CHEMICAL SCIENCES

CSIR-NET & GATE TOPICWISE COMPLETE SOLUTION

Vivek C. Badgujar
(M.Sc. Chemistry, CSIR-NET-JRF, SET, GATE)
Assistant Professor,

Department of Chemistry, Pratap College,
Amalner 425401 (M.S.)

Email : vivekbadgujar@pca.ac.in

Kirtikumar C. Badgujar
(M.Sc. Chemistry, Gold-Medalist, 2008-
University topper, CSIR-NET-JRF, SET, GATE,
MRSC), Senior CSIR Research Fellow

Department of Chemistry, Institute of Chemical
Technology (ICT), **Mumbai 400019 (M.S.)**

Email : kirrtti@gmail.com

Harshal B. Saraf
(M.Sc. Chemistry, UGC-NET-JRF, SET, GATE)
Lecturer in Chemistry,

Department of Chemistry, Pratap College,
Amalner 425401 (M.S.)

Email : harshal.saraf5@gmail.com

Harshal C. Badgujar
(M.Sc. Chemistry, B. SC. Gold-Medalist, 2010-
University topper, CSIR-NET-JRF, SET, GATE)
'Suman' Chemistry Classes,
Amalner 425401 (M.S.)

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Nagpur : Kundanlal Chandak Industrial Estate, Ghat Road, Nagpur - 440 018.
Phones: 2738731, 3296733 Telefax: 0712-2721216.
Bengaluru : Plot No. 91-33, 2nd Main Road Seshadripuram, Behind Nataraja Theatre,
Bengaluru - 560 020. Phones: 08041138821, 9379847017, 9379847005.
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Chennai : New-20, Old-59, Thirumalai Pillai Road, T. Nagar, Chennai - 600 017 .
Mobile: 09380460419.
Pune : First Floor, "Laksha" Apartment, No. 527, Mehunpura, Shaniwarpeth,
(Near Prabhat Theatre), Pune - 411 030. Phones: 020-24496323, 24496333.
Lucknow : House No. 731, Shekhupura Colony, Near B.D. Convent School, Vikas Nagar,
Aliganj, Lucknow - 226022. Mob: 09307501549.
Ahmedabad : 114, "SHAIL",1st Floor, Opp. Madhu Sudan House, C.G.Road, Navrang Pura,
Ahmedabad - 380 009. Phone: 079-26560126, Mobile: 0937708847.
Ernakulam : 39/176 (New No: 60/251) 1ST Floor,Karikkamuri Road,Ernakulam,
Kochi - 682011, Kerala. Tel : 0484-2378012, 2378016, Mobile: 09344199799
Bhubaneswar : 5 Station Square, Bhubaneswar (Orissa) - 751 001.
Phone: 0674-2532129,9338746007, Mobile: 09883055590
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Preface

The basic principle in writing of this CSIR-NET-GATE book is to create a guiding text for students- a text which represents the material in a way that encourages the students for the logical thinking about what they have learned theoretically in their bachelors/masters.

At present in India, the national level competitive examinations such as CSIR-NET-JRF, UGC-SLET (SET), IIT-JAM, TIFR, IISc, BARC, ONGC and DRDO exams are of great importance to start advance career after basic graduation/ post graduation studies. These above competitive exams test the in-depth and practical knowledge of various basic concepts. Cracking of any above national competitive examination opens several doors of opportunities in the field of industrial/scientific research and may offer excellent job opportunities in the research as well as teaching field. However, the percentage of qualifying students is varied from the 1-10 %. Hence, an attempt has been made by authors to design the book in such a way that students will become more familiar with the type of conceptual questions that are asked in above said competitive exams.

The attempt has been made by us to ensure an error free version, however, if any errors or typos have noticed then we sincerely regret for the same. We would like to hear appreciation, suggestions and comments from fellow teachers and students to improve the book. The suggestions can be send to email: netgate.badgujar@gmail.com

Finally we are greatly thankful to **Shri. G. N. Pandey** (Director of **Himalaya Publishing House**, Nagpur) for this opportunity and Mr. Dinesh Dhawane, Area Manager for his invaluable support to bring out this book in time. We sincerely hope that present book will be helpful for Graduate/ Post Graduate students, lecturers and professors throughout the Nation.

Authors

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We (authors) would like to express special thanks to our family who encourage and support in preparation of this book. Also we are greatly thankful to the all faculties/ professors and lectures from the Pratap College, Amalner (North Maharashtra University, Jalgaon); especially from the Department of Chemistry for their kind suggestions. We are sincerely thankful to Prof. T. V. Rajale (from Department of Chemistry, Pratap College, Amalner) for their kind assistance in reviewing of this book. Also we are sincerely thankful to Prof. P. M. Yeole (from Department of Chemistry, R. L. College, Parola), Prof. B. M. Bhanage (from Department of Chemistry, Institute of Chemical Technology, Mumbai) and Prof. S. D. Samant (from Department of Chemistry, Institute of Chemical Technology, Mumbai) for their constant inspiration regarding this activity. We are also thankful to our students and friends for their valuable suggestions.

Authors

Authors Opinion

Welcome, it gives us great pleasure to present/introduce one of the unique book for all of Graduate as well as Post Graduate students from chemical sciences branch those are willing to crack CSIR-UGC-NET-JRF & GATE. This book will also constructive to get ready for prestigious state and national level competitive exams such as UGC-SLET (SET), IIT-JAM, PET, TIFR, IISc, BARC, ONGC and DRDO in Chemistry or Chemical Science related branches.

Most common question asked by students is "how should I prepare for this exam?"

One of the best and easy method to crack any of these exams is to......

- ✓ ***Go through the syllabus and pattern of examination***
- ✓ ***Prepare according to the syllabus***
- ✓ ***Collect the previous question papers***
- ✓ ***Solve the topic wise questions, after studying and reading that particular topic***
- ✓ ***This will not only improve the confidence levels to face any exam but also in-depth knowledge of respective field/ topic.***

In this book we make an attempt to provide topic wise questions that are asked from last many question papers of CSIR-NET/ SET/ GATE of Chemical Science branch. We try to cover most of the syllabus topics wise in this book. Questions from more than 25 topics are included in these books which are frequently asked in CSIR-NET/ SET/ GATE exams. The previously asked questions are not repeated exactly in the same format. However, previously asked questions are repeated by modifying the questions in a different pattern/ format. One of the most essential thing is that, although modified questions are different, but the concept and logic behind it is nearly same. Hence, if you go through previously solved question papers and prepare a note of frequently asked facts, then it will be very much worthwhile to crack the competitive exams such as CSIR-UGC-NET/JRF etc. Now-a-days comparative exam are applied everywhere to screen the suitable candidate. However, the percentage of qualifying students is varied from 1-10 %. These topic-wise questions bank offer a rich store-house of conceptual questions to check the theory and understanding. In addition to this, the carefully graded challenging questions that are asked in CSIR-NET/ GATE exam bring a special perspective in teaching and learning context. Thus, the present book will be definitely important to students. Furthermore, the book will also be very important for Lecturers/ Professors for Undergraduate and Post Graduate university level teaching to build up a competitive exam aspect in students.

- Authors

About the exam........

Precisely talking about the CSIR-NET exam, Council of Scientific and Industrial Research, (CSIR) and University Grant Commission (UGC) jointly conducted CSIR-UGC-NET exam for (i) Junior Research Fellowship (JRF) and (ii) Eligibility for Lectureship (LS) in various basic sciences. This exam conducted twice in a year, mostly in month of June & December. The notification for the same is announced most probably in the month of March and September respectively on web address: http://csirhrdg.res.in/ (website for NET exam).

The GATE exam is conducted jointly by the Indian Institute of Science, Bangalore and the seven Indian Institutes of Technology (Bombay, Delhi, Guwahati, Kanpur, Kharagpur, Madras and Roorkee) on behalf of the National Coordination Board- GATE, Department of Higher Education, Ministry of Human Resources Development (MHRD), and Government of India. The notification for the same is announced most probably in the month of September.

The new pattern implemented from June 2011 onwards for CSIR-UGC-NET-EXAM of Chemical Science branch involves:

- *A single test paper test having multiple choice questions (MCQs)*
- *It carries maximum of 200 marks.*
- *It is divided into three parts (A, B & C).*
- *It is conducted for duration of 3 hours.*

Part A: Carries 20 questions. The candidate is required to answer any 15 questions. Each correct answer is awarded with 2 marks. The total marks allocated to this section shall be 30 out of 200. This part will test general aptitude

Part B: Contains 50 multiple choice questions generally covering the topics given in the syllabus. A candidate is required to answer any 35 questions and each correct answer is awarded with 2 marks. The total marks allocated to this section shall be 70 out of 200.

Part C: Consists of 75 questions. A candidate shall be required to answer any 25 questions, each carrying 4 marks. The maximum marks allocated to this section are 100 out of 200.

*Note- There will be **negative marking @ 25%** for each wrong answer.

Part	No. of questions	To be attempted	Marks allotted per question	Maximum marks
A	20	15	2	30
B	50	35	2	70
C	75	25	4	100
				Total Marks- 200

Research Fellowships awarded after clearing CSIR-NET-JRF exam

YEAR	Amount of fellowships
1 to 2 (JRF)	25,000 per month + 20 % or 30 % HRA + Contingency
3 to 5 (SRF)	28,000 per month + 20 % or 30 % HRA + Contingency

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11) The average value of the radius <r> in the 1s state of the hydrogen atom is (a_0 is Bohr radius) ***[June 2012]***

(a) a_0 (b) $1.5\ a_0$ (c) $0.75\ a_0$ (d) $0.5\ a_0$.

12) The difference in energy levels of n = 2 and n = 1 of a particle-in-a one dimensional box is 6 units of energy In the same units, what is the difference in energy levels of n = 3 and n = 2 for the above system? ***[June 2013]***

(a) 4 (b) 5 (c) 9 (d) 10

13) The wave function ψ of a certain system is the linear combination ***[June 2013]***

$$\Psi = \sqrt{\frac{1}{4}}\Psi_1 + \sqrt{\frac{3}{4}}\Psi_2$$

where ψ_1 and ψ_2 are energy eigen functions with eigen values (non-degenerate) E_1 and E_2, respectively. What is the probability that the system energy will be observed to be E_1?

a) $\sqrt{\frac{3}{16}}$ (b) $\sqrt{\frac{3}{4}}$ c) $\frac{1}{4}$ (d) $\sqrt{\frac{1}{4}}$

14) Calculate the total number of microstates for 6 identical particles with their occupation numbers {1, 2, 3} In three states is: ***[June 2013]***

(a) 6 (b) 12 (c) 60 (d) 720

15) The hermitian conjugate of operator d/dx, called (d/ dx)†, is actually equal to ***[June 2013]***

(a) –d/dx (b) d/dx (c) *i*(d/dx) (d) –*i*(d/dx)

16) A constant of motion is defined by the equation: ***[June 2013]***

(a) [H, A] = 0 (b) <[H,A]> =0 (c) A = f(H) (d) A†= A

17) The orbital with two radial and two angular nodes is ***[Dec 2013]***

(a) 3p (b) 5d (c) 5f (d) 8d

18) The energy of 2s and 2p orbitals is the same for ***[Dec 2013]***

(a) Li (b) Li^{+2} (c) Be_2^+ (d) H^-

19) The number of configurations in the most probable state, according to Boltzmann formula, is ***[June 2014]***

(a) e^{S/K_B} (b) e^{-S/K_B} (c) e^{-E/K_BT} (d) $-\Delta G/K_BT$

20) The commutator of the kinetic energy operator, $\hat{T}_x$ and the momentum operator, $\hat{p}_x$ for the one dimensional case is ***[June 2014]***

(a) $i\hbar$ (b) $i\hbar\frac{d}{dx}$ (c) 0 (d) $i\hbar x$

21) For a particle of mass m confined in a box of length L, assume Δx = L. Assume further that $\Delta p(\min) = \langle p^2\rangle^{1/2}$. Use the uncertainty principle to obtain an estimate of the energy of the particle. The value will be ***[Dec 2014]***

(a) $h^2/(8mL^2)$ (b) $\hbar^2/(8mL^2)$ (c) $h^2/(32mL^2)$ (d) $h^2/(2mL^2)$

22) The exact differential *df* of a state function f(x,y), among the following is ***[Dec 2014]***

(a) xdy (b) $dx - \frac{x}{y}dy$ (c) $ydx - xdy$ (d) $\frac{1}{y}dx - \frac{x}{y^2}dy$

Topic 1

ATOMIC STRUCTURE AND QUANTUM CHEMISTRY

Questions with TWO marks

1) The energy levels for cyclobutadiene are $\alpha+2\beta, \alpha\ \alpha$ and $\alpha-2\beta$. The delocalization energy in this molecule is ***[June 2011]***

(a) 0 (b) -4β (c) -8β (d) 4α

2) An operator A is defined as $= -\frac{d}{dx} + x$. Which one of the following statements is true? ***[June 2011]***

(a) A is a Hermitian operator.
(b) $A^\dagger$ is an antihermitian operator.
(c) Both $A A^\dagger$ and $A^\dagger A$ are Hermitian operator.
(d) $A A^\dagger$ is Hermitian, but $A^\dagger A$ is antihermitian operator.

3) Identify which of the following operators is <u>not</u> hermitian? ***[Dec 2011]***

(a) $\frac{\hbar}{i}\frac{d}{dx}$ (b) $i\frac{d^2}{dx^2}$ (c) $\frac{d^2}{dx^2}$ (d) x^2

4) A particle is constrained in one dimensional box of a length 2a with potential $V(x) = \infty$; $x < -a$, $x > a$ and $V(x) = 0$; $-a \le x \le a$. Energy difference between levels n= 3 and n = 2 is ***[Dec 2011]***

(a) $\frac{5h^2}{8ma^2}$ (b) $\frac{9h^2}{8ma^2}$ (c) $\frac{9h^2}{32ma^2}$ (d) $\frac{5h^2}{32ma^2}$

5) When a hydrogen atom is placed in an electric field along the y-axis, the orbital that mixes most with the ground state 1s orbital is ***[Dec 2011]***

(a) 2s (b) $2p_x$ (c) $2p_y$ (d) $2p_x$

6) If A and B are non-commuting hermitian operators, all eigenvalues of the operator given by the commutator [A,B] are ***[Dec 2011].***

(a) complex (b) real (c) imaginary (d) zero

7) The value of commutator $[x, p_x^2]$ is given by ***[Dec 2011]***

(a) $2i$ (b) $2i\hbar$ (c) $2i\hbar x$ (d) $2i\hbar p_x$

8) The correlation coefficient between two arbitrary variables x and y is zero, if ***[Dec 2011]***

(a) $<xy> =<yx>$ (b) $<x^2> =<x>^2$
(c) $<y^2> =<y>^2$ (d) $<xy = <x>< y>$

9) For any operator A and its adjoint $A^\dagger$, the INCORRECT statement is ***[June 2012]***

(a) $A A^\dagger$ is a hermitian. (b) $A A^\dagger + A^\dagger A$ is hermitian
(c) $A+A^\dagger$ hermitian (d) $A - A^\dagger$ is hermitian

10) For hydrogen-like atom with a nuclear charge Z, the energy of orbital with principal quantum number 'n' follows the relation. ***[June 2012]***

(a) $E_n \propto n^2Z^2$ (b) $E_n \propto -\frac{Z^2}{n}$ (c) $E_n \propto -\frac{Z}{n}$ (d) $E_n \propto -\frac{Z^2}{n^2}$

Questions with FOUR marks

23) The probability of finding the particle in a one dimensional box of length 'L' in the region between $\frac{L}{4}$ and $\frac{3L}{4}$ for quantum number n = 1 is 0 *[June 2012]*

(a) $\frac{1}{2}$ (b) $\frac{1}{2}+\frac{1}{\pi}$ (c) $\frac{1}{2}-\frac{1}{\pi}$ (d) $\frac{2}{3}$

24) A particle in three dimensional cubic box of a L has energy of $\frac{14h^2}{8mL^2}$. The degeneracy of the state is *[June 2012]*

(a) 2 (b) 3 (c) 6 (d) 9

25) Using Huckel molecular orbital approximation, the two roots of secular equation of ethene are *[June 2012]*

(a) $\alpha+\sqrt{2}\,\beta, \alpha-\sqrt{2}\,\beta$ (b) $\alpha+\beta, \alpha$
(c) $\alpha+\beta, \alpha-\beta$ (d) $\alpha+2\beta, \alpha-2\beta$

26) For H_2 molecule in the excited state $\sigma_g^{\,1}\,\sigma_u^{\,1}$ the spin part of the triplet state with m_s is proportional to *[June 2012]*

(a) $\alpha(1)\beta(2)$ (b) $[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$ (c) $\alpha(1)\alpha(2)$ (d) $[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

27) The energy of a harmonic oscillator in its ground state is $\frac{1}{2}\hbar\omega$. According to the virial theorem, the average kinetic (T) and potential (V) energies of the above are *[Dec 2012]*

(a) $T=\frac{1}{4}\hbar\omega;\ V=\frac{1}{4}\hbar\omega$ (b) $T=\frac{1}{8}\hbar\omega;\ V=\frac{3}{8}\hbar\omega$

(c) $T=\hbar\omega;\ V=-\frac{1}{2}\hbar\omega$ (d) $T=\frac{3}{8}\hbar\omega;\ V=\frac{1}{8}\hbar\omega$

28) For the particle-in-a-box problem in (0,L), the value of $\langle x^3\rangle$ in the n ⟶ ∞ limit would be *[June 2013]*

(a) $L^3/6$ (b) $L^3/3$ (c) $L^3/4$ (d) $L^4/4$

29) The energy of a hydrogen atom in a state is $-\frac{hcR_H}{25}$ ($R_H = Rydberg\ constant$) The degeneracy of the state will be *[Dec 2012]*

(a) 5 (b) 10 (c) 25 (d) 50

30) The energy for a single electron excitation in cyclopropenium cation in Huckel theory is *[Dec 2013]*

(a) β (b) 2β (c) 3β (d) 4β

31) For an electronic configuration of two non-equivalent π electrons $[\pi^1, \pi^1]$ which of the following terms is not possible? *[Dec 2013]*

(a) $^1\Sigma$ (b) $^3\Sigma$ (c) $^3\Delta$ (d) $^3\Phi$

32) The spatial part of the wave function of the atom in its ground state is 1s(1) 1s(2). The spin part would be *[June 2014]*

(a) $\alpha(1)\beta(2)$ (b) $\beta(1)\alpha(2)$ (c) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$ (d) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$

33) Simple Huckel molecular orbital theory *[June 2014]*

(a) considers electron-electron repulsion explicitly (b) distinguishes cis-butadiene and trans-butadiene
(c) disinguishes cis-butadiene and cyclobutadiene (d) has different coulomb integrals for non-equivalent carbons.

34) Consider a particle confined in a cubic box. The degeneracy of the level, that has an energy twice that of the lowest level, is ***[June 2014]***

(a) 3 (b) 1 (c) 2 (d) 4

35) If $\psi = 0.8\ \varphi_A + 0.4\ \varphi_B$ is a normalized molecular orbital of a diatomic molecule AB, constructed from φ_A and φ_B which are also normalized, the overlap between φ_A and φ_B is ***[June 2014]***

(a) 0.11 (b) 0.31 (c) 0.51 (d) 0.71

36) A particle in a 1-dimensional box of length L is perturbed by a delta function potential , $\delta(x-L/2)$, in the middle of the box. The first order energy correction to the ground state will be ***[Dec 2014]***

(a) 0 (b) 1 (c) $L/2$ (d) $2/L$

$[Hint: \int_{+\infty}^{-\infty} f(x)\delta(x-a)dx = f(a)]$

37) According to the Huckel theory , the π electron charge on central carbon atom in propenyl cation is $(CH_2CHCH_2)^+$ is (in unit of electronic charge) ***[Dec 2014]***

(a) 1/2 (b) $1/\sqrt{2}$ (c) 1 (d) 2

38) The number of microstates that are possible, when two particle are distributed in four states such that resulting wave functions are anti-symmetric with respect to exchange of the particle , is – ***[Dec 2014]***

(a) 16 (b) 12 (c) 8 (d) 6

<u>(Questions from GATE EXAM)</u>

<u>Questions with ONE OR TWO marks</u>

39) The set of eigenfunction $\sqrt{\frac{2}{a}}\,sin\frac{n\pi x}{a}\ \ (0 \le x \le a, n = 1, 2, 3, ...)$ [GATE 2005]

(a) orthogonal (b) normalized

(c) both orthogonal and normalized (d) unnormalized

40) The function e^{ax^2} $(\alpha > 0)$ is not an acceptable wave function for bound system, because ***[GATE 2005]***

(a) it is not continuous (b) it is multivalued

(c) it is not normalized (d) all of these

1) The 2s orbital of H–atom has a radial node at 2a because Ψ_{2s} is proportional to ***[GATE 2005]***

(a) $(1/2 + r/a_0)$ (b) $(2 + r/a_0)$ (c) $(2 - r/a_0)$ (d) $(2 - r/2a_0)$

2) In the Huckel model for benzene, the π electronic transitions from the occupied to the unoccupied molecular orbitals do not occur at ***[GATE 2006]***

(a) 4β (b) 3β (c) 2β (d) 1β

) Which of the following pairs of operators commute? ***[GATE 2006]***

(a) x and $\frac{d}{dx}$ (b) $\frac{d}{dx}$ and $\frac{d^2}{dx^2} + 2\frac{d}{dx}$

(c) $x^2\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ (d) x^3 and $\frac{d}{dx}$

Linked Answer Questions (44 and 45) [GATE 2007]

44) Consider a particle of mass m moving in a one-dimensional box under the potential V=0 for $0 \le x \le a$ and V = ∞ outside the box. When the particle is in its lowest energy state the average momentum ($\langle p_x \rangle$) of the particle is

(a) $\langle p_x \rangle = 0$ (b) $\langle p_x \rangle = \frac{h}{a}$ (c) $\langle p_x \rangle = \frac{h}{2a}$ (d) $\langle p_x \rangle = \frac{h}{2\pi a}$

45) The uncertainty in the momentum (Δp_x) of the particle in its lowest energy state is

(a) $\Delta p_x = 0$ (b) $\Delta p_x = \frac{h}{a}$ (c) $\Delta p_x = \frac{h}{2a}$ (d) $\Delta p_x = \frac{h}{2\pi a}$

46) A particle is confined to a one-dimensional box of length 1 mm. If the length is changed by 10^{-12} m the % change in the ground state energy is ***[GATE 2008]***

(a) 2×10^{-4} (b) 2×10^{-7} (c) 2×10^{-2} (d) 0

47) The operation of the commutator [x, d/dx] on a function f(x) is equal to ***[GATE 2008]***

(a) 0 (b) f(x) (c) –f(x) (d) x df/dx

Common Data Questions [GATE 2008]

Common Data for Questions 48 ,49 and 50:

An electron accelerated through a potential difference of φ volts impinges on a nickel surface, whose (100) planes have a spacing d = 351.8×10^{-12} m (351.8 pm).

48) The de-Broglie wavelength of the electron is The value of λ / pm = $(a / \varphi)^{1/2}$ in volts is

(a) 1.5×10^{-18} (b) 1.5×10^{6} (c) 6.63×10^{-5} (d) 2.5×10^{18}

49) The condition for observing diffraction from the nickel surface is

(a) $\lambda >> 2d$ (b) $\lambda \le 2d$ (c) $\lambda \le ad$ (d) $\lambda \ge ad$

50) The minimum value of φ (V) for the electron to diffract from the (100) planes is

(a) 3000 (b) 300 (c) 30 (d)3

51) The degeneracy of a quantum particle in a cubic box having energy four times that of the lowest energy is ***[GATE 2009]***

(a) 3 (b) 6 (c) 1 (d) 4

52) The de Broglie wavelength for a He atom travelling at 1000 ms^{-1} (typical speed at room temperature) is ***[GATE 2009]***

(a) 99.7×10^{-12} m (b) 199.4×10^{-12} m (c) 199.4×10^{-18} m (d) 99×10^{-6} m

53) An electron of mass '*m*' confined to a one dimensional box of length '*b*'. If it makes a radiative Transition from second excited state to the ground state, the frequency of the photon emitted is ***[GATE 2010]***

(a) $\frac{9h}{8mb^2}$ (b) $\frac{3h}{8mb^2}$ (c) $\frac{h}{mb^2}$ (d) $\frac{2h}{mb^2}$

54) For eigenfunction $\Psi = \sqrt{\frac{1}{b}}\sin\left(\frac{\pi x}{b}\right)$ and $\Psi = \sqrt{\frac{2}{b}}\sin\left(\frac{2\pi x}{b}\right)$ of a particle in a 1-D box of length $b(0 \le x \le b)$ **[GATE 2010]**

(a) Ψ_1 is normalized and orthogonal to Ψ_2
(b) Ψ_1 is normalized but orthogonal to Ψ_2
(c) $\Psi_2$is normalized and orthogonal to Ψ_1
(d) $\Psi_2$is neither normalized nor orthogonal to Ψ_1

55) The wave function for a quantum mechanical particle in a 1-dimensional box of length *'a'* is given by $\Psi = A\sin\frac{\pi x}{a}$. The value of *'A'* for a box of length 200 nm is ***[GATE 2011]***

(a) $4\times10^4\ (\text{nm})^2$ (b) $10\sqrt{2}\ (\text{nm})^{1/2}$ (c) $\sqrt{2}/10\ (\text{nm})^{-1/2}$ (d) $0.1\ (\text{nm})^{-1/2}$

56) If Δy and Δp_y are the uncertainties in the y-coordinate and the y component of the momentum of a particle respectively, then, according to uncertainty principle $\Delta y\Delta p_y$ is($\hbar = \frac{h}{2\pi}$ and h is Planck's constant) ***[GATE 2012]***

(a) $\geq \hbar$ (b) $> \hbar/2$ (c) $> \hbar$ (d) $\geq \hbar/2$

57) Let $\emptyset_x^C$ and $\emptyset_z^C$ denote the wavefunctions of the $2p_x$ and $2p_z$ orbitals of carbon, respectively, and $\emptyset_x^O$ and $\emptyset_z^O$ represent the wavefunctions of the $2px$ and $2pz$ orbitals of oxygen, respectively. If c_1 and c_2 are constants used in linear combinations and the CO molecule is oriented along the z axis, then, according to molecular orbital theory, the π-bonding molecular orbital has a wavefunction given by ***[GATE 2012]***

(a) $c_1\emptyset_z^C + c_2\emptyset_x^O$ (b) $c_1\emptyset_z^C + c_2\emptyset_z^O$ (c) $c_1\emptyset_x^C + c_2\emptyset_z^O$ (d) $c_1\emptyset_x^C + c_2\emptyset_x^O$

<u>Statement for Linked Answer Questions 58 and 59: [GATE 2012]</u>

Hückel molecular orbital theory can be applied to the allene radical ***[GATE 2012]***

$$H_2C{=}CH{-}\dot{C}H_2$$

58) The secular determinant (where α, β and *E* have their usual meanings) is given by

(a) $\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$ (b) $\begin{vmatrix} \alpha-E & 0 & 0 \\ 0 & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$

(c) $\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & 0 \\ 0 & 0 & \alpha-E \end{vmatrix}$ (d) $\begin{vmatrix} \alpha-E & -\beta & 0 \\ -\beta & \alpha-E & -\beta \\ 0 & -\beta & \alpha-E \end{vmatrix}$

59) The possible values of *E* are

(a) $\alpha+\sqrt{2}\beta, \alpha, \alpha-\sqrt{2}\beta$ (b) $\alpha+2\sqrt{2}\beta, \alpha, \alpha-2\sqrt{2}\beta$

(c) $\alpha+\beta, \alpha, \alpha-\beta$ (d) $\alpha+2\beta, \alpha, \alpha-2\beta$

60) e^{-2x^2} is an eigen function of the operator $(\frac{d^2}{dx^2} - 16x^2)$ The corresponding eigen value is [GATE 2013]

(a) + 4 (b) – 4 (c) + 2 (d) – 2

61) The value of the magnetic quantum number of a p_x orbital is ***[GATE 2014]***

(a) –1 (b) 0 (c) +1 (d) undefined

62) $\Psi = N\,r(6-Z\,r)e^{-Zr/3}\cos\theta$, is a proposed hydrogenic wavefunction, where Z = Atomic number, r = radial distance from the nucleus, θ = azimuthal angle, N is a constant. The <u>*INCORRECT*</u> statement about Ψ is ***[GATE 2014]***

(a) $\Psi = 0$ in the *xy*-plane

(b) two radial nodes are present in Ψ

(c) one angular node is present in Ψ

(d) the size of the orbital decreases with increase in atomic number

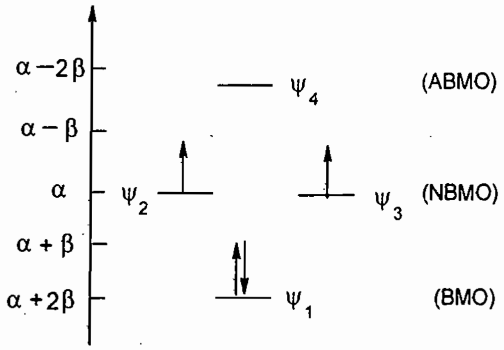
Answer Key

Topic: 1:- Atomic structure and Quantum chemistry

1	a	2	c	3	b	4	d	5	c	6	c	7	d	8	d	9	d	10	d
11	b	12	d	13	c	14	c	15	c	16	a	17	b	18	b	19	a	20	c
21	a	22	d	23	b	24	c	25	c	26	d	27	a	28	c	29	c	30	c
31	d	32	d	33	c	34	a	35	b	36	d	37	c	38	d	39	c	40	d
41	c	42	d	43	b	44	a	45	b	46	a	47	c	48	a	49	b	50	d
51	c	52	a	53	c	54	c	55	d	56	d	57	d	58	a	59	a	60	b
61	d	62	b																

Hint & solutions

1) Ans (a):- HMO diagram for cyclobutadiene:-



HMO diagram for cyclobutadiene

4 π electron occupying the Mo's, as shown above. Hence, total π electron energy

$$E\pi = 2(\alpha + 2\beta) + 2\alpha$$
$$= 4\alpha + 4\beta$$

$$\text{Hence DE} = 4\alpha + 4\beta - 4(\alpha + \beta)$$
$$= 4\alpha + 4\beta - 4\alpha - 4\beta$$
$$= 0$$

2) Ans (c):- Let

$$A = -\frac{d}{dx} + x \quad \& \quad A^{\dagger} = i\left(-\frac{d}{dx} + x\right)$$
$$AA^{\dagger} = \left(-\frac{d}{dx} + x\right)\left[i\left(-\frac{d}{dx} + x\right)\right]$$
$$= \left(-\frac{d}{dx} + x\right)\left(-i\frac{d}{dx} + ix\right)$$
$$= i\frac{d^2}{dx^2} - ix\frac{d}{dx} - ix\frac{d}{dx} + ix^2$$

$$= i\left(\frac{d}{dx} - x\right)^2 \underline{\qquad\qquad\qquad} (1)$$

$$A^{\dagger}A = \left[i\left(-\frac{d}{dx} + x\right)\right]\left(-\frac{d}{dx} + x\right)$$

$$= \left(-\frac{id}{dx} + ix\right)\left(-\frac{d}{dx} + x\right)$$

$$= i\frac{d^2}{dx^2} - ix\frac{d}{dx} - ix\frac{d}{dx} + ix^2$$

$$= i\left(\frac{d}{dx} + x\right)^2 \underline{\qquad\qquad\qquad} (2)$$

From equation (1) and (2), we get

$AA^{\dagger} = A^{\dagger}A$

Hence, both $AA^{+} = A^{+}A$ are Hermitian operator.

3) Ans (b):- Condition for Hermiton operator is

$A.A^{\dagger} = A^{\dagger}.A \underline{\qquad\qquad\qquad\qquad} (1)$

But, for $A = i\frac{d^2}{dx^2}$, equation (1) is not satisfied, Hence $i\frac{d^2}{dx^2}$ is not a hermitian operator.

4) Ans (d):- $E_n = \frac{n^2\hbar^2}{8ma^2}, n = 1, 2, 3 \ldots\ldots$.

Energy difference between n = 3 and n = 2 is

$$\Delta E = \frac{h^2}{8ma^2}[(3)^2 - (2)^2]$$

$$\Delta E = \frac{5h^2}{8ma^2}$$

Here $a = 2a$, So

$$\Delta E = \frac{5h^2}{8m(2a)^2} = \frac{5h^2}{8m(4a^2)}$$

$$\left[\Delta E = \frac{5h^2}{32ma^2}\right]$$

5) Ans (c):- When a hydrogen atom is placed in an electric field along the y – axis, the orbital that mixes most with the ground state 1s orbital is $2p_y$ as magnetic field will be oriented along y – axis.

6) Ans (c):- If A and B are non-commuting hermitian operator, all the eigen values are purely imaginary.

7) Ans (d):- Value of commutator

$[x, P_x^n] = ni\hbar P_x^{\,n-1} \underline{\qquad\qquad\qquad\qquad} (1)$

In this case n = 2

By putting value of n = 2 is equation (1)

$$[x, P_x^2] = (2)i\hbar P_x^{\,2-1}$$

$$= (2)i\hbar P_x$$

$$= 2i\hbar P_x$$

Ans (d):- Correlation coefficient between two arbitrary variables x and y is zero, if $< XY > = < X >< Y >$

Ans (d):- Let A = operator and $A^{\dagger}$ = Adjoint of A then

$AA^{\dagger} = A^{\dagger}A \qquad \underline{\qquad\qquad\qquad} (1)$

This equation (1) is the condition for hermitian operator. This condition is not valid for $A - A^{\dagger}$ is not an hermitian.

10) Ans (d):- For hydrogen atom, Energy will be $E_n = -13.6\,\frac{z^2}{n^2}$

$$E_n = -R_H\,\frac{z^2}{n^2}$$

$$\therefore\ E_n\ \alpha\ \frac{-z^2}{n^2}$$

11) Ans (b):- In quantum mechanics, Average value of the radius $\langle r\rangle$ is

$$\langle r\rangle = \int \Psi n.\, r.\, \Psi n d\tau$$

$$\langle r\rangle = \int \Psi_{1s}.\, r.\, \Psi_{1s} d\tau$$

Since, $d\tau = r^2 dr\ \sin\theta d\theta d\Phi$

Hence Integrating between appropriate limit

$$\langle r\rangle = \frac{1}{\pi a_0^3}\int_0^\infty r^3\, e^{-2r/ao}\, dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi$$

$$= \frac{1}{\pi a_0^3}\left[\frac{3!}{\left(\frac{2}{a_0}\right)^4}\,(2)(2\pi)\right]$$

$$= \frac{3}{2}a_0 = 1.5\ a_0$$

12) Ans (d):- $E_n = \frac{n^2h^2}{8ma^2}, n = 1, 2, 3 \ldots\ldots$

Energy difference between n = 3 and n = 2 is

$$\Delta E = \frac{h^2}{8ma^2}\,[(3)^2 - (2)^2]$$

$$\Delta E = \frac{5h^2}{8ma^2}$$

Here a $= 2a$, So

$$\Delta E = \frac{5h^2}{8m\,(2a)^2} = \frac{5h^2}{8m(4a^2)}$$

$$\left[\Delta E = \frac{5h^2}{32ma^2}\right]$$

The difference in energy level of n = 2 and n = 1 of particle in box is 6 units

i.e. $\Delta E = E_2 - E_1 = 6$

As $\Delta E = E_2 - E_1 = [(2)^2 - (1)^2]\frac{h^2}{8ma^2} = 6$

$$= [4 - 1]\frac{h^2}{8ma^2} = 6$$

$$\therefore\ \frac{3h^2}{8ma^2} = 6$$

$$= \left[\frac{h^2}{8ma^2} = 2\right]\text{units}$$

Now, n = 3 ⟶ n = 2

$$\Delta E = [(3)^2 - (2)^2]\frac{h^2}{8ma^2}$$

$$= [9 - 4]\frac{h^2}{8ma^2}$$

$$= \frac{5h^2}{8ma^2}$$

$= 5 \times (2) \qquad \because \frac{h^2}{8ma^2}$

$\Delta E = 10$ units

13) Ans (c):- In LCAO-MO system.

$\Psi_{mo} = C_A\phi_A + C_B\phi_B$

Probability of finding the electron in ϕ_A and ϕ_B atomic orbitals.

$[C_A]^2$ and $[C_B]^2$

Similarly; $\Psi = \sqrt{\frac{1}{4}}\Psi_1 + \sqrt{\frac{3}{4}}\Psi_2$

$\Psi = C_A\Psi_1 + C_B\Psi_2$

Probability $[C_A]^2 = \left(\sqrt{\frac{1}{4}}\right)^2$ for E_1

$= \frac{1}{4}$

14) Ans (c):- Microstate $= \frac{N!}{n_x!\, n_y!\, n_z!}$

N = Total number of particles = 6

n_x, n_y, n_z = number of state particle <u>*or*</u> $[n_x, n_y, n_z] = [1, 2, 3]$

$\therefore$ Microstate $= \frac{N!}{n_x!\, n_y!\, n_z!}$

$= \frac{6!}{1!2!\,3!}$

$= \frac{6 \times 5 \times 4 \times 3\,!}{1! \times 2 \times 1 \times 3!}$

Microstate = 60

15) Ans (c):- Operator $A = \frac{d}{dx}$

It's conjugate operator $A^\dagger = i\frac{d}{dx}$

Since $AA^\dagger = A^\dagger A$ ____________(1) which is the condition for Hermitian operator

1st $\quad AA^+ = \left(\frac{d}{dx}\right)\left(\frac{i\,d}{dx}\right)$

$= i\frac{d^2}{dx^2}$ ____________(i)

2nd $\quad A^+A = \left(\frac{i\,d}{dx}\right)\left(\frac{d}{dx}\right) = i\frac{d^2}{dx^2}$ ____________(ii)

From equation (i) and (ii), we get

$AA^+ = A^+A$

Hence $A^\dagger = i\frac{d}{dx}$ will be conjugate operator of A.

16) Ans (a):- A constant of motion is quantity that is conserved throughout the motion, A quantity is conserved, if $[H, A] = 0$

17) Ans (b):- Orbital with two radial and two angular nodes is 5d.

Radial Nodes = $(n-l-1)$

For 5d; $(n = 5\ \&\ l = 2)$

So, Radial Nodes =2

And, Angular Node = $l = 2$

18) Ans (b):- Li^{+2} ion has one electron is 1s orbital (i.e. hydrogen like atom). In case of H like atom, energy of orbital depends upon the principal quantum number $'n'$

$$\text{i.e.} \quad E_n \, \alpha - \frac{z^2}{n^2}$$

Hence, for 2s and 2p orbital, energy will be the same.

19) Ans (a):-Boltzmann's equation is a probability equation relating the entropy S of an ideal gas to the quantity W, which is the number of microstate corresponding to a given macrostate.

$$S = K_B \ln W \_\_\_\_\_\_\_\_\_\_\_\_ (1)$$

Here, $\ln W = \frac{S}{K_B}$

$$\therefore W = e^{S/K_B}$$

20) Ans (c):- Commutator $\Longrightarrow$ $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \_\_\_\_\_\_\_\_\_\_\_\_ (1)$

e.g. $[\hat{T}_x, \hat{P}_x]$, $\hat{A} = \hat{T}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\hat{B} = \hat{P}_x = -i\hbar\frac{d}{dx}$$

$$\hat{A}\hat{B} = \hat{T}_x\hat{P}_x = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\left(-i\hbar\frac{d}{dx}\right)$$

$$= i\frac{\hbar^3}{2m}\frac{d^3}{dx^3} \qquad \_\_\_\_\_\_\_\_\_\_\_\_ (2)$$

$$\hat{B}\hat{A} = \hat{P}_x\hat{T}_x = \left(-i\hbar\frac{d}{dx}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)$$

$$\hat{B}\hat{A} = i\frac{\hbar^3}{2m}\frac{d^3}{dx^3} \qquad \_\_\_\_\_\_\_\_\_\_\_\_ (3)$$

equation (1) $\Longrightarrow \hat{A}\hat{B} - \hat{B}\hat{A}$

$$= \hat{T}_x\hat{P}_x - \hat{P}_x\hat{T}_2$$

$$= \frac{i\hbar^3}{2m}\frac{d^3}{dx^3} - \frac{i\hbar^3}{2m}\frac{d^3}{dx^3}$$

$$= 0$$

Hence, $[\hat{T}_x, \hat{P}_x] = 0$

21) Ans (a):- Given: $\Delta P\,(\text{min}) = < p^2 >^{1/2}$

Also, we know that

$$< p^2 > = \frac{n^2\pi^2\hbar^2}{L^2} \text{ as } \hbar = \frac{h}{2\pi}$$

$$\text{Energy of particle} = \frac{[\Delta P]^2}{2m} = \frac{\left[<p^2>^{\frac{1}{2}}\right]^2}{2m}$$

$$= \frac{<p^2>}{2m}$$

By putting value of $< p^2 >$, we get

$$= \frac{n^2\pi^2\hbar^2}{L^2} \text{X} \frac{1}{2m}$$

$$= \frac{n^2\pi^2}{2mL^2} \text{X}\, \hbar^2$$

$$= \frac{n^2\pi^2}{2mL^2} \text{X} \left(\frac{h}{2\pi}\right)^2$$

$$= \frac{n^2\pi^2h^2}{2mL^2(4\pi^2)}$$

$$= \frac{n^2\pi^2h^2}{8mL^2\pi^2}$$

$$= \frac{n^2h^2}{8mL^2}$$

22) Ans (d):-$f(x, y) = Mdx + Ndy$ $\underline{\hspace{5cm}}$(1)

for exact differential equation

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \qquad \underline{\hspace{5cm}}(2)$$

Here, Given : $f(x, y) = \frac{1}{y}dx - \frac{x}{y^2}dy$ $\underline{\hspace{5cm}}$(3)

Will satisfy the eq^n (2), as

By comparing eq^n (1) and (3), we get

$$M = \frac{1}{y} \;\&\; N = -\frac{x}{y^2}$$

Differentiate M with respective to y.

$$\frac{\partial M}{\partial y} = \frac{\partial}{\partial y}\left(\frac{1}{y}\right) = -\frac{1}{y^2} \qquad \underline{\hspace{5cm}}(4)$$

Differentiate N with respective to x.

$$\frac{\partial N}{\partial x} = \frac{\partial}{\partial x}\left(-\frac{x}{y^2}\right) = -\frac{1}{y^2}\frac{\partial x}{\partial x}$$

$$\frac{\partial N}{\partial x} = -\frac{1}{y^2} \qquad \underline{\hspace{5cm}}(5)$$

From eq^n (4) and (5), we have

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

23) Ans (b):-Probability of finding particle in 1D Box of length L.

$$\Psi_n = \sqrt{\frac{2}{L}}\,\text{Sin}\left(\frac{n\pi x}{L}\right)$$

$$\text{for } 1D, 0 < x < L$$

$$n = 1\ \Psi_n = \sqrt{\frac{2}{L}}\,\text{Sin}\left(\frac{\pi x}{L}\right)$$

Probability for normalized wave function

$$= \int \Psi^*\Psi\, d\tau$$

$$= \int_{\frac{L}{4}}^{3L/4} \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right).\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)dx$$

$$= \left(\frac{2}{L}\right)\int_{\frac{L}{4}}^{3L/4} \sin^2\left(\frac{\pi x}{L}\right)dx$$

By solving this, we get

$$= \frac{1}{2} + \frac{1}{\pi}$$

24) Ans (c):-Degeneracy = $(nx^2 + ny^2 + nz^2)\frac{h^2}{8ma^2} = 14$

So, $(nx^2 + ny^2 + nz^2) = 14$ $\underline{\hspace{5cm}}$(1)

n_x +	n_y +	n_z
1	2	3
1	3	2
2	1	3

2	3	1
3	1	2
3	2	1

Equation (1) $\Rightarrow (1)^2 + (2)^2 + (3)^2$

$\Rightarrow 1 + 4 + 9$

$\Rightarrow 14$

All the above combination will satisfy Equation (1), hence, total degeneracy = 6

25) Ans (c):-Huckel secular equation for ethene is

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$\text{where } x = \frac{\alpha - E}{\beta}$$

$$\therefore x^2 - 1 = 0$$

$$\therefore x^2 = 1$$

$$\therefore x = \pm 1$$

$$\therefore \frac{\alpha - E}{\beta} = +1$$

$$\therefore \alpha - E = \beta$$

$$\therefore E = \alpha - \beta$$

$$\therefore \frac{\alpha - E}{\beta} = -1$$

$$\therefore \alpha - E = -\beta$$

$$\therefore E = \alpha + \beta$$

$\therefore$ Two roots are $\alpha + \beta$ and $\alpha - \beta$

26) Ans (d):- For H_2 molecule in the excited state $\sigma_g{}^1\sigma_s{}^1$ spin part of the triplet state with $m_s = 0$ is proportional to $[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

as, for $m_s = 0$, triplet state will be $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

27) Ans (a):- According to virial theorem for SHO

$E = K.E. + P.E.$

As, we know that, for SHO

$\therefore K.E. = P.E.$ ________________(1)

$\therefore E = K.E. + K.E.$

$E = 2KE$

Given : $E = \frac{1}{2}\hbar w$

$$\therefore \frac{1}{2}\hbar w = 2 \times K.E.$$

$$\therefore K.E. = \frac{1}{4}\hbar w$$

From equation (1), $P.E. = \frac{1}{4}\hbar w$

28) Ans (c):- value of $\langle x^3 \rangle = \int_0^L \Psi \langle x^3 \rangle \Psi^* \, d\tau$

$$\Psi = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\langle x^3\rangle = \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right).x^3\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L x^3.\sin^2\left(\frac{n\pi x}{L}\right)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L x^3\left[\frac{1-\cos\left(\frac{2n\pi x}{L}\right)}{2}\right]dx$$

$$= \left(\frac{2}{L}\right)\int_0^L \frac{x^3}{2}dx - \left(\frac{2}{L}\right)\int_0^L x^3.\cos\left(\frac{2n\pi x}{L}\right)dx$$

$$\text{As,} \therefore \int_0^L x^3.\cos\left(\frac{2n\pi x}{L}\right)dx = 0$$

$$= \left(\frac{2}{L}\right)\int_0^L \frac{x^3}{2}dx - 0$$

$$\langle x^3\rangle = \left(\frac{2}{L}\right)\left(\frac{1}{2}\right)\left[\frac{x^4}{4}\right]_0^L$$

$$= \left(\frac{1}{L}\right)\left[\frac{L^4}{4} - 0\right]$$

$$= \left(\frac{1}{L}\right)\left(\frac{L^4}{4}\right)$$

$$\langle x^3\rangle = \frac{L^3}{4}$$

29) Ans (c):-For hydrogen atom, energy is given by

$$E_n = -R_H\frac{z^2}{n^2}, \text{where } n = 1, 2, 3 \ldots\ldots\ldots\ldots\ldots$$

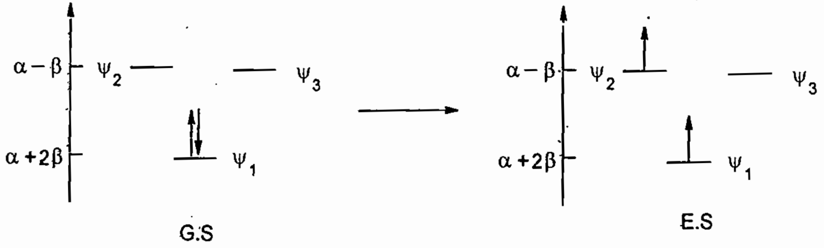
Degeneracy $= n^2$

Given $E = -\frac{hcR_H}{25} = -\frac{hcR_H}{n^2}$

$\therefore$ Degeneracy $= n^2 = 25$

$\therefore$ Degeneracy of state will be 25.

30) Ans (c):- Cyclopropenium cation ;



HMO diagram for cyclopropenium cation.

$E_{\pi(G.S.)} = 2(\alpha + 2\beta)$

$= 2\alpha + 4\beta$

Now, by single electron excitation in cyclopropenium cation in Huckel theory,

$E_\pi = (\alpha + 2\beta) + (\alpha - \beta)$

$= 2\alpha + \beta$

$\therefore$ Total π electron energy will be

$E_\pi = E_{\pi(G.S)} - E_{\pi(E.S)}$

$E_\pi = (2\alpha + 4\beta) - (2\alpha + B)$

$E_\pi = 3\beta$

31) Ans (d):-For π, $m\ell = \pm 1$

$\therefore M_L = |1+1| \ldots\ldots |1+1|$

$= |2| \ldots\ldots |0|$

$M_L = 2, 1, 0$

So, $M_L = 0$ Spectroscopic State $= \Sigma$

$M_L = 1$ Spectroscopic State $= \pi$

$M_L = 2$ Spectroscopic State $= \Delta$

$M_L = 3$ Spectroscopic State $= \phi$

For two non-equivalent π electrons

$M_L = 0, 1, 2$ but not 3

Hence, $^3\phi$ is not possible.

32) Ans (d):- According to the Pauli Exclusion Principle, the wave function of an electron must be antisymmetric.

i.e $\Psi(1,2) = -\Psi(2,1)$

Spin wave function can be

Ψ spin $= \alpha(1)\alpha(2)$ or $\beta(1)\beta(2)$ or

$[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$

Ψ spin $\equiv$ spin part of wave function. It is symmetrical in nature

As,

Ψ Total $= \Psi$ space $*$ Ψ spin

Ψ total is anti symmetrical with electron exchange

Ψ space $\equiv$ special part of wave function (symmetrical in nature)

So, spin part will be anti symmetric

$$= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

33) Ans (c):- Simple Huckel molecular orbital theory distinguishes cis butadience and cyclobutadiene on the basis of energy. As for cyclobutadiene DE = zero; While for Butadiene DE = 0.472 β

34) Ans (a):- For cubic box,

$$E = E_{nx,ny,nz} = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mL^2}$$

Degeneracy $= 1$ $n_x = n_y = n_z = 1$

$$E = [(1)^2 + (1)^2 + (1)^2]\frac{h^2}{8mL^2}$$

$$E = \frac{3h^2}{8mL^2}$$

If degeneracy = 3,

n_x	n_y	n_z
1	1	2
1	2	1
2	1	1

$$E = [(1)^2 + (1)^2 + (2)^2]\frac{h^2}{8mL^2} = \frac{6h^2}{8mL^2}$$

Hence, for degeneracy = 3, Energy will be double.

35) Ans (b):- Given, $\Psi = 0.8\,\phi_A + 0.4\,\phi_B$

$$\Psi = C_1\phi_A + C_2\phi_A$$

By comparing, $C_1 = 0.8$, $C_2 = 0.4$

Overlap between ϕ_A & ϕ_B

$C_1^2 + C_2^2 + 2C_1C_2S = 1$

Putting the values

$\therefore (0.8)^2 + (0.4)^2 + 2(0.8)(0.4)S = 1$

$\therefore 0.64 + 0.16 + 2.(0.32)S = 1$

$\therefore 0.645 = 1 - 0.80$

$\therefore S = \dfrac{0.20}{0.64}$

$\therefore S = 0.31$

36) Ans (d):- First order energy correction to the ground state will be

$E_n = <\Psi n\,|H|\,\Psi n>$

$= \Psi(x)\left\{\left|\delta\left(x - \frac{L}{2}\right)\right|\right\}\Psi(x)dx$

$\Psi(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$

We know that

$\int \Psi(x)\delta\left(x - \frac{L}{2}\right)\Psi(x)dx$

$= \int \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\delta\left(x - \frac{L}{2}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)dx$

$= \left(\frac{2}{L}\right)\int \sin^2\left(\frac{n\pi x}{L}\right)\delta\left(x - \frac{L}{2}\right)dx$

Given: $\int_{-\infty}^{\infty} f(x)\ \delta(x - a)dx$

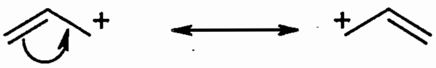
$= f(a)$

$= \left(\frac{2}{L}\right)\int \sin^2\left(\frac{n\pi x}{L} x \frac{L}{2}\right)dx$

$= \left(\frac{2}{L}\right)\int \sin^2\left(\frac{n\pi}{2}\right)dx$

$= \frac{2}{L}$ for $n = 1$

37) Ans (c):- Since the BMO is concentrated on the central carbon atom as most of the electron density of the allyl cation is located at C_2. Therefore, the positive charge is at C_1 and C_3 as (see the resonance structures of the allyl cation).



If one calculates the electron densities, there is exactly zero positive charge on the central carbon and exactly one-half unit of positive charge on each of the terminal atoms. As shown in the diagram above, the contribution to the electron density at a specific atom from a single electron in the BMO is given by the square of the coefficient of that atom in the BMO ¼ for atoms 1 and 3, & ½ for atom 2.

$$\psi_1 = \frac{1}{2}\phi_1 + \frac{1^{\frac{1}{2}}}{2}\phi_2 + \frac{1}{2}\phi_3$$

The square of the coefficient of C_2 atom = $\sqrt{\frac{1}{2}} \times \sqrt{\frac{1}{2}} = \frac{1}{2}$ = contribution of electron density.

The π electron charge on central carbon atom in propenyl cation = $\frac{1}{2} + \frac{1}{2}$ = 1 that is total contribution of electronic density.

38) Ans (d):-Microstate$= \frac{N!}{r!(N-r)!}$

Given $N = 4, r = 2$

Microstate $= \frac{4!}{2!2!} = 6$

39) Ans (c):-$\Psi(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a})$

For orthonormal function

$$\int \Psi_i\,\Psi_j d\tau = 1$$

$$\Psi(x) = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right).\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)dx$$

$$= \left(\frac{2}{a}\right)\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$= \left(\frac{2}{a}\right)\left\{\int_0^a \left[\frac{1-\cos\left(\frac{2n\pi x}{2}\right)}{2}\right]dx\right\}$$

$$= \left(\frac{2}{a}\right)\left(\frac{1}{2}\right)\int_0^a dx - \left(\frac{2}{a}\right)\left(\frac{1}{2}\right)\int_0^a \cos\left(\frac{2n\pi x}{a}\right)dx$$

$$= \left(\frac{2}{a}\right)\left(\frac{1}{2}\right)[x]_0^a - 0$$

$$= \frac{1}{a} x\, a$$

$$= 1$$

This function is orthonormal i.e. both orthogonal and normalized.

40) Ans (d):- Let, $f(x) = e^{ax^2}$

$$\Psi = \int_{-\infty}^{+\infty} \Psi.\Psi\,dx = 1 \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_}(1)$$

$$= \int_{-\infty}^{+\infty} e^{ax^2}.e^{ax^2}dx$$

$$= \int_{-\infty}^{+\infty} e^{2ax^2}dx$$

$$= \left[\frac{2ax^3}{3}e^{2ax^2}\right]_{-\infty}^{+\infty}$$

$$= e^{\infty} - e^{\infty}$$

$$= 0 \neq 1 \ldots\ldots$$

It is not normalized function. Given function is non-continuous.

41) Ans (c):- $\Psi_{2s} = \frac{1}{4\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}}\left(2 - \frac{zr}{a_0}\right)^{e^{-\frac{zr}{a_0}}}$ ______________(1)

At Node, $\Psi_{2S} = 0$

Equation (1) $\Longrightarrow \left(2 - \frac{zr}{a_0}\right) = 0$

$\therefore \frac{zr}{a_0} = 2$

$\therefore r = 2a_0$

$z = 1$ for H-atom

$\Psi_{2s}\alpha\left(2 - \frac{r}{a_0}\right)$

42) Ans (d):- In the Huckel model for benzene, the π electronic transitions from the occupied to the unoccupied molecular orbitals do not occur at 1β

43) Ans (b):- Two operator commute if following equation is true.

$[\hat{A}.\hat{B}] = [\hat{B}\,\hat{A}]$

$[\hat{A},\hat{B}] = [\hat{A}\,\hat{B}] - [\hat{B}\,\hat{A}] = 0$ ______________(1)

Let $\hat{A} = \frac{d}{dx}, \hat{B} = \frac{d^2}{dx^2} + 2\frac{d}{dx}$

$[\hat{A}\,\hat{B}]\Psi(x) \Longrightarrow$

$$= \left[\left(\frac{d}{dx}\right)\left(\frac{d^2}{dx^2} + 2\frac{d}{dx}\right)\right]\Psi(x)$$

$$= \left(\frac{d}{dx}\right)\left(\frac{d^2}{dx^2}\Psi(x) + 2\frac{d}{dx}\Psi(x)\right)$$

$$= \frac{d^3}{dx^3}\Psi(x) + 2\frac{d^2}{dx^2}\Psi(x) \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(2)}$$

$[\hat{B}\,\hat{A}]\Psi(x) \Longrightarrow$

$$= \left[\left(\frac{d^2}{dx^2} + 2\frac{d}{dx}\right)\left(\frac{d}{dx}\right)\right]\Psi(x)$$

$$= \left[\frac{d^3}{dx^3} + 2\frac{d^2}{dx^2}\right]\Psi(x)$$

$$= \frac{d^3}{dx^3}\Psi(x) + 2\frac{d^2}{dx^2}\Psi(x) \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(2)}$$

By substituting the values of equation (2) and (3) in equation (1), we get

equation (1) $\Longrightarrow [\hat{A},\hat{B}] = 0$

44) Ans (a):-Average momentum <P$_x$> is given by

$$\langle P_x\rangle = \int_0^a \Psi_n\langle P_x\rangle\Psi_n dx$$

$$= \int_0^a\left\{\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\left[-i\hbar\frac{d}{dx}\right]\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\right\}dx$$

$$= \left(\frac{2}{a}\right)(-i\hbar)\int_0^a\left\{\sin\left(\frac{n\pi x}{a}\right)\frac{d}{dx}\sin\left(\frac{n\pi x}{a}\right)\right\}dx$$

$$= \left(\frac{2}{a}\right)(-i\hbar)\int_0^a \sin\left(\frac{n\pi x}{a}\right).\cos\left(\frac{n\pi x}{a}\right)\frac{n\pi}{a}dx$$

$$= \frac{n\pi}{a}\left(\frac{2}{a}\right)(-i\hbar)\int_0^a \sin\left(\frac{n\pi x}{a}\right).\cos\left(\frac{n\pi x}{a}\right)dx$$

$$= \left(\frac{2}{a}\right)(-i\hbar)\left(\frac{n\pi}{a}\right)\int_0^a \sin\left(\frac{n\pi x}{a}\right).\cos\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{-2ni\pi\hbar}{a^2}\int_0^a \sin\left(\frac{n\pi x}{a}\right).\cos\left(\frac{n\pi x}{a}\right)dx$$

$$= 0$$

45) Ans (b):-The uncertainly in the momentum ΔP_x of particle in its lowest energy state $\Delta P_x = \frac{h}{a}$.

46) Ans (a):-% change in energy $\left(\frac{\Delta E}{E} x\, 100\right)$

$$E = \frac{n^2h^2}{8m\ell^2} \quad i.e. \quad E \,\alpha\, \frac{1}{\ell^2}$$

% change in energy $\left(\frac{\Delta E}{E} x\, 100\right)$

$$= \left(2x\,\frac{\Delta\ell}{\ell} x\, 100\right) \qquad \text{Given:- } \Delta\ell = 10^{-9} \,\&\, \ell = 10^{-3}$$

$$= \frac{2 \, x \, 10^{-9}}{10^{-3}} x\, 100 = 2 \, x \, 10^{-4}$$

47) Ans (c):-$\hat{A} = x\,;\quad \hat{B} = \frac{d}{dx}$

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \underline{\hspace{6cm}}(1)$$

$$[\hat{A}\hat{B}]\,f(x) = \left(x\,\frac{d}{dx}\right)f(x) = x.\frac{d}{dx}\,f(x)$$

$$= x.f'(x)\underline{\hspace{6cm}}(2)$$

$$[\hat{B},\hat{A}]f(x) = \left[\frac{d}{dx}.x\right]f(x)$$

$$= \frac{d}{dx}\,x.f(x)$$

$$= x\,\frac{d}{dx}\,f(x) + f(x)\frac{dx}{dx}$$

$$= x\,f'(x) + f(x)(1)\underline{\hspace{4cm}}(3)$$

equation (1) $\Rightarrow$

$$[\hat{A},\hat{B}] = x\,f'(x) - [x\,f'(x) + f(x)]$$

$$= x\,f'(x) - x\,f'(x) - f(x)$$

$$[\hat{A},\hat{B}] = -f(x)$$

48) Ans (a):- De-Broglie wavelength given by

$$\lambda = \frac{h}{mv}\underline{\hspace{4cm}}(1)$$

Also, E or K. E. $= \frac{1}{2}mv^2$

$$\therefore \quad v = \sqrt{\frac{2E}{m}}$$

Equation(1)become, $$\lambda = \frac{h}{m\sqrt{\frac{2E}{m}}}$$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

Given $\lambda = \left(\frac{a}{\phi}\right)^{1/2}$

$$\therefore \left(\frac{a}{\phi}\right)^{1/2} = \frac{h}{\sqrt{2mE}}$$

$$\therefore \frac{a}{\phi} = \frac{h^2}{2mE}$$

$$\therefore a = \frac{h^2}{2mE} \text{ x } \phi$$

$$a = \frac{h^2}{2meV} \phi$$

By substituting values, we geta $= 1.49 \text{ x } 10^{-18}$

49) Ans (b):- Bragg's equations is $n\lambda = 2d \sin\theta$

$$\therefore \sin\theta = \frac{n\lambda}{2d}$$

for diffraction, $\sin\theta \leq 1$

$$\therefore \frac{n\lambda}{2d} \leq 1$$

$$\therefore \frac{\lambda}{2d} \leq 1$$

$n = 1$ for 1st order diffraction

$\therefore \lambda \leq 2d$

50) Ans (d):- Bragg's equations is $n\lambda = 2d\sin\theta$______________________(1)

For minimum value of ϕ, λ must be maximum

λ = maximum when $\sin\theta = \sin 90^0 = 1$

for 1st order diffraction n = 1

$\lambda = 2d\sin\theta \qquad \theta = 90^0$

by putting values of n and $\sin\theta$ in eq^n (1) we get

$\lambda = 2d \ldots\ldots\ldots\ldots\ldots \sin 90^0 = 1$

Given : $$\lambda - \sqrt{\frac{a}{\phi}}$$

$$2d = \sqrt{\frac{a}{\phi}}$$

$$(2d)^2 = \frac{a}{\phi}$$

$$\therefore \phi = \frac{a}{(2d)^2} = \frac{a}{4d^2}$$

$$= \frac{1.5 \text{ x } 10^{-18}}{4\,(351.8 \text{ x } 10^{-12})^2}$$

$\therefore \phi = 3.0\text{ V}$

51) Ans (c):- Lowest energy state ; $(n_x, n_y, n_z) = (1,1,1)$

$$E_n = (n_x{}^2 + n_y{}^2 + n_z{}^2)\frac{h^2}{8mL^2}$$

$$E_{(1,1,1)} = [(1)^2 + (1)^2 + (1)^2]\frac{h^2}{8mL^2}$$

$$E_1 = \frac{3h^2}{8mL^2}$$

Given :- $E_2 = 4E_1$

$$= 4 \times \frac{3h^2}{8mL^2}$$

$$E_2 = \frac{12h^2}{8mL^2}$$

$$E_n = (n_x{}^2 + n_y{}^2 + n_z{}^2)\frac{h^2}{8mL^2}$$

By comparing, we get

$$(n_x{}^2 + n_y{}^2 + n_z{}^2) = 12$$

$$\therefore (n_x, n_y, n_Z) = (2,2,2)$$

$$\therefore \text{Degeneracy} = 1$$

52) Ans (a):- Given

$h = 6.63 \times 10^{-34}$

$m = 4 \ldots\ldots\ldots\ldots (\text{for He} - \text{atom})$

$v = 1000\ m/s$

de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.63 \times 10^{-34}}{4 \times 1.6 \times 10^{-27} \times 1000}$$

$$\lambda = 99.8 \times 10^{-12} m$$

53) Ans (c):-$E = \frac{n^2h^2}{8ml^2}$ ——————————(1)

Since, $E = h\nu, l = b$

Eq^n (1) becomes

$$h\nu = \frac{n^2h^2}{8mb^2} \text{——————————(2)}$$

For ground state n = 1

Eq^n (2) $\Rightarrow h\nu = \frac{(1)^2h^2}{8mb^2} = \frac{h^2}{8mb^2}$ ——————————(3)

For 2nd state existed state n = 3

Eq^n (2) $\Rightarrow h\nu = \frac{(3)^2h^2}{8mb^2} = \frac{9h^2}{8mb^2}$ ——————————(4)

$$\therefore h\nu = \frac{9h^2}{8mb^2} - \frac{h^2}{8mb^2}$$

$$= \frac{8h^2}{8mb^2}$$

$$h\nu = \frac{h^2}{mb^2}$$

$$\therefore \nu = \frac{h}{mb^2}$$

54) Ans (c):-Given

$$\Psi_1 = \sqrt{\frac{1}{b}}\sin\left(\frac{\pi x}{b}\right) \;\&\; \Psi_2 = \sqrt{\frac{2}{b}}\sin\left(\frac{2\pi x}{b}\right)$$

$\Psi_1 = \text{Orthogonal and } \Psi_2 = \text{Normalised}$

This is due to the condition for orthonormality are

$$\Psi(x) = \int \Psi i\, \Psi j\, d\tau = 0 \qquad \text{if } i \neq j$$

$$= 1 \qquad \text{if } i = j$$

55) Ans (d):- $\Psi = A.\sin\left(\frac{\pi x}{a}\right)$

For Normalization, we have

$$\int_0^a \Psi^2 dx = A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = 1$$

Let $\frac{\pi x}{a} = t$

$$x = \frac{a\,t}{\pi}$$

$$dx = \frac{a\,dt}{\pi}$$

as $x = 0 \Rightarrow t = 0$

$x = a \Rightarrow t = \pi$

$$\int_0^a \Psi^2 dx = A^2\left(\frac{a}{\pi}\right)\int_0^\pi \sin^2 t dt = 1$$

$$A^2\left(\frac{a}{\pi}\right) x\, \frac{\pi}{2} = 1$$

$$\therefore\ A^2 = \frac{2}{a}$$

$$\therefore\ A = \pm\sqrt{\frac{2}{a}}$$

$$\therefore\ A = \pm\sqrt{\frac{2}{200}}$$

$$= \pm\sqrt{0.01}$$

$$\therefore\ A = 0.1$$

56) Ans (d):- If Δy and Δp_y are the uncertainties in the y-coordinate and the y component of the momentum of a particle respectively, then, according to uncertainty principle $\Delta y \Delta p_y$ is ($\hbar = \frac{h}{2\pi}$ & h is Planck's constant) is $\geq \hbar/2$

57) Ans (d):- Since, CO molecule is oriented along z – axis, combination of Φz and Φz results in the formation of σ – Bonding orbital

$$\Phi z + \Phi z \longrightarrow \sigma - \text{BMO}$$

$$\Phi z - \Phi z \longrightarrow \sigma - \text{ABMO}$$

While, combination of either Φx and Φx or Φy and Φy result in formation of π –bonding orbital.

∴ wave function for π – BMO is

$$= C_1{\Phi_x}^c + C_2{\Phi_x}^0$$

58) Ans (a):- According to Huckel MOT, Secular determinant for allene radical is

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$$

59) Ans (a):-

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$$

$$= \begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

Let $\frac{\alpha - E}{\beta} = x$

$\therefore \alpha - E = x\beta$

$\therefore E = \alpha - x\beta$ ________________(1)

$$\therefore \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

By solving, we get

$x^2 = 0$; $x = 0$

$x^2 = 2$; $x = \pm\sqrt{2}$

on putting values of x in eq^n (1), we get

$E = \alpha + \sqrt{2}\beta, \ \alpha, \alpha - \sqrt{2}\beta$

60) Ans (b):- $\Psi = e^{-2x^2}$

$\hat{O} = \text{operator} = \left[\frac{d^2}{dx^2} - 16x^2\right]$

$\hat{O}\Psi = a\Psi$

$a = \text{eigen value}$

$$\left[\frac{d^2}{dx^2} - 16x^2\right]\left(e^{-2x^2}\right)$$

$$\Rightarrow \frac{d^2}{dx^2}\left(e^{-2x^2}\right) - 16x^2.e^{-2x^2}$$

$$\Rightarrow \frac{d}{dx}\left\{\frac{d}{dx}e^{-2x^2}\right\} - 16x^2.e^{-2x^2}$$

$$\Rightarrow \frac{d}{dx}\left\{-4x.e^{-2x^2}\right\} - 16x^2.e^{-2x^2}$$

$$\Rightarrow (-4)\left\{\frac{d}{dx}\left(x.e^{-2x^2}\right)\right\} - 16x^2.e^{-2x^2}$$

$$\Rightarrow (-4)\left\{x\frac{d}{dx}e^{-2x^2} + e^{-2x^2}\frac{d}{dx}x\right\} - 16x^2.e^{-2x^2}$$

$$\Rightarrow (-4)\left\{(-4x^2)e^{-2x^2} + e^{-2x^2}\right\} - 16x^2.e^{-2x^2}$$

$$\Rightarrow 16x^2.e^{-2x^2} - 4e^{-2x^2} - 16x^2.e^{-2x^2}$$

$\hat{O}\Psi = -4e^{-2x^2}$

$\hat{O}\Psi = -4\Psi$

$\therefore$ by comparing this with equation (1), we have $a = -4$, where a = eigen value

61) Ans (d):-In this case we cannot define the value of the magnetic quantum number of a $p_x$orbital& it may be +1, 0 or −1 (but the exact value depends upon symmetric axis.)

62) Ans (b):- For the given hydrogenic wave function

$$\Psi = \mathrm{Nr}\,(6 - \mathrm{zr})\mathrm{e}^{\frac{-\mathrm{zr}}{3}}\cos\theta$$

$n = 3, l = 1$ i.e. corresponds to 3p orbital

$\therefore$ Number of angular nodes $= l = 1$

$\therefore$ Also, Number of radial nodes

$$= n - l - 1$$
$$= 3 - 1 - 1$$
$$= 1$$

Hence, an angular and radial node is equal to one.

Also, $\Psi = 0$ in the xy plane and size of the orbital decreases with increase in atomic number.

List of Reference Books

1) Quantum Chemistry, by Ira N. Levine, Brooklyn, New York

2) Quantum Chemistry, by Donald A. McQuarrie, University Science Books, 2007Physical Chemistry by Peter

3) Atkins and Julio De Paula Oxford University Press

4) Quantum Chemistry, by R.K. Prasad, New Age International, 2001,

5) Principles of Physical Chemistry by Puri, Sharma and Pathania Vishal Publishing Co.

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Topic 2

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

Questions with TWO marks

1) Among SF_4, BF_4^-, XeF_4 and ICl_4^- the number of species having two lone pair of electrons on the central atom according to VSEPR theory is [*June 2011*]

(a) 2 (b) 3 (c) 4 (d) 0

2) In the molecules H_2O, NH_3 and CH_4. [*June 2011*]

(a) The bond angles are same
(b) The bond distances are same.
(c) The hybridizations are same
(d) The shapes are same.

3) The total number of lone pairs of electrons in I_3^- is [*June 2012*]

(a) Zero (b) Three (c) Six (d) Nine

4) Which ones among CO_3^{2-}, SO_3, XeO_3 and NO_3^- have planar structure? [*Dec 2012*]

(a) CO_3^{2-}, SO_3 and XeO_3,
(b) SO_3, XeO_3, and NO_3^-
(c) CO_3^{2-}, XeO_3, and NO_3^-
(d) CO_3^{2-}, SO_3, and NO_3^-

5) The number of lone-pairs are identical in the pairs [*June 2013*]

(a) XeF_4, ClF_3 (b) XeO_4, ICl_4^- (c) XeO_2F_2, ICl_4^- (d) XeO_4, ClF_3

6) According to VSEPR theory, the geometry (with lone pair) around the central iodine in I_3^+ and I_3^- ions respectively are [*Dec 2013*]

(a) tetrahedral and tetrahedal
(b) trigonal bipyramidal and trigonal bipyramidal
(c) tetrahedral and trigonal bipyramidal
(d) tetrahedral and octahedral

7) The structure of $SbPh_5$ and PPh_5 respectively are [*June 2014*]

(a) trigonal bipyramidal , square pyramidal
(b) square pyramidal , trigonal bipyramidal
(c) trigonal bipyramidal , trigonal bipyramidal
(d) square pyramidal , square pyramidal

8) The correct non-linear and iso-structural pair is [*June 2014*]

(a) SCl_2, I_3^- (b) SCl_2, I_3^+ (c) SCl_2, ClF_2^- (d) I_3^+, ClF_2^-

Questions with FOUR marks

9) According to VSEPR theory, the molecule/ion having ideal tetrahedral shape is [*June 2011*]

(a) SF_4 (b) SO_4^{2-} (c) S_2Cl_2 (d) SO_2Cl_2

10) The molecule with highest number of lone-pairs and has a linear shape based on VSEPR theory is [*June 2011*]

(a) CO_2 (b) I_3^- (c) NO_2^- (d) NO_2^+

11) Match list I (compounds) with list II (structures), and select the correct answer using the codes given below ***[Dec 2011]***

List I	***List II***
(A) XeO_4	(i) square planar
(B) BrF_4^-	(ii) tetrahedral
(C) $SeCl_4$	(iii) distorted tetrahedral.

(a) (A–ii) (B–iii) (C–i)
(b) (A–iii) (B–i) (C–ii)
(c) (A–ii) (B–i) (C–iii)
(d) (A–i) (B–ii) (C–iii)

12) Among the following pairs, those in which both species have similar structures are [*Dec 2011*]

(A) N_3^-, XeF_2
(B) $[ICl_4]^-$, $[PtCl_4]^{2-}$
(C) $[ClF_2]^+$, $[ICl_2]^-$
(D) XeO_3, SO_3

(a) (A) and (B) only
(b) (A) and (C) only
(c) (A), (B) and (C) only
(d) (B), (C) and (D) only

13) The decreasing order of dipole moment of molecules is [*June 2012*]

(a) $NF_3>NH_3>H_2O$
(b) $NH_3>NF_3>H_2O$
(c) $H_2O>NH_3>NF_3$
(d) $H_2O>NF_3>NH_3$

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

14) The shape of the molecule XeO_2F_2 is [*GATE 2005*]

(a) distorted octahedral
(b) square planar
(c) trigonal bipyramidal
(d) tetrahedral

15) $[XeO_6]^{4-}$ is octahedral whereas XeF_6 is a distorted one, because [*GATE 2006*]

(a) fluorine is more electronegative than oxygen
(b) Xe has a lone-pair in XeF_6
(c) XeF_6 is neural whereas is $[XeO_6]^{4-}$ anionic
(d) Xe–F has more ionic character

16) The pair of compounds having the same hybridization for the central atom is [*GATE 2007*]

(a) XeF_4 and $[SiF_6]^{2-}$
(b) $[NiCl_4]^{2-}$ and $[PtCl_4]^{2-}$
(c) $Ni(CO)_4$ and XeO_2F_2
(d) $[Co(NH_3)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$

17) If ClF_3, were to be stereochemically rigid, its ^{19}F NMR spectrum (I for $^{19}F = 1/2$,) would be (assume that Cl is not NMR active) ***[GATE 2008]***

(a) a doublet and a triplet
(b) a singlet
(c) a doublet and a singlet
(d) two singlets

18) The geometry around the central atom in ClF_4^+ is [*GATE 2009*]

(a) square planar
(b) square pyramidal
(c) octahedral
(d) trigonal bipyramidal

19) Among the following, the isoelectronic and isostructural pair is [*GATE 2009*]

(a) CO_2 and SO_2
(b) SO_3 and SeO_3
(c) NO_2^+ and TeO_2
(d) SiO_4^{4-} and PO_4^{3-}

20) According to VSEPR model, the shape of $[XeOF_5]^-$ is [*GATE 2010*]

(a) octahedral
(b) trigonal bipyramidal
(c) square pyramidal
(d) pentagonal monopyramidal

21) Among the following, the group of molecules that undergoes rapid hydrolysis is ***[GATE 2011]***

(a) SF_6, Al_2Cl_6, $SiMe_4$
(b) BCl_3, SF_6, $SiCl_4$
(c) BCl_3, $SiCl_4$, PCl_5
(d) SF_6, Al_2Cl_6, $SiCl_4$

22) The reaction of solid XeF_2 with AsF_5 in 1: 1 ratio affords ***[GATE 2011]***

(a) XeF_4 and AsF_3
(b) XeF_6 and AsF_3
(c) $[XeF]^+ [AsF_6]^-$
(d) $[Xe_2F_3]^+ [AsF_6]^-$

23) According to VSEPR theory, the shape of $[SF_2Cl]^+$ and $[S_2O_4]^{2-}$ should be ***[GATE 2011]***

(a) trigonal planar for $[S_2O_4]^{2-}$ and trigonal pyramidal for $[SF_2Cl]^+$
(b) both are trigonal planar
(c) trigonal pyramidal for $[S_2O_4]^{2-}$ and trigonal planar for $[SF_2Cl]^+$
(d) both trigonal pyramidal

24) The order of polarity of NH_3, NF_3 and BF_3 is ***[GATE 2012]***

(a) $NF_3 < NH_3 < BF_3$
(b) $BF_3 < NF_3 < NH_3$
(c) $BF_3 < NH_3 < NF_3$
(d) $NF_3 < BF_3 < NH_3$

25) Conversion of boron trifluoride to tetrafluoroborate accompanies ***[GATE 2013]***

(a) increase in symmetry and bond elongation
(b) increase in symmetry and bond contraction
(c) decrease in symmetry and bond contraction
(d) decrease in symmetry and bond elongation

Answer Key

Topic : 2:-Valence shell electron pair repulsion theory (VSEPR)

1	a	2	c	3	d	4	d	5	a	6	c	7	b	8	b	9	b	10	b
11	c	12	a	13	c	14	c	15	b	16	a	17	a	18	d	19	d	20	d
21	c	22	c	23	a	24	b	25	a										

Hint & solution

VSEPR theory is useful to predict the shapes of molecules, and type of hybridization,based on the number of electron pairs (bond pair + lone pair) present in valence shell of central atom. Refer table-

Steric Number ↓ lone pair ⇒	0 lp	1 lp	2 lp	3 lp
2 (sp hybridization)	linear	-	-	-
3 (sp^2 hybridization)	Trigonal planar	Angular (Bent shape)	-	-
4 (sp^3 hybridization)	Tetrahedral	Trigonal Pyramidal	Angular	
5 (sp^{3}d hybridization)	Trigonal bipyramidal	See saw *or* Distorted tetrahedral	T-shape	Linear
6 (sp^{3}d^2 hybridization)	Octahedral	Square pyramidal	Square planar	-
7 (sp^{3}d^3 hybridization)	Pentagonal bipyramidal	Pentagonal pyramidal	-	-

The shapes of molecules, and type of hybridization can be predicted by following formula which give us steric number-

$$\text{Steric number on central atom} = \frac{\text{Valence electron in central atom} + \text{no. of bonded atom(s)} - \text{positive charge} + \text{negative charge}}{2}$$

Note: - If oxygen is bonded; consider it as zero as it forms double bond.

Example:-

Steric number on xenon in XeO_2F_4 = $\frac{\text{Valence electron in central atom} + \text{no.of bonded atom(s)}}{2}$

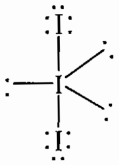
$$= \frac{8+4}{2} = 6 \text{ i.e. octahedral shape } (6 \text{ bond pair } \& \ 0 \text{ lone pair}) \ \& \text{ hybridization is } sp^3d^2$$

---

1) Ans (a):- According to VSEPR theory XeF_4 and ICl_4^- have two lone pair of electrons on the central atom.

2) Ans (c):- The hybridizations of H_2O, NH_3 and CH_4 are same (sp^3 hybridization in all)

3) Ans (d):- The shape of I_3^- is linear & the <u>total number of lone pairs</u> of electrons in I_3^- is nine



4) Ans (d):- Among CO_3^{2-}, SO_3, XeO_3 and NO_3^-; CO_3^{2-}, SO_3, and NO_3^- have planar structure

Molecule or ion	lone pair + bond pair	shape
CO_3^{2-}	0 *lp* + 3 *bp*	Trigonal planar
SO_3	0 *lp* + 3 *bp*	Trigonal planar
XeO_3	1*lp* + 3 *bp*	Tetrahedral
NO_3^-	0 *lp* + 3 *bp*	Trigonal planar

5) Ans (a):- The number of lone-pairs are identical in the XeF_4, ClF_3 & ICl_4^-

Molecule or ion	lone pair + bond pair	shape
XeF_4,	2 *lp* + 4 *bp*	Square planar
ClF_3	2 *lp* + 3 *bp*	T-shape
XeO_4	0*lp* + 4 *bp*	Tetrahedral
ICl_4^-	2 *lp* + 4 *bp*	Square planar
XeO_2F_2	1 *lp* + 4 *bp*	See saw *or* Distorted tetrahedral

6) Ans (c):- the geometry (with lone pair) around the central iodine in I_3^+ and I_3^- ions are Tetrahedral and Trigonal bipyramidal respectively

Molecule or ion	lone pair + bond pair	Geometry	Shape
I_3^+	2 *lp* + 2 *bp*	Based on Tetrahedral	Angular (Bent shape)
I_3^-	3 *lp* + 2 *bp*	Based on Trigonal bipyramidal	Linear

7) Ans (b):- The structure of $SbPh_5$ and PPh_5 are square pyramidal, trigonal bipyramidal respectively. (Hint:- due larger size of Sb, the structure of $SbPh_5$ rearrange from trigonal bipyramidal to square pyramidal shape.)

8) Ans (b):- The non-linear and iso-structural pair is SCl_2, I_3^+

Option	Molecule or ion	shape	Molecule or ion	shape
a	SCl_2,	Angular	I_3^-	Linear
b	SCl_2,	Angular	I_3^+	Angular
c	SCl_2,	Angular	ClF_2^-	linear
d	I_3^+	Angular	ClF_2^-	Linear

9) Ans (b):- Hint: - Shape of SO_2Cl_2 is not regular tetrahedral as bonded atoms are different (oxygen & chlorine)

Molecule or ion	*lp* & *bp* on central atom	shape
SF_4	1 *lp* + 4 *bp*	Distorted tetrahedral
SO_4^{2-}	0 *lp* + 4 *bp*	ideal tetrahedral
S_2Cl_2	1 *lp* + 3 *bp*	Trigonal Pyramidal
SO_2Cl_2	0 *lp* + 4 *bp*	Irregular tetrahedral

10) Ans (b):- I_3^- ion has highest number of lone-pairs and a linear shape based on VSEPR theory.

Molecule or ion	*lp* & *bp* on central atom	total no. of *lp*	shape
CO_2	0 *lp* + 2 *bp*	4 *lp*	Linear
I_3^-	3 *lp* + 2 *bp*	9 *lp*	Linear
NO_2^-	1 *lp* + 2 *bp*	6 *lp*	Angular
NO_2^+	0 *lp* + 2 *bp*	4 *lp*	Linear

11) Ans (c):-

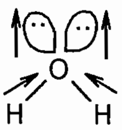
Molecule or ion	lone pair + bond pair	shape
XeO_4	0 *lp* + 4 *bp*	Tetrahedral
BrF_4^-	2 *lp* + 4 *bp*	Square planar
$SeCl_4$	1 *lp* + 4 *bp*	Distorted tetrahedral

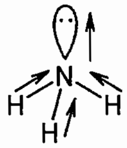
12) Ans (a):-

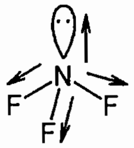
Option	Molecule or ion	shape	Molecule or ion	shape
A	N_3^-	Linear	XeF_2	Linear
B	$[ICl_4]^-$,	Square planar	$[PtCl_4]^{2-}$	Square planar
C	$[ClF_2]^+$,	Angular	$[ICl_2]^-$	linear
D	XeO_3	Trigonal Pyramidal	SO_3	Trigonal planar

13) Ans (c):- Dipole moment is vector quantity, & in H_2O & NH_3; dipole moment is due to lone pair & bond pair which reinforce in same direction but in NF_3 it is in opposite direction.

Among the H_2O & NH_3; dipole moment of H_2O is greater than NH_3 due to 2 lone pair of electron in water Therefore decreasing order of dipole moment is $H_2O > NH_3 > NF_3$







14) Ans (c):- The shape of the molecule XeO_2F_2 is trigonal bipyramidal (see-saw) with 1 *lp* + 4 *bp*

15) Ans (b):- $[XeO_6]^{4-}$ is octahedral whereas XeF_6 is a distorted one, because Xe has a one lone-pair in XeF_6

Molecule or ion	lone pair + bond pair	shape
$[XeO_6]^{4-}$	0 *lp* + 6 *bp*	Octahedral
XeF_6	1 *lp* + 6 *bp*	Pentagonal pyramidal or distorted octahedral

16) Ans (a):- The XeF_4 and $[SiF_6]^{2-}$ have the same hybridization for the central atom.

Molecule or ion	hybridization	Molecule or ion	hybridization
XeF_4	sp^3d^2	$[SiF_6]^{2-}$	sp^3d^2
$[NiCl_4]^{2-}$	sp^3	$[PtCl_4]^{2-}$	dsp^2
$Ni(CO)_4$	sp^3	XeO_2F_2	sp^3d
$[Co(NH_3)_6]^{3+}$	d^2sp^3	$[Co(H_2O)_6]^{3+}$	sp^3d^2

17) Ans (a):- The ^{19}F NMR spectrum of ClF_3 (T-shaped) shows a doublet and a triplet. Two axial F nuclei split into a doublet by the single equatorial ^{19}F nucleus, and single equatorial F nucleus split into a triplet by the two axial ^{19}F nuclei

18) Ans (d):- The geometry around the central atom in ClF_4^+ is trigonal bipyramidal with see saw shape
Total no. of pair = 5 (1*lp* + 4 *bp*)

19) Ans (d):- Among all SiO_4^{-4} & PO_4^{-3} is the isoelectronic and isostructural pair

Pair	Molecular/ion	Total electrons	Structure according to VSEPR
(a)	CO_2	22	linear
	SO_2	32	Bent or V shaped
(b)	SO_3	40	trigonal planar
	SeO_3	58	trigonal planar
(c)	NO_2^-	24	bent or V shaped
	TeO_2	68	bent or V shaped
(d)	**SiO_4^{-4}**	**50**	tetrahedral
	PO_4^{-3}	**50**	tetrahedral

20) Ans (d):- The shape of $[XeOF_5]^-$ is pentagonal monopyramidal. (1 *lp* + 6 *bp*)

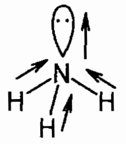
21) Ans (c):- SF_6 is very unreactive due to steric hindrance of six F^- around the central S atom & high strength of S−F bond it undergoes hydrolysis very slowly. Al_2Cl_6 exists as the dimer & therefore do undergo hydrolysis. While BCl_3, $SiCl_4$, PCl_5 undergoes rapid hydrolysis.

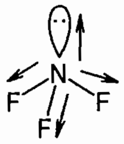
22) Ans (c):- Fluoride acceptors such as BF_3, AsF_5 and SbF_5 readily form the anions $[BF_4]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ respectively. Thus the reaction of XeF_2 with AsF_5 in 1: 1 ratio affords $[XeF]^+[AsF_6]^-$

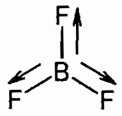
$$XeF_2 + AsF_5 \rightarrow [XeF]^+ [AsF_6]^-$$

23) Ans (a):- According to VSEPR theory, the shape of $[SF_2Cl]^+$ and $[S_2O_4]^{2-}$ should be trigonal pyramidal and unusual trigonal planar due to long sulfur-sulfur bond respectively.

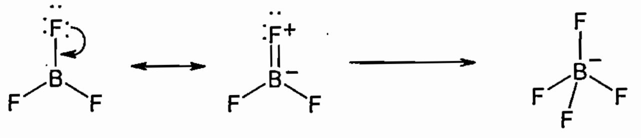
24) Ans (b):- Dipole moment is vector quantity, & in NH_3, dipole moment is due to lone pair & bond pair which reinforce in same direction but in NF_3 it is in opposite direction. In case of BF_3 dipole moment due to bond pair cancel out each other & it is non-polar. Therefore the order of polarity is $BF_3 < NF_3 < NH_3$







25) Ans (a):- In BF_3 (D_{3h}) due to stronger 2p(B)−2p(F) π back bonding; bond order of each B−F bond is greater than one while in BF_4^- (T_d) bond order of B−F is one therefore conversion of BF_3 to BF_4^- accompanies with bond elongation. Point group T_d is group of high symmetry than D_{3h}



average bond order is greater than one

average bond order is one
(bond elongation)

$$\underset{(D_{3h})}{BF_3} \longrightarrow \underset{(T_d)}{\bar{B}F_4}$$

List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited
2) Concise inorganic chemistry, By J. D. Lee, John Wiley & Sons. India.
3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.
4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press
5) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.
6) Principles of Inorganic Chemistry by Puri, Sharma and Kalia, Milestone Publisher.
7) Inorganic Chemistry by James E. House, Elsevier Science Publication.

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Topic 3

MOT OF DIATOMIC MOLECULES

Questions with two marks

1) The number of antibonding electrons in NO and CO according to MO theory are respectively. ***[Dec 2011]***
(a) 1, 0 (b) 2, 2 (c) 3, 2 (d) 2, 3

2) If a homonuclear diatomic molecule is oriented along the Z-axis, the molecular orbital formed by linear combination of p_x, orbitals of the two atoms is ***[Dec 2013]***
(a) σ (b) σ^* (c) π (d) δ

3) The molecule in which the bond order increases upon addition of an electron is ***[Dec 2013]***
(a) O_2 (b) B_2 (c) P_2 (d) N_2

4) The reason for the chemical inertness of gaseous nitrogen at room temperature is best given by its ***[Dec 2013]***
(a) high bonding energy only (b) electronic configuration
(c) HOMO-LUMO gap only (d) high bond energy and HOMO-LUMO gap

Questions with four marks

5) The highest occupied MO in N_2 and O_2^+ respectively are (take x-axis as internuclear axis) ***[June 2011]***
(a) $\sigma\ 2p_x$, $\pi^*\ 2p_y$ (b) $\pi\ 2p_y$, $\pi\ 2p_z$ (c) $\sigma^*\ 2p_x$, $\sigma\ 2p_x$ (d) $\pi^*\ 2p_y$, $\pi^*\ 2p_z$

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

) Match the following items of column I with the appropriate items in column II ***(GATE 2005)***

Column I **column II**

Molecular species **Bond order and magnetic property**

P) O_2^-
Q) O_2
R) O_2^+
S) O_2^{-2}

I 2.5 paramagnetic
II 2.0 diamagnetic
III 1.5 diamagnetic
IV 1.0 diamagnetic
V 2.0 paramagnetic
VI 1.5 paramagnetic

(a) P-III, Q-V, R-IV, S-III (b) P-III, Q-II, R-I, S-IV (c) P-III, Q-V, R-IV, S-VI (d) P-VI,Q-V, R-I, S-IV

or a homonuclear diatomic molecule, the bonding molecular orbital is ***(GATE 2007)***
(a) σ_u of lowest energy (b) σ_u of second lowest energy (c) π_g of lowest energy (d) π_u of lowest energy

he highest occupied molecular orbital of HF is ***(GATE 2008)***
(a) bonding (b) antibonding (c) ionic (d) nonbonding

ne bond order of C_2 molecule is ***(GATE 2010)***
(a) 0 (b) 1 (c) 2 (d) 3

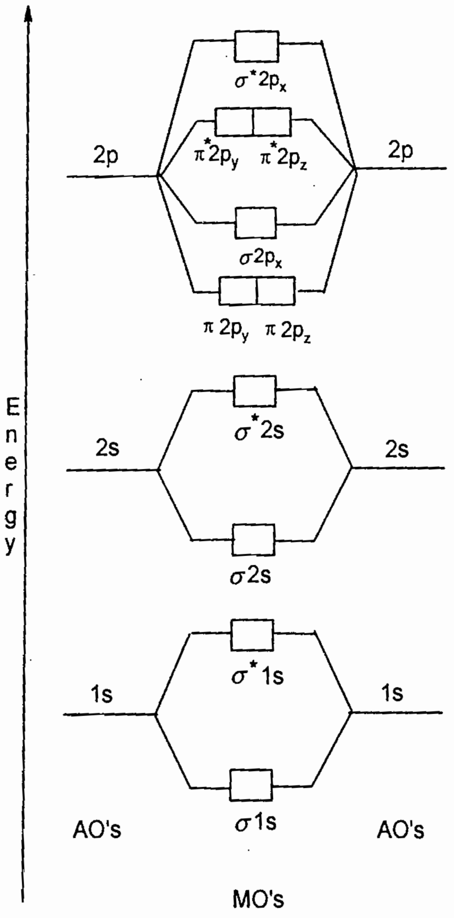
Answer Key

Topic: 3:-Molecular orbital theory of diatomic molecules

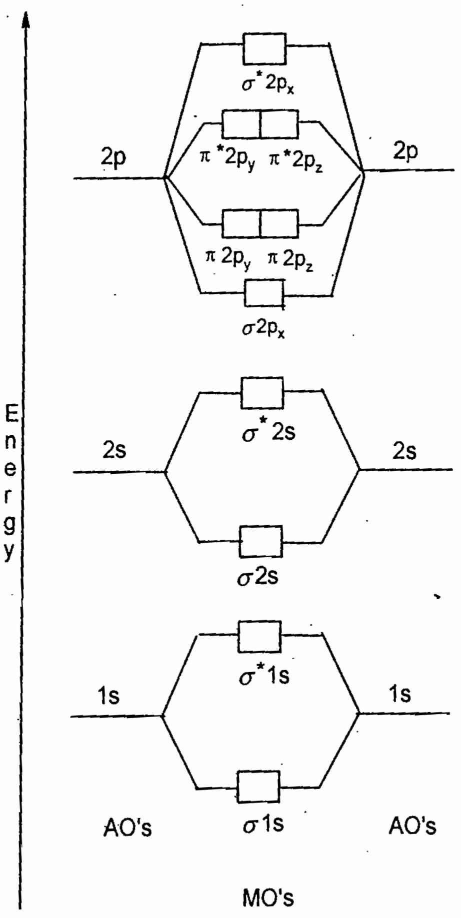
1	2	3	4	5	6	7	8	9
a	c	b	d	a	d	d	d	c

Hint & solution

General Molecular orbital diagram for diatomic molecules:-



General Molecular orbital diagram
For a molecule with or upto the14 electrons



General Molecular orbital diagram
For a molecule with a more than 14 electrons

General MO electronic configuration for diatomic molecules, ions with a or upto the 14 electrons :-

$$\sigma 1s \quad \sigma^{*}1s \quad \sigma 2s \quad \sigma^{*}2s \quad \begin{matrix}\pi 2p_y \\ \pi 2p_z\end{matrix} \quad \sigma 2p_x \quad \begin{matrix}\pi^{*}2p_y \\ \pi^{*}2p_z\end{matrix} \quad \sigma^{*}2p_x$$

$$\xrightarrow{\hspace{10cm}}$$

Energy increases

General MO electronic configuration for diatomic molecules, ions with a more than 14 electrons :-

$$\sigma 1s \quad \sigma^{*}1s \quad \sigma 2s \quad \sigma^{*}2s \quad \sigma 2p_x \quad \begin{matrix}\pi 2p_y \\ \pi 2p_z\end{matrix} \quad \begin{matrix}\pi^{*}2p_y \\ \pi^{*}2p_z\end{matrix} \quad \sigma^{*}2p_x$$

$$\xrightarrow{\hspace{10cm}}$$

Energy increases

1) Ans (a):-The number of antibonding electrons in NO and CO according to MO theory are respectively 1, 0

MO electronic configuration Of CO molecule:- (14 electrons)

$$\sigma 1s^2 \quad \sigma^*1s^2 \quad \sigma 2s^2 \quad \sigma^*2s^2 \quad \begin{matrix}\pi 2p_y^2\\ \pi 2p_z^2\end{matrix} \quad \sigma 2p_x^2 \quad \begin{matrix}\pi^* 2p_y\\ \pi^* 2p_z\end{matrix} \quad \sigma^* 2p_x$$

$$\xrightarrow{\hspace{12em}}$$

Energy increases

MO electronic configuration Of NO molecule :-(15 electrons)

$$\sigma 1s^2 \quad \sigma^*1s^2 \quad \sigma 2s^2 \quad \sigma^*2s^2 \quad \sigma 2p_x^2 \quad \begin{matrix}\pi 2p_y^2\\ \pi 2p_z^2\end{matrix} \quad \begin{matrix}\pi^* 2p_y^1\\ \pi^* 2p_z\end{matrix} \quad \sigma^* 2p_x$$

$$\xrightarrow{\hspace{12em}}$$

Energy increases

2) Ans (c):- If a homonuclear diatomic molecule is oriented along the Z-axis, the molecular orbital formed by linear combination of p_z, orbitals results in a σ bond formation while the molecular orbital formed by combination of p_x or p_y orbitals results in a π bond formation

3) Ans (b):- An extra electron always add into lower unoccupied molecular orbital (LUMO) & if LUMO is antibonding molecular orbital; it results in a decrease in bond order & if LUMO is bonding molecular orbital; it results in a increase in bond order. Note: - consider P_2 as like N_2

Molecule	LUMO
O_2	Antibonding molecular orbital
B_2	Bonding molecular orbital
P_2	Antibonding molecular orbital
N_2	Antibonding molecular orbital

Therefore bond order of B_2 molecule is increases upon addition of an electron

4) Ans (d):- The reason for the chemical inertness of gaseous nitrogen at room temperature is best given by its high bond energy and HOMO-LUMO gap. Bond order of N_2 molecule is three. Bond order & bond energy are directly related.

5) Ans (a):- The highest occupied MO in N_2 and O_2^+ respectively are $\sigma\ 2p_x$, $\pi^*\ 2p_y$

MO electronic configuration Of N_2 molecule:- (14 electrons)

$$\sigma 1s^2 \quad \sigma^*1s^2 \quad \sigma 2s^2 \quad \sigma^*2s^2 \quad \begin{matrix}\pi 2p_y^2\\ \pi 2p_z^2\end{matrix} \quad \overset{\text{HOMO}}{\sigma 2p_x^2} \quad \begin{matrix}\pi^* 2p_y\\ \pi^* 2p_z\end{matrix} \quad \sigma^* 2p_x$$

$$\xrightarrow{\hspace{12em}}$$

Energy increases

MO electronic configuration Of O_2^+ molecule :-(15 electrons)

$$\sigma 1s^2 \quad \sigma^*1s^2 \quad \sigma 2s^2 \quad \sigma^*2s^2 \quad \sigma 2p_x^2 \quad \begin{matrix}\pi 2p_y^2\\ \pi 2p_z^2\end{matrix} \quad \begin{matrix}\overset{\text{HOMO}}{\pi^* 2p_y^1}\\ \pi^* 2p_z\end{matrix} \quad \sigma^* 2p_x$$

$$\xrightarrow{\hspace{12em}}$$

Energy increases

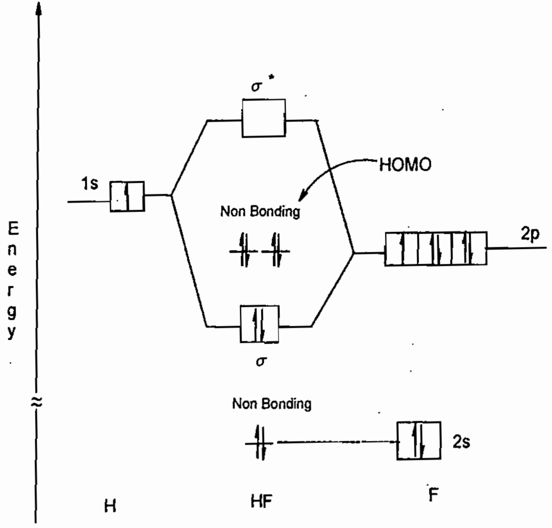
6) Ans (d):- Use MO diagram:-

Molecule/ion	Total electrons	Nb electrons	Na electrons	bond order	Magnetic properties
O_2^-	17	10	7	1.5	paramagnetic
O_2	16	10	6	2	paramagnetic
O_2^+	15	10	5	2.5	paramagnetic
O_2^{-2}	18	10	8	1	diamagnetic

7) Ans (d):- For a homonuclear diatomic molecule, the bonding molecular orbital is π_u of lowest energy

Molecular orbital
σ_u of lowest energy = Antibonding MO
σ_u of second lowest energy = Antibonding MO
π_g of lowest energy = Antibonding MO
π_u of lowest energy = bonding MO

8) Ans (d):- The highest occupied molecular orbital of HF molecule is nonbonding



9) Ans (c):-The bond order of C_2 molecule is 2.

The term bond order, (B) gives us number of bonds between two atoms & is a measure of the *net* number of electron pairs used in bonding& is given by equation:-

$$B = \frac{1}{2}N_b - N_a$$

Where N_b is number of electrons in bondingmolecular orbital& N_a is number of electrons in antibonding molecular orbital.

MO electronic configuration Of C_2 molecule :- (12 electrons)

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \begin{matrix}\pi\, 2p_y^2 \\ \pi\, 2p_z^2\end{matrix} \quad \sigma 2p_x \quad \begin{matrix}\pi^* 2p_y \\ \pi^* 2p_z\end{matrix} \quad \sigma^* 2p_x$$

$$\xrightarrow{\hspace{12cm}}$$

Energy increases

$$\textbf{Bond order of } C_2 \textbf{ molecule} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-4) = 2$$

List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited

2) Concise inorganic chemistry, By J. D. Lee, John Wiley & Sons. India.

3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.

4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press

5) Inorganic Chemistry by James E. House, Elsevier Science Publication.

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Topic 4

s AND p-BLOCK ELEMENTS

Questions with two marks

1) The correct order of stability of difluorides is ***[June 2011]***

(a) $GeF_2 > SiF_2 > CF_2$ (b) $CF_2 > SiF_2 > GeF_2$
(c) $SiF_2 > GeF_2 > CF_2$ (d) $CF_2 > GeF_2 > SiF_2$

2) Lewis acidity of BCl_3, BPh_3 and BMe_3 with respect to pyridine follows the order ***[DEC 2011]***

(a) $BCl_3 > BPh_3 > BMe_3$ (b) $BMe_3 > BPh_3 > BCl_3$
(c) $BPh_3 > BMe_3 > BCl_3$ (d) $BCl_3 > BMe_3 > BPh_3$

3) The material that exhibits the highest electrical conductivity among the following sulfur–nitrogen compounds is ***[DEC 2011]***

(a) S_4N_4 (b) S_7NH (c) S_2N_2 (d) $(SN)_X$

4) Among the following pairs ***[DEC 2011]***

(1) oxygen-sulfur (2) nitrogen -phosphorus
(3) phosphorus arsenic (4) chlorine- iodine

Those in which the first ionization energies differ by more than 300kJ mole^{-1}
(a) (1) and (3) only (b) (1) and (2) only (c) (2) and (3) only (d) (3) and (4) only

5) The size of the d orbitals in Si, P, S and Cl follows the order. ***[June 2012]***

(a) Cl > S > P > Si (b) Cl > P > S > Si (c) P > S > Si > Cl (d) Si > P > S > Cl

6) In the reactions (A) and (B), ***[June 2012]***

$$nH_2O + Cl^- \longrightarrow \left[Cl(H_2O)_n\right]^- \quad \text{..... (A)}$$

$$6\,H_2O + Mg^{2+} \longrightarrow \left[Mg(H_2O)_6\right]^{2+} \quad \text{..... (B)}$$

water behaves as
(a) An acid in both (A) and (B) (b) An acid in (A) and a base in (B)
(c) A base in (A) an acid in (B) (d) A base in both (A) and (B)

7) The electronegativity differences is the highest for the pair ***[Dec 2012]***

(a) Li, Cl (b) K, F (c) Na, Cl (d) Li, F

8) Which of the following pairs has the highest difference in their first ionization energy? ***[June 2013]***

(a) Xe, Cs (b) Kr, Rb (c) Ar, K (d) Ne, Na

9) Among the compounds A-D, those which hydrolyse easily are - ***[June 2013]***

(A) NCl_3 (B) NF_3 (C) $BiCl_3$ (D) PCl_3.

(a) A and B only (b) A, C and D only (c) B, C and D only (d) A, B and C only

10) Among the molten alkali metals, the example of an immiscible pair (in all proportions) is ***[Dec 2013]***

(a) K and Na (b) K and Cs (c) Li and Cs (d) Rb and Cs

Among the following, an example of a hypervalent species is ***[Dec 2013]***

(a) $BF_3 \cdot OEt_2$ (b) SF_4 (c) $[PF_6]^-$ (d) Sb_2S_3

Treatment of ClF_3 with SbF_5 leads to the formation of a/an ***[Dec 2013]***

(a) polymeric material (b) covalent cluster

(c) ionic compound (d) lewis acid-base adduct

When Si is doped with a group V element. ***[June 2014]***

(a) donor levels are created close to the valence band

(b) donor levels are created close to the conduction band

(c) acceptor levels are created close to the valence band

(d) acceptor levels are created close to the conduction band

The pair of solvents in which PCl_5 does NOT ionize, is ***[June 2014]***

(a) CH_3CN, CH_3NO_2 (b) CH_3CN, CCl_4 (c) C_6H_6, CCl_4 (d) CH_3CN, C_6H_6

Questions with four marks

Alkali metal superoxides are obtained by the reaction of ***[June 2011]***

(a) Oxygen with alkali metals in liquid ammonia. (b) Water with alkali metals in liquid ammonia

(c) H_2O_2 with alkali metals. (d) H_2O_2 with alkali metals in liquid ammonia.

The strength of p_π–d_π bonding in E–O (E = Si, P, S and C) follows the order ***[June 2012]***

(a) Si – O > P – O > S – O > Cl – O (b) P – O > Si – O > S – O > Cl – O

(c) S – O > Cl – O > P – O > Si – O (d) Cl – O > S – O > P – O > Si – O

Among the halides, NCl_3 (A), PCl_3 (B) and $AsCl_3$ (C), those which produce two different acids pon hydrolysis are ***[June 2012]***

ı) A and B (b) A and C (c) B and C (d) A, B and C

Match each item from the List-I (compound in solvent) with that from the List-II (its behavior) nd select the correct combination using the codes given below. ***[Dec 2012]***

List-I	**List-II**
\. CH_3COOH in pyridine	(i) strong acid.
3. CH_3COOH in H_2SO_4	(ii) weak acid
Ↄ. $HClO_4$ in H_2SO_4	(iii) strong base
). SbF_5 in HF	(iv) weak base

) (A–i), (B–ii), (C–iii), (D–iv) (b) (A–ii), (B–i), (C–iii), (D–iv)

) (A–iii), (B–iv), (C–ii), (D–i) (d) (A–iv), (B–ii), (C–iii), (D–i)

3oric acid is a weak acid in aqueous solution. But its acidity increases significantly in the ›resence of ethylene glycol, because ***[Dec 2012]***

ı) ethylene glycol releases additional H^+

›) $B(OH)_4^-$ is consumed in forming a compound with ethylene glycol.

:) ethylene glycol neutralizes H^+ released by boric acid.

l) Boric acid dissociates better in the mixed-solvent.

'he compound that will behave as an acid in H_2SO_4 is ***[June 2013]***

ɜ) CH_3COOH (b) HNO_3 (c) $HClO_4$ (d) H_2O

21) Xenon forms several fluorides and oxofluorides which exhibit acidic behavior. The correct sequence of descending Lewis acidity among the given species is represented by ***[Dec 2013]***

(a) $XeF_6 > XeOF_4 > XeF_4 > XeO_2F_2$ (b) $XeOF_4 > XeO_2F_2 > XeOF_4 > XeF_6$

(c) $XeF_4 > XeO_2F_2 > XeOF_4 > XeF_6$ (d) $XeF_4 > XeF_6 > XeOF_4 > XeO_2F_2$

22) The correct order of decreasing electronegativity of the following atoms is ***[June 2014]***

(a) As>Al>Ca>S (b) S> As>Al>Ca (c) Al > Ca >S >As (d) S> Ca >As> Al

23) The correct order of the size of S, S^{2-}, S^{2+} and S^{4+} species is ***[June 2014]***

(a) $S > S^{+2} > S^{+4} > S^{-2}$ (b) $S^{+2} > S^{+4} > S^{-2} > S$

(c) $S^{-2} > S > S^{+2} > S^{+4}$ (d) $S^{+4} > S^{-2} > S > S^{+2}$

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

24) The number of hydroxy (OH) groups present in phosphorus acid is ***(GATE 2005)***

(a) one (b) two (c) three (d) four

25) Among the following, the incorrect statement about SiC is that ***(GATE 2005)***

(a) it is known as corundum

(b) it is prepared by reducing quartz with a slight excess of coke in an electric furnace at 2000-2500°C

(c) pure SiC is almost colourless or pale yellow

(d) its hardness is slightly less than diamond

26) The incorrect statement for solid sodium chloride is that ***(GATE 2005)***

(a) both sodium and chloride ions adopt inert gas configuration

(b) the conduction band is full

(c) the conduction band is empty

(d) the valence band is full

27) The series with correct order of decreasing ionic size is ***(GATE 2006)***

(a) $K^+ > Ca^{+2} > S^{-2} > Cl^-$ (b) $S^{-2} > Cl^- > K^+ > Ca^{+2}$

(c) $K^+ > Cl^- > Ca^{+2} > S^{-2}$ (d) $Cl^- > K^+ > S^{-2} > Ca^{+2}$

28) When Al_4C_3 and Mg_2C_3 reacts with H_2O , then major products formed respectively, are ***(GATE 2006)***

(a) ethyne and ethane (b) methane and propyne

(c) propane and propene (d) methane and propene

29) The Lewis acid character of BF_3, BCl_3 and BBr_3 follows the order ***(GATE 2007)***

(a) $BF_3 < BBr_3 < BCl_3$ (b) $BCl_3 < BBr_3 < BF_3$

(c) $BF_3 < BCl_3 < BBr_3$ (d) $BBr_3 < BCl_3 < BF_3$

30) The coordination number of the Ba^{2+} ions in barium fluoride is 8. The coordination number of the fluoride ion is ***[GATE 2009]***

(a) 8 (b) 4 (c) 1 (d) 2

31) Among the following, the isoelectronic and isostructural pair is ***[GATE 2009]***

(a) CO_2 and SO_2 (b) SO_3 and SeO_3

(c) NO_2^+ and TeO_2 (d) SiO_4^{4-} and PO_4^{3-}

Statement for Linked Answer Questions 32 and 33: **[*GATE 2009*]**

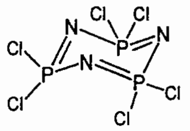
Triphosphazene is prepared by reacting X and Y in equimolar ratio at 120 -150°C using appropriate solvents.

32) The reactants X and Y, respectively, are

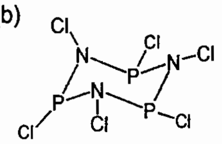
(a) PCl_3; NH_3 (b) PCl_5; NH_3 (c) PCl_5; NH_4Cl (d) PCl_3; NH_4Cl

33) The structure of triphosphazene is

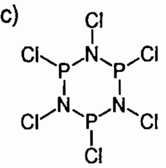
(a)



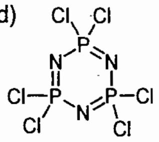
(b)



(c)



(d)



34) The Lewis acidity BF_3 is less than BCl_3 even though fluorine is more electronegative than chlorine, it is due to **[*GATE 2010*]**

(a) stronger 2p(B)–2p(F) σ bonding (b) stronger 2p(B)–2P(F) π bonding

(c) stronger 2p(B)–3p(Cl) σ bonding (d) stronger 2p(B)–3p(Cl) π bonding

35) Among the following pentachlorides the one which does not exist due to the 'inert-pair effect' is **[*GATE 2010*]**

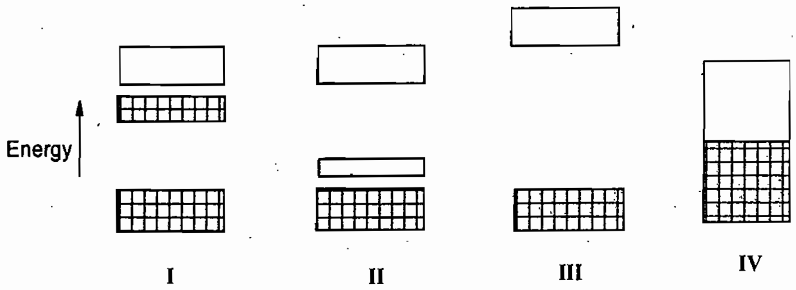
(a) PCl_5 (b) $BiCl_5$ (c) $SbCl_5$ (d) $AsCl_5$

36) Band theory predicts that magnesium is an insulator. However in practice it acts as conductor due to **[*GATE 2010*]**

(a) presence of filled 3s orbital (b) overlap of filled 2p and filled 3s orbital

(c) overlap of filled 3s and empty 3p orbital (d) presence of unfilled 3p orbital

37) The band structure in an n-type semiconductor is **[*GATE 2011*]**



(a) I (b) II (c) III (d) IV

38) Among the following, the group of molecules that undergoes rapid hydrolysis is **(*GATE 2011*)**

(a) SF_6, Al_2Cl_6, $SiMe_4$ (b) BCl_3, SF_6, $SiCl_4$

(c) BCl_3, $SiCl_4$, PCl_5 (d) SF_6, Al_2Cl_6, $SiCl_4$

39) The reaction of solid XeF_2 with AsF_5 in 1: 1 ratio affords **(*GATE 2011*)**

(a) XeF_4 and AsF_3 (b) XeF_6 and AsF_3

(c) $[XeF]^+ [AsF_6]^-$ (d) $[Xe_2F_3]^+ [AsF_6]^-$

40) Among the following donors, the one that forms most stable adduct with the Lewis acid $B(CH_3)_3$ is **[*GATE 2012*]**

(a) 4-methylpyridine (b) 2,6-dimethylpyridine

(c) 4-nitropyridine (d) 2,6-di-*tert*-butylpyridine

Statement for Linked Answer Questions 41 and 42:

Heating a mixture of ammonium chloride and sodium tetrahydridoborate gives one liquid product(X), along with other products, under ambient conditions. ***[GATE 2013]***

41) Compound X is

(a) $NH_4[BH_4]$ (b) $[(NH_3)_2BH_2][BH_4]$ (c) $N_3B_3H_6$ (d) $N_3B_3H_{12}$

42) Compound X in above reaction is an example of ***[GATE 2013]***

(a) ionic liquid (b) saturated heterocycle (c) molecular cage (d) unsaturated heterocycle

43) The number of S–S bonds in $H_2S_5O_6$ is ***[GATE 2014]***

(a) 2 (b) 3 (c) 4 (d) 5

44) The BCl_3 and NH_4Cl were heated at 140^0C to give a compound X, which when treated with $NaBH_4$ gave another compound Y. Compound X and Y are ***[GATE 2014]***

(a) X = $B_3N_3H_3Cl_3$ and Y = $B_3N_3H_6$ (b) X = $B_3N_3H_9Cl_3$ and Y = $B_3N_3H_6$

(c) X = $B_3N_3H_9Cl_3$ and Y = $B_3N_3H_{12}$ (d) X = $B_3N_3Cl_6$ and Y = $B_3N_3H_6$

← **Answer Key** →

Topic: 4:-s and p-block elements

1	a	2	b	3	d	4	b	5	d	6	b	7	b	8	d	9	b	10	c
11	c	12	d	13	b	14	c	15	a	16	d	17	c	18	c	19	b	20	c
21	a	22	b	23	c	24	b	25	a	26	b	27	b	28	b	29	c	30	b
31	d	32	c	33	d	34	b	35	b	36	c	37	a	38	c	39	c	40	a
41	c	42	d	43	c	44	a												

Hint & solution

1) Ans (a):- Hint:- Inert pair effect (As we move down the group there is a reluctance of *ns* electrons to participate in bond formation) Therefore +2 state stability will be in the order:- Ge > Si >C. Therefore the correct order of stability of difluorides is therefore $GeF_2 > SiF_2 > CF_2$

2) Ans (b):- Lewis acidity of BCl_3, BPh_3 and BMe_3 with respect to pyridine follows the order: - $BMe_3 > BPh_3 > BCl_3$. Among BCl_3, BMe_3 & BPh_3; BCl_3 is weak Lewis acidic due 2p(B)–3p(Cl) π back bonding. Among BMe_3, and BPh_3; BMe_3 is strong Lewis acid with respect to pyridine due to steric factor in BPh_3.

3) Ans (d):- Sulfur forms a variety of covalent binary nitrides, but the two most interesting ones are tetrasulfur & tetranitride S_4N_4, and disulfur dinitride, S_2N_2, because they are precursors to an unusual polymer called polythiazyl, $(SN)_x$. This polymeric sulfur nitride is unusual because, even though it is composed solely of two nonmetals, it exhibits some properties normally associated only with metals like electrical and thermal conductivity & It becomes a superconductor at 0.26 kelvin

4) Ans (b):- In case of oxygen-sulfur & nitrogen –phosphorus; the first ionization energies differ by more than $300kJmole^{-1}$. Because compared with the rest of Group; first element has the smaller size & highest electronegativity which makes it the most nonmetallic in the group & hence first ionization energy is always more compared with the rest of group & therefore ionization energies difference is more.

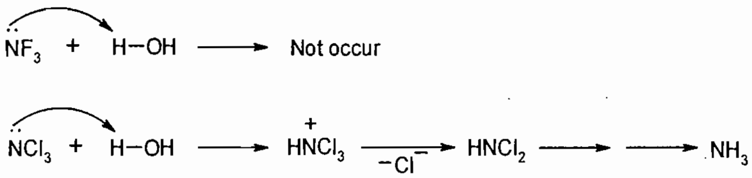
5) Ans (d):- Hint:-The size of the s, p and d orbitals generally decreases with decrease in size of an element
And as we know in periods, the atomic radius decreases across the period from left to right,
Therefore order of the size of d orbitals is Si > P > S > Cl.

6) Ans (b):- Water behaves as an acid with negatively charged species (as water donate H^+) & base with positively charged species (as water acts as electron pair donor to metal cation)

7) Ans (b):- Among metal, order of electronegativity is Li > Na > K & among halide order of electronegativity is F > Cl. Therefore an electronegativity difference is the highest for the K and F.

8) Ans (d):- Order of size of alkali metal is Na< K < Rb < Cs & first ionization energy is Na> K > Rb > Cs while that of Nobel gases; order of size is Ne< Ar <Kr < Xe & first ionization energy is Ne> Ar > Kr > Xe. Difference in first ionization energy between alkali metal & nobel gases of same period is decreases top to bottom. Thus the Na, Ne pairs has the highest difference in their first ionization energy.

9) Ans (b):- Among NCl_3, NF_3, $BiCl_3$ & PCl_3; NF_3 do not undergo hydrolyse because in NF_3 fluorine is more electronegative so attack on proton by lone of nitrogen is not possible due to decrease in basisty & polarity factor while in case of NCl_3 it is possible due despite similarity of electronegativity of both Cl & N



$BiCl_3$ rapidly undergoes hydrolysis reaction due to incomplete octect & PCl_3 also undergo hydrolysis because it acts as electron pair acceptor due to availability of *d* orbital in P

10) Ans (c):- Due to the small size; the first members in each group displays an anomalous behavior when compared to the rest of the family members. Similarly due to the very small size of lithium in the group; lithium displays an anomalous behavior when compared to sodium and rest of the family members of the alkali metal family e.g. Li is miscible with Na only and immiscible with K, Rb & Cs, whereas all other pairs of alkali metals are miscible with each other.

11) Ans (c):- A hypervalent molecule (expanded octet) is a molecule that contains one or more main group elements with more than eight electrons in their valence shells e.g. $[PF_6]^-$

12) Ans (d):- BF_3, AsF_5 and SbF_5 are the F^- acceptor & readily form the anions $[BF_4]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ respectively, due to great affinity towards F^- & it leads to the formation of a lewis acid-base adduct

$$ClF_3 + SbF_5 \rightarrow [ClF_2]^+ + [SbF_6]^-$$

13) Ans (b):- When Si is doped with a group V element element like P or As, which contains five valence electrons, donor levels are created close to the conduction band & result in increase in conductivity.

14) Ans (c):- Ionization is not possible in non-polar solvent i.e. in benzene & carbon tetra chloride.

15) Ans (a):- When the alkali metals (K, Rb and Cs) dissolve in liquid ammonia & if the solution is heated in an excess of air or in O_2, it gives electron & the result in superoxides. (KO_2, RbO_2 and CsO_2).
In short one of the electron is lose by alkali metals & gain by the oxygen.

16) Ans (d):- As the size increases, strength of p_π–d_π bonding decreases because inter nuclear distance between two atoms increases & strength of π bond decreases due to poor overlap as π bond is formed by side by side overlap. As increasing order of size is Si > P > S > Cl & therefore order of strength of p_π–d_π bonding is Cl – O > S – O > P – O > Si – O

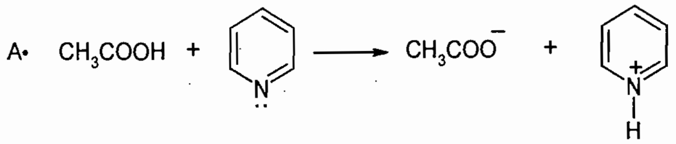
17) Ans (c):- PCl_3 and $AsCl_3$, produce two different acids upon hydrolysis.

$$NCl_3 + 3H_2O \longrightarrow NH_3\text{ (Base)} + 3\,HOCl\text{ (Acid)}$$
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3\text{ (Acid)} + 3HCl\text{ (Acid)}$$
$$AsCl_3 + 3H_2O \longrightarrow H_3AsO_3\text{ (Acid)} + 3HCl\text{ (Acid)}$$

Now question arise why NCl_3 produce NH_3 (Base) upon hydrolysis while PCl_3 & $AsCl_3$ produce H_3PO_3 (Acid) & H_3AsO_3 (Acid) respectively upon hydrolysis. It is due to the fact that NCl_3 acts as electron pair donor due to unavailability of d orbital in nitrogen whereas PCl_3 & $AsCl_3$ acts as electron pair acceptor due to availability of d orbital, (refer answer of question no. 9)

18) Ans (c):- The correct combination is:-

List-I	List-II
CH_3COOH in pyridine	strong base
CH_3COOH in H_2SO_4	weak base
$HClO_4$ in H_2SO_4	weak acid
SbF_5 in HF	strong acid

A.


B. $CH_3COOH + H_2SO_4 \longrightarrow CH_3COOH_2^+ + HSO_4^-$

C. $HClO_4 + H_2SO_4 \longrightarrow ClO_4^- + H_3SO_4^+$

D. $SbF_5 + 2\,HF \longrightarrow {}^{-}SbF_6 + H_2F^+$

19) Ans (b):- In aqueous solution, Boric acid $B(OH)_3$ form BO_4^{-4} & is consumed in forming a compound with ethylene glycol by simple condensation reaction & therefore rejoining of BO_4^{-4} with H^+ ion is not possible. Therefore acidity of boric acid increases significantly in the presence of ethylene glycol.

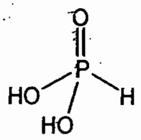
20) Ans (c):- $HClO_4$ is a stronger acid than H_2SO_4 & will behave as an acid in H_2SO_4.
Hint: - Resonance stabilization of ClO_4^- (conjugate base of $HClO_4$) is more than HSO_4^- (conjugate base of H_2SO_4) so $HClO_4$ act as a stronger acid than H_2SO_4

21) Ans (a):- Lewis acidity of a xenon fluorides and xenon oxofluorides depends upon the number of fluorine & oxidation number of Xe. Lewis acidity of a xenon fluorides and xenon oxofluorides increases with increase in the number of fluorine & higher oxidation state of Xe. So the general order of Lewis acidity of xenon fluorides and xenon oxofluorides is $XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 > XeF_2$

22) Ans (b):- The correct order of decreasing electronegativity is:- S(2.58) > As (2.18) > Al(1.61) > Ca(1).
In periodic table elctronegativity increases from left to right in period & decreases top to bottom in group.

23) Ans (c):- The correct order of the size of $S^{-2} > S > S^{+2} > S^{+4}$.
General order of size:- Anoinic species > Neutal atom > Cation species

24) Ans (b):- The number of hydroxy (OH) groups present in phosphorus acid is two



Phosphorous acid

25) Ans (a):- Silicon carbide (SiC), is also known as carborundum while Al_2O_3 is known as corundum.

26) Ans (b):- Na (Z = 11) gives up its outermost shell electron to Cl (Z=17) atom, thus the crystal is made up of ions with the electronic structures of the inert atoms Ne and Ar. In NaCl the valence band is completely filled, and the conduction band is completely empty.

27) Ans (b):- The series with correct order of decreasing ionic size is $S^{-2} > Cl^{-} > K^{+} > Ca^{+2}$
General order of size:-:- Anoinic species > Neutal atom > Cation species

28) Ans (b):- Al_4C_3 and Mg_2C_3 reacts with H_2O gives methane and propyne respectively:-

$$Al_4C_3 + 12\,H_2O \rightarrow 3\,CH_4 + 4\,Al(OH)_3$$

$$Mg_2C_3 + 4\,H_2O \rightarrow CH_3{-}C{\equiv}CH + 2\,Mg(OH)_2$$

29) Ans (c):- The Lewis acidity BF_3 is less than BCl_3 because of stronger 2p(B)−2p(F) π back bonding in case of BF_3 which is not effective in case of BCl_3 due to weaker 2p(B)−3p(Cl) π back bonding and this π back bonding become worse in case of BBr_3; due to poorer 2p(B)−4p(Br) π back bonding. Therefore Lewis acidity order is $BF_3 < BCl_3 < BBr_3 < BI_3$

30) Ans (b):- BaF_2 crystallize with the fluorite structure. Coordination number of F^- is 4 (tetrahedral)

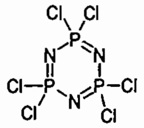
31) Ans (d):- Among all SiO_4^{-4} & PO_4^{-3} is the isoelectronic and isostructural pair

Pair	Molecular/ion	Total electrons	Structure according to VSEPR
(a)	CO_2	22	linear
	SO_2	32	Bent or V shaped
(b)	SO_3	40	trigonal planar
	SeO_3	58	trigonal planar
(c)	NO_2^-	24	bent or V shaped
	TeO_2	68	bent or V shaped
(d)	SiO_4^{-4}	50	tetrahedral
	PO_4^{-3}	50	tetrahedral

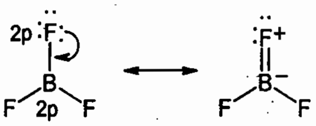
32) Ans (c):- The reactants X and Y are PCl_5; NH_4Cl respectively.

$$n PCl_5 + n NH_4Cl \xrightarrow{120\text{-}150\,^0C} (PNCl_2)_n$$

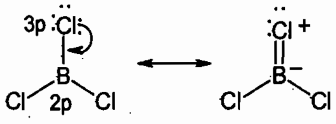
33) Ans (d):- The structure of triphosphazene is



34) Ans (b):- The Lewis acidity of BF_3 is less than BCl_3 because of stronger 2p(B)−2p(F) π back bonding in case of BF_3 which is not effective in case of BCl_3 due to weaker 2p(B)−3p(Cl) π back bonding.



back bonding is more effective



back bonding is less effective

35) Ans (b):- Inert pair effect (As we move down the group there is a reluctance of *ns* electrons to participate in bond formation). Therefore +5 state is not stable for Bi

36) Ans (c):- Filled 3s and empty 3p orbital of the Mg are very close & so result in overlapping bands due to this Mg is acts as conductor. Similarly Na & Al also acts as conductor due to the same reason.

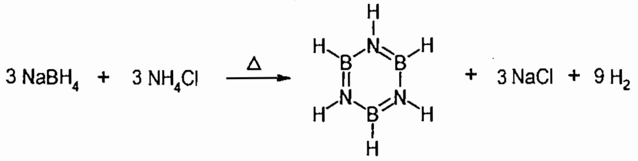
37) Ans (a):- The band structure in an n-type semiconductor is I

38) Ans (c):- Among all SF_6, Al_2Cl_6 doesn't undergo hydrolysis. In SF_6, S is in high oxidation state (VI) & as F is bad leaving group) nucleophilic attack of water is not possible while Al_2Cl_6 is dimeric structure therefore doesn't undergo hydrolysis. In case of BCl_3, $SiCl_4$ & PCl_5 water can attack on central atom & undergoes rapid hydrolysis

39) Ans (c):-The reaction of solid XeF_2 with AsF_5 in 1: 1 ratio affords $[XeF]^+ [AsF_6]^-$
Hint:- BF_3, AsF_5 and SbF_5 are the F^- acceptor & readily form the anions $[BF_4]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ respectively, due to great affinity towards F^- & it leads to the formation of a lewis acid-base adduct

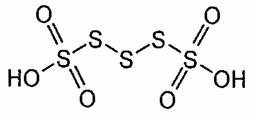
40) Ans (a):-Among 4-methylpyridine (A), 2,6-dimethylpyridine(B) & 4-nitropyridine (C) 2,6-di-*tert*-butylpyridine(D); (A) will form stable adduct because (C) will act as weak Lewis base due to electron withdrawing nitro group while in case of (B) & (D) it leads to steric crowding in adduct.

41) Ans (c):- Heating a mixture of ammonium chloride and sodium tetrahydridoborate gives borazine ($N_3B_3H_6$) known as inorganic benzene i.e. unsaturated heterocycle

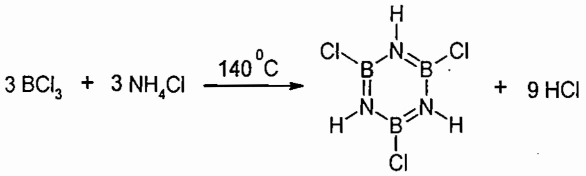


42) Ans (d):- unsaturated heterocycle

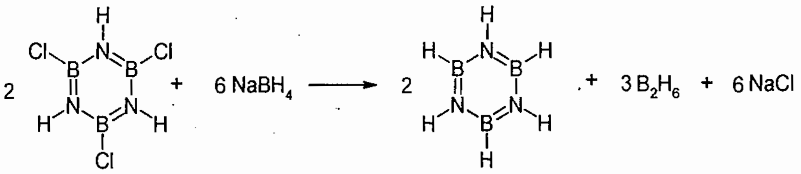
43) Ans (c):- There are four S−S bonds in $H_2S_5O_6$



44) Ans (a):- BCl_3 is first converted to trichloroborazine:



The B-Cl bonds are subsequently reduced to B-H bonds by $NaBH_4$:



List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited
2) Concise inorganic chemistry, By J. D. Lee, John Wiley & Sons. India.
3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.
4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press
5) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.
6) Inorganic Chemistry by James E. House, Elsevier Science Publication.
7) Principles of Inorganic Chemistry by Puri, Sharma and Kalia, Milestone Publisher.
8) Modern Inorganic Chemistry, By R.D.Madan & Satya Prakash, S. Chand publication

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Topic 5

TRANSITION/INNER-TRANSITION ELEMENTS

Questions with two marks

1) According to crystal field theory, Ni^{2+} can have two unpaired electrons in *[June 2011]*

(a) Both octahedral and tetrahedral geometry (b) Square-planar geometry only
(c) Tetrahedral geometry only (d) Octahedral geometry only

2) $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ complex ions are *[June 2011]*

(a) Both diamagnetic (b) Both paramagnetic
(c) Diamagnetic and paramagnetic respectively (d) Antiferromagnetic and diamagnetic respectively

3) Which of the following compounds show a charge-transfer band? *[June 2011]*

(a) Lanthanum nitrate (b) Ceric ammonium nitrate
(c) Manganese (II) acetate (d) Copper (II) sulphate pentahydrate

4) The number of possible isomers for $[Ru(bpy)_2Cl_2]$ is (where bpy = 2,2'-bipyridine) *[June 2011]*

(a) 2 (b) 3 (c) 4 (d) 5

5) The ligand system present in vitamin B_{12} is *[June 2011]*

(a) Porphyrin (b) Corrin (c) Phthalocyanine (d) Crown ether

6) The actual magnetic moment shows a large deviation from the spin-only formula in the case of *[Dec 2011]*

(a) Ti^{3+} (b) V^{3+} (c) Gd^{3+} (d) Sm^{3+}

7) The complex that absorbs light of shortest wavelength is *[Dec 2011]*

(a) $[CoF_6]^{3-}$ (b) $[Co(H_2O)_6]^{3+}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(OX)_3]^{3-}$ (OX = $C_2O_4^{2-}$)

8) Green coloured $Ni(PPh_2Et)_2Br_2$ has a magnetic moment of 3.20 B.M. The geometry and the number of isomers possible for the complex respectively, are *[Dec 2011]*

(a) square planar and one (b) tatrahedral and one
(c) Square planer and two (d) tetrahedral and two

9) Uranium fluorides co-precipitate with *[Dec 2011]*

(a) CaF_2 (b) AgF (c) LiF (d) MgF_2

10) As a ligand Cl^- *[June 2012]*

(a) Only σ- donor (b) Only π- donor (c) Both σ- & π- donor (d) A σ- donor & a π- acceptor

11) The correct d-electron configuration showing spin-orbit coupling is *[June 2012]*

(a) $t_{2g}^6 e_g^2$ (b) $t_{2g}^6 e_g^0$ (c) $t_{2g}^4 e_g^0$ (d) $t_{2g}^3 e_g^2$

12) Among the following the strongest oxidizing agent is *[June 2012]*

(a) $[WO_4]^{-2}$ (b) $[CrO_4]^{-2}$ (c) $[MoO_4]^{-2}$ (d) $[ReO_4]^{-1}$

13) The least basic among the following is ***[June 2012]***

(a) $Al(OH)_3$ (b) $La(OH)_3$ (c) $Ce(OH)_3$ (d) $Lu(OH)_3$

14) Which one of the following shows the highest solubility in hot concentrated aqueous NaOH? ***[Dec 2012]***

(a) $La(OH)_3$ (b) $Nd(OH)_3$ (c) $Sm(OH)_3$ (d) $Lu(OH)_3$

15) The light pink color of $[Co(H_2O)_6]^{2+}$ and the deep blue color of $[CoCl_4]^{2-}$ are due to ***[Dec 2012]***

(a) MLCT transition in the first and d-d transition in the second (b) LMCT transition in both
(c) d-d transition in the first and MLCT transition in the second. (d) d-d transitions in both.

16) The number of possible isomers of $[Ru(PPh_3)_2(acac)_2]$ (acac = acetylacetonate) is ***[Dec 2012]***

(a) 2 (b) 3 (c) 4 (d) 5

17) Among the following, the correct acid strength trend is represented by ***[Dec 2013]***

(a) $[Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{2+}$ (b) $[Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{2+}$
(c) $[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$ (d) $[Fe(H_2O)_6]^{2+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+}$

18) An octahedral metal ion M^{2+} has magnetic moment of 4.0 B.M. The correct combination of metal ion and d- electron configuration is given by ***[Dec 2013]***

(a) $Co^{2+}, t_{2g}^{5}e_g^{2}$ (b) $Cr^{2+}, t_{2g}^{4}e_g^{2}$ (c) $Mn^{2+}, t_{2g}^{3}e_g^{1}$ (d) $Fe^{2+}, t_{2g}^{4}e_g^{2}$

Questions with four marks

19) Among the following statements, identify the correct ones for complexes of lanthanide(III) ion ***[June 2011]***

(A) Metal-ligand bond is significantly ionic.
(B) Complexes rarely show isomerism.
(C) The coordination number is not more than 8.
(D) The magnetic moments are not accounted even approximately by spin only value for majority of lanthanides.

(a) A, B and D only (b) A, B and C only (c) B and C only (d) A and D only.

20) The correct order of LMCT energies is ***[June 2011]***

(a) $MnO_4^- > CrO_4^{-2} > VO_4^{-3}$ (b) $MnO_4^- < CrO_4^{-2} < VO_4^{-3}$
(c) $MnO_4^- > CrO_4^{-2} < VO_4^{-3}$ (d) $MnO_4^- < CrO_4^{-2} > VO_4^{-3}$

21) The complex $[Mn(H_2O)_6]^{2+}$ has very light pink color. The best reason for it is ***[June 2011]***

(a) The complex does not have a charge transfer transition.
(b) d-d transitions here are orbital forbidden but spin allowed.
(c) d-d transitions here are orbital allowed but spin forbidden.
(d) d-d transitions here are both orbital forbidden and spin forbidden.

22) *Statement I:* The sizes of Zr and Hf are similar
Statement II:* Size of Hf is affected by lanthanide contraction.** ***[June 2011]

(a) Statement I and II are correct and II is correct explanation of I.
(b) Statement I and II are correct but II is not a correct explanation of I.
(c) Statement I is correct and II is incorrect
(d) Statements I and II both are incorrect.

23) For the given complexes (A), (B), (C) & (D) the ideal octahedral geometry will not be observed in ***[June 2011]***

(A) $[\mathrm{Ni(H_2O)_6}]^{2+}$ (B) $[\mathrm{Mn(H_2O)_6}]^{2+}$ (C) $[\mathrm{Cr(H_2O)_6}]^{3+}$ (D) $[\mathrm{Ti(H_2O)_6}]^{3+}$

(a) (A) and (D) (b) (C) and (D) (c) (B) only (d) (D) only

24) The electronic configuration for gadolinium (Gd) is [Xe] $4f^7 5d^1 6s^2$ where as that of Gd^{2+} is ***[June 2011]***

(a) [Xe] $4f^5 5d 6s^2$ (b) [Xe] $4f^6 6s^2$ (c) [Xe] $4f^6 5d^1 6s^1$ (d) [Xe] $4f^7 5d^1$

25) H_2O_2 reduces ***[June 2011]***

(A) $[\mathrm{Fe(CN)_6}]^{3-}$ (B) KIO_4 (C) $Ce(SO_4)_2$ (D) SO_3^{2-}

(a) A and B only (b) B and C only (c) C and D only (d) B and D only

26) The electronic spectrum of $[\mathrm{CrF_6}]^{3-}$ shows three bands at 14,900cm^{-}, 22400cm^{-} & 34800 cm^{-}
The value of Δ_o in this case is ***[Dec 2012]***

(a) 5,500 cm^{-} (b) 14,900cm^{-} (c) 22400cm^{-} (d) 34800 cm^{-}

27) The coordination number and geometry of cerium in $[\mathrm{Ce(NO_3)_6}]^{2-}$ are respectively, ***[Dec 2011]***

(a) 6 and octahedron (b) 6 and trigonal prism (c) 8 and cubic (d) 12 and icosahedron

28) The correct order of acidity among the following species is ***[Dec 2011]***

(a) $[\mathrm{Na(H_2O)_6}]^+ > [\mathrm{Ni(H_2O)_6}]^{2+} > [\mathrm{Mn(H_2O)_6}]^{2+} > [\mathrm{Sc(H_2O)_6}]^{3+}$
(b) $[\mathrm{Sc(H_2O)_6}]^{3+} > [\mathrm{Ni(H_2O)_6}]^{2+} > [\mathrm{Mn(H_2O)_6}]^{2+} > [\mathrm{Na(H_2O)_6}]^+$
(c) $[\mathrm{Mn(H_2O)_6}]^{2+} > [\mathrm{Ni(H_2O)_6}]^{2+} > [\mathrm{Sc(H_2O)_6}]^{3+} > [\mathrm{Na(H_2O)_6}]^+$
(d) $[\mathrm{Sc(H_2O)_6}]^{3+} > [\mathrm{Na(H_2O)_6}]^+ > [\mathrm{Ni(H_2O)_6}]^{2+} > [\mathrm{Mn(H_2O)_6}]^{2+}$

29) The correct order of d-orbital splitting in a trigonal bipyramidal geometry is ***[Dec 2011]***

(a) $d_{z^2} > d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy}$ (b) $d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy} > d_{z^2}$

(c) $d_{x^2-y^2}, d_{xy} > d_{z^2} > d_{xz}, d_{yz}$ (d) $d_{z^2} > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$

30) Statement I. U(VI) is more stable than Nd(VI).
Statement II. The valence electrons in U are in *5f*, *6d* and *7s* orbitals. ***[Dec 2011]***

(a) Statements I and II are correct and Statement II is correct explanation of I.
(b) Statements I and II are correct but Statement II is not an explanation for Statement I.
(c) Statements I is correct and Statement II is incorrect.
(d) Statements I and II both are incorrect

31) The pair of lanthanides with the highest third-ionization energy is ***[June 2012]***

(a) Eu, Gd (b) Eu, Yb (c) Dy, Yb (d) Lu, Yb

32) The lanthanide(III) ion having the highest partition coefficient between tri-n-butylphosphate and conc. HNO_3 is ***[June 2012]***

(a) La(III) (b) Eu(III) (c) Nd(III) (d) Lu(III)

33) The metal complex that exhibits a triplet as well as doublet in its ^{31}P NMR spectrum is ***[June 2012]***

(a) *mer*–$[\mathrm{IrCl_3(PPh_3)_3}]^+$ (b) *trans*–$[\mathrm{IrCl(CO)(PPh_3)_2}]$
(c) *fac*–$[\mathrm{IrCl_3(PPh_3)_3}]^+$ (d) $[\mathrm{Ir(PPh_3)_4}]^+$

34) The correct spinel structure of Co_3O_4 is. ***[Dec 2012]***

(a) $(Co^{2+})_t(2Co^{3+})_oO_4$ (b) $(Co^{3+})_t(2Co^{2+}Co^{3+})_oO_4$

(c) $(Co^{2+}Co^{3+})_t(Co^{3+})_oO_4$ (d) $(2Co^{3+})_t(Co^{2+})_oO_4$

35) Consider the ions Eu(III), Gd(III), Sm(III) and Lu(III). The observed and calculated magnetic moment values are closest for the pair ***[Dec 2012]***

(a). Gd(III), Lu(III) (b) Eu(III), Lu(III) (c) Sm(III), Gd(III) (d) Sm(III), Eu(III)

36) In the solid state, the $CuCl_5^{-3}$ ion has two types of bonds. These are ***[Dec 2012]***

(a) three long and two short (b) two long and three short

(c) one long and four short (d) four long and one short

37) Identify the order representing increasing π- acidity of the following ligands C_2F_4, NEt_3, CO and C_2H_4 ***[June 2013]***

(a) $CO < C_2F_4 < C_2H_4 < NEt_3$ (b) $C_2F_4 < C_2H_4 < NEt_3 < CO$

(c) $C_2H_4 < NEt_3 < CO < C_2F_4$ (d) $NEt_3 < C_2H_4 < C_2F_4 < CO$

38) The species with highest magnetic moment (spin only value) is ***[June 2013]***

(a) $[VCl_6]^{4-}$ (b) $[\eta^5\text{–}C_5H_5)_2]Cr$ (c) $[Co(NO_2)_6]^{3-}$ (d) $[Ni(EDTA)]^{2-}$

39) Identify the pairs in which the covalent radii of elements are almost similar ***[June 2013]***

(A) Nb , Ta (B) Mo, W (C) La, Lu (D) Sc, Y

(a) A and B only (b) A and C only (c) B and C only (d) A, B and C only

40) Consider the lanthanide(III) ions......... (A) Nd(III) (B) Gd(III) (C) Dy(III)
The magnetic moment closest to the spin only value is(are) for ***[June 2013]***

(a) B only (b) A and B only (c) A and C only (d) B and C only

41) The Δ_t of the following complexes follows the order ***[June 2013]***

(A) $[CoCl_4]^{2-}$ (B) $[CoBr_4]^{2-}$ (C) $[Co(NCS)_4]^{2-}$

(a) C > A > B (b) A > B > C (c) B > A > C (d) C > B > A

42) Identify the chiral complexes from the following ***[June 2013]***

(A) $[Cr(EDTA)]^-$ (B) $[Ru(bipy)_3]^{3+}$ (C) $[PtCl(dine)]^+$

(a) A only (b) A and B only (c) A and C only (d) B and C only

43) Which of the pairs will generally result in tetrahedral coordination complexes, when ligands are Cl^- or OH^-:- (A) Be(II), Ba(II) (B) Ba(II), Co(II) (C) Co(II), Zn(II) (D) Be(II), Zn(II) ***[June 2013]***

(a) A and B (b) B and C (c) C and D (d) A and D

44) Among the following, the correct combination of complex and its color is ***[Dec 2013]***

	Complex	Color
(a)	$[Co(CN)_4]^{2-}$	Red
(b)	$[CoCl_4]^{2-}$	Orange
(c)	$[Co(NCS)_4]^{2-}$	Blue
(d)	$[CoF_4]^{2-}$	Yellow

45) $MnCr_2O_4$ is likely to have a normal spinel structure because ***[Dec 2013]***

(a) Mn^{2+} will have a LFSE in the octahedral site whereas the Cr^{3+} will not

(b) Mn is +2 oxidation state and both the Cr are in +3 oxidation state.

(c) Mn is +3 oxidation state and 1 Cr is in +2 and the other is in +3 state.

(d) Cr^{3+} will have a LFSE in the octahedral site whereas the Mn^{2+} ion will not.

46) Compounds $K_2Ba[Cu(NO_2)_6]$ (A) and $Cs_2Ba[Cu(NO_2)_6]$ (B) exhibit tetragonal elongation and tetragonal compression, respectively. The unpaired electron in A and B are found respectively, in orbitals, *[Dec 2013]*

(a) d_{z^2} and $d_{x^2-y^2}$ (b) $d_{x^2-y^2}$ and d_{z^2} (c) $d_{x^2-y^2}$ and $d_{x^2-y^2}$ (d) d_{z^2} and d_{z^2}

47) The typical electronic configurations of the transition metal centre for oxidative addition are *[June 2014]*

(a) d^0 and d^8 (b) d^5 and d^8 (c) d^8 and d^{10} (d) $d^5$and d^{10}

48) $NiBr_2$ reacts with $(Et)(Ph)_2P$ at -78^0C in CS_2 to give red compound, 'A' which upon standing at room temperature turns green to give the compound 'B' of the same formula. The measured magnetic moments of 'A' and 'B' are 0.0 & 3.2 B.M respectively. The geometry of 'A' and 'B' are *[June 2014]*

(a) Square-planar and Tetrahedral (b) Tetrahedral and Square-planar

(c) Square-planar and Octahedral (d) Tetrahedral and Octahedral

49) The maximum bond order obtained from the molecular orbitals of a transition metal dimer formed as linear combinations of d-orbitals alone is *[June 2014]*

(a) 3 (b) 4 (c) 5 (d) 6

50) In bis(dimethylglyoximato)nickel(II), the number of Ni-N , Ni-O & and intramolecular hydrogen bond(s) respectively, are *[June 2014]*

(a) 4, 0 and 2 (b) 2, 2 and 2 (c) 2, 2 and 0 (d) 4, 0 and 1

51) If L is a neutral monodentate ligand, the species $[AgL_4]^{2+}$,$[AgL_6]^{2+}$ and $[AgL_4]^{3+}$ respectively are *[June 2014]*

(a) paramagnetic, paramagnetic and diamagnetic (b) paramagnetic, diamagnetic and paramagnetic

(c) diamagnetic, paramagnetic and diamagnetic (d) paramagnetic, diamagnetic and diamagnetic

52) $[CoL_6]^{3+}$ is red in colour where as $[CoL'_6]^{3+}$is green. L and L' respectively corresponds to, *[June 2014]*

(a) NH_3 and H_2O (b) NH_3 and 1,10-phenanthroline

(c) H_2O and 1,10-phenanthroline (d) H_2O and NH_3

53) Identify the correct statement about $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ *[June 2014]*

(a) All Ni–O and Cu–O bond lengths of individual species are equal

(b) Ni–O(equatorial) and Cu–O(equatorial) bond lengths are shorter than Ni–O(axial) and Cu–O(axial) ones respectively

(c) All Ni–O bond lengths are equal whereas Cu–O (equatorial) bonds are shorter than Cu–O(axial) bonds

(d) All Cu–O bond lengths are equal whereas Ni–O(equatorial) bonds are shorter than Ni–O(axial) bonds.

54) A comparison of the valence electron configuration of the elements, Sm and Eu suggests that *[June 2014]*

(a) Sm is a better one electron reductant than Eu (b) Sm is a better one electron oxidant than Eu

(c) Facile oxidation state is +2 for both the elements (d) Both of these display similar redox behaviour.

55) Molybdoenzymes can both oxidize as well as reduce the substrates, because *[June 2014]*

(a) Mo(VI) is more stable than Mo(IV)

(b) Mo(IV) can transfer oxygen atom to the substrate and Mo(VI) can abstract oxygen atom from the substrate

(c) Conversion of Mo(VI) to Mo(IV) is not favoured

(d) Mo(VI) can transfer oxygen atom to the substrate and Mo(IV) can abstract oxygen atom from the substrate.

56) The number of stereoisomers of trans $[CoCl_2(\text{triethylenetetramine})]Br$ is *[Dec 2014]*

(a) One (b) Two (c) Three (d) Four

57) The spin-only magnetic moment and the spectroscopic ground state term symbol of manganese centre in $[MnF_6]^{3-}$ ion respectively, are *[Dec 2014]*

(a) 4.9 BM and ^5D (b) 4.9 BM and ^4F (c) 3.9 BM and ^3D (d) 4.9 BM and ^3F

58) The spin-only (μ_S) and spin plus-orbital (μ_{S+L}) magnetic moment of $[CrCl_6]^{3-}$ are ***[Dec 2014]***

(a) 3.87 BM and 5.20 BM (b) 2.84 BM and 5.20 BM

(c) 3.87 BM and 6.34 BM (d) 2.84 BM and 6.34 BM

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

59) The complexes $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$ are examples of ***(GATE 2005)***

(a) ionization isomerism (b) linkage isomerism

(c) geometric isomerism (d) optical isomerism

60) In the trigonal bipyramidal crystal field the d orbital with the highest energy is ***(GATE 2005)***

(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{yz} (d) d_{z^2}

61) The magnetic moment of the complex $K_3[CoF_6]$ is 5.0 μ_B. The total stabilization energy will be ***(GATE 2005)***

(a) $-0.4\ \Delta_0$ (b) $-0.4\ \Delta_0+P$ (c) $-2.4\Delta_0+3P$ (d) $-1.8\ \Delta_0+3P$

62) Ligand field stabilization energies are smaller for lanthanides compared to transition metals in the same oxidation state because ***(GATE 2005)***

(a) Size of lanthanide ions are larger (b) F orbitals interact less effectively with ligands

(c) Size of lanthanide ions are smaller (d) Lanthanides favour oxygen donor ligands

63) The lanthanide complex (acac = acetylacetonate; phen = 1, 10-phenanthroline that do not have square antiprismatic structure is ***(GATE 2005)***

(a) $[Ce(NO_3)_6]^{2-}$ (b) $[La(acac)_3(H_2O)_2]$ (c) $[Ce(acac)_4]$ (d) $[Eu(acac)_3(phen)]$

Linked Answer Questions (64 and 65)

64) For the complex ion $[Cu(NH_3)_6]^{2+}$, the coordination geometrical will be ***(GATE 2005)***

(a) Octahedral (b) tetragonally distorted octahedral

(c) trigonal prismatic (d) trigonal antiprismatic

65) The number of possible *d–d* transitions will be ***(GATE 2005)***

(a) One (b) two (c) three (d) four

66) The homogeneous catalyst that is used in the hydroformylation or hydrocarbonylation is based on ***(GATE 2006)***

(a) Co (b) Cr (c) Ti (d) V

67) The pair of ions that most commonly forms complexes with coordination number 2 is ***(GATE 2006)***

(a) Cd(II) and Hg(II) (b) Cu(II) and Hg(I) (c) Cd(II) and Hg(I) (d) Cu(I) and Hg(II)

68) The experimental magnetic moment of $K_3[Fe(CN)_6]$ is 2.3 μ_B and is attributable to the ***(GATE 2006)***

(a) spin–only value of low–spin Fe (b) spin–only value of high–spin Fe

(c) low–spin Fe with orbital contribution (d) high–spin Fe with orbital contribution

69) The CORRECT order of the soft character (as per HSAB principle) of the central metal ion is ***(GATE 2006)***

(a) $[CrO_4]^{2-} < [CrCl_4]^- < [Cr(bipy)_3] < [Cr(CO)_5]^{2-}$ (b) $[CrCl_4]^- < [Cr(bipy)_3] < [CrO_4]^{2-} < [Cr(CO)_5]^{2-}$

(c) $[CrO_4]^{2-} < [Cr(bipy)_3] < [Cr(CO)_5]^{2-} < [CrCl_4]^-$ (d) $[CrCl_4]^- < [CrO_4]^{2-} < [Cr(CO)_5]^{2-} < [Cr(bipy)_3]$

70) The metal ion that is expected to shift the C_1-methylene group in heptanol from 2 to 10 ppm in ^{1}H NMR is *(GATE 2006)*

(a) Eu (III) (b) Tl (III) (c) Al (III) (d) Sc(III)

71) Among, RO^- , $AsMe_3$, ROR' , CN^-, $AsMe_3$,RCO_2^- , SCN^- , the set of ligands with good π-acceptor nature are *(GATE 2006)*

(a) RO^-, RCO_2^-, SCN^- (b) RO^-, RCO_2^-, $AsMe_3$,

(c) $AsMe_3$, CN^-, SCN^- (d) RO^-, ROR', RCO_2^-

72) The set of ions expected to show Jahn-Teller distortion in their complexes is *(GATE 2006)*

(a) Ti(III), Cu(II), high-Spin Fe (III) (b) Cu(I), Ni(II), High-spin Fe (III)

(c) Cu(II), Low-Spin Fe (III), Ti (III) (d) Low-Spin Fe (III), Mn (II), Cu(I)

73) The series with correct order of increasing Δ_O in their complexes is *(GATE 2006)*

(a) $I^- < PR_3 < CH_3^- < CO$ (b) $PR_3 < CH_3^- < I^- < CO$ (c) $CH_3^- < PR_3 < I^- < CO$ (d) $I^- < CH_3^- < PR_3 < CO$

74) Coordinatede water moecules of a Cd(II) complex can be successively replaced by Br^- finally to result in $[CdBr_4]^{2-}$. In this process, the fourth equilibrium constant is observed to be higher than the third one, because *(GATE 2006)*

(a) equilibrium constant for the last step is always the highest

(b) three molecules of H_2O are released during the fourth step

(c) the aquo-Cd(II) species is a octrahedral

(d) an anion (Br^-) replaces a neutral (H_2O) molecule from the coordination sphere

75) The CORRECT statement regarding the thermodynamic stability and kinetic reactivity of metal ion complexes is that *(GATE 2006)*

(a) more stable complexes are less reactive

(b) there exists a dependence on the bulkiness of the ligand

(c) there exists no direct relation between these two phenomenon

(d) there exists a dependence on the size of the metal ion

76) The octahedral complex *or* complex ion which shows both facial and meridianal isomers is *(GATE 2007)*

(a) Triglycinatocobalt(III) (b) Tris(ethylenediamine)cobalt(III)

(c) Dichlorodiglycinatocobalt(III) (d) Trioxalatocobaltate(III)

77) The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is observed for *(GATE 2007)*

(a) Pm^{3+} (b) Eu^{3+} (c) Dy^{3+} (d) Lu^{3+}

78) The separation of trivalent lanthanide ions, Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+} can be effectively done by a cation exchange resin using ammonium o-hydroxy isobutyrate as the eluent. The order in which the ions will be separated is *(GATE 2007)*

(a) Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+} (b) Eu^{3+}, Dy^{3+}, Yb^{3+}, Lu^{3+} (c)Dy^{3+}, Yb^{3+}, Eu^{3+}, Lu^{3+} (d) Yb^{3+}, Dy^{3+}, Lu^{3+}, Eu^{3+}

79) Arrange the following metal complexes in order of their increasing hydration energy *(GATE 2007)*

$[Mn(H_2O)_6]^{2+}$	$[V(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$	$[Ti(H_2O)_6]^{2+}$
P	Q	R	S

(a) P < S < Q < R (b) P < Q < R < S (c) Q < P < R < S (d) S < R < Q < P

80) The compound which shows L ← M charge transfer is ***(GATE 2007)***

(a) $Ni(CO)_4$ (b) $K_2Cr_2O_7$ (c) HgO (d) $[Ni(H_2O)_6]^{2+}$

81) Zeise's salt is represented as ***(GATE 2007)***

(a) H_2PtCl_6 (b) $[PtCl_4]^{2-}$ (c) $[ZnCl_4]^{2-}$ (d) $[PtCl_3(\eta^2-C_2H_4)]^-$

82) The total number of isomers of $Co(en)_2Cl_2$ (en = ethylenediamine) is ***(GATE 2008)***

(a) 4 (b) 3 (c) 6 (d) 5

83) The magnetic moment of $[Ru(H_2O)_6]^{2+}$ corresponds to the presence of ***(GATE 2008)***

(a) four unpaired electrons (b) three unpaired electrons
(c) two unpaired electrons (d) zero unpaired electrons

84) The structures of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)$ in solution respectively are ***(GATE 2008)***

(a) square planar and tetrahedral (b) octahedral and square pyramidal
(c) octahedral and trigonal bipyramidal (d) tetrahedral and square planar

85) The expected magnetic moments of the first-row transition metal complexes and those of the lanthanide metal complexes are usually calculated using ***(GATE 2008)***

(a) $\mu_{s.o.}$ equation (s.o = spin only) for both lanthanide and transition metal complexes
(b) $\mu_{s.o.}$ equation for lanthanide metal complexes and μ_J equation for transition metal complexes
(c) $\mu_{s.o.}$ equation for transition metal complexes and μ_J equation for lanthanide metal complexes
(d) μ_{L+S} equation for transition metal complexes and $\mu_{s.o.}$ equation for lanthanide metal complexes

86) $CaTiO_3$, has a perovskite crystal structure. The coordination number of titanium in $CaTiO_3$ is ***(GATE 2008)***
(a) 9 (b) 6 (c) 3 (d) 12

87) Among the compounds Fe_3O_4, $NiFe_2O_4$ and Mn_3O_4 ***(GATE 2008)***

(a) $NiFe_2O_4$ and Mn_3O_4 are normal spinels (b) Fe_3O_4 and Mn_3O_4 are normal spinels
(c) Fe_3O_4 and Mn_3O_4, are inverse spinels (d) Fe_3O_4 and $NiFe_2O_4$ are inverse spinels

88) The correct statement about the Cu-N bond distances in $[Cu(NH_3)_6]^{2+}$ is ***[GATE 2009]***

(a) all the bond distances are equal
(b) the axial bonds are longer than the equatorial ones
(c) the equatorial bonds are longer than the axial ones
(d) all the bond distances are unequal

89) The number of unpaired electron(s) present in the species $[Fe(H_2O)_5(NO)]^{2+}$ which is formed during 'brown ring test' is ***[GATE 2010]***

(a) 2 (b) 3 (c) 4 (d) 5

90) Fe_3O_4 and Co_3O_4 are metal oxides having spinel structure. Considering their CFSEs, the correct statement regarding their structure is ***[GATE 2010]***

(a both have normal spinel structure
(b) both have inverse spinel structure
(c) Fe_3O_4 has a normal and Co_3O_4, are inverse spinels
(d) Fe_3O_4 has a inverse and Co_3O_4, are normal spinels

91) The d-d absorption band of $[Fe(H_2O)_6]^{2+}$ is split due to **[GATE 2010]**

(a) presence of octahedral geometry
(b) static Jahn-Teller distortion
(c) dynamic Jahn-Teller distortion
(d) presence of trigonal bipyramidal geometry

92) $[CoCl_4]^{2-}$ a blue coloured complex. Controlled-treatment of this complex with water generates two isomeric light pink coloured complexes, of composition $[Co(H_2O)_4Cl_2]$. Identify the correct point groups for $[CoCl_4]^{2-}$ and two isomeric complexes $[Co(H_2O)_4Cl_2]$. **[GATE 2010]**

(a) D_{4h} and (C_{2v} & C_{2h})
(b) Td and (C_{2v} & D_{4h})
(c) D_{4h} and (C_{2v} & D_{4h})
(d) Td and (C_{2v} & C_{4v})

93) Jahn-Teller distortion of $CuSO_4.5H_2O$ acts to **(GATE 2011)**

(a) raise symmetry
(b) remove an electronic degeneracy
(c) cause loss of H_2Oligand
(d) promote a d-electron to an antibonding molecular orbital

94) The complex that exists as a pair of enantiomers is **(GATE 2011)**

(a) *trans*-$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$
(b) *cis*-$[Co(NH_3)_4Cl_2]^+$
(c) $[Pt(PPh_3)(Cl)(Br)(CH_3)]^-$
(d) $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$

95) The crystal field stabilization energy (CFSE) value, for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is **(GATE 2011)**

(a) 20,325 cm^{-1}
(b) 12,195 cm^{-1}
(c) 10,162 cm^{-1}
(d) 8,130 cm^{-1}

96) In the isoelectronic series, VO_4^{-3}, CrO_4^{-2} and MnO_4-, all members have intense charge transfer (CT) transitions. The INCORRECT statement is **(GATE 2011)**

(a) CT transitions are attributed to excitations of electrons from ligand (σ) to metal (e)
(b) MnO_4^- exhibits charge transfer at shortest wavelength among the three
(c) The wavelengths of transitions increase in the order $VO_4^{-3} < CrO_4^{-2} < MnO_4^-$
(d) The charge on metal nucleus increases in the order $VO_4^{-3} < CrO_4^{-2} < MnO_4^-$

97) The increasing order of wavelength of absorption for the complex ions **(GATE 2011)**
i) $[Cr(NH_3)_6]^{3+}$, ii) $[CrCl_6]^{3-}$, iii) $[Cr(OH_2)_6]^{3+}$, iv) $[Cr(CN)_6]^{3-}$ is

(a) iv < ii < i < iii
(b) iv < iii < ii < i
(c) iv < i < iii < ii
(d) ii < iii < i < iv

98) The complex with *inverse*-spinel structure is **[GATE 2012]**

(a) Co_3O_4
(b) Fe_3O_4
(c) $MgAlO_4$
(d) Mn_3O_4

99) The enthalpies of hydration of Ca^{2+}, $Mn^{2+}$and Zn^{2+} follow the order **[GATE 2012]**

(a) $Mn^{2+} > Ca^{2+} > Zn^{2+}$
(b) $Zn^{2+} > Ca^{2+} > Mn^{2+}$
(c) $Mn^{2+} > Zn^{2+} > Ca^{2+}$
(d) $Zn^{2+} > Mn^{2+} > Ca^{2+}$

100) The IUPAC nomenclature of $Na[PCl_6]$ is **[GATE 2012]**

(a) sodium hexachlorophosphine(V)
(b) sodium hexachlorophosphate(V)
(c) sodium hexachlorophosphine
(d) sodium hexachlorophosphite(V)

101) The INCORRECT statement about Zeise's salt is **[GATE 2012]**

(a) Zeise's salt is diamagnetic
(b) The oxidation state of Pt in Zeise's salt is +2
(c) All the Pt−Cl bond lengths in Zeise's salt are equal
(d) C−C bond length of ethylene moiety in Zeise's salt is longer than that of free ethylene molecule

102) The number of possible isomers for the square planar mononuclear complex [$(NH_3)_2M(CN)_2$] of a metal M is ***[GATE 2012]***

(a) 2 (b) 4 (c) 6 (d) 3

103) The correct statement with respect to the bonding of the ligands, Me_3N and Me_3P with the metal ions Be^{2+} and Pd^{2+} is, ***[GATE 2013]***

(a) The ligands bind equally strong with both the metal ions as they are dicationic
(b) The ligands bind equally strong with both the metal ions as both the ligands are pyramidal
(c) The binding is stronger for Me_3N with Be^{2+} and Me_3P with Pd^{2+}
(d) The binding is stronger for Me_3N with Pd^{2+} and Me_3P with Be^{2+}

104) The correct electronic configuration and spin only magnetic moment of Gd^{3+} (At.No. 64) are ***[GATE 2013]***

(a) [Xe]$4f^7$ and 7.9 BM (b) [Xe]$4f^7$ and 8.9 BM
(c) [Xe]$4f^6 5d^1$ and 7.9 BM (d) [Rn]$5f^7$ and 7.9 BM

105) Among the following octahedral complexes, the one that has the highest enthalpy of hydration is ***[GATE 2013]***

(a) $[Ca(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{2+}$ (c) $[V(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

106) The geometries of $Ni(CO)_4$ and $[NiCl_4]^{2-}$, respectively, are ***[GATE 2014]***

(a) tetrahedral and square planar (b) square planar and tetrahedral
(c) tetrahedral and tetrahedral (d) square planar and square planar

107) The complexes $[Co(H_2O)_4Cl_2]NO_2$ and $[Co(H_2O)_4Cl(NO_2)]Cl$ are ***[GATE 2014]***

(a) linkage isomers (b) positional isomers (c) ionization isomers (d) optical isomers

108) Amongst the following, the complex ion that would show strong Jahn-Teller distortion is ***[GATE 2014]***

(a) $[Cr(H_2O)_6]^{2+}$ (b) $[Ti(H_2O)_6]^{3+}$ (c) $[Co(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{2+}$

109) Amongst the following, the complex ion that is expected to show the highest magnetic moment at room temperature is ***[GATE 2014]***

(a) $[Ni(CN)_4]^{2-}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Cu(H_2O)_6]^{2+}$ (d) $[Co(CN)_6]^{3-}$

110) $MnCr_2O_4$ is ***[GATE 2014]***

(a) normal spinel with total CFSE of −15.5 Dq

(b) inverse spinel with total CFSE of −15.5 Dq

(c) normal spinel with total CFSE of −24 Dq

(d) inverse spinel with total CFSE of −24 Dq

Answer Key

Topic: 5:-Transition/Inner-transition Elements:-

1	a	2	c	3	b	4	d	5	b	6	d	7	c	8	b	9	a	10	c
11	c	12	b	13	a	14	d	15	d	16	b	17	c	18	a	19	d	20	b
21	d	22	a	23	d	24	d	25	a	26	b	27	d	28	a	29	d	30	b
31	b	32	d	33	a	34	a	35	a	36	a	37	d	38	a	39	a	40	b
41	a	42	b	43	c	44	c	45	d	46	b	47	c	48	a	49	c	50	a
51	a	52	a	53	c	54	b	55	d	56	c	57	a	58	a	59	a	60	d
61	a	62	b	63	a	64	b	65	a	66	a	67	d	68	c	69	a	70	a
71	c	72	c	73	a	74	b	75	c	76	a	77	b	78	a	79	a	80	a
81	d	82	b	83	d	84	a	85	c	86	b	87	d	88	b	89	d	90	d
91	c	92	b	93	b	94	d	95	a	96	b	97	c	98	b	99	d	100	b
101	c	102	a	103	c	104	a	105	c	106	c	107	c	108	a	109	b	110	c

Hint & solution

1) Ans (a):- According to crystal field theory, Ni^{2+} can have two unpaired electrons in both octahedral and tetrahedral geometry. Square-planar complexes are always diamagnetic.

2) Ans (c):- According to crystal field theory, $[Ni(CN)_4]^{2-}$ is a square-planar diamagnetic complex and $[NiCl_4]^{2-}$ is a tetrahedral paramagnetic complex

3) Ans (b):- Ceric ammonium nitrate show a charge-transfer band.(Ligand-to-metal charge-transfer transitions are observed in the visible region of the spectrum when the metal is in a high oxidation state; here Ce is in high oxidation state i.e. Ce(IV))

4) Ans (d):- The number of possible isomers for $[Ru(bpy)_2Cl_2]$ are 5

5) Ans (b):- The ligand system present in vitamin B_{12} is Corrin.
The ligand system present in haemoglobin (Fe) and in chlorophyll (Mg) is Porphyrin.

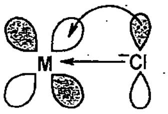
6) Ans (d):- Magnetic moment of transition metal is calculated by spin only formula while magnetic moment of lanthanides is calculated by both spin as well as orbital contribution but in case of Gd^{+3} the value of L= 0 i.e. orbital contribution is zero so it does not show a large deviation from the spin-only formula so answer is Sm^{3+} which belongs to lanthanides series with $L \neq 0$.

7) Ans (c):- The complex that absorbs light of shortest wavelength is [$Co(NH_3)_6$ $]^{3+}$
Hint:- Spectrochemical series of ligand

8) Ans (b):- $Ni(PPh_2Et)_2Br_2$ is a tetrahedral complex according to given magnetic moment and therefore do not show isomerism unless all four ligands are different or where there are two unsymmetrical bidentate chelating ligands. Therefore the geometry and the number of isomers possible for the complex are tatrahedral and one respectively

9) Ans (a):- Uranium fluorides co-precipitate with CaF_2

10) Ans (c):- As a ligand Cl^- is both σ- & π- donor (π-bases) other examples are OH^-, H_2O etc.



11) Ans (c):- Spin-orbit coupling is shown by the d-electron configuration with unsymmetrical electrons in t_{2g} Orbital i.e. $t_{2g}{}^4e_g{}^0$

12) Ans (b):- The strongest oxidizing agent is $[CrO_4]^{-2}$ due to smaller size of Cr^{+6} it is more electronegative so it has strong oxidizing power among all.

13) Ans (a):- The least basic is $Al(OH)_3$. The acidic character of hydroxides of lanthanides increases as the size decreases from $La^{3+}$to Lu^{3+} (consequences of lanthanide contraction). However basic strength decreases. $La(OH)_3$ thus is most basic whereas Lu $(OH)_3$ is least basic but size of Al^{+3} is smaller than Lu^{+3} so it is least basic among the all. Similarly, the basicity of oxides also decreases in the order from La^{3+} to Lu^{3+}.

14) Ans (d):- Among all Lu $(OH)_3$ is acts as acidic (consequences of lanthanide contraction) so it has highest solubility in hot concentrated aqueous NaOH

15) Ans (d):- because of d-d transitions in both as no possibility of LMCT & MLCT in both (according to concept of LMCT & MLCT)

16) Ans (b):- The number possible isomers of $[Ru(PPh_3)_2(acac)_2]$ are cis & trans. The cis isomer does exist as optical isomers because it does not have a mirror plane or centre of inversion (it does have a C_2 axis); while the trans isomer has mirror planes and an centre of inversion and therefore cannot be optical active. The number possible isomers of $[Ru(PPh_3)_2(acac)_2]$ are 3

17) Ans (c):- The acidic character of hydroxides is directly proportional to the charge density on a metal ion. Generally cation with smaller size has a greater charge density.
Size increase in the order:- $Al^{+3}<Fe^{+3}<Fe^{+2}$ &
hence order of acidic character is reverse i.e. $[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$

18) Ans (a):- An octahedral metal ion M^{2+} with three unpaired electrons has magnetic moment of 4.0 B.M. i.e. high spin Co^{+2}

unpaired electrons	Formula = $\sqrt{n(n+2)}$	magnetic moment (by spin only formula)
1	$\sqrt{1(1+2)} = \sqrt{3}$	1.73 B.M.
2	$\sqrt{2(2+2)} = \sqrt{8}$	2.82 B.M.
3	$\sqrt{3(3+2)} = \sqrt{15}$	3.87 B.M.
4	$\sqrt{4(4+2)} = \sqrt{24}$	4.9 B.M.
5	$\sqrt{5(5+2)} = \sqrt{35}$	5.91 B.M.

19) Ans (d):- Lanthanide(III) ion complexes show isomerism & the coordination number generally 6 to 12. So option (b) & (c) are incorrect & option (a) & (d) are correct options

20) Ans (b):- As the size of central metal ion increases trend in LMCT energies is also increases. Order of size is $V^{+5} > Cr^{+6} > Mn^{+7}$ ∴ $MnO_4^- < CrO_4^{-2} < VO_4^{-3}$

21) Ans (d):- In complex $[Mn(H_2O)_6]^{2+}$, Mn^{2+} is in the high spin d^5 system so there is both orbital forbidden and spin forbidden therefore it is light pink in colour.

22) Ans (a):- Hint:- consequences of lanthanide contraction & each element beyond lanthanum has similar atomic radius as that of the element lying above it in the group (e.g. Zr 145 pm, Hf 144 pm); (Nb 134 pm, Ta 134 pm); (Mo 129 pm, W 130 pm).

23) Ans (d):- $[Ti(H_2O)_6]^{3+}$ shows distortion in octahedral geometry due to weak Jahn Teller distortion

24) Ans (d):- The electronic configuration for gadolinium Gd^{2+} is [Xe] $4f^7\,5d^1$

25) Ans (a):- H_2O_2 reduces $[Fe(CN)_6]^{3-}$, KIO_4 only

26) Ans (b):- In $[CrF_6]^{3-}$ Cr is in +3 oxidation state i.e. d^3system & for d^3 system the value of $\Delta_o = \nu_1$ that is 14,900 cm^-, in this case. (On the basis of orgel diagram)

Configuration	stabilization energy (in D_q)	Frequencies
d^2	10 D_q	$\nu_3-\nu_1$
d^3, d^8	10 D_q	ν_1
d^7	10 D_q	$\nu_2-\nu_1$

27) Ans (d):- In $[Ce(NO_3)_6]^{2-}$ each NO_3^- ligand is bonded to the ceric ion by two O atoms and therefore Coordination Number = 2 × $6NO_3^-$ = 12 and icosahedron

28) Ans (a):- Hint:-Hydration energy is proportional to CFSE. But when CFSE is same metal ion with smaller size have more hydration energy. (in period left to right size decreases).
Among all size of Na^+ ion is smallest
so order of acidic character of hydroxides is $[Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+}$

Complex	Configuration	CFSE
$[Sc(H_2O)_6]^{3+}$	$t_{2g}^0 e_g^0$	0 Δ_0
$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3 e_g^2$	0 Δ_0
$[Ni(H_2O)_6]^{2+}$	$t_{2g}^6 e_g^2$	−1.2 Δ_0

29) Ans (d):- Order of d-orbital splitting in a trigonal bipyramidal geometry is $d_{z^2} > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$.

	Energies of *d*-Orbitals in Ligand Fields in Dq Units				
Energy Δ_0	7.07	−0.82	−0.82	−2.72	−2.72
d-orbital	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}

30) Ans (b):- Statements I and II are correct but Statement II is not an explanation for Statement I.

31) Ans (b):- Because for Eu, Yb; +2 oxidation state is more stable than +3 therefore energy required for third-ionization energy is high.

32) Ans (d):- Lu(III) has highest partition coefficient due smaller in size

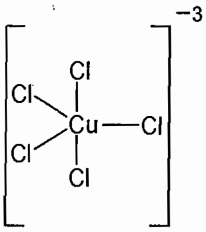
33) Ans (a):- The metal complex *mer*–[$IrCl_3(PPh_3)_3]^+$ exhibits a triplet as well as doublet in its ^{31}P NMR spectrum. Note:- In the *fac* and *mer* isomers, all P atoms are equivalent in the *fac* isomer while two environments exist in case of *mer* isomer.

34) Ans (a):- The correct spinel structure of Co_3O_4 is $(Co^{2+})_t(2Co^{3+})_oO$.
Here Co^{3+} is a low spin system even in presence of weak field oxo ligands due to high charge on the Co^{3+} metal ion

35) Ans (a):- The observed and calculated magnetic moment values are closest for the pair Gd(III), Lu(III)

Metal ion	Calculated Magnetic moment	Observed Magnetic moment
Sm(III),	0.84	1.5-1.6
Eu(III)	0	3.4-3.5
Gd(III),	7.94	7.8-7.9
Lu(III)	0	0

36) Ans (a):- In the solid state, the $CuCl_5^{-3}$ ion two types of bonds (three long and two short)



37) Ans (d):- increasing π- acidity order of $:NEt_3$ (not acts as π acceptor) < $H_2C=CH_2$ < $F_2C=CF_2$ < $:C\equiv O^+$

38) Ans (a):- The species with highest magnetic moment (spin only value) is $[VCl_6]^{4-}$

Complex	Unpaired electron	Magnetic moment
$[VCl_6]^{4-}$	3	~3.9
$[\eta^5-C_5H_5)_2]Cr$	2	~2.8
$[Co(NO_2)_6]^{3-}$	0 (low spin)	0
$[Ni(EDTA)]^{2-}$	2	~2.8

39) Ans (a):- It is consequences of lanthanide contraction & each element beyond lanthanum has same atomic radius as that of the element lying above it in the group (e.g. Zr 145 pm, Hf 144 pm); (Nb 134 pm, Ta 134 pm); Mo 129 pm, W 130 pm).

40) Ans (b):- The magnetic moment closest to the spin only value are for Nd(III) & Gd(III)

Metal ion	Magnetic moment	
	Spin only	Spin + orbital
Nd(III) = $4f^3$	3.9	3.62
Gd(III) = $4f^7$	7.9	7.94
Dy(III) = $4f^9$	2.7	10.63

41) Ans (a):- Hint:- Spectrochemical series

42) Ans (b):- In$[\text{Cr(EDTA)}]^-$ & $[\text{Ru(bipy)}_3]^{3+}$ has a neither mirror plane of symmetry nor a centre of inversion; so both are chiral while in case of $[\text{PtCl(dine)}]^+$ plane of symmetry and hence it is achiral.

43) Ans (c):- Co(II), Zn(II) & Be(II) will form tetrahedral coordination complexes, when ligands are Cl^- or OH^-

44) Ans (c):- Hint:- Spectrochemical series

45) Ans (d):- $MnCr_2O_4$ is likely to have a normal spinel structure because Cr^{3+} (d^3) will have a LFSE in the octahedral site whereas the Mn^{2+} (d^5) ion will not. Generally metal ion (M^{+2}/M^{+3}) with greater LFSE will occupy in an octahedral site.

46) Ans (b):- Hint:- Jahn Teller distortion [d^9 system of Cu(II) shows dynamic Jahn Teller distortion

The energy order of tetragonal elongation for an octahedral complex {$K_2Ba[Cu(NO_2)_6]$}

$$d_{xz} \sim d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$$

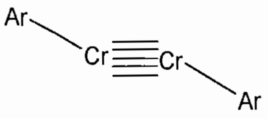
The energy order of tetragonal compression for an octahedral complex { $Cs_2Ba[Cu(NO_2)_6]$}

$$d_{xy} < d_{xz} \sim d_{yz} < d_{x^2-y^2} < d_{z^2}$$

47) Ans (c):- Oxidative addition reactions are favoured by electron rich metal centers (d^8 & d^{10}) as during oxidative addition reactions there is increase in oxidation number of the metal centre by 2 (0 to +2 or +1 to +3 etc).

48) Ans (a):- From the given magnetic data geometry of A & B is square-planar and tetrahedral respectively.

49) Ans (c):- Recent study showed that the concept of metal-metal multiple bonds are extended to *five* known as Quintuple Bonds; e.g



quintuple bonding

In such cases the ligand forms a bond with the 4s orbitals of Cr & hence d-orbitals available for Cr-Cr bonding. Quintuple bond results in a trans-bent geometry rather than linear geometry.

50) Ans (a):- Refer structure of $Ni(DMG)_2$ complex

51) Ans (a):- Hint:- d^8 system of 4d & 5d series generally form Square planar complexes

Complex	System	Geometry	Magnetism
$[AgL_4]^{2+}$	d^9	Tetrahedral	Paramagnetic
$[AgL_6]^{2+}$	d^9	Octahedral	Paramagnetic
$[AgL_4]^{3+}$	d^8	Square planar	Diamgnetic

52) Ans (a):- $[CoL_6]^{3+}$ is red in colour (absorb shorter wavelength) where as $[CoL'_6]^{3+}$ is green (absorb longer wavelength). Therefore L and L' are, NH_3 and H_2O; according to spectrochemical series

53) Ans (c):- In $[Ni(H_2O)_6]^{2+}$ it is a d^8 system no Jahn Teller distortion (symmetrical filling in t_{2g} & e_g orbital) and in case of $[Cu(H_2O)_6]^{2+}$ it is a d^9 system shows dynamic Jahn Teller distortion (due to unsymmetrical filling in e_g orbital). Therefore in $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$, all Ni–O bond lengths are equal whereas Cu–O (equatorial) bonds are shorter than Cu–O(axial) bonds

54) Ans (b):- Sm ($4f^6 5d^0 6s^2$) is a better one electron oxidant than Eu so that it attain more stable configuration ($4f^7 5d^0 6s^2$)

55) Ans (d):- Due to characteristic property of transition metal to show variable oxidation state and that is why they are involved in biological electron transfer reaction. Molybdoenzymes can both oxidize as well as reduce the substrates, because Mo(VI) can transfer oxygen atom to the substrate and Mo(IV) can abstract oxygen atom from the substrate.

56) Ans (c):- The number of stereoisomers of trans $[CoCl_2(triethylenetetramine)]Br$ is 3

57) Ans (a):- In $[MnF_6]^{3-}$ Mn^{3+} is in +3 i.e. d^4 system (with 4 unpaired electron (high spin complex))
∴ magnetic moment is 4.9 BM
Ground state term symbol = ^{2S+1}L (where *s* is total spin angular momentum quantum number & *L* is a total orbital angular momentum quantum number). 2S+1 = 5 & L= 2 i.e. D term ∴ Ground state term symbol = ^5D

58) Ans (a):- The spin-only (μ_S) and spin plus-orbital (μ_{S+L}) magnetic moment of $[CrCl_6]^{3-}$ 3.87 BM and 5.20 BM & is calculated by formulae:-

$$\mu_{\text{(spin only)}} = \sqrt{n(n+2)} \quad \text{and} \quad \mu_{\text{(eff.)}} = \sqrt{4S(S+1) + L(L+1)}$$

59) Ans (a):- The complexes $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$ are examples of ionization isomerism

60) Ans (d):- Splitting of the d orbitals in trigonal bipyramidal crystal field with increasing energy is:-
In the trigonal bipyramidal crystal field the d_{z^2} orbital is with the highest energy ($d_{z^2} > d_{xy} \sim d_{x^2-y^2} > d_{xz} \sim d_{yz}$)

	Energies of *d*-Orbitals in Ligand Fields in Dq Units				
Energy Δ_o	7.07	−0.82	−0.82	−2.72	−2.72
d-orbital	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}

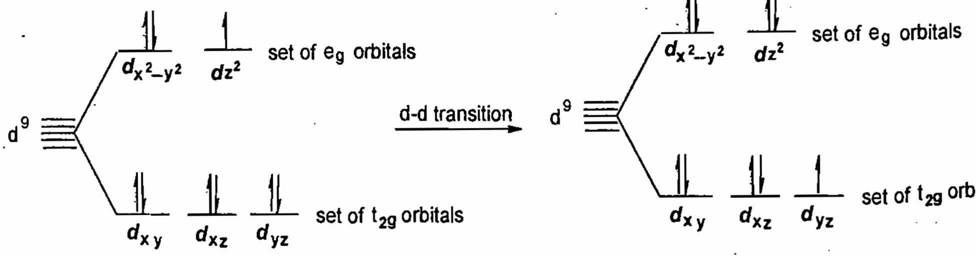
61) Ans (a):- Magnetic moment of complex $K_3[CoF_6]$, is 5.0 μ_B which clearly indicate that Co is in +3 oxidation state with high spin $t_{2g}^4e_g^2$ electrons. Therefore the total stabilization energy will be −0.4 Δ_0.
(each electron in t_{2g} orbital corresponds to −0.4 Δ_0 & each electron in e_g orbital corresponds to +0.6 Δ_0)
The total stabilization energy = (electrons in t_{2g} orbital × −0.4 Δ_0) + (electrons in e_g orbital × 0.6 Δ_0)

62) Ans (b):- Ligand field stabilization energies are smaller for lanthanides compared to transition metals in the same oxidation state because f orbitals interact less effectively with ligands since the 4f electrons are well shielded and not affected by the environment of the ion

63) Ans (a):- The coordination number of metal ion in case of square antiprismatic structure is 8 but in $[Ce(NO_3)_6]^{2-}$ the coordination number of Ce(IV) ion is 12 & is icosahedrons structure.
(Each NO_3^- ligand is bonded to the ceric by two O atoms in $[Ce(NO_3)_6]^{2-}$)

64) Ans (b):- For the complex ion $[Cu(NH_3)_6]^{2+}$, the coordination geometry will be tetragonally distorted octahedral (Hint:- Jahn Teller distortion [d^9 system of Cu(II) shows dynamic Jahn Teller distortion]

65) Ans (a):- According to Spin selection rule the number of possible d-d transition for the $[Cu(NH_3)_6]^{2+}$ complex ion is only one i.e. degenerate t_{2g} orbital to e_g orbital.



Cu^{+2} in octahedral complexes
ground state

Cu^{+2} in octahedral complexes
excited state

66) Ans (a):- The homogeneous catalyst that is used in the hydroformylation or hydrocarbonylation is based on Co

67) Ans (d):- Metal ions that most commonly forms complexes with coordination number 2 are Cu(I), Ag(I), and Hg(II), & all d^{10} ions.

68) Ans (c):- The experimental magnetic moment of $K_3[Fe(CN)_6]$ is 2.3 μ_B and is attributable to the low–spin Fe^{+3} $(t_{2g}^5 e_g^0)$ electrons with orbital contribution

69) Ans (a):- As per HSAB principle, the central metal ion with high positive charge & small size are said to be hard acid & those having low positive charge, large size, and completely filled outer orbitals are said to be soft acids. Thus in table size of metal/metal ion increases top to bottom & hence order of the soft acid character is $[CrO_4]^{2-} < [CrCl_4]^- < [Cr(bipy)_3] < [Cr(CO)_5]^{2-}$

Metal complex	oxidation state of chromium
$[CrO_4]^{2-}$	Cr^{6+}
$[CrCl_4]^-$	Cr^{3+}
$[Cr(bipy)_3]$	Cr^0
$[Cr(CO)_5]^{2-}$	Cr^{2-}

70) Ans (a):- β-Diketone complexes of some of the lanthanides e.g. Eu(III) have interesting and useful properties as NMR shift reagents.

71) Ans (c):- Among, RO^-, $AsMe_3$, ROR' , CN^-, $AsMe_3$,RCO_2^- , SCN^- , the set of ligands with good π-acceptor nature is $AsMe_3$, CN^-, SCN^-

72) Ans (c):- Cu(II), Low-Spin Fe (III), Ti (III) ions expected to show Jahn-Teller distortion in their complexes (Jahn-Teller distortion is shown by metal ion with an unsymmetrical filling of d-electrons in t_{2g} and e_g orbital.

73) Ans (a):- The series with correct order of increasing Δ_O in their complexes is $I^- < PR_3 < CH_3^- < CO$

74) Ans (b):- Reaction occur in this way:-

$$[Cd(H_2O)_6]^{+2} \xrightarrow{K_1} [Cd(H_2O)_5Br]^{+1} \xrightarrow{K_2} [Cd(H_2O)_4Br_2] \xrightarrow{K_3} \underset{\text{octahedral complex}}{[Cd(H_2O)_3Br_3]^{-1}} \xrightarrow{K_4} \underset{\text{tetrahedral complex}}{[CdBr_4]^{-2}}$$

Thus during the fourth step; three molecules of H_2O are released and formation of tetrahedral complex take place with release in steric hindrance & therefore the fourth equilibrium constant is observed to be higher than the third one

75) Ans (c):- Thermodynamic stability refers to the change in energy on going from reactants to products while Kinetic stability refers to reactivity, generally ligand substitution. Substitution occurs extremely rapidly (labile) in some cases and extremely slowly (inert.) in others. Sometimes these two types of stability parallel one another, but often they do not, in short there exists no direct relation between these two phenomenon.

76) Ans (a):- *mer* and *fac* isomers are possible for complexes of formula $[MA_3B_3]$ or $[M(A–B)_3]$
Among all; Triglycinatocobalt(III) will show both facial and meridianal isomers

77) Ans (b):- The difference in observed and calculated magnetic moment is seen in Eu(III)

Metal ion	Calculated Magnetic moment	Observed Magnetic moment
Pm(III),	2.68	2.7
Eu(III)	0	3.4-3.5
Dy(III),	10.63	10.4
Lu(III)	0	0

78) Ans (a):- The ion with smaller size is eluted first & therefore the order of separation is Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+}

Metal ion	Ionic radius M^{+3} (in ppm)
Eu^{3+}	107
Dy^{3+}	103
Yb^{3+}	99
Lu^{3+}	98

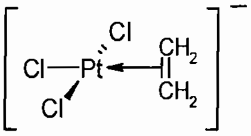
79) Ans (a):- Hint:-Hydration energy is proportional to CFSE. But when CFSE is same metal ion with smaller size have more hydration energy.(in period left to right size decreases)

$$[Mn(H_2O)_6]^{2+} < [Ti(H_2O)_6]^{2+} < [V(H_2O)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

Complex	Configuration	CFSE
$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3e_g^2$	$0\ \Delta_o$
$[V(H_2O)_6]^{2+}$	$t_{2g}^3e_g^0$	$-1.2\ \Delta_o$
$[Ni(H_2O)_6]^{2+}$	$t_{2g}^6e_g^2$	$-1.2\ \Delta_o$
$[Ti(H_2O)_6]^{2+}$	$t_{2g}^2e_g^0$	$-0.8\ \Delta_o$

80) Ans (a):- Charge-transfer transitions from metal to ligand (MLCT) are observed when the metal is in a low oxidation state and the ligands have low-lying acceptor orbitals. i.e. $Ni(CO)_4$, While all other shows LMCT.

81) Ans (d):- Zeise's salt is represented as $K[PtCl_3(\eta^2\text{-}C_2H_4)]$;

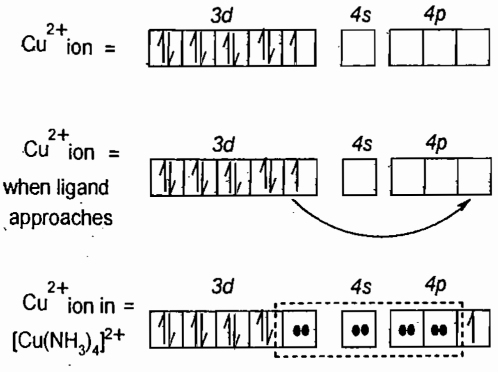


82) Ans (b):- The total number of isomers of $Co(en)_2Cl_2$ (en = ethylenediamine) are cis & trans. The cis isomer does exist as optical isomers because it does not have a mirror plane or centre of inversion that is cannot be superimposed on its mirror image. It is therefore chiral while the trans isomer has mirror planes and an centre of inversion and therefore cannot be optical active. The number possible isomers of $Co(en)_2Cl_2$ are 3

83) Ans (d):- In $[Ru(H_2O)_6]^{2+}$; Ru^{+2} is d^6 low spin system & the magnetic moment of $[Ru(H_2O)_6]^{2+}$ corresponds to the presence of zero unpaired electrons. This is because for a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: [Δ_o (3d) < Δ_o (4d) < Δ_o (5d).]

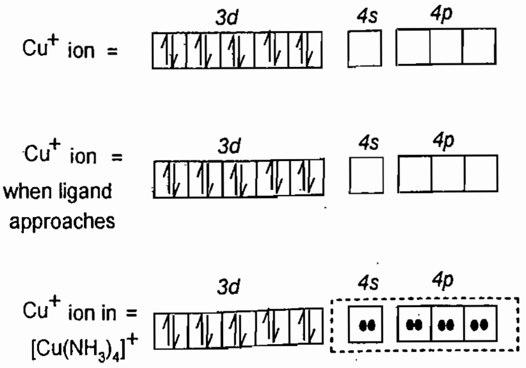
84) Ans (a):- According to VBT; the structures of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)$ in solution are square planar and tetrahedral respectively.

Hybridization of $[Cu(NH_3)_4](ClO_4)_2 = [Cu(NH_3)_4]^{2+}$



dsp^2 square planar complex

Hybridization of $[Cu(NH_3)_4]ClO_4 = [Cu(NH_3)_4]^+$



sp^3 tetrahedral complex

85) Ans (c):- Magnetic moment of the first-row transition metal complexes is calculated only by spin only formula ($\mu_{s.o.}$equation) because the crystal field quenches the orbital angular momentum due to direct interaction of metal orbital with ligand orbital & hence there is no contribution from orbital motion. while in case of lanthanide metal complexes the 4f orbitals being deeply buried and well shielded (from outside environment) by the $5s^2$ and $5p^6$ orbitals and therefore not affected by the environment of the ion therefore magnetic moments of the lanthanide metal complexes is calculated by both spin as well as orbital contribution (μ_J equation)

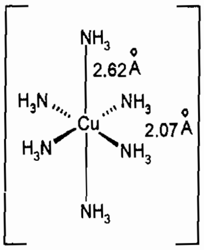
86) Ans (b):- The coordination number of Ti in $CaTiO_3$ is 6 (octahedral) & that of Ca is 12 (cuboctahedral)

87) Ans (d):- Generally when Δ_O CFSEs of M^{+3} ion is greater than M^{+2} ion it will adopt normal spinels structure otherwise it will adopt inverse spinels structure.

Metal oxides	Δ_O CFSE of M^{+3}	Δ_O CFSE of M^{+2}	Conclusion
Fe_3O_4	High spin $Fe^{+3} = 0.0\ \Delta_O$	High spin $Fe^{+2} = -0.4\ \Delta_O$	*inverse spinel*
$NiFe_2O_4$	High spin $Fe^{+3} = 0.0\ \Delta_O$	High $Ni^{+2} = -1.2\ \Delta_O$	*inverse spinel*
Mn_3O_4	High spin $Mn^{+3} = -0.6\ \Delta_O$	High spin $Mn^{+2} = -0.0\ \Delta_O$	normal spinels

Thus Fe_3O_4 & $NiFe_2O_4$ are *inverse spinel* while Mn_3O_4 is a normal spinels

88) Ans (b):- In $[Cu(NH_3)_6]^{2+}$ (d^9 system) ; axial Cu-N bond distances & equatorial bonds distances are not same due to unsymmetrical filling of electrons in e_g orbitals (Jahn-Teller distortion which leads to removal of degeneracy in the system). Generally in the d^9 system; the d_{z^2} orbital is lowered in energy in comparison to the $d_{x^2-y^2}$ & the odd electron resides in $d_{x^2-y^2}$ and the degeneracy in the system is removed & it leads to the 2 axial bonds (along the z–axis) are longer than the 4 equatorial ones (along the x,y–axis)



$[Cu(NH_3)_6]^+$
(D_{4h})

89) Ans (d):- The Mössbauer and EPR parameters suggest five number of unpaired electron(s) that is (high spin Fe^{+3}) present in the species $[Fe(H_2O)_5(NO)]^{2+}$ i.e. complex is $[Fe^{III}(H_2O)_5(NO)^-]^{2+}$ & not $[Fe^{I}(H_2O)_5(NO)^+]^{2+}$

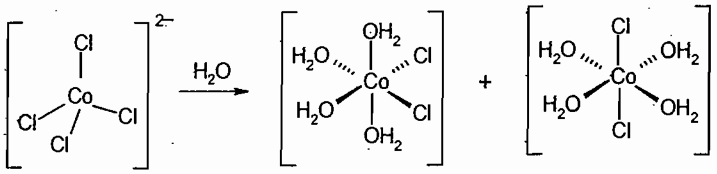
90) Ans (d):- Generally when Δ_O CFSEs of M^{+3} ion is greater than M^{+2} ion it will adopt normal spinels structure otherwise it will adopt inverse spinels structure.

Metal oxides	Δ_O CFSE of M^{+3}	Δ_O CFSE of M^{+2}	Conclusion
Fe_3O_4	High spin $Fe^{+3} = 0.0\ \Delta_O$	High spin $Fe^{+2} = -0.4\ \Delta_O$	*inverse spinel*
Co_3O_4	Low spin $Co^{+3} = -2.4\ \Delta_O$	High spin $Co^{+2} = -0.8\ \Delta_O$	normal spinels

Note:-Co^{3+} is a low spin system even in presence of oxo ligands due to high charge on the ion & hence greater Δ_O

91) Ans (c):- The d-d absorption band of $[Fe(H_2O)_6]^{2+}$ is split due to dynamic Jahn-Teller distortion (Note:- dynamic Jahn-Teller distortion means Jahn-Teller distortion due to unsymmetrical filling of electron in t_{2g} orbital) e.g. $[Fe(H_2O)_6]^{2+}$ is a high spin Fe^{+2} complex with $t_{2g}^4 e_g^2$ configuration that is unsymmetrical filling of electron in t_{2g} orbital.

92) Ans (b):- Two isomeric complexes $[Co(H_2O)_4Cl_2$ are as given below,



$[CuCl_4]^{2-}$ Td   *trans* $Cu(H_2O)_4Cl_2$ (C_{2v})   *cis* $Cu(H_2O)_4Cl_2$ (D_{4h})

93) Ans (b):- $CuSO_4.5H_2O$ is a d^9 system; due to unsymmetrical filling of electrons in e_g orbitals (Jahn-Teller distortion) which leads to removal of degeneracy in the system.

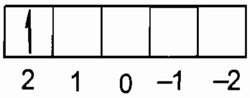
94) Ans (d):- Among all *trans*-$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ & *cis*–$[Co(NH_3)_4Cl_2]^+$ have a two plane of symmetry (can be superimposed on its mirror image) and therefore nonchiral.

$[Pt(PPh_3)(Cl)(Br)(CH_3)]^-$ is a square-planar complex & do not show optical isomerism

$[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$ is exists as a pair of enantiomers. In such $M(L{-}L)_3$ complexes clockwise rotation is designated Δ & anticlockwise rotation is designated Λ

95) Ans (a):-

$Ti^{+3} = d^1$



Thus L = 2; S = ½ ∴ The term symbol is:- $^{2S+1}L = {}^2D$

The term for ^2D is $^2T_{2g} + {}^2E_g$

Given:- absorption maxima (λ) = 492nm (492×10^{-7}cm)

∴In the case of d^1 system CFSE = frequency(ν) = $\frac{1}{\lambda} = \frac{1}{492\times10^{-7}} = 20325\ cm^{-1}$

96) Ans (b):- The incorrect statement is (b) as MnO_4^- exhibits charge transfer at longest wavelength among the three

97) Ans (c):- Hint:- spectrochemical series of ligands. The increasing order of wavelength of absorption for the complex ions: - $[Cr(CN)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(OH_2)_6]^{3+} < [CrCl_6]^{3-}$

98) Ans (b):- In inverse spinel CFSE of M^{+3} is zero or smaller than M^{+2}; e.g. Fe_3O_4

In the *inverse spinel* structure, the octahedral holes are occupied by half of the +3 ions and by the +2 ions while the tetrahedral holes are occupied by the half of the +3 ions

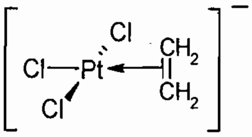
99) Ans (d):- In case of d^0, $d^5$and d^{10} system smaller the size of the cation; greater is a enthalpies of hydration.

Size of cation:- $Ca^{2+} > Mn^{2+} > Zn^{2+}$.

Hence order of the enthalpies of hydration $Zn^{2+} > Mn^{2+} > Ca^{2+}$

100) Ans (b):- The IUPAC nomenclature of $Na[PCl_6]$ is sodium hexachlorophosphate(V)

101) Ans (c):- In Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$; all the Pt–Cl bond lengths are not equal. (Bond length of one Pt–Cl is different.)



102) Ans (a):- The number of possible isomers for the square planar mononuclear complex $[(NH_3)_2M(CN)_2]$ of a metal M is 2 (cis & trans)

103) Ans (c):- According to the hard-soft interaction principle; soft electron donors in which the donor atom is sulfur or phosphorus form more stable complexes with soft metal ions such as Pd^{2+} or Ag^+ etc., or with metal atom. Hard electron donors such as H_2O, NH_3, or F^- generally form stable complexes with hard metal ions like Cr^{3+} or Be^{2+} etc.

104) Ans (a):- The correct electronic configuration and spin only magnetic moment of Gd^{3+} (At.No. 64) are $[Xe]4f^7$ and 7.9 BM

105) Ans (c):- Hint:-Hydration energy is proportional to CFSE. But when CFSE is same metal ion with smaller size have more hydration energy.(in period left to right size decreases)

Complex	Configuration	CFSE
$[Ca(H_2O)_6]^{2+}$	d^0	$0\ \Delta_o$
$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3e_g^2$	$0\ \Delta_o$
$[V(H_2O)_6]^{2+}$	$t_{2g}^3e_g^0$	$-1.2\ \Delta_o$
$[Cr(H_2O)_6]^{2+}$	$t_{2g}^3e_g^1$	$-0.6\ \Delta_o$

106) Ans (c):- According to valence bond theory geometries of both $Ni(CO)_4$ and $[NiCl_4]^{2-}$ is tetrahedral

107) Ans (c):- The complexes $[Co(H_2O)_4Cl_2]NO_2$ and $[Co(H_2O)_4Cl(NO_2)]Cl$ are ionization isomers

108) Ans (a):- Strong Jahn-Teller distortion is shown by metal ion with an unsymmetrical filling of d-electrons in e_g orbital. $[Cr(H_2O)_6]^{2+}$ complex is a high spin d^4 system with an $t_{2g}^3\ e_g^1$ configuration & shows Strong Jahn-Teller distortion.

109) Ans (b):- Among $[Fe(CN)_6]^{3-}$ & $[Cu(H_2O)_6]^{2+}$, the effective magnetic moment of $[Fe(CN)_6]^{3-}$ is greater than $[Cu(H_2O)_6]^{2+}$ due to spin orbit coupling in $[Fe(CN)_6]^{3-}$ (observed magnetic moment is greater than calculated).

Complex	structure	System	Unpaired electron	Magnetic moment
$[Ni(CN)_4]^{2-}$	Square planar	d^8	0	0
$[Fe(CN)_6]^{3-}$	Octahedral	low spin d^5	1	>1.7
$[Cu(H_2O)_6]^{2+}$	Octahedral	high spin d^9	1	~1.7
$[Co(CN)_6]^{3-}$	Octahedral	low spin d^6	0	0

110) Ans (c):- $MnCr_2O_4$ is normal spinel with total CFSE of −24 Dq.
In $MnCr_2O_4$; Mn^{+2} is with high spin d^5 system; CFSE = 0 Dq so occupied tetrahedral site & Cr^{+3} is with high spin d^3 system; CFSE = −12 Dq ($2Cr^{+3}$; CFSE = −24 Dq) & occupied octahedral site. In the *normal spinel* structure, the octahedral holes are occupied by the +3 ions and the tetrahedral holes are occupied by the +2 ions (AB_2O_4).

List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited
2) Concise inorganic chemistry, By J. D. Lee, John Wiley & Sons. India.
3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.
4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press
5) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.
6) Inorganic Chemistry by James E. House, Elsevier Science Publication.
7) Concise Coordination Chemistry, by R Gopalan and V Ramalingam Vikas Publishing House Pvt Ltd.
8) Modern Inorganic Chemistry, By R.D.Madan & Satya Prakash, S. Chand publication

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Topic 6

BIO-INORGANIC

Questions with two marks

1) The ligand system present in vitamin B_{12} is ***[June 2011]***

(a) Porphyrin (b) Corrin (c) Phthalocyanine (d) Crown ether

2) Superoxide dismutase contains the metal ions ***[Dec 2011]***

(a) Zn (II) and Ni (II) (b) Cu (II) and Zn(II) (c) Ni (II) and Co(III) (d) Cu (II) and Fe(III)

3) The oxidation state of iron in met-haemoglobin is ***[June 2012]***

(a) Three (b) Two (c) Four (d) Zero

4) The correct set of the biologically essential elements is, ***[Dec 2012]***

(a) Fe, Mo, Cu, Zn (b) Fe, Cu, Co, Ru (c) Cu, Mn, Zn, Ag (d) Fe, Ru, Zn, Mg

5) Patients suffering from Wilson's disease have ***[Dec2013]***

(a) Low level of Cu-Zn superoxide dismutase (b) High level of Cu-Zn superoxide dismutase
(c) Low level of copper-storage protein, ceruloplasmin (d) High level of copper-storage protein ceruloplasmin

6) High dose of dietary supplement $ZnSO_4$ for the cure of Zn deficiency ***[Dec2013]***

(a) reduces myoglobin (b) increases iron level in blood
(c) increases copper level in brain (d) reduces copper, iron and calcium levels in body

7) The extent of π electron conjugation in macrocyclic rings of (i) heme, (ii) coenzyme B_{12} and (iii) chlorophyll follows the order ***[Dec 2014]***

(a) (i) > (iii) > (ii) (b) (i) > (ii) > (iii) (c) (iii) > (i) > (ii) (d) (ii) $\approx$ (i) >(iii)

8) The number of histidine amino acid nitrogen atoms coordinated to bimetallic active site of oxyhemocyanin and oxyhemerythrine, respectively, are ***[Dec 2014]***

(a) 2, 3 and 3, 3 (b) 3, 3 and 2, 3 (c) 3, 3 and 2, 2 (d) 2, 4 and 3, 2

Questions with four marks

9) Carboxypeptidase contains ***[June 2011]***

(a) Zn(II) and hydrolyses CO_2. (b) Mg(II) and hydrolyses CO_2.
(c) Zn(II) and hydrolyses peptide bonds. (d) Mg(II) and hydrolyses peptide bonds

10) The reduction of nitrogen to ammonia, carried out by the enzyme nitrogenase, needs, ***[Dec 2011]***

(a) 2 electrons (b) 4 electrons (c) 6 electrons (d) 8 electrons

11) In bacterial rubredoxin, the number of iron atoms, sulfur bridges and cysteine ligands are ***[Dec 2011]***

	Fe atom	**sulfur bridge**	**cysteine**
(a)	4	4	4
(b)	2	2	4
(c)	2	2	2
(d)	1	0	4

12) A metal ion that replace manganese (II) ion in mangano-proteins without changing its function, is ***[Dec 2011]***

(a) Fe (II) (b) Zn (II) (c) Mg (II) (d) Cu (II)

13) The changes (from A-D given below) which occur when O_2 binds to hemerythrin are ***[June 2012]***

(A) One iron atom is oxidized
(B) Both the iron atoms are oxidized
(C) O_2 binds to one iron atom and is also hydrogen bonded.
(D) O_2 binds to both the iron atoms and is also hydrogen bonded.

(a) B and C (b) B and D (c) A and D (d) A and C

14) In metalloenzymes, the metal centres are covalently linked through the side chains of the amino acid residues. The correct set of amino acids which are involved in the primary coordination spheres of metalloenzymes is ***[Dec 2012]***

(a) Ala, Leu, His (b) Glu, His, Cys (c) Leu, Glu, Cys (d) Ala, His, Glu

15) Based on the behavior of the metalloenzymes, consider the following statements ***[Dec 2012]***

(A) In the enzymes, the zinc activates O_2 to form peroxide species.
(B) In the enzymes, the zinc activates H_2O and provides a zinc bound hydroxide.
(C) In the oxidases, the iron activates O_2 to break the bonding between the two oxygens
(D) Zinc ion acts as a nucleophile and attacks at the peptide carbonyl

The set of correct statements is,

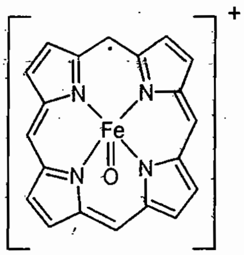
(a) A and B (b) B and C (c) C and D (d) A and D

16) Fe^{2+} -porphyrins fail to exhibit reversible oxygen transport and cannot differentiate CO from O_2. However, the hemoglobin is free from both these pit falls. Among the following the correct set of statements is ***[Dec 2012]***

(A) Fe^{2+}– porphyrins undergo μ-oxodimer formation and the same is prevented in case of the hemoglobin.
(B) Fe–CO bond strength is much low in case of hemoglobin when compared to the Fe^{2+} - porphyrins.
(C) While Fe–CO is linear, Fe–O_2 is bent and is recognized by hemoglobin
(D) The interlinked four monomeric units in the hemoglobin are responsible to overcome the pitfalls.

(a) A and B (b) A and C (c) C and D (d) B and D

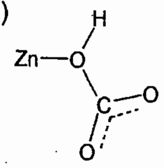
17) Oxidized form of enzyme catalase (structure A); prepared by the reaction of [Fe(P) $]^+$ (P = porphyrin) with H_2O_2 has a green color because of ***[Dec2013]***

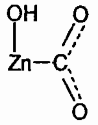


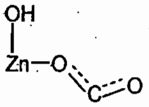
A (substituents on ring are removed for clarity)

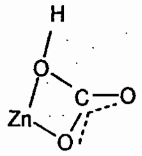
(a) Oxidation state of iron changed from Fe^{III} to Fe^{IV}.
(b) Porphyrin ring is oxidized by one electron
(c) π–π* transition appears in the visible region
(d) Fe^{IV} is coordinated with anionic tyrosinate ligand in axial position.

18) At pH 7, the zinc(II) ion in carbonic anhydrase reacts with CO_2 to give ***[June 2014]***

(a)


(b)


(c)


(d)


19) The cooperative binding of O_2 in hemoglobin is due to ***[June 2014]***

(a) a decrease in size of iron followed by changes in the protein conformation
(b) an increase in size of iron followed by changes in the protein conformation
(c) a decrease in size of iron that is NOT accompanied by the protein conformational changes
(d) an increase in size of iron that is NOT accompanied by the protein conformational changes

20) Molybdoenzymes can both oxidize as well as reduce the substrates, because ***[June 2014]***

(a) Mo(VI) is more stable than Mo(IV)
(b) Mo(IV) can transfer oxygen atom to the substrate and Mo(VI) can abstract oxygen atom from the substrate
(c) Conversion of Mo(VI) to Mo(IV) is not favoured
(d) Mo(VI) can transfer oxygen atom to the substrate and Mo(IV) can abstract oxygen atom from the substrate.

21) Under physiological condition, oxygen is binding to deoxyhemoglobin and deoxymyoglobin, the binding curve and its pH dependence, respectively, are ***[Dec 2014]***

(a) Sigmoidal and pH dependent; hyperbolic and pH independent
(b) Hyperbolic and pH independent; sigmoidal and pH dependent
(c) Sigmoidal and pH independent; hyperbolic and pH dependent
(d) Hyperbolic and pH dependent; sigmoidal and pH independent

22) Match the metalloproteins in column A with their function in column B ***[Dec 2014]***

Column A	**Column B**
I. Oxyhemocyanin	(A) hydrolysis of C-terminal peptide bond
II. Carbonic anhydrase	(B) methylation
III. Cytochrome P_{450}	(C) conversion of CO_2 to H_2CO_3
IV. Carboxy peptidase A	(D) oxidation of alkene
	(E) oxygen storage
	(F) oxygentransport

The correct answer is

(a) I-(F); II-(C); III-(D); IV-(A)
(b) I-(E); II-(C); III-(A); IV-(F)
(c) I-(F); II-(B); III-(C); IV-(A)
(d) I-(E); II-(D); III-(C); IV-(A)

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

23) The metal present at the active site of the protein carboxypeptidase A is ***(GATE 2005)***

(a) zinc
(b) molybdenum
(c) magnesium
(d) cobalt

24) Match the following items of column I with the appropriate items in column II *(GATE 2005)*

Column I	**column II**
P) cytochrome c	I molybdenum
Q) calmodulin	II potassium
R) Chlorophyll	III magnesium
S) Alcohol dehydrogenase	IV zinc
	V iron
	VI calcium

R — III
P — V

(a) P- I Q-II R -III S- IV
(b) P-II Q-III R - IV S-V
(c) P-V Q-IV R-VI S-II
(d) P-V Q -VI R-III S-IV

25) In biological systems, the metal ion involved in the dioxygen transport besides Fe is *(GATE 2006)*

(a) Co (b) Zn (c) Mg (d) Cu

26) Iron–sulphur clusters in biological systems are involved in *(GATE 2006)*

(a) proton transfer (b) atom transfer (c) group transfer (d) electron transfer

27) The amino acid side chain high affinity for Ca^{2+} and Cu^{2+} in metallo-proteins is *(GATE 2006)*

− 0.5

(a) Carboxylate in both the cases
(b) Imidazole in both the cases
(c) Carboxylate for Ca^{2+} and imidazole for Cu^{2+}
(d) Imidazole for Ca^{2+} and carboxylate for Cu^{2+}

28) When a reduced cytochrome transfers an electron from its Fe(II) to the bound O_2, *(GATE 2006)*

(a) The bond order of O_2 is reduced by one and ν_{O2} decreases
(b) A metal bound superoxide is formed and ν_{O2} decreases
(c) A metal bound superoxide is formed and ν_{O2} increases
(d) The bond order of O_2 is reduced by one and ν_{O2} increases

O_2 Fe 2 O_2 H+1
O — O_2^-

29) In photosynthesis, the predominant metal present in the reaction centre of photo-system II is *(GATE 2007)*

(a) Zn (b) Cu (c) Mn (d) Fe

30) Zn in carbonic anhydrase is coordinated by three histidine and one water molecule. The reaction of CO_2 with this enzyme is an example of *(GATE 2007)*

(a) electrophilic addition (b) electron transfer (c) nucleophilic addition (d) electrophilic substitution

31) In biological systems, the metal ions involved in electron transport are *(GATE 2008)*

(a) Na^+ and K^+ (b) Zn^{2+} and Mg^{2+} (c) Ca^{2+} and Mg^{2+} (d) Cu^{2+} and Fe^{3+}

32) In the transformation of oxyhaemoglobin to deoxyhaemoglobin *[GATE 2009]*

(a) Fe^{3+} in the low spin state changes to Fe^{2+} in the high spin state
(b) Fe^{2+} in the low spin state changes to Fe^{3+} in the low spin state
(c) Fe^{2+} in the high spin state changes to Fe^{2+} in the low spin state
(d) Fe^{2+} in the high spin state changes to Fe^{3+} in the high spin state

33) Among the following pair of metal ions present in Nature. The first one functions as an electron transfer agent and the second one catalyzes the hydrolysis reactions. The correct pair is *[GATE 2010]*

(a) Fe and Zn (b) Mg and Fe (c) Co and Mo (d) Ca and Cu

34) A well known naturally occurring organometallic compound is *(GATE 2011)*

(a) vitamin B_{12} coenzyme
(b) chlorophyll
(c) cytochrome P-450
(d) myoglobin

35) The red color of oxyhaemoglobin is mainly due to the *(GATE 2011)*

(a) d-d transition
(b) metal to ligand charge transfer transition
(c) ligand to metal charge transfer transition
(d) intraligand π-π^* transition

36) Hemoglobin is an oxygen carrying protein. The correct statement about oxy-hemoglobin is that *[GATE 2012]*

(a) the metal is low-spin in +3 oxidation state while dioxygen is in O_2^- form
(b) the metal is high-spin in +3 oxidation state while dioxygen is in O_2^- form
(c) the metal is low-spin in +3 oxidation state while dioxygen is in neutral form
(d) the metal is high-spin in +3 oxidation state while dioxygen is in neutral form

37) Oxymyoglobin $Mb(O_2)$ and oxyhaemoglobin $Hb(O_2)_4$, respectively, are *[GATE 2013]*

(a) Paramagnetic and paramagnetic
(b) Diamagnetic and diamagnetic
(c) Paramagnetic and diamagnetic
(d) Diamagnetic and paramagnetic

38) The number of oxygen molecule(s) that a molecule of hemerythrin can transport is *[GATE 2013]*

(a) One (b) Two (c) Three (d) Four

39) Mg^{2+} is preferred in photosynthesis by chlorophyll because ***[GATE 2014]***

(a) it has strong spin-orbit coupling
(b) it has weak spin-orbit coupling
(c) it is a heavy metal
(d) it binds strongly with chlorophyll

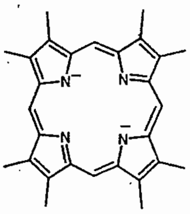
Answer Key

Topic 6:- Bioinorganic

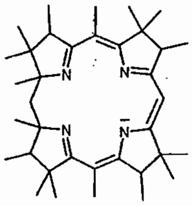
1	b	2	b	3	a	4	a	5	d	6	d	7	a	8	b	9	c	10	d
11	a	12	c	13	a	14	b	15	b	16	b	17	a	18	a	19	a	20	d
21	a	22	a	23	a	24	d	25	d	26	d	27	c	28	b	29	c	30	c
31	d	32	a	33	a	34	a	35	d	36	a	37	b	38	a	39	b		

Hints &Solution

1) Ans (b):-The ligand system present in vitamin B_{12} is Corrin.
Macrocycle ligand:- The porphyrin group was first identified in haemoglobin (Fe) and a similar macrocycle is found in chlorophyll (Mg). The corrin ligand has a slightly smaller ring size and coordinates Co in cobalamin.



Porphyrin^{-2}



Corrin^{-}

2) Ans (b):- Superoxide dismutase converts superoxide ion into oxygen and hydrogen peroxide. It contains the Cu (II) and Zn(II) metal ions

3) Ans (a):- Met-hemoglobin is a form of hemoglobin that contains ferric [Fe^{3+}] iron. Met-hemoglobin cannot bind oxygen, unlike oxyhemoglobin. In human blood a trace amount of methemoglobin is normally produced spontaneously, but when present in excess the blood becomes abnormally dark bluish brown & disorder is known as Met-hemoglobinemia or blue skin syndrome

4) Ans (a):- Mn & Ru are not biologically essential elements.

5) Ans ([illegible]:- Patients suffering from Wilson's disease have high level of copper-storage protein, ceruloplasmin (Cu accumulation)

6) Ans (d):- High dose of dietary supplement $ZnSO_4$ for the cure of Zn deficiency reduces copper, iron and calcium levels in body

7) Ans (a):- The extent of π electron conjugation in macrocyclic rings:-
heme > chlorophyll > coenzyme B_{12}

8) Ans (b):- The number of histidine amino acid nitrogen atoms coordinated to bimetallic active site of oxyhemocyanin and oxyhemerythrine; (from the structure) are 3, 3 and 2, 3 respectively.

9) Ans (c):- Carboxypeptidase contains Zn(II) and hydrolyses peptide bonds (catalyses the cleavage of a peptide link in a polypeptide chain.)

10) Ans (d):- The reduction of nitrogen to ammonia, carried out by the enzyme nitrogenase needs $8e^-$

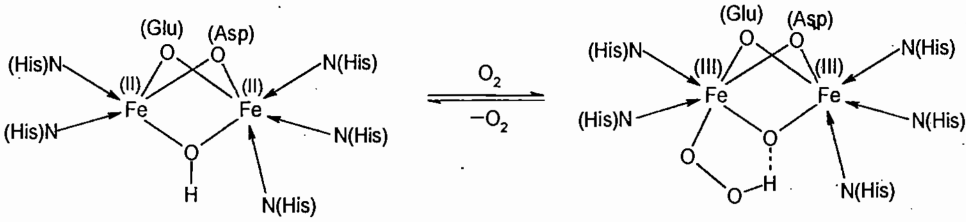
$$N_2 + 8H^+ + 8e^- \rightarrow 2\,NH_3 + H_2$$

11) Ans (a):- In bacterial rubredoxin, the number of iron atoms, sulfur bridges and cysteine ligands are 4,4 & 4 respectively

Fe atom	sulfur bridge	cysteine	Example
2	2	4	spinach (Spinacia oleracea)
3	4	3	bacterium Azotobacter vinelandii,
4	4	4	bacterium Chromatium vinosum.

12) Ans (c):- EPR studies showed that, Mn^{2+}, an ion which can often replace Mg^{2+} in nucleic acid processing enzymes.

13) Ans (a):- Both the iron atoms are oxidized when O_2 binds to hemerythrin i.e. Fe^{II} to Fe^{III}. O_2 binds to only one iron atom by peroxide linkage and hydrogen on hydroxyl group participates in O_2 binding, becoming part of an $[HO_2]^-$ ligand.



14) Ans (b):- Amino acid namely Glutamate, histidine and cysteine are involved in the primary coordination spheres of metalloenzymes.

15) Ans (b):- In the enzymes, the zinc acts as a Lewis acid & activates H_2O and provides a zinc bound hydroxide & in the oxidases, the iron activates O_2 to break the bonding between the two oxygens.

Oxidases are the metalloenzymes that catalyse the reduction of O_2 to H_2O and, at the same time, an organic substrate undergoes a one electron oxidation *i.e.* RH to ROH

16) Ans (b):- Fe^{2+}– porphyrins undergo μ-oxodimer formation and the same is prevented in case of the hemoglobin & Fe–CO is linear, Fe–O_2 is bent and is recognized by hemoglobin (In hemoglobin end-on, bent coordination mode of the O_2 group which is not possible in case of linear CO.

Evidences for the end-on, bent coordination mode of the O_2 :- O–O bond length is 125pm and the Fe–O–O bond angle is 136.8°. The vibrational spectrum of the complex also suggest end-on, bent coordination mode of the O_2

17) Ans (a):- Oxidation state of iron changed from Fe^{III} to Fe^{IV}.

18) Ans (a):- At pH 7, the zinc(II) ion in carbonic anhydrase reacts with CO_2 to give $(His)_3Zn^+\text{-}OH\text{-}CO_2^-$

$$(His)_3Zn^+\text{-}OH + CO_2 \longrightarrow (His)_3Zn^+\text{-}OH\text{-}CO_2^-$$

19) Ans (a):- The cooperative binding of O_2 in hemoglobin is due to a decrease in size of iron (Fe^{II} to Fe^{III}). Fe^{+3} moves into the plane of the porphyrin ring followed by changes in the protein conformation.

20) Ans (d):- Molybdoenzymes can both oxidize as well as reduce the substrates, because Mo(VI) (oxidized form) can transfer oxygen atom to the substrate and Mo(IV) (reduced form) can abstract oxygen atom from the substrate

21) Ans (a):- The binding curve and its pH dependence, when oxygen is binding to deoxyhemoglobin is sigmoidal and pH dependent and in case of deoxymyoglobin; it is hyperbolic and pH independent

22) Ans (a):-

Column I	Column II
Oxyhemocyanin	oxygen transport
Carbonic anhydrase	conversion of CO_2 to H_2CO_3
Cytochrome P_{450}	oxidation of alkene
Carboxy peptidase A	hydrolysis of C-terminal peptide bond

23) Ans (a):- Tetrahedrally coordinated Zn^{2+} ion is present at the active site of the protein carboxypeptidase A

24) Ans (d):-

Column I	Column II
cytochrome c	iron
calmodulin	calcium
Chlorophyll	magnesium
Alcohol dehydrogenase	zinc

25) Ans (d):- Haemocyanins are O_2-carrying copper-containing proteins in molluscs (e.g. whelks, snails, and squid) and arthropods (e.g.lobsters, crabs, shrimps, horseshoe crabs, scorpions), and although the name suggests the presence of a haem group, haemocyanins are not haem proteins. The deoxy-form of a haemocyanin is colourless and contains Cu(I), while O_2 binding results in the blue Cu(II) form.

26) Ans (d):- Iron–sulphur clusters in biological systems are involved in biological redox reactions. (electron transfer)

27) Ans (c):- Hint:- Concept of HSAB:- Hard nucleophiles tend to react hard acid (metal) & Soft nucleophiles tend to react soft acid (metal). Carboxylate (Hard base) for Ca^{2+} (Hard acid) and imidazole (Borderline base) for Cu^{2+} (Borderline Acids)

28) Ans (b):- A metal bound superoxide is formed and V_{O_2} decreases as bond order decreases.

$$O_2 \text{(bond order 2)} \rightarrow O_2^- \text{(bond order 1.5)}$$

29) Ans (c):- Mn is the predominant metal present in the reaction centre of photo-system II

30) Ans (c):- The reaction of CO_2 with this enzyme is an example of nucleophilic addition; (water adds to CO_2 molecule)

$$(His)_3Zn^+\text{–}OH + CO_2 \longrightarrow (His)_3Zn^+\text{–}OCO_2H$$

31) Ans (d):- In biological systems, Cu^{2+} and Fe^{3+} are involved in electron transport reaction. (A characteristic property of *d*-block elements is their ability to exhibit a variety of oxidation states in their compounds.)
i.e. $Cu^{2+} \rightarrow Cu^+$ & $Fe^{3+} \rightarrow Fe^{2+}$

32) Ans (a):- In the transformation of oxyhaemoglobin to deoxyhaemoglobin; Fe^{3+} in the low spin state changes to Fe^{2+} in the high spin state

33) Ans (a):- Fe is an electron transfer agent and Zn catalyzes the hydrolysis reactions.

34) Ans (a):- Vitamin B_{12} coenzyme is an organometallic as there is a Co-C bond (metal-carbon bond).

35) Ans (d):- The red color of oxyhaemoglobin is mainly due to the intraligand π–π^* transition.

36) Ans (a):- In oxy- haemoglobin the metal Fe is low-spin in +3 oxidation state while dioxygen is in O_2^- form

37) Ans (b):- Both Oxymyoglobin $Mb(O_2)$ and oxy haemoglobin $Hb(O_2)_4$, are diamagnetic. O_2 binding to deoxymyoglobin and deoxy haemoglobin, result in oxidation of high-spin Fe(II) to low- spinFe(III) and reducing O_2 to $[O_2]^-$. Both low-spin Fe(III) (d^5) and $[O_2]^-$ contain an unpaired electron, but due to antiferromagnetic coupling between the Fe(III) centre and $[O_2]^-$ ligand; oxy-forms of both oxymyoglobin $Mb(O_2)$ and oxyhaemoglobin $Hb(O_2)_4$, are therefore diamagnetic.

38) Ans (a):- In marine invertebrates such as annelids (segmented earthworms), molluscs and arthropods, O_2 is transported by haemerythrin, (a non-haem Fe-containing protein). Hemerythrin can transport one oxygen molecule.

39) Ans (b):- Mg^{2+} is preferred in photosynthesis by chlorophyll because it has weak spin-orbit coupling

List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited

2) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.

3) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press

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Topic 7

TERM SYMBOL AND ELECTRONIC SPECTROSCOPY

Questions with two marks

1) The term symbol of a molecule with electronic configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^1(1\pi_u)^1$ is *[June 2011]*

(a) $^1\Sigma_g^+$ (b) $^1\Sigma_g^-$ (c) $^3\Sigma_g^-$ (d) $^3\Sigma_g^+$

2) The term symbol for the ground state of nitrogen atom is *[Dec 2011]*

(a) $^3P_0$ (b) $^4P_{3/2}$ (c) $^1P_1$ (d) $^4S_{3/2}$

3) The electric dipole allowed transition in a d^2 atomic system is *[Dec 2012]*

(a) $^3F \longrightarrow {}^1D$ (b) $^3F \longrightarrow {}^1P$ (c) $^3F \longrightarrow {}^3D$ (d) $^3F \longrightarrow {}^3P$

4) What is the atomic term symbol for helium atom with electronic configuration $1s^2$? *[June 2013]*

(a) $^2S_{1/2}$ (b) $^1P_0$ (c) $^1S_0$ (d) $^1S_1$

5) The Mulliken symbols for the spectroscopic states arising from the free-ion term F are *[June 2013]*

(a) $T_{2g} + E_g$ (b) $T_{1g} + T_{2g} + T_{1u}$ (c) $T_{1g} + T_{2g} + A_{2g}$ (d) $A_{1g} + T_{2g} + T_{1g}$

6) Calculate the total number of microstates for 6 identical particles with their occupation numbers {1, 2, 3} in three states is *[June 2013]*

(a) 6 (b) 12 (c) 60 (d) 720

7) Three bands in the electronic spectrum of $[Cr(NH_3)_6]^{+3}$ are due to the following transitions *[June 2013]*

(A) $^4A_{2g} \longrightarrow {}^4T_{1g}$ (B) $^4A_{2g} \longrightarrow {}^4T_{2g}$ (B) $^4A_{2g} \longrightarrow {}^2E_g$

Identify the correct statement about them

(a) Intensity of (A) is lowest (b) Intensity of (C) is lowest
(c) Intensities of (A), (B) and (C) are similar (d) Intensities of (B) and (C) are similar

8) In the presence of an external magnetic field (normal Zeeman effect), the transition $^1D_2 \longrightarrow {}^1P_1$ splits into *[June 2013]*

(a) 9 lines (b) 8 lines (c) 7 lines (d) 6 lines

9) The term symbol that is NOT allowed for the *np*^{2} configuration is *[June 2014]*

(a) ^1D (b) ^3P (c) ^1S (d) ^3D

10) The *S* and *L* values for ^{15}N atom respectively are *[Dec 2014]*

(a) ½ and 1 (b) ½ and 0
(c) 1 and 0 (d) 3/2 and 0

Questions with four marks

11) The possible J values for ^3D term symbol are ***[June 2011]***

(a) 2 (b) 3 (c) 4 (d) 5

12) Observe the following electronic transitions of a diatomic molecule. ***[Dec 2011]***

(a) $^1\Sigma_g^+ \longrightarrow {}^3\Sigma_g^+$ (b) $^1\Sigma_u^+ \longrightarrow {}^1\Sigma_g^+$ (c) $^1\Delta_u \longrightarrow {}^1\Sigma_g^+$ (d) $^1\Pi_g \longrightarrow {}^1\Sigma_u^+$

The allowed transitions are

(a) (A) and (C) only (b) (B) and (D) only

(c) (A), (B) and (C) only (d) (A), (C) and (D) only

13) One of the excited states of Ti has the electronic configuration [Ar] $4s^2 3d^1 4p^1$ .The number of microstates with zero total spin (S) for this configuration is ***[Dec 2012]***

(a) 9 (b) 15 (c) 27 (d) 60

14) The ground state term symbol for Nb (atomic number 41) is ^6D. The electronic configuration corresponding to this term symbol is ***[June 2013]***

(a) [Kr] $4d^3 5s^2$ (b) [Kr] $4d^4 5s^1$ (c) [Kr] $4d^5 5s^0$ (d) [Kr] $4d^3 5s^1 5p^1$

15) The ground state term of Sm^{3+} and Eu^{3+} respectively, are ***[Dec 2013]***

(a) $^7F_0$ and $^6H_{5/2}$ (b) $^6H_{5/2}$ and $^7F_0$ (c) $^2F_{5/2}$ and $^5I_4$ (d) $^7F_6$ and $^2F_{7/2}$

16) For an electronic configuration of two non-equivalent π electrons $[\pi^1, \pi^1]$ which of the following terms is not possible? ***[Dec 2013]***

(a) $^1\Sigma$ (b) $^3\Sigma$ (c) $^3\Delta$ (d) $^3\Phi$

17) In its electronic spectrum, $[V(H_2O)_6]^{3+}$ exhibits two absorption bands, one at 17,800 (ν_1) and the second at 25,700 (ν_2) cm^{-1}. The correct assignment of these bands, respectively, is ***[June 2014]***

(a) $\nu_1 = {}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$; $\nu_2 = {}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$

(b) $\nu_1 = {}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$; $\nu_2 = {}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(P)$

(c) $\nu_1 = {}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$; $\nu_2 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$

(d) $\nu_1 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$; $\nu_2 = {}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$

18) An aqueous solution of $[Mn(H_2O)_6]^{2+}$ complex is pale pink in color. The probable reasons for it are ***[Dec 2014]***

A. presence of $^6A_{1g}$ ground state B. disallowed transition by spin selection rule

C. presence of $^2T_{2g}$ ground state D. charge transfer transition

The correct answer is

(a) A and B (b) A and C (c) B and C (d) C and D

19) The spin-only magnetic moment and the spectroscopic ground state term symbol of manganese centre in $[MnF_6]^{3-}$ ion respectively, are ***[Dec 2014]***

(a) 4.9 BM and ^5D (b) 4.9 BM and ^4F
(c) 3.9 BM and ^3D (d) 4.9 BM and ^3F

20) The configuration $[Ne]2p^13p^1$ has a ^3D term. Its levels are ***[Dec 2014]***

(a) $^3D_{3/2}$, $^3D_{1/2}$ (b) $^3D_{5/2}$, $^3D_{3/2}$, $^3D_{1/2}$
(c) $^3D_3$, $^3D_2$, $^3D_1$ (d) $^3D_3$, $^3D_2$, $^3D_1$, $^3D_0$

21) The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is ***[Dec 2014]***

(a) 16 (b) 12 (c) 8 (d) 6

<u>(Questions from GATE EXAM)</u>

<u>Questions with ONE OR TWO marks</u>

22) The ground state term for V^{+3} ion is ***(GATE 2007)***

(a) ^3F (b) ^2F (c) ^3P (d) ^2D

23) The spectroscopic ground state symbol and the total number of electronic transitions of $[Ti(H_2O)_6]^{2+}$ are ***(GATE 2008)***

(a) $^3T_{1g}$ and 2 (b) $^3A_{2g}$ and 3 (c) $^3T_{1g}$ and 3 (d) $^3A_{2g}$ and 2

24) The lowest energy state of the $(1s)^2$ $(2s)^1$ $(3s)^1$ configuration of Be is ***(GATE 2008)***

(a) $^1S_0$ (b) $^1D_2$ (c) $^3S_1$ (d) $^3P_1$

25) The crystal field symbol for the ground state of $[Mn(CN)_6]^{4-}$ is ***[GATE 2010]***

(a) $^2T_{2g}$ (b) $^1A_{1g}$ (c) ^5E_g (d) $^6A_{1g}$

26) The crystal field stabilization energy (CFSE) value, for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is ***(GATE 2011)***

(a) 20,325 cm^{-1} (b) 12,195 cm^{-1} (c) 10,162 cm^{-1} (d) 8,130 cm^{-1}

27) Choose the allowed transition ***[GATE 2012]***

(a) $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ (b) $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^-$ (c) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ (d) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$

28) The ground states of high-spin octahedral and tetrahedral Co(II) complexes are, respectively ***[GATE 2012]***

(a) $^4T_{2g}$ and $^4A_2$ (b) $^4T_{1g}$ and $^4A_2$
(c) $^3T_{1g}$ and $^4A_2$ (d) $^4T_{1g}$ and $^3T_1$

29) The ground state term of $[Ni(H_2O)_6]^{2+}$ is ***[GATE 2013]***

(a) $^3T_{1g}$ (b) $^3T_{2g}$ (c) $^3A_{2g}$ (d) $^4T_{1g}$

30) The number of microstates in term ^1G is ***[GATE 2014]***

(a) 13 (b) 11 (c) 9 (d) 7

Answer Key

Topic: 7:- Term Symbol and electronic spectroscopy

1	c	2	d	3	c	4	c	5	c	6	c	7	b	8	a	9	d	10	d
11	b	12	b	13	b	14	b	15	b	16	d	17	a	18	a	19	a	20	c
21	d	22	a	23	c	24	c	25	a	26	a	27	c	28	b	29	c	30	c

Hint & solution

1) Ans (c):- The molecular term symbol is represented as:- $^{2S+1}|M_L|$

Molecular orbital (HOMO)	$\lvert M_L \rvert$	Letter
σ	0	Σ
π	1	Π
δ	2	Δ

The molecule electronic configuration:- $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^1(1\pi_u)^1$

HOMO is $(1\pi_u)^1(1\pi_u)^1$; $2S+1 = 2(^1/_2 + ^1/_2) + 1 = 3$

$|M_L| = m_{l1} + m_{l2} = (+1) + (-1) = 0 \quad \therefore |M_L| = 0$ that is Σ

The symmetry of $(1\pi_u)^1(1\pi_u)^1$ is $u \times u = g$

The sign is negative (−) for unpaired electrons in π orbital while positive (+) for paired electrons in π orbital;

Therefore the complete molecular term symbol is $^3\Sigma_g^-$

2) Ans (d):- The term symbol is represented as:- $^{2S+1}L_J$

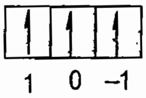
S is the total spin quantum number. 2*S* + 1 is the spin multiplicity:

L is the total orbital quantum number in spectroscopic notation.

L =	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	S	P	D	F	G	H	I	K	L	M	N	O	Q	R	T	U	V

J is the total angular momentum quantum number, J = |L+S| for more than half filled & |L−S| for less than half filled;

N(7) = p^3



Thus L = 0; S = 3/2 & J = |L+S| = |0 + 3/2| = 3/2

The term symbol is :- $^{2S+1}L_J = {}^4S_{3/2}$

3) Ans (c):- For electronic transition selection rule is:- $\Delta S = 0$; $\Delta l = \pm1$ & $\Delta J = 0, \pm1$

$^3F \rightarrow {}^1D$; $\Delta S \neq 0$ ∴ it is spin forbidden transition.

$^3F \rightarrow {}^1P$; $\Delta S \neq 0$ & $\Delta l \neq \pm1$ ∴ it is spin as well as laporte forbidden transition.

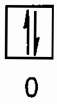
$^3F \rightarrow {}^3P$; $\Delta S = 0$ but $\Delta l \neq \pm1$ ∴ it is spin allowed but laporte forbidden transition.

$^3F \rightarrow {}^3D$; $\Delta S = 0$; $\Delta l = \pm1$ ∴ it is spin allowed as well as laporte allowed.

Therefore according to a selection rule the electric dipole allowed transition is $^3F \rightarrow {}^3D$

4) Ans (c):-

He(2) = $1s^2$



Thus L = 0; S = 0 & J = 0

The term symbol is :- $^{2S+1}L_J = {}^1S_0$

5) Ans (c):-The Mulliken symbols for the spectroscopic states

S (1)	A_{1g}
P (3)	T_{1g}
D (5)	E_g , T_{2g}
F (7)	A_{2g} , T_{1g} , T_{2g}
G (9)	A_{1g} , E_g , T_{1g} , T_{2g}
H (11)	E_g , 2 x T_{1g} , T_{2g}
I (13)	A_{1g} , A_{2g} , E_g , T_{1g} , 2 x T_{2g}

The Mulliken symbols for the spectroscopic states arising from the free-ion term for F is $T_{1g} + T_{2g} + A_{2g}$

6) Ans (c):- The total number of microstates for N identical particles with their occupation numbers {1, 2, 3} in three states is given by

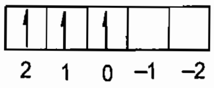
Total number of microstates = $\dfrac{N!}{n_x!n_y!n_z!}$

Identical particles (N) = 6; the states $\{n_x, n_y, n_z\} = \{1,2,3\}$

∴ Total number of microstates = $\dfrac{6!}{1!2!3!} = 60$

7) Ans (b):- $[Cr(NH_3)_6]^{+3}$ that is Cr^{+3} ion & it is d^3 system

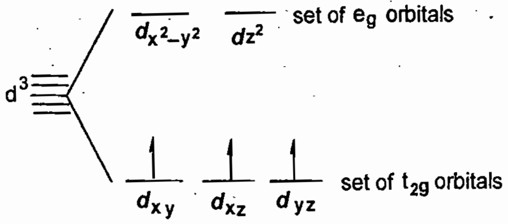
$Cr^{+3} = d^3$



Thus L = 3; S = 3/2 ∴ The term symbol is :- $^{2S+1}L = {}^4F$

The free-ion term for F is $T_{1g} + T_{2g} + A_{2g}$

Splitting pattern of Cr^{+3} ion in $[Cr(NH_3)_6]^{+3}$

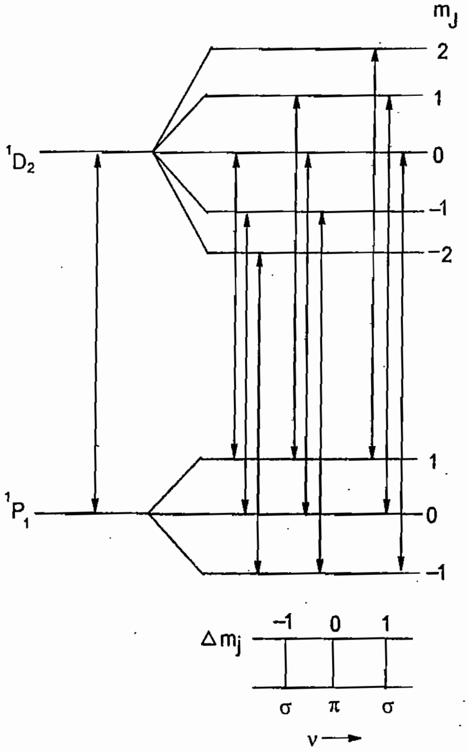


The ground state spectroscopic term is $^4A_{2g}$ & according to orgel diagram it has three type of transition:-

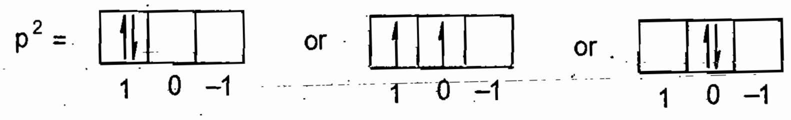
$^4A_{2g} \rightarrow {}^4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}$ & $^4A_{2g} \rightarrow {}^4T_{1g}(P)$

All the above three transition are spin allowed but transition $^4A_{2g} \rightarrow {}^2E_g$ is spin forbidden transition (according to a spin selection rule) . Therefore Intensity of this transition is lowest among three.

8) Ans (a):- In the presence of an external magnetic field (normal Zeeman effect), the transition $^1D_2 \rightarrow {}^1P_1$ splits into 9 lines

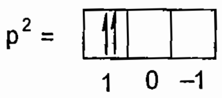


9) Ans (d):- The possible arrangement of electron for np^2 configuration & their term symbols are:



Term symbol = ^1D ^3P ^1S

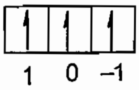
^3D term symbol that is NOT allowed for the np^2 configuration as it is violating the Pauli Exclusion Principle



Term symbol = ^3D (not possible)

10) Ans (d):- ^{15}N is a Isotopes of ^{14}N (Isotopes are nuclides of a particular element that differ in the number of neutrons with same number of electron)

N(7) = p^3



Thus L = 0; S = 3/2 & J = |L+S| = |0 + 3/2| = 3/2

The term symbol is :- $^{2S+1}L_J = {}^4S_{3/2}$

11) Ans (b):- For ^3D term symbol; S = 1 & for D term L = 2

Possible values of J = |L+S| to |L−S| = |2+1| to |2−1| = 3,2,1

∴ The possible J values for ^3D term symbol are 3

12) Ans (b):- The allowed transitions are (b) & (d) in options

Selection Rules for Electronic Transitions in Diatomic Molecules

Allowed Transitions	Examples
$\Delta\Lambda = 0, \pm 1$	$\Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Pi, \Sigma \leftrightarrow \Pi, \ \Delta \leftrightarrow \Pi$
$\Delta S = 0$	$^1\Sigma \leftrightarrow {}^1\Sigma, {}^3\Pi \leftrightarrow {}^3\Pi, {}^1\Sigma \leftrightarrow {}^1\Pi, \ {}^3\Sigma \leftrightarrow {}^3\Pi$
$+ \leftrightarrow +$	$\Sigma^+ \leftrightarrow \Sigma^+$
$- \leftrightarrow -$	$\Sigma^- \leftrightarrow \Sigma^-$
$g \leftrightarrow u$	$\Sigma_g^+ \leftrightarrow \Sigma_u^+, \ \Sigma_g \leftrightarrow \Pi_u$

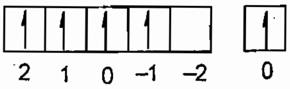
13) Ans (b):- The number of microstates of the excited states of Ti with electronic configuration [Ar] $4s^2 3d^1 4p^1$ with zero total spin (S) are 15.

The number of microstates of d^1 with zero total spin (S) = (2L + 1)(2S + 1) = 2(2) + 1 = 5 &

The number of microstates of p^1 with zero total spin (S) = (2L + 1)(2S + 1) = 2(1) + 1 = 3

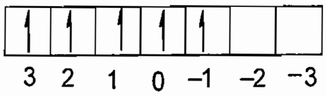
The total number of microstates of d^1p^1 with zero total spin (S) = 5×3 = 15

14) Ans (b):- The ground state term symbol for Nb (atomic number 41) is ^6D & for this term symbol the value of L is 2 & S is =5/2. The only electronic configuration corresponding to the value of L & S is [Kr] $4d^4\,5s^1$



15) Ans (b):- The ground state term of Sm^{3+} is

Sm^{+3} = $[Xe]4f^5$ =

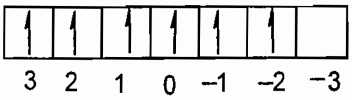


Thus L = 5; S = 5/2 & J = |L−S| = |5 − 5/2| = 5/2

The term symbol is :- $^{2S+1}L_J = {}^6H_{5/2}$

<u>The ground state term of Eu^{3+} is</u>

Eu^{+3} = $[Xe]4f^6$ =



Thus L = 3; S = 3 & J = |L−S| = |3 − 3| = 0

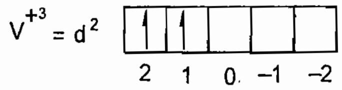
The term symbol is :- $^{2S+1}L_J = {}^7F_0$

Thus the ground state term of Sm^{3+} and Eu^{3+} respectively, are $^6H_{5/2}$ and $^7F_0$

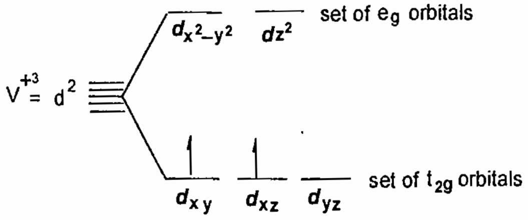
16) Ans (d):- For an electronic configuration of two non-equivalent π electrons [π^1, π^1] value of m_l is 1 & value of $M_L = | m_l + m_l |$.........$| m_l - m_l | = 2, 1, 0$; Thus spectroscopic state term $^3\Phi$ is not possible.

M_L	spectroscopic state
0	Σ
1	Π
2	Δ
3	Φ

17) Ans (a):- In $[V(H_2O)_6]^{3+}$; V is in +3 oxidation state i.e. d^2 system



Thus L = 3; S = 1 $\therefore$ The term symbol is :- $^{2S+1}L = {}^3F$



Ground state term = $^3T_{1g}$

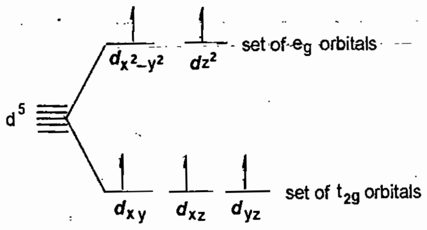
The free-ion term for ^3F is $^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$

The ground state spectroscopic term is $^3T_{1g}$ & according to orgel diagram it has three type of transition:-

$^3T_{1g} \rightarrow {}^3T_{2g}$; $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ & $^3T_{1g} \rightarrow {}^3A_{2g}$

Electronic transition	absorption band
$^3T_{1g} \rightarrow {}^3T_{2g}$ (V_1)	17800 cm^{-1}
$^3T_{1g} \rightarrow {}^3T_{1g}(P)$ (V_2)	25700 cm^{-1}

18) Ans (a):- According to spin selection rule; the transition is spin forbidden in $[Mn(H_2O)_6]^{2+}$ complex ion

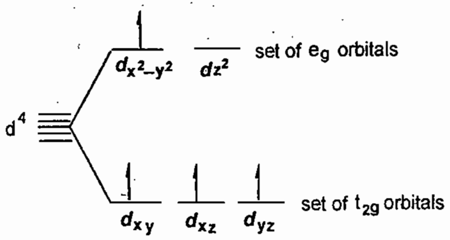


Mn^{+2} in high spin octahedral complexes

Ground state term = $^6A_{1g}$

Therefore the correct reason for pale pink color of $[Mn(H_2O)_6]^{2+}$ complex is the presence of $^6A_{1g}$ ground state & disallowed transition by spin selection rule

19) Ans (a):-



Mn^{+3} in high spin octahedral complexes

Ground state term symbol = ^5D

The spin-only magnetic moment = $\sqrt{n(n+2))}$ = $\sqrt{4(4+2)}$ = $\sqrt{24}$ = 4.9

The spectroscopic ground state term symbol: L = 2; S = 2 ∴ The term symbol is :- ^{2S+1}L = ^5D

20) Ans (c):- The configuration $[Ne]2p^1 3p^1$ has a ^3D

For term L= 2 & S = 1 & possible values of J = |L+S| to |L−S| = |2+1| to |2−1| = 3,2,1

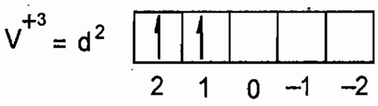
The configuration $[Ne]2p^1 3p^1$ has a ^3D term. Its levels are $^3D_3$, $^3D_2$, $^3D_1$

21) Ans (d):- Total number of microstates = $\frac{N!}{r!(N-r)!}$

Given N = 4 & r = 2

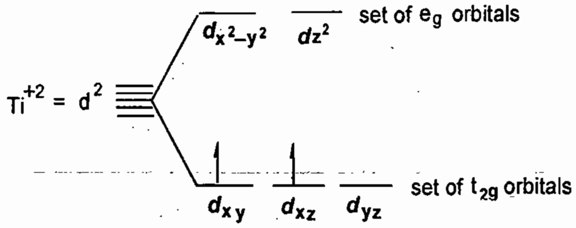
∴ Total number of microstates = $\frac{4!}{2!(4-2)!}$ = 6

22) Ans (a):- V is in +3 oxidation state i.e. d^2 system



Thus L = 3; S = 1 ∴ The term symbol is :- ^{2S+1}L = ^3F

23) Ans (c):- The spectroscopic ground state symbol and the total number of electronic transitions of $[Ti(H_2O)_6]^{2+}$ are $^3T_{1g}$ and 3



Ground state term = $^3T_{1g}$

Thus L = 3; S = 1 ∴ The term symbol is :- ^{2S+1}L = ^3F

The free-ion term for ^3F is $^3T_{1g}$ + $^3T_{2g}$ + $^3A_{2g}$

The ground state spectroscopic term is $^3T_{1g}$ & according to orgel diagram it has three type of transition:-

$^3T_{1g} \rightarrow {}^3T_{2g}$; $^3T_{1g} \rightarrow {}^3A_{2g}$ & $^3T_{1g} \rightarrow {}^3T_{1g}(P)$

24) Ans (c):- The lowest energy state of the $(1s)^2$ $(2s)^1$ $(3s)^1$ configuration of Be is $^3S_1$

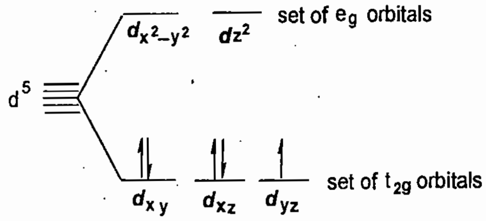
$(1s^2)(2s^1)(3s^1)$ =

Resultant S =1 & Resultant L= 0

Thus L = 0; S = 1 & J = |L+S| = |0 + 1| = 1

The term symbol is :- $^{2S+1}L_J = {}^3S_1$

25) Ans (a):- The crystal field symbol for the ground state of $[Mn(CN)_6]^{4-}$ is $^2T_{2g}$

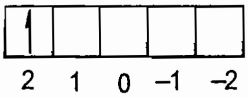


Mn^{+2} in low spin octahedral complexes

Ground state term = $^2T_{2g}$

26) Ans (a):-

$Ti^{+3} = d^1$



Thus L = 2; S = ½ ∴ The term symbol is:- $^{2S+1}L = {}^2D$

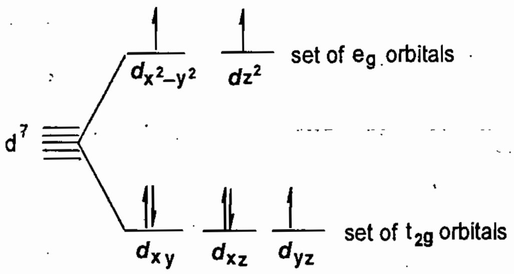
The term for ^2D is $^2T_{2g} + {}^2E_g$

Given:- absorption maxima (λ) = 492nm (492×10^{-7}cm)

∴In the case of d^1 system CFSE = frequency(ν) = $\frac{1}{\lambda} = \frac{1}{492\times10^{-7}} = 20325\ cm^{-1}$

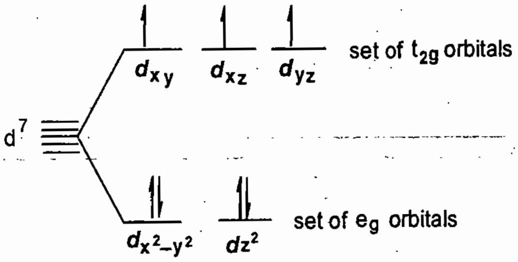
27) Ans (c):- The allowed transition $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ (Refer the chart of Q.no. 12)

28) Ans (b):- The ground states of high-spin octahedral and tetrahedral Co(II) complexes are $^4T_{1g}$ and $^4A_2$ respectively



Co^{+2} in high spin octahedral complexes

Ground state term = $^4T_{1g}$



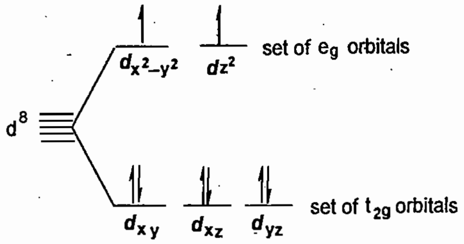
Co^{+2} in tetrahedral complexes

Ground state term = $^4A_2$

As L = 3; S =3/2 ∴ The term symbol is :- $^{2S+1}L = {}^4F$

The free-ion term for ^4F is $^4T_{1g} + {}^4T_{2g} + {}^4A_{2g}$

29) Ans (c):- The ground state term of $[Ni(H_2O)_6]^{2+}$ is $^3A_{2g}$ (according to the orgel diagram)



Thus L = 3; S = 1 ∴ The term symbol is :- $^{2S+1}L = {}^3F$

The free-ion term for ^3F is $^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$

The ground state spectroscopic term is $^3A_{2g}$ & according to orgel diagram it has three type of transition:-

$^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}$ & $^3A_{2g} \rightarrow {}^3T_{1g}(P)$

30) Ans (c):- The number of microstates in term ^1G is 9 (for G; L = 4)

The number of microstates for this type of term = (2S+1) (2L+1)

= 1×[2(4)+1] = 9

List of Reference Books

1) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited

2) Concise inorganic chemistry, By J. D. Lee, John Wiley & Sons. India.

3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.

4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press

5) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.

6) Physical Chemistry a molecular approach, by Donald A. McQuarrie and John D. Simon, University Science Book

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Topic 8

ORGANO–METALLIC CHEMISTRY & CATALYSIS

Questions with two marks

1) In Ziegler-Natta catalysis the commonly used catalyst system is *[June 2011]*

(a) $TiCl_4$, $Al(C_2H_5)_3$ (b) $(\eta^5\text{-}Cp)_2TiCl_2$, $Al(OC_2H_5)_3$
(c) $VO(acac)_2$, $Al_2(CH_3)_6$ (d) $TiCl_4$, BF_3

2) Oxidation occurs very easily in case of *[June 2011]*

(a) $(\eta^5\text{-}C_5H_5)_2Fe$ (b) $(\eta^5\text{-}C_5H_5)_2Co$ (c) $(\eta^5\text{-}C_5H_5)_2Ru$ (d) $(\eta^5\text{-}C_5H_5)_2Co^+$

3) Complex in which organic ligand is having only σ– bond with metal is *[June 2011]*

(a) $W(CH_3)_6$ (b) $(\eta^5\text{-}C_5H_5)_2Fe$ (c) $K[PtCl_3(C_2H_4)]$ (d) $(\eta^6\text{-}C_6H_6)_2Ru$

4) The correct combination of metal, number of carbonyl ligands and the charge for a metal carbonyl complex $[M(CO)_x]^{z-}$ that satisfies the 18 electron rule is *[Dec2011]*

(a) M = Ti, x = 6, z = 1 (b) M = V, x = 6, z = 1
(c) M = Co, x = 4, z = 2 (d) M = Mo, x = 5, z = 1

5) The stable cyclopentadienyl complex of beryllium is *[Dec2011]*

(a) $[Be(\eta^5\text{-}C_5H_5)_2]$ (b) $[Be(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$
(c) $[Be(\eta^1\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)]$ (d) $[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$

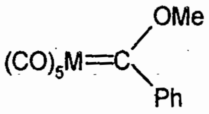
) For a reaction, $trans[IrCl(CO)(PPh_3)_2] + Cl_2 \longrightarrow trans[IrCl_3(CO)(PPh_3)_2]$ the correct observation *[June 2012]*

(a) ν_{CO}(product) > ν_{CO}(reactant) (b) ν_{CO} (product) < ν_{CO} (reactant)
(c) ν_{CO} (product) = ν_{CO} (reactant) (d) ν_{CO} (product) = ν_{CO} (free CO)

The substitution of η^5– Cp group with nitric oxide is the easiest for *[Dec2012]*

(a) $\eta^5\text{-}Cp_2Fe$ (b) $\eta^5\text{-}Cp_2CoCl$ (c) $\eta^5\text{-}Cp_2Ni$ (d) $\eta^5\text{-}Cp_2Co$

The molecule shown below obeys 18 e rule. The two 'M' satisfying the condition are *[Dec2012]*



$(CO)_5M{=}C(OMe)(Ph)$

(a) Cr, Re^+ (b) Mo, V (c) V, Re^+ (d) Cr, V

he ligand in uranocene is *[June 2013]*

(a) $C_8H_8^{2-}$ (b) $C_5H_5^{2-}$ (c) C_6H_6 (d) $C_4H_4^{2-}$

n metal-olefin interaction, the extent of increase in metal → olefin π–back donation would *[June 2013]*

a) lead to a decrease in C = C bond length
b) change the formal oxidation state of the metal
c) change the hybridization of the olefin carbon from sp^2 to sp^3.
d) increase with the presence of electron donating substituent on the olefin.

11) The oxidation state of molybdenum in $[(\eta^7-\text{tropylium})Mo(CO_3)]^+$ is **[June 2013]**

(a) +2 (b) +1 (c) 0 (d) −1

12) The number of metal-metal bonds in $[W_2(OPh)_6]$ is: **[June 2013]**

(a) 1 (b) 2 (c) 3 (d) 4

13) The reaction given below is an example of **[June 2013]**

$$\left[(CO)_5Mn(Me)\right] + CO \longrightarrow \left[(CO)_5Mn\{C(O)(Me)\}\right]$$

(a) oxidative addition (b) electrophilic substitution
(c) nucleophilic substitution (d) migratory insertion

14) Which of the following is NOT suitable as catalyst for hydroformylation? **[Dec2013]**

(a) $HCo(CO)_4$ (b) $HCo(CO)_3PBu_3$ (c) $HRh(CO)(PPh_3)_3$ (d) $H_2Rh(PPh_3)_2Cl$

15) The ligand(s) that is (are) fluxional in $[(\eta^5-C_5H_5)(\eta^1-C_5H_5)Fe(CO)_2]$ in the temperature range 221–298K, is (are) **[June 2014]**

(a) $\eta^5-C_5H_5$ (b) $\eta^1-C_5H_5$ (c) $\eta^5-C_5H_5$ and CO (d) $\eta^1-C_5H_5$ and CO

16) The oxidation state of Ni and number of metal-metal bonds in $[Ni_2(CO)_6]^{2-}$ that are consistent with the 18 electron rule are **[June 2014]**

(a) Ni (−II), 1 bond (b) Ni (IV), 2 bond (c) Ni (−I), 1 bond (d) Ni (IV), 3 bonds

17) The product of the reaction of propene, CO and H_2 in the presence of $Co_2(CO)_8$ as a catalyst is **[Dec 2014]**
(a) Butanoic acid (b) Butanal (c) 2-butanone (d) Methylpropanoate

18) The hapticities 'x' and 'y' of the arene moieties in the diamagnetic complex $[(\eta^x-C_6H_6)Ru(\eta^y-C_6H_6)]$ respectively are **[Dec 2014]**

(a) 6 and 6 (b) 4 and 4 (c) 4 and 6 (d) 6 and 2

19) Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh) **[Dec 2014]**

(a) T-shaped $[Rh(PPh_3)_2Cl]$ (b) Trigonal-planar $[Rh(PPh_3)_2Cl]^{2+}$

(c) T-shaped $[Rh(H)(PPh_3)Cl]^+$ (d) Trigonal-planar $[Rh(H)(PPh_3)_2]$

Questions with four marks

20) The oxidative addition and reductive elimination steps are favoured by **[June 2011]**

(a) Electron rich metal centers.
(b) Electron deficient metal centers
(c) Electron deficient and electron rich metal centers respectively.
(d) Electron rich and electron deficient metal centers respectively.

21) Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)_4$, $Ti(i\text{-}Pr)_4$ and $TiEt_4$. **[June 2011]**

(a) $Ti(CH_2Ph)_4 < Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4$ (b) $TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

(c) $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$ (d) $TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

22) Among the metals, Mn, Fe, Co and Ni, the ones those would react in its native form directly with CO giving metal carbonyl compounds are ***[June 2011]***

(a) Co and Mn (b) Mn and Fe (c) Fe and Ni (d) Ni and Co

23) In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$ ***[June 2011]***

(a) Forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$
(b) Forms an adduct with an olefin reactant.
(c) Reacts with H_2.
(d) Eliminates propane.

24) Reaction of $Fe(CO)_5$ with OH^- leads to complex A which on oxidation with MnO_2 gives B. Compounds A and B respectively are ***[Dec2011]***

(a) $[HFe(CO)_4]^-$ and $Fe_3(CO)_{12}$ (b) $[Fe(CO)_5(OH)]^-$ and $Fe_2(CO)_9$
(c) $[Fe(CO)_4]^{2-}$ and $Mn_2(CO)_{10}$ (d) $[HFe(CO)_4]^-$ and Fe_2O_3

25) The number of metal-metal bonds in the dimers $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2$ respectively, are ***[Dec2011]***

(a) two and two (b) two and three (c) one and two (d) zero and one

26) In the trans-$PtCl_2L(CO)$ complex, the CO stretching frequency for L = NH_3, pyridine, NMe_3 decreases in the order ***[Dec2011]***

(a) pyridine > NH_3 > NMe_3 (b) NH_3 > pyridine > NMe_3
(c) NMe_3 > NH_3 > pyridine (d) pyridine > NMe_3 > NH_3

27) The greater stability of $((CH_3)_3C{-}CH_2{-})_4Ti$ (A) compared to that of $((CH_3)_2CH{-}CH_2{-})_4$ Ti(B) due to ***[Dec2011]***

(a) Hyperconjugation present in complex (A)
(b) β–hydride elimination is not possible in complex (A)
(c) Steric protection of titanium from reactive species in complex (A)
(d) The stronger nature of Ti–C bond in complex (A).

28) A compound A having the composition $FeC_9H_8O_3$ shows one signal at 2.5 ppm and another one around 5.0 ppm in its ^1H NMR spectrum. The IR spectrum of this compound shows two bands around 1900 and 1680 cm^{-1}. The compound follows the 18 electron rule of the following statements for A, the correct one is/are ***[Dec2011]***

(A) It has η^5– Cp group (B) It has terminal CO ligand
(C) It has CH_3 ligand (D) It has Fe–H bond

(a) (A) and (B) only (b) (C) only (c) (A) and (C) only (d) (B) and (D) only.

29) The carbonyl resonance in ^{13}C NMR spectrum of $[(\eta^5\text{– }C_5H_5)\,Rh\,(CO)]_3$ (^{103}Rh, nuclear spin, I = ½, 100%) shows a triplet at –65° C owing to the presence of ***[June 2012]***

(a) Terminal CO (b) μ_2–CO (c) μ_3–CO (d) η^5– C_5H_5

30) The complex that *<u>DOES NOT</u>* obey 18- electron rule is: ***[June 2012]***

(a) $[(\eta^5\text{– }C_5H_5)]\,RuCl(CO(PPh_3)]$ (b) $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$

(c) $[IrCl_3(PPh_3)_2(AsPh_2)]^-$ (d) $[Os(N)Br_2(PMe_3)(NMe_2)]^-$

31) The final product of the reaction $[\,Mn(CO)_6]^+ + MeLi \longrightarrow$ is ***[June 2012]***

(a) $[\,Mn(CO)_6]^+\,Me^-$ (b) $[\,Mn(CO)_5Me]$ (c) $[\,Mn(CO)_6]$ (d) $[\,(MeCO)Mn(CO)_5]$

32) Complexes of general formula, fac–[Mo(CO)$_3$(phosphines)$_3$] have the C–O stretching bands as given below. Phosphines:- PF$_3$(A); PCl$_3$(B); P(Cl)Ph$_2$(C); PMe$_3$(D)

ν_{CO} cm^{-1} = 2090(i); 2040(ii); 1977(iii); 1945(iv)

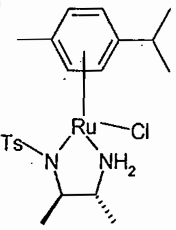
The correct combination of the phosphine and the streching frequency is, ***[Dec2012]***

(a) (A–i), (B–ii), (C–iii), (D–iv)
(b) (A–ii), (B–i), (C–iv), (D–iii)
(c) (A–iv), (B–iii), (C–ii), (D–i)
(d) (A–iii), (B–iv), (C–i), (D–ii)

33) In the cluster [Co$_3$(CH)(CO)$_9$] obeying 18 electron rule, the number of metal-metal bonds and the bridging ligands respectively, are ***[Dec2012]***

(a) 3 and 1 CH
(b) 0 and 3 CO
(c) 3 and 1 CO
(d) 6 and 1 CH

34) Consider the catalyst in column-I and reaction in column-II ***[Dec2012]***

Column - I	**Column - II**
A) [(R)-BINAP]Ru^{-2}	i) Hydroformylation
B) [Rh(CO)$_2$I$_2$]$^-$	ii) Asymmetric hydrogenation
C) Pd(PPh$_3$)$_4$	iii) Asymmetric hydrogen transfer
D) 	iv) Heck coupling

The best match of a catalyst of column-I with the reaction under column-II is

(a) (A–ii), (B–i), (C–iv), (D–iii)
(b) (A–i), (B–ii), (C–iii), (D–iv)
(c) (A–iii), (B–i), (C–iv), (D–ii)
(d) (A–iv), (B–iii), (C–ii), (D–i)

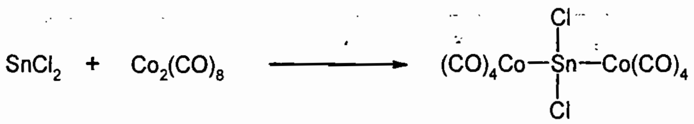
35) Which one of the following will NOT undergo oxidative addition by methyl iodide? ***[Dec2012]***

(a) [Rh(CO)$_2$I$_2$]$^-$
(b) [Ir(PPh$_3$)$_2$ (CO)Cl]
(c) [η^5– CpRh(CO)$_2$]
(d) [η^5– Cp$_2$ Ti(Me)Cl]

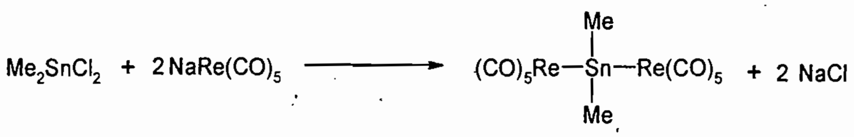
36) In hydrofomylation reaction using [Rh(PPh$_3$)$_3$ (CO)(H)] as the catalyst, addition of excess PPh$_3$ would ***[Dec2012]***

(a) increase the rate of reaction
(b) decrease the rate of reaction.
(c) not influence the rate of reaction
(d) stop the reaction.

37) Reactions A and B are, termed as respectively. ***[Dec2012]***

A) 

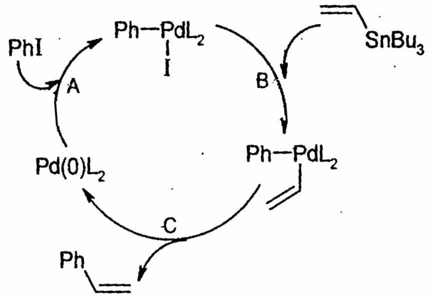
$$SnCl_2 + Co_2(CO)_8 \longrightarrow (CO)_4Co\text{–}SnCl_2\text{–}Co(CO)_4$$

B) 

$$Me_2SnCl_2 + 2\,NaRe(CO)_5 \longrightarrow (CO)_5Re\text{–}SnMe_2\text{–}Re(CO)_5 + 2\,NaCl$$

(a) Insertion, Metathesis
(b) Metathesis, insertion
(c) Oxidative addition, metathesis
(d) Oxidative addition, insertion

38) Consider the following reaction mechanism *[Dec2012]*



The steps A, B and C, respectively, are

(a) Oxidative addition; transmetallation; reductive elimination.
(b) Oxidative addition; carbopalladation; β–hydride elimination.
(c) Carbopalladation; transmetallation; reductive elimination.
(d) Metal halogen exchange; transmetallation; metal extrusion.

39) Though cyclobutadiene (C_4H_4) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because *[June 2013]*

(a) it engages in long-range interaction with transition metals.
(b) it gains stability due to formation of $C_4H_4^{2-}$ on binding to transition metals.
(c) its polymerization ability reduces in presence of transition metal.
(d) it becomes stable in presence of transition metals due to formation of $C_4H_4^{2+}$.

40) The number of metal-metal bonds in $Ir_4(CO)_{12}$ is *[June 2013]*

(a) 4 (b) 6 (c) 10 (d) 12

41) The orders of reactivity of ligands, NMe_3, PMe_3 and CO with complexes $MeTiCl_3$ and $(CO)_5Mo(thf)$ are *[June 2013]*

(a) CO > PMe_3 > NMe_3 and CO > NMe_3 > PMe_3 (b) PMe_3 > CO > NMe_3 and NMe_3 > CO > PMe_3
(c) NMe_3 > PMe_3 > CO and CO > PMe_3 > NMe_3 (d) NMe_3 > CO > PMe_3 and PMe_3 > NMe_3 > CO

42) The correct statement regarding terminal/bridging CO groups in solid $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ is *[Dec2013]*

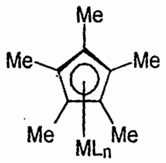
(a) both have equal number of bridging CO groups
(b) number of bridging CO groups in $Co_4(CO)_{12}$ is 4
(c) the number of terminal CO groups in $Co_4(CO)_{12}$ is 8
(d) the number of bridging CO groups in $Ir_4(CO)_{12}$ is zero.

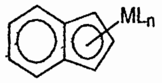
43) On reducing $Fe_3(CO)_{12}$ with an excess of sodium, a carbonylate ion is formed. The iron is isoelectronic With *[Dec2013]*

(a) $[Mn(CO)_5]^-$ (b) $[Ni(CO)_4]$ (c) $[Mn(CO)_5]^+$ (d) $[V(CO)_6]^-$

4) Substitution of L with other ligands will be easiest for the species *[Dec2013]*

(a)


(b)


(c)


(d)


45) ^{1}H NMR spectrum of [η^5–C_5H_5)Rh(C_2H_4)$_2$] at –20^{0}Cshows a typical AA' XX' pattern in the olefinic region. on increasing the temperature to ~70°C, the separate lines collapse into a single line which is due to ***[June 2014]***

(a) free rotation of the ethylene ligand about the metal-olefin bond
(b) intramolecular exchange between the ethylene ligands
(c) intermolecular exchange between the ethylene ligands
(d) change in hapticity of the cyclopentadienyl ligand

46) Reaction of nitrosyl tetrafluoroborate to Vaska's complex gives complex A with an ∠M–N–O = 124^0. The complex A and its N–O stretching frequency are, respectively ***[June 2014]***

(a) [IrCl(CO)(NO)(PPh_3)$_2$]BF_4, 1620 cm^{-1}
(b) [IrCl(CO)(NO)$_2$(PPh_3)](BF_4)$_2$, 1730 cm^{-1}
(c) [IrCl(CO)(NO)$_2$(PPh_3)](BF_4)$_2$, 1520 cm^{-1}
(d) [IrCl(CO)(NO)(PPh_3)$_2$], 1820 cm^{-1}

47) Na [η^5–C_5H_5)Fe(CO)$_2$] reacts with Br_2 to give A. Reaction of A with $LiAlH_4$ results in B. The proton NMR spectrum of B consists of two singlets of relative intensity 5:1. Compounds A and B, respectively are ***[Dec 2014]***

(a) (η^5–C_5H_5)Fe(CO)$_2$Br and (η^5–C_5H_5)Fe(CO)$_2$H
(b) (η^4–C_5H_5)Fe(CO)$_2$Br$_2$ and (η^4–C_5H_5)Fe(CO)$_2$HBr
(c) (η^5–C_5H_5)Fe(CO)$_2$Br and (η^4–C_5H_5)Fe(CO)$_2$(H)$_2$
(d) (η^5–C_5H_5)Fe(CO)$_2$Br and (η^5–C_5H_5)Fe(CO)$_2$HBr

48) ^{1}H NMR spectrum of free benzene shows a peak at ~ 7.2 ppm. The expected chemical shift (in ppm) of C_6H_6 ligand in ^{1}H NMR spectrum of [η^6–C_6H_6)Cr(CO)$_3$] and the reason for it, if any, is/are ***[Dec 2014]***

(a) 4.5; disruption of ring current
(b) 9.0; inductive effect
(c) 7.2
(d) 2.5; combination of inductive effect and disruption of ring current.

49) Complexes of HM(CO)$_5$ and [η^5–C_5H_5)M'(CO)$_3$]$_2$ obey the 18–electron rule. Identify M and M' and their ^{1}H NMR chemical shifts relative to TMS. ***[Dec 2014]***

(a) M = Mn, –7.5; M' = Cr, 4.10
(b) M = Cr, 4.10; M' = Mn, –7.5
(c) M = V, –7.5; M' = Cr, 4.10
(d) M = Mn, 10.22; M' = Fe, 2.80

50) The compound that undergoes oxidative addition reaction in presence of H_2 is ***[Dec 2014]***

(a) [Mn (CO)$_5$]$^-$
(b) [η^5–C_5H_5)Mo(CO)$_3$]$^-$
(c) IrCl(CO)(PPh_3)$_2$]
(d) [η^5–C_5H_5)$_2$ReH]

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

51) The neutral complex which follows the 18-electron rule is ***(GATE 2005)***

(a) (η^5–C_5H_5)Fe(CO)$_2$
(b) (η^5–C_5H_5)Mo(CO)$_3$
(c) (η^5–C_5H_5)$_2$Co
(d) (η^5–C_5H_5)Re(η^6-C_6H_6)

52) For the metal-olefin complexes (i) [PtCl$_3$(C_2H_4)]$^-$ and (ii) [PtCl$_3$(C_2F_4)]$^-$, the Correct statement is that ***(GATE 2005)***

(a) Carbon-carbon bond length is same both in (i) and (ii)
(b) Carbon-carbon bond length in (i) is smaller compared to that of (ii)
(c) Carbon-carbon bond length in (i) is larger compared to that of (ii)
(d) a metallacycle is formed in each complex

53) The values of M-C stretching frequencies of (i) $[V(CO)_6]^-$, (ii) $[Cr(CO)_6]$ and (iii) $[Mn(CO)_6]^+$ follow the trend ***(GATE 2005)***

(a) (ii)>(i)>(iii) (b) (ii)>(iii)>(i) (c) (i)>(ii)>(iii) (d) (iii)>(ii)>(i)

54) Match the following items of column I with the appropriate items in column II ***(GATE 2005)***

Column I	**column II**
P) Wilkinsons catalyst	I Trans-$IrCl(CO)(PPh_3)_2$
Q) speiers catalyst	II Hydrosilylation
R) Water gas shift catalyst	III $RhCl(PPh_3)_3$
S) Zeolite ZSM-5 catalyst	IV Synthetic gasoline
	V Hydroformylation
	VI Zinc- copper oxide

(a) P-III, Q-II, R-VI, S-IV (b) P-I, Q-V, R-III, S-IV

(c) P-V, Q-II, R-VI, S-IV (d) P-III,Q-VI, R-IV, S-II

55) The CORRECT order of the CO stretching vibrational frequency is ***(GATE 2006)***

(a) $[Ti(CO)_6]^{2-} > [V(CO)_6]^- > CO > [Cr(CO)_6]$ (b) $[Cr(CO)_6] > CO > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$

(c) $CO > [V(CO)_6]^- > [Ti(CO)_6]^{2-} > [Cr(CO)_6]$ (d) $CO > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$

56) Zn in carbonic anhydrase is coordinated by three histidine and one water molecule. The reaction of CO_2 with this enzyme is an example of ***(GATE 2007)***

(a) electrophilic addition (b) electron transfer

(c) nucleophilic addition (d) electrophilic substitution

57) Match the compounds in List I with the corresponding structure / property given in List II ***(GATE 2007)***

List I	***List II***
(A) $(Ph_3P)_3RhCl$	(i) Spinel
(B) LiC_6	(ii) Intercalation
(C) PtF_6	(iii) Oxidising agent
(D) Ni_3S_4	(iv) Catalyst for alkene hydrogenation

(a) (A–iii) (B–i) (C–ii) (D–iv) (b) (A–iv) (B–ii) (C–iii) (D–i)

(c) (A–iii) (B–ii) (C–i) (D–iv) (d) (A–iv) (B–iii) (C–ii) (D–i)

58) $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives a compound X, X is represented as ***(GATE 2007)***

(a) WMe_6 (b) $(CO)_5W{-}Me$ (c) $(CO)_5W{=}C(Me)OMe$ (d) $(CO)_5W{\equiv}CMe$

59) In the complexes $[Ni_2(\eta^5-C_5H_5)_2(CO)_2]$ the IR stretching frequency appears at 1857cm^{-1} (strong) and 1897cm^{-1} (weak). The valence electron count and the nature of the M-CO bond respectively are ***(GATE 2007)***

(a) 16 e^-, bridging (b) 17 e^-, bridging (c) 18 e^-, terminal (d) 18 e^-, bridging

0) In the reaction shown below, X and Y respectively are ***(GATE 2007)***

$$Mn_2(CO)_{10} \xrightarrow{Na} (X) \xrightarrow{CH_3COCl} (Y)$$

(a) $[Mn(CO)_4]^{2-}$, $[CH_3C(O)Mn(CO)_5]^{1-}$ (b) $[Mn(CO)_5]^-$, $CH_3C(O)Mn(CO)_5$

(c) $[Mn(CO)_5]^-$, $[Cl\,Mn(CO)_5]$ (d) $[Mn(CO)_5]^{2-}$, $[Cl\,Mn(CO)_5]^-$

61) The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is *(GATE 2007)*

(a) $HCo(CO)_4$ (b) $[PdCl_4]^{2-}$

(c) V_2O_5 (d) [$TiCl_4$in presence of $Al(C_2H_5)_3$

62) The number of M-M bonds in $Ir_4(CO)_{12}$ are *(GATE 2008)*

(a) four (b) six (c) eight (d) zero

63) Schrock carbenes are

(a) triplets and nucleophilic (b) triplets and electrophilic

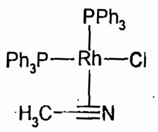
(c) singlets and nucleophilic (d) singlets and electrophilic

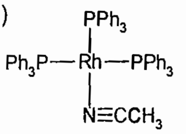
<u>Consider a reaction for Linked Answer Questions (64 and 65)</u> *(GATE 2008)*

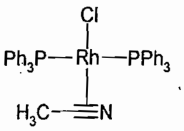
In the reaction,

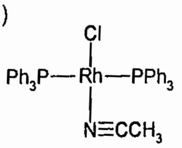
$$(PPH_3)_3RhCl \xrightarrow{CH_3CN} X + Y$$

64) Compound X is

(a)


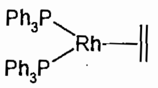
(b)


(c)


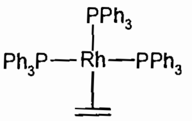
(d)


65) $Rh(PPh_3)_3Cl$ reacts very fast with a gaseous mixture of H_2 and C_2H_2 to immediately give Z. The structure of Z is

(a) H_3C-CH_3

(b)


(c) $(PPH_3)_2RhCl(\eta^2-C_2H_4)$

(d)


66) The number of metal - metal bonds in $[(C_5H_5)Fe(CO)]_2$ is *[GATE 2009]*

(a) zero (b) one (c) two (d) three

67) The correct order of ν_{CO} for the compounds $[Mo(CO)_3(NMe_3)_3$; $[Mo(CO)_3(P(OPh)_3)_3$; $[Mo(CO)_3(PMe_3)_3$; $[Mo(CO)_3(PCl_3)_3$ in the IR spectrum is *[GATE 2009]*

(a) $[Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(PCl_3)_3]$

(b) $[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3]$

(c) $[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3]$

(d) $[Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3] > [Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3]$

68) The reaction between $[PdCl_4]^{-2}$ and C_2H_4 produces a new compound compared to free C_2H_4 the C–C bond order of the product is *[GATE 2010]*

(a) between 1 and 2 (b) less than I (c) unaltered (d) greater than 2

69) Structurally nickellocene is similar to ferrocene. Nickellocene attains stability due to formation of *[GATE 2010]*

(a) a monocation (b) a dication (c) a monoanion (d) a dianion

70) A well known naturally occurring organometallic compound is *(GATE 2011)*

(a) vitamin B_{12} coenzyme (b) chlorophyll (c) cytochrome P-450 d) myoglobin

71) The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$, respectively, is ***(GATE 2011)***

(a) 3 and 6 (b) 4 and 5 (c) zero and 4 (d) 3 and 4

72) The product of the reaction between $CH_3Mn(CO)_5$ and ^{13}CO is ***(GATE 2011)***

(a) $(CH_3\,^{13}CO)Mn(CO)_5$ (b) $(CH_3CO)Mn(CO)_4(^{13}CO)$
(c) $(^{13}CH_3CO)Mn(CO)_5$ (d) $CH_3Mn(CO)_4$

73) The number of terminal carbonyl groups present in $Fe_2(CO)_9$ is ***[GATE 2012]***

(a) 2 (b) 5 (c) 6 (d) 3

74) The INCORRECT statement about Zeise's salt is ***[GATE 2012]***

(a) Zeise's salt is diamagnetic
(b) The oxidation state of Pt in Zeise's salt is +2
(c) All the Pt−Cl bond lengths in Zeise's salt are equal
(d) C−C bond length of ethylene moiety in Zeise's salt is longer than that of free ethylene molecule

75) An intermediate formed during the hydroformylation of olefins using $Co_2(CO)_8$ as catalyst is ***[GATE 2012]***

(a) $HCo(CO)_6$ (b) $H_4Co(CO)_3$ (c) $H_2Co(CO)_4$ (d) $HCo(CO)_4$

76) The by-product formed in the characteristic reaction of $(CO)_5Cr{=}C(OMe)(Me)$ with $MeNH_2$ is ***[GATE 2013]***

(a) CO (b) MeOH (c) MeCHO (d) $MeCONH_2$

77) The catalyst and co-catalyst used in the Wacker process, respectively, are ***[GATE 2013]***

(a) $PdCl_2$ and Cu (b) $CuCl_2$ and $[PdCl_4]^{2-}$
(c) Pd and CuCl (d) $[PdCl_4]^{2-}$ and $CuCl_2$

78) Hapticity of cycloheptatrienein $Mo(C_7H_8)(CO)_3$ is ***[GATE 2013]***

(a) Five (b) Six (c) Seven (d) Eight

79) Amongst the following, the metal that does NOT form homoleptic polynuclear metal carbonyl is
(a) Mn (b) Fe (c) Cr (d) Co ***[GATE 2014]***

80) In Monsanto acetic acid process shown below, the role of HI is ***[GATE 2014]***

$$CH_3OH + CO \xrightarrow[180^0C,\ 30\ bar]{Rh(I)\ Catalyst\ /\ HI} CH_3COOH$$

(a) to convert CH_3OH to a stronger nucleophile (CH_3O^-)
(b) to reduce the Rh(I) catalyst to a Rh(0) species
(c) to reduce a Rh(III) active species to a Rh(I) species in the catalytic cycle
(d) to convert CH_3OH to CH_3I

81) Amongst the following, the metal carbonyl species having the highest ν_{CO} stretching frequency is ***[GATE 2014]***
(a) $[Mn(CO)_6]^+$ (b) $Cr(CO)_6$ (c) $[V(CO)_6]^-$ (d) $[Fe(CO)_4]^{2-}$

82) The correct order of thermal stability for the given compounds is ***[GATE 2014]***

(a) $TiMe_4 > Ti(CH_2CMe_3)_4 > TiEt_4$ (b) $TiEt_4 > Ti(CH_2CMe_3)_4 > TiMe_4$
(c) $TiMe_4 > TiEt_4 > Ti(CH_2CMe_3)_4$ (d) $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

Answer Key

Topic:- 8 Organo-metallic Chemistry & catalysis

1	a	2	b	3	a	4	b	5	d	6	a	7	c	8	a	9	a	10	c
11	b	12	c	13	d	14	d	15	b	16	c	17	b	18	c	19	a	20	d
21	c	22	c	23	a	24	a	25	d	26	a	27	b	28	a	29	b	30	d
31	d	32	a	33	a	34	a	35	d	36	b	37	a	38	a	39	b	40	b
41	c	42	d	43	b	44	c	45	a	46	a	47	a	48	a	49	a	50	c
51	d	52	c	53	c	54	a	55	d	56	c	57	b	58	c	59	d	60	b
61	b	62	b	63	a	64	b	65	c	66	d	67	c	68	a	69	b	70	a
71	a	72	b	73	c	74	c	75	d	76	b	77	d	78	b	79	c	80	d
81	a	82	d																

Hint and solution

1) Ans (a):- $TiCl_4$, $Al(C_2H_5)_3$ is used in Ziegler-Natta catalysis. The commonly used catalyst in polymerization of ethylene.

2) Ans (b):- In $(\eta^5-C_5H_5)_2Co$; Oxidation occur easily to form 18 e^- complex

Complex	Electrons	conclusion
$(\eta^5-C_5H_5)_2Fe$	18	stable
$(\eta^5-C_5H_5)_2Co$	19	Oxidation occur easily to form 18 e^- complex
$(\eta^5-C_5H_5)_2Ru$	18	stable
$(\eta^5-C_5H_5)_2Co^+$	18	stable

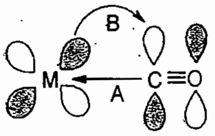
3) Ans (a):- In $W(CH_3)_6$ Complex in which organic ligand is having only σ- bond with W

4) Ans (b):- Among all complex; $[V(CO)_6]^{1-}$ satisfies the 18 electron rule.

complex $[M(CO)_x]^z$	Electrons
M = Ti($4e^-$), x = 6($12e^-$), z =1	17
M = V($5e^-$), x = 6($12e^-$), z =1	18
M = Co($9e^-$), x = 4($8e^-$), z=2	19
M = Mo($6e^-$), x = 5($10e^-$), z = 1	17

5) Ans (d):- The stable cyclopentadienyl complex of beryllium is $[Be(\eta^1-C_5H_5)(\eta^5-C_5H_5)]$ as octet of Be is complete. (valence electron of Be = 2)

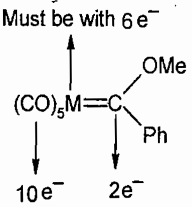
6) Ans (a):- In a given reaction, trans[$IrCl(CO)(PPh_3)_2$] + $Cl_2 \longrightarrow$ trans[$IrCl_3(CO)(PPh_3)_2$]; Ir(I) is changes to Ir(III), (oxidative addition); so metal to :C≡O$^+$ back bonding decreases in product.(Arrow B in fig.) hence ν_{CO}(product) > ν_{CO} (reactant)



7) Ans (c):- According to covalent model of electron count of η^5– Cp is 5e$^-$ donor & nitric oxide is 3e$^-$ donor therefore the complex with 20 e$^-$ will substitute faster to form 18 e$^-$ complex.

Complex	Electrons	conclusion
η^5– Cp_2 Fe	18	stable
η^5– Cp_2 CoCl	20	But Co is already in Co(III) state; oxidation occur very slowly
η^5– Cp_2 Ni	20	Ni is in Ni(II) state; oxidation occur easily
η^5– Cp_2 Co	19	Will not substitute by nitric oxide

8) Ans (a):- In $(CO)_5M$=CRR', according to covalent model of electron count; each CO is 2e$^-$ donor & double bonded carbon ligand is also 2e$^-$ donor therefore pair of metal with 6 valence electron will obeys 18 e$^-$ rule. i.e. Cr, Re$^+$



9) Ans (a):- The ligand in uranocene is $C_8H_8^{2-}$

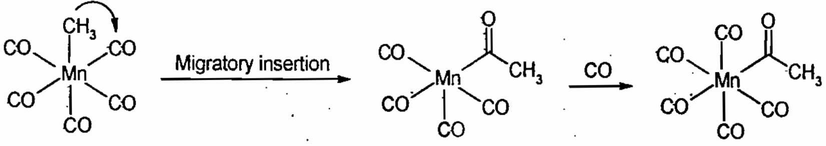
10) Ans (c):- In metal-olefin interaction, the extent of increase in metal$\longrightarrow$ olefin π–back donation would lead to a increase in C=C bond length as it takes place in the alkene π^* antibonding MO, reducing the C=C bond order to one. & change the hybridization of the olefin carbon from sp^2 to sp^3.
Metal to ligand back donation decrease with the presence of electron donating substituent on the olefin & increase with the presence of electron withdrawing substituent on the olefin.

11) Ans (b):- In [(η^7– tropylium)Mo(CO_3)]$^+$; Both η^7– tropylium & CO are neutral ligand so oxidation state of metal is equal to charge on complex therefore the oxidation state of Mo in [(η^7–tropylium)Mo(CO_3)]$^+$ is +1

12) Ans (c):- According to 18e rule the number of electron count in homoleptic polynuclear metal= n×18 e$^-$ (where n= Number of metal atoms) (valence electron of W = 6 e$^-$) and each -OPh is 3 electron donor

Metal complex	n × 18 e$^-$	Total electron count	Metal-Metal bond
[$W_2(OPh)_6$]	2 × 18e = 36	30	36–30 = 6/2 = 3

13) Ans (d):- Migratory insertion reactions result from the migration of a species such as a hydride or alkyl group to an adjacent ligand such as carbonyl or alkene to give a metal complex with two fewer electrons on the metal atom(B) & result in a addition of another ligand.



(B)

14) Ans (d):- $H_2Rh(PPh_3)_2Cl$ is NOT suitable as catalyst for hydroformylation.

15) Ans (b):- In (η^5– C_5H_5) ligand all five carbon atoms are equally bonded to the transition metal while in (η^1– C_5H_5) only one C atom is bonded to the transition metal & therefore (η^1– C_5H_5) usually shows fluxional process.

$$[(\eta^5\text{– }C_5H_5)(\eta^1\text{– }C_5H_5)Fe(CO)_2] \rightarrow [(\eta^5\text{– }C_5H_5)_2Fe]$$

16) Ans (c):- In $[Ni_2(CO)_6]^{2-}$; CO are neutral ligand so oxidation state of metal is equal to charge on complex therefore the oxidation state of each Ni is −1.

According to $18e^-$ rule the number of electron count in homoleptic dinuclear metal= 2×18 = 36 e^- (valence electron of Ni^- = 11) and each CO is 2 e^- electron donor

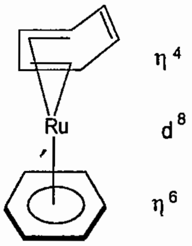
Metal complex	n × 18 e^-	Total electron count	Metal-Metal bond
$[Ni_2(CO)_6]^{2-}$	2 × 18e = 36	34	36–34 = 2/2 = 1

17) Ans (b):- This is a Hydroformylation reaction, also known as oxo synthesis, In a hydroformylation reaction, an alkene, CO, and H_2 react in presence of catalyst $Co_2(CO)_8$ to form an aldehyde containing one more C atom than in the original alkene

$$H_3C{-}CH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} CH_3{-}CH_2{-}CH_2{-}CHO$$

Butanal

18) Ans (c):- The hapticities 'x' and 'y' of the arene moieties are 4 & 6 respectively in the diamagnetic complex $[(\eta^x\text{–}C_6H_6)Ru(\eta^y\text{-}C_6H_6)]$ i.e. $[(\eta^4\text{–}C_6H_6)Ru(\eta^6\text{-}C_6H_6)]$ = 18 e complex



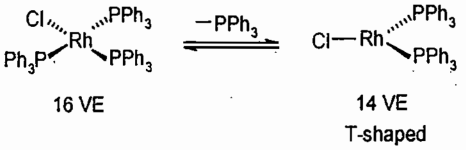
Ru = 8

η^6–C_6H_6 = 6

η^4–C_6H_6 = 4

18 e complex

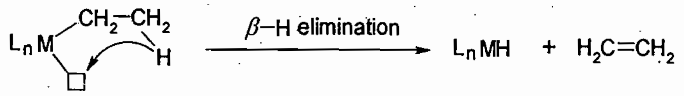
19) Ans (a):- Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in T-shaped $[Rh(PPh_3)_2Cl]$



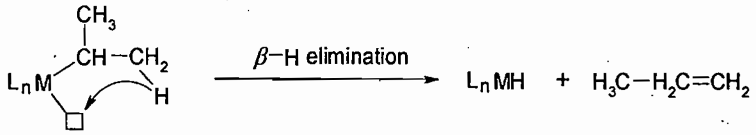
20) Ans (d):- Oxidative addition reactions are favoured by electron rich metal centers as in oxidative addition reactions there is increase in oxidation number of the metal centre by 2 (0 to +2 or +1 to +3 etc). Reductive elimination is the reverse of oxidative addition & therefore favoured by electron deficient metal centers

21) Ans (c):- Metal-alkyl complexes are stable if they do not have β hydrogen because Metal-alkyl complexes with β hydrogen undergoes decomposition via β -H elimination (beta hydride elimination) therefore $Ti(i\text{-}Pr)_4$ $TiEt_4$ are least stable as shown below. Now among $TiMe_4$ & $Ti(CH_2Ph)_4$; $Ti(CH_2Ph)_4$ is more stable than $TiMe_4$ because if the ligand is bulky & it does not induce α or γ-H elimination. So the increasing stability of the following organometallic compounds $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

β-H elimination in $TiEt_4$



β-H elimination in $Ti(i\text{-}Pr)_4$



22) Ans (c):- Among the metals, Mn, Fe, Co and Ni; Fe and Ni react in its native form directly with CO to form $Fe(CO)_5$ and $Ni(CO)_4$ respectively.

23) Ans (a):- In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$ forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$ (Migratory insertion reaction) (See hydroformylation reaction)

24) Ans (a):- Reaction of $Fe(CO)_5$ with OH^- leads to complex $[HFe(CO)_4]^-$ which on oxidation with MnO_2 gives $Fe_3(CO)_{12}$.

$$Fe(CO)_5 + 2OH^- \rightarrow [HFe(CO)_4]^- + CO_3^{-2} + H^+$$

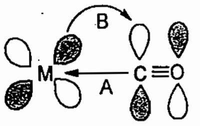
$$3\,[HFe(CO)_4]^- + 3MnO_2 + H^+ \rightarrow Fe_3(CO)_{12} + 3Mn^{2+} + 6H_2O$$

25) Ans (d):- According to $18e^-$ rule the number of electron count in homoleptic polynuclear metal= n×18 (where n= Number of metal atoms) (VE of Fe = 8 & Mo = 6) and Cp = 5; CO = 2 & linear NO = 3 & & bent NO = 1) (Note:- according to covalent electron count)

Metal complex	n × 18e	Total electron count in the dimers	Metal-Metal bond
$[CpFe(CO)(NO)]_2$	2 × 18e = 36	36 (if NO is linear)	36–36 = 0/2 = 0
$[CpFe(CO)(NO)]_2$	2 × 18e = 36	32 (if NO is bent)	36–32 = 4/2 = 2
$[CpMo(CO)_3]_2$	2 × 18e = 36	34	36–34 = 2/2 = 1

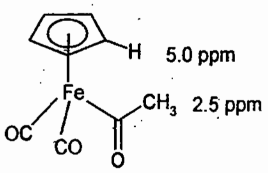
Thus the number of metal-metal bonds in the dimers $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2$ are zero and one respectively,
Note: - if we consider bent NO then the number of metal-metal bonds in the dimers $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2$ are two and one respectively, but it doesn't match with given options

26) Ans (a):- Stronger σ– donor ligand increases metal electron density & as electron density on the metal increases (i.e. negative charge on complex); metal to ligand π back donation increases (B in fig.) & result in increase in $\nu_{M\text{-}C}$ & decrease in ν_{CO} frequency. Order of σ–donation is $NMe_3 > NH_3 >$ pyridine & hence in the trans-$PtCl_2L(CO)$ complex, the CO stretching frequency decreases in the order pyridine $>NH_3>NMe_3$



27) Ans (b):- β–hydride elimination is not possible in complex (A); Refer solution of Q.No.-21

28) Ans (a):- From spectroscopic data & as compound obey $18e^-$ Complex; the structure of $FeC_9H_8O_3$ has η^5– Cp group & terminal CO ligand. The IR spectrum at1900 and 1680 cm^{-1} indicate terminal M-C–O & C–H stretching frequency respectively.



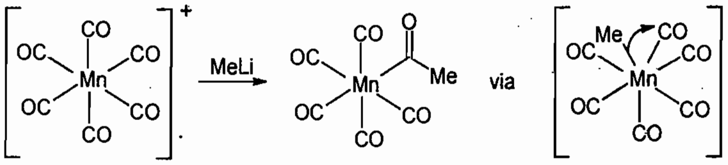
29) Ans (b):- In ^{13}C NMR spectrum of [(η^5– C_5H_5) Rh (CO)]$_3$ (^{103}Rh, nuclear spin, I = ½, 100%) in the presence of μ_2–CO shows a triplet due to heteronuclear spin–spin coupling: ^{13}C–^{103}Rh

Bridging mode	In ^{13}C NMR spectrum (^{103}Rh, nuclear spin, I = ½, 100%)
Terminal CO	doublet due to heteronuclear spin–spin coupling: ^{13}C–^{103}Rh
μ_2–CO	triplet due to heteronuclear spin–spin coupling: ^{13}C–^{103}Rh
μ_3–CO	quartet due to heteronuclear spin–spin coupling: ^{13}C–^{103}Rh
η^5– C_5H_5	doublet due to heteronuclear spin–spin coupling: ^{13}C–^{103}Rh

30) Ans (d):- $[Os(N)Br_2(PMe_3)(NMe_2)]^-$ does not obey 18- electron rule

Complex	Covalent Electron count	Total electron
[(η^5– C_5H_5)] RuCl(CO)(PPh$_3$)]	5+8+1+2+2	18e$^-$ Complex
[W(CO)$_3$ (SiMe$_3$)(Cl)(NCMe)$_2$]	6+6+1+1+4	18e$^-$ Complex
$[IrCl_3(PPh_3)_2(AsPh_2)]^-$	9+3+4+1+1(–ve charge)	18e$^-$ Complex
$[Os(N)Br_2(PMe_3)(NMe_2)]^-$	8+3+2+2+1+1(–ve charge)	17e$^-$ Complex

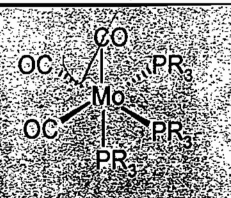
31) Ans (d):- $[Mn(CO)_6]^+$ + MeLi → [(MeCȮ)Mn(CO)$_5$]



32) Ans (a):- In fac–[Mo(CO)$_3$(phosphines)$_3$] when R in PR$_3$ is electron withdrawing; π acceptor ability of phosphine ligand increases & result in decrease in π backbonding to the CO π *. This result in a strengthening of the CO bond, & the higher ν_{co} stretching frequency.

The order of π acceptor ability of phosphine ligand is:-

$PF_3 > PCl_3 > P(OR)_3 > PCl_2 (Ph) > PCl(Ph)_2 > P(Ph)_3 > PRPh_2 > PR_2Ph_2 > PR_3$

Complex	ν_{co} stretching frequency	 fac-[Mo(CO)$_3$(PR$_3$)$_3$
[fac–[Mo(CO)$_3$(PF$_3$)$_3$	2090 cm^{-1}	
[fac–[Mo(CO)$_3$(PCl$_3$)$_3$	2040 cm^{-1}	
[fac–[Mo(CO)$_3$(P(Cl)Ph$_2$)$_3$	1977 cm^{-1}	
[fac–[Mo(CO)$_3$(PMe$_3$)$_3$	1945 cm^{-1}	

33) Ans (a):- In the cluster [$Co_3(CH)(CO)_9$] 3 metal-metal bonds & 1 bridging CH ligands

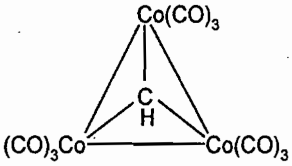
In the cluster [$Co_3(CH)(CO)_9$] according to 18e rule; the number of total electrons should be 54 (18×3)

∴ 54 = 48 electrons(Co= 9; CH= 3 & CO= 2) + metal-metal bond

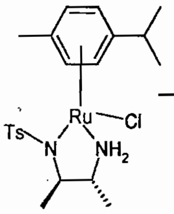
∴ Metal-metal bond = 54 – 48 electrons = 6 electrons

∴ Metal-metal bond = 6/2 = 3

And as valency of Carbon is four ∴ the structure of [$Co_3(CH)(CO)_9$]



34) Ans (a):-

Column - I	Column - II
$[(R)\text{-BINAP}]Ru^{-2}$ →	Asymmetric hydrogenation
$[Rh(CO)_2I_2]^-$ →	Hydroformylation
$Pd(PPh_3)_4$ →	Heck coupling
 →	Asymmetric hydrogen transfer

35) Ans (d):- Oxidative addition reactions are favoured by electron rich metal centers as in oxidative addition reactions there is increase in oxidation number of the metal centre by 2 (0 to +2 or +1 to +3 etc).

Oxidative addition reaction is not possible in complex with d^0 metal centers. In [η^5– $Cp_2Ti(Me)Cl$]; Ti is in Ti^{+4} with d^0 system so further oxidation is not possible.

36) Ans (b):- Addition of excess PPh_3 would decrease the rate of reaction as replacement by a bulky ligand disfavours the formation of complexes with alkene

37) Ans (a):- Reactions A and B are termed as Insertion, Metathesis respectively .The word metathesis comes from the Greek for a exchange. Metathesis reactions are concerted reactions that sometimes occurs when oxidative addition cannot take place.

38) Ans (a):-

Step A	is an oxidative addition reactions as there is increase in oxidation number of the metal centre by 2 (Pd(0) to Pd(+2)
Step B	is a transmetallation reaction, which involves breaking a metal-carbon bond and forming a metal-carbon bond to a different metal.
Step C	is a reductive elimination (Pd(+2) to Pd(0) (the reverse of oxidative addition) Note:- β–hydride elimination is not possible as do not have β hydrogen.

39) Ans (b):- Cyclobutadiene in its neutral form, being anti-aromatic (4π–electrons), is unstable as a free molecule, but its dianionic ($C_4H_4^{2-}$) form is stable because of being aromatic (6π–electrons).

On binding to transition metals the cyclobutadiene ligand is stabilized by significant metal to ligand π–back donation to the vacant ligand orbitals & result in formation of $C_4H_4^{2-}$.

40) Ans (b):- According to 18e rule the number of electron count in homoleptic polynuclear metal= n×18 (where n= Number of metal atoms) (VE of Rh = 9) and each CO = 2.

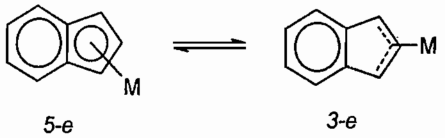
Metal carbonyl	n × 18e	Total electron count	Metal-Metal bond
$Ir_4(CO)_{12}$	4 × 18e = 72	60	72−60 = 12/2 = 6

41) Ans (c):- In complexes $MeTiCl_3$; Ti is in +4 oxidation number & is hard acid so orders of reactivity of ligands NMe_3 (Hard base) > PMe_3 > CO (soft base) and in $(CO)_5Mo(thf)$; Mo is in zero oxidation state & is soft acid so orders of reactivity of ligands is reverse i.e. CO (soft base) > PMe_3 > NMe_3 (Hard base). The most favorable interactions occur when the hard acid interact with hard base & when soft acid interact with soft base

42) Ans (d):- In solid $Co_4(CO)_{12}$ the number of bridging CO groups are three and in $Ir_4(CO)_{12}$number of bridging CO group is zero.

43) Ans (b):- $Fe_3(CO)_{12}$ with an excess of sodium gives $[Fe(CO)_4]^{2-}$ ion & is isoelectronic With $[Ni(CO)_4]$

44) Ans (c):- Several ligands can rearrange between n-*e* and (n-2)-*e*. For example linear NO to bent NO and $\eta^5 \rightarrow \eta^3$ as shown below. So substitution of L with other ligands will be easiest for the species (c)



45) Ans (a):- In metal-olefin interaction, the hybridization of the olefin carbon from sp^2 to sp^3 but at low temperature at -20^0C; ^1H NMR spectrum of $[\eta^5\text{–}C_5H_5)Rh(C_2H_4)_2]$ shows a typical AA' XX' pattern in the olefinic region because at this temperature there in no free rotation of the ethylene ligand about the metal-olefin bond but at $\sim 70^0C$; there is a free rotation of the ethylene ligand about the metal-olefin bond & result in the separate lines collapse into a single line

46) Ans (a):- Linear (N≡O) M-N-O groups absorb in the range 1650–1900 cm^{-1}, whereas bent (N=O) nitrosyls absorb in the range 1525–1690 cm^{-1}. $\angle M\text{–}N\text{–}O = 124^0$ suggest the complex A is with bent nitrosyl i.e complex $[IrCl(CO)(NO)(PPh_3)_2]BF_4$, with 1620 cm^{-1}

47) Ans (a):- Compounds A and B, are $(\eta^5\text{–}C_5H_5)Fe(CO)_2Br$ and $(\eta^5\text{–}C_5H_5)Fe(CO)_2H$ respectively. The proton NMR spectrum of B consists of two singlets; one for $(\eta^5\text{–}C_5H_5)$ & second for H in B with relative intensity 5:1

$$\underset{\text{18e}^- \text{ complex}}{Na^+[\eta^5\text{–}C_5H_5)Fe(CO)_2]^-} \xrightarrow[-NaBr]{Br_2} \underset{\text{(A)}}{\underset{\text{18e}^- \text{ complex}}{[\eta^5\text{–}C_5H_5)Fe(CO)_2Br]}} \xrightarrow{LiAlH_4} \underset{\text{(B)}}{\underset{\text{18e}^- \text{ complex}}{[\eta^5\text{–}C_5H_5)Fe(CO)_2H]}}$$

48) Ans (a):- The expected chemical shift (in ppm) of C_6H_6 ligand in ^1H NMR spectrum of $[\eta^6\text{–}C_6H_6)Cr(CO)_3]$ is 4.5; disruption of ring current (loss of planarity & hence aromaticity.)

49) Ans (a):- $HM(CO)_5$ = 18 electrons; ∴ M = 7e i.e. Mn (H = 1 & each CO = 2)
And in $[(\eta^5\text{–}C_5H_5)M'(CO)_3]_2$ = 36 electrons (as it is dimer). ∴ M = 6e i.e. Cr ($\eta^5\text{–}C_5H_5$ = 5 & each CO = 2) with one metal-metal bond.
H in M−H bond is electron rich so ^1H NMR chemical shifts relative to TMS is −7.5 & H of $C_5H_5^-$ are already electron rich than benzene & become more electron rich when form bond with metal so ^1H NMR chemical shifts of H of $(\eta^5\text{–}C_5H_5)M$ relative to TMS is 4.10 rather than 5.4 in $C_5H_5^-$

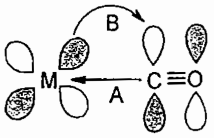
50) Ans (c):- $IrCl(CO)(PPh_3)_2]$ (Vaska's compound) undergoes oxidative addition reaction in presence of H_2

51) Ans (d):- According to covalent model of electron count of (η^5–C_5H_5), (η^6-C_6H_6) & CO ligands are $5e^-$, $6e^-$ & $2e^-$ donor respectively. (Valence electron of metal Fe = 8; Mo = 6; Co = 9 & Re = 7)

Metal complex	Covalent Electron count	Total electron count
(η^5–C_5H_5)$Fe(CO)_2$	5+8+4	17 e^-
(η^5–C_5H_5)$Mo(CO)_3$	5+6+6	17 e^-
(η^5–C_5H_5)$_2$Co	10+9	19 e^-
(η^5–C_5H_5)Re(η^6-C_6H_6)	5+7+6	18 e^-

52) Ans (c):- Carbon-carbon bond length in (i) is larger compared to that of (ii) due to electron withdrawing group of F in C_2F_4

53) Ans (c):- As electron density on the metal increases (negative charge on complex); metal to ligand π back donation increases (B in fig.) & result in increase in $\nu_{M\text{-}C}$ & decrease in ν_{CO} frequency. $\nu_{M\text{-}L}$ stretching frequency is therefore highest in $[V(CO)_6]^-$ & order is $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+$



54) Ans (a):-

Column I	Column II
Wilkinsons catalyst	$RhCl(PPh_3)_3$
speiers catalyst	Hydrosilylation
Water gas shift catalyst	Zinc- copper oxide
Zeolite ZSM-5 catalyst	Synthetic gasoline

55) Ans (d):- As electron density on the metal increases (negative charge on complex); metal to ligand π back donation increases & result decrease in ν_{CO} frequency.

Metal carbonyl	ν_{CO} frequency in cm^{-1}
CO	2143
$[Mn(CO)_6]^+$	2090
$Cr(CO)_6$	2000
$[V(CO)_6]^-$	1860

56) Ans (c):- The reaction of CO_2 with this enzyme is an example of nucleophilic addition

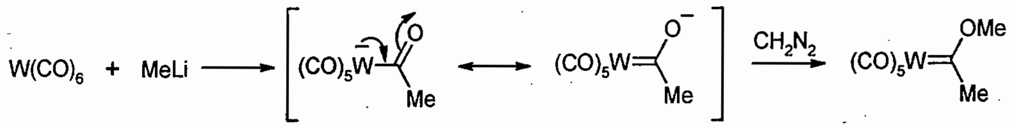
$$(His)_3Zn^+\text{-}OH + CO_2 \longrightarrow (His)_3Zn^+\text{-}OCO_2H$$

57) Ans (b):-

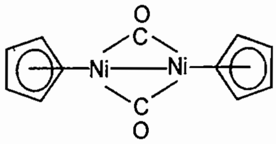
List I	List II
$(Ph_3P)_3RhCl$	Catalyst for alkene hydrogenation
LiC_6	Intercalation
PtF_6	Oxidising agent
Ni_3S_4	Spinel(AB_2X_4) Where X = O,S or Se

In Li-ion batteries Graphite is the standard anode material in these devices. Upon charging of the battery, lithium diffuses into the graphite anode particles forming lithiated graphite intercalation structures (C→LiC_6)
PtF_6 strong oxidant e.g. reacts with oxygen to form $[O_2]^+[PtF_6]^-$

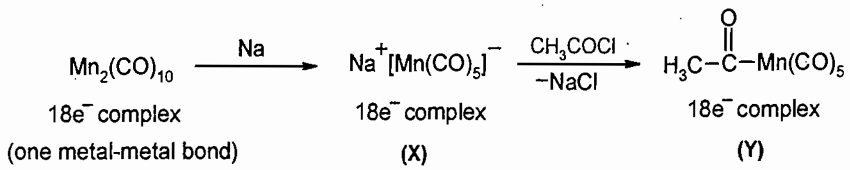
58) Ans (c):- Product of reaction is $(CO)_5W{=}C(Me)OMe$;
Note:-It is synthesis & reaction of Fisher carbene Complexes



59) Ans (d):- The IR stretching frequency appears at 1857cm^{-1} (strong) and 1897cm^{-1} strongly indicate the presence of μ_2–CO bridging & logically the valence electron count is 18 e$^-$, with one metal-metal bond



60) Ans (b):-



61) Ans (b):- The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is $[PdCl_4]^{2-}$

62) Ans (b):- The number of M-M bonds in $Ir_4(CO)_{12}$ are six
According to 18e rule the number of electron count in homoleptic polynuclear metal= n×18
(where n= Number of metal atoms) (valence electron of Ir = 9)

Metal carbonyl	n × 18e	Total electron count	Metal Metal bond
$Ir_4(CO)_{12}$	4 × 18e = 72	60	54–60 = 12/2 = 6

63) Ans (a):- Schrock carbenes are triplets and nucleophilic

Fischer-type carbene Complex	Schrock-type Carbene Complex
Singlets Carbene Complex	Triplets Carbene Complex
Low oxidation state metal center	High oxidation state metal center
Middle and late transition metals Fe(0), Mo(0), Cr(0)	Early transition metals Ti(IV), Ta(V)
Good π acceptor	Good σ & π donor
Pi-donor substituents on the carbene atom such as alkoxy and alkylated amino groups.	Hydrogen and alkyl substituents on carbenoid carbon.

64) Ans (b):- Hint: - Trans effect

65) Ans (c):- $Rh(PPh_3)_3Cl + H_2 + C_2H_4 \longrightarrow (PPh_3)_2RhCl(\eta^2\text{-}C_2H_4)$

66) Ans (d):- The number of metal - metal bonds in $[(C_5H_5)Fe(CO)]_2$ are three.
According to 18e rule the number of electron count in dinuclear metal= 2×18 = 36
But in $[(C_5H_5)Fe(CO)]_2$ total electron count is 30e. Therefore remaining six electrons will form three M - M bonds

67) Ans (c):- ν_{CO} for the compounds $[Mo(CO)_3(L)_3]$ type ; ν_{CO} increases with increasing π acceptor ability of L and ν_{CO} decreases with increase in σ donation. General order of π acceptor ability decreases in the Order:- $NO^+ > CO > PF_3 > AsCl_3 > RN{\equiv}C > PCl_3 > As(OR)_3 > P(OR)_3 > PR_3 > RC{\equiv}N > NH_3$
Therefore correct order of ν_{CO} for the compounds in the IR spectrum is:-

$$[Mo(CO)_3(PCl_3)_3] > [Mo(CO)_3(P(OPh)_3)_3] > [Mo(CO)_3(PMe_3)_3] > [Mo(CO)_3(NMe_3)_3]$$

68) Ans (a):- In $K[PdCl_3(\eta^2\text{-}C_2H_4)]$ The C atoms of the alkene rehybridize close to sp^3 therefore the C−C bond order of the product is between 1 and 2

69) Ans (b):- Nickellocene (Cp_2Ni) is 20e system therefore will form dication $(Cp_2Ni)^{+2}$ *i.e.* 18e system

70) Ans (a):- Vitamin B_{12} is an organometallic as there is a Co-C bond (metal-carbon bond).

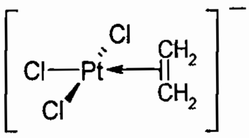
71) Ans (a):- The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$, are 3 and 6 respectively. According to 18e rule the number of electron count in homoleptic polynuclear metal= n×18 (where n= Number of metal atoms) (valence electron of Ru & Co are 8 & 9 respectively.)

Metal carbonyl	n × 18e	Total electron count	Metal-Metal bond
$Ru_3(CO)_{12}$	3 × 18e = 54	48	54−48 = 6/2 = 3
$Co_4(CO)_{12}$	4 × 18e = 72	60	72−60 = 12/2 = 6

72) Ans (b):- $CH_3Mn(CO)_5 + {}^{13}CO \rightarrow cis\text{-}(CH_3CO)Mn(CO)_4({}^{13}CO)$

73) Ans (c):- The number of terminal carbonyl groups present in $Fe_2(CO)_9$ are 6 and three bridging CO ligands

74) Ans (c):- In Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$ two Pt−Cl bond lengths are equal out of three.



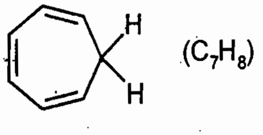
75) Ans (d):- $HCo(CO)_4$ an intermediate formed during the hydroformylation of olefins using $Co_2(CO)_8$

76) Ans (b):- It is a simple nucleophilic reaction on Fisher carbene complexes

$$(CO)_5Cr{=}C(OMe)(Me) + MeNH_2 \longrightarrow (CO)_5Cr{=}C(NHMe)(Me) + MeOH$$

77) Ans (d):- The catalyst and co-catalyst used in the Wacker process are $[PdCl_4]^{2-}$ and $CuCl_2$ respectively

78) Ans (b):- Hapticity of cycloheptatrienein $Mo(C_7H_8)(CO)_3$ is Six

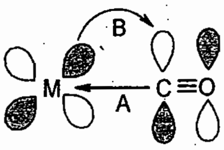


Cycloheptatrienein is 6e donor (sp^3 hybridized carbon is not involved in bond formation)

79) Ans (c):- Cr does NOT form homoleptic polynuclear metal carbonyl while all other form homoleptic polynuclear metal carbonyl e.g. $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ & $Co_2(CO)_8$

80) Ans (d):- In Monsanto acetic acid process, the role of HI is to convert CH_3OH to CH_3I

81) Ans (a):- As electron density on the metal increases (negative charge on complex); metal to ligand π back donation increases(B in fig.) & result in decrease in ν_{CO} frequency. ν_{CO} stretching frequency is highest in $[Mn(CO)_6]^+$



Metal carbonyl	ν_{CO} frequency in cm^{-1}
$[Mn(CO)_6]^+$	2090
$Cr(CO)_6$	2000
$[V(CO)_6]^-$	1860
$[Fe(CO)_4]^{2-}$	1750

82) Ans (d):- Metal-alkyl complexes are stable if they do not have β hydrogen because Metal-alkyl complexes with β hydrogen undergoes decomposition via β -H elimination(beta hydride elimination) therefore $TiEt_4$ is least stable. Now among $TiMe_4$ & $Ti(CH_2CMe_3)_4$; $Ti(CH_2CMe_3)_4$ is more stable than $TiMe_4$ because if the ligand is bulky it does not induce α or γ-H elimination so correct order of thermal stability $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

List of Reference Books

1) The organometallic Chemistry of the transition metals by Robert H. Crabtree, John Wiley & Sons

2) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited

3) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.

4) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press

5) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.

6) Inorganic Chemistry by James E. House Elsevier Science Publication.

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Topic 9

BORANE, SILICATES, ISOLOBAL FRAGMENTS, CAGES & METAL CLUSTERS

Questions with two marks

1) The correct statement regarding closo-{B_nH_n} species is ***[Dec2011]***

(a) it always has –2 charge (b) it always has +2 charge
(c) it is a neutral species (d) it is more reactive than nido arachno-, and hypo-boranes

2) The number of metal-metal bonds in [$W_2(OPh)_6$] is: ***[June 2013]***

(a) 1 (b) 2 (c) 3 (d) 4

3) In a cluster, $H_3CoRu_3(CO)_{12}$, total number of electrons considered to be involved in its formation is ***[Dec 2013]***

(a) 57 (b) 60 (c) 63 (d) 72

4) The bond order of metal-metal bonds in dimeric complex $[Re_2Cl_4(PMe_2Ph)_4]^+$ is ***[Dec 2013]***

(a) 4.0 (b) 3.5 (c) 3.0 (d) 2.5

5) The maximum bond order obtained from the molecular orbitals of a transition metal dimer, formed as linear combinations of d-orbitals alone is ***[June 2014]***

(a) 3 (b) 4 (c) 5 (d) 6

6) The δ-bond is formed via the overlap of ***[Dec 2014]***

(a) $d_{x^2-y^2}$ and $d_{x^2-y^2}$ orbitals (b) d_{xz} and d_{xz} orbitals (c) d_{xy} and d_{xy} orbitals (d) d_{yz} and d_{yz} orbitals

7) $Co_4(CO)_{12}$ adopts the ***[Dec 2014]***

(a) Closo - structure (b) Nido – structure (c) Arachno - structure (d) Hypho - structure

Questions with four marks

8) The styx code of B_4H_{10} is ***[Dec2011]***

(a) 4120 (b) 4220 (c) 4012 (d) 3203

9) Bayer's process involves. ***[Dec2011]***

(a) Synthesis of B_2H_6 from $NaBH_4$ (b) Synthesis of $NaBH_4$ from borax
(c) Synthesis of $NaBH_4$ from B_2H_6 (d) Synthesis of $B_3N_3H_6$ from B_2H_6

10) The cluster having arachno type structure is ***[June 2012]***

(a) [$Os_5(CO)_{16}$] (b) [$Os_3(CO)_{12}$] (c) [$Ir_4(CO)_{12}$] (d) [$Rh_6(CO)_{16}$]

11) Structure of a carborane with formula, $C_2B_4H_8$ is formally derived from ***[Dec2012]***

(a) Closo-borane (b) Nido-borane (c) Arachno-borane (d) Conjuncto-borane

12) In the cluster [$Co_3(CH)(CO)_9$] obeying 18e rule, the number of metal-metal bonds and the bridging ligands respectively, are ***[Dec2012]***

(a) 3 and 1 CH (b) 0 and 3 CO (c) 3 and 1 CO (d) 6 and 1 CH

13) Silicates with continuous 3D frame work are

(a) Neso-silicates (b) Soro-silicates (c) Phyllo-silicates (d) Tecto-silicates

14) Intense band at 15000 cm^{-1} in the UV-visible spectrum of $[Bu_4N]_2Re_2Cl_8$ is due to the transition ***[June 2013]***

(a) $\pi-\pi^*$ (b) $\delta-\delta^*$ (c) $\delta-\pi^*$ (d) $\pi-\delta^*$

15) The number of metal-metal bonds in $Ir_4(CO)_{12}$ is ***[June 2013]***

(a) 4 (b) 6 (c) 10 (d) 12

16) Number of isomeric derivatives possible for the neutral closo-carborane, $C_2B_{10}H_{12}$ is ***[Dec2013]***

(a) three (b) two (c) four (d) six

17) For higher boranes 3c-2e 'BBB' bond may be a part of their structures. In B_5H_9, the number of such electron deficient bond(s) present is/are ***[Dec2013]***

(a) four (b) two (c) zero (d) one

18) Among the following clusters, H is encapsulated in ***[Dec2013]***

A = $[(H)Co_6(CO)_{15}]^-$ B = $[(H)_2Os_6(CO)_{18}]$ C = $[(H)_2Os_5(CO)_{16}]$

(a) A only (b) B only (c) B and C only (d) A and B only

19) Among the following, the correct statement is ***[Dec2013]***

(a) CH is isolobal to $Co(CO)_3$ (b) CH_2 is isolobal to $Ni(CO)_2$
(c) CH is isolobal to $Fe(CO)_4$ (d) CH_2 is isolobal to $Mn(CO)_4$

20) The total valence electron count and the structure type adopted by the complex $[Fe_5(CO)_{15}C]$ respectively are ***[June 2014]***

(a) 74 and *nido* (b) 60 and *closo* (c) 84 and *arachno* (d) 62 and *nido*

21) The compound $[Re_2(Me_2PPh)_4Cl_4]$ (M) having configuration of $\sigma^2\pi^4\delta^2\delta^{*2}$ can be oxidized to M^+ and M^{+2}. The formal metal–metal bond order in M, M^+ and M^{+2} respectively, are ***[June 2014]***

(a) 3.0, 3.5 and 4.0 (b) 3.5, 4.0 and 3.0 (c) 4.0, 3.5 and 3.0 (d) 3.0, 4.0 and 3.5

22) Amongst the following which is not isolobal pairs ***[June 2014]***

(a) $Mn(CO)_5$, CH_3 (b) $Fe(CO)_4$, O (c) $Co(CO)_3$, R_2Si (d) $Mn(CO)_5$, RS

23) According to Wade's rule, anion $C_2B_9H_{12}^-$ adopts ***[Dec 2014]***

(a) Closo structure (b) Nido structure (c) Arachno structure (d) Hypho structure

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

24) The $[Re_2Cl_8]^{-2}$ is strong royal blue colour is due to ***(GATE 2005)***

(a) Absorption band due to $\pi-\pi^*$ transition in the visible region
(b) Absorption band due to $\pi-\delta^*$ transition in the visible region
(c) Absorption band due to $\delta-\delta^*$ transition in the visible region
(d) Absorption band due to $\pi-\pi^*$ and $\delta-\delta^*$ transition in the visible region

25) $Mg_6Si_4O_{10}(OH)_8$ is commercially known as ***(GATE 2006)***

(a) asbestos (b) water glass (c) soda glass (d) zeolite

26) $[Co(CO)_4]$ is isolobal with *(GATE 2006)*

(a) CH_4 (b) CH_3 (c) CH_2 (d) CH

27) $BaTi[Si_3O_9]$ is a class of *(GATE 2007)*

(a) ortho silicate (b) cyclic silicate (c) chain silicate (d) sheet silicate

28) Considering the quadrupolar nature of M-M bond in $[Re_2Cl_8]^-$, the M–M bond order in $[Re_2(Me_2PPh)_4Cl_4]^+$ and $[Re_2(Me_2PPh)_4Cl_4]$ respectively, are *(GATE 2007)*

(a) 3.0 and 3.0 (b) 3.0 and 3.5 (c) 3.5 and 3.5 (d) 3.5 and 3.0

29) The correct classification of $[B_5H_5]^{2-}$, B_5H_9 and B_5H_{11} respectively is *(GATE 2007)*

(a) closo, arachno, nido (b) arachno, closo, nido (c) closo, nido, arachno (d) nido, arachno, closo,

30) Metal-metal quadruple bonds are well-known for the metal *(GATE 2008)*

(a)Ni (b) Co (c) Fe (d) Re

31) White phosphorus,P_4 belongs to the *(GATE 2008)*

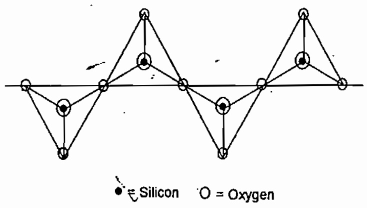
(a) closo system (b) Nido system (c) arachno system (d) hypho system

$(BH_2)_4$

B_4H_8 $4-$

(B_4H_4)

32) Pyroxenes are a class of silicate minerals. Which exhibit a polymeric chain structure, as shown below *[GATE 2010]*



Its simplest repeat unit is

(a) $[SiO_4]^{4-}$ (b) $[SiO_3]^{2-}$ (c) $[Si_2O_7]^{6-}$ (d) $[Si_4O_{11}]^{6-}$

33) The number of 'framework electron pairs' present in the borane cluster $[B_{12}H_{12}]^{-2}$ *[GATE 2010]*

(a) 10 (b) 11 (c) 12 (d) 13

$1 \times 12 + 1 = 13$

34) According to *polyhedral electron count rule*, the structure of $Rh_6(CO)_{16}$ is ***[GATE 2013]***

(a) Closo (b) Nido (c) Arachno (d) Hypho

35) An example of *nido*-borane from the following is *[GATE 2014]*

(a) B_4H_{10} (b) B_6H_{10} (c) B_6H_{12} (d) B_8H_{14}

Answer Key

Topic 9:- Boran , Silicates, Isolobal fragments, Cages & Metal Clusters

1	a	2	c	3	b	4	b	5	c	6	c	7	b	8	c	9	b	10	b
11	b	12	a	13	d	14	b	15	b	16	a	17	d	18	a	19	a	20	a
21	a	22	c	23	b	24	c	25	a	26	b	27	b	28	d	29	c	30	d
31	b	32	b	33	d	34	a	35	b										

Hints &Solution

1) Ans (a):- The general formula of closo borane species is always $B_nH_n^{2-}$

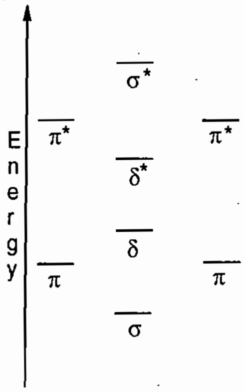
2) Ans (c):- In $[W_2(OPh)_6]$, Each W is in +3 oxidation state (due to 6 OPh^-)

Electronic configuration of W is $[Xe]4f^{14}5d^{4}6s^{2}$

∴Both W^{+3} = $[Xe]4f^{14}5d^{3}6s^{0}$ *i.e.* total six electrons (three electrons of each W)

Electronic configurationaccording to molecular orbital diagram formed by *d*– orbital interactions = $\sigma^2\pi^4$

&bond order i.e. number of metal metal bond is 3



Approximate molecular orbital energy level scheme for M—M intreaction

3) Ans (b):- In a cluster, $H_3CoRu_3(CO)_{12}$, (H= 1; Co= 9; Ru= 8 & CO= 2 electrons)

∴ (1×3) + (9×1) + (8×3) + (2×12) = 60

4) Ans (b):- In $[Re_2Cl_4(PMe_2Ph)_4]^+$, Each Re is in +2.5 oxidation state

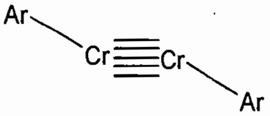
Electronic configuration of Re is $[Xe]4f^{14}5d^{5}6s^{2}$

∴ Both $Re^{+2.5}$ = $[Xe]4f^{14}5d^{4.5}6s^{0}$ *i.e.* total nine electrons

According to molecular orbital diagram formed by *d*– orbital interactions; electron configuration:-$\sigma^2\pi^4\delta^2\ \delta^{*1}$

& bond order i.e. number of metal metal bond is 3.5

5) Ans (c):- Recent study showed that the concept of metal-metal multiple bonds are extended to *five* known as Quintuple Bonds; e.g



quintuple bonding

In such cases the ligand forms a bond with the 4s orbitals of Cr & hence d-orbitals available for Cr-Cr bonding. Quintuple bond results in a trans-bent geometry rather than linear geometry.

6) Anc (c):- The δ-bond is formed via the overlap of d_{xy} and d_{xy} orbitals.

The π-bond is formed via the overlap of $d_{xz}$and d_{xz} orbitals and $d_{yz}$and d_{yz} orbitals.

The σ-bond is formed via the overlap of d_{z^2} and d_{z^2} orbitals.

7) Ans (b):- $Co_4(CO)_{12}$ adopts the nido structure.

For transition metal cluster the structure is determined according to the following chart

Structure	valence electrons (n = number of vertices or metal atoms in the cluster)
Closo	14n + 2 valence electrons
Nido	14n + 4 valence electrons
Arachno	14n + 6 valence electrons
Hypho -	14n + 8 valence electrons

In $Co_4(CO)_{12}$; (Valence electron of Co= 9 & CO= 2) so (9×4) + (2×12) = 60 electrons.

$\frac{60}{14}$ = 4 with remainder 4

Transition metal cluster with (14n + 4) valence electrons adopts the nido structure (where 4 is remainder)

8) Ans (c):- According to styx code; the styx code of B_4H_{10} is 4012

According to styx code	According to this styx code for	
s = Number of 3c−2e B−H−B bonds	B_2H_6 = 2002	B_6H_{10} = 4220
t = Number of 3c−2e B−B−B bonds	B_4H_{10} = 4012	$B_{10}H_{14}$ = 4620
y = Number of 2c−2e B−B bonds	B_5H_9 = 4120	
x = Number of BH_2 group	B_5H_{11} = 3203	

9) Ans (b):-The Bayer process involves a reaction of borax and quartz sand with hydrogen and metallic sodium to form sodium borohydride. The Bayer process is one of the best known commercial $NaBH_4$ production methods.

10) Ans (b):- The structure $[Os_3(CO)_{12}]$ cluster is arachno type

cluster	Valence electrons	valence electrons (n = number of vertices or metal atoms in the cluster)	Structure
$[Os_5(CO)_{16}]$	72	14n + 2 valence electrons	closo
$[Os_3(CO)_{12}]$	48	14n + 6 valence electrons	arachno
$[Ir_4(CO)_{12}]$	60	14n + 4 valence electrons	nido
$[Rh_6(CO)_{16}]$	86	14n + 2 valence electrons	closo

11) Ans (b):- $C_2B_4H_8 = B_6H_{10}$ (Consider C= BH unit) & is Nido-borane

Structure	formula
Closo	$B_nH_n^{2-}$
Nido	B_nH_{n+4}
Arachno	B_nH_{n+6}
Hypho -	B_nH_{n+8}

12) Ans (a):- In the cluster $[Co_3(CH)(CO)_9]$ 3 metal-metal bonds & 1 bridging CH ligands

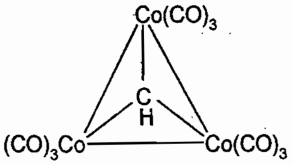
In the cluster $[Co_3(CH)(CO)_9]$ according to 18e rule; the number of total electrons should be 54 (18×3)

∴ 54 = 48 electrons(Co= 9; CH= 3 & CO= 2) + metal-metal bond

∴ Metal-metal bond = 54 – 48 electrons = 6 electrons

∴ Metal-metal bond = 6/2 = 3

And as valency of Carbon is four ∴ the structure of $[Co_3(CH)(CO)_9]$



13) Ans (d):- Tecto-silicates are the Silicates with continuous 3D frame work

14) Ans (b):- Intense band at 15000 cm^{-1} in the UV-visible spectrum is due to $\delta-\delta^*$ due to quadruple bonding in $[Bu_4N]_2Re_2Cl_8$ i.e. $[2Bu_4N]^+$ $[Re_2Cl_8]^{2-}$ (see hint of question no. 4).

15) Ans (b):-The number of metal-metal bonds in $Ir_4(CO)_{12}$ is six

In the $Ir_4(CO)_{12}$ according to 18e rule; the total number of electrons must be 72(18×4)

∴ 72 = 60 electrons (Ir= 9; & CO= 2) + metal-metal bond

∴ Metal-metal bond = 72 – 60 electrons = 12 electrons

∴ Metal-metal bond = 12/2 = 6

16) Ans (a):- Three (ortho, meta & para)

17) Ans (d):- In B_5H_9, the number of 3c-2e 'BBB' bond is one (Refer the solution of Que. No. 8)

18) Ans (a):- Many of the anions carbonyl cluster species are with encapsulated H e.g. $[(H)Co_6(CO)_{15}]^-$ In such clusters generally one of the CO is replaced by one hydrogen & one negative charge.

19) Ans (a):- The isolobal principle (the isolobal analogy) is a used in organometallic chemistry to relate the structure of organic and inorganic molecular fragments in order to predict bonding properties of organometallic compounds. Isolobal fragments are given in table

Organic	Organometallic
5-electron fragments	15-electron fragments
6-electron fragments	16-electron fragments
7-electron fragments	17-electron fragments
8-electron fragments	18-electron fragments

<table>
<tr><th>Organic</th><th>Organometallic</th></tr>
<tr><td colspan="2">CH = 5 electron fragments is isolobal with $Co(CO)_3$ = 15 electron fragments</td></tr>
<tr><td colspan="2">CH_2 = 6 electron fragments is not isolobal with $Ni(CO)_2$ = 12 electron fragments</td></tr>
<tr><td colspan="2">CH = 6 electron fragments is not isolobal with $Fe(CO)_4$ = 14electron fragments</td></tr>
<tr><td colspan="2">CH_2 = 6 electron fragments is not isolobal with $Mn(CO)_4$= 15 electron fragments</td></tr>
</table>

So from above table CH is isolobal with $Co(CO)_3$

$$CH \underset{\bigcirc}{\longleftrightarrow} Co(CO)_3$$

20) Ans (a):- total valence electron count of the complex $[Fe_5(CO)_{15}C]$ = 74 (Fe = 8; each CO = 2 & C= 4)

$$structure\ type = \frac{total\ valence\ electron\ count}{14} = \frac{74}{14} = 5\ with\ 4\ remainder\ i.e.nido$$

21) Ans (a):-

Complex	oxidation state of each Re	Number of d electrons	electron configuration	bond order
$[Re_2(Me_2PPh)_4Cl_4]$	2	10	$\sigma^2\pi^4\delta^2\ \delta^{*2}$	3
$[Re_2(Me_2PPh)_4Cl_4]^+$	2.5	9	$\sigma^2\pi^4\delta^2\ \delta^{*1}$	3.5
$[Re_2(Me_2PPh)_4Cl_4]^{++}$	3	8	$\sigma^2\pi^4\delta^2$	4

22) Ans (c):- R_2Si & $Co(CO)_3$ are not isolobal

Organic	Organometallic
CH_3 = 7 electron fragments	$Mn(CO)_5$ = 17 electron fragments
O = 6 electron fragments	$Fe(CO)_4$ = 16 electron fragments
R_2Si = 6 electron fragments	$Co(CO)_3$ = 15 electron fragments
RS = 7 electron fragments	$Mn(CO)_5$ = 17 electron fragments

23) Ans (b):- According to Wade's rule, anion $C_2B_9H_{12}^- = B_{11}H_{14}^-$ is a Nido structure (Consider C= BH unit)

24) Ans (c):- The electron configuration of $[Re_2Cl_8]^{-2}$ is $\sigma^2\pi^4\delta^2$. Complexes with electron in δ orbitals are dark in coloured as energy difference of the δ and δ* orbitals is very small & δ to δ* transition occurs in visible region. Therefore $[Re_2Cl_8]^{-2}$ is strong royal blue colour.

25) Ans (a):- $Mg_6Si_4O_{10}(OH)_8$ is commercially known as asbestos.

26) Ans (b):- $[Co(CO)_4]$ is isolobal with CH_3. Refer solution of question no. 19 & 22

27) Ans (b):- $BaTi[Si_3O_9]$ is a class of cyclic silicate

28) Ans (d):- the M−M bond order in $[Re_2(Me_2PPh)_4Cl_4]^+$ and $[Re_2(Me_2PPh)_4Cl_4]$ 3.5 and 3.0

Complex	oxidation state of each Re	Number of d electrons	electron configuration	bond order
$[Re_2(Me_2PPh)_4Cl_4]^+$	2.5	9	$\sigma^2\pi^4\delta^2\ \delta^{*1}$	3.5
$[Re_2(Me_2PPh)_4Cl_4]$	2	10	$\sigma^2\pi^4\delta^2\ \delta^{*2}$	3

29) Ans (c):- $[B_5H_5]^{2-}$, B_5H_9 and B_5H_{11} classified as closo, nido, arachno respectively

30) Ans (d):- Metal-metal quadruple bonds are well-known for the Re metal

31) Ans (b):- $P_4 = B_4H_8$ (Consider each P= BH_2 unit) & is Nido-borane

32) Ans (b):- Simplest repeat unit of Pyroxenes is $[SiO_3]^{2-}$

Type	General formula
Ortho silicates or Neso silicates	SiO_4^{4-}
Pyro silicates or Soro silicates	$Si_2O_7^{6-}$
Cyclic silicates	$(SiO_3)_n^{2n-}$
Chain silicates or pyroxenes	$(SiO_3)_n^{2n-}$
double chain silicates or Amphiboles	$(Si_4O_{11})_n^{6n-}$
Sheet or Phyllo silicates	$(Si_2O_5)_n^{2n-}$
three dimensional or tecto silicates is	$(SiO_2)_n$

33) Ans (d):- The number of 'framework electron pairs' present in the $[B_{12}H_{12}]^{-2}$ is 13

The number of 'framework electron pairs' = 1 × each BH unit (& add $^1/_2$ for each negative charge)

∴ The number of 'framework electron pairs' of $[B_{12}H_{12}]^{-2}$ = 1 × 12 + 1 = 13

34) Ans (a):- The structure of $Rh_6(CO)_{16}$ is Closo structure.

In $Rh_6(CO)_{16}$; (Valence electron of Rh = 9 & CO= 2)So (9×6) + (2×16) = 86 electrons.

$\frac{86}{14}$ = 6 with remainder 2

Transition metal cluster with (14n + 2) valence electrons adopts the closo structure (where 2 is remainder)

35) Ans (b):- B_6H_{10} is an example of *nido*-borane

List of Reference Books

1) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.

2) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.

3) Molecular orbitals of transition metal complexes, by Yves Jean, Oxford University Press

4) Inorganic Chemistry by Catherine E. Housecroft and Alan Sharpe Pearson Education Limited

5) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press

6) Principles of Inorganic Chemistry by Puri, Sharma and Kalia, Milestone Publisher.

1× each BH unit
add [illegible]

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Topic 10

INORGANIC REACTION MECHANISM

Questions with two marks

1) **The reactions of $Ni(CO)_4$ with the ligand L (L= PMe_3 or P $(OMe)_3$) yields $Ni(CO)_3$ L. The reaction is** *[June 2012]*

(a) Associative (b) Dissociative (c) Interchange (Ia) (d) Interchange (Id)

2) **The reaction of $[PtCl_4]^{-2}$ with two equivalent of NH_3 produces** *[June 2013]*

(a) *cis* $-[Pt(NH_3)_2Cl_2]$ (b) *trans*$-[Pt(NH_3)_2Cl_2]$
(c) both *cis* $-[Pt(NH_3)_2Cl_2]$ and *trans*$-[Pt(NH_3)_2Cl_2]$ (d) *cis* $-[Pt(NH_3)_2Cl_4]^{-2}$

3) **The rate of the given reaction depends on** *[Dec 2014]*

$$Ni(CO)_4 + PPh_3 \xrightarrow{h\nu} [Ni(CO)_3(PPh_3)] + CO$$

(a) Concentration of both the reactants (b) Concentration of $Ni(CO)_4$ only
(c) Concentration of PPh_3 only (d) The steric bulk of PPh_3

4) **In the following reaction compound B is** *[Dec 2014]*

$$[PtCl_4]^{2-} + NO_2^- \longrightarrow A \xrightarrow{NH_3} B$$

(a) Trans-$[PtCl_2(NO_2)(NH_3)]^-$ (b) cis-$[PtCl_2(NO_2)(NH_3)]^-$

(c) Trans-$[PtCl_2(NH_3)_2]$ (d) cis-$[PtCl_2(NO_2)_2]^{2-}$

Questions with four marks

5) **Consider two redox pairs** *[June 2011]*
(1) Cr(II)/Ru(III) (2) Cr(II)/Co(III)
The rate of acceleration in going from a outer-sphere to a inner-sphere mechanism is lower for (1) Relative to (2). Its correct explanation is:

(a) HOMO/LUMO are σ^* and σ^* respectively. (b) HOMO/LUMO are σ^* and π^* respectively.
(c) HOMO/LUMO are π^* and σ^* respectively. (d) HOMO/LUMO are π^* and π^* respectively.

6) **A true statement about base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$** *[Dec 2011]*

(a) It is a first order reaction
(b) The rate determining step involves the dissociation of chloride in $[Co(NH_3)_4(NH_2)Cl]^+$
(c) The rate is independent of the concentration of the base
(d) The rate determining step involves the abstraction of a proton from $[Co(NH_3)_5Cl]^{2+}$

7) **For the following outer sphere electron transfer reactions** *[Dec 2011]*

$$[Co(NH_3)_6]^{2+} + [Co^*(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co^*(NH_3)_6]^{2+}$$
$$[Ru(NH_3)_6]^{2+} + [Ru^*(NH_3)_6]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Ru^*(NH_3)_6]^{2+}$$

the rate constants are 10^{-6} M^{-1} s^{-1} and 8.2×10^2 $M^{-1}s^{-1}$ respectively. This difference in the rate constants is due to

(a) a change from high spin to low spin in Co* and high spin to low spin in Ru.
(b) a change from high spin to low spin in Co* and low spin to high spin in Ru*.

(c) a change from low spin to high spin in Co* and the low spin state remains unchanged in Ru.
(d) a change from low spin to high spin in Co* and high spin to low spin in Ru*.

8) The platinum complex of NH_3 and Cl^- ligands is an anti-tumor agent. The correct isomeric formula of the complex and its precursor are ***[Dec 2012]***

(a) *cis* $-[Pt(NH_3)_2Cl_2]$ and $[PtCl_4]^{-2}$
(b) *trans* $-[Pt(NH_3)_2Cl_2]$ and $[PtCl_4]^{-2}$
(c) *cis* $-[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]^{+2}$
(d) *trans*$-[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]^{+2}$

9) The rate of exchange of OH_2 present in the coordination sphere by $^{18}OH_2$ of, (i) $[Cu(OH_2)_6]^{2+}$, (ii) $[Mn(OH_2)_6]^{2+}$, (iii) $Fe(OH_2)_6]^{2+}$, (iv) $[Ni(OH_2)_6]^{2+}$, follows an order ***[Dec 2012]***

(a) (i) > (ii) > (iii) > (iv)
(b) (i) > (iv) > (iii) > (ii)
(c) (ii) > (iii) > (iv) > (i)
(d) (iii) > (i) > (iv) > (ii)

10) Consider the second order rate constants for the following outer-sphere electron transfer reactions:

$[Fe(H_2O)_6]^{3+} / [Fe(H_2O)_6]^{2+}$	$4.0 M^{-1} sec^{-1}$
$[Fe(phen)_3]^{3+} / [Fe(phen)_3]^{2+}$	$3.0 \times 10^7 M^{-1} sec^{-1}$

(Phen = 1,10–phenanthroline)

The enhanced rate constant for the second reaction is due to the fact that ***[June 2014]***

(a) The 'phen' is a π-acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer.
(b) The 'phen' is a π-donor ligand that enhances the rate of electron transfer
(c) The 'phen' forms charge transfer complex with iron and facilitates the electron transfer
(d) The 'phen' forms, kinetically labile complex with iron and facilitates the electron transfer.

11) Reduction of $[Ru(NH_3)_5(isonicotinamide)]^{3+}$ with $[Cr(H_2O)_6]^{2+}$ occurs by inner sphere mechanism and rate of the reaction is determined by dissociation of the successor complex. It is due to the ***[June 2014]***

(a) Inert ruthenium bridged to inert chromium centre
(b) Inert ruthenium bridged to labile chromium centre
(c) Labile ruthenium bridged to inert chromium centre
(d) Labile ruthenium bridged to labile chromium centre

12) Base hydrolysisof $[CoCl(NH_3)_5]^{2+}$ is an overall second order reaction, whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rates depend in both cases solely on the concentrations of the cobalt complex. This may be due to ***[Dec 2014]***

A. presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ but not in $[Co(CN)_6]^{3-}$
B. $S_N{}^1{}_{CB}$ mechanism in the case of $[CoCl(NH_3)_5]^{2+}$ only
C. $S_N{}^1{}_{CB}$ mechanism in the case of $[Co(CN)_6]^{3-}$ only
D. $S_N{}^1{}_{CB}$ mechanism in both the complexes

Correct explanation (s) is/are

(a) A and B
(b) A and C
(c) B only
(d) A and D

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

13) The rate of exchange of cyanide ligands in the complexes (i) $[Ni(CN)_4]^{2-}$, (ii) $[Mn(CN)_6]^{3-}$ and (iii) $[Cr(CN)_6]^{3-}$ by ^{14}CN follow the order ***(GATE 2005)***

(a) (ii)>(i)>(iii)
(b) (iii)>(i)>(ii)
(c) (i)>(iii)>(ii)
(d) (i)>(ii)>(iii)

14) The CORRECT order of the rate of exchange of water molecules between the coordination sphere and the bulk is ***(GATE 2006)***

(a) $Cr^{3+}<Al^{3+}<Cr^{2+}<Ni^{2+}$
(b) $Cr^{3+}<Al^{3+}<Ni^{2+}<Cr^{2+}$
(c) $Cr^{3+}<Ni^{2+}<Cr^{2+}< Al^{3+}$
(d) $Cr^{3+}<Cr^{2+}<Al^{3+}<Ni^{2+}$

15) Consider the reactions *(GATE 2007)*

A. $[Cr(H_2O)_6]^{2+} + [CoCl(NH_3)_5]^{2+} \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$
B. $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$

Which one of the following is the correct statement?

(i) Both involve an inner sphere mechanism
(ii) Both involve an outer sphere mechanism
(iii) Reaction A follows inner sphere and reaction B follows outer sphere mechanism
(iv) Reaction A follows outer sphere and reaction B follows inner sphere mechanism

(a) i (b) ii (c) iv (d) iii

16) The reaction of $[PtCl_4]^{2-}$ with NH_3, gives rise to *(GATE 2007)*

(a) $[PtCl_4(NH_3)_2]^{2-}$ (b) *trans*- $[PtCl_2(NH_3)_2]$ (c) $[PtCl_2(NH_3)_4]$ (d) *cis*- $[PtCl_2(NH_3)_2]$

17) Designate the following complexes X, Y and Z as inert or labile [*GATE 2009*]

$X = [Al(C_2O_4)_3]^{3-}$ $Y = [V(H_2O)_6]^{2+}$ $Z = [Cr(C_2O_4)_3]^{3-}$

(a) X and Yare inert; Z is labile (b) X and Z are labile; Y is inert
(c) X is inert; Y and Z are labile (d) X is labile; Y and Z are inert

18) The mechanism of the reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine) is [*GATE 2010*]

(a) outer-sphere electron-transfer (b) inner-sphere electron-transfer
(c) self -exchange reaction (d) ligand exchange followed by electron-transfer

19) Consider the following pairs of complexes *[GATE 2012]*

$[CoF(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$
$[Co(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
$[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
$[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$

The electron transfer rate will be fastest in the pair

(a) $[CoF(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$ (b) $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
(c) $[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$ (d) $[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$

Answer Key

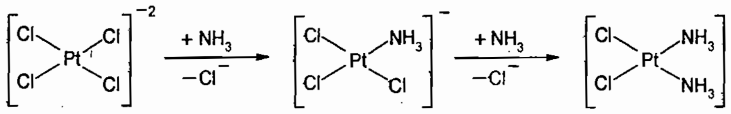
Topic 10 :– Inorganic Reaction Mechanism

1	b	2	a	3	b	4	a	5	b	6	b	7	c	8	a	9	a	10	a
11	b	12	a	13	d	14	b	15	d	16	d	17	d	18	a	19	d		

Hints & Solution

1) Ans (b):- Dissociative Mechanism ($S_N{}^1$-like) – typically occurs with 18 electron complexes;

2) Ans (a):- The reaction of $[PtCl_4]^{-2}$ with two equivalent of NH_3 produces *cis* $-[Pt(NH_3)_2Cl_2]$

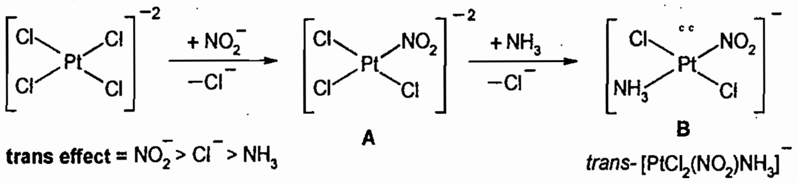


trans effect = Cl⁻ > NH₃

cis-$[Pt(NH_3)_2Cl_2]$

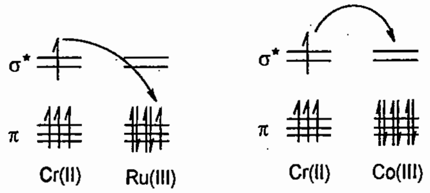
3) Ans (b):- Dissociative Mechanism ($S_N{}^1$-like) so rate of reaction depends on concentration of $Ni(CO)_4$ only

4) Ans (a):- The reaction of $[PtCl_4]^{-2}$ with NO_2^- & then NH_3 produces Trans-$[PtCl_2(NO_2)(NH_3)]^-$



5) Ans (b):- When both HOMO & LUMO are σ*; massive acceleration is seen in rates from outer to inner sphere But in case of Cr(II)/Ru(III) as HOMO/LUMO are σ* and π* therefore the rate of acceleration in going from a outer-sphere to a inner-sphere mechanism is lower.

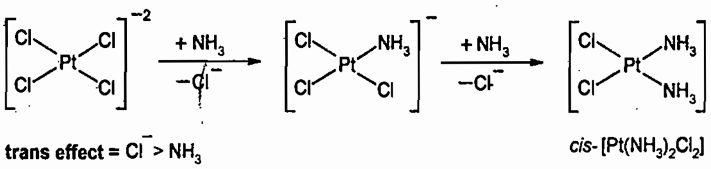
Reaction	HOMO	LUMO
Cr(II)/Ru(III)	$\sigma^*(e_g)$	$\pi^*(t_{2g})$
Cr(II)/Co(III)	$\sigma^*(e_g)$	$\sigma^*(e_g)$



6) Ans (b):- Base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ follow the $S_N{}^1$(CB) mechanism & the dissociation of chloride ion in $[Co(NH_3)_4(NH_2)Cl]^+$ is a rate determining step for base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$.

7) Ans (c):- A change from low spin to high spin in Co* and the low spin state remains unchanged in Ru. (Hint;- factors affecting Δ_0 & also check for oxidation state of metal ion in reaction)

8) Ans (a):- Isomeric formula of the complex and its precursor are *cis* −$[Pt(NH_3)_2Cl_2]$ and $[PtCl_4]^{-2}$



9) Ans (a):- The rates of water exchange in high-spin hexaaqua ions follow the sequences:

$$V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cr^{2+} < Cu^{2+}$$

A series is based on loss or gain of CFSE (labile/inert). A loss of CFSE means an increase in the activation energy for the reaction and hence a decrease in its rate & vice a versa. Therefore the order of rate of exchange of OH_2 present in the coordination sphere by $^{18}OH_2$ is
(i) $[Cu(OH_2)_6]^{2+}$ > (ii) $[Mn(OH_2)_6]^{2+}$ > (iii) $Fe(OH_2)_6]^{2+}$ > (iv) $[Ni(OH_2)_6]^{2+}$

10) Ans (a):- The 'phen' is a π-acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer.

11) Ans (b):- Reduction of $[Ru(NH_3)_5(isonicotinamide)]^{3+}$ with $[Cr(H_2O)_6]^{2+}$ occurs by inner sphere mechanism in which inert ruthenium bridged to very labile chromium centre. In this electron transfer reaction; electron transfer from Cr^{+2} to bridged isonicotinamide ligand by forming the successor complex.
In the next step isonicotinamide transfer the electron through the π system into the t_{2g} levels of Ru(III) & dissociation of the successor complex is take place

12) Ans (a):- Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is $S_N{}^1{}_{CB}$ mechanism due to presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$. $S_N{}^1{}_{CB}$ mechanism is not possible in the case of $[Co(CN)_6]^{3-}$.

13) Ans (d):- The rate of exchange of cyanide ligands by ^{14}CN follows the order:
$[Ni(CN)_4]^{2-} > [Mn(CN)_6]^{3-} > [Cr(CN)_6]^{3-}$
The general increasing order for lability low spin M^{+3} metal ion is:-

$$Co(III) < Cr(III) < Mn(III) < Fe(III) < Ti(III) < V(III)$$

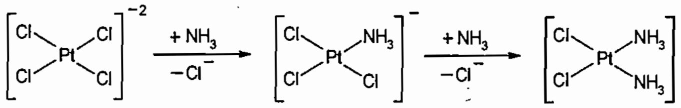
14) Ans (b):- The rates of water exchange in high-spin hexaaqua ions follow the sequences:

$$V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cr^{2+} < Cu^{2+}$$

A series is based on loss or gain of CFSE (labile/inert). A loss of CFSE means an increase in the activation energy for the reaction and hence a decrease in its rate & vice a versa

15) Ans (d):- Reaction 'A' follows inner sphere and reaction 'B' follows outer sphere mechanism

16) Ans (d):- The reaction of $[PtCl_4]^{2-}$ with NH_3, gives rise to *cis*- $[PtCl_2(NH_3)_2]$



cis-$[Pt(NH_3)Cl_2]$

17) Ans (d):- Hint:- High spin metal complexes with d^3 & d^8 metal ion configurations are inert.

$[Al(C_2O_4)_3]^{3-}$ is labile (d^0system); $[V(H_2O)_6]^{2+}$ & $[Cr(C_2O_4)_3]^{3-}$ are inert (d^3system)

18) Ans (a):- The mechanism of the reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine) is outer-sphere electron-transfer

19) Ans (d):- The reaction of $[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$ have outer sphere mechanism because ligands cannot form bridge between two metal ion while in all other cases bridging is possible due to extra lone pair with which to form bond to the reactant. Bridging is more favorable with I^- so rate of $[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$ pair is found to be much faster

Pair of reactant	Rate of The electron transfer reaction
$[CoF(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$	2.5×10^5
$[Co(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{2+}$	5×10^{-1}
$[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$	8.9×10^{-5}
$[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$	3×10^6

List of Reference Books

1) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter Pearson Education India.
2) Inorganic Chemistry, by Shriver and Atkins, Oxford University Press
3) Inorganic Chemistry, by Gary L. Miessler and Donald A. Tarr Pearson Education.
4) Principles of Inorganic Chemistry by Puri, Sharma and Kalia, Milestone Publisher.
5) Concise Coordination Chemistry, by R Gopalan and V Ramalingam, Vikas Publishing House.

◆◆◆

Topic 11

POINT GROUP/SYMMETRY ELEMENT

Questions with two marks

1) The symmetry point group of ethane in its staggered conformation is **[*Dec 2011*]**

(a) C_{3V} (b) C_{3d} (c) D_{3h} (d) S_6

2) Among the following, the CORRECT statement is **[*June 2012]***

(a) The number of irreducible representations is equal to classes of symmetry operations.
(b) The number of irreducible representations is equal to the order of the symmetry point group.
(c) The irreducible representations contained in any point group are always of one dimension.
(d) A symmetry point group may not contain a totally symmetric irreducible representation.

3) The molecule that has an S_6 symmetry element is **[*Dec 2012*]**

(a) B_2H_6 (b) CH_4 (c) PH_5 (d) SF_6

4) A molecule contains the following symmetry operations- E, $2C_6$, $2C_3$, C_2, $3\sigma_d$ & $3\sigma_v$. . The number of classes and order of the symmetry point group is **[*June 2013]***

(a) 3, 12 (b) 5, 12 (c) 6, 12 (d) 6, 6

5) The symmetry point group of propyne is **[*June 2014]***

(a) C_3 (b) C_{3V} (c) D_3 (d) D_{3d}

6) The point group symmetries for trans $[Cr(en)_2F_2]^+$ and $[TiCl_6]^{3-}$, respectively are **[*Dec 2014]***

(a) D_{4d} and D_{3d} (b) D_{3d} and D_{4d} (c) D_{4h} and D_{3h} (d) D_{3h} and D_{4h}

Questions with four marks

7) Given the character table of the point group C_{3V} [*June 2011*]

	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	
E	2	−1	0	(x,y)

Consider the reducible representation, τ

	E	$2C_3$	$3\sigma_v$
τ	6	3	0

Its irreducible components are

(a) $E + 2A_1 + 2A_2$ (b) $2E + A_1 + A_2$ (c) $3A_1 + 3A_2$ (d) $E^2 + 2A_1$

8) Character table of C_{2v} point group is **[June 2012]**

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	—
B_1	1	−1	1	−1	x
B_2	1	−1	−1	1	y

If the initial and final states belong to A_1 and B_1 irreducible representation respectively, the allowed electronic transition from A_1 to B_1 is

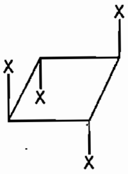
(a) z-polarized (b) y-polarized (c) x-polarized (d) x, z-polarized

9) Identify the Mulliken notation for the following irreducible representation ***[June 2013]***

E	C_n	nC_2	i	σ_h
1	1	−1	−1	−1

(a) A'_{1u} (b) A''_{2u} (c) B'_{2u} (d) A'_{2u}

10) Identify the point group symmetry of the following molecule (all C−C bond lengths are equal) ***[June 2013]***



(a) C_{2V} (b) S_4 (c) D_{2d} (d) D_{4d}

11) The transition that is allowed by x-polarized light in trans-butadiene is ***[Dec 2013]***
(The character table for C_{2h} is given below)

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	R_x, x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y, xz, yz
A_u	1	1	−1	−1	z
B_u	1	−1	−1	1	x, y

(a) $^1A_u \longrightarrow {}^1A_u$ (b) $^1A_u \longrightarrow {}^1B_g$ (c) $^1B_u \longrightarrow {}^1B_g$ (d) $^3B_g \longrightarrow {}^1A_g$

12) The low temperature (−98°C) ^{19}F NMR spectrum of SF_4 shows doublet of triplets. It is consistent with the point group symmetry ***[June 2014]***

(a) C_{3V} (b) C_{4V} (c) T_d (d) C_{2V}

13) The result of the product $C_2(x)\,C_2(y)$ ***[June 2014]***

(a) E (b) σ_{xy} (c) $C_2(z)$ (d) *i*

14) The E⊗E direct product in D_3 point group contains the irreducible representations ***[June 2014]***

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	–1
E_2	2	–1	0

(a) $A_1 + A_2 + E$ (b) $2A_1 + E$ (c) $2A_2 + E$ (d) $2A_1 + 2A_2$

15) The product $\sigma^{xy}.S_4^z$ (S_4^z is the four fold improper axis of rotation around the z axis, and σ^{xy} is the reflection in the xy plane is) ***[Dec 2014]***

(a) C_4^z (b) $C_4^z\,.\,i$ (c) C_4^y (d) C_2^z

<u>(Questions from GATE EXAM)</u>

<u>Questions with ONE OR TWO marks</u>

16) A molecule has a 2–fold axis and a mirror plane perpendicular to that. The point group must have a ***(GATE 2006)***

(a) C_2 axis (b) Centre of inversion (c) σ_h plane (d) σ_v plane

17) The symmetry elements that are present in BF_3 are ***(GATE 2006)***

(a) C_3, σ_v, σ_h, $3C_2$ (b) C_3, $3C_2$, S_2, σ_v (c) C_3, $3C_2$, σ_h, S_2 (d) C_3, σ_h, σ_v, *i*

18) The S_2 operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to ***(GATE 2007)***

(a) (-x, -y, z) (b) (x, -y, -z) (c) (-x, y, -z) (0) (-x, -y, -z)

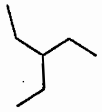
19) The point group of NSF_3 is ***(GATE 2008)***

(a) D_{3d} (b) C_{3h} (c) D_{3h} (d) C_{3v}

20) The T_d point group has 24 elements and 5 classes. Given that it has two 3-dimensional irreducible representations, the number of one dimensional irreducible representations is ***(GATE 2008)***

(a) 1 (b) 6 (c) 2 (d) 3

21) The point group symmetry of the given planar shape is ***(GATE 2011)***



(a) D_{3h} (b) C_3 (c) C_{3h} (d) C_{3v}

Statement for Linked Answer Questions 22, 23 and 24:

Trans 1,2 difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre. Answer the following three questions *(GATE 2007)*

22) The number of distinct symmetry operations that can be performed on the molecule is

(a) 2 (b) 4 (c) 6 (d) 8

23) The number of irreducible representations of the point group of the molecule is

(a) 1 (b) 2 (c) 3 (d) 4

24) When two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be

(a) C_i (b) C_{2h} (c) C_{2v} (d) D_{2h}

Linked Answer Questions (25 and 26)

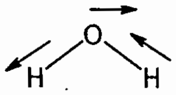
Character table for the point group C_{2v} is given below: *[GATE 2009]*

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	Z	X^2, y^2, z^2
A_2	1	1	−1	−1	R_Z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

25) The reducible representation corresponding to the three translational degrees of freedom, τ_{tr}

(a) 3,1,1,1 (b) 3,−1, 1,1 (c) 3,−1,−1,−1 (d) 3,1,−1,−1

26) The asymmetric stretching mode of the H_2O is shown below. The molecular plane is *yz* and the symmetry axis of H_2O is *z*.



This vibration transforms as the irreducible representation

(a) A_1 (b) B_1 (c) A_2 (d) B_2

27) $[CoCl_4]^{2-}$ a blue coloured complex. Controlled-treatment of this complex with water generates two isomeric light pink coloured complexes, of composition $[Co(H_2O)_4Cl_2]$. Identify the correct point groups for $[CoCl_4]^{2-}$ and two isomeric complexes $[Co(H_2O)_4Cl_2]$. *[GATE 2010]*

(a) D_{4h} and (C_{2v} & C_{2h}) (b) Td and (C_{2v} & D_{4h})

(c) D_{4h} and (C_{2v} & D_{4h}) (d) Td and (C_{2v} & C_{4v})

28) The point group of ClF_3 molecule and its corresponding number of irreducible representations are respectively *[GATE 2010]*

(a) C_{3v} & 4 (b) C_{2v} & 4 (c) C_{3v} & 3 (d) C_{2v} & 3

29) Symmetry operations of the four C_2 axes perpendicular to the principal axis belong to the same class in the point group(s) *[GATE 2012]*

(A) D_4 (B) D_{4d} (C) D_{4h} (D) D_{4h} and D_{4d}

30) The point group symmetry of $CH_2=C=CH_2$ is **[GATE 2013]**

(a) D_{2h} (b) C_{2h} (c) C_{2v} (d) D_{2d}

31) Conversion of boron trifluoride to tetrafluoroborate accompanies **[GATE 2013]**

(a) increase in symmetry and bond elongation (b) increase in symmetry and bond contraction
(c) decrease in symmetry and bond contraction (d) decrease in symmetry and bond elongation

32) The number of C_2 axes in CCl_4 is **[GATE 2014]**

(a) Two (b) Three (c) Four (d) Five

Answer Key

Topic 11: –Point group/Symmetry element

1	b	2	a	3	d	4	c	5	b	6	c	7	a	8	c	9	c	10	c
11	b	12	d	13	c	14	a	15	a	16	b	17	a	18	d	19	d	20	c
21	a	22	b	23	d	24	d	25	b	26	d	27	b	28	b	29	c	30	d
31	a	32	b																

Hints & Solution

1) Ans (b):- The symmetry point group of ethane in its staggered conformation is D_{3d}

2) Ans (a):- The CORRECT statement is the number of irreducible representations is equal to classes of symmetry operations according to assumptions of the Great Orthogonality Theorem

3) Ans (d):- The molecule that has an S_6 symmetry element is SF_6. Here, S_6 is improper axis of rotation
Condition for the improper axis (S_n):- There must be either rotation followed by reflection or reflection followed by rotation occurs that is $S_n = C_n. \sigma_h$ or $\sigma_h.C_n$ this type of rotation only when $C_n \perp^{er} \sigma_h$.

4) Ans (c):- The number classes is equal to the number of symmetry operations &
Order of point group = Total number of symmetry elements.

Symmetry element	E	$2C_6$	$2C_3$	C_2	$3\sigma_d$	$3\sigma_v$	Total
Operations/ classes	1	1	1	1	1	1	6
Order	1	2	2	1	3	3	12

5) Ans (b):- The symmetry point group of propyne is C_{3v}

6) Ans (c):- The point group symmetries for trans $[Cr(en)_2F_2]^+$ and $[TiCl_6]^{3-}$, are D_{4h} and D_{3h} respectively

7) Ans (a):- $n_j = \frac{1}{h}\sum_{Rp} g_p \chi_i(R_p)\chi_j(R_p)$

Order h of C_{3v} point group is 6. Hence using the character table of the C_{3v} point group & the above equation we get;

$$A_1 = \frac{1}{6}[(1)(1)(6) + (2)(1)(3) + (3)(1)(0)] = 2 \text{ that is } 2A_1$$

$$A_2 = \frac{1}{6}[(1)(1)(6) + (2)(1)(3) + (3)(-1)(0)] = 2 \text{ that is } 2A_2$$

$$E = \frac{1}{6}[(1)(2)(6) + (2)(-1)(3) + (3)(0)(0)] = 1 \text{ that is } E$$

Therefore irreducible component are $E + 2A_1 + 2A_2$

8) Ans (c):- The initial and final states belong to A_1 and B_1 is x-polarized that is

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	z
B_1	1	–1	1	–1	x
$A_1 \longleftrightarrow B_1$	1	–1	1	–1	

9) Ans (c):- B'_{2u} (Use following rule to determine the Mulliken notation)

The Mulliken notation used to describe the symmetry species of point groups including their meaning with respect to molecular symmetry	
A	Symmetric with respect to principal axis of symmetry
B	Antisymmetric with respect to principal axis of symmetry
E	Doubly degenerate, two-dimensional irreducible representation
T	Triply degenerate, three-dimensional irreducible representation
g	Symmetric with respect to a center of symmetry
u	Antisymmetric with respect to a center of symmetry
1 (subscript)	Symmetric with respect to a C_2 axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a σ_v plane of symmetry is symmetric.
2 (subscript)	Antisymmetric with respect to a C_2 axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a σ_v plane of symmetry is antisymmetric.
' (prime)	Symmetric with respect to reflection in a horizontal plane of symmetry
" (prime)	Antisymmetric with respect to reflection in a horizontal plane of symmetry

10) Ans (c):- The point group symmetry of the given molecule is D_{2d}

11) Ans (b):- The transition that is allowed by x-polarized light in trans-butadiene is $^1A_u \rightarrow {}^1B_g$

C_{2h}	E	C_2	i	σ_h	
B_g	1	–1	1	–1	R_x, R_y, xz, yz
A_u	1	1	–1	–1	z
B_u	1	–1	−1	1	x, y

12) Ans (d):- According to VSEPR shape of SF_4 is sea-saw and point group of molecule with sea-saw structure is C_{2v}

13) Ans (c):- $C_2(x)\ C_2(y) = C_2(z)$ This is the Element transformation (Matrix method)

$$\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix}\begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{bmatrix} = \begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

14) Ans (a):-

D_3	E	$2C_3$	$3C_2$
E	2	−1	0
E	2	−1	0
E⊗E	4	1	0

E⊗E is a reducible representation, with the help of reducible representation we can calculate the set of irreducible representation of D_3 point group.

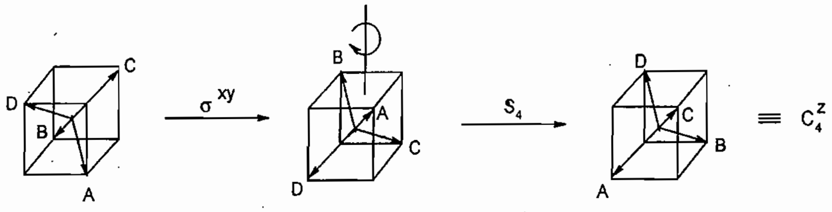
η_{A_1} = 1/6 [4+2+0] = 1

η_{A_2} = 1/6 [4+2+0] = 1

η_{E} = 1/6 [8−2+0] = 1

Therefore E⊗E direct product in D_3 point group contains the irreducible representations $A_1 + A_2 + E$.

15) Ans (a):- The product of $\sigma^{xy}.s_4^z$ is C_4^z



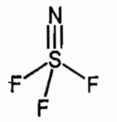
16) Ans (b):- The D_{nh} group that have n-two fold axes perpendicular to the principal axes (n-fold) in addition σ_h plane. It has three mutually perpendicular two fold axes, σ_h plane & as consequences a center of inversion (that is n-two fold axes & σ_h is perpendicular).

17) Ans (a):- The symmetry elements that are present in BF_3 are C_3, σ_v, σ_h, $3C_2$ because BF_3 has D_{3h} point group. (symmetry elements for D_{3h} point group are E, $2C_3$, $3C_2$, σ_h, $3\sigma_v$, $2S_3$)

18) Ans (d):- The S_2 operation on a molecule with the axis of rotation as the z axis, moves a nucleus at (x, y, z) to (-x, -y, -z). As S_2 operation is equal to C_2 operation followed by σ_h operation. If the C_2 axis as 'z', the effect of first would be to convert every point (x, y, z) into & equivalent point at (−x, −y, z). Second step the reflection xy plane would transpose every coordinate z into −z that is:-(−x, −y, z) → (−x, −y, −z)

Therefore net effect is $(x,y,z) \xrightarrow{S_2} (-x,-y,-z)$

19) Ans (d):- The shape of NSF_3 is like a trigonal pyramidal so point group of NSF_3 is C_{3v}



C_{3v}

20) Ans (c):- Hint:- From the character table of Td point group, the irreducible set are A_1, A_2, E, T_1, T_2. From the given data the T_d point group have 5 classes & two 3-dimensional irreducible representations, the number of one dimensional irreducible representations is two (A_1 & A_2)
(A term belongs to one dimension; E term belongs two dimension & T term belongs to three dimension)

21) Ans (a):- The point group symmetry of the given planar shape is D_{3h}

22) Ans (b):- Trans 1,2 difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre. The number of distinct symmetry operations is equal to the numbers of classes. In this example numbers of classes are identity, 2-fold rotational axis, a symmetry plane perpendicular to the rotational axis and an inversion centre that is equal to four.

Symmetry element C_{2h}	E	$C_2(z)$	i	$\sigma(xz)$	Total
classes	1	1	1	1	4

23) Ans (d):- The number of irreducible representations of the point group of the molecule is 4.
Hint:- The number of irreducible representations is equal to the number of classes.

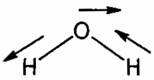
24) Ans (d):- When two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be D_{2h}

C_{2h} D_{2h}

25) Ans (b):- The reducible representation corresponding to the three translational degrees of freedom, τ_{tr} 3,−1, 1,1 In this case translational degree of freedom τ_{tr} from C_{2v} character table $\tau_{tr} = A_1 + B_1 + B_2$ corresponding to T_x, T_y & T_z respectively.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	X^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
τ_{tr}	3	−1	1	1		

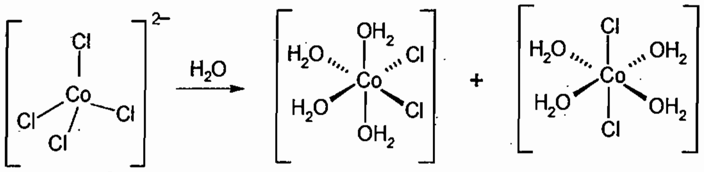
26) Ans (d):- The asymmetric stretching mode of the H_2O is shown below. The molecular plane is *yz* and the symmetry axis of H_2O is z.



The molecular plane σ_{yz} corresponds to B_2 irreducible representation & symmetry axis of H_2O is $C_2(z)$ corresponds to A_1 irreducible representation from the given character table. Therefore $A_1 \rightarrow B_2$ transformation equal to B_2 irreducible representation.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	
B_2	1	−1	−1	1	
$A_1 \times B_2$	1	−1	−1	1	corresponds to B_2

27) Ans (b):- Two isomeric complexes [Co(H_2O)$_4$Cl$_2$ are as given below,



[CuCl$_4$]$^{2-}$ Td — *trans Cu(H$_2$O)$_4$Cl$_2$* (C$_{2v}$) — *cis Cu(H$_2$O)$_4$Cl$_2$* (D$_{4h}$)

28) Ans (b):- The point group of ClF$_3$ molecule and its corresponding number of irreducible representations are respectively C_{2v} & 4

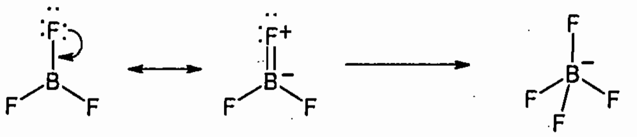
Symmetry element of C_{2v}	E	$C_2(z)$	σ_v	σ'_v	Total
classes	1	1	1	1	4

Therefore number of irreducible representation = number of classes = 4.

29) Ans (c):- Symmetry operations of the four C_2 axes perpendicular to the principal axis belong to the same class in the point group(s) D_{4h} (Refer the solution of question number 16).

30) Ans (b):- The point group symmetry of $CH_2=C=CH_2$ is D_{2d}.

31) Ans (a):- In BF_3 (D_{3h}) due to stronger 2p(B)−2p(F) π back bonding; bond order of each B−F bond is greater than one while in BF_4^- (T_d) bond order of B−F is one therefore conversion of BF_3 to BF_4^- accompanies with bond elongation. Point group T_d is group of high symmetry than D_{3h}



average bond order is greater than one — average bond order is one (bond elongation)

$$\underset{(D_{3h})}{BF_3} \longrightarrow \underset{(T_d)}{\overset{-}{BF_4}}$$

32) Ans (b):- The number of C_2 axes in CCl_4 is three. The point group of CCl_4 is tetrahedral. The symmetry elements for tetrahedral point group are E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

List of Reference Books

1) Chemical application and group Theory: F.A. Cotton, 3rd edition (1999)
2) Molecular symmetry and Group Theory by Robert L. Carter John Wiley & Sons
3) Group theory and its chemical application: P.K. Bhattacharya 2nd edn. (1989) (Himalaya Publication)
4) Concept and Application of Group Theory by Kishor Arora Anmol Publications Pvt. Ltd.
5) Principles of Physical Chemistry by Puri, Sharma and Pathania Vishal Publishing Co.

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Topic 12

SOLID STATE

Questions with two marks

1) The value of d_{111} in a cubic crystal is 325.6 pm. The value of d_{333} is ***[Dec 2011]***

(a) 325.6 pm (b) 976.8 pm (c) 108.5 pm (d) 625.6 pm

2) How many atoms are there in an element packed in a fcc structure ***[June 2012]***

(a) 1 (b) 2 (c) 4 (d) 8

3) The structure obtained when all the tetrahedral holes are occupied in a fcc structure is of the type ***[June 2012]***

(a) NaCl (b) CsCl (c) CaF_2 (d) ZnS

4) The angle between the two planes represented by the Miller indices (110) and (111) in a simple cubic lattice is: ***[Dec 2012]***

(a) 30° (b) 45° (c) 60° (d) 90°

5) The packing fraction of a simple cubic lattice is close to

(a) 0.94 (b) 0.76 (c) 0.52 (d) 0.45

6) The coordinates for the atoms in a body centred cubic unit cell are ***[June 2013]***

(a) (0, 0, 0) and (1/2, 0, 0) (b) (0, 0, 0) and (1/2, 1/2, 1/2)
(c) (0, 0, 0) and (0, 1/2, 0) (d) (0, 0, 0) and (0, 0, 1/2)

7) The inter planar distance (Å) for a (100) plane in a cubic structure with the lattice parameter of 4 Å is: ***[June 2013]***

(a) 1 (b) 2 (c) 4 (d) 8

8) When Frenkel defects are created in an otherwise perfect ionic crystal, the density of the ionic crystal ***[Dec 2013]***

(a) increases (b) decreases
(c) remains same (d) oscillates with the number of defects

9) A compound of M and X atoms has a cubic unit cell. M atoms are at the corners and body centre position and X atoms are at face centre positions of the cube. The molecular formula of the compound is ***[Dec 2013]***

(a) MX (b) MX_2 (c) M_3X_2 (d) M_2X_3

10) The angle at which the first order Bragg reflection is observed from (110) plane in a simple cubic unit cell of side 3.238 Å when chromium K_α radiation of wavelength 2.29 Å is used, is ***[Dec 2013]***

(a) 30° (b) 45° (c) 60° (d) 90°

11) Number of rotational symmetry axes for triclinic crystal system is ***[June 2014]***

(a) 4 (b) 3 (c) 1 (d) 0

Questions with four marks

12) The lattice parameter of an element stabilized in a fcc structure is 4.04 Å. The atomic radius of the element is ***[June 2012]***

(a) 2.86 Å (b) 1.43 Å (c) 4.29 Å (d) 5.72 Å

13) Coordination number of "C" in Be_2C_3 whose structure is correlated with that of CaF_2, is: ***[Dec 2012]***

(a) 2 (b) 4 (c) 6 (d) 8

14) Crystal A diffracts from (111) and (200) planes but not from (110) plane, while the crystal B diffracts from (110) and (200) planes but not from the (111) plane. From the above, we may conclude that ***[Dec 2012]***

(a) A has fcc lattice while B has bcc lattice (b) A has bcc lattice while B has fcc lattice
(c) A and B both have fcc lattice (d) A and B both have bcc lattice.

15) A metal crystallizes in fcc structure with a unit cell side of 500 pm. If the density of the crystal is 1.33 g/cc, the molar mass of the metal is close to ***[Dec 2012]***

(a) 23 (b) 24 (c) 25 (d) 26

16) A plane of spacing 'd' shows first order Bragg diffraction at angle θ. A plane of spacing 2d ***[June 2013]***

(a) shows Bragg diffraction at 2θ (b) shows Bragg diffraction at $\theta/2$

(c) shows Bragg diffraction at $\sin^{-1}\left(\frac{\sin\theta}{2}\right)$ (d) shows Bragg diffraction at $\sin^{-1}\left(\frac{\sin 2\theta}{2}\right)$

17) An element exists in two crystallographic modifications with FCC and BCC structures. The ratio of the densities of the FCC and BCC modifications in terms of the volumes of their unit cells (V_{FCC} and V_{BCC}) is ***[Dec 2013]***

(a) $V_{BCC} : V_{FCC}$ (b) $2V_{BCC} : V_{FCC}$ (c) $V_{BCC} : 2V_{FCC}$ (d) $V_{BCC} : \sqrt{2}V_{FCC}$

18) Metallic gold crystallizes in fcc structure with unit cell dimension of 4.00 Å The atomic radius of gold is ***[Dec 2013]***

(a) 0.866 Å (b) 1.414 Å (c) 1.732 Å (d) 2.000 Å

19) Both NaCl and KCl crystallize with the Fcc structure. However, the X-ray powder diffraction pattern corresponds to the fcc structure whereas, that of KCl corresponds to simple cubic structure. This is because ***[Dec 2013]***

(a) K^+ and Cl^- are isoelectronic (b) Na^+ and Cl^- are isoelectronic
(c) K^+ and Cl^- are disordered in the crystal lattice (d) KCl has anti-site defects.

20) A compound A_xB_y has a cubic structure with A atoms occupying all corners of the cube as well as all the face centre positions. The B atoms occupy four tetrahedral voids. The values of x and y respectively, are ***[June 2014]***

(a) 4, 4 (b) 4, 8 (c) 8, 4 (d) 4, 2

21) The interplanar spacing of (110) planes in a cubic unit cell with lattice parameter a = 4.242 Å is

(a) 3 Å (b) 6 Å (c) 7.35 Å (d) 2.45 Å

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

22) The arrangement of sulphur in zinc blende and wurtzite structures, respectively, are *(GATE 2006)*

(a) hexagonal close packing and cubic close packing (b) cubic close packing and hexagonal close packing
(c) hexagonal close packing in both the structures (d) simple cubic packing in both the structures

23) For a face centered cubic lattice, the Miller indices for the first Bragg's peak (smallest Bragg angle) are *[GATE 2012]*

(A) 0 0 2 (B) 1 1 1 (C) 0 0 1 (D) 1 1 0

24) A crystal has the lattice parameters $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$. The crystal system is *[GATE 2013]*

(a)Tetragonal (b) Monoclinic (c) Cubic (d) Orthorhombic

25) The increasing order of melting points of the halides NaCl, CuCl and NaF is *[GATE 2013]*

(a) CuCl<NaCl<NaF (b) NaF<NaCl<CuCl (c) NaF<CuCl<NaCl (d) CuCl<NaF<NaCl

26) A metal crystallizes in face-centered cubic lattice with a lattice parameter of 4.20 Å. The shortest atom to atom contact distance in the lattice is *[GATE 2013]*

(a) 4.20 Å (b) 2.97 Å (c) 2.42 Å (d) 2.10 Å

27) The lattice parameters for a monoclinic crystal are *[GATE 2008]*

(a) $a \neq b \neq c$; $\alpha = \gamma = 90^0$ (b) $a = b \neq c$; $\alpha \neq \beta \neq \gamma$
(c) $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$ (d) $a = b = c$; $\alpha = \gamma = 90^0$

28) Molybdenum crystallizes in a *bcc* structure with unit cell dimensions of 0.314 nm. Considering the atomic mass of molybdenum to be 96, its density (in kg m^{-3}) is in the range of: *[GATE 2014]*

(a) 8000-10000 (b) 10000-10200 (c) 10000-10300 (d) 10000-10500

Answer Key

Topic : 12 :- solid state

1	c	2	c	3	c	4	b	5	c	6	b	7	c	8	c	9	d	10	a
11	d	12	b	13	d	14	a	15	c	16	c	17	b	18	b	19	a	20	a
21	a	22	b	23	b	24	d	25	a	26	b	27	a	28	d				

Hint & solution

1) Ans (c):- The distance between the parallel planes in crystals are designated as d_{hkl}. For different cubic lattices these interplanar spacing are given by the general formula,

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Where a is the length of cube side while h, k and l are the Miller indices of the plane. For a cubic crystal,

$$d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{a}{\sqrt{3}}$$

$$d_{333} = \frac{a}{\sqrt{3^2+3^2+3^2}} = \frac{a}{\sqrt{27}} = \frac{a}{3\sqrt{3}} \; but \; \frac{a}{\sqrt{3}} = d_{111}$$

$$\therefore d_{333} = \frac{d_{111}}{3} = \frac{325.6}{3} = 108.5\,pm$$

2) Ans (c):- Number of atoms in different types of unit cells:-

Types of unit cells	Number of atoms (z) present in a unit cell
Primitive unit cell:	1 atom
Face centred unit cell:	4 atoms
Body centred unit cell:	2 atoms
Edge centred unit cell:	1.5 atoms

3) Ans (c):-

Structure	arrangements
NaCl	Cl^- with Na^+ in all octahedral holes
CsCl	bcc structure
CaF_2	Ca^{2+} with F^- in all Tetrahedral holes
ZnS	S^{2-} with Zn^{2+} in half Tetrahedral holes

4) Ans (b):- In a simple cubic lattice the angle between any two planes can be calculated as

$$cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2+k_1^2+l_1^2)}\ \sqrt{(h_2^2+k_2^2+l_2^2)}}$$

$$cos\theta = \frac{1\times1 + 1\times1 + 0\times1}{\sqrt{1^1+1^1+0^1}\ \sqrt{1^1+1^1+1^1}}$$

$$cos\theta = \frac{2}{\sqrt{6}} = 0.82$$

$$\theta = cos^{-1}(0.82) = 35^0$$

Thus the angle between the two planes (110) and (111) in a simple cubic lattice is: $\theta = 35.3°$ i.e. 45° in option
The angles between the two planes are given in table:-

ANGLE	100	110	010	001	101
100	0.00	45.0	90.0	90.0	45.0
011	90.0	60.0	45.0	45.0	60.0
111	54.7	35.3	54.7	54.7	35.3
211	35.2	30.0	65.9	65.9	30.0
311	25.2	31.4	72.4	72.4	31.4
511	15.8	35.2	78.9	78.9	35.2
711	11.4	37.6	81.9	81.9	37.6

5) Ans (c):-

Types of unit cells	Packing fraction (in %)
Simple cubic arrangement	52
Body centered cubic (BCC) arrangement	68
Face centered cubic (FCC) arrangement	74
Hexagonal close cubic (HCC) arrangement	74

6) Ans (b):- The coordinates for the atoms in a body centred cubic unit cell e.g. CsCl are (0,0,0) & (1/2,1/2,1/2.). There is a Cl^- ion at the coordinates 0,0,0; & there is a Cs^+ ion at the coordinates 1/2,1/2,1/2.

7) Ans (c):- Given a = 4

We have,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{100} = \frac{4}{\sqrt{1^2 + 0^2 + 0^2}} = 4$$

8) Ans (c):- Frenkel defects is a point defect formed due to shifting of an atom or ion from its normal lattice point to an interstitial site & therefore density of the ionic crystal remains same in Frenkel defects as ions are not missing from the lattice

9) Ans (d):-

Types of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face centered	1/2
Body centre	1

M atoms = $8 \times \frac{1}{8} + 1 \times 1 = 2$ & X atoms = $6 \times \frac{1}{2} = 3$

∴ The molecular formula of the compound is M_2X_3

10) Ans (a):- We know; 2dsinθ = nλ but d is not given therefore $d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = d_{110} = a/\sqrt{2}$

Now; equation nλ = 2dsinθ now become $n\lambda = \frac{2a\sin\theta}{\sqrt{2}}$

$$\therefore \sin\theta = \frac{2.29\text{Å}\sqrt{2}}{2 \times 3.238\,\text{Å}} = 0.5$$

$$\theta = sin^{-1}(0.5) = 30^0$$

11) Ans (d):- Number of rotational symmetry axes is zero for triclinic crystal system. Axial distances & Angles in case of triclinic crystal system are $a \neq b \neq c$ & $\alpha \neq \beta \neq \gamma \neq 90°$ respectively, therefore no axis of symmetry.

12) Ans (b):- Given a = 4.04 Å.

In a fcc structure; the atomic radius of the element (r) = $\frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 4.04\text{Å}}{4} = 1.4284$ Å

13) Ans (d):- Coordination number of "C" in Be_2C_3 is 8

Structure	Cation	Anion
CaF_2	Ca^{+2} *(divalent)* ; CN = 8	F^- *(monovalent)*; CN = 4
Be_2C_3	Be^+ *(monovalent)* ; CN = 4	C_3^{-2} *(divalent)* ; CN = 8

14) Ans (a):- A has fcc lattice while B has bcc lattice

Selection Rules for Diffraction Peaks in Cubic Systems		
Bravais lattice	Allowed reflections	Forbidden reflections
Simple cubic	Any h, k, l	None
Body-centered cubic	$h + k + l$ = even	$h + k + l$ = odd
Face-centered cubic	h, k, l all odd or all even	h, k, l mixed odd and even

15) Ans (c):- Density is given by formula:-

$$Density(\rho) = \frac{Z.M}{N_A a^3}$$

Where Z = no. of atoms in unit cell; in case of fcc structure the number of atoms are **4**

M = molar mass =?

A= Avogadro number = 6.022×10^{23} m

& a = edge length = 500 pm = 500×10^{-12} m $=500\times10^{-10}$cm

Density (ρ) = 1.33 g/cc

$$M = \frac{\rho.N_A a^3}{Z}$$

By solving we get the molar mass of the metal is close to = 25

16) Ans (c):- We know Bragg equation:- $n\lambda = 2d\sin\theta$ or $d = \frac{\lambda}{2\sin\theta}$ (for first order n = 1)

By rearranging equation: - $\sin\theta = \frac{n\lambda}{2d}$ But d = 2d ....(1)

$$\sin\theta = \frac{\lambda}{4d} \quad \text{.......................(2)}$$

Now putting the value of $d = \frac{\lambda}{2\sin\theta}$ in equation (2) & by solving we get

$$\sin\theta = \frac{\sin\theta}{2}$$

$$\therefore\ \theta = \sin^{-1}.\frac{\sin\theta}{2}$$

17) Ans (b):- Density is given by formula:-

$$Density(\rho) = \frac{Z.M}{N_A a^3}$$

Where Z =4 for FCC & 2 BCC

$$Thus;\ Density(\rho_{FCC}) = \frac{4.M}{N_A V_{FCC}} \quad \& \quad Density(\rho_{BCC}) = \frac{2.M}{N_A V_{BCC}}$$

$$\therefore\ \frac{\rho_{FCC}}{\rho_{BCC}} = \frac{2V_{BCC}}{V_{FCC}}$$

18) Ans (b):-

Relation between unit cell dimension & atomic radius	
Simple cubic	$r = \frac{a}{2}$
Body-centered cubic	$r = \frac{\sqrt{3}a}{4}$
Face-centered cubic	$r = \frac{\sqrt{2}a}{4}$

The atomic radius of gold (FCC structure) is = $r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2}\ 4}{4}$ = 1.414 Å

19) Ans (a):- The two ions in KCl (K^+ & Cl^-) have the same number of electrons (isoelectronic) and identical scattering power. So the net effect is that the two reflections cancel and the 111 reflection appears to be absent. This means the first reflection is the 200, which is same as 100 reflection from simple cubic structure. Therefore; the X-ray powder diffraction pattern of KCl corresponds to simple cubic structure.

20) Ans (a):- A compound A_xB_y has a cubic structure with A atoms occupying all corners of the cube as well as all the face centre positions. The B atoms occupy four tetrahedral voids. Then the values of x and y are 4 and 4 respectively. [Hint:- remind the structure of ZnS (Zinc Blende)]

21) Ans (a):- We know

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{4.242}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{4.242}{\sqrt{2}} = 2.99\text{Å} \cong 3\text{Å}$$

22) Ans (b):- Arrangement of sulphur in zinc blende and wurtzite structures are cubic close packing and hexagonal close packing respectively.

23) Ans (b):- For a face centered cubic lattice, the Miller indices for the first Bragg's peak (smallest Bragg angle) are 111

24) Ans (d):- The lattice parameters for an orthorhombic crystal system are: - a ≠ b ≠ c and $\alpha = \beta = \gamma = 90^\circ$.

Crystals class	Bravais lattices	Axial distances	Angles	Possible types of unit cells	Examples
Cubic	3 (P, I, F)	a = b = c	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC	Copper , KCl, NaCl ,diamond, zinc blende,
Tetragonal	2(P, I)	a = b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC	SnO_2, White tin, TiO_2
Orthorhombic	4(P, I, F,C)	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC, end centred	Rhombic sulphur, KNO_3, $CaCO_3$
Hexagonal	1 (P)	a = b ≠ c	$\alpha = \beta = 90^\circ$ & $\gamma = 120^\circ$	SC	Graphite, Mg, ZnO
Trigonal or Rhombohedral	1 (P)	a = b = c	$\alpha = \beta = \gamma \neq 90^\circ$	SC	($CaCO_3$) Calcite, HgS(Cinnabar)
Monoclinic	2 (P,C)	a ≠ b ≠ c	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	SC, end centred	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	1 (P)	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	SC	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

25) Ans (a):- Metal halides with more ionic character generally have higher melting point. According to Fajan's rules order of ionic character & hence melting point CuCl < NaCl < NaF

26) Ans (b):- The shortest atom to atom contact distance in the fcc lattice is:- $\frac{a}{\sqrt{2}}$

$\therefore 4.20 / \sqrt{2} = 2.97$ Å

27) Ans (a):- The lattice parameters for a monoclinic crystal are $a \neq b \neq c$; $\alpha = \gamma = 90^0$

28) Ans (d):- Density of crystal can be calculated from the dimensions of unit cell and mass of atoms in it.

$$Density(\rho) = \frac{Z.M}{N_A a^3}$$

Where Z = no. of atoms in unit cell ; in case of bcc structure number of atoms are 2

M = molar mass = 96 $gmol^{-1}$

A = Avogadro number = 6.022×10^{23} m

& a = edge length = 0.314 nm = 3.14×10^{-10} m

By calculation we get 10322.5 kgm^{-3}

List of Reference Books

1) Fundamental of Physical Chemistry by Moron and Prutton, Oxford and IBH Publishing Co. Pvt. Ltd

2) Inorganic Chemistry, by Sharpe, Pearson Education India.

3) Concise inorganic chemistry, by J. D. Lee, John Wiley & Sons. India.

4) Inorganic Chemistry: Principles of Structure and Reactivity, by J. H. Huheey, E.A. Keiter and R.L.Keiter, Pearson Education.

5) Principles of Physical Chemistry by Puri, Sharma and Pathania Vishal Publishing Co.

6) Essential of Physical Chemistry by Arun Bahl, B.S.Bahl, G.D. Tuli, S Chand Publishing.

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Topic 13

MOLECULAR SPECTROSCOPY

Questions with two marks

1) Which one of the following exhibits rotational spectra? ***[June 2011]***

(a) H_2 (b) N_2 (c) CO (d) CO_2

2) The microwave spectrum of a molecule yields three rotational constants. The molecule is ***[June 2011]***

(a) Prolate symmetric top (b) Spherical top (c) Asymmetric top (d) Oblate symmetric top

3) The Q band in the vibrational spectrum of acetylene is observed in the ***[June 2011]***

(a) C–C stretching mode (b) C-H symmetric stretching mode
(c) Bending mode (d) C-H antisymmetric stretching mode.

4) Which of the following spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes? ***[June 2011]***

(a) NMR (b) IR (c) EPR (d) Mass

5) If Mössbauer spectrum of $Fe(CO)_5$ is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with ***[June 2012]***

(a) Three lines (b) Four lines (c) Five lines (d) Six lines

6) For a diatomic molecule AB, the energy for the rotational transition from J = 0 to J = 1 state is 3.9 cm^{-1}. The energy for the rotational transition from J = 3 to J = 4 state would be ***[June 2012]***

(a) 3.9 cm^{-1} (b) 7.8 cm^{-1} (c) 11.7 cm^{-1} (d) 15.6 cm^{-1}

7) For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is ***[June 2012]***

(a) $\Delta v = 0$ only (b) $\Delta v = \pm 1$ only (c) $\Delta v = \pm 2$ only (d) $\Delta v = 0, \pm 1$

8) In the vibrational spectrum of CO_2, the number of fundamental vibrational modes common in both infrared and Raman are ***[Dec 2012]***

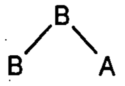
(a) Three (b) Two (c) One (d) Zero

9) The number of lines exhibited by a high resolution EPR spectrum of the species, $[Cu(ethylenediamine)_2]^{2+}$ is [Nuclear spin (I) of Cu = 3/2 and that of N = 1] ***[Dec 2012]***

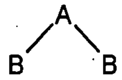
(a) 12 (b) 15 (c) 20 (d) 36

10) A triatomic molecule of the type AB_2 shows two IR absorption lines and one IR-Raman line. The structure of the molecule is ***[June 2013]***

(a) B—B—A (b) B—A—B (c)



(d)



11) Consider the reaction:- ***[June 2013]***

Non linear molcule + Non linear molcule $\rightleftharpoons$ Non linear activated complexes

The number of vibrational degrees of freedom in the activated complex, containing N atoms, is

(a) 3N–5 (b) 3N–6 (c) 3N–7 (d) 3N–8

12) The number of EPR signals observed for octahedral Ni(II) complexes is ***[June 2013]***

(a) One (b) Two (c) Three (d) Zero

13) The correct order of the isomeric shift in Mössbauer spectra (^{57}Fe source) of iron compounds is ***[Dec 2014]***

(a) Fe(II) > Fe(III) > Fe(IV) (b) Fe(III) > Fe(II) > Fe(IV)
(c) Fe(IV) > Fe(III) > Fe(II) (d) Fe(IV) > Fe(II) > Fe(III)

14) If the component of the orbital angular momentum along the molecular axis of a heteronuclear diatomic molecule is nonzero, the rotational-vibrational spectrum will show ***[Dec 2014]***

(a) P and R branches only (b) P and Q branches only
(c) Q and R branches only (d) All the P, Q and R branches

15) Bond lengths of homonuclear diatomic molecules can be determined with the help of both ***[Dec 2014]***

(a) Rotational and vibrational spectroscopy (b) Rotational and rotational Raman spectroscopy
(c) Rotational Raman and electronic spectroscopy (d) Vibrational and electronic spectroscopy

Questions with four marks

16) In IR spectrum of $[Co(CN)_5H]^{3-}$ the Co–H stretch is observed at 1840 cm^{-1}. The (Co– D) stretch in $[Co(CN)_5D]^{3-}$ will appear at nearly ***[June 2011]***

(a) 1300 cm^{-1} (b) 1400 cm^{-1} (c) 1500 cm^{-1} (d) 1600 cm^{-1}

17) The rotational constant of $^{14}N_2$ is 2 cm^{-1}. The wave number of incident radiation in a Raman spectrometer is 20487cm^{-1}. What is the wave number of first scattered Stokes line (in cm^{-1}) of $^{14}N_2$? ***[June 2011]***

(a) 20479 (b) 20475 (c) 20499 (d) 20495

18) Consider the compounds, (A) SnF_4, (B) $SnCl_4$ and (C) R_3SnCl. The nuclear quadrupole splitting are observed for ***[June 2011]***

(a) (A), (B) and (C) (b) (A) and (B) only (c) (B) and (C) only (d) (A) and (C) only

19) In the EPR spectrum of tetragonal Cu(II) complex when $g_{||} > g_{\perp} > g_e$ unpaired electron resides in the orbital ***[June 2011]***

(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) d_{xz}

20) The vibrational energy levels, $v'' = 0$ and $v' = 1$ of a diatomic molecule are separated by 2143 cm^{-1}. Its anharmonicity constant ($\omega_e x_e$) is 14 cm^{-1}.The values of ω_e (in cm^{-1}) and first overtone (cm^{-1}) of this molecule are respectively. ***[Dec 2011]***

(a) 2143 and 4286 (b) 2157 and 4286 (c) 2157 and 4314 (d) 2171 and 4258

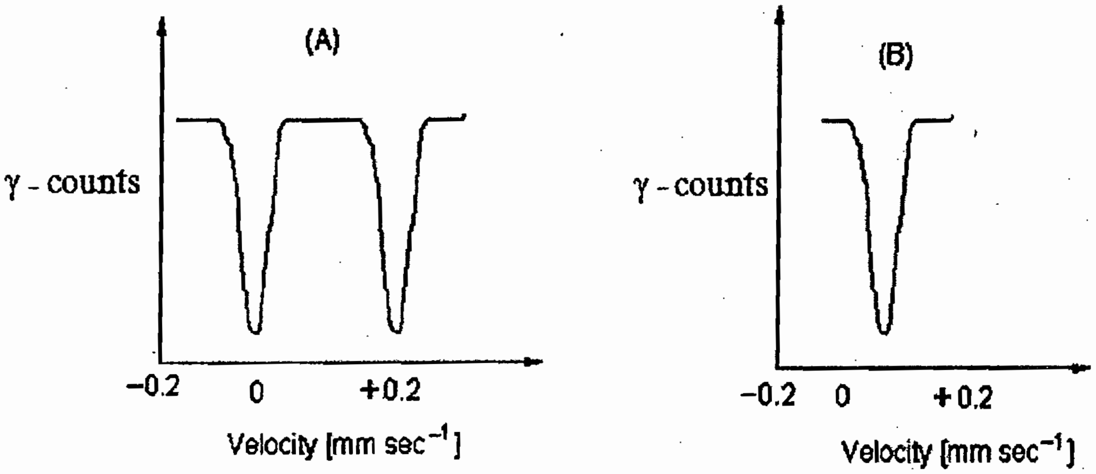
21) In $^{57}Fe^*$ Mössbauer experiment, a source at 14.4 KeV (equivalent to 3.48×10^{12} MHz) is moved towards absorber at a velocity 2.2 mm s^{-1} for resonance. The shift in the frequency of the source for this sample is ***[Dec 2011]***

(a) 35.5 MHz (b) 25.5 MHz (c) 20.2 MHz (d) 15.5 MHz

22) The total numbers of fine and hyperfine EPR lines expected for octahedral high-spin Mn(II) complexes are respectively (I = 5/2 for Mn) ***[June2012]***

(a) 3 and 30 (b) 5 and 33 (c) 5 and 30 (d) 4 and 24

23) The Mössbauer spectra of two iron complexes are shown below. They may arise from (i) high-spin iron(III), (ii) high-spin iron(II) and (iii) low-spin iron(III)



The correct matches of spectra (A) and (B) with the iron complexes are ***[June 2012]***

(a) A with (i) and B with (ii) (b) A with (ii) and B with (i)
(c) A with (iii) and B with (ii) (d) A with (ii) and B with (iii)

24) The following data were obtained from the vibrational fine structure in the vibronic spectrum of a diatomic molecule. Given:- $\omega_e = 512\ \text{cm}^{-1}$ and $\omega_e X_e = 8\ \text{cm}^{-1}$ where ω_e is the energy associated with the natural frequency of vibration and X_e is the anharmonicity constant. The dissociation energy (D_e) of the molecule is ***[June 2012]***

(a) 4096 cm^{-1} (b) 6144 cm^{-1} (c) 8192 cm^{-1} (d) 16384 cm^{-1}

25) The vibrational frequency and anharmonicity constant of an alkali halide are 300 cm^{-1} and 0.0025 respectively. The positions (in cm^{-1}) of its fundamental mode and first overtone are respectively. ***[Dec 2012]***

(a) 300, 600 (b) 298.5, 595.5 (c) 301.5, 604.5 (d) 290, 580

26) Among the following, those can act as Mössbauer nuclei are ***[June 2013]***

(A) ^{129}I, (B) ^{57}Co (C) ^{57}Fe (D) ^{121}Sb

(a) A, B, C and D (b) B, C and D only (c) A, B, and D only (d) A, C and D only

27) In Mössbauer experiment, a source emitting at 14.4 KeV (3.48 X 10^{18} Hz) had to be moved towards absorber at 2.2 mm s^{-1} for resonance. The shift in the frequency between the source and the absorber is ***[Dec 2013]***

(a) 15.0 MHz (b) 20.0 MHz (c) 25.5 MHz (d) 30.0 MHz

28) The number of lines in the ESR spectrum of CD_3 is (the spin of D is 1) ***[June 2014]***

(a) 1 (b) 3 (c) 4 (d) 7

29) The C=O bond length is 120 pm in CO_2. The moment of inertia of CO_2 would be close to (masses of C and O are 1.9×10^{-27} kg and 2.5×10^{-27} kg, respectively) ***[June 2014]***

(a) 1.8×10^{-45} kg m^2 (b) 3.6×10^{-45} kg m^2 (c) 5.4×10^{-45} kg m^2 (d) 7.2×10^{-45} kg m^2.

30) EPR spectrum of free radical containing nuclei with non zero nuclear spin is obtained if the following selection rules are observed ***[Dec 2014]***

(a) $\Delta m_S = 0 \quad \Delta m_I = 0$ (b) $\Delta m_S = \pm 1 \quad \Delta m_I = 0$ (c) $\Delta m_S = \pm 1 \quad \Delta m_I = \pm 1$ (d) $\Delta m_S = 0 \quad \Delta m_I = \pm 1$

31) if the bond length of heteronuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption lines of P-Branch ***[Dec 2014]***

(a) Increases non linearly (b) Decreases non linearly (c) Increases linearly (d) Decreases linearly

(Questions from GATE EXAM)

Questions with ONE OR TWO marks

32) Out of the following the one which is not an excitation source for IR spectrometer is ***(GATE 2005)***

(a) tungsten filament lamp (b) nerst glower (c) deuterium lamp (d) mercury arc

33) Resonant frequencies for EPR and NMR are respectively in the spectral region ***(GATE 2005)***

(a) microwave and far-IR (b) far-IR and microwave
(c) radiofrequency and microwave (d) microwave and radiofrequency

34) Match the following items of column I with the appropriate items in column II ***(GATE 2005)***

Column I **Spectral technique**	**column II** **Selection Rule**
P) rotational transition	I $\Delta v = \pm 1$
Q) vibrational transition	II $\Delta J = 0$
R) electronic transition-in atoms	III $\Delta J = \pm 1$
S) nmr spectroscopy	IV $\Delta I = \pm 1$
	V $\Delta m_L = \pm 1$
	VI $\Delta v = 0$
	VII $\Delta I = 0$

(a) P-I, Q-VI, R-VII, S-V (b) P-II, Q-I, R-IV, S-V (c) P-III, Q-I, R-IV, S-V (d) P-I, Q-VI, R-VII, S-V

35) The zero-point energy of the vibration of $^{35}Cl_2$ mimicking a harmonic oscillator with a force constant k=2293.8 Nm^{-1} is ***(GATE 2006)***

(a) 10.5×10^{-21} J (b) 14.8×10^{-21} J (c) 20.9×10^{-21} J (d) 29.6×10^{-21} J

36) The molecule active in rotational microwave, infrared absorption as well as rotational Raman spectra is ***(GATE 2006)***

(a) CO_2 (b) SF_6 (c) HCl (d) H_2

37) A radical contains ^{14}N (I=1) with hyperfine constant 1.61 mT and two equivalent protons (I=1/2) with hyperfine constant 0.35 mT. The ESR spectrum will exhibit ***(GATE 2006)***

(a) 3 lines (b) 6 lines (c) 7 lines (d) 9 lines

38) The selection rules for the appearance of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor- harmonic oscillator model are ***(GATE 2007)***

(a) $\Delta v = \pm 1$ and $\Delta J = \pm 1$ (b) $\Delta v = +1$ and $\Delta J = +1$ (c) $\Delta v = +1$ and $\Delta J = -1$ (d) $\Delta v = -1$ and $\Delta J = -1$

39) The J = 0 to J = 1 rotational transition for $^{1}H^{79}Br$ occurs at 500.72 GHz. Assuming the molecule to be a rigid rotor, the J = 3 to J = 4 transition occurs at *(GATE 2007)*

(a) 50.1 cm^{-1} (b) 66.8 cm^{-1} (c) 16.7 cm^{-1} (d) 83.5 cm^{-1}

40) If ClF_3, were to be stereochemically rigid, its ^{19}F NMR spectrum (I for ^{19}F = 1/2,) would be (assume that Cl is not NMR active) *(GATE 2008)*

(a) a doublet and a triplet (b) a singlet (c) a doublet and a singlet (d) two singlets

Statement for Linked Answer Questions 41 and 42:

An iron complex $[FeL_6]^{+2}$ (L = neutral monodentate ligand) catalyses the oxidation of $(CH_3)_2S$ by per benzoic acid. *(GATE 2008)*

41) The formation of the organic product in the above reaction can be monitored by

(a) gas chromatography (b) cyclic voltammetry
(c) electron spin resonance (d) fluorescence spectroscopy

42) The oxidation state of the metal ion in the catalyst can be detected by

(a) atomic absorption spectroscopy (b) Mössbauer spectroscopy
(c) HPLC (d) gas chromatography

Common Data Questions

Common Data for Questions 43 and 44:

The infrared spectrum of a diatomic molecule exhibits transitions at 2144, 4262 and, 6354 cm^{-1} corresponding to excitations from the ground state to the first, second and, third vibration States respectively. *(GATE 2008)*

43) The fundamental transition (cm^{-1}) of the diatomic molecule is at *(GATE 2008)*

(a) 2157 (b) 2170 (c) 2183 (d) 2196

44) The anharmonicity constant (cm^{-1}) of the diatomic molecule is *(GATE 2008)*

(a) 0.018 (b) 0.012 (c) 0.006 (d) 0.003

45) Two samples have been given to you: $[NiCl_2(PPh_3)_2]$ and $[[PdCl_2(PPh_3)_2]$. A physical method that can be used to identify these compounds unambiguously is *[GATE 2009]*

(a)HPLC (b) magnetic susceptibility
(c) ^{13}C NMR spectroscopy (d) Mössbauer spectroscopy

46) The rotational Raman spectrum of $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.238 cm^{-1} and 19223.707 cm^{-1}.The rotational constant for ^{19}F, in GHz is *[GATE 2009]*

(a) 26.484 (b) 52.968 (c) 105.936 (d) 3.531

47) The most populated rotational state for HCl (B = 8.5 cm^{-1}) at 300 K is *[GATE 2010]*

(a) 2 (b) 3 (c) 5 (d) 7

Common Data Questions

Common Data for Questions 48 and 49:

A six coordinate transition metal complex is ESR and Mössbauer active. The effective magnetic moment of this complex is ≈ 5.9 B.M. *[GATE 2010]*

48) The metal ion along with its oxidation state and the number of unpaired electron present are

(a) Fe(II) and 4 (b) Mn(II) and 5 (c) Fe(III) and 1 (d) Fe(III) and 5

49) The complex is

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

50) The region of electromagnetic spectrum employed in the electron spin resonance (ESR) spectroscopy is *(GATE 2011)*

(a) radiowave (b) microwave (c) infrared (d) visible

51) The bond that gives the most intense band in the infrared spectrum for its stretching vibration is *[GATE 2012]*

(a) C–H (b) N–H (c) O–H (d) S–H

52) The extent of Mössbauer quadrupole splitting of iron follows the order *[GATE 2012]*

(a) $FeCl_2{\bullet}4H_2O > K_2[Fe(CN)_5(NO)] > FeCl_3{\bullet}6H_2O$ (b) $K_2[Fe(CN)_5(NO)] > FeCl_2{\bullet}4H_2O > FeCl_3{\bullet}6H_2O$

(c) $FeCl_3{\bullet}6H_2O > K_2[Fe(CN)_5(NO)] > FeCl_2{\bullet}4H_2O$ (d) $FeCl_2{\bullet}4H_2O > FeCl_3{\bullet}6H_2O > K_2[Fe(CN)_5(NO)]$

Statement for Linked Answer Questions 53 and 54 ***[GATE 2012]***

A 20491 cm^{-1} laser line was used to excite oxygen molecules (made of ^{16}O only) to obtain the rotational Raman spectrum. The resulting rotational Raman spectrum of oxygen molecule has the first Stokes line at 20479 cm^{-1}.

53) The rotational constant (usually denoted as B) for the oxygen molecule is

(a) 1.2 cm^{-1} (b) 2.0 cm^{-1} (c) 3.0 cm^{-1} (d) 6.0 cm^{-1}

54) The next rotational Stokes line is expected at

(a) 20467cm^{-1} (b) 20469 cm^{-1} (c) 20471 cm^{-1} (d) 20475 cm^{-1}

55) The infrared spectrum of HCl gas shows an absorption band centered at 2885 cm^{-1}. The zero point energy of HCl molecule under harmonic oscillator approximation is *[GATE 2013]*

(a) 2.8665×10^{-22} J (b) 2.8665×10^{-20} J (c) 5.7330×10^{-22} J (d) 5.7330×10^{-20} J

56) The number of IR active vibrational normal modes of CO_2 is *[GATE 2014]*

(a) Two (b) Three (c) Four (d) Five

57) In atomic absorption spectroscopy, the atomization process utilizes *[GATE 2014]*

(a) flame (b) electric field (c) magnetic field (d) electron beam

Answer Key

1	c	2	c	3	a	4	b	5	d	6	d	7	b	8	d	9	d	10	b
11	c	12	a	13	a	14	d	15	c	16	a	17	a	18	d	19	b	20	d
21	b	22	c	23	b	24	c	25	b	26	d	27	c	28	d	29	d	30	b
31	a	32	c	33	d	34	c	35	b	36	c	37	d	38	c	39	b	40	a
41	c	42	b	43	b	44	c	45	b	46	a	47	b	48	d	49	d	50	b
51	c	52	a	53	b	54	c	55	b	56	b	57	a						

Hint & solution

1) Ans (c):- A pure rotation spectrum can only arise when the molecule possesses a permanent dipole moment. Therefore among all only CO will exhibits rotational spectra

2) Ans (c):- A Rotational constant is inversely proportional to moments of inertia. Among Prolate symmetric top; Spherical top; Asymmetric top; Oblate symmetric top only Asymmetric top has all three principal moments of inertia are unequal so yields three rotational constant (B).

$$B = \frac{h}{8\pi^2 Ic}$$

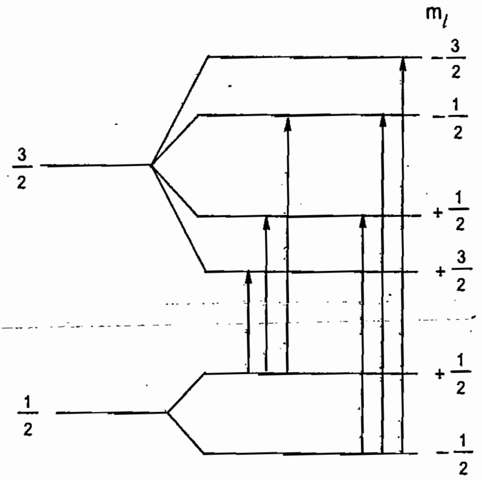
Type of molecule	Moments of inertia	Rotational constant
Linear molecules	$I_A < I_B = I_C$	two
spherical top	$I_A = I_B = I_C$	one
Oblate symmetric tops	$I_A = I_B < I_C$	two
Prolate symmetric tops	$I_A < I_B = I_C$	two
Asymmetric tops	$I_A \neq I_B \neq I_C$	three

3) Ans (a):- The Q band in the vibrational spectrum of acetylene is observed in the C–C stretching mode

4) Ans (b):- IR will be useful to distinguish between M-SCN and M-NCS binding modes. (Frequency will be different for M–N bond in M-NCS & M–S bond in M-SCN)

5) Ans (d):- Magnetic splitting (hyperfine splitting) is a result of the interaction between the nucleus and any surrounding magnetic field. Transitions between the excited state and ground state can only occur where m_l changes by 0 or 1. This gives six possible transitions for a 3/2 to 1/2 transition, giving a sextet

i.e. $+\frac{3}{2}$ to $-\frac{3}{2}$ & $+\frac{1}{2}$ to $-\frac{1}{2}$



6) Ans (d):- $\Delta\varepsilon_{J=1} - \Delta\varepsilon_{J=0} = 2B = 3.9\ \text{cm}^{-1}$ i.e. $B = 1.95\ \text{cm}^{-1}$

Now; $\Delta\varepsilon_{J=4} - \Delta\varepsilon_{J=3} = 8B = 8 \times 1.95 = 15.6\ \text{cm}^{-1}$

7) Ans (b):- $\Delta v = \pm 1$ only

8) Ans (d):- In the vibrational spectrum of CO_2, the number of fundamental vibrational modes common in both infrared and Raman are Zero. (According to Rule of mutual exclusion)

9) Ans (d):- The number of lines exhibited by a high resolution EPR spectrum is given by formula;

$[(2n_aI_a+1)\,(2n_bI_b+1)]$, where n is equivalent nuclei & I is a Nuclear spin.

For $[Cu(ethylenediamine)_2]^{2+}$; $I_N = 1$ & $I_{Cu} = 3/2$

$$[(2n_NI_N+1)\,(2n_{Cu}I_{Cu}+1)] = [(2\times4\times1+1)\,(2\times1\times\frac{3}{2}+1)] = 36$$

10) Ans (b):- The structure of the molecule is like CO_2 or CS_2 (B–A–B) (According to Rule of mutual exclusion)

11) Ans (c):- For non-linear system, you will have (3N–6) vibration degrees of freedom. (3 translation, 3 rotation). In case of nonlinear activated complex if we apply transition-state theory, one of the vibrational degrees of freedom will be taken off and that should be added to the translation. So therefore, for non-linear activated complex, you will have (3N–7) vibrational degrees of freedom. (4 translation, 3 rotation)

12) Ans (a):- The number of EPR signals observed for octahedral Ni(II) complexes is one because octahedral Ni(II) contain even number of unpaired electrons and even electron system seldom give ESR spectra.

13) Ans (a):-The correct order of the isomeric shift in Mössbauer spectra (^{57}Fe source) of iron compounds is Fe(II) > Fe(III) > Fe(IV) ; This can be explained on the basis of s-electron density.
The s-electron density at the nucleus is reduced in Fe(II) $3d^6$, compared with Fe(0) $4s^23d^6$, producing a large positive isomer shift. When a 3d electron is removed to produce Fe(III) from Fe(II), there is a small increase in s-electron density at the nucleus (as the 3d electrons partly screen the nucleus from the inner s electrons) and the isomer shift becomes less positive; similarly there is a large increase in s-electron density at the nucleus as we move from Fe(III) to Fe(IV) & therefore isomer shift of Fe(IV) becomes even less positive than Fe(III).

14) Ans (d):- All the P, Q and R branches.

15) Ans (c):- Bond lengths of homonuclear diatomic molecules can be determined with the help of both Rotational Raman and electronic spectroscopy

16) Ans (a):- The frequency of the vibration is inversely related to the mass of the atoms attached, so heavier atoms vibrate at lower frequencies. ($m_{Co} = 59$ $m_H = 1$ & $m_D = 2$)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} \propto \sqrt{\frac{1}{\mu}}$$

$$\frac{\bar{\nu}_{Co-D}}{\bar{\nu}_{Co-H}} = \sqrt{\frac{\mu_{Co-H}}{\mu_{Co-D}}}$$

$$\bar{\nu}_{Co-D} = \sqrt{\frac{m_{Co}m_H}{m_{Co}+m_H} \times \frac{m_{Co}+m_D}{m_{Co}m_D}} \times \bar{\nu}_{Co-H}$$

By solving; The (Co– D) stretch in $[Co(CN)_5D]^{3-}$ will appear at nearly 1300 cm^{-1}

17) Ans (a):- The gap between incident radiation & first scattered stokes line in a Raman spectrometer = 4*B*

$\therefore$ 20487 $cm^{-1} - x = 4B$ (B= 2 cm^{-1})

$\therefore x = 20479$ cm^{-1}

$\therefore$ Wave number of first scattered Stokes line = 20479 cm^{-1}

18) Ans (d):- The nuclear quadrupole splitting are observed for SnF_4, and R_3SnCl but not for $SnCl_4$ because in case of $SnCl_4$ spherical electrical field is expected at the nucleus so no quadrupole splitting, while the SnF_4

form polymeric structure that is non spherical electrical field & gives doublet. Similarly in R_3SnCl ligand field is non-equivalent so it also gives doublet.

19) Ans (b):- Hint:- Jahn Teller distortion; so either $d_{x^2-y^2}$ or d_{z^2} is possible. When $g_{||} > g_{\perp}$ the unpaired electron resides in the $d_{x^2-y^2}$ orbital & when $g_{||} < g_{\perp}$ the unpaired electron is in the d_{z^2} orbital

20) Ans (d):- $\Delta\epsilon_{0\to1} = \omega_e - 2\omega_e x_e = 2143\ cm^{-1}$ (But $\omega_e x_e = 14\ cm^{-1}$)

$\therefore \omega_e = 2143\ cm^{-1} + 2(14) = 2171\ cm^{-1}$

Now first overtone = $\Delta\epsilon_{0\to2} = 2\omega_e - 6\omega_e x_e = (2\times2171) - 6(14) = 4258\ cm^{-1}$

The values of ω_e is 2171 cm^{-1} and first overtone 4258 cm^{-1}.

21) Ans (b):- $\text{The shift in the frequency} = \dfrac{\text{velcity of source} \times \text{frequency}}{\text{speed of light}}$

$$= \frac{2.2\ mms^{-1} \times 3.48 \times 10^{12}\ MHz}{3 \times 10^{8}\ ms^{-1}}$$

$$= 25.5\ MHz$$

22) Ans (c):- In general, the EPR spectrum of Mn(II) i.e high spin d^5 system, the fine EPR lines are expected due to the interaction of the free electron spins within themselves, that is equal to number of unpaired electrons. While hyperfine arises from the interaction of the free electron with the nuclear spin of Mn(II) nucleus. When an external magnetic field is applied, these spin states split further resulting in five EPR transitions with selection rule Ms = ±1 & in addition each of these five lines split further into a sextet, due to the nuclear spin of Mn (I = 5/2). Hence a 30-lines

In short:-

The total numbers of fine EPR lines = Number of unpaired electrons i.e five in this case

The total numbers of hyperfine EPR lines = Number of unpaired electrons × $(2n_b I_b+1)]$,

(where n is equivalent nuclei & I is a Nuclear spin.)

$\therefore$ The total numbers of hyperfine EPR lines = 5 × [2(1)(5/2)+1)] = 30.

23) Ans (b):- A Mössbauer spectrum of iron complex shows either singlet or doublet.

Octahedral Iron complexes with symmetrical electrical filling in t_{2g} & e_g orbitals that is high spin d^5 & low spin d^6 system & with identical six ligands (spherical electrical field) shows singlet in Mössbauer spectra.

While all other iron complexes shows doublet in the Mössbauer spectra.

Comlex	Filling of electron	electronic field	Mössbauer spectra
high-spin iron(III),	$t_{2g}^3\ e_g^2$	Symmetrical	singlet
high-spin iron(II)	$t_{2g}^4\ e_g^2$	unsymmetrical	doublet
low-spin iron(III)	$t_{2g}^5\ e_g^0$	unsymmetrical	doublet

Thus high-spin iron(II) & low-spin iron(III) will give spectra (A) and high-spin iron(III) will give spectra (B)

24) Ans (c):- Given:- $\omega_e = 512\ cm^{-1}$ and $\omega_e x_e = 8\ cm^{-1}$

$$\therefore x_e = \frac{8}{512} = 0.0156$$

$$\text{Dissociation energy} = \frac{\omega_e}{4x_e} = \frac{512}{4\times0.0156} = 8192\ cm^{-1}$$

25) Ans (b):- Given:- $\omega_e = 300\,\text{cm}^{-1}$ & $x_e = 0.0025$

Fundamental mode = $\Delta\epsilon_{0\to1} = \omega_e - 2\omega_e x_e = 300 - 2\,(300\times0.0025)$

$$\Delta\epsilon_{0\to1} = 300 - 1.5 = 298.5$$

Now first overtone = $\Delta\epsilon_{0\to2} = 2\omega_e - 6\omega_e x_e = 2 \times 300 - 6\,(300\times0.0025) = 595.5$.

26) Ans (d):- The Mössbauer active nuclei are ^{129}I, ^{57}Fe & ^{121}Sb.

The Mössbauer active nuclei are-:

^{57}Fe	^{109}Ag	^{127}I	^{161}Dy	^{181}Ta
^{61}Ni	^{119}Sn	^{129}I	^{166}Er	^{183}W
^{67}Zn	^{121}Sb	^{151}Eu	^{169}Tm	^{193}Ir
^{99}Ru	^{125}Te	^{155}Gd	^{170}Yb	^{197}Au
^{237}Np	^{243}Am			

27) Ans (c):- Refer the solution of question no.21

28) Ans (d):- The number of lines exhibited by a high resolution EPR spectrum is given by formula; $[(2n_a I_a+1)]$ where n is equivalent nuclei & I is a Nuclear spin. (for D, I = 1)

$\therefore 2(3)(1) + 1 = 7$

29) Ans (d):- For a triatomic linear rotor like OCS; $I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$

but for a centrosymmetric triatomic linear rotor like CO_2 :- $m_A = m_C$ & $R = R'$

$\therefore$ Above equation becomes: - $I = 2m_A R^2 = 2 \times 2.5 \times 10^{-27} \times (120 \times 10^{-12}\text{m})^2 = 7.2 \times 10^{-45}\text{Kgm}^2$

30) Ans (b):- Selection rule is $\Delta m_S = \pm1$; $\Delta m_I = 0$ in a EPR spectrum of free radical containing nuclei with non zero nuclear spin. ($\Delta m_I = 0$ in a EPR spectrum because nuclear motion is much slower than electronic motion so that during the time electron changes its spin orientation, the nucleus being heavier has no time to reorient its spin so that $\Delta m_I = 0$ & $\Delta m_S = \pm1$)

31) Ans (a):- If the bond length of heteronuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption lines of P-Branch increases non-linearly & that of R-Branch decreases non-linearly

32) Ans (c):- Deuterium lamp is not an excitation source for IR spectrometer & is a general light source for UV range spectroscopic applications.

33) Ans (d):- The ESR spectroscopy falls in the microwave region & NMR fall in radiofrequency region

34) Ans (c):-

Spectral technique	Selection Rule
rotational transition	$\Delta J = \pm 1$
vibrational transition	$\Delta v = \pm 1$
electronic transition-in atoms	$\Delta l = \pm 1$
nmr spectroscopy	$\Delta m_L = \pm 1$

35) Ans (b):- The zero-point energy of the $^{35}Cl_2$ under harmonic oscillator = $\frac{1}{2}h\nu$

Given = k = 2293.8 Nm^{-1}

First we have to calculate ν; We know that

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\text{But } \mu = \frac{m_1 m_2}{m_1+m_2} = \frac{35.5amu \times 35.5amu}{35.5\,amu + 35.5\,amu} \times 1.66 \times 10^{-27}kg$$

$$\mu = 29.47 \times 10^{-27}kg$$

The zero-point energy of the $^{35}Cl_2$ under harmonic oscillator = $\frac{1}{2}h\nu = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$

$$= \frac{6.636\times10^{-34}}{4\times3.14}\sqrt{\frac{2293.8}{29.47\times 10^{-27}}} = 14.8 \times 10^{-21}\,J$$

36) Ans (c):- The molecule active in rotational microwave, infrared absorption as well as rotational Raman spectra is HCl (that is the molecule with a permanent dipole moment.)

37) Ans (d):- The number of lines exhibited by a high resolution EPR spectrum is given by formula;

$[(2n_aI_a+1)\,(2n_bI_b+1)]$, where n is equivalent nuclei & I is a Nuclear spin.

For NH_2 radical $I_N = 1$ & $I_H = 1/2$

$[(2n_NI_N+1)\,(2n_HI_H+1)] = [(2\times1\times1+1)\,(2\times2\times\frac{1}{2}+1)] = 3\times3 = 9$ lines

38) Ans (c):- The selection rules for the appearance of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor- harmonic oscillator model are $\Delta\nu = +1$ and $\Delta J = -1$

39) Ans (b):- We know that for rotational transition J = 0 to J = 1; $\Delta\epsilon_{0\rightarrow1} = 2B = 500.72$ GHz.

∴ B= 250.36 GHz.

Now rotational transition J = 3 to J = 4; $\Delta\epsilon_{3\rightarrow4} = 8B = 8 \times 250.36 = 2002.88$ GHz.

But 1cm^{-1} = 30GHz

∴ the J = 3 to J = 4 transition = $\frac{2002.88}{30}$ = 66.76 cm^{-1}

40) Ans (a):- The ^{19}F NMR spectrum of ClF_3 (T-shaped) shows a doublet and a triplet. Two axial F nuclei is split into a doublet by the single equatorial ^{19}F nucleus, and single equatorial is split into a triplet by the two axial ^{19}F nuclei

41) Ans (c):- The formation of the organic product can be monitored by electron spin resonance that is presence of unpaired electrons in an iron complex

42) Ans (b):- The oxidation state of the metal ion in the catalyst can be detected by Mössbauer spectroscopy that is electrical field of iron in an iron complex

43) Ans (b):- Given:- ν_1= 2144 cm^{-1} ν_2= 4262 cm^{-1} & ν_3 = 6354 cm^{-1}

$\nu_1 = \Delta\epsilon_{0\rightarrow1} = \omega_e(1-2X_e) = 2144$ cm^{-1} & $\nu_2 = \Delta\epsilon_{1\rightarrow2} = 2\omega_e(1-3X_e) = 4262$ cm^{-1}

$$\frac{\nu_1}{\nu_2} = \frac{\omega_e(1-2X_e)}{2\omega_e(1-3X_e)} = \frac{(1-2X_e)}{2(1-3X_e)} = \frac{2144}{4262} = 0.5030$$

$$\frac{(1-2X_e)}{2(1-3X_e)} = 0.5030$$

By solving Xe = 0.0058;

Now $\nu_1 = \Delta\epsilon_{0\rightarrow1} = \omega_e(1-2X_e) = 2144\ cm^{-1}$

Put Xe = 0.0058 in above equation;

$\omega_e[1-2(0.0058)] = 2144\ cm^{-1}$

$$\omega_e = \frac{2144}{0.9884} = 2169.16\ cm^{-1}$$

44) Ans (c):- The anharmonicity constant (cm^{-1}) of the diatomic molecule is 0.0058 ~ 0.006

45) Ans (b):- According to crystal field theory [$NiCl_2(PPh_3)_2$] is a tetrahedral complex (paramagnetic) and [$PdCl_2(PPh_3)_2$] is a square planar complex (diamagnetic) therefore magnetic susceptibility can be used to identify these compounds

46) Ans (a):- the gap between first Stokes line & next rotational Stokes line = 4*B*

$\therefore$ 19230.769 cm^{-1} − 19227.238 cm^{-1} = 4B

$\therefore$ 3.531 = 4B

$\therefore$ B = 0.88275 cm^{-1} (But 1cm^{-1} = 30GHz)

$\therefore$ B = 0.88275 cm^{-1} × 30 = 26.4825 GHz

47) Ans (b):- The most populated rotational state for HCl can be calculated by

$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Where;

Boltzmann constant	*k* =	$1.381\times10^{-23}\ J\ K^{-1}s$
Planck constant	*h*=	$6.626\times10^{-34}\ J\ s$
Speed of light	*c* =	$3\times10^{10}\ cm\ s^{-1}$
Temperature	T =	300 K
Rotational constant	B =	$8.5\ cm^{-1}$

By solving we get; the most populated rotational state for HCl = 3

48) Ans (d):- The effective magnetic moment of this complex is ≈ 5.9 B.M. it means transition metal complex is with five unpaired electron; that is d^5 system with high spin complex i.e. Mn(II) and 5 or Fe(III) and 5 in $[Mn(H_2O)_6]^{2+}$ & $[Fe(H_2O)_6]^{3+}$ respectively. But as Mn is Mössbauer inactive; the complex is $[Fe(H_2O)_6]^{3+}$

49) Ans (d):- the complex is $[Fe(H_2O)_6]^{3+}$

50) Ans (b):- The ESR spectroscopy falls in the microwave region.

51) Ans (c):- Intensities of IR absorption is directly proportional to relative bond polarities & hence more intense band in the IR absorption is of O−H

52) Ans (a):- The order of extent of Mössbauer quadrupole splitting of iron is:-

$FeCl_2{\bullet}4H_2O > K_2[Fe(CN)_5(NO)] > FeCl_3{\bullet}6H_2O$

Complex	$FeCl_2 \cdot 4H_2O$	$K_2[Fe(CN)_5(NO)]$	$FeCl_3 \cdot 6H_2O$
Oxidation state of Fe	Fe^{II}	Fe^{II}	Fe^{III}
Configuration	High spin; $t_{2g}^4\ e_g^2$	Low spin; $t_{2g}^6\ e_g^0$	High spin; $t_{2g}^3\ e_g^2$
Electrical field	Unsymmetrical	Symmetrical	Symmetrical
Ligand field	equivalent	non-equivalent	equivalent
Quadrupole splitting	$3.00 mms^{-1}$	$1.85\ mms^{-1}$	$0.2\ mms^{-1}$

Hint:- In $FeCl_2 \cdot 4H_2O$ high value of quadrupole splitting is due to unsymmetrical electrical field while high value of quadrupole splitting in $K_2[Fe(CN)_5(NO)]$ due to non-equivalent ligand field & π–backbonding with NO ligand

53) Ans (b):- A gap between ν_0 and 1st lines of each branch is of 6*B*

$\therefore$ $20491\ cm^{-1} - 20479\ cm^{-1} = 6B$

$\therefore$ $B = 2.0\ cm^{-1}$

54) Ans (c):- the gap between first Stokes line & next rotational Stokes line = 4*B*

$\therefore$ next rotational Stokes line = 1st lines – 4B ..... (But B= 2)

$\therefore$ next rotational Stokes line = $20479\ cm^{-1} - 4(2) = 20471\ cm^{-1}$

55) Ans (b):- zero point energy of HCl molecule under harmonic oscillator = $\frac{1}{2}h\nu$

Given = $\bar{\nu} = 2885\ cm^{-1}$

We know that $\nu = c\bar{\nu}$

$\therefore$ zero point energy of HCl molecule under harmonic oscillator = $\frac{1}{2}hc\bar{\nu}$

$$= \frac{1}{2}6.626 \times 10^{-34} \text{J.s} \times 3 \times 10^{10} \text{cms}^{-1} \times 2885 \text{cm}^{-1}$$

$$= 28674.015 \times 10^{-24}\ \text{J}$$

$$= 2.8674 \times 10^{-20}\ \text{J}$$

56) Ans (b):- For a linear (except diatomic) system, you will have 3 translation, 2 rotation & (3N–5) vibration degrees of freedom. $\therefore$ Vibration degrees of freedom of CO_2 is (3N–5) = [(3×3)–5] = 4

But out of four; one is symmetric stretching mode which is IR inactive vibrational modes while two are bending modes & one is asymmetric stretching mode which is IR active vibrational modes

Thus the number of IR active vibrational normal modes of CO_2 is 3

57) Ans (a):- In atomic absorption spectroscopy, the atomization process utilizes flame.

List of Reference Books

1) Fundamentals of Molecular & Spectroscopy, By C. N. Banwell and E. M. Mccash, Tata McGraw-Hill Education

2) Physical Methods in Chemistry, R. S. Drago, Saunders College Publishing (1977)

3) Physical Chemistry by Peter Atkins and Julio De Paula Oxford University Press

4) Principles of Physical Chemistry by Puri, Sharma and Pathania Vishal Publishing Co.

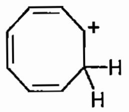
❖❖❖

Topic 14

AROMATICITY

Questions with two marks

1) Among the carbocations given below ***[June 2011]***

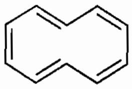

A

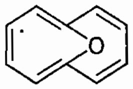

B

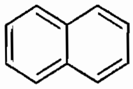

C

(a) A is homoaromatic, B is antiaromatic and C is aromatic.
(b) A is aromatic, B is antiaromatic and C is homoaromatic.
(c) A is antiaromatic, B is aromatic and C is homoaromatic.
(d) A is homoaromatic, B is aromatic and C is antiaromatic.

2) Among A-C, the aromatic compounds are ***[Dec 2011]***


A


B


C

(a) A, B and C (b) A and B only (c) B and C only (d) A and C only

3) With respect to electrophilic aromatic substitution, reactivity order of pyrrole, pyridine and indole is ***[Dec 2011]***

(a) indole > pyrrole > pyridine (b) pyrrole > pyridine > indole
(c) pyrrole > indole > pyridine (d) indole > pyridine > pyrrole

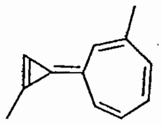
4) Consider the following statements for [18]-annulene ***[Dec 2012]***

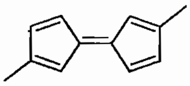
(A) It is aromatic
(B) The inner protons resonate at δ 9.28 in its ^{1}H NMR spectrum
(C) There are six protons in the shielded zone.

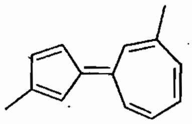
The correct statements are

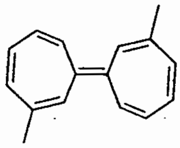
(a) A, B, C (b) A and B only (c) B and C only (d) A and C only

5) Among the following, the compound which has the lowest energy barrier for the cis-trans isomerisation is ***[Dec 2013]***

(a)


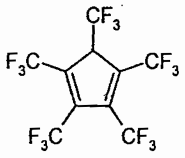
(b)


(c)


(d)


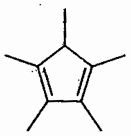
Questions with four marks

6) The correct order of acidity of the following compound A–C is *[June 2011]*



A

B

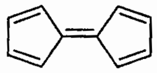


C

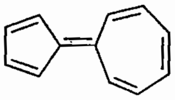
(a) B > C > A (b) C > B > A (c) A > C > B (d) A > B > C

7) Among the following compounds, the one which has highest dipole moment is *[June 2013]*

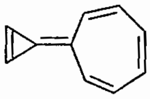
(a)



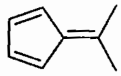
(b)



(c)

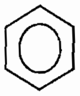


(d)

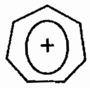


8) The correct match of the ^{1}H NMR chemical shifts δ of the following species/compound is *[June 2014]*

I



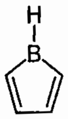
II



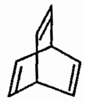
III

(a) I : 5.4; II : 7.2: III : 9.2
(b) I : 9.2; II : 7.2: III : 5.4
(c) I : 9.2; II : 5.4: III : 7.2
(d) I : 7.2; II : 9.2: III : 5.4

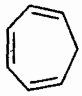
9) The compound that is antiaromatic is *[Dec 2014]*



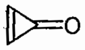
I



II



III



IV

(a) I (b) II (c) III (d) IV

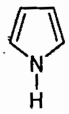
(Questions from GATE EXAM)

Questions with ONE OR TWO marks

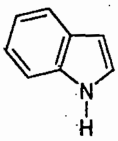
10) ^{1}H NMR spectrum of [18]–annulene shows *(GATE 2005)*

(a) only one peak at δ 7.2 (18H)
(b) only one peak at δ 5.0 (18H)
(c) two peaks at δ 9.0 (12H) and δ −3.0 (6H)
(d) two peaks at δ 9.0 (6H) and δ −3.0 (12H)

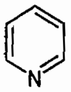
11) The correct order of the basicity of the following compounds is *(GATE 2006)*



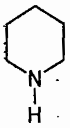
I



II



III



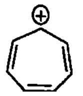
IV

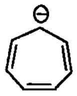
(a) IV > III > II > I (b) III > IV > II > I (c) IV > III > I > II (d) III > IV > I > II

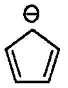
12) The correct statement about C_{60} is ***(GATE 2008)***

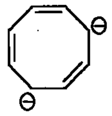
(a) C_{60} is soluble in benzene
(b) C_{60} does not react with *tert-butyllithium*
(c) C_{60} is made up of 10 five-membered and 15 six-membered rings
(d) Two adjacent five-membered rings share a common edge

13) The compound that is NOT aromatic is ***(GATE 2008)***

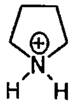
(a)


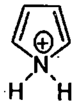
(b)


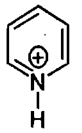
(c)


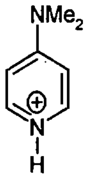
(d)


14) The most acidic species is ***(GATE 2008)***

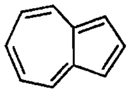
(a)


(b)


(c)


(d)


15) The compound is A is **[*GATE 2009*]**



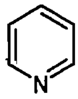
A

(a) aromatic and has high dipole moment
(b) aromatic and has no dipole moment
(c) non-aromatic and has high dipole moment
(d) anti-aromatic and has no dipole moment

16) The decreasing order of the reactivity of the following compounds towards electrophiles is **[*GATE 2010*]**

I

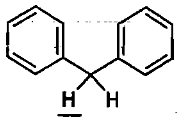
II



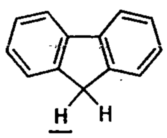
III

(a) II >I > III
(b) II >III > I
(c) III >I > II
(d) I >II > III

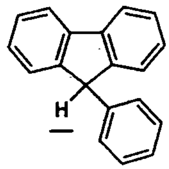
17) The decreasing order of the acidity of the marked $\underline{H}$ of the following molecules is **[*GATE 2010*]**



I



II



III

(a) I >II > III
(b) III >I > II
(c) III > II > I
(d) II > I > III

Answer Key

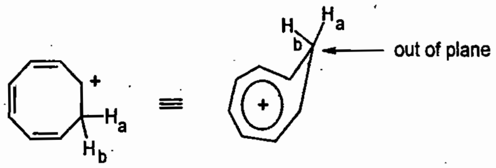
Topic: 14:-Aromaticity

1	a	2	c	3	c	4	d	5	c	6	c	7	b	8	a	9	a	10	c
11	a	12	a	13	b	14	b	15	a	16	d	17	c						

Hint & solution

1) Ans (a):- A is homoaromatic, B is antiaromatic and C is aromatic.

A) Homoaromatic compounds are stabilized cyclic conjugated system containing one or more sp^3 carbon atoms.



Homoaromatic

B) Antiaromatic compounds are cyclic, conjugated , planner & must contain $(4n)$ π electrons.

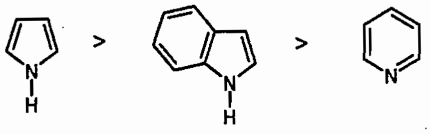
C) Aromatic compounds are cyclic, conjugated , planner & must contain $(4n + 2)$ π electrons.

2) Ans (c):- A is Non-aromatic, B & C are aromatic.

[10]-Annulene would be aromatic as it has $(4n + 2)$ π e^- but it is a nonaromatic compound because it is nonplannar.

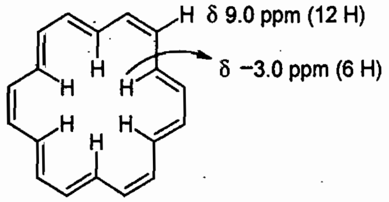
Note:-[10]-Annulene that has only *cis* double bonds cannot have the planar conformation because of angle strain. [10]-Annulene that has two *trans* double bonds cannot adopt a planar conformation because two internal hydrogen atoms interfere with each other & disturb the planarity

3) Ans (c):- Reactivity order of pyrrole, pyridine and indole to electrophilic aromatic substitution is pyrrole > indole > pyridine. Among pyrrole and indole, indole is less reactive than pyrrole because of withdrawing effect of –Ph ring in case of indole. Pyridine is very much less reactive due to electron-withdrawing nitrogen atom. Pyridine, therefore, is less reactive than benzene. Indeed, it is even less reactive than nitrobenzene.

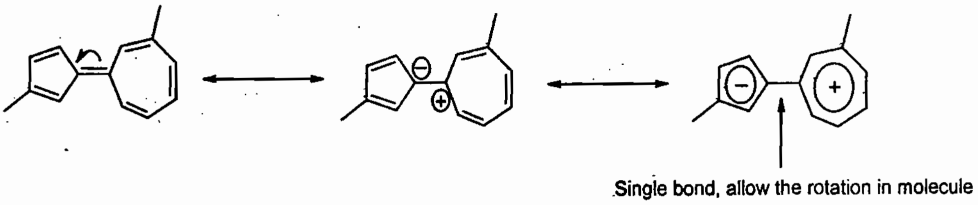


4) Ans (d):- The correct statements are A and C only.

Because the inner protons of [18]-annulene resonate at $\delta = -3.00$ in its ^1H NMR spectrum

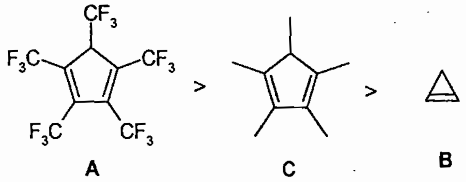


5) Ans (c):- Among A to D compound, only in C, the resonance stabilization energies arises the aromatization of both ring (as shown below) & delocalization result in formation of single bond which allow the rotation *i.e.* cis-trans isomerisation



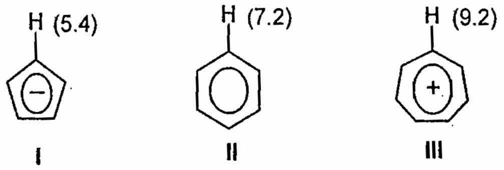
while in A,B & D the resonance stabilation energies (delocalization) arises the anti aromatization of the one of the ring so there is a no delocalization.

6) Ans (c):- Since the resulting carbanion formation on loss of a proton, is greatly stabilized due to aromatization in A & C while in case of B loss of a proton & the resulting carbanion formation is destabilized due to antiaromatization so it is not acidic at all. Now among A & C; A is more acidic due presence of electron withdrawing -CF_3 group which stabilizes the carbanion while in B due presence of electron donating -CH_3 group which destabilizes the carbanion. Therefore correct order of acidity is:-

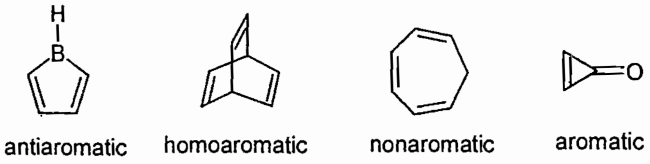


7) Ans (b):- Amongst A to D compound, only in B the resonance stabilization energies arises the aromatization of both ring & result in dipolar structure which possesses a significant dipole moment. While in A,C & in D the resonance stabilation energies arises the anti-aromatization of the one of the ring so no delocalization.

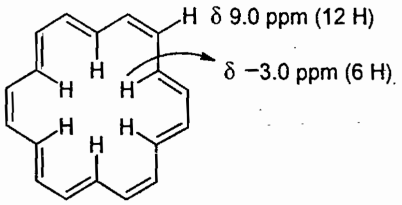
8) Ans (a):- The chemical shifts of protons on negatively charged (electron rich) carbon resonate at upfield (shielded) while that of protons on positively charged (electron deficient) carbon resonate at downfield (deshielded)



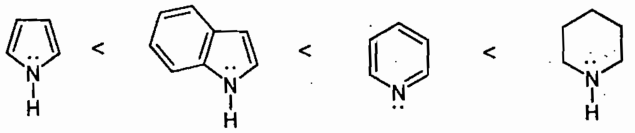
9) Ans (a):- The compound I is antiaromatic is as it obey Huckel's rule for Antiaromaticity. (In this case borane is sp^2 hybridized) Antiaromatic compounds are cyclic, conjugated, planner & must contain (4n) π electrons.



10) Ans (c):- ^1H NMR spectrum of [18]-annulene shows two peaks; the external protons are far downfield at δ 9.0 (12H) and the internal protons are at very up field δ −3.0 (6H)



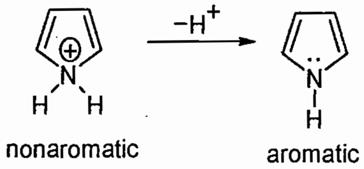
11) Ans (a):- Localized lone pair on saturated nitrogen atom is more basic than unsaturated so IV is more basic than III. I & II are very weakly basic since lone pair on N-atom is involved in aromatization. Pyrrole is an extremely weak base because when it is protonated, its aromaticity is destroyed while in indole aromaticity of benzene remain intact after protonation. So the correct order is IV > III > II > I.



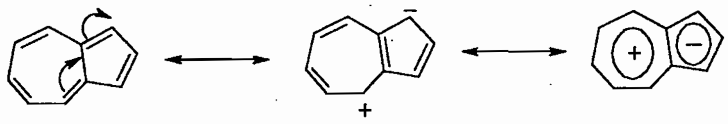
12) Ans (a):- Being organic in nature C_{60} is soluble in non polar solvent such as benzene & react with *tert-butyllithium.* C_{60} is made up of 12 five-membered and 20 six-membered rings & adjacent five-& six membered ring share a common edge

13) Ans (b):- (b) is not aromatic as it doesn't obey Huckel rule of aromaticity that is $(4n+2)\pi$ electrons

14) Ans (b):- The most acidic species is (b) as deprotonation result in aromatization



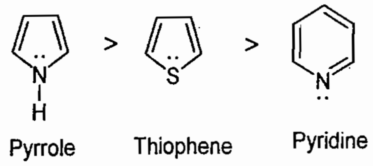
15) Ans (a):- Aromatic and has high dipole moment (0.8 D).



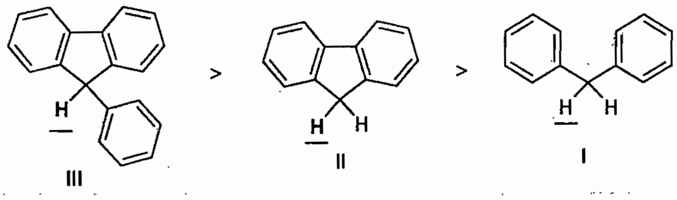
16) Ans (d):- Pyrrole (I) is more reactive than thiophene (II) due to better overlapping of 2p(C) & 2p(N) in case of pyrrole than weaker overlapping of 2p(C) & 3p(S) in case of thiophene, Pyridine (III) is very much less reactive than both I & II due to electron-withdrawing nitrogen atom.

Pyridine, therefore, is less reactive than benzene. Indeed, it is even less reactive than nitrobenzene.

so reactivity order is I >II > III



17) Ans (c):- since on loss of a proton, the resulting carbanion is greatly stabilized due to aromatization in case of II & III only so marked **H** of II & III are more acidic than I. Now among II & III, resultant carbanion formed by deprotonation in case of III is more resonance stabilized than II so decreasing order of the acidity of the marked H is III > II > I.



List of Reference Books

1) Advanced Organic Chemistry: Part A- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication.

2) March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure by Jerry March John Wiley & Sons

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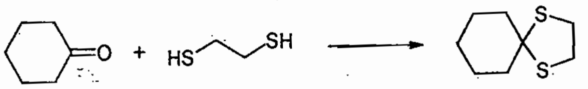
Topic 15

ORGANIC REACTION MECHANISM

(ORM, REAGENTS, REARRANGEMENTS & NAME REACTIONS)

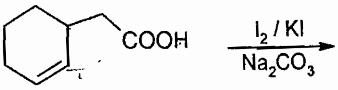
Questions with two marks

1) A suitable catalyst for bringing out the transformation given below is ***[June 2011]***

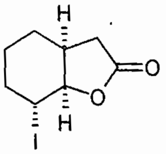


(a) $BF_3.Et_2O$ (b) NaOEt (c) Tungsten lamp (d) Dibenzoyl peroxide

2) The major product formed in the reaction given below is ***[June 2011]***



(a)



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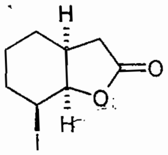

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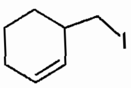

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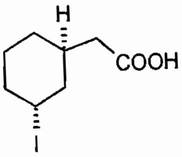
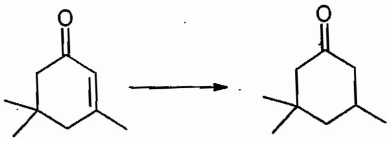
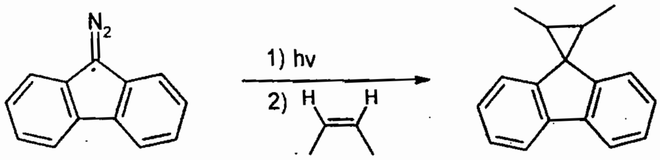


3) The most suitable reagent for the following transformation is ***[June 2011]***



(a) $LiAlH_4$ (b) NH_2NH_2/KOH (c) $NaBH_4/CeCl_3$ (d) Li/liq.NH_3

4) The intermediate involved in the reaction given below is ***[June 2011]***



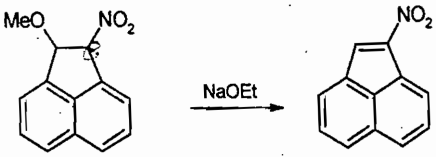
(a) Free radical (b) Carbocation (c) Carbanion (d) Carbene

5) Addition of BH_3 to a carbon-carbon double bond is ***[June 2011]***

(a) anti-Markovnikov syn addition (b) anti-Markovnikov anti addition

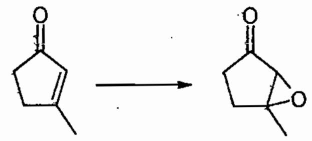
(c) Markovnikov syn addition (d) Markovnikov anti addition.

6) The reaction given below is an example of ***[June 2011]***



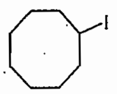
(a) E_2-elimination (b) E_1-elimination (c) syn-elimination (d) E_1cb-elimination

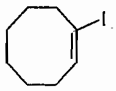
7) The suitable reagent for the following conversion is ***[June 2011]***

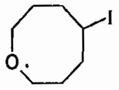


(a) m–CPBA (b) H_2O_2/AcOH (c) ^tBuOOH/HCl (d) H_2O_2/NaOH

8) The relative rates of solvolysis of iodides A-C are ***[June 2011]***


A


B

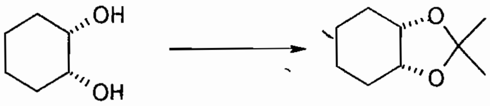

C

(a) C > A > B (b) C > B > A (c) B > C > A (d) B > A > C

9) Among the following compounds, the formyl anion equivalent is ***[Dec 2011]***

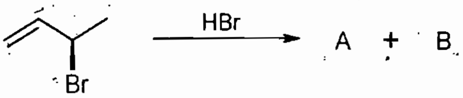
(a) acetylene (b) nitromethane (c) ethyl chloroformate (d) 1, 4-dithiane

10) A suitable reagent combination for carrying out the following conversion is ***[Dec 2011]***



(a) trimethyl orthoacetate and p- toluenesulfonic acid (b) trimethyl ortho acetate and sodium hydroxide
(c) 2-methoxypropene and p-toluenesulfonic acid (d) 2- methoxypropene and sodium hydroxide

11) In the following Markovnikov's addition reaction, the products A and B are ***[Dec 2011]***

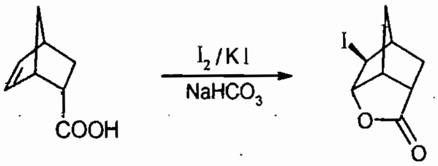


(a) homomers (b) enantiomers (c) diastereomers (d) regioisomers

12) The most appropriate reagent suitable for the conversion of 2-octyne into trans-2-octene is ***[Dec 2011]***

(a) zinc and acetic acid (b) 10% Pd/C
(c) lithium in liquid ammonia (d) hydrazine hydrate

13) The reaction given below proceeds through ***[Dec 2011]***



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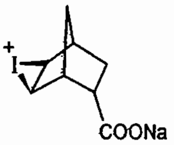

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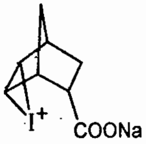

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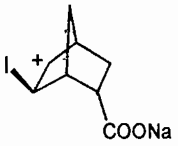

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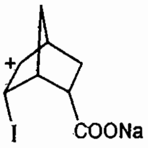
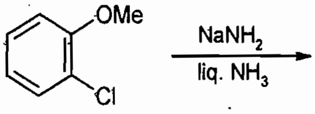


14) The major product formed in the following reaction is ***[Dec 2011]***



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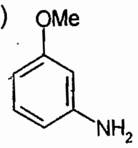

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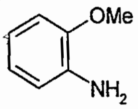

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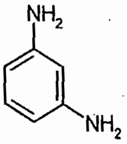

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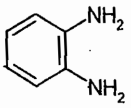
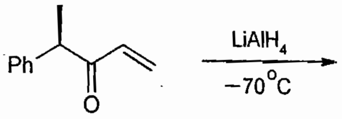


15) The major product formed in the following reaction is ***[Dec 2011]***



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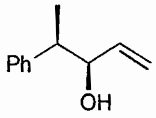

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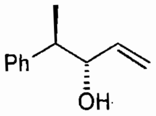

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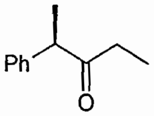

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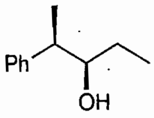


16) The reaction that involves the formation of both C-C and C-O bonds is ***[Dec 2011]***

(a) Diels-Alder reaction
(b) Darzen's glycidic ester condensation
(c) aldol reaction
(d) Beckmann rearrangement

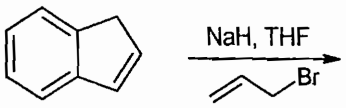
17) The nucleophilic attack on olefins under mild conditions ***[June 2012]***

(a) is always facile
(b) is more facile than electrophilic attack on olefins
(c) is facile for electron-rich olefins
(d) requires activation by coordination to metal.

18) Among the following, the synthetic equivalent for acyl anion is ***[June 2012]***

(a) Nitroethane and base
(b) α – chloroacrylonitrile
(c) Ethylmagnesium bromide
(d) Acetyl chloride and triethylamine

19) The major product formed in the following reaction is ***[June 2012]***



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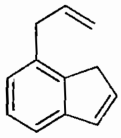

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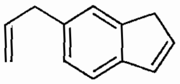

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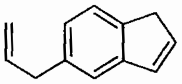

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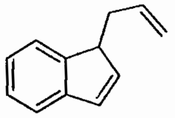
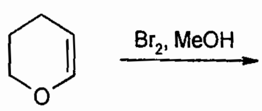
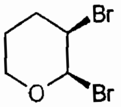


20) The major product formed in the following reaction is ***[June 2012]***



a)


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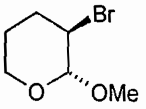

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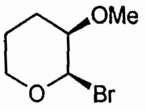

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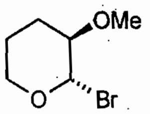
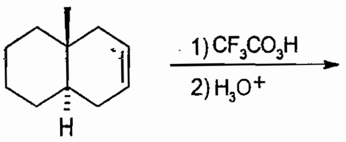


21) The major product formed in the following reaction is *[June 2012]*



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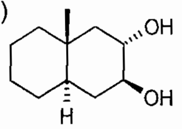

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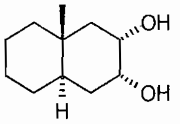

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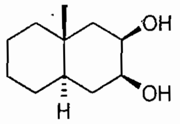

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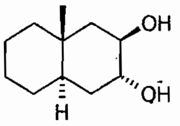
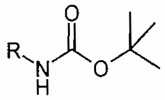


22) Among the following, the compound that undergoes deprotection easily on treatment with hydrogen in the presence of 10% Pd/C to generate RNH_2 is *[June 2012]*

(a)


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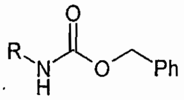

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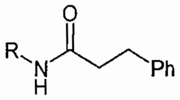

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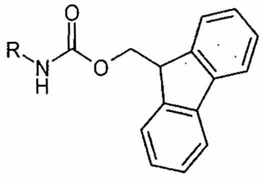
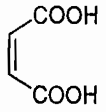


23) Among the following diacids, the one that forms an anhydride fastest on heating with acetic anhydride is *[June 2012]*

(a)


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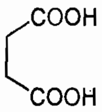

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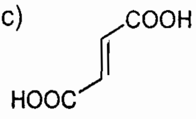
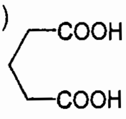
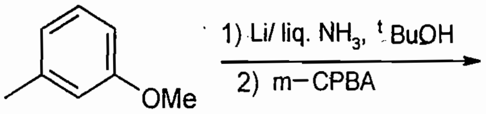
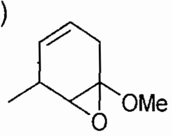


(d)


24) The major product formed in the following reaction sequence is *[June 2012]*



(a)


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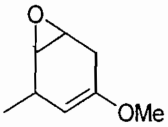
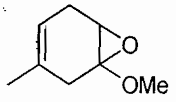
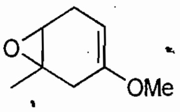
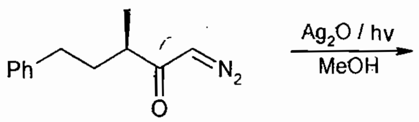
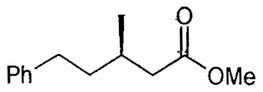


(c)


(d)


25) The major product formed in the following reaction is *[Dec 2012]*



(a)


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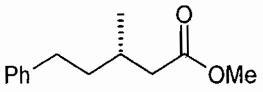

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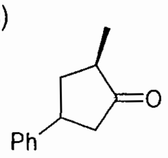

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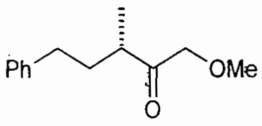
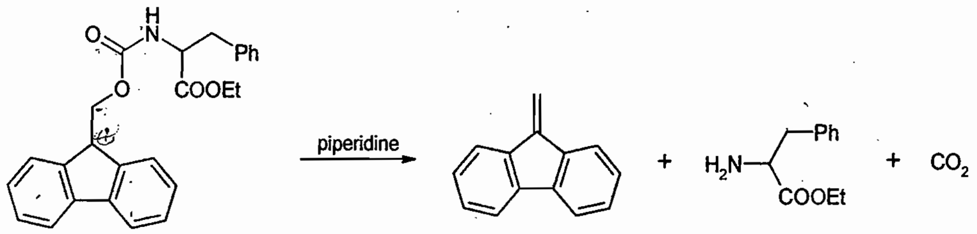


26) If the pKa value for p-methoxybenzoic acid is 4.46 and that of benzoic acid is 4.19, the σ_{para} for methoxy group is ***[Dec 2012]***

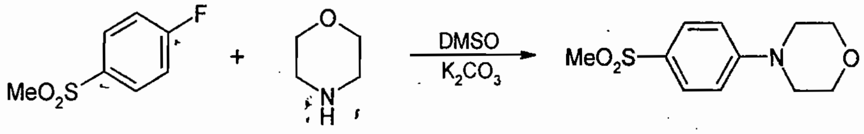
(a) 8.65 (b) 4.32 (c) 0.27 (d) – 0.27

27) The mechanism involved in the following conversion is ***[Dec 2012]***



(a) E2-elimination (b) E1-elimination (c) syn-elimination (d) E1 cb-elimination.

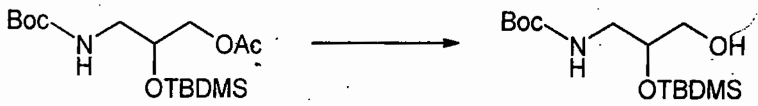
28) The correct statement(s)-A-D are given for the following reaction. The correct one(s) is (are) ***[Dec 2012]***



(A) aromatic ipso substitution reaction (B) aromatic nucleophilic substitution
(C) aromatic electrophilic substitution (D) aromatic free radical substitution.

(a) A and C only (b) A and B only (c) C and D only (d) C only

29) The most appropriate reagent to effect the following chemoselective conversion is ***[Dec 2012]***

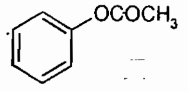


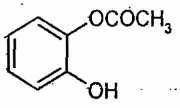
(a) HCl, EtOH, reflux (b) Bu_4NF (c) K_2CO_3, MeOH (d) CF_3COOH, EtOH, rt.

30) Among the following, an example of a "Green Synthesis" is ***[Dec 2012]***

(a) Synthesis of malachite green
(b) Friedel-Craft's acylation of anisole with Ac_2O/anhydrous $AlCl_3$.
(c) Jones' oxidation of benzyl alcohol to benzoic acid.
✓(d) Diels-Alder reaction of furan and maleic acid in water.

31) Among the following esters, the one that undergoes acid hydrolysis fastest is ***[June 2013]***

(a)


(b)


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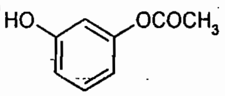
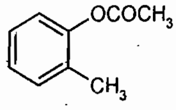
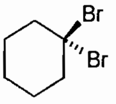


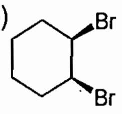
(d)


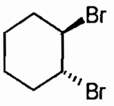
32) Rection of cyclohexyl benzyl ether with hydrogen in the presence of 10% Pd/C yields ***[June 2013]***

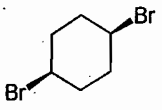
(a) cyclohexanol and toluene (b) cyclohexanol and benzyl alcohol
(c) cyclohexane and benzyl alcohol (d) cyclohexane and toluene

33) Among the following dibromocyclohexanes, the one that reacts fastest with sodium iodide to give cyclohexene is ***[June 2013]***

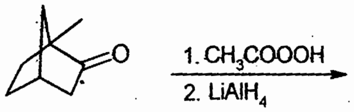
(a)


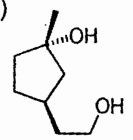
(b)


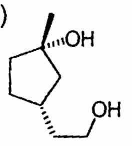
(c)


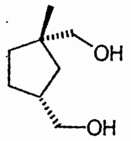
(d)


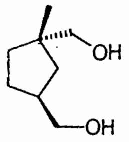
34) The major product formed in the following reaction sequence is ***[June 2013]***



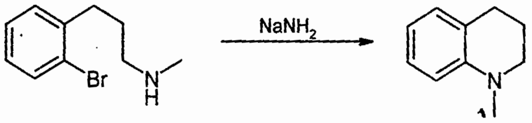
(a)


(b)


(c)


(d)


35) The reactive intermediate involved in the following reaction is ***[June 2013]***

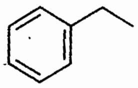


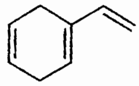
(a) a carbocation (b) a carbanion (c) a free radical (d) an aryne

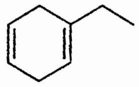
36) In the mechanism of reaction, $H_2 + Br_2 \longrightarrow 2HBr$ the first step is ***[Dec 2013]***

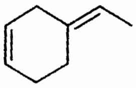
(a) dissociation of H_2 into $H^\bullet$ radicals (b) dissociation of Br_2 into $Br^\bullet$ radicals
(c) reaction of $H^\bullet$ radical with Br_2 (d) reaction of $Br^\bullet$ radical with H_2

37) The major product formed in the reaction of styrene with an excess of lithium in liquid ammonia and t-butyl alcohol is ***[Dec 2013]***

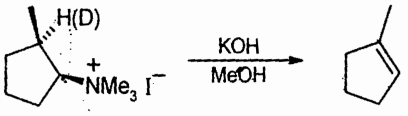
(a)


(b)


(c)


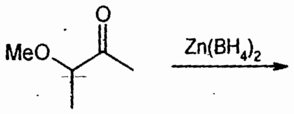
(d)


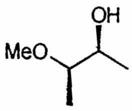
38) Deuterium kinetic isotope effect for the following reaction was found to be 4.0. Based on this information, mechanism of the reaction is ***[Dec 2013]***

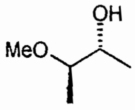


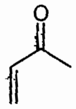
(a) E$_1$ (b) E$_2$ (c) E$_{1CB}$ (d) free radical

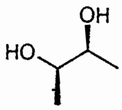
)The major product formed in the following reaction is ***[Dec 2013]***



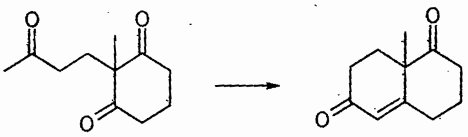
(a)


(b)


(c)


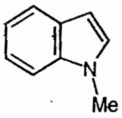
(d)


A suitable organocatalyst for enantioselective synthesis of Wieland-Miescher ketone (A) is ***[Dec 2013]***

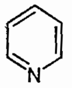


(–)-proline (b) (+)-menthone (c) guanidine (d) (+)–BINOL

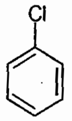
41) The correct order for the rates of electrophilic aromatic substitution of the following compound is ***[June 2014]***



I



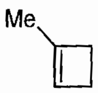
II

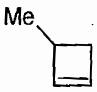


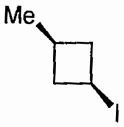
III

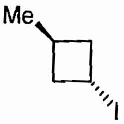
(a) I > II > III (b) II > I > III (c) III > II > I (d) I > III > II

42) The major product formed in the reactions of trans-1-bromo-3-methylcyclobutane with sodium iodide in DMF is ***[June 2014]***

(a)


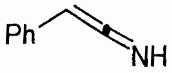
(b)


(c)


(d)


43) Consider the statements about the following structures X and Y. ***[June 2014]***

X



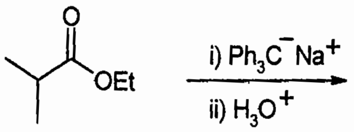
Y

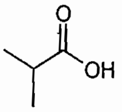
(A) X and Y are resonance structure
(B) X and Y are tautomers
(C) Y is more basic than X
(D) X is more basic than Y

The correct statement(s) among the above is (are)

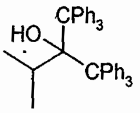
(a) A and C (b) C (c) B and D (d) B and C

44) The major products formed in the following reaction are ***[June 2014]***

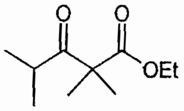


(a)


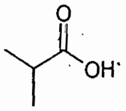
\+ $Ph_3C-CH_2CH_3$

(b)


\+ EtOH

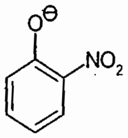
(c)


\+ EtOH

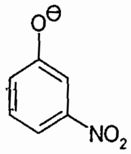
(d)


\+ $H_2C{=}CH_2$

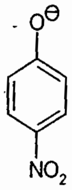
45) The correct order of basicity for the following anion is ***[June 2014]***



I



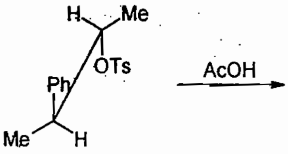
II

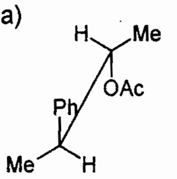


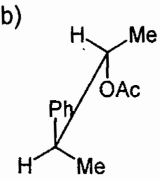
III

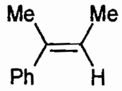
(a) II > III > I (b) I > II > III (c) II > I > III (d) III > II > I

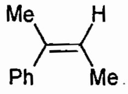
46) The major product formed in the following reaction is *[June 2014]*



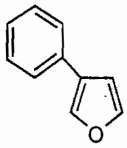
(a)


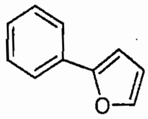
(b)


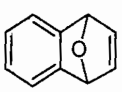
(c)


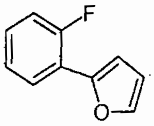
(d)


47) The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives *[Dec 2014]*

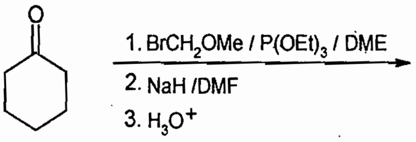
(a)


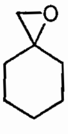
(b)


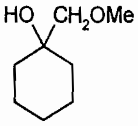
(c)


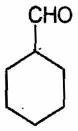
(d)


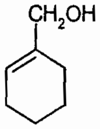
48) The product for the following sequence of the reaction is *[Dec 2014]*



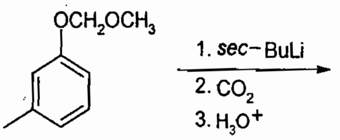
(a)


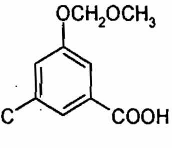
(b)


(c)


(d)


49) The major product formed in the following reaction is *[Dec 2014]*



(a)


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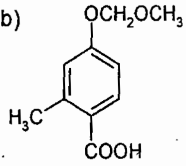

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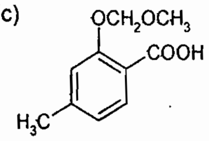
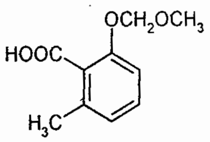
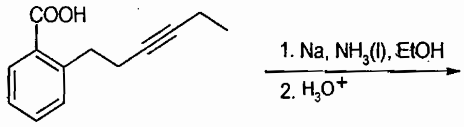
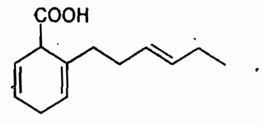
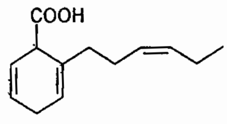


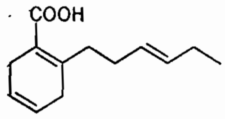
(d)


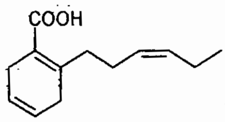
50) The major product of the following reaction is *[Dec 2014]*



(a)


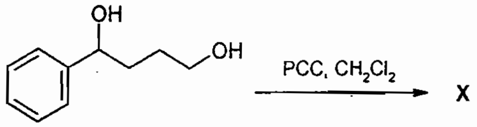
(b)


(c)


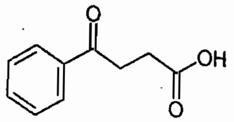
(d)


Questions with four marks

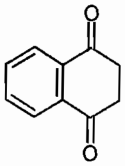
1) The major compound X formed in the following reaction exhibited a strong absorption at ν– max 1765 cm^{-1} in the IR spectrum. The structure of X is ***[June 2011]***



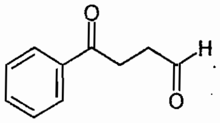
(a)



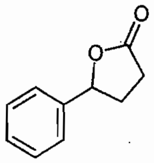
(b)



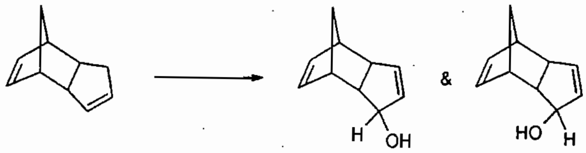
(c)



(d)

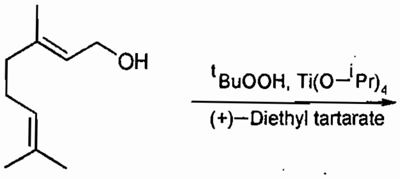


2) In allylic oxidation reaction, the appropriate statement, among the choices given below is ***[June 2011]***

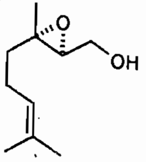


(a) Suitable reagent is $KMnO_4$ and the major product is A. (b) Suitable reagent is $KMnO_4$ and the major product is B.
(c) Suitable reagent is SeO_2 and the major product is A. (d) Suitable reagent is SeO_2 and the major product is B.

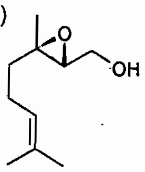
3) The major product formed in the following reaction is ***[June 2011]***



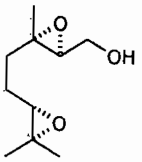
(a)



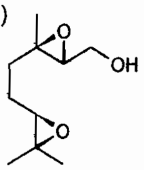
(b)



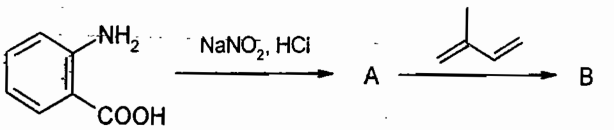
(c)



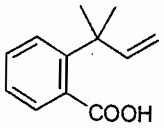
(d)



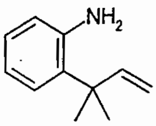
4) The intermediate A and the major product B in the following conversion are ***[June 2011]***



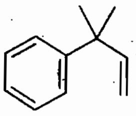
(a) A is carbocaion & B is



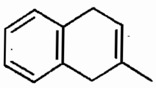
(b) A is carbanion & B is



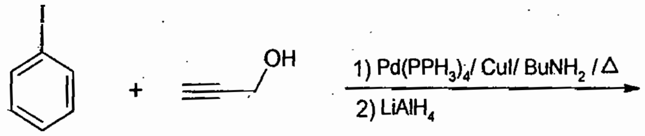
(c) A is free radical & B is

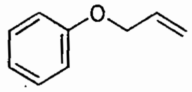


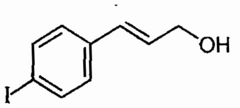
(d) A is benzyne & B is

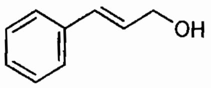


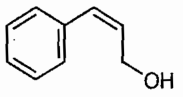
5) The major product formed in the following reaction is ***[June 2011]***



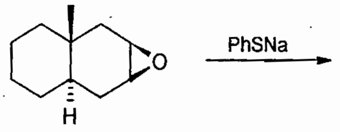
(a)


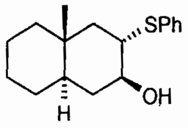
(b)


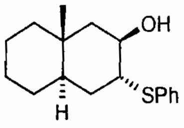
(c)


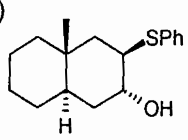
(d)


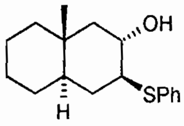
6) The major product formed in the following reaction is ***[June 2011]***



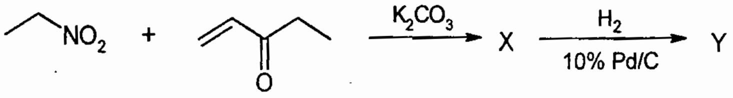
(a)


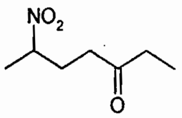
(b)


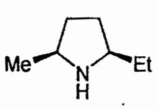
(c)


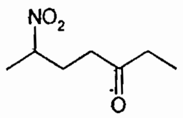
(d)


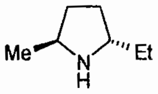
7) In the following reaction sequence, the correct structures for the major products X and Y are ***[June 2011]***

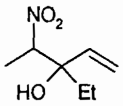


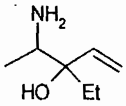
(a) X =


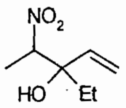
Y =


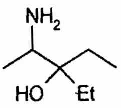
(b) X =


Y =


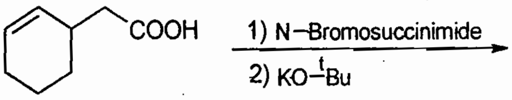
(c) X =


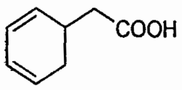
Y =


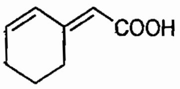
(d) X =


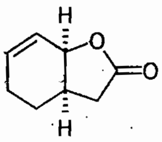
Y =


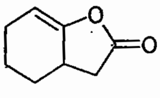
8) The major product formed in the following transformation is ***[June 2011]***



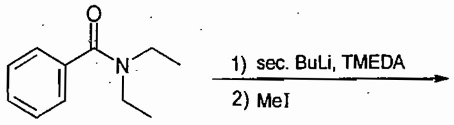
(a)


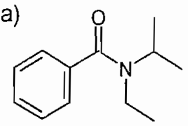
(b)


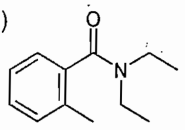
(c)


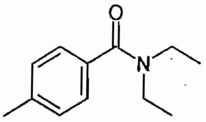
(d)


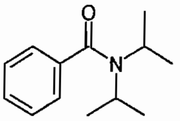
9) The major product formed in the following reaction is ***[June 2011]***



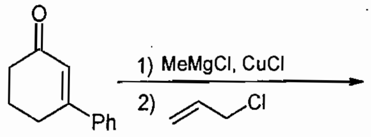
(a)


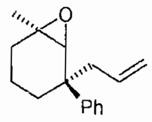
(b)


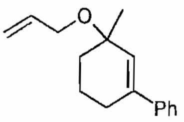
(c)


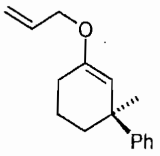
(d)


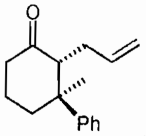
10) The major product formed in the following transformation is ***[June 2011]***



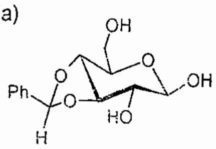
(a)


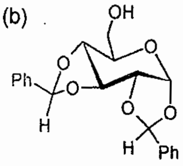
(b)


(c)


(d)


11) The major product formed in the reaction of glucose with benzaldehyde and p-TSA is ***[June 2011]***

(a)


(b)


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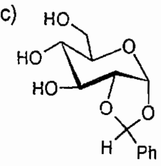

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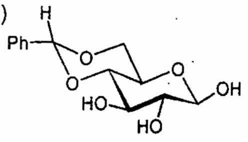
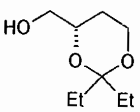


12) The major product formed in the reaction of (S)-1,2,4-butanetriol with 3-pentanone in the presence of a catalytic amount of p-TSA is ***[June 2011]***

(a)


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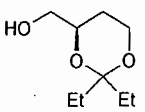

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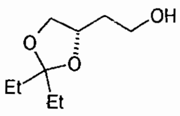

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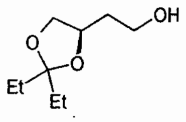
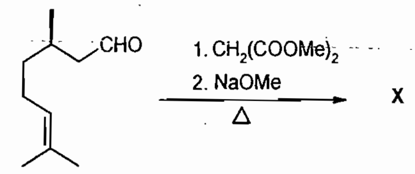
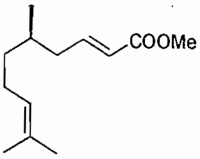


13) The major product formed in the reaction sequence is ***[June 2011]***



(citronellal)

(a)


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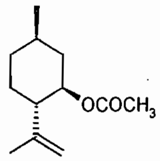

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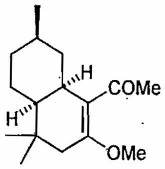

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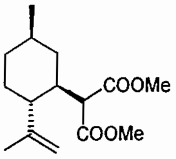
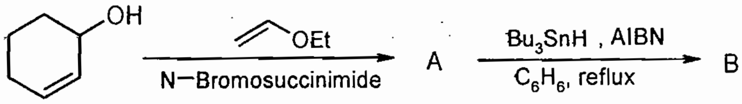
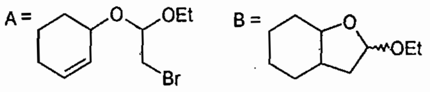


14) The major products A and B in the following reaction sequence are ***[Dec 2011]***



(a)


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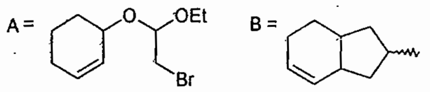
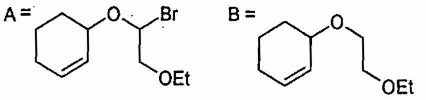


(c)


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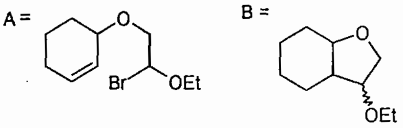
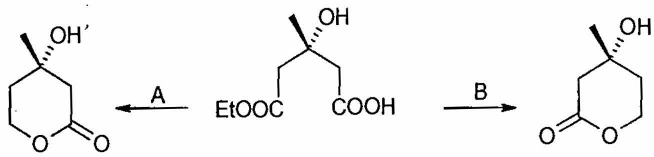


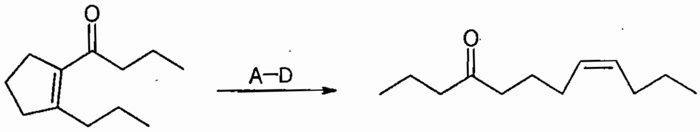
15) Identify appropriate reagents A and B in the following reactions. ***[Dec 2011]***



(a) A = $LiAlH_4$, B = $BH_3.Me_2S$ (b) A = $BH_3.Me_2S$, B = $LiAlH_4$

(c) A = $LiBH_4$, B = $BH_3.Me_2S$ (d) A = $BH_3.Me_2S$, B = $LiBH_4$

16) The correct sequence of the reagents to be employed in the following transformation is: ***[Dec 2011]***



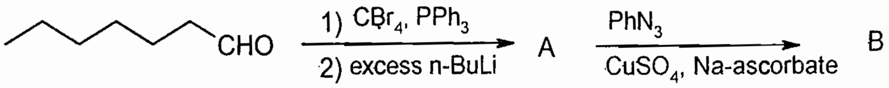
(a) (A) m–CPBA; (B) $TsNHNH_2$; (C) AcOH; (D) H_2 , Pd / $BaSO_4$

(b) (A) H_2O_2, NaOH; (B) NH_2NH_2 ; (C) AcOH; (D) H_2 , Pd / C

(c) (A) m–CPBA; (B) $TsNHNH_2$; (C) NaOH; (D) H_2 , Pd / C

(d) (A) H_2O_2, NaOH; (B) $TsNHNH_2$; (C) AcOH; (D) H_2 , Lindlar's catalyst

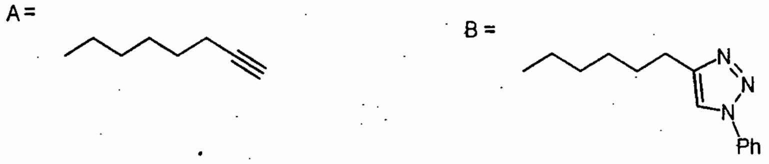
17) The major products A and B in the following reaction sequence are ***[Dec 2011]***



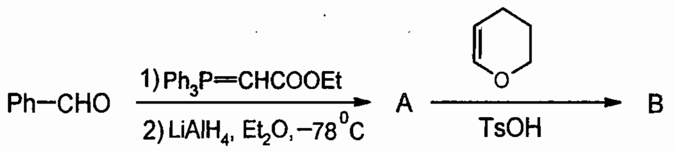
(a)


(b)


(c)


(d)


18) The major products A and B in the following reaction sequence are ***[Dec 2011]***



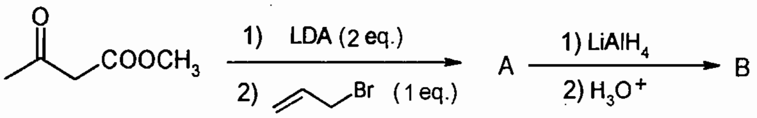
(a)

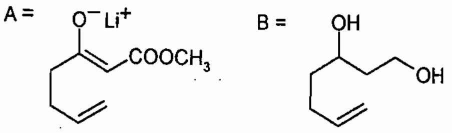

(b)


(c)


(d)


19) The major products A and B in the following reaction sequence are ***[Dec 2011]***



(a)


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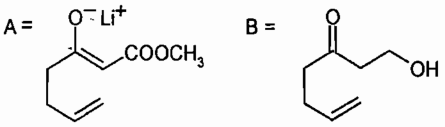

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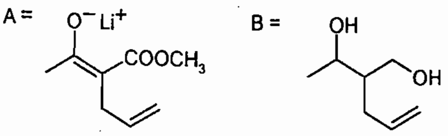

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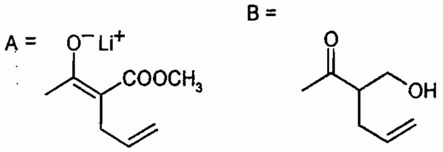
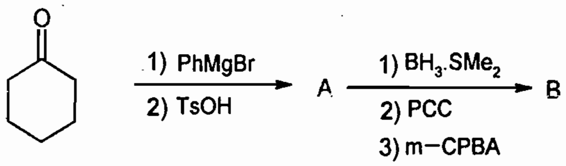
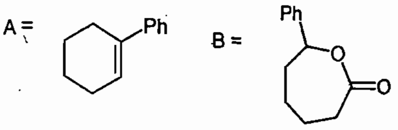


20) The major products A and B of the following reaction sequence are ***[Dec 2011]***



(a)


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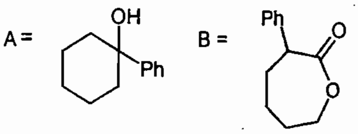

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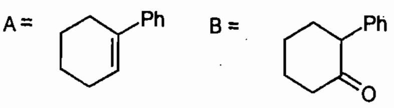

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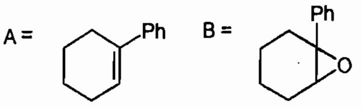
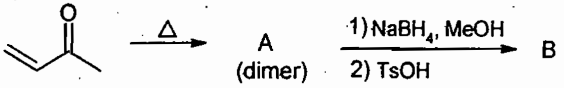
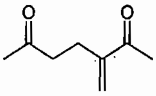
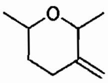
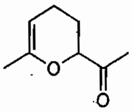
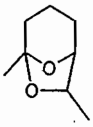
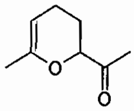
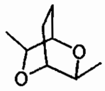


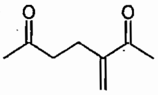
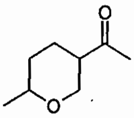
21) The major products A and B in the following reaction sequence are ***[Dec 2011]***



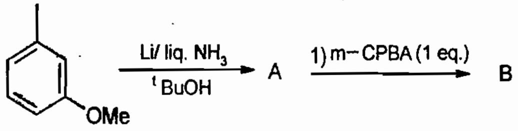
(a) A =  B = 

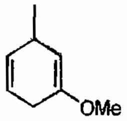
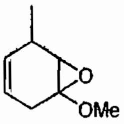
(b) A =  B = 

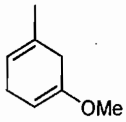
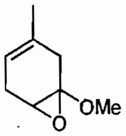
(c) A =  B = 

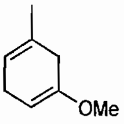
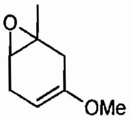
(d) A =  B = 

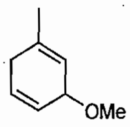
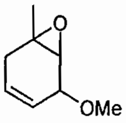
22) The major products A and B in the following reaction sequence are ***[Dec 2011]***



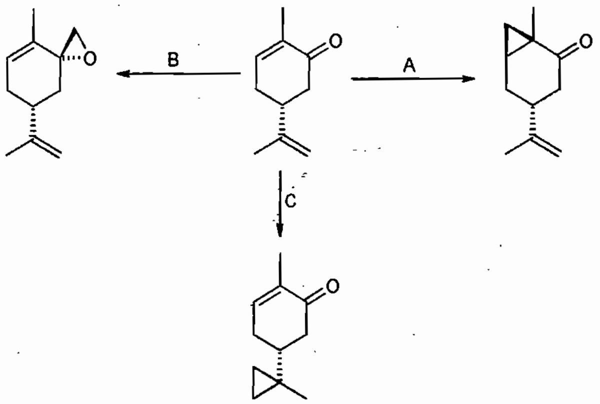
(a) A =  B = 

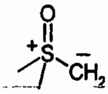
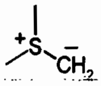
(b) A =  B = 

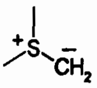
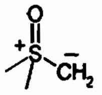
(c) A =  B = 

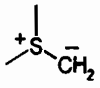
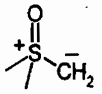
(d) A =  B = 

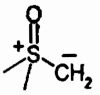
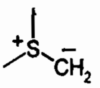
23) The correct reagents for effecting the following reactions are ***[Dec 2011]***



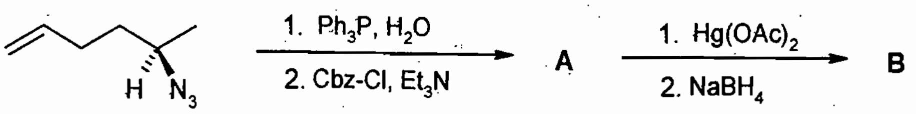
(a) A =  B =  C = CH$_2$I$_2$, Zn−Cu

(b) A =  B =  C = CH$_2$I$_2$, Zn−Cu

(c) A CH$_2$I$_2$, Zn−Cu B  C = 

(d) A =  B =  C = Tebbe's Reagent

24) **The major product A and B of the following reaction sequence are** ***[Dec 2011]***



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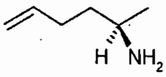

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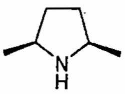

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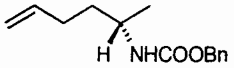

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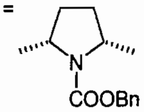

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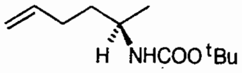

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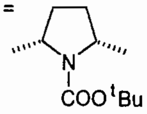

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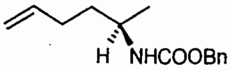

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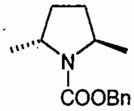
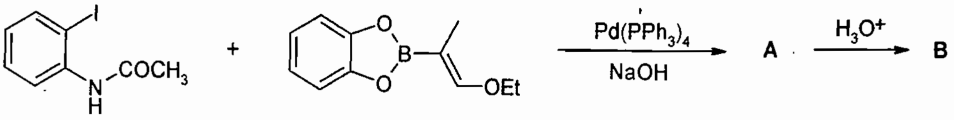
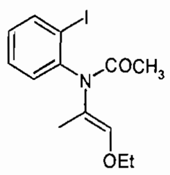


25) **The major products A and B in the following synthetic sequence are** ***[Dec 2011]***



(a) A =


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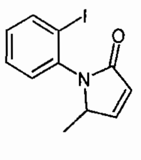
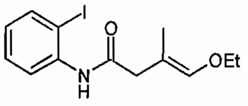


(b) A =


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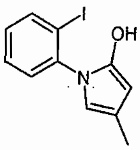
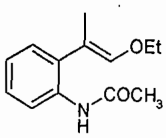


(c) A =


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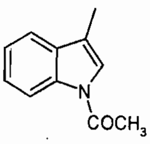
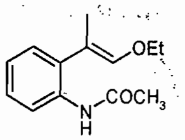


(d) A =


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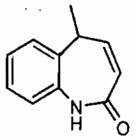
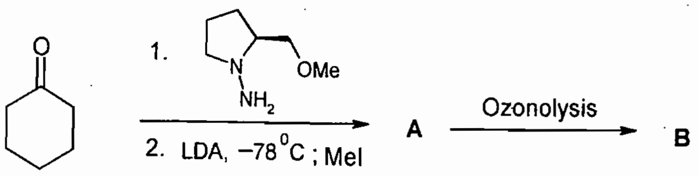
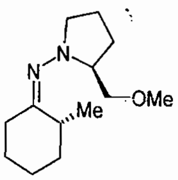


26) **The major products A and B in the following synthetic strategy are** ***[Dec 2011]***



(a) A =


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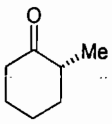
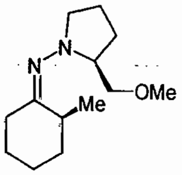


(b) A =


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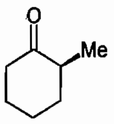
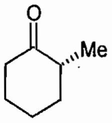


(c) A =


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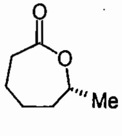
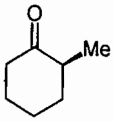
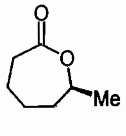
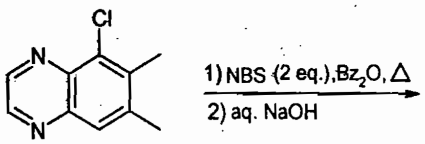


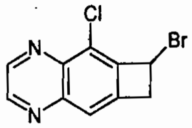
(d) A =


B =


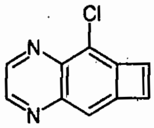
27) The structure of the tricyclic compound formed in the following two step sequence is ***[June 2012]***



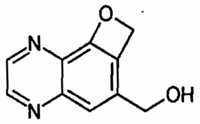
(a)



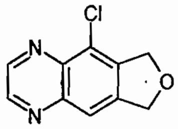
(b)



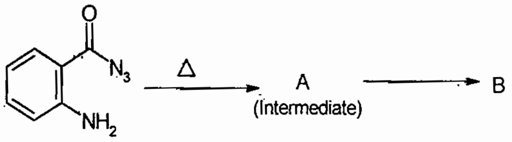
(c)



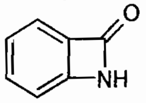
(d)



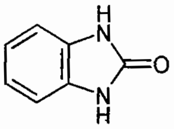
28) The intermediate A and the major product B in the following reaction are ***[June 2012]***



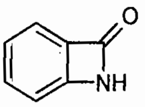
(a) A is acyl cation & B is



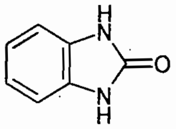
(b) A is acyl cation & B is



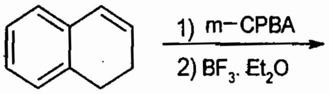
(c) A is acyl nitrene & B is



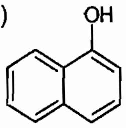
(d) A is acyl nitrene & B is



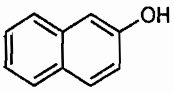
29) The major product formed in the following reaction sequence is ***[June 2012]***



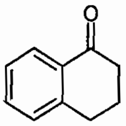
(a)



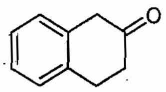
(b)



(c)

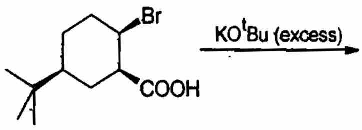


(d)

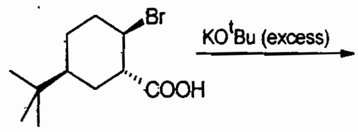


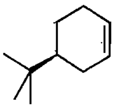
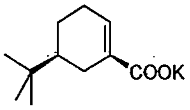
30) For the following two reactions A and B, the correct statement is: ***[June 2012]***

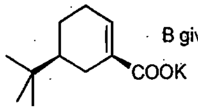
A)

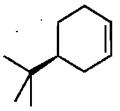


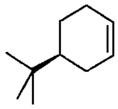
and B)

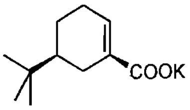


(a) A gives  B gives 

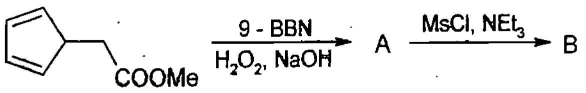
(b) A gives 

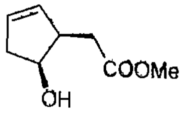
B gives 

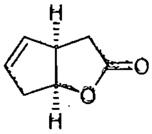
(c) Both A and B give 

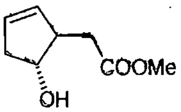
(d) Both A and B give 

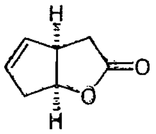
31) The major compound B formed in the reaction sequence given below exhibited a carbonyl absorption band at 1770 cm^{-1} in the IR spectrum. The structure A and B are ***[June 2012]***

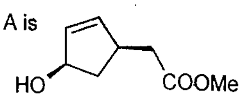


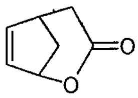
(a) A is 

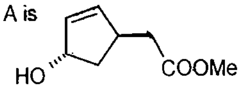
B is 

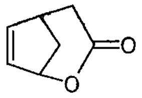
(b) A is 

B is 

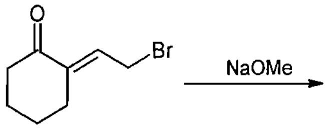
(c) A is 

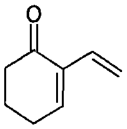
B is 

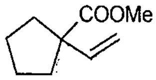
(d) A is 

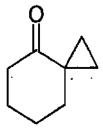
B is 

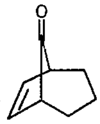
32) The major product formed in the following reaction is: ***[June 2012]***



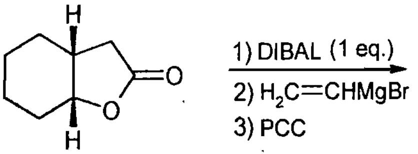
(a) 

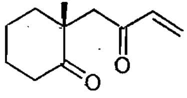
(b) 

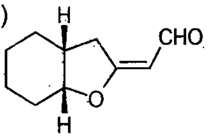
(c) 

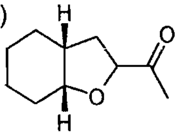
(d) 

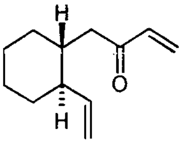
33) The major product formed in the following reaction sequence is: ***[June 2012]***



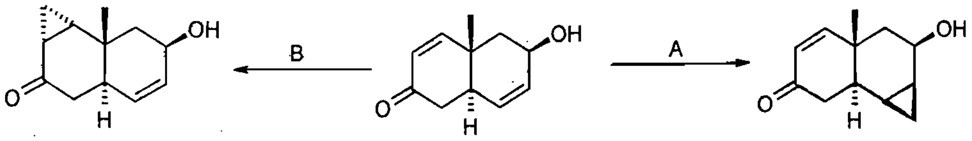
(a) 

(b) 

(c) 

(d) 

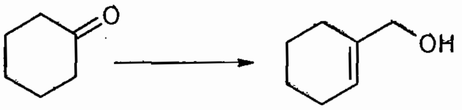
34) The reagents A and B in the following reactions are ***[June 2012]***



(a) A = CH_2I_2, Zn–Cu   B = $Me_3S^+ I^-$, NaH   (b) A = CH_2I_2, Zn–Cu   B = $Me_3S^+(O)\ I^-$, NaH

(c) A = $Me_3S^+ I^-$, NaH   B = $Me_3S^+(O)\ I^-$, NaH   (d) A = $Me_3S^+(O)\ I^-$, NaH   B = CH_2I_2, Zn–Cu

35) The correct reagent combination/reaction sequence for effecting the following conversion is: ***[June 2012]***



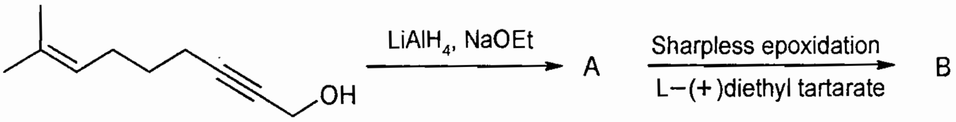
(a) (1) Me_3SiCH_2OMe, ^nBuLi; (2) H_3O^+; (3) $NaBH_4$, MeOH

(b) (1) $Ph_3P^+CH_2OMeCl^-$, ^nBuLi; (2) H_3O^+; (3) $NaBH_4$, MeOH

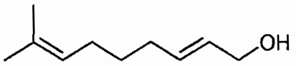
(c) (1) NH_2NHTs; (2) NaOEt; (3) ClCOOEt

(d) (1) NH_2NHTs; (2) 2 eq. ^nBuLi; (3) HCHO

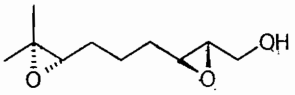
36) The major products A and B formed in the following reaction sequence are ***[June 2012]***



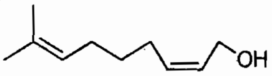
(a) A =



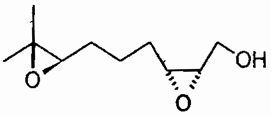
B =



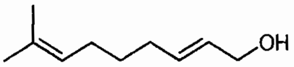
(b) A =



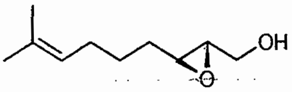
B =



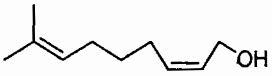
(c) A =



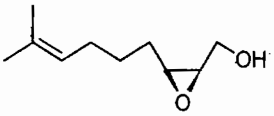
B =



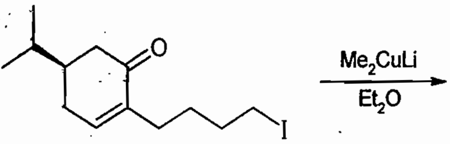
(d) A =

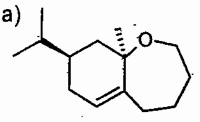


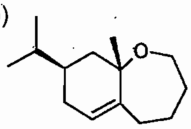
B =

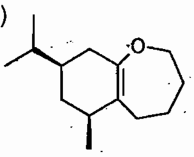


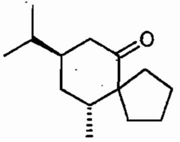
37) The major product formed in the following reaction is: ***[June 2012]***



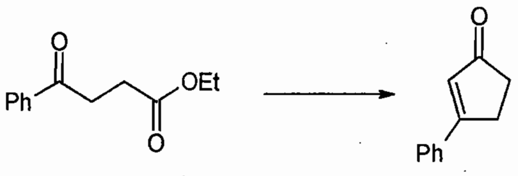
(a)


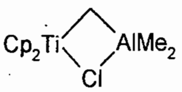
(b)


(c)


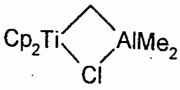
(d)


38) The correct sequence of reagents for effecting the following conversion is: ***[June 2012]***



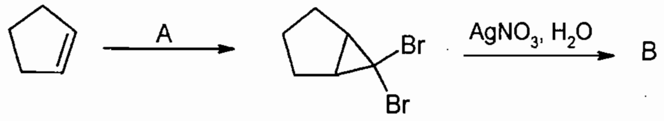
(a) 1) $(CH_2OH)_2$, PTSA, Δ 2)  (Tebbe's reagent) 3) H_3O^+ 4) KOH

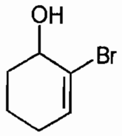
(b) 1) $(CH_2OH)_2$, PTSA, Δ 2) $Ph_3P{=}CH_2$ 3) H_3O^+ 4) KOH

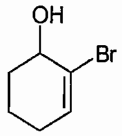
(c) 1)  (Tebbe's reagent) 2) H_3O^+ 3) KOH

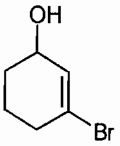
(d) 1) $Ph_3P{=}CH_2$ 2) H_3O^+ 3) KOH

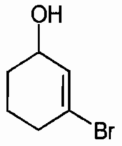
39) The reagent A required, and the major product B formed in the following reaction sequence are ***[June 2012]***



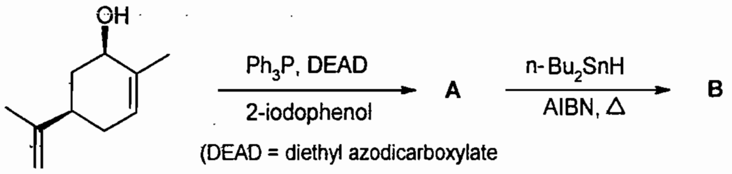
(a) A = CH_2Br_2 & KO^tBu B =


(c) A = $CHBr_3$ & KO^tBu B =


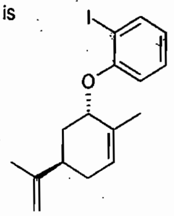
(b) A = CH_2Br_2 & KO^tBu B =


(d) A = $CHBr_3$ & KO^tBu B =


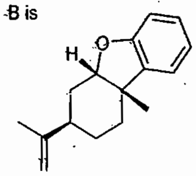
40) The major products A and B the following reaction sequence, are ***[June 2012]***



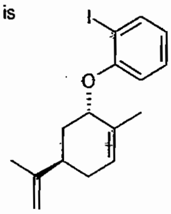
(a) A is



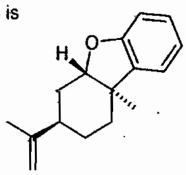
B is



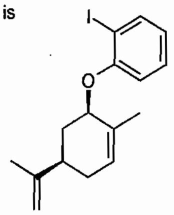
(b) A is



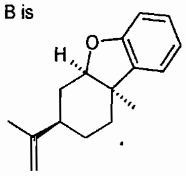
B is



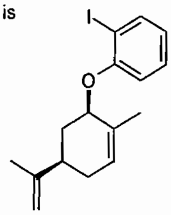
(c) A is



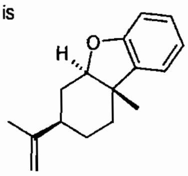
B is



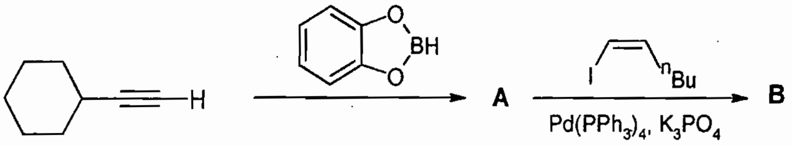
(d) A is



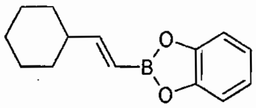
B is



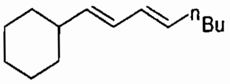
41) The major products A and B the following reaction sequence, are ***[June 2012]***



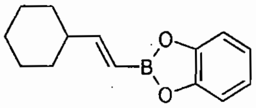
(a) A is



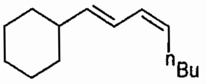
B is



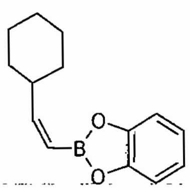
(b) A is



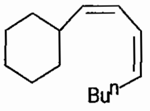
B is



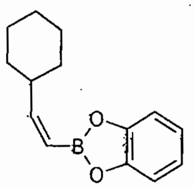
(c) A is



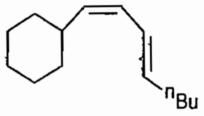
B is



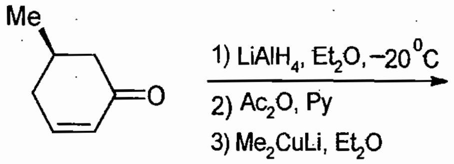
(d) A is



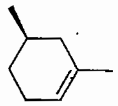
B is



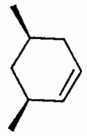
42) The major product formed in the following reaction sequence is ***[Dec 2012]***



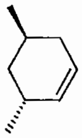
(a)



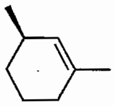
(b)



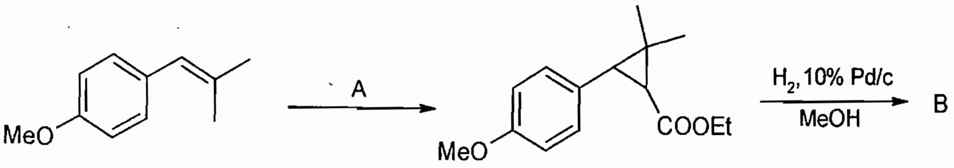
(c)



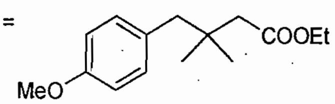
(d)



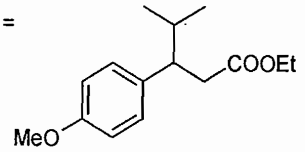
43) In the following reaction, the reagent A and the major product B are **[Dec 2012]**



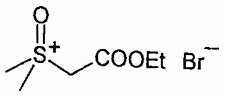
(a) A = $N_2CHCOOEt$, Cu(acac)$_2$ B =



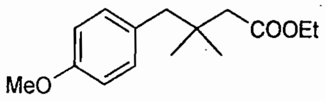
(b) A = $N_2CHCOOEt$, Cu(acac)$_2$ B =



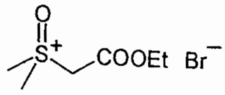
(c) A = NaH &



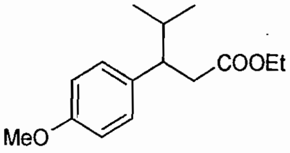
B =



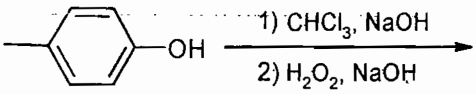
(d) A = NaH &



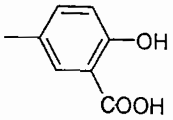
B =



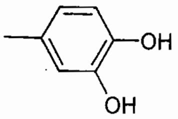
44) The major product formed in the following reaction sequence is **[Dec 2012]**



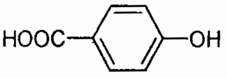
(a)



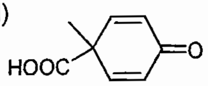
(b)



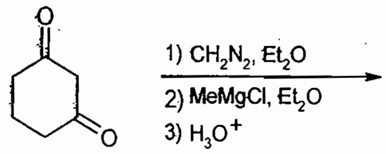
(c)

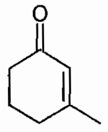


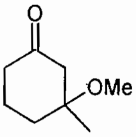
(d)

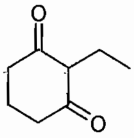


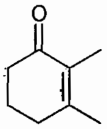
45) The major product formed in the following reaction sequence is **[Dec 2012]**



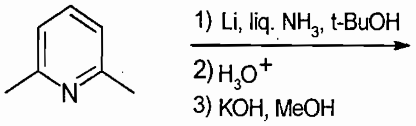
(a)


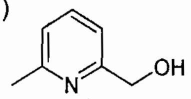
(b)


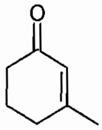
(c)


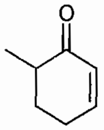
(d)


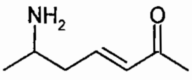
46) The major product formed in the following reaction is **[Dec 2012]**



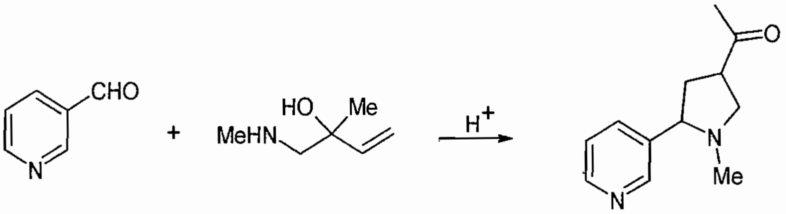
(a)


(b)


(c)


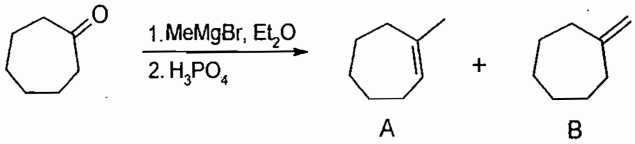
(d)


47) The following transformation involves **[Dec 2012]**



(a) an iminium ion, [3,3]-sigmatropic shift and Mannich reaction.
(b) a nitrenium ion, [3,3]-sigmatropic shift and Michael reaction.
(c) an iminium ion, [1,3]-sigmatropic shift and Mannich reaction.
(d) a nitrenium ion, [1,3]-sigmatropic shift and Michael reaction.

48) Among the following, the correct statement for the following reaction is **[June 2013]**

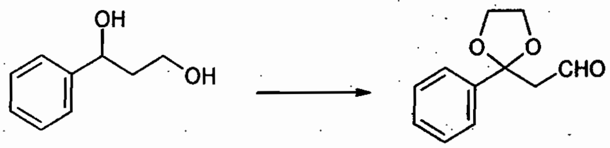


(a) A is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum
(b) A is the minor product and it will have eight signals in the proton decoupled ^{13}C NMR spectrum
(c) B is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum
(d) B is the minor product and it will have five signals in the proton decoupled ^{13}C NMR spectrum

49) The treatment of PhBr with n-BuLi yields: **[June 2013]**

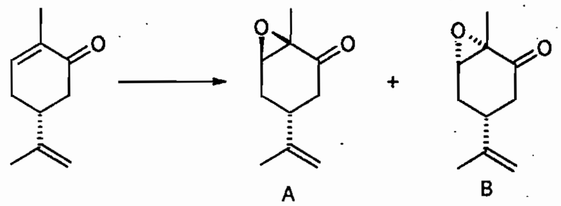
(a) 2 n−BuPh + Br_2 + Li_2 (b) PhPh + octane + 2 LiBr (c) n−BuPh + LiBr (d) PhLi + n-BuBr

50) For the following three step conversion of A to B, the appropriate sequence of reactions is **[June 2013]**



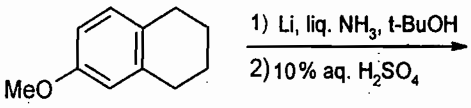
(a) MnO_2; $(CH_2OH)_2$/p-TSA; PCC
(b) PCC; MnO_2; $(CH_2OH)_2$/p-TSA;
(c) PCC; $(CH_2OH)_2$/p-TSA; Jones' reagent
(d) Jones' reagent; $(CH_2OH)_2$/p-TSA; MnO_2.

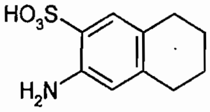
51) Which one of the following statements is true for the following transformation? ***[June 2013]***

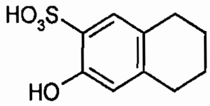


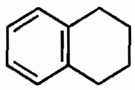
(a) Suitable reagent is m-CPBA and B is the major product
(b) Suitable reagent in m-CPBA and A is the major product.
(c) Suitable reagent is aq. H_2O_2/NaOH and B is the major product.
(d) Suitable reagent is aq. H_2O_2/NaOH and A is the major product.

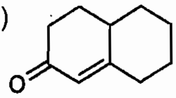
52) The compound formed in the following reaction sequence is ***[June 2013]***



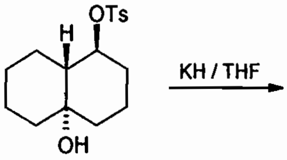
(a)


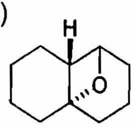
(b)


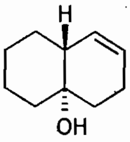
(c)


(d)


53) The major product formed in the following reaction is ***[June 2013]***



(a)


(b)


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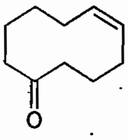
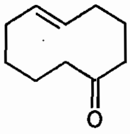
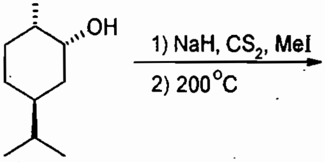
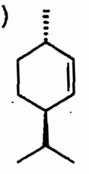
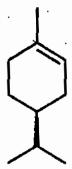


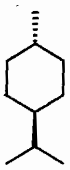
(d)


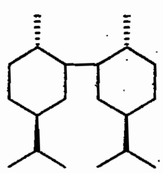
54) The major product formed in the following reaction is ***[June 2013]***



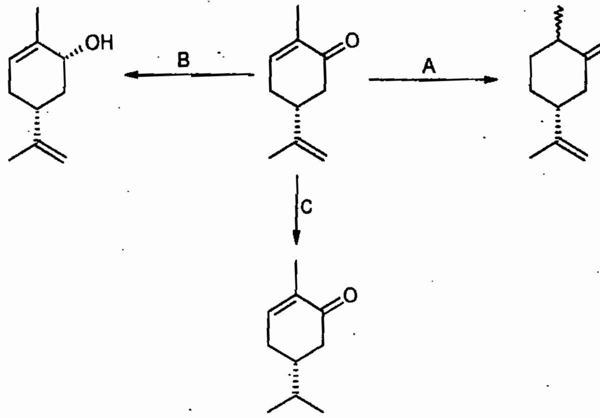
(a)


(b)


(c)


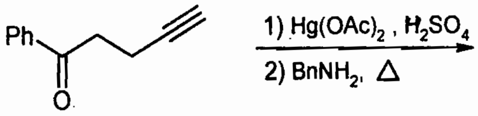
(d)


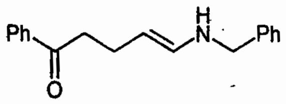
55) The most suitable reagent combination of A-C, required in the following conversions are ***[Dec 2013]***

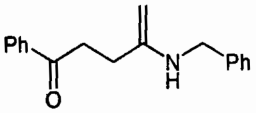


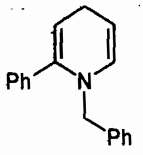
(a) A = Li/liq. NH_3; B = $NaBH_4$, $CeCl_3.7H_2O$; C = H_2, $(Ph_3P)_3RhCl$.
(b) A = Li/liq. NH_3; B = $NaBH_4$, $CeCl_3.7H_2O$; C = H_2, 10% Pd/C.
(c) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. NH_3; C = H_2, $(Ph_3P)_3RhCl$.
(d) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. NH_3; C = H_2, 10% Pd/C

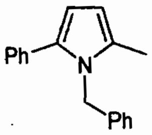
56) The major product formed in the following reaction sequence is ***[Dec 2013]***



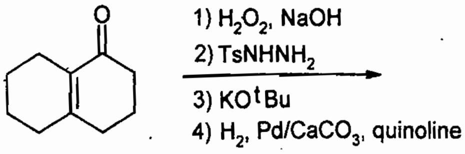
(a)


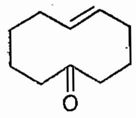
(b)


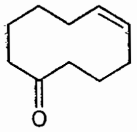
(c)


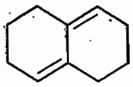
(d)


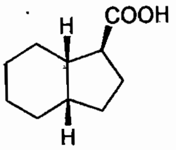
57) The major product formed in the following reaction sequence is ***[Dec 2013]***



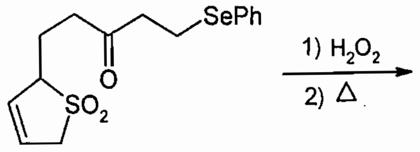
(a)


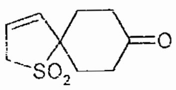
(b)


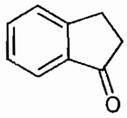
(c)


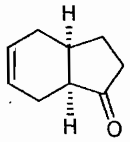
(d)


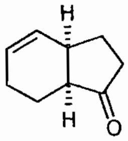
58) **The major product formed in the following reaction sequence is** *[Dec 2013]*



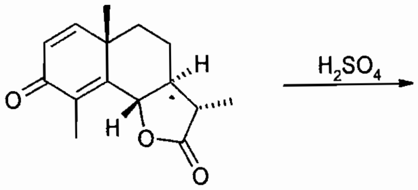
(a)


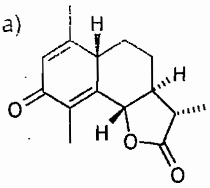
(b)


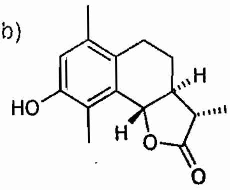
(c)


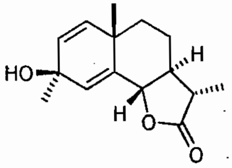
(d)


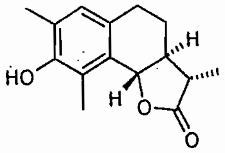
59) **The major product formed in the sulfuric acid mediated rearrangement of the sesquiterpene santonin A is** *[Dec 2013]*



(a)


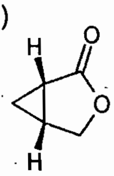
(b)


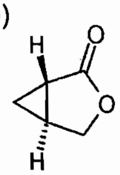
(c)


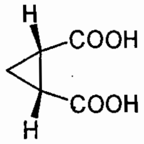
(d)


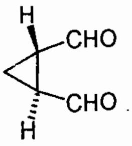
60) **The major product formed in the following reaction sequence is** *[Dec 2013]*

cis−but−2ene−1,4−diol $\xrightarrow[\text{2) PCC, } CH_2Cl_2]{\text{1) } CH_2I_2\text{, Zn−Cu, } CH_2Cl_2}$

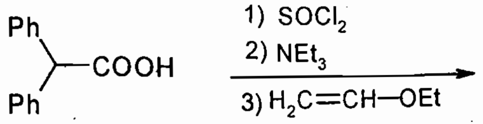
(a)


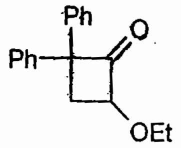
(b)


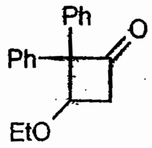
(c)


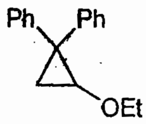
(d)


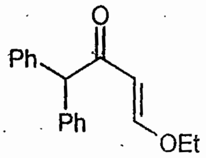
61) **The major product formed in the following reaction sequence is** *[Dec 2013]*



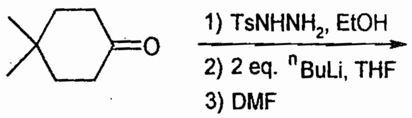
(a)


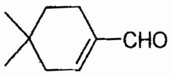
(b)


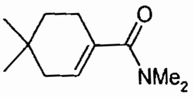
(c)


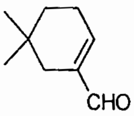
(d)


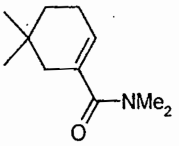
62) The major product formed in the following reaction sequence is *[Dec 2013]*



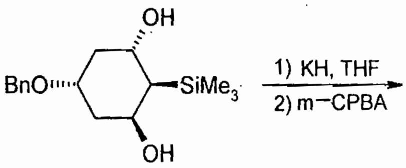
(a)


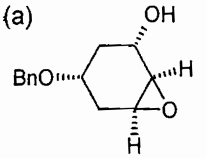
(b)


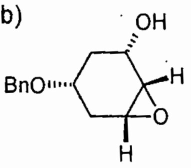
(c)


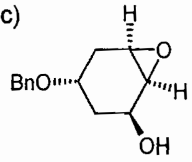
(d)


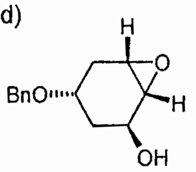
63) The major product formed in the following reaction sequence is *[Dec 2013]*



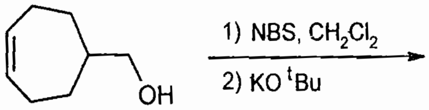
(a)


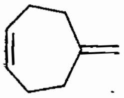
(b)


(c)


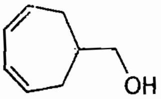
(d)


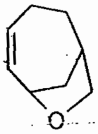
64) The major product formed in the following reaction sequence is *[Dec 2013]*



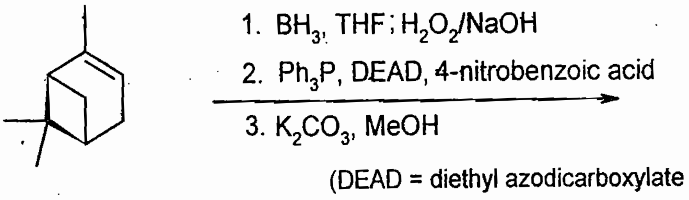
(a)


(b)


(c)


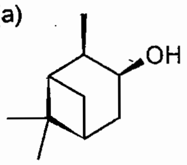
(d)


65) The major product formed in the following reaction sequence is *[Dec 2013]*

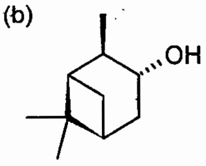


(DEAD = diethyl azodicarboxylate)

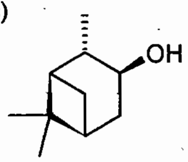
(a)



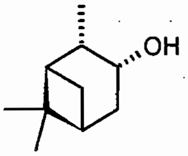
(b)



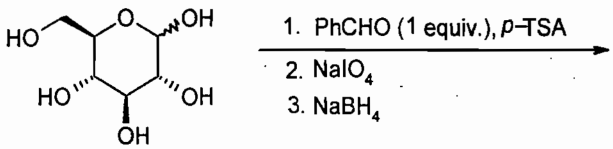
(c)



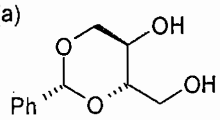
(d)



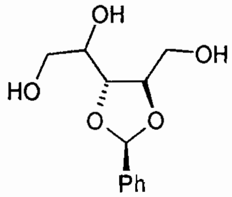
66) The major product formed in the following reaction sequence is ***[Dec 2013]***



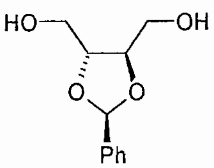
(a)



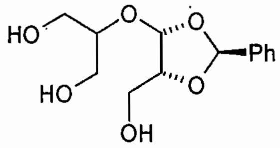
(b)



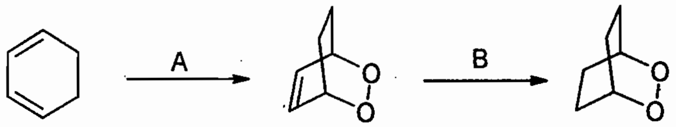
(c)



(d)



67) The correct combination of reagents for effecting the following sequence of reactions is ***[June 2014]***



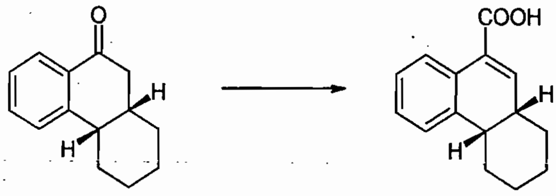
(a) A = O_3/O_2; B = $K^{+-}OOC-N=N-COO^-K^+$, AcOH

(b) A = O_2, Rose Bengal, hv; B = $K^{+-}OOC-N=N-COO^-K^+$, AcOH

(c) A = O_2, Rose Bengal, hv; B = H_2, Pd/C

(d) A = O_2, Rose Bengal; Δ; B = H_2, Pd/C

68) The correct combination of reagents to effect the following conversion is ***[June 2014]***



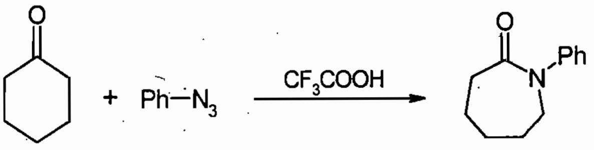
(a) (1) $Ph_3P^+CH_2OMeCl^-$, BuLi; (2) H_3O^+; (3) Jone's reagent

(b) (1) NH_2NHTs; (2) 2 eq. BuLi; (3) DMF

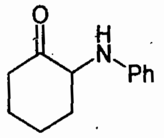
(c) (1) NH_2NHTs; (2) 2 eq. BuLi; (3) CO_2

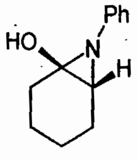
(d) (1) $ClCH_2CO_2Et$; LDA (2) $BF_3 \cdot OEt_2$ (3) DMSO,$(COCl)_2$, Et_3N, -78^0C to rt

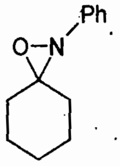
69) Consider the following reaction. ***[June 2014]***

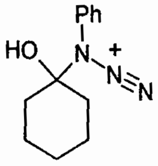


The appropriate intermediate involved in this reaction

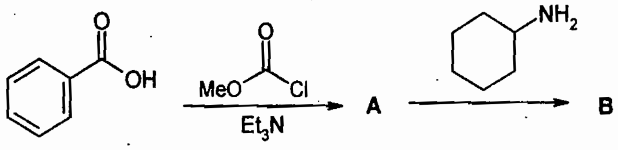
(a)


(b)


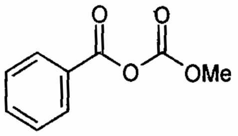
(c)


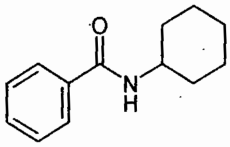
(d)


70) The products A and B in the following reaction sequence are *[June 2014]*

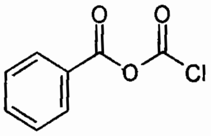


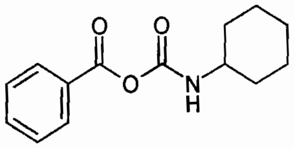
(a)

A :


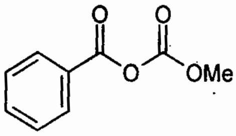
B :


(b)

A :


B :


(c)

A :


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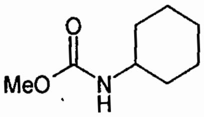
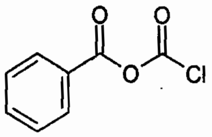


(d)

A :


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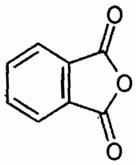
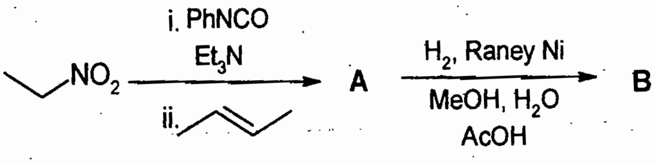
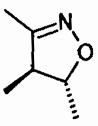
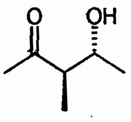


71) The major products A and B in the following reaction sequence are *[June 2014]*

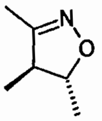


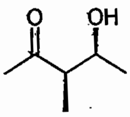
(a)

A :


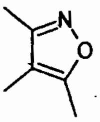
B :


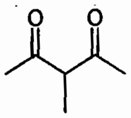
(b)

A :


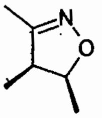
B :


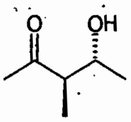
(c)

A :


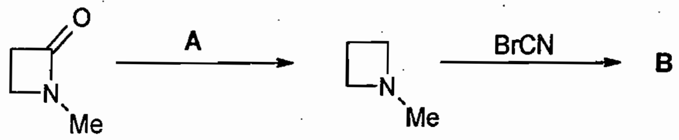
B :


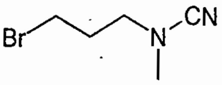
(d)

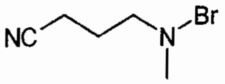
A :


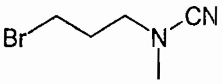
B :


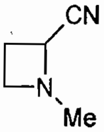
72) The reagent A used and the major product B formed in the following reaction sequence are ***[June 2014]***



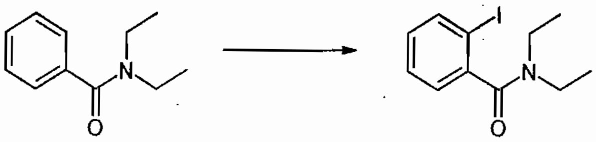
(a) A : LiAlH$_4$ B :


(b) A : LiAlH$_4$ B :


(c) A : NaBH$_4$ B :


(d) A : H_2 / Pd−C B :


73) The correct combination of reagents required to effect the following conversion is ***[June 2014]***



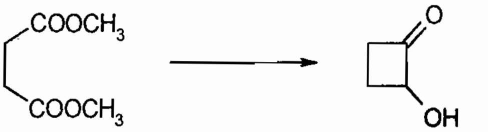
(a) I_2, HNO3

(b) s-BuLi, −78^{0}C followed by KI

(c) NaOEt followed by ICH_2CH_2I

(d) s-BuLi, −78^{0}C followed by ICH_2CH_2I

74) The correct combination of reagents required to effect the following conversion is ***[June 2014]***



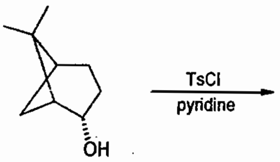
(a) (1) Na, xylene, Me_3SiCl, heat (2) H_3O^+;

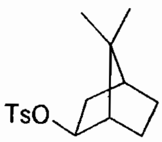
(b) (1) Na, xylene, heat (2) H_2O_2, NaOH

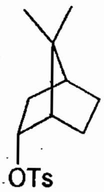
(c) (1) NaOEt, EtOH (2) Na, xylene, heat

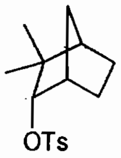
(d) (1) $TiCl_3$, Zn-Cu, Me_3SiCl, heat (2) H_3O^+;

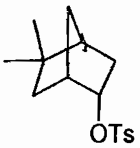
75) The major product formed in the following photochemical reaction is ***[June 2014]***



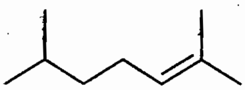
(a)


(b)


(c)


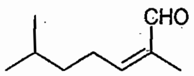
(d)


76) The products A & B formed in the following reaction sequence are ***[June 2014]***

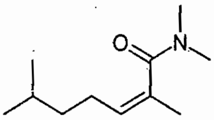


$\xrightarrow[\text{dioxane reflux}]{SeO_2}$ **A** $\xrightarrow[i\text{-PrOH, } Me_2NH]{\text{aq. NaCN, } MnO_2}$ **B**

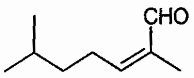
(a) A:



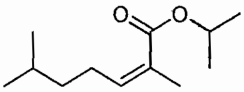
B:



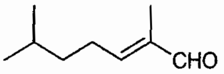
(b) A:



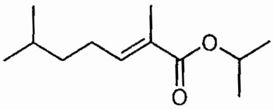
B:



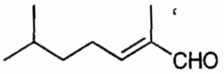
(c) A:



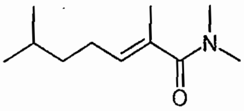
B:



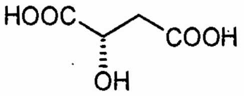
(d) A:



B:

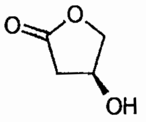


77) The major product formed in the following reaction is **[Dec 2014]**

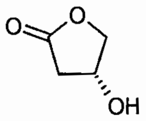


1. $Me_2C(OMe)_2$, TsOH (cat)
2. BH_3, THF
3. H_3O^+

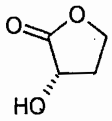
(a)



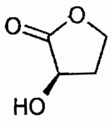
(b)



(c)



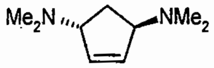
(d)



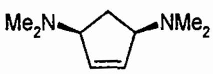
78) The product B in the following reaction sequence is **[Dec 2014]**

$\xrightarrow[\text{hexane, rt}]{Br_2 \text{ (1 equiv)}}$ **A** $\xrightarrow{\text{excess } Me_2NH}$ **B**

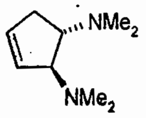
(a)



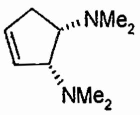
(b)



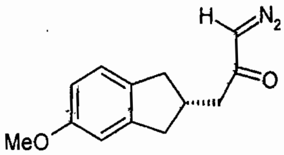
(c)



(d)

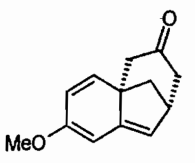


79) The major product of the following reaction is **[Dec 2014]**

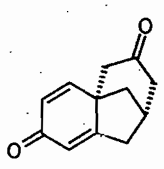


$\xrightarrow{CF_3COOH}$

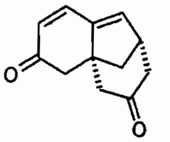
(a)



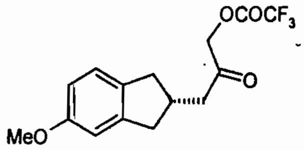
(b)



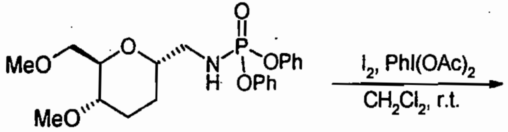
(c)



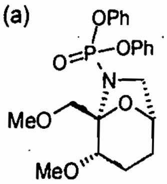
(d)



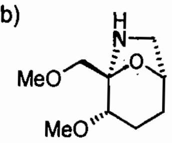
80) The major product of the following reaction is ***[Dec 2014]***



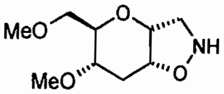
(a)



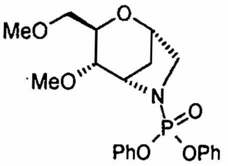
(b)



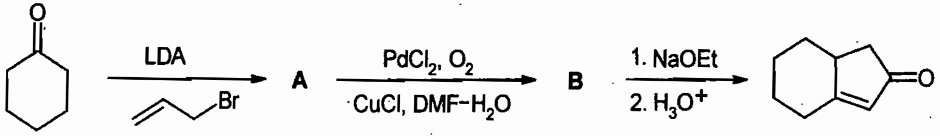
(c)



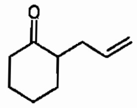
(d)



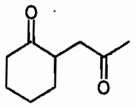
81) The products A and B formed in the following reaction sequence are ***[Dec 2014]***



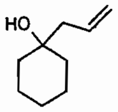
(a) A =



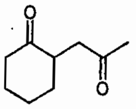
B =



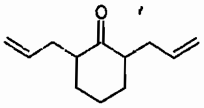
(b) A =



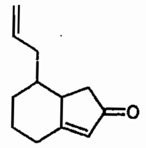
B =



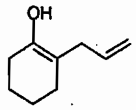
(c) A =



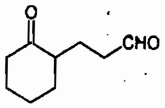
B =



(d) A =

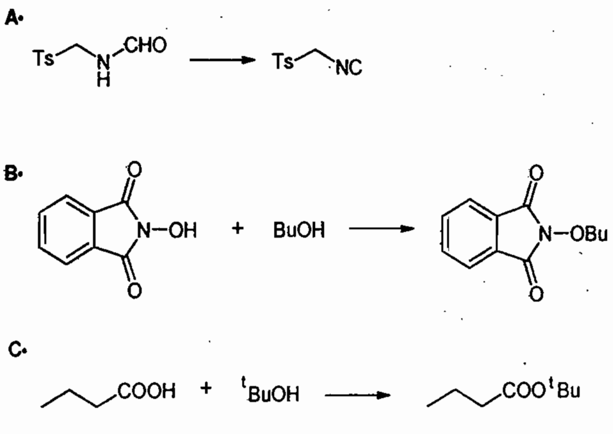


B =



82) The correct combinations of the reactions and the reagents are ***[Dec 2014]***

Reactions



Reagents

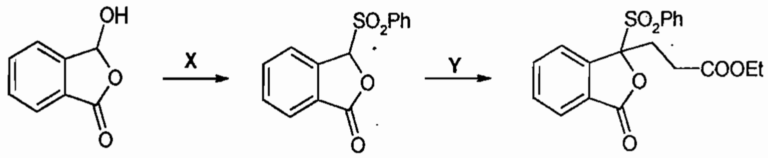
P. PPh_3 and $EtO_2CN{=}NCO_2Et$

Q. $POCl_3$, Et_3N

R. H_2SO_4

(a) A-P, B-Q, C-R (b) A-Q, B-R, C-P (c) A-P, B-R, C-Q (d) A-Q, B-P, C-R

83) In the following reaction sequence, the reagent X and Y are respectively ***[Dec 2014]***



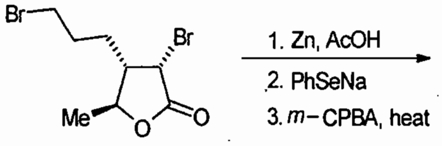
(a) X = $PhSO_2H$, $BF_3.OEt_2$ **and** Y = $CH_2{=}CHCOOEt$, $BF_{3}.OEt_2$.

(b) X= 1.PhSH, PTSA; 2. m-CPBA **and** Y= $CH_2{=}CHCOOEt$, $BF_3.OEt_2$.

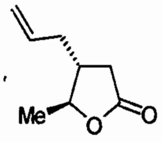
(c) X = $PhSO_3H$, $BF_3.OEt_2$ **and** Y = LDA, $CH_2{=}CHCOOEt$.

(d) X= 1. PhSH, PTSA; 2. m-CPBA **and** Y=LDA, $CH_2{=}CHCOOEt$

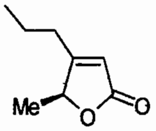
84) The major product of the following reaction is ***[Dec 2014]***



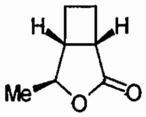
(a)



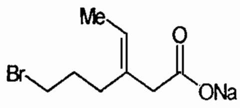
(b)



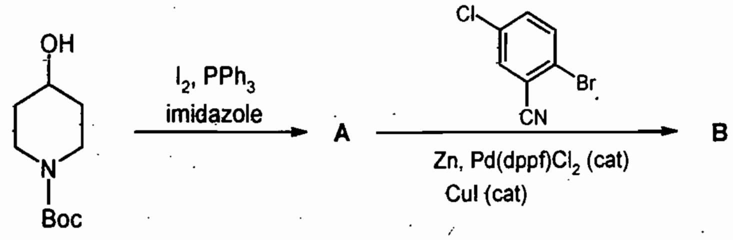
(c)



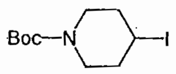
(d)



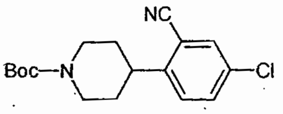
85) In the following reaction sequence, the structure of A and B are respectively ***[Dec 2014]***



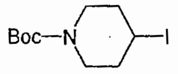
(a) A =



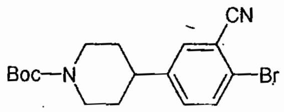
B =



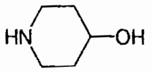
(b) A =



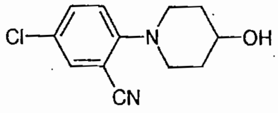
B =



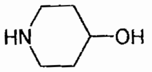
(c) A =



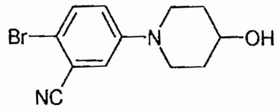
B =



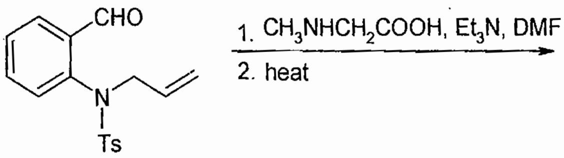
(d) A =



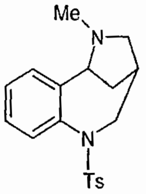
B =



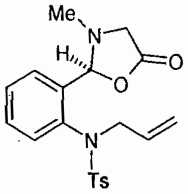
86) The major product of the following reaction is ***[Dec 2014]***



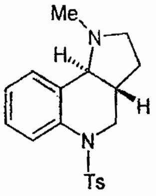
(a)



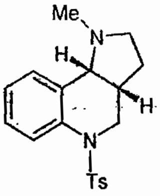
(b)



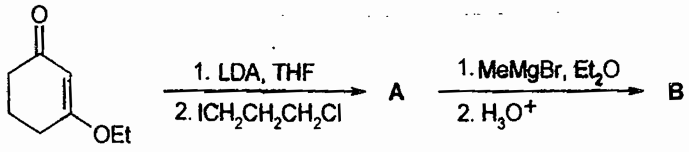
(c)



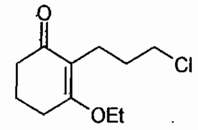
(d)



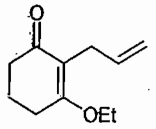
7) The major products A and B formed in the following reaction sequence are ***[Dec 2014]***



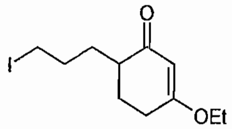
(a) A =



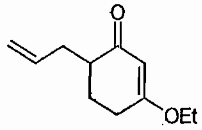
B =



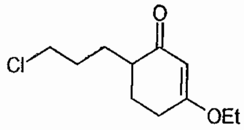
(b) A =



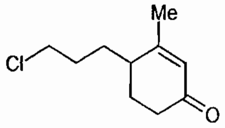
B =



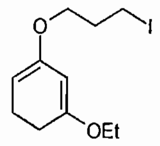
(c) A =



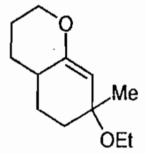
B =



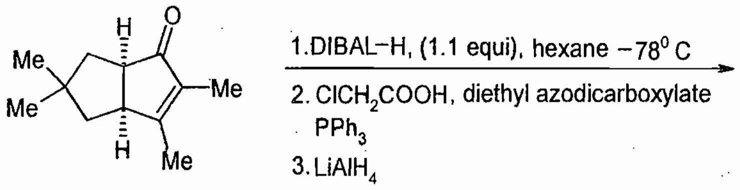
(d) A =



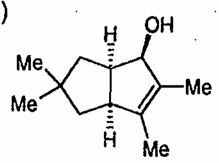
B =



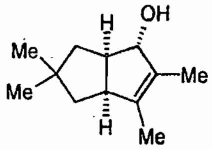
88) In the following reaction sequence, the structure product formed is **[Dec 2014]**



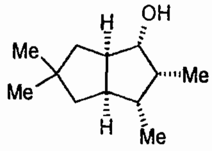
(a)



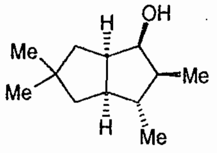
(b)



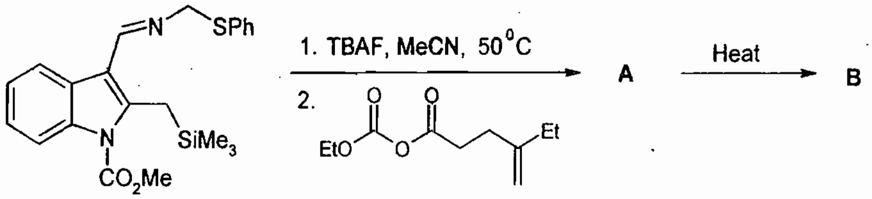
(c)



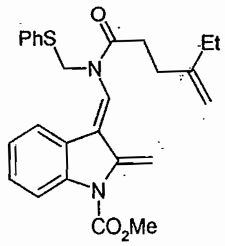
(d)



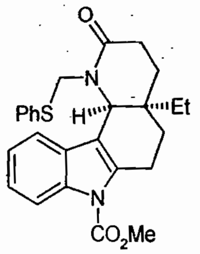
89) The product A and B in the following reaction sequence are **[Dec 2014]**



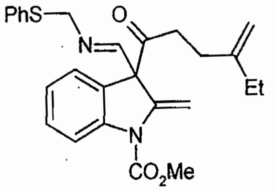
(a) A =



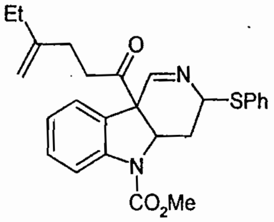
B =



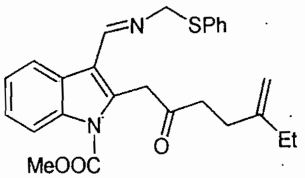
(b) A =



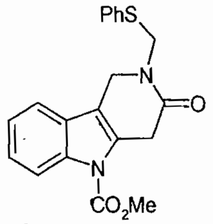
B =



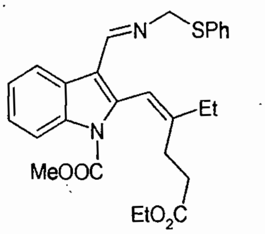
(c) A =



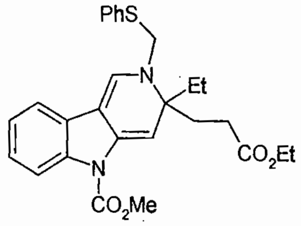
B =



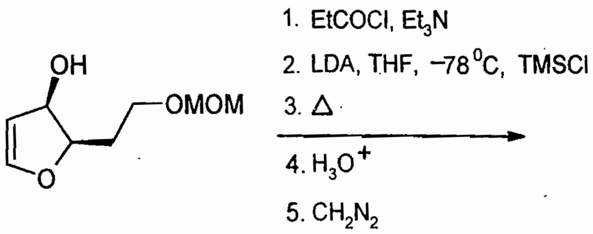
(d) A =



B =

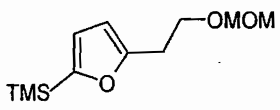


The major product formed in the following reaction sequence is **[Dec 2014]**

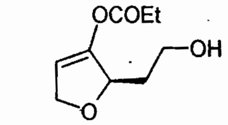


1. EtCOCl, Et_3N
2. LDA, THF, $-78\,^0C$, TMSCl
3. Δ
4. H_3O^+
5. CH_2N_2

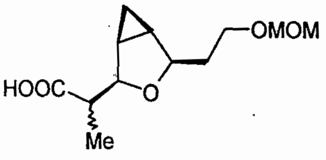
(a)



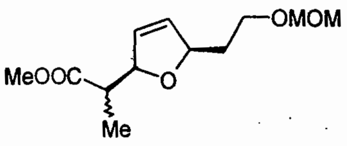
(b)



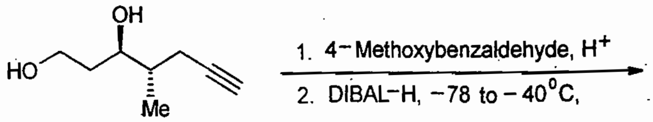
(c)



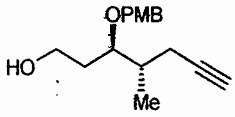
(d)

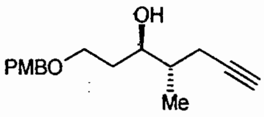


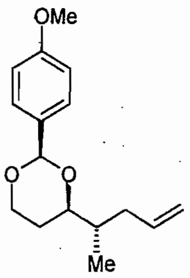
The major product formed in the following reaction sequence is **[Dec 2014]**

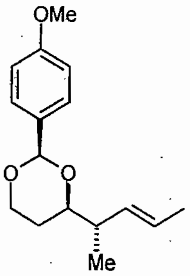


1. 4−Methoxybenzaldehyde, H^+
2. DIBAL−H, −78 to − 40^0C,

(a)


(b)


(c)


(d)


92) The correct combinations of the following reactions and their ρ values is ***[Dec 2014]***

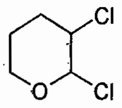
Entry	Reactions	Entry	ρ value
A	$ArNH_2$ + PhCOCl in benzene	P	+ 2.01
B	ArO^- + EtI in ethanol	Q	− 0.99
C	$ArCO_2Et$ + aq. NaOH in ethanol	R	− 2.69
		S	+ 0.78

(a) A-P; B-R; C-P (b) A-R; B-Q; C-P (c) A-R; B-P; C-Q (d) A-Q ; B-R; C-S

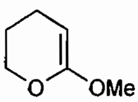
(Questions from GATE EXAM)

Questions with ONE OR TWO marks

1) The compound formed on methanolysis of P is ***(GATE 2005)***



P

(a)


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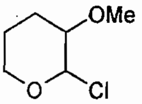
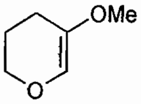


(c)


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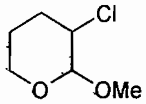
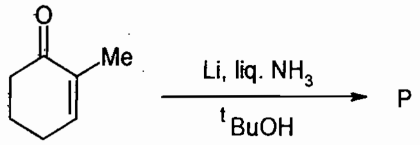
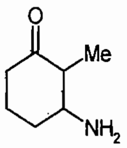


2) The major product P of the given reactions is ***(GATE 2005)***



(a)


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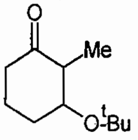

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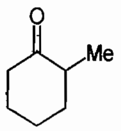

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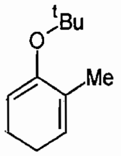
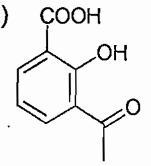


3) The major product of acetylation of salicyclic acid with Ac_2O/H^+ followed by heating with anhydrous $AlCl_3$ is

(GATE 2005)

(a)


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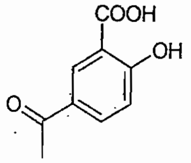

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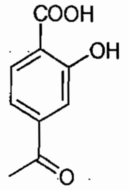

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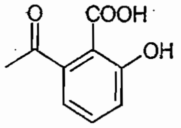
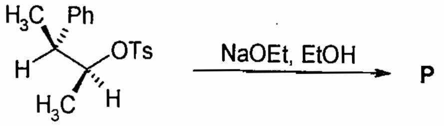
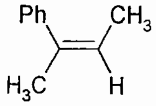


4) The major product P of the given reaction is

(GATE 2005)



(a)


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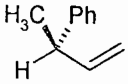

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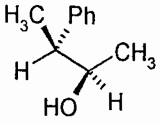

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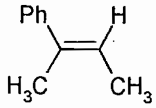
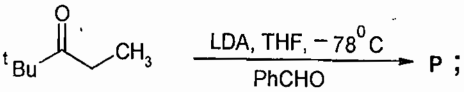
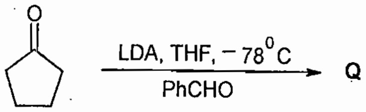
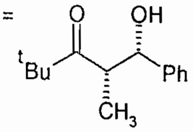


5) In the following reactions identify the correct combination of their major products P and Q [LDA = LiN(i-Pr)₂]

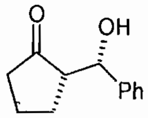
(GATE 2005)





(a) P =


and

Q =


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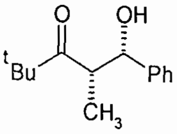
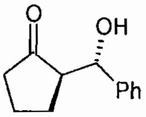
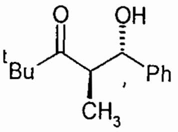


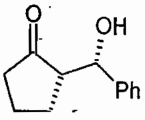
and

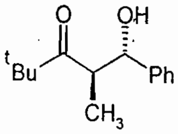
Q =


(c)

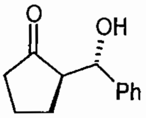
P =


and

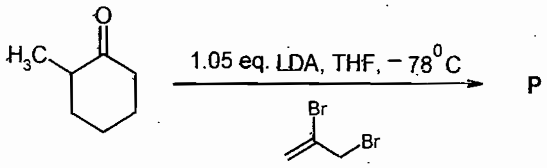
Q =


(d) P =


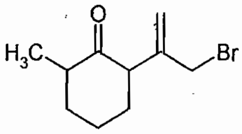
and

Q =


6) The major product P formed in the following reaction is *(GATE 2005)*



(a)



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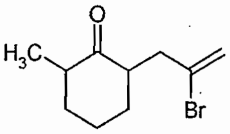
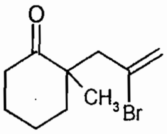


(c)



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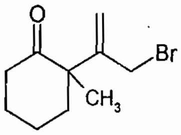
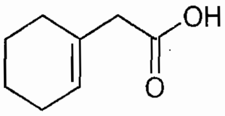
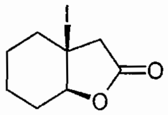


7) Iodo−lactonization of β,γ unsaturated carboxylic acid X with I_2 and $NaHCO_3$ gives *(GATE 2005)*

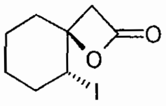


X

(a)



(b)



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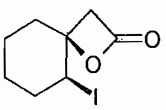
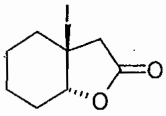
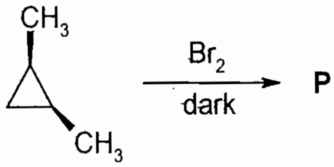


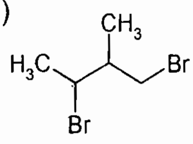
(d)



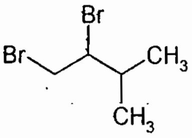
8) The major product P of the following reaction is *(GATE 2005)*



(a)



(b)



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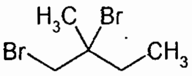
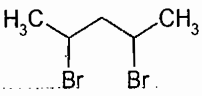
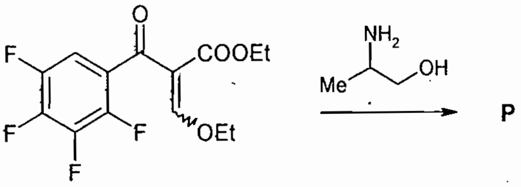


(d)

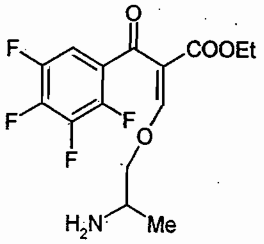


Linked answer questions 9 & 10

9) The major product P of the following of reaction is *(GATE 2005)*



(a)



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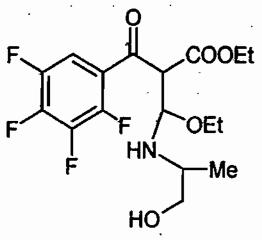

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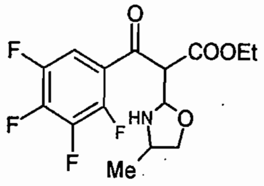

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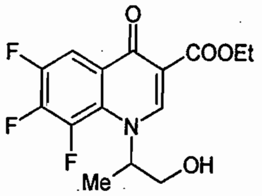
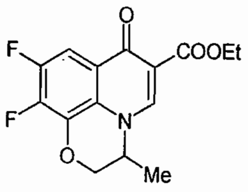
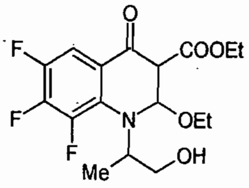


10) The major compound Q obtained on reaction of P with NaH in DMF ***(GATE 2005)***

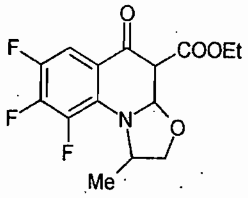
(a)



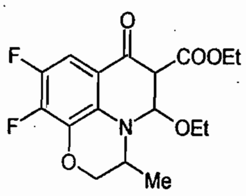
(b)



(c)

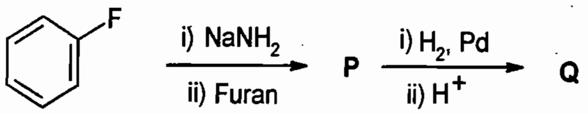


(d)

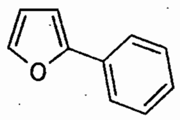


Linked answer questions 11 & 12

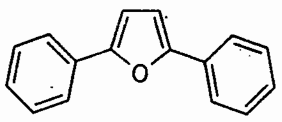
11) In the following sequence of reactions, the major product Q is ***(GATE 2005)***



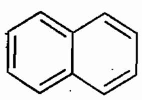
(a)



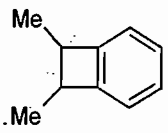
(b)



(c)

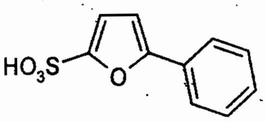


(d)



12) The major product on sulphonation of Q with H_2SO_4 at 160° C is ***(GATE 2005)***

(a)



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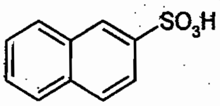
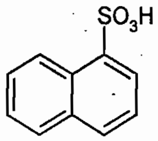
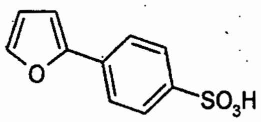


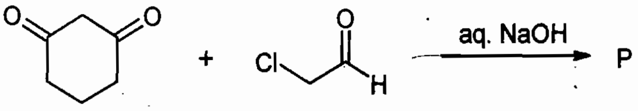
(c)



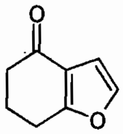
(d)



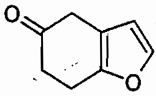
13) Identify the major product P in the following reaction ***(GATE 2006)***



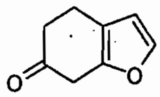
(a)



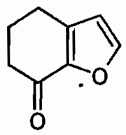
(b)



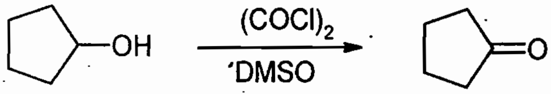
(c)

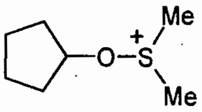


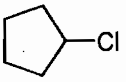
(d)

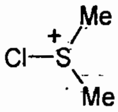


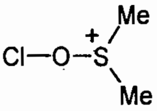
14) Which of the statement is correct about the mechanism of the following reaction? ***(GATE 2006)***



(a) DMSO reacts with the alcohol initially to give  , which reacts with $(COCl)_2$

(b) $(COCl)_2$ reacts with the alcohol initially to give  , which reacts with DMSO

(c) DMSO reacts with $(COCl)_2$ initially to give  $\mathrm{Cl{-}\overset{+}{S}(Me)_2}$, which reacts with the alcohol

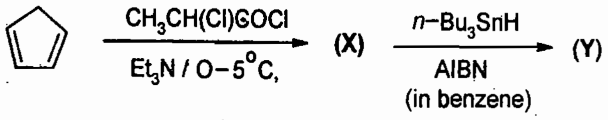
(d) $(COCl)_2$ reacts with DMSO initially to give  $\mathrm{Cl{-}O{-}\overset{+}{S}(Me)_2}$, which reacts with the alcohol

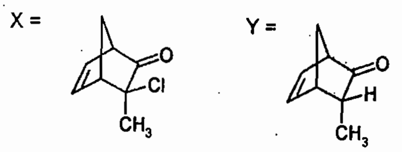
15) Match the reaction of some *p*–substituted benzene derivatives A–D given in List I with the Hammett's ρ–values (i) – (iv) in list II and identify the correct match *(GATE 2006)*

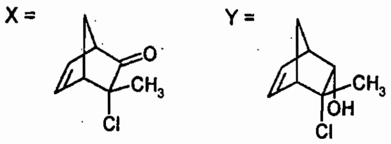
List- I	List- II
A) $ArCH_2{-}Cl \xrightarrow[70^\circ C,]{aq.\ acetone} ArCH_2{-}OH + HCl$	i) + 8.50
B) $ArCH_2{-}COOH \underset{25^\circ C,}{\overset{H_2O}{\rightleftharpoons}} ArCH_2{-}COO^- + H^+$	ii) +1
C) $Ar{-}Cl \xrightarrow[50^\circ C,]{MeONa,\ MeOH} Ar{-}OMe + Cl^-$	iii) +0.49
D) $Ar{-}COOH \underset{25^\circ C,}{\overset{H_2O}{\rightleftharpoons}} Ar{-}COO^- + H^+$	iv) −1.88

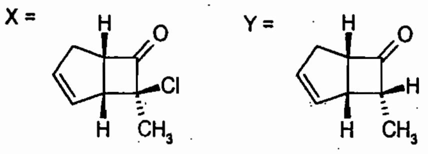
(a) (A–i), (B–iv), (C–iii), (D–ii)
(b) (A–iv), (B–i), (C–ii), (D–iii)
(c) (A–i), (B–ii), (C–iv), (D–iii)
(d) (A–iv), (B–iii), (C–i), (D–ii)

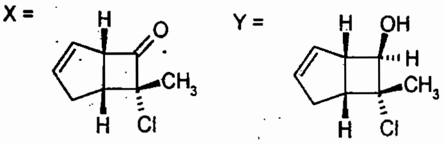
16) The major products X and Y formed in the following reaction sequence are *(GATE 2006)*



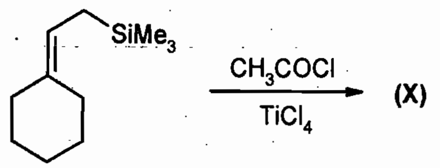
(a)


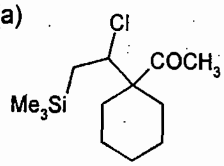
(b)


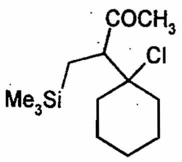
(c)


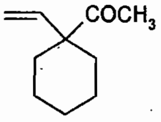
(d)


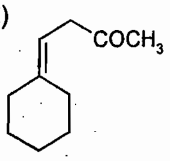
17) Identify the major product (X) in the following reaction *(GATE 2006)*



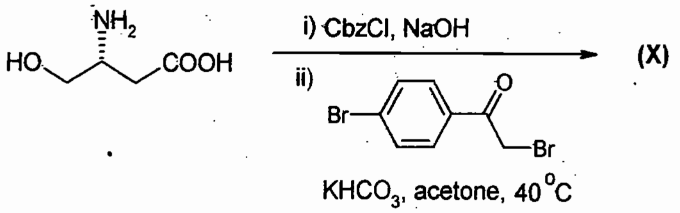
(a)


(b)


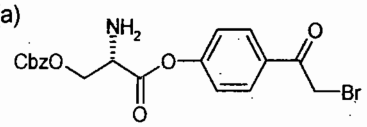
(c)


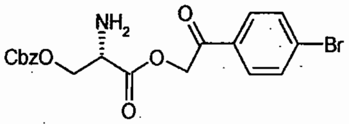
(d)


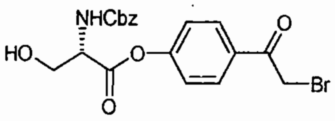
18) Identify the major product (X) in the following reaction *(GATE 2006)*

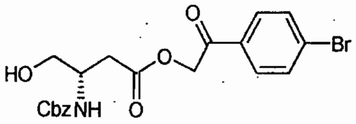


CbzCl is $PhCH_2OCOCl$

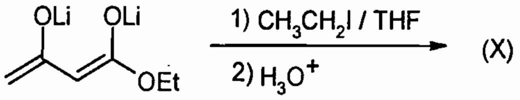
(a)


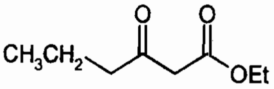
(b)


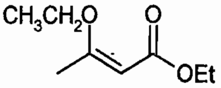
(c)


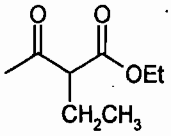
(d)


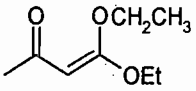
19) Identify the major product (X) in the following reaction *(GATE 2006)*



(a)


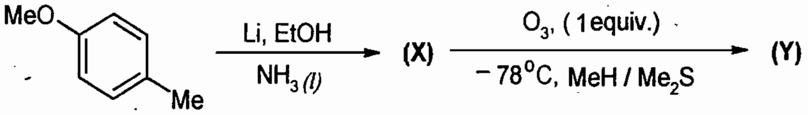
(b)


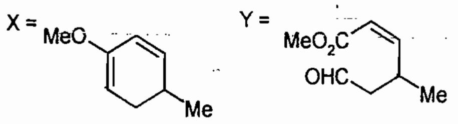
(c)


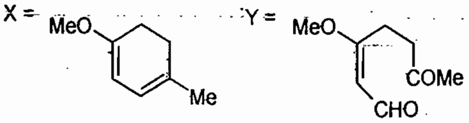
(d)


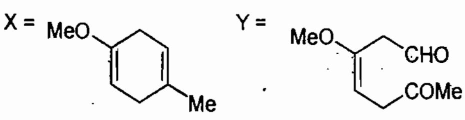
***Linked answer questions* 20 & 21**

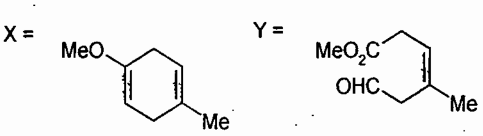
20) The major products X and Y formed in the following reaction sequence are *(GATE 2006)*



(a)


(b)


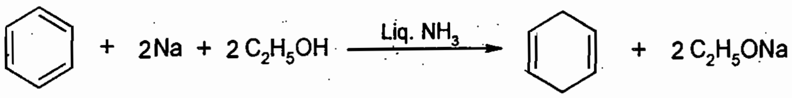
(c)


(d)


21) The reagent for selective reduction of an aldehyde group in Y obtained in above reaction is *(GATE 2006)*

(a) H_2, $(Ph_3P)_3RhCl$
(b) $((H_3C)_2CHCH_2)_2AlH$
(c) $Na(CH_3COO)_3BH$
(d) $LiAlH_4$

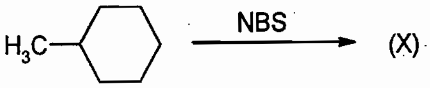
22) The reaction is an example of a ***(GATE 2007)***

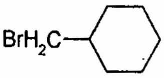


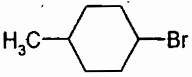
(a) Birch reduction (b) Clemmenson reduction

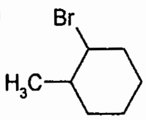
(c) Wolff-Kishner reduction (d) hydride reduction

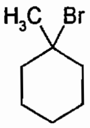
23) The major product (X) of the monobromination reaction is ***(GATE 2007)***



(a) 

(b) 

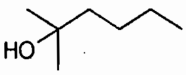
(c) 

(d) 

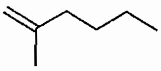
24) Benzene cannot be iodinated with I_2 directly. However, in presence of oxidants such as HNO_3, iodination is possible. The electrophile formed in this case is ***(GATE 2007)***

(a) $\left[I^+\right]$ (b) $\left[I^\cdot\right]$ (c) $\left[\overset{+\delta}{I}\cdots\cdots\overset{+\delta}{OH_2}\right]^+$ (d) $\left[\overset{+\delta}{I}\cdots\cdots\overset{-\delta}{OH_2}\right]^+$

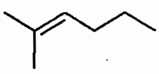
25) The major product obtained upon treatment of compound X with H_2SO_4 at 80°C is ***(GATE 2007)***

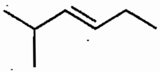


(X)

(a) 

(b) 

(c) 

(d) 

26) Classify the following species as electrophiles (E) and nucleophiles (N) in routine organic synthesi SO_3, Cl^+, CH_3NH_2, H_3O^+, BH_3, CN^- ***(GATE 2007)***

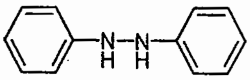
(a) E = SO_3, Cl^+, BH_3; N = CH_3NH_2, H_3O^+, CN^-

(b) E = Cl^+, H_3O^+; N = SO_3, CH_3NH_2, BH_3, CN^-

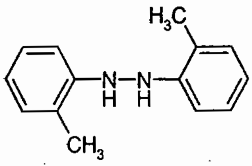
(c) E = Cl^+, H_3O^+, BH_3; N = SO_3, CH_3NH_2, H_3O^+, CN^-

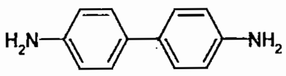
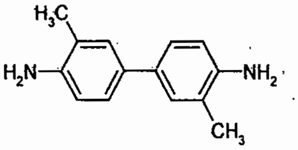
(d) E = SO_3, Cl^+, H_3O^+, BH_3 ; N = CH_3NH_2, CN^-

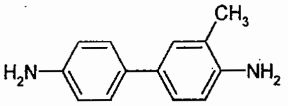
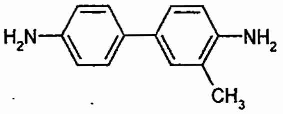
27) The major products obtained upon treating a mixture of with a strongly acidic solution of H_2SO_4 is ***(GATE 2007)***

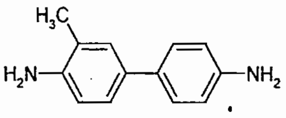
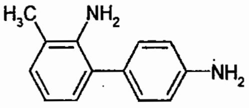


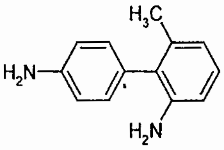
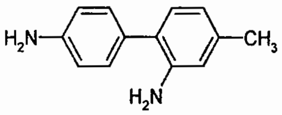
and



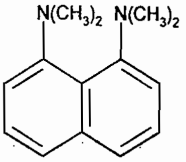
(a)  and 

(b)  and 

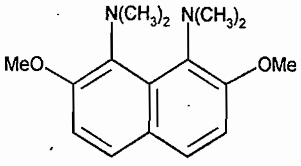
(c)  and 

(d)  and 

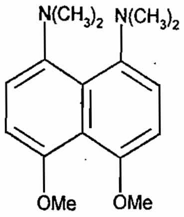
28) The increasing order of basicity among the following is **(GATE 2007)**



(X)



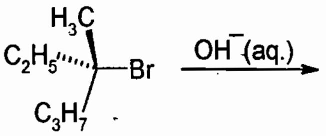
(Y)



(Z)

(a) Y< X< Z (b) Y< Z< X (c) X< Z< Y (d) X< Y< Z

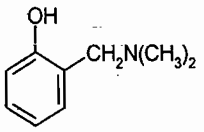
29) In the reaction if the concentration of both the reactants is doubled, then the rate of the reaction will **(GATE 2007)**

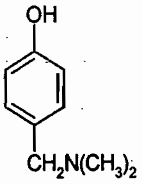


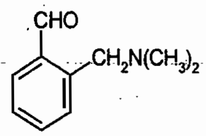
(a) remain unchanged (b) quadruple

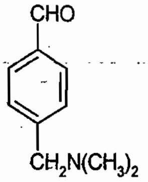
(c) reduce to one fourth (d) double

30) Phenol on reaction with formaldehyde and dimethyl amine mainly gives **(GATE 2007)**

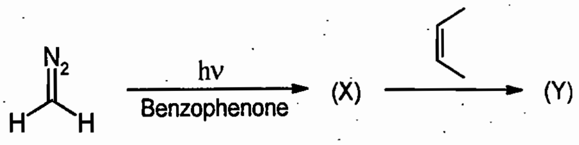
(a) 

(b) 

(c) 

(d) 

31) In the following reaction (X) and (Y) respectively are **(GATE 2007)**



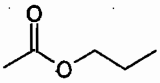
(a) 1:CH$_2$ and cis 1,2 dimethylcyclopropane

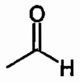
(b) ^{3}:CH$_2$ and cis 1,2 dimethylcyclopropane

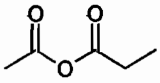
(c) ^{1}:CH$_2$ and a mixture of cis / trans 1,2 dimethylcyclopropane

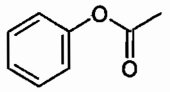
(d) ^{3}:CH$_2$ and a mixture of cis / trans 1,2 dimethylcyclopropane

32) The compound which on reacting with aniline will NOT form an acetanilide is ***(GATE 2007)***

(a)


(b)


(c)


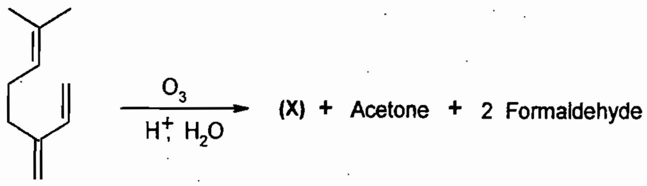
(d)


33) Aniline can be distinguished from methylamine by its reaction with ***(GATE 2007)***

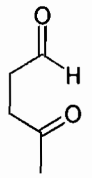
(a) p-toluene sulphonyl chloride / KOH
(b) (i) $NaNO_2/HCl, 0{-}5^0C$ ii) alkaline β naphthol
(c) Sn / HCl
(d) acetyl chloride

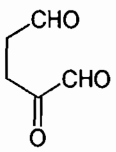
Linked answer questions 34 & 35

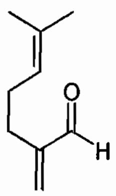
In the reaction ***(GATE 2007)***



34) Compound (X) is

(a)


(b)


(c)


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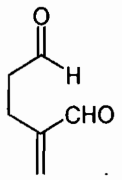
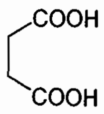
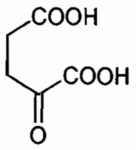
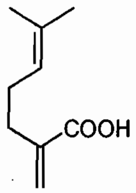
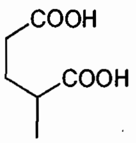


35) Oxidation of X with chromic acid chiefly gives

(a)


(b)


(c)


(d)


36) The order of stability for the following cyclic olefins is ***(GATE 2008)***


I

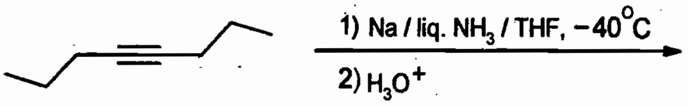

II

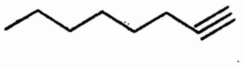

III


IV

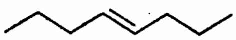
(a) I < II < III < IV (b) II < III < IV < I (c) II < III < I < IV (d) IV < II < I < III

37) The major product of the following reaction is ***(GATE 2008)***



(a)


(b)


(c)


(d)

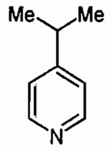

38) In the carbylamine reaction, R–X is converted to R–Y *via* the intermediate Z. R–X, R–Y and Z, respectively, are ***(GATE 2008)***

(a) $R-NH_2$, R–NC, carbene (b) $R-NH_2$, R–NC, nitrene

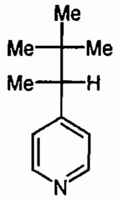
(c) R–NC, $R-NH_2$, carbene (d) R–OH , R–NC , nitrene

39) The compound that is NOT oxidized by $KMnO_4$ is ***(GATE 2008)***

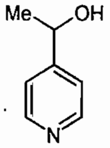
(a)



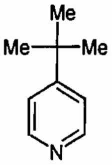
(b)



(c)



(d)



40) The Hammett reaction constant ρ is based on ***(GATE 2008)***

(a) the rates of alkaline hydrolysis of substituted ethyl benzoates

(b) the dissociation constants of substituted acetic acids

(c) the dissociation constants of substituted benzoic acids

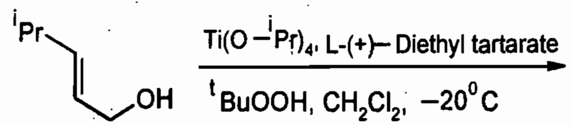
(d) the dissociation constants of substituted phenols

41) Schrock carbenes are ***(GATE 2008)***

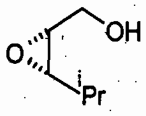
(a) triplets and nucleophilic (b) triplets and electrophilic

(c) singlets and nucleophilic (d) singlets and electrophilic

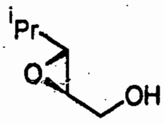
42) The major product of the following reaction is ***(GATE 2008)***



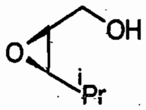
(a)



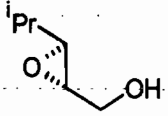
(b)



(c)



(d)



43) *o*-Bromophenol is readily prepared from phenol using the following conditions ***(GATE 2008)***

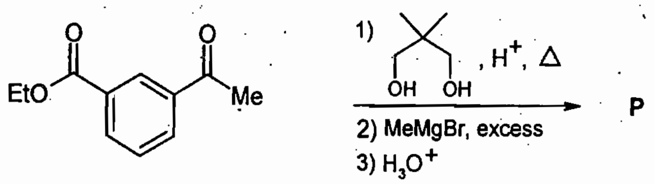
(a) i) $(CH_3CO)_2O$; ii) Br_2 iii) $HCl-H_2O$, Δ

(b) i) H_2SO_4, 100^0C ii) Br_2 iii) H_3O^+, 100^0C

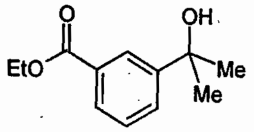
(c) N-Bromosuccinimide, dibenzoyl peroxide, CCl_4, Δ

(d) $Br_2/FeBr_3$

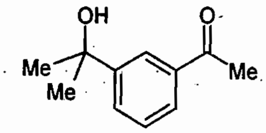
44) The major product P of the following reactions is *(GATE 2008)*



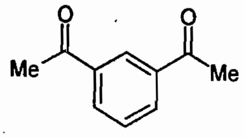
(a)



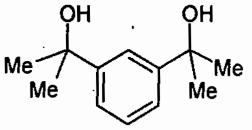
(b)



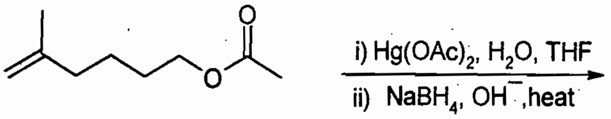
(c)



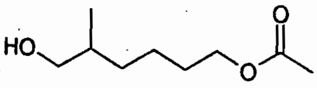
(d)



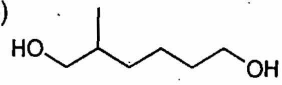
5) The major product of the following reactions is *(GATE 2008)*



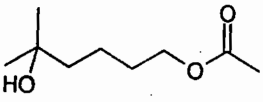
(a)



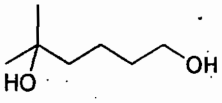
(b)



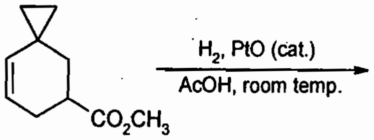
(c)



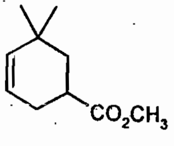
(d)



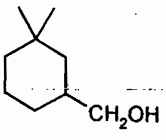
) The major product of the following reaction is *(GATE 2008)*



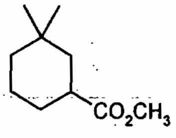
(a)



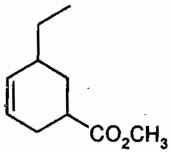
(b)



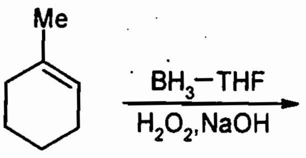
(c)



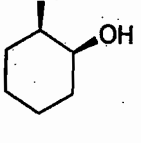
(d)



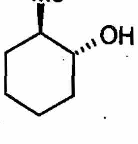
) The major product of the following reactions is *(GATE 2008)*



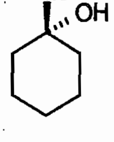
(a)



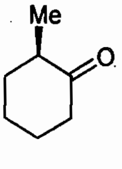
(b)



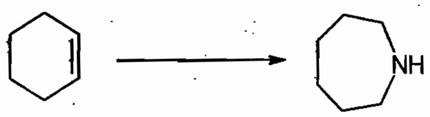
(c)



(d)



48) The most appropriate sequence of reactions for carrying out the following transformation is *(GATE 2008)*



(a) i) O_3/H_2O_2; ii) excess $SOCl_2$/pyridine; iii) excess NH_3; iv) $LiAlH_4$,

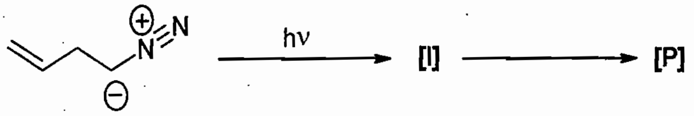
(b) i) O_3/Me_2S; ii) excess $SOCl_2$/pyridine; iii) $LiAlH_4$; iv) excess NH_3,

(c) i) O_3/H_2O_2; ii) excess $SOCl_2$/pyridine; iii) $LiAlH_4$; iv) excess NH_3,

(d) i) O_3/Me_2S; ii) excess $SOCl_2$/pyridine; iii) excess NH_3; iv) $LiAlH_4$.

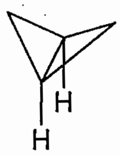
Linked answer questions 49 & 50

In the following reaction, *(Linked que.)* *(GATE 2008)*

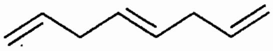


49) The reactive intermediate I and the product P are

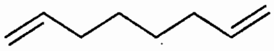
(a) carbene and



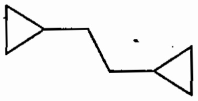
(b) radical and



(c) carbene and



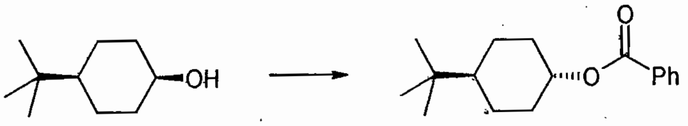
(d) radical and



50) The product P shows 'm' and ' n' number of signals in ^1H and ^{13}C NMR spectra, respectively. The values of 'm' and 'n' are

(a) m = 3 and n = 2 (b) m = 2 and n = 3 (c) m = 2 and n = 2 (d) m = 4 and n = 3

51) The most suitable reagent combination to bring out the following transformation *[GATE 2009]*



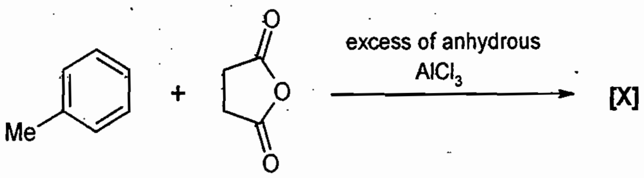
(a) PhCOCl and pyridine

(b) DCC and PhCOOH

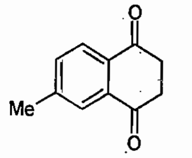
(c) PhBr, CO and $Pd(PPh_3)_4$

(d) EtOOC–N=N–COOEt, PPh_3 and PhCOOH

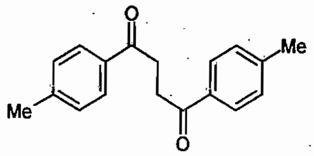
52) In the reaction the major product X is *[GATE 2009]*



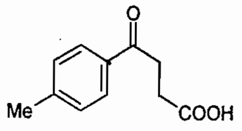
(a)



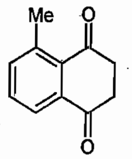
(b)



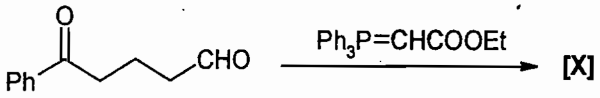
(c)



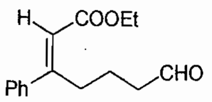
(d)



53) In the reaction the major product X is **[*GATE 2009*]**



(a)



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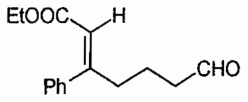

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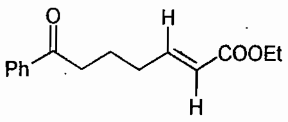
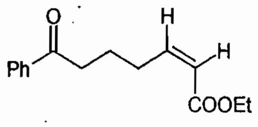
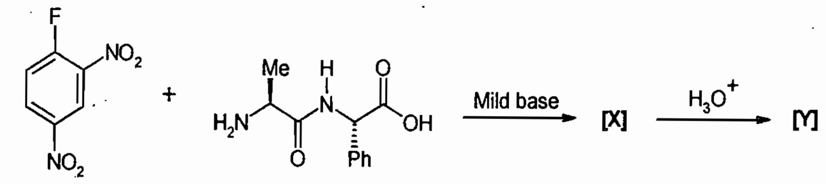


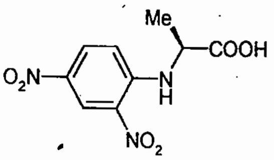
(d)



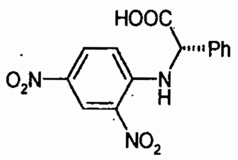
54) In the two steps reaction sequence the major product Y is **[*GATE 2009*]**



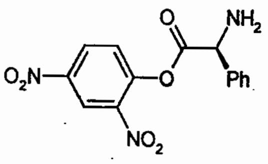
(a)



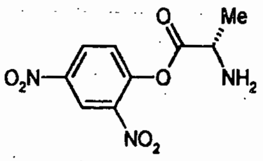
(b)



(c)



(d)



55) In the reaction the compounds X and Y, respectively, are **[*GATE 2009*]**

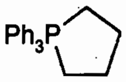
$$Ph_3P \xrightarrow{MeI} [X] \xrightarrow{n-BuLi} [Y]$$

(a) $[Ph_3P(Me)]$ [I] ; $Ph_3P{=}CHCH_2CH_2CH_3$

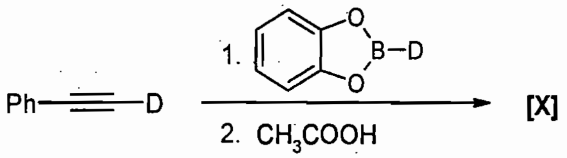
(b) $[Ph_3P(Me)]$ [I] ; $Ph_3P{=}CH_2$

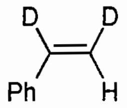
(c) $[Ph_3P(Me)_2]$; $Ph_3P{=}CH_2$

(d) $[Ph_3P(Me)]$ [I] ;



56) In the reaction the major product X is **[*GATE 2009*]**



(a)


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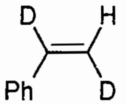

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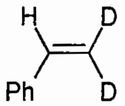

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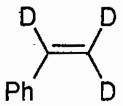
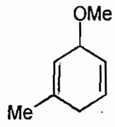


57) Reaction of m-methylanisole with lithium in liquid ammonia and *t*-butyl alcohol at -33°C generates compound X as the major product. Treatment of the compound X with dilute sulphuric acid producescompound Y as the major product. The compounds X and Y, respectively, are **[*GATE 2009*]**

(a)


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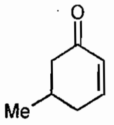

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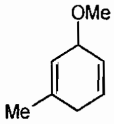

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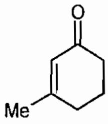

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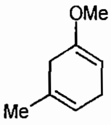

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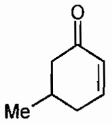

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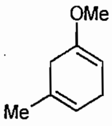
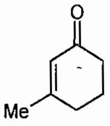
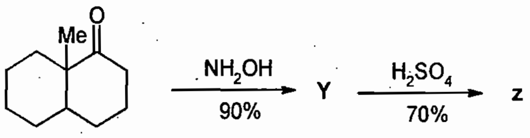


and

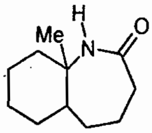


58) In the reaction sequence **[*GATE 2009*]**

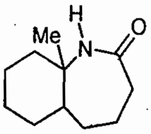


X

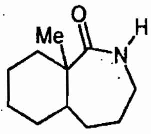
the structure of the major product Z and the overall yield for its formation from the ketone X, are

(a)


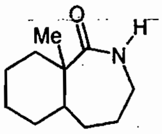
and 80%

(b)


and 63%

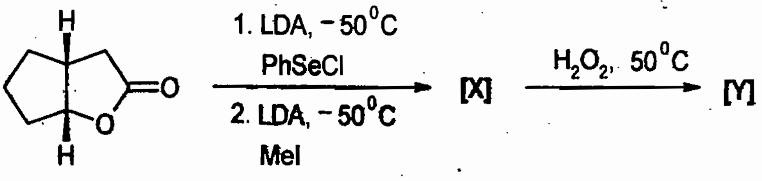
(c)


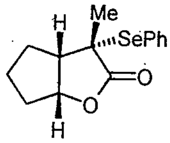
and 63%

(d)


and 80%

59) In the reaction sequence the major products X and Y, respectively, are **[*GATE 2009*]**





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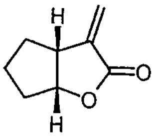
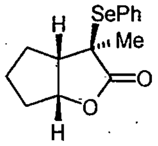


(b)



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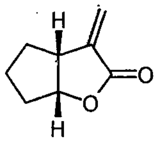

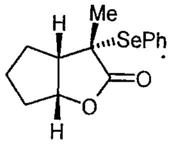

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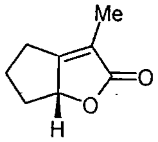
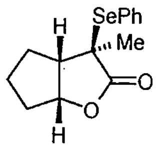


(d)



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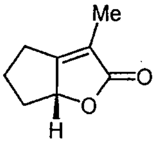
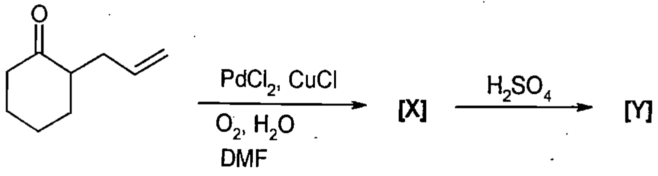
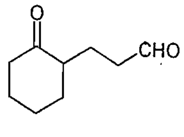


In the reaction sequencethe major products X and Y, respectively, are **[*GATE 2009*]**



(a)



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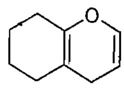
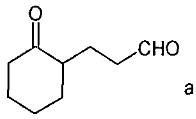
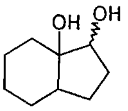


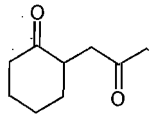
(b)



and



(c)



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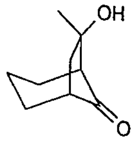

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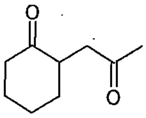

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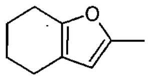
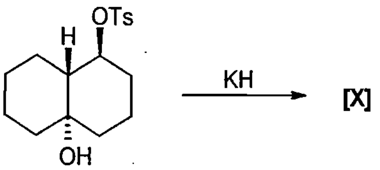
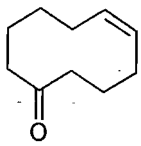


The major product X (based on the preferred conformation) in the reaction is **[*GATE 2009*]**

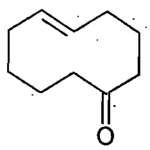


(Ts = p-toluenesolfonyl)

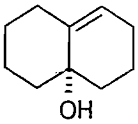
(a)



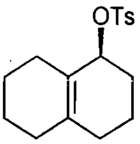
(b)



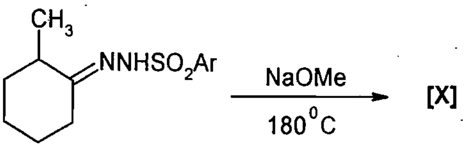
(c)



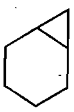
(d)



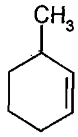
In the following reaction the major product [X] is **[*GATE 2010*]**



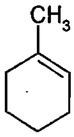
a)



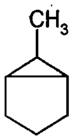
(b)



(c)



(d)



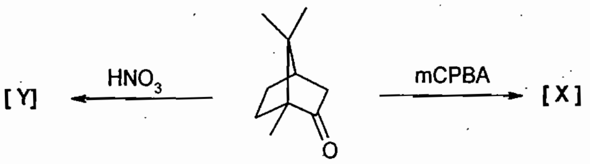
63) The decreasing order of nucleophility for the following anions is **[*GATE 2010*]**

CH_3COO^-, CH_3O^-, $C_6H_5O^-$, NO_3^-

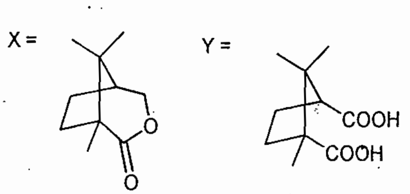
(a) $CH_3COO^- > CH_3O^- > C_6H_5O^- > NO_3^-$ (b) $CH_3O^- > NO_3^- > C_6H_5O^- > CH_3COO^-$

(c) $CH_3O^- > C_6H_5O^- > CH_3COO^- > NO_3^-$ (d) $C_6H_5O^- > CH_3O^- > NO_3^- > CH_3COO^-$

64) The major products X and Y formed in the following reaction sequence are **[*GATE 2010*]**



(a)



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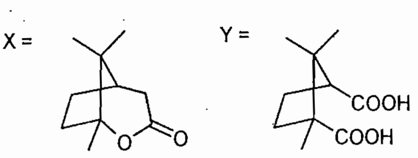

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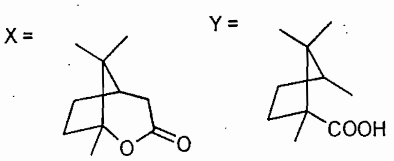
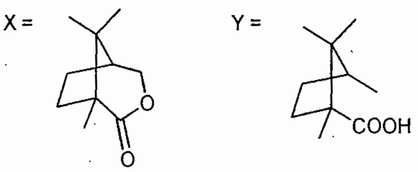
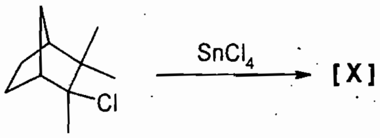


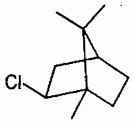
(d)



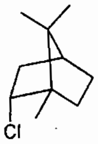
65) In the following reaction the major product [X] is **[*GATE 2010*]**



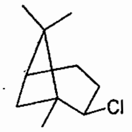
(a)



(b)

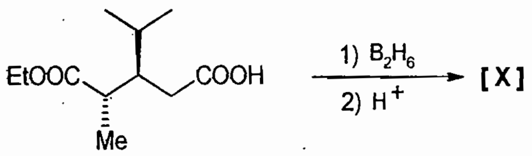


(c)

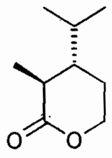


(d)

66) In the following reaction the major product [X] is **[*GATE 2010*]**



(a)



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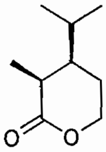

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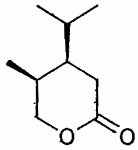
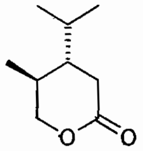
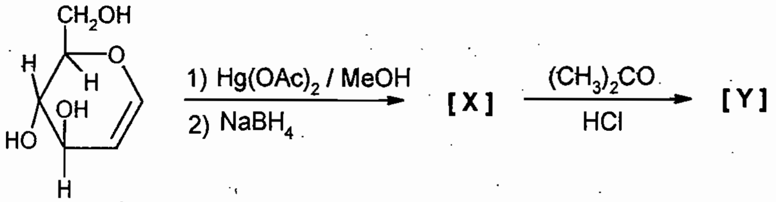
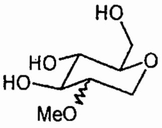


(d)



’) The major products X and Y formed in the following reaction sequence are **[*GATE 2010*]**



)


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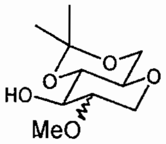
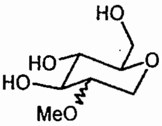
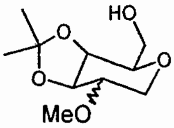


(b)


and


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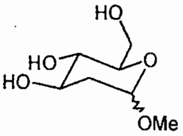

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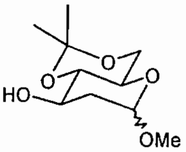
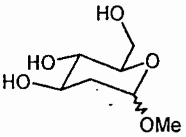


(d)


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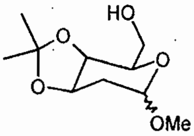
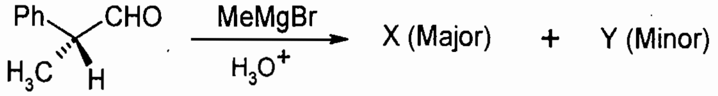
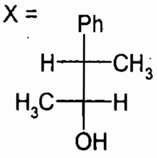
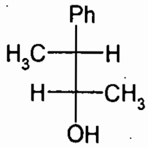


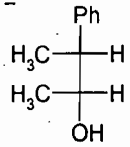
inked answer questions 68 & 69

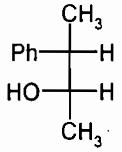
8) The major product X formed in the following reaction is **[*GATE 2010*]**



(a) X =


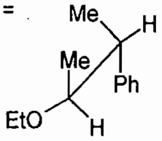
(b) X =


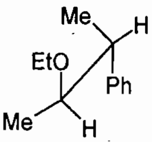
(c) X =


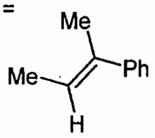
(d) X =


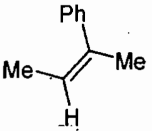
9) The compound [Z] is

$$[X] \xrightarrow[\text{2) NaOEt / EtOH}]{\text{1) TsCl / Py}} [Z]$$

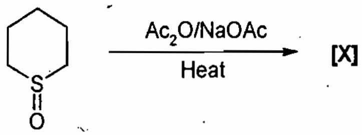
(a) Z =


(b) Z =


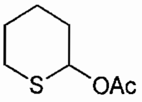
(c) Z =


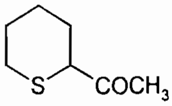
(d) Z =


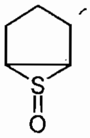
’0) In the following reaction the major product [X] is **(*GATE 2011*)**



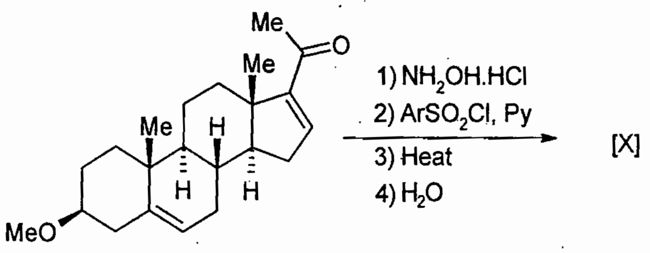
(a)


(b)


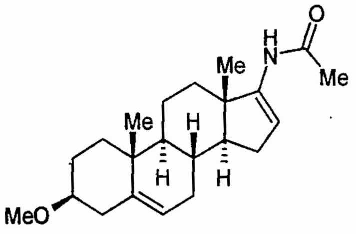
(c)


(d)


71) In the following reaction sequence the major product [X] is ***(GATE 2011)***



(a)



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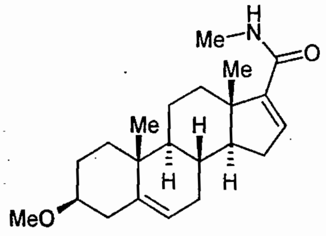

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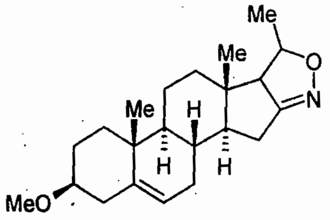
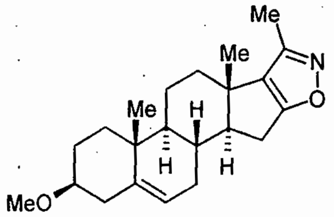
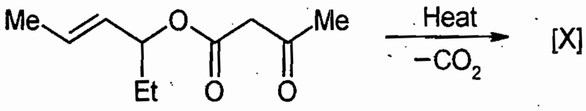


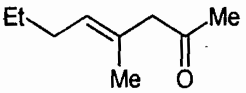
(d)



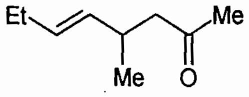
72) In the following reaction the major product [X] is ***(GATE 2011)***



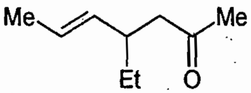
(a)



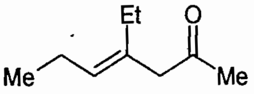
(b)



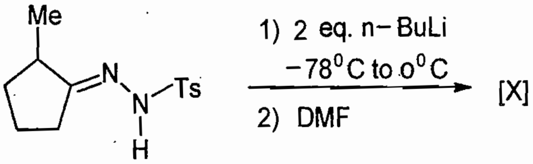
(c)



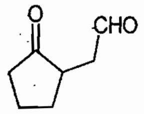
(d)



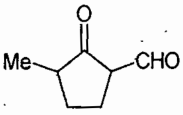
73) In the following reaction the major product [X] is ***(GATE 2011)***



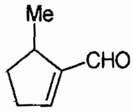
(a)



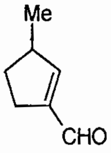
(b)



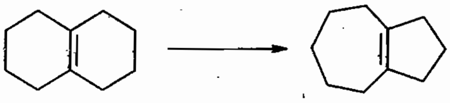
(c)



(d)



74) The most appropriate sequence of reactions for carrying out the following conversion is ***(GATE 2011)***



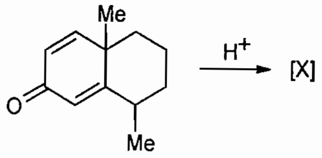
(a) (i) Peracid; (ii) H^+; (iii) Zn / dil. HCl

(b) (i) Alkaline $KMnO_4$; (ii) $NaIO_4$; (iii) N_2H_4 / KOH

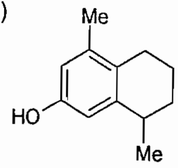
(c) (i) Alkaline $KMnO_4$; (ii) H^+; (iii) Zn / dil. HCl

(d) (i) O_3 / Me_2S; (ii) NaOEt; (iii) N_2H_4 / KOH

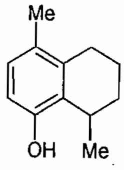
75) In the following reaction the major product [X] is ***(GATE 2011)***



(a)



(b)



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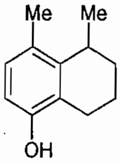
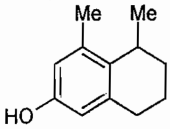
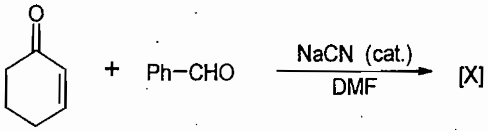


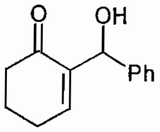
(d)



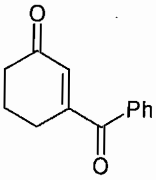
76) In the following reaction the major product [X] is ***(GATE 2011)***



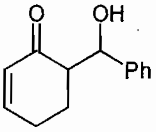
(a)



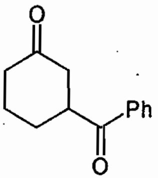
(b)



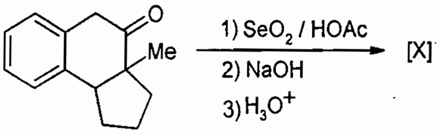
(c)



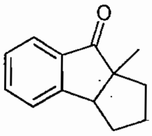
(d)



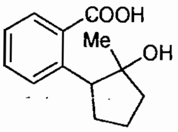
77) In the following reaction the major product [X] is ***(GATE 2011)***



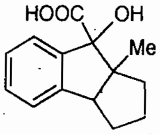
(a)



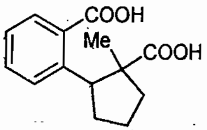
(b)



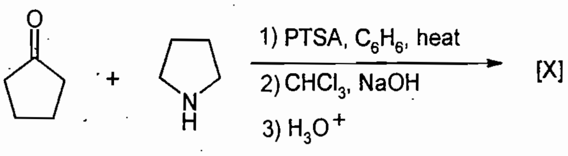
(c)



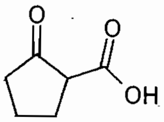
(d)



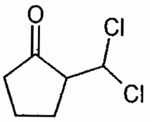
78) In the following reaction the major product [X] is ***(GATE 2011)***



(a)



(b)



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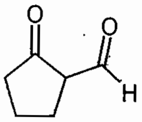
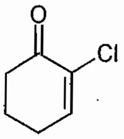
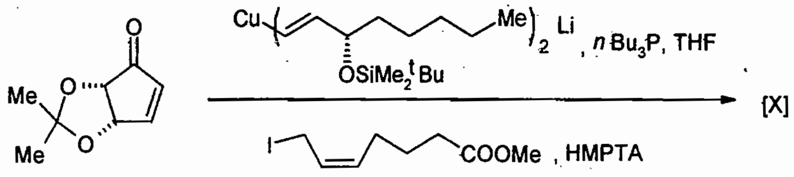


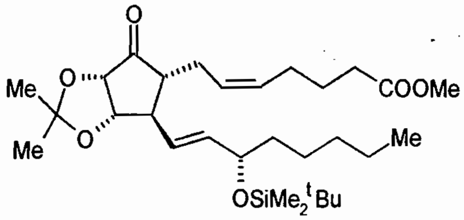
(d)



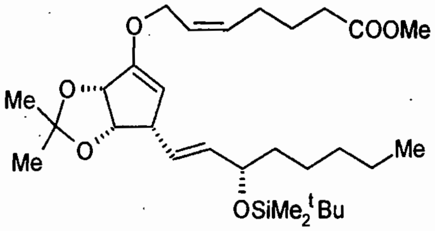
79) In the reaction the major product [X] is ***(GATE 2011)***



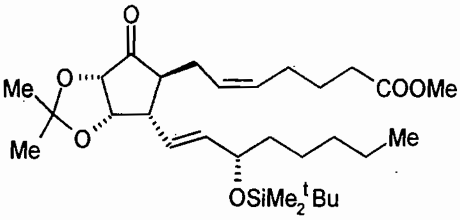
(a)



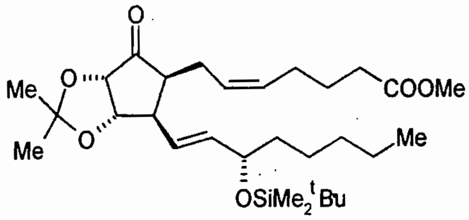
(c)



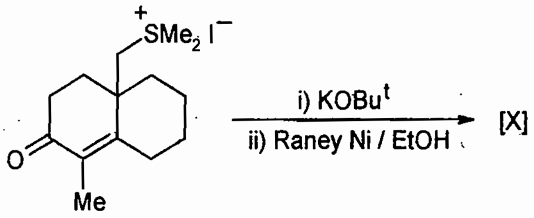
(b)



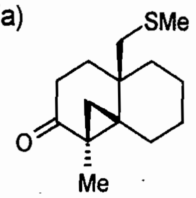
(d)



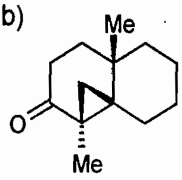
80) In the reaction the major product [X] is ***(GATE 2011)***



(a)



(b)



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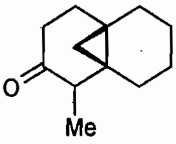

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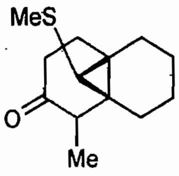
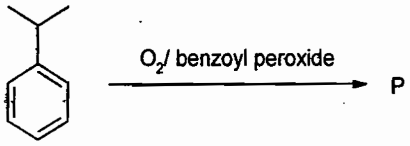
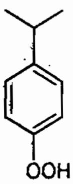


81) Identify the most probable product in the given reaction ***[GATE 2012]***



(a)



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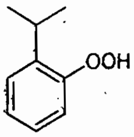

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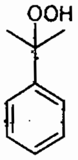
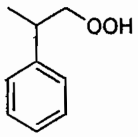
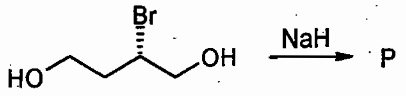
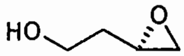


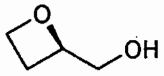
(d)

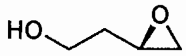


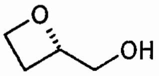
82) In the cyclization reaction given below, the most probable product formed is ***[GATE 2012]***



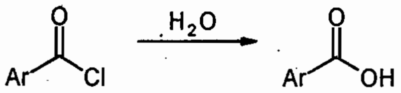
(a)


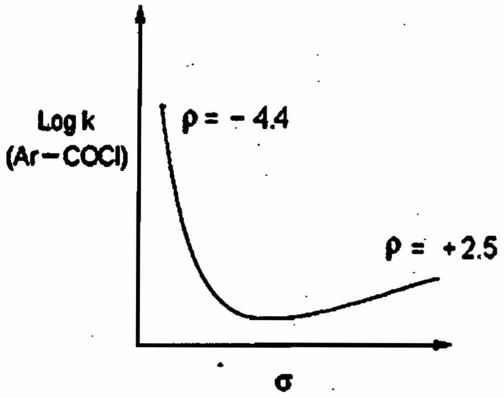
(b)


(c)


(d)


83) Shown below is a Hammett plot obtained for the reaction ***[GATE 2012]***





The change in slope of the plot indicates that

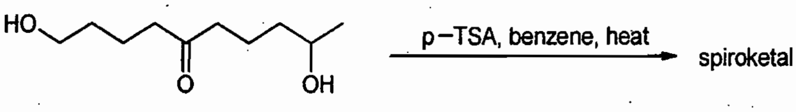
(a) the reaction does not follow linear free energy relationship

(b) electrons are being withdrawn from the transition state in the mechanism

(c) electrons are being donated to the transition state in the mechanism

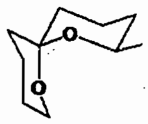
(d) the mechanism of the reaction is changing

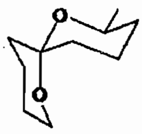
84) The acid catalyzed cyclization of 5−ketodecan−1,9−diol is given below ***[GATE 2012]***

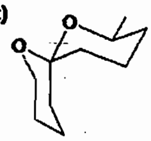


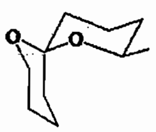
(p−TSA, = p−toluenesulfonic acid)

The most predominant spiroketal is

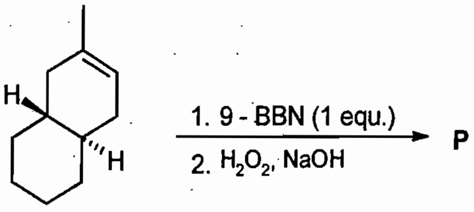
(a)


(b)


(c)


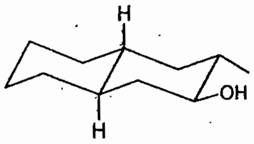
(d)


85) Identify the product from the following reaction ***[GATE 2012]***

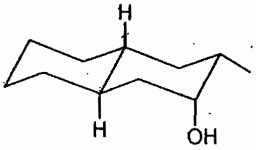


(BBN = 9−Borabicyclo[3•3•1]nonane)

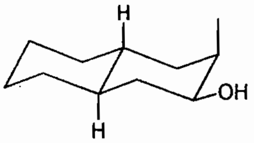
(a)



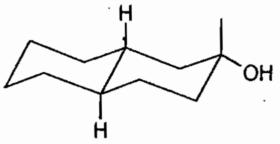
(b)



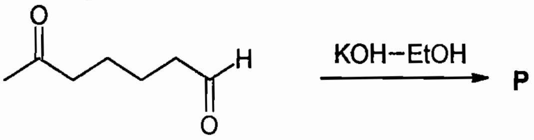
(c)



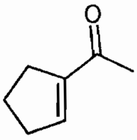
(d)



86) Identify the product from the following reaction *[GATE 2012]*



(a)



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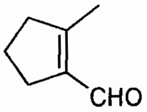
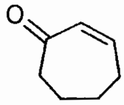
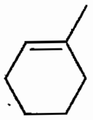


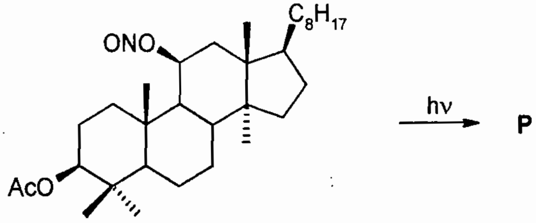
(c)



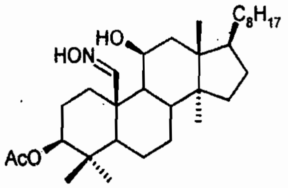
(d)



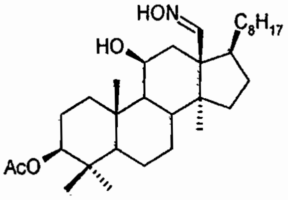
87) Identify the product from the following reaction *[GATE 2012]*



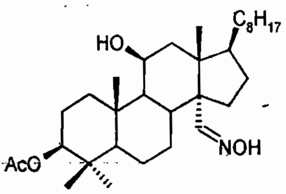
(a)



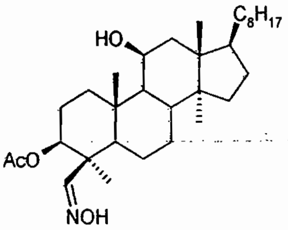
(b)



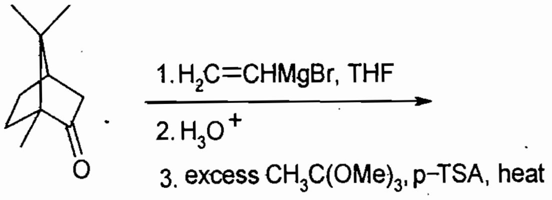
(c)



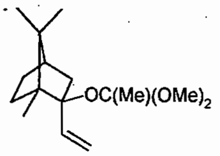
(d)

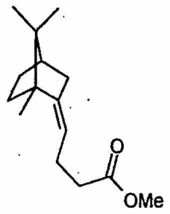


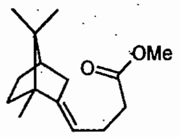
88) In the reaction given below, identify the product *[GATE 2012]*

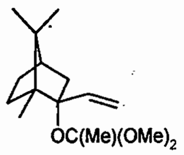


(*p*–TSA = p– toluenesulfonic acid; THF = tetrahydrofuran)

(a)


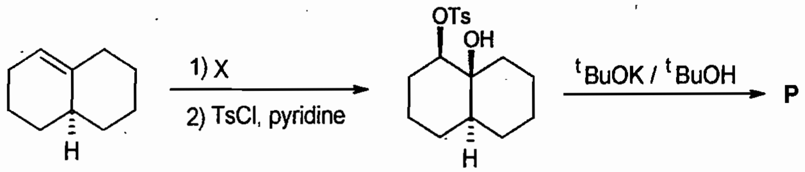
(b)


(c)


(d)


Common Data for Questions (Linked question 89 & 90

Consider the reaction sequence shown below: ***[GATE 2012]***

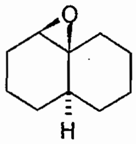


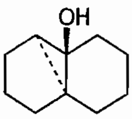
TsCl = p−toluenesulfonyl chloride

89) The oxidant X used in step 1 is

(a) CrO_3 (b) OsO_4 (c) $NaIO_4$ (d) *m*-CPBA followed by NaOH

90) The product is

(a)


(b)


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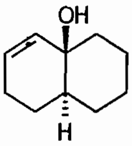
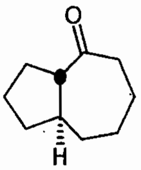
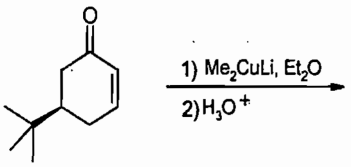


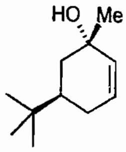
(d)


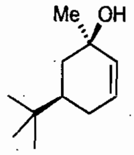
91) Among the compounds given in the options A-D, the one that can be used as a *formyl anion equivalent* (in the presence of a strong base) is ***[GATE 2013]***

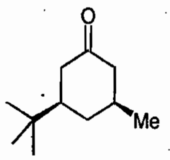
(a) ethylene (b) nitroethane (c) 1,3-dithiane (d) 1,4-dithiane

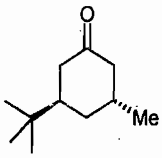
92) The major product formed in the reaction given below is ***[GATE 2013]***



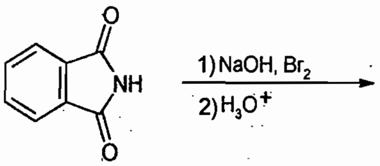
(a)


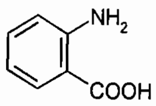
(b)


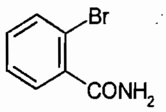
(c)


(d)


93) The major product formed in the reaction given below is ***[GATE 2013]***



(a)


(b)


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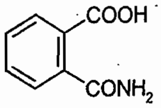
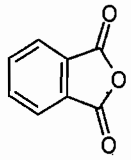
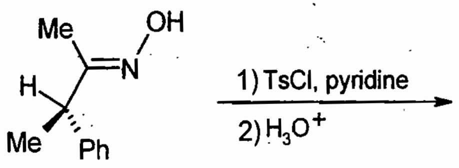
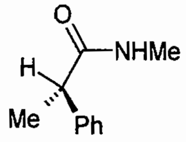


(d)


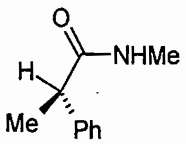
94) The major product formed in the Beckmann rearrangement of the compound given below is ***[GATE 2013]***



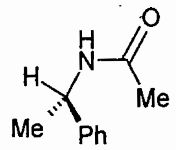
(a)



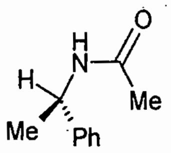
(b)



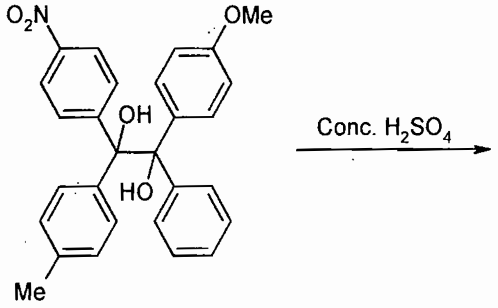
(c)



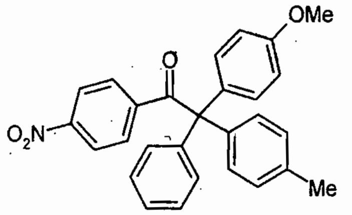
(d)



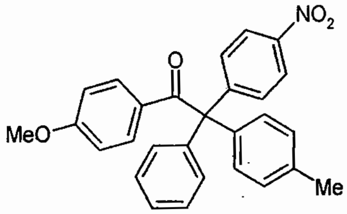
95) The major product formed in the reaction given below is ***[GATE 2013]***



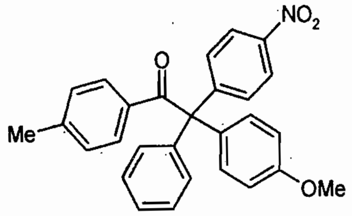
(a)



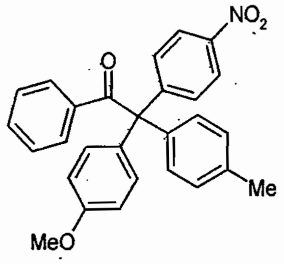
(b)



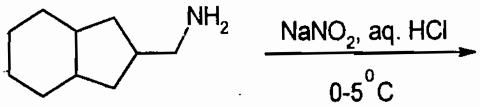
(c)



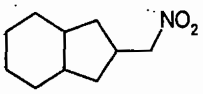
(d)



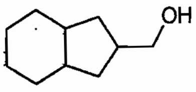
96) The major product formed in the reaction given below is ***[GATE 2013]***



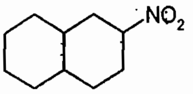
(a)



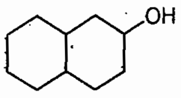
(b)



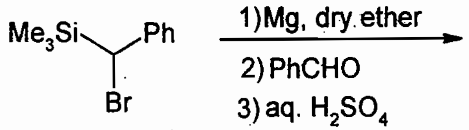
(c)

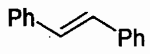
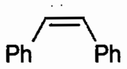


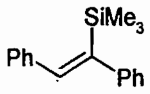
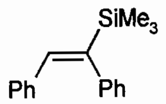
(d)

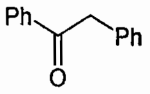


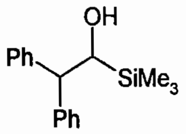
97) The major product(s) formed in the reaction sequence given below is (are) ***[GATE 2013]***



(a)  and 

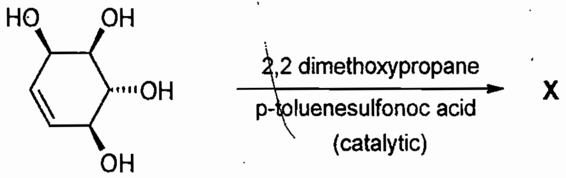
(b)  and 

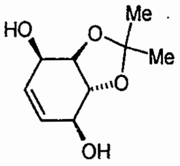
(c) 

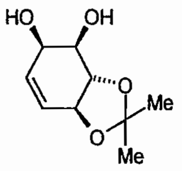
(d) 

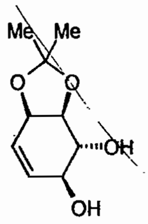
Linked Answer Questions 98 & 99:

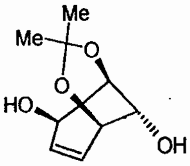
98) The major product X formed in the reaction given below is ***[GATE 2013]***



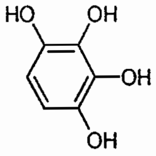
(a) 

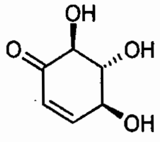
(b) 

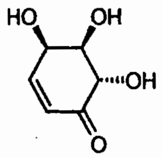
(c) 

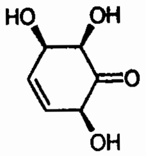
(d) 

99) Oxidation of the product X, obtained in the above reaction, with active manganese dioxide, followed by acidic hydrolysis gives ***[GATE 2013]***

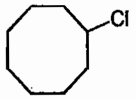
(a) 

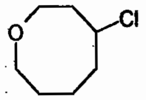
(b) 

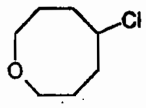
(c) 

(d) 

100) The correct order of the rate of solvolysis for the following chlorides in acetic acid is ***[GATE 2014]***

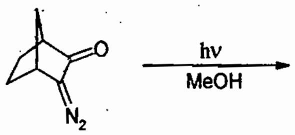

I


II

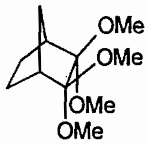

III

(a) II > I > III (b) III > II > I (c) III > I > II (d) I > III > II

101) The product of the following reaction gave 6 line ^{13}C NMR spectrum with peaks at δ 175, 52, 50, 46, 37, 33 ppm. The structure of the product is ***[GATE 2014]***



(a)



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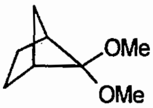

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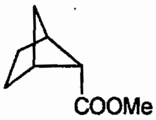
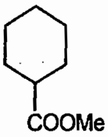
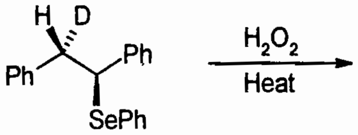


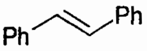
(d)



102) The major product formed in the following reaction is ***[GATE 2014]***



(a)



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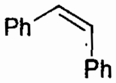

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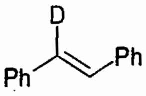

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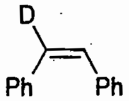
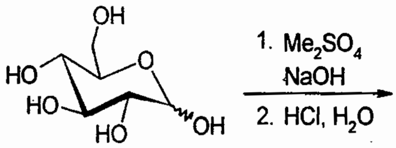
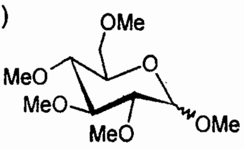


103) The major product formed in the following reaction is ***[GATE 2014]***



(a)



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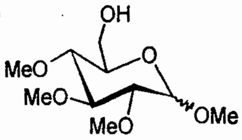

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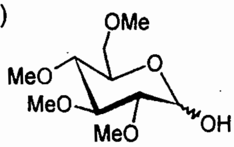

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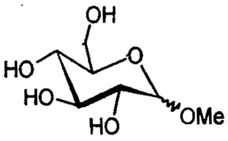
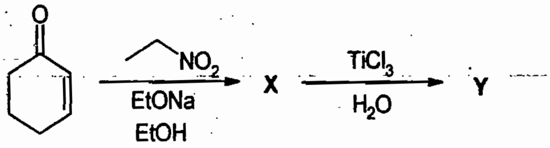
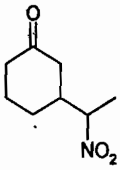


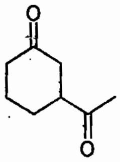
104) The major products X and Y formed in the following reaction sequence are ***[GATE 2014]***



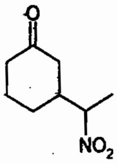
(a) X =



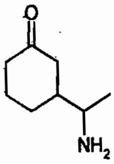
Y =



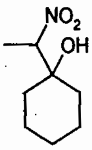
(b) X =



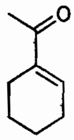
Y =



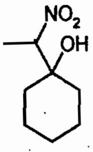
(c) X =



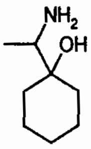
Y =



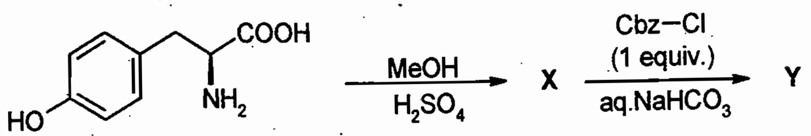
(d) X =



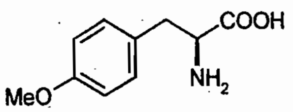
Y =



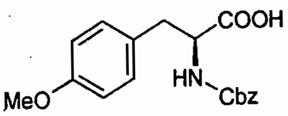
105) The major products X and Y formed in the following reaction sequence are **[GATE 2014]**



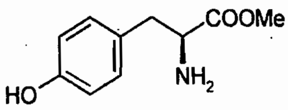
(a) X =



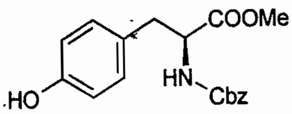
Y =



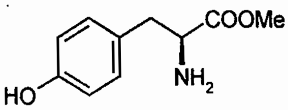
(b) X =



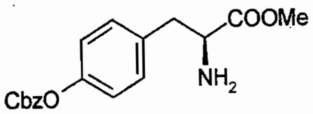
Y =



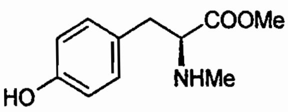
(c) X =



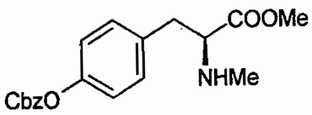
Y =



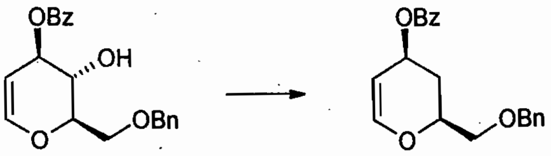
(d) X =



Y =



106) The most suitable reagent combination to effect the following conversion is **[GATE 2014]**



(a) i. NaH, CS_2, then MeI; ii. Bu_3SnH, AIBN, C_6H_6, reflux

(b) i. I_2, PPh_3, imidazole; ii. H_2, 10% Pd-C, AcOH, high pressure

(c) i. Me_3SiCl, pyridine, DMAP; ii. Bu_3SnH, AIBN, C_6H_6, reflux

(d) i. MsCl, pyridine, DMAP; ii. $LiAlH_4$, THF, reflux

Answer Key

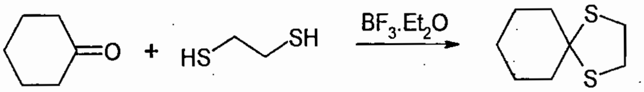
NET EXAM (TWO MARKS)

- **Topic- Organic Reaction Mechanism (ORM, Reagents, Rearrangements & Name Reactions)**

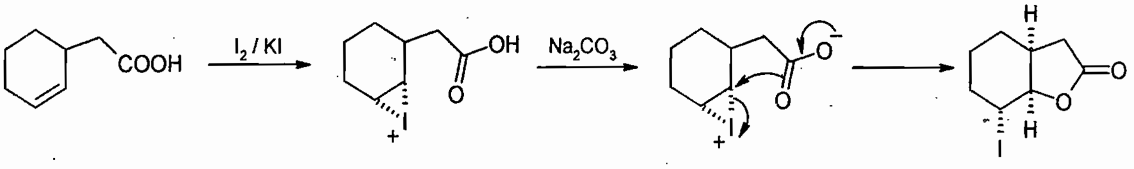
1	a	2	a	3	d	4	d	5	c	6	d	7	d	8	a	9	b	10	c
11	c	12	c	13	a	14	a	15	b	16	b	17	d	18	a	19	d	20	b
21	d	22	b	23	a	24	c	25	a	26	d	27	d	28	b	29	c	30	d
31	b	32	a	33	c	34	b	35	d	36	b	37	d	38	b	39	b	40	a
41	d	42	c	43	c	44	c	45	c	46	a	47	c	48	c	49	c	50	a

Hint & solution of Questions with two marks (NET EXAM)

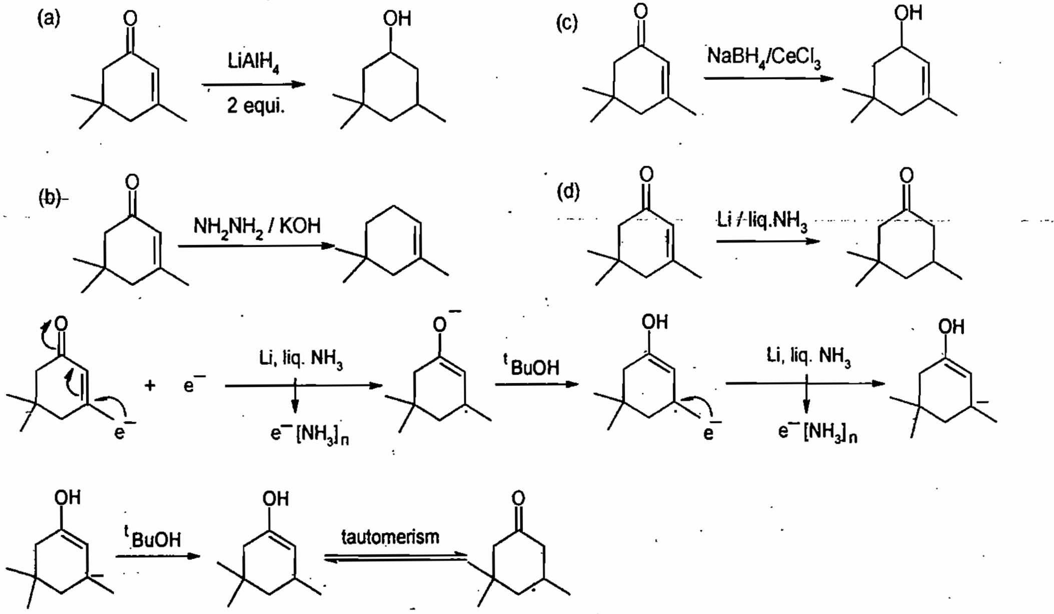
1) Ans (a):- A Lewis acid (BF_3) is usually needed rather than a protic acid for bringing out the following transformation.



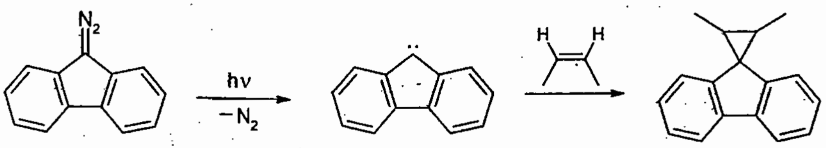
2) Ans (a):- One side of the alkene is sterically hindered by the carboxyl group. Therefore, I_2 will add to the other side of the double bond, forming a iodonium ion. We know that in the second step of the addition reaction, a nucleophile (in this case the carbonyl oxygen) will attack the iodonium ion.
The carbonyl oxygen is attack the back side of the iodonium ion, resulting in a compound with the observed configuration.



3) Ans (d):- Li/liq.NH_3 is used to reduce the C–C double bond in α,β– unsaturated aldehydes and ketones.

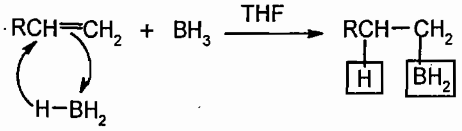


4) Ans (d):- Photolysis of diazo compound gives carbene which reacts with alkene to give cyclopropane



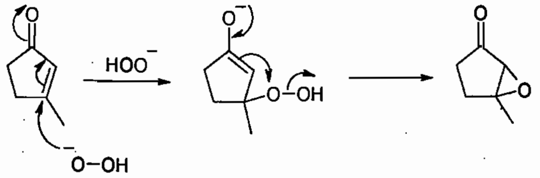
5) Ans (c):- Markovnikov's rule:- When an unsymmetrical reagent add to unsymmetrical alkene the negative part of reagent adds to the sp^2 carbon that is bonded to the less number of hydrogens.

The Boron is less electronegative (2.0) than hydrogen (2.1) so hydrogen must bond to the carbon of the alkene that had fewer hydrogens attached to it. The addition of borane to an alkene is an example of a syn addition. Thus addition of BH_3 to a carbon-carbon double bond is Markovnikov syn addition



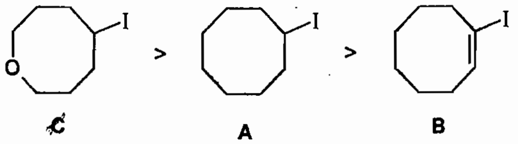
6) Ans (d):- The elimination reactions occur via E_1cB mechanism; when anion-stabilizing (electron withdrawing) group is present at β-carbon

7) Ans (d):- Epoxidation of unsaturated carbonyl compound is achieved by H_2O_2/NaOH

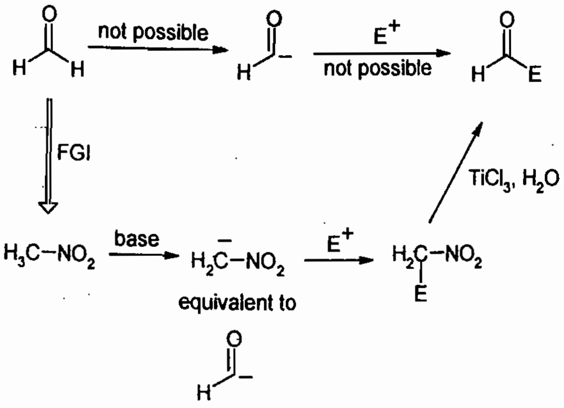


8) Ans (a):- Among A, B & C; C will react faster due to internal nucleophile while among A & B; A will react faster while B do not undergo S_N reaction; because, as the nucleophile approaches the back side of the sp^2 carbon, it is repelled by the π electron cloud of the double bond.

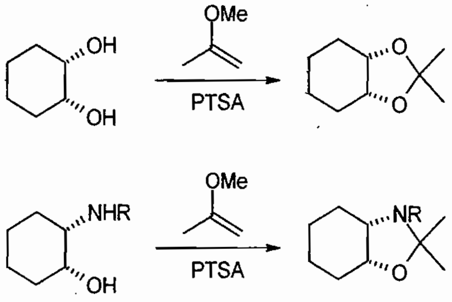
Therefore the relative rates of solvolysis of iodides A-C are C > A > B



9) Ans (b):- The formyl anion equivalent is nitromethane



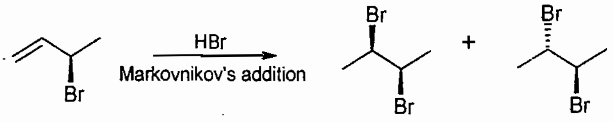
10) Ans (c):- 2-methoxypropene and p-toluenesulfonic acid is a suitable reagent combination for carrying out the following conversion



11) Ans (c):- Markovnikov's addition reaction will give diastereomers.

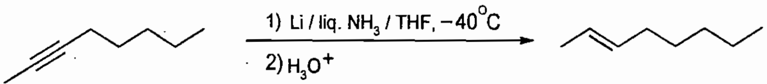
The term Diastereoisomers arises when there are more than one stereocentre.

Diastereoisomers are stereoisomers that are not enantiomers i.e.that are not mirror images.



diastereomers

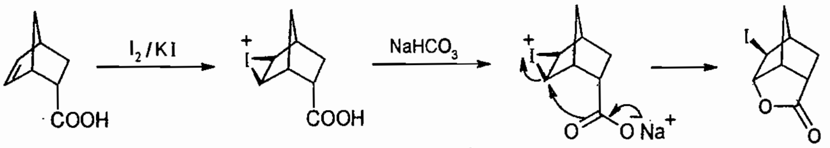
12) Ans (c):- Conversion of 2-octyne into trans-2-octene is partial reduction & is possible by using lithium metal in liquid ammonia; in contrast, reduction of 2-octyne into cis-2-octene is achieved by Lindlar's catalyst



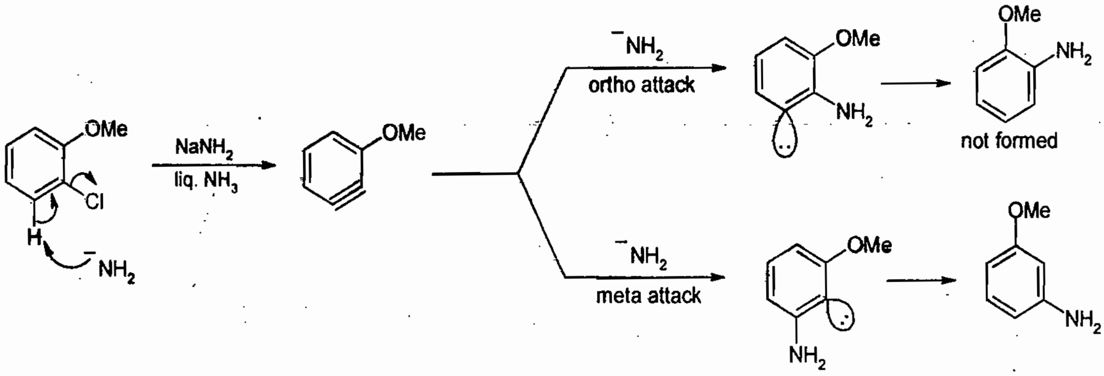
2-octyne

trans-2-octene

13) Ans (a):- Reaction proceed through iodonium ion,



14) Ans (a):- This is an example of nucleophilic aromatic substitution via benzyne intermediate sometimes called as the elimination–addition mechanism. Major product is formed by more stable aryl anion intermediate

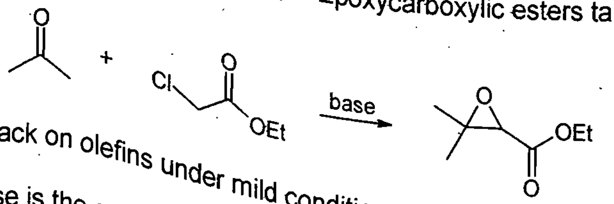


stabilized by -OMe group

15) Ans (b):- At low temperature (−70°C); $LiAlH_4$ only reduces carbonyl group of α,β-unsaturated carbonyl group. Among (a) & (b); (b) is obtained as a major product.

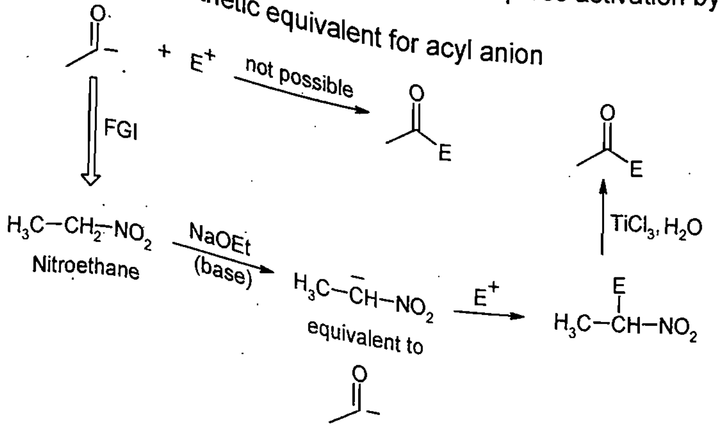
Hint:- The nucleophilic attacks at carbonyl compound take place through Felkin–Anh transition state conformation.

) **Ans (b):-** Darzen's glycidic ester condensation involves the formation of both C-C and C-O bonds. In Darzen's glycidic ester condensation formation of α,β- Epoxycarboxylic esters take place from aldehydes or ketones and α–halo esters.

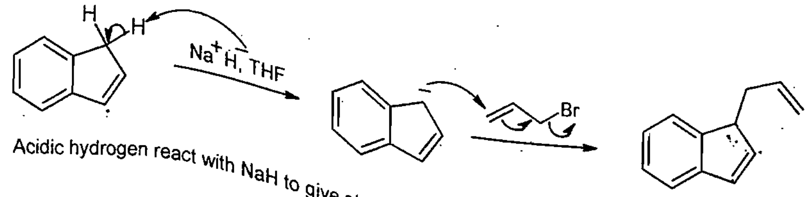


) **Ans (d):-** The nucleophilic attack on olefins under mild conditions requires activation by coordination to metal.

) **Ans (a):-** Nitroethane and base is the synthetic equivalent for acyl anion

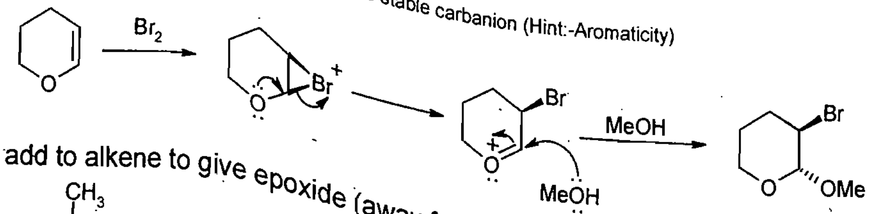


Ans (d):-

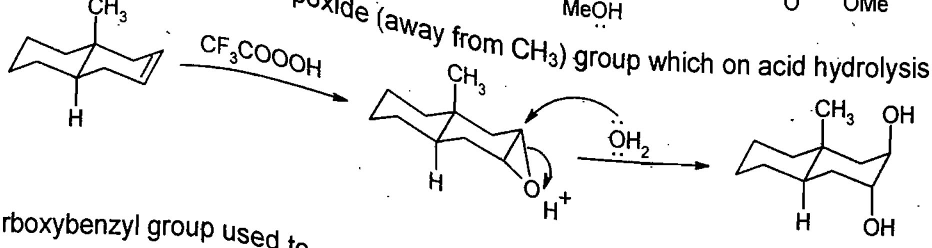


Acidic hydrogen react with NaH to give stable carbanion (Hint:-Aromaticity)

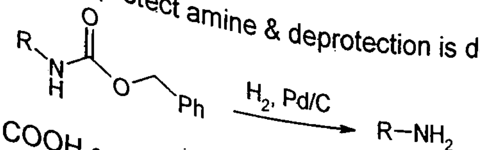
Ans (b):-



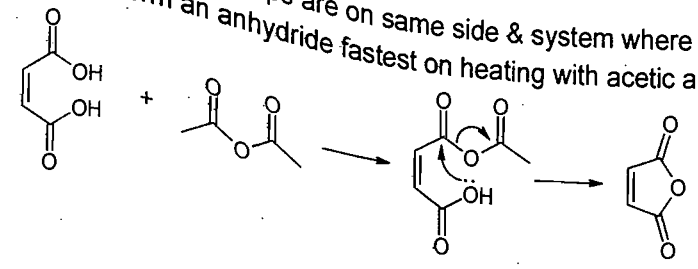
Ans (d):- Peracid add to alkene to give epoxide (away from CH_3) group which on acid hydrolysis gives trans diol.



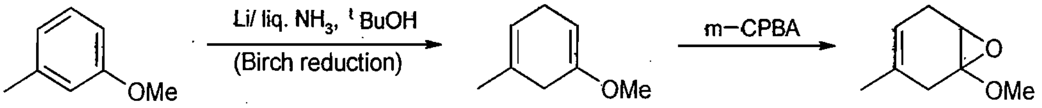
Ans (b):- It is carboxybenzyl group used to protect amine & deprotection is done by HBr or H_2,Pd/C



Ans (a):- The diacids in which both COOH groups are on same side & system where there is a restriction in rotation due to double bond, will form an anhydride fastest on heating with acetic anhydride .



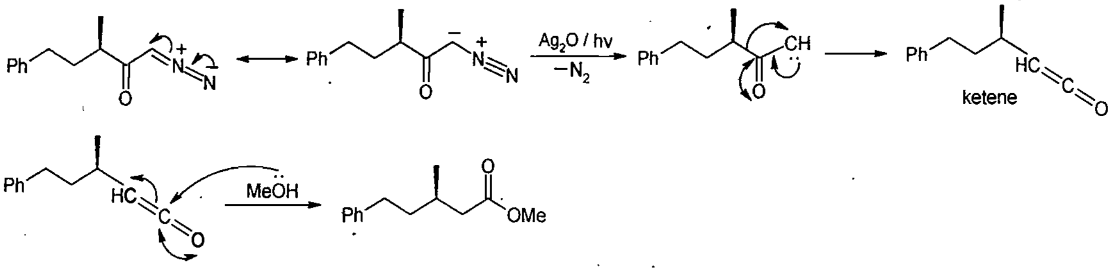
24) Ans (c):- In Birch reduction, 1,4 reduction of aromatic ring occur at ortho & meta position w.r.t. electron donating group (regioselective). In the next step epoxidation of more electron rich alkene take place



1) In Birch reduction1,4 reduction occur at ortho & meta position w.r.t electron donating group

2) Here peracid add to more electron rich alkene

25) Ans (a):- Wolff rearrangement:- Photolysis of diazocarbonyl compounds with a silver(I) salt to form ketene. Ketene on solvolysis gives an ester with one more carbon atom in the chain.

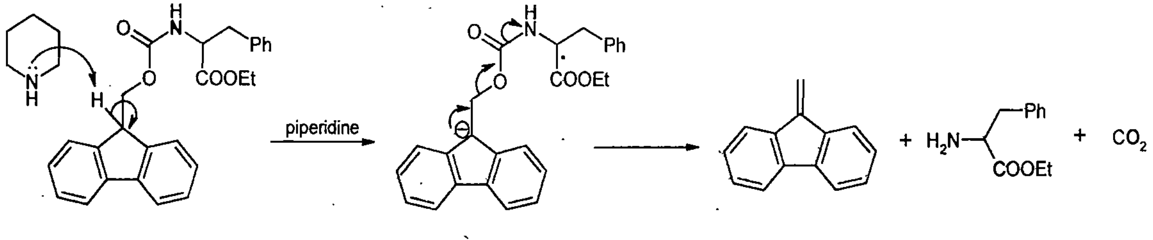


26) Ans (d):- the σ_{para} for methoxy group is – 0.27

σ_{para} = pKa(C_6H_5COOH)- pKa(p-OMe-C_6H_4COOH)

σ_{para} = 4.19- 4.46 = – 0.27

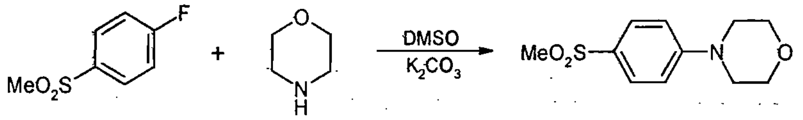
27) Ans (d):-The mechanism involved is E1cb-elimination. (The elimination reactions occur via E_1cB ; when anion-stabilizing (electron withdrawing) group is present at β-carbon)



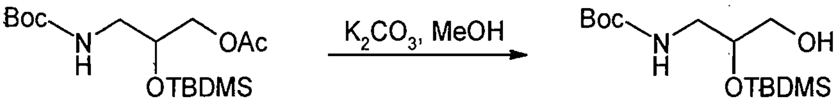
- Aromatic stable carbanion

(Elimination through conjugate base)

28) Ans (b):- A given reaction is aromatic ipso substitution reaction & aromatic nucleophilic substitution. Reaction will follow addition-elimination mechanism.



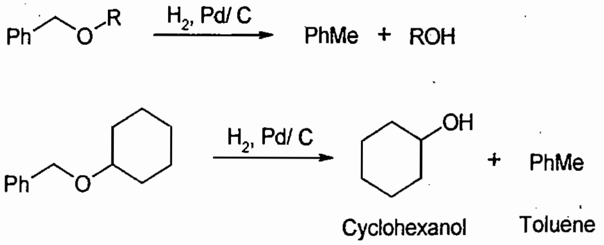
29) Ans (c):- Boc & t-butyl dimethyl silyl ether (R-OTBDMS) are protecting agent for amines & alcohols respectively. Deprotection of Boc is done in acidic condition & R-OTBDMS are usually removed with aqueous acid or fluoride salts, particularly $Bu_4N^+F^-$. So we can only apply K_2CO_3, MeOH for reaction.



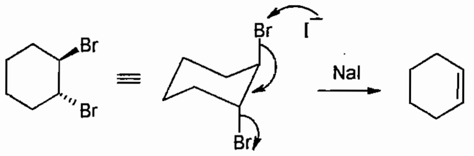
30) Ans (d):- Diels-Alder reaction of furan and maleic acid in water is an example of a "Green Synthesis"

31) Ans (b):- Electron donating groups at ortho/para position promote acid hydrolysis of esters.

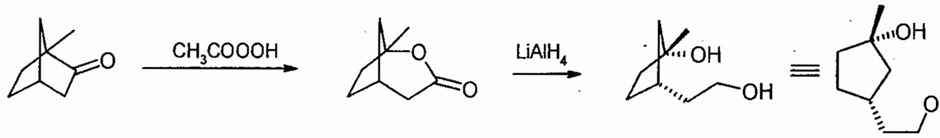
32) Ans (a):- Benzyl ether deprotection is done by catalytic hydrogenation by using 10% Pd/C



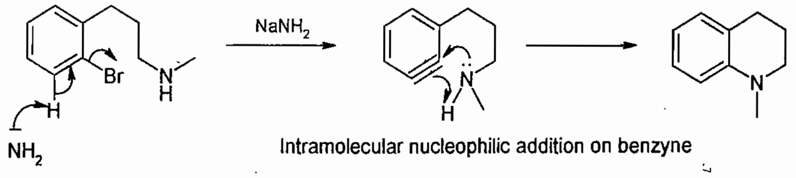
33) Ans (c):- Trans-1,2-dibromocyclohexanes reacts fastest with sodium iodide to give cyclohexene



34) Ans (b):- Baeyer–villiger oxidation of bridged bicyclic ketones to give lactone followed reduction by $LiAlH_4$



35) Ans (d):- an aryne (benzyne)



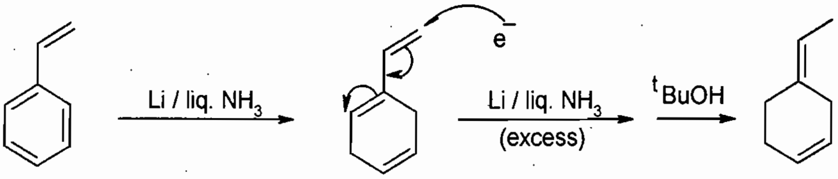
Intramolecular nucleophilic addition on benzyne

36) Ans (b):- The first step is dissociation of Br_2 into $Br^{\bullet}$ radicals

37) Ans (d):-

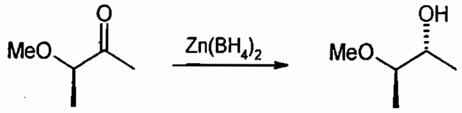
1) In Birch reduction1,4 reduction occur at ortho & meta position w.r.t electron donating group

2) Excess of Li / liq. NH_3 reduces 1,3 diene into isolated double bond as shown below.

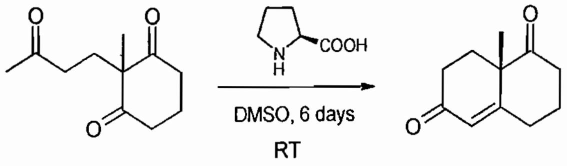


38) Ans (b):- When kinetic isotope effect(K_H/K_D) for the reaction was found to be 4.0; it indicates abstraction of β-hydrogen is involved in rate dertermine step i.e. E_2 elimination

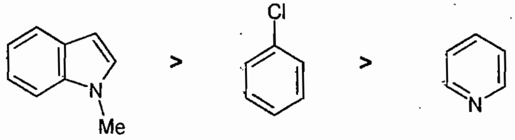
39) Ans (b):- $Zn(BH_4)_2$ is reducing reagent & it approaches to the less-hindered side of the carbonyl group in this reaction. The main product formed in this reactions can be predicted on the basis of the Felkin–Anh model.



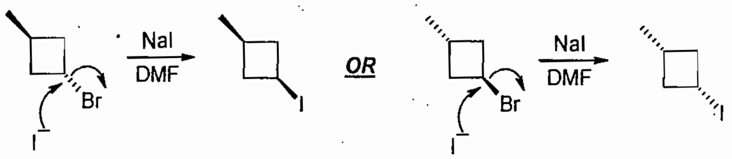
40) Ans (a):- This is an example of enantioselective Robinson annelation. It is an asymmetric synthesis by using (−)-proline (optically active) as the catalyst



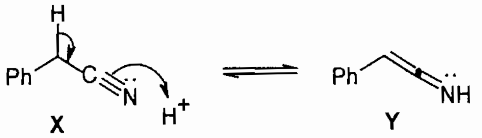
41) Ans (d):- Since the lone pair on the nitrogen atom in Indole can donate electrons into the ring by resonance & makes it more reactive than benzene. The electron-withdrawing nitrogen atom in pyridine makes it less reactive than benzene. Indeed, it is even less reactive than nitrobenzene. In cases of halogens, the negative inductive effect is more dominating than positive resonance effect & make it less reactive than benzene but more reactive than nitrobenzene. *Order for the rates of electrophilic aromatic substitution:-*



42) Ans (c):- NaI(I$^-$) is good nucleophile & DMF is a polar aprotic solvents & favors S_N^2 reaction with inversion in configuration. Thus reactions of trans-1-bromo-3-methylcyclobutane with sodium iodide in DMF is simple S_N^2 reaction with inversion in configuration

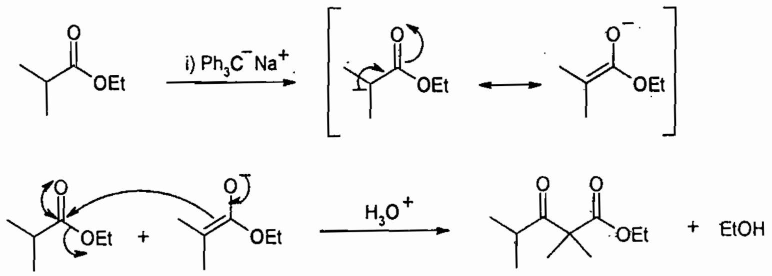


43) Ans (c):- Any reaction that simply involves the intramolecular transfer of a proton is called a tautomerism. Among X & Y; X is more basic (localized lone pair on nitrogen) than Y (delocalized lone pair on nitrogen)



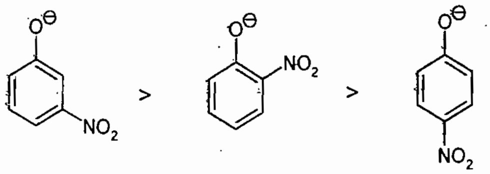
44) Ans (c):- This is the Claisen ester condensation (enolate of a carboxylic ester is formed at room temperature with base & then self condensation of the ester results and gives a β-keto ester product.

Claisen ester condensation

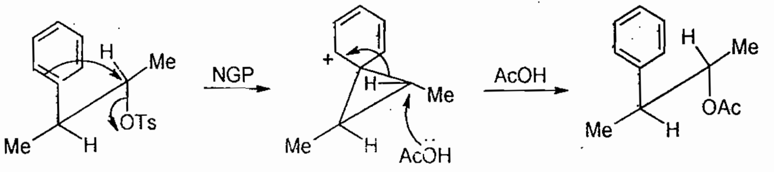


45) Ans (c):- Among three, m-nitrophenoxide ion is more basic as resonance stabilization is not possible in case of m-nitrophenoxide ion which is rather possible in o-nitrophenoxide ion & p-nitrophenoxide ion. Among o- nitrophenoxide ion & p-nitrophenoxide ion; o-nitrophenoxide ion is more basic as resonance stabilization in case of p-nitrophenoxide ion is more due to lengthening of conjugation & therefore shows less affinity towards proton. (A convenient way to look at basicity is based on electron pair availability, the more available the electrons, the more readily it can be donated to form a new bond to the proton and therefore the stronger base.)

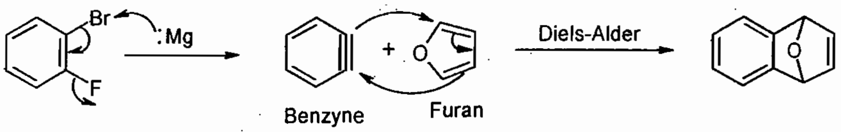
Order of Basisity



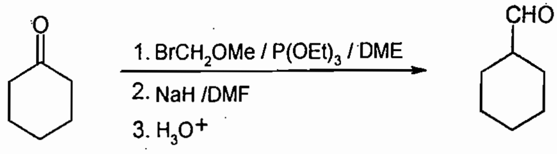
46) Ans (a):- It is an example of neighboring group participation (NGP) reaction:- a type of substitution reaction which goes with retention in configuration and abnormal increase in rate.



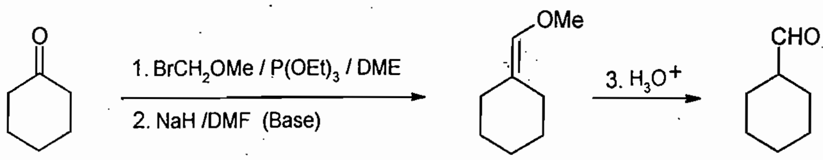
47) Ans (c):-



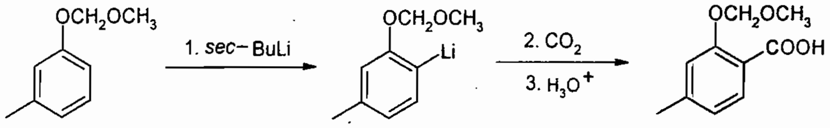
48) Ans (c):- It is a Wittig reaction followed by acid hydrolysis



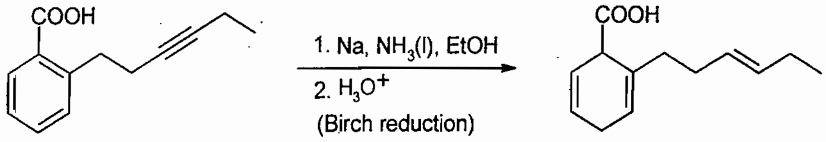
Wittig reaction followed by acid hydrolysis



49) Ans (c):- It is an example of lithiation reactions; lithiation occur at less hindered ortho position.



50) Ans (a):- In Birch reduction, 1,4 reduction occur at ipso & para position w.r.to electron withdrawing group (regioselective) & also brings out a partial reduction of alkynes to trans alkene (stereospecific)



Answer Key

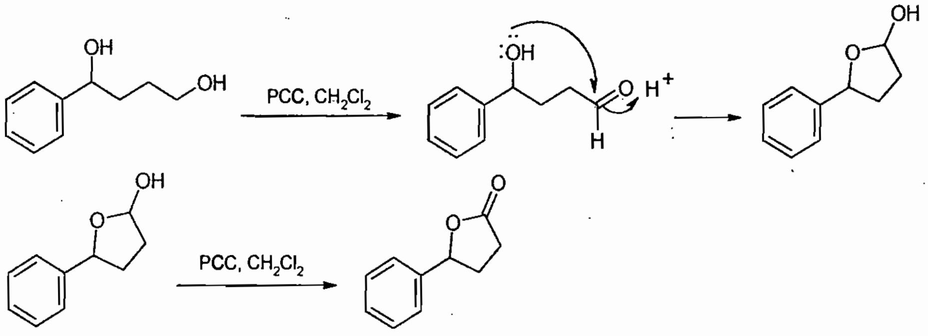
NET EXAM (FOUR MARKS)

Topic- 15:-Organic Reaction Mechanism (ORM, Reagents, Rearrangements & Name Reactions

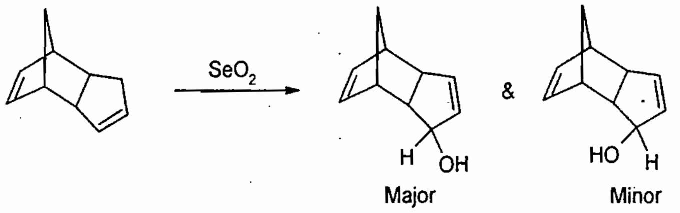
1	d	2	c	3	a	4	d	5	c	6	b	7	a	8	c	9	b	10	d
11	d	12	c	13	d	14	a	15	c	16	d	17	d	18	d	19	a	20	a
21	b	22	b	23	b	24	d	25	c	26	a	27	d	28	d	29	d	30	b
31	b	32	b	33	a	34	b	35	d	36	c	37	d	38	a	39	c	40	a
41	b	42	c	43	a	44	b	45	a	46	b	47	a	48	d	49	d	50	a
51	d	52	d	53	d	54	a	55	a	56	d	57	b	58	d	59	b	60	a
61	b	62	a	63	b	64	b	65	a	66	a	67	b	68	c	69	d	70	a
71	a	72	a	73	d	74	b	75	b	76	d	77	c	78	c	79	b	80	a
81	a	82	d	83	d	84	a	85	a	86	d	87	c	88	b	89	a	90	d
91	a	92	b																

Hint & solution of Questions with four marks (NET EXAM)

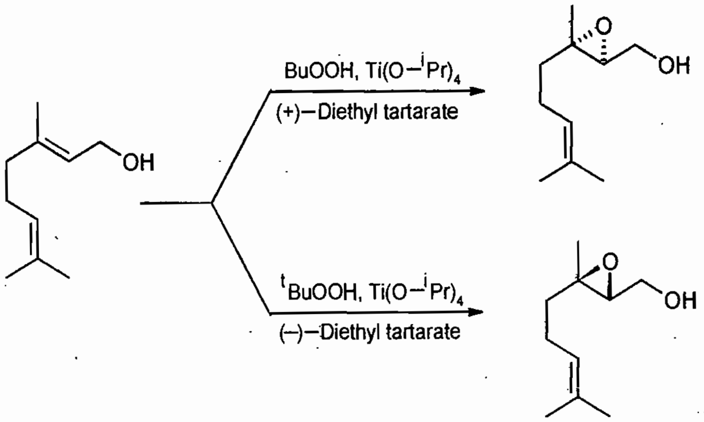
1) **Ans (d):-** The oxidation of a primary alcohol can be easily stopped at the aldehyde by pyridinium Chlorochromate pyH$^+$CrO$_3$Cl$^-$ (PCC) & no further oxidation takes place. Secondary alcohols are oxidized to corresponding ketones with PCC. The PCC is somewhat acidic and acid-catalyzed rearrangements have been observed. A strong absorption at ν_{max} 1765 cm^{-1} in the IR spectrum also suggest the formation of γ-lactone



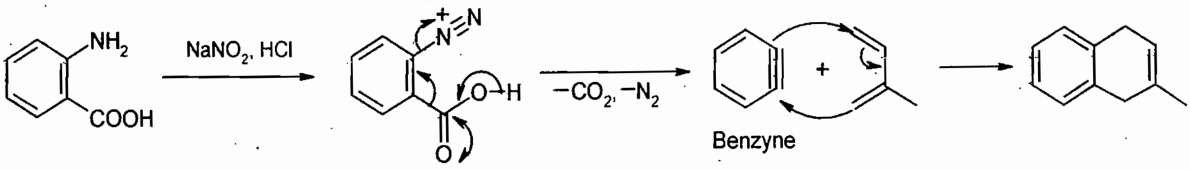
2) **Ans (c):-** SeO$_2$ is an oxidizing agent & is suitable reagent for the allylic oxidation of alkenes to allylic alcohols,



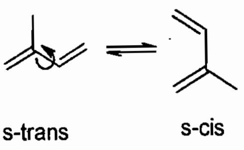
3) **Ans (a):-** The Sharpless Epoxidation allows the enantioselective epoxidation of prochiral allylic alcohols. (–)-diethyl tartrate delivers oxygen to top face of alkene while (+)-diethyl tartrate delivers oxygen to bottom face of alkene



4) **Ans (d):-**

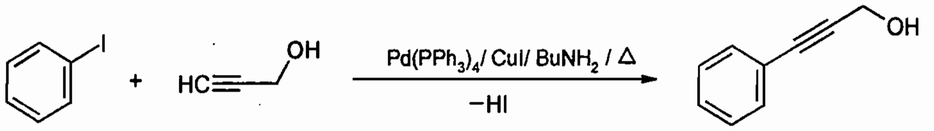


Hint:- s-trans diene undregoes single bond rotation to give s-cis diene

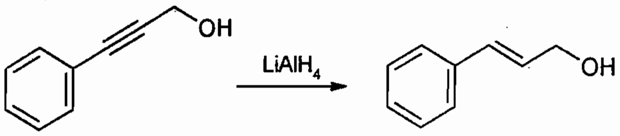


5) Ans (c):- New carbon–carbon bonds can be made using an organometallic reagent in which the metal ion is a transition metal. The reactions are called coupling reactions because two groups are coupled together (joined together).

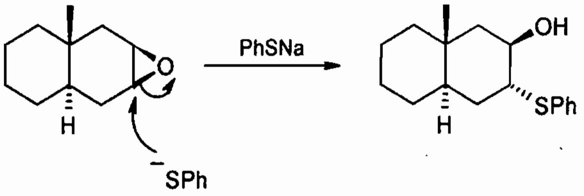
Step I is a coupling of terminal alkynes with aryl or vinyl halides under palladium catalysis



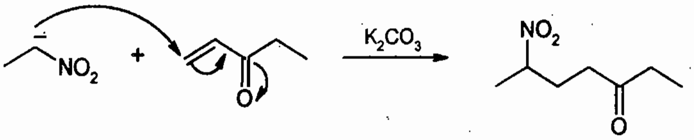
Step II is partial reduction of triple bond to trans alkene by $LiAlH_4$



6) Ans (b):- It is simple S_N^2 reaction of PhS^- on epoxide from less hinderd back side.

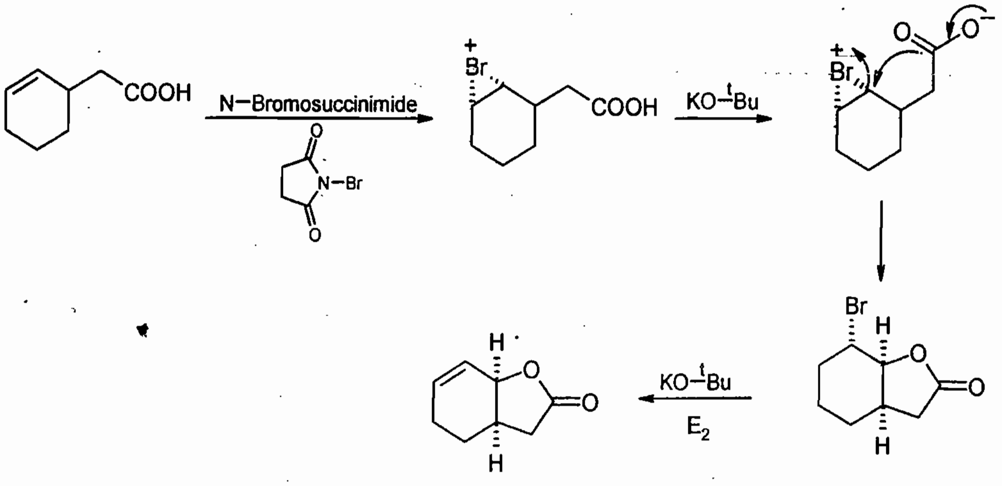


7) Ans (a):- Step I Nitroalkane readily undergoes multiple conjugate additions under basic condition.

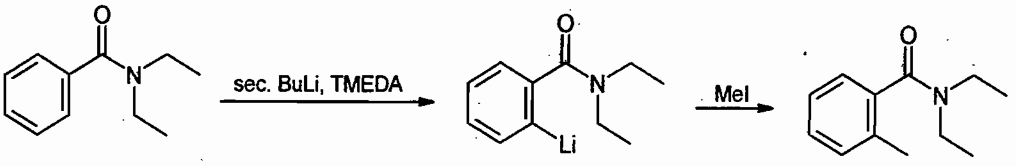


Step II:- The first stage involve reduction of nitro group to an amine, condensation with the ketone to give an imine & its reduction.

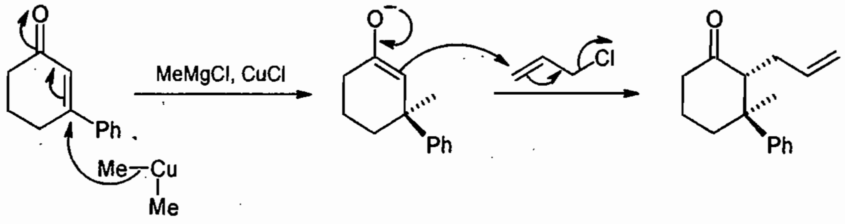
8) Ans (c):- NBS is a radical generator in nonpolar solvents, but in polar solvents, it supplies electrophilic Bromine.



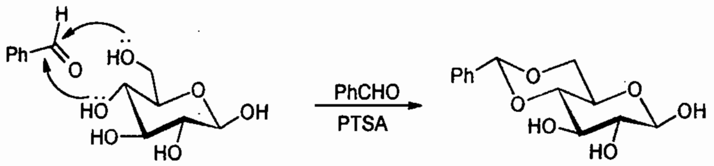
9) Ans (b):- It is a lithiation reaction. sec-BuLi is a strongly basic reagent & remove a more acidic ortho proton



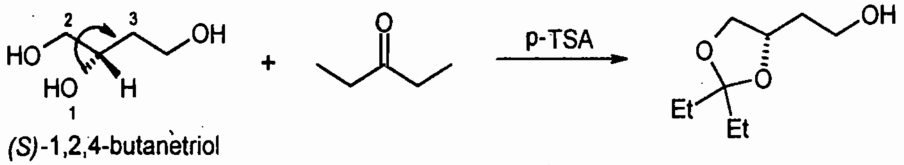
10) Ans (d):- Alkylcuprate undergoes conjugate addition when react with unsaturated α,β– aldehydes and ketones.



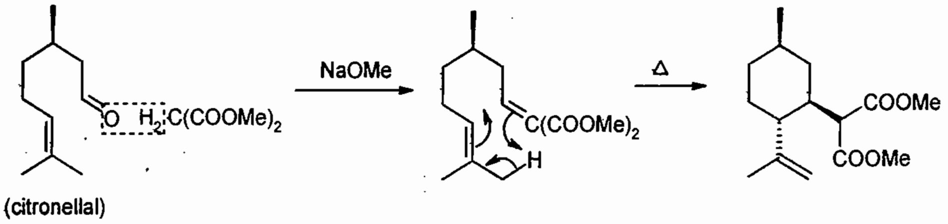
11) Ans (d):- The new chair acetal ring is formed between primary –OH group & its adjacent –OH group with benzaldehyde and p-TSA with the phenyl group in an equatorial position in the product



12) Ans (c):- It is a simply acetal ring formation between 1,2 diol of (S)-1,2,4-butanetriol with 3-pentanone in the presence of a catalytic amount of p-TSA

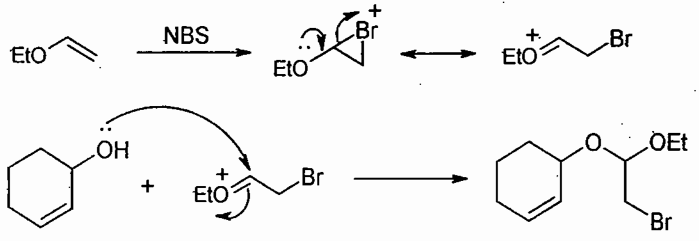


13) Ans (d):- First Step is base catalyzed condensation followed by cyclisation.



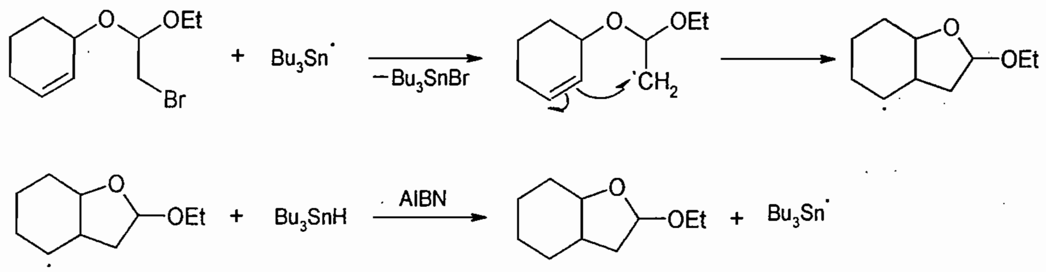
14) Ans (a):-

Step I :- formation of A

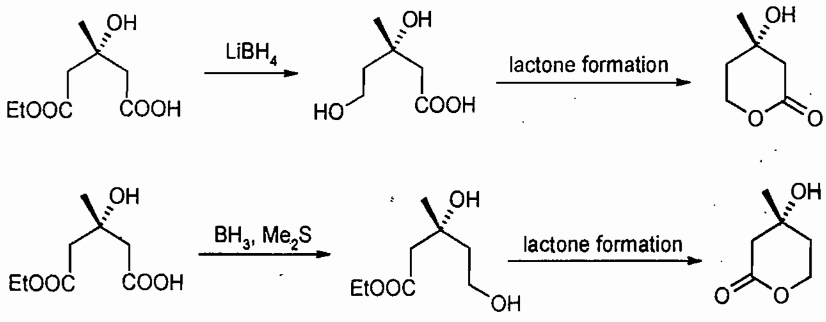


Step II :- formation of B

$$Bu_3SnH \xrightarrow{AIBN} Bu_3Sn^{\cdot}$$

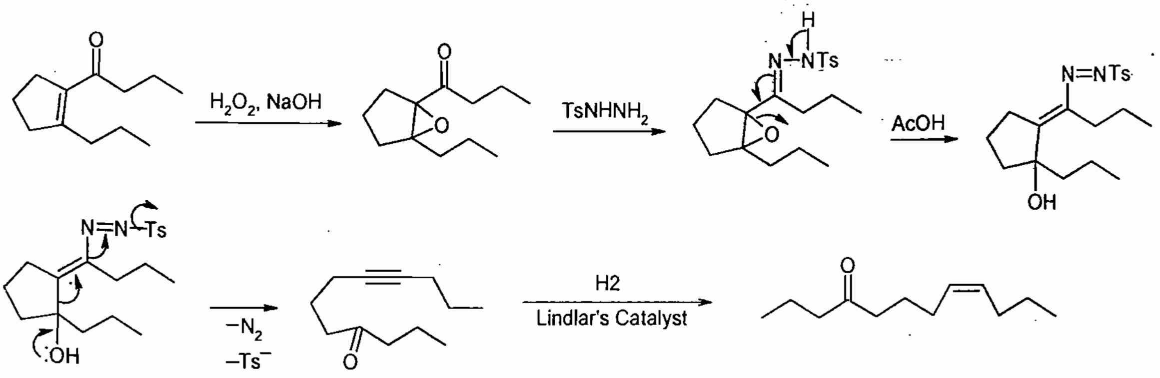


15) Ans (c):- $LiBH_4$, a milder reducing agent than $LiAlH_4$ & chemo-selectively reduces ester group in presence of acids and amide while Borane is a highly chemoselective reagent for the reduction of carboxylic acids in the presence of other reducible functional groups such as esters, and even ketones.

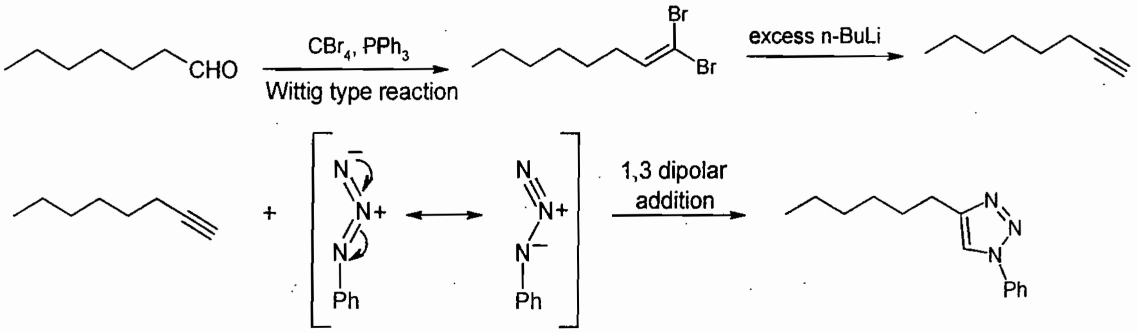


16) Ans (d):- The correct sequence of the reagents:

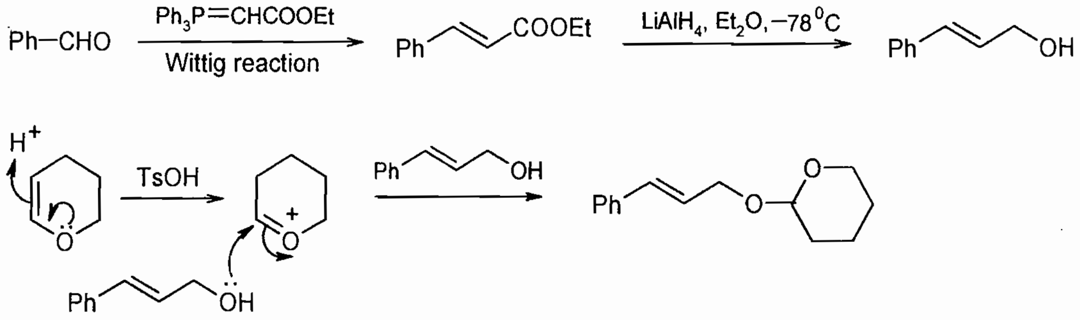
(A) H_2O_2, NaOH; (B) $TsNHNH_2$; (C) AcOH; (D) H_2, Lindlar's catalyst



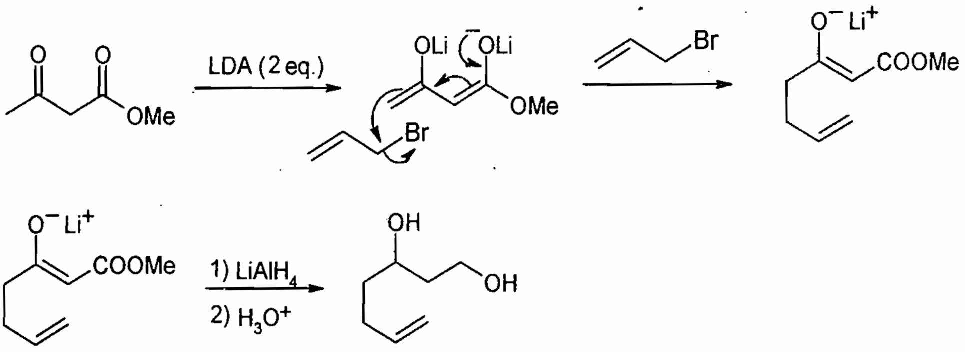
17) Ans (d):- First Step is Wittig type reaction (the phosphonium ylide $Ph_3P=CBr_2$, generated from carbon tetrabromide, triphenylphosphine) to give1,1 dibromo-alkene. 1,1 dibromo-alkene on tratement nBuLi result in the terminal alkyne. Last step is 1,3 dipolar cycloaddition reaction.



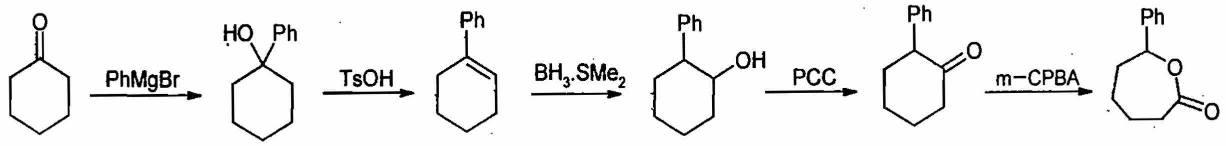
18) Ans (d):- First Step is Wittig reaction by using stabilized ylid to give E-alkene selectively. In next step at low temperature $LiAlH_4$ only reduces polar bond that is ester group into a primary alcohol.
Last step is protection of alcohol group by dihydropyran in presence of TsOH



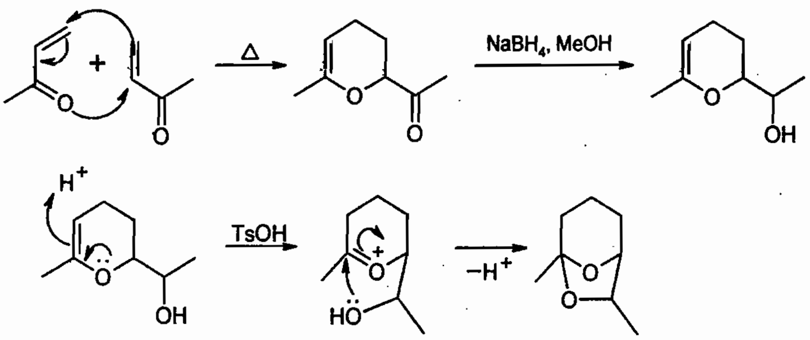
19) Ans (a):- Hint:-Dianion of ethyl acetoacetate is usually alkylated on the terminal carbon atom.



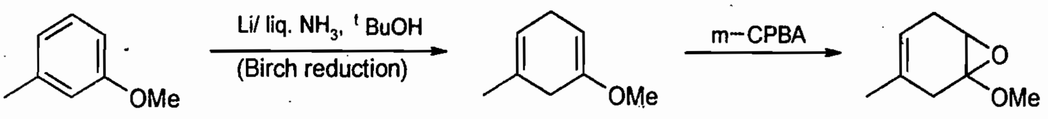
20) Ans (a):- First step is addition of Grignard reagent to ketone to form an alcohol which undergoes dehydration in acid solution with toluene sulfonic acid (TsOH). Next step is hydroboration; (used for the conversion of alkenes to alcohol) & subsequent oxidation by PCC.Last step is Baeyer–Villiger oxidation of ketone to ester by peroxy-acids.



21) Ans (b):- The major products of reaction are:-



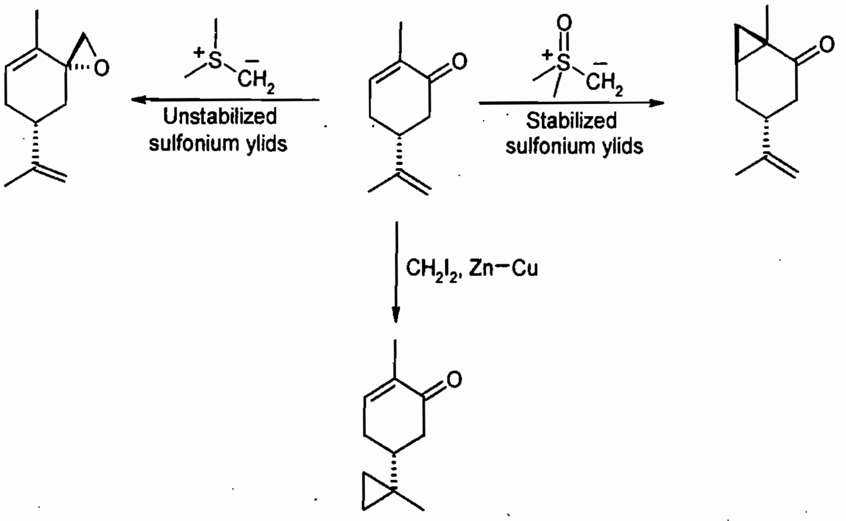
22) Ans (b):- In Birch reduction, 1,4 reduction of aromatic ring occur at ortho & meta position w.r.to electron donating group (regioselective). In the next step epoxidation of more electron rich alkene take place



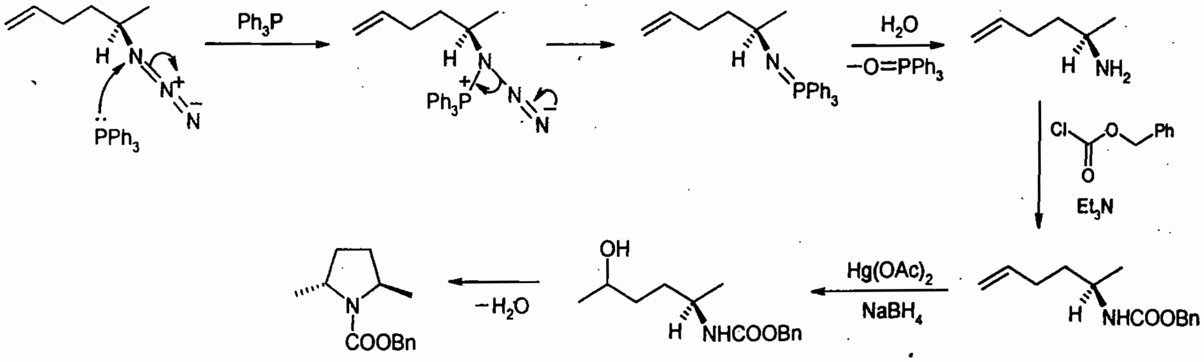
1) In Birch reduction1,4 reduction occur at ortho & meta position w.r.t electron donating group

2) Here peracid add to more electron rich alkene

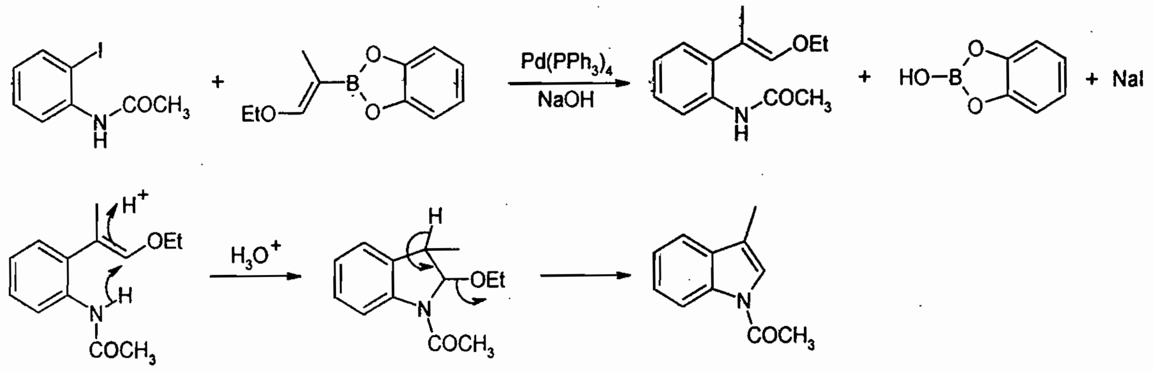
23) Ans (a):- The Simmons–Smith (CH_2I_2,Zn−Cu) adds to electron rich alkene and produce cyclopropanes. 'Unstabilized' sulfonium ylids give epoxides from α,β-unsaturated carbonyl compounds while 'stabilized' ylids (with an anion-stabilizing substituent) give cyclopropanes.



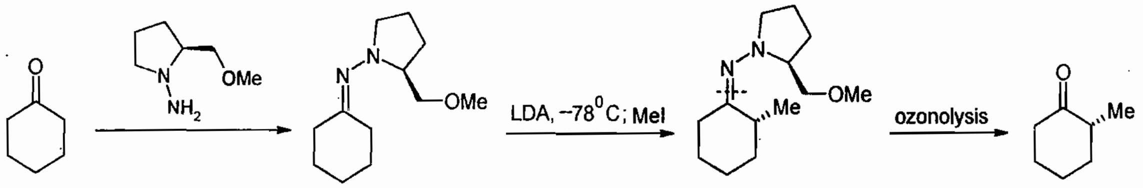
24) Ans (d):- First step is a reduction of an azide into the primary amine by using triphenylphosphine in water. In next step NH_2 group is protected benzyl chloroformate (BnOCOCl) and weak base. Third step is oxymercuration reaction to give an alcohol which undergoes cyclodehydration reaction.



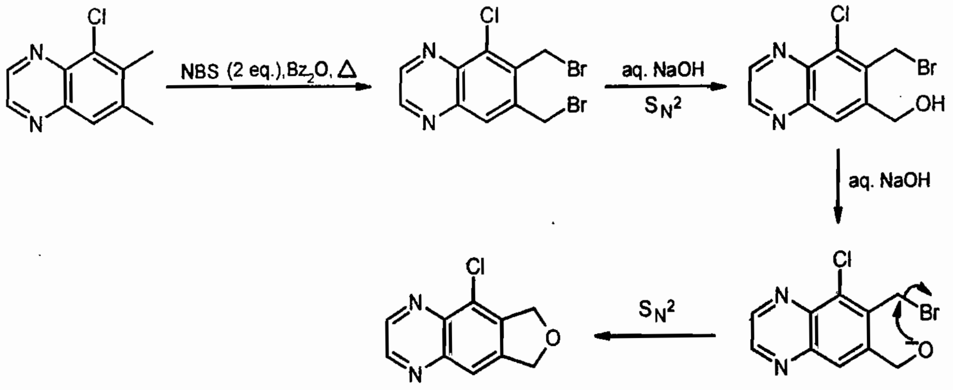
25) Ans (c):- First step is the Suzuki reaction (A reaction that couples an aryl, benzyl, or vinyl halide with an organoborane in a basic solution). Next step is cyclization & aromatisation to give substituted indol.



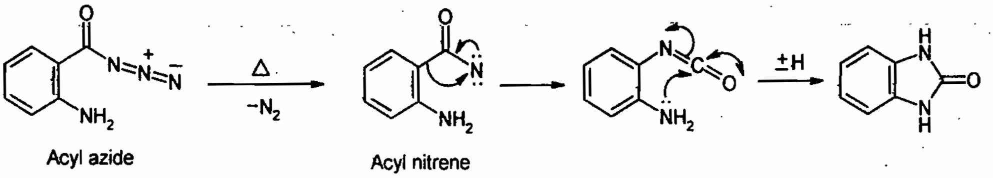
26) Ans (a):- First step is a oxime formation. Next step is methylation from the bottom face of enamine ion. Last step is ozonolysis of imine to ketone.



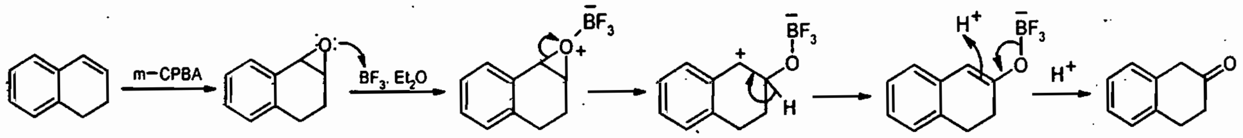
27) Ans (d):- *N*-bromo succinimide with radical initiator (here initiated by dibenzoyl peroxide,) is a versatile and commonly used reagent for allylic/benzylic bromination of alkenes to give allylic bromides. Second step is a simple nucleophilic substitution reaction to form cyclic product.



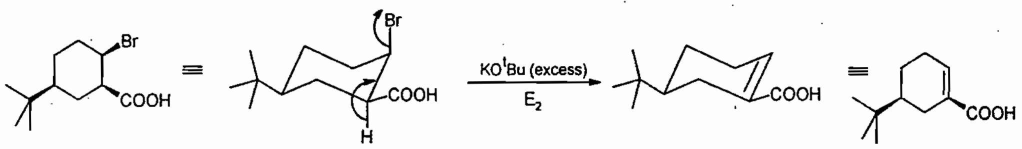
28) Ans (d):- Curtius Rearrangement - Formation of isocyanates by thermal decomposition (pyrolysis) of acyl azides. Reaction proceed through an intermediate acyl nitrene.

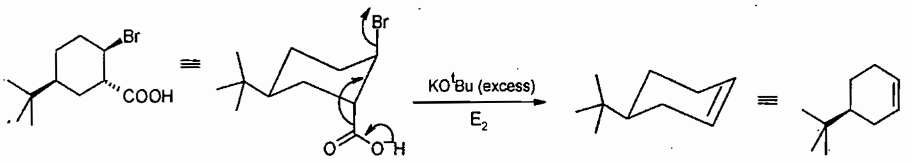


29) Ans (d):- First step is epoxidation of alkene. Epoxide opens in presence of lewis acid to form an alkene via formation more stable benzylic carbocation

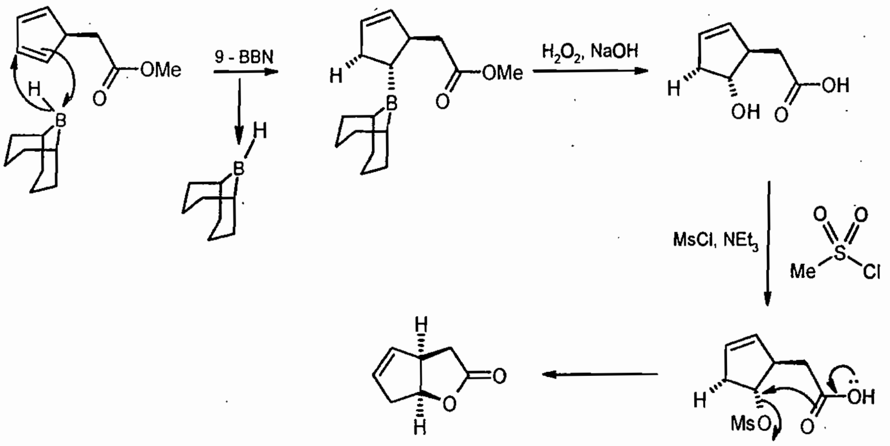


30) Ans (b):- An E_2 reaction involves the removal of two groups from adjacent carbons. It is a concerted reaction because the two groups are eliminated in the same step. The bonds to the groups to be eliminated must be in the same plane that is either antiperiplanar or synperiplanar. Therefore in first reaction gives dehydrohalgenation reaction(–H & –Br are anti-periplanar to each other). While in second reaction decarboxylation & loss of bromide is take place(–COOH & –Br are anti-periplanar to each other).

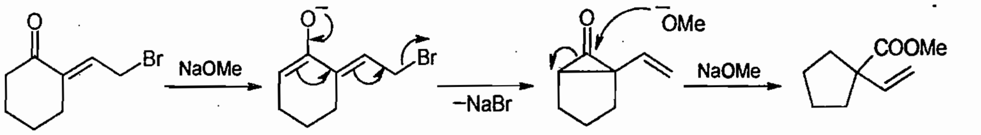




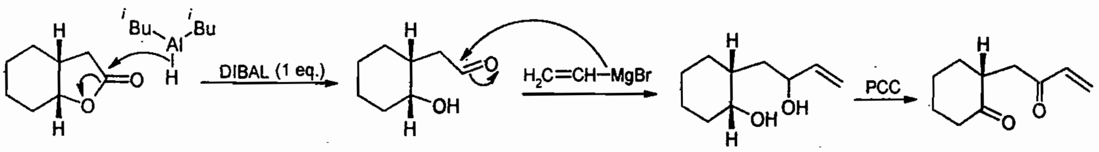
31) Ans (b):- Here 9–BBN add on opposite face of diene substituent & give an alcohol on oxidation. Methanesulfonyl chloride convert the hydroxyl into a good leaving group & result in cis-lactone formation by intramolecular nucleophilic reaction



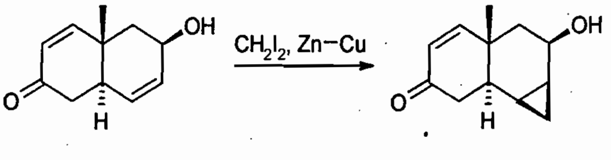
32) Ans (b):- It is an example of Favorskii rearrangement (rearrangement of an α-halo ketone to carboxylic acids or their derivatives.



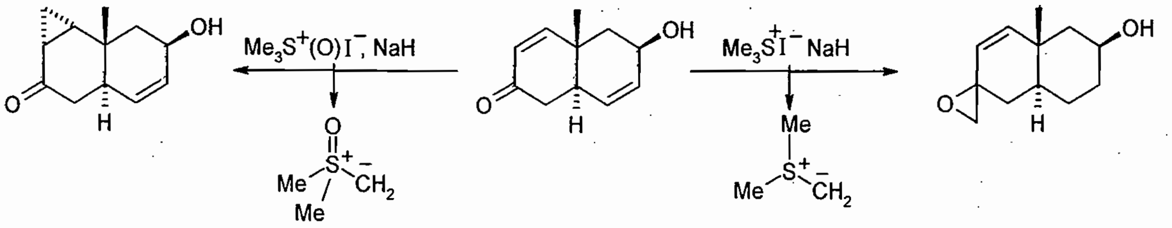
33) Ans (a):- One equivalents of DIBAL-H reduces lactones (cyclic esters) into lactols which rearrange into the aldehyde. In the next step of Grignard reagents adds to aldehyde to give alcohols. In last step pyridinium chlorochromate oxidizes the alcohol to ketone.



34) Ans (b):- The Simmons–Smith (CH_2I_2,Zn–Cu) adds to electron rich alkene and produce cyclopropanes. When an allylic alcohol is cyclopropanated by Simmons–Smith (CH_2I_2,Zn–Cu), the new methylene group adds stereoselectively to the same face of the double bond as the alcohol group.



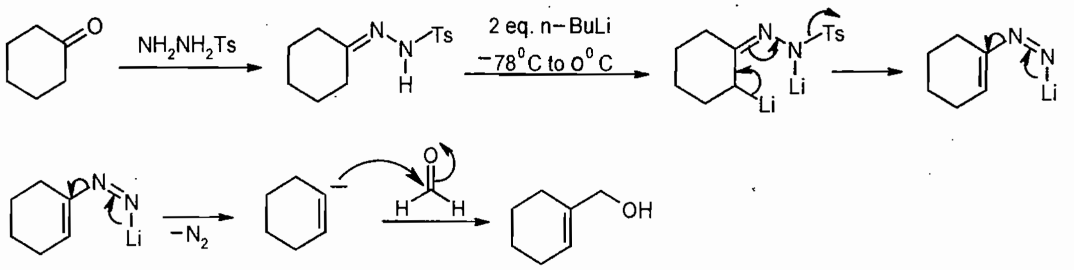
'Unstabilized' sulfonium ylids give epoxides from α,β-unsaturated carbonyl compounds while 'stabilized' ylids (with an anion-stabilizing substituent) give cyclopropanes.



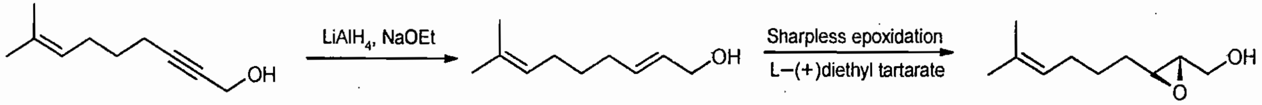
Stabilized sulfonium ylids

Unstabilized sulfonium ylids

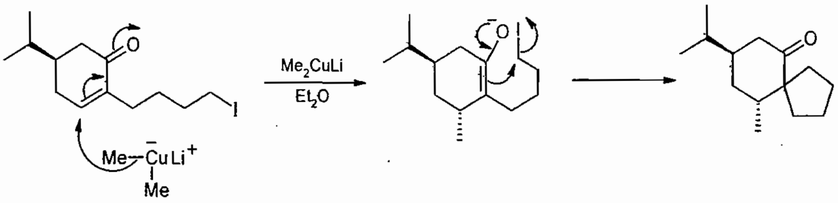
35) Ans (d):- It is an example of Shapiro reaction; (decomposition of the tosyl hydrazones of aliphatic aldehydes or ketones with very strong base, usually butyl lithium or LDA, to give corresponding vinyl lithium). Vinyl lithium then reacts with formaldehyde to give corresponding alcohol



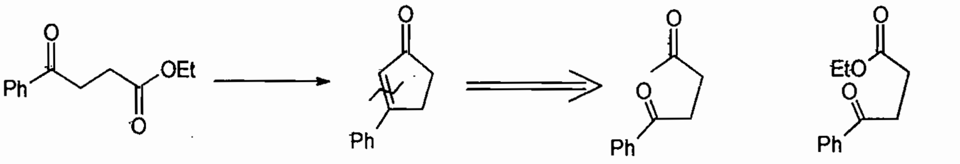
36) Ans (c):- First step is partial reduction of triple bond to trans alkene by $LiAlH_4$.Next step is Sharpless asymmetric epoxidation of allyl alcohol. D-(–)-diethyl tartrate delivers oxygen to top face of alkene & L-(+)-diethyl tartrate delivers oxygen to bottom face of alkene



37) Ans (d):- Alkylcuprate undergoes conjugate addition when react with unsaturated α,β– aldehydes and ketones. Lithium enolate formed in the reaction undergoes C-alkylation with alkyl hailde



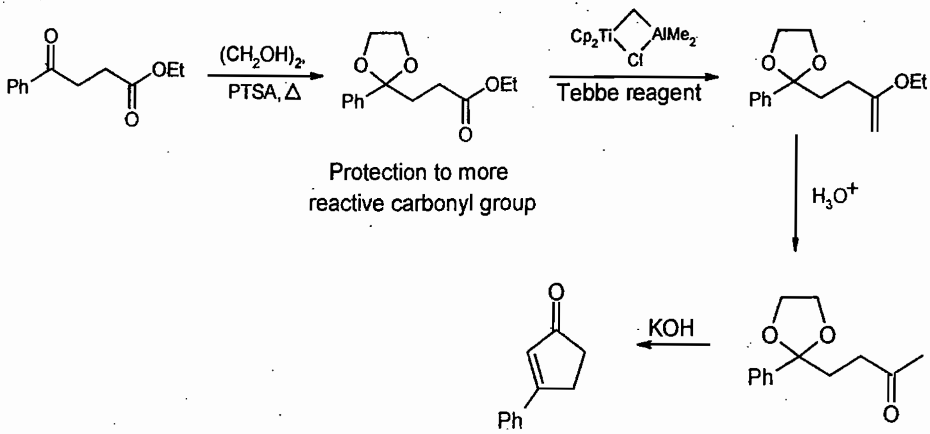
38) Ans (a):- Tebbe reagent, carry out the methylenation of carbonyl compounds, ester & even amide Protection is must to carry out the reaction at less reactive carbonyl group.(ketones are more reactive than ester). Last step is intramolecular aldol condensation reaction.



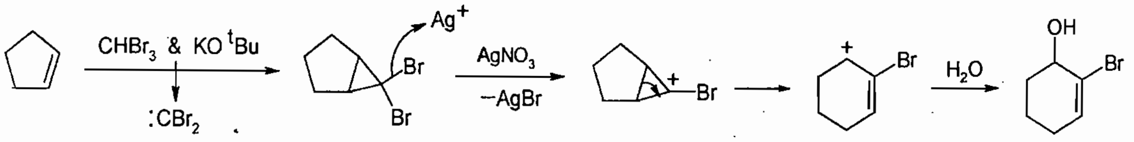
required molecule

starting compound

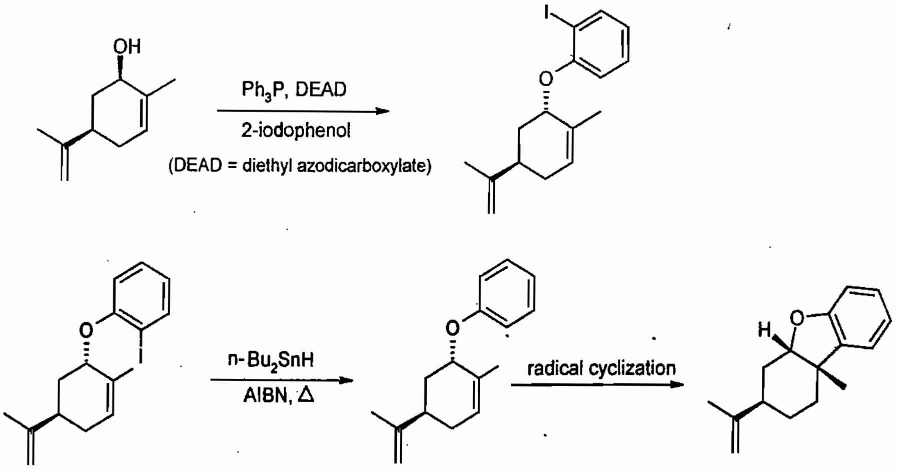
sequence of reagent & reaction:-



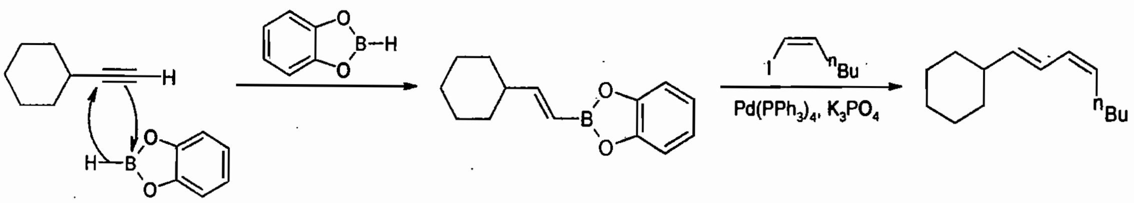
39) Ans (c):- First step is base-catalysed elimination of HBr from $CHBr_3$ gives a $:CBr_2$ & addition of $:CBr_2$ to cyclopentene. Next step is a formation of carbocation which is attacked by water molecule.



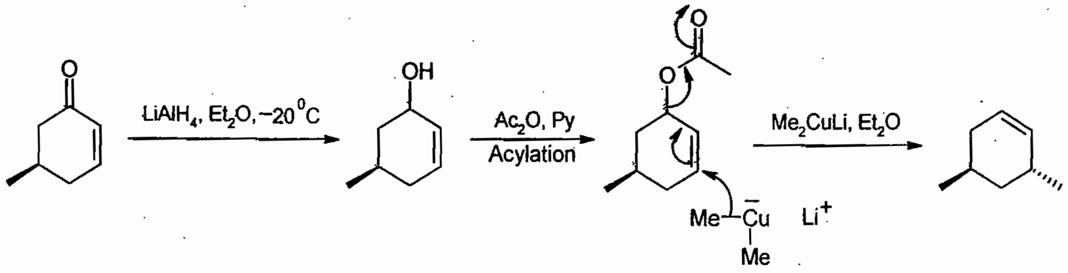
40) Ans (a):- First step is the Mitsunobu reaction:- A reaction give inversion of configuration at secondary alcohol by nucleophile. Next step is intramolecular radical cyclization.



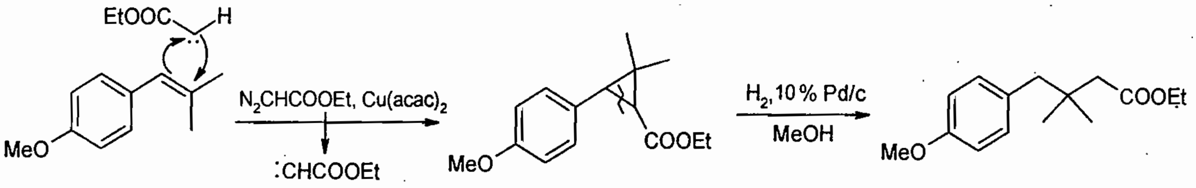
41) Ans (b):- First step is the hydroboration of an alkyne with catecholborane, The borane adds to less hindered side of alkynes and addition of boron and hydrogen occurs *cis* stereospecifically.
Second step is the Suzuki coupling couples boronic acids to halides that is vinyl boronate with a vinyl iodide.



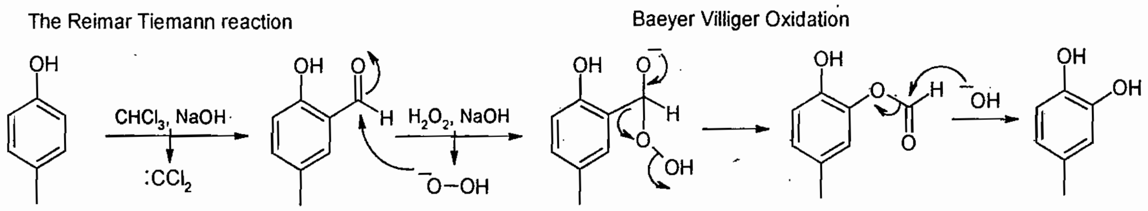
42) Ans (c):- $LiAlH_4$ often reduces double bond along with carbonyl compound in α,β– aldehydes and ketones. but selective reduction of the carbonyl group can generally be achieved by working at low temperatures. In next step acylation of hydroxyl group by acetic anhydride & pyrindine (base). In last step Gilman reagent approaches from the less hindered side & elimination of acyl group takes place to give desired product



43) Ans (a):- In first step carbene is generated by metal-catalysed decomposition of ethyl diazoacetate. Carbene form cyclopropane ring with alkene double bond. H_2,Pd/C reduces cyclopropane ring to the less hindered C−C bond.

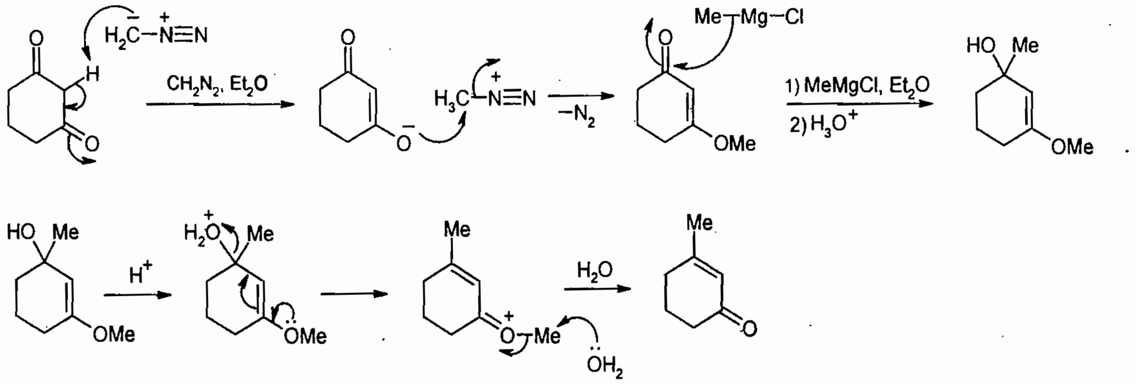


44) Ans (b):- First step is Reimer–Tiemann reaction & is used to carry out a formylation of electron rich aromatic compounds like phenols & next step is Bayer Villiger type oxidation reaction.

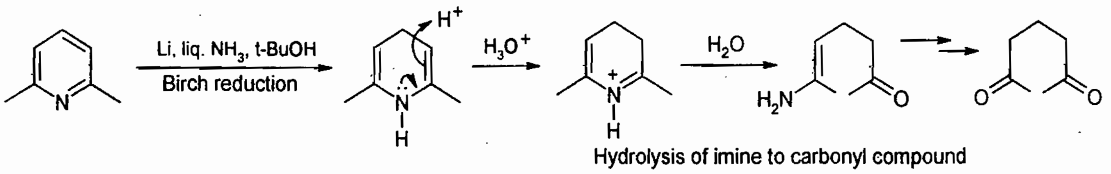

The Reimar Tiemann reaction

Baeyer Villiger Oxidation

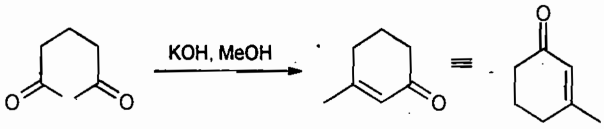
45) Ans (a):- In first step diazomethane remove acid hydrogen atom to form an extremely unstable diazonium cation & enolate & then result in O-methylation. In next Hard nucleophiles(Grignard reagent) react with hard electrophiles (carbonyl group) to form allyl alcohol which rearrange in acidic condition



46) Ans (b):- Birch reduction of pyridines gives 1,4- dihydropyridines which are readily hydrolysed to 1,5-dicarbonyl compounds. 1,5-dicarbonyl compounds undergo intramolecular aldol condensation under basic condtion.

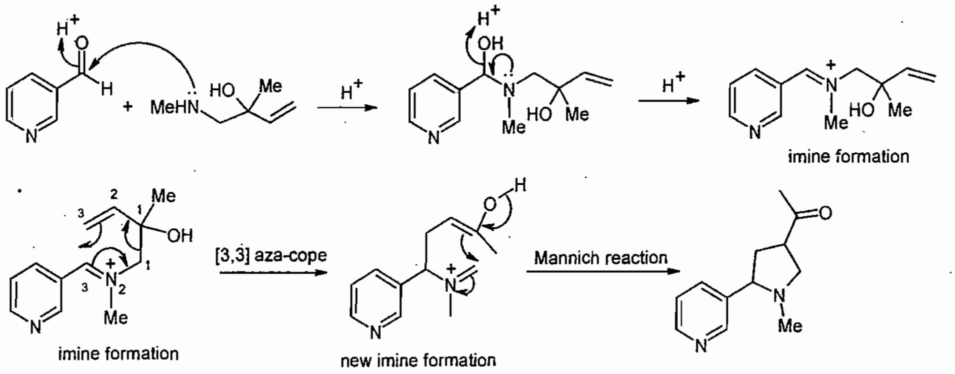


Hydrolysis of imine to carbonyl compound

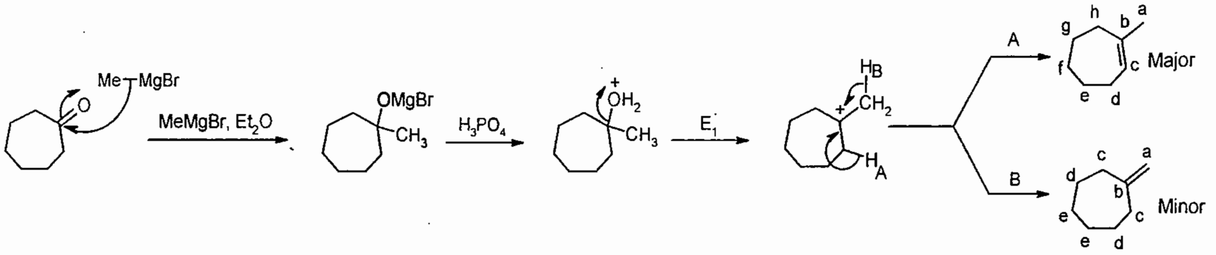


Intramolecular aldol condensation

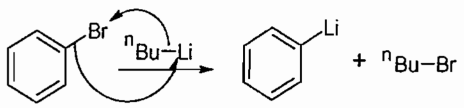
47) Ans (a):- The transformation involves an iminium ion, [3,3]-sigmatropic shift (aza cope) and Intramolecular Mannich reaction (reaction of enol with imine)



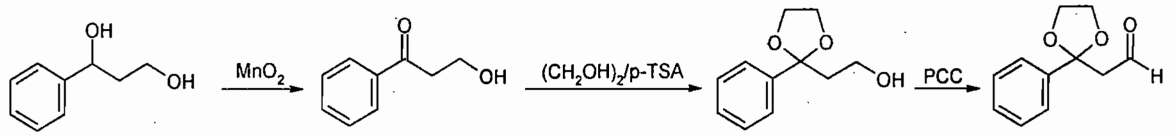
48) Ans (d):- In first step is the Grignard reagent adds to ketones to give tertiary alcohols. Tertiary alcohol readily undergoes dehydration with dehydrating agent like H_3PO_4 or H_2SO_4 via E_1 elimination to give More substituted alkenes (more stable) as a major product.



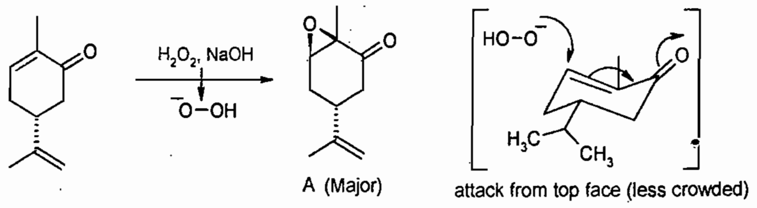
49) Ans (d):- The treatment of PhBr with n-BuLi yields PhLi + n-BuBr. Here butyllithiums remove halogen atom from aryl halides & reaction is known as halogen–metal exchange.

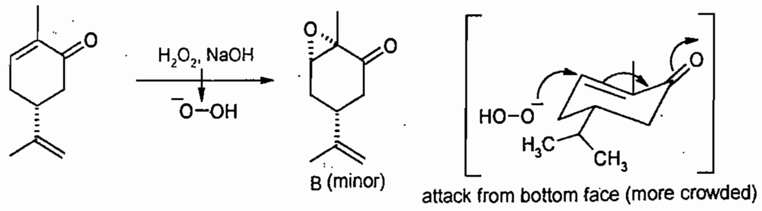


50) Ans (a):- PCC (Pyridinium Chlorochromate $[PyH]^+[CrO_3Cl]^-$ & Jones' reagent (CrO_3 + H_2SO_4 + H_2O) oxidizes both benzylic & primary alchol; so we cannot use them in first step otherwise $(CH_2OH)_2$/p-TSA will form acetal with more reactive aldehyde rather than ketone. While manganese dioxide (MnO_2) oxidizes only allylic or benzylic hydroxyl groups into the ketones. Therefore the appropriate sequence of reactions is MnO_2; $(CH_2OH)_2$/p-TSA; PCC

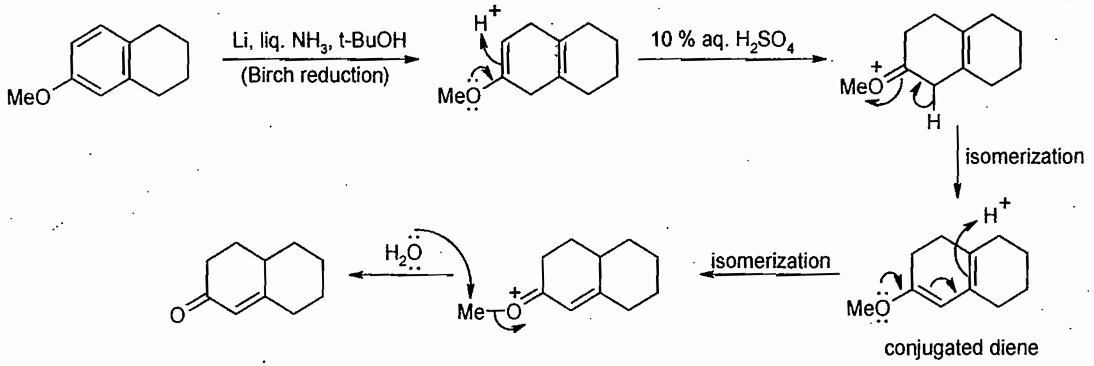


51) Ans (d):- Epoxidation of α,β– unsaturated aldehydes and ketones is achieved by aq. H_2O_2/NaOH. In this reaction hydroperoxide anion attack from top face of alkene (less crowded).

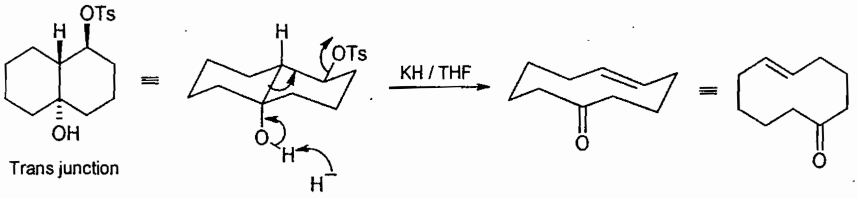




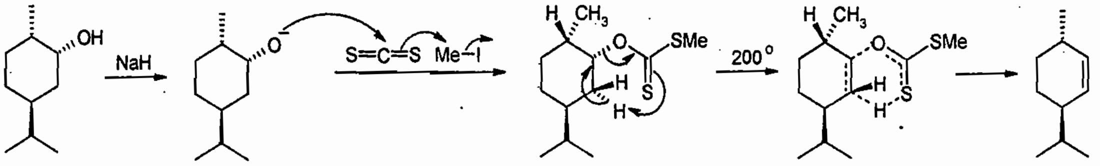
52) Ans (d):- In Birch reduction, 1,4 reduction of aromatic ring occur at ortho & meta position w.r.to electron donating group (regioselective). However, the product formed undergoes isomerization & hydrolysis to give α,β-unsaturated ketone in presence of strong acidic condition.



53) Ans (d):- The reaction is an example of the Grob fragmentation and takes place in a concerted manner to give an alkene. The stereochemistry of an alkene in a product is governed by the relative orientation of the groups in the starting compound. When tosyloxy group and the adjacent ring junction hydrogen atom are *cis*, it will give *E*-5-cyclodecenone in high yield, whereas when tosyloxy group and the adjacent ring junction hydrogen atom are *trans*, it will give *Z*-5-cyclodecenone in high yield.



54) Ans (a):- The reaction is an example of Pyrolytic syn eliminations of xanthates,
Pyrolytic elimination reactions take place in a concerted manner at elevated temperature, by way of a six-membered cyclic transition state which is possible only when β– hydrogen & leaving group are syn-periplanar to each other that is syn stereochemistry.

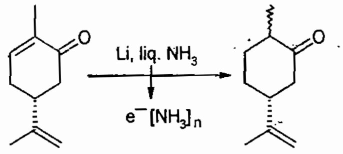


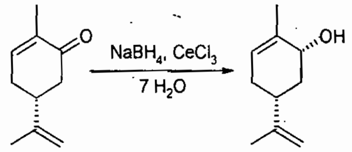
55) Ans (a):- The problem is based on chemoselectivity of reagents (selectivity for one functional group over another)

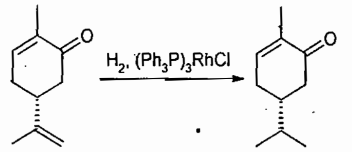
a) Li/liq.NH₃ reduces the C–C double bond in α,β– unsaturated aldehydes and ketones

b) NaBH₄, CeCl₃.7H₂O; reduces the C=O bond (carbonyl) group in α,β– unsaturated aldehydes or ketones.

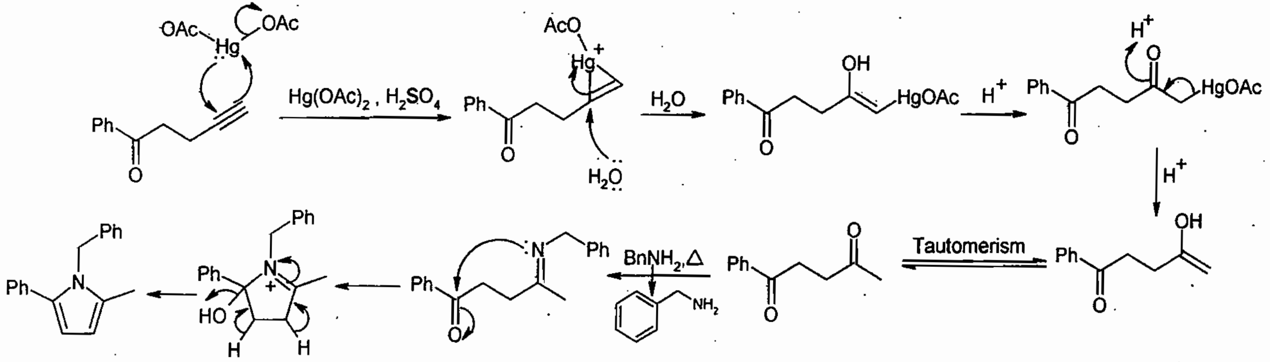
c) H₂, (Ph₃P)₃RhCl (Wilkinson's catalyst) is used for homogeneous hydrogenation of isolated multiple bond.





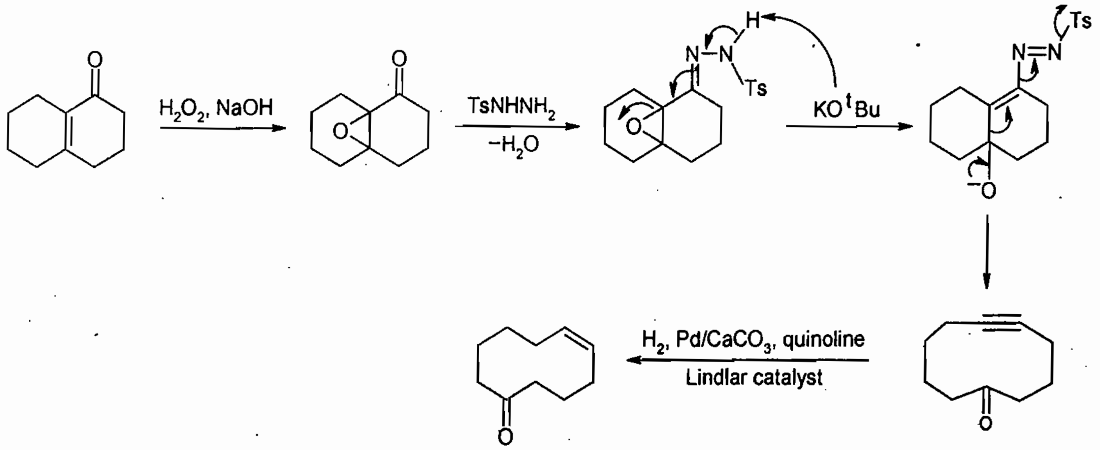


6) Ans (d):- First step is Oxymercuration of alkyne to give a ketone. Next step is condensation reaction of ketone with Benzyl amine. In last step forrmation of five-membered aromatic pyrrole is take place via cyclodehydration.

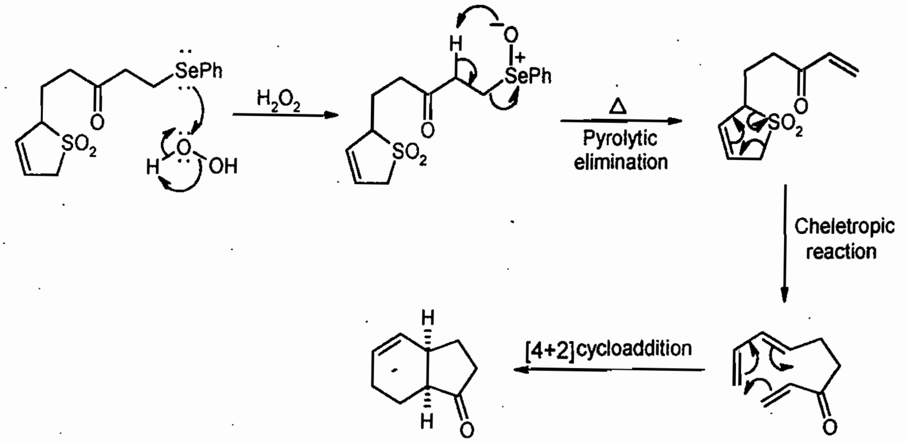


7) Ans (b):- First step is Epoxidation of α,β– unsaturated ketones by aq. H_2O_2/NaOH. In second step formation of the tosylhydrazone from the epoxy-ketone & followed by opening of the epoxide under basic condition gives alkoxide anion. Alkoxide anion then undergoes the Grob fragmentation & give a triple bond via irreversible concerted loss of a Ts$^-$ and N_2.

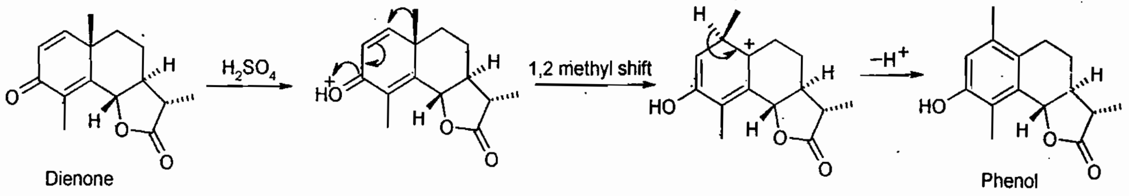
Last step is a partial reduction of triple bond to cis alkene by Lindlar's catalyst



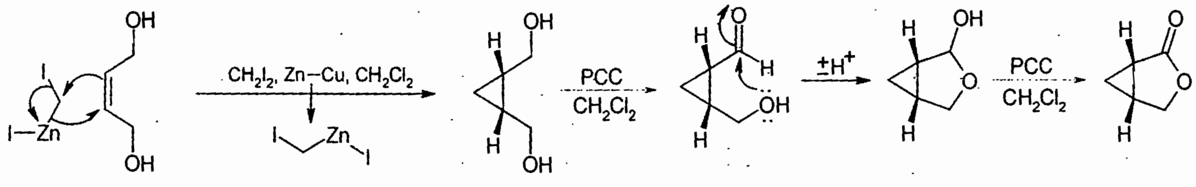
58) Ans (d):- First step is oxidation of phenylselenyl to selenoxide which at elevated temperature undergo pyrolytic elimination & retro Cheletropic reaction. Last step is intramolecular [4+2] cyloaddition to give desire product.



59) Ans (b):- It is an example of dienone–phenol rearrangement

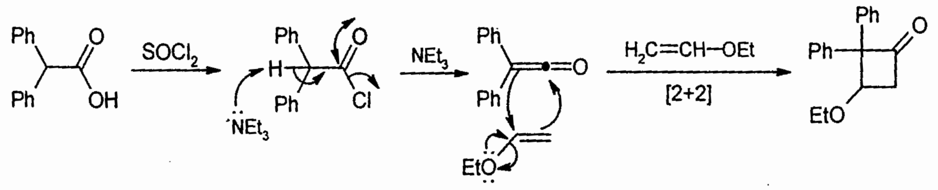


60) Ans (a):- First step is Simmons–Smith reaction, (Addition of Simmons–Smith reagent to alkene to form cyclopropane compounds). In second step PCC (Pyridinium Chlorochromate $[PyH]^+[CrO_3Cl]^-$) oxidizes the alcohol into the aldehyde which is readily attacked by internal hydroxy group to form lactol. Lactol formed is also oxidized into lactone

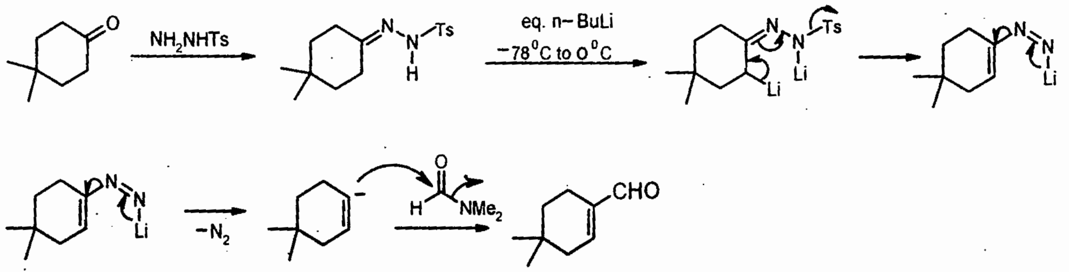


cis−but−2ene−1,4−diol

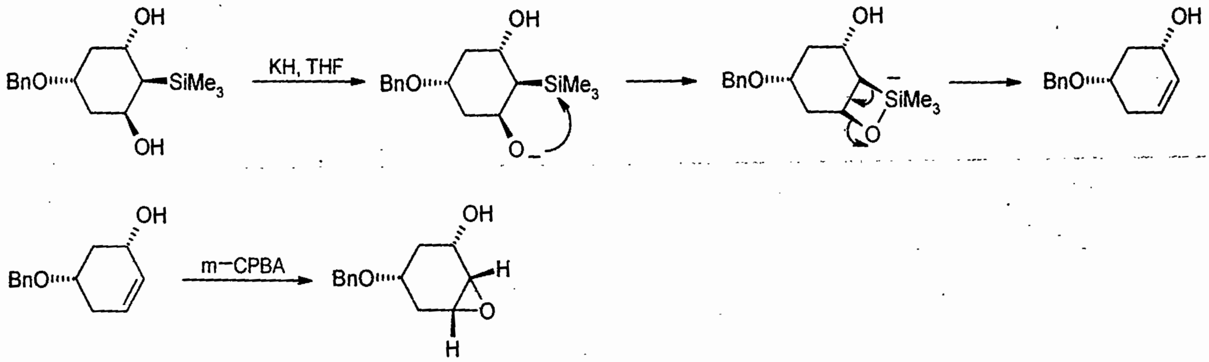
61) Ans (b):- $SOCl_2$ converts carboxylic acid into Acid chlorides & base converts it into the ketenes. Last step is thermal [2+2] cycloaddition giving four-membered rings which is possible only when the one of the systems must have two double bonds to the *same* carbon atom; that is ketene in this case..



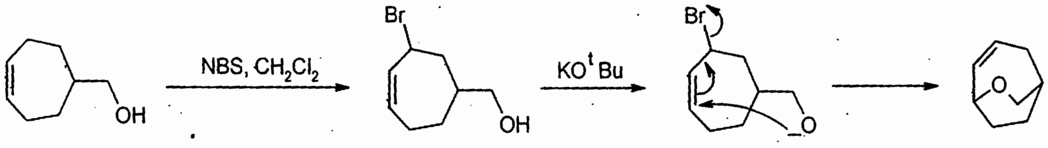
62) Ans (a):- It is an example of Shapiro reaction; (decomposition of the tosyl hydrazones of aliphatic aldehydes or ketones with very strong base, usually butyl lithium or LDA, to give corresponding vinyl lithium). Vinyl lithium then reacts with formaldehyde to give corresponding alcohol



63) Ans (b):- First KH deprotonate the hydroxyl group and the oxyanion attacks the silicon atom intramolecularly & elimination takes place via a syn-periplanar transition state. Next step is epoxidation of alkene by m-CPBA which delivers the oxygen atom stereoselectively to the same face of the double bond as the adjacent alcohol group.



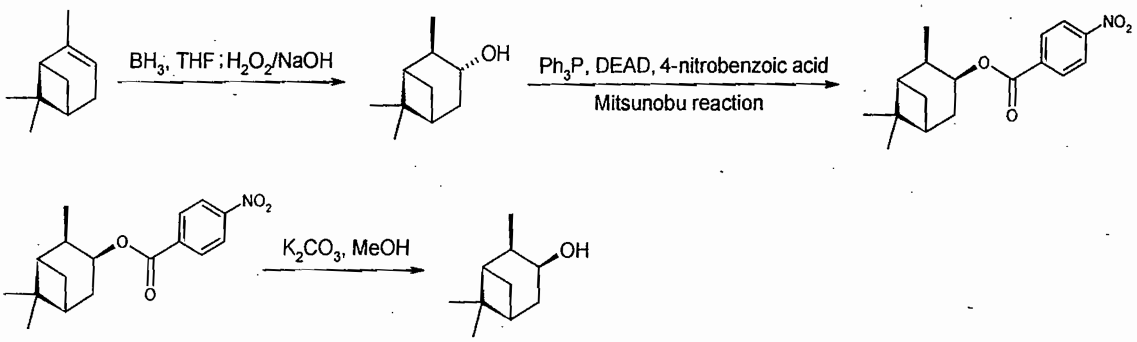
Ans (b):- NBS is a bromine radical generator in nonpolar solvents & carry out bromination at the allylic position. Next step is intramolecular nucleophilic substitution of allylic bromide



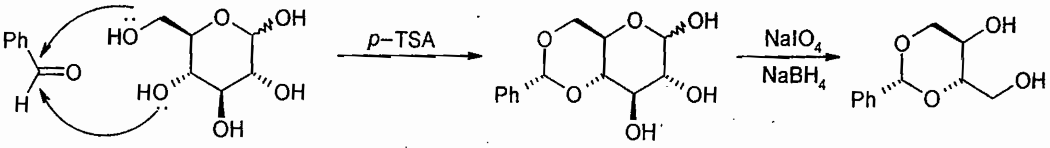
65) Ans (a):- First step is a Hydroboration reaction (the conversion of alkenes to alcohols by the syn (cis) addition of water (that is H & OH) with the OH group going to the less substituted end of the alkene.

Second step is the Mitsunobu reaction (used to replace OH by another acidic group with inversion of configuration.

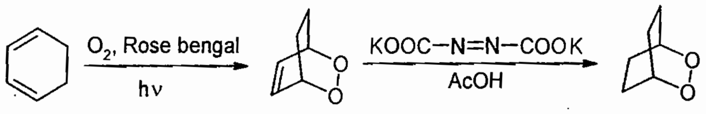
Last step is base catalyzed hydrolysis of ester



66) Ans (a):- First step is reaction of benzaldehyde in acid solution forms more stable & energetically favorable actal with trans decaline system. In next step periodate ions oxidatively cleave the C–C bond between the two oxygen substituents which on treatment with NaBH$_4$ gives product

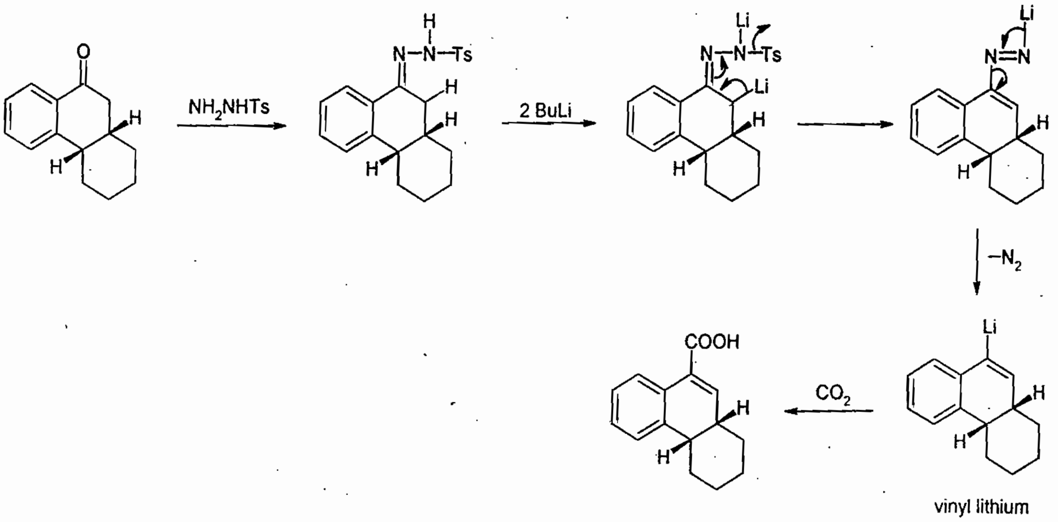


67) Ans (b):- Hint:- H$_2$/Pd will break the O–O bond.

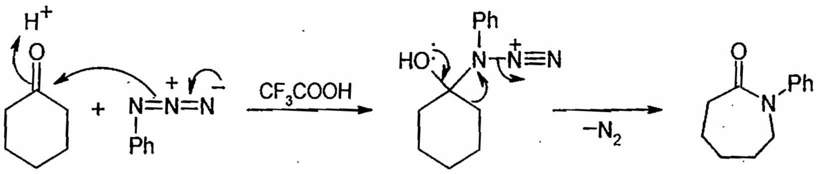


68) Ans (c):- The correct combination of reagents (1) NH$_2$NHTs; (2) 2 eq. BuLi; (3) CO$_2$

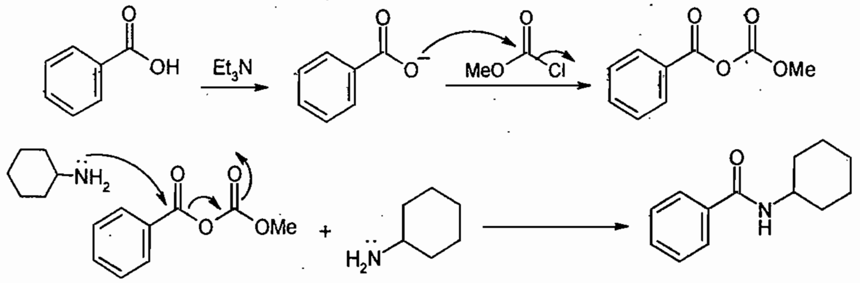
First step is the Shapiro reaction; (decomposition of the tosyl hydrazones of aliphatic aldehydes or ketones with very strong base, usually butyl lithium or LDA, to give corresponding vinyl lithium). In next step carbon dioxide reacts with vinyl lithium to give a carboxylic acid with one more carbon atom than the starting organometallic.



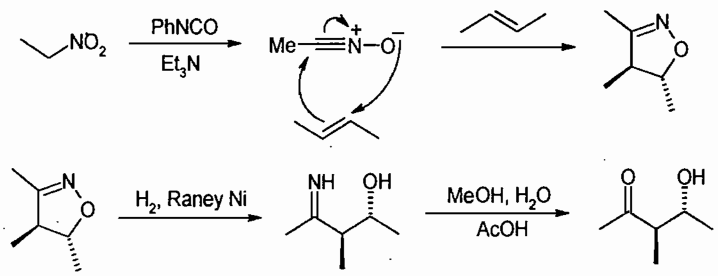
69) Ans (d):-



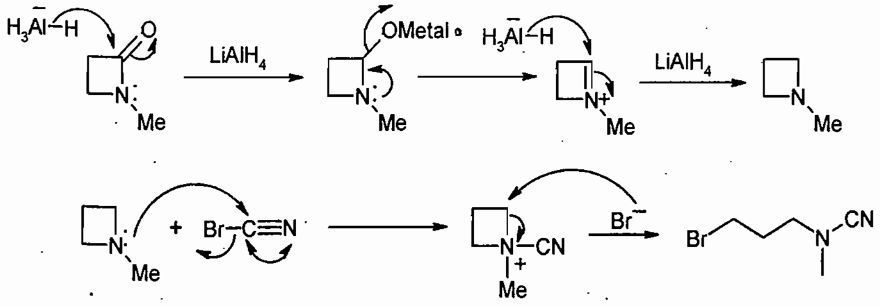
70) Ans (a):- First step is simple nucleophilic substitutuion on carbonyl carbon with loss of Cl^- (Cl^- is a better leaving group than MeO^-). Next step is also on nucleophilic substitutuion on more reactive carbonyl carbon of an anhydride.



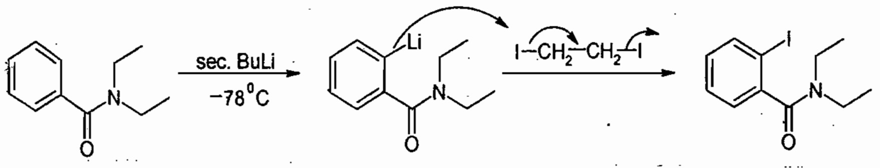
71) Ans (a):- In first step Nitrile oxide is generated by dehydration of primary nitro compounds with phenylisocyanate by treatment with a base. Next step is 1,3 dipolar cycloaddition with an alkene to form an isoxazoline. Last step is reduction of isoxazoline to form a β−hydroxy ketone



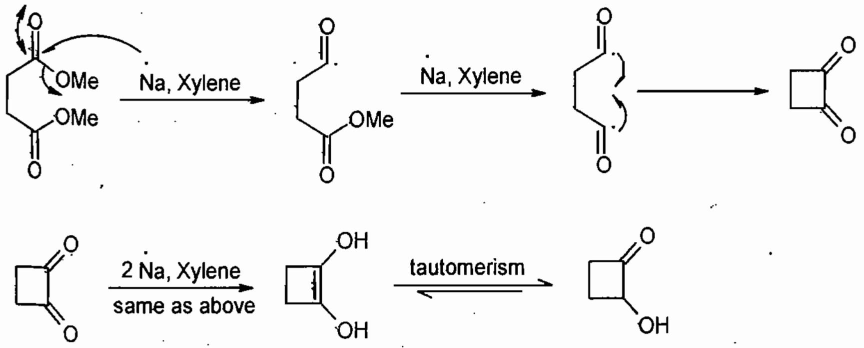
72) Ans (a):- Lithium aluminium hydride reduces amides to amines. In second step lone pair of nitrogen attacks on electrophilic carbon & leads to ring opening.



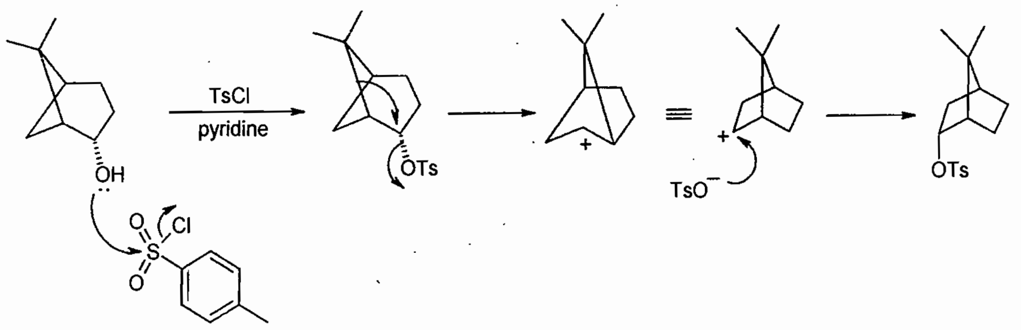
73) Ans (d):- The correct combination of reagents:- s-BuLi, -78^0C followed by ICH_2CH_2I



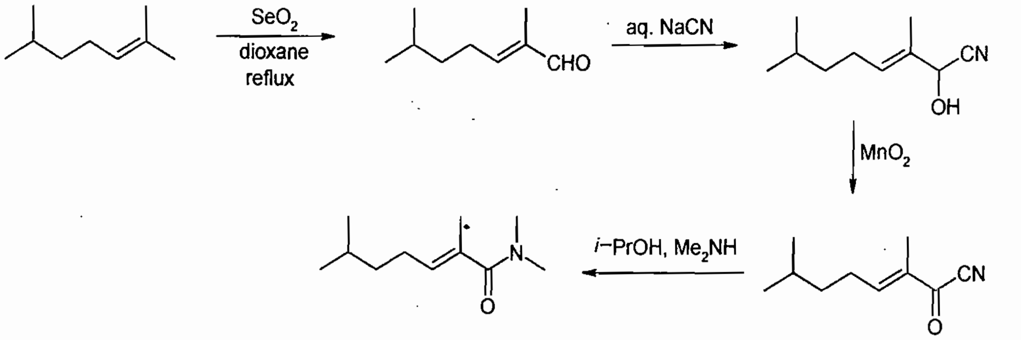
74) Ans (b):- The correct combination of reagents 1) Na, xylene, heat (2) H_2O, NaOH



75) Ans (b):- Toluene-para-sulfonyl chloride (TsCl) is used to convert the –OH (a bad leaving group) into the –OTs (a good leaving group). Endo product is formed to avoid the steric crowding.



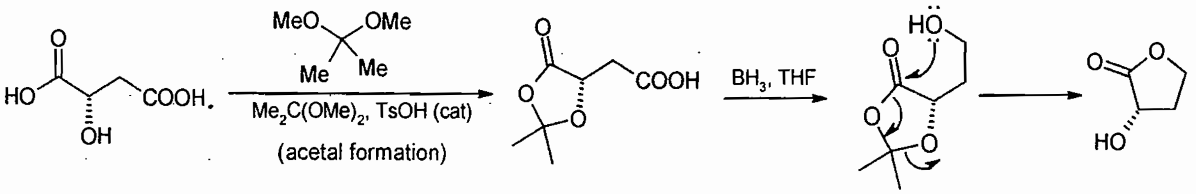
76) Ans (d):- In first step SeO_2 selectively oxidizes the less substituted allylic end of an alkene that is *E*- methyl group into the aldehyde. In next step aldehyde which reacts with cyanide to give the cyanohydrin. Oxidation of the cyanohydrin with manganese dioxide gives the acyl nitrile, which then reacts with the amine to give a amide by a loss of CN^- ion



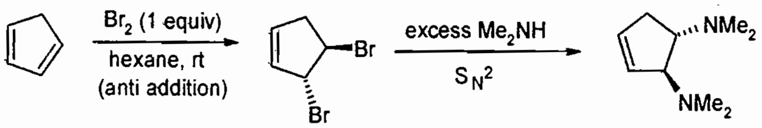
77) Ans (c):- First step is actal formation

In second step Borane reduce the carboxylic acid to give an alcohol. Borane is a highly chemoselective reagent for the reduction of carboxylic acids in the presence of other reducible functional groups.

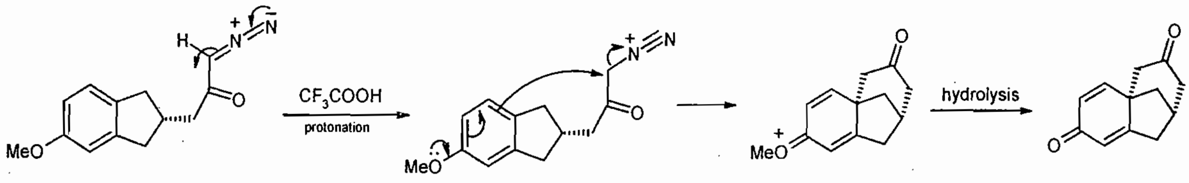
In the last step openeing of acetal via lactone formation.



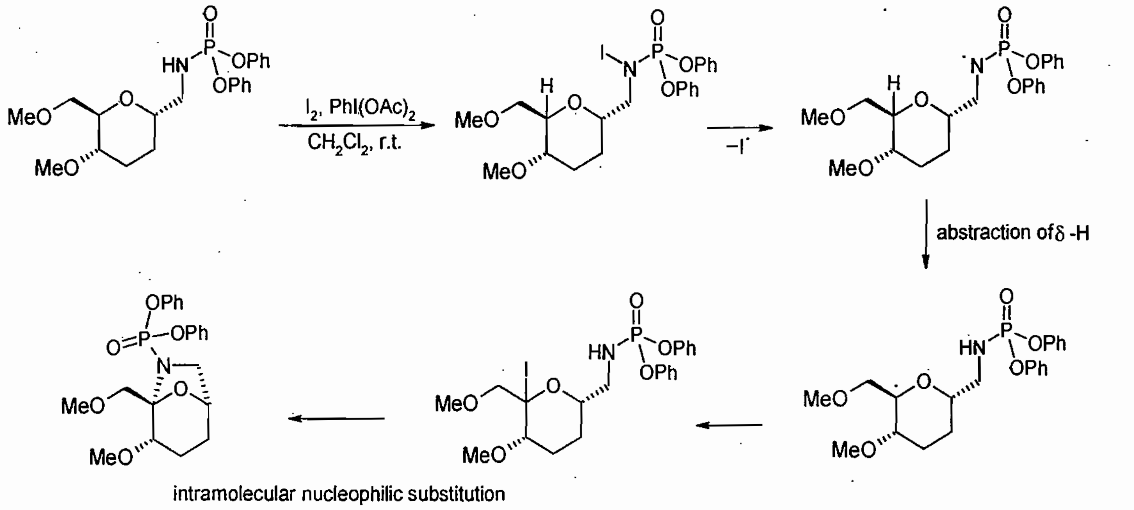
'8) Ans (c):- Addition of bromine with alkene in hexane, gives *anti*-1,2-dibromderivative; which undergoes nucleophilic substitution reaction with Me$_3$NH



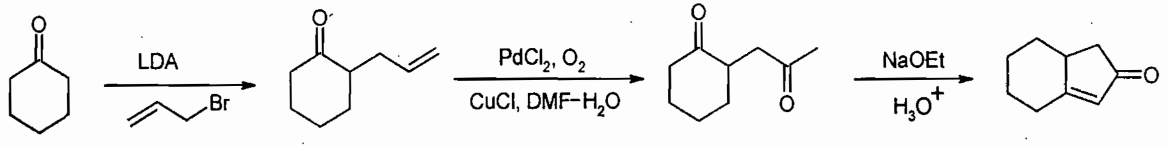
'9) Ans (b):- First step is protonation of the diazoketone followed by nucleophilic displacement of nitrogen from the resultant diazonium ion by the double bond or aromatic ring.

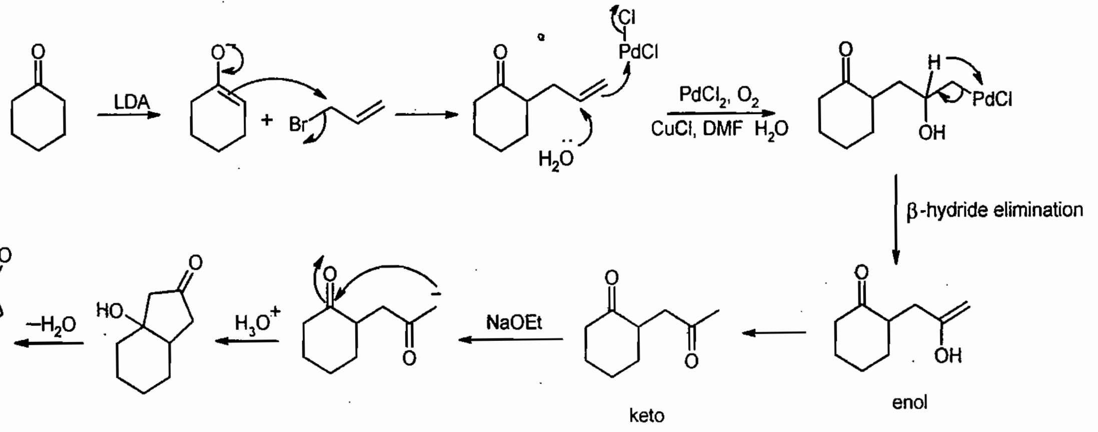


80) Ans (a):- The *N*-iodo compound is generated by reaction with iodine and iodobenzene diacetate. Warming or irradiating the reaction mixture promotes the formation of the nitrogen-centred radical and hence subsequent δ–hydrogen atom abstraction. Last step is a intramolecular displacement reaction.



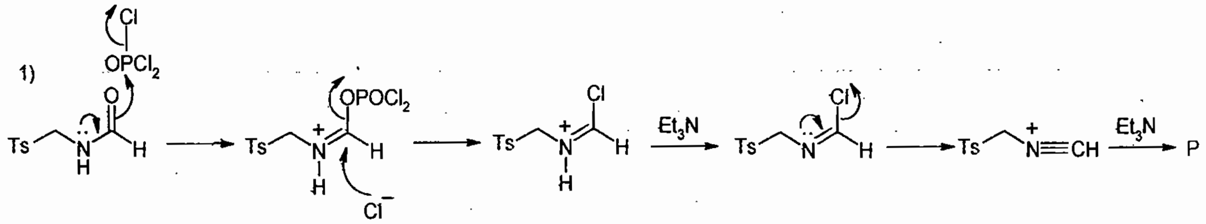
81) Ans (a):- First step is Michael reaction, followed by palladium-catalysed oxidation of the terminal alkene into the methyl ketones (Wacker oxidation). Last step is intramolecular aldol condensation.



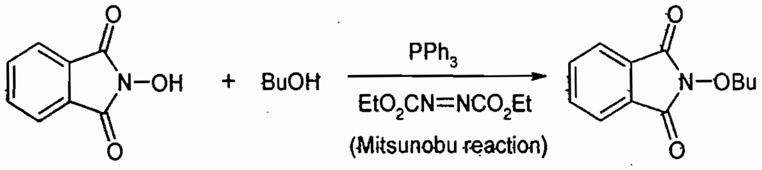


82) Ans (d):- The correct combinations of the reactions and the reagents are:-

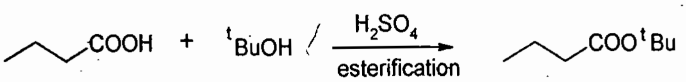
1)



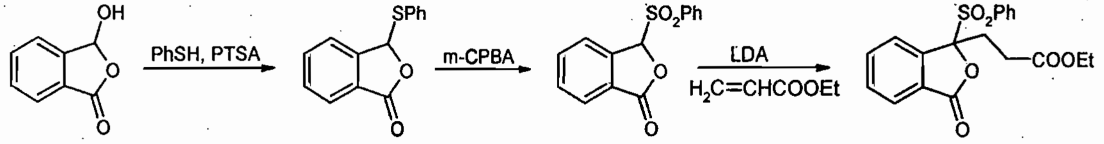
2)



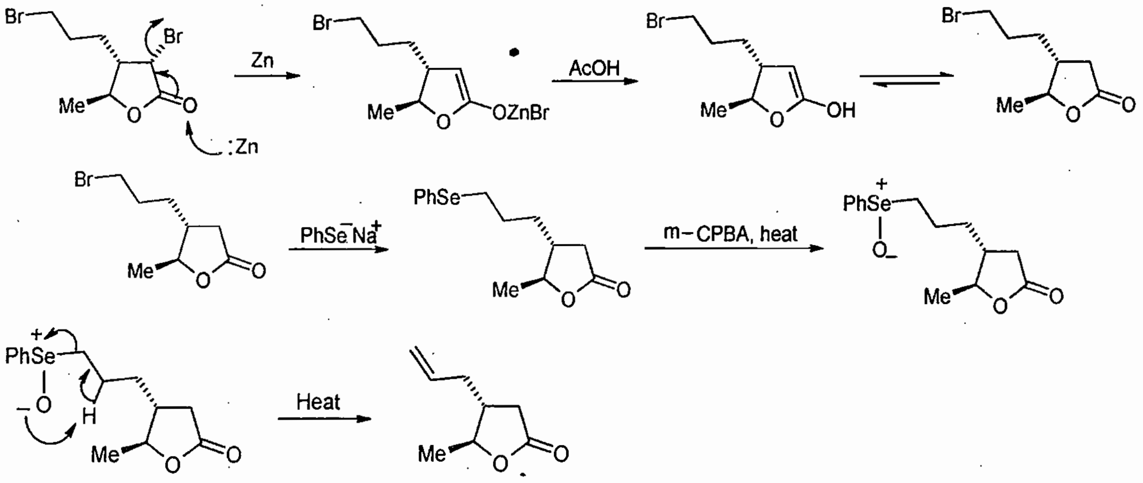
3)



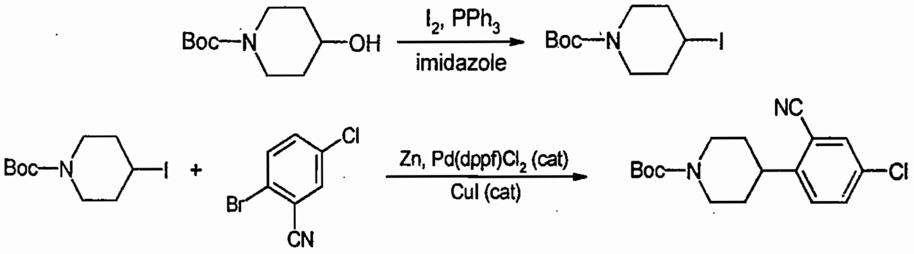
83) Ans (d):- First step is nucleophilic substitution reaction to give sulfide which on oxidation with m-CPBA give phenyl sulfones. Last step is Michael reaction



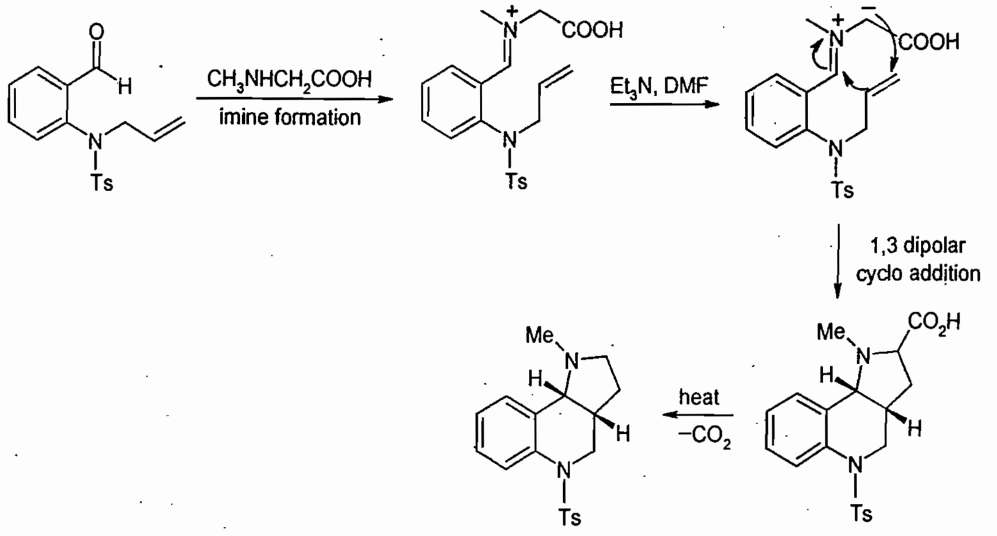
84) Ans (a):- In first step zinc remove halogen & forms a zinc enolate with α–halo ketone, which is converted into the ketone by the acid. In next step PhSe⁻ substitute Br & oxidized to selenoxides with *m*-CPBA. Last step is elimination step at elevated temperature



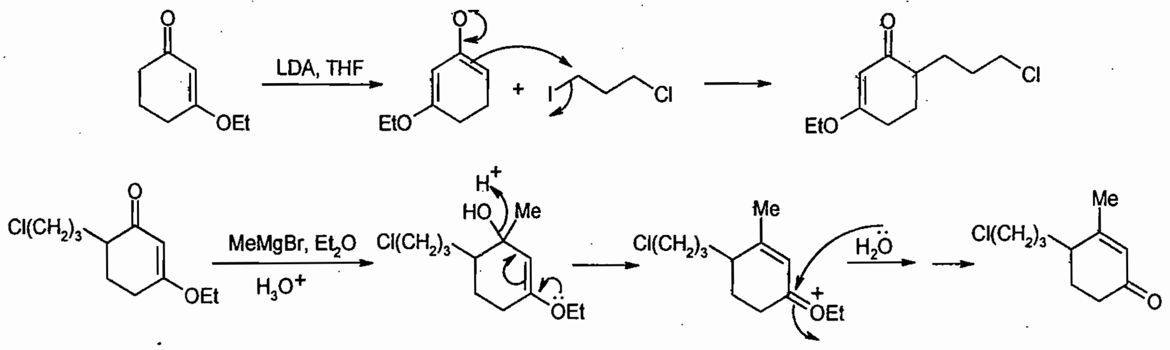
85) Ans (a):- First step is simple & selective reaction for conversion of *alcohols to their corresponding iodides* using PPh_3/I_2 & second step is coupling reactions.



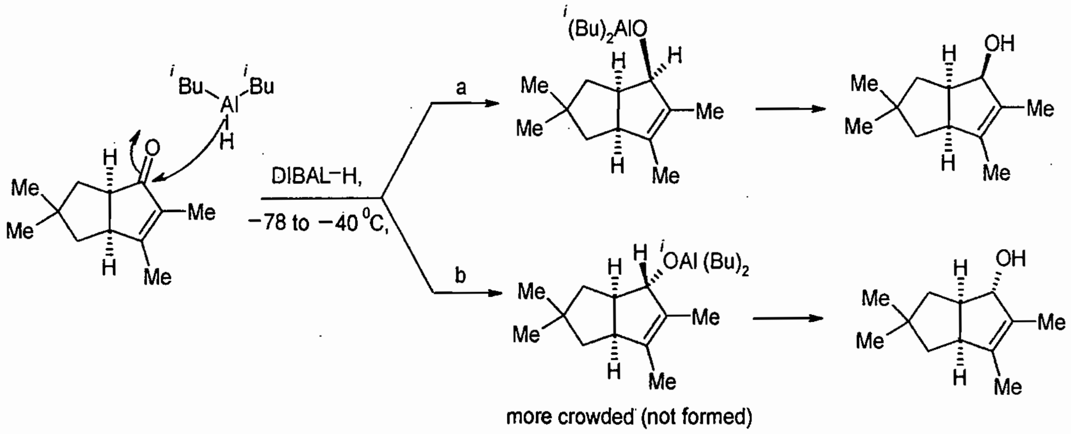
86) Ans (d):- First step is imine ion formation between sec.amine & aldehyde. Imine ion undergoes intramolecular 1,3 dipolar cycloaddition under basic medium.
Last step is a decarboxylation & leads formation of the pyrrolidine.



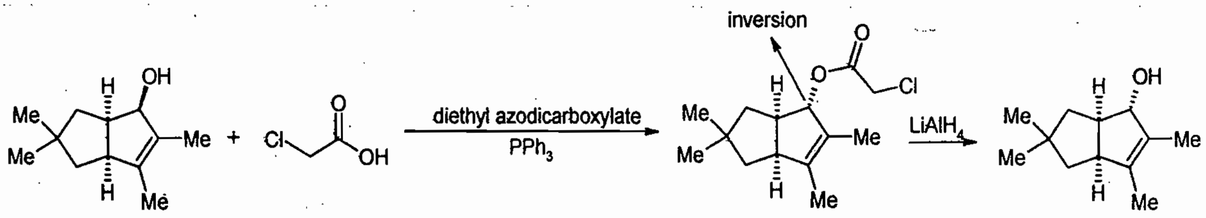
87) Ans (c):- First step is attack of enolate ion on carbon bearing iodine (iondine is better leaving group than chlorine.). In next step of Grignard reagent (hard nucleophile) adds to carbonyl carbon (hard elctrophile).



88) Ans (b):- In first step; DIBAL-H reduces α,β-unsaturated carbonyl compounds to allylic alcohols.

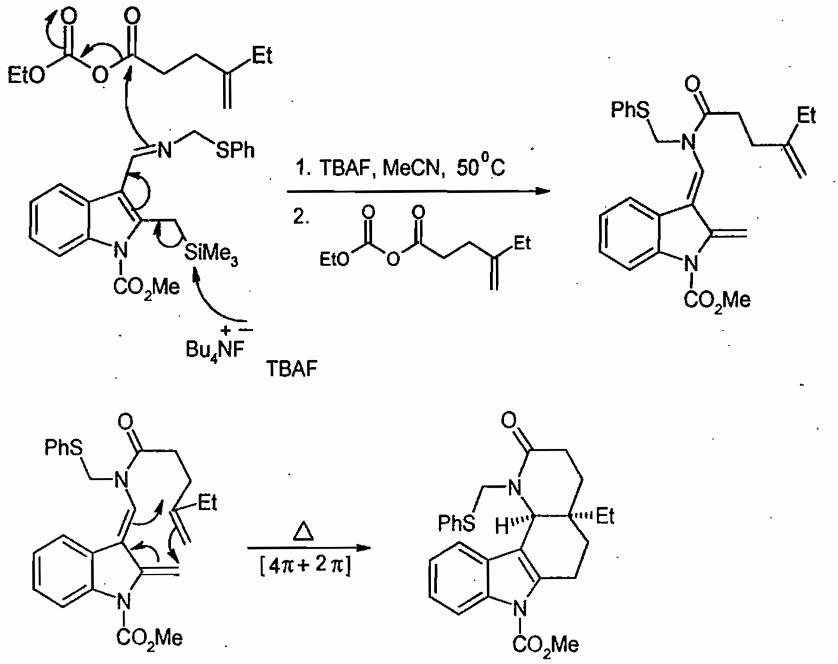


Second step is the Mitsunobu reaction & is used to replace −OH by another group with inversion of configuration. The nucleophile employed should be acidic, since one of the reagents (DEAD, diethylazodicarboxylate) must be protonated during the course of the reaction.
In last step; reduction of ester by LiAlH$_4$ to give an alcohol.

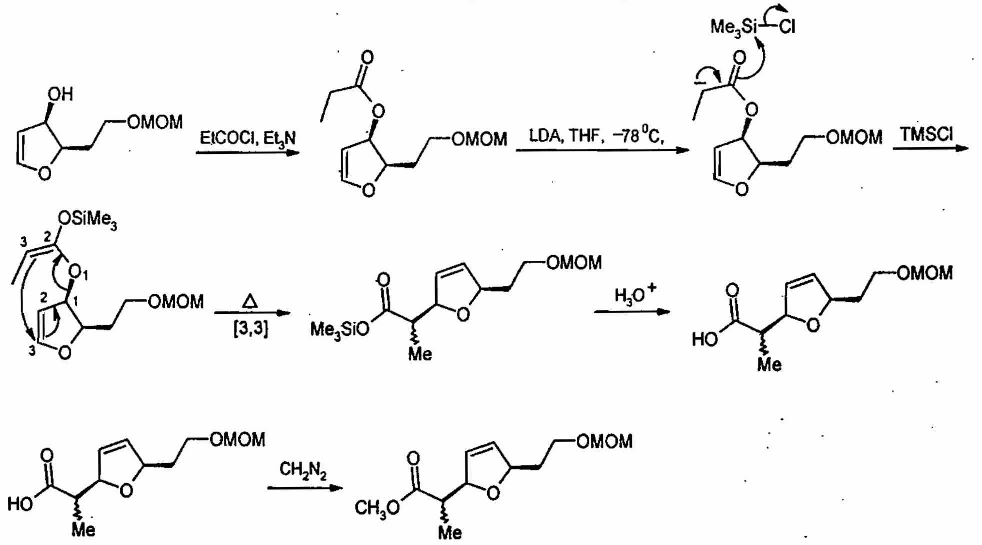


last step is S$_N$^{2} attack of nucleophile

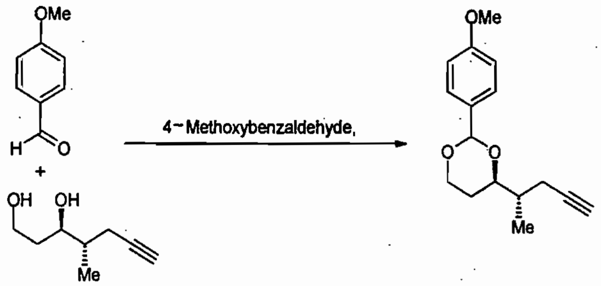
89) Ans (a):- In first step trialkylsilyl group is removed with fluoride salts (TBAF = $Bu_4N^+F^-$) to form a carbanion which via conjugation give N–acylation product. The resultant product on heating undergo [4n+2] cycloaddition in second step.

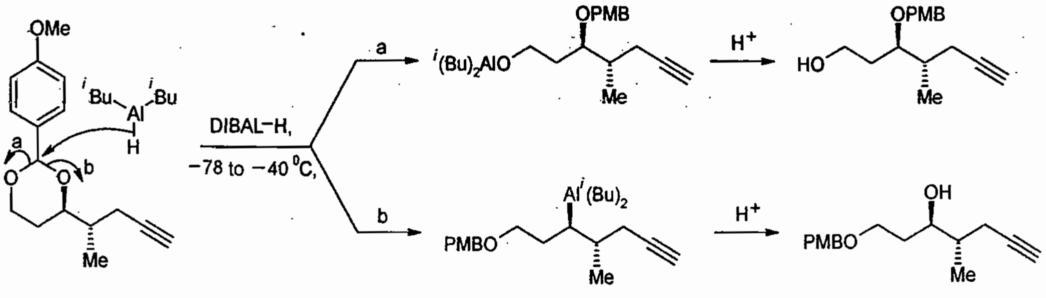


90) Ans (d):- Mechanism for the formation of major product is given below. Et_3N & LDA removes acidic proton in respective steps. In final step diazomethane methylates carboxylic acids



91) Ans (a):- In first step; reaction of 4-methoxybenzaldehyde with diols form six-membered cyclic acetal. In second step DIBAL-H reduces six-membered cyclic acetals & form a less crowded stable tetrahedral intermediate which on protic workup give product.

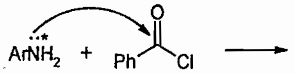




more crowded (not formed)

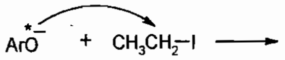
Not formed

92) Ans (b):- The Hammett reaction constant (ρ) indicate electron density in the transition state at the reaction centre. Positive value of ρ indicate increase electron density in the transition state at the reaction than in the starting material & negative value of ρ indicate decrease electron density in the transition state at the reaction centre than in the starting material.(* indicate the reaction centre)



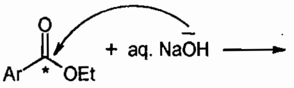
in benzene

Reaction costant(ρ) = -2.69 (electron density decreases at reaction centre)



in ethanol

Reaction costant(ρ) = -0.99 (electron density decreases at reaction centre)



in ethanol

Reaction costant(ρ) = $+2.01$ (electron density increases at reaction centre)

Answer Key

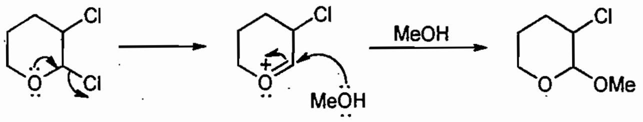
GATE EXAM (ONE OR TWO MARKS)

Topic: - Organic Reaction Mechanism (ORM, Reagents, Rearrangements & Name Reactions)

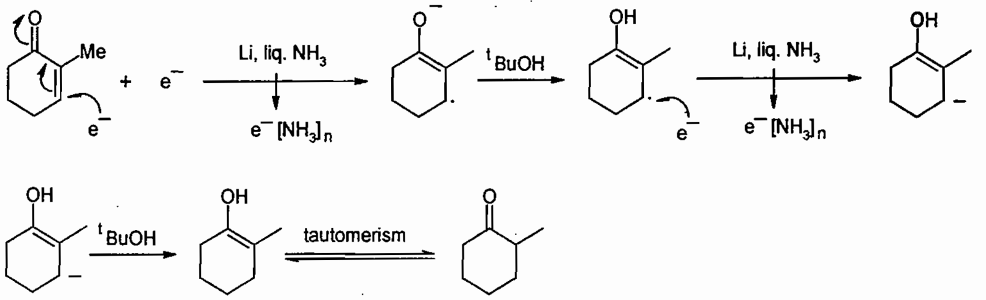
1	d	2	c	3	b	4	d	5	b	6	b	7	b	8	d	9	d	10	a
11	C	12	b	13	a	14	c	15	d	16	c	17	c	18	d	19	a	20	d
21	c	22	a	23	d	24	a	25	c	26	d	27	a	28	a	29	d	30	a
31	d	32	b	33	b	34	b	35	b	36	b	37	c	38	a	39	d	40	a
41	a	42	d	43	b	44	b	45	d	46	c	47	b	48	c	49	a	50	c
51	d	52	c	53	c	54	c	55	b	56	b	57	b	58	a	59	d	60	d
61	b	62	c	63	c	64	b	65	a	66	a	67	c	68	c	69	c	70	b
71	a	72	b	73	c	74	d	75	a	76	d	77	c	78	c	79	a	80	b
81	c	82	c	83	d	84	a	85	a	86	a	87	a	88	d	89	b	90	d
91	c	92	d	93	a	94	d	95	a	96	d	97	a	98	c	99	c	100	b
101	c	102	c	103	c	104	a	105	b	106	a								

Hint & solution of Questions from GATE EXAM

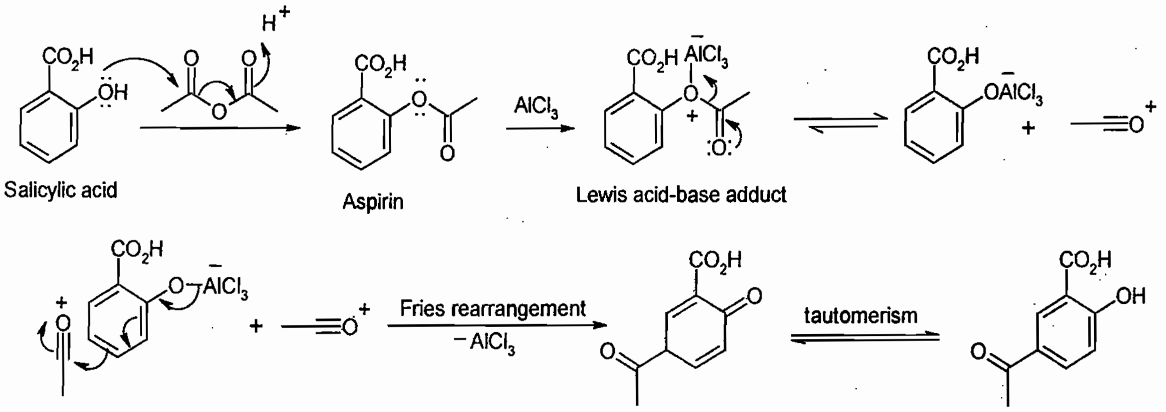
1) Ans (d):- Hint:- Oxygen acts as an internal nucleophile .



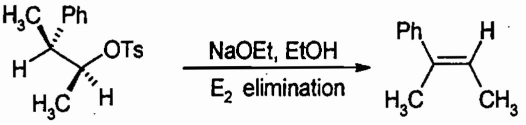
2) Ans (c):- When alkali metals dissolve in ammonia they give electrons (solvated electrons $e^-[NH_3]_n$) & is acts as reducing agent. Li, liq.NH_3 gives conjugate addition when react with unsaturated α,β– ketones.



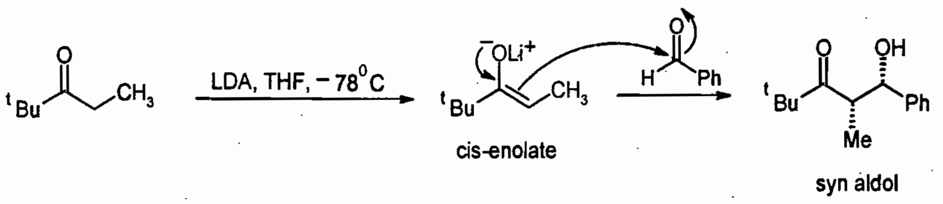
3) Ans (b):- First step is acylation of salicylic acid to give aspirin which is on heating with Lewis acid undergoes Fries rearrangement.

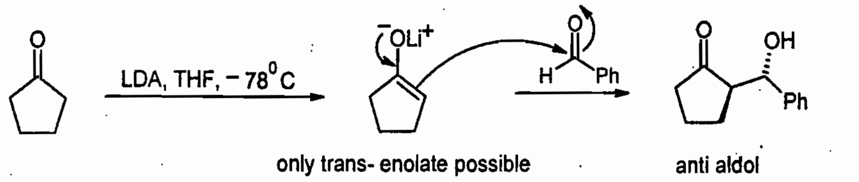


4) Ans (d):- It is a simple E_2 elimination reaction

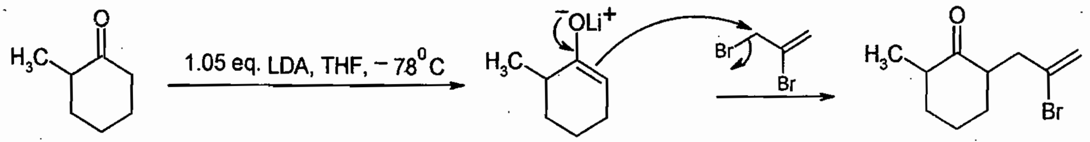


5) Ans (b):- Reactions are based on diastereoselectivity in aldol reactions.
In diastereoselective in aldol reactions generally cis-enolates give syn aldol & trans enolates give anti-aldol product.

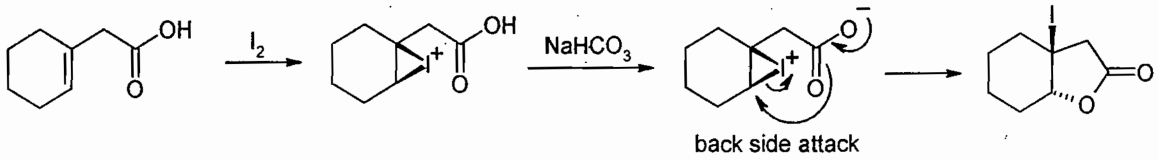




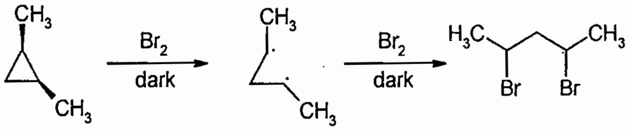
6) Ans (b):- LDA gives less-substituted enolate with unsymmetrical ketone. Enolate attack on allylic carbon bearing leaving group. Nucleophilic attack on vinylic carbon is difficult



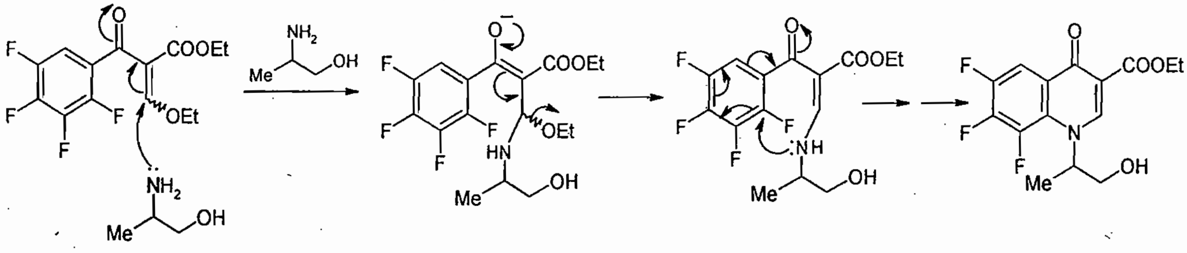
7) Ans (d):- I_2 will add to the double bond, forming a iodonium ion. In the second step of the addition reaction, the carbonyl oxygen is attack the back side of the iodonium ion, resulting in a compound with the observed configuration.



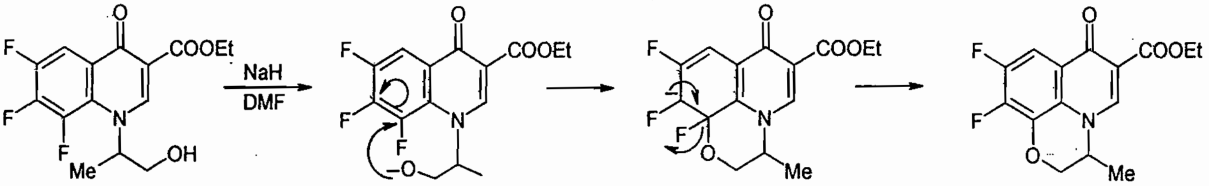
8) Ans (d):- It is an example of bromination via a more stable free-radical mechanism



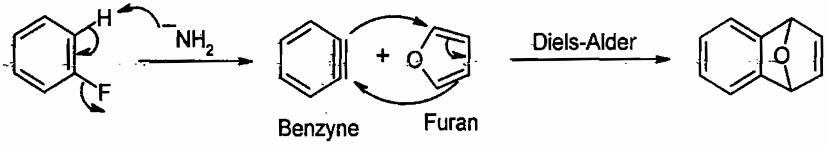
9) Ans (d):- First step is conjugate addition of amino group of an amino alcohol to unsaturated α,β– ketones (Nitrogen is better electron donor than oxygen). In the next step two nucleophilic aromatic substitution reactions take place via addition elimination meachanism. (first by nitrogen & second by alkoxide ion)

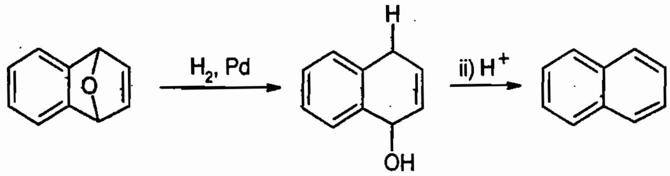


10) Ans (a):-

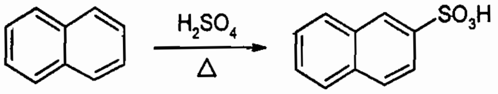


11) Ans (c):- First reaction give Naphthalene as major a product

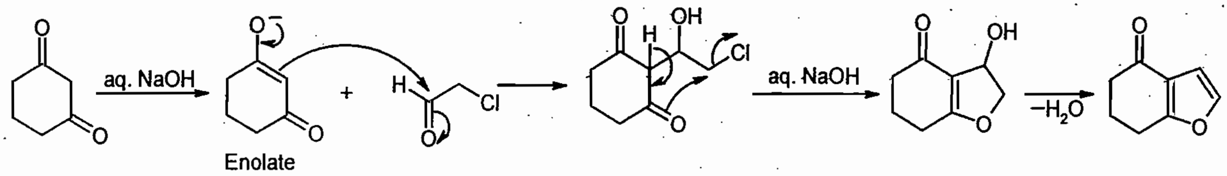




12) Ans (b):- Second step is sulphonation of Naphthalene with H_2SO_4 at 160⁰ C gives thermodynamic product that is 2-naphthalene sulfonic acid.

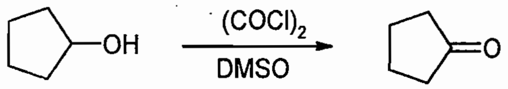


13) Ans (a):- It is the Feist–Benary Synthesis of furan:- (reaction of 1,3–dicarbonyl enolate with a 2–halo–ketone,

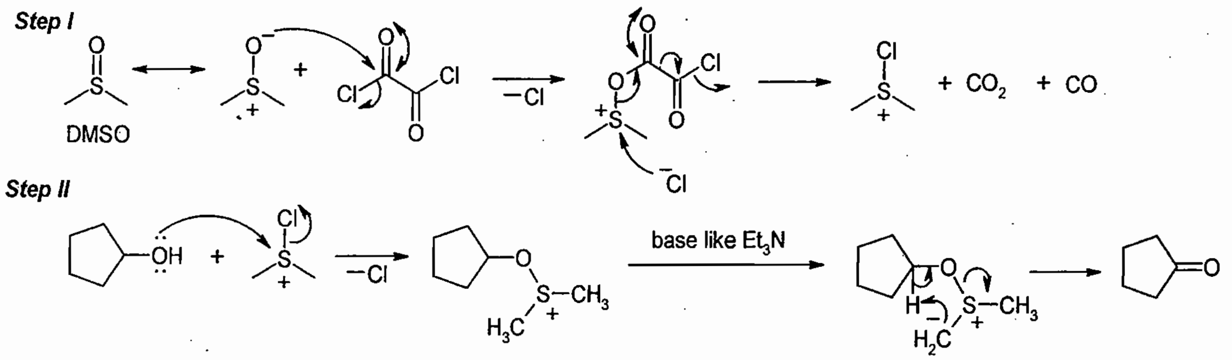


14) Ans (c):- This is the Swern oxidation useful to convert alcohols to aldehydes. It is two step reaction
In the first step, DMSO reacts with oxalyl chloride to give an electrophilic sulfur (Me_2S^+Cl)
In the second step alcohol attacks an electrophilic sulfur.

The Swern oxidation



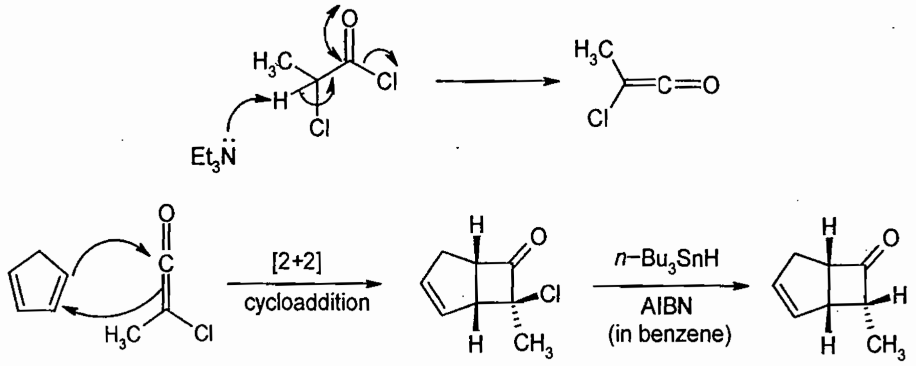
Mechanism



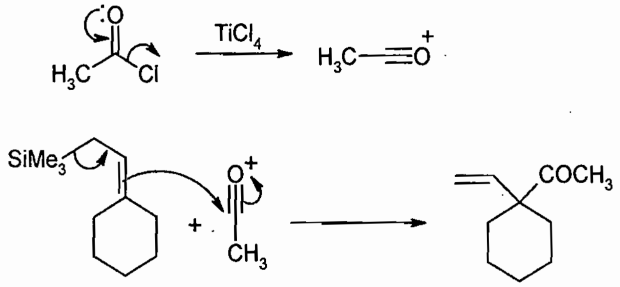
15) Ans (d):- The Hammett reaction constant (ρ) indicate the electron density in the transition state at the reaction centre. Positive value of ρ indicate; increase in electron density in the transition state at the reaction centre than in the starting material & negative value of ρ indicate; decrease in electron density in the transition state at the reaction centre than in the starting material.

Reaction	Intermediate	Reaction costant (ρ)
$ArCH_2{-}Cl \xrightarrow[70^\circ C,]{aq.\ acetone} ArCH_2{-}OH + HCl$	$Ar\overset{+}{C}H_2$	−1.88
$ArCH_2{-}COOH \underset{25^\circ C,}{\overset{H_2O}{\rightleftharpoons}} ArCH_2{-}COO^- + H^+$	simple ionisation	+0.49
$Ar{-}Cl \xrightarrow[50^\circ C,]{MeONa,\ MeOH} Ar{-}OMe + Cl^-$	via benzyne	+ 8.50
$Ar{-}COOH \underset{25^\circ C,}{\overset{H_2O}{\rightleftharpoons}} Ar{-}COO^- + H^+$	simple ionisation	+1

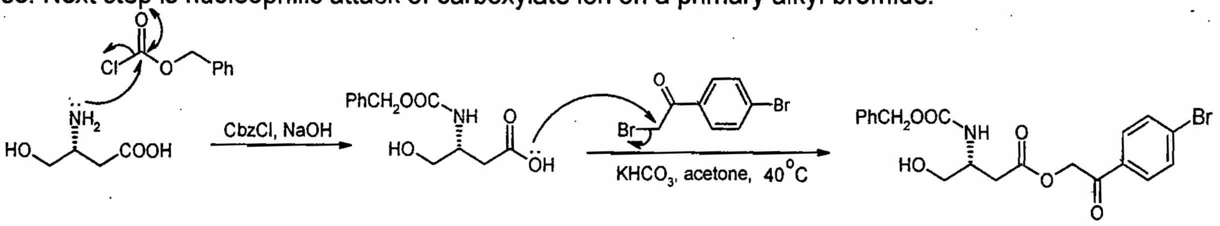
16) Ans (c):- First step is ketene formation which undergo [2+2] cycloaddition rather than [4+2] cycloaddition & form the cis-geometry at the ring junction. In the last step n-BuSnH with AIBN converts the C–Cl bond into C–H bond



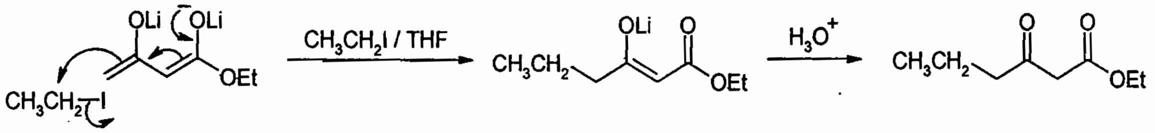
17) Ans (c):- In this reaction allyl silane reacts with acylium ions produced from acid chlorides & Lewis acid to form a product.,



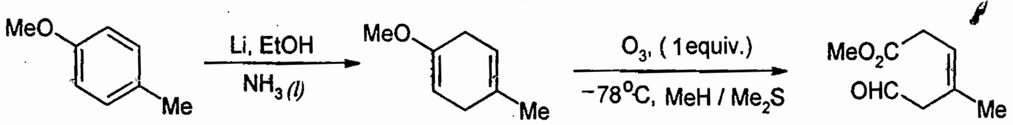
18) Ans (d):- First step is protection of NH_2 group by treating with benzyl chloroformate (BnOCOCl) and weak base. Next step is nucleophilic attack of carboxylate ion on a primary alkyl bromide.



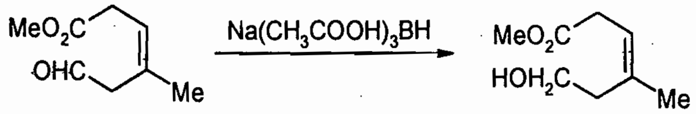
19) Ans (a):- Hint:-Dianion of ethyl acetoacetate is usually alkylated on the terminal carbon atom.



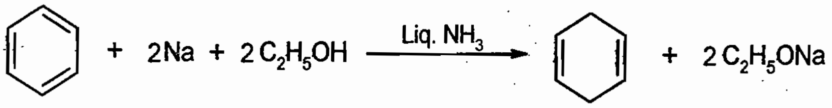
20) Ans (d):- In Birch reduction, 1,4 reduction of aromatic ring occur at ortho & meta position w.r.to electron donating group (regioselective). In the next step ozonolysis of more electron rich alkene take place



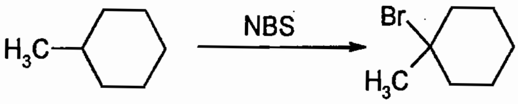
21) Ans (c):- $Na(CH_3COO)_3BH$ is like $NaBH_4$ & only reduces aldehyde & ketones.



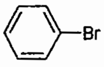
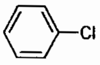
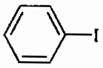
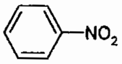
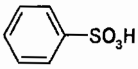
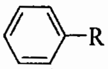
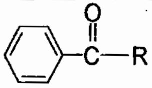
22) Ans (a):- It is Birch reduction (1,4 reduction of aromatic ring)



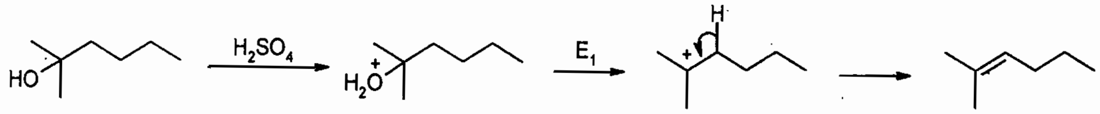
23) Ans (d):- It is an example of radical bromination of most stable free radical by *N*-bromosuccinimide (NBS)



24) Ans (a):- Benzene cannot be iodinated with I_2 directly. However, in presence of oxidants such as HNO_3, iodination is possible. The electrophile formed in this case is I^+

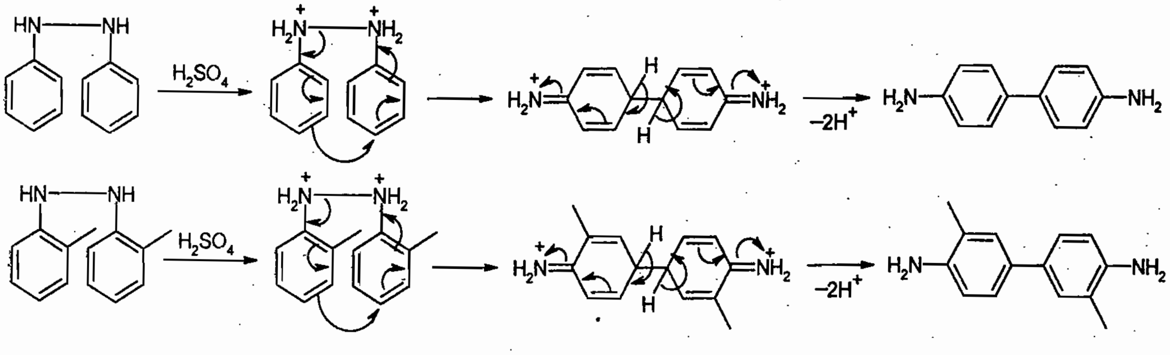
Reaction	Reagents	Electrophile	Product
Halogenation	Br_2 / $FeBr_3$	Br^+	
	Cl_2 / $FeCl_3$	Cl^+	
	I_2 / $CuCl_2$ or I_2 / HNO3	I^+	
Nitration	HNO_3/H_2SO_4	NO_2^+	
Sulfonation	SO_3/ H_2SO_4	SO_3	
Alkylation	R-Cl / $AlCl_3$	R^+	
Acylation	RCOCl / $AlCl_3$	$RC{\equiv}O^+$	

25) Ans (c):- It is an example of E_1 reaction to give more substituted alkenes (more stable) as a major product

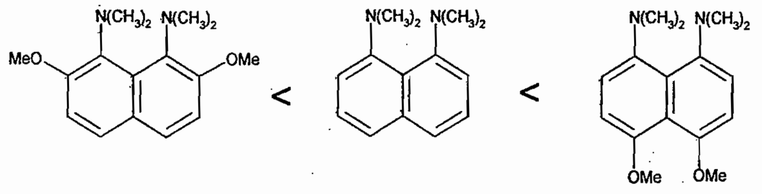


26) Ans (d):- Electrophiles (electron acceptor) are SO_3, Cl^+, H_3O^+, BH_3; Nucleophiles (electron donor) are CH_3NH_2, CN^-

27) Ans (a):- It is an example of Benzidine Rearrangement (Rearrangement of hydrazobenzene to yield benzidine). It has been demonstrated by crossover experiments that the rearrangement does not proceed *via* a dissociation/ recombination process.



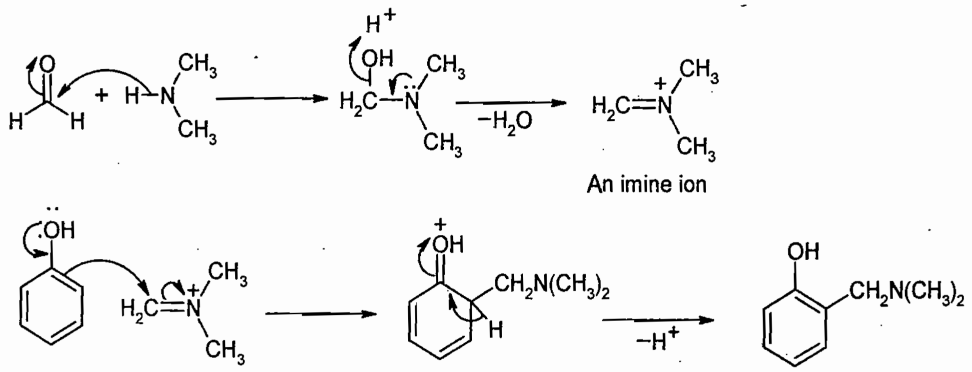
28) Ans (a):- Y is least basic due to steric crowding of o-methoxy group. Z is the most basic due electron donating effect of p-methoxy group. The increasing order of basicity is.



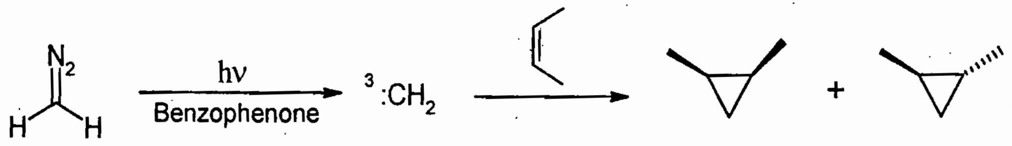
(Y) (X) (Z)

29) Ans (d):- Tertiary alkyl halides cannot undergo S_N^2 reactions due to steric hindrance to back-side attack. Therefore reaction follows S_N^1 mechanism & rate of the reaction depends on the concentration of alkyl halide only and not on the concentration of nucleophile thus the rate of the reaction will doubled if the concentration of both the reactants is doubled

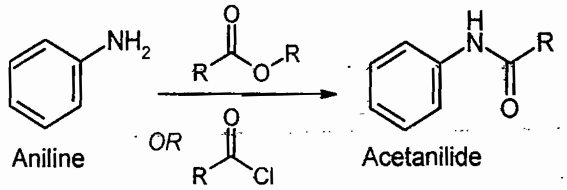
30) Ans (a):- It is an example of Mannich reaction. In first step dimethyl amine adds to formaldehyde to form an imine ion. In next step phenol attacks on imine ion.



31) Ans (d):- The alkene insertion reaction is stereospecific only for singlet carbenes (thermally). For triplet carbenes, the reaction is nonstereospecific but stereoselective (photochemically).

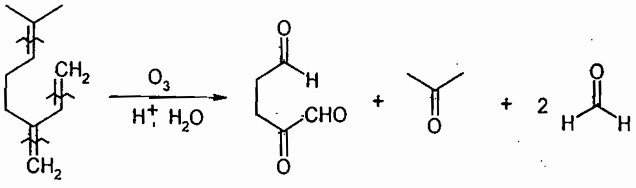


32) Ans (b):- Formaldehyde on reacting with aniline will NOT form an acetanilide.

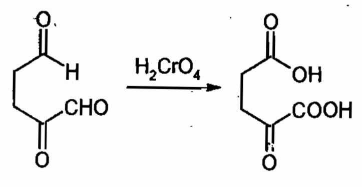


33) Ans (b):- aniline and methylamine can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with $NaNO_2$ + dil.HCl at 0-5°C, followed by a reaction with the alkaline solution of β naphthol. Aliphatic amines give a brisk effervescence due to the evolution of N_2 gas under similar conditions.

34) Ans (b):- First step is ozonolysis, Chromic acid oxidizes aldehyde into carboxylic acid



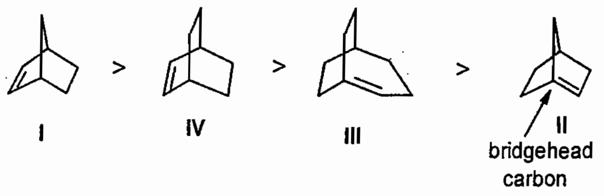
(X)



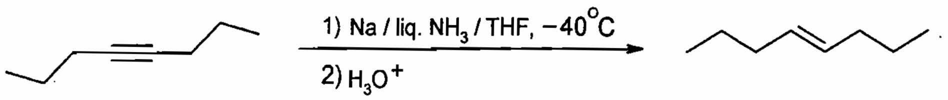
(X)

35) Ans (b):- Refer the solution of question number (34)

36) Ans (b):- Bredt's rule:- double bonds can never be formed to bridgehead carbons in bicyclic systems unless one of the rings contains at least eight carbon atoms. Among all (II) bicyclic olefin is not possible due to angle strain; therefore planar structure is not possible at bridgehead carbon.

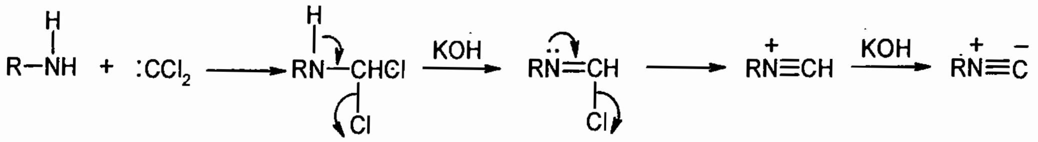


37) Ans (c):- It is a Birch reduction reaction. It brings out a partial reduction of alkynes to trans alkene (stereospecific)

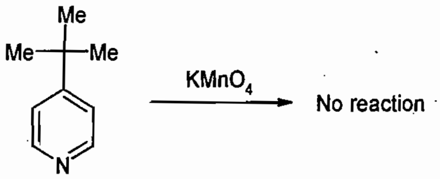


38) Ans (a):- In carbylamine reaction; primary amines are heated with chloroform and alcoholic KOH give isocynaides via carbene (dichlorocarbene) as the intermediate.

$$CHCl_3 + KOH \longrightarrow :CCl_2$$



39) Ans (d):- $KMnO_4$ oxidizes an alkyl group bonded to a benzene ring in to the carboxyl group (−COOH). If the alkyl group lacks a benzylic hydrogen, the oxidation reaction will not occur because the first step in the oxidation reaction is removal of a hydrogen from the benzylic carbon.

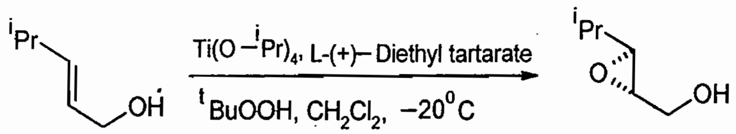


40) Ans (a):- The Hammett reaction constant ρ is based on the rates of alkaline hydrolysis of various *meta*- and *para*-substituted ethyl benzoates.

41) Ans (a):- Schrock carbenes are triplets and nucleophilic

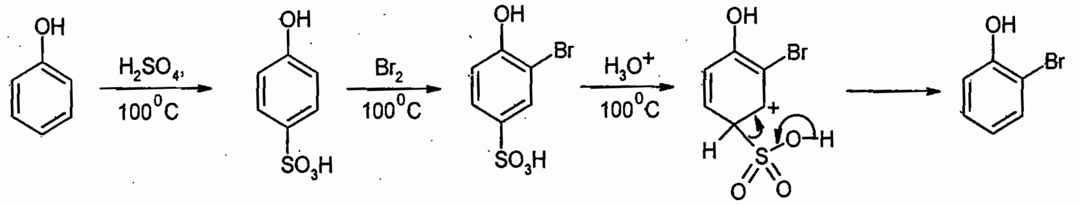
$$L_nM{=}CR_2 \longleftrightarrow L_n\overset{+}{M}{=}\overset{-}{C}R_2$$

42) Ans (d):- The Sharpless Epoxidation allows the enantioselective epoxidation of prochiral allylic alcohols. D-(−)-diethyl tartrate delivers oxygen to top face of alkene while L-(+)-diethyl tartrate delivers oxygen to bottom face of alkene

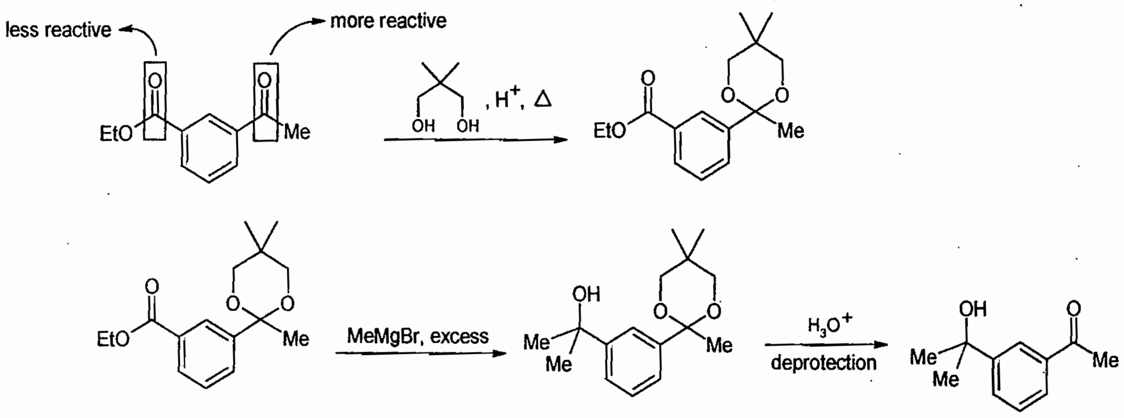


43) Ans (b):- at the higher temperature, thermodynamically stable para product is produced exclusively which on bromination gives 3-bromo-4-Hydroxybenzenesulfonic acid.

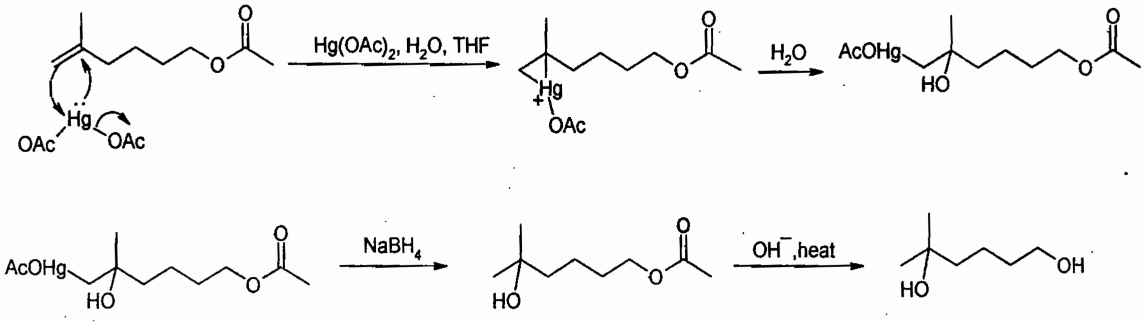
In last step the desulfonation of 3-bromo-4-Hydroxybenzenesulfonic acid is takes place when it is heated in dilute acid.



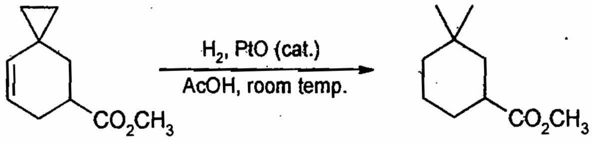
44) Ans (b):- The first step puts the protecting group on to the (more electrophilic) ketone carbonyl, making it unreactive towards nucleophilic addition. The Grignard reagent(in excess) then adds to the ester, to give a tertiary alcohol. Final step is 'deprotection' step, acid-catalysed hydrolysis of the acetal, gives us back the ketone.



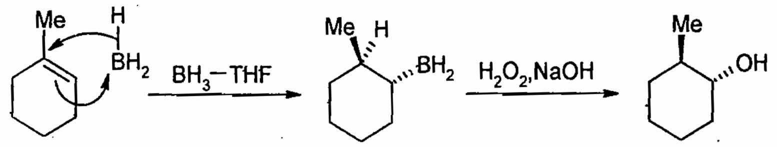
45) Ans (d):- First step is a oxymercuration (Markovnikov addition H-OH)(ester is not reduced by NaBH4). Final step is base-catalysed hydrolysis of an ester.



46) Ans (c):- It is a catalytic hydrogenation & chemoselectivily hydrogenate double bond in the presence of ester.

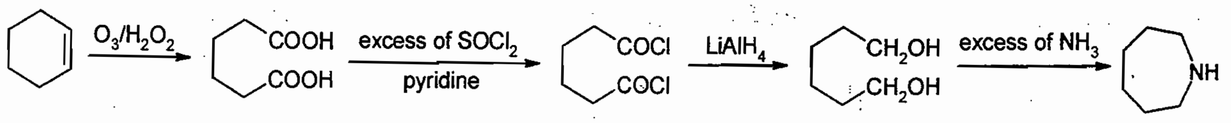


47) Ans (b):- Hydroboration is mostly used for the conversion of alkenes to alcohols by the syn (cis) addition of water (that is H & OH) .The –OH group going to the less substituted end of the alkene..

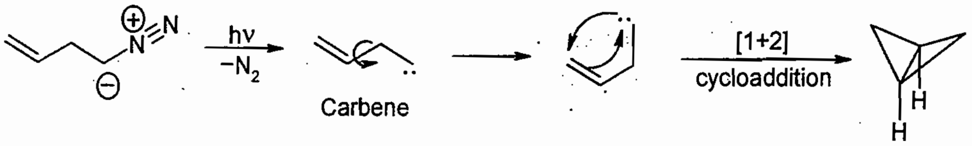


Syn addition of H—BH$_2$

48) Ans (c):- The most appropriate sequence of reactions for carrying out the formation is:-
i) O_3/H_2O_2; ii) excess $SOCl_2$/pyridine; iii) $LiAlH_4$; iv) excess NH_3,

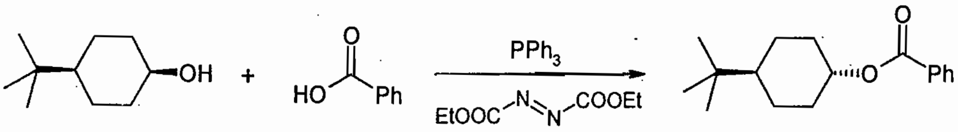


49) Ans (a):- First step is formation of carbenes from diazoalkenes followed by intramolecular [1+2] cycloaddition of singlet carbenes

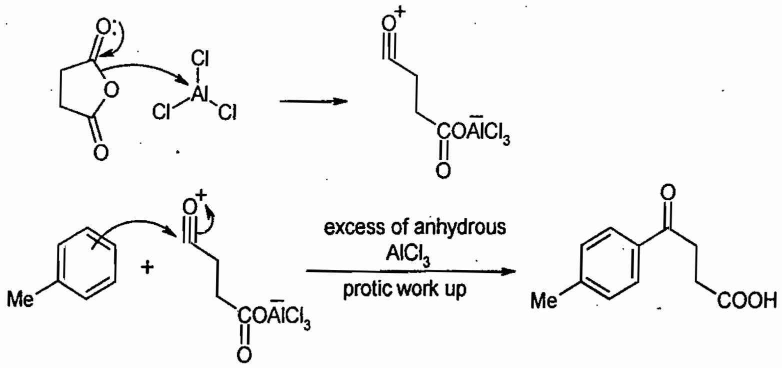


50) Ans (c):- The product shows 2 number of signals in ^1H and 2 number of signals in ^{13}C NMR spectra,

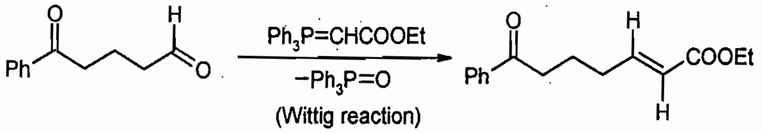
51) Ans (d):- It is the Mitsunobu reaction:- A reaction of secondary alcohol to ester with inversion of configuration



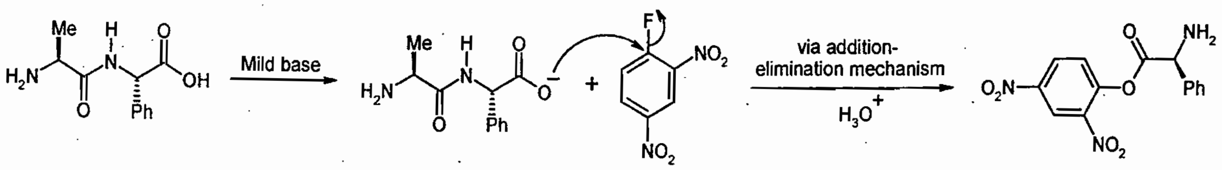
52) Ans (c):- It is a simple Friedel–Crafts acylation reaction



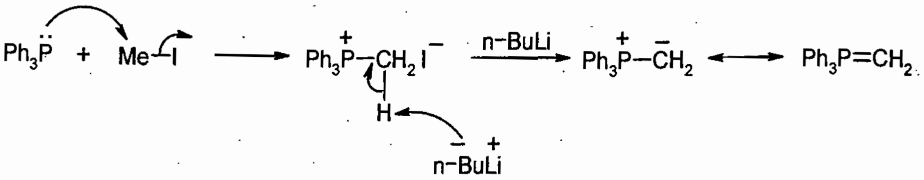
53) Ans (c):- It is the Wittig reaction with stabilized ylides to give E-alkene selectively. Wittig reagent adds to more electrophilic aldehyde carbonyl group.



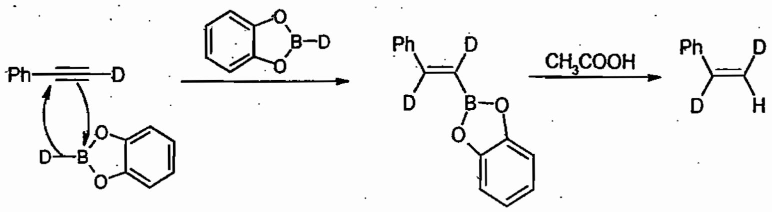
54) Ans (c):- It is example of nucleophilic aromatic substitution by the addition–elimination mechanism



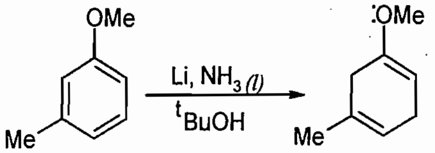
55) Ans (b):- It is the preparation of phosphonium ylide in Wittig reaction



56) Ans (b):- The boran adds to less hindered side of alkynes and addition of boron and deuterium occurs *cis* stereospecifically.

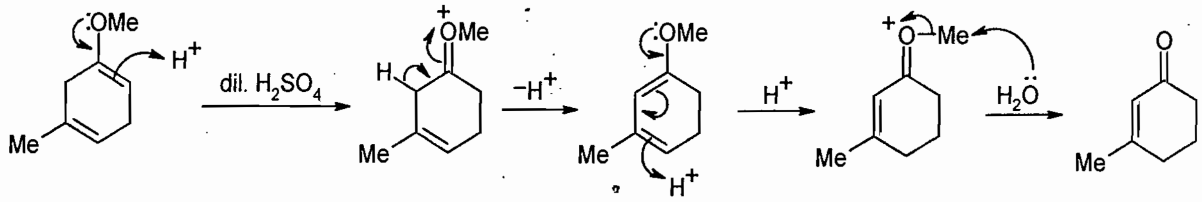


57) Ans (d):- In Birch reduction, 1,4 reduction of aromatic ring occur at ortho & meta position w.r.to electron donating group (regioselective). However, the product formed undergoes isomerization & hydrolysis to give α,β-unsaturated ketone in acidic condition.

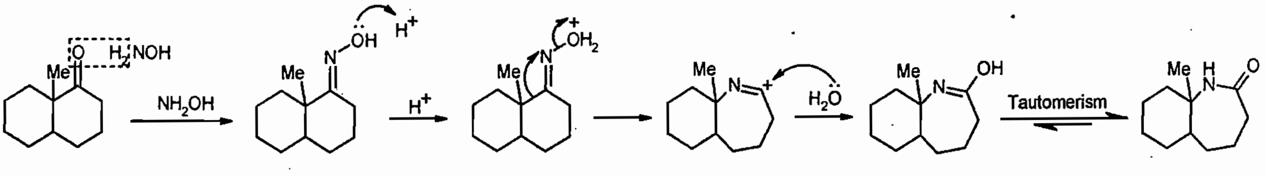


(Birch reduction)

m-methylanisole

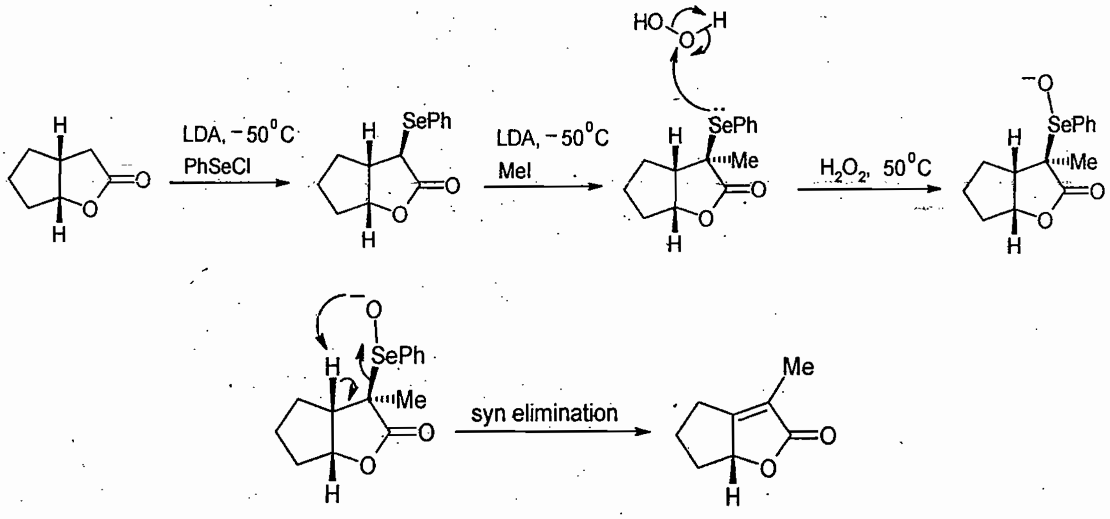


58) Ans (a):- It is an example of the Beckmann rearrangement



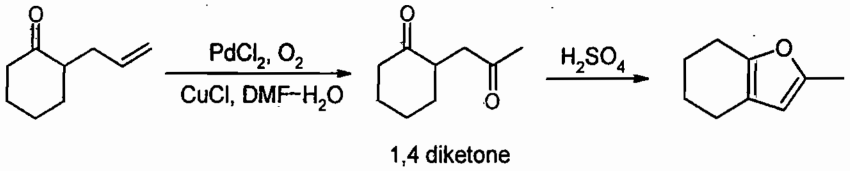
80%

59) Ans (d):- Reaction involve the oxidation of the selenide & then transformation of carbonyl compounds to α,β-unsaturated carbonyl compounds by syn elimination of selenoxide

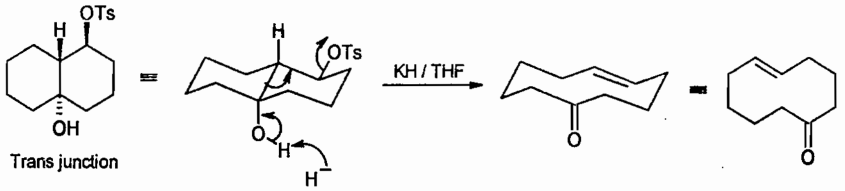


60) Ans (d):- First step is palladium-catalysed oxidation of the terminal alkene into the methyl ketones (Wacker oxidation).

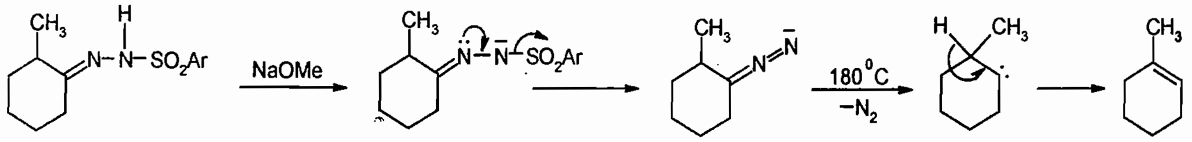
In second step 1,4 - Dicarbonyl Compounds with dehydrating agent undergoes cyclodehydration to form furans.



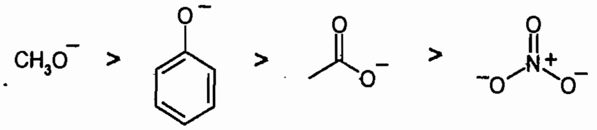
61) Ans (b):- The reaction is an example of the Grob fragmentation and takes place in a concerted manner to give an alkene. The stereochemistry of an alkene in a product is governed by the relative orientation of the groups in the starting compound. When tosyloxy group and the adjacent ring junction hydrogen atom are *cis*, it will give *E*-5-cyclodecenone in high yield, whereas when tosyloxy group and the adjacent ring junction hydrogen atom are *trans*, it will give *Z*-5-cyclodecenone in high yield.



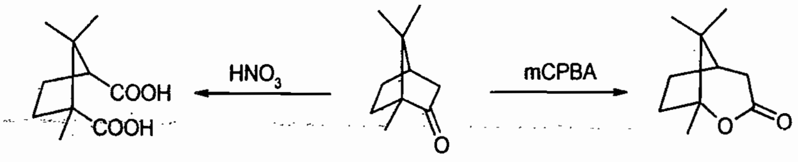
62) Ans (c):- Bamford–Stevens Reaction:- Reaction of tosylhydrazones with a mild base such as NaOMe or KH to give more substituted alkenes.



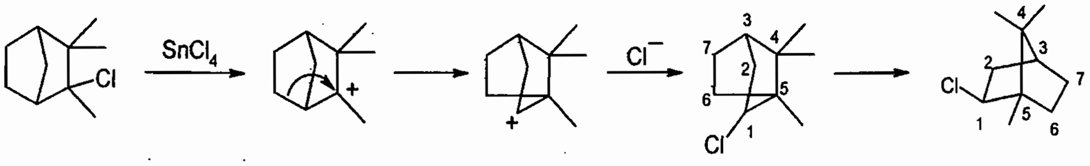
63) Ans (c):- Hint:- Conjugation decreases the nucleophilicity. Therefore nucleophilicity decreases left to right as conjugation become more effective



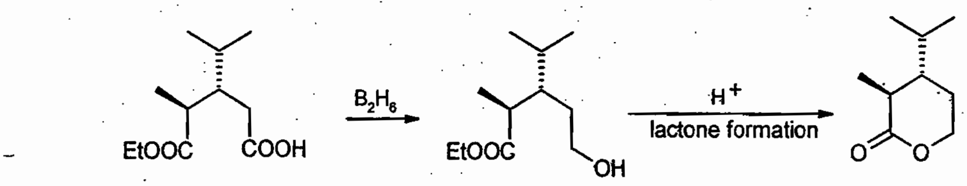
64) Ans (b):-



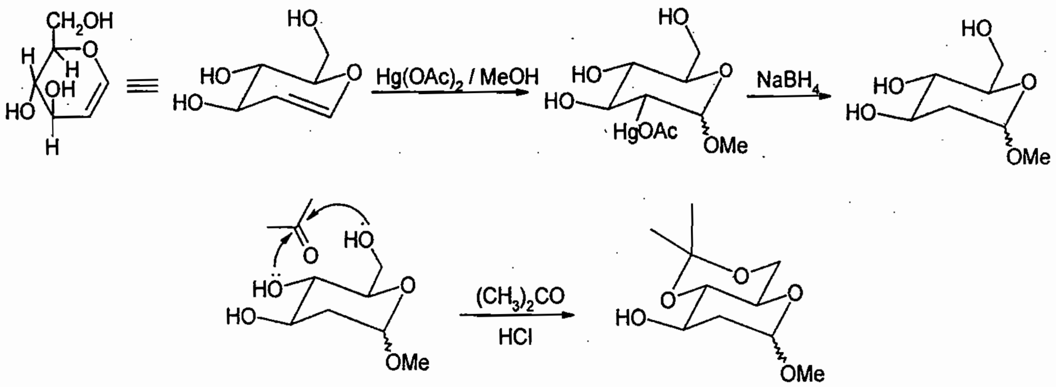
65) Ans (a):- It is an example of Wagner–Meerwein rearrangement (the migration of an alkyl group to a carbocation.)



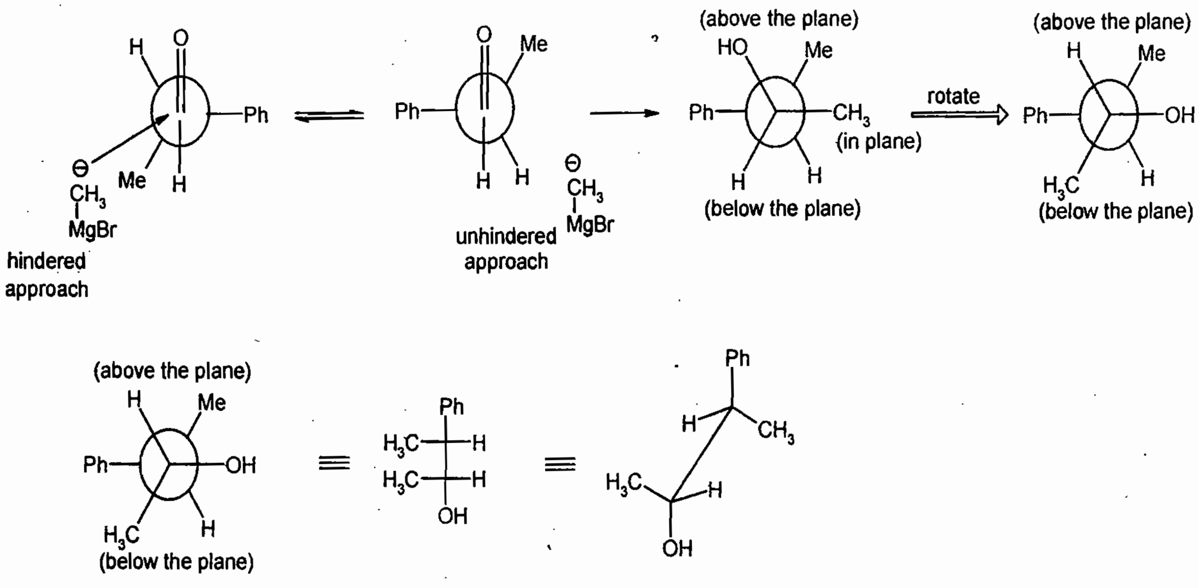
66) Ans (a):- Borane is a highly chemoselective reagent for the reduction of carboxylic acids in the presence of other reducible functional groups such as esters, and even ketones.



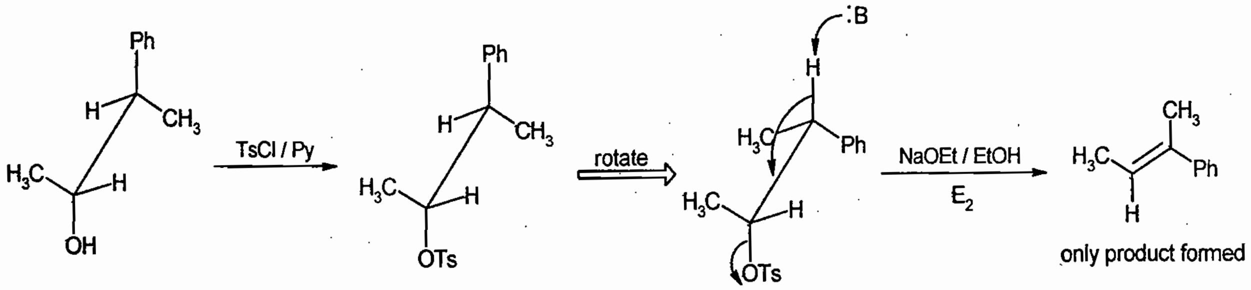
67) ans (c):- it in an example of oxymercuration followed by acetal formation



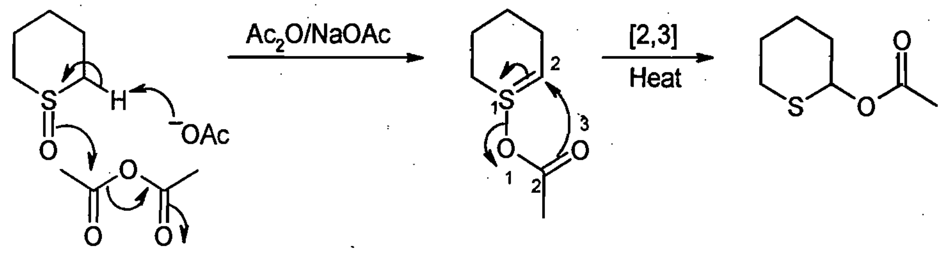
68) Ans (c):- The most important conformations of a carbonyl compound with a stereogenic centre adjacent to the carbonyl group are those that place the largest group perpendicular to the carbonyl group. The major product arises from the most reactive conformer in which approach of nuclophile is unhindered. Thus (c) is the major product.



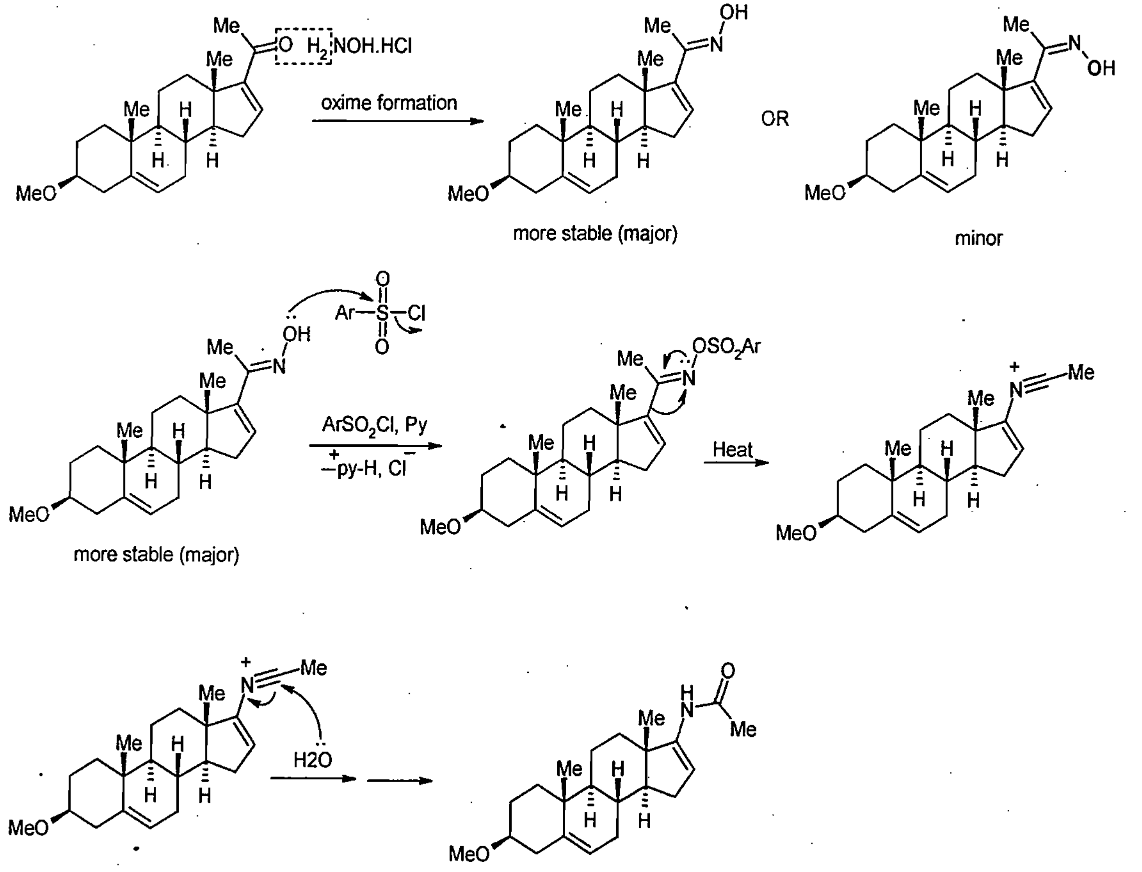
69) Ans (c):- It in an example of E_2 anti-elimination reaction



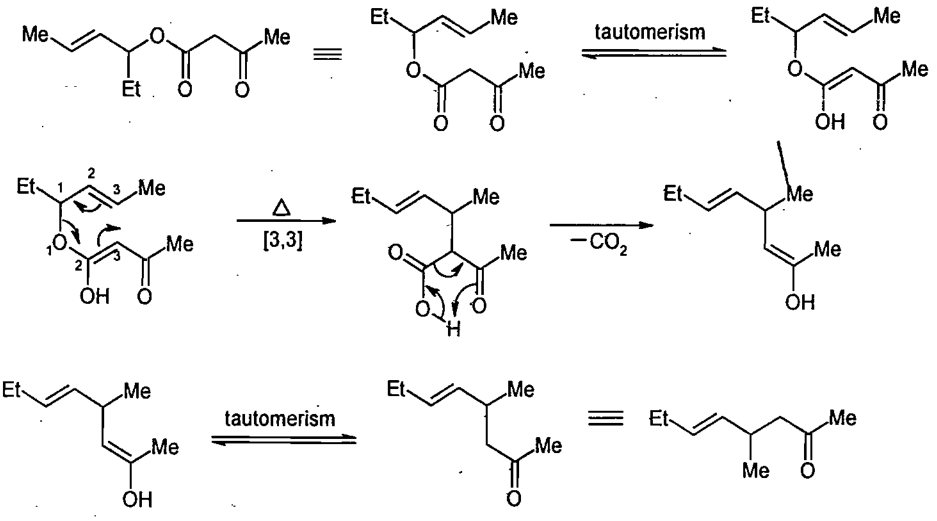
70) Ans (b):- It is simple acylation of oxygen of sulfoxide followed by [2,3]-sigmatropic rearrangement.



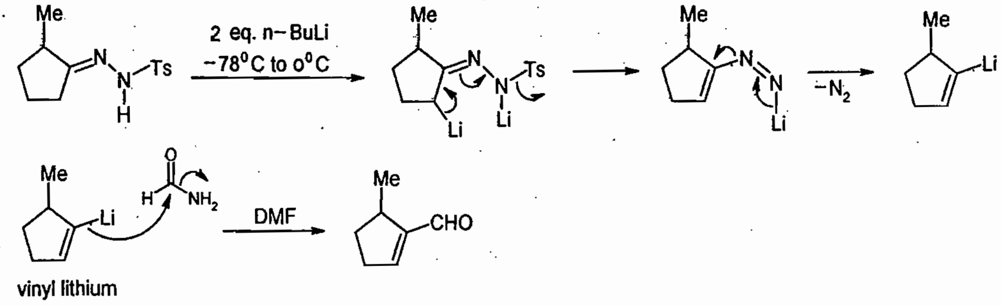
71) Ans (a):- First step is oxime formation & then rearrangement of oxime to N-substituted amide (Beckmann rearrangement)



72) Ans (b):- A Claisen rearrangement:-[3,3] sigmatropic rearrangement of an allyl vinyl ether.



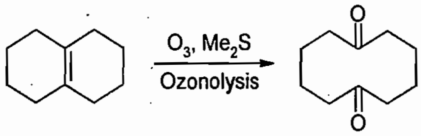
73) Ans (c):- It is an example of Shapiro reaction; (decomposition of the tosyl hydrazones of aliphatic aldehydes or ketones with very strong base, usually butyl lithium or LDA, to give corresponding vinyl lithium).

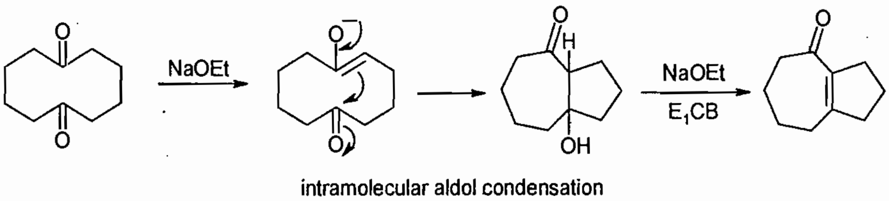


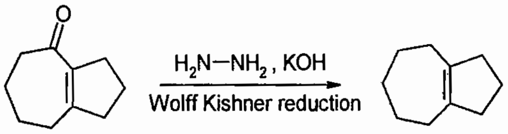
74) Ans (d):- The most appropriate sequence (i) O_3 / Me_2S (Ozonolysis);

(ii) NaOEt; (intramolecular aldol condensation)

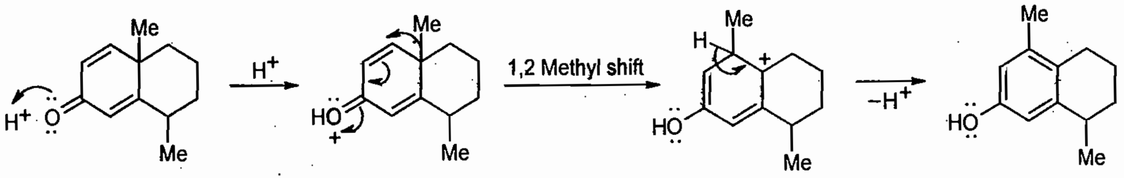
(iii) N_2H_4 / KOH The Wolff–Kishner reduction employs hydrazine under basic conditions & reduces a ketone carbonyl group to a methylene group





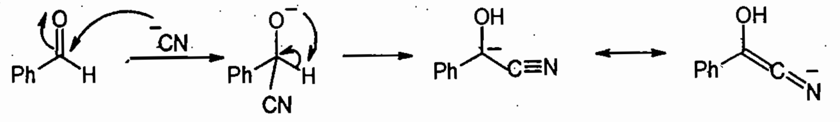


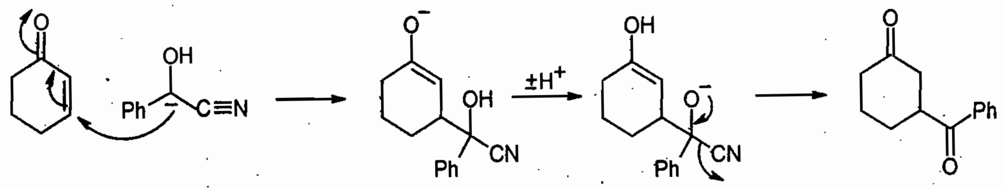
75) Ans (a):- It is a dienone–phenol rearrangement (acid catalyzed rearrangement of dienone to a phenol via tertiary carbocation).



76) Ans (d):- It is a benzoin condensation type reaction.

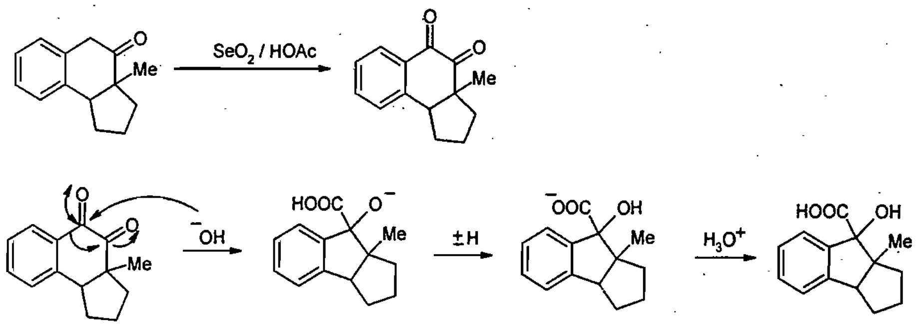
Cyanide ion is acts as catalyst because of three reason 1) Good nucleophile 2) carbanion stabilizer & 3) better leaving group





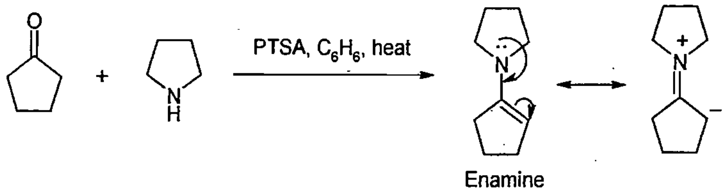
tautomerism & catalyst is regenerated

77) Ans (c):- In first step SeO_2 oxidizes active methylene group present adjacent to the carbonyl group to give 1,2-dicarbonyl compounds. In second step; the resultant 1,2-dicarbonyl compound undergoes benzilic acid rearrangement under basic condition

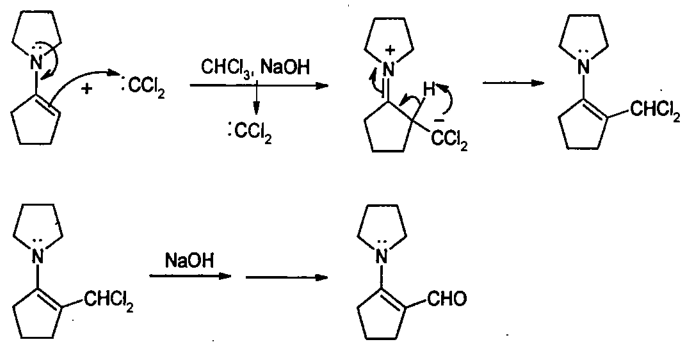


78) Ans (c):- It is a Stork enamine reaction in which enamines acts as nuclophile & it reacts with electrophiles in the same way that enolates do.

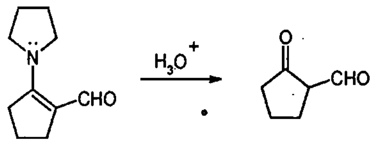
1) First step is enamine formation:-



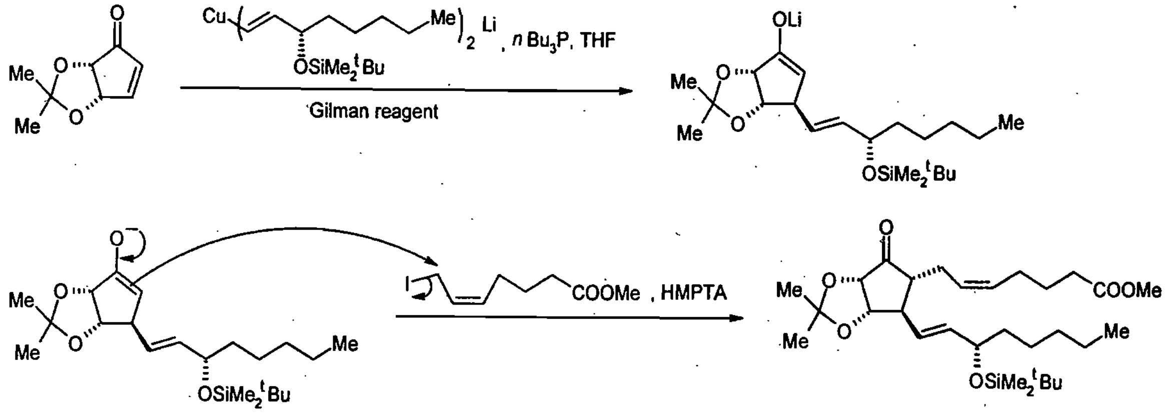
2) Second step is nucleophilic attack of enamine on electrophile(carbene):-
Note: It is the Reimer–Tiemann type reaction



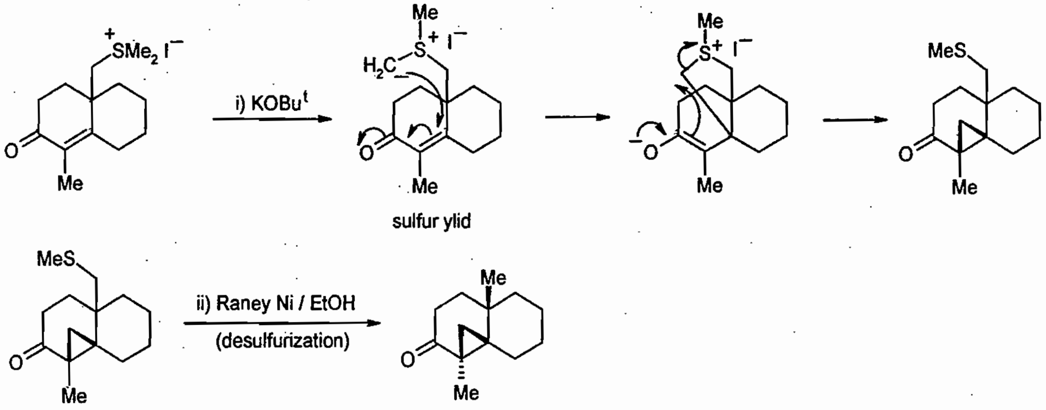
3) Third step is acid hydrolysis of enamine :-



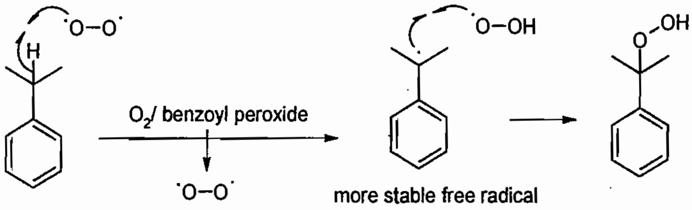
79) Ans (a):- lithium dialkylcuprates (Gilman reagent) undergoes conjugate addition when react with unsaturated α,β– aldehydes and ketones. Attack takes place from less hindered side.



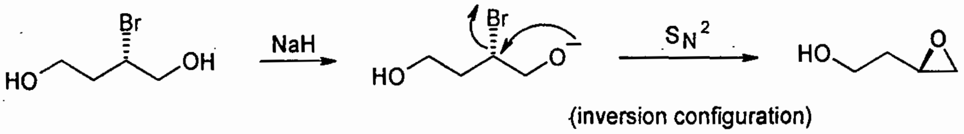
80) Ans (b):- The sulfur ylid forms in presence of base which undergoes conjugate addition with unsaturated α,β– ketones as shown below. In the next step Raney Ni removes sulfur atom (desulfurization)



81) Ans (c):- oxygen diradical forms and add to benzylic more stable free radical.

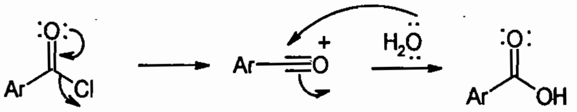


82) Ans (c):- Formation of three-membered rings is faster than four-membered ring and epoxide is only product. Reaction follows S_N^2 mechanism with inversion in configuration.



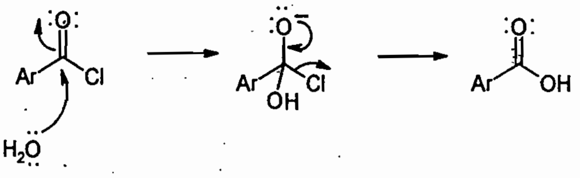
83) Ans (d):- The Hammett reaction constant (ρ) indicate electron density in the transition state at the reaction centre. Positive value of ρ indicate increase in electron density in the transition state at the reaction centre than in the starting material & negative value of ρ indicate decrease in electron density in the transition state at the reaction centre than in the starting material. If a sign of ρ is opposite for particular reaction with different substituent; it indicate the mechanism of the reaction is changing from one type of substituent (electron donating) to another type of sustituent (electron withdrawing).

Aryl group with electron donating substituent will follow such type mechanism:-



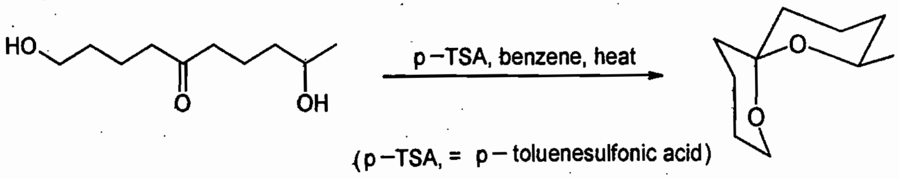
Reaction costant(ρ) with negtive value

Aryl group with electron withdrawing substituent will follow this type mechanism:-

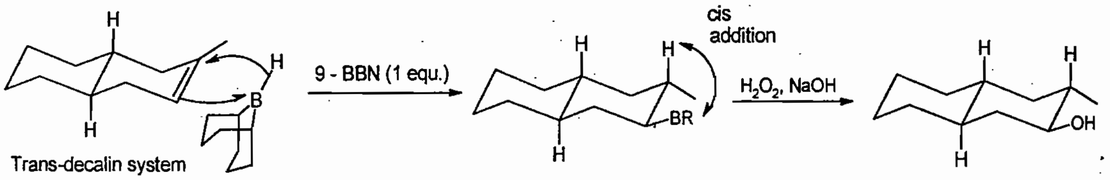


Reaction costant (ρ) with positive value

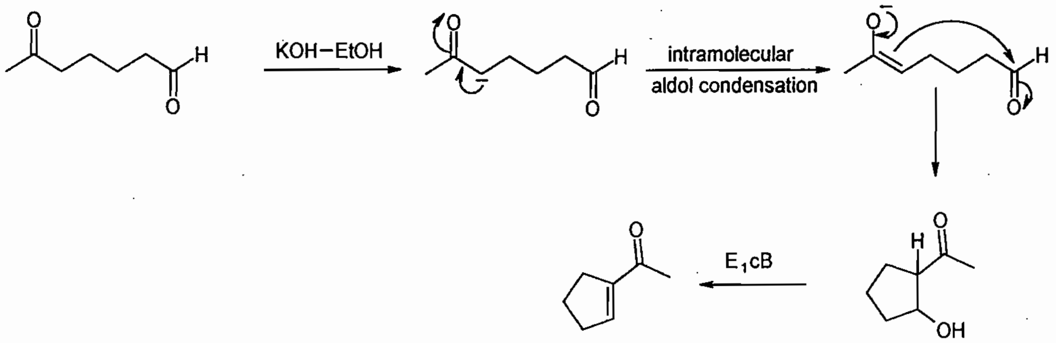
84) Ans (a):- The most predominant spiroketal is (a) which is stabilized by double anomeric effect.



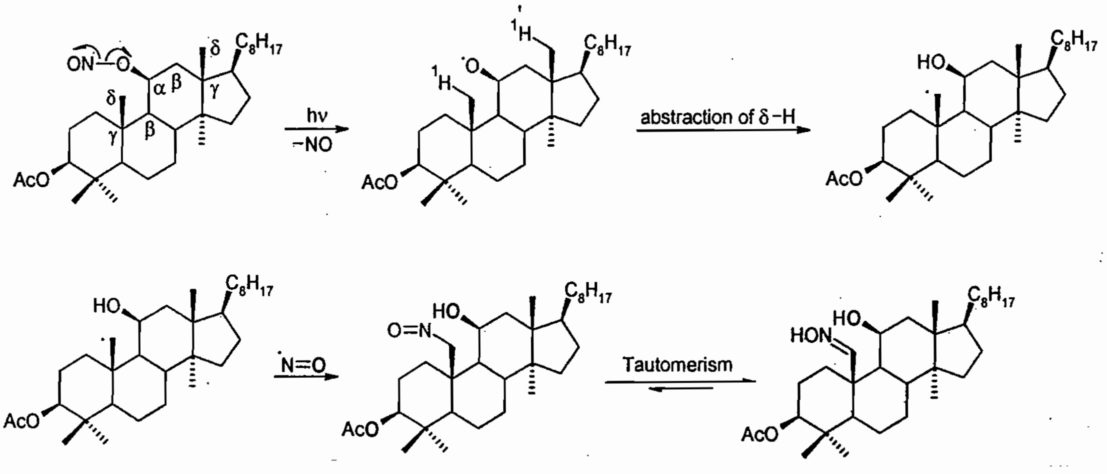
85) Ans (a):- Hydroboration is mostly used for the conversion of alkenes to alcohols by the syn (cis) addition of water (that is H & OH) with the OH group going to the less substituted end of the alkene..



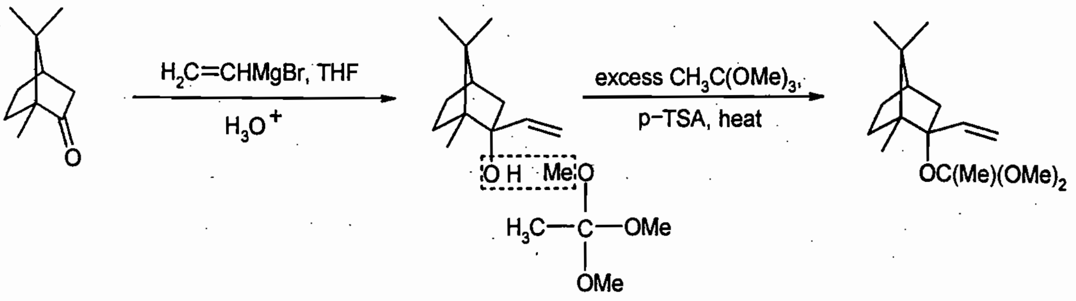
86) Ans (a):- It is an example of intramolecular aldol condensation reaction & five-membered ring is formed in preference to a seven-membered ring. The major product is the thermodynamic product formed from the more stable enolate that is α-H of the ketone



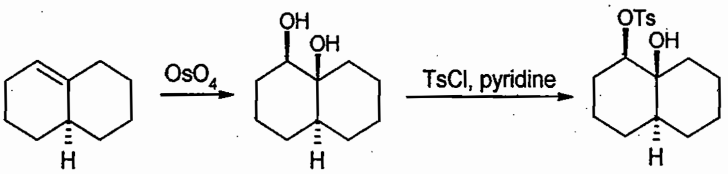
87) Ans (a):- It is an example of the Barton reaction. The photolytic conversion of organic nitrites into nitroso compounds. Reaction involve photolysis of an organic nitrite (R–O–N=O) gives an alkoxy radical and nitrogen monoxide. Subsequent intramolecular δ–hydrogen atom abstraction is followed by capture of nitrogen monoxide by the carbon radical and formation of a nitrosoalcohol, The product formed by abstraction of δ–^{1}hydrogen (activated) is more than the product formed by abstraction of δ–$^{1'}$hydrogen



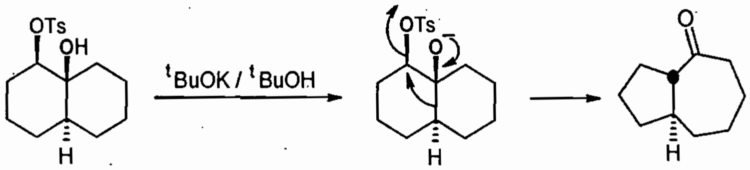
88) Ans (d):- The major product is observed to be the endo alcohol by addition of vinyl magnesium bromide to carbonyl group from exo carbonyl face The stereoselectivity observed in this reaction is due to decreased steric hindrance from the exo face carbonyl group, giving rise to the endo alcohol.



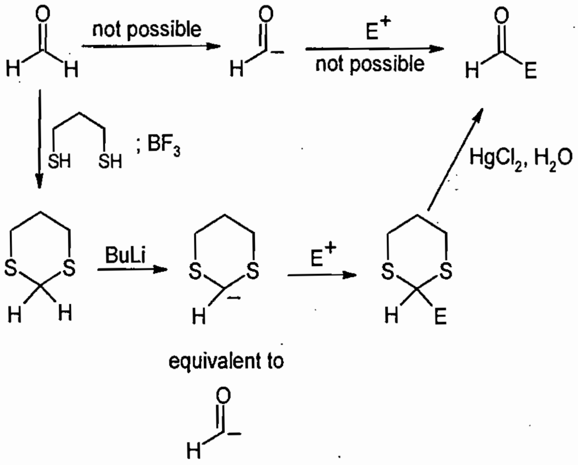
89) Ans (b):- OsO_4 is used for cis-hydroxylation of alkene



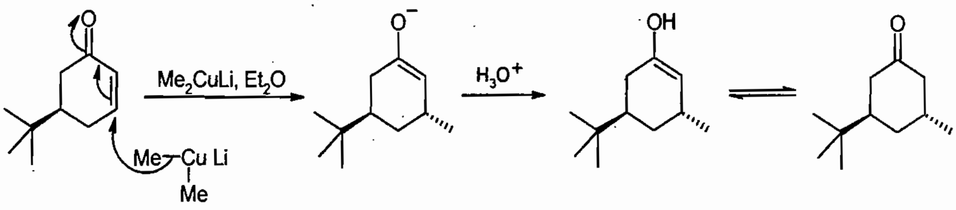
90) Ans (d):- It is an example of semipinacol rearrangements



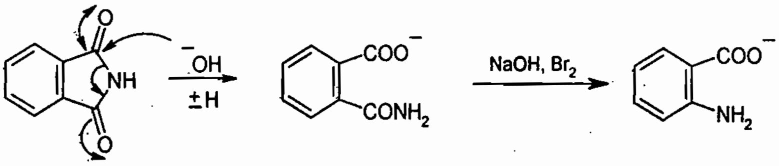
91) Ans (c):- 1,3-dithiane is act as a formyl anion equivalent (in the presence of a strong base). In this reaction thioacetal inverts the polarity at the carbonyl carbon atom.



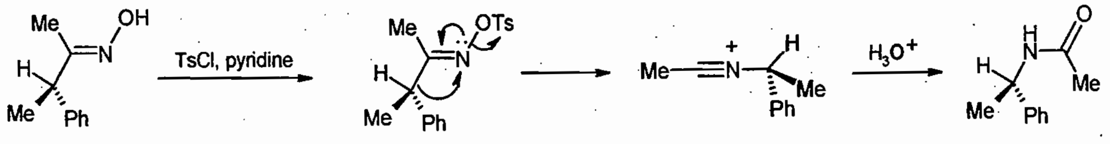
92) Ans (d):- lithium dialkylcuprates (Gilman reagent) undergoes conjugate addition when react with unsaturated α,β– aldehydes and ketones. Attack takes place from less hindered side.



93) Ans (a):- Hofmann rearrangement:-Reaction of primary amide to primary amine with one carbon atom less in presence of hypobromite ion (NaOH + Br_2 → NaOBr).

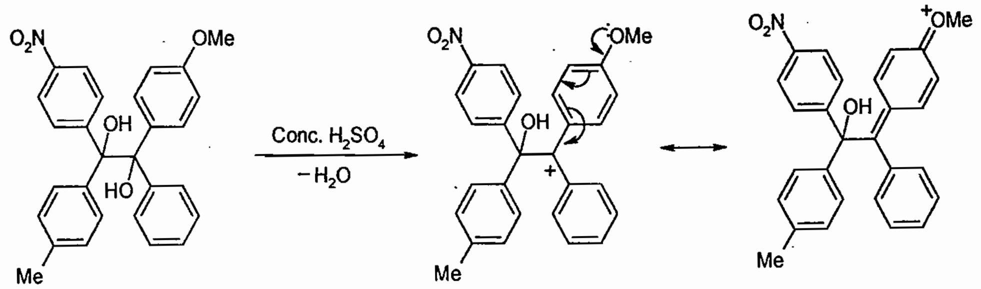


94) Ans (d):- In the Beckmann rearrangement (an oxime to an N-substituted amide) of unsymmetrical oxime; the alkyl group which is 'anti' to the -OH group will migrate to the electron deficient nitrogen with retention in configuration to give linear nitrilium ion. The linear nitrilium ion is then attacked by water to give an N-substituted amide.

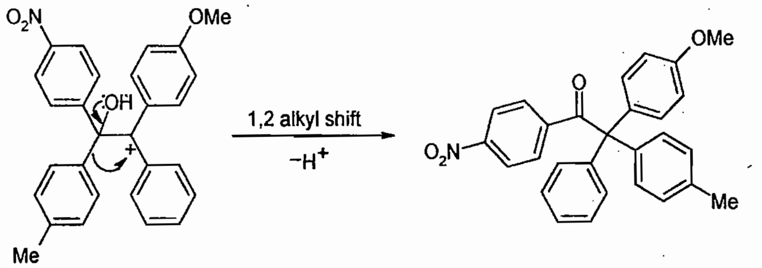


Migration of anti group

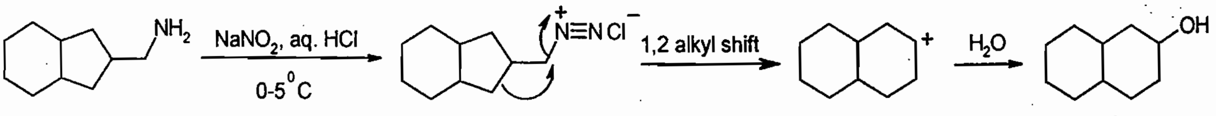
95) Ans (a):- Pinacol Rearrangement:-1,2-diol known as pinacol reacts with an acid, it leads to the formation of an ketone or aldehyde called pinacolone via more stable carbocation. The resultant carbocation is attacked by the most electron rich group.



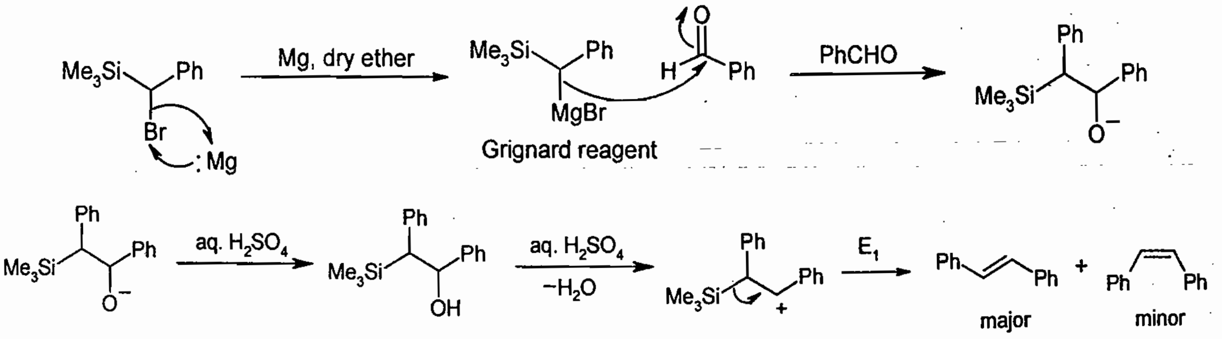
Resonance stabilized carbocation



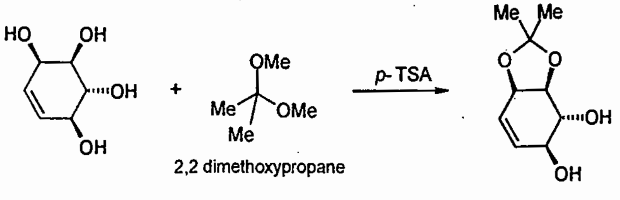
96) Ans (d):- A primary amine can be converted into a diazonium salt by treatment with nitrous acid (HNO_2) Because nitrous acid is unstable, it is formed in situ, using an aqueous solution of sodium nitrite and HCl ($NaNO_2$ + aq.HCl). Resultant diazonium salt give more stable carbocation by 1,2 alkyl shift. An alcohol is formed by nucleophilic (water) attack on carbocation.



97) Ans (a):- In first step Grignard reagent is prepared & then reaction of Grignard reagent with aldehyde to give an alcohol. Alcohol in acidic condition undergoes elimination reaction via E_1 mechanism.

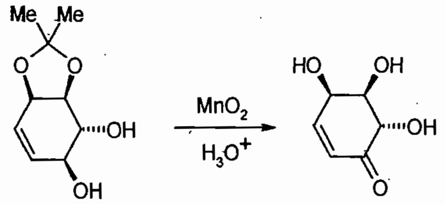


98) Ans (c):- Acetal formation is preferable with Cis-1,2-diol

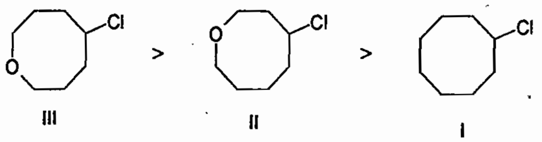


X

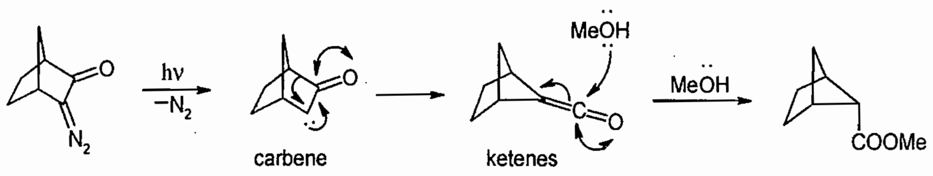
99) Ans (c):- Manganese dioxide chemoselective reagent for oxidation of the allylic/benzylic alcohol to give the aldehyde or ketone.



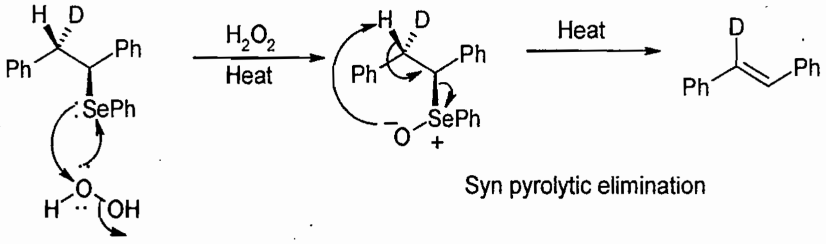
100) Ans (b):- Among I, II & III; II & III will react faster due to internal nucleophile but among II & III; III will react faster than II due to more stable five member ring intermediate. Compound I will react slowly since solvolysis process, solvent (acetic acid) acts as is a weak nucleophile. Therefore the relative rate of solvolysis of chlorides is:- III > II > I



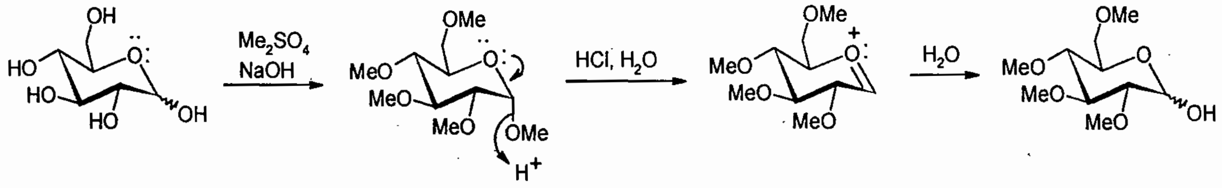
101) Ans (c):- It is an example of the Wolff rearrangement:- reaction of diazoketones to give carboxylic acid, or its derivative. In cyclic diazoketones, the rearrangement leads to ring contraction.



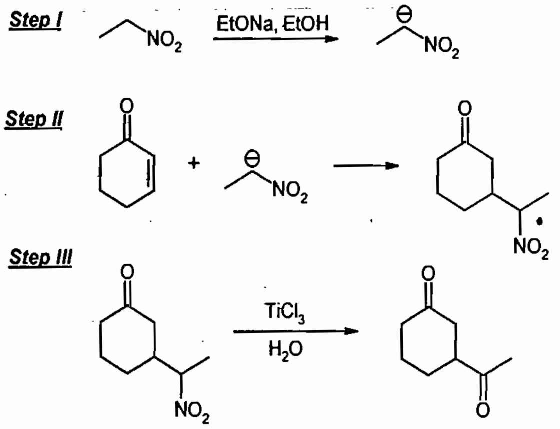
102) Ans (c):- First step is oxidation of phenylselenyl to selenoxide which at elevated temperature undergo pyrolytic elimination &



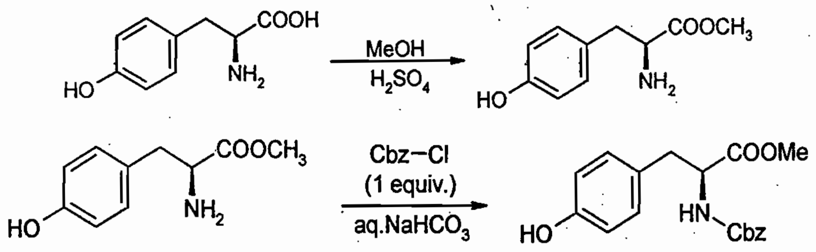
103) Ans (c):- The major product formed in the reaction is:-



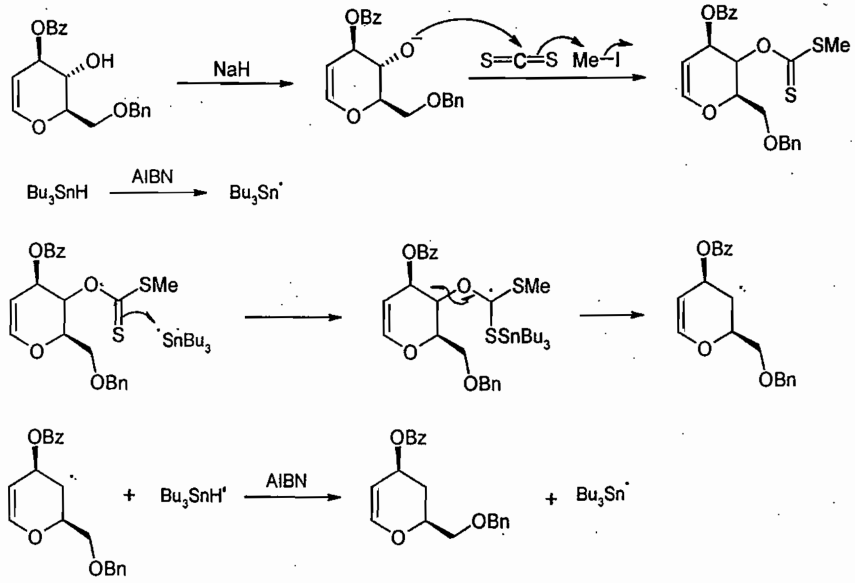
104) Ans (a):- Initially a resonance stabilized enolate ion (nucleophile) is produced in presence of a strong base.



105) Ans (b):- First step is simple esterification step to give X and in second step Cbz (carboxybenzyl) group is one of the most important nitrogen-protecting groups & are put on by treating with benzyl chloroformate (BnOCOCl) and weak base.



106) Ans (a):- The most suitable reagent combination is: - i. NaH, CS_2 then MeI; ii. Bu_3SnH, AIBN, C_6H_6, reflux



List of Reference Books

1) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford

2) Modern Methods of Organic Synthesis by W. Carruthers and L. Coldham, Cambridge University Press.

3) Advanced Organic Chemistry: Part A- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication

4) Advanced Organic Chemistry: Part B- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication

5) March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure by Jerry March John Wiley & Sons

6) Organic Synthesis by Michael B. Smith, McGraw Hill Higher Education

7) Organic Chemistry by Paula Bruice, Pearson Education

8) A guidebook to mechanisms in organic chemistry by Peter Sykes, Pearson India

9) Named Organic Reactions by Thomas Laue and Andreas Plagens, John Wiley & Sons.

10) Organic Synthesis: The Disconnection Approach, by S. Warren and P. Wyatt, John Wiley & Sons.

11) Mechanism and Structure in Organic Chemistry, by E.S Gould, Holt-Dryden, New York

12) Principles of Organic Synthesis, by R.O.C, Norman and J. M. Coxon, CRC Press.

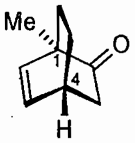
* * *

Topic 16

STEREOCHEMISTRY

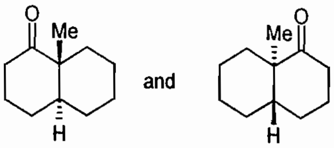
Questions with two marks

1) **The configuration at the two stereocentres in the compound given below are** ***[June 2011]***



(a) 1R, 4R (b) 1R, 4S (c) 1S, 4R (d) 1S, 4S

2) **The two compounds given below are** ***[June 2011]***



(a) Enantiomers (b) Identical (c) Diastereomers (d) Regioisomers.

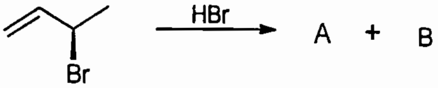
3) **In the most stable conformation of trans-1-t-butyl-3-methylcyclohexane, the substituents at C–1 and C–3, respectively, are** ***[June 2011]***

(a) Axial and equatorial (b) Equatorial and equatorial
(c) Equatorial and axial (d) Axial and axial.

4) **Addition of BH_3 to a carbon-carbon double bond is** ***[June 2011]***

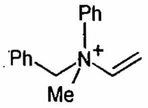
(a) anti-Markovinikov syn addition (b) anti-Markovnikov anti addition
(c) Markovnikov syn addition (d) Markovnikov anti addition.

5) **In the following Markonikov addition reaction, the products A and B are** ***[Dec 2011]***

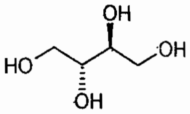


(a) homomers (b) enantiomers (c) diastereomers (d) regioisomers

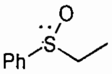
6) **Among A-C, the compounds which can exhibit optical activity are** ***[Dec 2011]***



A



B



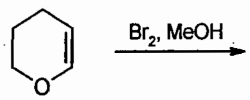
C

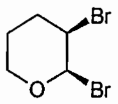
(a) A, B and C (b) A and B only (c) A and C only (d) B and C only

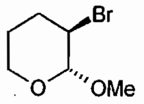
7) **Expoxidation of (R)-cyclohex-2-enol with peracetic acid yields a 95:5 mixture of compounds A and B. Compounds A and B are** ***[June 2012]***

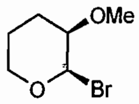
(a) Enantiomers (b) Diastereomers (c) Constitutional isomers (d) Homomers

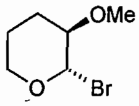
8) The major product formed in the following reaction is ***[June 2012]***



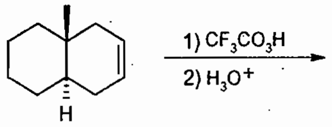
(a)


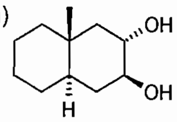
(b)


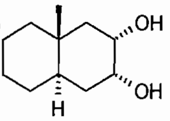
(c)


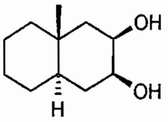
(d)


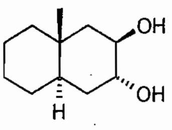
9) The major product formed in the following reaction is ***[June 2012]***



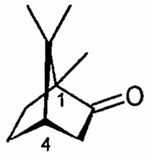
(a)


(b)


(c)


(d)


10) The absolute configuration at the two chiral centres of (−)-camphor is ***[Dec 2012]***

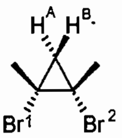


(a) 1R, 4R (b) 1R, 4S (c) 1S, 4R (d) 1S, 4S

11) The first person to separate a racemic mixture into individual enantiomers is ***[Dec 2012]***

(a) J, H van't Hoff (b) L. Pasteur (c) H.E. Fischer (d) F. Wohler

12) In the compound given below, the relation between H^A, H^B; and between Br^1, Br^2 is ***[Dec 2012]***



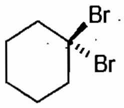
(a) H^A, H^B are enantiotropic; and Br^1 Br^2 are diastereotopic

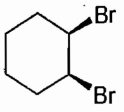
(b) H^A, H^B are diastereotopic; and Br^1, Br^2 are enantiotropic

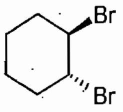
(c) H^A, H^B are diastereotopic; and Br^1, Br^2 are homotopic

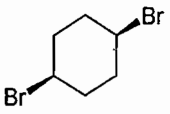
(d) H^A, H^B are enantiotropic; and Br^1, Br^2 are homotopic.

13) Among the following dibromocyclohexanes, the one that reacts fastest with sodium iodide to give cyclohexene is ***[June 2013]***

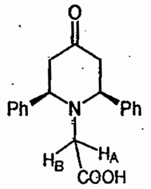
(a)


(b)


(c)


(d)


14) In the compound given below, the hydrogenes marked A and B are *[June 2013]*

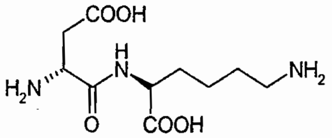


(a) homotopic (b) isotopic (c) enantiotopic (d) diastereotopic

15) The gauche conformation (θ = 60°) of n-butane possess *[June 2013]*

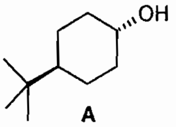
(a) plane of symmetry; and is achiral
(b) C_2-axis of symmetry; and is chiral
(c) centre of symmetry; and is achiral
(d) plane of symmetry; and is chiral

16) The constituent amino acids present in the following dipeptide, respectively, are *[Dec 2013]*

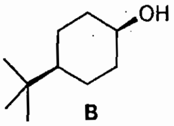


(a) (R)-aspartic acid and (S)-lysine
(b) (S)-aspartic acid and (R)-lysine
(c) (R)-glutamic acid and (S)-arginine
(d) (S)-glutamic and (S)-arginine

17) For acylation with acetic anhydride/triethylamine, and oxidation with chromium trioxide of the trans- and cis alcohols A and B, the correct statement is *[Dec 2013]*



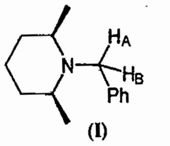
A



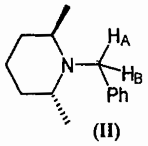
B

(a) A undergoes acylation as well as oxidation faster than B
(b) B undergoes acylation as well as oxidation faster than A
(c) A undergoes acylation faster than B, whereas B undergoes oxidation faster than A
(d) B undergoes acylation faster than A, whereas A undergoes oxidation faster than B

18) The two benzylic hydrogens H_A and H_B in the compounds I and II, are *[Dec 2013]*



(I)



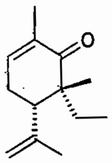
(II)

(a) diastereotopic in I and enantiotopic in II
(b) diastereotopic in II and enantiotopic in I
(c) diastereotopic in both I and II
(d) enantiotopic in both I and II

19) An aqueous solution of an optically pure compound of concentration 100 mg in 1 ml of water and measured in a quartz tube of 5 cm length was found to be -3^0. The specific rotation is *[June 2014]*

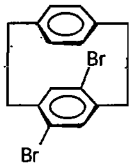
(a) -30^0 (b) -60^0 (c) -6^0 (d) $+6^0$

20) The absolute configuration of the two stereogenic (chiral) centres in the following molecule is *[June 2014]*



(a) 5*R*,6*R* (b) 5*R*,6*S* (c) 5*S*,6*R* (d) 5*S*,6*S*

21) The correct statement about the following molecule is ***[June 2014]***



(a) Molecule is chiral and possesses a chiral plane
(b) Molecule is chiral and possesses a chiral axis
(c) Molecule is achiral and possesses a plane of symmetry
(d) Molecule is achiral and possesses a centre of symmetry

22) Consider following the statements about *cis-* *and trans-*decalins ***[June 2014]***

(A) *cis*-isomer is more stable than *trans-* isomers
(B) *trans*-isomer is more stable than *cis-* isomers
(C) *trans-* isomers undergoes ring-flip
(D) *cis-* isomers undergoes ring-flip

The correct statements among the above are

(a) B and D (b) A and C (c) A and D (d) B and C

23) In the most stable conformation of neomenthol, stereochemical orientation of the three substituents on the cyclohexane ring are

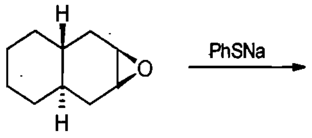
(a) OH: equatorial; i-Pr: equatorial and Me: equatorial (b) OH: axial; i-Pr: equatorial and Me: equatorial
(c) OH: equatorial; i-Pr: equatorial and Me: axial (d) OH: equatorial; i-Pr: axial and Me: equatorial

24) The absolute configuration of the chiral centres of starting ketone in the following reaction is ***[Dec 2014]***

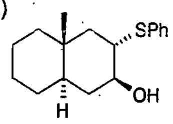
(a) 3R, 6S (b) 3S, 6S (c) 3R, 6R (d) 3S, 6R

<u>Questions with four marks</u>

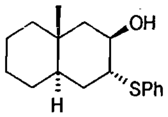
25) The major product formed in the following reaction is ***[June 2011]***



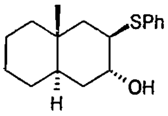
(a)



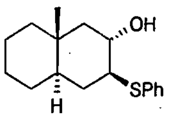
(b)



(c)



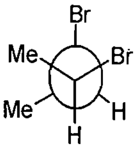
(d)



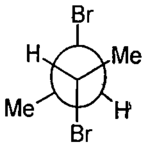
26) The gauche interaction values for Me/Me, Me/Br and Br/Br are 3.3, 0.8 and 3.0 kJ/mol, respectively.

Among the following, the most stable conformation of 2, 3-dibromobutane is ***[June 2011]***

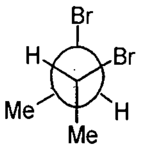
(a)



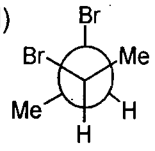
(b)



(c)



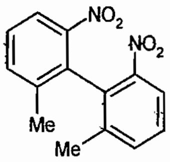
(d)



27) Match the following *[June 2011]*

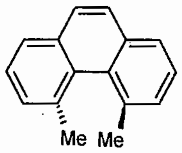
Column I

(A)



(B)

(C)



Column II

(i) chiral centre

(ii) chiral axis

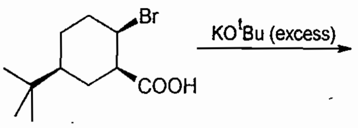
(iii) chiral plane

(iv) helical chirality

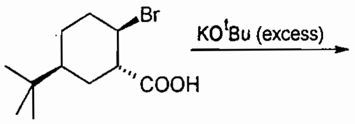
(a) (A)-iii (B)-ii (C)-iv (b) (A)-iv (B)-iii (C)-ii (c) (A)-ii (B)-iv (C)-iii (d) (A)-ii (B)-iii (C)-iv

28) For the following two reactions A and B, the correct statement is *[June 2012]*

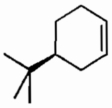
A)



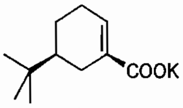
and B)



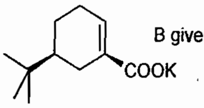
(a) A gives



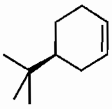
B gives



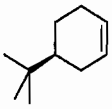
(b) A gives



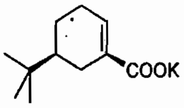
B gives



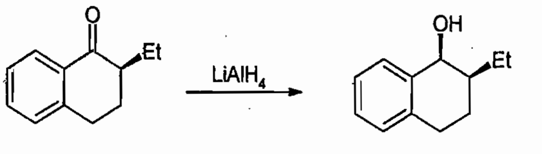
(c) Both A and B give



(d) Both A and B give



29) Considering the following reaction, among a-c, the correct statements are *[June 2012]*



85% de

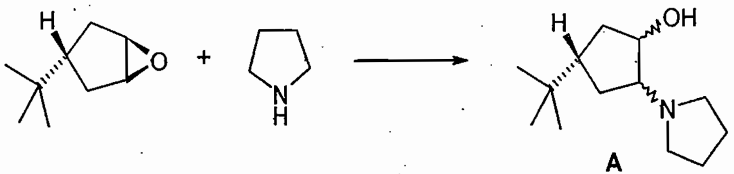
(A) The carbonyl group has enantiotopic faces;

(B) The hydride attack is re-facial;

(C) It is a diastereoselective reduction.

(a) (a) and (b) only (b) (a) and (c) only (c) (b) and (c) only (d) (a), (b) and (c)

30) Among the choices, the correct statements for A formed in the following reaction *[June 2012]*

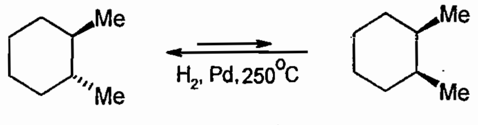


A

(a) A is a single enantiomer (b) A is a racemic mixture

(c) A is a mixture of two diastereomers (d) A is a mixture of two epimers.

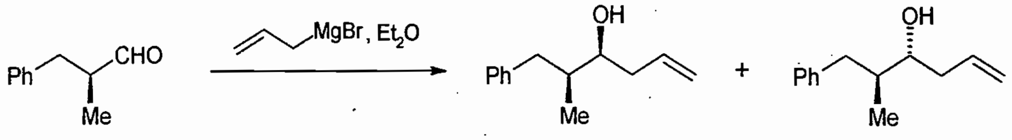
31) Given the energy of each gauche butane interaction is 0.9 kcal/mol, ΔG value of the following reaction is ***[Dec 2012]***



(e,e conformer)

(a) 0.9 kcal/mol (b) 1.8 kcal/mol (c) 2.7 kcal/mol (d) 3.6 kcal/mol

32) Which one of the following statements is true for the following transformation? ***[June 2013]***



(A) (B)

(a) A is the major product and it is a Cram product.

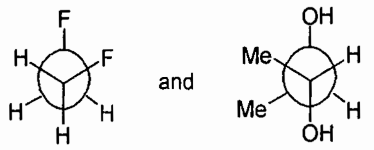
(b) A is the major product and it is anti-Cram product.

(c) B is the major product and it is a Cram product.

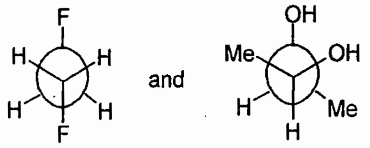
(d) B is the major product and it is anti-Cram product.

33) The most stable conformations of 1, 2-difluoroethane and dl-2, 3-butanediol are ***[June 2013]***

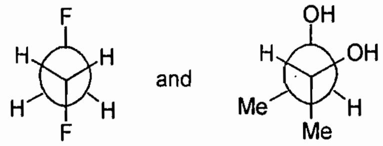
(a)



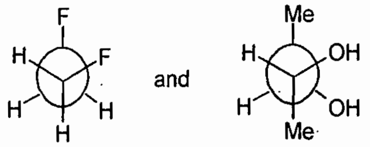
(b)



(c)



(d)

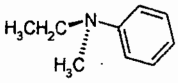


(Questions from GATE EXAM)

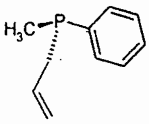
Questions with ONE OR TWO marks

34) Among the following, the optically inactive compound is ***(GATE 2005)***

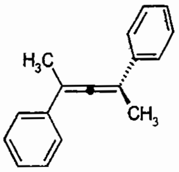
(a)



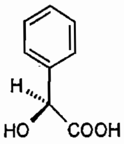
(b)



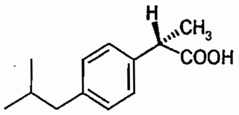
(c)



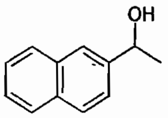
(d)



35) Esterification of the acid P with the alcohols Q will give ***(GATE 2005)***



(s)- P



(±)-Q

(a) only one enantiomer

(b) a mixture of diastereomers

(c) a mixture of enantiomers

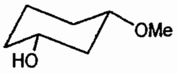
(d) only one diastereomer

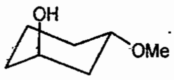
36) Bridge-head hydrogen of the conformer of cis-decalin is positioned as ***(GATE 2005)***

(a) a,a (b) e,e (c) a,e (d) pseudo-a, pseudo-e

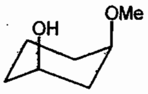
[a = axial; e = equatorial]

37) Among the following, the most stable isomer for 3-methoxycyclohexanol is ***(GATE 2005)***

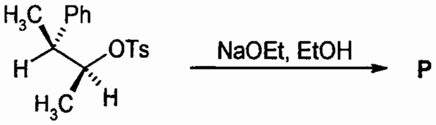
(a)


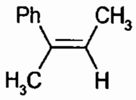
(b)


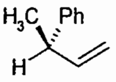
(c)

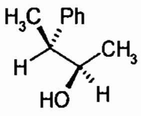

(d)


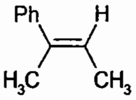
38) The major product P of the given reaction is ***(GATE 2005)***



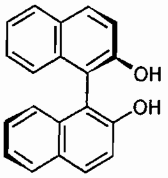
(a)


(b)


(c)


(d)


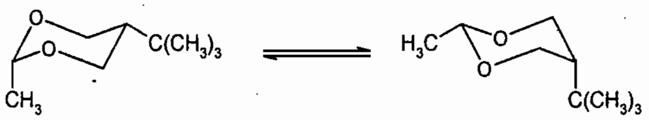
39) The binaphthol (Bnp) is ***(GATE 2005)***



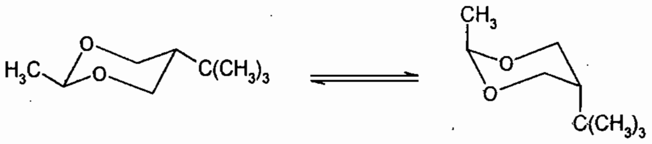
Bnp

(a) an optically active compound with (R)-configuration
(b) an optically inactive compound
(c) a meso compound
(d) an optically active compound with (S)-configuration

40) Cis and trans-2-methyl-5-t-butyl-1,3-dioxane each can exist as two conformers as shown below ***(GATE 2005)***



cis - P ***cis - Q***

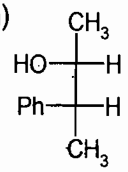


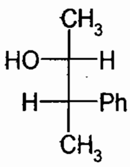
trans - R ***trans - S***

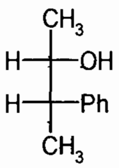
The preferred conformations for the cis- and trans-compoundS will be

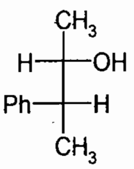
(a) P, R (b) Q, S (c) P, S (d) Q, R

41) The major stereoisomer obtained in the reaction of (S)-2-phenylpropanal with MeMgBr is ***(GATE 2005)***

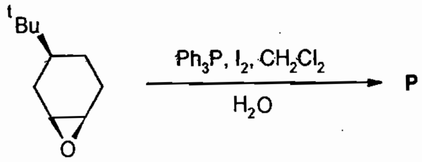
(a)


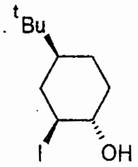
(b)


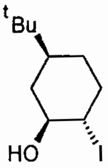
(c)


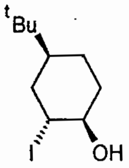
(d)


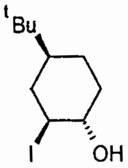
42) The major stereoisomer P obtained in the following reaction is *(GATE 2005)*



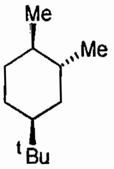
(a)


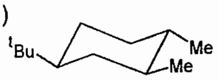
(b)


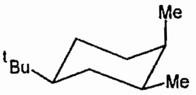
(c)


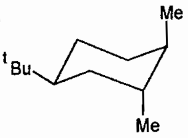
(d)


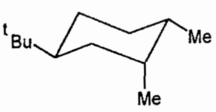
43) The most stable conformation of the following compound is *(GATE 2006)*



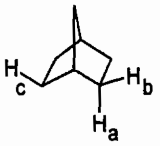
(a)


(b)


(c)


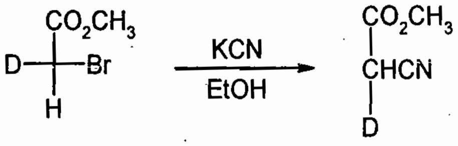
(d)


44) Identify the correct stereochemical relationship amongst the hydrogen atoms H_a, H_b, and H_c in the following compound *(GATE 2006)*



(a) H_a, and H_b : enantiotopic
(b) H_a, and H_b : diastereotopic
(c) H_a, and H_c : enantiotopic
(d) H_b, and H_c : diastereotopic

45) The configurations of the reactant and product in the following reaction, respectively, are *(GATE 2006)*



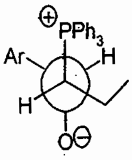
(a) R, R
(b) R, S
(c) S, R
(d) S,S

46) In the following Wittig reaction the structure of intermediate X and major products Y, respectively are *(GATE 2006)*

$$\text{ArCHO} + Ph_3P{=}CH{-}CH_2{-}CH_3 \xrightarrow[\text{free of inorganic salts}]{\text{Benzene}} (X) \longrightarrow (Y)$$

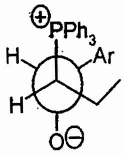
Ar = p-$CH_3C_6H_4$

(a) X =



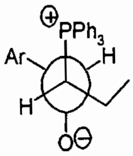
Y =

(b) X =

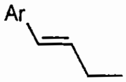


Y =

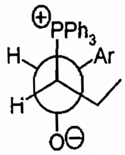
(c) X =



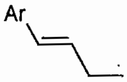
Y =



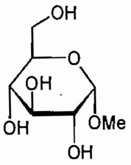
(d) X =



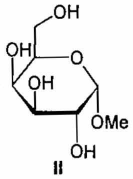
Y =



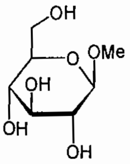
47) Identify the CORRECT set of stereochemical relationships amongst the following monosaccharides I–IV ***(GATE 2006)***



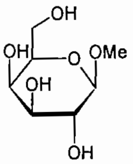
I



II



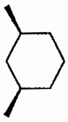
III



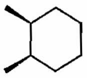
IV

(a) I and II are anomers; III and IV are epimers
(b) I and III are epimers; II and IV are anomers
(c) I and II are epimers; III and IV are anomers
(d) I and III are anomers; I and II are epimers

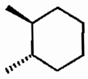
48) The molecule(s) that exist as *meso* structure(s) is / are ***(GATE 2007)***



(K)



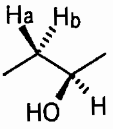
(L)



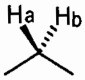
(M)

(a) only M (b) both K and L (c) only L (d) only K

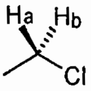
49) The stereochemical descriptors for the atoms labeled H$_a$, and H$_b$ in the structures respectively are ***(GATE 2007)***



(X)



(Y)



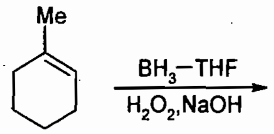
(Z)

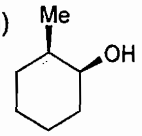
(a) X-homotopic, Y-enantiotopic and Z-diasterotopic
(b) X-enantiotopic, Y-homotopic and Z-diasterotopic
(c) X-diasterotopic, Y-homotopic and Z-enantiotopic
(d) X-homotopic, Y –diasterotopic and Z-enantiotopic

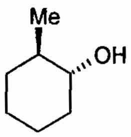
50) The result of the reduction of either (R) or (S) 2-methylcyclohexanone, in separate reactions, using LiAlH$_4$. is that the reduction of ***(GATE 2007)***

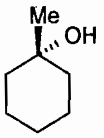
(a) the R enantiomer is stereoselective
(b) the R enantiomer is stereospecific
(c) the S enantiomer is stereospecific
(d) both the R and S enantiomers is stereoselective

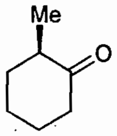
51) The major product of the following reactions is *(GATE 2008)*



(a)


(b)


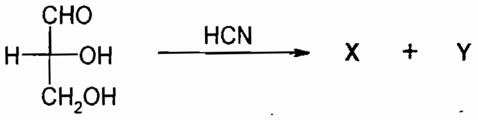
(c)


(d)


52) The number of optically active stereoisomers possible for 1,3-cyclohexanediol in its chair conformation is *(GATE 2008)*

(a) 4 (b) 3 (c) 2 (d) 1

53) In the following reaction, *(GATE 2008)*

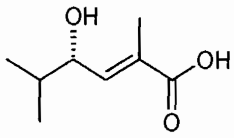


(D−Glyceraldehyde) (2 diastereomers)

The absolute configurations of the chiral centres in X and Y are

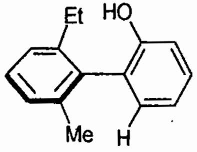
(a) 2S, *3R* and *2R, 3R* (b) *2R, 3R* and *2R,3S*
(c) 2S, *3S* and *2R, 3R* (d) 2S, *3R* and 2S, *3R*

54) For the compound the stereochemical notations are **[*GATE 2009*]**

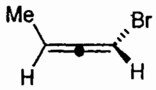


(a) *2Z, 4R* (b) *2Z, 4S* (c) *2E,4R* (d) *2E,4S*

55) The absolute configurations for compounds, X and Y respectively are **[*GATE 2010*]**



[X]



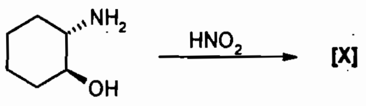
[Y]

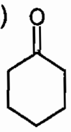
(a) *R,S* (b) *S,R* (c) *R,R* (d) *S,S*

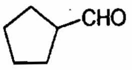
56) Among the following, a pair of resolvable configurational enantiomers is given by **[*GATE 2010*]**

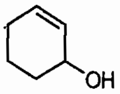
(a) *cis*−1,2 dimethylcyclohexane (b) *cis*−1,3 dimethylcyclohexane
(c) *cis*−1,4 dimethylcyclohexane (d) *trans*−1,3 dimethylcyclohexane

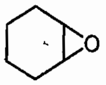
57) In the following reaction the major product [X] is **[*GATE 2010*]**



(a)


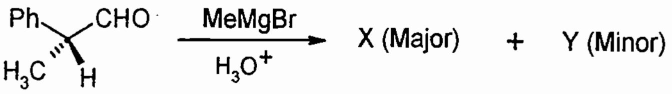
(b)


(c)


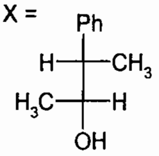
(d)


Linked question (Question no. 58 & 59)

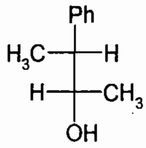
58) The major product X formed in the following reaction is ***[GATE 2010]***



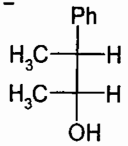
(a) X =



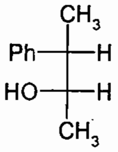
(b) X =



(c) X =



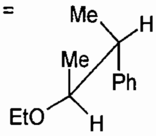
(d) X =



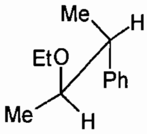
59) The compound [Z] is

$$[X] \xrightarrow[\text{2) NaOEt / EtOH}]{\text{1) TsCl / Py}} [Z]$$

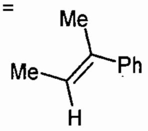
(a) Z =



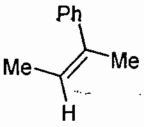
(b) Z =



(c) Z =



(d) Z =



60) In the reaction the major product [X] is ***(GATE 2011)***

Optically pure (+) − *trans*−acetoxycyclohexyl tosylate $\xrightarrow[\Delta]{\text{HOAc, KOAc}}$ [X]

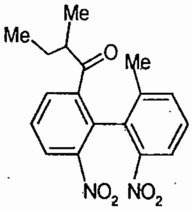
(a) racemic *trans*-1,2-cyclohexanediol diacetate

(b) optically active *trans*-1,2-cyclohexanediol diacetate

(c) racemic *cis-1* ,2-cyclohexanediol diacetate

(d) optically active *cis*-1,2-cyclohexanediol diacetate

61) The maximum number of stereoisomers possible for the compound given below is ***[GATE 2013]***



(a) Two (b) Four (c) Six (d) Eight

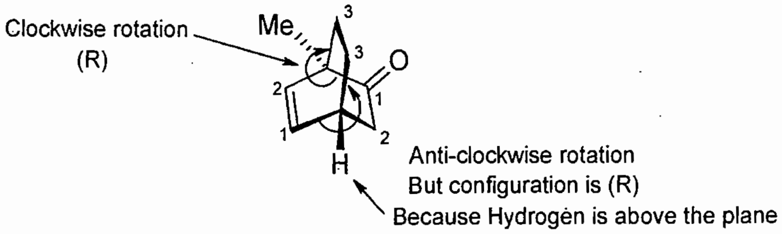
Answer Key

Topic : 16:- Stereochemistry

1	a	2	b	3	c	4	c	5	c	6	c	7	b	8	b	9	d	10	d
11	b	12	b	13	c	14	c	15	b	16	a	17	c	18	b	19	b	20	c
21	a	22	a	23	b	24	a	25	b	26	b	27	d	28	b	29	c	30	b
31	b	32	a	33	d	34	a	35	d	36	c	37	a	38	d	39	a	40	a
41	c	42	c	43	c	44	a	45	c	46	a	47	d	48	b	49	c	50	d
51	b	52	c	53	a	54	d	55	b	56	d	57	b	58	c	59	c	60	a
61	b																		

Hint & solution

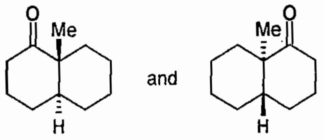
1) **Ans (a):-** The configuration at the two stereocentres in the compound given below is 1R, 4R as shown below.(Note:- If the hydrogen is shown above the plane the configuration of that chiral carbon is opposite to that of direction of rotation)



Clockwise rotation (R)

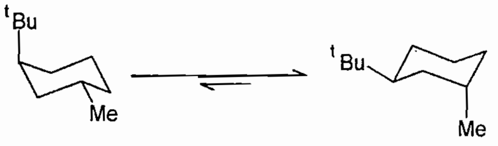
Anti-clockwise rotation
But configuration is (R)
Because Hydrogen is above the plane

2) **Ans (b):-** The two compounds given below are Identical. (Check out the configuration at the stereocentres)



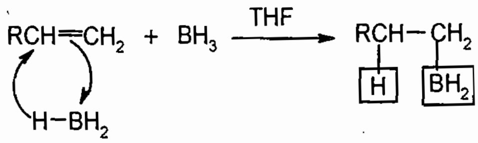
3) **Ans (c):-** In the most stable conformation of trans-1-t-butyl-3-methylcyclohexane, the substituents at C–1 and C–3, are equatorial and axial respectively (Note:- t-butyl group always stays in the equatorial position)

Conformation of trans-1-^{t}butyl-3-methyl cyclohexane

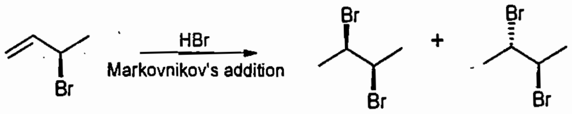


less stable more stable

4) **Ans (c):-** Addition of BH_3 to a carbon-carbon double bond is Markovnikov syn addition
Markovnikov's rule:- When an unsymmetrical reagent add to unsymmetrical alkene; the negative part of reagent adds to the sp^2 carbon that is bonded to the less number of hydrogens.
The Boron is less electronegative (2.0) than hydrogen (2.1) so hydrogen must bond to the carbon of the alkene that had fewer hydrogens attached to it. The addition of borane to an alkene is an example of a syn addition

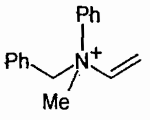


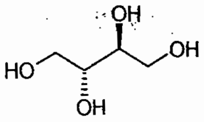
) **Ans (c):-**In the following Markonikov addition reaction, the products A and B are diastereomers.
The term Diastereoisomers arises when there is more than one stereocentre.
Diastereoisomers are stereoisomers that are not enantiomers i.e.that are not mirror images.

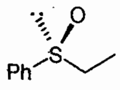


diastereomers

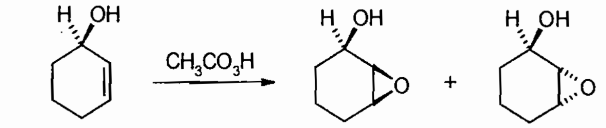
) **Ans (c):-** Quaternary ammonium ions with four different group are optically active(A); similary the sulfur is also optically active center if two alkyl group attached to sulfur in sulfoxide are different (C). Compound (B) is meso compound & is optically inactive due to plane of symmetry.


optically active


optically inactive
(meso)


optically active

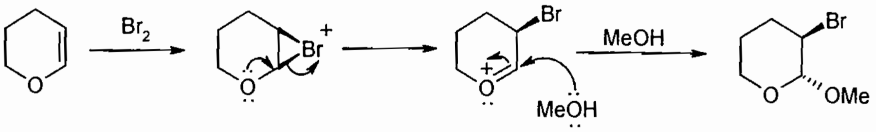
7) Ans (b):- The compound A & B are Diastereoisomers. The term Diastereoisomers arises when there are more than one stereocentre. Diastereoisomers are stereoisomers that are not enantiomers i.e. that are not mirror images.



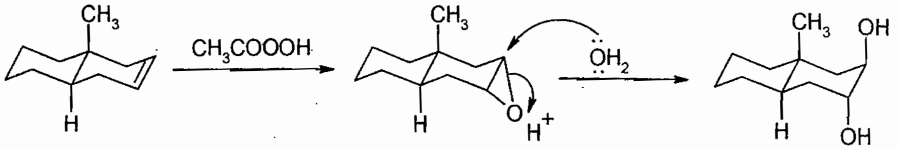
(R)-cyclohex-2-enol

Diastereomers

8) Ans (b):-

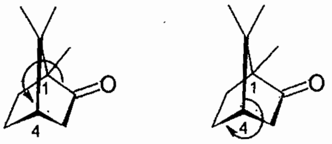


9) Ans (d):- Peracid add to alkene to give epoxide (away from CH_3) group which on acid hydrolysis gives trans diol.



10) Ans (d):- The absolute configuration at the two chiral centres of (–)-camphor is *1S, 4S.*

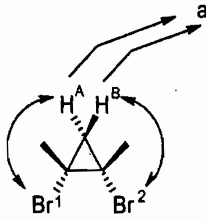
(Note: - In case of C-4 lowest priority group is on front side & therefore the configuration of that chiral carbon is opposite to that of direction of rotation)



1S *4S*

11) Ans (b):- L. Pasteur is the first person who separates a racemic mixture into individual enantiomers

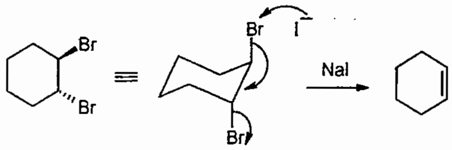
12) Ans (b):- If a carbon is bonded to two hydrogens and replacing each of them in turn with deuterium (or another group) creates a pair of diastereomers, the hydrogens are called diastereotopic hydrogens. They do not have the same reactivity (chemically different) with achiral reagents & appear at different chemical shifts in the NMR spectrum. Homotopic groups cannot be distinguished & they are chemically entirely identical. While enantiotopic groups can be distinguished still they appear identical in the NMR spectrum.



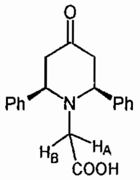
appear at different chemical shift
so they are diastreotopic

Environment of Br is different so they are enantiotropic.
But magnetically they are same.

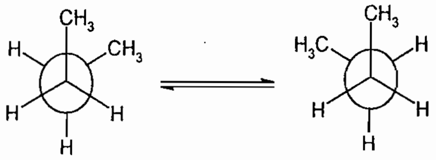
13) Ans (c):- Trans-1,2-dibromocyclohexanes reacts fastest with sodium iodide to give cyclohexene



14) Ans (c):- Two groups are enantiotopic if they are related to one another by a plane of symmetry or centre of symmetry. Transformations of enantiotopic groups give rise to enantiomers.
Thus two benzylic hydrogens H_A and H_B in the compounds I and II, are enantiotopic

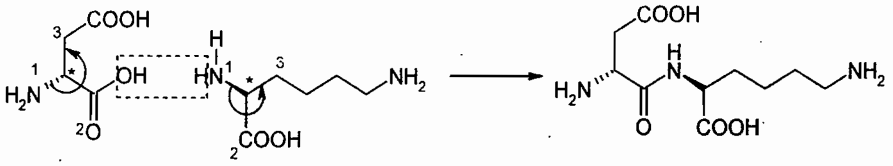


15) Ans (b):- The gauche conformation ($\theta = 60°$) of n-butane possess C_2-axis of symmetry; and is chiral.
Note:- It may possible that achiral molecule (butane) can have chiral conformation (gauche conformations of butane). The gauche butane has a two chiral, enantiomeric conformations.



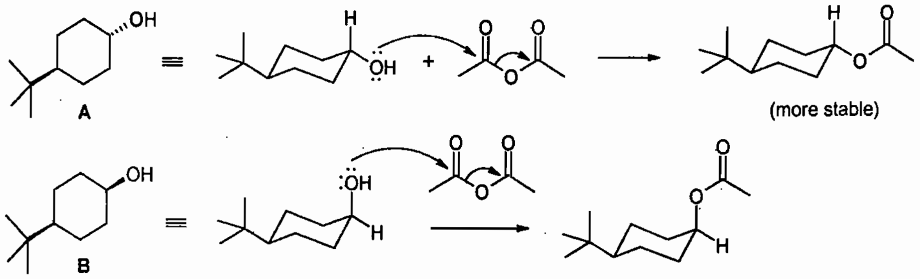
Gauche conformation of butane

16) Ans (a):- Amino acids present are (R)-aspartic acid and (S)-lysine respectively.
(Note:- If the hydrogen is shown above the plane the configuration is opposite to the direction of rotation; see the direction of rotation in aspartic acid which is anti-clockwise but we use (R) term because –H is above the plane)

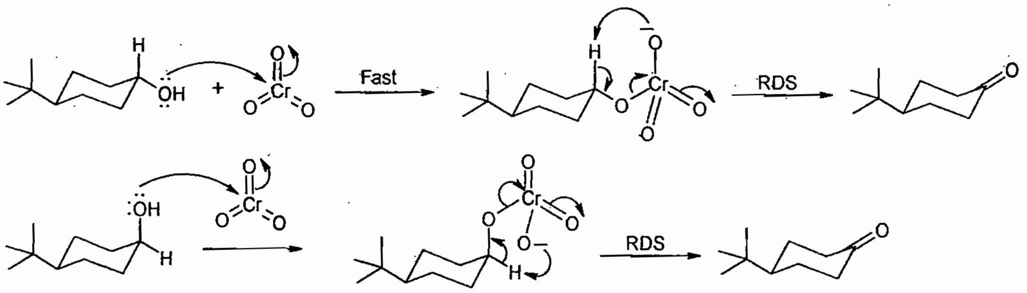


(R)-aspartic acid (S)-lysine

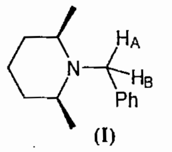
17) Ans (c):- A undergoes acylation faster than B, whereas B undergoes oxidation faster than A.
In cyclohexane bulky group always prefer equatorial position so acylation of equatorial alcohol takes place with faster rate & bulky acyl group stay at equatorial position.



But oxidation of axial alcohol with chromium trioxide is occur with faster rate than equatorial alcohol. because abstraction of equatorial hydrogen is more easily accessible in axial chromate ester than the abstraction of axial hydrogen in equatorial chromate ester

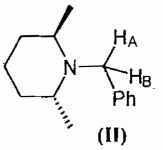


18) Ans (b):- Two groups are enantiotopic if they are related to one another by a plane of symmetry or centre of symmetry. Transformations of enantiotopic groups give rise to enantiomers (compound I). Two groups which cannot be interchanged by any symmetry operation are described as diastereotopic. Transformations of diastereotopic groups give rise to diastereomers (compound II). Thus two benzylic hydrogens H_A and H_B in the compounds I and II, are enantiotopic & diastereotopic respectively.



(I)

H_A & H_B are enantiotopic



(II)

H_A & H_B are diastereotopic

19) Ans (b):- The specific rotation is -60^0

Given:- optical rotation:- -3^0

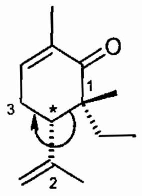
concentration: - 100 mg in 1 ml = 0.01 gcm^{-3}.

path length:- 5 cm

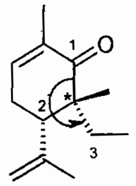
$$\text{Specific rotation} = \frac{\text{optical rotation}}{\text{concentration } \times \text{path length}}$$

$$[\propto] = \frac{\propto}{cl} = \frac{-3^0}{0.01 \times 5} = -60^0$$

20) Ans (c):- The absolute configuration of the two stereogenic (chiral) centres is 5*S*,6*R*



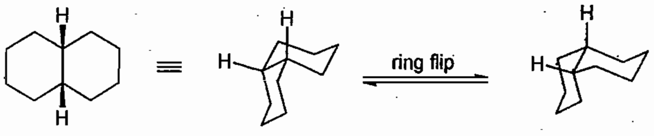
Clockwise rotation
But absolute configuration of C_5 is (S)
Because Hydrogen is shown above the plane



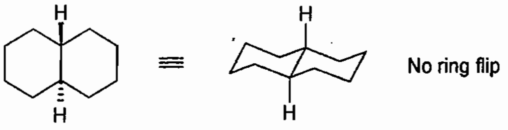
Anti-clockwise rotation
But absolute configuration of C_6 is (R)
Because lowest priority group is shown above the plane

21) Ans (a):- Molecule is chiral and possesses a chiral plane

22) Ans (a):- *cis*-decalin can undergo ring flips, but *trans*-decalin cannot undergo ring flip because of too much ring Strain. In *trans*-decalin, all carbons are equatorial, whereas in *cis*-decalin, one carbon is equatorial and the other is axial. T*rans*-decalin is more stable than *cis*-decalin & stability can be explained by guache butane interaction. In *cis*-decalin three such guache interactions are present while in *trans*-decalin no such gauche interaction is present since each ring is joined through equatorial bonds. Three gauche interaction in *cis*-decalin make it 8.8-11.4kJmol^{-1} less stable than *trans*-decalin.

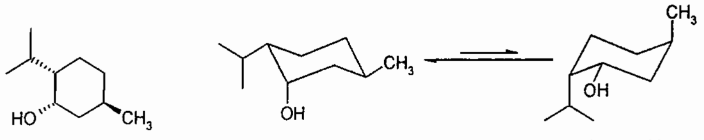


cis-decalin



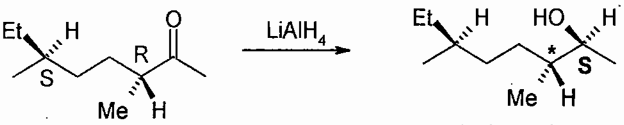
trans-decalin

23) Ans (b):- In the most stable conformation of neomenthol, OH: axial; i-Pr: equatorial and Me: equatorial



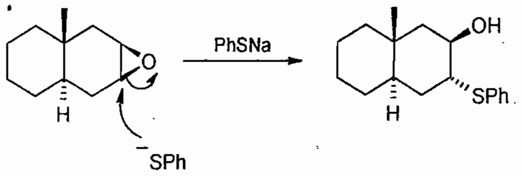
Neomenthol more stable less stable

24) Ans (a):- The *anti* stereoisomer of the alcohol predominates in the product in the reduction by using $LiAlH_4$ of the carbonyl compound with a stereogenic centre adjacent to the carbonyl group.

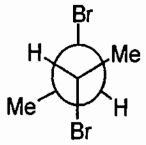


Anti streoisomer

25) Ans (b):- It is simple S_N^2 reaction of PhS^- on epoxide from less hinderd back side (away from methyl group).



26) Ans (b):- The most stable conformation of 2, 3-dibromobutane is (b) in which Me/Br are gauche to each other because gauche interaction values for Me/Br is only 0.8 kJ/mol, which is least among all



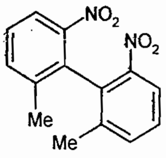
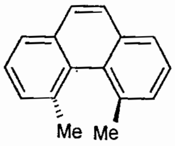
Both bulky groups are away from each other

27) Ans (d):- Axially chiral:- If two perpendicular planes which are not symmetry planes & if these *disymmetric* (chiral) planes cannot freely rotate against each other, the corresponding compounds are chiral. Compounds of this type are said to be *axially chiral e.g. Allenes*

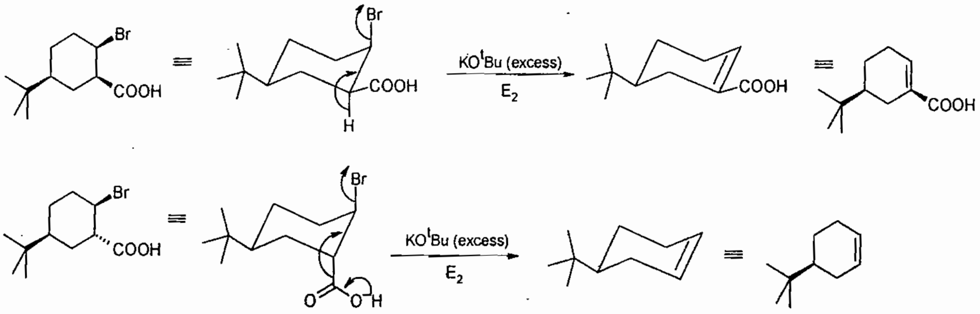
Axially chiral:- In biphenyl- and binaphtyl-derivatives if both aromatic ring systems are asymmetrically substituted, the compounds are chiral. As the chirality of these structures originates not from an asymmetrically substituted atom center, but from an asymmetric axis (chiral axis) around which rotation is hindered,

Helices:- Helices are chiral as they can exist in enantiomeric forms. Typical examples for helical strutures are provided by the helicenes (benzologues of phenanthrene).

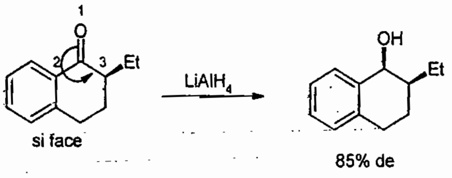
Planar chirality :-It may arise if an appropriately substituted planar group of atoms or ring system is bridged by a linker-chain extending into the space above or below of this plane. Common examples are the planar chirality of cyclophanes or alkenes

Molecule	Reason for chirality
	chiral axis
	chiral plane
	helical chirality

28) Ans (b):- An E_2 reaction involves the removal of two groups from adjacent carbons. It is a concerted reaction because the two groups are eliminated in the same step therefore the bonds to the groups to be eliminated must be in the same plane that is either antiperiplanar or synperiplanar. Therefore first reaction gives dehydrohalgenation reaction(−H & −Br are anti-periplanar to each other). While in second reaction decarboxylation & loss of bromide is take place(−COOH & −Br are anti-periplanar to each other).



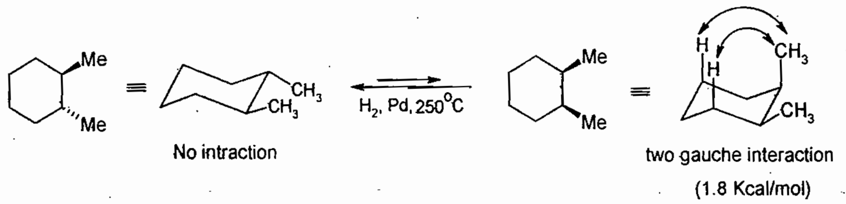
29) Ans (c):- A face is labeled *re* if; the the priorities of substituents at the trigonal atom decrease in clockwise order, and *si* if the priorities decrease in counter-clockwise order.
Note that the designation of the resulting chiral center as *S* or *R* depends on the priority of the incoming group. Back side attack on si face of carbonyl group; it means the hydride attack is re-facial (or you may say that the front side attack on si face of carbonyl group; it means the hydride attack is si-facial)



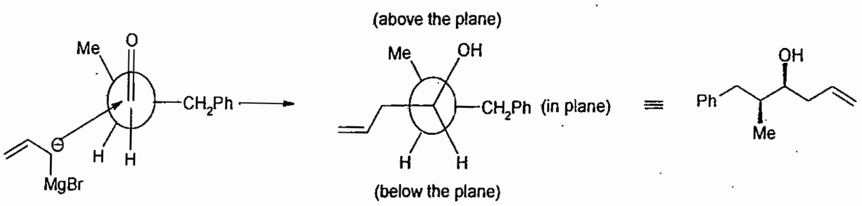
If the starting molecule is chiral, then the reaction at prochiral centre is always diastereoselective
Therefore the hydride attack is re-facial; & reaction is a diastereoselective reduction

30) Ans (b):- A is a racemic mixture

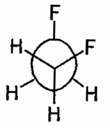
31) Ans (b):- ΔG value of the reaction is 1.8 kcal/mol (two gauche butane interaction ∴ 2 × 0.9 = 1.8 kcal/mol)



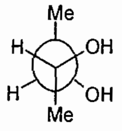
32) **Ans (a):-** The most important conformations of a carbonyl compound with a stereogenic centre adjacent to the carbonyl group are those that place the largest group perpendicular to the carbonyl group. The major product arises from the most reactive conformer in which approach of nuclophile is unhindered.
Thus A is the major product and it is a Cram product.



33) **Ans (d):-** Generally staggered conformation is lower in energy (more stable) as larger groups are away from each other but in 1, 2-difluoroethane gauche conformation extra stabilized by hyperconjugation that is the donation of electron density from the C–H σ bonding orbital to the C–F σ* antibonding orbital. Such stabilizing interactions is only possible in guache conformer which offset the energetic "cost" of steric hindrance.
Thus the most stable conformations of 1, 2-difluoroethane and dl-2, 3-butanediol are gauche (A) & staggered respectively (B).



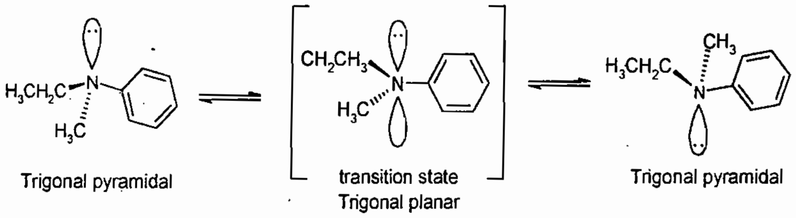
and



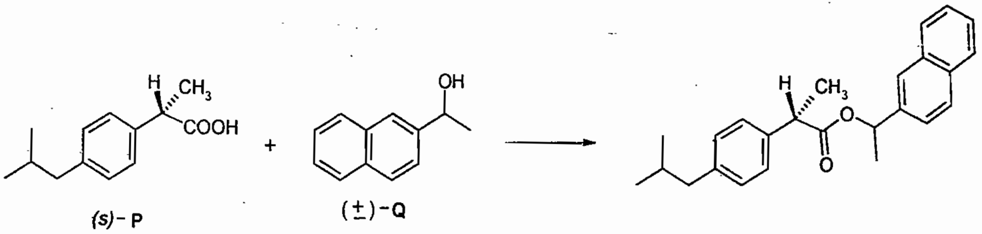
A

B

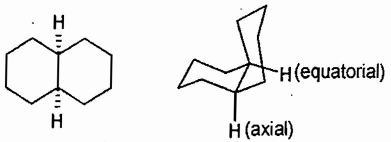
34) **Ans (a):-** Compound (a) is optically inactive compound because one of the four "groups" attached to nitrogen is a lone pair, the enantiomers cannot be separated because they interconvert rapidly at room temperature. This is called amine inversion.
But in case of phosphorous with one lone pair (b), there is a relatively high energy barrier to inversion of molecules, therefore they can be obtained as pure enantiomers.
Compound (c) is axially chiral in which the central atom is sp-hybridized, and the planes containing the substitutents on either end of the double bonds are aligned perpendicular to each other.
Compound (d) is also optically active as it has four different groups or atoms attached to it and it has a tetrahedral geometry,



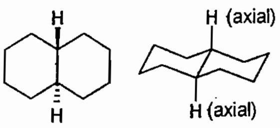
35) **Ans (d):-** Esterification of the acid P with the alcohols Q will give only one diastereoisomers to avoid steric crowing.



36) **Ans (c):-** Bridge-head hydrogen of the conformer of cis-decalin is axial & equatorial (a,e)

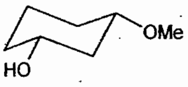


cis-decalin

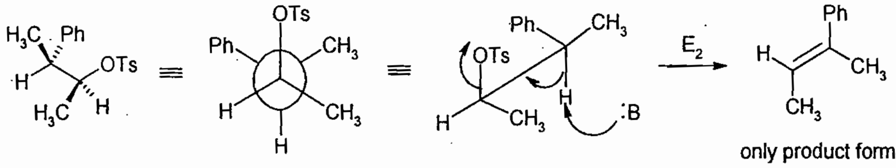


trans-decalin

37) Ans (a):- In cyclohexane bulky group always prefer equatorial position so (a) conformation is more stable

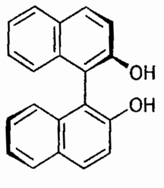


38) Ans (d):- It in an example of E_2 anti-elimination reaction

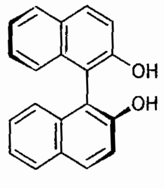


only product formed

39) Ans (a):- The binaphthol (Bnp) is an optically active compound with (R)–configuration & exist as two separate enantiomers because rotation about the bond is restricted.



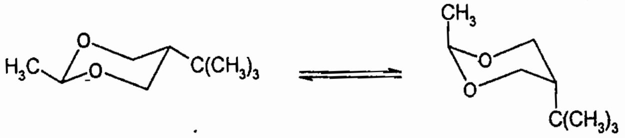
(R)-Binaphthol



(S)-Binaphthol

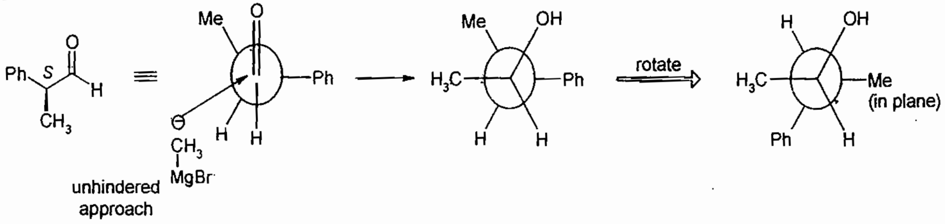
40) Ans (a):- In cyclohexane bulky group always prefer equatorial position (*t*-butyl group always stays in the equatorial position). Therefore cis-P & trans-R conformation is more stable preferred conformations for cis and trans–2–methyl–5–t–butyl–1,3–dioxane respectively.

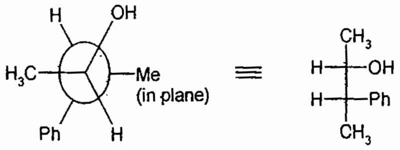
***cis* – P (more stable)** ***cis* – Q (less stable)**



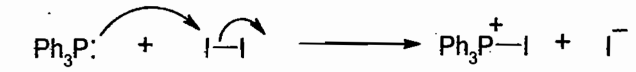
***trans* – R (more stable)** ***trans* – S (less stable)**

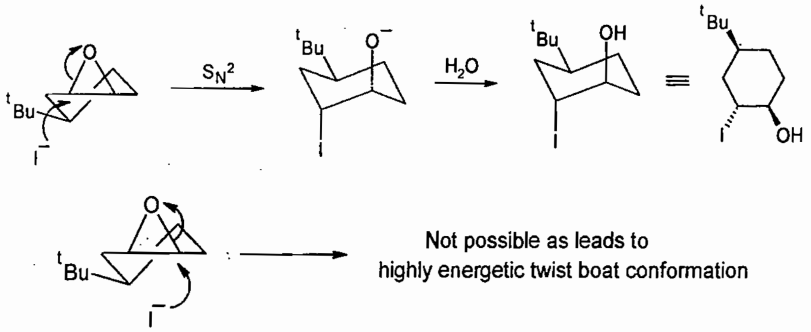
41) Ans (c):- The most important conformations of a carbonyl compound with a stereogenic centre adjacent to the carbonyl group are those that place the largest group perpendicular to the carbonyl group. The major product arises from the most reactive conformer in which approach of nucleophile is unhindered.



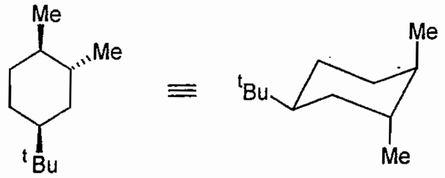


42) Ans (c):- Ring opening of cyclohexene oxides always leads directly to diaxial products.





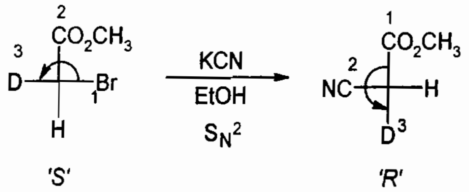
43) Ans (c):- The most stable conformation is:-



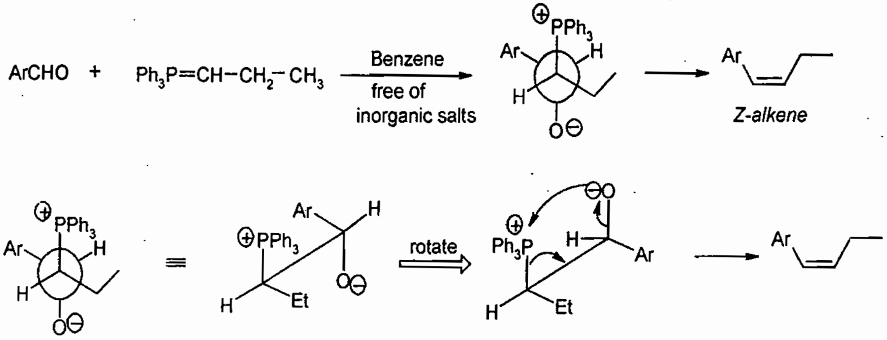
44) Ans (a):- H_a, and H_b : enantiotopic

<u>Enantiotopic:-</u> the atoms are said to be enantiotopic If one of two equivalent atoms in a molecule is replaced by a test group, it results in a enantiomers

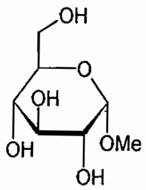
45) Ans (c):- The configurations of the reactant and product in the reaction is 'S' & 'R' respectively.
(In product hydrogen is in plane therefore the configuration of that chiral carbon is opposite to that of direction of rotation)

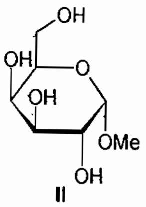


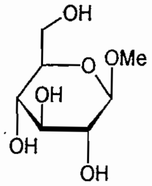
46) Ans (a):- Hint: - the Wittig reaction with unstabilized ylids is Z selective & therefore reaction must go through this conformation.

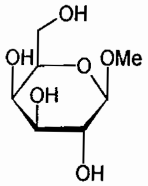


47) Ans (d):- <u>Anomers</u> are two sugars that differ in configuration only at the C-1 carbon.
<u>Epimers</u> differ in configuration at only one asymmetric carbon other than C-1


I

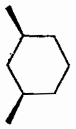

II


III

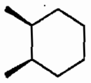

IV

I & III are anomers ; I & II are epimer

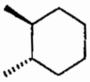
48) Ans (b):- K & L exist as *meso* structure(s) due to plane of symmetry



achiral (meso)
(Plane of symmetry)



achiral (meso)
(Plane of symmetry)

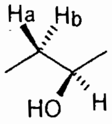


chiral

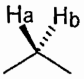
49) Ans (c):- X-diasterotopic, Y-homotopic and Z-enantiotopic

Enantiotopic:- the atoms are said to be enantiotopic If one of two equivalent atoms in a molecule is replaced by a test group, it results in a enantiomers

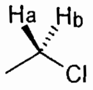
Diasterotopic: - the atoms are said to be diastereotopic If one of two equivalent atoms in a molecule is replaced by a test group, it results in a diastereomers



diastereotopic

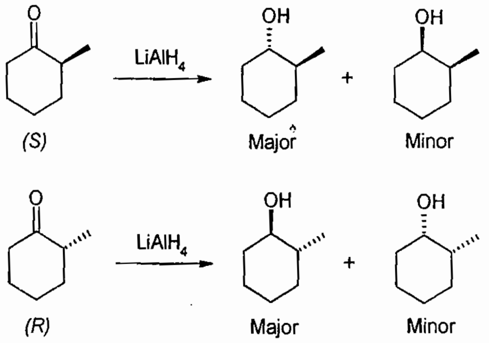


homotopic

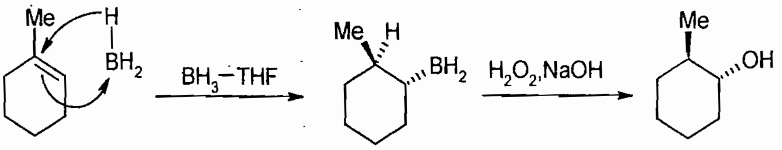


enantiotopic

50) Ans (d):- The reduction of either (R) or (S) 2-methylcyclohexanone is stereoselective. Trans product is major as both substituent stay at equatorial position.

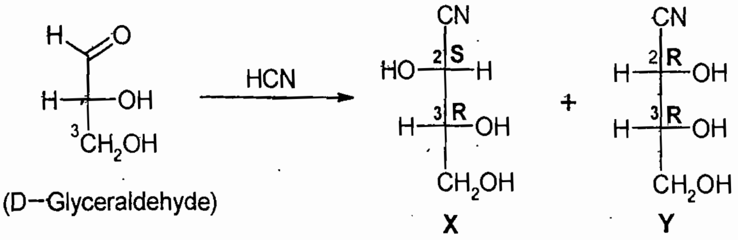


51) Ans (b):- The addition of borane to an alkene is an example of a syn addition



52) Ans (c):- Only trans-isomer of 1,3-cyclohexanediol is optically active while the cis isomer of 1,3-cyclohexanediol is optically inactive due to plane of symmetry. Therefore stereoisomers possible for 1,3-cyclohexanediol in its chair conformation is two

53) Ans (a):- The absolute configurations of the chiral centres in X and Y are 2S, *3R* and *2R, 3R*



(D–Glyceraldehyde)

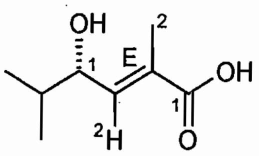
(2 diastereomers)

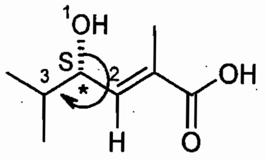
54) Ans (d):- The stereochemical notations for given compound are *2E,4S*

If the higher priority groups are on the opposite sides of double bond, the isomer is denoted by the E.

If the higher priority groups are on the same sides of double bond, the isomer is denoted by the Z.

And configuration of chiral carbon is *S* (Note: - If the hydrogen is shown above the plane then the configuration of that chiral carbon is opposite to that of direction of rotation)





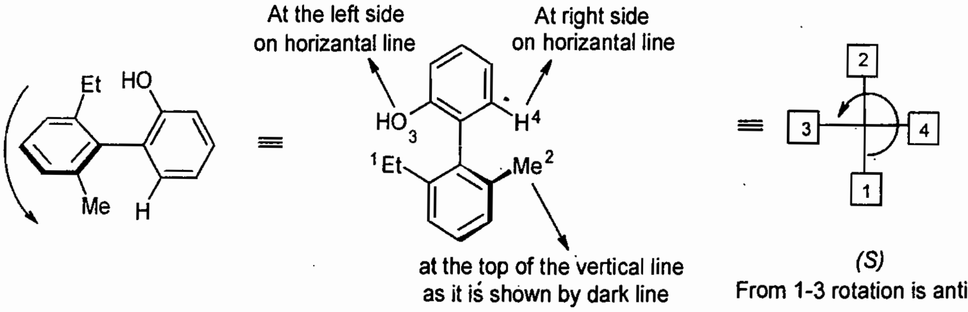
55) Ans (b):- Absolute configurations in allenes & biphenyls:-

Rule 1:- Turn the molecule to bring the perpendicular group at bottom.

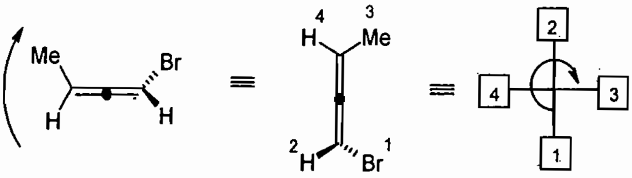
Rule 2:- View the molecule from bottom.

Rule 3:- Put the perpendicular group on vertical line (group shown by dark line put it on top side of vertical line & group shown by dotted line put it on bottom side of vertical line); & give an order of priority either 1 or 2 to either group

Rule 4:- the groups which are in plane put them on a horizontal line (left hand side group on left side & right hand side group on right side of a horizontal line) & give an order of priority (either 3 or 4 to either group).



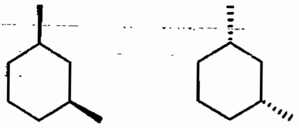
(S)
From 1-3 rotation is anticlockwise



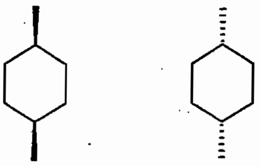
(R)
From 1-3 rotation is clockwise

56) Ans (d):- A pair of resolvable configurational enantiomers is given by *trans*–1,3 dimethylcyclohexane

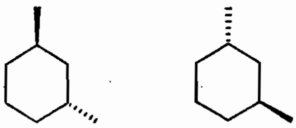
cis-1,2 dimethylcyclohexane
Achiral (plane of symmetry)



cis-1,3 dimethylcyclohexane
Achiral (plane of symmetry)

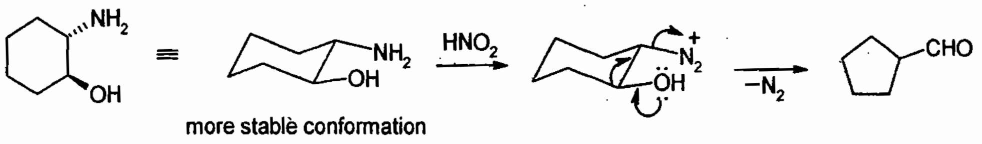


cis-1,4 dimethylcyclohexane
Achiral (plane of symmetry)

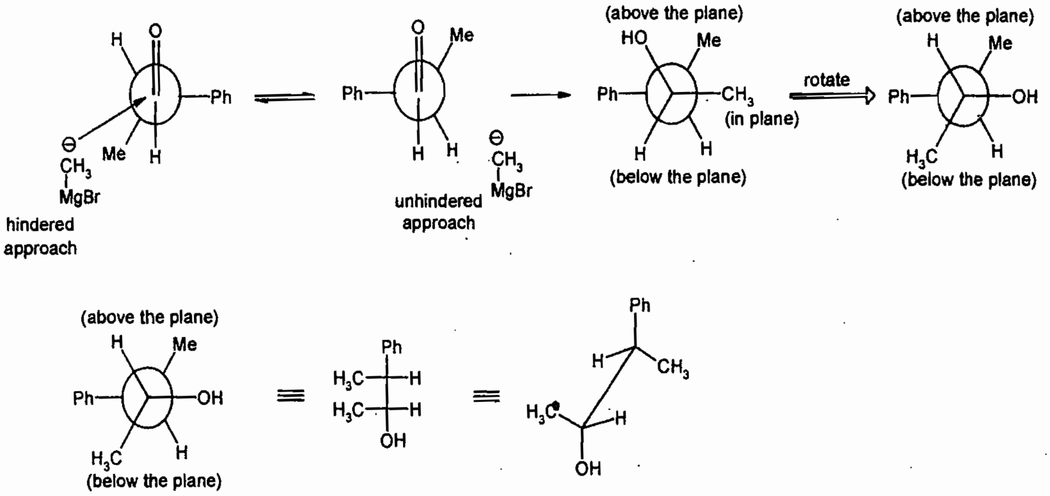


trans-1,3 dimethylcyclohexane
Chiral

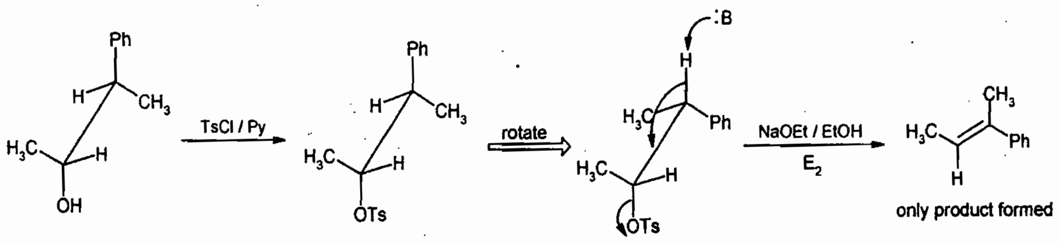
57) Ans (b):- First step is diazotization of amino alcohol followed by rearrangement where the OH group provides the electronic push & result in the ring contraction by an alkyl migration to give product & loss of N_2



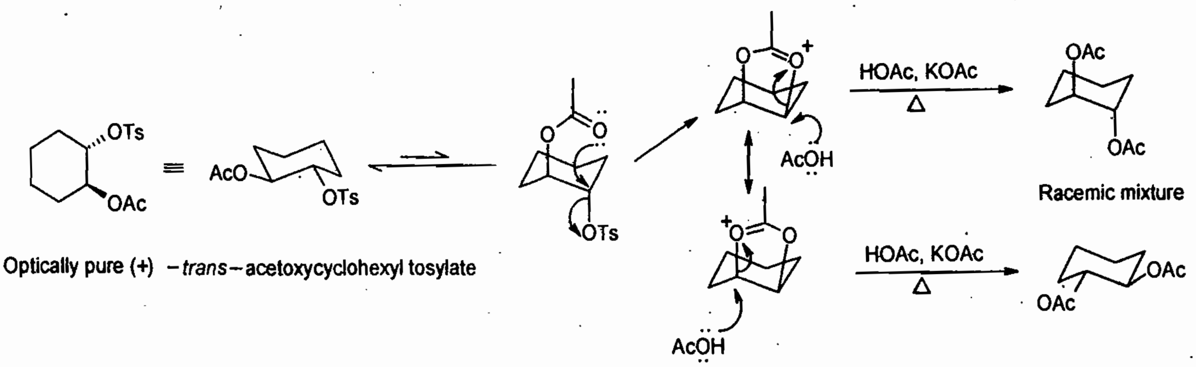
58) Ans (c):- The most important conformations of a carbonyl compound with a stereogenic centre adjacent to the carbonyl group are those that place the largest group perpendicular to the carbonyl group. The major product arises from the most reactive conformer in which approach of nuclophile is unhindered. Thus (c) is the major product.



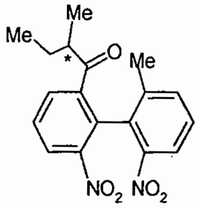
59) Ans (c):- It in an example of E_2 anti-elimination reaction



60) Ans (a):- The product of the reaction is racemic *trans*-1,2-cyclohexanediol diacetate by Neighboring Groups participation mechanism.



61) Ans (b):- The maximum number of stereoisomers possible for the compound is four.
(Two stereoisomers because of one chiral carbon atom & as a compound is biphenyl derivative with the chiral axis that is rotation around the single bond is restricted due to steric reason,so two more stereoisomers)



List of Reference books

1) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford

2) Stereochemistry of carbon compounds by E. L. Eliel and S. H. Wilen, John Wiley & Sons

3) Advanced Organic Chemistry: Part A- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication.

4) Modern Methods of Organic Synthesis by W. Carruthers and L. Coldham, Cambridge University Press.

5) Organic Reactions Stereochemistry and Mechanism, by D. Nashipuri, New Age International.

6) Organic Reactions Stereochemistry and Mechanism, By P. S. Kalsi, New Age International.

❖❖❖

Topic 17

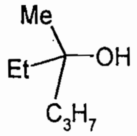
ORGANIC SPECTROSCOPY

Questions with two marks

1) The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is ***[June 2011]***

(a) Anhydride > amide > ketone
(b) Ketone > amide > anhydride
(c) Amide > anhydride > ketone
(d) Anhydride > ketone > amide

2) In the mass spectrum of the compound given below, during the α−cleavage, the order of preferential loss of groups is ***[June 2011]***

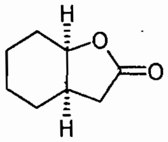


(a) Me > C_3H_7 > Et
(b) C_3H_7 > Et > Me
(c) Et > Me > C_3H_7
(d) Et > C_3H_7 > Me

3) The absorption at λ_{max} 279 nm (ε =15) in the UV spectrum of acetone is due to ***[June 2011]***

(a) π−π* transition
(b) n−π* transition
(c) σ − σ * transition
(d) π−σ* transition

4) In the IR spectrum, carbonyl absorption band for the following compound appears at ***[Dec 2011]***



(a) 1810cm^{-1}
(b) 1770cm^{-1}
(c) 1730cm^{-1}
(d) 1690cm^{-1}

5) In the mass spectrum of dodecahedrane $C_{20}H_{20}$, approximate ratio of the peaks at m/z 260 and 261 is ***[Dec 2011]***

(a) 1 : 1
(b) 5 : 1
(c) 10 : 1
(d) 20 : 1

6) An organic compound (MF:$C_8H_{10}O$) exhibited the following ^{1}H NMR spectral data :- δ 2.5 (3 H,s), 3.8 (3H,s), 6.8 (2 H, d, J 8 Hz), 7.2 (2 H, d, J 8 Hz) ppm. The compound among the choices, is ***[Dec 2011]***

(a) 4-ethylphenol
(b) 2-ethylphenol
(c) 4-methylanisole
(d) 4-methylbenzyl alcohol

7) The number of signals that appear in the broadband decoupled ^{13}C NMR spectrum of phenanthrene and anthracene, respectively are ***[June 2012]***

(a) ten and four
(b) ten and ten
(c) seven and four
(d) seven and seven.

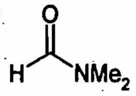
8) In the 400 MHz ^{1}H NMR spectrum, an organic compound exhibited a doublet. The two lines of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is ***[June 2012]***

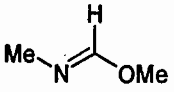
(a) 3 Hz
(b) 6 Hz
(c) 9 Hz
(d) 12 Hz

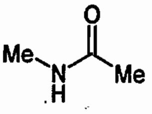
9) ^{1}H NMR spectrum of HD would show ***[Dec 2012]***

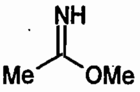
(a) a singlet
(b) a doublet
(c) a triplet with intensity ratio 1:2:1
(d) a triplet with intensity ratio 1:1:1

10) In the ^1H NMR spectrum recorded at 293 K, an organic compound (C_3H_7NO), exhibited signals at δ 7.8 (1H, s); 2.8 (3H, s) and 2.6 (3H, s). The compound is ***[Dec 2012]***

(a) 

(b) 

(c) 

(d) 

11) In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at ***[Dec 2012]***

(a) 1670 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1760 cm^{-1}

12) In NMR spectroscopy, the product of the nuclear 'g' factor (g_N), the nuclear magneton β_N and the magnetic field strength (B_0) gives the ***[June 2013]***

(a) energy of transition from α to β state (b) chemical shift
(c) spin-spin coupling constant (d) magnetogyric ratio

13) In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at ***[June 2013]***

(a) 1800 cm^{-1} (b) 1760 cm^{-1} (c) 1710 cm^{-1} (d) 1660 cm^{-1}

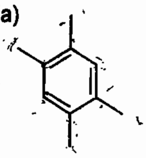
14) An AX system gave 4 lines at δ 4.72, 4.6, 1.12 and 1.0 ppm away from the TMS using an NMR spectrometer operating at 100 MHz. What are the values of J_{AX} (in Hz) & δ_{AX} in ppm , respectively ***[June 2013]***

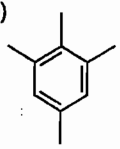
(a) 12 and 3.6 (b) 6 and 3.6 (c) 12 and 2.86 (d) 6 and 2.86

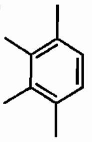
15) In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at ***[Dec 2013]***

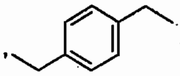
(a) 1660 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1770 cm^{-1}

16) An organic compound having the molecular formula $C_{10}H_{14}$ exhibited two singlets in the ^1H NMR spectrum and three signals in the ^{13}C NMR spectrum. The compound is ***[Dec 2013]***

(a) 

(b) 

(c) 

(d) 

17) The correct match of the ^1H NMR chemical shifts δ of the following species/compound is ***[June 2014]***


I


II

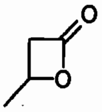

III

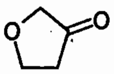
(a) I : 5.4; II : 7.2: III : 9.2 (b) I : 9.2; II : 7.2: III : 5.4
(c) I : 9.2; II : 5.4: III : 7.2 (d) I : 7.2; II : 9.2: III : 5.4

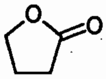
18) The ratio of relative intensities of the carbon signals in the first order ^{13}C NMR spectrum of CD_3Cl is ***[Dec 2014]***

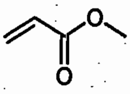
(a) 1:4:6:4:1 (b) 1:3:3:1
(c) 1:6:15:20:15:6:1 (d) 1:3:6:7:6:3:1

19) A compound with molecular formula $C_4H_6O_2$ shows band at 1770 cm^{-1} in IR spectrum and peaks at 178,68,28 and 22 ppm in ^{13}C NMR. The correct structure of the compound is ***[Dec 2014]***

(a) 

(b) 

(c) 

(d) 

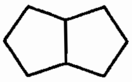
20) The mass of metastable ion is produced due to decomposition of F_1^+ in the following mass fragmentation sequence is ***[Dec 2014]***

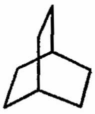
$$\underset{(M^{+\cdot}, 222)}{\text{Diethyl phthalate}} \longrightarrow \underset{(177)}{F_1^+} \longrightarrow F_2^+ + CO$$

(a) 141.2 (b) 125.4 (c) 45.0 (d) 210.2

Questions with four marks

21) In the broad band decoupled ^{13}C NMR spectrum, the number of signals appearing for the bicyclooctane A–C, respectively, are ***[June 2011]***


A


B


C

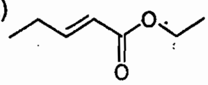
(a) Five, four and eight (b) Three, two and five
(c) Five, four and five (d) Three, two and eight

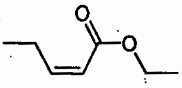
22) In the mass spectrum of dichlorobenzene the ratio of the peaks at m/z 146, 148 and 150, is ***[June 2011]***

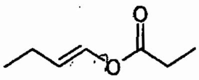
(a) 1:1:1 (b) 3:3:1 (c) 1:2:1 (d) 9:6:1

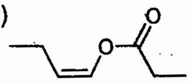
23) An organic compound ($C_7H_{12}O_2$) exhibited the following data in the ^{1}H NMR spectrum. ***[June 2011]***
δ 7.10 (1H, dt, J=16 & 7.2Hz), 5.90 (1H, dt, J=16 & 2Hz), 4.1 (2H, q, J=7.2 Hz), 2.10 (2H,m); 1.25(3H, t, J=7.2Hz), 0.90(3H, t, J=7.2Hz) ppm.

The compound, among the choices given below, is

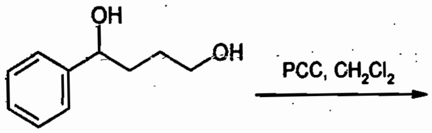
(a)


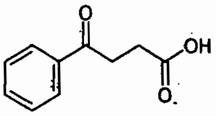
(b)


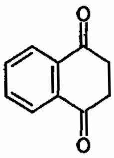
(c)


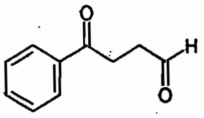
(d)


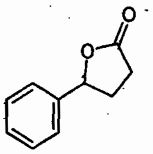
24) The major compound X formed in the following reaction exhibited a strong absorption at ν_{max} 1765 cm^{-1} in the IR spectrum. The structure of X is ***[June 2011]***



(a)


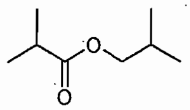
(b)


(c)


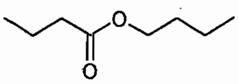
(d)


) An organic compound A ($C_8H_{16}O_2$) on treatment with an excess of methyl magnesium chloride generated two alcohols B and C, whereas reaction of A with lithium aluminum hydride generated only a single alcohol C. Compound B on treatment with an acid yielded an olefin (C_6H_{12}), which exhibited only a singlet at δ1.6 ppm in the ^{1}HNMR spectrum. The compound A is *[June 2011]*

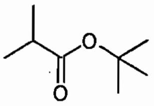
(a)



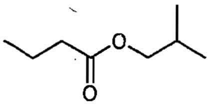
(b)



(c)



(d)



) The NMR spectrum of AX_3 exhibits lines at δ = 2.1 and 2.3 ppm (for X type protons) and δ = 4.1, 4.3, 4.5 and 4.7 ppm (for A type protons), measured from TMS with an instrument operating at 100 MHz. The chemical shift (in ppm) of A and X protons and coupling constant (in (Hz) are respectively. *[Dec 2011]*

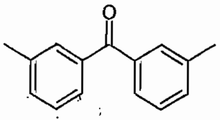
(a) 4.4, 2.2 and 20　(b) 2.2, 4.4 and 10　(c) 2.2, 4.4 and 5　(d) 4.3, 2.1 and 20

7) An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following ^{1}H and ^{13}C NMR spectral data. *[Dec 2011]*

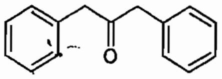
^{1}H NMR: - δ 2.4 (s), 7.2(d, J=8 Hz), 7.7(d, J=8 Hz)

^{13}C NMR: - δ 21.0, 129.0, 130.0, 136.0, 141.0, 190.0

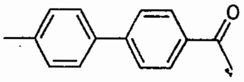
(a)



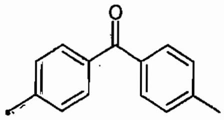
(b)



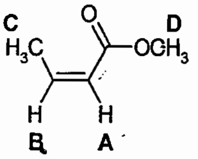
(c)



(d)



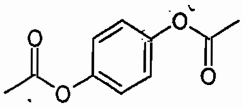
8) Appropriate ^{1}H NMR chemical shifts (δ) for the protons A-D for the following compound are *[Dec 2011]*



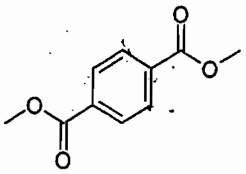
(a) A– 6.8; B –5.7; C–3.9; D –2.1ppm　(b) A– 6.8; B–5.7; C–2.1; D –3.9 ppm

(c) A–5.7; B–6.8; C–3.9; D –2.1 ppm　(d) A– 5.7; B – 6.8; C–2.1; D –3.9 ppm

9) Compounds A and B exhibit two singlet, each in their ^{1}H NMR spectra. The expected chemical shifts are at δ *[June 2012]*



A



B

(a) 6.9 and 2.1 for A; 7.7 and 3.9 for B　(b) 7.7 and 3.9 for A; 6.9 and 2.1 for B

(c) 6.9 and 3.9 for A; 7.7 and 2.1 for B　(d) 7.7 and 2.1 for A; 6.9 and 3.9 for B

30) Match the following ***[June 2012]***

Compound	**^{13}C NMR chemical shift (δ ppm)**
(A) Acetic acid	(i) 95
(B) Acetonitrile	(ii) 115
(C) Acetone	(iii) 175
(D) Carbon tetrachloride	(iv) 205

(a) (A)-(iii), (B)-(ii), (C)-(iv), (D)-(i)
(b) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)
(c) (A)-(i), (B)-(ii), (C)-(iv), (D)-(iii)
(d) (A)-(iii), (B)-(i), (C)-(iii), (D)-(iv)

31) 4-Hydroxybenzoic acid exhibited signals at δ 171, 162, 133, 122 and 116 ppm in its broadband decoupoled ^{13}C NMR spectrum. The correct assignment of the signals is ***[Dec 2012]***

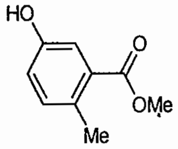
(a) δ 171(C–4), 162 (–COOH), 133(C–3 & 5), 122(C–1) and 116(C–2 & 6)

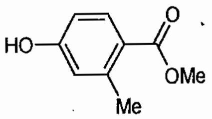
(b) δ 171(–COOH),162 (C–4), 133(C–2 & 6), 122(C–1) and 116(C–3 & 5)

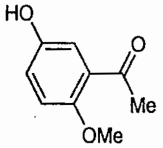
(c) δ 171(C–4),162(–COOH), 133(C–2 & 6), 122(C–1) and 116(C–3 & 5)

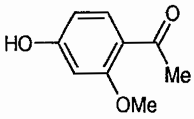
(d) δ 171(–COOH), 162 (C–4), 133(C–3 & 5), 122(C–1) and 116(C–2 & 6)

32) An organic compoound ($C_9H_{10}O_3$) exhibited the following spectral data ***[Dec 2012]***
IR: 3400, 1680 cm^{-1};
^{1}H NMR: δ 7.8(1H, d, J = 8 Hz), 7.0 (1 H, d, J = 8Hz), 6.5 (1 H, s), 5.8 (1 H, s, D_2O exchangeable), 3.9(3H,s), 2.3 (3 H, s). The compound is

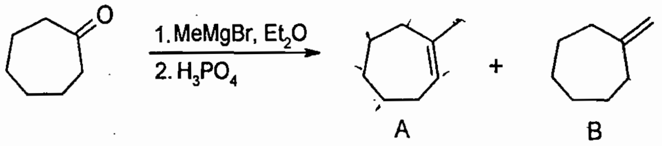
(a)


(b)


(c)


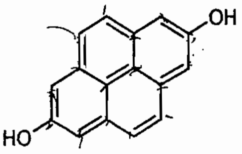
(d)


33) Among the following, the correct statement for the following reaction is ***[June 2013]***

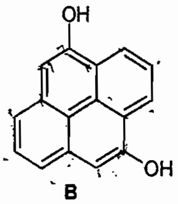


(a) A is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum
(b) A is the minor product and it will have eight signals in the proton decoupled ^{13}C NMR spectrum
(c) B is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum
(d) B is the minor product and it will have five signals in the proton decoupled ^{13}C NMR spectrum

34) In the broad band decoupled ^{13}C NMR spectrum, the number of signals appearing for the two pyrenediols A and B respectively are ***[June 2013]***



A

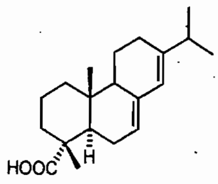


B

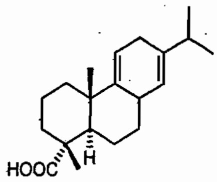
(a) eight and eight
(b) eight and sixteen
(c) five and ten
(d) five and eight.

35) In the UV-Vis is spectrum, a diterpenoid exhibited a λ_{max} at 275 nm. The compound, among the choices given below is ***[June 2013]***

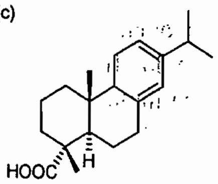
(a)



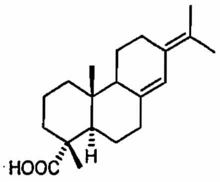
(b)



(c)



(d)

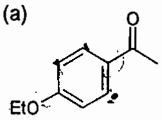


36) An organic compound exhibited the following ^{1}H NMR spectral data ***[June 2013]***

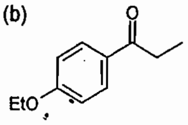
δ 7.80 (2 H, d, J 8 Hz), 6.80 (2 H, d, J 8 Hz), 4.10 (2H, q, J 7.2 Hz), 2.4 (3H, s),1.25 (3 H, t, J 7.2 Hz)

The compound, among the choices given below is, ***[June 2013]***

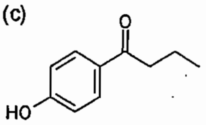
(a)



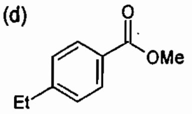
(b)



(c)

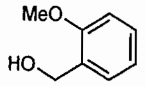


(d)

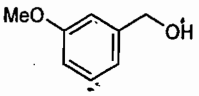


37) An organic compound ($C_6H_{10}O_2$), which does not change the color of ferric chloride solution, exhibited the following ^{1}H NMR spectral data- δ 7.3 (1H, t, J = 8 Hz), 7.0 (1H, d, J = 8 Hz), 6.95 (1H, s), 6.9 (1H, d, J =8 Hz), 5.3 (1H, brs, D_2O exchangeable), 4.6 (2H, s), 3.9 (3H, s). Structure of the compound is ***[Dec 2013]***

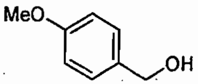
(a)



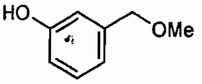
(b)



(c)



(d)



38) Methyl 4-oxopentanoate exchibited signals at δ 208, 172, 51, 37, 32 and 27 ppm in its ^{13}C NMR spectrum.The signals due to the methoxy, C1, C4 and C5 carbons are ***[Dec 2013]***

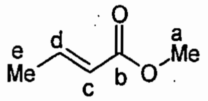
(a) OMe −32; C1−208; C4−172; C5−51

(b) OMe-51; C1−208; C4−172; C5−32

(c) OMe−32; C1−172; C4−208; C5−51

(d) OMe-51; C1−172, C4−208; C5−32

39) The correct ^{13}C NMR chemical shifts (δ) values of carbons labeled a−e in the following esters are ***[June 2014]***



(a) a :19; b:143; c:167; d:125; e:52

(b) a : 52; b:143; c:167; d:125; e:19

(c) a : 52; b:167; c:143; d:125; e:19

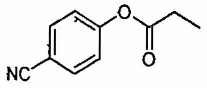
(d) a : 52; b: 167; c:125; d:143; e:19

40) An organic compound gives following spectral data:

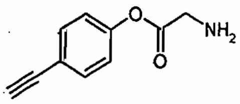
IR : 2210, 1724 cm^{-1}, ^{1}H NMR : δ 1.4 (t, J = 7.1 Hz, 3H), 4.4 (q, J = 7.1 Hz, 2H), 7.7 (d, J = 7.0 Hz, 2H); 8.2 (d, J = 7.0 Hz, 2H); ^{13}C NMR : δ 16, 62, 118, 119, 125, 126, 127, 168.

The compound is ***[June 2014]***

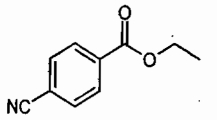
(a)



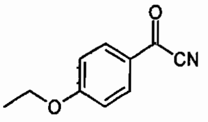
(b)



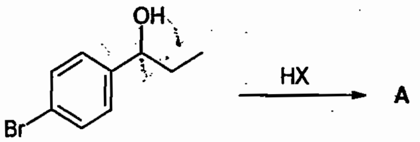
(c)



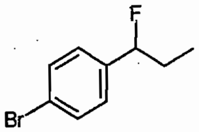
(d)



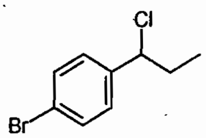
41) The mass spectrum of the product A, formed in the following reaction , exhibits M, M+2, M+4 peaks in the ratio of about 1:2:1. The reagent HX and the product A are ***[June 2014]***



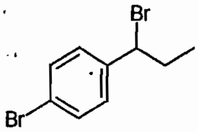
(a) HX = HF and **A** =



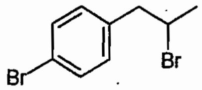
(b) HX = HCl and **A** =



(c) HX = HBr and **A** =

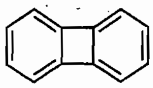


(d) HX = HBr and **A** =

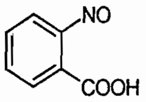


42) Anthranilic acid, on treatment with iso−amyl nitrite furnishes a product which displays a strong peak at 76 (m/e) in its mass spectrum. The structure of product is ***[June 2014]***

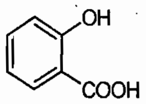
(a)



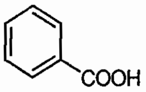
(b)



(c)



(d)

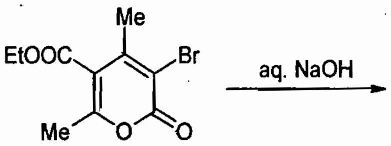


43) The following reaction gives a product (racemic) which exhibits the following NMR data: ***[Dec 2014]***

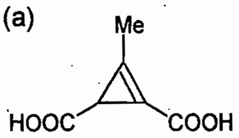
^{1}H NMR: δ 2.67 (2H, s), 5.60(2H,s) ppm

^{13}C NMR: δ 170.3, 129.0, 105.0, 25.4 ppm

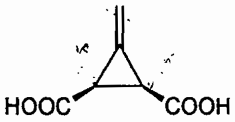
The structure of the product (racemic) is



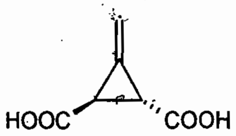
(a)



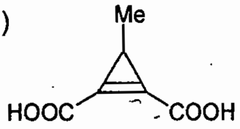
(b)



(c)



(d)



44) An organic compound having molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data :

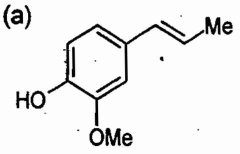
IR : 3400 (br), 1600 cm^{-1}

^{1}H NMR : δ 1.85 (3H, d, J=6Hz), 3.8 (3H, s), 5.0 (1H,s,D_2O exchangeable) , 6.0 (1H, dq , J=18, 6Hz) , 6.28 (1H,d, J=18 Hz) , 6.75(1H,d, J=8Hz) , 6.8 (1H,s) , 6.90 (1H, d, J=8Hz) ppm

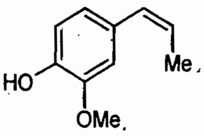
^{13}C NMR : δ 146.5 , 144.0 , 131.0 , 130.5, 123.0, 119.0 , 114.0 , 108.0 , 55.0 , 18.0 ppm

The structure of the compound is ***[Dec 2014]***

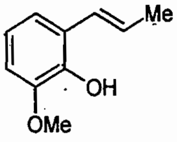
(a)



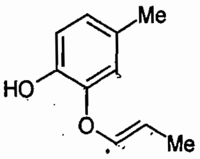
(b)



(c)



(d)



(Questions from GATE EXAM)

Questions with ONE OR TWO marks

5) ^{1}H NMR spectrum of [18]–annulene shows ***(GATE 2005)***

(a) only one peak at δ 7.2 (18H) (b) only one peak at δ 5.0 (18H)
(c) two peaks at δ 9.0 (12H) and δ −3.0 (6H) (d) two peaks at δ 9.0 (6H) and δ −3.0 (12H)

6) Resonant frequencies for EPR and NMR are respectively in the spectral region ***(GATE 2005)***

(a) microwave and far-IR (b) far-IR and microwave
(c) radiofrequency and microwave (d) microwave and radiofrequency

7) Match the following items of column I with the appropriate items in column II ***(GATE 2005)***

Column I **Compounds**	**column II** **carbonyl stretching frequency (cm^{-1})**
P) Cyclohexanone	I 1910
Q Cyclopentanone	II 1715
R) Cyclobutanone	III 1813
S) Cyclopropanone	IV 1650
	V 1780
	VI 1745

(a) P-I, Q-II, R-III, S-IV (b) P-II, Q-VI, R-V, S-III (c) P-VI, Q-V, R-IV, S-III (d) P-I,Q-V, R-IV, S-III

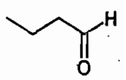
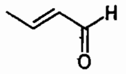
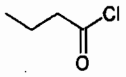
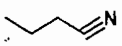
8) Which of the following absorption is shown by 1,3 butadiene in its UV absorption spectrum recorded in *n*–hexane (ε_{max} is the molar absorptivity) ***(GATE 2006)***

(a) λ_{max} 217 nm (ε_{max} = 21,000) (b) λ_{max} 214 nm (ε_{max} = 210)
(c) λ_{max} 253 nm (ε_{max} = 50,000) (d) λ_{max} 250 nm (ε_{max} = 500)

9) Which of the following compounds is expected to show a sharp singlet for one of its protons at δ ≥ 8 ppm in ^{1}H NMR spectrum, given that this signal remain unaffected on shaking the solution thoroughly with D_2O? ***(GATE 2006)***

(a) CH_3CO_2H (b) $CH_3CONHC_6H_5$ (c) n–$C_6H_{13}C{\equiv}CH$ (d) n–$C_6H_{13}CHO$

0) Match the compounds in List –I with the stretching frequencies (cm^{-1}) of principal functional group given in List–II ***(GATE 2006)***

List- I		List- II
A)		i) 2240
B)		ii) 1795
C)		iii) 1750
D)		iv) 1725
		v) 1695

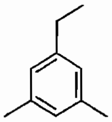
(a) (A–iii), (B–iv), (C–i), (D–v) (b) (A–iii), (B–iv), (C–ii), (D–i)
(c) (A–iv), (B–v), (C–ii), (D–i) (d) (A–iv), (B–iii), (C–v), (D–i)

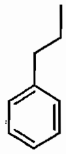
51) Match the observed principal absorbtions in the visible spectrum shown in List I with the bond that shows this absorption in List II ***(GATE 2007)***

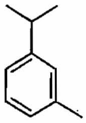
List I	***List II***
(A) $\sigma \rightarrow \sigma^*$	(i) C–C
(B) $n \rightarrow \sigma^*$	(ii) C–O
(C) n, π^*	(iii) C=O
(D) π, π^*	(iv) C=C

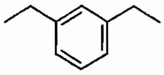
(a) (A–i) (B–ii) (C–iii) (D–iv)
(b) (A–i) (B–iii) (C–ii) (D–iv)
(c) (A–ii) (B–i) (C–iv) (D–iii)
(d) (A–iv) (B–ii) (C–iii) (D–i)

52) Among the isomers of $C_{10}H_{14}$ shown, the isomer that can be identified uniquely by mass spectrometry alone is ***(GATE 2007)***


P

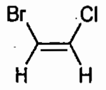

Q


S

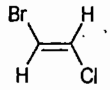

R

(a) P (b) Q (c) R (d) S

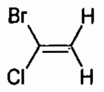
53) Match the structures in List I with the coupling constant [^{1}H J (Hz)] given in List II ***(GATE 2007)***

(A)


(i) ~1 Hz

(B)


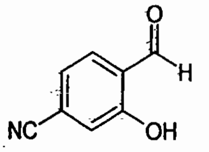
(ii) ~ 10 Hz

(C)


(iii) ~ 15 Hz

(a) A- i , B- ii , C- iii (b) A- ii , B- iii , C- I (c) A- iii , B- ii , C- i (d) A- iii , B- i , C- ii

54) The IR stretching frequencies (cm^{-1}) for the compound X are as follows: 3300-3500 (s, br); 3000(m); 2225 (s); 1680 (s). ***(GATE 2008)***



X

The correct assignment of the absorption bands is

(a) $\bar{\nu}_{(OH)} = 3300-3500$; $\bar{\nu}_{(CH)} = 3000$; $\bar{\nu}_{(CN)} = 2225$; $\bar{\nu}_{(CO)} = 1680$

(b) $\bar{\nu}_{(OH)} = 3000$; $\bar{\nu}_{(CH)} = 3300-3500$; $\bar{\nu}_{(CN)} = 2225$; $\bar{\nu}_{(CO)} = 2225$

(c) $\bar{\nu}_{(OH)} = 3300-3500$; $\bar{\nu}_{(CH)} = 3000$; $\bar{\nu}_{(CN)} = 1680$; $\bar{\nu}_{(CO)} = 2225$

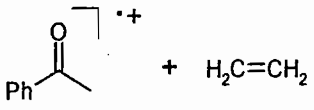
(d) $\bar{\nu}_{(OH)} = 3000$; $\bar{\nu}_{(CH)} = 3300-3500$; $\bar{\nu}_{(CN)} = 1680$; $\bar{\nu}_{(CO)} = 1680$

Linked answer question 55 & 56

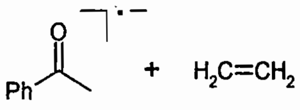
For butyrophenone ($PhCOCH_2CH_2CH_3$), In the reaction,

55) The most probable fragmentation observed in the electron impact ionization (EI) mass spectrometry is ***(GATE 2008)***

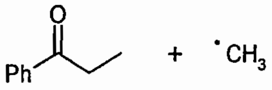
(a)



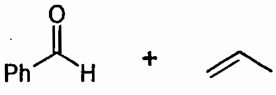
(b)



(c)

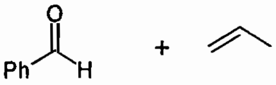


(d)

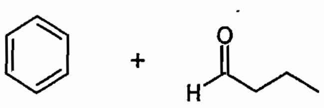


56) Photoirradiation leads to the following set of products.

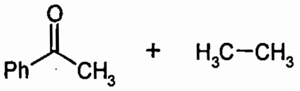
(a)



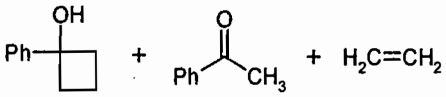
(b)



(c)



(d)



57) The ^1H NMR spectrum of HD consists of a **[*GATE 2009*]**

(a) singlet (b) 1:1 doublet [✓ (c) 1:1:1 triplet] (d) 1 :2:1 triplet

58) The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of *ortho-*, *meta-* and *para*-dichlorobenzenes, respectively, are **[*GATE 2009*]**

(a) 3, 4 and 2 (b) 3,3 and 2 (c) 4,4 and 2 (d) 3,4 and 4

Linked answer question 59 & 60

An organic compound X ($C_9H_{10}O$) exhibited the following spectral data.

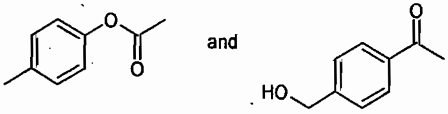
IR: 1680 cm^{-1}

^1H NMR: δ 7.8 (2 H, d, J 7.5 Hz), 7.2 (2 H, d, J 7.5 Hz), 2.7 (3 H, s) and 2.4 (3 H, s).

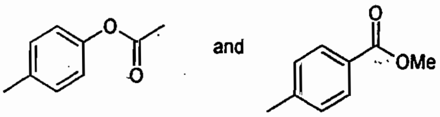
Compound X on treatment with m-chloroperbenzoic acid produced two isomeric compounds Y (major) and Z(minor). **[*GATE 2009*]**

59) Compounds Y and Z, respectively, are

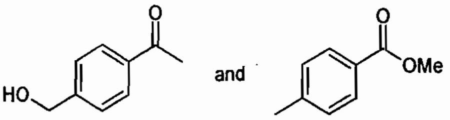
(a)



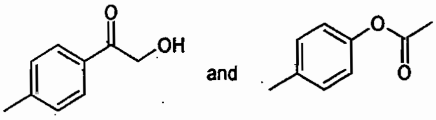
(b)



(c)



(d)



60) Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because

(a) Y produces 4-methylphenol and Z is unaffected

(b) Y produces 4-methylphenol and Z produces 4-methylbenzoic acid

(c) Y is unaffected and Z produces 4-methylbenzoic acid

(d) Y is unaffected and Z produces 4-methylphenol

Linked answer question 61 & 62

An organic compound [X] ($C_{12}H_{16}O_3$) exhibit the following spectral data **[*GATE 2010*]**

IR: - 1720cm^{-1}

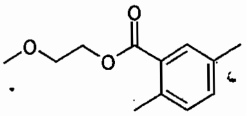
^{1}H NMR:- 2.35 (s, 6H), 3.30(s, 3H), 3.83(t, 2H), 4.42 (t, 2H), 7.07(s, 1H), 7.58(s, 2H)

The compound [X] with an excess of MeMgBr gives a 1:1 mixture of [Y] and [Z] compounds.

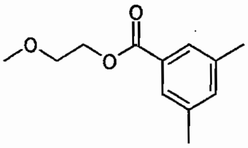
The compound [Z] exhibit the following ^{1}H NMR data:- 2.0 (bs, 1H), 3.30 (s, 3H), 3.56 (t, 2H), 3.70 (t, 2H),

61) The compound [X] is

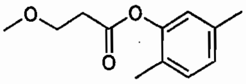
(a) X =



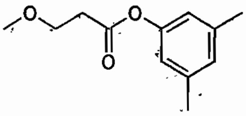
(b) X =



(c) X =

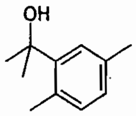


(d) X =

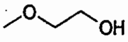


62) The compound [Y] is

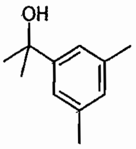
(a)



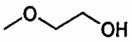
and



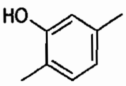
(b)



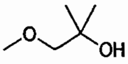
and



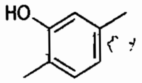
(c)



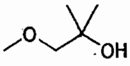
and



(d)



and

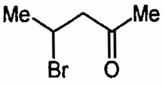


Linked answer question 63 & 64

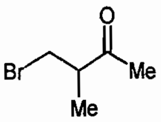
A ketone on treatment with bromine in methanol gives the corresponding monobromo compound [X] having molecular formula C_5H_9BrO. The compound [X] when treated with NaOMe in MeOH produces [Y] as the major product. The spectral data for compound [X] are: ^{1}H NMR: δ 1.17 (d, 6H), 3.02 (m, 1H), 4.10 (s, 2H); ^{13}C NMR: δ 17,37, 39,210. ***(GATE 2011)***

63) The compound [X] is

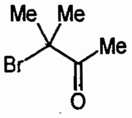
(a)



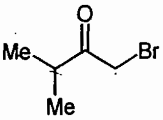
(b)



(c)

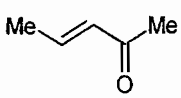


(d)

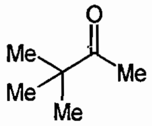


64) The compound [Y] is

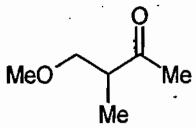
(a)



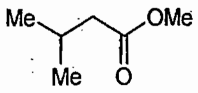
(b)



(c)



(d)



65) In the proton decoupled ^{13}C NMR spectrum of 7-norbornanone, the number of signals obtained is ***[GATE 2012]***

(a) 7 (b) 3 (c) 4 (d) 5

66) The ratio of relative intensities of the two molecular ion peaks of methyl bromide (CH_3Br) in the mass spectrum is ***[GATE 2012]***

(a) $M^+ : (M+2)^+ = 1:3$ (b) $M^+ : (M+2)^+ = 3:1$ (c) $M^+ : (M+2)^+ = 1:1$ (d) $M^+ : (M+2)^+ = 1:2$

67) The bond that gives the most intense band in the infrared spectrum for its stretching vibration is ***[GATE 2012]***

(a) C–H (b) N–H (c) O–H (d) S–H

68) The number of signals that appear in the proton decoupled ^{13}C NMR spectrum of benzonitrile (C_7H_5N) is ***[GATE 2013]***

(a) Four (b) Five (c) Six (d) Seven

69) Among the compounds given in the options A-D, the one that exhibits a sharp band at around 3300 cm^{-1} in the IR spectrum is ***[GATE 2013]***

(a) 1,2-butadiene (b) 1,3-butadiene (c) 1-butyne (d) 2-butyne

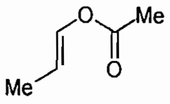
70) An organic compound Q exhibited the following spectral data: ***[GATE 2013]***

IR: 1760 cm^{-1}

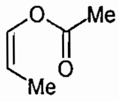
^{1}H NMR: δ (ppm): 7.2 (1H, d, J = 16.0 Hz), 5.1 (1 H, m), 2.1 (3 H, s), 1.8 (3H, d, J = 7.0 Hz)

^{13}C NMR: δ (ppm): 170 (carbonyl carbon). Compound Q is

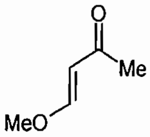
(a)



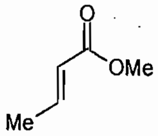
(b)



(c)



(d)



Linked answer question 71 & 72

N,N-Dimethylformamide (DMF) gives different patterns of signals for the methyl protons when its1H NMR spectrum is recorded at different temperatures. ***[GATE 2013]***

71) Match the patterns of the NMR signals given in column I with temperatures given in the column II.

Column I	columnII
(i) Two singlets,for three protons each, at δ 2.87 and 2.97 ppm	(x) 25 °C
(ii) One sharp singlet for six protons at δ 2.92 ppm	(y) 120 °C
(iii) One broad signal for six protons	(z) 150 °C

(a) (i)-(x); (ii)-(y); (iii)-(z) (b) (i)-(x); (ii)-(z); (iii)-(y) (c) (i)-(z); (ii)-(x); (iii)-(y) (d) (i)-(z); (ii)-(y); (iii)-(x)

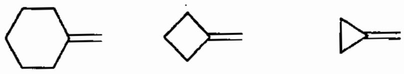
72) Based on the above data, the calculated difference in the frequencies of the two methyl singlets, if the spectrum is recorded on a 300 MHz spectrometer, is

(a) 30 (b) 60 (c) 90 (d) 120

73) At room temperature, the number of singlet resonances observed in the ^{1}H NMR spectrum of $Me_3CC(O)NMe_2$ (N,N-dimethyl pivalamide) is ***[GATE 2014]***

(a) Two (b) Three (c) Four (d) Five

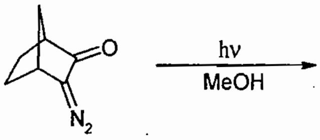
74) The correct order of IR stretching frequency of the C=C in the following olefins is ***[GATE 2014]***



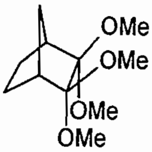
I II III

(a) I > II > III (b) II > III > I (c) III > II > I (d) III > I > II

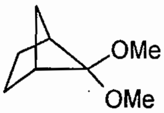
75) The product of the following reaction gave 6 line ^{13}C NMR spectrum with peaks at δ 175, 52, 50, 46, 37, 33 ppm. The structure of the product is ***[GATE 2014]***



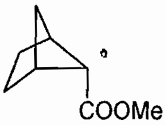
(a)



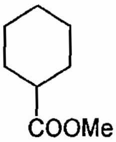
(b)



(c)



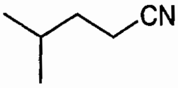
(d)



76) The set of protons (underlined) in $CH_3CH_2CH_2OCH_3$ that would exhibit different splitting patterns in high (500 MHz) and low (60 MHz) field ^{1}H NMR, is ***[GATE 2014]***

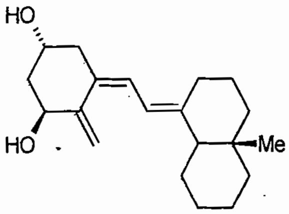
(a) $\underline{CH_3}CH_2CH_2OCH_3$ (b) $CH_3\underline{CH_2}CH_2OCH_3$ (c) $CH_3CH_2\underline{CH_2}OCH_3$ (d) $CH_3CH_2CH_2O\underline{CH_3}$

77) The *m/z* value of the detectable fragment formed by McLafferty like rearrangement of the following compound in mass spectrometer is ***[GATE 2014]***



(a) 31 (b) 39 (c) 41 (d) 43

78) Given the fact that 1,3-butadiene has a UV absorption of 217 nm, the absorption wavelength (in nm) for the conjugated system shown below is
(Use these absorption values for auxochromic groups: alkyl: +5; *exo*-cyclic double bond: +5; every additional conjugated C=C: +30) ***[GATE 2014]***



(a) 278 (b) 282 (c) 288 (d) 293

Answer Key

Topic :-17: Organic spectroscopy

1	d	2	b	3	b	4	b	5	b	6	c	7	c	8	d	9	d	10	a
11	d	12	a	13	b	14	a	15	d	16	a	17	a	18	d	19	c	20	b
21	b	22	d	23	a	24	d	25	a	26	a	27	d	28	d	29	a	30	a
31	b	32	d	33	d	34	c	35	c	36	a	37	b	38	d	39	d	40	c
41	c	42	a	43	c	44	a	45	c	46	d	47	b	48	a	49	d	50	b
51	a	52	b	53	b	54	a	55	a	56	d	57	c	58	a	59	b	60	b
61	b	62	b	63	d	64	d	65	b	66	c	67	c	68	b	69	c	70	a
71	b	72	a	73	b	74	c	75	c	76	b	77	c	78	b				

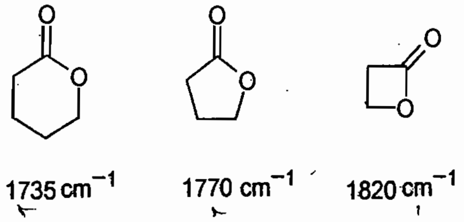
Hint & solution

1) **Ans (d):-** The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is Anhydride > ketone > amide
The general order of carbonyl stretching frequency in the IR spectra:-
acid chlorides > anhydrides > ester > aldehydes > ketones > carboxylic acids > amides

2) **Ans (b):-** The largest alky group is most readily lost in tertiary alcohol;
Therefore the order of α–clevage is: C_3H_7 > Et > Me.

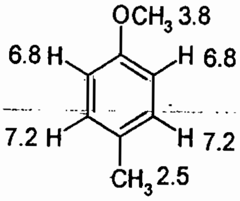
3) **Ans (b):-** The absorption at λ_{max} 279 nm (ε =15) in the UV spectrum of acetone is due to $n-\pi^*$ transition.

4) **Ans (b):-** In the IR spectrum, carbonyl absorption band for the following compound appears at 1770cm^{-1}

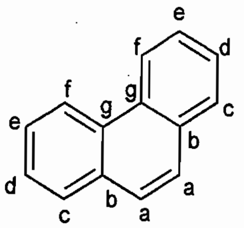


5) **Ans (b):-** In the mass spectrum of dodecahedrane $C_{20}H_{20}$, approximate ratio of the peaks at m/z 260 and 261 is 5:1

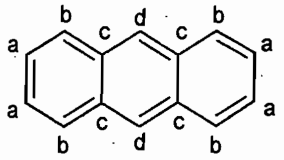
6) **Ans (c):-** The given ^{1}H NMR spectral data match with 4-methylanisole



7) **Ans (c):-**



7 signals



4 signals

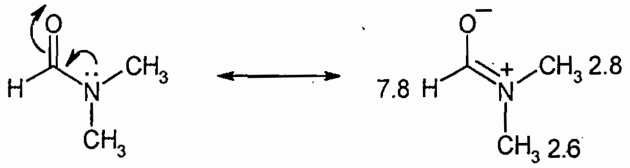
8) Ans (d):- The coupling constant (J) value for a doublet =
(Difference between the frequency of the two peaks) × (frequency of NMR machine)
= (2.38−2.35)400 = 0.03 × 400 = 12Hz

9) Ans (d):- ^1H NMR spectrum of HD would show a triplet with intensity ratio 1:1:1. In case of D the value of I = 1
∴ No. of signals = $[(2n_aI_a+1)]$, where n is equivalent nuclei & I is a Nuclear spin.
∴ No. of signals = [2(1)(1) +1] = 3.

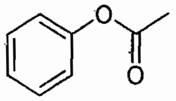
When I= ½ the relative intensity ratio is according to Pascal's triangle but when I = 1 the relative intensity ratio is given as

n	2n/+1	relative intensity ratio when I = 1
0	1	1
1	3	1:1:1
2	5	1:2:3:2:1
3	7	1:3:6:7:6:3:1
4	9	1:4:10:16:19:16:10:4:1
5	11	1:5:15:30:45:51:45:30:15:5:1

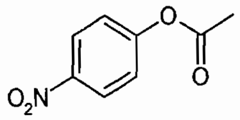
10) Ans (a):-At room temperature DMF has a partial double bond character due to the delocalization & therefore it gives singlet for each methyl group(one Me group is syn to oxygen & another is anti to oxygen)



11) Ans (d):- In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at 1760 cm^{-1} & in p-nitrophenyl acetate due to electron withdrawing effect of NO_2 group carbonyl frequency is shifted to a higher frequency & therefore among the given option it match with 1760 cm^{-1}



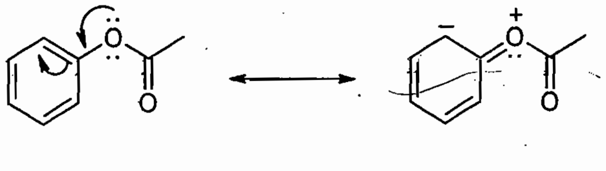
phenyl acetate



p-nitrophenyl acetate

12) Ans (a):- In NMR spectroscopy, the product of the nuclear 'g' factor (g_N), the nuclear magneton β_N and the magnetic field strength (B_0) gives the energy of transition from α to β state

13) Ans (b):- In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at 1760 cm^{-1}. Normal ester frequency of carbonyl group appears in the range from 1750 to 1735 cm^{-1} but in case of phenyl acetate due to the conjugation involving the single bonded oxygen with phenyl group shift of carbonyl frequency to a higher frequency that is at 1760 cm^{-1}.



phenyl acetate

phenyl acetate

14) Ans (a):- Given:- An AX system gave 4 lines at δ_1 =4.72, δ_2=4.6, δ_3 =1.12 and δ_4=1.0

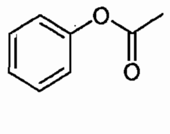
The coupling constant (J) value for a AX system =

[Difference between the frequency of the (δ_1− δ_2) OR (δ_3− δ_4)]× (frequency of NMR machine)

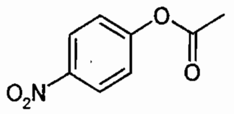
= (4.72−4.6)100 = 0.12 × 100 = 12Hz

Now $\delta_{AX} = (\delta_A - \delta_X) = \sqrt{(\delta_1 - \delta_4)(\delta_2 - \delta_3)} = \sqrt{(4.72 - 1.0)(4.6 - 1.12)} = \sqrt{12.95}$ = 3.6 ppm

15) Ans (d):- In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at 1760 cm^{-1} & in p-nitrophenyl acetate due to electron withdrawing effect of NO_2 group carbonyl frequency is shifted to a higher frequency & therefore it appear at 1770 cm^{-1}



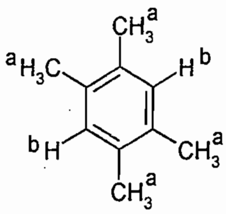
phenyl acetate



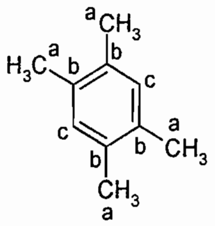
p-nitrophenyl acetate

16) Ans (a):- The compound (a) in a option exhibit two singlets in the ^{1}H NMR spectrum and three signals in the ^{13}C NMR spectrum.

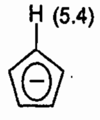
^{1}H NMR



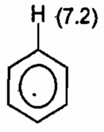
^{13}C NMR



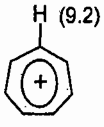
17) Ans (a):- The chemical shifts of protons on negatively charged (electron rich) carbon resonate at upfield (shielded) while that of protons on positively charged (electron deficient) carbon resonate at downfield (deshielded)



I



II



III

18) Ans (d):- ^{1}H NMR spectrum of CD_3Cl would show a septet with intensity ratio 1:3:6:7:6:3:1

In case of D the value of I = 1

∴ No. of signals = $[(2n_aI_a+1)]$, where n is equivalent nuclei & I is a Nuclear spin.

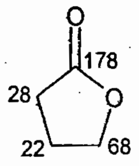
∴ No. of signals = [2(3)(1) +1] = 7.

When I= ½ the relative intensity ratio is according to Pascal's triangle but when I = 1 the relative intensity ratio is given as

n	2n+1	relative intensity ratio when I = 1
0	1	1
1	3	1:1:1
2	5	1:2:3:2:1
3	7	1:3:6:7:6:3:1
4	9	1:4:10:16:19:16:10:4:1
5	11	1:5:15:30:45:51:45:30:15:5:1

∴ The ratio of relative intensities of the carbon signals in the first order ^{13}C NMR spectrum of CD_3Cl is 1:3:6:7:6:3:1

19) Ans (c):- In the IR spectrum, carbonyl absorption band for the γ-lactone appears at 1770cm^{-1}



1770 cm^{-1}

20) Ans (b):- The metastable ion is appear at an m/e ratio that depends on its mass as well as the mass of original ion from which it formed in the mass spectrum. The metastable ion peaks are usually a broad peak. The apparent mass of the metastable ion (m*) is given by:-

$$m_1^+ \rightarrow m_2^+ + \text{fragment}$$

$$m^* = \frac{(m_2)^2}{m_1}$$

Where m_1 is the mass of original ion from which the fragment formed & m_2 is the mass of the new fragment ion

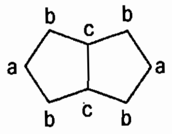
Thus the mass of metastable ion is produced due to decomposition of F_1^+ in the following mass fragmentation sequence is calculated as:-

$$\underset{(M^{+}, 222)}{\text{Diethyl phthalate}} \longrightarrow \underset{(177)}{F_1^+} \longrightarrow \underset{(149)}{F_2^+} + \underset{(28)}{CO}$$

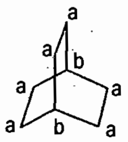
$$m^* = \frac{(m_2)^2}{m_1} = \frac{(149)^2}{177} = 125.4$$

21) Ans (b):-

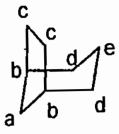
^{13}C NMR



A
3 signals



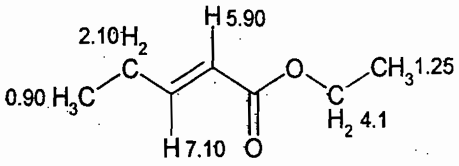
B
2 signals



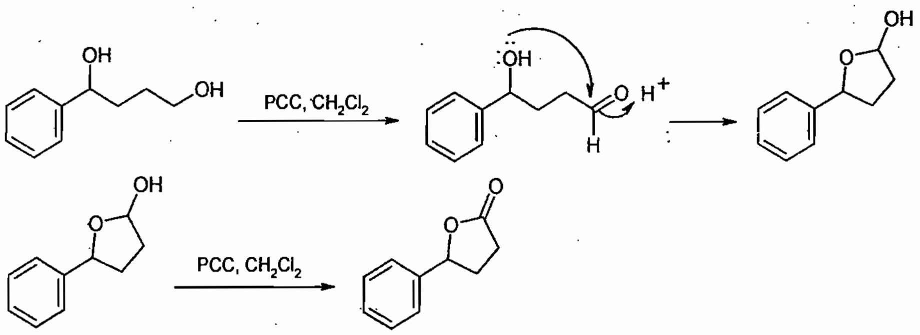
C
5 signals

22) Ans (d):- A compound that contain two chlorine atom will always have three ion peak namely molecular ion peak (M); M+2 & M+4 with 9:6:1 intensity because of ^{37}Cl isotope along with ^{35}Cl.

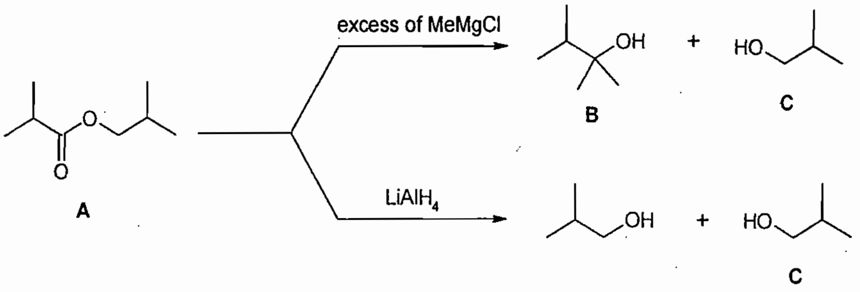
23) Ans (a):- Hint:- Protons substituted trans on double bond couple most strongly with typical value for ^{3}J of about 16 Hz. Protons substituted cis on double bond couple about 8 Hz; so option (b) & (d) are not possible & therefore the compound, of the choice is:-

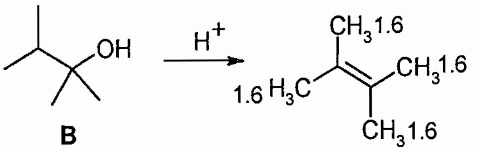


24) Ans (d):- A strong absorption at ν_{max} 1765 cm^{-1} in the IR spectrum also suggest the formation of γ-lactone In first step oxidation of a primary alcohol can be easily stopped at the aldehyde by pyridinium chlorochromate pyH$^+$CrO$_3$Cl$^-$ (PCC) & no further oxidation takes place. Secondary alcohols are oxidized to corresponding ketones with PCC. The PCC is somewhat acidic and acid-catalyzed rearrangements have been observed.



25) Ans (a):- The compound A is





(acid catalyzed dehydration via 1,2 hydride shift to carbocation)

26) Ans (a):- *The chemical shift (in ppm) of A protons* = Average of the outer lines = $\frac{(4.1+4.7)}{2} = \frac{8.8}{2} = 4.4$

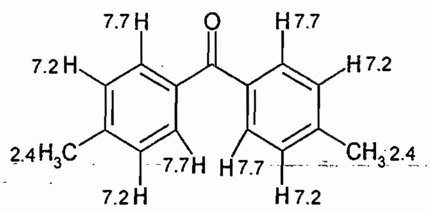
The chemical shift (in ppm) of X protons = Average of the outer lines = $\frac{(2.1+2.3)}{2} = \frac{4.4}{2} = 2.2$

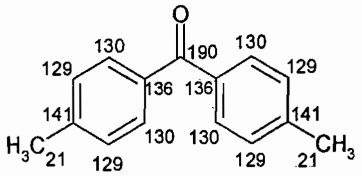
The coupling constant (in (Hz) =

(Difference between the frequency of the two adjacent peaks) × (frequency of NMR machine)

= (2.3−2.1)100 = 0.2 × 100 = 20Hz ***or*** (4.3−4.1)100 = 0.2 × 100 = 20Hz

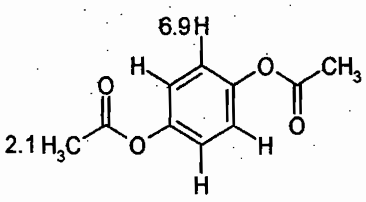
27) Ans (d):- The compound that match with given spectral data is:-



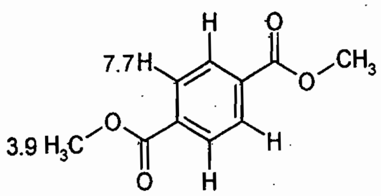


28) Ans (d):- Appropriate ^{1}H NMR chemical shifts (δ) for the protons A-D :- A– 5.7; B – 6.8; C–2.1; D –3.9 ppm.
C type of proton of methyl group attached to sp^2 carbon & therefore appears at δ 2.1ppm
D type of proton of methyl group of methyl ester appears at δ3.9 ppm.
Among A & B; B type of proton are more deshielded due to conjugation making it electron deficient than A type of proton; therefore A & B appears at δ 5.7 & 6.8 ppm respectively

29) Ans (a):- Hint:- The ring protons are more shielded in (A) due to electron donating substituent & therefore resonate at upfield (6.9) compare to the benzene proton(7.27 ppm) ; while the ring protons are more deshielded in (B) due to electron withdrawing substituent & therefore resonate at downfield (7.7) compare to the benzene proton(7.27 ppm). In ^{1}H NMR the chemical shifts (δ) for methyl proton of methyl ester always resonate at 3.5 to 4.8 ppm & α−hydrogen in the ketone always resonate at 2.1 to 2.4 ppm.



A

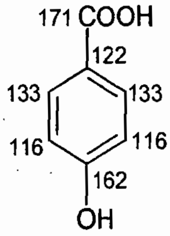


B

30) Ans (a):- The correct match is:-

Compound	^{13}C NMR chemical shift (δ ppm)
Acetic acid	175
Acetonitrile	115
Acetone	205
Carbon tetrachloride	95

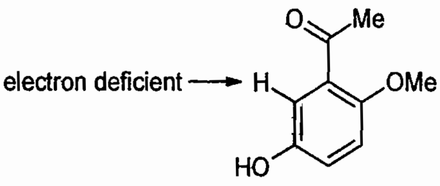
31) Ans (b):- 4-Hydroxybenzoic acid exhibited signals at δ 171(–COOH), 162 (C–4), 133(C–2 & 6), 122(C–1) and 116(C–3 & 5) in its broadband decoupoled ^{13}C NMR spectrum.



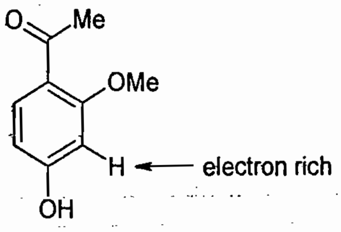
32) Ans (d):- The IR value 1680cm^{-1} is of aryl ketone & match with (c) & (d) in option.

Now in ^{1}H NMR: δ 6.5 (1 H, s) without coupling constant resonate at upfield (6.5) compare to the benzene proton(7.27 ppm) indicate that it is electron rich due to electron donating substituent.

Therefore the value at δ 6.5 (1 H, s) match with compound (d) in option

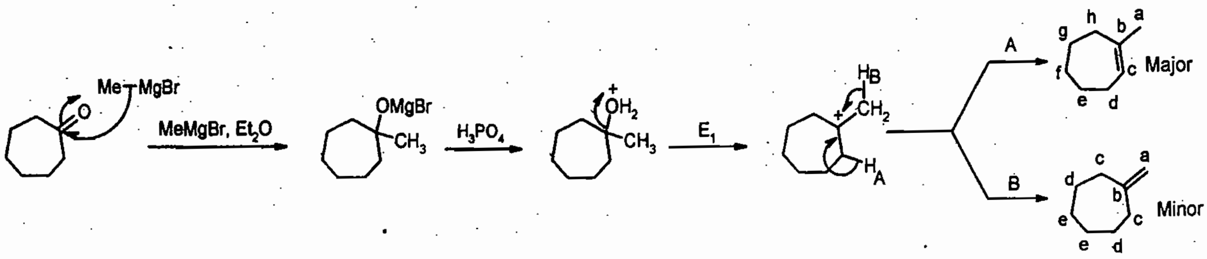


(c)

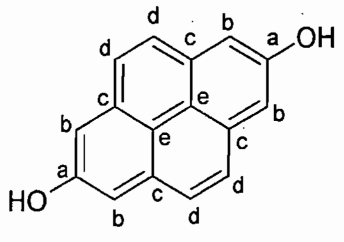


(d)

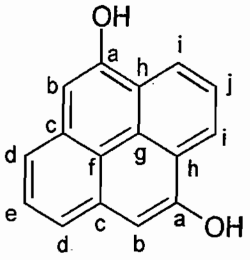
33) Ans (d):- In first step is the Grignard reagent adds to ketones to give tertiary alcohols. Tertiary alcohol readily undergoes dehydration with dehydrating agent like H_3PO_4 or H_2SO_4 via E_1 elimination to give More substituted alkenes (more stable) as a major product & it will have eight signals in the proton decoupled ^{13}C NMR spectrum



34) Ans (c):- In the broad band decoupled ^{13}C NMR spectrum, the number of signals appearing for the two pyrenediols A and B are five and ten respectively

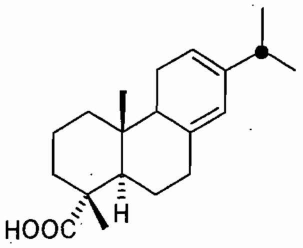


A



B

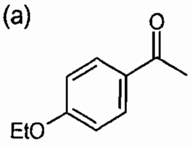
35) Ans (c):-



Cis 1,3-buadiene:	253 nm
three ring residue	15
one alkyl substituent:	5
one exocyclic double bond:	5
	278 nm

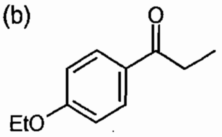
36) Ans (a):- Among the option 5 signals are possible only in the (a) & (d) compound. But singlet at δ 2.4 (3H, s), is characteristic of methyl proton of aryl methyl ketone therefore the spectral data is of compound (a) in option

(a)



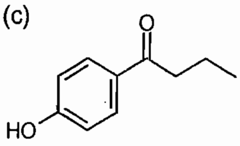
5 signals

(b)



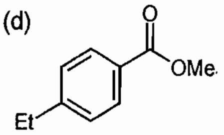
6 signals

(c)



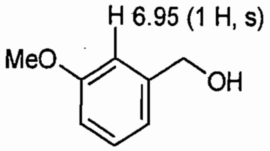
6 signals

(d)

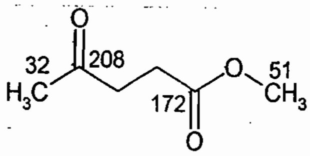


5 signals

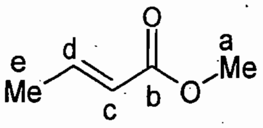
37) Ans (b):- Among the given option (c) is not possible because exhibit the five signal in ^{1}H NMR & option (d) a phenol which changes the colour of $FeCl_3$ solution so it is also not possible. The value in ^{1}H NMR at δ 6.95 (1H, s), is a without coupling constant indicates 1,3 disubstituted benzene that is option (b).



38) Ans (d):- Methyl 4-oxopentanoate exhibit the signals at δ OMe-51; Cl–172, C4–208; C5–32 in its ^{13}C NMR spectrum.

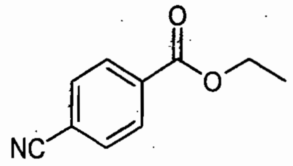


39) Ans (d):- ^{13}C NMR chemical shifts (δ) value for 'd' carbon appear at 143 ppm due to positive charge developed during conjugation.



a :52; b :167; c :125; d : 143; e :19

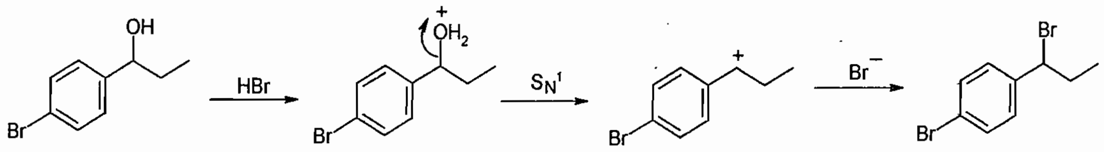
40) Ans (c):- Hint:- The IR stretching frequency at 1724 cm^{-1} strongly indicate $\nu_{C=O}$ due to the α–β or aryl conjugation.



$\nu_{C=O}$ 1725 cm^{-1}

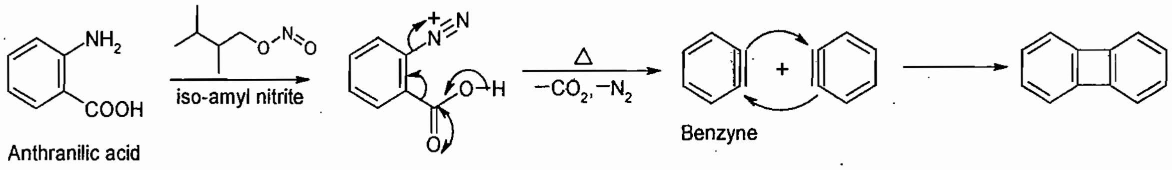
α, β or aryl conjugation

41) Ans (c):- A compound that contain two bromine atom will always have three ion peak namely molecular ion peak (M); M+2 & M+4 with 1:2:1 intensity because of ^{81}Br isotope along with ^{79}Br.



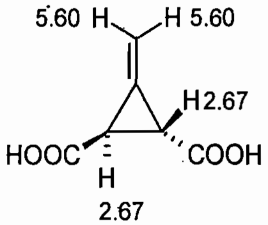
42) Ans (a):- In first step primary amine is converted into a diazonium salt by treatment with iso–amyl nitrite to give benzyne by decarboxylation & loss of N_2. Formation of benzyne gives, strong peak at 76, in mass spectrometer.

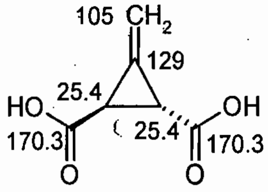
In second step benzyne itself to give a benzyne dimer having a four membered ring between two benzene rings.



43) Ans (c):- Hint:- The ^1H NMR data at δ 2.67 (2H, s), 5.60(2H,s) ppm ruled out the options (a) & (d) which would otherwise give singlet for three hydrogen.

Now among (b) & (c); compound (b) is achiral due to the plane of symmetry so would be achiral therefore the structure of the product (racemic) must be (c) which also match with given spectral data.



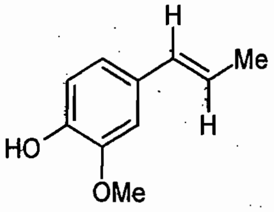


44) Ans (a):- From the given spectral data:-

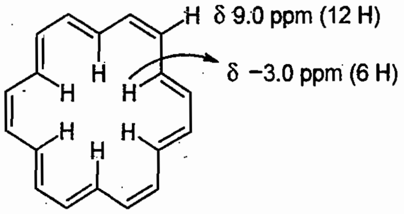
*Protons substituted trans on double bond couple most strongly with typical value for ^3J of about 16 Hz. Therefore the compound (b) is not possible in which protons substituted cis on double bond.

*The ^1H NMR data at δ 6.8 (1H,s) is a without coupling constant & is not possible in compound (c).

*Now the ^1H NMR data at δ 3.8 (3H, s), is indicate the presence of −OMe group which is present in compound (a) but absent in (d), Therefore the structure of the compound is :-

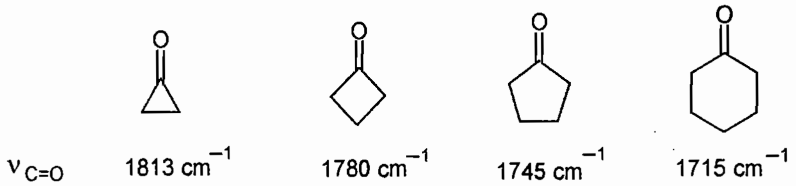


45) Ans (c):- ^{1}H NMR spectrum of [18]-annulene shows two peaks at δ 9.0 (12H; outer proton) and δ −3.0 (6H; inner proton).



46) Ans (d):- Resonant frequencies for EPR and NMR are microwave and radiofrequency respectively in the spectral region

47) Ans (b):- Hint:- As the ring strain increases the $\nu_{C=0}$ stretching frequency also increases

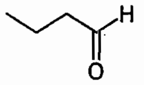
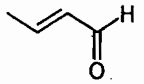
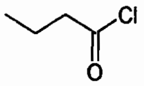
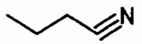


48) Ans (a):- 1,3 butadiene in its UV absorption spectrum recorded in *n*−hexane shows the absorption at λ_{max} 217 nm (ε_{max} = 21,000).

Alkenes	λ_{max} (nm)	ε_{max}
Ethylene	175	15000
1,3-butadiene	217	21000
1,3,5-hexatriene	258	35000

49) Ans (d):- The aldehyde hydrogen is shifted far downfield due to the anisotropy of the carbonyl group show a sharp singlet for one of its protons at δ ≥ 8 ppm that is at 9.0−10.0 ppm in ^{1}H NMR spectrum, which remain unaffected on shaking the solution thoroughly with D_2O.

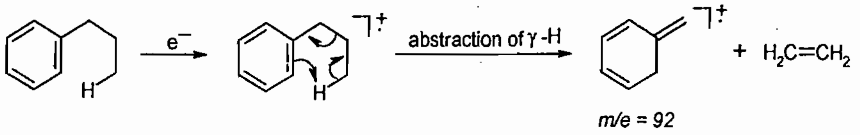
50) Ans (b):- The correct match is:-

	List- I	List- II
A)		1750
B)		1725
C)		1795
D)		2240

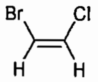
51) Ans (a):- The correct match is:-

Type of transition	Type of bond
$\sigma \rightarrow \sigma^*$	C−C
$n \rightarrow \sigma^*$	C−O
n, π^*	C=O
π, π^*	C=C

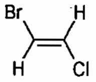
52) Ans (b):- Mass spectra of ortho, meta & para disubstituted aromatic rings are essentially identical as a result the position of substituent of polyalkyl substituted benzenes cannot be determined by mass spectrometry. So among the give option compound Q is identified uniquely by mass spectrometry. When alkyl group is attached to the benzene ring is propyl or larger group an important type of rearrangement called McLafferty rearrangement occurs.



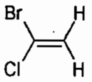
53) Ans (b):- The correct match of a coupling constant [^{1}H J (Hz)] is:-

(A)

cis

(ii) ~ 10 Hz

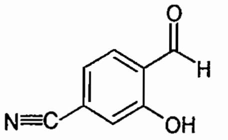
(B)

trans

(iii) ~ 15 Hz

(C)

geminal

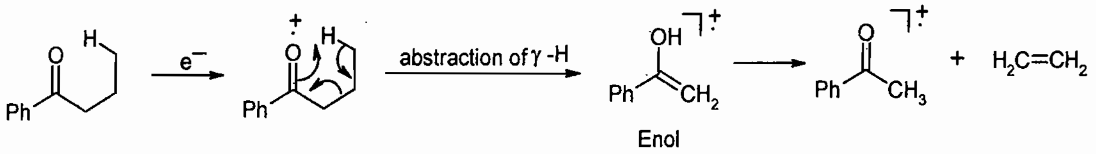
(i) ~1 Hz

54) Ans (a):- The IR stretching frequencies (cm^{-1}) for the compound X are:-


X

$$\bar{\nu}_{(OH)} = 3300-3500;\ \bar{\nu}_{(CH)} = 3000\ ;\ \bar{\nu}_{(CN)} = 2225;\ \bar{\nu}_{(CO)} = 1680$$

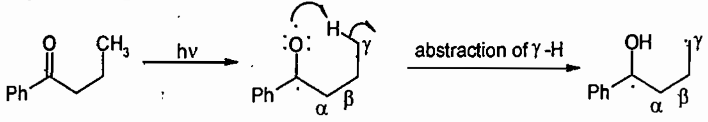
55) Ans (a):- The fragment formed by McLafferty like rearrangement in mass spectrometer of butyrophenone ($PhCOCH_2CH_2CH_3$).

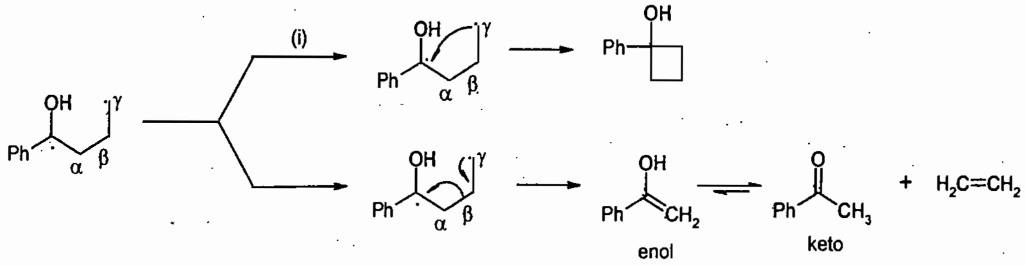


56) Ans (d):- In the Norrish Type II cleavage reaction, intramolecular abstraction of the γ hydrogen leads to two types of reaction

i) followed by cyclization of diradical to give a cyclobutanol.

ii) followed by cleavage of the resulting diradical to give an enol that tautomerizes to the ketone.

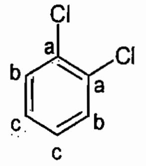




57) Ans (c):- The ^{1}H NMR spectrum of HD consists of a 1:1:1 triplet (Refer the solution of question no. 9)

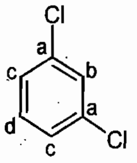
58) Ans (a):- The broad-band decoupled ^{13}C NMR spectrum of *ortho-*, *meta-* and *para*-dichlorobenzenes, gives 3, 4 and 2 number of signals respectively

^{13}C NMR



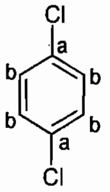
o-dichlorobenzene

3 signals



m-dichlorobenzene

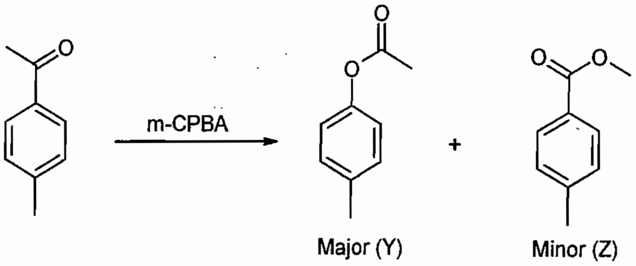
4 signals



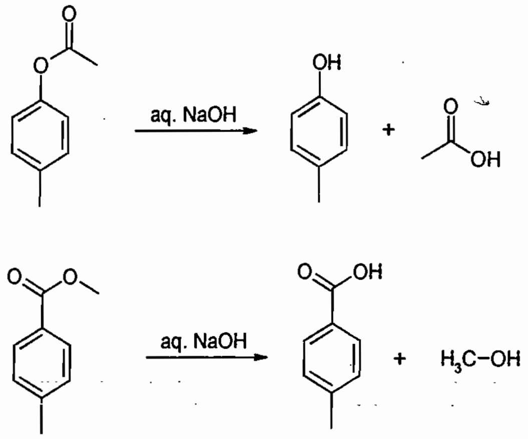
p-dichlorobenzene

2 signals

59) Ans (b):- An organic compound X ($C_9H_{10}O$) with IR: 1680 cm^{-1} that is conjugation of carbonyl group with phenyl & ^{1}H NMR with δ 7.8 (2 H, d, *J* 7.5 Hz),7.2 (2 H, d, *J* 7.5 Hz), 2.7 (3 H, s) and 2.4 (3 H, s) match with 4-methylacetophenone(X) which on treatment with m-chloroperbenzoic acid (that is Baeyer–Villiger oxidation) produced two isomeric compounds Y (major) and Z(minor).

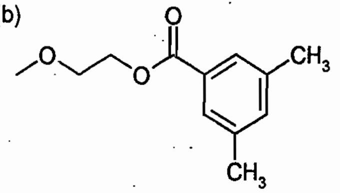


60) Ans (b):- Compounds Y and Z can be differentiated by carrying out basic hydrolysis, because Y produces 4-methylphenol and Z produces 4-methylbenzoic acid.



61) Ans (b):- The ^{1}H NMR signal at δ 2.35 (s, 6H) is not possible for compound (a) & (c) in given option. Now among (b) & (d) the IR value 1720cm^{-1} match with (b) option as shown below.

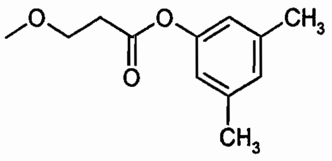
(b)



$\nu_{C=O}$ 1725 cm^{-1}

α, β or aryl conjugation

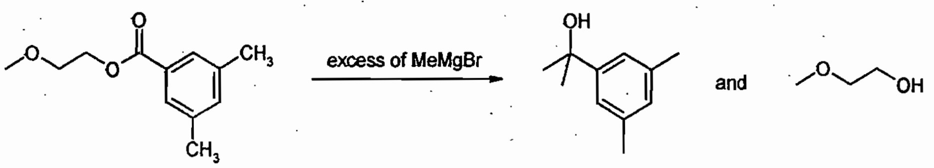
(d)



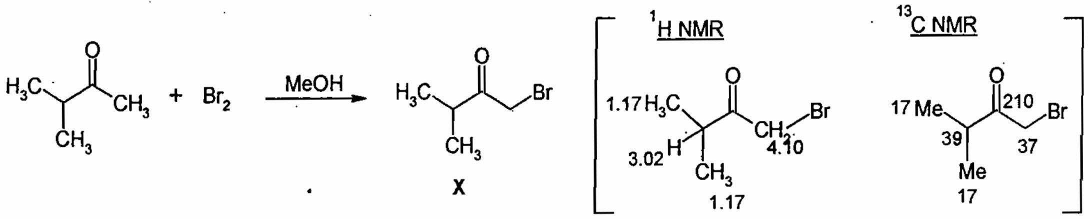
$\nu_{C=O}$ 1765 cm^{-1}

conjugation with oxygen

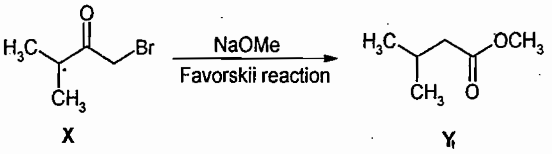
62) Ans (b):-



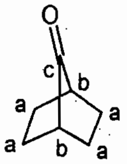
63) Ans (d):- The compound [X] with given spectral data is:



64) Ans (d):- The compound [Y] is:-



65) Ans (b):- The number of signals obtained in the proton decoupled ^{13}C NMR spectrum of 7-norbornanone are three

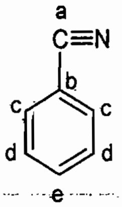


66) Ans (c):- A compound that contain one bromine atom will always have two ion peak namely molecular ion peak (M); M+2 with equal in intensity because of ^{81}Br isotope along with ^{79}Br that is $M^+ : (M+2)^+ = 1:1$

67) Ans (c):- Intensities of IR absorption is directly proportional to relative bond polarities & hence more intense band in the IR absorption is of O−H

68) Ans (b):- The number of signals that appear in the proton decoupled ^{13}C NMR spectrum of benzonitrile (C_7H_5N) are five

^{13}C NMR



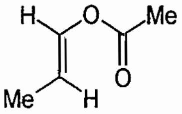
69) Ans (c):- A sharp band at around 3300 cm^{-1} in the IR spectrum is due to C−H stretching frequency in H−C≡C (C−H in terminal alkyne) which is present in 1-butyne.

70) Ans (a):- IR: At 1760 cm^{-1} is due to the conjugation of single bonded oxygen atom with C=C

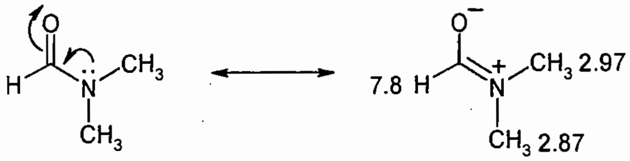
^{1}H NMR: Protons substituted trans on double bond couple most strongly with typical value for ^3J of about 16 Hz & methoxy proton are always appear in the range of δ 3.2−3.8ppm so given values indicate the absence of methoxy proton

^{13}C NMR: δ (ppm): 170 carbonyl carbon of ester (165−175)

An organic compound exhibited the above spectral data is:-



71) Ans (b):- At room temperature DMF has a partial double bond character due to the delocalization & therefore it gives singlet for each methyl group (one Me group is syn to oxygen & another is anti to oxygen) but at high temperature delocalization become so fast & sufficient energy available to overcome the rotational barrier and allow the two methyl groups to interchange & result in one broad signal for six protons 120 °C which become sharp singlet for six protons at δ 2.92 ppm 150 °C

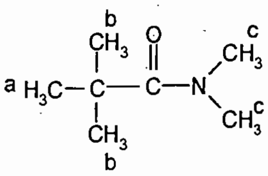


72) Ans (a):- Difference in the frequencies of the two methyl singlets is 30 Hz

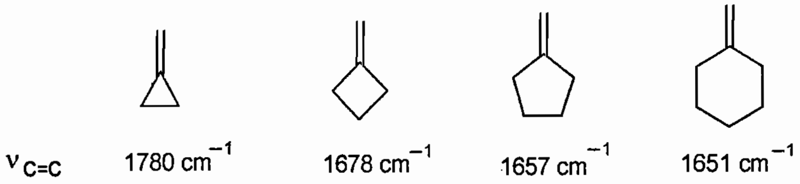
[Difference between the frequencies of the $(\delta_1 - \delta_2)] \times$ (Frequency of NMR machine)

$= (2.97 - 2.87)300 = 0.10 \times 300 = 30\text{Hz}$

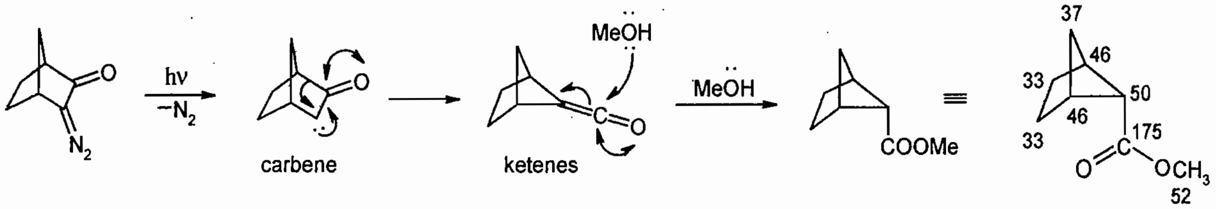
73) Ans (b):- At room temperature, the number of singlet resonances observed in the ^{1}H NMR spectrum of $Me_3CC(O)NMe_2$ (N,N-dimethyl pivalamide) is



74) Ans (c):- Hint:- As the ring strain increases the $\nu_{C=C}$ stretching frequency also increases

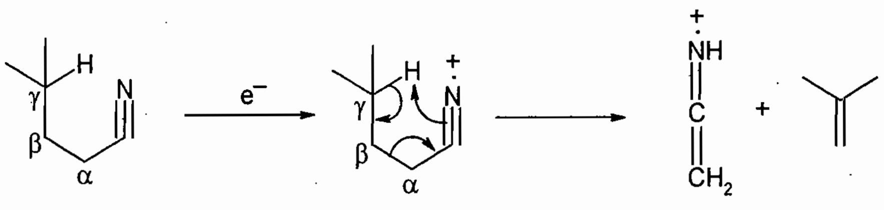


75) Ans (c):- It is an example of the Wolff rearrangement:- reaction of diazoketones to give carboxylic acid, or its derivative. In cyclic diazoketones, the rearrangement leads to ring contraction.



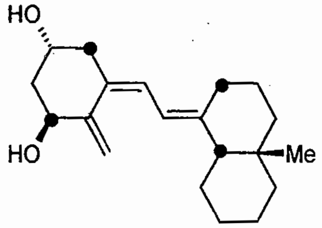
76) Ans (b):- The set of protons (underlined) in $CH_3\underline{CH_2}CH_2OCH_3$ would exhibit different splitting patterns in high (500 MHz)(the splitting patterns no longer overlap) and low (60 MHz)(signal overlap) field^{1}H NMR, due to spin-spin splitting.(spin-spin splitting gives the number of hydrogens on adjacent carbons).

77) Ans (c):- The *m/z* value of the detectable fragment formed by McLafferty like rearrangement in mass spectrometer is 41



m/e = 41

78) Ans (b):- The absorption wavelength (in nm) for given compound is 282 nm.



1,3-buadiene:	217 nm
one additional cojugation:	30
four alkyl substituent:	20
three exocyclic double bond:	15
	282 nm

List of Reference books

1) Organic spectroscopy by Donald L. Pavia, Gary M Lampman & George S. Kriz Spectroscopy.

2) Spectrometric identification of organic compounds, by R. M. Silverstein, F. X. Webster, 6th Ed. John Wiley and Sons.

3) Absorption spectroscopy of organic molecules, V. M. Parikh, Mehta Publishing House.

4) Organic Spectroscopy, by P. S. Kalsi, New age international publication

5) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford

❖❖❖

Topic 18

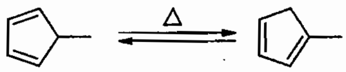
PERICYCLIC REACTIONS

Questions with two marks

1) Thermolysis of allyl phenyl ether generates ***[June 2011]***

(a) o-allyl phenol only
(b) o- and p-allyl phenols
(c) o-, m- and p-allyl phenols
(d) m-allyl phenol only

2) The reaction given below is an example of ***[June 2011]***

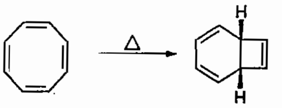


(a) 1, 3-sigmatropic hydrogen shift
(b) 1, 3-sigmatropic methyl shift
(c) 1, 5-sigmatropic hydrogen shift
(d) 1, 5-sigmatropic methyl shift.

3) The concerted photochemical reaction between two olefins leading to a cyclobutane ring is ***[June 2011]***

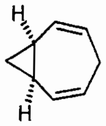
(a) ${}_{\pi}2_S + {}_{\pi}2_a$ cycloaddition
(b) ${}_{\pi}2_S + {}_{\pi}2_S$ cycloaddition
(c) ${}_{\sigma}2_S + {}_{\sigma}2_S$ cycloaddition
(d) ${}_{\pi}2_S + {}_{\sigma}2_a$ cycloaddition

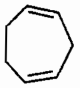
4) In the following concerted reaction, the product is formed by a ***[Dec 2011]***

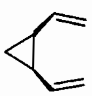


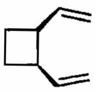
(a) 6π- disrotatory electrocyclisation
(b) 4π- disrotatory electrocyclisation
(c) 6π- conrotatory electrocyclisation
(d) 4π- conrotatory electrocyclisation

5) Among the following dienes, the one that undergoes a degenerate Cope rearrangement is ***[June 2013]***

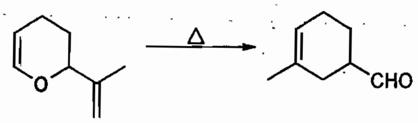
(a)


(b)


(c)


(d)


6) The following reaction proceeds through a ***[Dec 2013]***



(a) 1, 3-sigmatropic rearrangement
(b) 2, 3-sigmatropic rearrangement
(c) 3, 3-sigmatropic rearrangement
(d) 3, 5-sigmatropic rearrangement

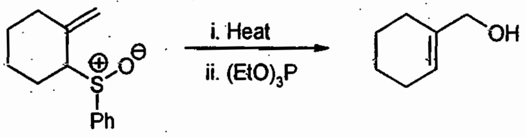
7) The number of nodes present in the highest occupied molecular orbital of 1, 3, 5-hexatriene in its ground state is ***[Dec 2013]***

(a) one
(b) two
(c) three
(d) four

8) In a Diels-Alder reaction, the most reactive diene amongst the following is ***[June 2014]***

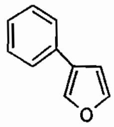
(a) (4*E*)-1,4-hexadiene
(b) (4*Z*)-1,4-hexadiene
(c) (2*E*,4*E*)-2,4-hexadiene
(d) (2*Z*,4*Z*)-2,4-hexadiene

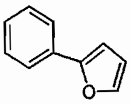
9) Pericyclic reaction involved in one of the steps of the following reaction sequence is *[June 2014]*

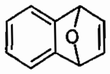


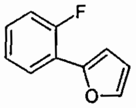
(a) [1,3] sigmatropic shift
(b) [3,3] sigmatropic shift
(c) [1,5] sigmatropic shift
(d) [2,3] sigmatropic shift

10) The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives *[Dec 2014]*

(a)


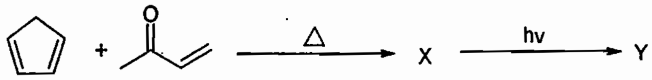
(b)


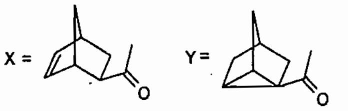
(c)


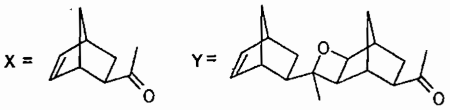
(d)


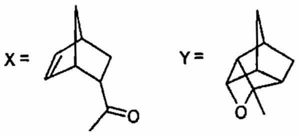
Questions with four marks

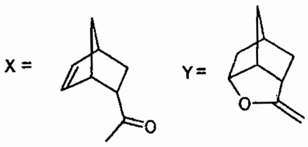
11) The structures of the major products X and Y in the following transformation are *[June 2011]*



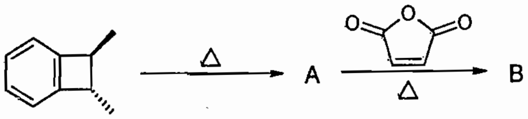
(a)


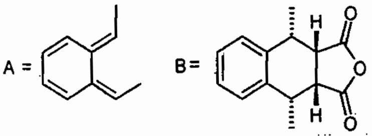
(b)


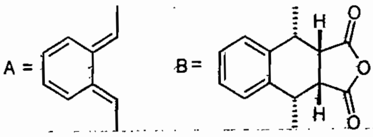
(c)


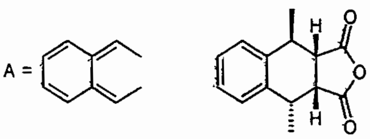
(d)


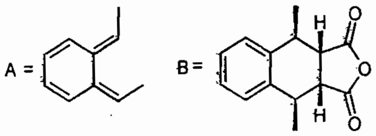
12) The major products A and B in the following reaction sequence are *[Dec 2011]*



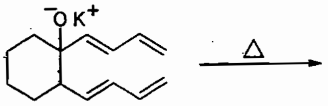
(a)


(b)


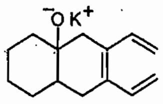
(c)


(d)


13) The product formed and the process involved in the following reaction is *[Dec 2011]*

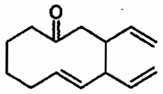


(a)



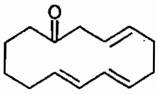
[3,3]- Sigmatropic rearramgement

(b)



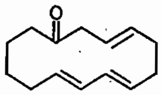
[1,3]- Sigmatropic rearramgement

(c)



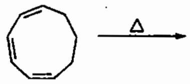
[5,5]- Sigmatropic rearramgement

(d)

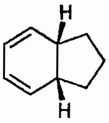


[1,5]- Sigmatropic rearramgement

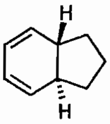
14) The major product formed in the following concerted reaction is ***[June 2012]***



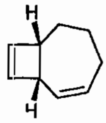
(a)



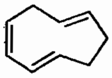
(b)



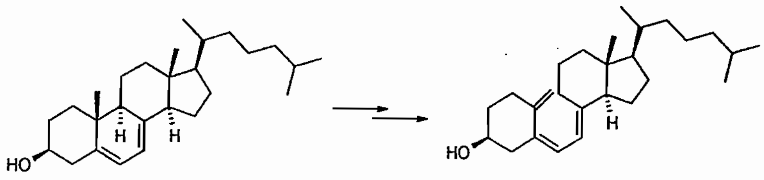
(c)



(d)



15) The two step conversion of 7-dehydrocholesterol to vitamin D_3 proceeds through ***[June 2012]***

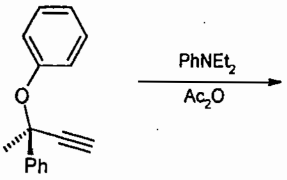


(a) Photochemical electrocyclic disrotatory ring opening; and thermal antarafacial [1, 7] -H shift.
(b) Photochemical electrocyclic conrotatory ring opening; and thermal antarafacial [1, 7] -H shift.
(c) Thermal electrocyclic conrotatory ring opening; and photochemical superafacial [1, 7] -H shift.
(d) Thermal electrocyclic disrotatory ring opening; and thermal suprafacial [1, 7] -H shift.

16) The major product formed when (3R, 4S)-3, 4-dimethylhexa-1, 5-diene is heated at 240° is ***[June 2012]***

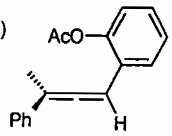
(a) (2Z, 6Z)-octa-2, 6-diene (b) (2E, 6E)-octa-2, 6-diene
(c) (2E, 6Z)-octa-2, 6-diene (d) (3Z, 5E)-octa-3, 5-diene

17) In the following pericyclic reaction, the structure of the allene formed and its configuration are ***[Dec 2012]***



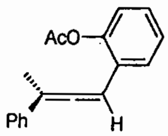
(Optically pure)

(a)



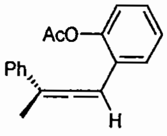
'R'

(b)



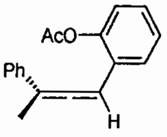
'S'

(c)



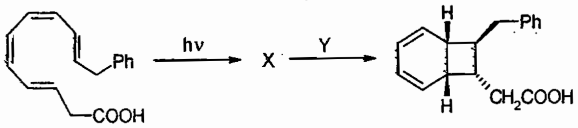
'R'

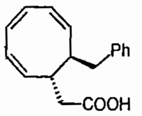
(c)

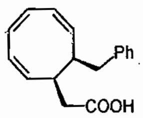


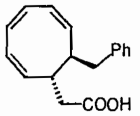
'S'

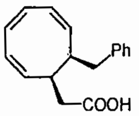
18) In the following sequence of pericyclic reactions X and Y are **[Dec 2012]**



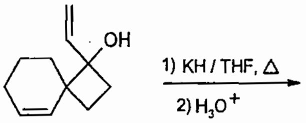
(a) X =  Y = hν / dis

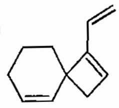
(b) X =  Y = hν / con

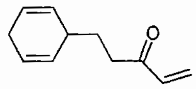
(c) X =  Y = Δ / dis

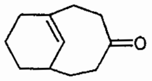
(d) X =  Y = Δ / con

19) The major product formed in the following reaction is **[Dec 2012]**



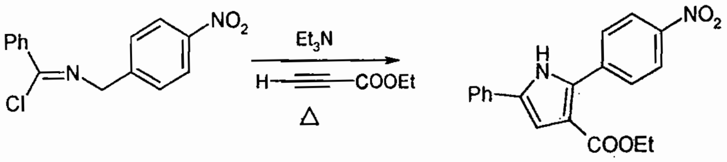
(a) 

(b) 

(c) 

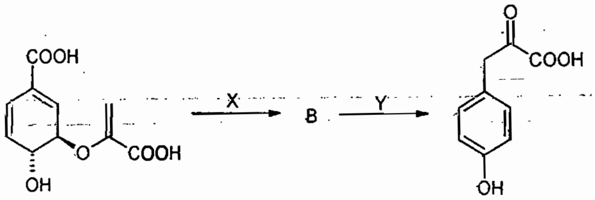
(d) 

20) The following conversion involves **[Dec 2012]**



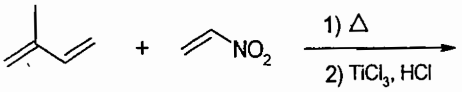
(a) a 1, 3-dipolar species as reactive intermediate, and a cycloaddition.
(b) a carbenium ion as reactive intermediate, and a cycloaddition.
(c) a 1, 3-dipolar species as reactive intermediate, and an aza Wittig reaction.
(d) a carbanion as reactive intermediate, and an aza Cope rearrangement.

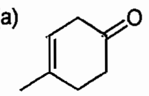
21) With respect to the following biogenetic conversion of chorismic acid (A) to 4-hydroxyphenylpyruvic acid (C), the correct statement is **[Dec 2012]**

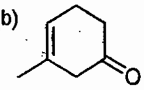


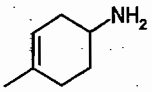
(a) X is Claisen rearrangement; Y is oxidative decarboxylation.
(b) X is Fries rearrangement; Y is oxidative decarboxylation.
(c) X is Fries rearrangement; Y is dehydration.
(d) X is Claisen rearrangement; Y is dehydration.

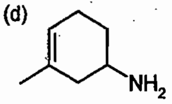
22) The major product formed in the following reaction is **[June 2013]**



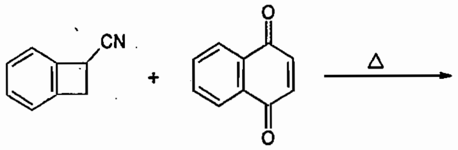
(a)


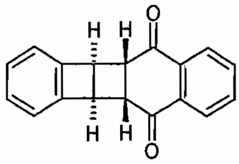
(b)


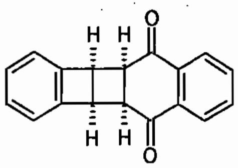
(c)


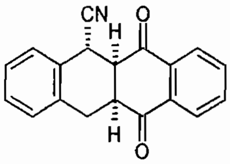
(d)


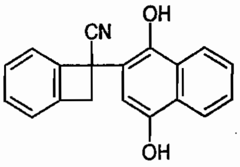
23) The major product formed in the following reaction is ***[June 2013]***



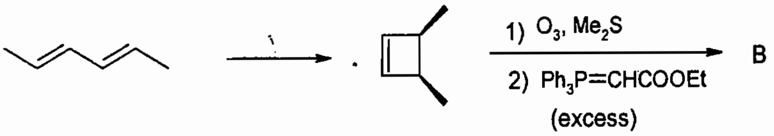
(a)


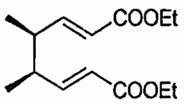
(b)


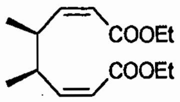
(c)


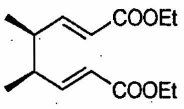
(d)


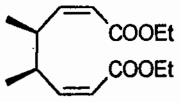
24) Predict the condition A and the structure of the major product B in the following sequence. ***[June 2013]***



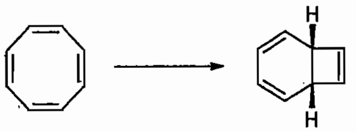
(a) A= hv B =


(b) A= hv B =


(c) A = Δ B =


(d) A = Δ B =


25) The most appropriate mode of cyclisation in the following transformation is ***[June 2013]***



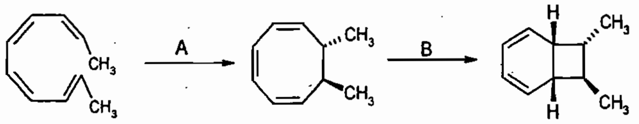
(a) con-rotatory in photochemical; and dis-rotatory in thermal conditions.

(b) con-rotatory in thermal; and dis-rotatory in photochemical conditions.

(c) con-rotatory in thermal; and con-rotatory in photochemical conditions.

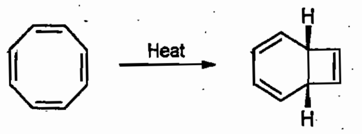
(d) dis-rotatory in photochemical; and dis-rotatory in thermal conditions.

26) The conditions A-B, required for the following pericyclic reactions are ***[Dec 2013]***



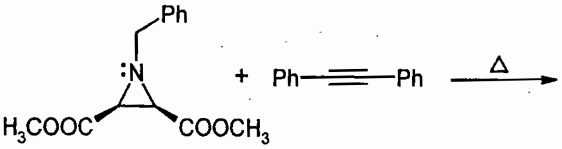
(a) A = Δ ; B= Δ (b) A = hv ; B= Δ (c) A = hv ; B = hv (d) A = Δ ; B = hv

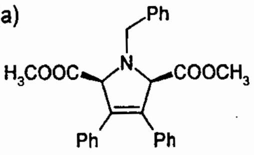
27) The number of π electrons participating and the pericyclic mode in the following reaction are ***[Dec 2013]***

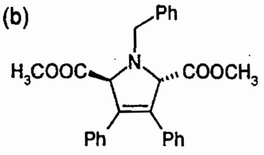


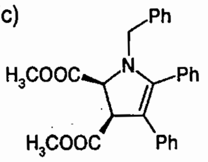
(a) 4 and conrotatory (b) 4 and disrotatory (c) 6 and conrotatory (d) 6 and disrotatory

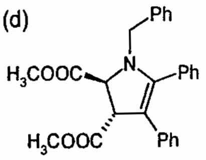
28) The major product formed in the following reaction is ***[June 2014]***



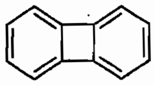
(a)


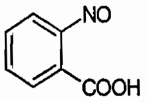
(b)


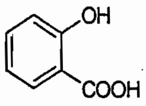
(c)


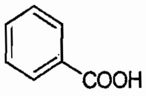
(d)


29) Anthranilic acid, on treatment with iso–amyl nitrite furnishes a product which displays a strong peak at 76 (m/e) in its mass spectrum. The structure of product is ***[June 2014]***

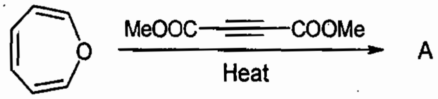
(a)


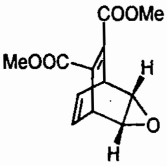
(b)


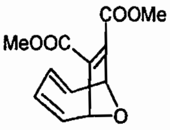
(c)


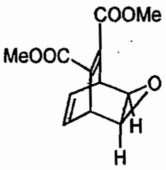
(d)


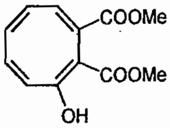
30) The major product A formed in the following reaction is ***[June 2014]***



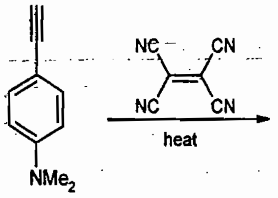
(a)


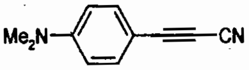
(b)


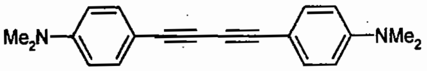
(c)


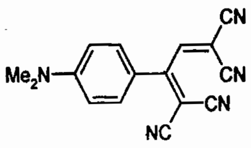
(d)


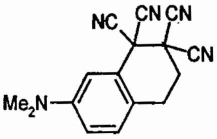
31) The major product of the following reaction is ***[Dec 2014]***



(a)


(b)


(c)


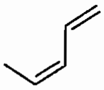
(d)


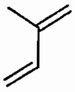
(Questions from GATE EXAM)

Questions with ONE OR TWO marks

32) Order of reactivity of the following dienes X,Y and Z in the Diels-Alder reaction is *(GATE 2005)*

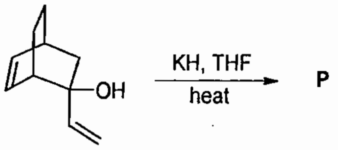

X

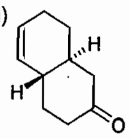

Y

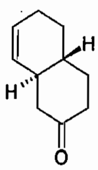

z

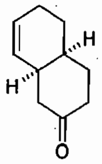
(a) X > Z > Y (b) Y > X > Z (c) Y > Z > X (d) X > Y > Z

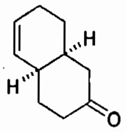
33) The major product P of the given reaction is *(GATE 2005)*



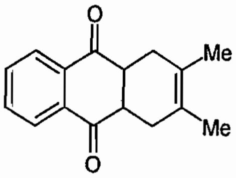
(a)


(b)


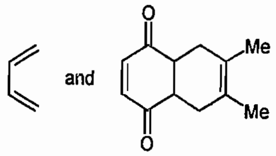
(c)


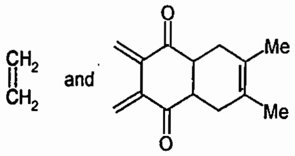
(d)


34) The most appropriate starting materials for one step synthesis of the compound (I) are *(GATE 2006)*



(I)

(a)


(b)


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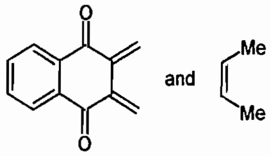
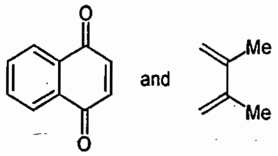
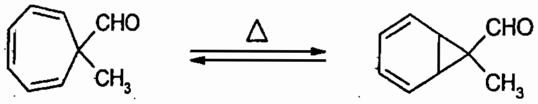


(d)


35) Select the correct classification in the following reaction from options I to IV gives below *(GATE 2006)*

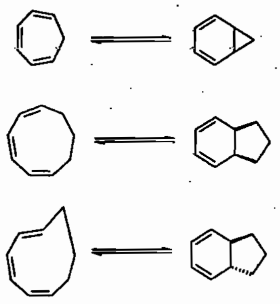


(I) Conrotatory electrocyclic reaction (II) Disrotatory electrocyclic reaction

(III) Valence isomerization (IV) $[_{\pi}4_s + _{\pi}2_a]$ Cycloaddition reaction

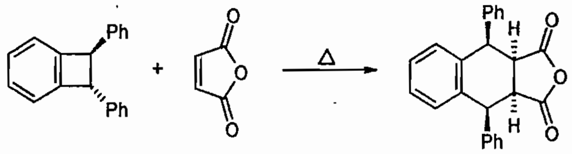
(a) I and III (b) II and IV (c) II and III (d) I and IV

36) The direction of rotation of the following thermal electrocyclic ring closures respectively are ***(GATE 2007)***



(a) disrotatory, disrotatory, disrotatory
(b) con rotatory, conrotatory, conrotatory
(c) disrotatory, disrotatory, con rotatory
(d) disrotatory, conrotatory, disrotatory

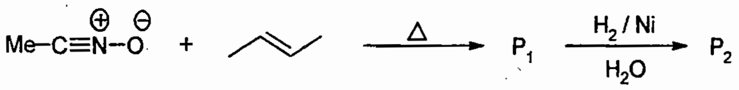
37) The reaction between X and Y to give Z proceeds ***via*** ***(GATE 2008)***



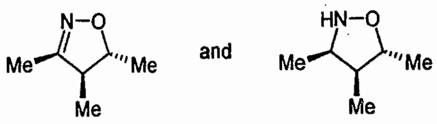
X Y z

(a) 4π-conrotatory opening of x followed by *endo* Diels-Alder cycloaddition
(b) 4π-disrotatory opening of x followed by *endo* Diels-Alder cycloaddition
(c) 4π-conrotatory opening of x followed by *exo* Diels-Alder cycloaddition
(d) 4π-disrotatory opening of x followed by *exo* Diels-Alder cycloaddilion

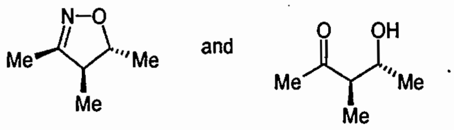
38) The major products P_1 and P_2 respectively, in the following reaction sequence are ***(GATE 2008)***



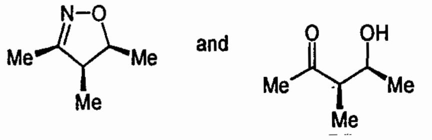
(a)



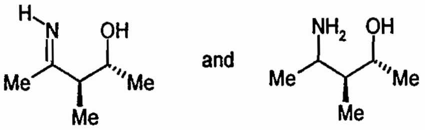
(b)



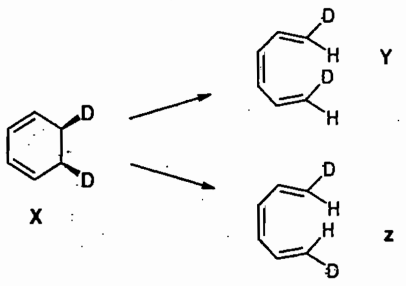
(c)



(d)

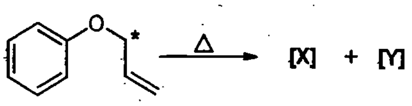


39) The products Y and Z are formed, respectively, from X ***via*** ***(GATE 2008)***

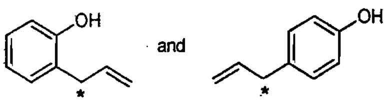


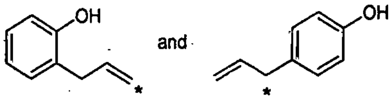
(a) hν conrotatory opening and Δ disrotatory opening
(b) hν disrotatory opening and Δ conrotatory opening
(c) Δ conrotatory opening and hν disrotatory opening
(d) Δ disrotatory opening and hν conrotatory opening

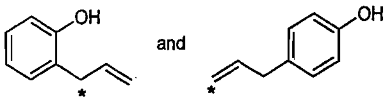
40) In the reaction the major products X and Y are **[*GATE 2009*]**

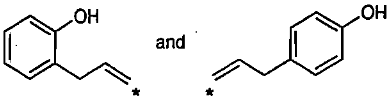


$*$ = ^{13}C labelled carbon atom

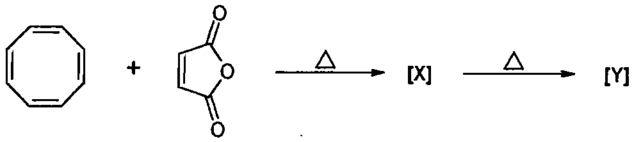
(a)


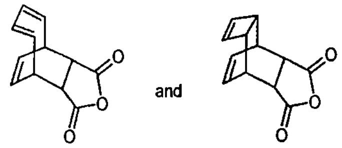
(b)


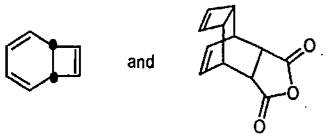
(c)


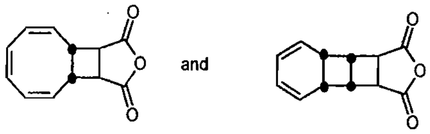
(d)


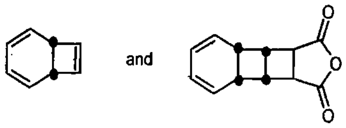
41) In the reaction sequence X and Y respectively, are **[*GATE 2009*]**



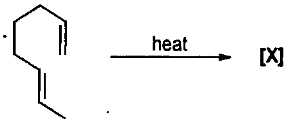
(a)


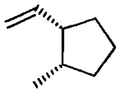
(b)


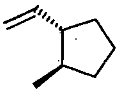
(c)


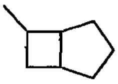
(d)


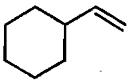
42) In the following reaction the major product [X] is **[*GATE 2010*]**



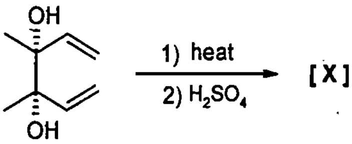
(a)


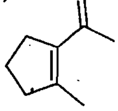
(b)


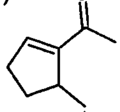
(c)


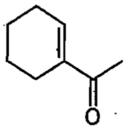
(d)


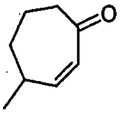
43) In the following reaction the major products [X] is **[*GATE 2010*]**



(a)


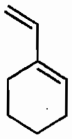
(b)


(c)


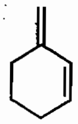
(d)


44) The diene which undergoes Diels-Alder reaction with maleic anhydride is ***(GATE 2011)***

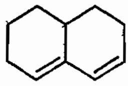
(a)



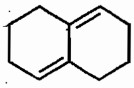
(b)



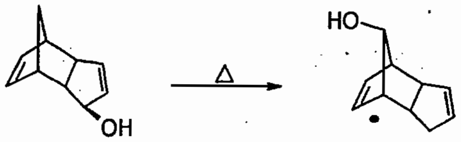
(c)



(d)

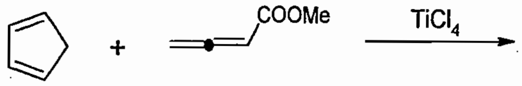


45) The pericyclic reaction given below is an example of ***[GATE 2013]***

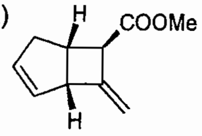


(a) [1,3]-sigmatropic shift (b) [1,5]-sigmatropic shift (c) [3,5]-sigmatropic shift (d) [3,3]-sigmatropic shift

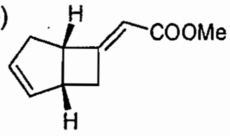
46) The major product formed in the following reaction is ***[GATE 2014]***



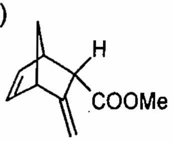
(a)



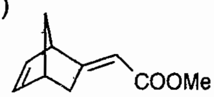
(b)



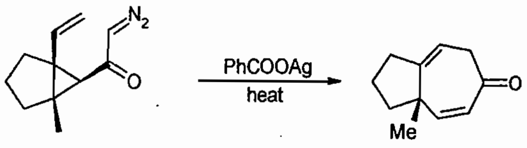
(c)



(d)

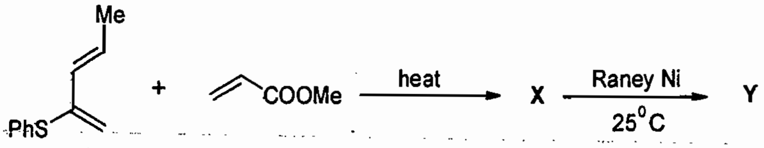


47) Formation of the ketone (II) from the diazoketone (I) involves ***[GATE 2014]***

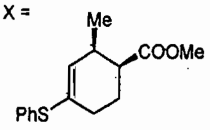


(a) generation of carbene and a [2,3]-sigmatropic rearrangement
(b) generation of carbene and an electrocyclic ring closing reaction
(c) generation of ketene and a [2+2] cycloaddition
(d) generation of ketene and a [3,3]-sigmatropic rearrangement

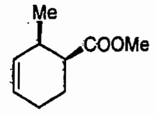
48) The major products X and Y formed in the following reaction sequence are ***[GATE 2014]***



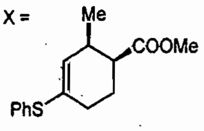
(a) X =



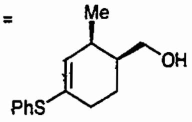
Y =



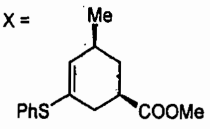
(b) X =



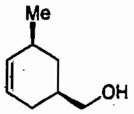
Y =



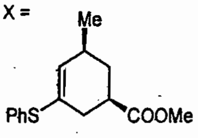
(c) X =



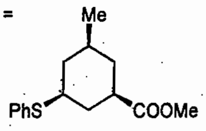
Y =



(d) X =



Y =



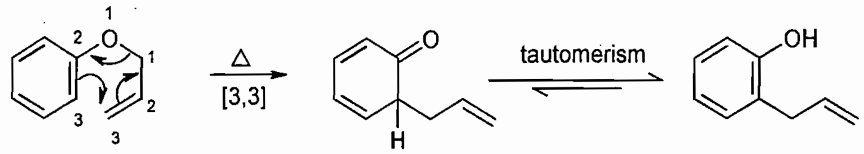
Answer Key

Topic 18 : Pericyclic reactions

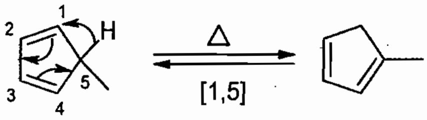
1	a	2	c	3	b	4	a	5	a	6	c	7	b	8	c	9	d	10	c
11	c	12	b	13	c	14	a	15	b	16	c	17	a	18	c	19	c	20	a
21	a	22	a	23	c	24	a	25	d	26	b	27	d	28	b	29	a	30	a
31	c	32	a	33	d	34	d	35	c	36	a	37	c	38	b	39	a	40	b
41	b	42	a	43	a	44	a	45	d	46	c	47	d	48	a				

Hint & solution

1) Ans (a):- Thermolysis of allyl phenyl ether (a Claisen rearrangement) generates o-allyl phenol only. Claisen rearrangement is a [3,3] sigmatropic rearrangement of an allyl vinyl ether or allyl phenyl ether.



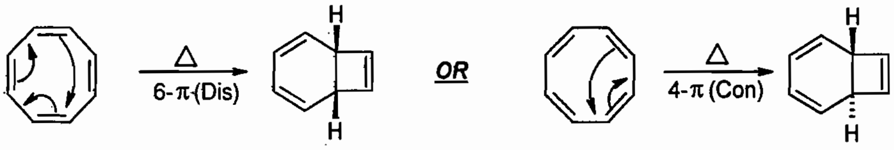
2) Ans (c):- It is an example of 1, 5-sigmatropic hydrogen shift



3) Ans (b):- The concerted photochemical reaction between two olefins leading to a cyclobutane ring is $_{\pi}2_S + _{\pi}2_S$ cycloaddition

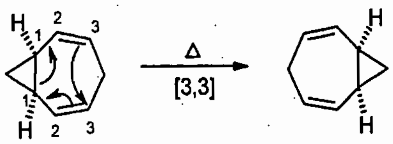
4) Ans (a):- Stereochemistry in case of thermally allowed electrocyclic ring closing if the reactants are in same plane:-

System	Thermally	stereochemistry
4n π	Con rotation	Trans product
4n + 2π	Dis rotation	cis product

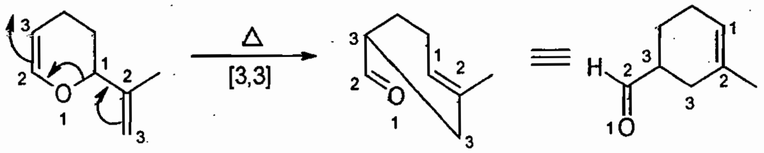


Thus the product is formed by a 6π- disrotatory electrocyclisation (giving the cis-junction)

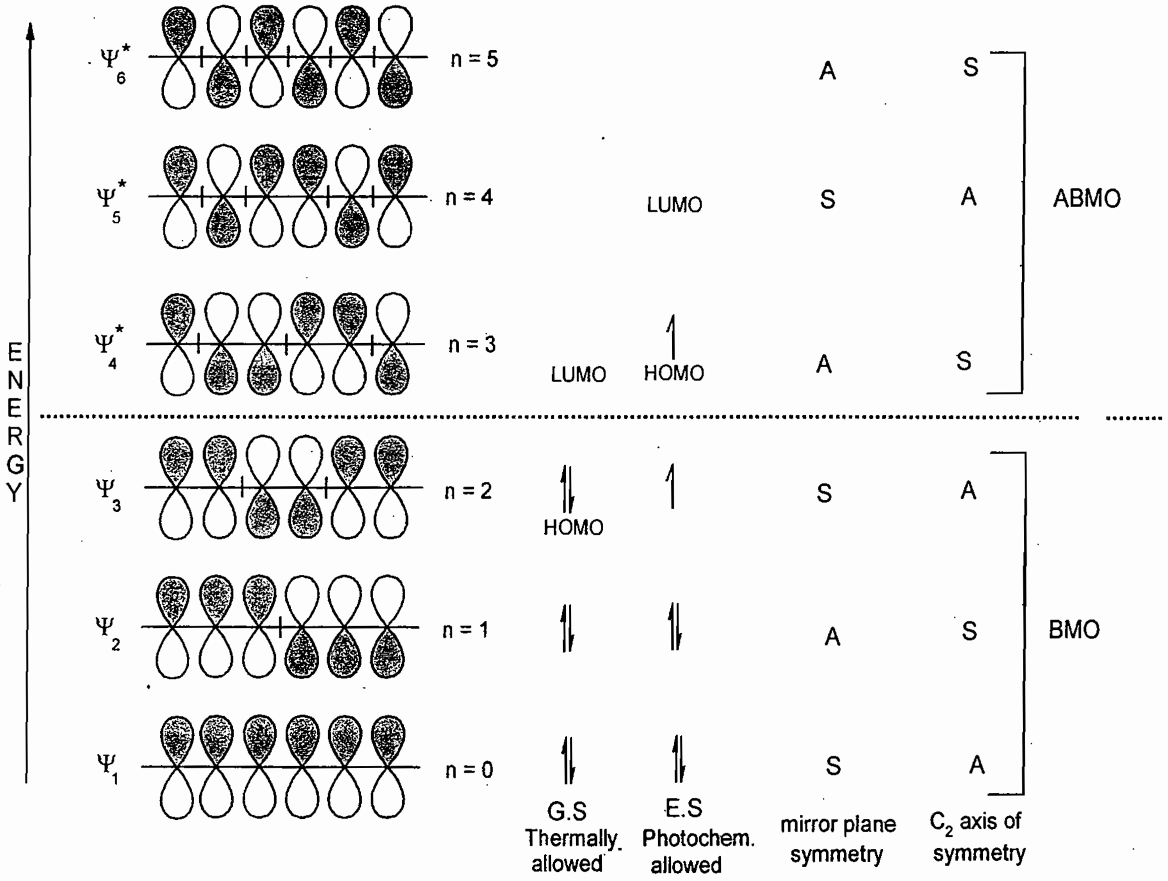
5) Ans (a):- Compound (a) will undergo a degenerate Cope rearrangement.



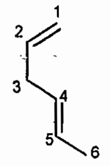
6) Ans (c):- The reaction proceeds through a 3,3-sigmatropic rearrangement as shown below.



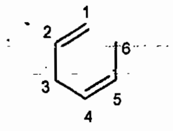
7) Ans(b):- The number of nodes present in the highest occupied molecular orbital of 1, 3, 5-hexatriene in its ground state (thermally allowed) is two.



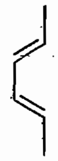
8) Ans (c):- Diels-Alder reaction is not possible in (4*E*)-1,4-hexadiene(a), (4*Z*)-1,4-hexadiene(b) as they are not conjugated diene. Among (c) and (d); (c) will react with faster rate. Cisoid conjugated diene are more reactive towards Diels-Alder reaction



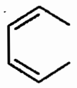
(4E)-1,4-hexadiene



(4Z)-1,4-hexadiene

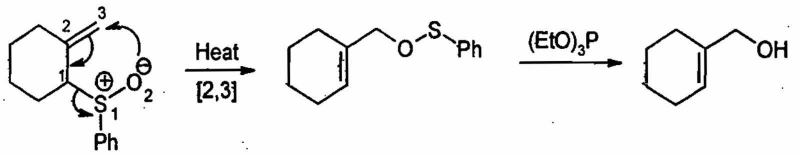


(2E,4E)-2,4-hexadiene

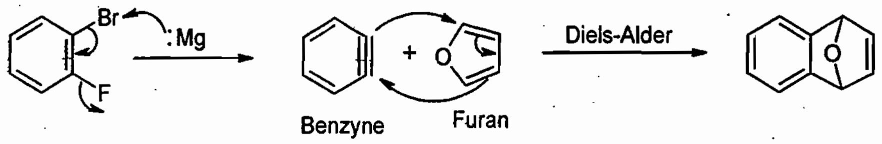


(2Z,4Z)-2,4-hexadiene

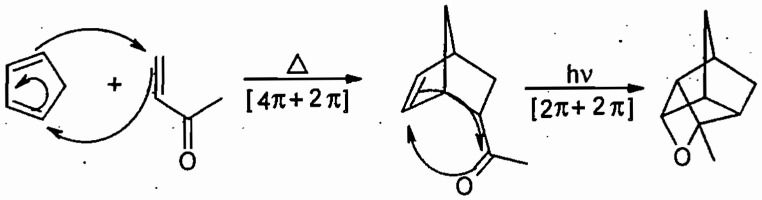
9) Ans (d):- It is a [2,3] sigmatropic shift



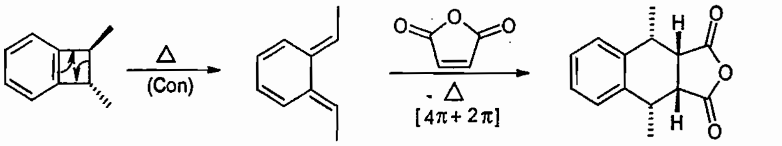
10) Ans (c):- It is a Diels-Alder reaction of furan & benzyne



11) Ans (c):-



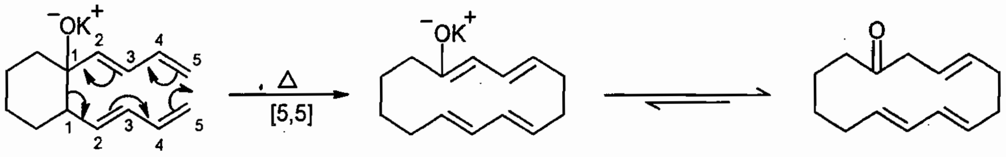
12) Ans (b):- First reaction is thermally allowed electrocyclic ring openining of trans-4n system to give diene with substituent in same plane. The resultant diene undergoes Diels Alder reaction with dienophile.



Substituent on diene are in same plane

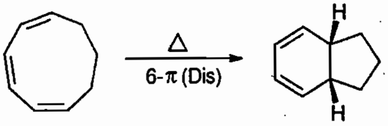
Cycloaddition with retension in configuration

13) Ans (c):- It is an example of oxy-Cope rearrangement & product is formed by [5,5] sigmatropic rearrangement

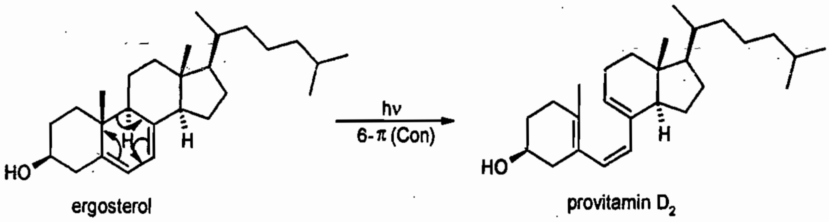


[5,5]- Sigmatropic rearramgement

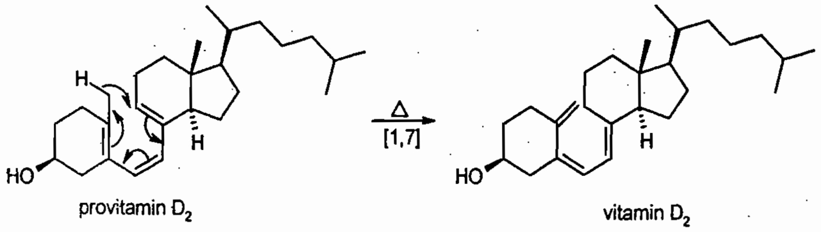
14) Ans (a):- Electrocyclic ring closure of 4n + 2π system under thermal conditions is disrotatory. Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product as substituent are in same plane



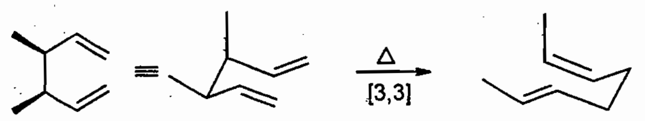
15) Ans (b):- Step I-Photochemical electrocyclic ring opening involving 4n + 2π electrons are occur via conrotatory rotation



Step II- happens spontaneously, without the need for light, so the [1,7] shift must be antarafacial.

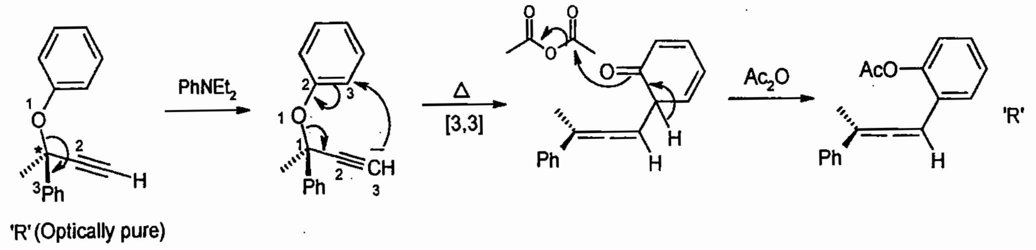


16) Ans (c):- (3R, 4S)-3, 4-dimethylhexa-1, 5-diene on heating undergoes [3,3] cope rearrangement to give (2E, 6Z)-octa-2, 6-diene

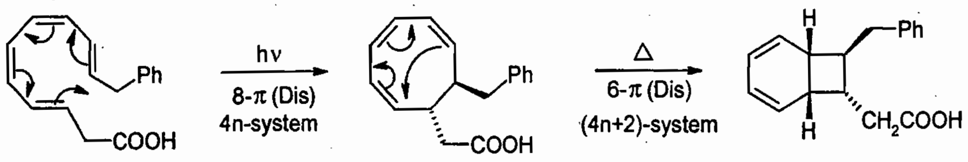


(3R, 4S)-3,4-dimethylhexa-1,5-diene (2E, 6Z)-octa-2,6-diene

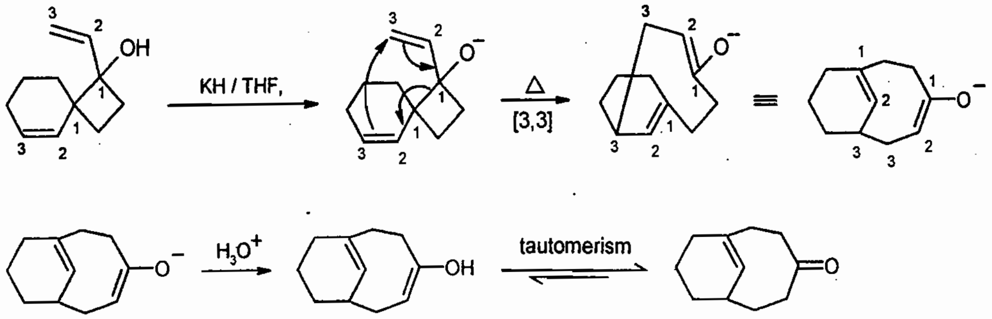
17) Ans (a):- Pericyclic reactions are all concerted reactions. This means that all the electron reorganization takes place in a single step with retention of configuration in product except when there is antarafacial migration



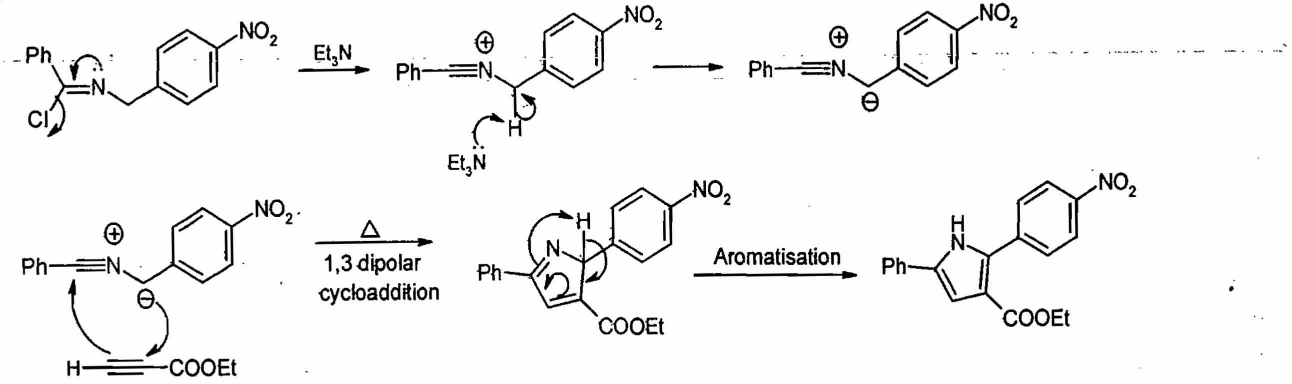
18) Ans (c):- Step I is disrotatory electrocyclic ring closure of 4n system under photochemical condition.(trans junction)
Step II is disrotatory electrocyclic ring closure of (4n + 2)π system under thermal conditions. (Cis junction)



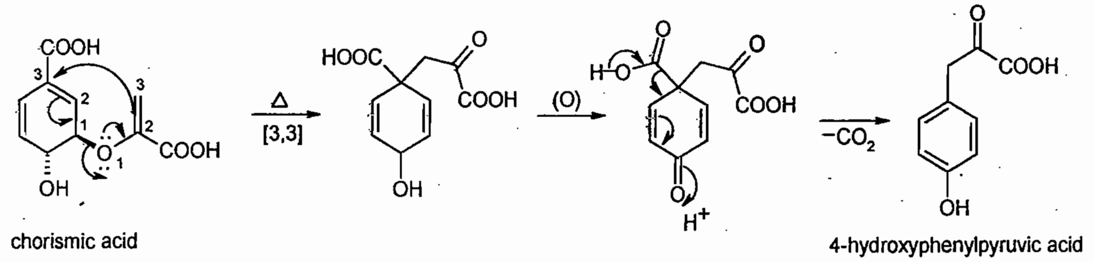
19) Ans (c):- It is an example of oxy-Cope rearrangement (thermally allowed 3,3-sigmatropic rearrangement)



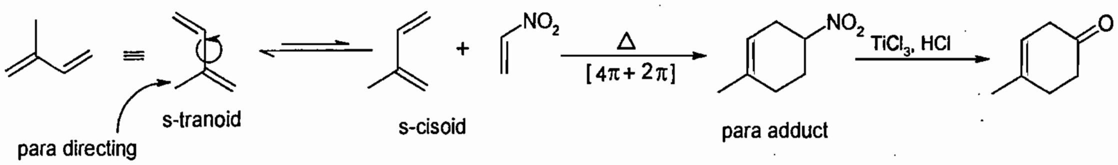
20) Ans (a):- Reaction involves a 1, 3-dipolar species as reactive intermediate, and a cycloaddition



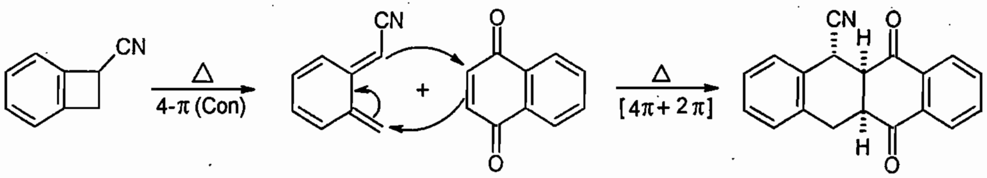
21) Ans (a):- Biogenetic conversion of chorismic acid to 4-hydroxyphenyl pyruvic acid take place via Claisen rearrangement; followed by oxidative decarboxylation.
Claisen rearrangement is a [3,3] sigmatropic rearrangement of an allyl vinyl ether or allyl phenyl ether.



22) Ans (a):- Regioselectivity in Diels-Alder reactions:- Diels-Alder reactions are highly ortho/para selective & it depends on a position of electron donating group on diene.$TiCl_3$ convert aliphatic nitro compounds into carbonyl compounds.

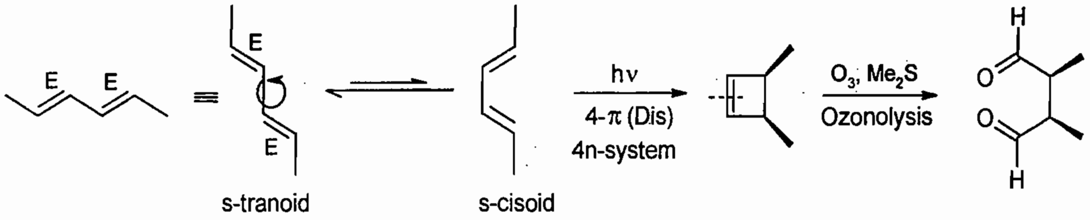


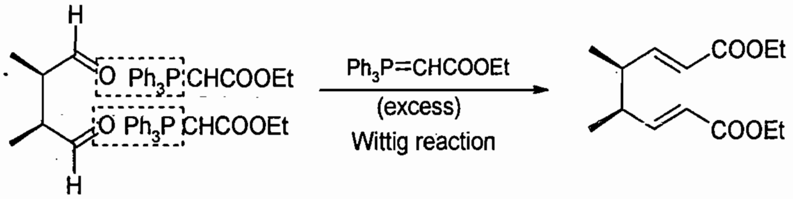
23) Ans (c):- Step I:- Electrocyclic ring opening of 4n system under thermal conditions is occur via conrotatory rotation. Step II is [4π +2π] cycloaddition.



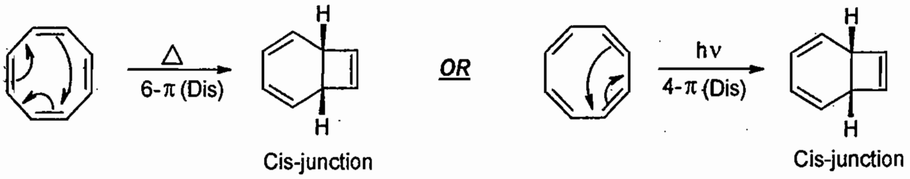
24) Ans (a):- Step I-Photochemical electrocyclic ring closure of 4n system is occur via disrotatory.(Note if same reaction under thermal condition will give trans product)

Step II- Ozonolysis reaction to give aldehyde. Aldehyde formed is react with stabilized phosphonium ylide to give trans alkene as a major product and a phosphine oxide (Wittig reaction)

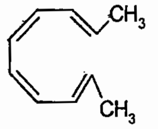




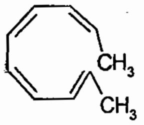
25) Ans (d):- Electrocyclic ring closure of 4n + 2π system under thermal conditions is disrotatory & electrocyclic ring closure of 4n system under photochemical conditions is also a disrotatory. Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product as substituent are in same plane.



26) Ans (b):- Substituents in electrocyclic reaction are either in same plane or in opposite plane as shown below.

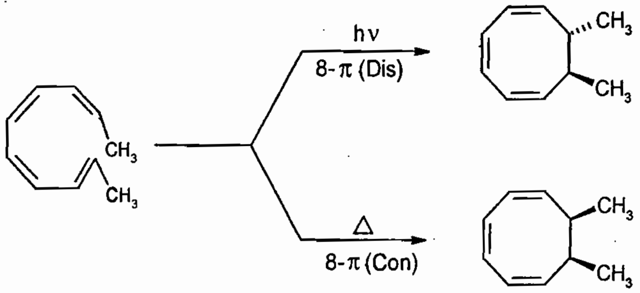


Substituents are in same plane

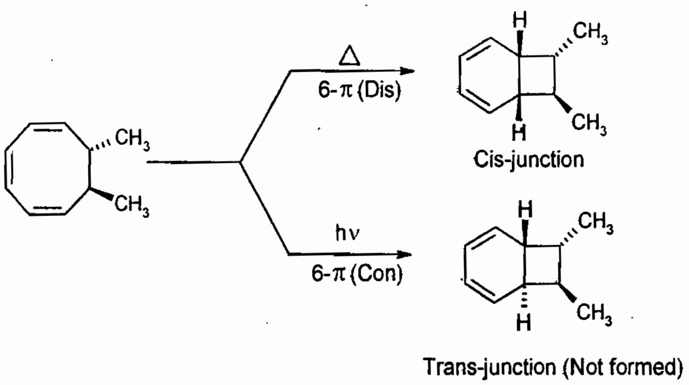


substituents are in opposite plane

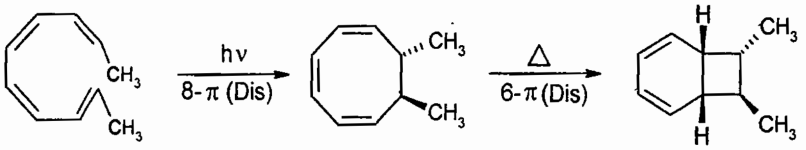
Thus first step is electrocyclic ring closure of 4nπ system under photochemical conditions is disrotatory if substituents are in opposite plane & the stereochemistry of product is trans. While same reaction under the thermal condition will give cis product & is occur conrotatory



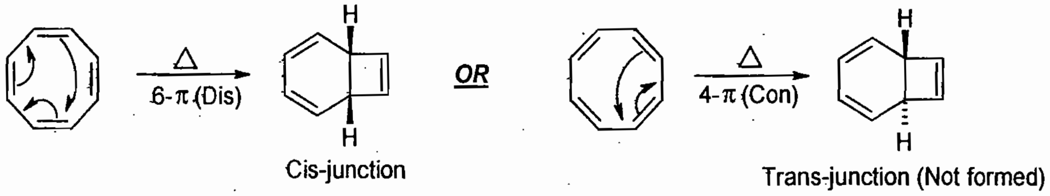
The second step Electrocyclic ring closure of 4n + 2π system under thermal conditions is disrotatory. Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product. Electrocyclic ring closure of 4n + 2π system Under photochemical conditions is conrotatory. Conrotatory ring closure of this reactant causes the hydrogens to be trans in the ring closed product.



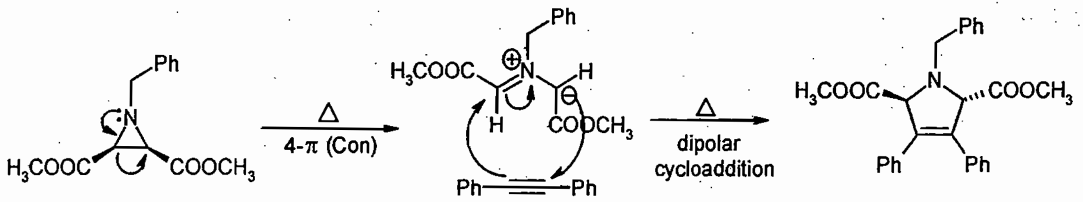
The overall reaction is :-



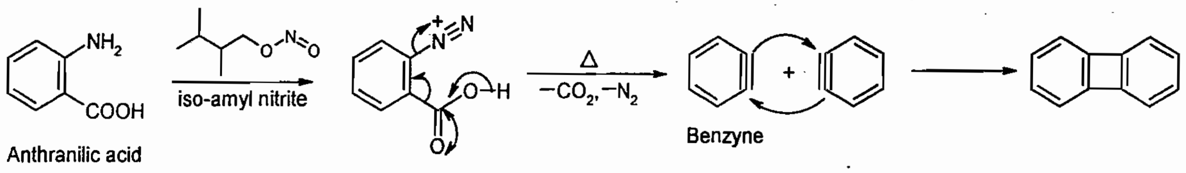
27) Ans (d):- Electrocyclic ring closure of 4n + 2π system under thermal conditions is disrotatory. Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product as substituent are in same plane. Thus the product is formed by a 6π- disrotatory electrocyclisation



28) Ans (b):- First step is three membered electrocyclic ring opening of a 4e$^-$ using the lone pair on nitrogen via conrotatory process under thermal condition to form 1,2 dipolar compound.
During electrocyclic ring opening one –COOEt group must rotate inwards and other outwards.
Second step is a cycloadditions of dipolar compound with dienophile.

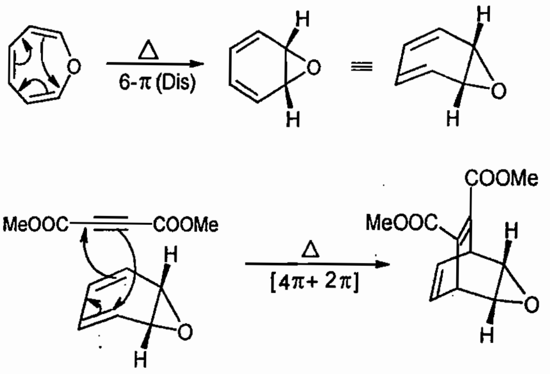


29) **Ans (a):-** In first step primary amine is converted into a diazonium salt by treatment with iso–amyl nitrite to give benzyne by decarboxylation & loss of N_2. Formation of benzyne gives, strong peak at 76, in mass spectrometer. In second step benzyne itself to give a benzyne dimer having a four membered ring between two benzene rings.



30) **Ans (a):-** First step is electrocyclic ring (intramolecular) closure of 4n + 2π system under thermal conditions is disrotatory to give benzene oxide. Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product (should not be confused with doing a cycloaddition reaction of 8 π system which is not possible under themal condition).

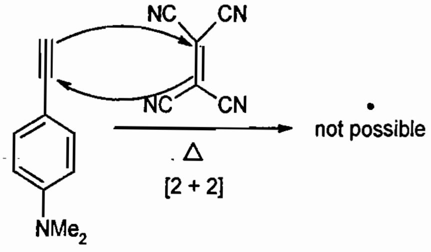
Second step is 4n + 2π cyloaddition of benzene oxide & acetylenedicarboxylate, under thermal conditions

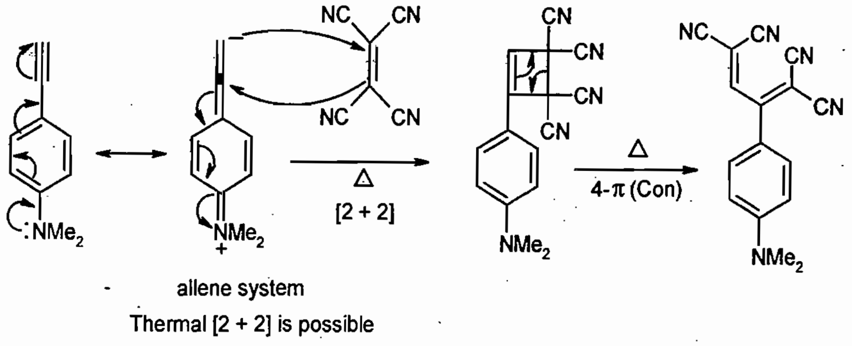


31) **Ans (c):-**Thermal [2 + 2] cycloadditions are not possible; but there are some thermal [2 + 2] cycloadditions giving four-membered rings but one of the system must have two double bonds to the *same* carbon atom.

The most important examples are ketenes, isocyanates and allenes. The structures have two π bonds at right angles.

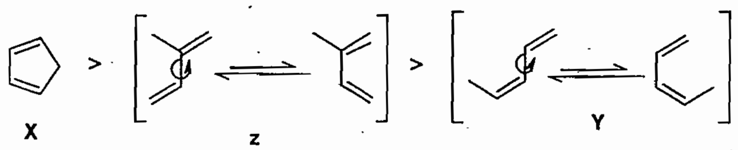
Second step is electrocyclic ring opening via conrotatory process under thermal condition



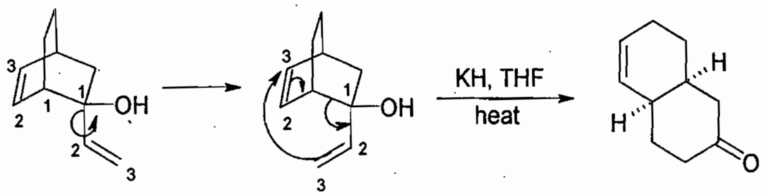


32) Ans (a):- Only dienes which can adopt the s-cis conformation undergo Diels-Alder reactions & the most reactive diene has the double bonds locked in an *s*-cis conformation therefore X is more reactive diene. Among Y & Z; Z is more reactive than Y due to steric crowding in Y

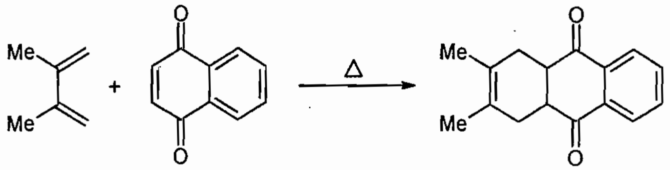
Reactivity of diene



33) Ans (d):- It is an example of oxy-Cope rearrangement (thermally allowed 3,3-sigmatropic rearrangement)

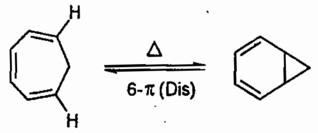


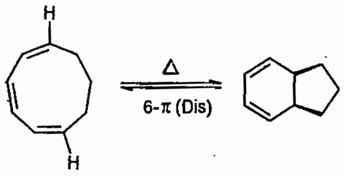
34) Ans (d):- Most successful Diels-Alder reactions involve electron rich (the donor) the diene and the electron poor (the acceptor) dienophile. Thus dienes with electron donating substituents & dienophiles with electron withdrawing substituents shows the increased reactivity. So the most appropriate starting materials are:-

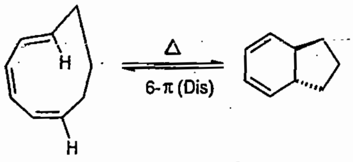


35) Ans (c):- The reaction is disrotatory electrocyclic valence isomerization reaction under thermal conditions

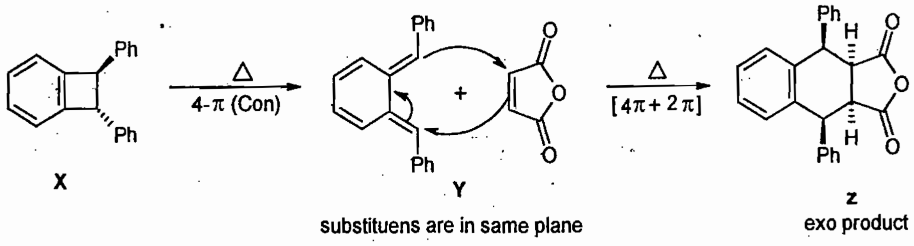
36) Ans (a):- Electrocyclic ring closure of 4n + 2π system under thermal conditions is disrotatory



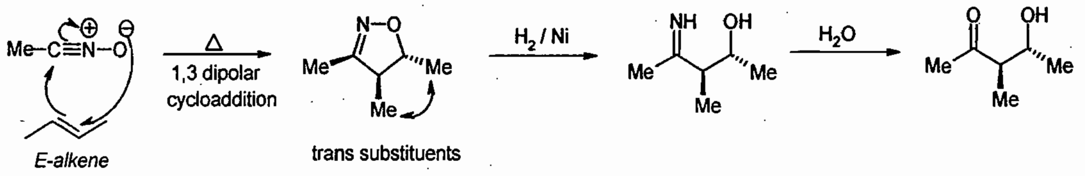




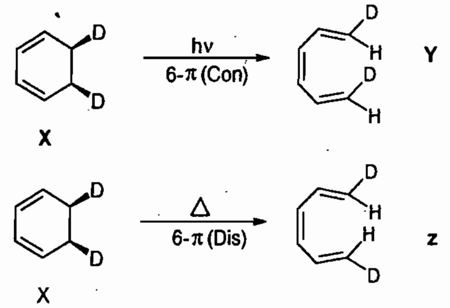
37) Ans (c):- 4π-conrotatory opening of x followed by *exo* Diels-Alder cycloaddition.



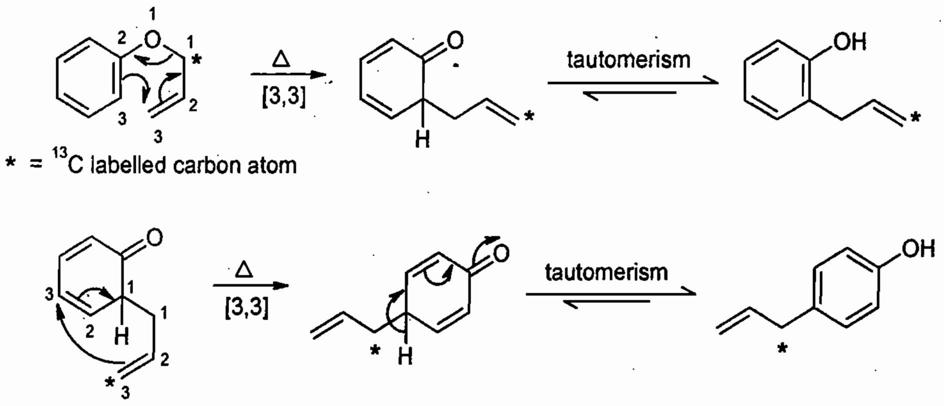
38) Ans (b):- First step is 1,3-dipolar cycloaddition of nitrile oxide and alkene to form five-membered ring. In second step H_2/Ni reduces weak N–O bond to give imine which on hydrolysis to give a ketone.



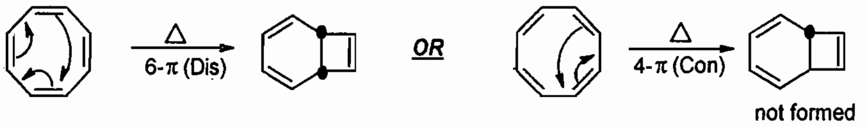
39) Ans (a):- The products Y and Z are formed, respectively, from X *via* ; hν conrotatory opening and Δ disrotatory opening



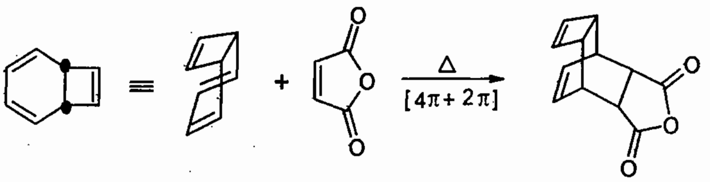
40) Ans (b):- Thermolysis of allyl phenyl ether (a Claisen rearrangement) generates allyl phenol. Claisen rearrangement is a [3,3] sigmatropic rearrangement of an allyl vinyl ether or allyl phenyl ether.



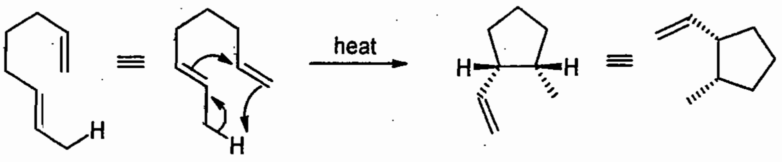
41) Ans (b):- First step is thermally allowed 6π- disrotatory electrocyclisation (intramolecular).Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring closed product.



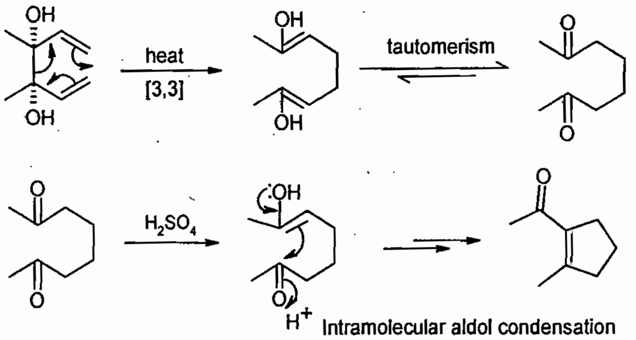
Second step is thermally allowed 4n + 2π cycloaddition reaction of diene with maleic anhydride.



42) Ans (a):- It is an example of intramolecular ene reaction to give a ring product with cis ring junction.

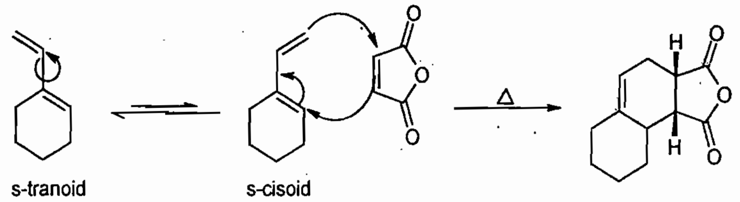


43) Ans (a):- It is an example of [3,3] sigmatropic rearrangement (oxy-Cope rearrangement) to form 2,7- octanedione. The next step is acid catalyzed intramolecular aldol condensation of 2,7-octanedione to form more stable five membered ring & not seven membered ring.

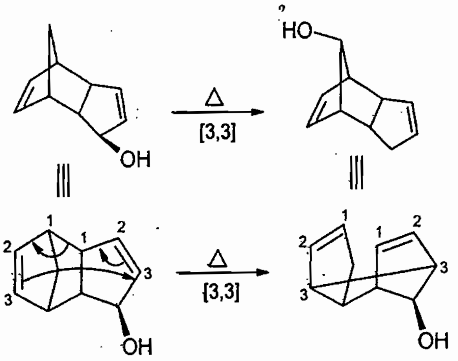


Intramolecular aldol condensation
(via more stable enol formation)

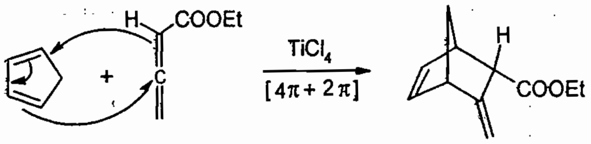
44) Ans (a):- Cycloaddition is only possible between a s-cisoid conjugated diene & dienophile or s-transoid which can isomerizes into the s-cisoid. Whereas cyclic s-transoid (b, c & d) is locked in an *s*-trans conformation & can't isomerizes into s-cisoid due to restriction in rotation of single bond in cyclic system.



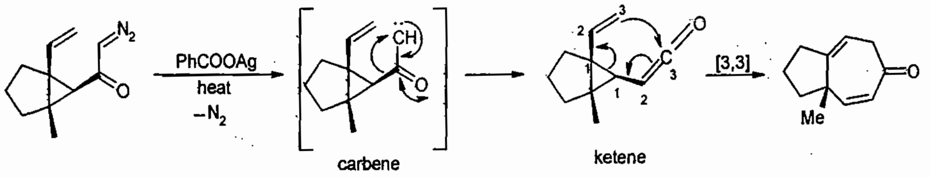
45) Ans (d):- [3,3]-sigmatropic shift



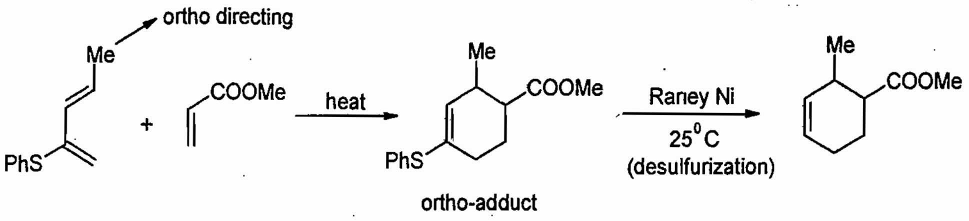
46) Ans (c):- It is Diels-Alder reaction of 4n + 2π system in the presence of the Lewis acid (here$TiCl_4$) which increases reactivity of dienophile by making it more electron deficient towards diene & reaction can be carried out at lower temperatures (below 25 °C). It also improves the regioselectivity of reaction. Now there are two possible products i.e. *exo* and *endo*. But endo product is preferred in irreversible Diels–Alder reactions as transition state during formation of endo product is extra stabilized by secondary interaction of orbitals.



47) Ans (d):- Wolff rearrangement is a useful reaction of diazocarbonyl compounds (not involving carbenes) to give ketene followed by cyclization by electrophilic attack on suitably situated carbon–carbon double bonds or aromatic rings. The Wolff rearrangement is normally effected by heat, photolysis or with a metal salt, often a silver(I) salt.



48) Ans (a):- Regioselectivity in Diels-Alder reactions:-Diels-Alder reactions are highly ortho/para selective & it depends on a position of electron donating group on diene. In the next step Raney Ni removes sulfur atom (desulfurization)



List of Reference books

1) Pericyclic reactions by Ian Fleming Oxford Science Publications

2) Conservation of orbital symmetry, R. B. Woodward and R. Hoffmann; Angewandte Chemie International Edition in English, 8, (11), 781–853,1969.

3) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford

4) Advanced Organic Chemistry: Part A & B- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication.

5) Modern Methods of Organic Synthesis by W. Carruthers and L. Coldham, Cambridge University Press.

6) March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure by Jerry March John Wiley & Sons

7) Principles of Organic Synthesis, by R.O.C, Norman and J. M. Coxon, CRC Press

8) Photochemistry and Pericyclic Reactions, by J. Singh, New Age International.

◆◆◆

Topic 19

PHOTOCHEMISTRY

Questions with two marks

1) The concerted photochemical reaction between two olefins leading to a cyclobutane ring is *[June 2011]*

(a) $_{\pi}2_S + _{\pi}2_a$ cycloaddition (b) $_{\pi}2_S + _{\pi}2_S$ cycloaddition

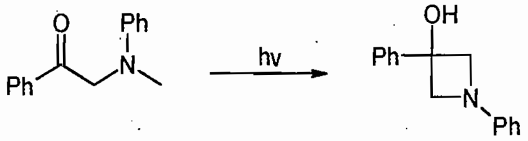
(c) $_{\sigma}2_S + _{\sigma}2_S$ cycloaddition (d) $_{\pi}2_S + _{\sigma}2_a$ cycloaddition

2) "Phosphorescence" is represented as *[June 2012]*

(a) $T_1 \longrightarrow S_0 + h\nu$ (b) $T_1 \longrightarrow S_0 + \Delta$

(c) $S_1 \longrightarrow S_0 + h\nu$ (d) $S_1 \longrightarrow T_1 + \Delta$

3) The following photochemical transformation proceeds through *[Dec 2012]*



(a) Norrish type I reaction (b) Norrish type II reaction

(c) Barton reaction (d) Paterno-Buchi reaction

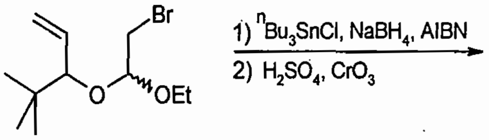
4) Appropriate reasons for the deviation form the Beer's law among the following are *[Dec 2012]*

(A) Monochromaticity of light **(C) Very high concentration of analyte**

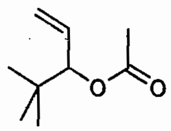
(B) Association of analyte **(D) Dissociation of analyte.**

(a) A, B and D (b) B, C and D (c) A, C and D (d) A, B and C

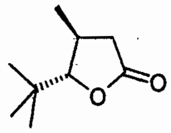
5) The major product formed in the following reaction sequence is *[June 2013]*



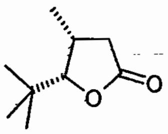
(a)



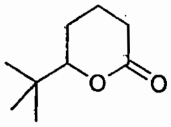
(b)



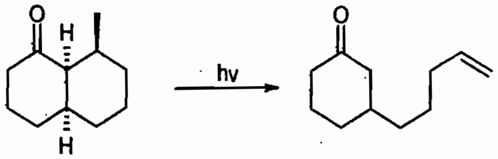
(c)



(d)



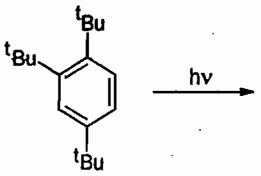
6) The following photochemical conversion proceeds through *[June 2013]*

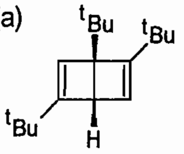


(a) Barton reaction (b) Paterno-Buchi reaction

(c) Norrish type I reaction (d) Norrish type II reaction

7) The major product formed in the following photochemical reaction is ***[June 2014]***



(a)


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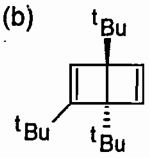

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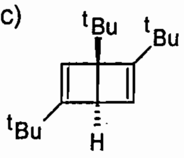

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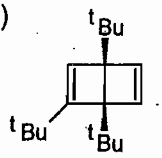
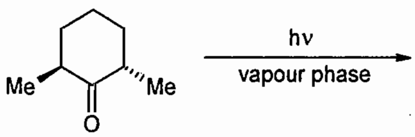


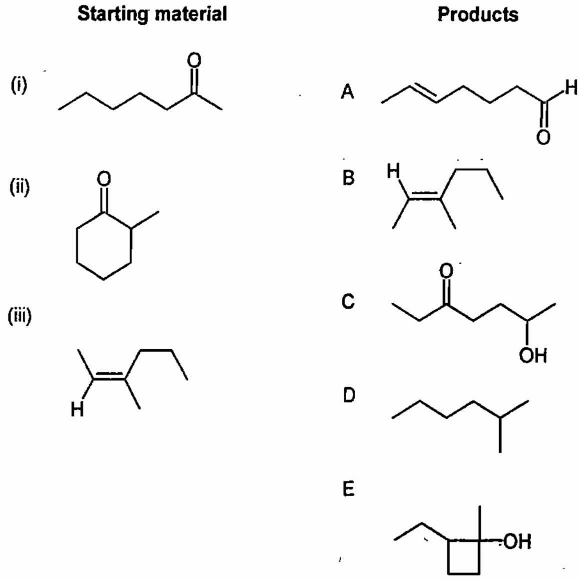
8) The cyclic product(s) of the following photochemical reaction is (are) ***[Dec 2014]***



(a) Only cis-1,2-dimethylcyclopentane
(b) Only trans-1,2-dimethylcyclopentane
(c) a mixture of cis and trans-1,2-dimethylcyclopentane
(d) Only 2,6-dimethylcyclohexanol

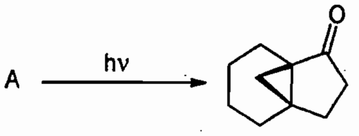
Questions with four marks

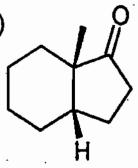
9) Match the following starting compounds with corresponding products in photochemical reactions ***[Dec 2011]***



(a) (i)–(E) (ii)–(A) (iii)–(B)
(b) (i)–(A) (ii)–(C) (iii)–(B)
(c) (i)–(D) (ii)–(C) (iii)–(A)
(d) (i)–(E) (ii)–(A) (iii)–(D)

10) Structure of the starting material A in the following photochemical Norrish reaction, is ***[June 2012]***



(a)


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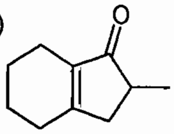

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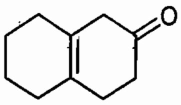
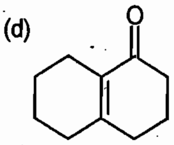
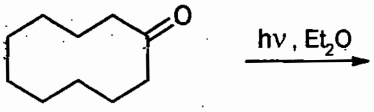
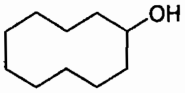


(d)


11) The major product formed in the following reaction is ***[June 2013]***



(a)


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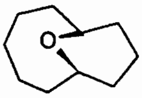

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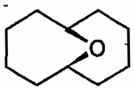

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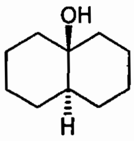
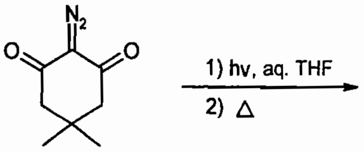


12) The major product formed in the following reaction is ***[June 2013]***



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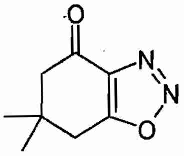

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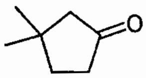
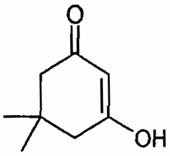
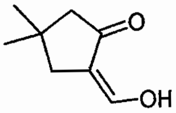
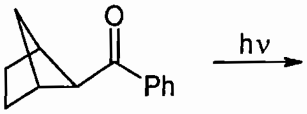
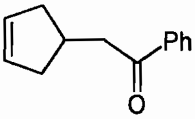


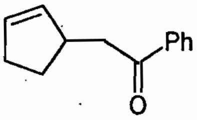
(c)


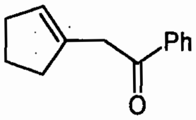
(d)


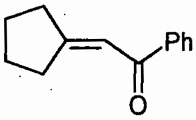
13) The major product formed in the following photochemical reaction is ***[Dec 2013]***



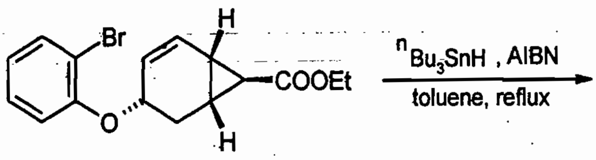
(a)


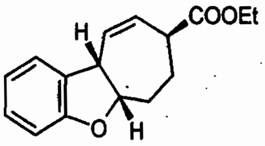
(b)


(c)


(d)


14) The major product formed in the following reaction sequence is ***[Dec 2013]***



(a)


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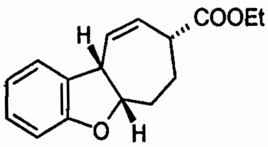

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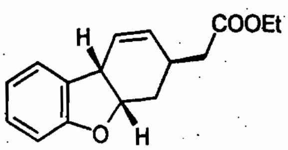
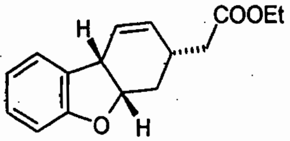
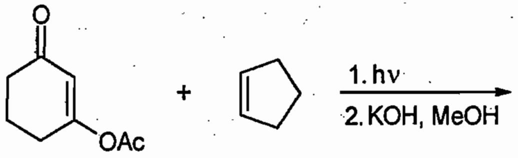
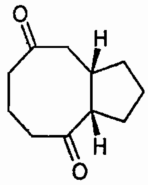
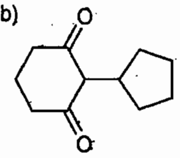


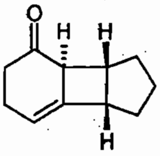
(d)


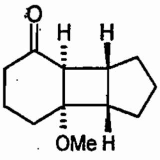
15) The major product formed in the following reaction sequence is ***[Dec 2013]***



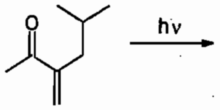
(a)


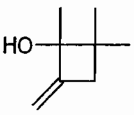
(b)


(c)


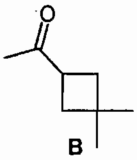
(d)


16) Amongst the following, the major products formed in the following photochemical reaction are ***[June 2014]***

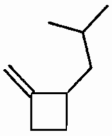




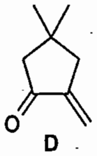
A



B



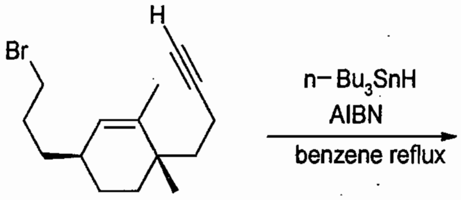
C

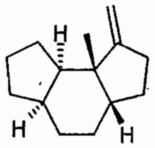


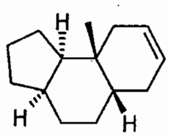
D

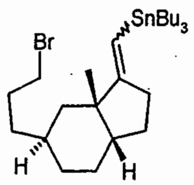
(a) A and C (b) B and C (c) A and D (d) A and B

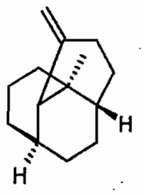
17) The major product formed in the following reaction ***[June 2014]***



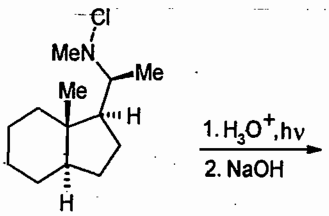
(a)


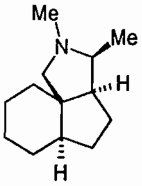
(b)


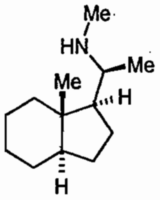
(c)


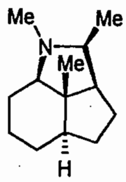
(d)


18) The major product of the following reaction is ***[Dec 2014]***



(a)


(b)


(c)


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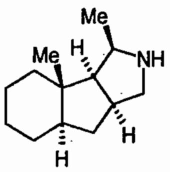
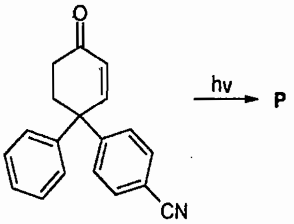
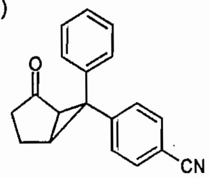


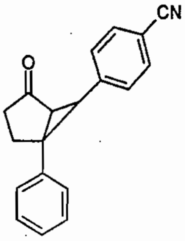
(Questions from GATE EXAM)

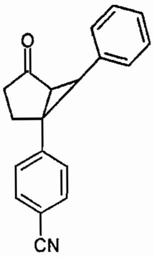
Questions with ONE OR TWO marks

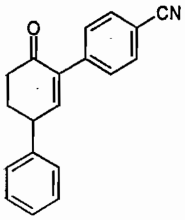
19) The major product P formed in the following photochemical reaction is ***(GATE 2005)***



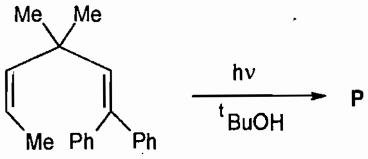
(a)


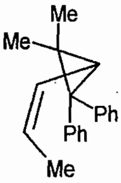
(b)


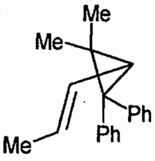
(c)


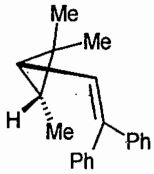
(d)


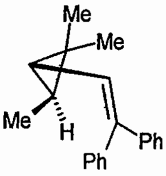
20) Identify the major product (P) in the following reaction ***(GATE 2006)***



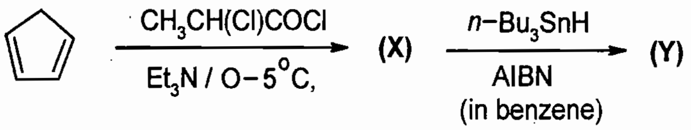
(a)


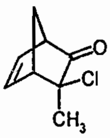
(b)


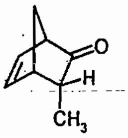
(c)


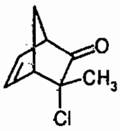
(d)


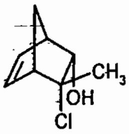
21) The major products X and Y formed in the following reaction sequence are ***(GATE 2006)***

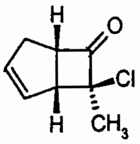


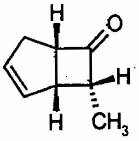
(a) X =


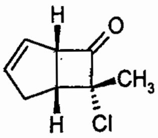
Y =


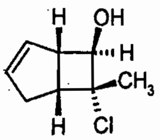
(b) X =


Y =


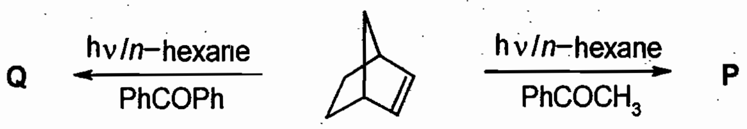
(c) X =


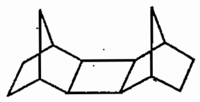
Y =


(d) X =


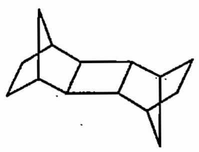
Y =


22) Identify the major product (P) and (Q) in the following reactions from the list of compounds I to IV
(GATE 2006)

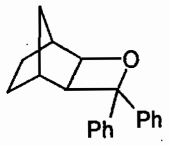




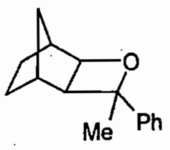
I



II



III



IV

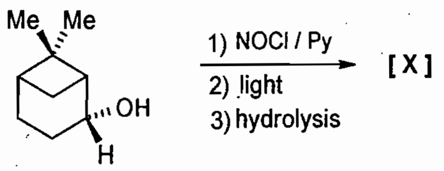
(a) P : I and Q : II

(b) P : II and Q : III

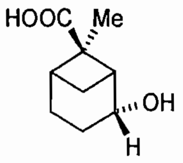
(c) P : IV and Q : II

(d) P : IV and Q : III

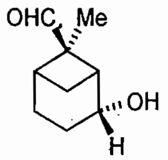
23) In the following reaction sequence the major product X **[*GATE 2010*]**



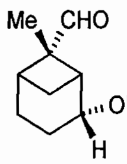
(a)



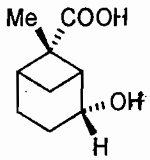
(b)



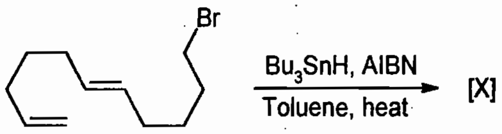
(c)



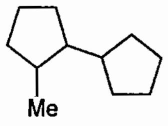
(d)



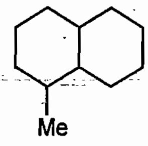
24) In the following reaction the major product [X] is ***(GATE 2011)***



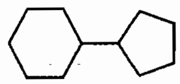
(a)



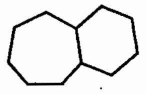
(b)



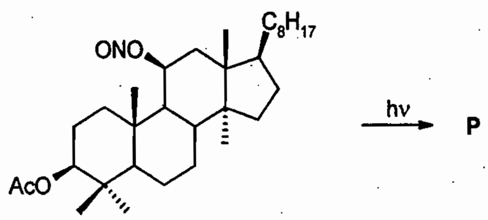
(c)



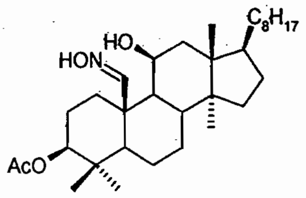
(d)



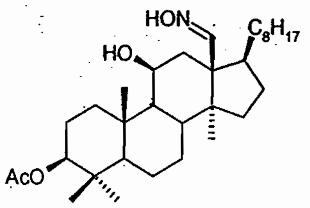
25) Identify the product from the following reaction ***[GATE 2012]***



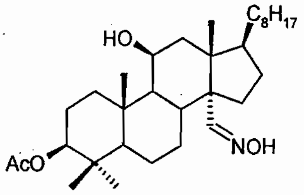
(a)



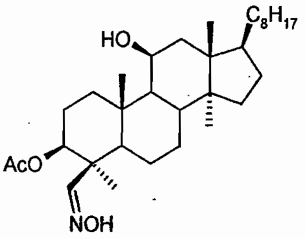
(b)



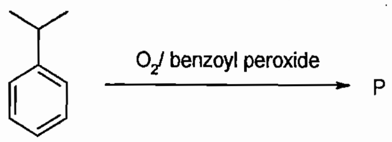
(c)



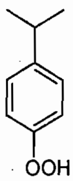
(d)



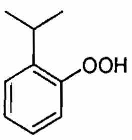
26) Identify the most probable product in the given reaction **[GATE 2012]**



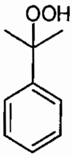
(a)



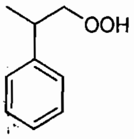
(b)



(c)



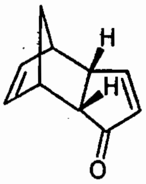
(d)



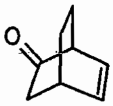
27) Match the compounds in the column I with the photochemical reactions that they can undergo given in the column II **[GATE 2013]**

Column I

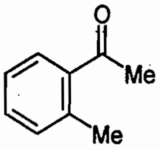
i)



ii)



iii)



Column II

(p) oxa-di-pi methane rearrangement

(q) Paterno Buchi reaction

(r) Intramolecular [2 + 2] cycloaddition

(s) photoenolisation

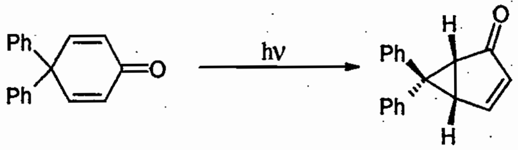
(a) (i)-(q); (ii)-(s); (iii)-(p)

(b) (i)-(r); (ii)-(p); (iii)-(s)

(c) (i)-(p); (ii)-(r); (iii)-(q)

(d) (i)-(r); (ii)-(q); (iii)-(s)

28) Formation of the product in the following photochemical reaction involves ***[GATE 2014]***



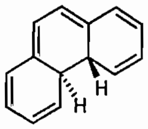
(a) di-π-methane rearrangement (b) Paterno-Buchi reaction

(c) [2,3]-sigmatropic rearrangement (d) Norrish type I reaction

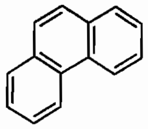
29) The major products X and Y formed in the following reaction sequence are ***[GATE 2014]***

$$Cis\text{−stilbene} \xrightarrow[C_6H_6]{h\nu} X \xrightarrow[\text{air}]{I_2} Y$$

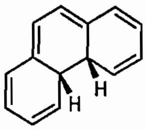
(a) X =



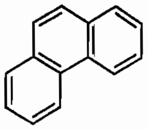
Y =



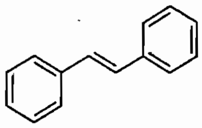
(b) X =



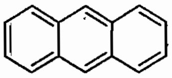
Y =



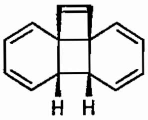
(c) X =



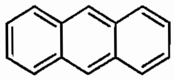
Y =



(d) X =



Y =



Answer Key

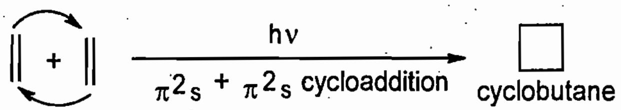
Topic 19:- Photochemistry

1	b	2	a	3	b	4	b	5	b	6	d	7	a	8	c	9	a	10	c
11	d	12	b	13	b	14	d	15	a	16	d	17	a	18	a	19	b	20	a
21	c	22	b	23	c	24	a	25	a	26	c	27	b	28	a	29	a		

Hint & solutions

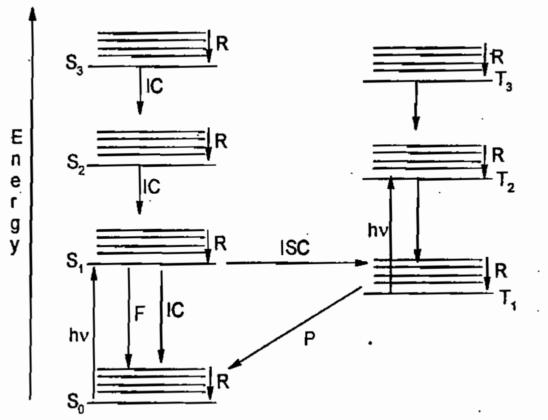
1) Ans (b):- First step is the concerted $_{\pi}2_S + _{\pi}2_S$ cycloaddition under photochemical condition between two olefins leading to a cyclobutane ring is. Selection rule:-

System	Thermally	Photochemically
4n	supra-antra or antra-supra	Supra-supra or antra-antra
4n+2	Supra-supra or antra-antra	supra-antra or antra-supra



2) Ans (a):- "Phosphorescence" is represented as $T_1 \rightarrow S_0 + h\nu$

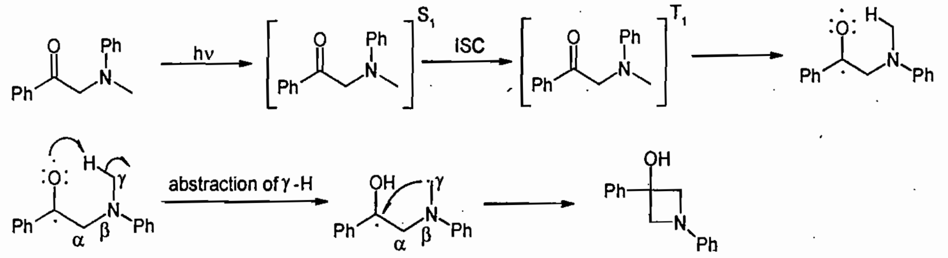
A Jablonski diagram



S = singlet state
F = fluorescence
IC = internal crossing
R = Relaxation
T = triplet state
ISC = intrnal system crossing
P = phosphorescence

Process	Transition
Light Absorption (Excitation)	$S_0 \rightarrow S_n$
Internal Conversion	$S_n \rightarrow S_1$
Vibrational Relaxation	$S_n^{*} \rightarrow S_n + \Delta$
Intersystem Crossing	$S_1 \rightarrow T_1 + \Delta$
Fluorescence	$S_1 \rightarrow S_0$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu$
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$

3) Ans (b):- It is a Norrish Type II cleavage reaction, involves intramolecular abstraction of the γ hydrogen followed by cyclization of diradical to give a cyclobutanol.



4) Ans (b):- According to Beer's Law; $A = \varepsilon bc$

Where A is absorbance

e is the molar absorbtivity with units of L mol^{-1} cm^{-1}

b is the path length of the sample - that is, the path length of the cuvette (in cm^{-1})

c is the concentration of the compound in solution, expressed in mol L^{-1}

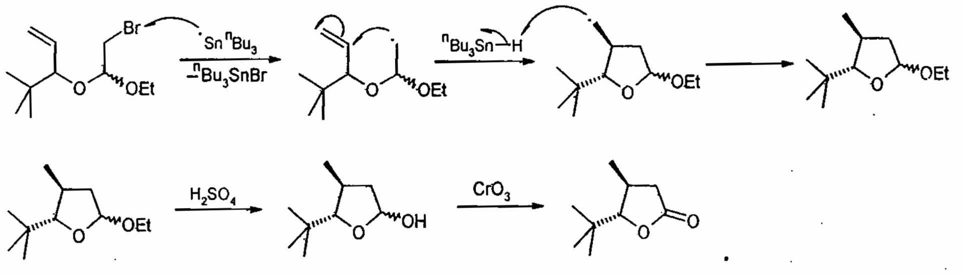
Thus among given option:- very high concentration of analyte & association of analyte or dissociation of analyte are associated with concentration of the compound in solution so they may cause the deviation from the Beer's law ($A = \varepsilon bc$)

5) Ans (b):- In Bu_3SnH; the Sn–H bond is weak and Bu_3SnH will react with alkyl halides to replace the halogen atom with H, producing Bu_3SnHal as a by-product.

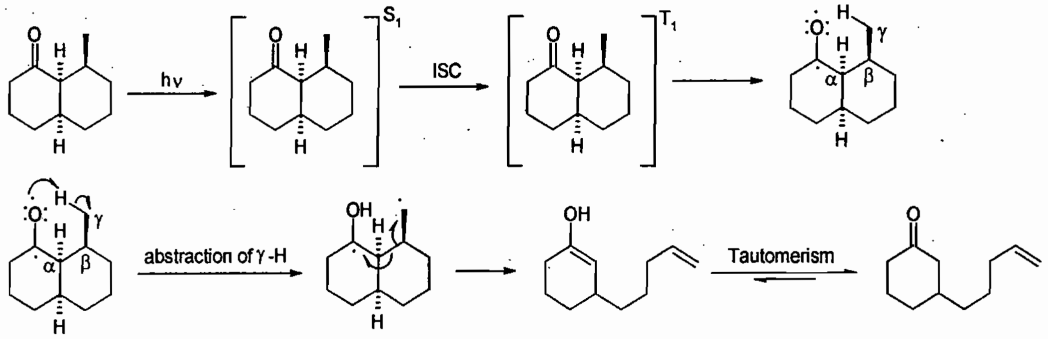
Note: - A formation of five membered ring is more favourable & adopts the more stable *trans* geometry.

$$^{n}Bu_3SnCl \xrightarrow{NaBH_4} {}^{n}Bu_3SnH$$

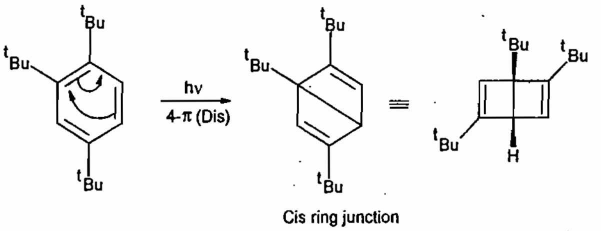
$$Bu_3SnH \xrightarrow{AIBN} Bu_3Sn^{\cdot}$$



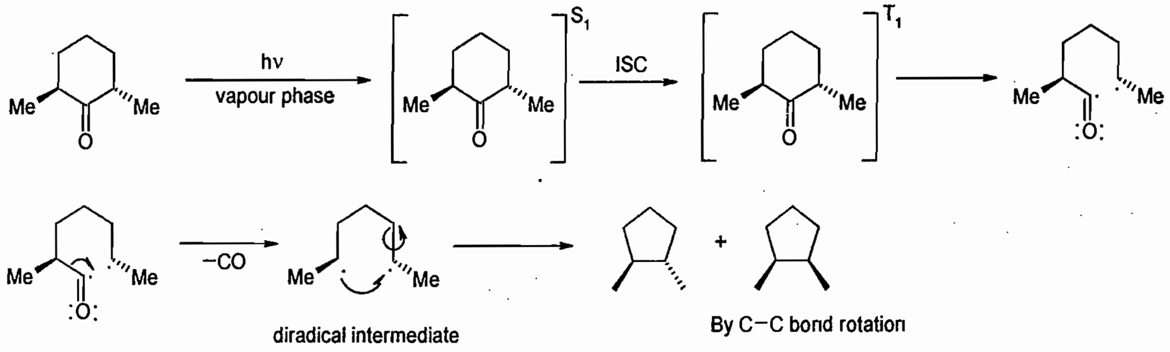
6) Ans (d):- It is a Norrish Type II cleavage reaction. Reaction involves intramolecular abstraction of the γ–hydrogen followed by cleavage of the resulting diradical to give an enol that tautomerizes to the aldehyde or ketone product



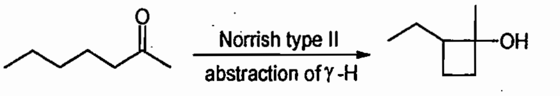
7) Ans (a):- This is an example of disrotatory electrocyclic ring closure of 1,2,4-tri-tert-butylbenzene via photolysis to give 1,2,5-tri-tert-butyl[2.2.0]hexadiene (a Dewar benzene) with cis ring junction..

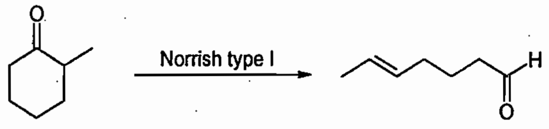


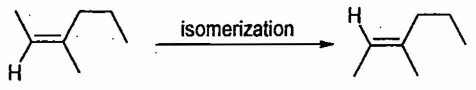
8) Ans (c):- It is an example of Norrish Type I decarbonylation reaction in which the acyl radical RCO$^\bullet$ can then lose CO to give R$^\bullet$ radicals (diradical triplet) intermediate. This diradical (triplet) intermediate must wait until one of the spins inverts so that the C–C bond can be formed & time required for this process is more than the time required for C–C bond rotation & result in a mixed product.



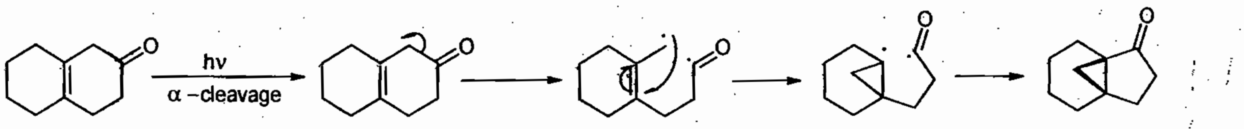
9) Ans (a):- Note:- Norrish Type I is slow reaction when α-cleavage leads to relatively unstable radical ($^\bullet$Ph, $^\bullet CH_3$, primary $^\bullet$R) or when γ-H available in carbonyl compound.



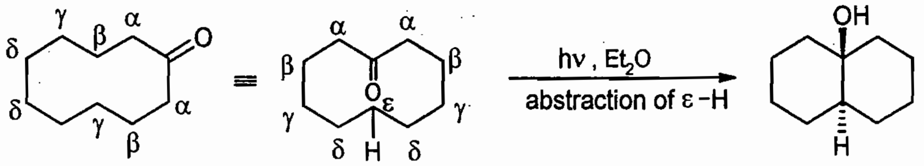




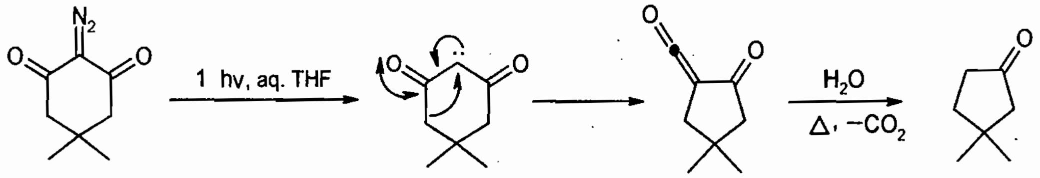
10) Ans (c):- It is an example of Norrish Type I reaction



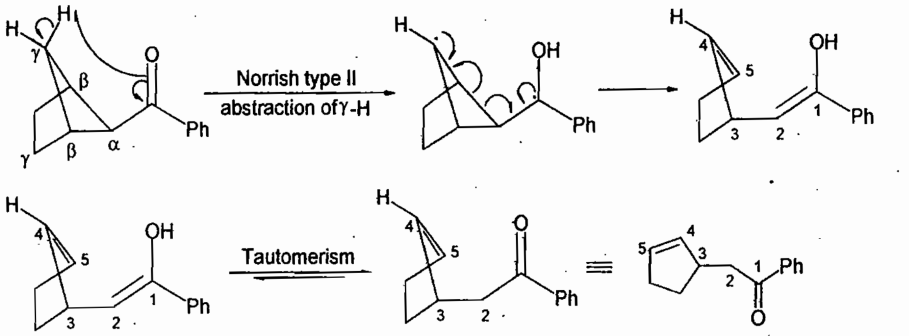
11) Ans (d):- It is a Norrish Type II cleavage reaction. Reaction involves intramolecular abstraction of ε–hydrogen followed by cyclization of diradical.



12) Ans (b):- It is a rearrangement of carbene formed by loss of N_2 from diazoketone to give ketene which cannot be isolated but is hydrolysed under aqueous condition & undergo subsequent decarboxylation.

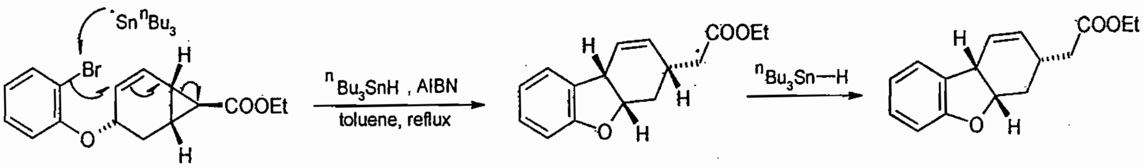


13) Ans (b):- It is a Norrish Type II cleavage reaction. Reaction involves intramolecular abstraction of the γ–hydrogen followed by cleavage of the resulting diradical to give an enol that tautomerizes to the aldehyde or ketone product. Abstraction of the γ–hydrogen takes place with a formation of six membered transition state become a difficult with the two other γ–hydrogen)

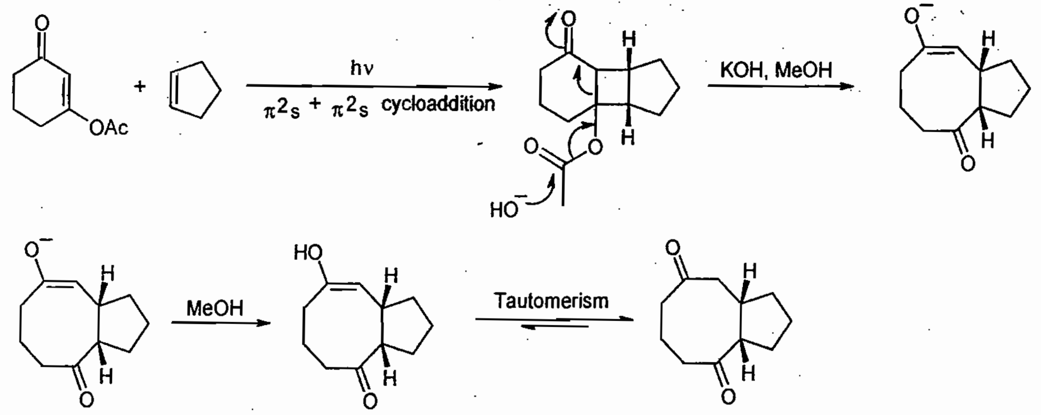


14) Ans (d):- In Bu_3SnH; the Sn–H bond is weak and Bu_3SnH reacts with alkyl halides to replace the halogen atom with H, producing Bu_3SnHal as a by-product.

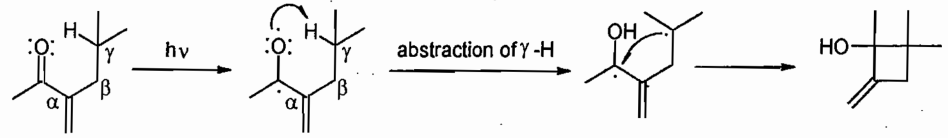
$${}^{n}Bu_3SnH \xrightarrow{AIBN} {}^{n}Bu_3Sn^{\cdot}$$



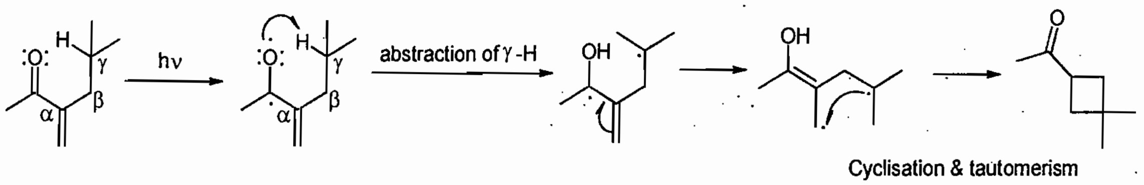
15) Ans (a):- First step is the concerted $_{\pi}2_s + _{\pi}2_s$ cycloaddition under photochemical condition between two olefins leading to a cyclobutane ring. Second step is rearrangement under basic condition.



16) Ans (d):- Formation of product (a) is a Norrish Type II cleavage reaction, involves intramolecular abstraction of the γ hydrogen followed by cyclization of diradical to give a cyclobutanol.

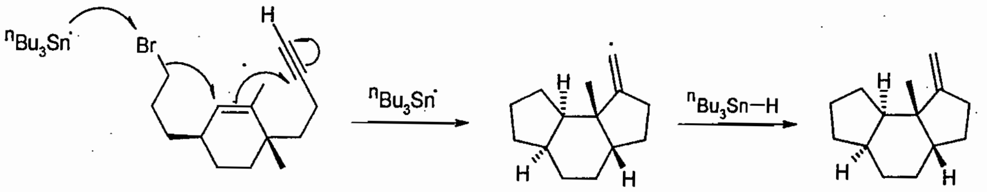


Formation of product (b) is also a Norrish Type II cleavage reaction. Reaction involves intramolecular abstraction of the γ-hydrogen followed by cyclization of rearranged diradical to give a rearranged product

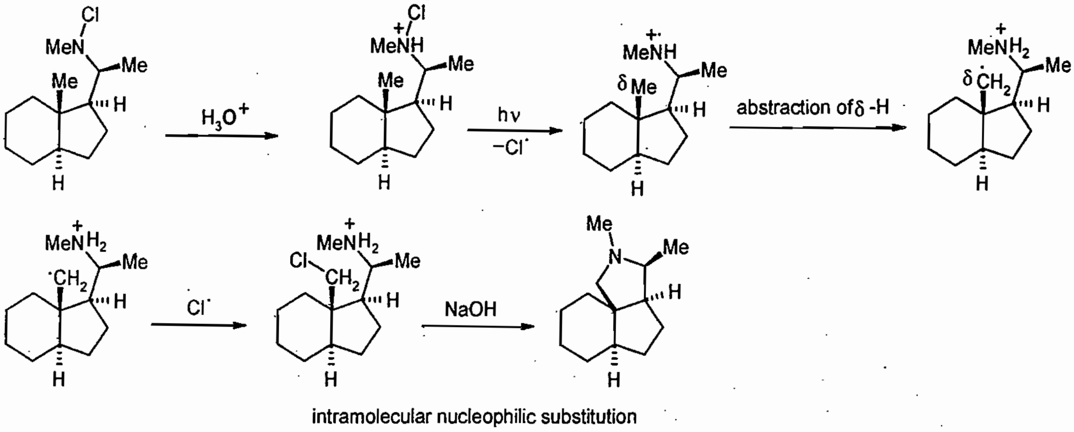


17) Ans (a):- In Bu_3SnH; the Sn–H bond is weak and Bu_3SnH reacts with alkyl halides to replace the halogen atom with H, producing Bu_3SnHal as a by-product. A formation of five membered ring is more favourable & the rate of radical cyclization to give a six membered or larger ring is considerably slower than that to a five-membered ring.

$^{n}Bu_3SnH \xrightarrow{AIBN} {}^{n}Bu_3Sn^{\cdot}$

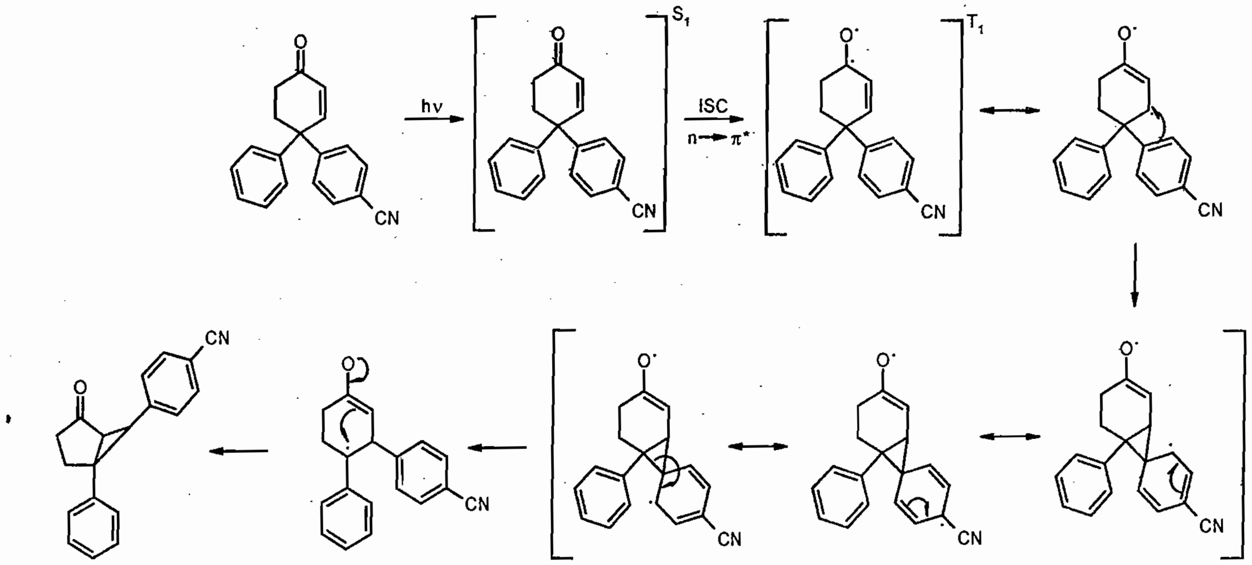


18) Ans (a):- It is an example of the *Hofmann–Loeffler–Freytag* reaction. Reaction involves photolytically initiated decomposition of N-haloamines in acidic solution, to give δ-haloamines. But formed δ-haloamines are usually converted to pyrrolidines by intramolecular nucleophilic substitution in basic condition

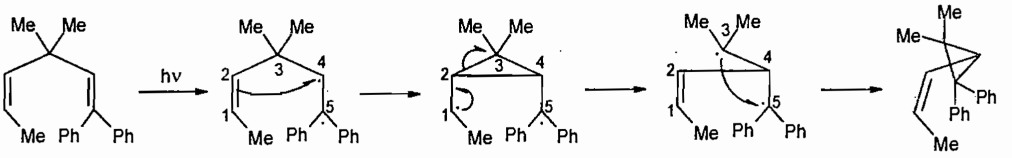


intramolecular nucleophilic substitution

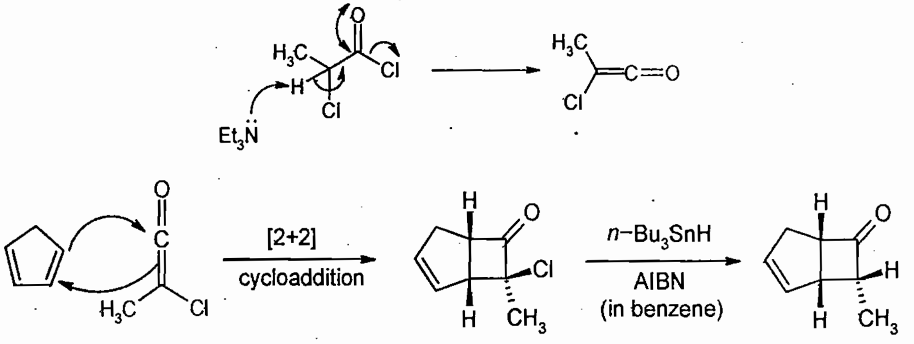
19) Ans (b):- It is Di-π-methane rearrangement.4,4diaryl systems undergoes this type of rearrangement. If two aryl groups are different ; the aryl group which stabilize the radical effectively will migrate preferentially.



20) Ans (a):- It is an example of the di-π-methane rearrangement:- 1,4-Dienes carrying alkyl or aryl substituents on C-3 can be photochemically rearranged to vinylcyclopropanes. Reaction occurs via a more stable free radical.

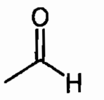
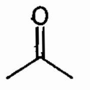
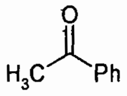
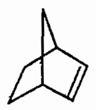
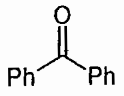


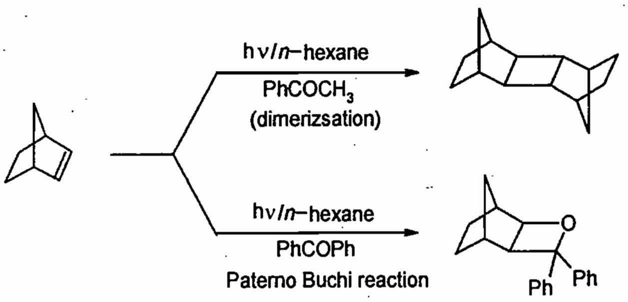
21) Ans (c):- First step is ketene formation which undergo [2+2] cycloaddition rather than [4+2] cycloaddition & form the cis-geometry at the ring junction. In the last step n-BuSnH with AIBN converts the C−Cl bond into C−H bond



22) Ans (b):- If the energy of the triplet excited state of carbonyl compound is less than the energy of the triplet excited state of olefinic compound then Paterno–Buchi Reaction take place.

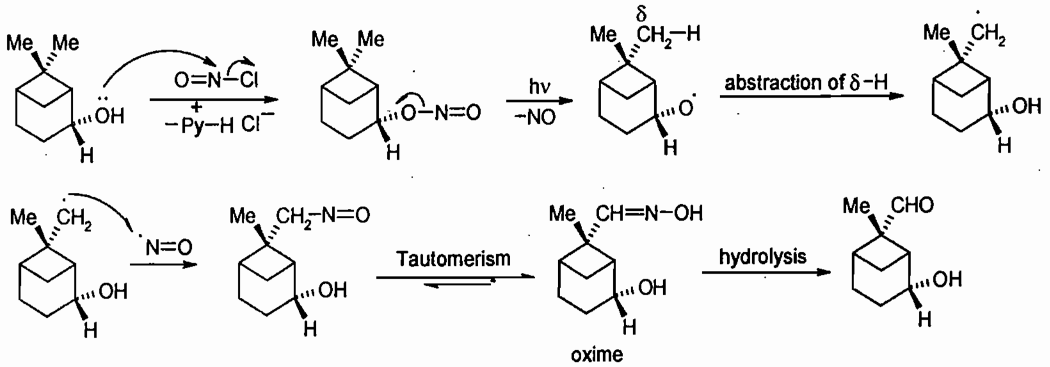
If the energy of the triplet excited state of carbonyl compound is more than the energy of the triplet excited state of olefinic compound then Dimerization of olefins take place.

Molecule	$H_2C{=}CH_2$					
E_T (kcal/mol)	84	80	78	74	72	69

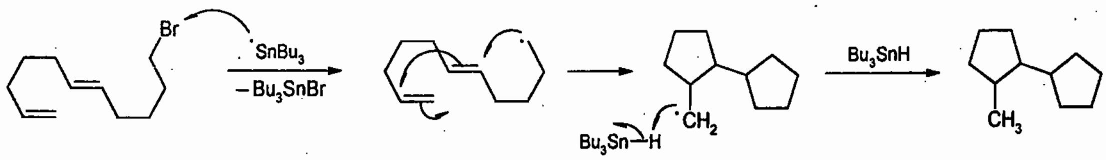


23) Ans (c):- It is an example of the Barton reaction. In reaction the alcohol is first converted to the nitrite ester. Photolysis of the nitrite results in conversion of the nitrite group to the OH group and nitrosation of the methyl group. Hydrolysis of the oxime tautomer gives the aldehyde.

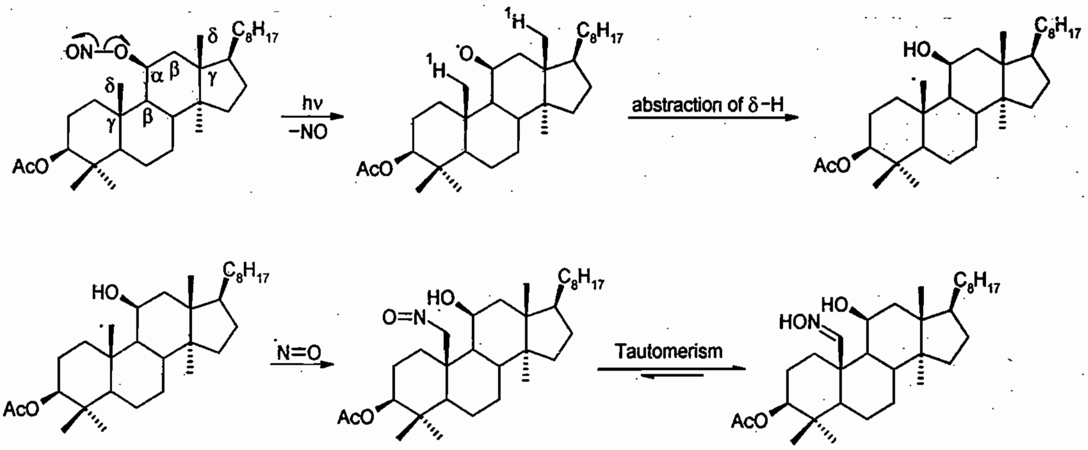
Stereoselectivity:- Abstraction intramolecular δ−hydrogen atom from the methyl group which is to the same face of alcohol.



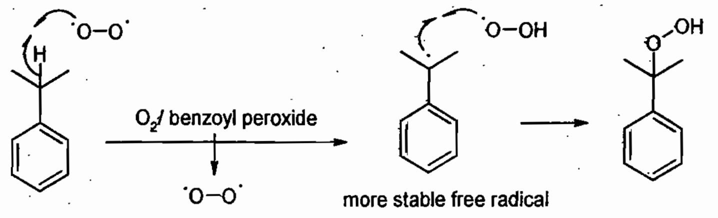
24) Ans (a):- The rate of radical cyclization to give a six membered or larger ring is considerably slower than that to a five-membered ring



25) Ans (a):- It is an example of the Barton reaction. The photolytic conversion of organic nitrites into nitroso compounds. Reaction involve photolysis of an organic nitrite (R−O−N=O) gives an alkoxy radical and nitrogen monoxide. Subsequent intramolecular δ−hydrogen atom abstraction is followed by capture of nitrogen monoxide by the carbon radical and formation of a nitrosoalcohol, The product formed by abstraction of δ−^{1}hydrogen (activated) is more than the product formed by abstraction of δ−$^{1'}$hydrogen

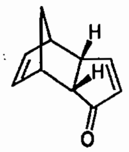


26) Ans (c):- oxygen diradical forms and add to benzylic that is stable free radical.



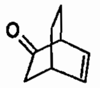
27) Ans (b):- The correct match is:-

i)



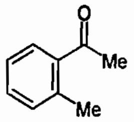
(r) Intramolecular [2 + 2] cycloaddition

ii)



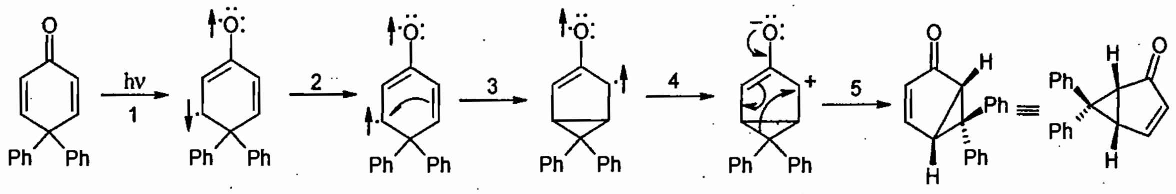
(p) oxa-di-pi methane rearrangement

iii)

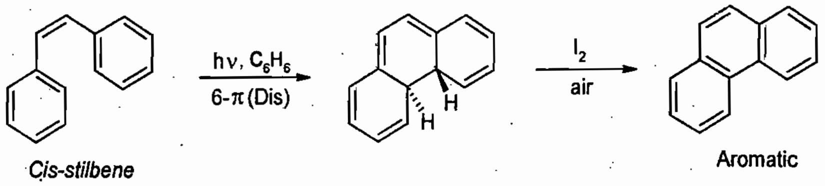


(s) photoenolisation

28) Ans (a):- It is photolyzed, rearrangement of 2,5-cyclohexadienones to give bicyclo[3.1.0]hexenone It is same as the di-pi-methane rearrangement Step 1 & 2 is singlet & triplet state after n−π* transition. Step 3 is a rearrangement from one excited state to another. Step 4 is π*−n electron demotion. Step 5 is migration of alkyl to a carbocation center



29) Ans (a):- Electrocyclic ring closure of (4n+2)π system under photochemical conditions is conrotatory. Conrotatory ring closure of this reactant causes the hydrogens to be trans in the ring closed product. polycyclic aromatic structure result on a subsequent oxidation of the product



List of Reference books

1) Introduction to Organic Photochemistry by J. D. Coyle, John Wiley & sons
2) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford
3) Photochemistry and Pericyclic Reactions, by J. Singh, New Age International.
4) Advanced Organic Chemistry: Part A- Reaction and Synthesis by F. A. Carey, R. J. Sundberg, Springer publication.
5) Modern Methods of Organic Synthesis by W. Carruthers and L. Coldham, Cambridge University Press.
6) March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure by Jerry March John Wiley & Sons
7) Mechanism and Structure in Organic Chemistry, by E.S Gould, Holt-Dryden, New York
8) Principles of Organic Synthesis, by R.O.C, Norman and J. M. Coxon, CRC Press.

* * *

Topic 20

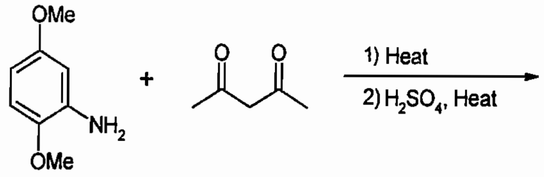
HETEROCYCLIC COMPOUNDS

Questions with two marks

1) With respect to electrophilic aromatic substitution, reactivity order of pyrrole, pyridine and indole is ***[Dec 2011]***

(a) indole > pyrrole > pyridine (b) pyrrole > pyridine > indole
(c) pyrrole > indole > pyridine (d) indole > pyridine > pyrrole

2) The major product formed in the following reaction is ***[Dec 2013]***



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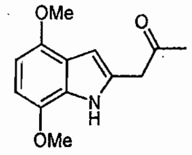

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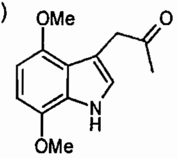

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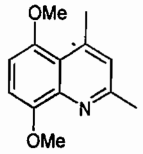

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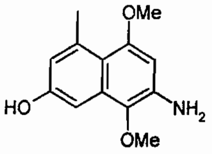
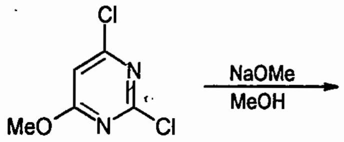


3) The major product formed in the following reaction is ***[Dec 2013]***



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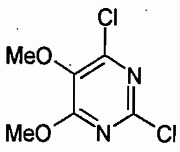

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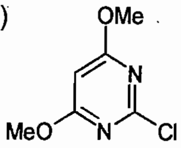

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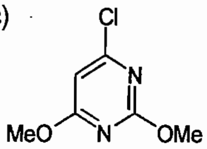

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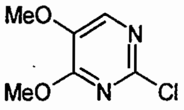
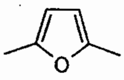


4) The major product formed in the reaction of 2,5-hexanedione with P_2O_5 is

(a)


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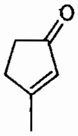

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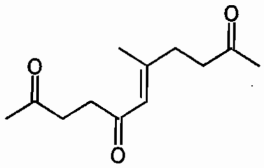

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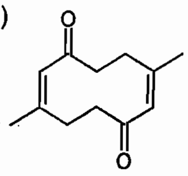
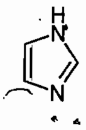
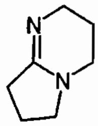


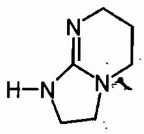
5) The decreasing order of basicity of the following compounds is ***[Dec 2014]***



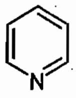
I



II



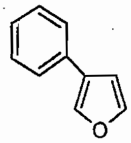
III

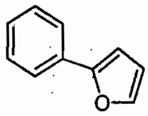


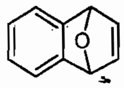
IV

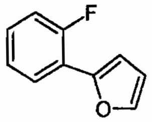
(a) I > II > III > IV (b) IV > I > II > III (c) III > II > I > IV (d) IV > III > II > I

6) The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives ***[Dec 2014]***

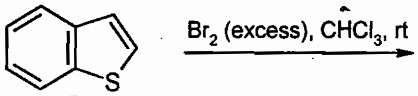
(a)


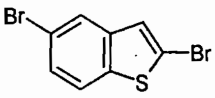
(b)


(c)


(d)


7) The major product of the following reaction is ***[Dec 2014]***



(a)


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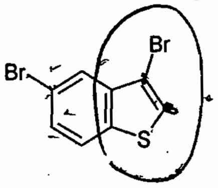

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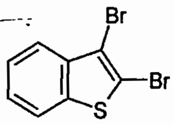

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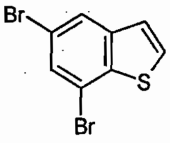


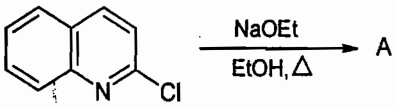
Questions with four marks

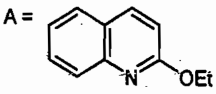
8) Match the following ***[June 2011]***

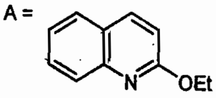
Column I	Column II
A. Pyrrole	i. Pictet-Spengler
B. 1, 4-dihydropyridine	ii. Chichibabin
C. Isoquinoline	iii. Paal-Knorr
	iv. Hantzsch

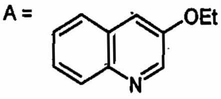
(a) (A)-i (B)-ii (C)-iii (b) (A)-ii (B)-iii (C)-iv (c) (A)-iv (B)-i (C)-ii (d) (A)-iii (B)-iv (C)-i

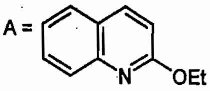
9) In the following reaction, the product formed and the mechanism involved is ***[Dec 2011]***



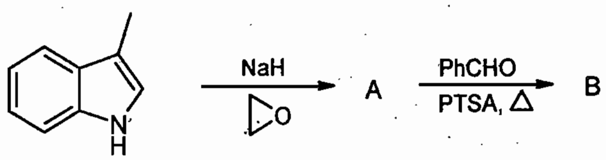
(a)

& is formed by addition - elimination mechanism

(b)

& is formed by benzyne mechanism

(c)

& is formed by benzyne mechanism

(d)

& is formed by S$_N$2 displacement

10) The major products A and B formed in the following reaction sequence are ***[June 2012]***



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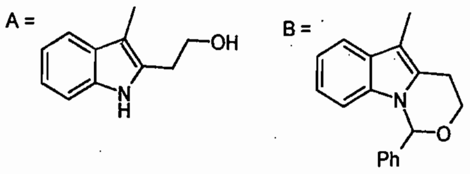

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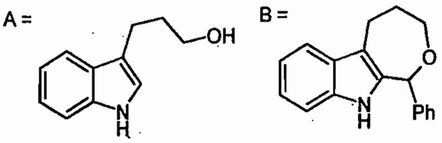

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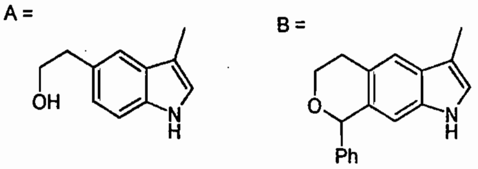

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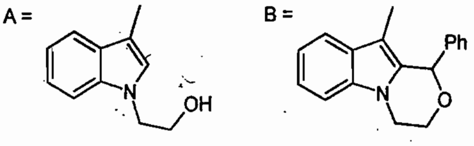
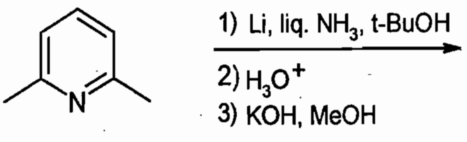
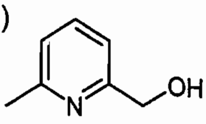


11) The major product formed in the following reaction is: ***[Dec 2012]***



(a)


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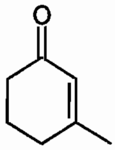

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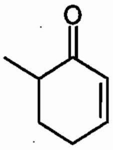

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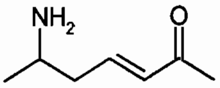
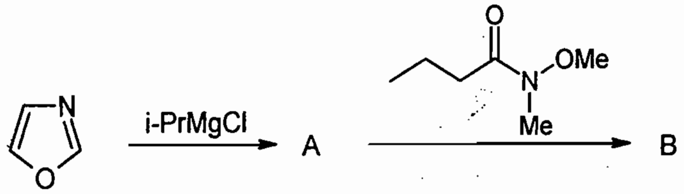
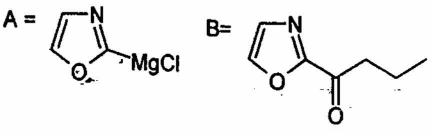


12) In the following reaction A and B are ***[Dec 2012]***



(a)


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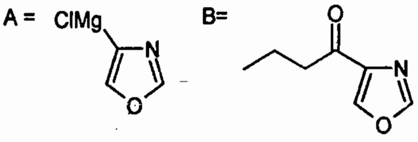

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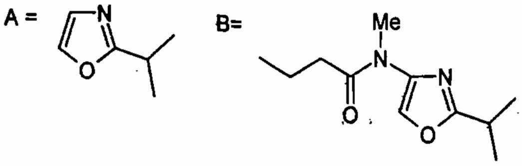

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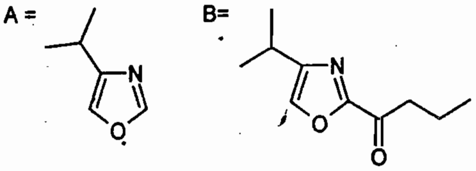
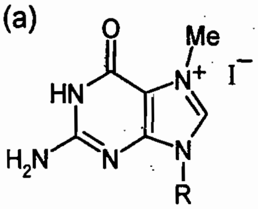


13) The heterocyclic ring present in the amino acid histidine is ***[June 2013]***

(a) pyridine (b) tetrahydropyrrole (c) indole (d) imidazole

14) The major product formed in the reaction of guanosine with one equivalent of methyl iodide is ***[June 2013]***

(a)



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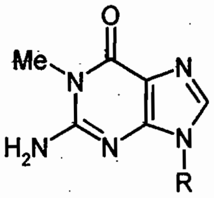

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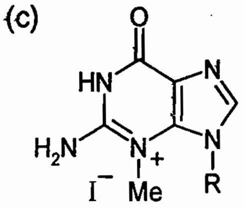
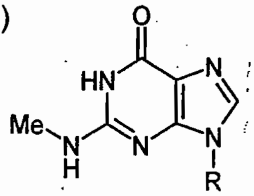
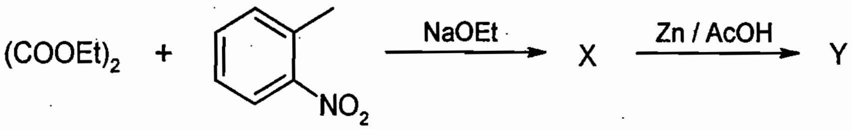


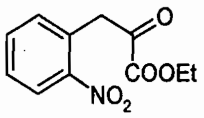
(d)



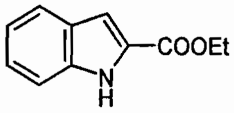
15) In the following reaction sequence, structures of the major product X and Y are ***[June 2013]***



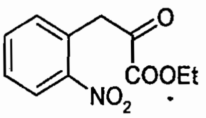
(a) X =



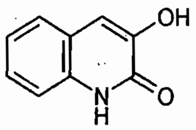
Y =



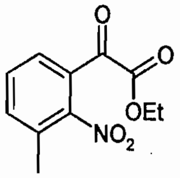
(b) X =



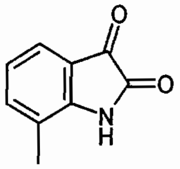
Y =



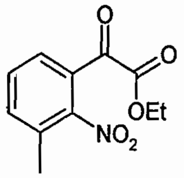
(c) X =



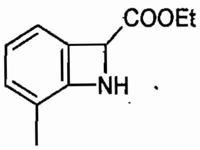
Y =



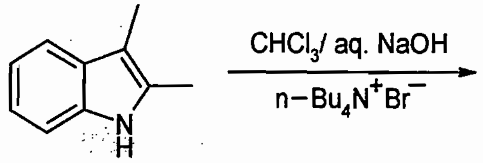
(d) X =



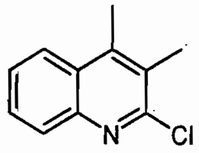
Y =



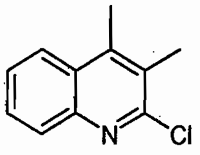
16) In the following reaction, the intermediate and the major product A are ***[Dec 2013]***



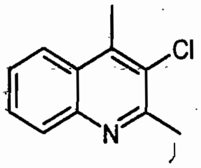
(a) :CHCl and



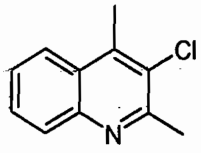
(b) :CCl$_2$ and



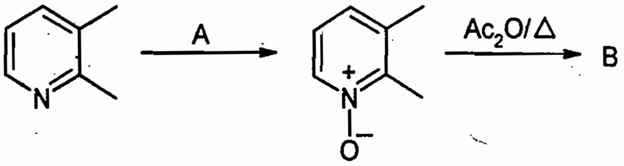
(c) :CHCl and



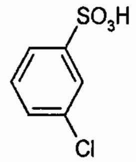
(d) :CCl$_2$ and



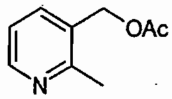
17) In the following transformation, the reagent A and the major product B, respectively, are ***[Dec 2013]***



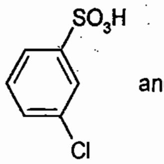
(a)



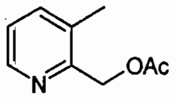
and



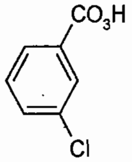
(b)



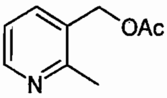
and



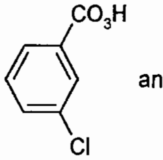
(c)



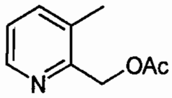
and



(d)



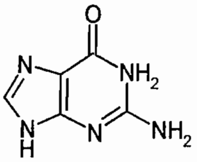
and



18) The reactive position of nicotinamide adenine dinucleotide (NAD) in biological redox reactions is ***[Dec 2013]***

(a) 2-position of the pyridine ring
(b) 6-position of the pyridine ring
(c) 4-position of the pyridine ring
(d) 5-position of the pyridine ring

19) In low chloride ion concentration, the anticancer drug cis-platin hydrolyses to give a diaquo complex and this binds to DNA via adjacent guanine ***[June 2014]***



(guanine)

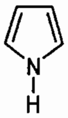
The coordinating atom of guanine to Pt(II) is

(a) N1
(b) N3
(c) N7
(d) N9

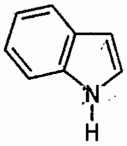
(Questions from GATE EXAM)

Questions with ONE OR TWO marks

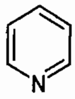
20) The correct order of the basicity of the following compounds is ***(GATE 2006)***



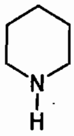
I



II



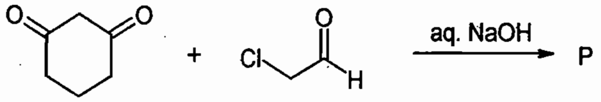
III



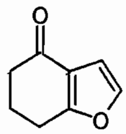
IV

(a) IV > III > II > I
(b) III > IV > II > I
(c) IV > III > I > II
(d) III > IV > I > II

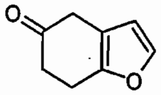
21) Identify the major product P in the following reaction ***(GATE 2006)***



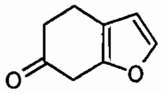
(a)



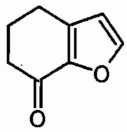
(b)



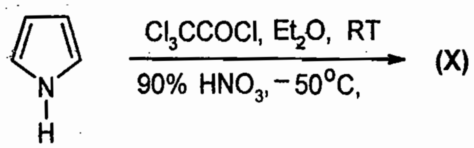
(c)

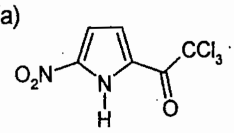


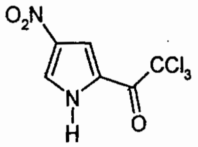
(d)

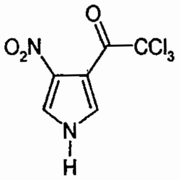


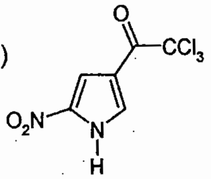
22) Identify the major product (X) in the following two–step reaction ***(GATE 2006)***



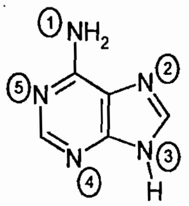
(a)


(b)


(c)


(d)


23) The mono protonation of adenine (X) in acidic solution mainly occurs at ***(GATE 2007)***

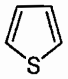


(x)

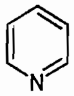
(a) position 1 (b) position 2 (c) position 3 (d) either position 4 or 5

24) The decreasing order of the reactivity of the following compounds towards electrophiles is ***[GATE 2010]***

I



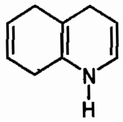
II

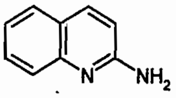


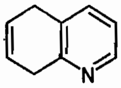
III

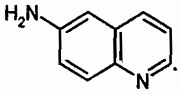
(a) II >I > III (b) II >III > I (c) III >I > II (d) I >II > III

25) The major product formed in the reaction of quinoline with potassium amide (KNH_2) in liquid ammonia is ***[GATE 2013]***

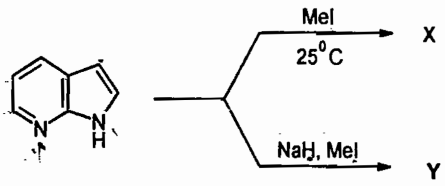
(a)


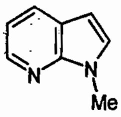
(b)


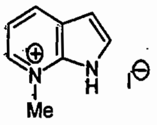
(c)


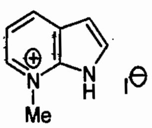
(d)


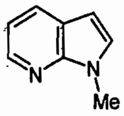
26) The major products X and Y formed in the following reactions are ***[GATE 2014]***

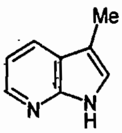


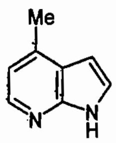
(a) X =


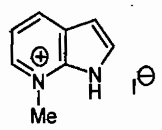
Y =


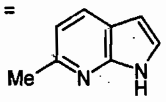
(b) X =


Y =


(c) X =


Y =


(d) X =


Y =


Answer Key

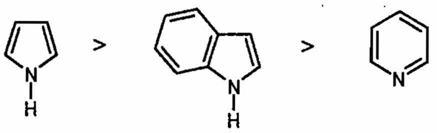
Topic 20:-Heterocyclic compounds

1	c	2	c	3	c	4	a	5	c	6	c	7	c	8	d	9	a	10	d
11	b	12	a	13	d	14	a	15	a	16	d	17	d	18	c	19	c	20	a
21	a	22	b	23	d	24	d	25	b	26	b								

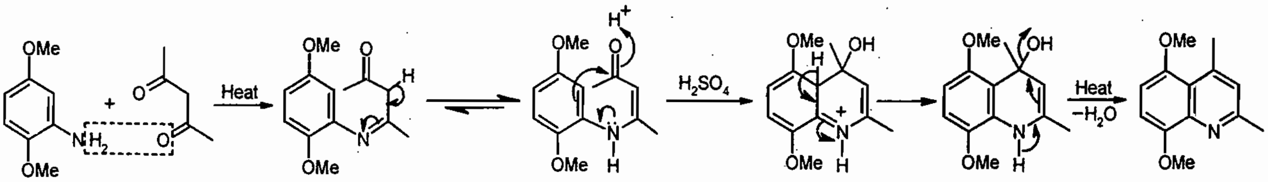
Hint & solutions

1) Ans (c):- Reactivity order of pyrrole, pyridine and indole to electrophilic aromatic substitution is pyrrole > indole > pyridine. Among pyrrole and indole, indole is less reactive than pyrrole because of withdrawing effect of –Ph ring in case of indole. Pyridine is very much less reactive to electrophilic aromatic substitution due to electron-withdrawing nitrogen atom. Pyridine, therefore, is less reactive than benzene. Indeed, it is even less reactive than nitrobenzene.

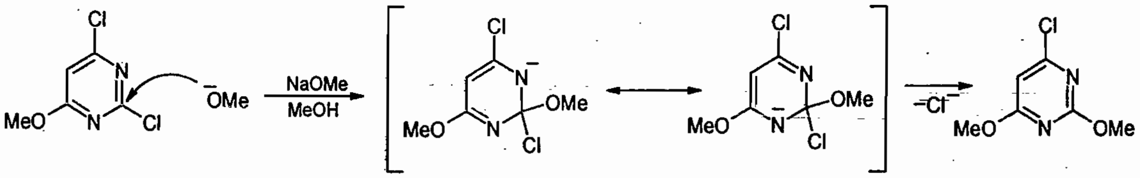
Therefore Reactivity order of pyrrole, pyridine and indole to electrophilic aromatic substitution is:-



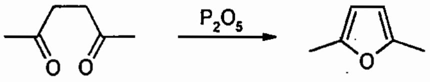
2) Ans (c):- It is the Combes Quinoline Synthesis:- Condensation of a 1,3 - dicarbonyl compound with an arylamine gives a high yield of a β-amino -enone, which on cyclodehydration with concentrated acid yields quinoline



3) Ans (c):- In this reaction nucleophile adds to the most electrophilic position between the two electron-withdrawing groups that is ring nitrogen. The product is formed by addition-elimination mechanism.

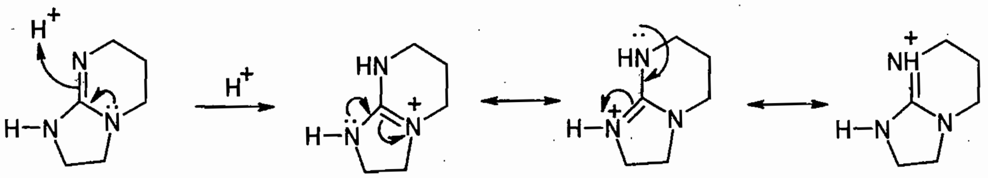


4) Ans (a):- 1,4 - Dicarbonyl Compounds with dehydrating agent undergoes cyclodehydration to form furans. The process involves addition of the enol oxygen of one carbonyl group to the other carbonyl group & then elimination of water.

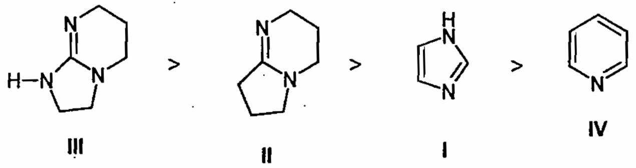


2,5-hexanedione Furan

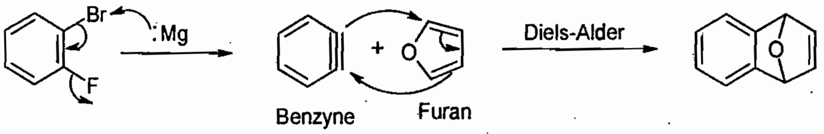
5) **Ans (c):-** Basicity is a measure of a compound's affinity for a proton. The stronger the base, the weaker is its conjugate acid. The base is stronger when its conjugate acid is stabilized by conjugation of an electron- donating group. Among all I, II & III are more basic than IV as the electron density on the sp^2 nitrogen is increased through conjugation with the sp^3 nitrogen as shown below. In case of pyridine (IV) no such stabilization of conjugate acid.



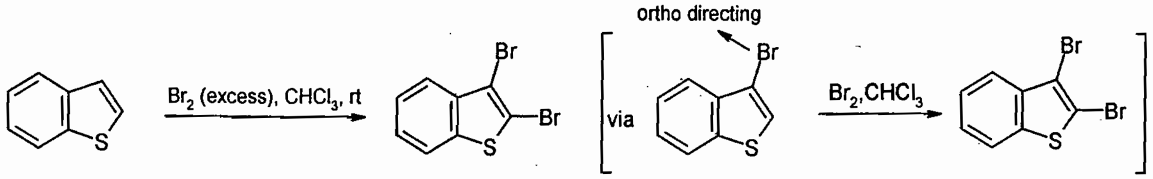
Thus the overall order of basicity is:-



6) **Ans (c):-**

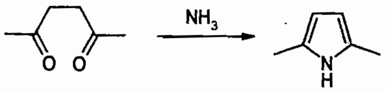


7) **Ans (c):-** The major product of the reaction is 2,3–dibromo-benzothiophene

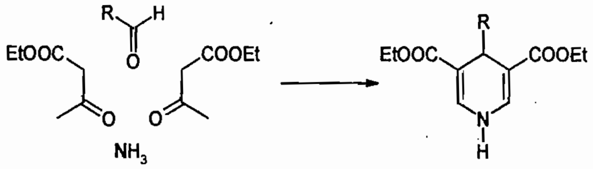


8) **Ans (d):-**

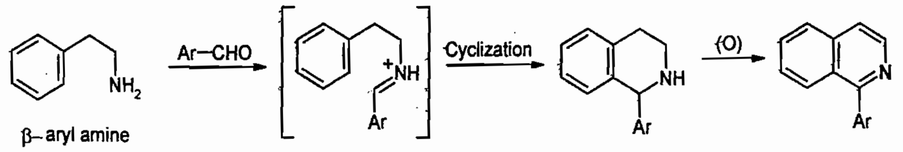
The Paal Knorr synthesis



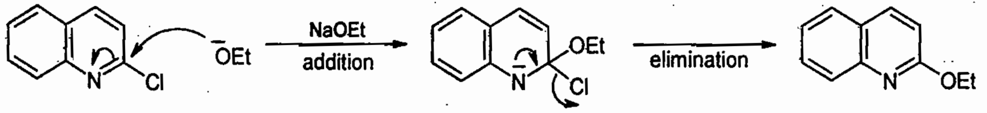
The Hantzsch synthesis



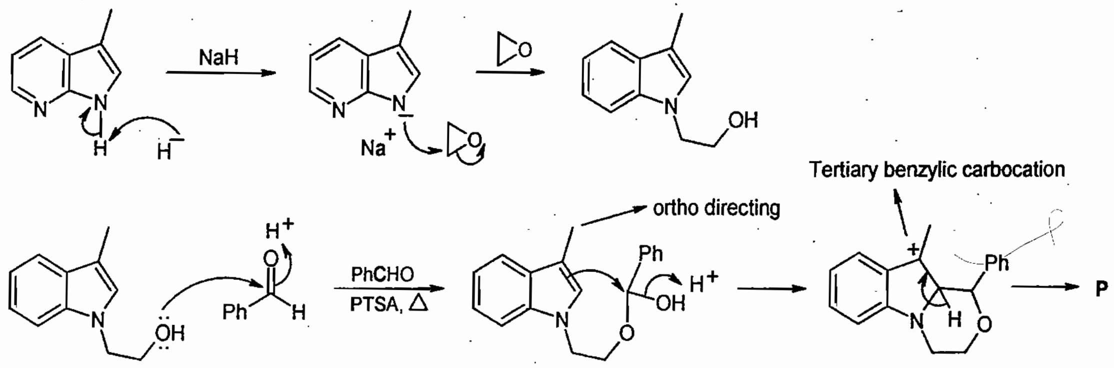
The Pictet-Spengler synthesis



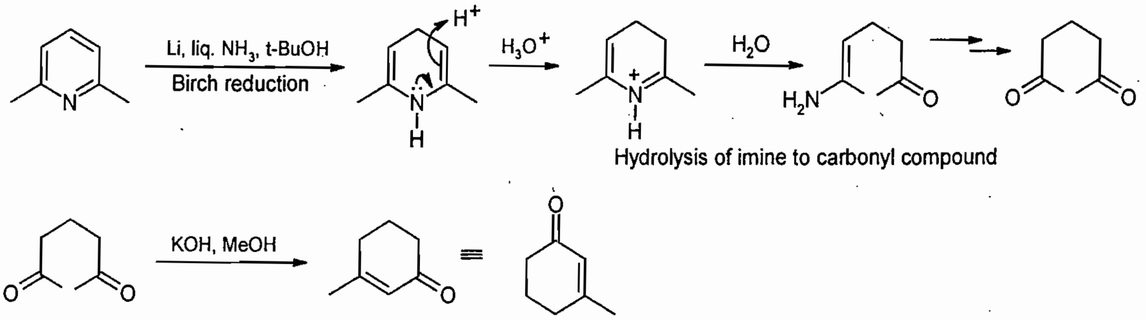
9) **Ans (a):-** The product is formed by addition-elimination mechanism.



10) Ans (d):- In first step NaH (base) abstract an acidic proton to form Na-salt of indole which give nucleophilic substitution reactions on indole nitrogen.
In the second step indole undergo electrophilic aromatic substitution at C-2 rather than C-3 as C-3 is blocked.

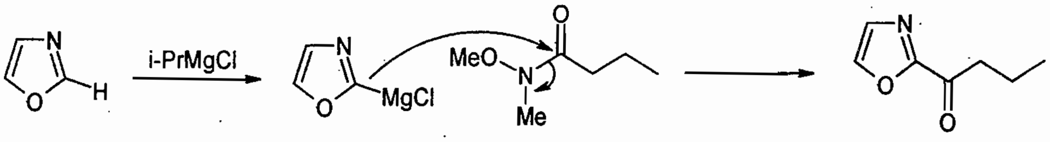


11) Ans (b):- Birch reduction of pyridines gives 1,4- dihydropyridines which are readily hydrolysed to 1,5-dicarbonyl compounds. 1,5-dicarbonyl compounds undergo intramolecular aldol condensation under basic condtion.

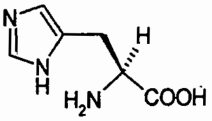


Intramolecular aldol condensation

12) Ans (a):- In the first step C–Metallation of oxazoles takes place preferentially at C – 2 position.
Second step is nucleophilic substitution of Grignard reagent with an electrophile

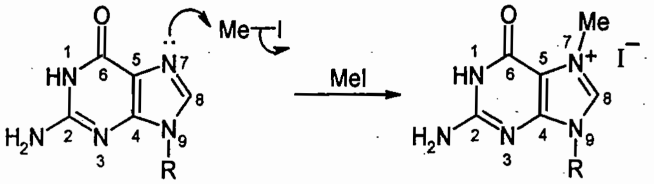


13) Ans (d):- Imidazole ring present in the amino acid histidine

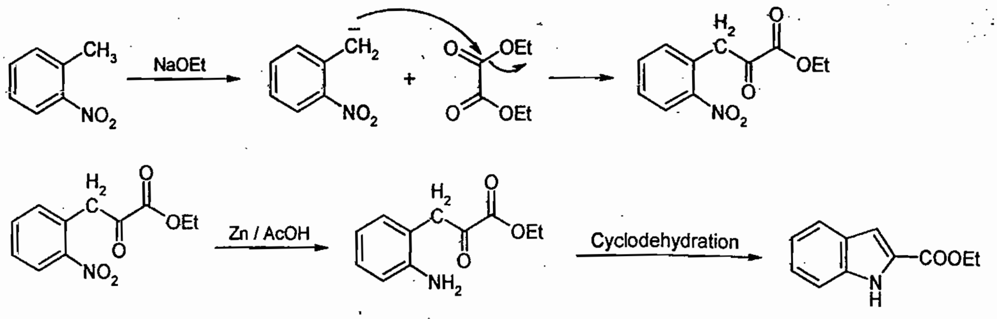


Histidine

14) Ans (a):- In guanosine the N7-nitrogen is more nucleophilic than other ring nitrogen.

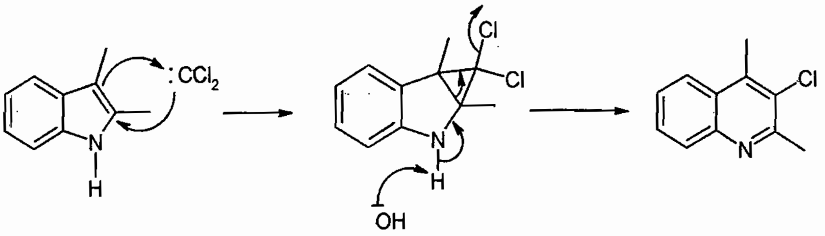


15) Ans (a):- The reaction is Reissert Indole synthesis. The reaction involves the reduction of o-nitrophenylpyruvic acid & its derivative with a reducing agent like Zn/AcOH to give o-aminophenylpyruvic acid. The intermediate o-aminophenylpyruvic acid give indole via cyclodehydration



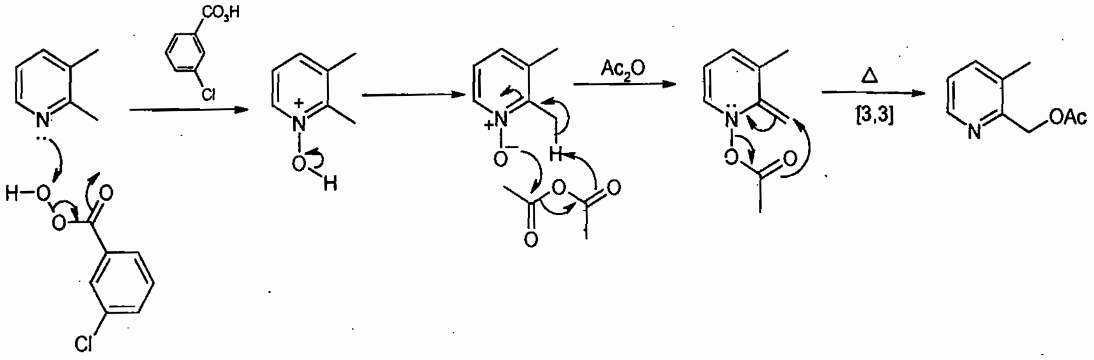
16) Ans (d):- In first step α−elimination of HX from $CHCl_3$ gives dichlorocarbene $:CCl_2$, which adds to the double bond in pyrrole & gives a bicyclic intermediate. The bicyclic intermediate rearrange in to the 3-chloroquinoline.

$$CHCl_3 + NaOH \xrightarrow{\alpha\text{-elimination}} :CCl_2$$

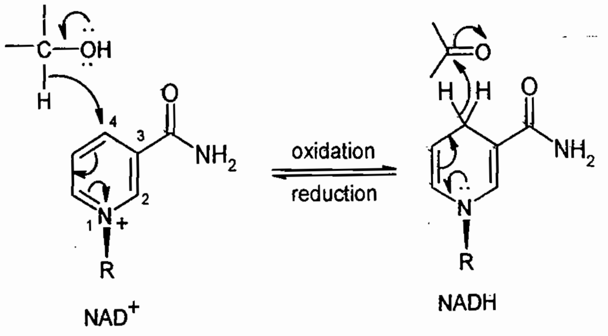


17) Ans (d):- In first step Pyridine is oxidized to pyridine *N*-oxide with reagents such *m*-CPBA .

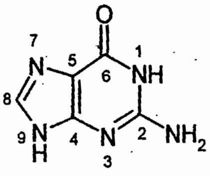
In secod step acylation occurs on oxygen of Pyridine *N*-oxides to form a compound which rearranges with migration of the acetate group by [3,3] sigmatropic rearrangement to the side chain and the restoration of aromaticity



18) Ans (c):- The reactive position of nicotinamide adenine dinucleotide (NAD) in biological redox reactions is 4-position of the pyridine ring

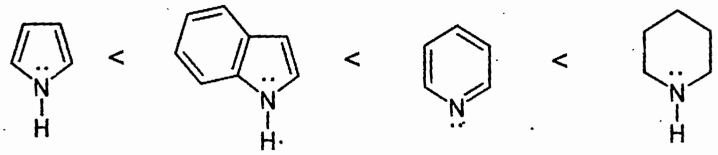


19) Ans (c):- The coordinating atom of guanine to Pt(II) is the N7-position of guanine

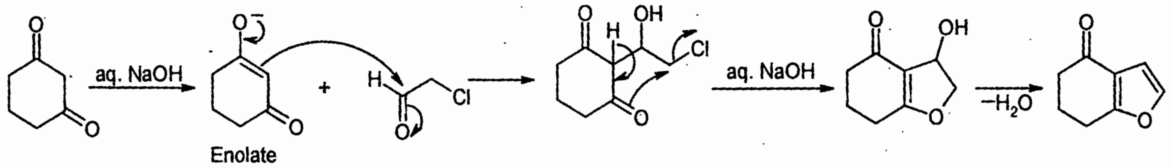


(guanine)

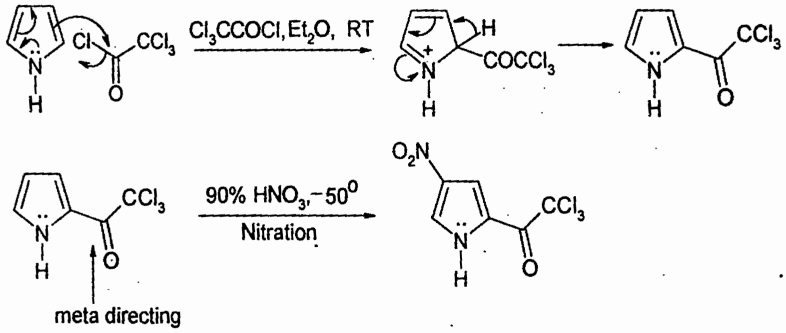
20) Ans (a):- Indole is more basic than pyrrole because in *N* - protonated indolium cation aromaticity of benzene is retain while aromaticity of pyrrolium ion is loss after protonation of indole & pyrrole respectively. Among pyridine & piperidine; piperidine is more basic (localized lone pair on sp^3 hybridized atom is more basic than the localized lone pair on sp^2 hybridized atom. Order of the basicity:-



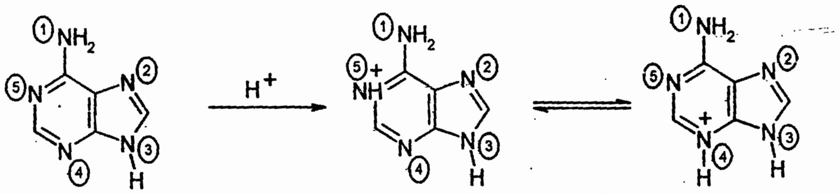
21) Ans (a):- It is the Feist–Benary Synthesis of furan
(Reaction of 1,3–dicarbonyl enolate with a α–halo–ketone,



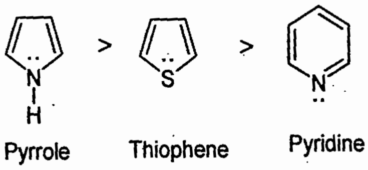
22) Ans (b):- Pyrrole undergo electrophilic substitution preferentially at C-2. Next step is nitration at meta to electron withdrawing acyl group



23) Ans (d):- The mono protonation of adenine in acidic solution mainly occurs at either position 4 or 5

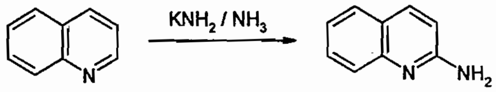


24) Ans (d):- Reactivity order of pyrrole, thiophene & pyridine to electrophilic aromatic substitution is pyrrole > thiophene > pyridine.

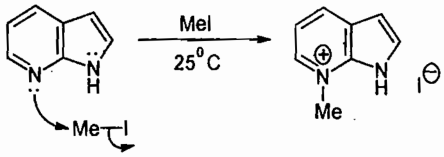


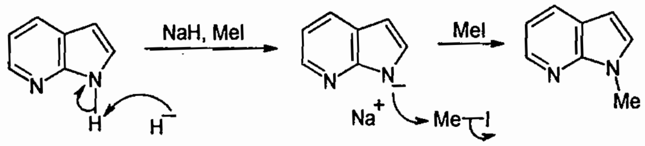
Among pyrrole and thiophene, pyrrole is more reactive than thiophene, because in pyrrole there is effective overlap between the $2sp^2$ orbital on carbon and the $2sp^2$ orbital on nitrogen & it make delocalization effective than delocalization due to poor overlap between the $2sp^2$ orbital on carbon and the $3sp^2$ orbital on sulfur in thiophene. Pyridine is very much less reactive due to electron-withdrawing nitrogen atom. Pyridine, therefore, is less reactive than benzene. Indeed, it is even less reactive than nitrobenzene.

25) Ans (b):- This is an example of Chichibabin reaction:- is a method for producing 2–aminopyridine or 2–aminoquinoline derivative by the reaction of pyridine/quinoline with sodium amide.



26) Ans (b):- Lone pair of nitrogen is localized & basic and a reasonably good nucleophile. In second reaction NaH (base) abstract an acidic proton to form Na-salt of indole & nucleophilic substitution reactions on indole nitrogen.





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2) Heterocyclic Chemistry by J. A. Joule and G. F. Smith, Chapman and Hall

3) Heterocyclic Chemistry by R. K. Bansal, New Age International

4) Name Reactions in Heterocyclic Chemistry, Edited by Jie Jack Li, John Wiley & Sons.

5) Organic Chemistry, by J. Clayden, N. Greeves, S. Warren and P. Wothers, Oxford University Press, Oxford

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