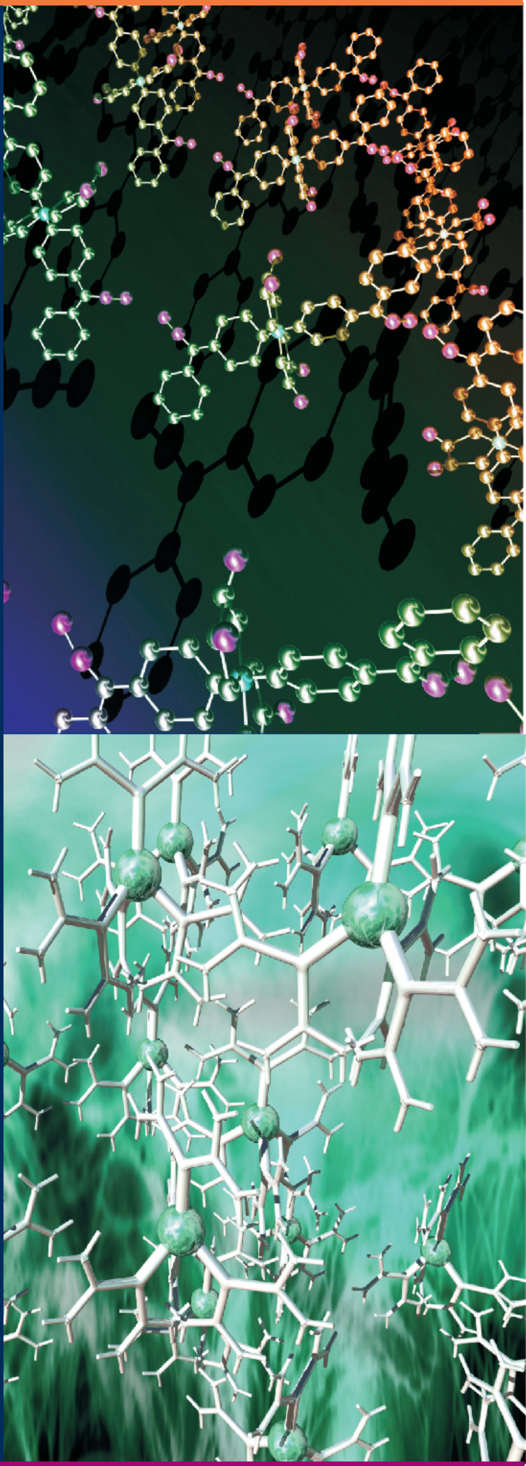
3rd Edition

Photochemistry and Pericyclic Reactions



JAGDAMBA SINGH
JAYA SINGH

New Academic Science

Photochemistry and Pericyclic Reactions

Photochemistry and Pericyclic Reactions

(THIRD EDITION)

JAGDAMBA SINGH
M.Sc., D. Phil.
Professor, Department of Chemistry
University of Allahabad
Allahabad, India

JAYA SINGH
M.Sc., D.Phil. (University of Allahabad)
Lecturer, Department of Chemistry
L.R.P.G. College, Sahibabad
Ghaziabad, U.P., Indiap

New Academic Science Limited
The Control Centre, 11 A Little Mount Sion
Tunbridge Wells, Kent TN1 1YS, UK
www.newacademicscience.co.uk • e-mail: info@newacademicscience.co.uk

The Control Centre, 11 A Little Mount Sion, Tunbridge Wells, Kent TN1 1YS, UK
www.newacademicscience.co.uk • e-mail: info@newacademicscience.co.uk

---

ISBN : 978 1 906574 51 2

British Library Cataloguing in Publication Data
A Catalogue record for this book is available from the British Library

Preface to the Third Edition

The use of light and heat to effect chemicals has been recognized for many years, but it is only recently that sufficient knowledge has been attained to place photochemical and pericyclic reactions in the realm of organic synthesis. The application of the principle of conservation of orbital symmetry to concerted reaction has made an important contribution to the understanding of many thermal and photochemical processes. This book has been written to provide an introduction to the principles and applications of **pericyclic** and organic **photochemistry** at a level suitable for undergraduate and postgraduate students in universities and technical institutes. It is intended to provide an exhaustive survey of the field and an up-to-date background of the subject to the students.

Jagdamba Singh
Jaya Singh

This page intentionally left blank

Preface to the First Edition

In the course of teaching under-graduate and post-graduate classes, we have constantly been feeling the need of a concise volume that gives details of the pericyclic reactions and photochemistry.

The goal of this book is to build on the foundation of photochemistry and pericyclic reactions. Our purpose is to solidify the students' understanding of the basic concepts of pericyclic reactions and photochemistry. The students have often expressed their difficulty caused by the absence of such a book. The book is intended to meet the need and requirement of under-graduate and post-graduate students. The book will also be useful to those students who are preparing for the various competitive examinations.

Chapter 1 of the present book encompasses the details of the molecular orbital theory of conjugated polyenes and allylic systems.

Chapters 2 to 5 deal with all the four pericyclic reactions viz. electrocyclic reactions, cycloaddition reactions, sigmatropic rearrangements and group transfer reactions. These reactions are discussed on the basis of Woodward-Hofmann orbital correlation method, Frontier molecular orbital method, Woodward-Hofmann rule and PMO method. The last two method should be particularly welcomed by the students as these offer simple mnemonics of selection rules for predictions of the stereochemical courses of the pericyclic reactions. Also retrocyclic addition reactions, 1,3-dipolar cycloaddition reactions and chelotropic reactions are discussed in detail.

Chapter 6 gives a general introduction to the basic concepts of photochemistry and the principles of absorption and emission of radiation. Chapter 7 deals with the photochemistry of carbonyl compounds. All molecular rearrangements of photochemistry with their mechanism are described in chapter 8. Chapter 9 deals with the photo-oxidation and reduction reactions and chapter 10 describes photochemistry of olefins and aromatic compounds. Chapter 11 deals with the photo-substitution reactions which includes Barton reaction and Hofmann-Loeffler-Freytag reaction. Chapters 12 and 13 deal with photochemistry in natural products and photochemistry of atmosphere and applied photochemistry. The topic of applied photochemistry includes photography, vision, photochromism and photopolymerisation. The most important aspects of this book is the number of problems given and their solutions in chapter 14.

It is hoped that this book would be useful and effective in helping the students of chemistry. We shall welcome constructuve criticism and suggestions with a view to improving upon our present effort.

Jagdamba Singh

Jaya Singh

Contents

CHAPTER 4 Sigmatropic Rearrangement 111–152

CHAPTER 5 Group Transfer Reactions 153–159

CHAPTER 6 Introduction and Basic Principles of Photochemistry 160–183

CHAPTER 7 Photochemistry of Carbonyl Compounds 184–228

CHAPTER 8 Photo Rearrangements 229–261

CHAPTER 9 Photo Reduction and Photo Oxidation 262–268

CHAPTER 10 Photochemistry of Alkenes, Dienes and Aromatic Compounds 269–300

1

CHAPTER

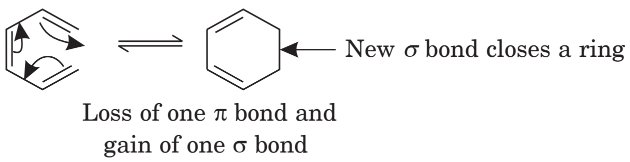
Pericyclic Reactions

1.1 INTRODUCTION

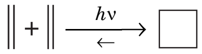
Pericyclic reactions are defined as the reactions that occur by a concerted cyclic shift of electrons. This definition states two key points that characterise a pericyclic reaction. First point is that reaction is concerted. In concerted reaction, reactant bonds are broken and product bonds are formed at the same time, without intermediates. Second key point in pericyclic reactions involves a cyclic shift of electrons. The word pericyclic means around the circle. Pericyclic word comes from cyclic shift of electrons. Pericyclic reactions thus are characterised by a cyclic transition state involving the π bonds.

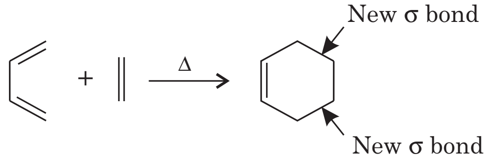
The energy of activation of pericyclic reactions is supplied by heat (Thermal Induction), or by UV light (Photo Induction). Pericyclic reactions are stereospecific and it is not uncommon that the two modes of induction yield products of opposite stereochemistry.

We shall concern with four major types of pericyclic reactions. The first type of reaction is the *electrocyclic reaction*: A reaction in which a ring is closed (or opened) at the expense of a conjugated double (or triple bond) bond.



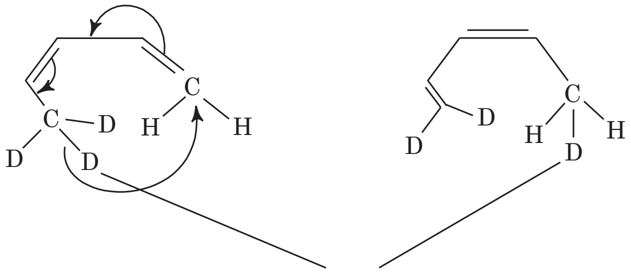
The second type of reaction is the *cycloaddition reaction*: A reaction in which two or more π electron systems react to form a ring at the expense of one π bond in each of the reacting partners.





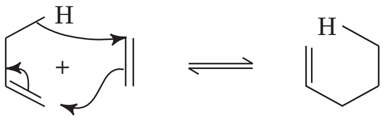
In this reaction formation of two new σ (*sigma*) bonds takes place which close a ring. Overall there is loss of two π (*pi*) bonds in reactants and gain of two σ (*sigma*) bonds in a product.

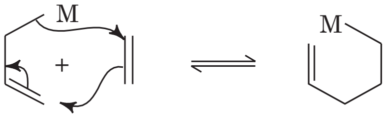
The third type of reaction is the *sigmatropic rearrangement* (or reaction): A reaction in which a σ (*sigma*) bond formally migrates from one end to the other end of π (*pi*) electron system and the net number of π bonds remains the same.



σ Bonded group moved from one end to the other end of the π electron system

The fourth type of reaction is the *group transfer reaction*: A reaction in which one or more groups or atoms transfer from one molecule to another molecule. In this reaction both molecules are joined together by σ (*sigma*) bond.

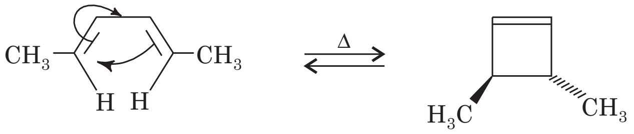




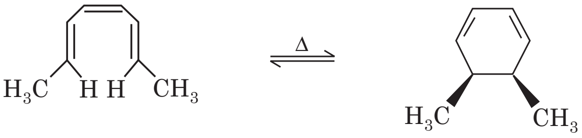
The three features of any pericyclic reaction are intimately interrelated. These are:

1. *Activation:* Pericyclic reactions are activated either by thermal energy or by UV light. However, many reactions that require heat are not initiated by light and *vice-versa*.
2. The number of π (*pi*) bonds involved in the reaction.
3. The stereochemistry of the reaction.

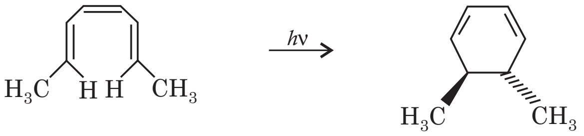
Consider the following three reactions:



...(1)



...(2)



...(3)

First two reactions are thermal reactions activated by heat and third reaction is photochemical reaction activated by light. The relationship between the mode of activation and the stereochemistry is exemplified by a comparison of reactions (2) and (3). When starting material is heated it gives *cis* product and when starting material is irradiated the product is *trans*.

These results had been observed for many years but the reasons for them were not known. Several theories have been developed to rationalise these pericyclic reactions. *R.B. Woodward* and *R. Hoffmann* have proposed explanation based upon the symmetry of the molecular orbitals of the reactants and products. The theory proposed is known as *Conservation of Orbital Symmetry*. *K. Fukuii* proposed another explanation based upon the frontier molecular orbitals. The theory proposed is known as *Frontier Molecular Orbital (FMO)* method. The *Woodward-Hoffmann* rule and *Hückel-Mobius* (H-M) methods are also used for the explanation of pericyclic reactions. These four theories make the same predictions for pericyclic reactions. These four are the alternate ways for looking at the same reaction.

In order to understand the theories of pericyclic reactions, we must first understand molecular orbitals of compound containing π (*pi*) bonds.

1.2 CONSTRUCTION OF π MOLECULAR ORBITALS OF ETHYLENE AND 1, 3-BUTADIENE

We know that, the number of molecular orbitals is always equal to the number of atomic orbitals that combine to form them. The same principle applies to π molecular orbitals. A π electron system derived from the interaction of number *m* of *p* orbitals contain *m* molecular orbitals, that differ in energy. Half of the molecular orbitals are bonding molecular orbitals and remaining half are antibonding molecular orbitals. π molecular orbitals of ethylene from the two *p* atomic orbitals of the two carbons can be constructed as follows:

Each *p* orbital consists of two lobes, with opposite phases of the wave function of the two lobes. The plus and minus signs used in drawing these orbitals indicate the phase of the wave function.

In the bonding orbital of ethylene, there is overlap of similar signs (+ with + and – with –) in the bonding region between the nuclei. This reinforcement of the wave function is called *constructive* overlap. In the antibonding orbital there is cancelling of opposite signs (+ and –) in the bonding region. This cancelling of the wave function is called *destructive* overlap (Fig. 1.1).

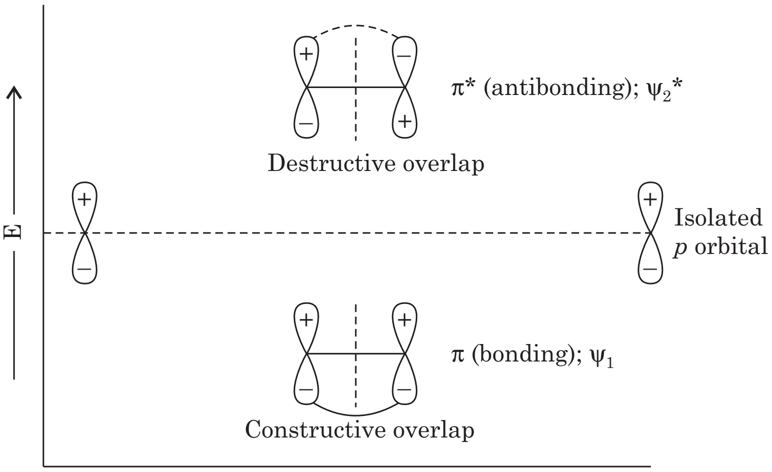


Fig. 1.1 The combination of two *p* orbitals results in the formation of two molecular orbitals

In 1, 3-butadiene, we have a system of four *p* orbitals on four adjacent carbons. These four *p* orbitals will overlap to produce four π molecular orbitals. We can get four new MOs in a number of equivalent ways. One of the ways to obtain four new molecular orbitals is by linear combination of two molecular orbitals of ethylene. Linear combination of orbitals is also known as *perturbation theory or perturbation molecular orbital* (*PMO*) *theory*. Linear combination always takes place between two orbitals (two atomic orbitals, two molecular orbitals or one atomic and one molecular orbitals) having minimum energy difference. This means that we need to look only at the results of the π ± π and π* ± π* interactions and do not have to consider π ± π* (Fig. 1.2).

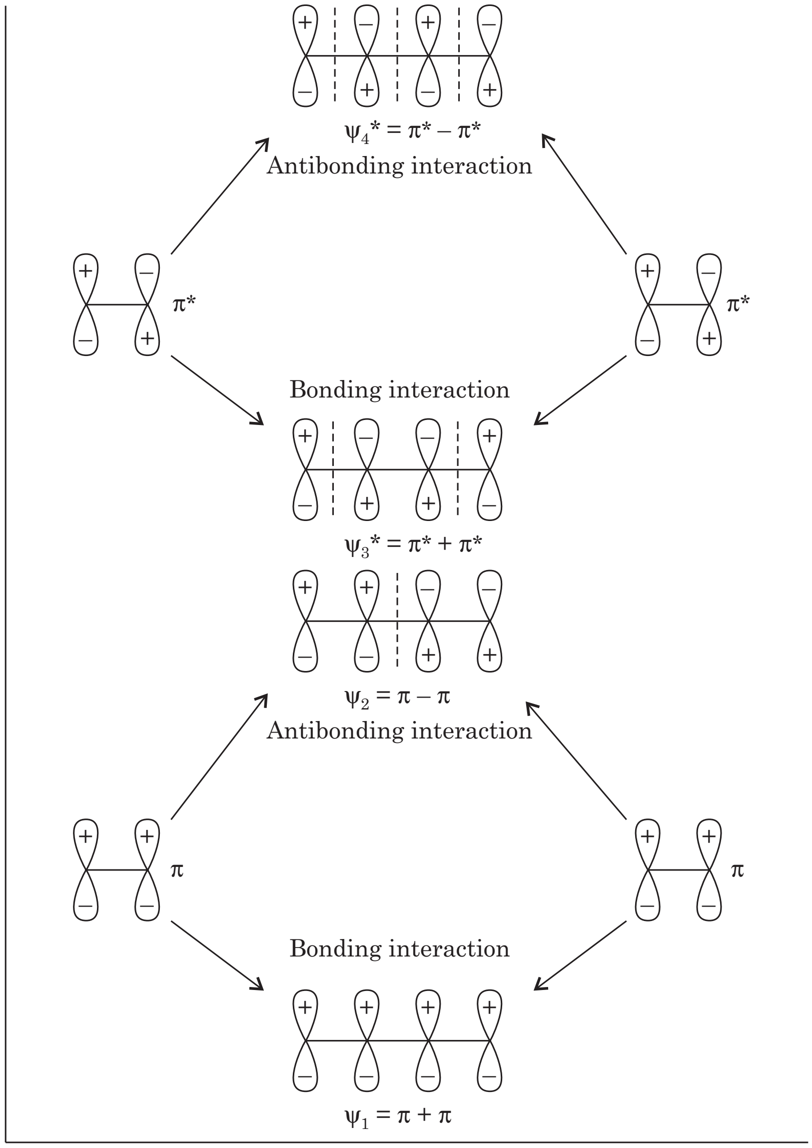


Fig. 1.2 The schematic formation of the π molecular orbitals of 1, 3-butadiene from the π molecular orbitals of ethylene

The lowest energy orbital (ψ_1) of 1, 3-butadiene is exceptionally stable for two reasons: There are three bonding interactions, and the electrons are delocalised over four nuclei (Fig. 1.3).

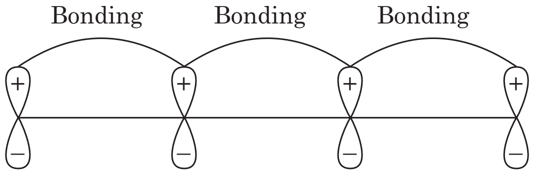


Fig. 1.3 ($\psi_1 = \pi + \pi$) Bonding interaction between two ethylene bonding MOs

The second molecular orbital ψ_2 of 1, 3-butadiene is obtained from the antibonding interaction between two bonding molecular orbitals of ethylene. The ψ_2 orbital has two bonding and one antibonding interaction, so we would expect it to be a bonding orbital (two bonding – one antibonding = one bonding). Thus, energy of ψ_2 is more than that of ψ_1. ψ_2 molecular orbital has one node between C_2–C_3. A node is a plane where the wave function drops to zero (Fig. 1.4).

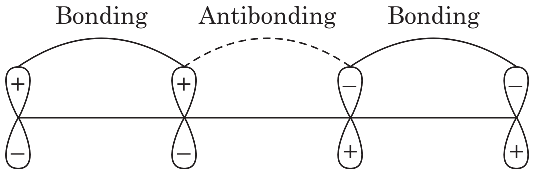


Fig. 1.4 $\psi_2 = \pi - \pi$ (Antibonding interaction between two ethylene π molecular orbitals)

The third butadiene MO, ψ_3^* has two nodes. This molecular orbital is obtained from the bonding interaction between π^* and π^* of two ethylene molecules. There is a bonding interaction of the C_2—C_3 bond and there are two antibonding interactions: One at C_1–C_2 bond and the other at the C_3—C_4 bond. This is an antibonding orbital (one bonding – two antibonding = one antibonding) having two nodes. Thus energy of this ψ_3^* orbital is more than the energy of ψ_2 MO (Fig. 1.5).

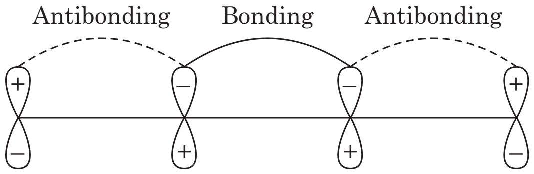


Fig. 1.5 ($\psi_3^* = \pi^* + \pi^*$) Bonding interaction between two antibonding MOs of ethylene

The fourth molecular orbital (ψ_4^*) is obtained from the antibonding interaction between π^* and π^* of two ethylene molecules. This molecular orbital has three nodes and is totally antibonding. This MO has the highest energy (Fig. 1.6).

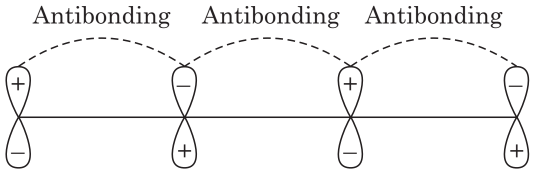


Fig. 1.6 ($\psi_4^* = \pi^* - \pi^*$) Antibonding interaction between π^* and π^* of ethylene

Following generalisations can be made to construct the molecular orbitals of the conjugated polyenes from the π molecular orbitals of ethylene and 1, 3-butadiene:

1. A π electron system derived from the interaction of a number of *m* of *p* orbitals contain *m* molecular orbitals (MOs) that differ in energy. Thus, the number of π MOs are always equal to the number of atomic *p* orbitals. In 1, 3-butadiene, four *p* orbitals are used in the formation of the π MOs, thus four π MOs results, which we shall abbreviate as ψ_1, ψ_2, ψ_3 and ψ_4 (or π_1, π_2, π_3 and π_4).
2. Half of the molecular orbitals (*i.e., m*/2) have lower energy than the isolated *p* orbitals. These are called bonding molecular orbitals (BMOs). The other half have energy higher than the isolated *p* orbitals. These are called antibonding molecular orbitals (ABMOs). To emphasise this distinction, antibonding MOs will be indicated with asterisks. Thus, 1, 3-butadiene has two bonding MOs (ψ_1 and ψ_2) and two antibonding MOs (ψ_3* and ψ_4*).
3. The bonding MO of lowest energy ψ_1 has no node. Each molecular orbital of increasingly higher energy has one additional node. Thus, in 1, 3-butadiene ψ_1 has zero node, ψ_2 has one node, ψ_3* has two nodes and ψ_4* has three nodes.
4. The nodes occur between atoms and are arranged symmetrically with respect to the centre of the π electron system.

The node in ψ_2* of ethylene is between two carbon atoms, in the centre of the π system (Fig. 1.1). The node in ψ_2 of 1, 3-butadiene is also symmetrically placed in the centre of the π system. The two nodes in ψ_3* are placed between carbon-1 and carbon-2 and between carbon-3 and carbon-4 respectively—equivalent distance from the centre of the π system. Each of the three nodes in ψ_4*, the orbital of highest energy, must occur between carbon atoms. Thus the highest level has a node between each adjacent carbon pair (Fig. 1.2).

The next generalisation relates to the symmetry of the molecular orbitals. Various molecular orbitals are classified according to their two independent symmetrical properties.

1.3 SYMMETRY IN π MOLECULAR ORBITAL

A π molecular orbital possesses either mirror plane symmetry or centre of symmetry. Both symmetries are not present together in a given π molecular orbital.

m-Symmetry: Some molecular orbitals have the symmetry about the mirror plane (*m*) which bisects the molecular orbitals and is perpendicular to the plane of the molecule (Fig. 1.7).

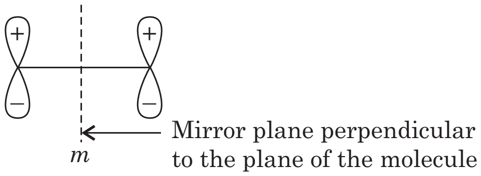


Fig. 1.7

Both orbitals in Fig. 1.7 are mirror images to each other hence in this MO there is mirror plane symmetry, abbreviated as *m*(S).

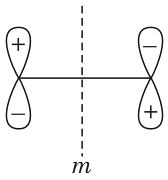


Fig. 1.8 (a)

In Fig. 1.8 (*a*) both orbitals are not mirror images to each other. Thus in this MO there is mirror plane asymmetry, abbreviated as *m*(A).

C_2-Symmetry: The centre of symmetry is a point in the molecular axis from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same phases of the orbitals [Fig.1.8 (*b*)].

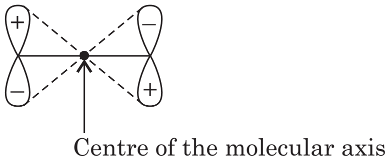
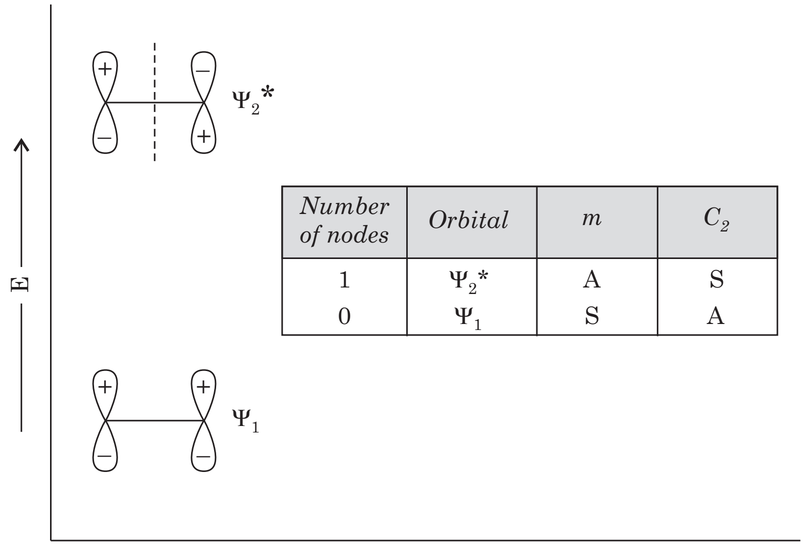


Fig. 1.8 (b)

Both orbitals in Fig. 1.8 (*b*) are symmetrical with respect to centre of the molecular axis. Thus in this MO there is centre of symmetry, abbreviated as C_2(S).

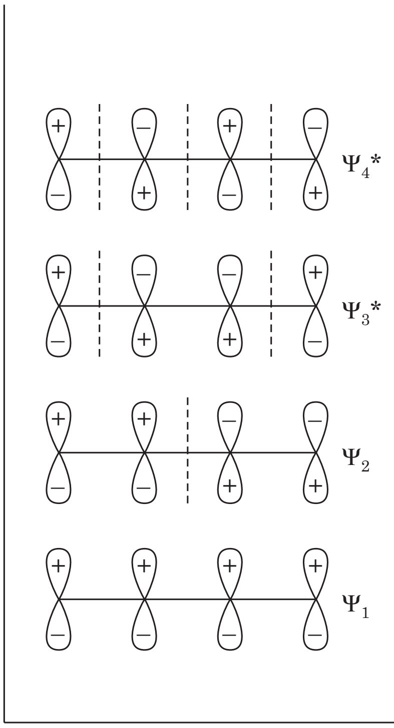
m(S) means plane of symmetry.
C_2(S) means centre of symmetry.

Let us take examples for the purpose of symmetry properties in ethylene (Fig. 1.9) and 1, 3-butadiene (Fig. 1.10).



Number of nodes	*Orbital*	*m*	C_2
1	$\Psi_2{}^*$	A	S
0	Ψ_1	S	A

Fig. 1.9 Symmetries in the π molecular orbitals of ethylene



Number of nodes	*Orbital*	*m*	*C_2*
3	Ψ_4^*	A	S
2	Ψ_3^*	S	A
1	Ψ_2	A	S
0	Ψ_1	S	A

Fig. 1.10 Symmetries in the π molecular orbitals of 1, 3-butadiene

On the basis of the above two examples we can conclude the following *very important points* for linear conjugated π systems:

1. The wave function ψ_n will have $(n - 1)$ nodes.
2. When n is odd, ψ_n will be symmetric with m and asymmetric with C_2.
3. When n is even, ψ_n will be symmetric with C_2 and asymmetric with m. Table 1.1.

Table 1.1 Symmetry elements in the orbital ψ_n of a linear conjugated polyene

Wave function	*nodes (n – 1)*	*m*	*C_2*
ψ_{odd} : ψ_1, ψ_3, ψ_5, ...	0 or even	S	A
ψ_{even} : ψ_2, ψ_4, ψ_6, ...	odd	A	S

1.4 FILLING OF ELECTRONS IN π MOLECULAR ORBITALS IN CONJUGATED POLYENES

Conjugated polyenes always contain even number of carbon atoms. These polyenes contain either $(4n)\pi$ or $(4n + 2)\pi$ conjugated electrons. The filling of electrons in the π molecular orbitals of a conjugated polyene is summarised below:

1. Number of bonding π MOs and antibonding π MOs are same.
2. Number of electrons in any molecular orbital is maximum two.

3. If a molecular orbital contains two electrons then both electrons are always paired.
4. Molecular orbitals follow Aufbau principle and Hund's rule.
5. Energy of the π molecular orbital is directly proportional to the number of the nodal planes.
6. There will be no degenerate molecular orbitals in any energy level, *i.e.*, each and every energy level contains one and only one molecular orbital.

1.5 CONSTRUCTION OF MOLECULAR ORBITALS OF CONJUGATED IONS AND RADICALS

Conjugated unbranched ions and radicals have an odd number of carbon atoms. For example, the allyl system (cation, anion or radical) has three carbons and three *p* orbitals—hence, three molecular orbitals. We can get three new molecular orbitals by linear combination of one molecular orbital of ethylene and two isolated *p* orbital. As already mentioned that the linear combination always takes place between two orbitals having minimum energy difference. In allylic system linear combination takes place between one ethylene MO and one *p* orbital. This means that we need to look at the results of the π ± *p* and π* ± *p* interactions (Fig. 1.11).

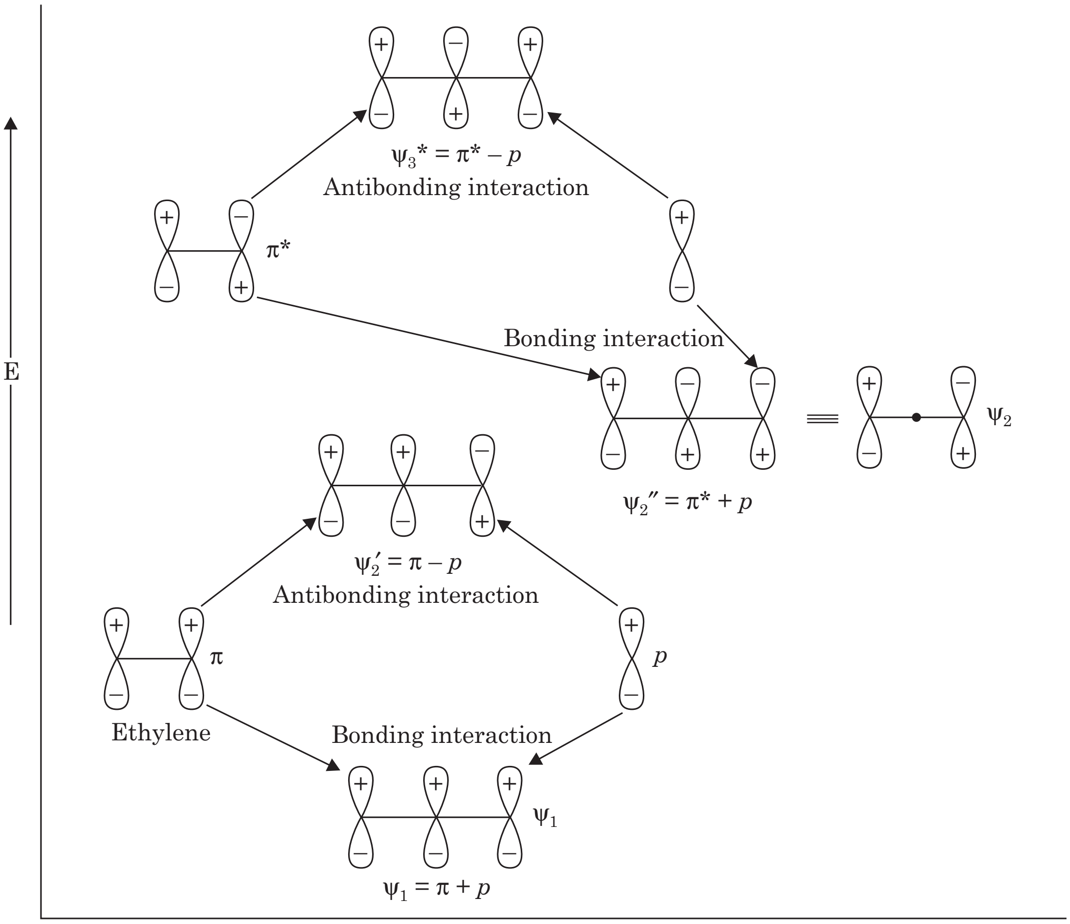


Fig. 1.11

(*i*) The ethylene bonding orbital, π gives linear combination with the *p* orbital in a bonding way and moving down in energy to give ψ_1.

(*ii*) The ethylene antibonding orbital (π^*) gives linear combination with *p* orbital in an antibonding way and moving up in energy to give $\psi_3{}^*$.

(*iii*) The *p* orbital mixes with both the bonding and antibonding orbitals of ethylene. Thus, there is double mixing for the *p* orbital. The lower energy ethylene bonding orbital (π) mixing in an antibonding way to push the *p* orbital up in the energy ($\psi_2{}' = \pi - p$) but the ethylene antibonding orbital mixing in a bonding way to push to *p* orbital down in energy ($\psi_2{}'' = \pi^* + p$). Thus, the net result in the energy change is zero. Under this situation a nodal plane always passes through the central carbon of the chain. This means an electron in ψ_2 has no electron density on the central carbon. Thus, the ψ_2, *i.e.*, central molecular orbital must be non-bonding molecular orbital. Thus, the molecular orbitals of the allylic system is represented as follows (Fig. 1.12).

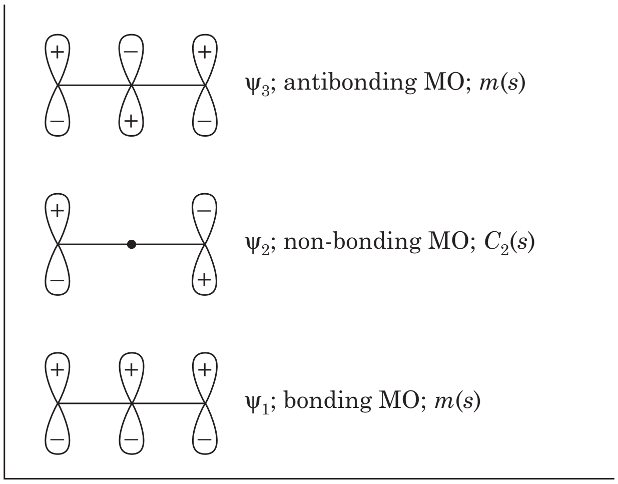


Fig. 1.12 π molecular orbitals of allyl system

From the example of allyl system following generalisation can be made to construct the molecular orbitals of the conjugated open chain system (cation, anion and radical) containing odd number of carbon atoms:

1. Number of conjugated atoms (or *p* orbitals) are always odd. For example, allyl system has three orbitals and 2, 4-pentadienyl system has five orbitals.
2. These systems have always one non-bonding molecular orbital whose energy is always equal to the unhybrid *p* orbital. Non-bonding molecular orbital is always central molecular orbital of the system (Fig. 1.12).
3. If system has *m* (which is always odd) atomic *p* orbitals then it has:
   (*i*) $\frac{m-1}{2}$ bonding molecular orbitals,
   (*ii*) $\frac{m-1}{2}$ antibonding molecular orbitals, and
   (*iii*) one non-bonding molecular orbital.
4. In non-bonding molecular orbital all the nodal planes (*i.e.*, $n - 1$ nodal planes for ψ_n wave function) pass through the carbon nucleus (or nuclei) (Fig. 1.13).

5. For odd ψ_n (ψ_1, ψ_3, ψ_5, ...), all nodal planes pass between two carbon nuclei (Fig. 1.13).
6. For even ψ_n (ψ_2, ψ_4, ψ_6, ...), one nodal plane passes through the central carbon atom and remaining nodal planes pass between two carbon atoms (Fig. 1.13).

Figure 1.13 illustrates schematically the forms of the molecular orbitals for chains up to seven carbon atoms in length with symmetries and nodal planes.

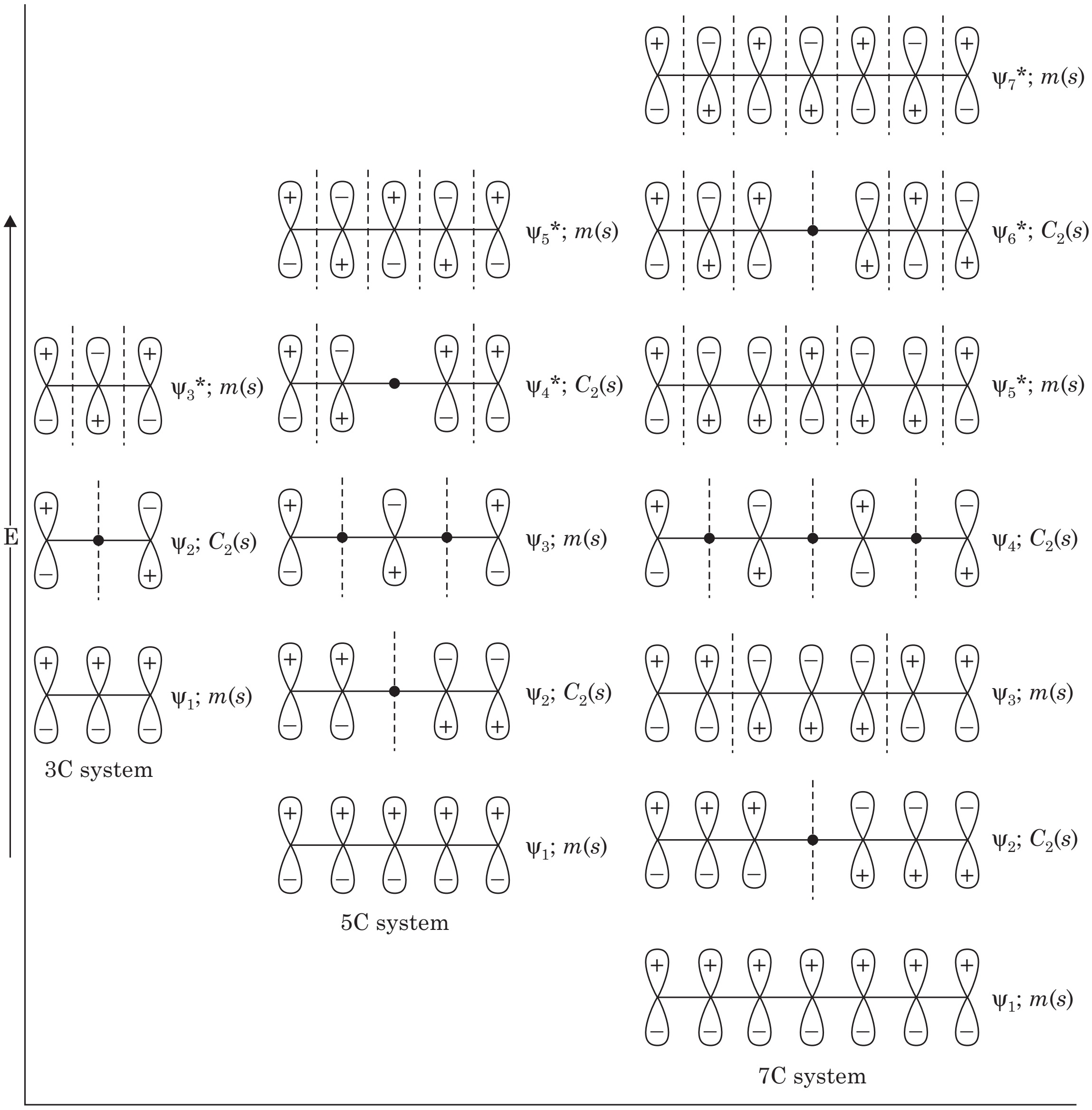


Fig. 1.13 π molecular orbitals of allyl 2, 4-pentadienyl and 2, 4, 6-heptatrienyl system

Electron occupancy of allyl carbocation, allyl free radical and allyl carbanion is shown in Fig. 1.14.

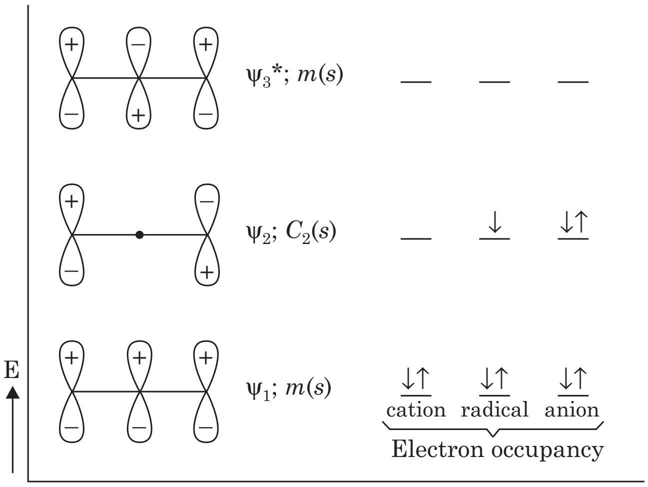


Fig. 1.14 π molecular orbitals with electron occupancy of the allyl system

Similarly, electron occupancy of 2, 4-pentadienyl systems are shown in Fig. 1.15.

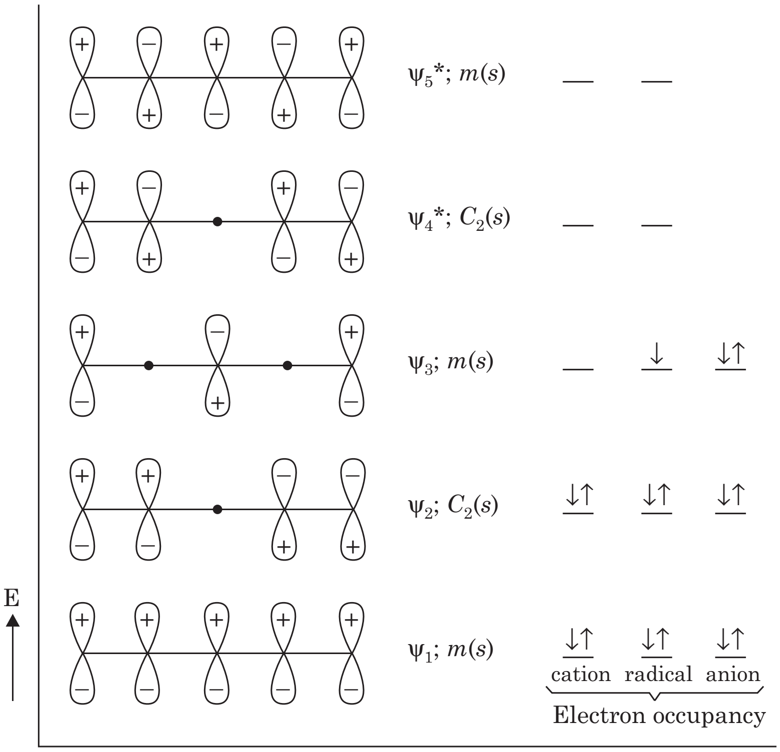


Fig. 1.15 π molecular orbitals with electron occupancy of the 2, 4-pentadienyl system

Notice that cations, radicals and anions involving the same π system have the same molecular orbitals. For example, the MOs of the allyl system apply equally well to the allyl cation, allyl radical and allyl carbanion because all the three species contain the same *p* orbitals. These species differ only in the *number* of π electrons, as shown in the "*electron occupancy*" column of Fig. 1.14.

1.6 FRONTIER MOLECULAR ORBITALS

Two π molecular orbitals are of particular importance in understanding pericyclic reactions. One is the occupied molecular orbital of highest energy, known as *highest occupied molecular orbital* (HOMO). The other is the unoccupied molecular orbital of lowest energy known as *lowest unoccupied molecular orbital* (LUMO). HOMO and LUMO of any given compound have opposite symmetries (Fig 1.16). HOMO and LUMO are referred to as *frontier molecular orbitals*.

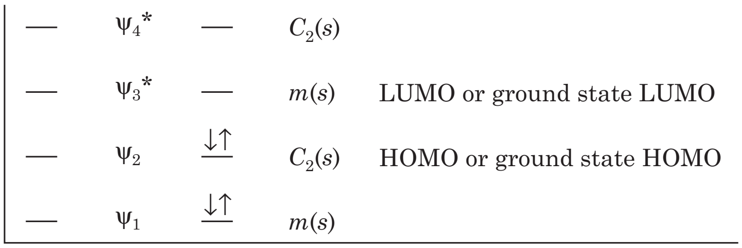


Fig. 1.16 Electronic state of ground state of 1, 3-butadiene

HOMO of the ground state species is also known as ground state HOMO. Similarly, LUMO of the ground state of the species is known as ground state LUMO.

Why are the LUMO and HOMO so important in determining the course of a concerted reaction? The electrons in the HOMO of a molecule are like the outer shell electrons of an atom. They can be removed with the least expenditure of energy because they are already in a highest energy level than any of the other electrons in the molecule. The LUMO of a molecule is the orbital to which electrons can be transformed with the least expenditure of energy.

The higher is the energy of HOMO of a molecule, the more easily electrons can be removed from it. The lower is the energy of the LUMO of the molecule, the more easily electrons can be transferred into it. Therefore, the interaction between a molecule with a high HOMO and a low LUMO is particularly strong.

In general, the smallest the difference in energy between HOMO of one molecule and the LUMO of another with which it is reacting, the stronger is the interaction between the two molecules.

1.7 EXCITED STATES

The molecules and ions we have been discussing can absorb energy from electromagnetic radiation of certain wavelengths. This process is shown schematically in Fig. 1.17 for 1, 3-butadiene. Let us refer to the normal electronic configuration of 1, 3-butadiene as the *ground state*. When 1, 3-butadiene absorbs a photon of proper wavelength *an electron* is promoted from the HOMO (ψ_2) to the LUMO (ψ_3*). The species with the promoted electron is an *excited* *state* of 1, 3-butadiene. The orbital ψ_3^* becomes HOMO and ψ_4^* becomes LUMO of the excited state. HOMO of excited state is termed as excited state HOMO or photochemical HOMO. Similarly, LUMO of the excited state is termed as excited state LUMO or photochemical LUMO (Fig. 1.17).

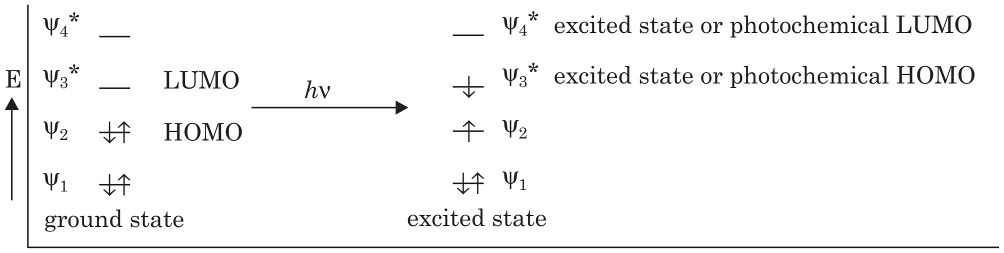


Fig. 1.17

Notice that the HOMO of ground state and excited state have opposite symmetries. Similarly, LUMO of the ground state and excited state also have opposite symmetries.

1.8 SYMMETRIES IN CARBON-CARBON SIGMA BOND

The sigma orbital of a carbon-carbon covalent bond has a mirror plane symmetry, and since a rotation of 180° through its midpoint regenerates the same sigma orbital, it also has a C_2 symmetry. A sigma antibonding molecular orbital is asymmetric with respect to both *m* and C_2 (Table 1.2).

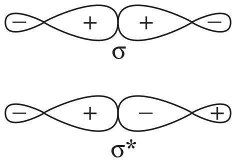


Table 1.2 Symmetric properties of σ and σ* molecular orbitals

Orbital	*m*	C_2
σ*	A	A
σ	S	S

1.9 THEORY OF PERICYCLIC REACTIONS

Pericyclic reactions are defined as reactions that occur by concerted cyclic shift of electrons. According to the Woodward and Hoffmann symmetry of the molecular orbitals that participate in the chemical reaction determines the course of the reaction. They proposed what they called the principle of the *conservation of orbital symmetry*; in the concerted reactions. In the most general terms, the principle means that in concerted pericyclic reactions, the molecular orbitals of the starting materials must be transformed into the molecular orbitals of the product in smooth continuous way. This is possible only if the orbitals have similar symmetry, *i.e.*, orbitals of the reactant and product have similar symmetries.

In concerted reaction product formation takes place by formation of cyclic transition state. The transition state of pericyclic reactions should be intermediate between the electronic ground states of the starting material and product. Obviously, the most stable transition state will be one which conserves the symmetry of the reactant orbitals in passing to product orbitals. In other words, a symmetric (S) orbital in the reactant must transform into a symmetric orbital in the product and that an asymmetric (A) orbital must transform into an asymmetric orbital. If the symmetries of the reactants and product orbitals are not the same, the reaction will not take place in a concerted manner.

If symmetry is conserved during the course of the reaction then reaction will take place and process is known as *symmetry allowed* process. If symmetry is not conserved during the course of the reaction, the reaction is known as *symmetry-forbidden* process. The energy of the transition state (*i.e.*, energy of activation of the transition state) of symmetry allowed process is always lower than the symmetry-forbidden process.

GLOSSARY

Allylic position: The carbon atom adjacent to a carbon-carbon double bond.

Constructive overlap: An overlap of orbitals that contributes to bonding. Overlap of lobes with similar phases is generally constructive overlap.

Delocalised orbitals: A molecular orbital that results from the combination of three or more atomic orbitals. When filled, these orbitals spread electron density over all the atoms involved.

Destructive overlap: An overlap of orbitals that contributes to antibonding. Overlap of lobes with opposite phases is generally destructive overlap.

HOMO: An abbreviation for “highest occupied molecular orbital”. In a photochemically excited state, this is represented as HOMO*.

LUMO: An abbreviation for lowest unoccupied molecular orbital.

Molecular orbitals: Orbitals that include more than one atom in a molecule. Molecular orbital can be bonding, antibonding, or nonbonding.

Bonding molecular orbitals: MOs that are lower in energy than the isolated atomic orbitals from which they are made. Electrons in these orbitals serve to hold the atoms together.

Antibonding molecular orbitals: MOs that are higher in energy than the isolated atomic orbitals from which they are made. Electrons in these orbitals tend to push the atoms apart.

Nonbonding molecular orbitals: MOs that are similar in energy to the isolated atomic orbitals from which they are made. Electrons in these orbitals have no effect on the bonding of the atoms.

Pericyclic reactions: A reaction involving concerted reorganisation of electrons within a closed loop of interacting orbitals.

FURTHER READING

1. R.B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970.

2. T.L. Gilchrist and R.C. Storr, *Organic Reactions and Orbital Symmetry*, 2nd ed. Cambridge University Press, Cambridge, U.K., 1979.

3. J.M. Coxon and B.Halton, *Organic Photochemistry*, Cambridge University Press, Cambridge, U.K., 1974.

PROBLEMS

1. Sketch the *pi* molecular orbitals of

(*a*) 1, 3-butadiene (*b*) 1, 3, 5-hexatriene

2. Sketch the *pi* molecular orbitals of the allyl system. Give electron occupancy in allyl carbonation, allyl free radical and allyl carbanion.

3. Sketch the *pi* molecular orbitals of 2, 4-pentadienyl system. Also draw nodal points in molecular orbitals. Show electron occupancy in its carbocation, free radical and carbanion.

4. Give symmetric properties of HOMO and LUMO of the following systems:

(*i*) Butadiene (*ii*) Excited state butadiene

(*iii*) 1, 3, 5-hexatriene (*iv*) Excited state hexatriene.

5. Show the electronic configuration of the ground state of 1, 3, 5-hexatriene. Give symmetric properties of all the molecular orbitals of 1, 3, 5-hexatriene.

6. Show the electronic configuration of the excited state of 2, 4-pentadienyl cation. Give symmetric properties of HOMO and LUMO of the system.

7. Draw molecular orbitals of 1, 3-butadiene from the linear combination of molecular orbitals of two ethylene molecules.

8. Draw molecular orbitals of allyl system by the use of the linear combination of molecular orbital of one ethylene molecule and one *p*-atomic orbital.

9. Explain why ψ_3 of butadiene has higher energy than the ψ_2?

10. Explain why energy of ψ_5 of 1, 3, 5-hexatriene is less than the ψ_6?

11. What are HOMO and LUMO? Why these two orbitals are so important in pericyclic reactions?

12. Give classification of pericyclic reactions with one example each.

13. (*i*) Draw the *p*-orbital array in the π molecular orbitals of the following ions (*ii*) Draw diagrams showing the occupied orbitals of the ground states and indicate the HOMOs.

(*i*) $CH_3{-}CH{=}CH{-}\overset{\oplus}{C}H{-}CH_3$ (*ii*) $CH_2{=}CH{-}\overset{\ominus}{C}H{-}CH_3$

(*iii*) $CH_3{-}CH{=}CH{-}CH{=}CH{-}\overset{\ominus}{C}H{-}CH_3$.

14. How many approaches have been made to explain the results of pericyclic reactions?

15. What do you understand from frontier orbital and orbital symmetry?

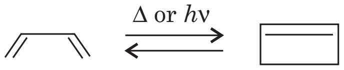
2

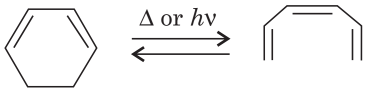
CHAPTER

Electrocyclic Reactions

2.1 INTRODUCTION

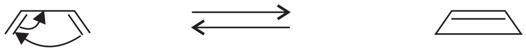
An electrocyclic reaction is the concerted interconversion of a conjugated polyene and a cycloalkene. Electrocyclic reactions are induced either thermally or photochemically.





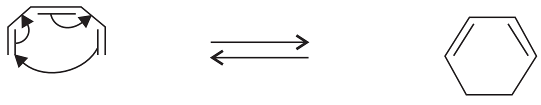
All electrocyclic reactions are reversible reactions. Open-chain partner of the reaction is always conjugated system whereas cyclic partner may or may not contain conjugated system.

In electrocyclic reactions either a ring is formed with the generation of a new σ bond and the loss of a π bond (*i.e.*, gain of one σ bond and loss of one π bond) or ring is broken with the loss of one σ bond and gain of one π bond.



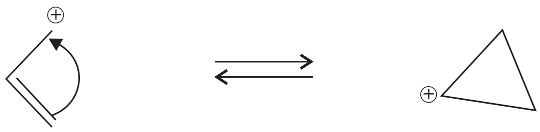
*k*π electrons
(*k* = 4)

(*k*π – 2) electrons + one
σ bond (loss of one π bond
and gain of one σ bond)



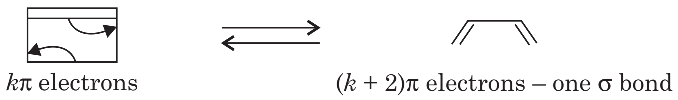
*k*π electrons
(*k* = 6)

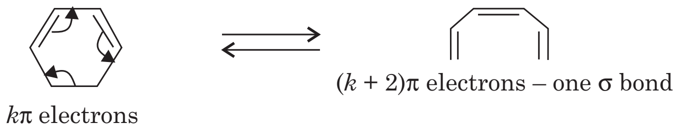
(*k*π – 2) electrons + one σ bond



*k*π electrons

(*k*π – 2)π electrons + one σ bond





Thus electrocyclic reactions can be classified into two categories:

(*i*) Electrocyclic opening of the ring, and

(*ii*) Electrocyclic closure of the conjugated system.

In electrocyclic closure of the ring (or ring closing electrocyclic reaction) if the π system of the open-chain partner contains $k\pi$ electrons, the corresponding cyclic partner contains $(k - 2)\pi$ electrons and one additional σ bond. In ring opening electrocyclic reaction if ring partner contains $k\pi$ electrons, the open chain partner will contain $(k + 2)\pi$ electrons with the loss of one σ bond.

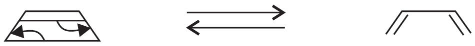
There are two possible stereochemistries for the ring-opening and ring-closing of electrocyclic reactions. They are:

1. Conrotatory process (or motion), and
2. Disrotatory process (motion).

2.2 CONROTATORY AND DISROTATORY MOTIONS IN RING-OPENING REACTIONS

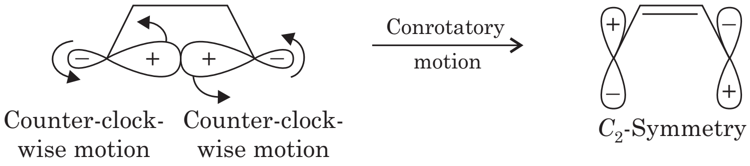
The most common example of the ring opening reaction is the conversion of cyclobutene to 1, 3-butadiene.

This conversion can only be possible if a σ (*sigma*) bond between C_3—C_4 of cyclobutene must break during the course of the reaction.



Ring opening reaction

This σ (*sigma*) bond may break in two ways. *First*, the two atomic orbital components of the σ (*sigma*) bond may both rotate in the same direction, clockwise or counter-clockwise. This process is known as **conrotatory motion** (Fig. 2.1).



Or

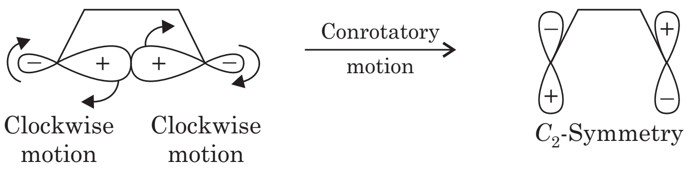


Fig. 2.1 Conrotatory ring-opening

Second, the atomic orbitals may rotate in opposite directions, one clockwise and the other counter-clockwise. This process of ring-opening is known as **disrotatory motion** (Fig. 2.2).

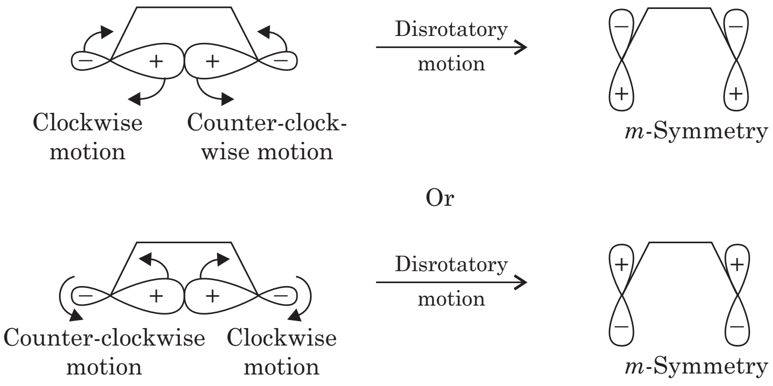


Fig. 2.2 Disrotatory ring-opening

The substituents present on the carbons of the rotating orbitals may also rotate in the direction of the rotating orbitals. Thus in the conrotatory motion substituents rotate in the same direction (Fig. 2.3) and in disrotatory motion substituents rotate in the opposite directions (Fig. 2.4).

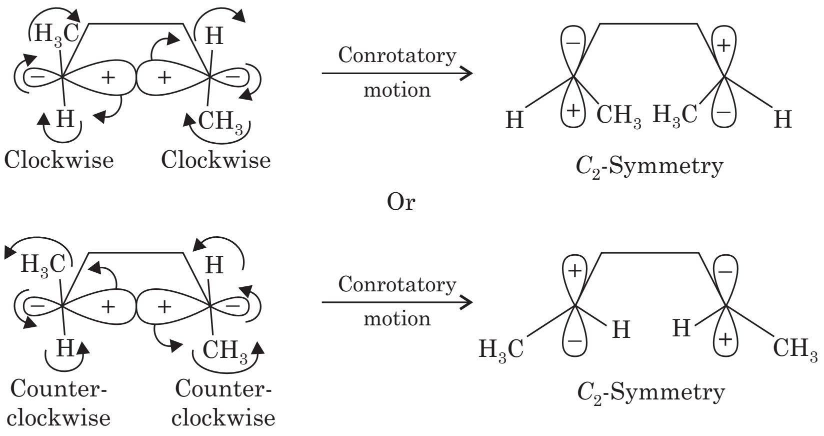


Fig. 2.3 Conrotatory ring-opening, orbitals and groups migrate in the same direction

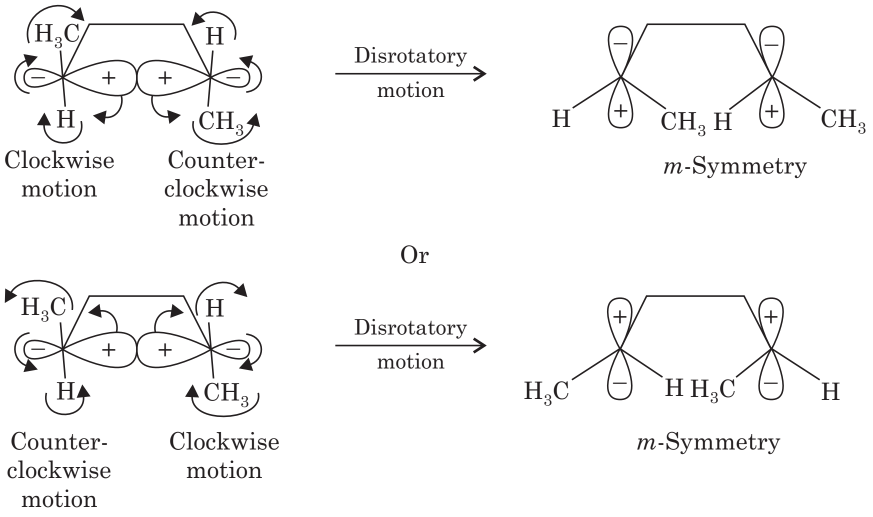


Fig. 2.4 Disrotatory ring-opening, orbitals and groups migrate in the opposite directions

2.3 CONROTATORY AND DISROTATORY MOTION IN RING-CLOSING REACTIONS

When an electrocyclic reaction takes place, the carbon at each end of the conjugated π system must turn in a concerted fashion so that the *p* orbitals can overlap (and rehybridised) to form σ bond that closes the ring. This turning can also occur in two stereochemically distinct ways.

In a conrotatory closure the orbitals and groups of the two carbon atoms turn in the same direction, clockwise or counter-clockwise (Fig. 2.5).

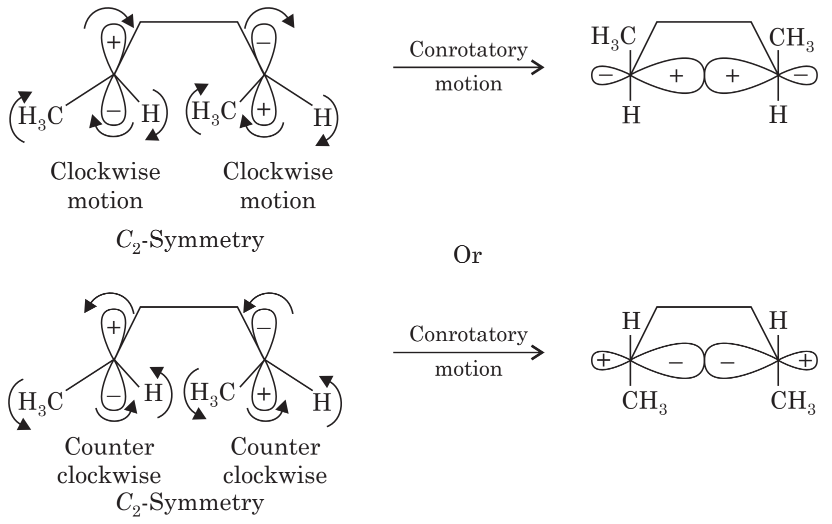


Fig. 2.5 Conrotatory closure of the ring

In a disrotatory closure the orbitals and groups of the two carbon atoms turn in the opposite direction, one clockwise and other counter-clockwise (Fig. 2.6).

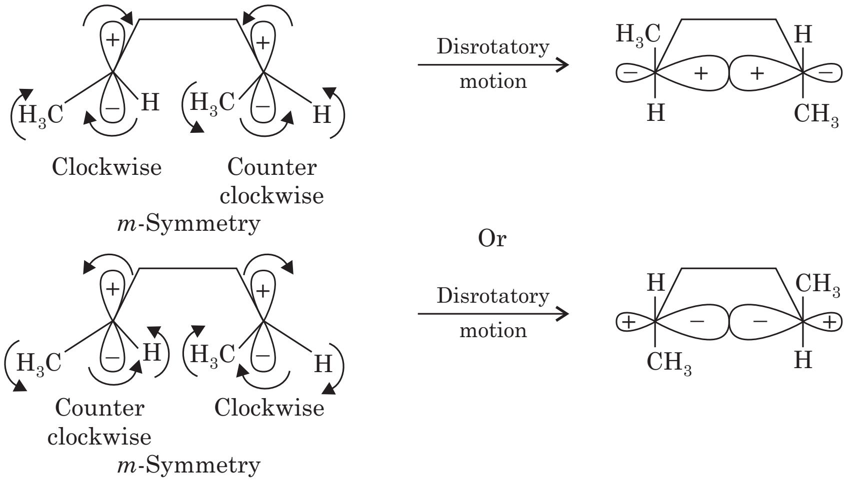


Fig. 2.6 Disrotatory ring-closure

From these examples it is clear that **orbitals having *m*-symmetry always give disrotatory motion.** (Fig. 2.4 and Fig. 2.6) whereas **orbitals having C_2-symmetry give conrotatory motion** (Fig. 2.3 and Fig. 2.5).

The reason behind this rule can be easily understood by recalling that overlap of wave functions of the same sign is bonding (and symmetry allowed reaction) whereas overlap of wave functions of opposite sign is antibonding (and symmetry forbidden process).

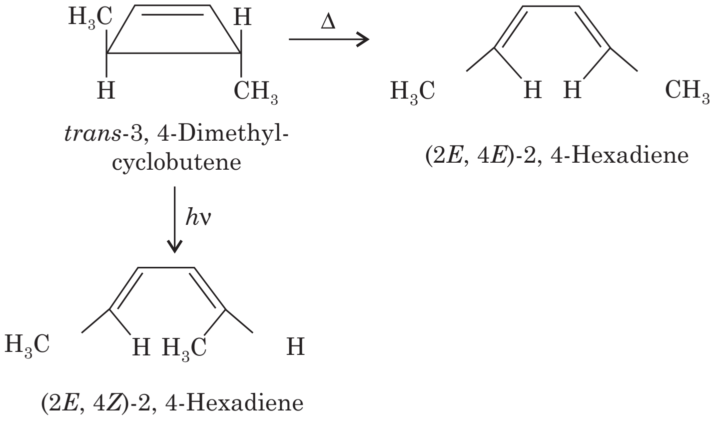
Electrocyclic reactions are highly stereospecific. An intriguing feature about electrocyclic reactions is that the stereochemistry of the product is dependent on whether the reaction is thermally **induced or photo-induced.**

2.3.1 Open Chain Conjugated System having 4nπ Conjugated Electrons

Let us consider the simplest example in which a cyclobutene derivative opens to a 1, 3-butadiene derivative, *i.e.,* open-chain conjugated system has **4*n* conjugated π electrons.**

In thermal condition *trans*-3, 4-dimethylcyclobutene gives (2*E*, 4*E*)-2, 4-hexadiene. Thus, this reaction is completely stereospecific.

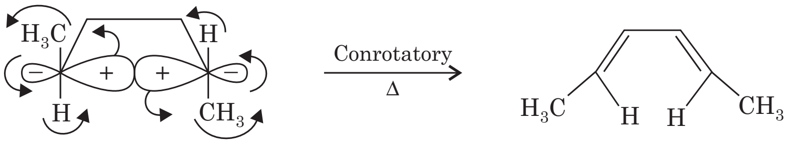
In the photochemical condition the same substrate gives (2*E*, 4*Z*)-2, 4-hexadiene. In this case too, the reaction is completely stereospecific. Thus the reaction can be performed thermally or photochemically, and under either condition the reaction is completely stereospecific.



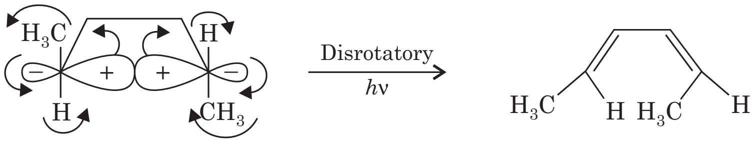
...(1)

...(2)

Stereochemistry of the thermal reaction-1 (of the $4n\pi$ system) can only be explained if process should be conrotatory.



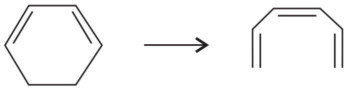
Stereochemistry of the photochemical reaction-2 (of the $4n$, π system) can only be explained if process should be disrotatory.



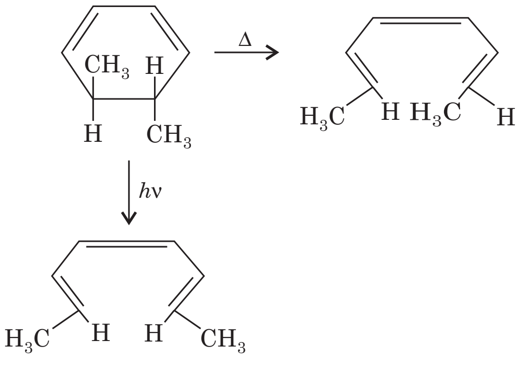
From the above two examples it is clear that **thermally induced electrocyclic reaction involving $4n\pi$ conjugated electrons require conrotatory motion and photochemically induced electrocyclic reaction require disrotatory motion.**

2.3.2 Open Chain Conjugated System having (4n + 2)π Conjugated Electrons

The simplest example of this category is the ring-opening of 1, 3-cyclohexadiene into 1, 3, 5-hexatriene.



In thermal condition 5, 6-*trans*-dimethyl-1, 3-cyclohexadiene is converted exclusively to (2*E*, 4*Z*, 6*Z*)-2, 4, 6-octatriene. In the photochemical condition the same substrate is converted exclusively to (2*E*, 4*Z*, 6*E*)-2, 4, 6-octatriene.



...(3)

...(4)

These two conversions are also highly stereospecific. Stereochemistry of these two reactions (*i.e.,* reaction-3 and 4) can only be explained if process should be disrotatory in thermal condition and conrotatory in photochemical condition.

On the basis of these experimental results the stereochemistry of electrocyclic reactions can be summarised by noting that thermally induced electrocyclic reactions involving $4n\pi$ electrons require conrotatory motion. Under similar conditions, electrocyclic reactions involving $(4n + 2)\pi$ electrons follow disrotatory motion. Similarly, photo-induced electrocyclic reactions involving $4n\pi$ electrons require disrotatory motion. Under similar conditions, electrocyclic reactions involving $(4n + 2)\pi$ electrons follow conrotatory motion.

A summary of the type of motion to be expected from different polyenes under thermal and photochemical conditions is shown in Table 2.1.

Table 2.1

Number of π electrons	*Condition (mode of activation)*	*Motion*
$4n$	(*i*) Thermal (*ii*) Photochemical	Conrotatory Disrotatory
$4n + 2$	(*i*) Thermal (*ii*) Photochemical	Disrotatory Conrotatory

The above experimental results can be explained by the four theories given for pericyclic reactions.

2.4 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

A methodology for quickly predicting whether a given pericyclic reaction is allowed by examining the symmetry of the highest occupied molecular orbital (HOMO) (in case of unimolecular reaction) and, if the reaction is bimolecular, the lowest unoccupied molecular orbital (LUMO) of the second partner.

Thus, electrocyclic reaction is analysed by HOMO of the open chain partner because reaction is unimolecular reaction. The stereochemistry of an electrocyclic process is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the open chain partner, regardless of which way the reaction actually runs. In thermal condition HOMO is always ground state HOMO whereas in photochemical condition HOMO is always first excited state HOMO.

If the highest occupied molecular orbital has m symmetry, the process will be disrotatory. On the other hand, if HOMO has C_2-symmetry then the process will be conrotatory (Table 2.2).

Table 2.2

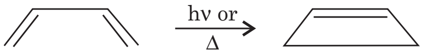
Symmetry in HOMO	*Mode of rotation*
m-Symmetry	Disrotatory
C_2-Symmetry	Conrotatory

For any electrocyclic reaction there are two conrotatory and two disrotatory modes of ring cleavage and ring closure. The two conrotatory modes can give same or different products. Similarly, the two disrotatory modes can also give the same or different products.

Now we are in a position to consider specific examples of the application of the FMO method.

2.4.1 Cyclisation of 4nπ Systems

1. Electrocyclic ring-closure reaction given by butadiene: 1, 3-butadiene is the first member of the conjugated polyene having 4*n*π electrons.



Thermal-induced cyclisation: When 1, 3-butadiene is heated, reaction takes place from the ground state. The electrons that are used for the σ (*sigma*) bond formation are in the HOMO (ψ_2 in this case). Pertinent *p* orbitals in ground state HOMO has C_2-symmetry. For the new σ (*sigma*) bond to form, rotation must be conrotatory. Disrotatory motion would not place the in-phase lobes together.

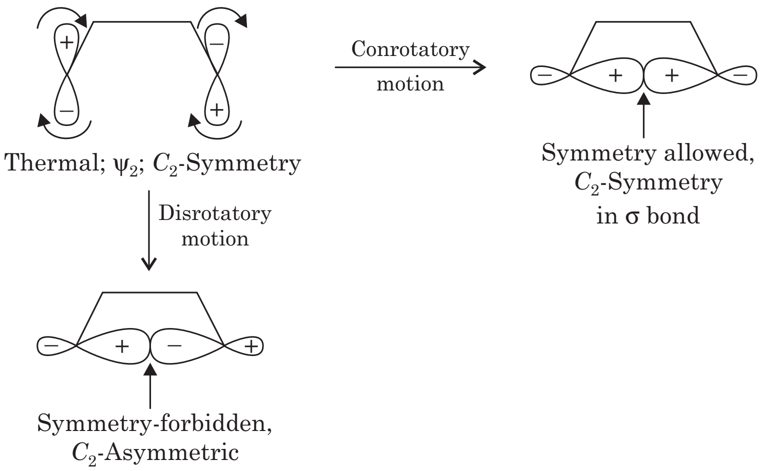
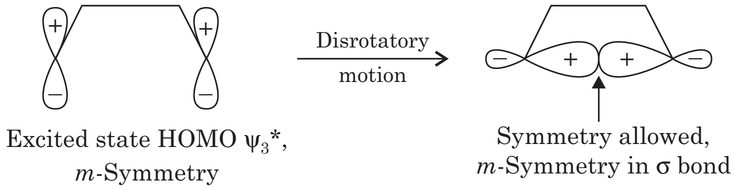
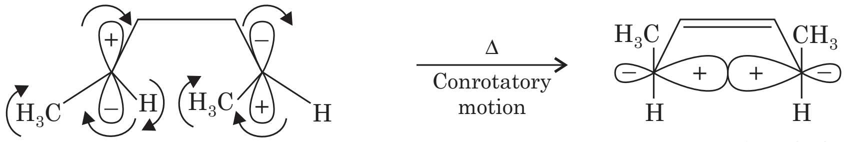


Photo-induced cyclisation: In photo-induced cyclisation, the first excited HOMO of 1, 3-butadiene is ψ_3^* which has *m* symmetry. For the new σ (*sigma*) bond to form, rotation must be disrotatory.



Let us return to (2*E*, 4*Z*)-2, 4-hexadiene to see why the *cis*-3, 4-dimethylcyclobutene results from the thermal cyclisation and the *trans*-isomer from the photo cyclisation.

In the case of the thermal cyclisation the ground state HOMO is ψ_2 which has C_2-symmetry. Thus, conrotatory motion is required for σ (*sigma*) bond formation. Both methyl groups rotate in the same direction, as a result they end up on the same side of the ring or *cis* is the product.

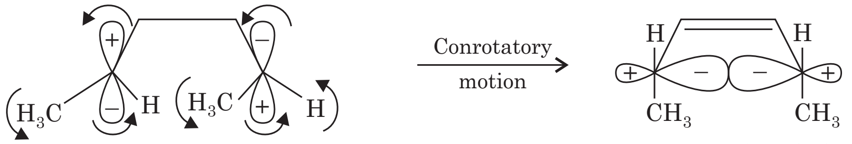


Clockwise Clockwise

(2*E*, 4*Z*)-2, 4-Hexadiene ψ_2, C_2-Symmetry

cis-3, 4-Dimethyl-cyclobutene

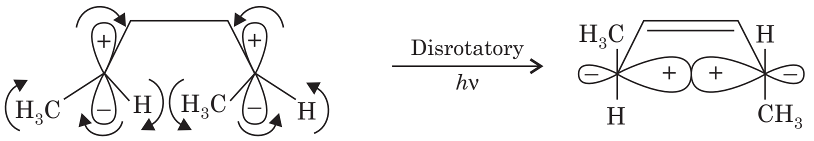
Or



Counter clockwise Counter clockwise

cis-3, 4-Dimethyl-cyclobutene

In the case of photocyclisation the excited state HOMO is ψ_3^* which has *m*-symmetry. Thus, disrotatory motion is required for the σ bond formation. In disrotatory motion, one of the methyl groups, rotates up and the other rotates down. The result is that both methyl groups are *trans* in the product.

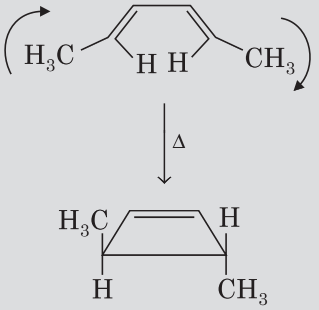


Excited state HOMO ψ_3^*, *m*-Symmetry

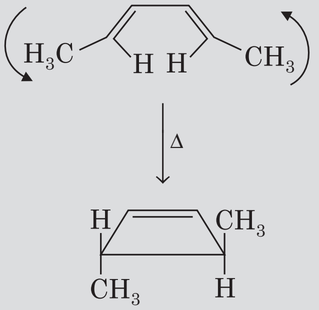
trans-3, 4-Dimethyl-cyclobutene

Problem 1: *Show both conrotatory processes for the thermal electrocyclic conversion of (2E, 4E)-2,4-hexadiene into 3,4-dimethylcyclobutene. Explain why the two processes are equally alike?*

Solution: The two different conrotatory motions are as follows:



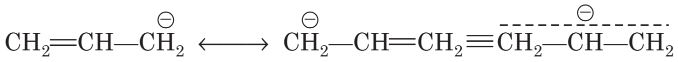
(1)



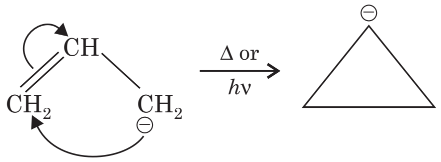
(2)

They are equally likely because they [(1) and (2)] are enantiomeric. Enantiomers have equal energies. Enantiomeric pathways have identical energies at all points and therefore identical rates.

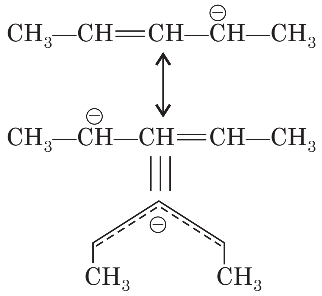
2. Electrocyclic ring-closure given by allyl carbanion: Allyl carbanion is also a $4n\pi$ conjugated system.

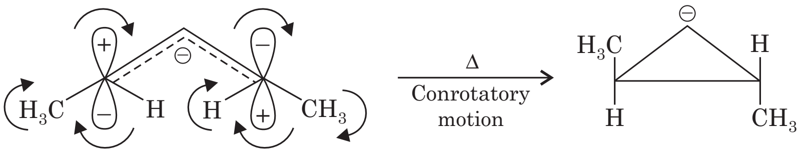


$$CH_2{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH_2 \equiv \overset{\ominus}{CH_2{-}CH{-}CH_2}$$

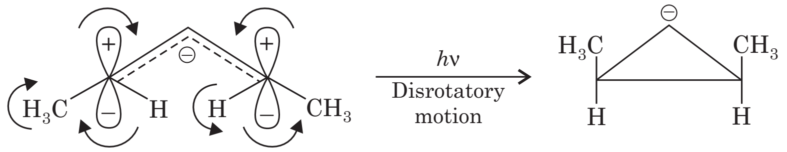


HOMO of the allyl carbanion in the ground state is ψ_2 which has C_2-symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition.





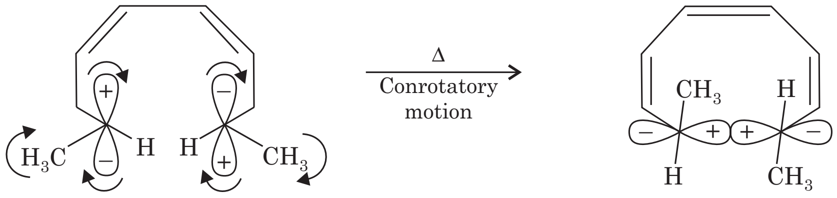
In case of photocyclisation, the excited HOMO is ψ_3^* which has m-symmetry. Thus, disrotatory motion is required for σ (*sigma*) bond formation.



3. Electrocyclic ring-closure reaction given by 1, 3, 5, 7-octatetraene: 1, 3, 5, 7-octatetraene and its derivatives contain $4n\pi$ conjugated electrons.

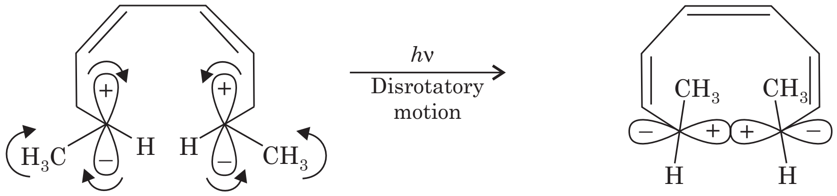
Consider the electrocyclic ring-closure of (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene in thermal and photochemical conditions.

Thermal-induced cyclisation: The tetraene is a $4n$ polyene. Its ground state HOMO is ψ_4 which has C_2-symmetry. Therefore, conrotatory motion is the mode of cyclisation.



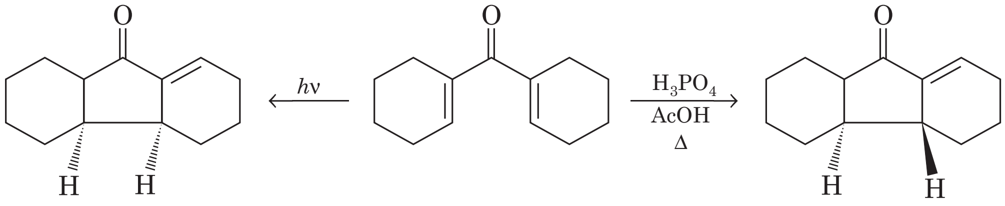
trans-7, 8-Dimethyl-1, 3, 5-cyclotriene

Photo-induced cyclisation: In case of photo-induced cyclisation the excited state HOMO is ψ_5^* which has *m*-symmetry. Thus disrotatory motion is the mode of cyclisation.

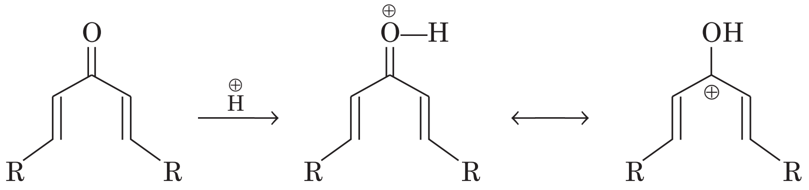


cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

4. Nazarov cyclisation: Nazarov cyclisation is given by 1, 4-pentadiene-3-one and its derivatives. The product of the reaction is cyclopentenone. The reaction is conrotatory electrocyclic ring-closure under thermal condition and disrotatory ring-closure under photochemical conditions.

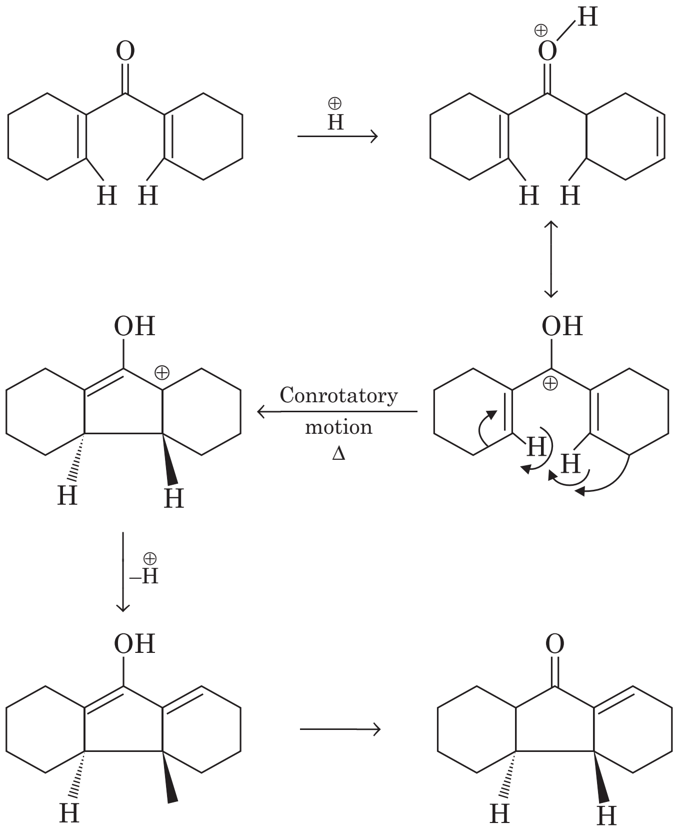


Nazarov cyclisations require acid. Under acidic condition the substrate converts into cation which has 4π conjugated electrons.

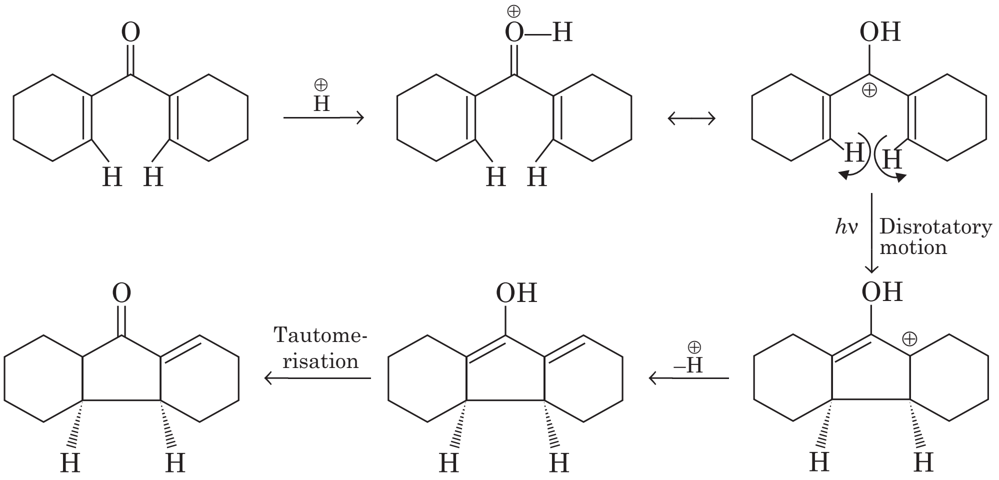


Under thermal condition, the motion is conrotatory and under photochemical conditions the motion is disrotatory because the conjugated system has $(4n)\pi$ conjugated electrons.

The reaction under thermal condition



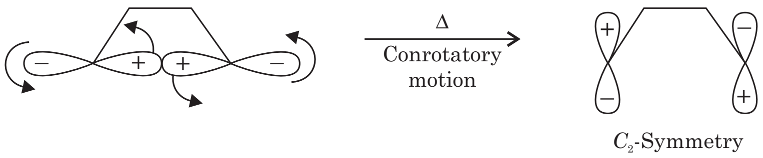
The reaction under photochemical conditions



2.4.2 Electrocyclic Ring-Opening in which Polyene has 4nπ Electrons

Conversion of cyclobutene to butadiene

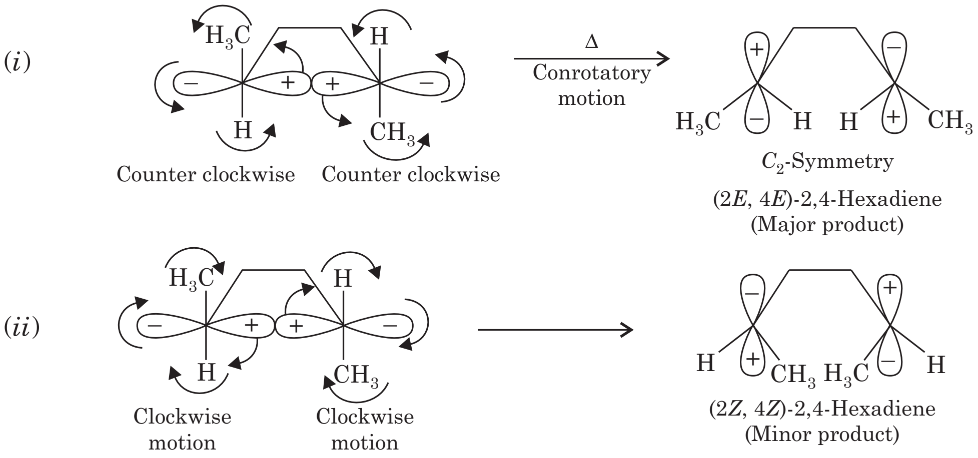
(A) ***Thermal-induced ring opening:*** In the ring-opening reactions stereochemistry of the product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the butadiene and its derivative will be ψ_2 which has C_2-symmetry. The cyclobutene ring must open in such a fashion that the σ bond orbitals transform into the HOMO of the product having C_2-symmetry. To get C_2-symmetry in the product HOMO, motion should be conrotatory in the ring opening of the reaction.



Thus, if the open-chain polyene has 4*n*π electrons then the process is always *conrotatory* in thermal condition whether the reaction is ring-closure or ring opening.

Let us take the stereochemistry of the ring opening of *trans*-3, 4-dimethylcyclobutene.

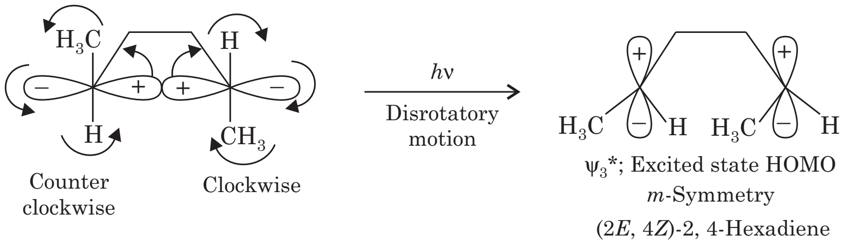
There is possibility of two modes of conrotatory motion, counter clockwise and clockwise motions.



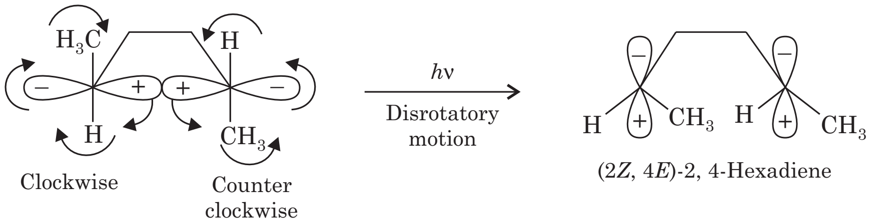
Thus, the thermal process is conrotatory with two products possible in the above case. The conrotation in the second case (clockwise rotation) leads to severe steric interactions between two methyl groups. This interaction is avoided in the first process (rotation is counter clockwise) in which two methyl groups move away from each other, and this is the favoured process.

(B) ***Photo-induced ring opening:*** The photo state HOMO of the open chain butadiene and its derivative will be $\psi_3{*}$ which has *m*-symmetry. Thus, the cyclobutene ring must be open in such a fashion that the σ bond orbitals transform into the excited state HOMO of the product having *m*-symmetry. To get *m*-symmetry in excited state HOMO of the product, motion should be disrotatory in the ring-opening of the reaction. There is also possibility of two modes of disrotatory motion.

(*i*)



(*ii*)

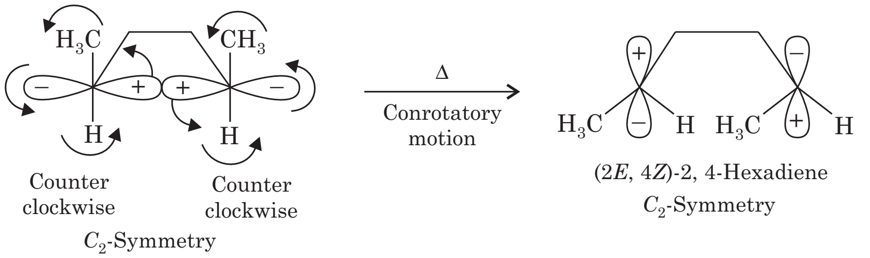


Thus, photo-induced process is disrotatory with either possible disrotation giving same product.

Let us take the conversion of *cis*-3, 4-dimethylcyclobutene into 2, 4-hexadiene.

Thermal ring-opening

(*i*)



(*ii*)

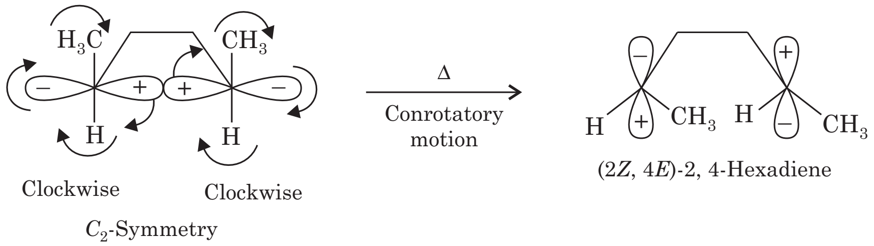
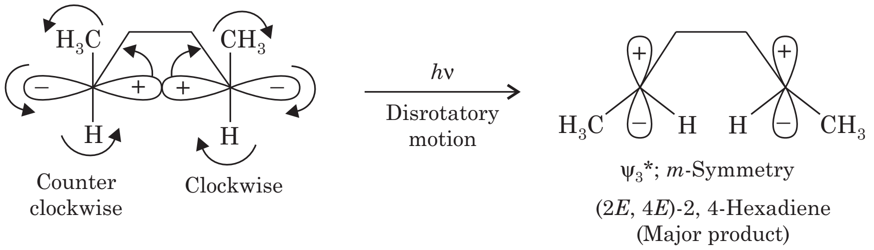
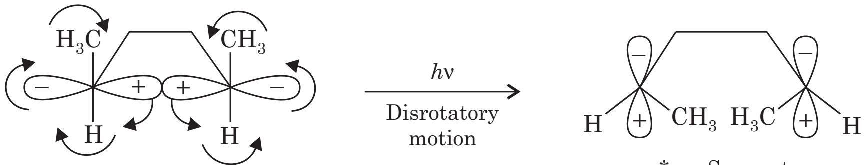


Photo-induced ring-opening

(*i*)



(*ii*)



Clockwise Counter clockwise

ψ_3*; *m*-Symmetry

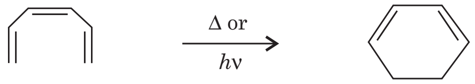
(2*Z*, 4*Z*)-2, 4-Hexadiene
(Minor product)

In case of *cis*-3, 4-dimethylcyclobutene, the thermal process is conrotatory with either possible conrotation giving the same product. The photochemical process is disrotatory with two possible products.

2.4.3 Cyclisation of (4n + 2)π Systems

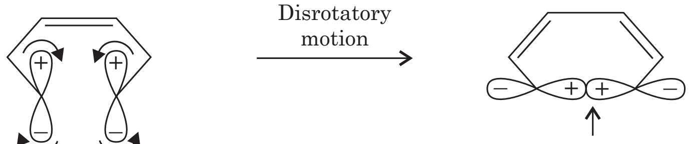
1. Electrocyclic ring-closure reaction given by 1, 3, 5-hexatriene

1, 3, 5-Hexatriene is the most common example of the polyene having (4*n* + 2)π conjugated electrons.



1, 3, 5-Hexatriene 1, 3-Cyclohexadiene

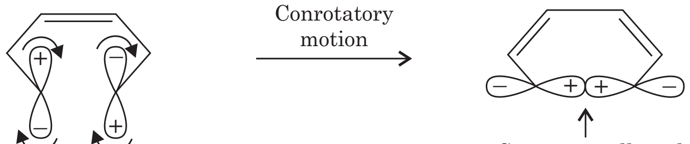
(A) ***Thermal-induced cyclisation:*** ψ_3 is the ground state HOMO of 1, 3, 5-hexatriene which has *m*-symmetry. Therefore, the thermal cyclisation proceeds by disrotatory motion.



ψ_3, Ground state HOMO
m-Symmetry

Symmetry-allowed
(*m*-Symmetry)

(B) ***Photo-induced cyclisation:*** When an electron of 1, 3, 5-hexatriene is promoted by photon absorption, ψ_4* becomes the HOMO. This excited state HOMO has C_2-symmetry. Therefore, photo-induced cyclisation proceeds by conrotatory motion.

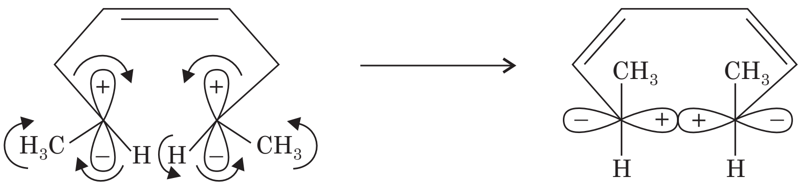


ψ_4*; Excited HOMO
(C_2-Symmetry)

Symmetry-allowed
(C_2-Symmetry)

Consider the stereochemistry of the thermal and photo-induced closure of (2*E*, 4*Z*, 6*E*)-2, 4, 6-octatriene to 5, 6-dimethyl-1, 3-cyclohexadiene.

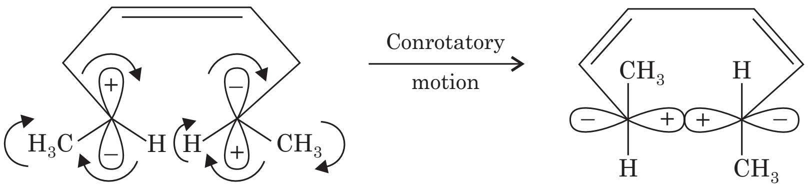
(A) ***Thermal-induced cyclisation:*** In the case of the thermal induced cyclisation, the ground state HOMO is ψ_3 which has *m*-symmetry. Thus, disrotatory motion is required for sigma bond formation.



ψ_3, Ground state HOMO
(*m*-Symmetry)

cis-5, 6-Dimethyl-1, 3-cyclohexadiene

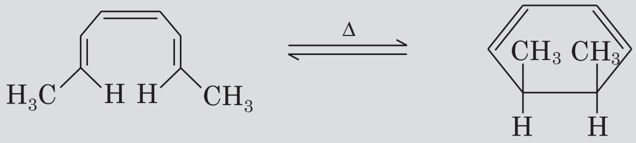
(B) ***Photo-induced cyclisation:*** In case of photo-induced cyclisation, the excited state HOMO is ψ_4^* which has C_2-symmetry. Therefore, conrotatory motion is required for σ (*sigma*) bond formation.



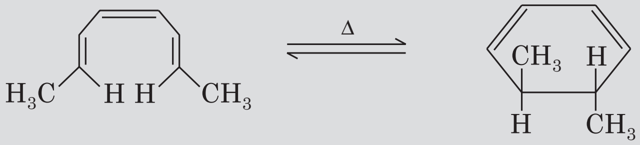
trans-5, 6-Dimethyl-1, 3-cyclohexadiene

Problem 2: *Which one of the following electrocyclic reactions should occur readily by a concerted mechanism?*

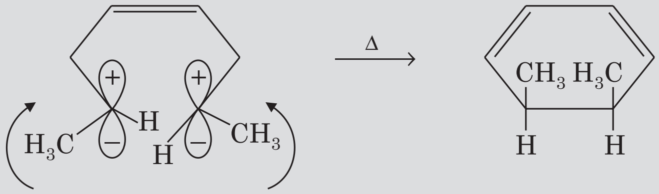
Reaction 1



Reaction 2

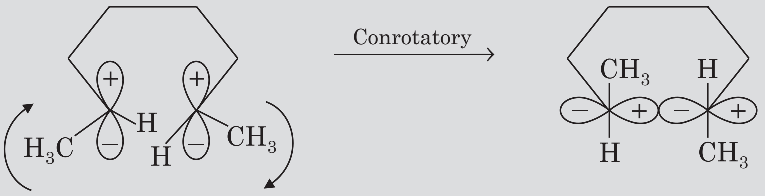


Solution: Reaction 1 is a disrotatory reaction involving $(4n + 2)\pi$ electrons because this will give *cis* product. This reaction is allowed reaction. This reaction, therefore, can occur readily by a converted mechanism.



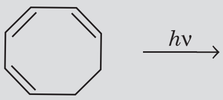
HOMO is ψ_3 *m*-Symmetry
disrotatory motion

Reaction 2 is a conrotatory reaction involving $(4n + 2)\pi$ electrons because conrotatory motion will give *trans* product. It does not allow because the reaction is symmetry forbidden reaction.

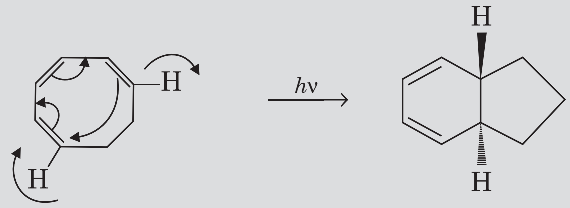


Thus, the reaction does not occur readily.

Problem 3: *Complete the following reaction and give stereochemistry of the product.*

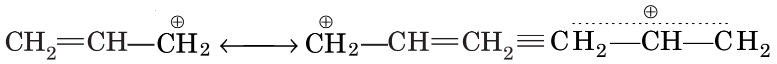


Solution: Reaction is photo-induced reaction. Reactant has $(4n + 2)\pi$ electrons. Its excited HOMO is ψ_4^* which has C_2-symmetry. Thus, motion is conrotatory motion.

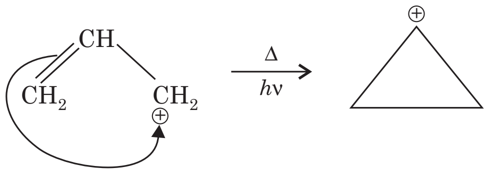


2. Electrocyclic ring-closure reaction given by allyl carbocation

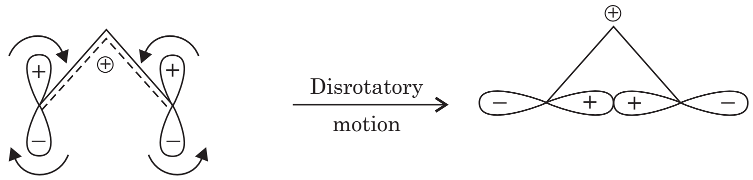
Allyl carbocation contains $(4n + 2)\pi$ conjugated electrons.



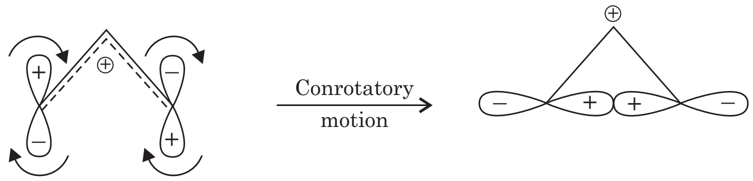
$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2 \equiv \overset{\oplus}{\overline{CH_2{-}CH{-}CH_2}}$$



(A) ***Thermal-induced cyclisation:*** HOMO of the allyl carbocation in the ground state is ψ_1 which has *m*-symmetry. Therefore, disrotatory motion is the mode of cyclisation in the thermal condition.



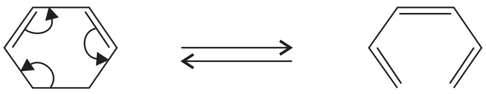
(B) ***Photo-induced cyclisation:*** HOMO of the allyl carbocation in the excited state is ψ_2 which has C_2-symmetry. Thus, conrotatory motion is required for σ (*sigma*) bond formation.



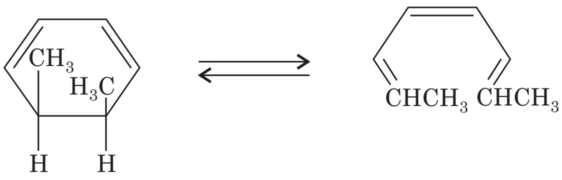
2.4.4 Electrocyclic Ring-opening in which Polyene has (4*n* + 2)π Electrons

1. Conversion of 1, 3-cyclohexadiene to 1, 3, 5-hexatriene system

The most common example of this class is the conversion of 1, 3-cyclohexadiene to 1, 3, 5-hexatriene.

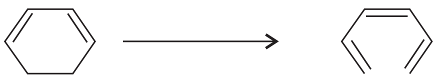


Let us take the example of the ring opening of a *cis*-5, 6-dimethyl-1, 3-cyclohexadiene into 2, 4, 6-octatriene.



(A) ***Thermal ring-opening:*** As mentioned earlier that in the ring opening reactions stereochemistry of product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the triene will be ψ_3 which has *m*-symmetry. The cyclohexadiene ring therefore, must open in such a fashion that σ bond orbitals transform into the ground state HOMO of the product having *m*-symmetry. To get *m*-symmetry in the HOMO of the product, motion should be disrotatory in the ring opening of the reaction.

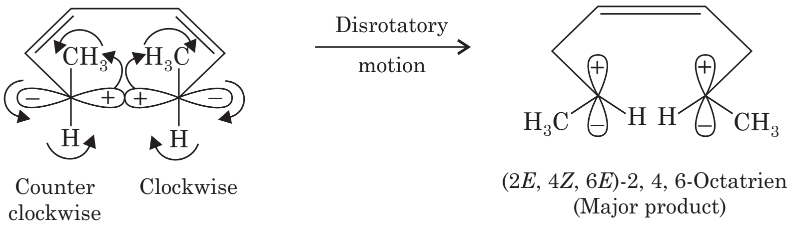
The above results can be obtained in short as follows:



Ground state HOMO is ψ_3 which has *m*-symmetry. Therefore, motion is disrotatory

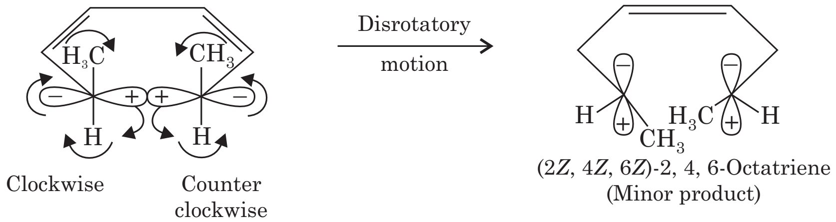
Two modes of disrotatory motions can take place as follows:

(*i*)



(2*E*, 4*Z*, 6*E*)-2, 4, 6-Octatriene
(Major product)

(*ii*)



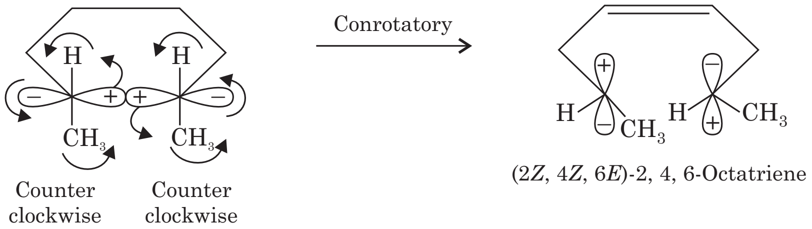
(2*Z*, 4*Z*, 6*Z*)-2, 4, 6-Octatriene
(Minor product)

Thus, the thermal process is disrotatory with two possible products, one is major and the other is minor due to the steric reasons.

(B) ***Photo-induced ring-opening:*** The photo state HOMO of the triene system is ψ_4^* which has C_2-symmetry. To get C_2-symmetry in the product, motion should be conrotatory in the ring opening reaction.

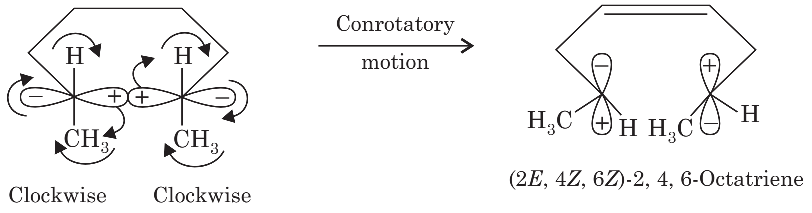
Consider the two modes of conrotatory motions:

(*i*)



(2*Z*, 4*Z*, 6*E*)-2, 4, 6-Octatriene

(*ii*)

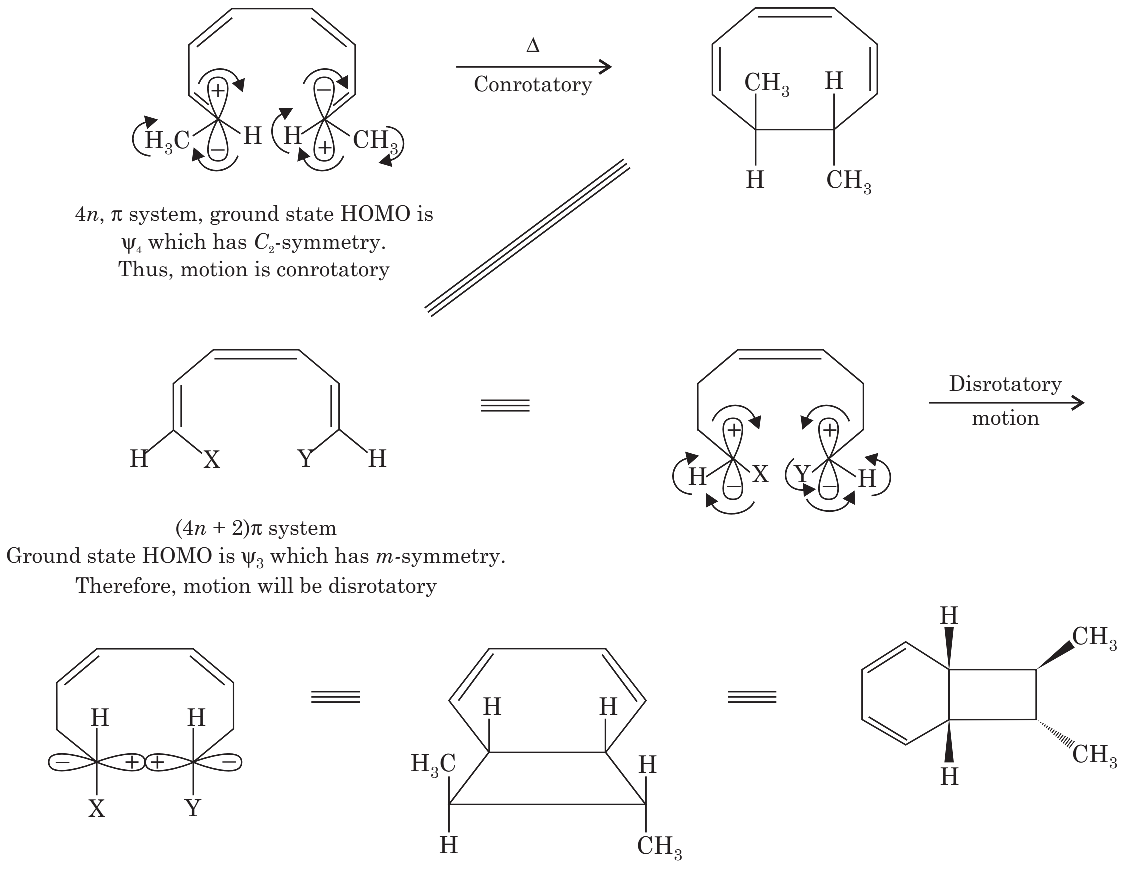


In this case either possible conrotation giving the same product.

2. Thermal electrocyclic reaction given by (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene

The thermally induced electrocyclic reaction of (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene provide elegant examples of electrocyclic reactions.

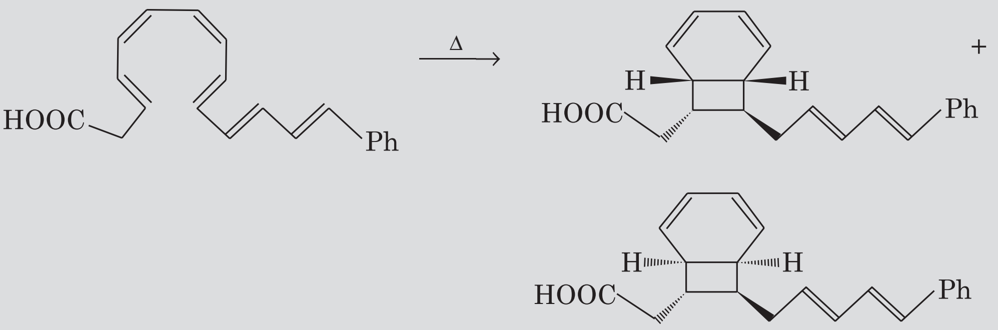
The starting tetraene forms a cyclooctatriene at room temperature. The tetraene is a 4*n* polyene; therefore, conrotatory motion is the expected mode of cyclisation. Indeed the *trans*-7, 8-dimethyl-1, 3, 5-cyclooctatriene is the product of this initial cyclisation. When this cyclooctatriene is heated above room temperature, another electrocyclic ring closure occurs. However, the cyclooctatriene is a (4*n* + 2)π polyene; therefore, this thermally induced electrocyclic reaction proceeds with disrotatory motion, and a *cis* ring junction is formed.



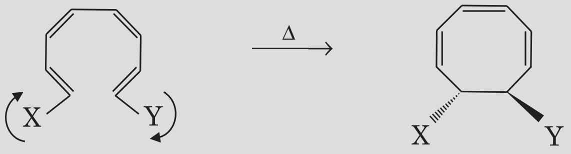
4*n*, π system, ground state HOMO is ψ_4 which has C_2-symmetry. Thus, motion is conrotatory

(4*n* + 2)π system
Ground state HOMO is ψ_3 which has *m*-symmetry.
Therefore, motion will be disrotatory

Problem 4: *Give mechanism of the following reaction:*

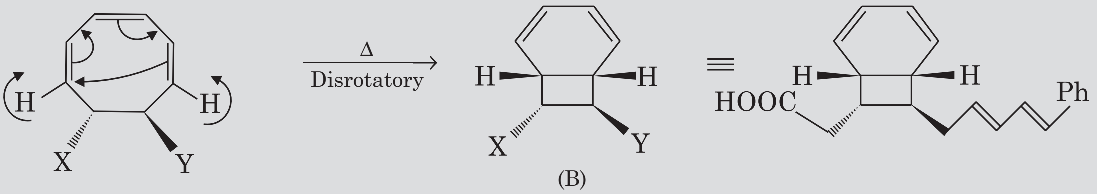


Solution: The first step is electrocyclic ring closure. Compound has $(4n)$ π electrons, hence motion is conrotatory.



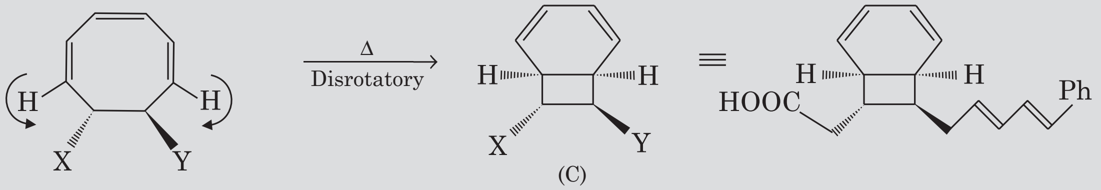
(A)

Compound (A) can further undergo electrocyclic ring-closure reaction. Since (A) has $(4n + 2)\pi$ electrons, hence mode will be disrotatory.



(B)

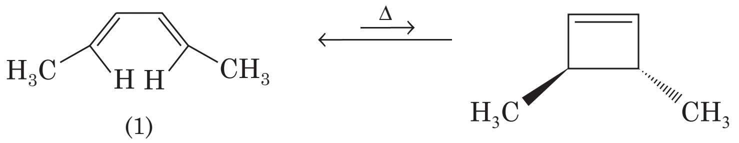
Or



(C)

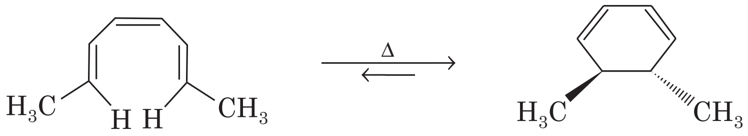
2.4.5 Selection Rules and Microscopic Reversibility

The selection rules in Table 2.1 are based on the orbital symmetry of the open-chain conjugated polyene reactant. However, it is important to understand that these rules refer to the rates of pericyclic reactions. These rules have nothing to say about the positions of the equilibrium involved. Thus, the electrocyclic reaction of the diene (1) to give a cyclobutene favours the diene at equilibrium because of the strain in the cyclobutene.



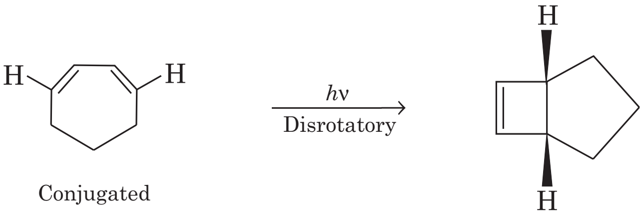
(1)

On the other hand, electrocyclic reaction of conjugated triene (2) favours the cyclic compound because σ (*sigma*) bonds are stronger than π (*pi*) bonds, and because six-membered rings are relatively stable.



(3)

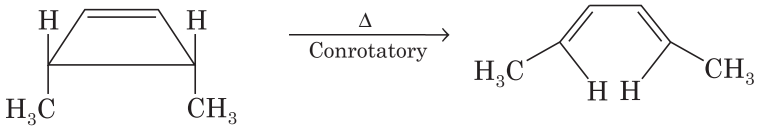
It is also common for a photochemical reaction to favour the less stable isomer of an equilibrium. For example, in the given reaction, the conjugated diene absorbs UV light, but the bicyclic compound does not, hence, the photochemical reaction favours the latter.



Non-conjugated

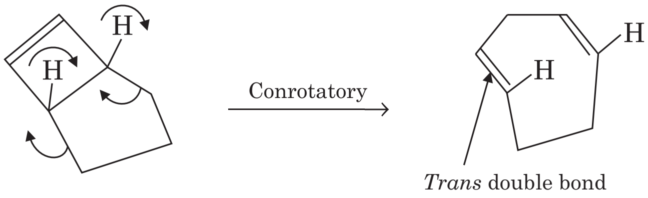
In summary, the selection rules (of Table 2.1) do not indicate which component of the equilibrium will be favoured—only whether the equilibrium will be established at a reasonable rate.

The principle of microscopic reversibility (*i.e.,* any reaction and its reverse proceed by the forward and reverse of the same mechanism) assures us that selection rules apply equally well to the forward and reverse of any pericyclic reaction, because the reaction in both directions must proceed through the same transition state. Hence, an electrocyclic ring-opening must follow the same selection rules as its reverse, an electrocyclic ring closure. Thus, the thermal ring-opening reaction of the cyclobutene (3), like the reverse ring closure reaction, must be a conrotatory process.



(3)

In the following electrocyclic ring opening reaction, the allowed thermal conrotatory process would give a highly strain molecule containing a *trans* double bond within a small ring.



Although the selection rules suggest that the reaction could occur, it does not because of the strain in the product (*trans* cycloalkenes with seven or fewer carbons have never been observed). Thus, allowed reactions are sometimes prevented from occurring for reasons having nothing to do with selection rules.

2.5 CORRELATION DIAGRAM

The diagram that shows the correspondence in energy and symmetry between relevant reactant and product orbitals is called orbital correlation diagram or simply correlation diagram. This method can be used for any pericyclic reaction, but is usually utilised only for electrocyclic reactions. The relevant orbitals are those that undergo change during the reaction. Correlation diagram is based on the fundamental rule of the conservation of orbital symmetry as proposed by Woodward and Hoffmann. According to this rule orbital symmetry be conserved throughout the course of reaction in concerted reactions. Thus, as a concerted reaction proceeds it must do so with conservation of orbital symmetry. This means that a symmetric orbital in the starting material must transform into a symmetric orbital in the product and that an asymmetric orbital must transform into an asymmetric orbital. The orbitals that correlate (transform into each other) are connected by lines (Fig. 2.9) keeping in view that there is correlation between orbitals of same symmetry having minimum energy difference. The diagram is constructed as follows: in separate columns the relevant orbitals of reactant and product are listed in their order of relative energies; each orbital is classified on the basis of the symmetry elements retained at all points along the reaction coordinate; line are drawn between the reactant and product orbitals connecting the lowest energy orbitals of the same symmetry type.

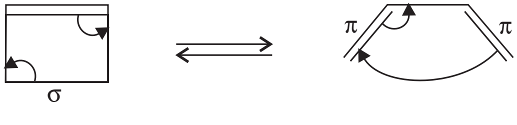
The following two conclusions can be drawn by correlation diagram:

(*i*) Thermal transformation is symmetry allowed reaction when the ground state orbitals of the reactant correlate with ground state orbitals of the product.

(*ii*) Photochemical transformation is symmetry allowed when first excited state orbitals of the reactant correlate with first excited state orbitals of the product.

2.5.1 Correlation Diagram of the Electrocyclic Reaction in which Polyene has 4nπ Electrons

We are now in a position to consider an electrocyclic reaction in terms of orbital symmetry. Let us exemplify the above principle by analysing the cyclobutene-butadiene transformation.



The orbitals that undergo direct changes in cyclobutene are σ, π and the related antibonding orbitals, σ* and π*; these orbitals pass on to the four π molecular orbitals of butadiene, *viz.*, ψ_1, ψ_2, ψ_3* and ψ_4*. For correlation diagram, all these orbitals are listed in order of increasing energy alongwith their mirror plane (*m*) and C_2-symmetric properties (Fig. 2.7).

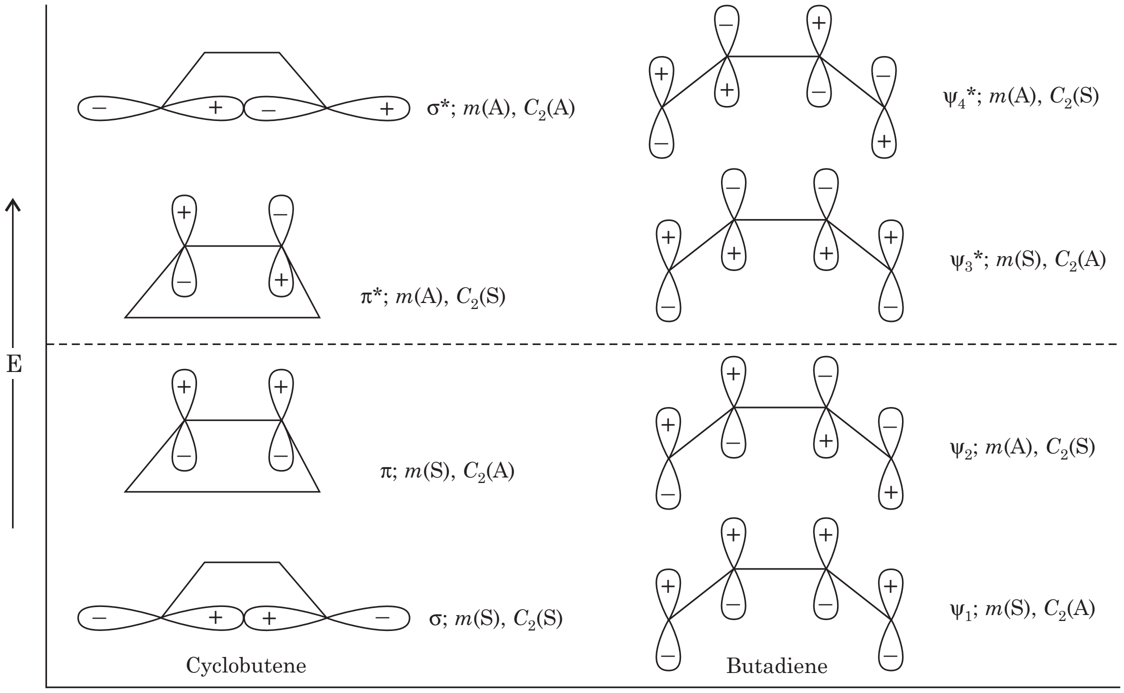


Fig. 2.7 Symmetric properties of molecular orbitals of cyclobutene and butadiene

Fig. 2.7 is shown in more simplified fashion as Fig. 2.8.

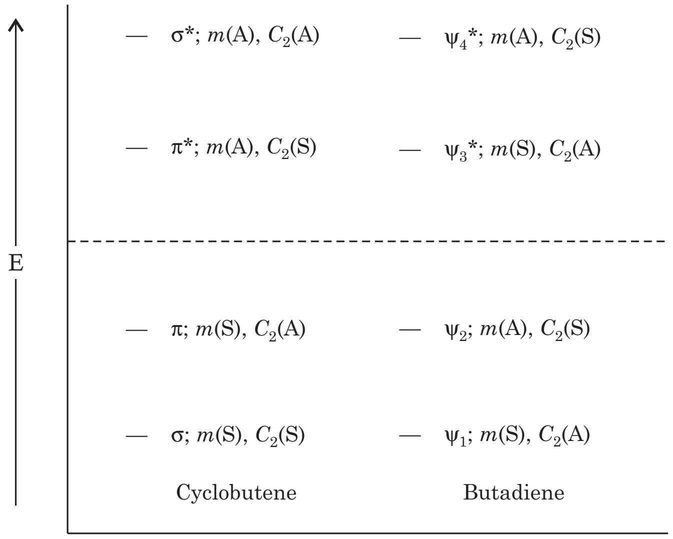
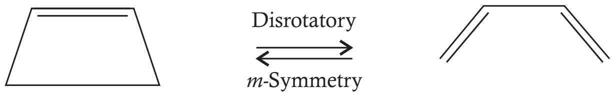


Fig. 2.8 Symmetric properties of molecular orbitals of cyclobutene and butadiene

We know that for bonding overlap (*i.e.,* symmetry allowed reaction) disrotatory mode of rotation is needed for orbitals having *m*-symmetry and conrotatory mode of rotation for C_2-symmetry.



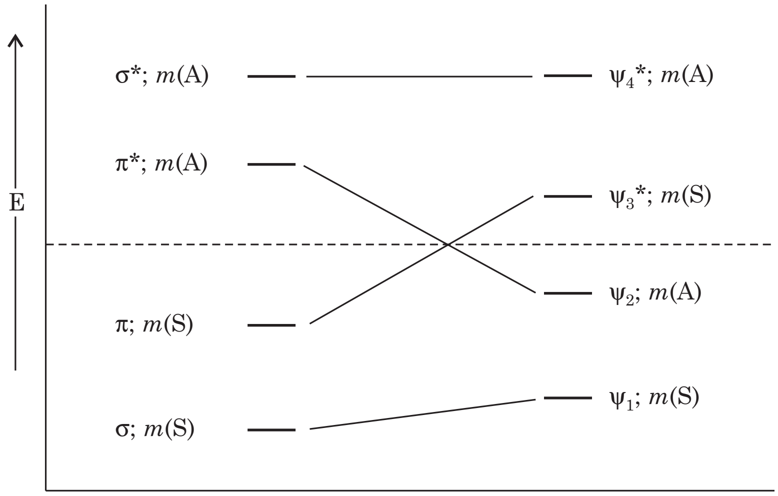


Fig. 2.9 Correlation diagram for disrotatory interconversion of cyclobutene-butadiene system

Let us analyse whether disrotatory mode ring-opening of cyclobutene to butadiene is thermal allowed or photochemical allowed process in which *m*-symmetry is maintained throughout the course of the reaction.

Inspection of correlation diagram (Fig. 2.9) shows that this process is thermally forbidden because π in cyclobutene containing two electrons would pass to the antibonding orbital (ψ_3*) of butadiene. In the correlation diagram (Fig. 2.9) the ground state σ orbital of cyclobutene correlate with the ground state ψ_1 orbital of butadiene. The ground state π orbital of cyclobutene does not correlate with the ground state ψ_2 orbitals of butadiene. Instead it correlates with ψ_3* which is an excited state and antibonding orbitals.

$$\sigma^2\pi^2 \overset{\Delta\quad\text{dis}}{\underset{\otimes}{\rightleftharpoons}} \psi_1^2\psi_2^2$$

Correlation diagram shows that the first excited state of the cyclobutene σ^2, π, π* correlates with the first excited state of butadiene ψ_1^2, $\psi_2\psi_3$*. Thus, disrotatory process in either direction is photochemically allowed. In the first excited state of cyclobutene π* contains an electron and it is transformed into bonding orbital (ψ_2) in butadiene.

$$\begin{array}{ccccccc} \sigma^2\pi^2 & \xrightarrow{h\nu} & \sigma^2\pi\pi^* & \rightleftharpoons & \psi_1^2\psi_2\psi_3^* & \xleftarrow{h\nu} & \psi_1^2\psi_2^2 \\ \text{Ground} & & \text{First excited state} & & \text{First excited state} & & \text{Ground state} \end{array}$$

Thus, following conclusions can be drawn from this correlation diagram:

Correlation	*Conclusion*	*Reason*
$\underset{\text{ground state}}{\sigma^2\pi^2} \longrightarrow \underset{\text{upper excited state}}{\psi_1^2\psi_3^{2*}}$	Disrotatory thermal conversion of cyclobutene to butadiene is forbidden.	π in cyclobutene containing two electrons in the ground state would pass to antibonding orbital (ψ_3*) of butadiene. An energy barrier would have to be overcome.
$\underset{\text{ground state}}{\psi_1^2\psi_2^2} \longrightarrow \sigma^2\pi^{*2}$	Disrotatory thermal conversion of butene to butadiene is forbidden.	ψ_2 of butadiene containing two electrons in the ground state would pass to antibonding orbital (π*) of cyclobutene. An energy barrier would have to be overcome.
$\sigma^2\pi\pi^* \longrightarrow \psi_1^2\psi_2\psi_3{}^*$	Disrotatory photochemical coversion in either direction is allowed.	First excited state of cyclobutene (π*) containing an electron is transformed into bonding orbital (ψ_2) of butadiene. Similarly, first excited state of butadiene (ψ_3*) containing an electron transformed into bonding orbital (π) of cyclobutene.

Now consider the conrotatory conversion of cyclobutene to butadiene in which a C_2-symmetry is maintained (Fig. 2.10).

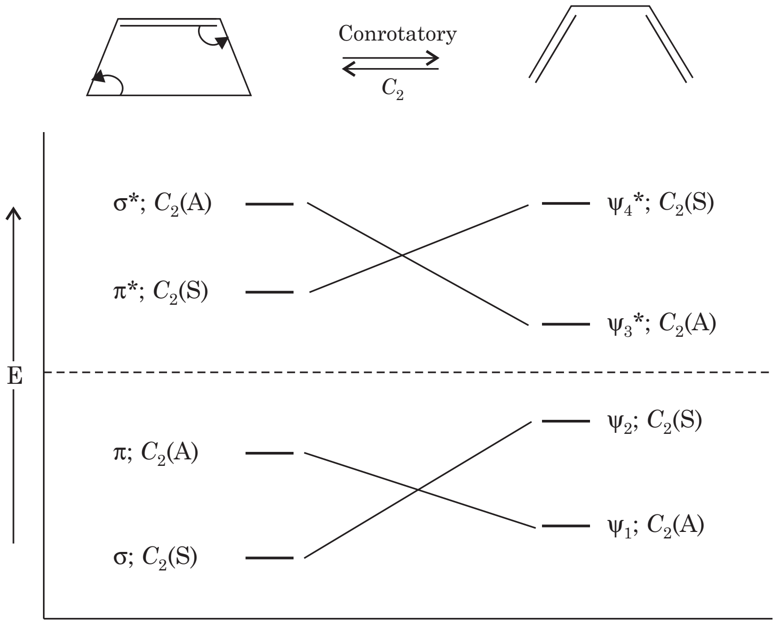


Fig. 2.10 Correlation diagram for conrotatory interconversion of cyclobutene-butadiene system

The orbitals now correlate in such a way that the ground state of cyclobutene $\sigma^2\pi^2$ correlates with the ground state of butadiene $\psi_1^2\psi_2^2$. The thermal conrotatory process is thus allowed in either direction.

$$\underset{\text{Ground state}}{\sigma^2\pi^2} \quad \overset{\Delta}{\rightleftarrows} \quad \underset{\text{Ground state}}{\psi_1^2\psi_2^2}$$

Inspection of correlation diagram shows that this process is photochemically forbidden. The first excited state of cyclobutene ($\sigma^2\pi\pi^*$) correlates with the upper excited state ($\psi_1^2\psi_2\psi_4^*$) of butadiene thus making it a high energy symmetry-forbidden process. Similarly, the first excited state of butadiene ($\psi_1^2\psi_2\psi_3^*$) correlates with a high energy upper excited state ($\sigma^2\pi\sigma^*$) of cyclobutene. In other words, a photochemical conrotatory process in either direction is symmetry-forbidden.

Thus, it becomes clear from the correlation diagrams that thermal opening of the cyclobutene proceeds in a conrotatory process while photochemical interconversion involves a disrotatory mode. These generalisations are true for all systems containing $4n\pi$ electrons.

2.5.2 Correlation Diagram of Electrocyclic Reaction in which Polyene has (4n + 2)π Electrons

A typical system of this category is the interconversion of 1, 3-cyclohexadiene and 1, 3, 5-hexatriene.

In this transformation six molecular orbitals (ψ_1, ψ_2, ψ_3, ψ_4^*, ψ_5^* and ψ_6^*) of hexatriene and six molecular orbitals (four π molecular orbitals π_1, π_2, π_3^* and π_4^* and two σ molecular orbitals) of cyclohexadiene are actually involved and, therefore, need to be considered.

Consider the conrotatory conversion of cyclohexadiene to hexatriene in which a C_2-symmetry is maintained (Fig. 2.11).

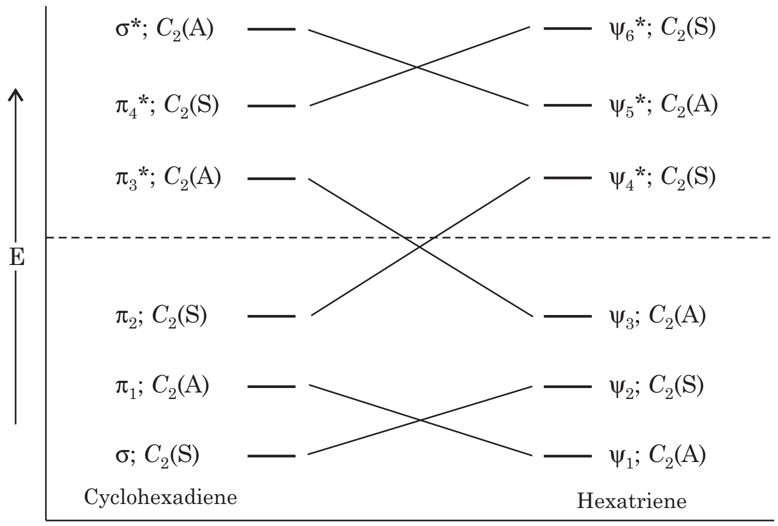


Fig. 2.11 Correlation diagram for conrotatory interconversion of cyclohexadiene-hexatriene system

(*i*) Inspection of the correlation diagram shows that this process is thermally forbidden because ground state orbitals of the reactant does not correlate with the ground state orbitals of the product.

$$\sigma^2\pi_1^2\pi_2^2 \;\cancel{\rightleftharpoons}\; \psi_1^2\psi_2^2\psi_3^2$$

In the correlation diagram, the ground state σ and π_1, orbitals of cyclohexadiene correlate with the ground state ψ_1 and ψ_2 orbitals of hexatriene. The ground state orbital π_2 of cyclohexadiene does not correlate with the ground state orbitals ψ_3 of hexatriene. Instead it correlates with $\psi_4{}^*$ which is an excited state and antibonding.

$$\sigma^2\pi_1^2\pi_2^2 \longrightarrow \psi_1^2\psi_2^2\psi_4{}^*$$

Thus, in thermal condition $\pi(\pi_2)$ in cyclohexadiene containing two electrons would pass to the antibonding orbital ($\psi_4{}^*$) of hexatriene. An energy barrier would have to be overcome in this process and thus process is forbidden.

(*ii*) Correlation diagram shows that the first excited state of cyclohexadiene $\sigma^2\pi_1^2\pi_2\pi_3{}^*$ correlates with the first excited state of hexatriene $\psi_1^2\psi_2^2\psi_3\psi_4{}^*$. Thus, conrotatory process in either direction is photochemically allowed.

$$\underset{\text{Ground state}}{\sigma^2\pi_1^2\pi_2^2} \xrightarrow{h\nu} \underset{\text{First excited state}}{\sigma^2\pi_1^2\pi_2\pi_3{}^*} \rightleftharpoons \underset{\text{First excited state}}{\psi_1^2\psi_2^2\psi_3\psi_4{}^*} \longleftarrow \underset{\text{Ground state}}{\psi_1^2\psi_2^2\psi_3^2}$$

In this case first excited state of cyclohexadiene $\pi_3{}^*$ containing an electron is transformed into bonding orbital ψ_3 of hexatriene. Similarly, first excited state of hexatriene $\psi_4{}^*$ containing an electron also transformed into bonding orbital π_2 of cyclohexadiene. Thus, process is allowed process.

$$\sigma^2\pi_1^2\pi_2\pi_3{}^* \rightleftharpoons \psi_1^2\psi_2^2\psi_3\psi_4{}^*$$

Now consider the disrotatory conversion of cyclohexadiene to hexatriene in which *m*-symmetry is maintained (Fig. 2.12).

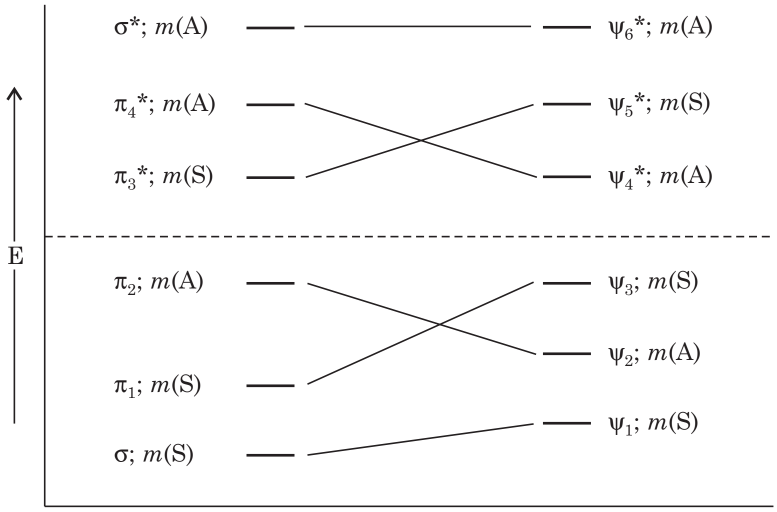


Fig. 2.12 Correlation diagram for disrotatory interconversion of cyclohexadiene-hexatriene system

(*i*) Inspection of the correlation diagram shows that the orbitals correlate in such a way that the ground state of cyclohexadiene $\sigma^2\pi_1^2\pi_2^2$ correlates with the ground state of hexatriene $\psi_1^2\psi_2^2\psi_3^2$. The thermal disrotatory process is thus allowed in either direction.

$$\sigma^2\pi_1^2\pi_2^2 \underset{\longleftarrow}{\overset{\Delta}{\longrightarrow}} \psi_1^2\psi_2^2\psi_3^2$$

(*ii*) Inspection of the correlation diagram shows that this process is photochemically forbidden. The first excited state of cyclohexadiene π_3* correlates with the upper excited state ψ_5* of hexatriene. Similarly, the first excited state of hexatriene ψ_4* correlates with a high energy upper excited state of cyclohexadiene. An energy barrier would have to be overcome in this process and thus process is forbidden.

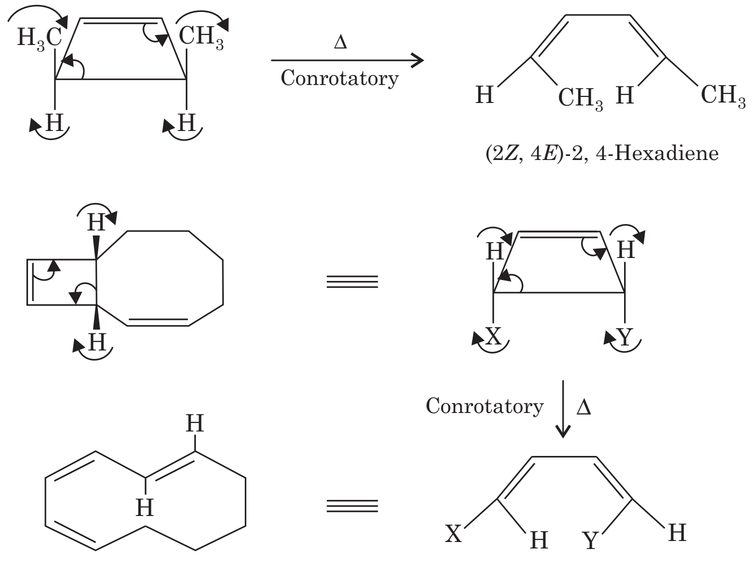
Thus, it becomes clear from the above considerations that thermal opening of the cyclohexadiene proceeds in a disrotatory process while photochemical interconversion involves a conrotatory mode. There generalisations are true for all conjugated systems containing $(4n + 2)\pi$ electrons.

Thus Woodward-Hoffmann rules for electrocyclic reactions on the basis of correlation diagrams may be summed up as in Table 2.3.

Table 2.3 Selection rules for electrocyclic reactions

Number of π electrons	*Thermal*	*Photochemical*
$4n$	Conrotatory	Disrotatory
$4n + 2$	Disrotatory	Conrotatory

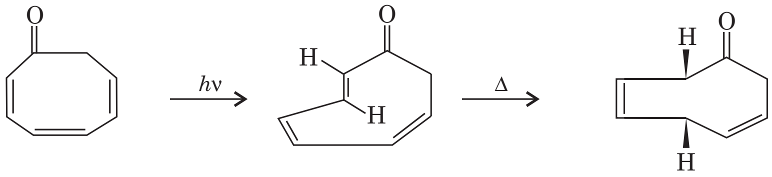
The above predictions are in accord with experimental results. Thermal isomerisation of *cis*-3, 4-dimethylcyclobutene gives (2*Z*, 4*E*)-2, 4-hexadiene and *cis*-bicyclo [6, 2, 0] deca-2, 9-diene gives (1*E*, 3*Z*, 5*Z*)-1, 3, 5-cyclodecatriene.



(2*Z*, 4*E*)-2, 4-Hexadiene

(1*E*, 3*Z*, 5*Z*)-1, 3, 5-Cyclodecatriene

Photochemical isomerisation of (2*Z*, 4*Z*, 6*Z*)-2, 4, 6-cyclooctatrione gives (2*E*, 4*Z*, 6*Z*)-2, 4, 6-cyclooctatrienone, which cyclises thermally in a conrotatory process to *cis*-bicyclo [4, 2, 0] octa-3, 6-dien-2-one.



2.6 THE WOODWARD-HOFFMANN RULE FOR ELECTROCYCLIC REACTIONS

Fortunately, all the conclusions that can be drawn laboriously from correlation diagrams can be drawn more easily from a pair of rules, known as the *Woodward-Hoffmann* rules. Rules distil the essence of the idea into two statements governing all pericyclic reactions, one rule of thermal reactions and its opposite for photochemical reactions. Correlation diagrams explain why they work, but we no longer depend upon constructing such diagrams.

2.6.1 Woodward-Hoffmann Rule for Electrocyclic Thermal Reactions

A thermal (ground state) electrocyclic reactions is symmetry allowed when the total number of $(4q + 2)s$ and $(4r)a$ components is odd.

2.6.2 Photochemical Electrocyclic Reactions

An electrocyclic reaction in the first electronically excited state is symmetry allowed when the total number of $(4q + 2)\ a$ and $(4r)s$ is odd.

These rules need some explanation.

Component

A component is a bond or orbital taking part in a pericyclic reaction as a single unit. A double bond is a π^2 component. The number *two* is the most important part of this designation and simply refers to the number of electrons. The prefix π tells us the type of electrons. A component may have any number of electrons, for example 1, 3-butadiene is a π^4 component. Component may not have mixtures of π and σ electrons. Component either contains only σ electrons or contains only π electrons. Designations $(4q + 2)$ and $(4r)$ simply refer to the number of electrons in the component where q and r are integers $(0, 1, 2, 3, 4, ..., n)$. An alkene is a π^2 component and so it is of the $(4q + 2)$ kind where $q = 0$ while diene is a π^4 component and so it is of the $(4r)$ kind where $r = 1$.

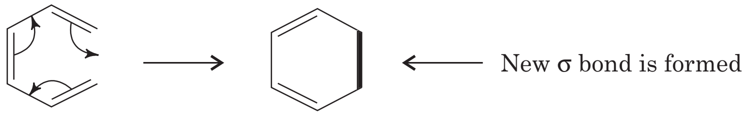
Suffix *s* and *a*

In electrocyclic reaction *s* means when upper (or lower) lobe of one frontier orbital overlaps with upper (or lower) lobe of other frontier orbital and *a* means when upper lobe of one orbital overlaps with lower lobe of other.

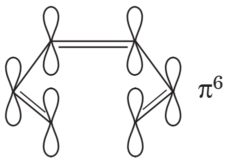
Let us start with hexatriene ring closure. As a preliminary, we would just note that hexatriene is, of course, a 6π electrons (π^6) conjugated system and, on forming cyclohexadiene, the end two orbitals have to form a σ bond.

So, now for the Woodward-Hoffmann treatment:

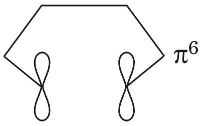
1. Draw the mechanism for the reaction



2. Choose the components. All the bonds taking part in the mechanism must be included and no others.



3. Make the three-dimensional drawing of the way the components come together for the reaction putting in orbitals at the ends of the components.

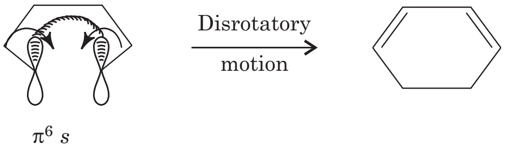


These orbitals are simple *p*-orbitals and do not make up HOMOs or LUMOs or any particular MOs. Do not attempt to mix frontier orbitals and Woodward-Hoffmann description of correlation of pericyclic reactions.

4. Join up the component(s) where new bond(s) are to be formed. Make sure you join orbitals that are going to form new bonds.

In this case formation of new σ bond takes place by two possible cases:

Case I: *When component is s. In this case overlapping will be possible if motion is disrotatory.*



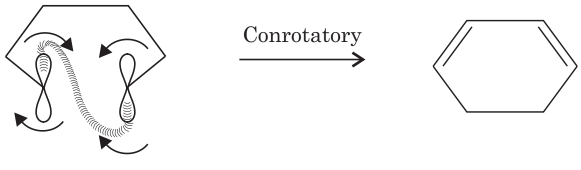
Notice that we call the component '*s*' because the upper lobes of the two *p*-orbitals were joining together. If upper lobe of one orbital and lower lobe of another orbital is joined together then component will be '*a*'.

Number of $(4q + 2)$ *s* component = 1
Number of $(4r)$ *a* component = 0
Total = 1 (odd)

Thermal: Allowed

Photochemical: Forbidden

Case II: *When component is 'a'. In this case overlapping will be possible if motion is conrotatory.*



$\pi^6 a$

Number of $(4q + 2)a = 1$

Number of $(4r)\ s = 0$

Total = 1 (odd)

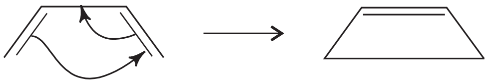
Thermal: Forbidden

Photochemical: Allowed

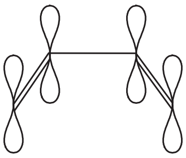
Similarly, take the example of conversion of cyclobutene to 1, 3-butadiene.

But for the use of Woodward-Hoffmann rule always consider the process in which open system converts into cyclic system.

1. Draw the mechanism for the reaction.

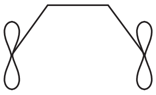


2. Choose the components. All the bonds taking part in the mechanism must be included and no others.



π^4

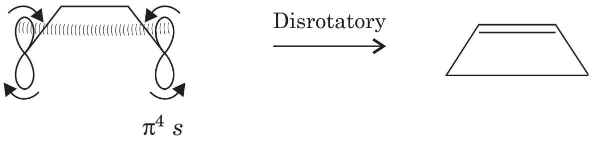
3. Make the three-dimensional drawing of the way in which the component comes together for the reaction, putting the orbitals at the ends of the component.



π^4

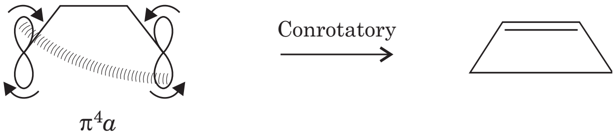
4. Join up the component(s) where new bond(s) are to be formed.
5. Show bond formation by conrotatory as well as disrotatory motion. Label each component s or a.

(*i*)



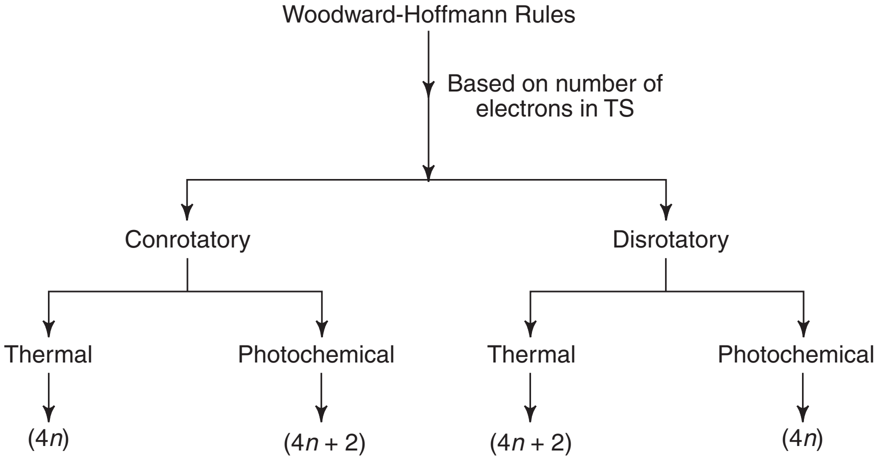
Number of $(4q + 2)$ s component = 0
Number of $(4r)$ a component = 0
Total = 0
Thermally: Disallowed
Number of $(4q + 2)$ a component = 0
Number of $(4r)$ s component = 1
Total = 1 (odd)
Photochemically: Allowed

(*ii*)



Number of $(4r)a$ = 1
Number of $(4q + 2)$ s = 0
Total = 1 (odd)
Thermally: Allowed

Thus, we can conclude the following results from Woodward-Hoffmann rule for electrocyclic reactions:



2.7 HÜCKEL-MOBIUS (H-M) METHOD OR PERTURBATION MOLECULAR ORBITAL (PMO) METHOD

Another method for quickly assessing whether a given pericyclic process is allowed is to examine the cyclic array of orbitals at the transition state of the pericyclic reaction. This method was popularised by H. Zimmerman and M.J.S. Dewar.

Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has $(4n + 2)$ π conjugated or delocalised electrons and consequently stable in ground state. Similarly, monocyclic planar conjugated system is anti-aromatic if it has $(4n)$ π conjugated or delocalised electrons. This system is unstable in ground state. However, further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals. Thus, system with $(4n + 2)$ π electrons and a node is antiaromatic while system with $(4n)$ π electrons and a node is aromatic.

Thus, system has no node then:

$(4n + 2)\pi$ electrons → aromatic → stable in ground state.

$(4n)\pi$ electrons → antiaromatic → unstable in ground state.

Similarly, system having a node then

$(4n)$ π electron → aromatic → stable in ground state.

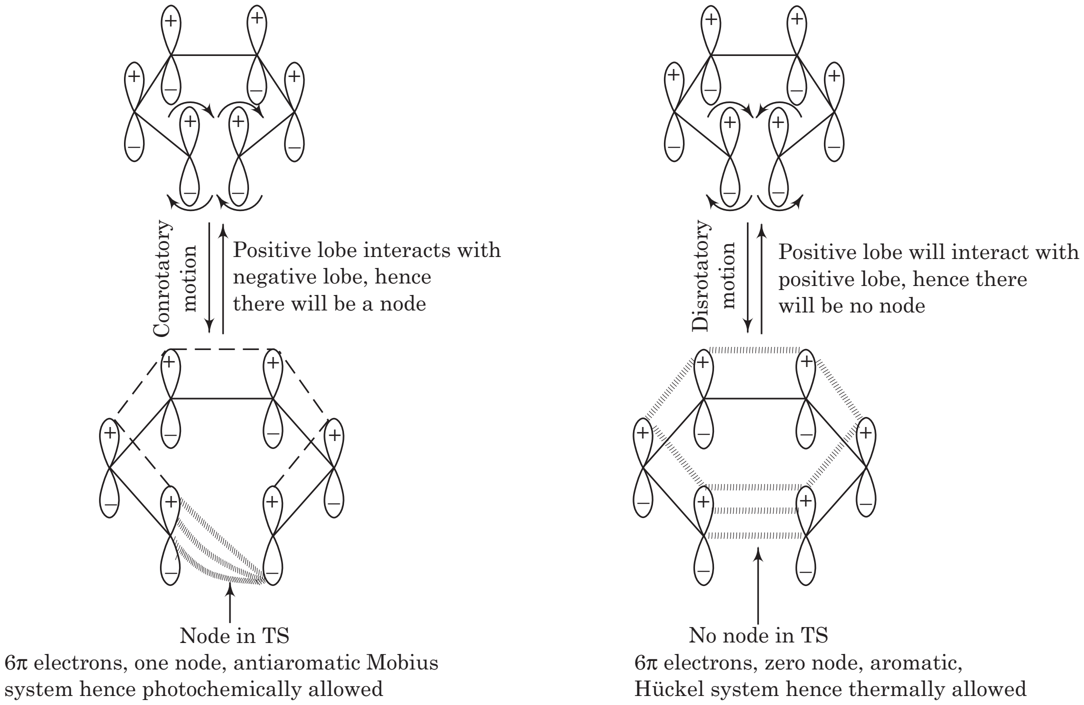
$(4n + 2)$ π electrons → antiaromatic → unstable in ground state.

If system has no node then it is called Hückel system and array is called Hückel array. Similarly, if system has node then it is called Mobius system and array is called Mobius array. Application of these rules to pericyclic reactions led to the generalisation that thermal reactions take place via aromatic transition state [*i.e.*, $(4n + 2)$ π electrons having no node or $(4n)$ π electrons having one node] whereas photochemical reactions proceed via antiaromatic transition state [*i.e.*, $(4n)\pi$ electrons having no node or $(4n + 2)$ π electrons having one node].

A cyclic transition state is said to be aromatic or isoconjugated with the corresponding aromatic system if the number of the conjugated atoms and that of the π (*pi*) electrons involved are the same as in the corresponding aromatic system. Similarly, a cyclic transition state is said to be antiaromatic or isoconjugated with the corresponding antiaromatic system if the number of conjugated atoms and that of the π (*pi*) electrons involved are the same as in the corresponding antiaromatic system. We have only to consider a cyclic array of atomic orbitals representing those orbitals which undergo change in the transition state and assign signs to the wave function in the best manner for overlap. Then the number of nodes in the array and number of electrons involved are counted.

Let us consider the following electrocyclic reaction (Fig. 2.13 and Fig. 2.14).

Cis-1, 3, 5-hexatriene $\rightleftharpoons$ Cyclohexadiene



Positive lobe interacts with negative lobe, hence there will be a node

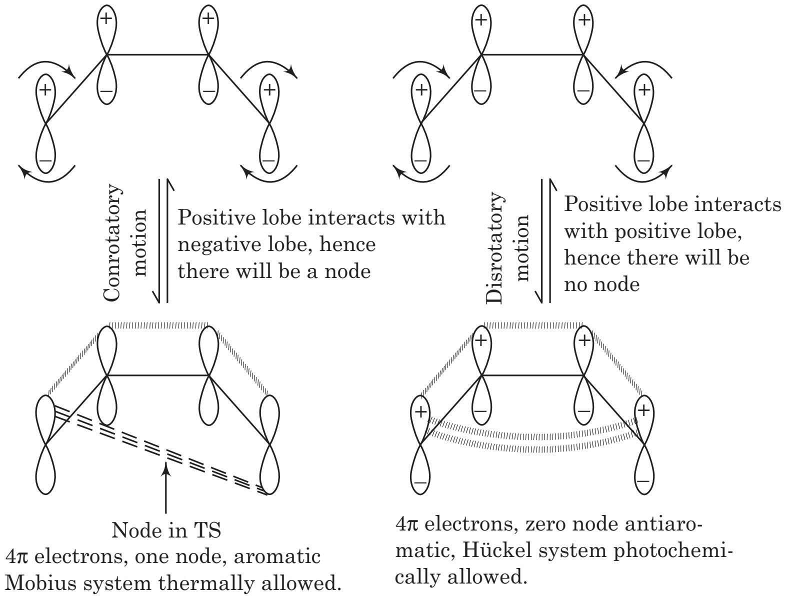
Positive lobe will interact with positive lobe, hence there will be no node

6π electrons, one node, antiaromatic Mobius system hence photochemically allowed

6π electrons, zero node, aromatic, Hückel system hence thermally allowed

Fig. 2.13 Array diagram for (4*n* + 2)π system

Similarly for
1, 3-butadiene ⇌ Cyclobutene



Positive lobe interacts with negative lobe, hence there will be a node

Positive lobe interacts with positive lobe, hence there will be no node

4π electrons, one node, aromatic Mobius system thermally allowed.

4π electrons, zero node antiaromatic, Hückel system photochemically allowed.

Fig. 2.14 Array diagram for (4*n*)π system

Thus, for the thermal reactions involving $(4n + 2)\pi$ electrons will be disrotatory and involved Hückel type transition whereas those having $(4n)$ π electrons will be conrotatory and the orbital array will be of the Mobius type. Similarly, for photochemical reactions involving $(4n + 2)$ π electrons will be conrotatory and involved Mobius type transition whereas those involving $(4n)$ π electrons will be disrotatory and the orbital array will be Hückel type.

Thus for convenience, the selection rules by this approach to electrocyclic reactions are given in Table 2.4.

Table 2.4 Selection rules for electrocyclic reactions by H.M. method

Array of π electrons involved	*Number of nodes*	*Aromaticity*	*Δ allowed*	*hν allowed*
$4n$	zero	antiaromatic	—	disrotatory
$4n$	one	aromatic	conrotatory	—
$(4n + 2)$	zero	aromatic	disrotatory	—
$(4n + 2)$	one	antiaromatic	—	conrotatory

GLOSSARY

Conrotatory motion: Rotation of bonds in the same direction, *i.e.,* both clockwise or both counterclock wise.

Disrotatory motion: Rotation of bonds in opposite directions, *i.e.,* one clockwise and one counterclock wise.

Electrocyclic reaction: Conversion of a conjugated polyene into an isomeric cyclic compound. The bond responsible for ring formation occurs between the two ends of the conjugated system of the starting material.

Photochemically allowed reaction: A reaction that will be concerted and will possess a comparatively low energy of activation when initiated by light.

Symmetry allowed reaction: A reaction that will occur by a concerted process and will not involve radical or ionic intermediate. A symmetry-allowed process may be accelerated either by heat or by light.

Symmetry-forbidden reaction: A reaction that cannot occur by concerted process under a given set of conditions. Reactions that are "symmetry-forbidden" do occur. However, when they do occur they are not concerted but, instead, involve classical intermediates (often radicals). They usually have high energy of activation.

Thermally allowed reaction: A reaction that will be concerted and will possess a comparatively low energy of activation when initiated by heat.

Orbital correlation diagram: A diagram that shows the correspondence in energy and symmetry between relevant reactant and product orbitals in a pericyclic reaction. The relevant orbitals frequently called the **basic set of orbitals**, are those that undergo change during the reaction.

Frontier-orbital approach: A methodology for quickly predicting whether a given pericyclic reaction is allowed by examining the symmetry of HOMO and, if the reaction is bimolecular, the LUMO of the second partner.

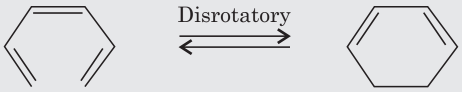
The Woodward-Hoffmann rule: A series of generalised symmetry selection rules elaborated by R.B. Woodward and R. Hoffmann, based on arguments such as correlation diagrams, which predict whether given pericyclic reaction will be allowed under a given set of conditions. In its most general form the rules state that a pericyclic reaction is ground state allowed (excited state forbidden) if the total number of suprafacial ($4q + 2$) and antarafacial ($4r$) reacting components (electronic fragments) is odd (q and r are any integer including zero). Note that the antarafacial ($4q + 2$) fragments and suprafacial ($4r$) components are not counted.

FURTHER READING

1. A.P. Marchand and R.E. Lehr, *Pericyclic Reactions,* Vol. I and II, Academic Press, New York, 1977.
2. E.N. Marvell, *Thermal Electrocyclic Reactions,* Academic Press, New York, 1980.
3. R.B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry,* Academic Press, New York, 1970.
4. M.J.S. Dewar and R.C. Dougherty, *The PMO Theory of Organic Chemistry,* Plenum Press, New York, 1975.
5. Francis A. Carey and R.J. Sunberg, *Advanced Organic Chemistry*, Part A and Part B, Plenum Press, New York, 2000.

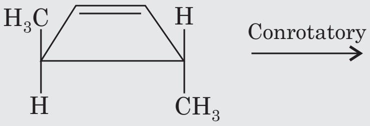
PROBLEMS

1. Construct a correlation diagram (depicting the orbitals undergoing change alongwith their symmetries) for the following transformations:

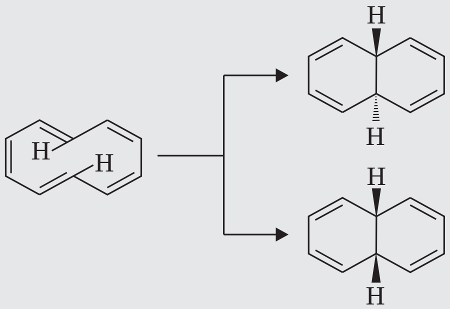


With the help of the diagram so constructed, predict whether these transformations are allowed thermally or photochemically. Do you arrive at the same conclusions using PMO method?

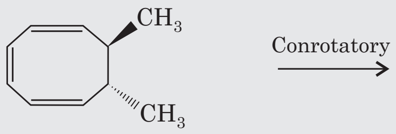
2. There are two ways of stereochemical modes in the following electrocyclic transformation. Write structures of the products expected from both modes and tell which one is preferred and why?



3. Sketch a suitable mechanistic scheme for the following transformations:



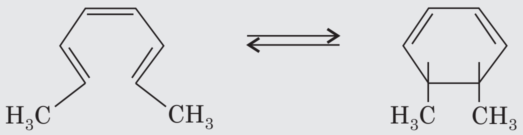
4. Write down the structure(s) of the most favourable product(s) in the given transformation:



5. What are electrocyclic reactions? With the help of correlation diagram, analyse the *cis*-3, 4-dimethylcyclobutene $\rightleftharpoons$ 2, 4-hexadiene system, giving stereochemistry under thermal and photochemical conditions.

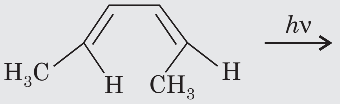
6. Construct correlation diagrams for conrotatory and disrotatory processes from interconversion of cyclohexadiene $\rightleftharpoons$ hexatriene system. Out of these processes, which process is photochemically allowed? Do you arrive at the same conclusion using FMO method?

7. With the help of FMO approach, explain whether the following reaction will be allowed thermally or photochemically.

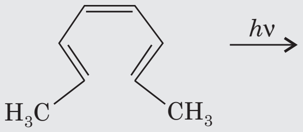


8. Write the products of the following electrocyclic reactions and write whether the reaction proceeds in a conrotatory or disrotatory fashion. Also give the stereochemistry of the products.

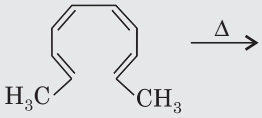
(*i*)



(*ii*)

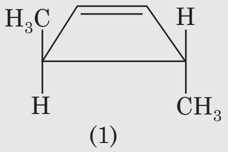


(*iii*)



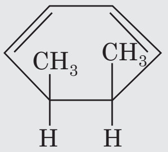
9. Why *cis*-3, 4-dimethylcyclobutene on heating gives (2*Z*, 4*E*)-2, 4-hexadiene while on photochemical the product is (2*E*, 4*E*)-2, 4-hexadiene?

10. In some cases, electrocyclic reactions proceed through more than one conrotatory or disrotatory manner. Show that cyclobutene (1) can open by two alternate conrotatory pathways giving two different products. Comment upon the relative yields of these products with suitable reasons.



(1)

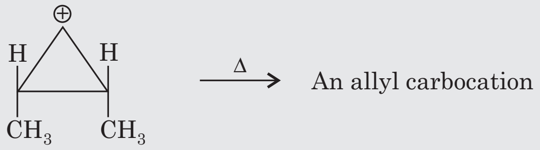
11. In some cases electrocyclic reactions proceed through more than one conrotatory or disrotatory manner. Show that cyclohexadiene (1) can open by two alternate disrotatory pathways giving two different products. Comment upon relative yields of these two products with suitable reasons.

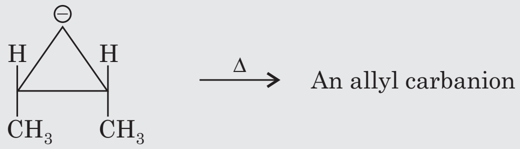


(1)

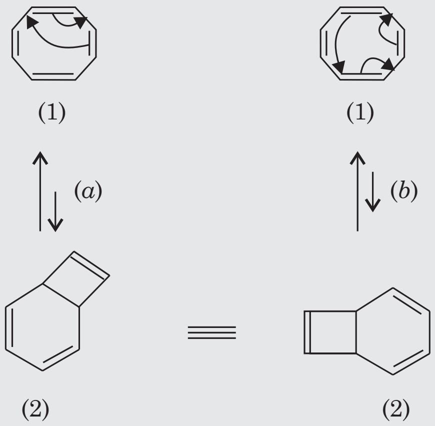
12. Predict the structure of the 2, 4-heptadiene produced by the thermal ring opening of *cis*-3-ethyl-4methyl-cyclobutene.

13. Analyse the thermal ring-opening to allyl ions of the two cyclopropyl ions shown below. What stereochemistry do you expect in the product ? Will the reaction involve conrotation or disrotation? Explain.





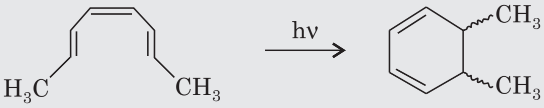
14. The thermally induced interconversion of cyclooctatetraene (COT) (1) and bicyclo [4, 2, 0] octa 2, 4, 7-triene (2) can be described with two different sets of arrows. Although these arrow formalisms may seem to give equivalent results, one of them is, in fact, not a reasonable depiction of the reaction. Explain.



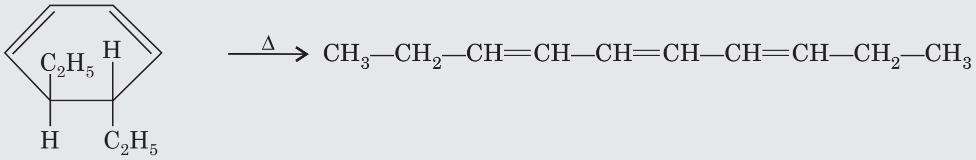
15. Draw the structures showing conrotatory motion of 1, 3-butadiene in the excited state (ψ_3*). Are the potential, bonding *p* orbitals in a symmetry-allowed or symmetry-forbidden orientation?

16. Predict the stereochemistry of the products.

(*i*)

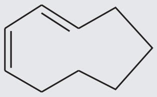


(*ii*)

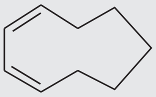


$CH_3—CH_2—CH=CH—CH=CH—CH=CH—CH_2—CH_3$

17. The following compounds both undergo photo-induced electrocyclic reactions. What are the structures and stereochemistry of the products?

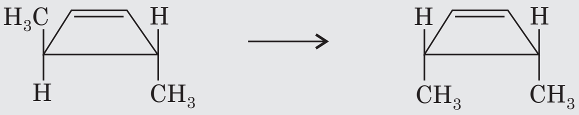


(1)



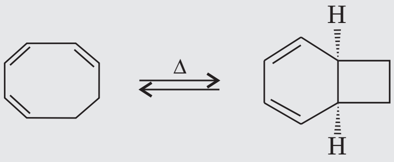
(2)

18. How would you carry out the following conversions?

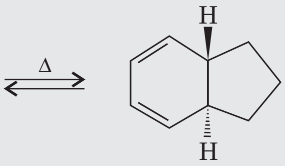


19. Which of the following electrocyclic reactions should occur readily by a concerted mechanism?

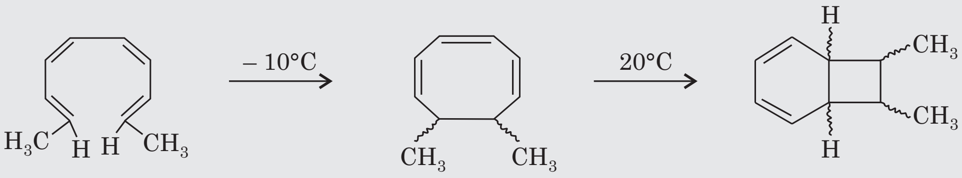
(*a*)



(*b*) 1, 3, 5-Cyclononatriene



20. Predict the stereochemistry of compounds (B) and (C).



(A) (B) (C)

21. Write a note on conrotatory and disrotatory motion.

22. Why on thermal reaction *cis*-3, 4-dimethylcyclobutene gives (2*E*, 4*Z*)-2, 4-hexadiene while the *trans* isomer gives the (2*E*, 4*E*)-2, 4-hexadiene?

23. How one can account for the opposite stereochemistry in the photochemical cyclisation of a 1, 3-butadiene to a cyclobutene than the thermal reaction?

24. The electrocyclic ring-opening of cyclobutenes is allowed thermally in the conrotatory mode. Two products could be formed by the conrotatory opening of *trans*-3,4-dimethylcyclobutene, but in practice only one is formed. Explain.

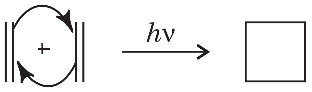
25. The electrocyclic transformation of (2*E*, 4*Z*, 6*E*)-2,4,6-octatriene gives *cis*-5,6-dimethyl-1,3-cyclohexadiene under thermal conditions but gives the *trans*-isomer on photochemical conditions. Explain.

3
CHAPTER

Cycloaddition Reactions

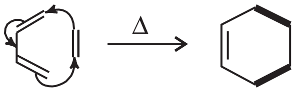
3.1 INTRODUCTION

A cycloaddition is a reaction in which two unsaturated molecules undergo an addition reaction to yield a cyclic product. Formation of cyclic product takes place at the expense of one π (*pi*) bond in each of the reacting partner and gain of two σ (*sigma*) bonds at the end of the both components having π (*pi*) bonds. Thus, in this reaction there is loss of two π (*pi*) bonds of the reactants and gain of two σ (*sigma*) bonds in the product.



...(1)

Loss of two π bonds and gain of two σ bonds



...(2)

Loss of two π bonds and gain of two σ bonds. Formation of σ bonds at the end of the two components.

The cycloaddition reactions are classified with respect to three facts of the reaction:

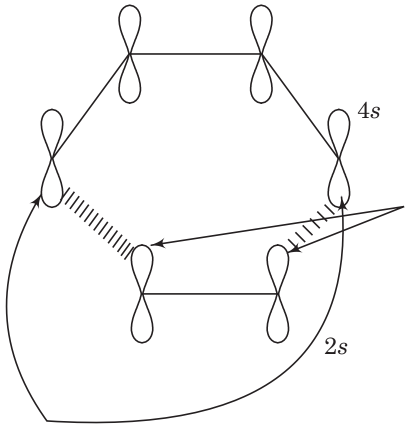
(*i*) The number of electrons of each unit participating in cycloaddition.

(*ii*) The nature of orbitals undergoing change (π or σ).

(*iii*) The stereochemical mode of cycloaddition (*supra*, *syn* or *antara*, *anti*).

The reaction in equation (1) is a [2 + 2] cycloaddition reaction because the reaction involves two electrons from one reacting component and also two electrons from the other. The reaction in equation (2) is a [4 + 2] cycloaddition.

The stereochemical mode is given by a subscript *s* or *a* which indicates whether the addition occurs in a *supra* or *antara* mode on each unit. A cycloaddition may in principle occur either across the same face or across the opposite faces of the planes in each reacting component. If reaction occurs across the same face of a π system, the reaction is said to be *suprafacial* with respect to that π system. The suprafacial is nothing more than a *syn* addition.

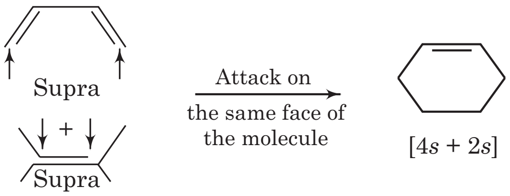


Both lobes are above the plane of the molecule or both lobes are in same plane, hence suprafacial

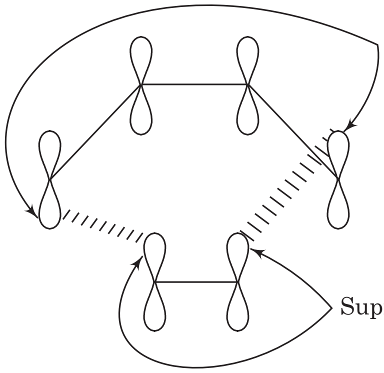
Both lobes are below the plane of the molecule or both lobes are in same plane, hence suprafacial

This addition reaction is thus [4*s* + 2*s*] cycloaddition reaction.

This can also be represented as follows:



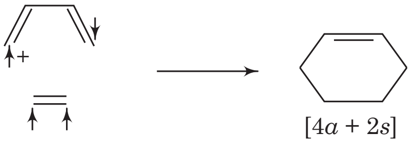
If the reaction bridges opposite faces of a π system, it is said to be antarafacial. An antarafacial is just an *anti* addition.

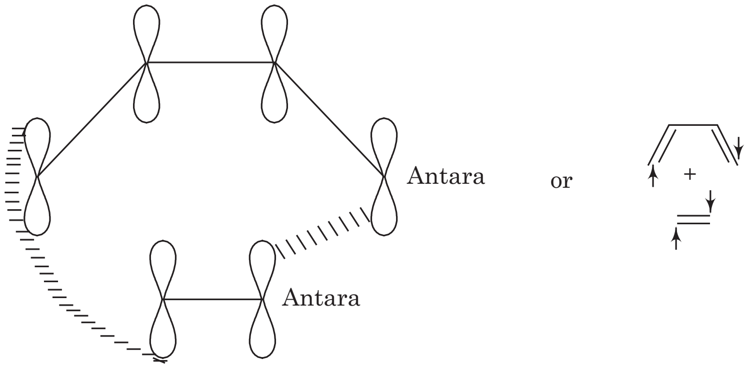


Antarafacial hence 4*a*

Suprafacial hence 2*s*

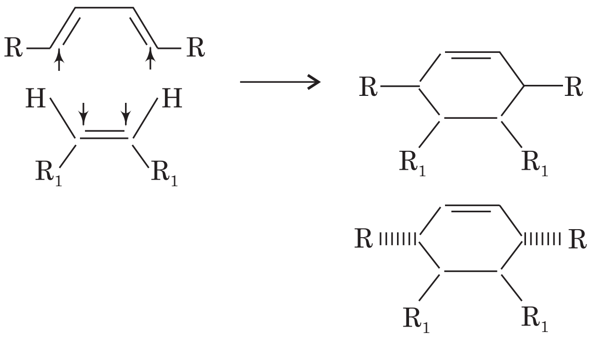
This mode of addition reaction is thus [4*a* + 2*s*] cycloaddition reaction. This can be represented as:





[4a + 2a] Cycloaddition reaction

In antarafacial, attack takes place with one bond forming to one surface but other bond forming to other surface. It is rare, it does not occur in any reaction. **Almost all cycloaddition reactions are suprafacial on both components.**



3.2 THEORY OF CYCLOADDITION REACTIONS: FMO METHOD

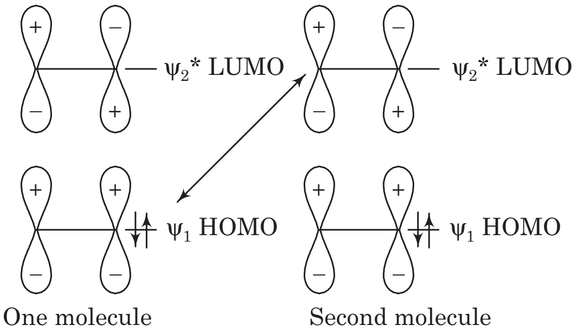
In order, for a cycloaddition to occur, there must be bonding overlap between *p*-orbitals at the terminal carbons of each π-electron system, this is where the new σ bonds are formed. Let us explain this point with a [4 + 2] cycloaddition. Let us suppose that diene (4π component) behaves as electron donor and the dienophile (2π component) as the electron acceptor (or vice-versa). What electrons will the 4π component donate? Obviously there will be its valence electrons—the electrons in its HOMO (ψ_2). The 2π component will accept these electrons to form the new bonds. The molecular orbital used to accept these electrons must be empty since molecular orbital cannot contain more than two electrons. Therefore, the molecular orbital which accepts electron should be LUMO of the 2π component. Thus, one component used its HOMO and the other component used its LUMO for overlapping. Simultaneously with the merging of the π orbitals, these orbitals also undergo hybridisation to yield the new sp^3 σ bonds.

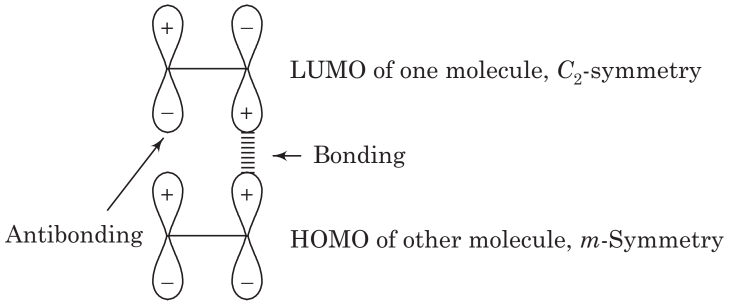
3.2.1 [2 + 2] Cycloaddition Reactions

(A) Thermal Induced [2 + 2] Cycloaddition Reactions

Thermal induced [2 + 2] cycloaddition reactions are symmetry forbidden reactions.

When ethylene is heated, its π electrons are not promoted, but remain in the ground state ψ_1. If we examine the phase of the ground state HOMO of one ethylene molecule and the LUMO of another ethylene molecule we can see why cyclisation does not occur by the thermal induction.





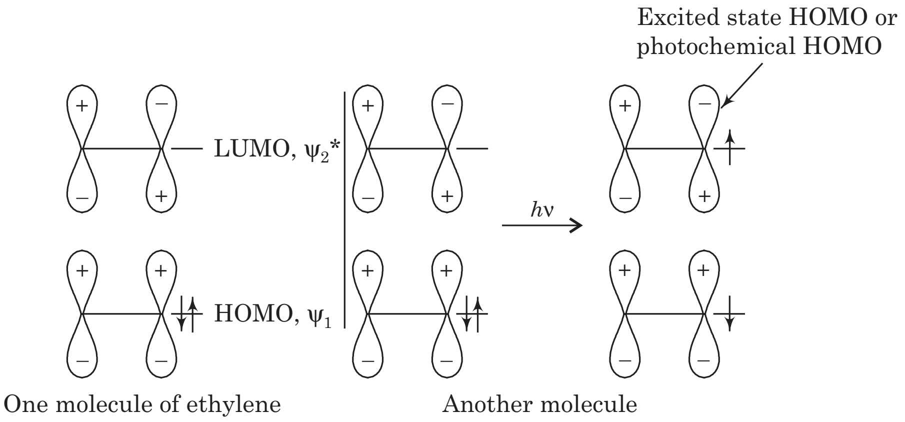
Phase wrong for overlap, symmetry forbidden.

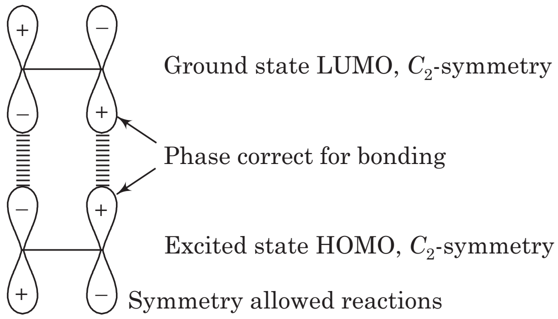
For bonding to occur, the phase of the overlapping orbitals must be same. This is not the case for the ground state HOMO and LUMO of two ethylene molecule or any other [2 + 2] system. Because the phase of the orbitals are incorrect for bonding, a thermally induced [2 + 2] cycloaddition is said to a symmetry forbidden reaction.

(B) Photo-Induced [2 + 2] Cycloaddition Reactions

When ethylene is irradiated with photon of UV light, a π electron is promoted from ψ_1 to ψ_2^* orbital in some, but not all, of the molecules. The result is a mixture of ground state and excited state ethylene molecules.

Thus photo-induced cycloaddition takes place between photochemical HOMO of one molecule and ground state LUMO of other molecule.

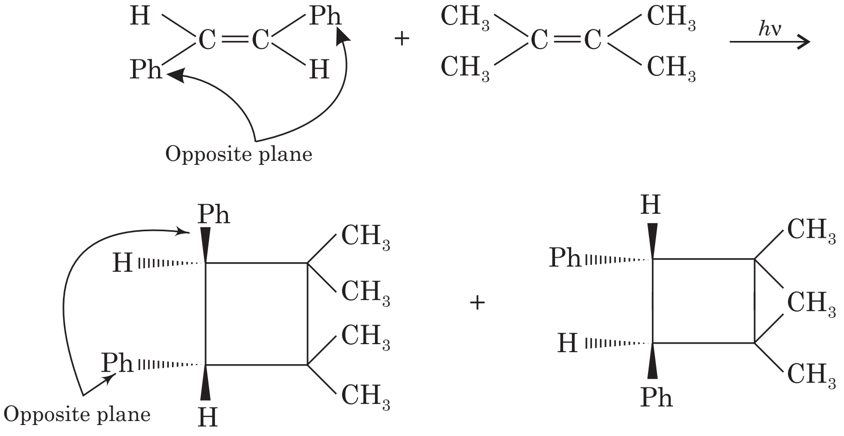


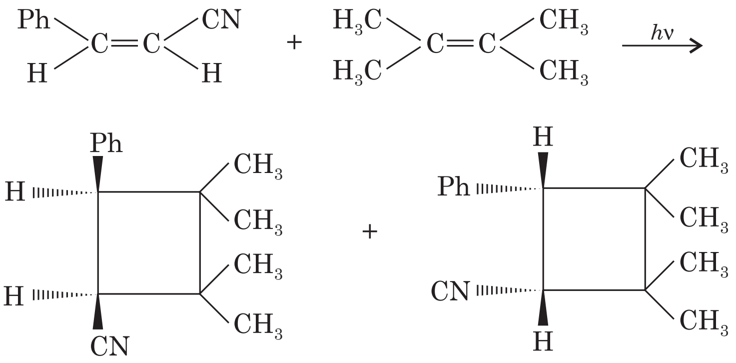


From the example it is clear that for cycloaddition reaction both HOMO and LUMO should have same symmetry otherwise reaction will be symmetry forbidden. For symmetry allowed reaction if HOMO has *m*-symmetry then LUMO should also have *m*-symmetry. Similarly if HOMO has C_2-symmetry then LUMO should also have C_2-symmetry.

Stereochemistry

Stereochemical integrity is maintained in cycloaddition reaction because reaction is concerted reaction,





3.2.2 [4 + 2] Cycloaddition Reactions

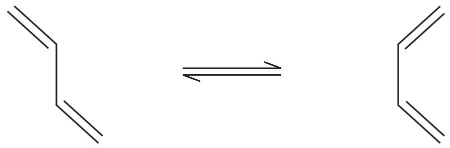
Diels-Alder reaction is the best known [4 + 2] cycloaddition reaction. This reaction is thermally allowed reaction. Diels-Alder reaction is photochemically forbidden. Since Diels-Alder reaction is the most common [4 + 2] cycloaddition reaction, let us first discuss the general description of this reaction.

Diels-Alder reactions occur between a conjugated **diene** and an alkene (or alkyne), usually called the **dienophile**.

(A) The Dienes

The diene of the Diels-Alder reaction is electron rich, while the dienophile is electron poor. Some Diels-Alder reactions with electron-poor dienes and electron-rich dienophiles are also known, but these are relatively rare. Simple dienes such as 1, 3-butadiene are sufficiently electron-rich to be effective dienes for Diels-Alder reaction. The presence of electron releasing groups such as alkyl groups, phenyl groups or alkoxy groups may further enhance the reactivity of dienes.

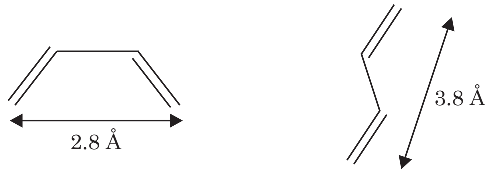
The diene component of the Diels-Alder reaction can be open-chain or cyclic but it must have *s-cis* conformation. Butadiene normally prefers the *s-trans* conformation with the two double bonds as far away from each other as possible for steric reasons. The barrier to rotation about the central σ bond is small (about 30 kJ/mole at 25°C) and rotation to the less favourable but reactive *s-cis* conformation is rapid.



Favoured but cannot
give Diels-Alder reaction

Disfavoured but can
give Diels-Alder reaction

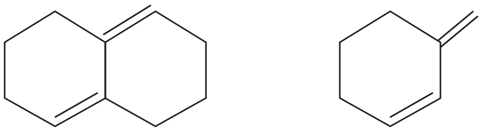
Cyclic dienes that are permanently in the *s-cis* conformation are exceptionally good for Diels-Alder reaction. On the other hand, cyclic dienes that are permanently in the *s-trans* conformation and cannot adopt the *s-cis* conformation will not give the Diels-Alder reaction at all. (Why ?) If the diene is in the *s-trans* conformation, the dienophile could not '**reach**' both ends of the diene at the same time.



s-cis Conformation, a requirement for the Diels-Alder reaction

s-trans Conformation

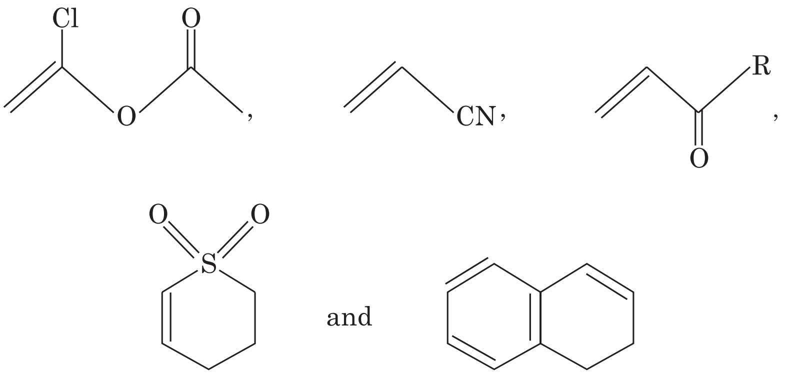
This explains why dienes such as those given below will not serve as dienes in the Diels-Alder reaction.



(B) The Dienophile

The most common dienophiles are the electron-poor alkenes and alkynes. Since electron-poor alkenes and alkynes are prone to react with a diene, these are called dienophiles (lover of dienes). Thus the simple alkenes and alkynes such as ethylene and acetylene are not good dienophiles. A good dienophile generally has one or more electron-withdrawing groups pulling electron density away from the π bond.

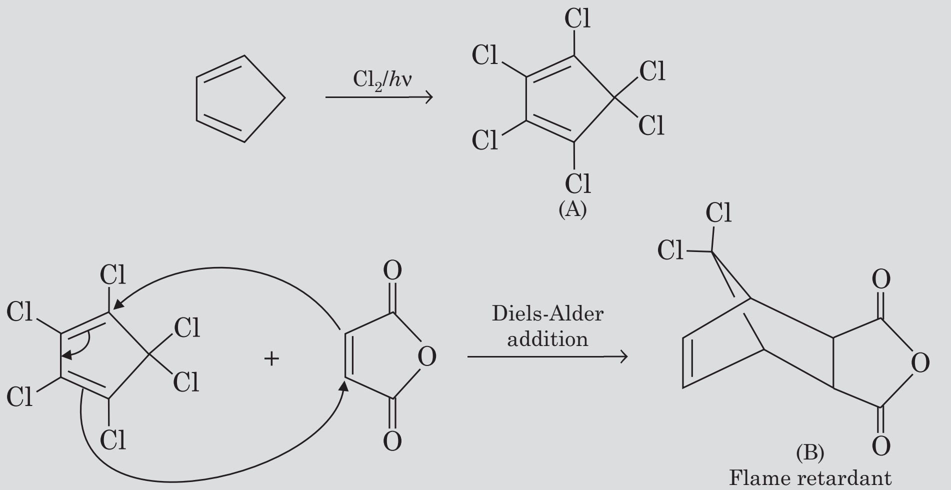
Dienophiles that do undergo the Diels-Alder reaction include conjugated carbonyl compounds, nitro compounds, nitriles, sulphones, arylalkenes, arylalkynes, vinyl ethers, vinyl esters, haloalkenes and dienes.



Some dienophiles for the Diels-Alder reaction

Problem 1: *1, 3-cyclopentadiene on chlorination gives hexachlorocyclopentadiene (A). Compound (A) reacts with maleic anhydride to give compound (B) which is used as flame retardant. Give the structure of (A) and (B).*

Solution:

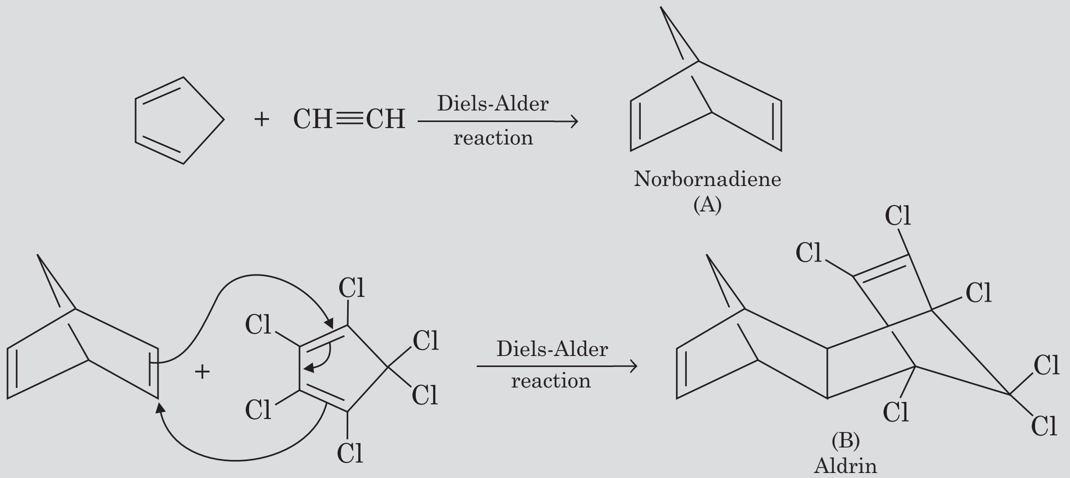


(A)

(B)
Flame retardant

Problem 2: *Cyclopentadiene reacts with acetylene at room temperature to give compound (A). Compound (A) reacts with hexachlorocyclopentadiene to give compound (B). Compound (B) is aldrin which is used as pesticide. Give the structure of (A) and (B).*

Solution:



Norbornadiene
(A)

(B)
Aldrin

(C) Mechanism of Diels-Alder Reaction

The mechanism of the Diels-Alder reaction is a simultaneous cyclic movement of six electrons: four in the diene and two in the dienophile. The simple representation of the mechanism shown below is fairly accurate. This is called a concerted reaction because all the bond making and bond breaking occurs simultaneously. For these three pairs of electrons to move simultaneously, however, the transition state must have a geometry that allows overlap of the two end *p*-orbitals of the diene with those of the dienophile (Fig. 3.1).

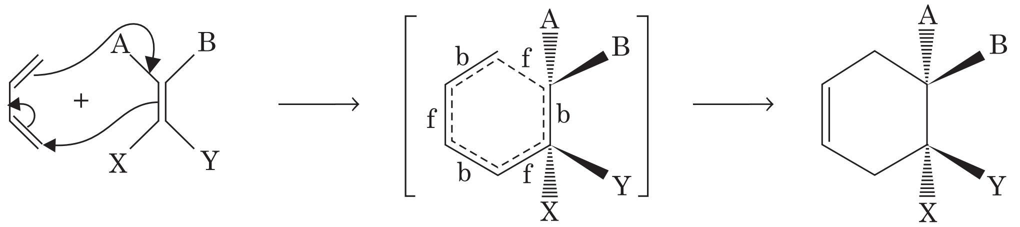
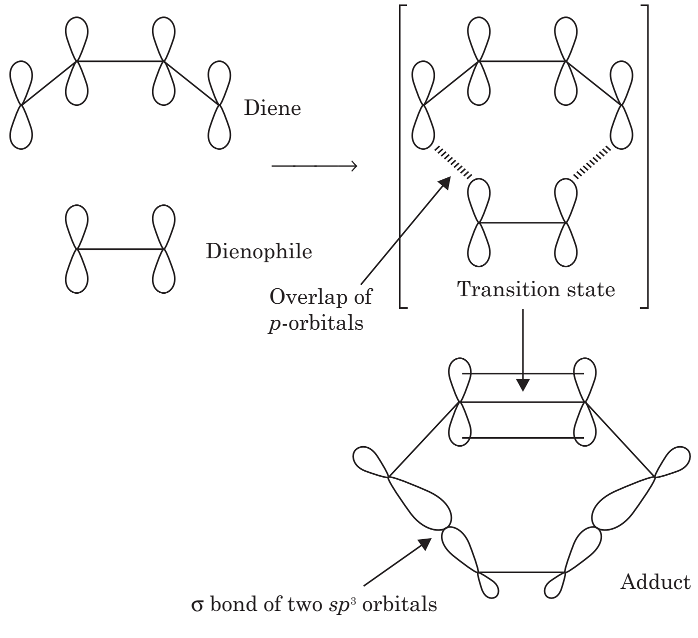


Fig. 3.1 Transition state

There are three major **stereochemical** features of the Diels-Alder reaction that are controlled by the requirements of the T.S.

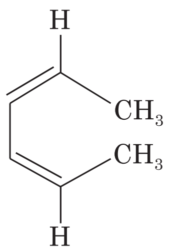
(*i*) ***s-cis* conformation of the diene:** This mechanism explain why the **diene** should be in *s-cis* conformation.

Diels-Alder reaction is a one step reaction that proceeds through a cyclic transition state. Bond formation occurs at both ends of the diene system, and the Diels-Alder transition state involves a cyclic array of six carbons and six π electrons. For this the diene adopts the *s-cis* conformation in the transition state.

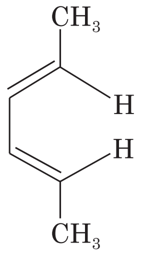


When the diene is in the *s-trans* conformation, the end *p*-orbitals are too far apart to overlap with the *p*-orbitals of the dienophile.

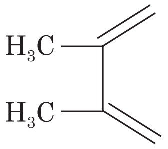
Structural feature that aid or hinder the diene in achieving the *s-cis* conformation affect its ability to participate in the Diels-Alder reaction. Thus the diene with functional groups that hinder the *s-cis* conformation react slower than butadiene. Dienes with functional groups that hinder the *s-trans* conformation react faster than butadiene.



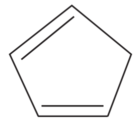
Much slower than butadiene



Similar to butadiene



Faster than butadiene

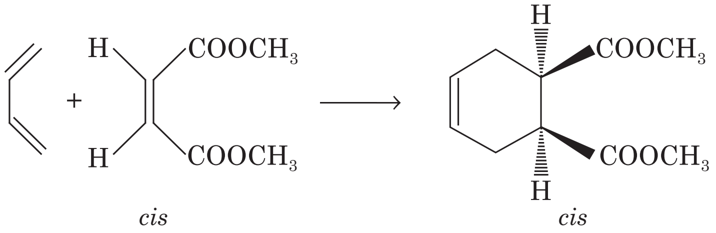


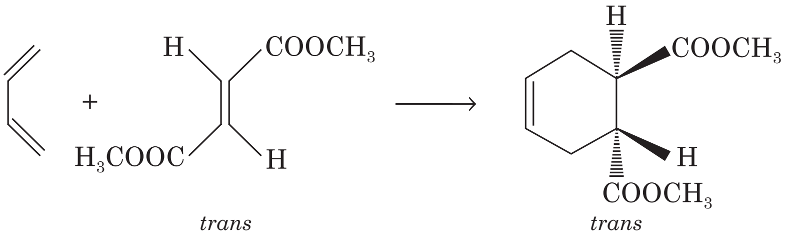
Much faster than butadiene

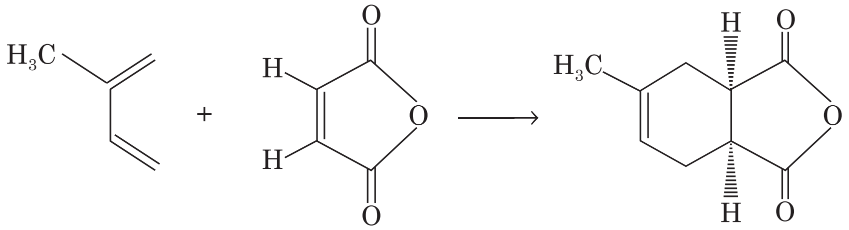
(*ii*) *syn* **stereochemistry:** The Diels-Alder reaction is a *syn* addition with respect to both the diene and dienophile. The dienophile adds to one face of the diene, and the diene adds to one face of the dienophile. As you can see from the transition state in Fig. 3.1, there is no opportunity for any of the substituents that are on the same side of the diene or dienophile will be *cis* on the newly formed ring. Thus, the stereochemistry of the diene and dienophile are preserved during the adduct formation.

(*a*) *Stereochemistry of the adduct due to stereochemistry of the dienophile*

The Diels-Alder reaction is stereospecific. Substituents that are *cis* in the dienophile remain *cis* in the product; substituents that are *trans* in the dienophile remain *trans* in the product.





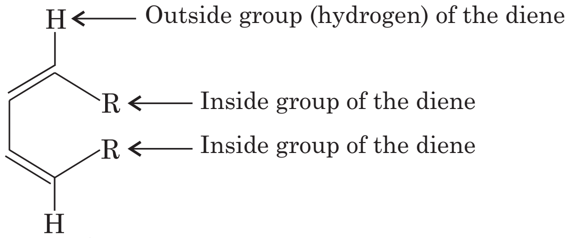


(b) Stereochemistry of the product due to the stereochemistry in the diene

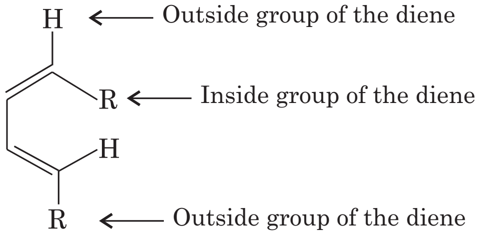
The product stereochemistry is controlled by the geometry of the diene.

This is slightly more complicated as the diene can be *cis*, *cis*; *trans*, *trans* or *cis*, *trans*.

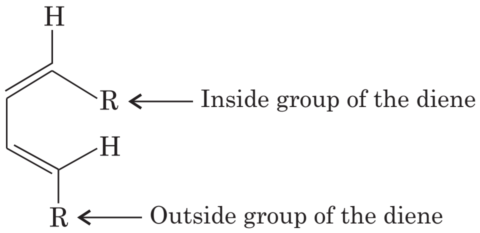
Terminal vinylic carbons (1 and 4 in butadiene) of the *s-cis* diene contain two substituents. One is designated as outside group and other is designated as inside group of the diene. For example,



cis-cis Diene



cis-trans Diene

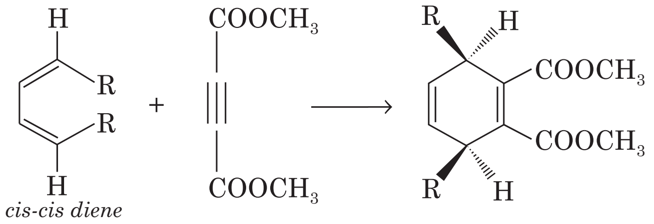


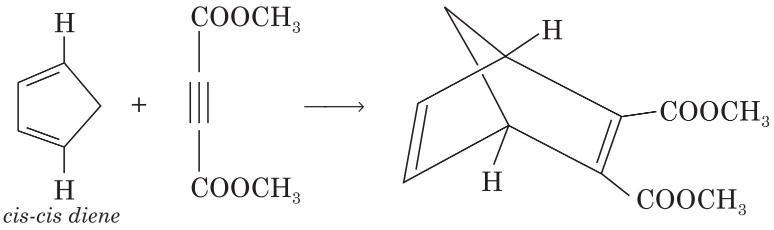
cis-trans Diene

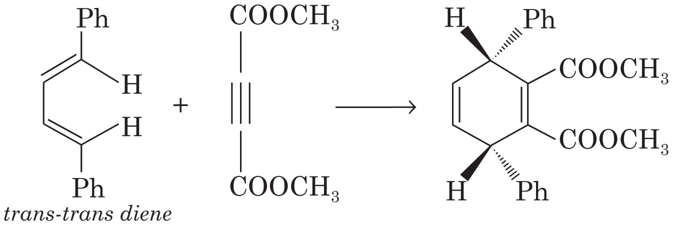
Outside groups at C-1 and C-4 are always *trans* to each other. Similarly, two inside groups at C-1 and C-4 are *cis* to each other.

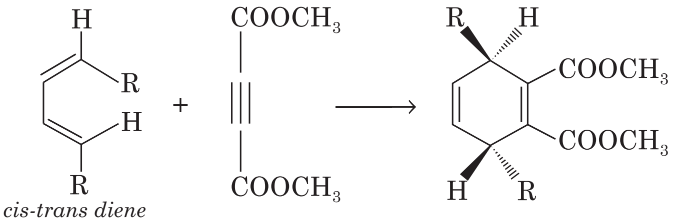
As mentioned earlier that the Diels-Alder reaction is stereospecific. According to the structure of the transition state of the Diels-Alder reaction the *outside substituents of the diene are always below the plane of the new six-membered ring of the adduct.*

Thus the inside substituents of the diene should always be above the plane of the new six-membered ring of the adduct.



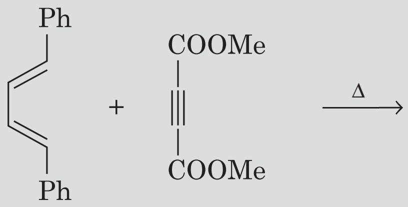




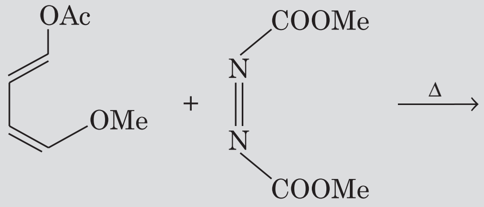


Problem 3: *Give stereochemistry of the product of the given reactions.*

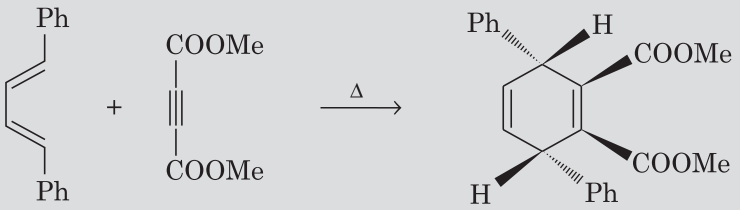
(*i*)



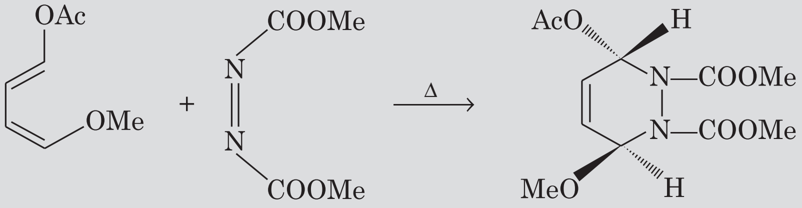
(*ii*)



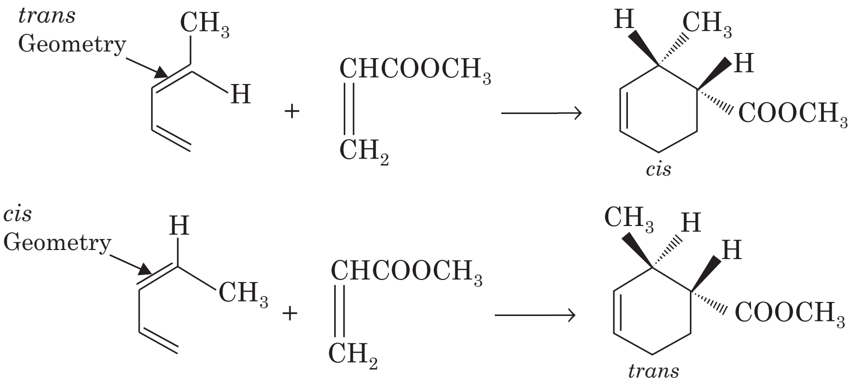
Solution: (*i*) The reaction is Diels-Alder addition. In this reaction the inside substitutions of the diene will be above the plane of the six-membered ring.



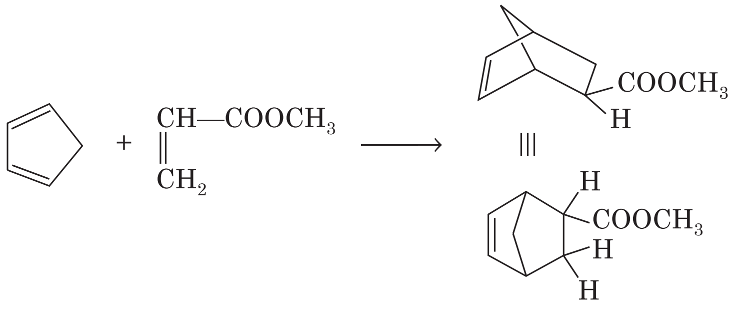
(*ii*) The second reaction is also a Diels-Alder addition. In this reaction too, the inside substituents will be above the plane of the six-membered ring.



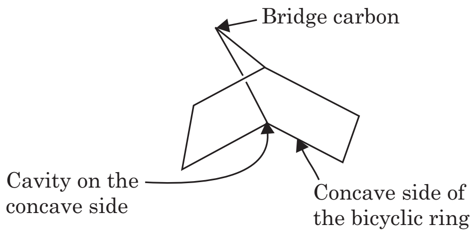
We also need to consider the stereochemistry in the product of the substituents on the diene relative to those on the dienophile. If *trans* 1, 3-pentadiene reacts with methyl propenoate we know that in the product the methyl and ester groups could be either *cis* or *trans*. It is found, in fact, that the *cis* product is formed from *trans* diene and the *trans* product is formed from *cis* diene.

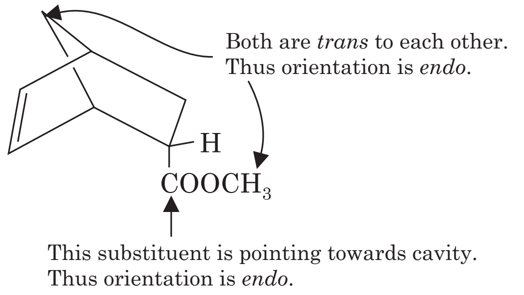


(*iii*) ***Endo* and *Exo* stereochemistry:** The Diels-Alder reaction will produce a bicyclic ring system if the diene is monocyclic. Cyclic dienes are particularly reactive in Diels-Alder reaction because the two double bonds are held in an *s-cis* conformation in five or six-membered rings. This can be seen in the reaction of 1, 3-cyclopentadiene with methyl propenoate.



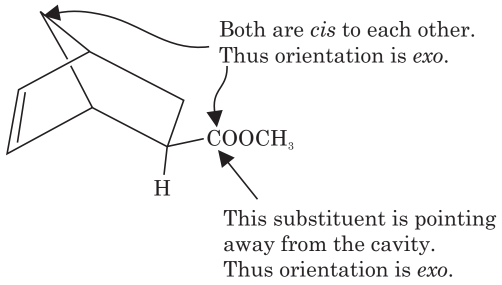
When a compound like this is synthesised, we introduce another stereochemical question. What will be the relative stereochemistry of the methylene bridge and the substituent (in this case $COOCH_3$)? Will they be *cis* or *trans* to one another? Asking these questions is the same as asking whether the substituent will be *endo* or *exo* in the product. An orientation is said to be *endo* meaning that the substituent is *trans* to the bridge carbon or substituent projects into the cavity on the concave side of the bicyclic ring. Similarly, an orientation is said to be *exo* meaning that the substituent is *cis* to the bridge carbon or substituent projects out of the cavity on the concave side of the bicyclic ring.





Both are *trans* to each other. Thus orientation is *endo*.

This substituent is pointing towards cavity. Thus orientation is *endo*.

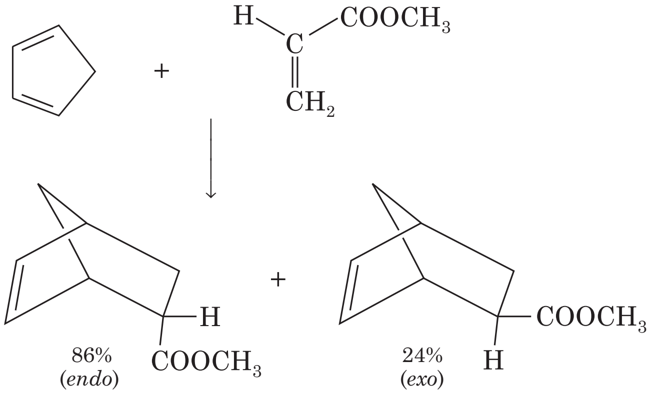


Both are *cis* to each other. Thus orientation is *exo*.

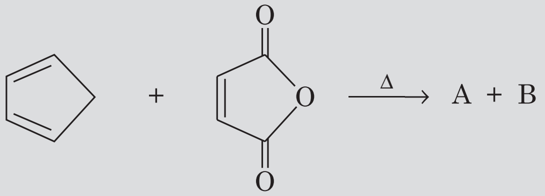
This substituent is pointing away from the cavity. Thus orientation is *exo*.

The *exo* product is expected to be more stable than the *endo* product for steric reasons. In *exo* product the *exo* substituent points away from the more congested part, *i.e.,* bicyclic ring but in *endo* product the *endo* substituent points towards the more congested part. Thus steric repulsion in *endo* is more than the *exo*. Due to this reason *exo* is expected to be more stable than the *endo*.

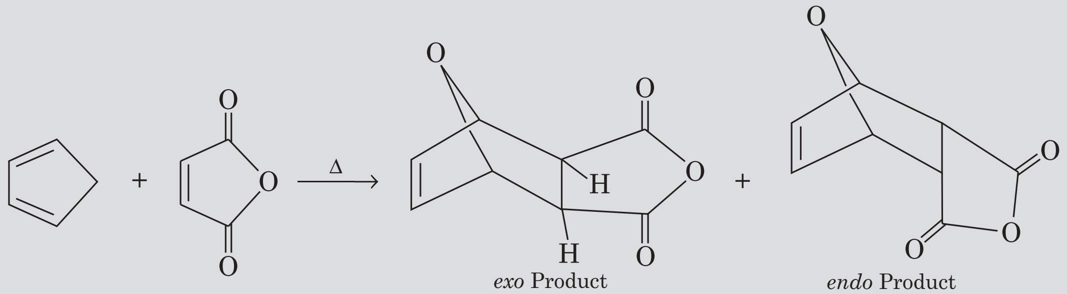
But in practice it has been found that if the diene has a π bond in its electron-withdrawing group then the *endo* product is more stable than the expected *exo* product. This stereochemical preference for the *endo* position is often called the *endo rule*. The reaction of 1, 3-butadiene with methyl propenoate produces three times as much as *endo* as *exo* product. Endo product is major product due to the secondary interactions.



Problem 4: *In the given reaction, there is possibility for the formation of two isomeric products. Write the structures of both products. Explain which will be the major product.*



Solution: The two isomeric products will be *endo* and *exo* products.



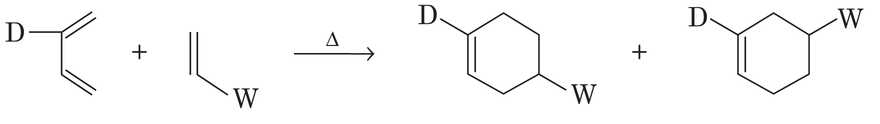
exo Product

endo Product

(D) Orientation Effects in Diels-Alder Reaction

Even when the diene and dienophile are both unsymmetrically substituted, the Diels-Alder product is usually a single isomer rather than a mixture. The product is the isomer that results from orienting the diene and dienophile so that we can imagine a hypothetical reaction intermediate with a “push-pull” flow of electrons from the electron-donating group to the electron-withdrawing group.

Case I: *When electron-donating group (D) is present on the middle carbon of the diene.*

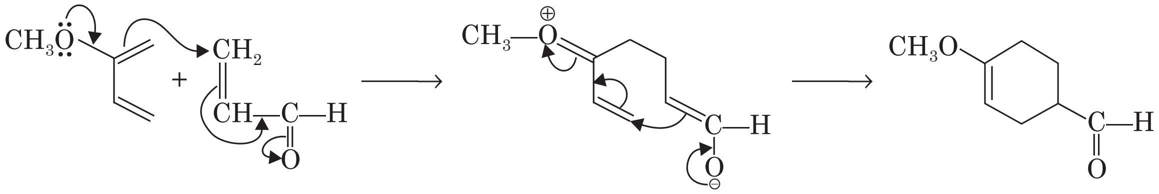


W = electron withdrawing group

1, 4-Product (formed)

1, 3-Product (not formed)

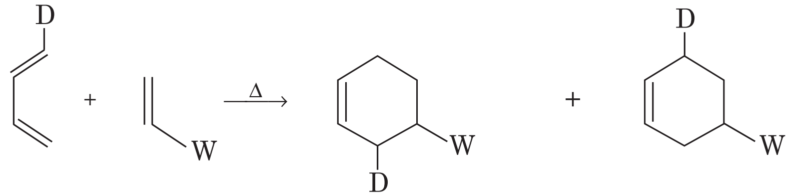
Imaginary flow of electrons in the above case is as follows:



Hypothetical intermediate 1, 4-Product

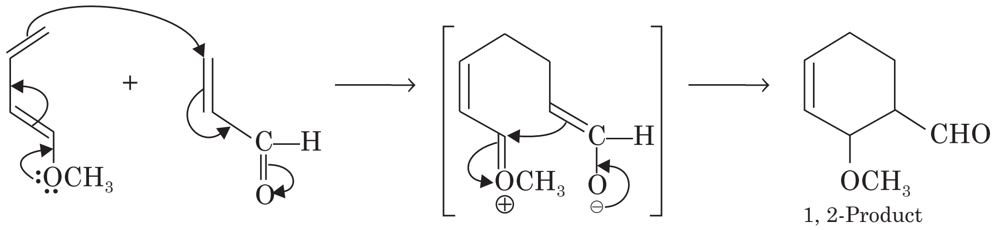
Thus, if electron-donating group is present either at C-2 or at C-3 then in this case product is always 1, 4 and not 1, 3.

Case II: *When an electron-donating group is present at terminal carbon of the diene.*



1, 2-Product (formed) 1, 3-Product (not formed)

Imaginary flow of electrons in this case is as follows:

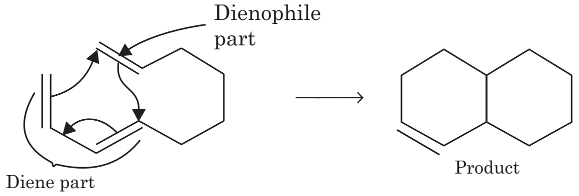


1, 2-Product

Thus, if electron-donating group is present either at C-1 or C-4 then in this case the product is always 1, 2 and not 1, 3.

(E) Intramolecular Diels-Alder Reactions

When diene and the dienophile are part of the same molecule then such type of molecule gives Diels-Alder reaction known as intramolecular Diels-Alder reaction.

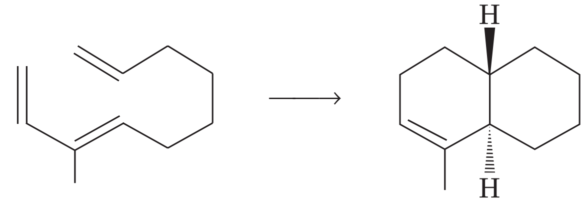


The above example is an intramolecular Diels-Alder reaction.

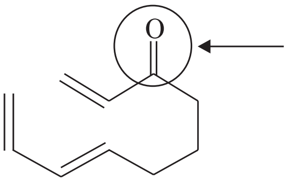
In intramolecular Diels-Alder reaction the stereochemistry at fused ring carbons depends on the nature of the substituent on the dienophile part of the molecule.

Case I: *When electron-withdrawing group is not present on dienophile*

In this case both ring junctions are *trans* to each other. Thus the substituents (*i.e.,* hydrogens) on both fused carbons are always *trans* to each other.

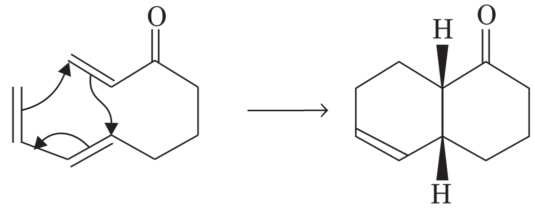


Case II: *When dienophilic part has electron-withdrawing group which is present on inner carbon of the dienophile*



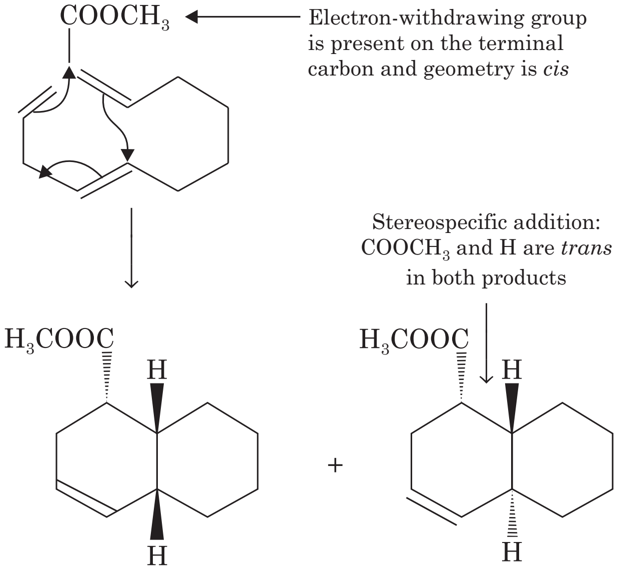
Electron-withdrawing group is present on the inner carbon of the dienophile

In this case both bridge hydrogens are *cis* to each other and perpendicular to the plane of the ring.



Case III: *When electron-withdrawing group is present on terminal carbon of the diene and geometry is cis*

In this case a mixture of two products are formed. In one product both hydrogens of the fused ring carbons are *cis*. In other product both hydrogens are *trans.* Electron-withdrawing group is always below the plane of the ring and *trans* to the bridge hydrogen.

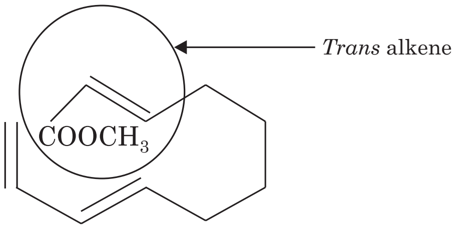


Electron-withdrawing group is present on the terminal carbon and geometry is *cis*

Stereospecific addition: $COOCH_3$ and H are *trans* in both products

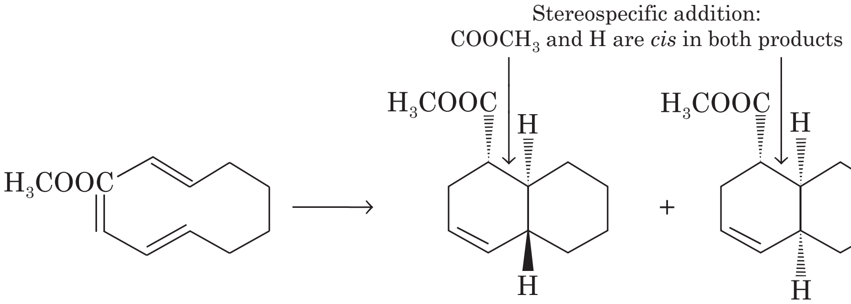
(Both hydrogens are *cis*) (Both hydrogens are *trans*)

Case IV: *When electron-withdrawing group is present on terminal carbon of the dienophile and geometry is trans*

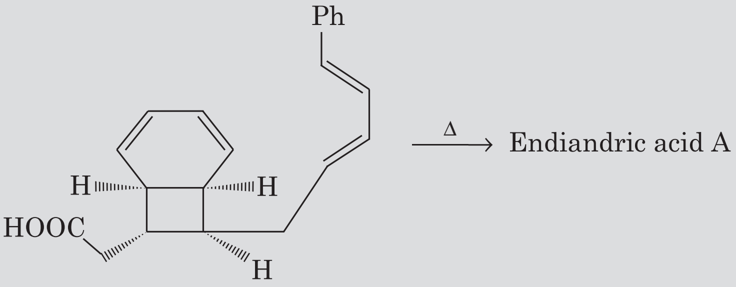


In this case also mixture of two products are formed. In one product both hydrogens of the bridge carbons are *cis* and in other product both are *trans*.

Electron-withdrawing group is always below the plane of the ring and *cis* to adjacent hydrogen of the bridge carbon.

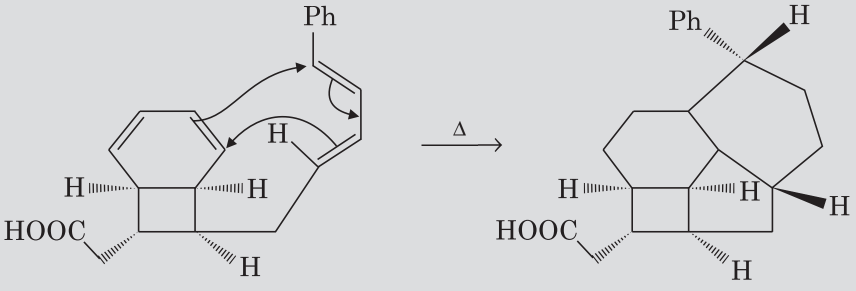

Stereospecific addition:
$COOCH_3$ and H are *cis* in both products

Problem 5: *Endiandric acid E on heating converts into endiandric acid A. Give the structure and stereochemistry of endiandric acid A.*



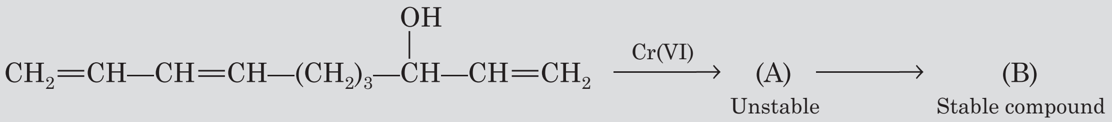
Endiandric acid E

Solution: Endiandric acid E will give intramolecular Diels-Alder addition.



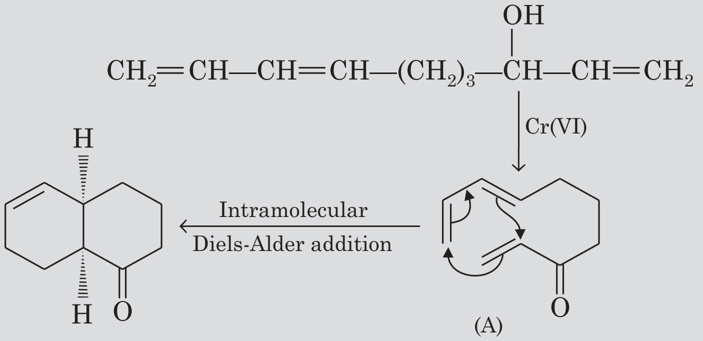
Endiandric acid A

Problem 6: *Complete the following reaction:*



$$CH_2{=}CH{-}CH{=}CH{-}(CH_2)_3{-}\overset{\overset{OH}{|}}{C}H{-}CH{=}CH_2 \xrightarrow{Cr(VI)} \underset{\text{Unstable}}{(A)} \longrightarrow \underset{\text{Stable compound}}{(B)}$$

Solution:

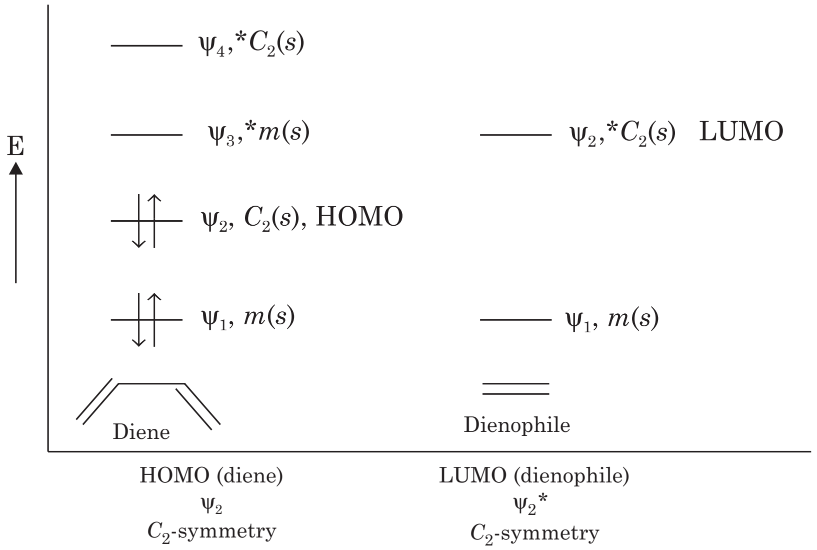


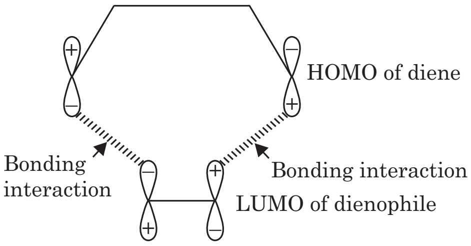
(F) The Frontier Orbital Description of [4 + 2] Cycloadditions

The reaction condition of [4 + 2] cycloaddition reactions are different from [2 + 2] cycloaddition reactions. [4 + 2] cycloaddition reaction is thermally allowed whereas [2 + 2] cycloaddition reaction is photochemically allowed. To see why this is so, we will examine the HOMO-LUMO interactions of only the *p*-orbital components that will form the new σ (*sigma*) bonds in a [4 + 2] cycloaddition. We will compare the HOMO-LUMO interactions for the ground state (for a thermal induced reaction) and those for the excited state (for photo induced reaction).

(*i*) **Thermal induced reaction:** There are two possible interactions, HOMO (diene)-LUMO (dienophile) and HOMO (dienophile)-LUMO (diene).

Case I: *HOMO of diene and LUMO of dienophile*

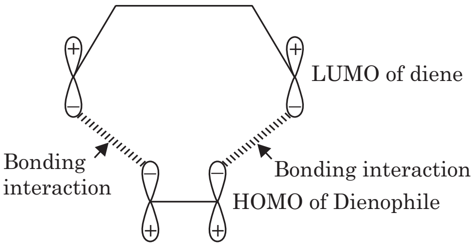




Phase correct for bonding symmetry allowed process

Case II: *LUMO of diene and HOMO of dienophile*

LUMO (diene)—HOMO (dienophile)
ψ_3^* ψ_1
m-Symmetry *m*-Symmetry



Phase correct for bonding symmetry allowed process

The stronger of these two interactions will control the reaction. In this case, the stronger interaction is between the HOMO and LUMO pair closer in energy. The strength of the orbital overlap and the magnitude of the resulting stabilisation, depends on the relative energies of the two orbitals. The closer the two are in energy, the stronger the interaction.

In the Diels-Alder reaction of ethylene and butadiene, the two HOMO-LUMO interactions are of equal energy and orbital symmetry is same in both reactions. Both interactions involve bonding overlap at the point of formation of the two new σ (*sigma*) bonds. Accordingly this reaction is symmetry allowed reaction.

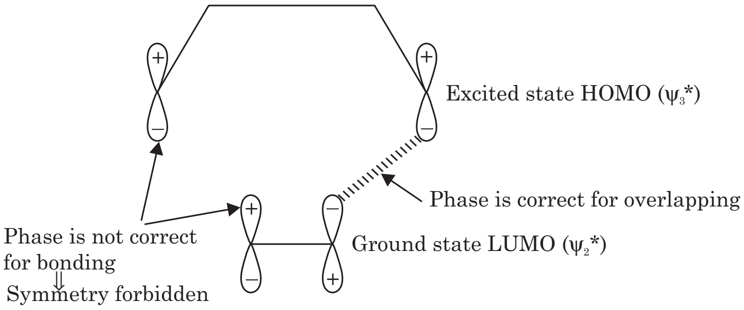
(*ii*) **Photo induced reaction:** In photo-induced cycloaddition reaction, interaction always takes place between excited state HOMO(HOMO*) of diene and ground state LUMO of dienophile and *vice-versa*. Thus, there are two possible interactions.

(*i*) Excited state HOMO (diene) and ground state LUMO (dienophile), and

(*ii*) Excited state HOMO (dienophile) and ground state LUMO (diene).

Let us take the example of excited state HOMO of diene and ground state LUMO of dienophile.

When butadiene is excited by light its HOMO becomes ψ_3* which has *m*-symmetry. This MO cannot overlap with ground state LUMO of the ethylene which has C_2-symmetry.



Phase is not correct for overlapping symmetry forbidden process

Thus, photochemical cycloaddition of [4 + 2] system is symmetry forbidden reaction. On the basis of the results we can obtain the following selection rules for the cycloaddition reactions.

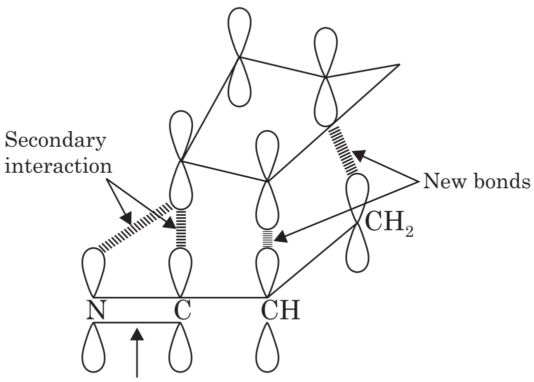
Table 3.1 Selection rules for cycloaddition reactions

Number of electrons	*Mode of activation*	*Allowed stereochemistry*
$(4n)\pi$	Photochemical	Supra-Supra
$(4n + 2)\pi$	Thermal	Supra-Supra

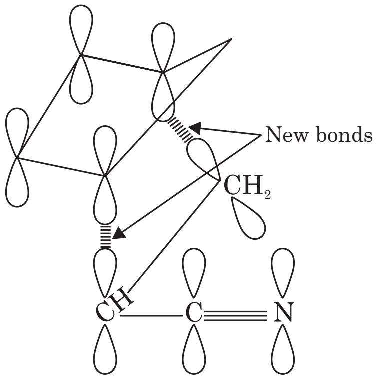
(*iii*) **Endo orientation in bicyclic compounds:** As mentioned earlier that the *exo* product is more stable (*i.e.,* it is thermodynamic product) than the *endo* product (*i.e.,* it is kinetically controlled product) in Diels-Alder reaction. Diels-Alder reaction always gives *endo* product as a major product when dienophile has a π bond in its electron-withdrawing group.

This clearly confirms that transition state of *endo* product in this case is more stable than the transition state of *exo* product due to some other factor, which overwhelms steric considerations.

In *endo* orientation the electron-withdrawing group having a π bond of a dienophile is directed to the inside of the cyclic ring, *i.e.,* electron-withdrawing group is nearer to the conjugated system of diene in the formation of transition state. In this orientation the *p*-orbital of the electron-withdrawing group approach the central carbon atoms (*C*-2 and *C*-3) of the diene. This proximity results in a weak secondary overlap: An overlap of the *p*-orbitals of the electron-withdrawing group with the *p*-orbitals of *C*-2 and *C*-3 of the diene. This fancy-phrase simply means that there can be interaction between the *back* diene orbitals and orbitals on the substituent only in the *endo* transition state. In *exo* orientation the electron-withdrawing group of the dienophile is directed away from the cyclic diene conjugated system.



Group is near to the conjugated system of diene *endo* transition state



Exo transition state has no possible secondary interactions

3.3 CORRELATION DIAGRAMS OF CYCLOADDITION REACTIONS

3.3.1 Orbital Symmetry in Cycloaddition

Orbital symmetry arguments make useful predictions about concerted cycloaddition reaction which is suprafacial-suprafacial. Consider the [$\pi 2s + \pi 2s$] cycloaddition of ethylene molecules in parallel planes approaching each other vertically (Fig. 3.2).

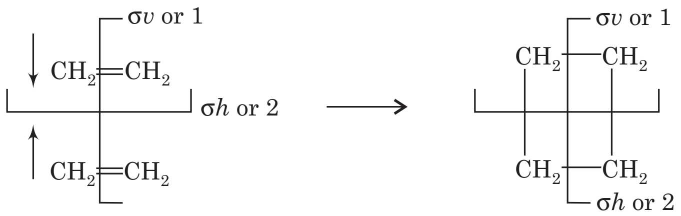
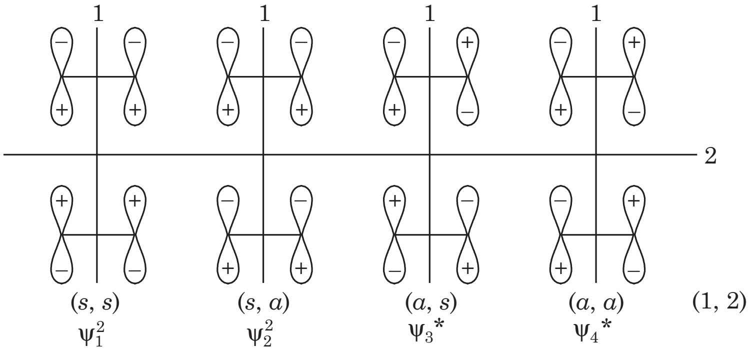


Fig. 3.2 Two ethylene molecules approaching each other vertically and approach is suprafacial-suprafacial

This system contains vertical and horizontal plane of symmetry (*i.e.*, mirror plane of symmetry) denoted by σv (or 1) and σh (or 2) which are useful in characterising the orbitals. In the transformation of ethylene molecules to cyclobutane we are mainly concerned with the four π (*pi*) orbitals of two ethylene molecules and the four σ (*sigma*) orbitals of cyclobutane.

Let us first take the σv and σh in two ethylene molecules



(A)

Now let us take the σv and σh in cyclobutane

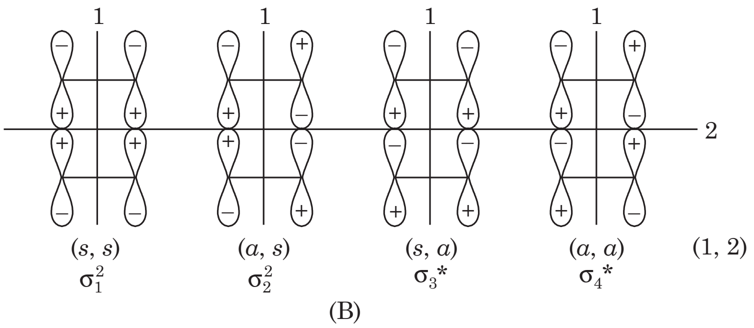


Fig. 3.3 Symmetry properties of (A) ethylene π orbitals and (B) cyclobutane σ orbitals

Note that more will be symmetry in the system less will be energy of the system for π as well as σ orbitals. Energy of π (*pi*) system is as follows in increasing order:

ss sa as aa

Energy of σ (*sigma*) system is as follow in increasing order:

ss as sa aa

We can now construct the orbital correlation diagram. But before this we must classify the symmetry of the orbitals twice over once for the plane bisecting the π bonds represented by the vertical line, *i.e.*, σv (or 1) (Fig. 3.3) and then for the plane between the two ethylene molecules, the horizontal line, *i.e.*, σh (or 2). Thus, the lowest energy orbital in the starting materials is the bonding combination ψ_1 (both ψ_1 has mirror symmetry) of the bonding π orbitals. This orbital has both symmetry (and hence represented as *s*, *s*). The next orbital up is the antibonding combination of ψ_2 (both ψ_2 has *m*-symmetry) of the two bonding π orbitals. This orbital has σv symmetry and σh asymmetry so it is classified as *sa*.

The next orbital up is the bonding combination of ψ_3^* (both ψ_3^* has C_2-symmetry) of the two antibonding π orbitals. This orbital has σv asymmetry and σh symmetry so it is classified as *as*. The next orbital up is the antibonding combination of ψ_4* (both ψ_4* has C_2-symmetry) of the two antibonding π orbitals. This orbital has σv as well as σh asymmetry so it is classified as *aa*. Thus, the orbitals of the interacting ethylenes are the result of forming bonding and antibonding combination of π and π^* orbitals of two ethylene molecules. The interacting σ orbitals are similar combination of the σ (σ_1, *s*, *s* and σ_2, *a*, *s*) and σ^* (σ_3*, *sa* and σ_4*, *aa*) (Fig. 3.3B).

We can now complete (Fig. 3.3) by correlating the energy levels, feeding the orbitals in the starting materials into orbitals of the same symmetry in the product, *ss* to *ss*.

sa to *sa*
sa to *sa*
as to *as*
aa to *aa*.

On the basis of the above information, a correlation diagram (Fig. 3.4) may be drawn in which the levels of like symmetry are connected by lines.

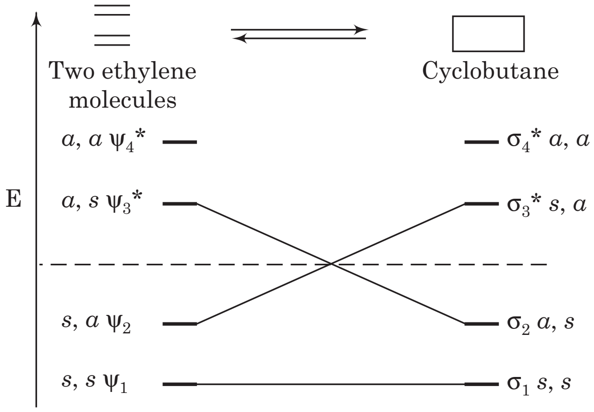


Fig. 3.4 Correlation diagram for cycloaddition of ethylene into cyclobutane

A close examination of the diagram leads us to the following two conclusions:

1. The ground state orbitals of ethylene correlate with an excited state of cyclobutane, $\psi_1^2\psi_2^2 \rightleftharpoons \sigma_1^2\sigma_3^{*2}$. Consequently, the combination of two ground state ethylene molecules cannot result in the formation of ground state cyclobutane while conserving the orbital symmetry. Hence the thermal process is symmetry-forbidden.
2. As there is correlation between the first excited state of the ethylene and cyclobutane, $\psi_1^2\psi_2\psi_3^* \rightleftharpoons \sigma_1^2\sigma_2\sigma_3^*$ the photochemical process is symmetry allowed.

3.3.2 Correlation Diagram of [4 + 2] Cycloaddition Reaction

As mentioned earlier correlation diagrams provide a complete explanation of concerted reaction in which symmetry is preserved throughout the reaction. For correlation diagram of [4 + 2] cycloaddition this can be done by the following steps:

1. Draw the concerted reaction and indicate the migration of electrons by curly arrows for the backward and forward reaction (Fig. 3.5).

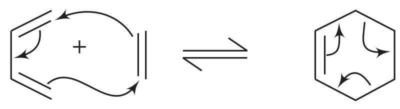


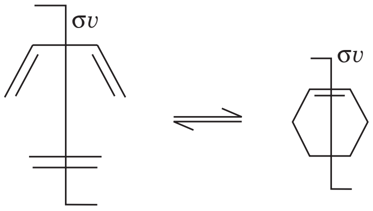
Fig. 3.5

Any substituent(s) present in any reactant (in this case diene and dienophile) symmetrical or unsymmetrical do not disturb the symmetry of the orbitals directly involved.

2. Identify the orbitals undergoing change. The curly arrow helps to focus on what they are, *i.e.*, which orbitals are undergoing change. For the starting materials, they are the π (*pi*) orbitals (ψ_1, ψ_2, ψ_3^* and ψ_4^*) of diene unit and π (*pi*) orbitals (π and π^*) of the dienophile. For the product, they are the π bond (π and π* orbitals) and two newly formed σ bonds (σ_1, σ_2, σ_3^* and σ_4^*).

3. Identify any symmetry elements maintained throughout the reaction, *i.e.*, the same symmetry should be present in reactants, cyclic transition state and product. The symmetry may be of one or two types (σv and σh).

   In Diels-Alder reaction there is only one symmetry and that is vertical plane of symmetry bisecting the bond between C-2 and C-3 of the diene and the double bond of the dienophile.



4. Rank the orbitals in increasing order of energy (vertical on the paper) with the reactants on the left and the product(s) on the right (Fig. 3.6).
5. Besides each energy level, draw the orbitals showing signs of the lobes of atomic orbitals.
6. Identify the symmetry of the orbitals with respect to σv or σh or both (which one is possible) of reactant and product. In this case symmetry is σv.
7. Construct an orbital correlation diagram. Following the assumption that an orbital in the starting material must feed into an orbital of same symmetry in the product, draw lines connecting the orbitals of the starting materials to those of the products nearest in energy (*i.e.,* energy difference between correlating orbitals of reactant and product should be minimum and of the same symmetry. Thus $\psi_1(s)$ connects to σ_1 (s), $\pi(s)$ to $\pi(s)$ and $\psi_2(a)$ connect to $\sigma_2(a)$ and similarly with unoccupied orbitals $\psi_3^*(s)$ connects to σ_3^*, π^* (a) connects to π^* (a) and ψ_4^* (a) connects to σ_4^* (a).

Since ground state orbitals of reactants correlate with the ground state orbitals of the product therefore Diels-Alder reaction is thermally allowed.

$$\psi_1^2\pi^2\psi_2^2 \longrightarrow \sigma_1^2\sigma_2^2\pi^2$$

On the other hand, photochemical transformation is not possible as the first excited state of the reactant does not correlate with the first excited state of the product. Rather it correlates with the upper excited state of the product.

$$\psi_1^2\pi^2\psi_2\psi_3^* \not\longrightarrow \sigma_1^2\sigma_2^2\pi\sigma_3^*$$

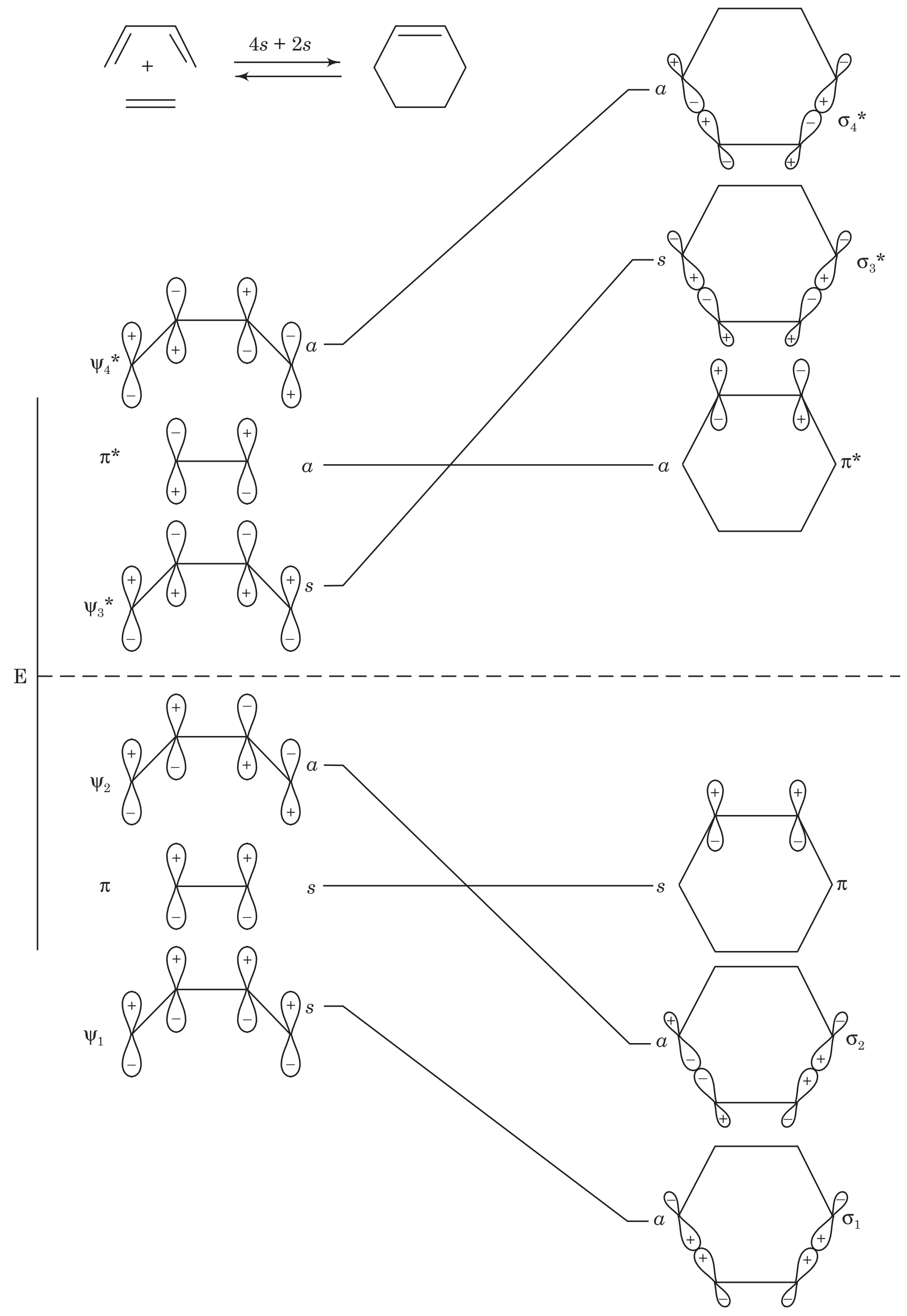


Fig. 3.6 Correlation diagram of [4 + 2] cycloaddition reaction

3.4 THE WOODWARD-HOFFMANN RULE FOR CYCLOADDITION REACTIONS

Thermal Reactions

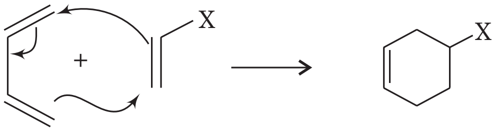
A thermal (ground state) pericyclic change is symmetry-allowed when the total number of $(4q + 2)s$ and $(4r)\ a$ components is odd.

Photo Chemical Reactions

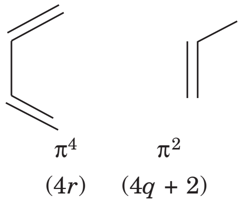
A pericyclic change in the first electronically excited state is symmetry-allowed when the total number of $(4q + 2)\ s$ and $(4r)\ a$ component is even.

3.4.1 The Woodward-Hoffmann Rule in | 4 + 2 | Cycloadditions

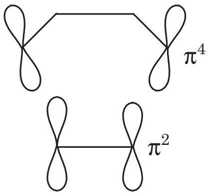
1. Draw the general mechanism of the reaction



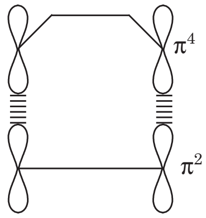
2. Choose the components. All the bonds taking part in the mechanism must be included and ignore all substituents which are not directly involved.



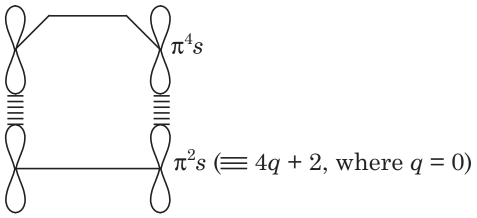
3. Make a three-dimensional drawing of the way the components come together for the reaction putting the orbitals at the ends of the components.



4. Join the components where new bonds are to be formed.



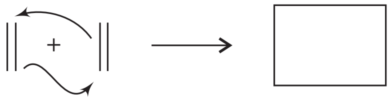
5. Label each component s or a depending on whether new bonds are formed on the same side or opposite sides.

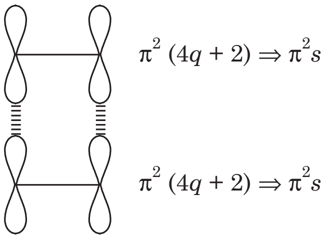


6. Count the number of $(4q + 2)$ s and $(4r)$ a components.

Number of $(4q + 2)$ s component = 1
Number of $(4r)$ a component = 0
Total = 1 (odd)
Thermally allowed.

3.4.2 Woodward-Hoffmann Rule in [2 + 2] Cycloadditions





Number of $(4q + 2)$ s component = 2
Number of $(4r)$ a component = 0
Total = 2 (even)
Photochemically allowed.

3.5 HÜCKEL-MOBIUS METHOD

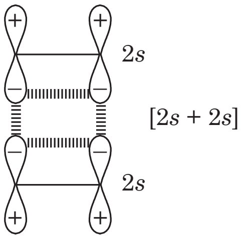
Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has $(4n + 2)\pi$ conjugated or delocalised electrons and consequently stable in ground state. Similarly, monocyclic planar conjugated system is anti-aromatic if it has $(4n)\pi$ conjugated or delocalised electrons. This system is unstable in ground state. However, further calculation shows that these rules are reversed by the presence of *a node* in the array of atomic orbitals. Thus system with $(4n + 2)\pi$ electrons and a node is anti-aromatic while system with $(4n)\pi$ electrons and a node is aromatic.

If system has no node then it is called *Hückel* system and array is called *Hückel* array. Similarly, if system has node then it is called *Mobius* system and array is called *Mobius* array.

Application of above rules to cycloaddition reactions led to the generalisation that thermal reactions take place via aromatic transition state whereas photochemical reactions proceed via antiaromatic transition state.

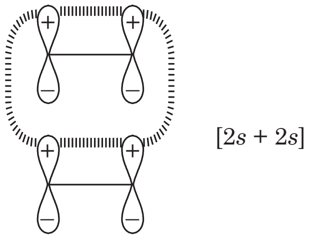
Consider the [2 + 2] cycloaddition reaction:

(*i*)



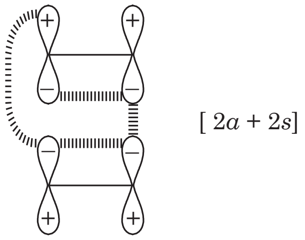
4 Electrons, zero node.
Hückel system, antiaromatic, *h*ν allowed.

(*ii*)



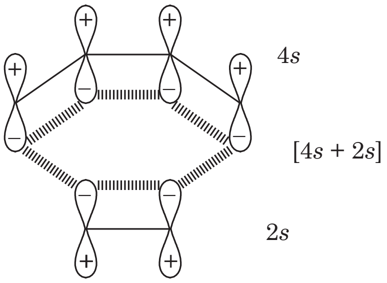
4 Electrons, zero node.
Hückel system, antiaromatic *h*ν allowed.

(*iii*)

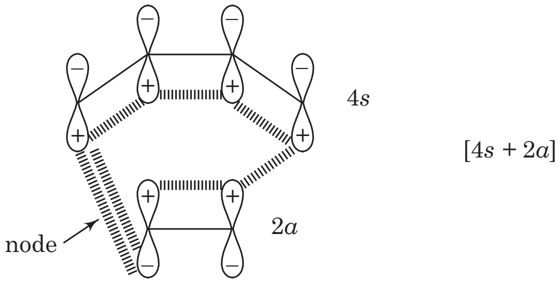


4 Electrons, one node.
Mobius system, aromatic Δ allowed.

Now consider the [4 + 2] cycloadditions:



6 Electrons, zero node.
Hückel system, aromatic, Δ allowed.



6 Electrons, one node.
Antiaromatic, Mobius system, $h\nu$ allowed.

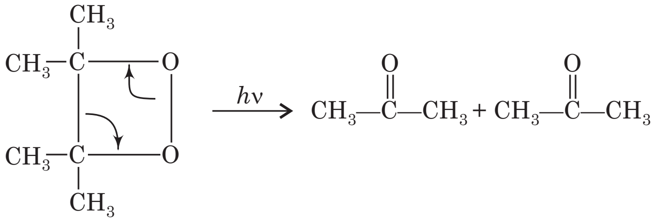
On the basis of the results we can obtain the following selection rules for the cycloaddition reactions:

Table 3.2 Selection rules for cycloaddition reactions

m + n electrons	*Number of nodes*	*Aromaticity*	*Thermally allowed*	*Photochemically allowed*
$4n$	0	antiaromatic		supra-supra antara-antara
$4n$	1	aromatic	supra-antara antara-supra	
$4n + 2$	0	aromatic	supra-supra antara-antara	
$4n + 2$	1	antiaromatic		supra-antara antara-supra

3.6 CYCLOREVERSION OR RETROCYCLOADDITION REACTIONS

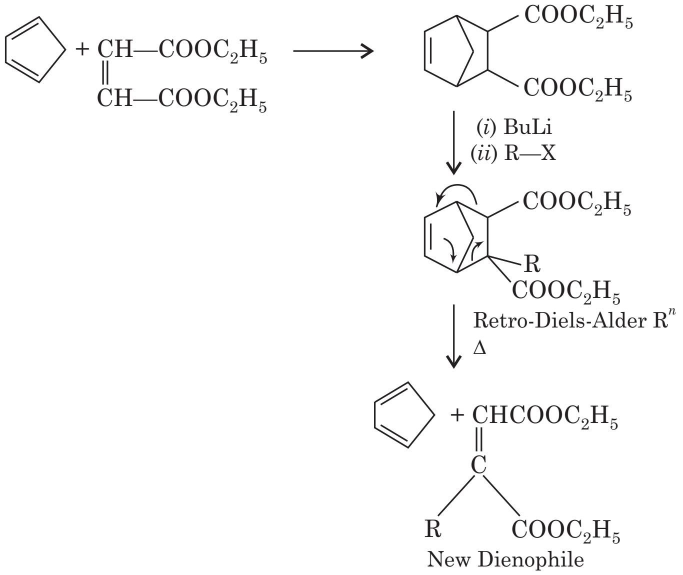
Cycloaddition reactions are, in theory and usually in practice, reversible reactions. The reverse of cycloaddition reactions are known as cycloreversions or retrograde cycloadditions. Such reactions follow same symmetry selection rules as does the cycloaddition itself. For example:



$$(CH_3)_2C(O)-C(O)(CH_3)_2 \xrightarrow{h\nu} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \quad ...(1)$$

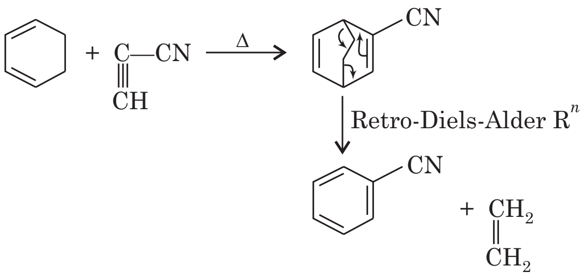
This reaction is represented as –[2 + 2] cycloreversion. A minus sign before the designation indicates a cycloreversion reaction. The most common cycloreversion reaction is – [4 + 2] cyclo reversion. This reaction is commonly known as retro-Diels-Alder reaction.

Diels-Alder reaction is reversible, and on heating many adducts dissociate into their components. In most of the cases retro-Diels-Alder reactions take place under quite mild conditions. Retro-Diels-Alder reaction is very important in those cases where adduct obtained in Diels-Alder reaction is chemically modified and than give new diene or dienophile by retro-Diels-Alder reaction.

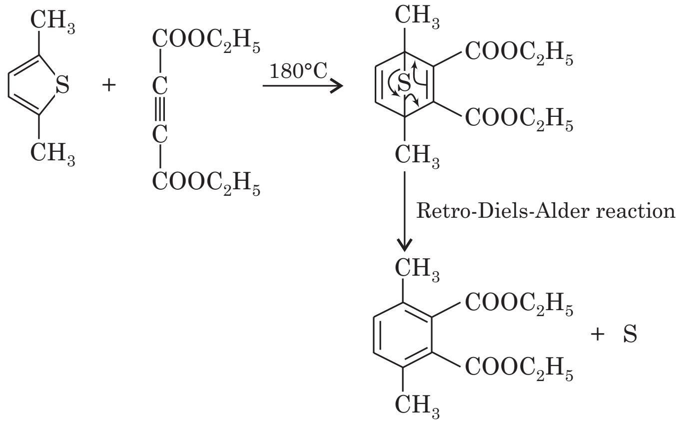


...(2)

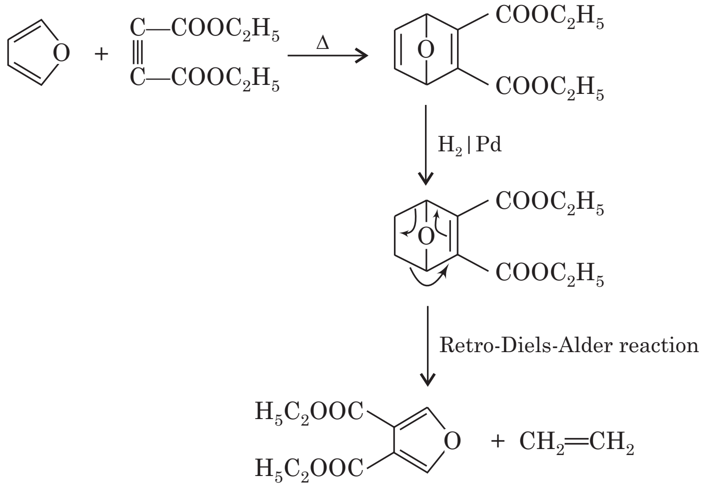
It is not always the bonds formed in Diels-Alder addition is broken in retro-Diels-Alder reaction



...(3)

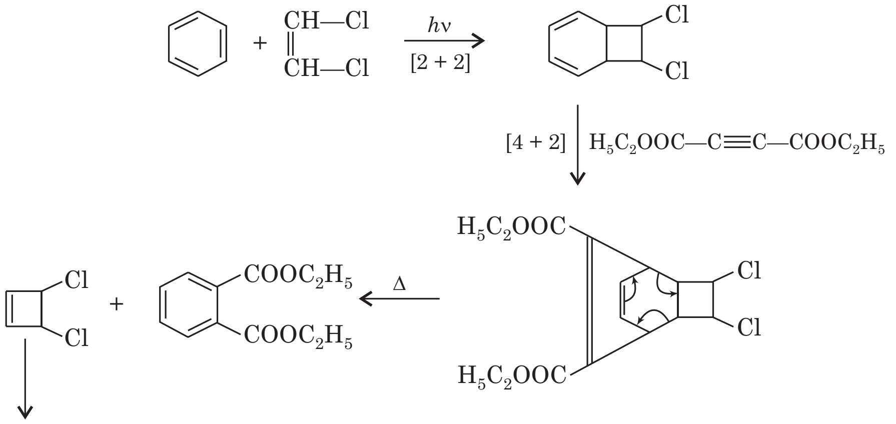


...(4)



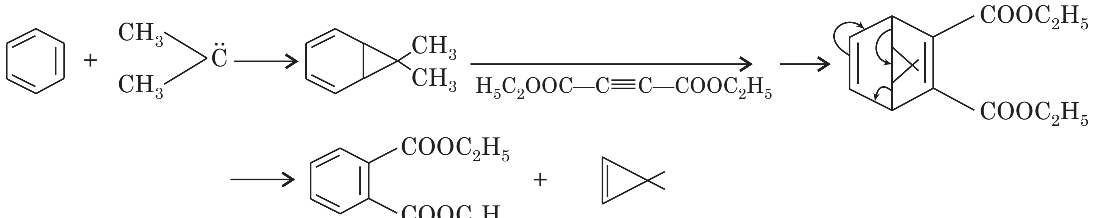
...(5)

Retro-Diels-Alder reaction can also be used for the preparation of some reactive compounds in vapour phase (in the absence of solvent and catalyst) that are difficult to prepare by other methods.



...(6)

This compound is highly reactive and used as synthetic reagent for the preparation of various compounds



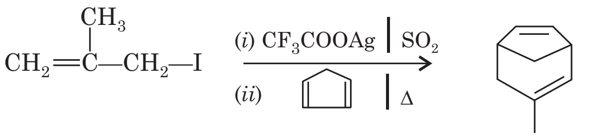
(Highly reactive compound)

3.7 [4 + 2] CYCLOADDITIONS OF CATIONS AND ANIONS

Conjugated ions like allyl cations, allyl anions and pentadienyl cations also give [4 + 2] cycloaddition reaction. Allyl cation is a two electron system in a [4 + 2] cycloaddition reaction. Allyl carbanion and pentadienyl cation is four electron system in a [4 + 2] cycloaddition reaction.

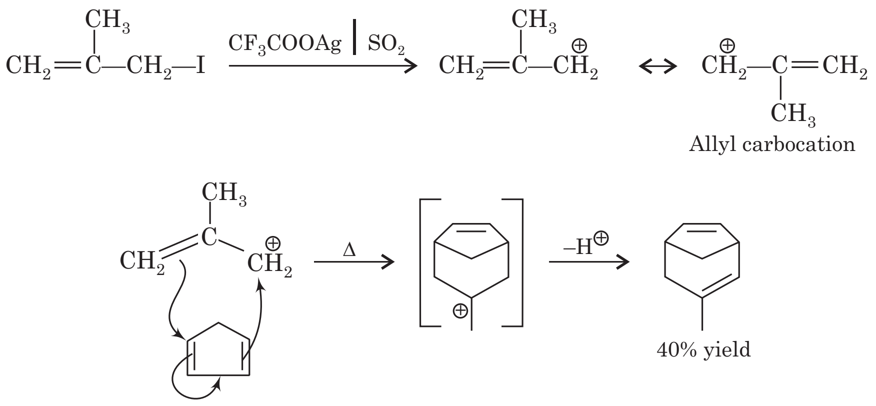
Examples of [4 + 2] cycloaddition reaction given by allyl carbocation.

(*i*)

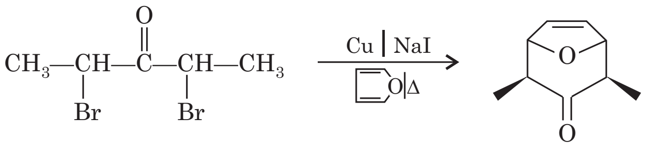


...(1)

The reaction takes place as follows:

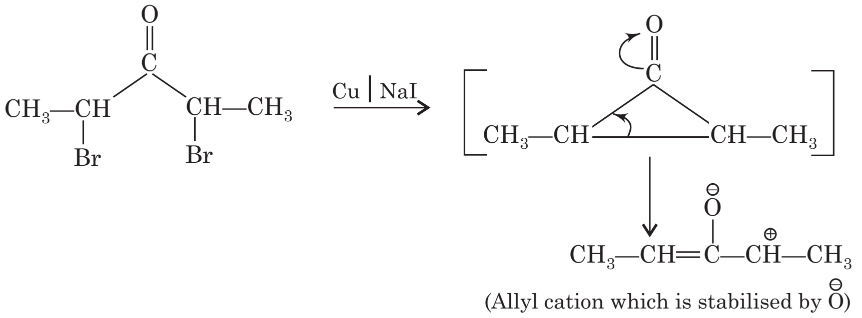


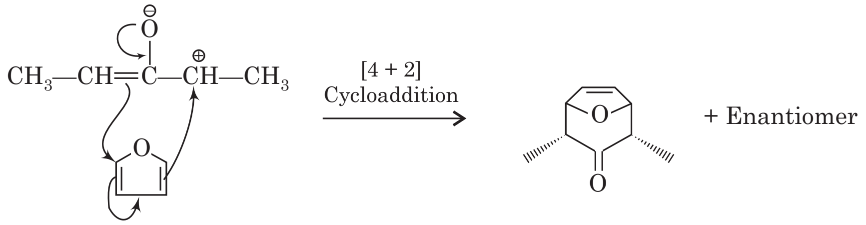
(*ii*)



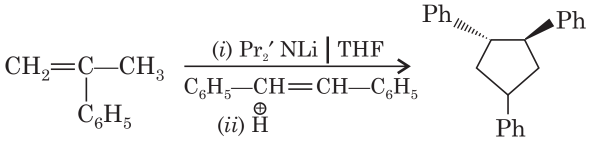
...(2)

The above reaction takes place as follows:

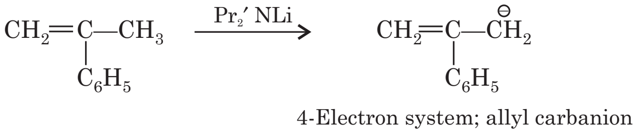


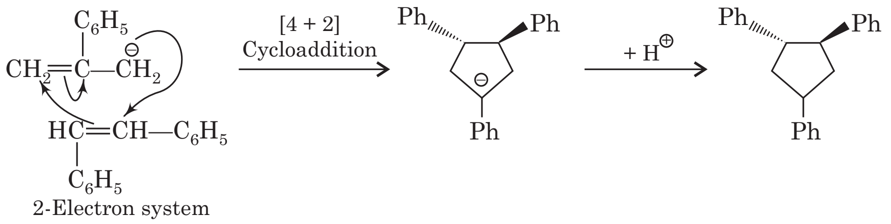


Example of [4 + 2] cycloaddition given by allyl carbanions



The above reaction takes place as follows:

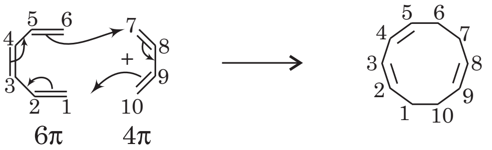


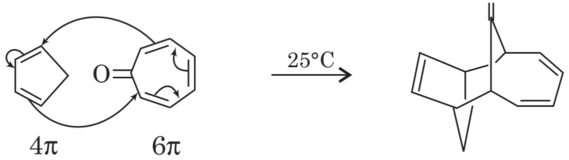


3.8 CYCLOADDITIONS INVOLVING MORE THAN [4 + 2] ELECTRONS

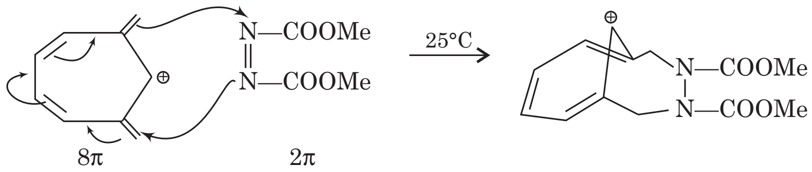
All the reactions described so far have used six electrons in the transition state. In some cycloaddition reaction more than six electrons take part in cyclic transition state. The common examples are [8 + 2] and [6 + 4] cycloadditions

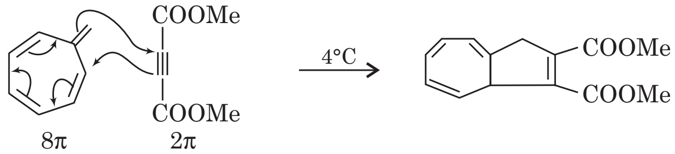
[6 + 4] *cycloaddition*



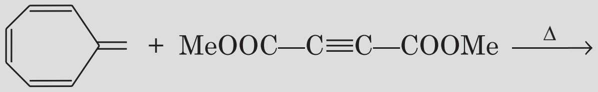


[8 + 2] cycloadditions

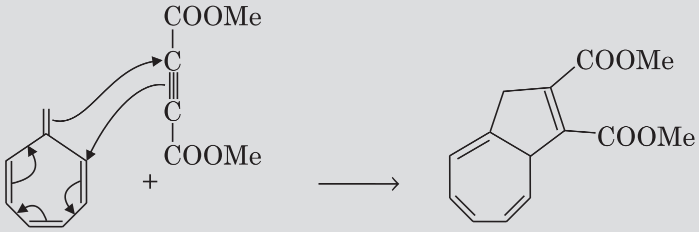




Problem 7: *Give the product of the following reaction:*

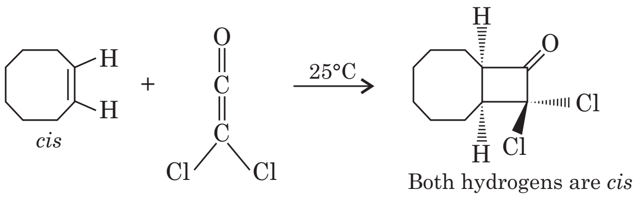


Solution: The reaction is [8 + 2] cycloaddition reaction.

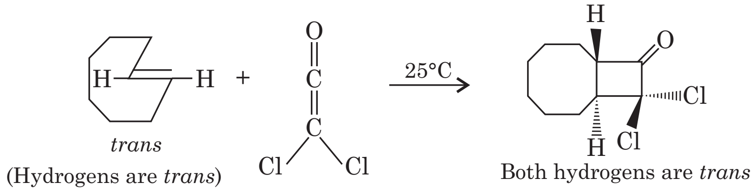


3.9 SOME ANOMALOUS [2 + 2] CYCLOADDITIONS

Let us first take some addition reactions of ketene with alkenes. The reaction has some characteristics of pericyclic cycloaddition. The reaction is *syn* addition and geometry of reactant is maintained in the product.



...(1)



...(2)

In the given two examples stereochemistry of reactant is maintained in the product. These two reactions are pericyclic [2 + 2] cycloaddition reaction and thermally allowed reactions. We know very well that [2 + 2] cycloaddition is photochemical reaction and suprafacial-suprafacial. If reaction is thermally allowed then reaction should be suprafacial-antarafacial reaction, *i.e.*, [$\pi 2s + \pi 2a$] cycloaddition (see Table 3.2). If this is [$2\pi s + 2\pi a$] than how does it overcome the symmetry-imposed barrier?

One suggestion is that two molecules approach each other at right angles for overlapping in an antarafacial sense of the ketene. Making the reaction the allowed [$\pi 2s + 2\pi a$] cycloaddition that we have dismissed as being unreasonable. This is the most simplest explanation. The [2 + 2] cycloadditions of ketenes being concerted is more likely to be a consequence of the fact that ketenes have two sets of π orbitals at right angle to each other and overlap can be developed to orthogonal orbitals (dashed lines) and in addition there is transmission of information from one orbital to its orthogonal neighbour (heavyline) (Fig. 3.7).

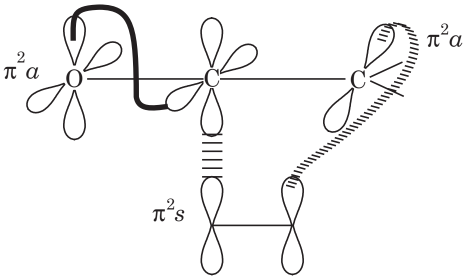


Fig. 3.7 Overlapping orbitals of ketene and alkene

The vision identifies the reaction as an allowed [$\pi 2s + \pi 2a + \pi 2s$] cycloaddition reaction.

The FMO treatment shows that the bond formation between C-1 and C-1′ develops mainly from the interaction of the LUMO of ketene (π^* of C=O) and HOMO of alkene (Fig. 3.7) and that the bond between C-2 and C-2′ develops mainly from the interaction of HOMO ketene [(ψ_2) the three atom linear set of orbitals analogous to the allyl anion] and LUMO of the alkene (Figs. 3.8 and 3.9).

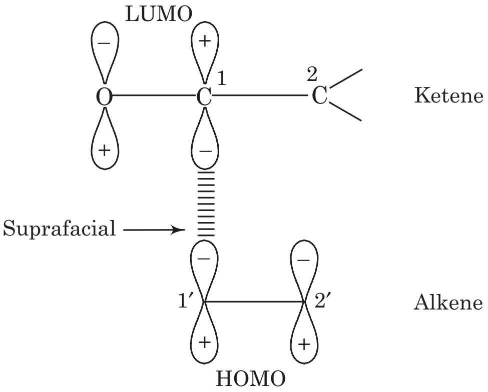


Fig. 3.8 Bond formation between C-1 of ketene and C-1′ of alkene

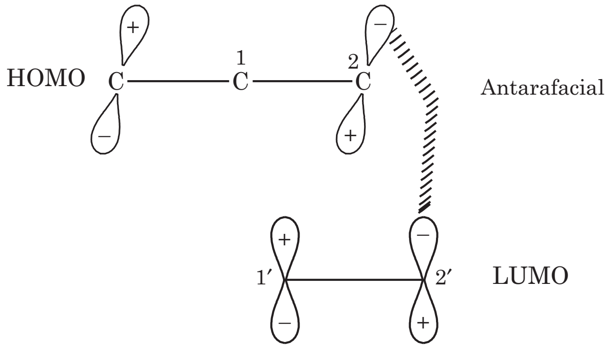
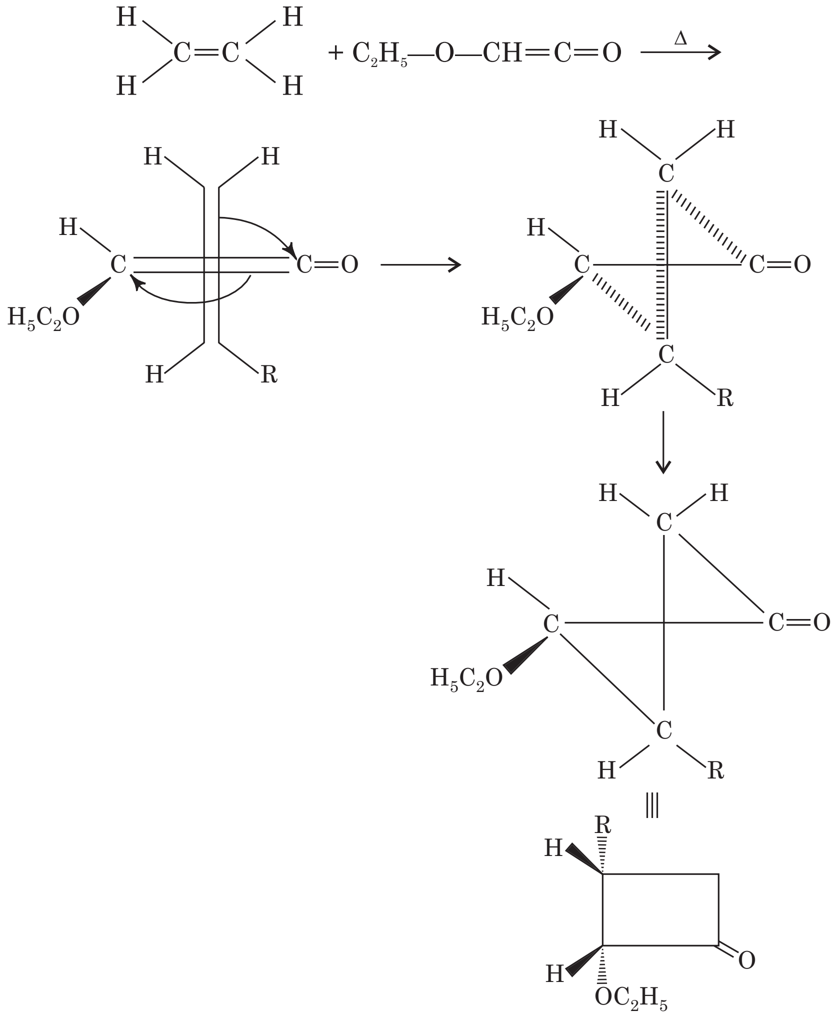
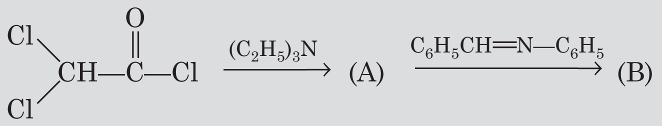


Fig. 3.9 Bond formation between C-2 of ketene and C-2′ of alkene

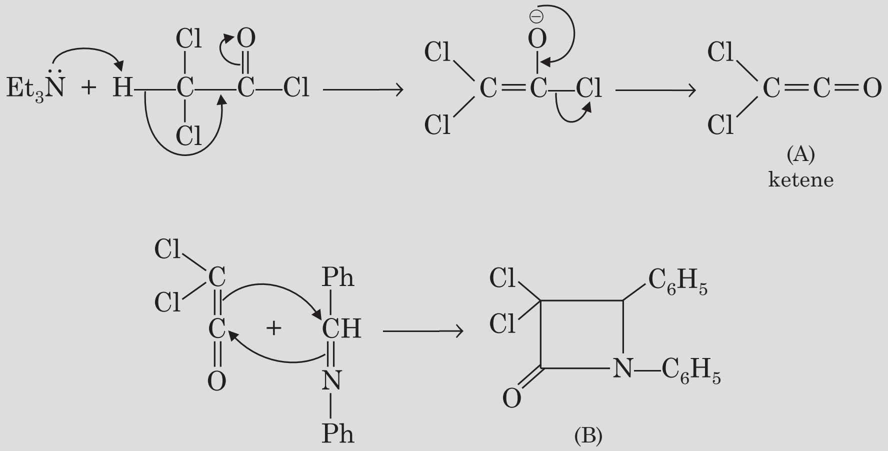
The reaction can be represented as follows:



Problem 8: *Complete the following reaction:*

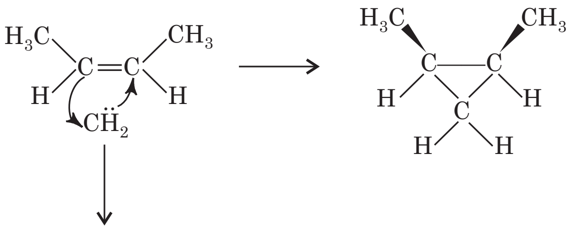


Solution:



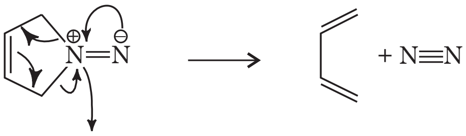
3.10 CHELOTROPIC REACTIONS

Chelotropic reactions are those reactions in which two σ bonds are formed on same atom or two σ bonds are broken on same atom.



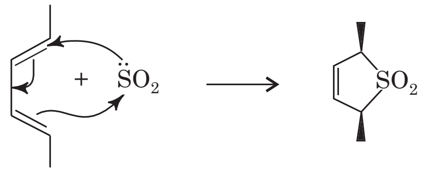
...(1)

Two σ bonds are formed on this carbon in the product.



...(2)

Two σ bonds are broken on nitrogen



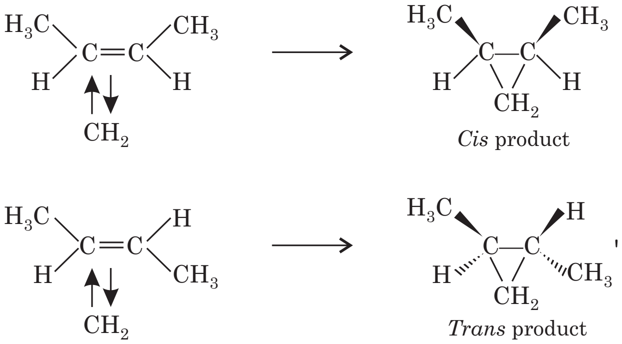
...(3)

Two σ bonds are formed on sulphur

3.10.1 [2 + 2] Chelotropic Cycloadditions

(*A*) *Chelotropic Reactions of Alkenes with Singlet Carbenes*

Alkene reacts with carbene to form cyclopropane or substituted cyclopropane. This addition reaction is stereospecific with singlet carbenes. Reaction is thermal allowed reaction.



...(4)

...(5)

The reaction is concerted reaction. An examination of the orbitals of carbene shows that a bonding overlap between HOMO of a carbene and LUMO of an alkene or LUMO of carbene and HOMO of alkene is possible.

In singlet carbene hybridisation of carbon is sp^2. It has three sp^2 hybrid orbitals and one empty p-orbital perpendicular to the plane defined by the carbon atom and the two substituents on it. Out of three sp^2 hybrid orbitals two are bonding and one is non-bonding having two electrons in it (Fig. 3.10).

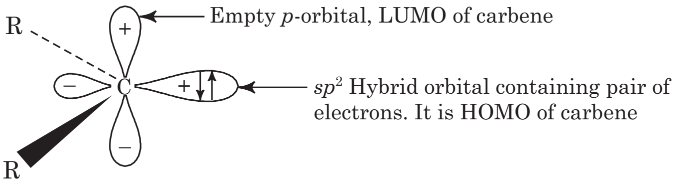


Fig. 3.10 MO diagram of singlet carbene

Concerted cycloaddition reaction between alkene and carbene is [2 + 2] cycloaddition reaction. This reaction is possible only if the carbene approaches the alkene sideways so that the plane defined by the carbon atom and its two substituents parallels the plane of the alkene. In this orientation, the empty p-orbital of the carbene pointing towards the electrons of the π bond of alkene [Figs. 3.11(*a*) and 3.11(*b*)].

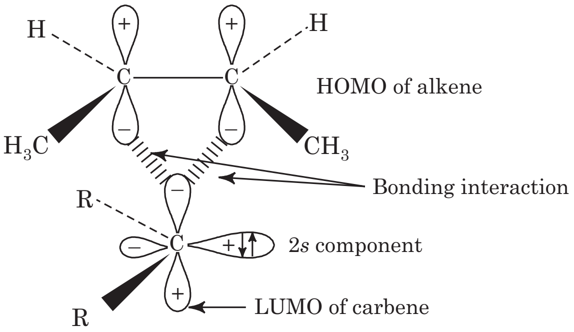


Fig. 3.11(a) Interaction between HOMO of alkene and LUMO of carbene

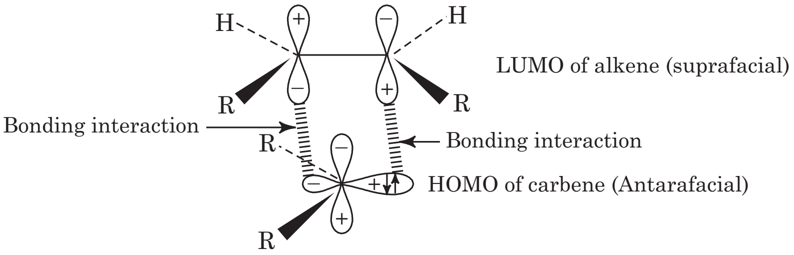
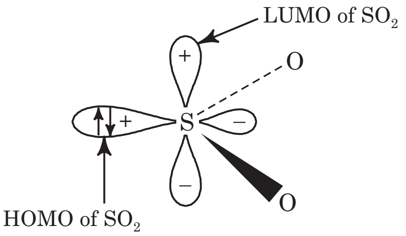


Fig. 3.11(b) Interaction between LUMO of alkene and HOMO of carbene

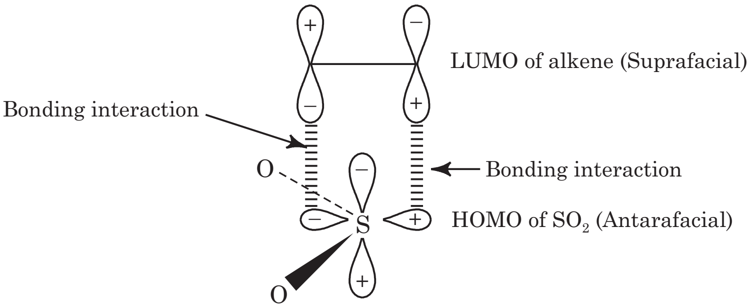
Chelotropic reaction of carbene is [2 + 2] cycloaddition reaction. Thus, chelotropic reaction of carbene with alkene is symmetry forbidden if both components interact suprafacially (Fig. 3.11*a*). Antarafacial reaction of a simple alkene is sterically very unlikely, so that the reaction is likely to involve the $\ddot{C}H_2$ antarafacially [Fig. 3.11 (*b*)].

(B) Chelotropic Reaction of Alkene with SO_2

Result of SO_2 is identical to carbene.

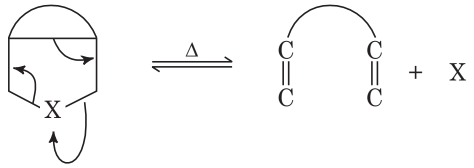


The orbital interaction between SO_2 and alkene is as follow:

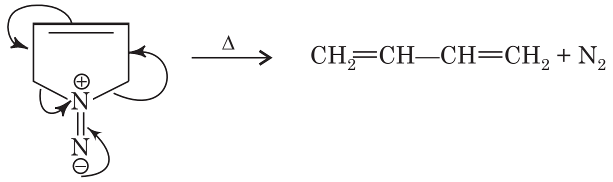


3.11 CHELOTROPIC ELIMINATION

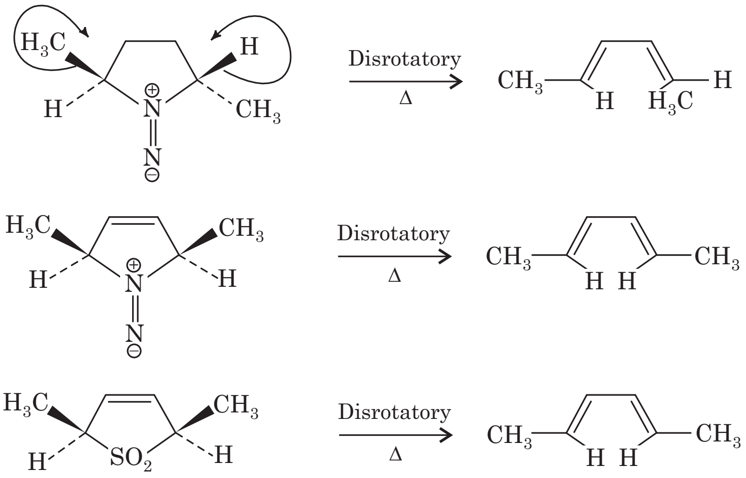
In chelotropic elimination, the atom X is normally bound to other atoms in such a way that elimination will give rise to a stable molecule. The most common examples involves five membered rings.



A good example of a concerted chelotropic elimination is the elimination of diazene in which elimination of nitrogen takes place.

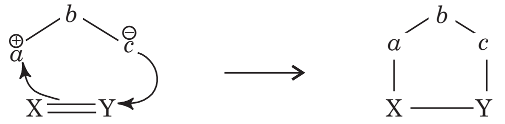


Use of substituted systems has shown that the reactions is completely stereospecific. The groups on C-2 and C-5 of the pyrroline ring rotate in the *disrotatory* mode on going to product. This stereochemistry is consistent with conservation of orbital symmetry.



3.12 1, 3-DIPOLAR CYCLOADDITIONS

There is a large class of reactions, known as 1, 3-dipolar cycloaddition reactions, that are analogous to the Diels-Alder reaction in that they are concerted [4π + 2π] cycloadditions. These reactions can be represented as in the given equation:



The species $\overset{\oplus}{a}—b—\overset{\ominus}{c}$ is called the 1, 3-dipolar molecule and X═Y is the dipolarophile. The 1, 3-dipolar molecules are isoelectronic with the allyl carbanion and have four electrons in a π (*pi*) system encompassing the 1, 3-dipole. All 1, 3-dipoles contain 4π (*pi*) electrons in three parallel *p*-orbitals of *a*, *b* and *c*.

In 1, 3-dipolar species $\overset{\oplus}{a}—b—\overset{\ominus}{c}$

(*i*) **a** has six electrons in its outermost orbit. **b** has its complete octet having at least one lone pair of electrons. **c** has its complete octet having negative charge.

(*ii*) **a** may be carbon, oxygen or nitrogen,
b may be nitrogen or oxygen, and
c may be carbon, oxygen or nitrogen.

(*iii*) If **b** is nitrogen then it has single or double bond.
If **b** is oxygen then it has single bond only.

Some typical 1, 3-dipolar species are given in Table 3.3.

Table 3.3 Some 1, 3-dipoles

Name	*Structure*		
Azoxy compounds	$-\overset{\oplus}{N}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{O}$	⟷	$-\ddot{N}=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{O}$
Nitrosoxides	$-\overset{\oplus}{N}-\underset{..}{\ddot{O}}-\overset{\ominus}{O}$	⟷	$-\ddot{N}=\overset{\oplus}{O}-\overset{\ominus}{O}$
Nitrous oxide	$\overset{\oplus}{N}=\ddot{N}-\overset{\ominus}{O}$	⟷	$\ddot{N}\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$
Carbonyl oxides	$>\overset{\oplus}{C}-O-\overset{\ominus}{O}$	⟷	$>C=\overset{\oplus}{O}-\overset{\ominus}{O}$
Ozone	$\overset{\oplus}{O}-\underset{..}{\ddot{O}}-\overset{\ominus}{O}$	⟷	$O=\overset{\oplus}{O}-\overset{\ominus}{O}$
Nitrile oxide	$-\overset{\oplus}{C}=\ddot{N}-\underset{..}{O}:$	⟷	$-C\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$
Nitrile imine	$-\overset{\oplus}{C}=\ddot{N}-\overset{\ominus}{N}$	⟷	$-C\equiv\overset{\oplus}{N}-\overset{\ominus}{N}$
Diazoalkanes	$\overset{\oplus}{N}=\ddot{N}-\overset{\ominus}{C}$	⟷	$\ddot{N}\equiv\overset{\oplus}{N}-\overset{\ominus}{C}<$
Nitrosoimines	$-\overset{\oplus}{N}-\underset{..}{\ddot{O}}-\overset{\ominus}{N}-$	⟷	$-\ddot{N}=\overset{\oplus}{O}-\overset{\ominus}{N}-$
Azides	$\overset{\oplus}{N}=\ddot{N}-\overset{\ominus}{N}-$	⟷	$\ddot{N}\equiv\overset{\oplus}{N}-\overset{\ominus}{N}-$
Carbonyl ylides	$>\overset{\oplus}{C}-\underset{..}{\ddot{O}}-\overset{\ominus}{C}<$	⟷	$>C=\overset{\oplus}{O}-\overset{\ominus}{C}<$
Nitrones	$>\overset{\oplus}{C}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{O}$	⟷	$>C=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{O}$
Azomethine imines	$>\overset{\oplus}{C}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{N}$	⟷	$>C=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{N}-$

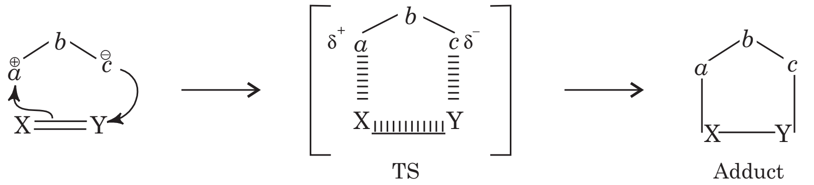
Contd...

Azomethane ylide	$>\overset{\oplus}{C}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{C}<$	⟷	$>C=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{C}<$
Azimines	$-\overset{\oplus}{N}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{N}-$	⟷	$-\ddot{N}=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{N}-$
Nitro compounds	$\overset{\oplus}{O}-\underset{\vert}{\ddot{N}}-\overset{\ominus}{O}$	⟷	$O=\underset{\vert}{\overset{\oplus}{N}}-\overset{\ominus}{O}$
Carbonyl imines	$>\overset{\oplus}{C}-\underset{..}{\ddot{O}}-\overset{\ominus}{N}$	⟷	$>C=\overset{\oplus}{O}-\overset{\ominus}{N}$
Carbonyl imides	$>\overset{\oplus}{C}-\underset{..}{\ddot{O}}-\overset{\ominus}{C}$	⟷	$>C=\overset{\oplus}{O}-\overset{\ominus}{C}<$
Nitrile ylide	$-\overset{\oplus}{C}=\ddot{N}-\overset{\ominus}{C}<$	⟷	$-C\equiv\overset{\oplus}{N}-\overset{\ominus}{C}<$

The dipolarophiles (X═Y) are alkenes, alkynes, imines, nitriles and carbonyl compounds.

3.12.1 Stereochemistry of 1, 3-Dipolar Cycloadditions

The stereochemistry of 1, 3-dipolar cycloaddition reaction is analogous to that of the Diels-Alder reaction and hence it is stereospecific *syn* addition.



When both the 1, 3-dipole and the dipolarophile are unsymmetrical then there are two possible orientations for addition (*i.e.*, two isomeric products are formed). Both steric and electronic factors play a role in determining the regioselectivity of the addition. The most generally satisfactory interpretation of regioselectivity of dipolar cycloaddition is based on *Frontier orbital* concepts. As with the Diels-Alder reaction, the most favourable orientation is that which involves complementary interaction (secondary interaction) between the FMO of the 1, 3-dipole and the dipolarophile in suprafacial-suprafacial manner. *In most of the dipolar addition LUMO of the dipolarophile interacts with the HOMO of the 1, 3-dipole. But in certain cases relationship is reversed.*

1, 3-Dipolar species has three *p*-orbitals having four electrons hence HOMO will be ψ_2 which has c_2-symmetry. The π orbitals of the 1, 3-dipolar species can be represented (Fig. 3.12) as follows:

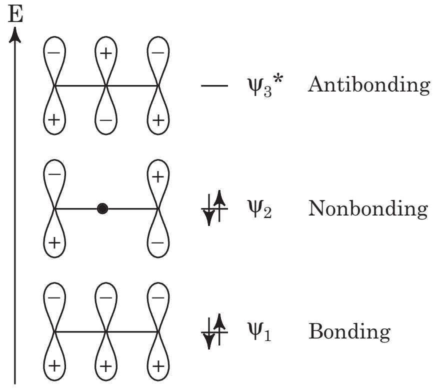
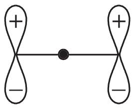


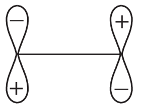
Fig. 3.12 MOs of 1, 3-dipolar species

Suppose 1, 3-dipole is diazomethane $(\overset{\oplus}{C}H_2—\ddot{N}=\overset{\ominus}{N})$. Its HOMO will be ψ_2.



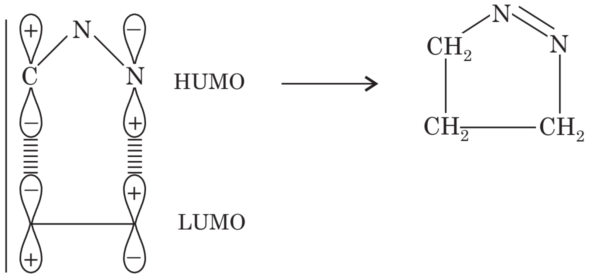
HOMO of 1, 3-dipole

Suppose dipolarophile is ethylene $(CH_2=CH_2)$ its LUMO is ψ_2^*.



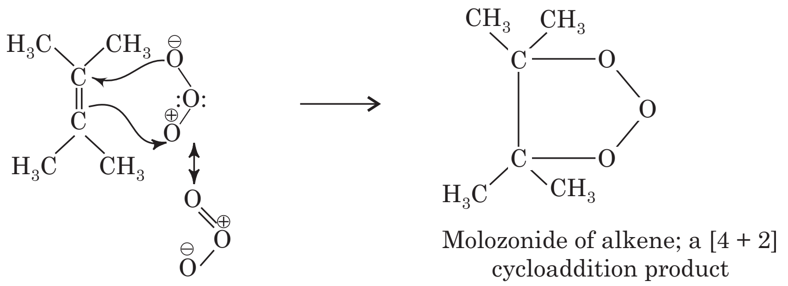
LUMO of dipolarophile; ψ_2^*

1, 3-dipolar addition between diazomethane and ethylene for example, can take place as follows:



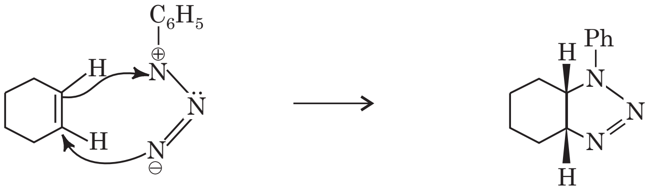
Symmetry allowed reaction

Some of the dipoles are stable compounds like ozone, diazomethane and suitably substituted azides, nitrones and nitrile oxides. Others, like the ylides, imines and carbonyl oxides are reactive intermediates that have to be made *in situ*. In most reactions the 1, 3-dipole is not isolated but generated *in situ* in the presence of the dipolarophile. Some examples of common 1, 3-dipolar cycloadditions are on the next page.



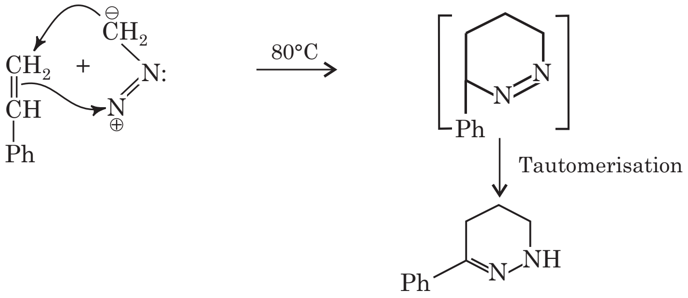
Molozonide of alkene; a [4 + 2] cycloaddition product

...(1)



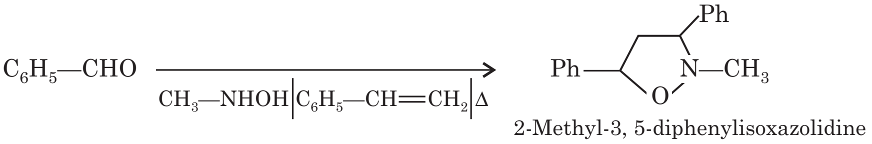
Triazoline

...(2)



2-Pyrazoline

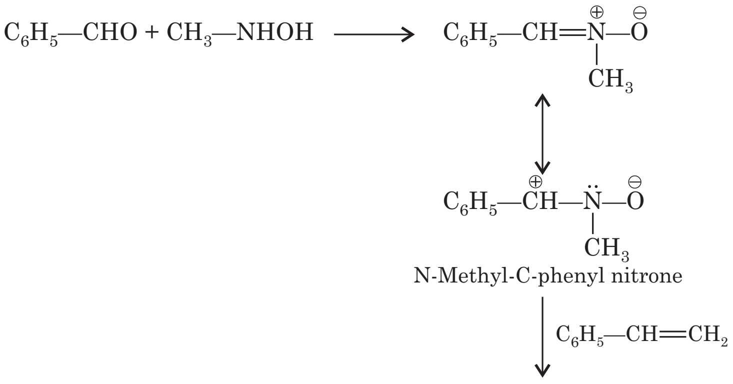
...(3)



2-Methyl-3, 5-diphenylisoxazolidine

...(4)

Reaction (*iv*) takes place as follows:

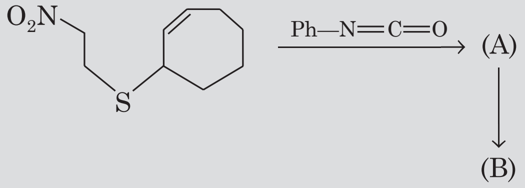


$$C_6H_5\text{—}CHO + CH_3\text{—}NHOH \longrightarrow C_6H_5\text{—}CH{=}\overset{\oplus}{N}\text{—}\overset{\ominus}{O}$$

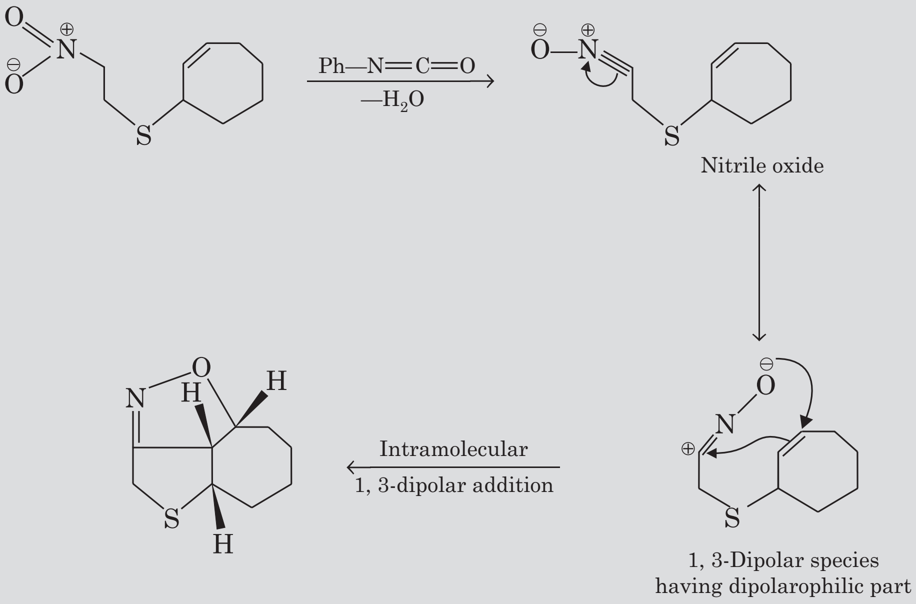
N-Methyl-C-phenyl nitrone

Product

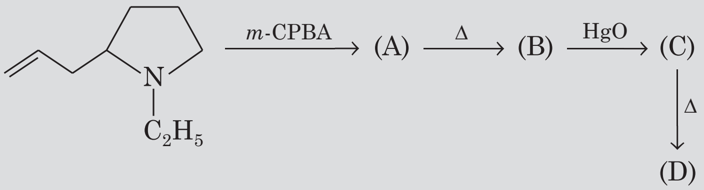
Problem 9: *Nitroalkane undergoes dehydration with C_6H_5—N=C=O to give nitrile oxide. Keeping this in mind, complete the following reaction:*



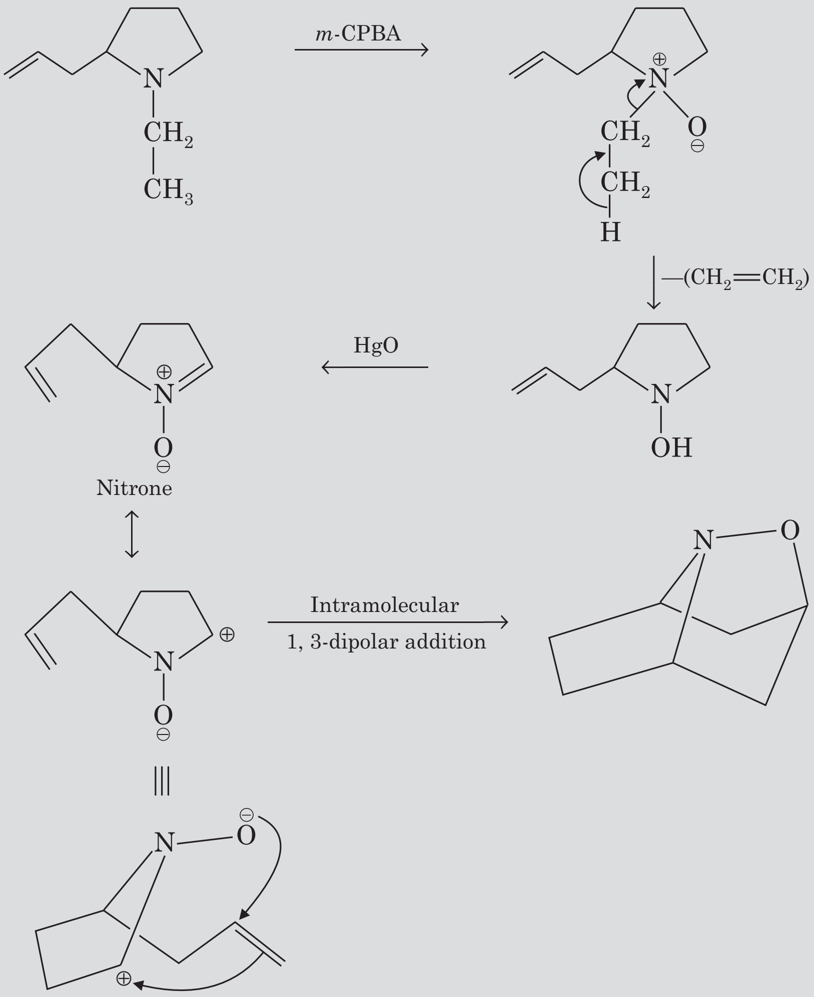
Solution:



Problem 10: *Complete the following reaction sequence:*



Solution:



GLOSSARY

Cycloaddition: A reaction in which two unsaturated molecules react to produce a cyclic compound. During the process π bonds are converted to σ bonds, and new π bonds may appear. If $(4n + 2)\pi$ electrons participate in the transition state, the reaction occurs in ground state or thermally. Diels-Alder reactions and 1, 3-dipolar additions are examples of thermal cycloadditions reactions. When $(4n)\pi$ electrons participate in the transition state, the reaction is photochemical; one of the reactants must be in an excited state.

Suprafacial process: A term describing the stereochemical relationship between the reacting termini of a molecule involved in a pericyclic reaction, when attachment occurs on the same face (side) of the molecule.

Antarafacial process: A process in which bonds are being made or broken on opposite sides (faces) of a π bond.

1, 3-Dipole: A three atom linkage, one resonance form of which has a negative change at one end and a positive change (hence an empty orbital) at the other. Such species are considered to have $4p\pi$ electrons.

1, 3-Dipolar addition: A cycloaddition involving a 1, 3-dipolar molecule or fragment and another (usually π) fragment. If the second fragment were a single bond, such a cycloaddition would be described as [4 + 2] addition, and would follow the same symmetry selection rules as any other [4 + 2] cycloaddition.

Cycloreversion or retrograde cycloaddition: The microscopic reverse of a cycloaddition reaction. Such a fragmentation follows the same symmetry selection rules as does the cycloaddition itself. A minus sign before the designation indicates a cycloreversion.

Chelotropic reaction: A cycloaddition in which one of the reacting species or fragments acts through a single atom possing both a filled and empty orbital.

FURTHER READING

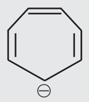
1. M.J.S. Dewar and R.C. Dougherty, *The PMO Theory of Organic Chemistry,* Plenum Press, New York, 1975.
2. T.L. Gilchrist and R.C. Storr, *Organic Reactions and Orbital Symmetry,* 2nd ed. Cambridge University Press, Cambridge, U.K. 1979.
3. L. Salem, *Electrons in Chemical Reactions,* John Wiley and Sons, New York, 1982.
4. R.B. Woodward and R. Hoffmann, *The Convervation of Orbital Symmetry,* Academic Press, New York, 1970.
5. I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley-Interscience, New York, 1976.
6. A.P. Marchand and R.E. Lehr, *Pericyclic Reactions,* Vol-I and II, Academic Press, New York, 1977.
7. W. Carruthers, *Cycloaddition Reactions in Organic Synthesis,* Pergamon Press, Oxford, 1990.
8. A. Williams, *Concerted Organic and Bio-organic Mechanism,* CRC Press, Boca Raton, FL, 2000.
9. A. Padwa (ed). *1, 3-Dipolar Cycloaddition Chemistry*, Wiley, New York, 1984.

PROBLEMS

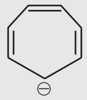
1. With the help of correlation diagram and PMO method, show that the Diels-Alder reaction is thermally allowed process.

2. What are the products of concerted cycloaddition of ethylene and *cis*-2-butene, addition being *suprafacial* on both components? It is symmetry-allowed under thermal or photochemical condition?

3. Determine whether the following *supra-supra* cycloaddition reactions are symmetry-allowed thermally or photochemically?

(*i*) $CH_2{=}CH{-}CH{=}CH{-}\overset{\ominus}{C}H_2 + CH_2{=}CH_2 \longrightarrow$ 

(*ii*) $CH_2{=}CH{-}CH{=}CH{-}\overset{\ominus}{C}H_2 + CH_2{=}CH_2 \longrightarrow$



[**Hint:** (*i*) It is $\pi^6s + \pi^2s$ process and is therefore allowed under photochemical condition.
(*ii*) It is $\pi^4s + \pi^2s$ process and therefore allowed under thermal condition.]

4. Using FMO, explain why cyclopentadiene undergoes thermal cycloaddition reaction with acrolein to give preferentially the *endo* product.

5. Draw correlation diagram to establish that $[\pi^4s + \pi^2s]$ cycloaddition is a thermally allowed process.

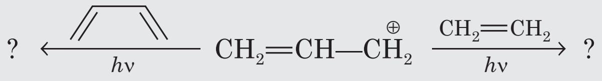
6. With the help of correlation diagram, show that [2 + 2] cycloaddition reaction is photochemically allowed process.

7. With the help of FMO method and PMO method, show that [2 + 2] cycloaddition reaction is photochemically allowed reaction.

8. Describe [2 + 2] cycloaddition, in detail with special reference to dimerisation of ethylene.

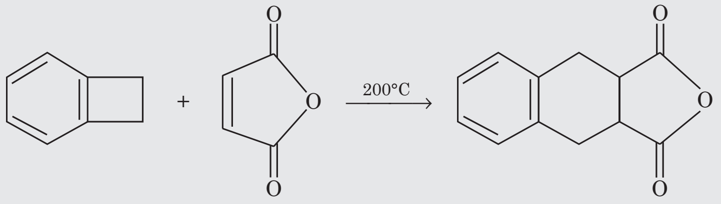
9. Predict the stereochemistry of the [2 + 2] cycloaddition of a pair of substituted ethylene, X—CH═CH—X.

10. Orbital symmetry permits one of the two following photochemical cycloaddition reactions to take place in a concerted fashion. What would be the products, which reaction is the concerted one, and why?

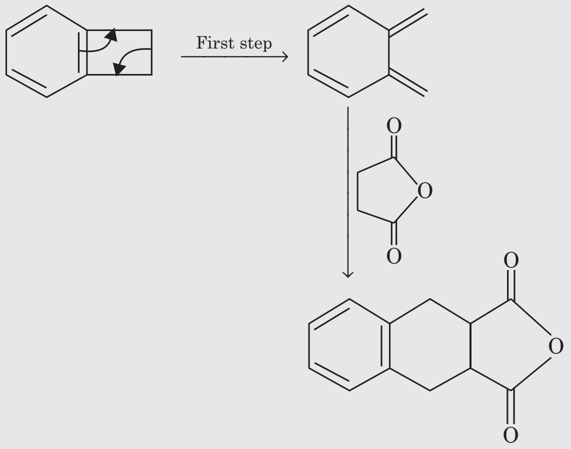


$$? \xleftarrow[h\nu]{} CH_2{=}CH{-}\overset{\oplus}{C}H_2 \xrightarrow[h\nu]{CH_2{=}CH_2} ?$$

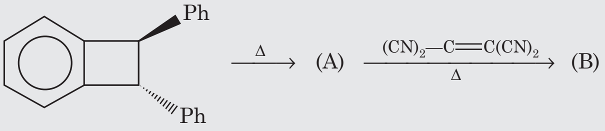
11. Benzocyclobutene (1) reacts with maleic anhydride when heated at 200°C to give the single product shown below. Write mechanism for this reaction.



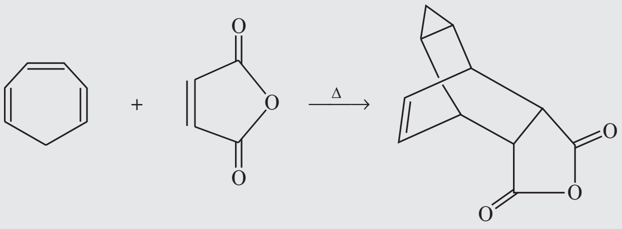
[**Hint:** Reaction takes place in two steps. First step is electrocyclic ring opening of cyclobutene and second step is Diels-Alder addition.]



12. Complete the given reaction sequence and give mechanism of each step.

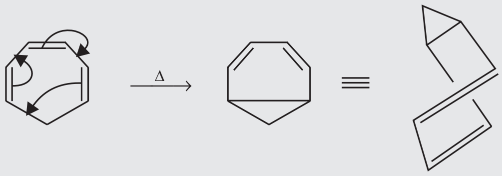


13. Write a mechanism for the following reaction:



(1) (2) (3)

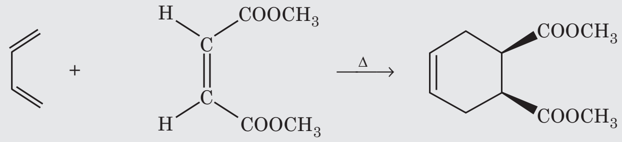
[**Hint:** The reaction is two step reaction. In the first step cycloheptatriene undergoes electrocyclic ring closer to give diene.]



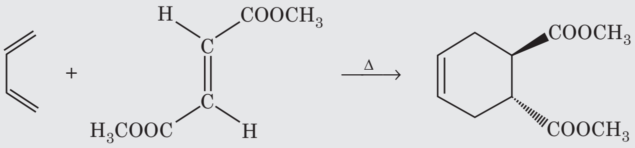
14. Would you expect that vinylacetylene could function as a diene in the Diels-Alder reaction? Explain your answer.

15. What is the importance, if any, of the following in understanding the mechanism of the Diels-Alder reaction?

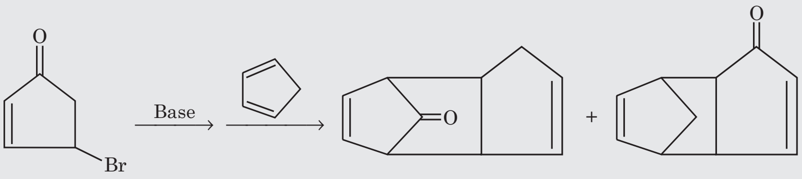
(*i*)



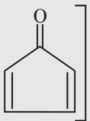
(*ii*)



16. The reaction of (A) with base, in the presence of 1, 3-cyclopentadiene, produced (B) and (C). Account for their formation.

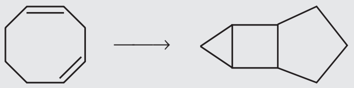


(A) (B) (C)

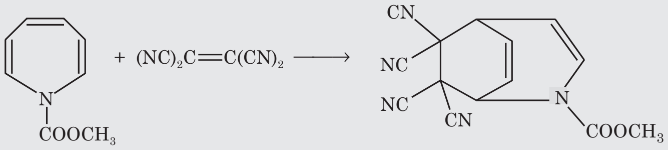
[**Hint:** A $\xrightarrow{\text{Base}}$ ]

17. Would you expect the reactions shown below to be accelerated by heat or by light? Explain.

(*i*)



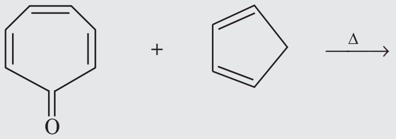
(*ii*)



[**Hint:** (*i*) [2 + 2] cycloaddition accelerated by light.
(*ii*) [4 + 2] cycloaddition, accelerated by heat.]

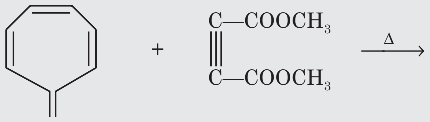
18. Give the product of the following cycloaddition reactions:

(*i*)



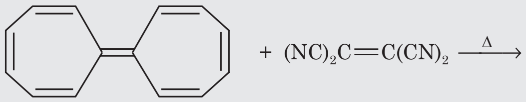
[**Hint:** It is [6 + 4] cycloaddition reaction]

(*ii*)

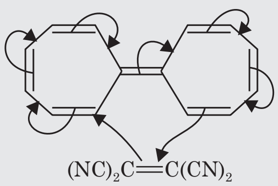


[**Hint:** It is [8 + 2] cycloaddition reaction]

(*iii*)

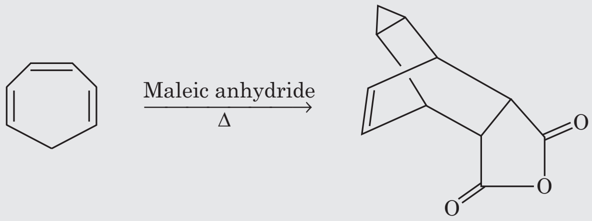


[**Hint:** It is [14 + 2] cycloaddition reaction]



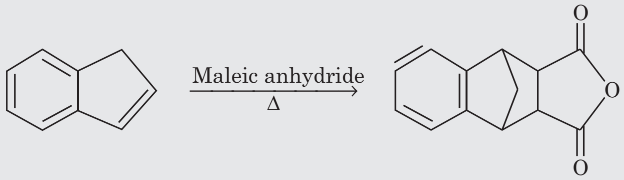
19. When each of the compound below is heated in the presence of maleic anhydride, an intermediate is trapped as a Diels-Alder adduct. What is the intermediate formed in each reaction, and how is it formed from the starting material?

(*i*)

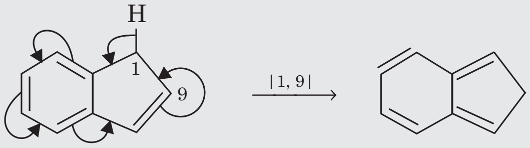


[**Hint:** Intermediate is formed by the ring closure electrocyclic reaction of the starting material].

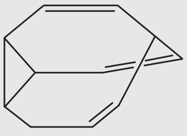
(*ii*)



[**Hint:** Intermediate is formed by the [1, 9] sigmatropic shift of hydrogen].



20. Bullvalene has a complex NMR spectrum at low temperature, consisting of resonance in both the allylic and vinylic region of the spectrum. As the temperature is raised, the NMR spectrum changes, and at 100°, consists of one singlet. Account for their change in the NMR spectrum with temperature in terms of what is known about the structure of bullvalene.



21. Predict whether a [4 + 2] cycloaddition could be photo-induced if the dienophile, instead of the diene, were the excited reactant. Explain your answer.

22. Which of the following types of cycloadditions would you predict to proceed easily upon heating?

(*a*) [6 + 2] (*b*) [6 + 4] (*c*) [8 + 2] (*d*) [8 + 4].

23. With the help of FMO method show that the [2 + 2] cycloaddition reaction between alkene and ketene is thermal allowed reaction.

24. Give the mechanism of the chelotropic cycloaddition reactions between

(*i*) alkene and carbene.

(*ii*) alkene and SO_2.

25. What are the characteristic of 1, 3-dipolar species in 1, 3-dipolar cycloaddition reactions?

26. Analyse 1, 3 dipolar cycloaddition reaction on the basis of FMO method.

27. In thermal [2 + 2] cycloadditions a supra-supra process is geometrically possible but symmetry forbidden on the other hand, a supra-antara process is symmetry allow but geometrically difficult. Photochemical formation of cyclobutanes from 2π components is however, a well process. Explain.

28. The Diels-Alder reaction is a concerted [4 + 2] process. In particular, the reaction is stereospecific and is a *syn* (suprafacial addition with respect to both the dienes and dienophile. Explain.

29. What is the *endo*-rule as applied to Diels-Alder reaction?

30. (*a*) Why the reactivity of the diene is increased by electron-releasing substituents.

(*b*) Cycloaddition of an unsymmetrically substituted diene and dienophile can in principle lead to regio isomers. Write the structures of the possible and main products by taking examples.

31. Explain the relation between Diels-Alder reaction and 1, 3-dipolar addition.

4

CHAPTER

Sigmatropic Rearrangement

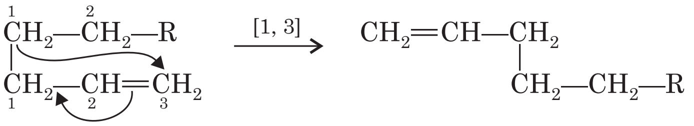
4.1 INTRODUCTION AND CLASSIFICATION

Sigmatropic rearrangements are another class of concerted pericyclic reactions governed by orbital symmetry. This rearrangement involves a concerted reorganisation of electrons during which a group attached by a σ (*sigma*) bond migrates to the terminus of an adjacent π (*pi*) electron system. The reactions are called sigmatropic rearrangement because a σ (*sigma*) bond appears to move from one place to another during the reaction. There is a simultaneous shift of the π (*pi*) electrons. The number of the π (*pi*) and σ (*sigma*) bonds remain separately unchanged.

4.1.1 Classification of Sigmatropic Rearrangements

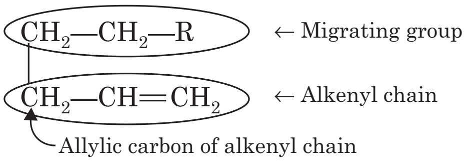
Sigmatropic rearrangements are classified by a double numbering system (*i*, *j* or *m*, *n*) that refers to the relative positions of the atom or group involved in the migration. This method of classification is different from those for cycloaddition or electrocyclic reactions which are classified by the number of π (*pi*) electrons involved in the cyclic transition state.

The method used in classifying sigmatropic rearrangement is best explained by the following examples:



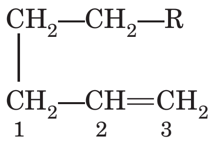
$$\begin{matrix}\overset{1}{C}H_2-\overset{2}{C}H_2-R\\ |\\ \underset{1}{C}H_2-\underset{2}{C}H=\underset{3}{C}H_2\end{matrix}\xrightarrow{[1,\,3]}\begin{matrix}CH_2=CH-CH_2\\ \qquad\quad |\\ \qquad\qquad CH_2-CH_2-R\end{matrix}\qquad ...(1)$$

In sigmatropic rearrangement substrate can be divided in two parts: Alkenyl (or polyalkenyl) chain and migrating group. All substrates have at least one allylic carbon in alkenyl chain for sigmatropic rearrangement.



Numbering of Alkenyl Chain

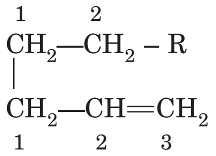
Numbering of alkenyl chain is always started from the allylic carbon and this carbon is numbered-1



$$\begin{array}{l} CH_2—CH_2—R \\ | \\ \underset{1}{CH_2}—\underset{2}{CH}=\underset{3}{CH_2} \end{array}$$

Numbering for Migrating Group

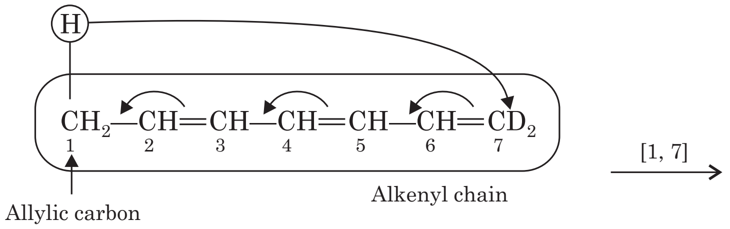
Atom (H, C or heteroatom) of migrating group bonded with allylic carbon by σ (*sigma*) bond is always given number-1



$$\begin{array}{l} \overset{1}{CH_2}—\overset{2}{CH_2} - R \\ | \\ \underset{1}{CH_2}—\underset{2}{CH}=\underset{3}{CH_2} \end{array}$$

4.1.2 Name of the Rearrangement

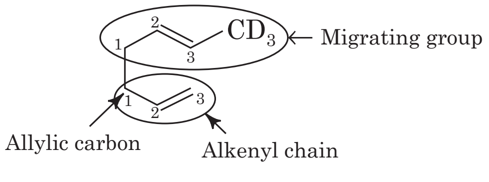
In the example (1) atom-1 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement would be classified as a [1, 3] sigmatropic rearrangement. In 1, 3 [(*i.e., i, j*) $i = 1$ and $j = 3$] *i* indicates position of atom in the migrating group and *j* indicates position of atom in the alkenyl chain.

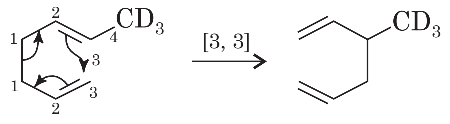


$CH_2=CH—CH=CH—CH=CH—CHD_2$ ...(2)

The above reaction is example of [1, 7] sigmatropic rearrangement.

It is not always the first atom of the migrating group that becomes bonded to the alkenyl chain in the rearrangement. Consider the following example:



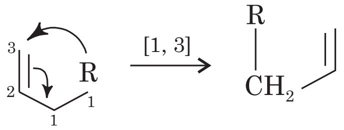


...(3)

In this rearrangement atom-3 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement is an example of [3, 3] sigmatropic rearrangement.

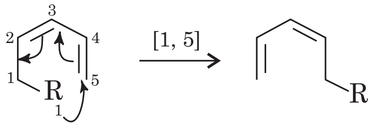
The sigmatropic rearrangements can be divided into *two classes*.

1. Those where the migrating atom or group is bonded through the same atom in both reactant and product.



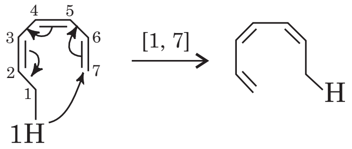
...(4)

R is bonded to carbon in reactant as well as in product



...(5)

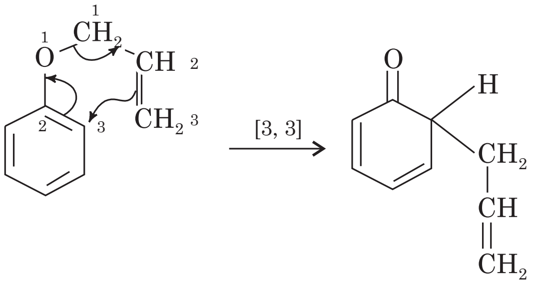
1, 5-shift of alkyl group, R is bonded to carbon in reactant as well as in product



...(6)

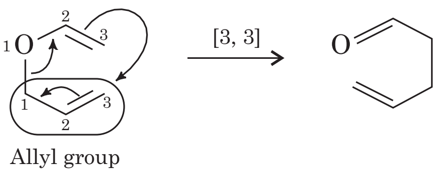
1, 7-shift of hydrogen. H is bonded to carbon in reactant as well as in product

2. Those where the migrating atom or group is bonded through different atoms in reactant and in product.



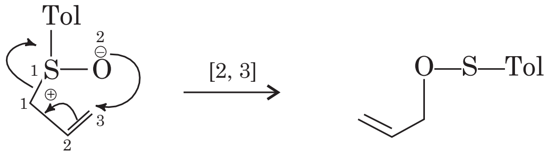
...(7)

This is [3, 3] sigmatropic rearrangement in which carbon of allyl group is bonded to oxygen in the reactant and carbon in the product.



...(8)

This is [3, 3] sigmatropic rearrangement of an allyl vinyl ether. Migrating group is bonded to the oxygen in the reactant which is bonded to the carbon in the product.



...(9)

Allyl group is bonded to sulphur

Allyl group is bonded to oxygen

[2, 3] Sigmatropic rearrangement of an allyl sulphoxide

...(10)

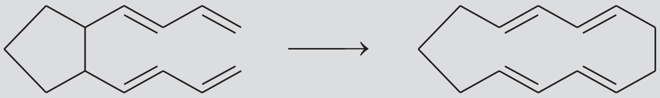
Allyl group is bonded to nitrogen

Allyl group is bonded to oxygen

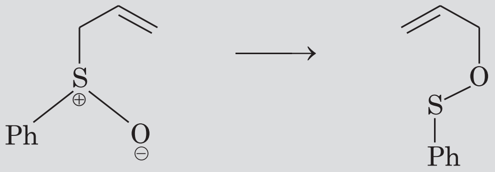
[2, 3] Sigmatropic rearrangement of an amine oxide

Problem 1: *Classify the following sigmatropic rearrangements with bracketed numbers.*

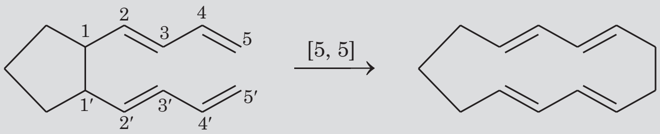
(*i*)



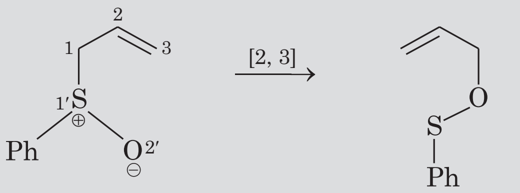
(*ii*)



Solution: (*i*) This is [5, 5] sigmatropic rearrangement.



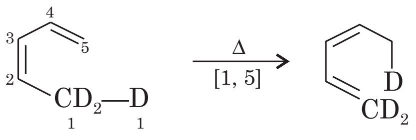
(*ii*) This is a [2, 3] sigmatropic rearrangement.



4.2 MECHANISM OF SIGMATROPIC REARRANGEMENT

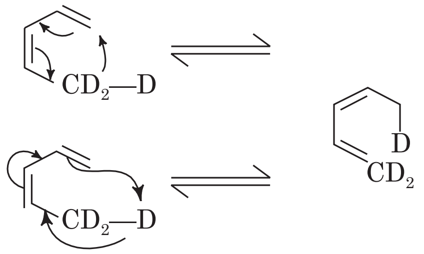
FMO Method

Consider the following reaction:



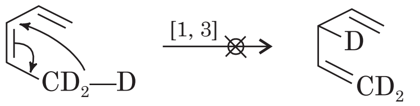
1, 3-Pentadiene

When 1, 3-pentadiene is heated, it gives [1, 5] sigmatropic rearrangement. It is simple to construct an arrow formalism picture of the reaction. The arrow could run in either direction, clockwise or anticlockwise. That is not true for a polar reaction in which the convention is to run the arrow from pair of electrons towards the electron deficient.



An arrow formalism description of the [1, 5] shift of deuterium in 1, 3-pentadiene.

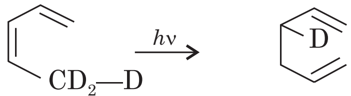
In the given example deuterium of sp^3 hybrid carbon migrates on to the sp^2 hybrid carbon (carbon-5). The given compound has also carbon-3 as sp^2 hybrid carbon. Thus this compound can also give [1, 3] sigmatropic rearrangement on heating, but [1, 3] shift is not observed.



Not observed

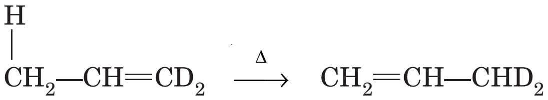
An arrow formalism can easily be written and it might be reasonably argued that the [1, 3] shift requiring a shorter path than the [1, 5] shift, should be easier than why [1, 3] shifts not observed on heating?

A second strange aspect of this reaction comes from photochemical experiments. When 1, 3-pentadienes are irradiated the product of the reaction include the molecules formed through [1, 3] shift but not those of [1, 5] shifts.



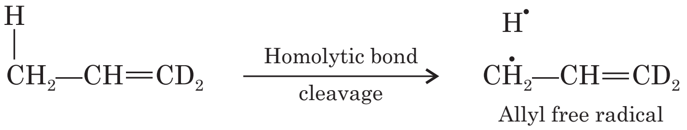
Product of a [1, 3] shift

So any mechanism proposed must include an explanation of why thermal shifts are [1, 5] whereas photochemically induced shifts are [1, 3]. We can use the frontier orbital approach to analyse these reactions and see why this is so. Let us first consider the following thermally induced sigmatropic rearrangement which is a [1, 3] shift.



$$\overset{\displaystyle H}{\overset{|}{CH_2}}{-}CH{=}CD_2 \xrightarrow{\Delta} CH_2{=}CH{-}CHD_2$$

For the purpose of analysing the orbitals, it is assumed that the σ (*sigma*) bond connecting the migrating group to its original position undergoes homolytic cleavage to yield two free radicals. This is not how the reaction takes place because reaction is concerted. But this assumption does allow analysis of the molecular orbitals.



$$\overset{\displaystyle H}{\overset{|}{CH_2}}{-}CH{=}CD_2 \xrightarrow[\text{cleavage}]{\text{Homolytic bond}} \overset{\displaystyle H^{\bullet}}{\dot{C}H_2}{-}CH{=}CD_2$$

Allyl free radical

The products of the hypothetical cleavage are a hydrogen atom and an allyl free radical, which contains three *p*-orbitals. The π (*pi*) molecular orbitals of allyl free radical are shown in Fig. 4.1.

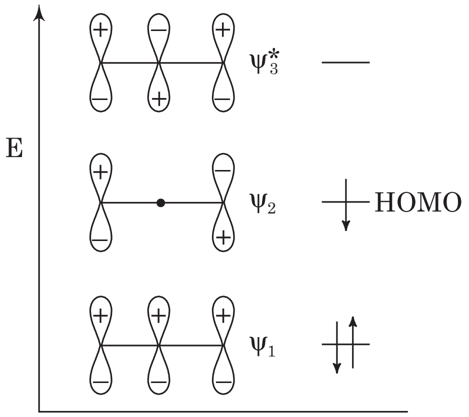
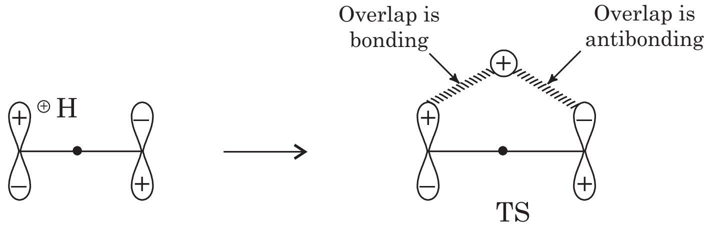


Fig. 4.1 Molecular orbitals of allyl free radical

The actual shift of hydrogen could take place in one of the two directions.

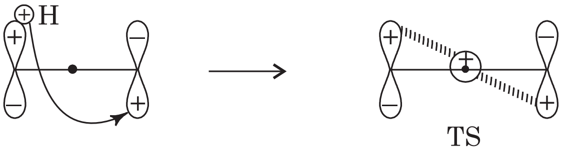
In the first case, the migrating group could remain on the same side of the π (*pi*) orbital system. Such a migration is known as a *suprafacial process*. In the thermal 1, 3 sigmatropic rearrangement a suprafacial migration is geometrically feasible but symmetry forbidden.



In the C—H bond the overlapping lobes are of the same sign

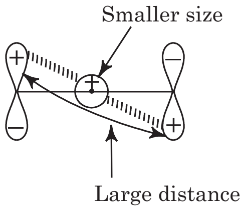
Symmetry forbidden (phase incorrect for overlapping)

Let us consider the second mode of migration for a symmetry allowed [1, 3] sigmatropic shift to occur, the migrating group must shift by an antarafacial process—that is, it must migrate to the *opposite face* of the orbital system.



Overlap is bonding, symmetry allowed but geometry difficult

While symmetry-allowed a [1, 3] antarafacial sigmatropic rearrangement of hydrogen is not geometrically favorable. Why? The problem is that the 1*s* orbital is smallest and cannot effectively span the distance required for an antarafacial migration. In other words, size of 1*s* orbital of hydrogen is smallest and distance between two lobes of interacting *p*-orbitals of carbon is maximum hence orbital of 1*s* cannot interact effectively with *p*-orbitals at same time in the formation of transition state.



Symmetry allowed but geometrically difficult

[1, 3] sigmatropic shifts take place in the presence of UV light but examples are rare. Consider again what happens when a molecule absorbs a photon. LUMO of ground state will become HOMO of excited state known as photochemical HOMO (Fig. 4.2).

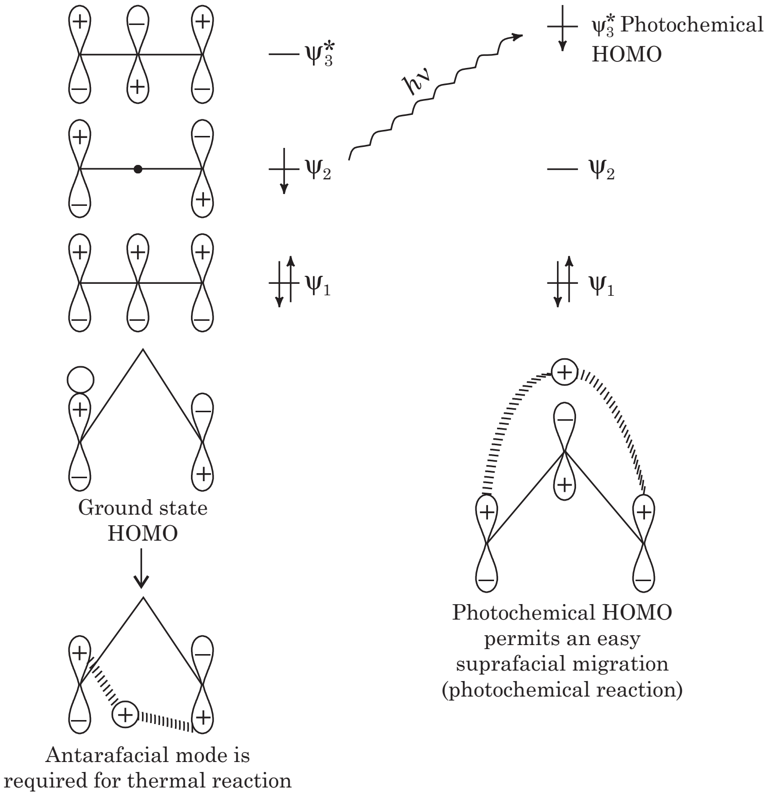


Fig. 4.2 Suprafacial migration is possible in ψ_3^* photochemical HOMO of the reaction

[1, 5] Sigmatropic Rearrangement: The products of hypothetical cleavage in this case are hydrogen free radical and pentadienyl radical. π MOs of pentadienyl radical is given below :

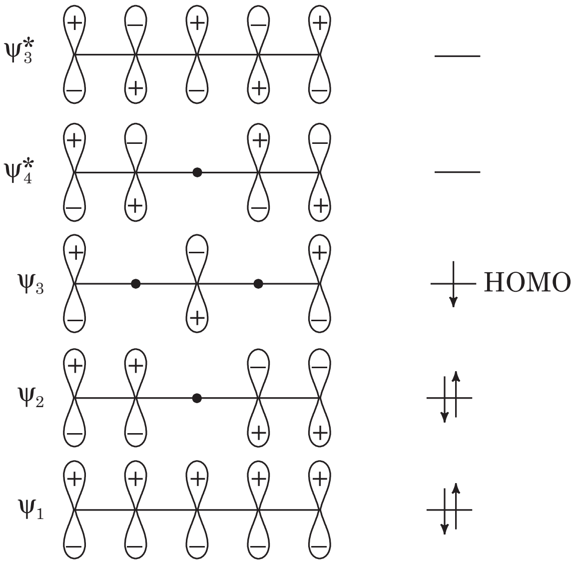
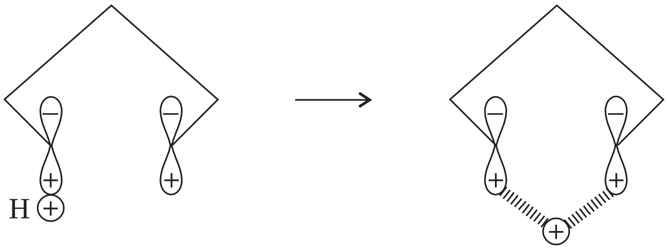


Fig. 4.3 π Molecular orbitals of the pentadienyl radical

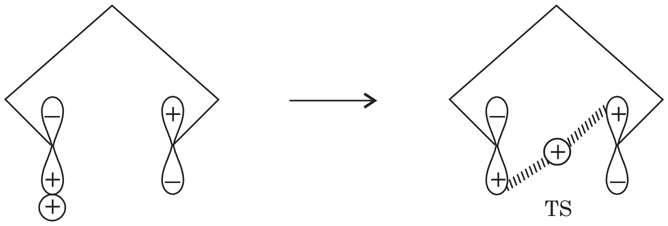
[1, 5] Sigmatropic shift is thermally allowed and photochemically forbidden. If we again assume a homolytic bond cleavage for purpose of analysis, we must consider the molecular orbitals of pentadienyl radical (Fig. 4.3).



Ground state HOMO TS

Suprafacial migration: *The [1, 5] suprafacial shift is symmetry allowed and geometrically feasible.*

Consider photochemical [1, 5] sigmatropic rearrangement. In this case ψ_4^* will be photochemical HOMO.



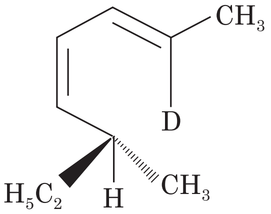
TS

Photochemical HOMO

Antarafacial migration, symmetry allowed but geometrically difficult.

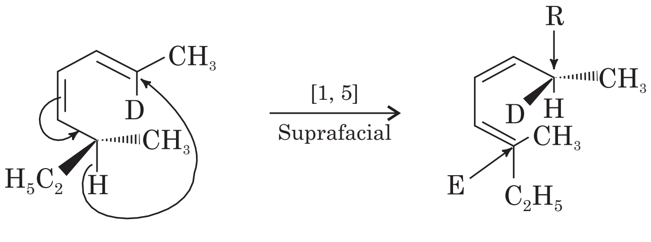
Stereochemistry of [1, 5] sigmatropic Rearrangement

Consider the following compound:



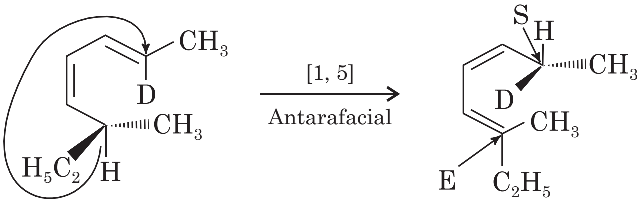
Compound has *S*-configuration at C-6 and *E* configuration at C-2.

Case I: *Suppose migration is suprafacial*



If migration is suprafacial then product has *R*-configuration at C-5 and *E*-configuration at C-1.

Case II: *Suppose migration is antarafacial*

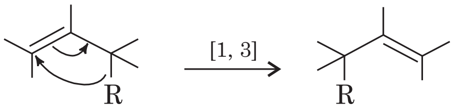


If migration is antarafacial then product has *S*-configuration at C-7 and *E*-configuration at C-2.

Experimentally it has been found that the product of the reaction is due to suprafacial migration. Thus, the theory is confirmed by this experimental result.

4.2.1 Sigmatropic Shifts of Alkyl Group

Sigmatropic migration involving alkyl group shifts can also occur.

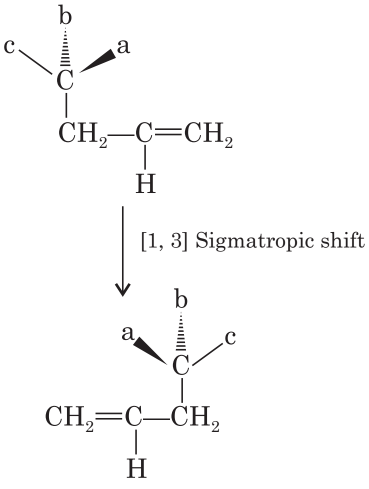


1, 3-Alkyl shift

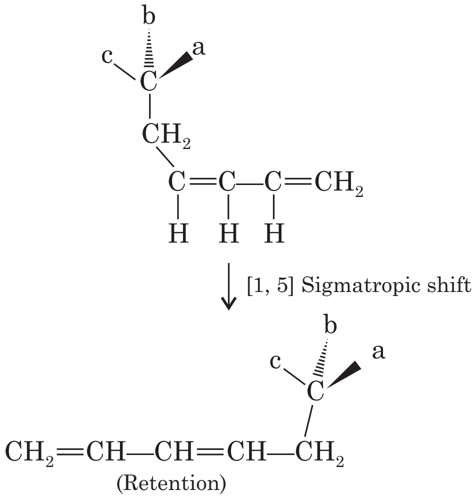
When an alkyl group migrates, there is additional stereochemical feature to consider. The shift can occur with retention or inversion at the migrating centre. The allowed process includes the suprafacial 1, 3-shift with inversion and the suprafacial 1, 5-shift with retention.

Thus, if the group that migrates is bonded to the backbone by a **chiral** carbon, then:

1. [1, 3] Suprafacial migration of the group proceeds with inversion of configuration at the chiral centre.
2. [1, 5] Suprafacial migration of the group proceeds with retention of configuration at the chiral centre.

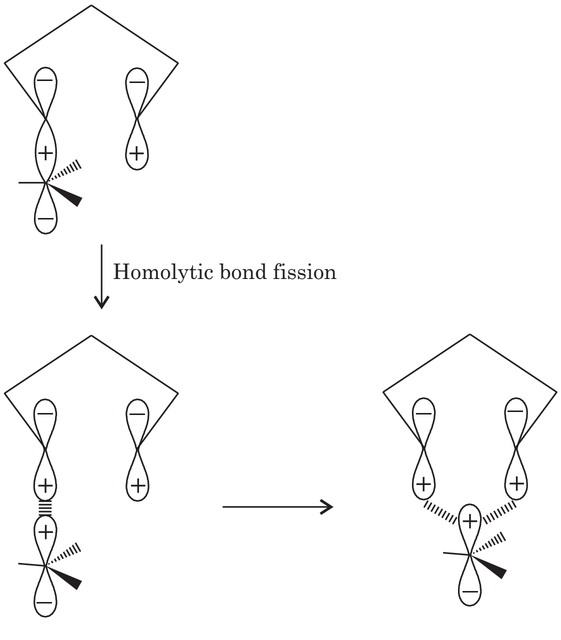


(Inversion)



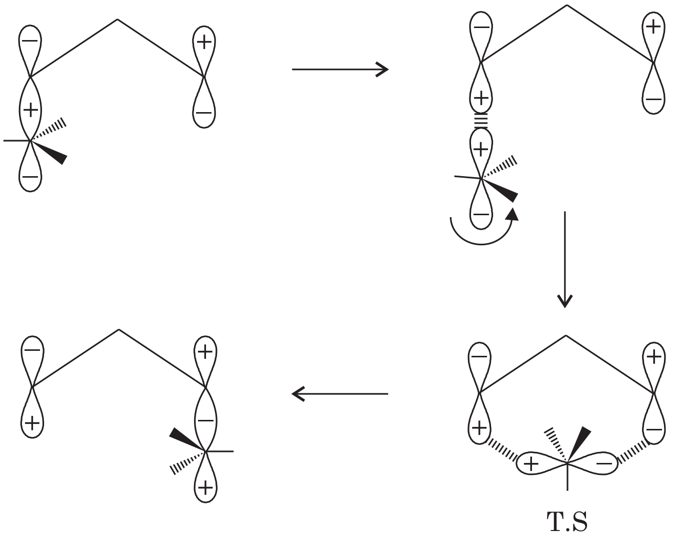
As compared to a hydrogen atom which has its electron in a 1*s* orbital that has only one lobe, a carbon free radical (for imaginary TS) has its odd electron in a *p*-orbital which has two lobes of opposite sign.

A consideration of the imaginary TS, shows that if in place of hydrogen one has carbon, then during a thermal suprafacial [1, 5] process, symmetry can be conserved only provided the migration carbon moves in a manner that the lobe which was originally attached to the π (*pi*) system remains attached to it (see figure given below)



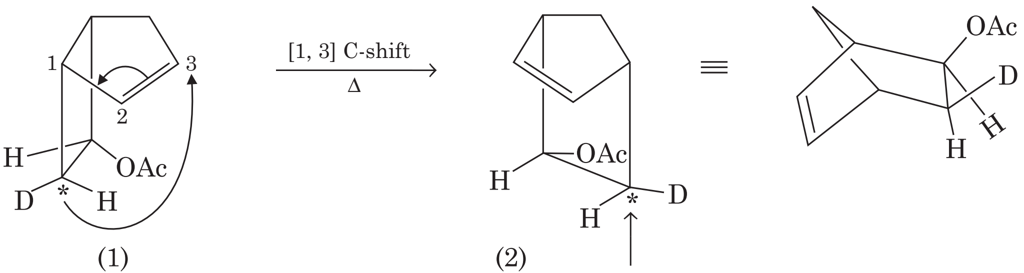
A thermal suprafacial [1, 5] migration. Configuration is retained within the migrating group.

The only way for this to happen is the retention of configuration within the migrating group. However, a related [1, 3] thermal suprafacial would involve opposite lobes. Thus, if the migrating carbon was originally bonded via its positive lobe, it must now use its negative lobe to form the new C—C bond. The stereochemical outcome of such a process is the inversion of configuration in the migrating group is shown below:



A thermal supraficial [1, 3] migration. Configuration in the migrating group will be inverted.

Compound (1) when heated at 300°C it gives compound (2). This is 1, 3 sigmatropic shift with inversion at the migrating centre.

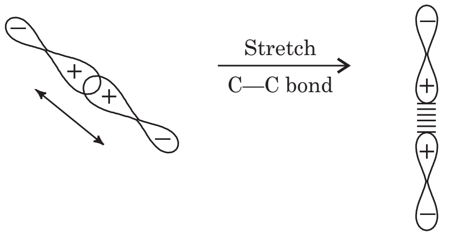


(1) (2)

Inversion of configuration

Let us use orbital symmetry to explain the observed result.

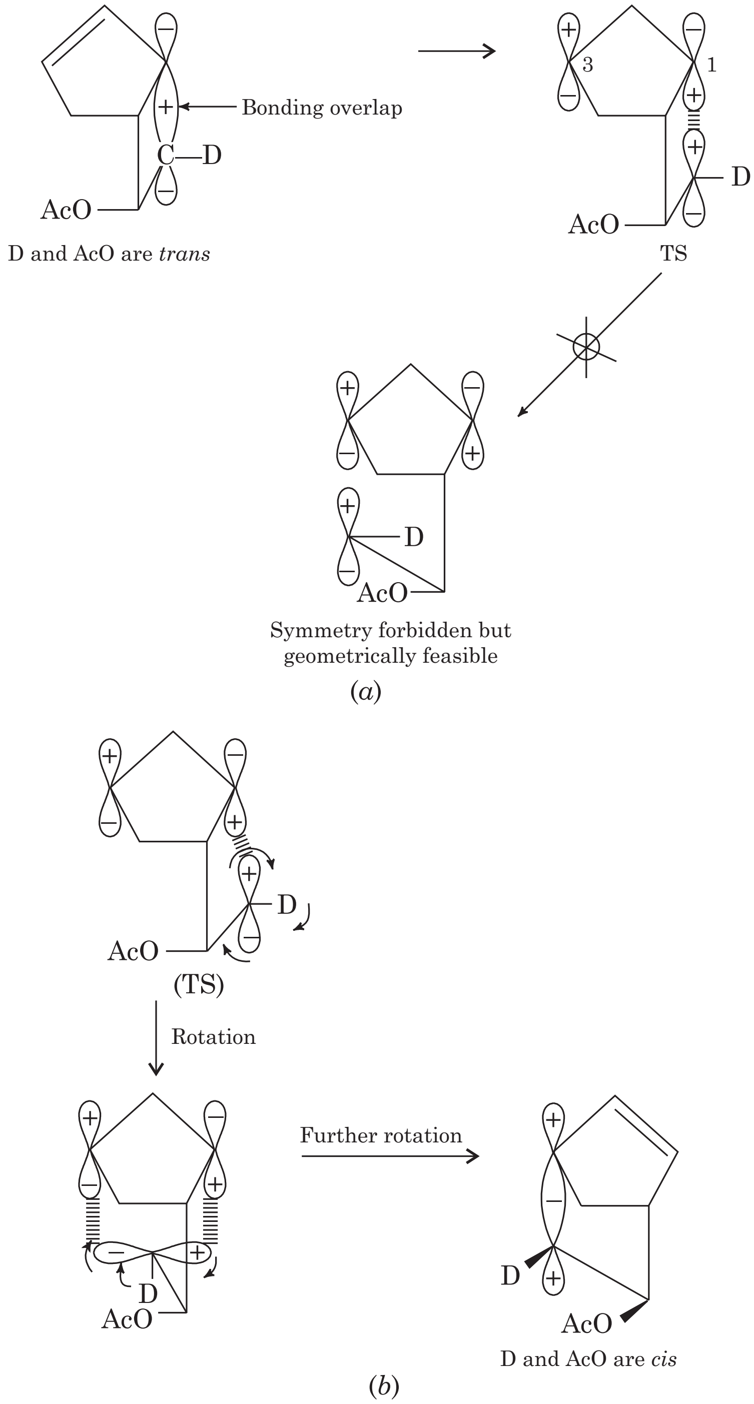
As the crucial bond between the alkyl system and the migrating carbon stretches, during the course of formation of transition state, the phase relationship between two bonded lobes must be mentioned.



Developing two *p*-orbitals

Inversion of configuration

We also know the symmetry of HOMO of the developing allyl systems and can fill in the lobes as in Fig. 4.4.

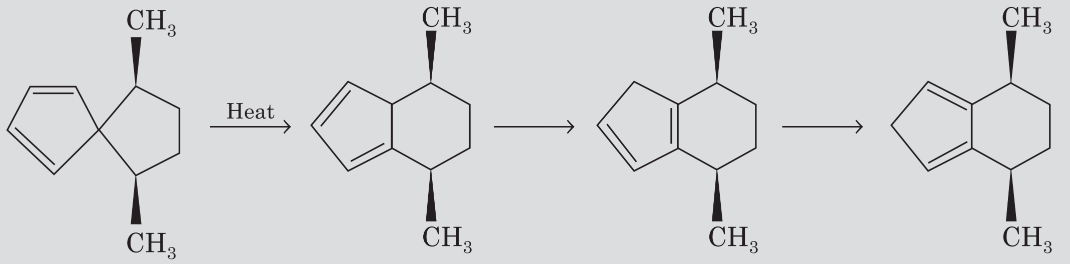


(*b*)

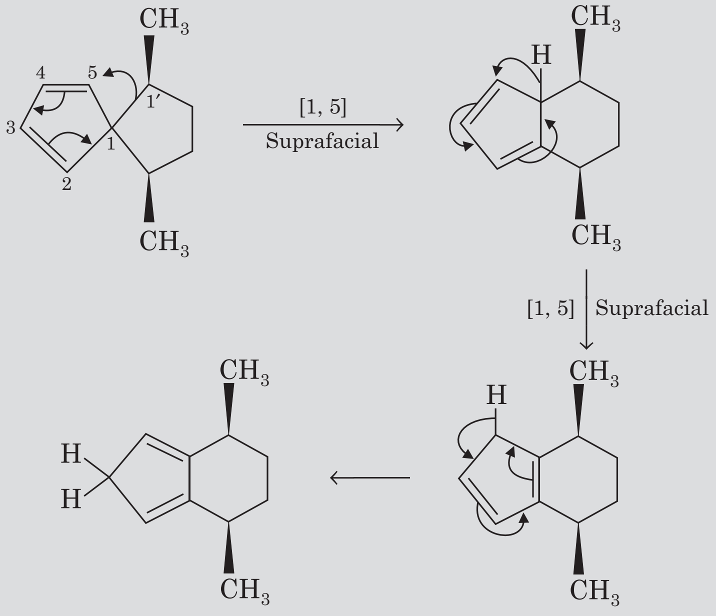
Fig. 4.4

In this case migration occurs using the back lobe of migrating carbon, and now a bonding interaction is created. The migrating carbon suffers inversion as reattachment takes place to the position-3 of the allyl framework. In order to preserve bonding overlap with C-1 and C-3 rotation must occur, and the *trans* starting material is thus converted into *cis* product.

Problem 2: *Indicate what type of sigmatropic reactions are involved in the following transformations:*



Solution: The first step is a [1, 5] sigmatropic rearrangement. Because the stereochemistry of the methyl group on the migrating carbon does not change, the rearrangement occurs with retention of configuration. The remaining steps are [1, 5] sigmatropic hydrogen migrations.



4.2.2 Selection Rules for Sigmatropic Rearrangement

The stereochemistry (*i.e.,* migration of group is suprafacial or antarafacial) of sigmatropic rearrangement is a simply function of number of electrons involved (as with other pericyclic reactions, the number of electrons involved is easily determined from the curved-arrow formalism: Simply count the curved arrow and multiply by two). All suprafacial sigmatropic reactions occurs when there are ($4q$ + 2) electrons involved in the reaction—that is an odd number of electron pairs or curved arrows.

Selection rule of [1, *n*] sigmatropic rearrangement when migrating group is hydrogen atom.

If sigmatropic reaction of the order ($m + n$) (for hydrogen $m = 1$) has $m + n = 4q + 2$ then thermal reaction is suprafacial and photochemical reaction will be antarafacial. However, for those cases in which $m + n = 4q$ then thermal reaction is antarafacial and photochemical reaction will be suprafacial (Table 4.1).

Table 4.1 Selection rule for [1 + *n*] in which migrating group is hydrogen

m+ n	*Thermal allowed photochemical forbidden*	*hν allowed Δ forbidden*
$4q$	antara	supra
$4q + 2$	supra	antara

Table 4.2 Selection rule for [1 + *n*] in which migrating atom is carbon

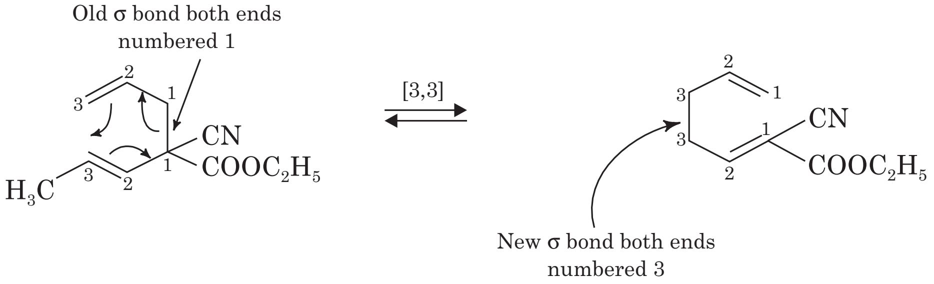
m + n	*Δ allowed*	*hν allowed*
$4q$	ar	sr
	si	ai
$4q + 2$	sr	ar
	ai	si

In the table *s* and *a* refer to supra and antara and *r* and *i* refer to retention and inversion in the configuration of the migrating centre.

4.3 OTHER SIGMATROPIC SHIFTS

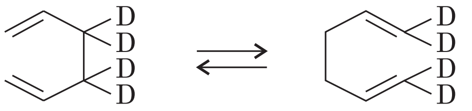
4.3.1 Cope Rearrangement

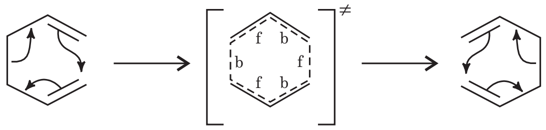
The most important sigmatropic rearrangement are the [3, 3] process involving carbon-carbon bond. The thermal rearrangement of 1, 5-dienes by [3, 3] sigmatropy is called Cope rearrangement. The reaction proceeds in the thermodynamically favoured direction.



This particular reaction is called a [3, 3] sigmatropic rearrangement because the new σ bond has a 3, 3 relationship to the old σ (*sigma*) bond.

The equilibrium in this case is controlled by the conjugation present in the product. The rearrangement of the simplest possible case, 1, 5-hexadiene, has been studied using deuterium labelling. For this reaction activation energy is 33.5 kcal/mole and the entropy of activation is – 13.8 *eu*. The substantially negative entropy conforms the formation of cyclic transition state.





Ea = +33.5 kcal/mole

Conjugated substituents at C-2, C-3, C-4 or C-5 accelerate the rearrangement. Donor substituents at C-2 and C-3 have an accelerating effect. The effect of substituents can be rationalised in terms of the stabilisation of the transition state by depicting their different effect on two interacting system (Fig. 4.5).

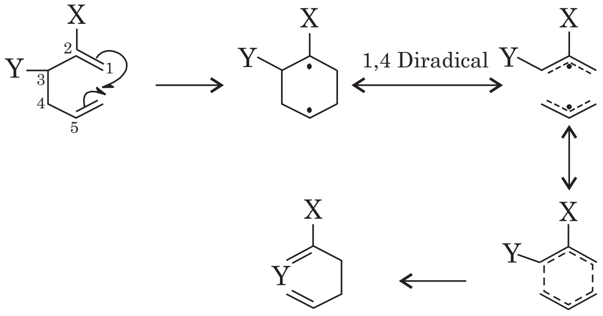


Fig. 4.5

The transition state involves six partially delocalised electrons being transformed from one 1, 5-diene system to another. The transition state could range in character from a 1, 4-diradical to two nearly independent allyl radical, depending on whether bond making or bond breaking is more advanced. The general framework for understanding the substituent effects is that the reaction are concerted with relatively late transition state with well developed C-1-C-6 bonds (Figs. 4.5 and 4.6)

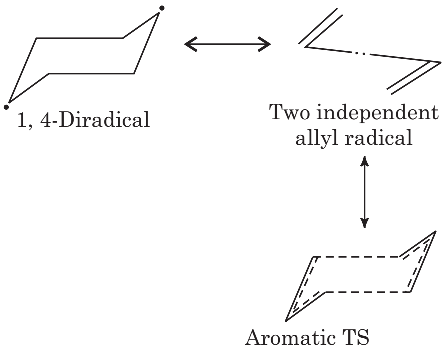


Fig. 4.6

The most advanced molecular orbital calculations support the idea of an aromatic transition state having six partially delocalised electrons. The net effect on reaction rate of any substituent is determined by whether it stabilises the transition state or the ground state more effectively. The aromatic concept of transition state predicts that it could be stabilised by conjugated substituents at all positions.

In Cope rearrangement the migrating group is allyl radical. An analysis of the symmetry of the orbitals involved shows why this reaction is a relatively facile thermal process but is not commonly observed on photochemical activation. As we break the C(1)–C(1) bond (Fig. 4.7) the phases of the overlaping lobes must be the same. The HOMO of the allyl radical is ψ_2 (Fig. 4.1) and that information allows us to fill the symmetries of the two allyl radicals making up of transition state (Fig. 4.7).

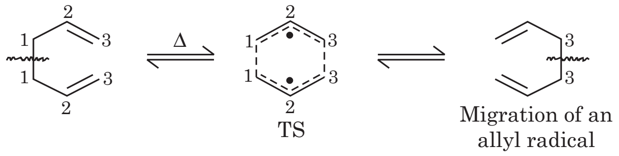


Fig. 4.7

Reattachment at the two C(3) positions (Fig. 4.7) is allowed because the interaction of the two lobes on the two C(3) carbons is bonding (Fig. 4.8).

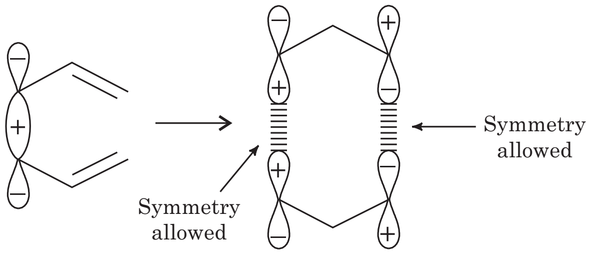


Fig. 4.8 Transition state: Two partially bonded allyl radicals—ψ_2 is the HOMO of each

If interaction is carried out in the presence of UV light then one electron is promoted from the HOMO to the LUMO and LUMO will become photochemically HOMO (Fig. 4.9).

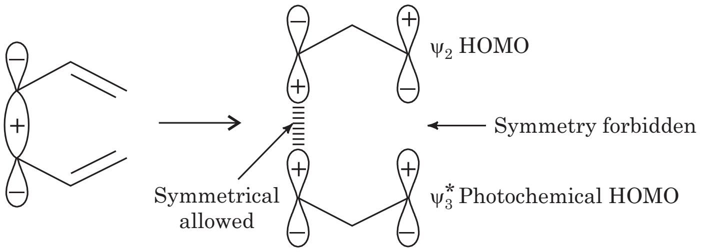
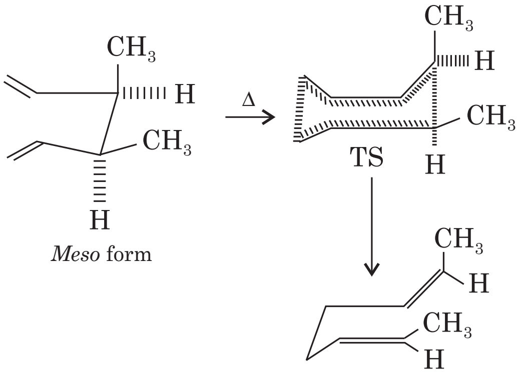


Fig. 4.9 Interaction between HOMO ground and HOMO photochemical symmetry forbidden process

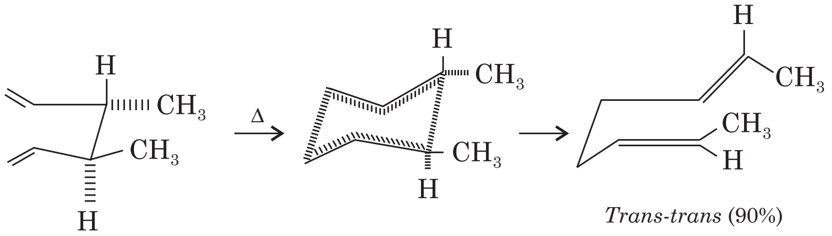
Stereochemistry of Cope Rearrangement

The Cope rearrangement usually proceeds through the chair like transition state. The stereochemical features of the reaction can usually be predicted and analysed on the basis of a chair transition state that minimises steric interactions between substituents. Rearrangement of the *meso* diene through such transition state then would give the *cis-trans* isomer while in the case of the rearrangement of the *racemic* mixture the *trans-trans* isomer is the major product and this is actually the result.



Meso form

Cis-trans 99.7%

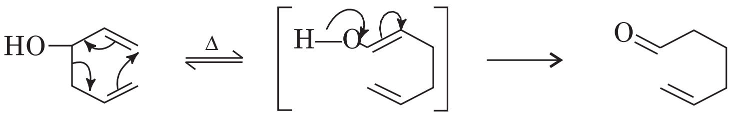


Trans-trans (90%)

The above result establishes that chirality is maintained throughout the course of the reaction. This stereospecificity is a general feature of [3, 3] sigmatropic shifts and has made them valuable reactions in enantiospecific synthesis.

Preparation of Carbonyl Compounds from Cope Rearrangement

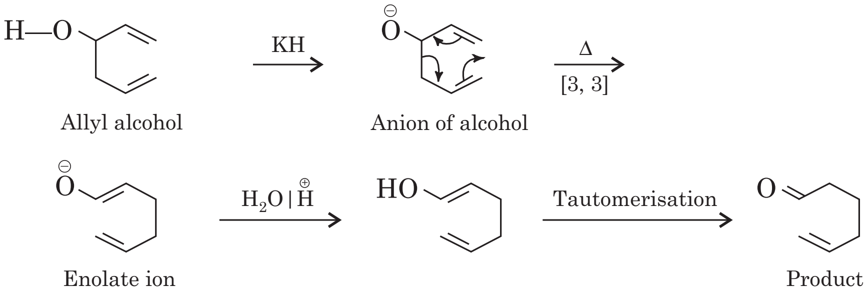
1, 5-Hexadiene-3-ol on heating undergoes Cope rearrangement with formation of unsaturated carbonyl compounds. Cope rearrangement given by such compounds is known as oxy-Cope rearrangement.



Enol

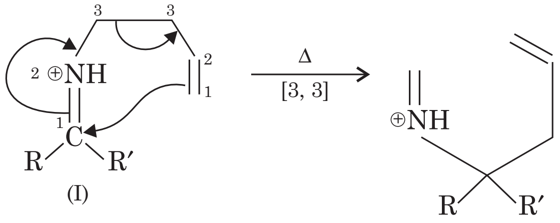
Unsaturated carbonyl compound

The reaction is accelerated when it is carried out in the presence of strong base. In the presence of strong base allyl alcohol converts into alkoxide ion which is very stable. Cope rearrangement given by anion of 1, 5-hexadiene-3-ol is known as anionic oxy-Cope rearrangement.



Alkoxide ion undergoes Cope rearrangement to give the product in which negative charge is in conjugation to π (*pi*) bond. This conjugation makes the anion very stable.

Iminium compound of type (I) also gives Cope rearrangement. Which is known as Aza Cope rearrangement.



Compound (I) can be prepared from 4-aminoalkenes.

$$H_2N—CH_2—CH_2—CH{=}CH_2$$

4-Aminoalkene

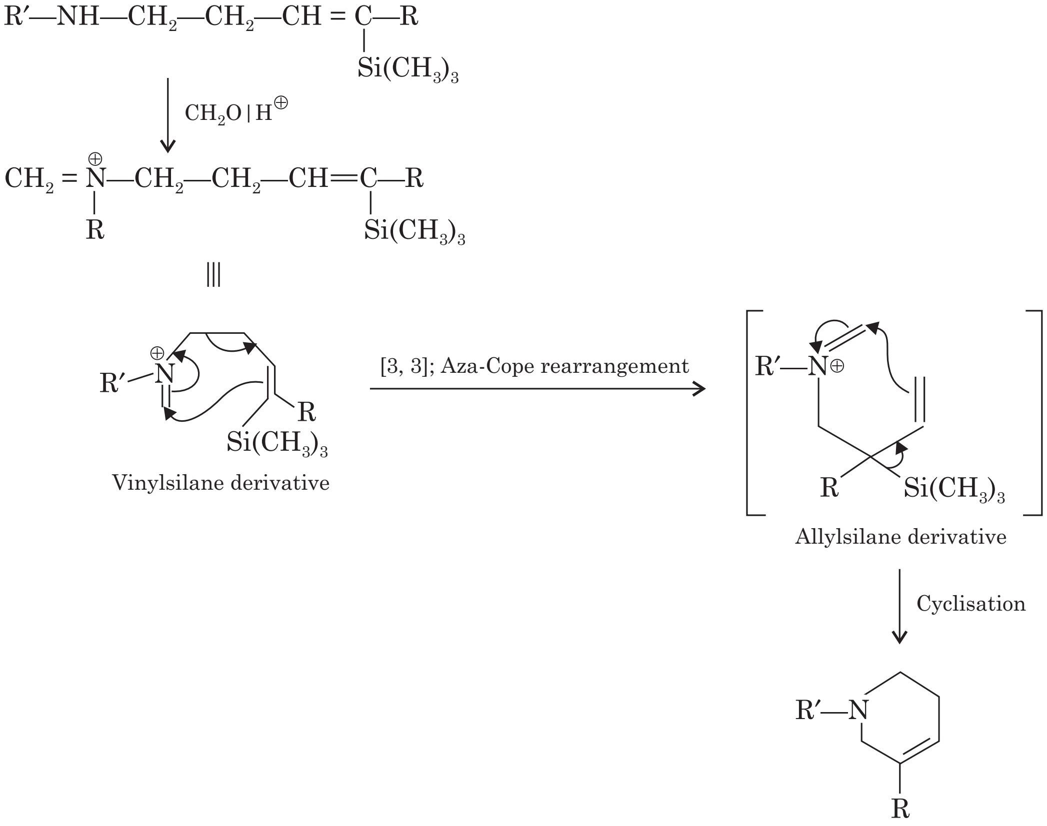
4-Aminoalkenes react with carbonyl compounds to give iminium compound of type (I).

$$H_2N—CH_2—CH_2—CH{=}CH_2$$

$$\Big\downarrow\ CH_2O \mid \overset{\oplus}{H}$$

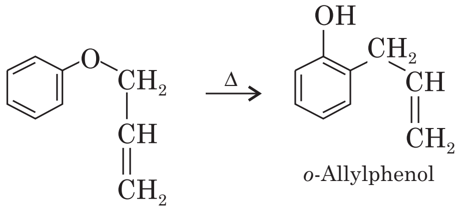
$$CH_2{=}\overset{\oplus}{N}H—CH_2—CH_2—CH{=}CH_2$$

Iminium compound of type (I) is very useful when it is prepared from 4-(trimethylsilyl)-3-alkenylamines because in this case rearranged product undergoes cyclisation to give six membered nitrogen heterocyclic compound. Thus, the overall reaction is as follows:



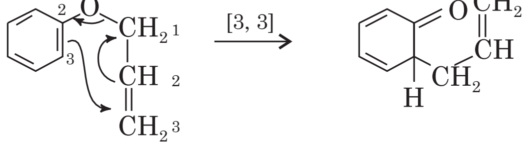
4.3.2 Claisen Rearrangement

Claisen rearrangement is the first sigmatropic rearrangement which was discovered. The original sigmatropic rearrangement occurs when allyl phenyl ether is heated without solvent. The product of the rearrangement is *o*-allylphenol.

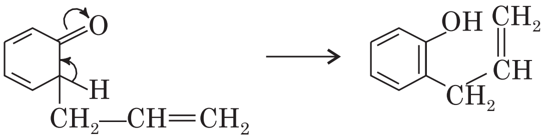


o-Allylphenol

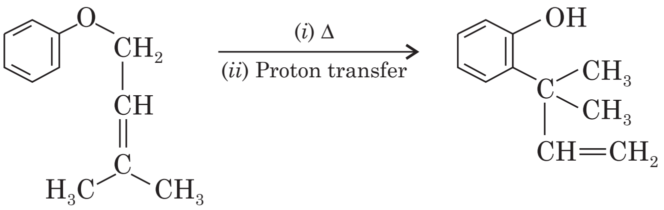
The above Claisen rearrangement is two step reaction. The first step in this reaction is [3, 3] sigmatropic rearrangement



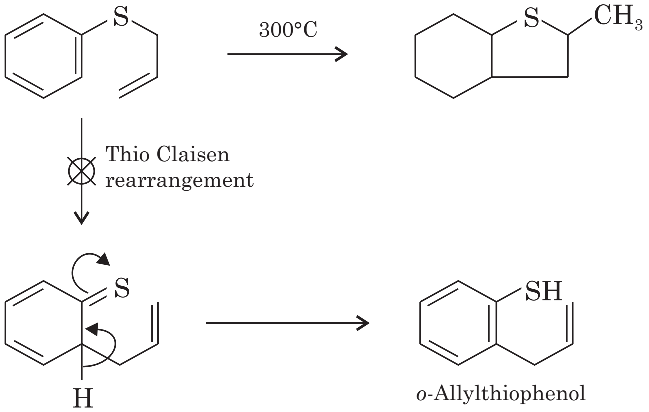
This is one step mechanism without ionic intermediates. In this case numbering start from the heteroatom oxygen having σ (*sigma*) bond and allylic carbon of the allyl group. The second step in the reaction is a simple ionic proton transfer to regenerate aromaticity.



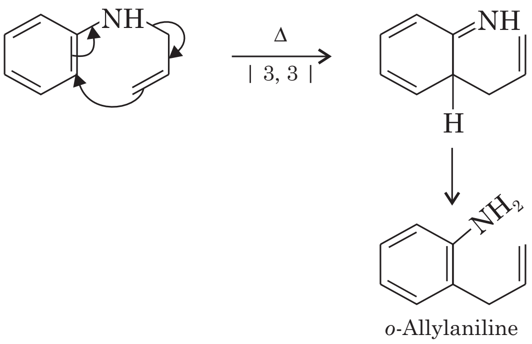
In this reaction allyl group turns inside out which is confirmed by unsymmetrical allyl ether.



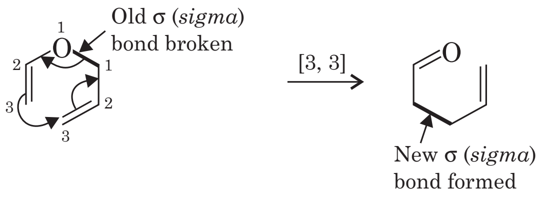
The conversion of allyl phenyl thioethers to *o*-allyl thiophenols, referred to as the thio-Claisen rearrangement, is not possible as the latter compounds are unstable but they instead give bicyclic compound.



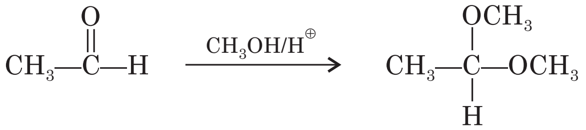
But if the oxygen atom in allyl phenyl ether is replaced by nitrogen, then the normal Claisen rearrangement takes place to afford the amino derivatives.



Claisen rearrangement is also given by allyl vinyl ether and in this case rearrangement is known as *aliphatic Claisen rearrangement* or *Claisen-Cope* rearrangement.

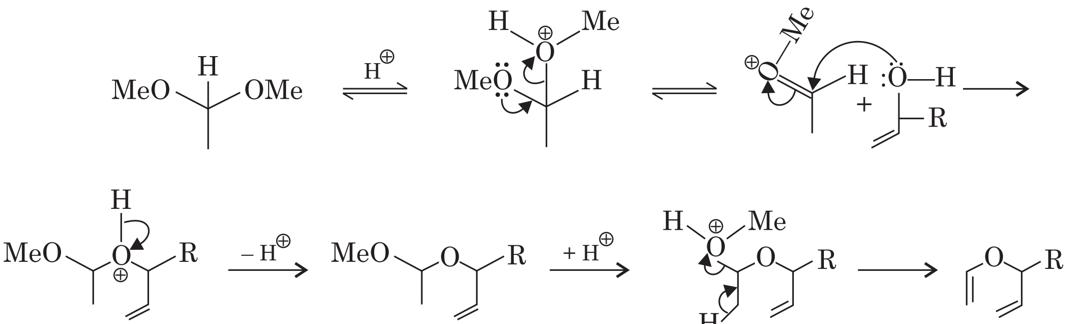


The starting material of aliphatic Claisen rearrangement is allyl vinyl ether which can be prepared with allyl alcohol and vinyl alcohol. Allyl alcohol is stable compound but vinyl alcohol is not. Thus, instead of vinyl alcohol acetal of acetaldehyde and methyl alcohol is used.



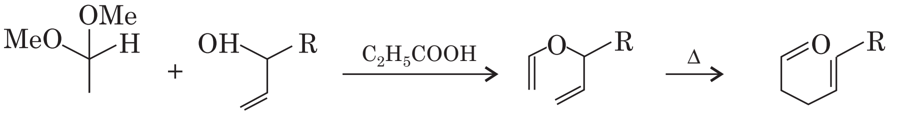
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{CH_3OH/H^{\oplus}} CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OCH_3}{|}}{C}}-OCH_3$$

When this acetal is treated with allyl alcohol, formation of vinyl allyl ether takes place.



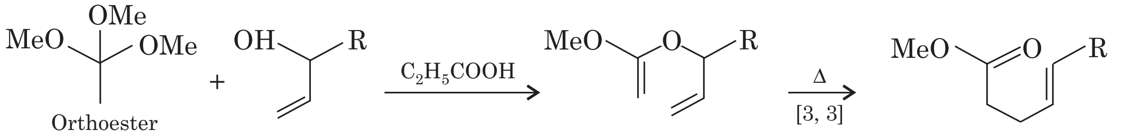
Allyl vinyl ether

Thus, overall reaction can be written as follows:



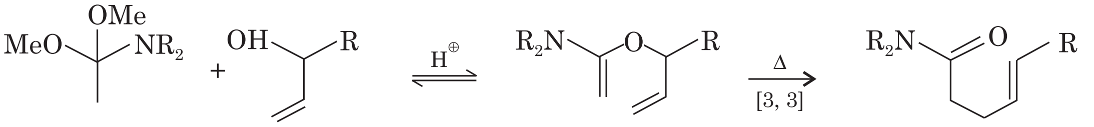
γ, δ-Unsaturated aldehyde

In this reaction orthoesters and orthoamides or amide acetals can be used in place of acetal or ketal and product of the reaction is γ, δ unsaturated ester and amide respectively.



Orthoester

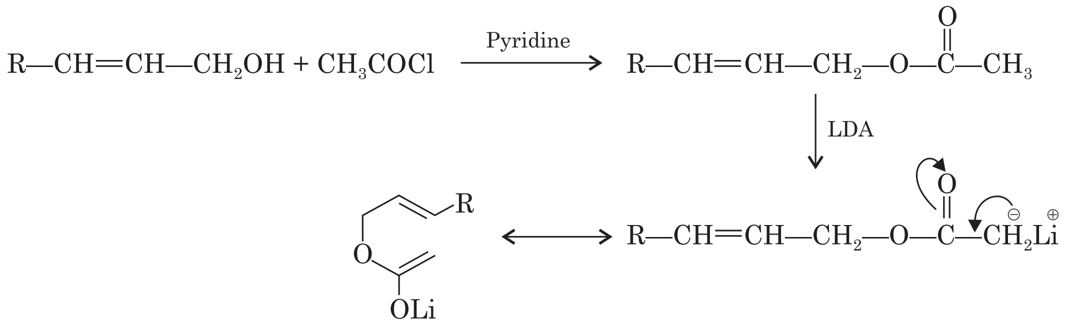
γ, δ-Unsaturated ester



γ, δ-Unsaturated amide

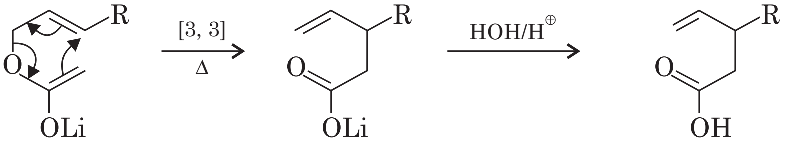
Formation of γ, δ-unsaturated ester from *ortho* ester and allyl alcohol is known as Johnson-Claisen rearrangement. Similarly formation of γ, δ-unsaturated amide from orthoamides and allyl alcohol is known as Eschenmoser-Claisen rearrangement.

Allyl vinyl ether can also be prepared from allyl alcohols and acid chlorides.



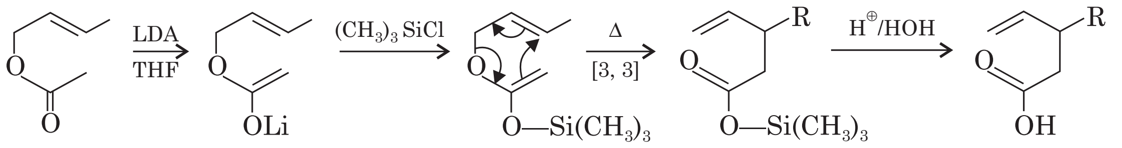
Lithium enolate

A combination of an oxygen atom in the chain and another out of the chain (at inner vinylic carbon) is very powerful at promoting [3, 3] sigmatropic rearrangement. Such type of compound can be used for the preparation of γ, δ-unsaturated carboxylic acid *via* [3, 3] sigmatropic rearrangement.



γ, δ-Unsaturated acid

Sometimes it is better to convert the lithium enolate into the silyl enol ether before [3, 3] sigmatropic rearrangement.

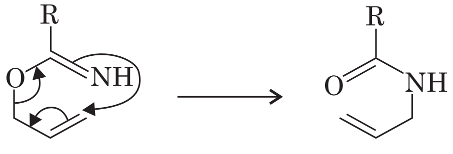


Silylenol ether

γ, δ-Unsaturated acid

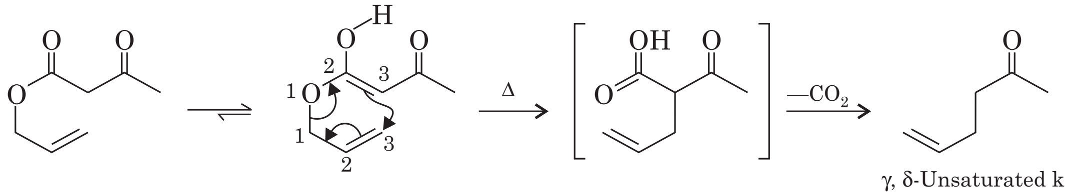
Cope rearrangement given by silyl enol ether is known as *Ireland-Claisen* rearrangement.

o-Allyl imidates also give Claisen rearrangement known as Aza-Claisen rearrangement.



N-Allylamide

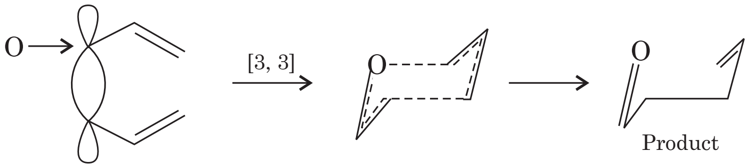
β-ketoesters can rearrange to give β-ketoacids which will decarboxylate to give γ, δ-unsaturated ketone. This rearrangement is known as Kimel-Cope rearrangement.



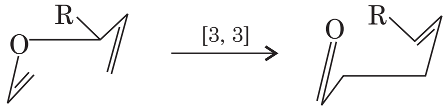
γ, δ-Unsaturated ketone

Stereochemistry

These [3, 3] sigmatropic rearrangements happen through a chair-like six membered cyclic transition state as in case of Cope rearrangement. This chair like transition state allows us both to get the orbitals right and to predict the stereochemistry (if any) of the new double bond in the product.



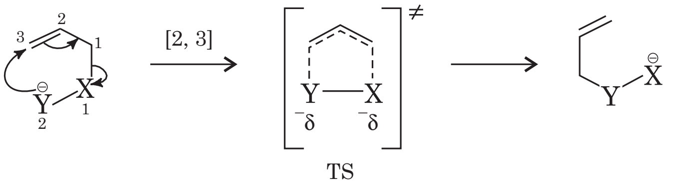
The substituent prefers an equatorial position as the material reacts and substituent retains this position in the product.

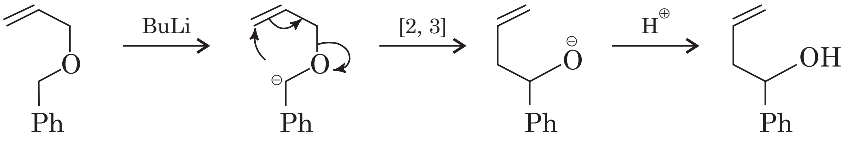


Thus the resulting double bond strongly favours *trans* (*E*) geometry.

4.4 [2, 3] SIGMATROPIC REARRANGEMENTS

All [3, 3] sigmatropic rearrangements have six-membered cyclisation transition state. It is no accident that the size of the ring in transition state is given by the sum of the two numbers in the square brackets as this is universally the case for sigmatropic rearrangements. In [2, 3] sigmatropic rearrangement transition state should have five membered ring structure. [2, 3] sigmatropic rearrangements have many variants depending upon which atoms are present in the chain of five atoms. All atoms may be carbons but most have Y(= carbon) and X(= oxygen, nitrogen, sulphur and carbon).





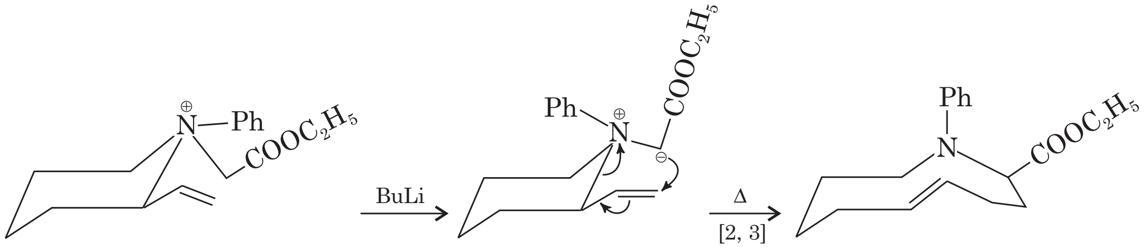
Benzylallyl ether

In the given case Y = Carbon and X = Oxygen.

If X is oxygen and Y is carbon then [2, 3] sigmatropic rearrangement is known as *Wittig* rearrangement.

When X = N and Y = C

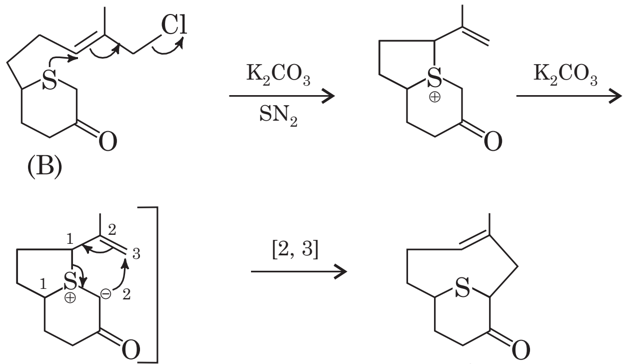
The quaternary ammonium ion (A) is deprotonated adjacent to ester group to give the nitrogen ylide which rearranges with ring expansion to give nine membered ring compound.



(A)

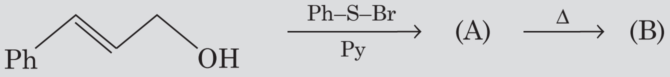
When X = S and Y = C

Intramolecular alkylation of the sulphide (B) followed by deprotonation gives a sulphur ylide which undergoes [2, 3] sigmatropic rearrangement.

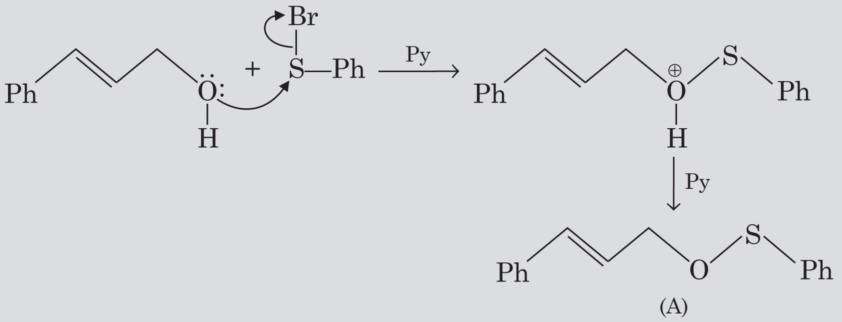


Product

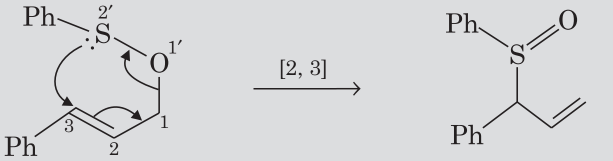
Problem 3: *Complete the following reaction sequences:*



Solution: First step is nucleophilic substitution reaction which gives (A) as follows:



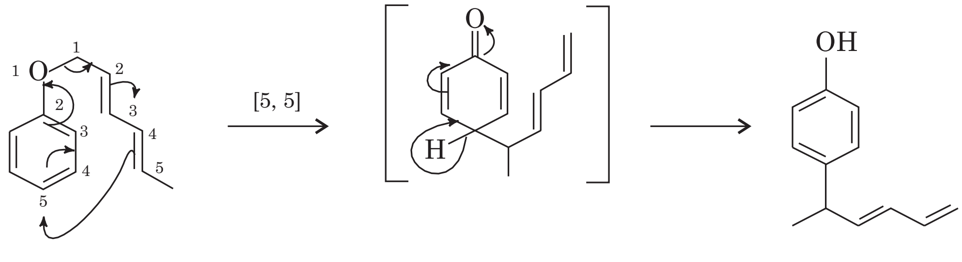
Compound (A) on heating undergoes [2, 3] sigmatropic rearrangement. In this rearrangement both oxygen and sulphur are involved.



Allylic sulphoxide

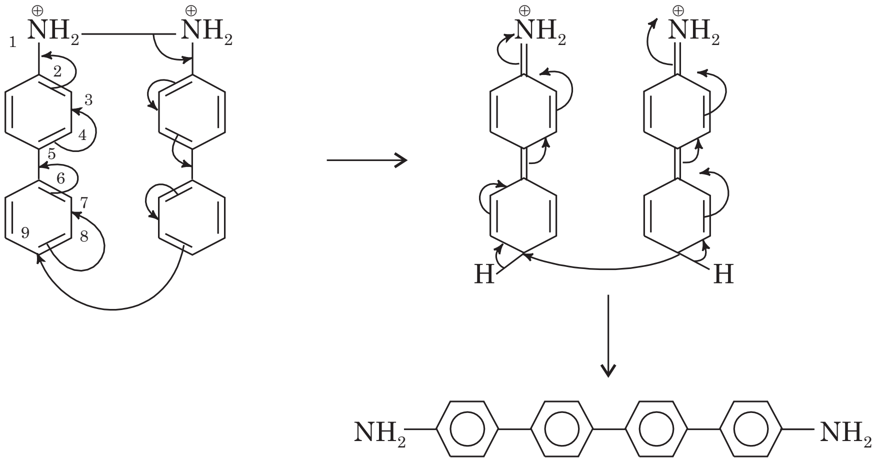
4.5 SOME OTHER [*m*, *n*] SIGMATROPIC REARRANGEMENTS

[5, 5], Sigmatropic rearrangement



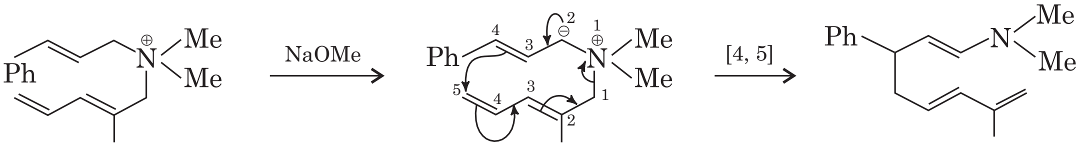
[9, 9] Sigmatropic rearrangement

Benzidine is example of [9, 9] sigmatropic rearrangement



[4, 5] Sigmatropic rearrangement

The given quaternary ammonium ion gives [4, 5] sigmatropic rearrangement.



4.6 THE WOODWARD-HOFFMANN RULE FOR SIGMATROPIC REARRANGEMENT

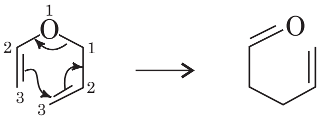
According to Woodward-Hoffmann rule a thermal (ground state) sigmatropic rearrangement is symmetry allowed when total number of $(4q + 2)s$ component and $(4r)a$ component is odd.

Similarly a sigmatropic change in the first excited state is symmetry allowed when total number of $(4q + 2)s$ and $(4r)a$ component is even.

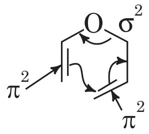
4.6.1 The Woodward-Hoffmann Rule for (m, n) Sigmatropic Rearrangement where Migrating Group is not Hydrogen

Here we will discuss [3, 3] sigmatropic rearrangement and in this case we will consider the Claisen rearrangement.

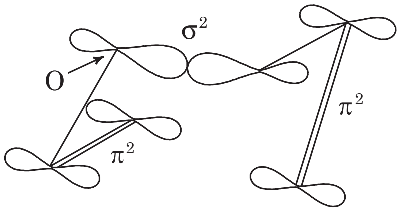
1. Draw the mechanism for the reaction.



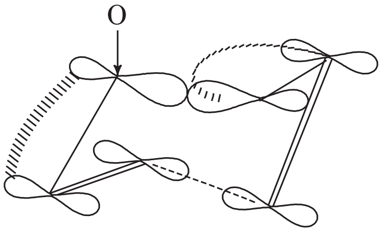
2. Choose the components. Only the bonds taking part in the reaction mechanism must be included.



3. Make a three-dimensional drawing of the way the components come together for the reaction, putting orbitals at the ends of the components.



4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.

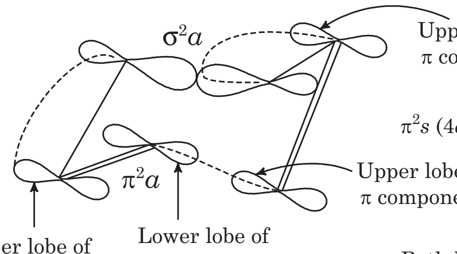


5. Label each component s or a. See below for the π and σ bond symmetries.

(a) **Whether π component is *s* or *a***

If both upper lobes or both lower lobes of the π (*pi*) component are involved in the reaction then the component will be *s* and it is label as π^2s.

If one upper lobe and other lower lobe of the π (*pi*) component are involved in the reaction then the component will be *a* and it is label as π^2a.



Upper lobe of π component

π^2s ($4q + 2$, $q = 0$)

Upper lobe of π component

Upper lobe of π component

Lower lobe of π component

Both lobes are upper of this π component which are taking part in the reaction hence this π component is π^2s.

One lobe is upper and one lobe is lower of this π component hence this component is π^2a

(b) **Whether σ component is *s* or *a* (when migrating atom is not hydrogen)**

(*i*) If sp^3-hybrid orbital uses its large lobe for reaction then there will be retention or the small lobe then there will be inversion.

Or

If large lobe of one orbital of the σ bond (which is undergoing cleavage) interacts with *p*-orbital of the adjacent atom (say atom-2 of allyl system) then at this end there will be retention.

If small lobe of the other orbital of the σ bond (which is undergoing cleavage) interacts with *p*-orbital of the adjacent atom (say atom-2 of vinyl system) then at this end there will be inversion (Fig. 4.10).

(*ii*) If there is retention at both ends or inversion at both ends then σ component is $\sigma^2 s$.

If there is retention at one end and inversion at other end then σ component is $\sigma^2 a$ (Fig. 4.10).

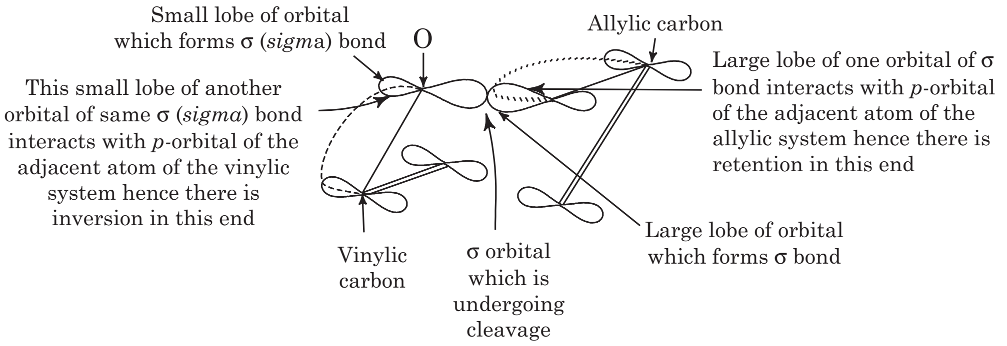


Fig. 4.10

Thus, σ component has retention at one end and inversion at another end hence σ component is $\sigma^2 a$.

6. Count the number of $(4q + 2)s$ and $(4r)\,a$ components.

Number of $(4q + 2)s$ component = 1

Number of $(4r)a$ component = 0

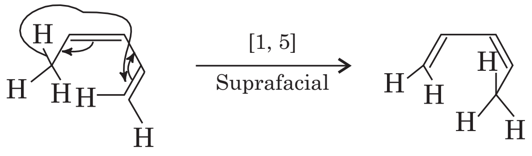
Total = 1 (odd) thermally allowed.

Note: $\pi^2\, a\ (4q + 2)a$ and $\sigma^2 a\ (4q + 2)$ components have irrelevant symmetry and are not counted.

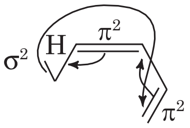
4.6.2 The Woodward-Hoffmann Rule for (m, n) Sigmatropic Rearrangement where Migrating Group is Hydrogen

Consider [1, 5] Sigmatropic hydrogen shifts

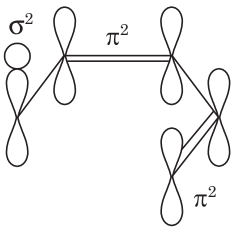
1. Draw mechanism for the reaction.



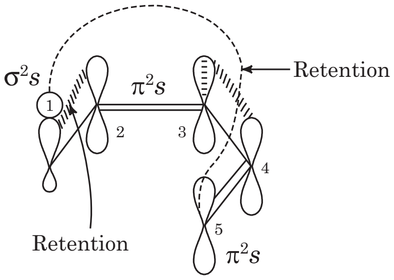
2. Choose the components. All bonds taking part in the reaction mechanism must be included and no others



3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components.



4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.

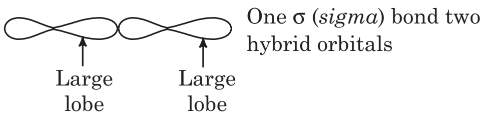


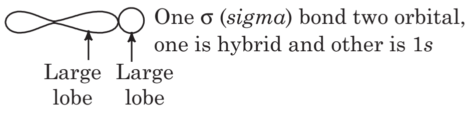
5. Label each components *s* or *a*. See below the σ (C—H) bond symmetry.

(*i*) The 1*s* orbital is spherically symmetrical and has no node, so whenever you draw the dotted line from 1*s* orbital it always means retention.

Or

Orbital of hydrogen which forms σ (*sigma*) bond is always treated as large lobe





(*ii*) If large lobe of one orbital of σ (C—H) bond (which is undergoing cleavage) interacts with *p*-orbital of the adjacent atom (atom-2) then at this end there will be retention.

If small lobe of the one orbital of σ (C—H) bond (which is undergoing cleavage) interacts with *p*-orbital of the adjacent atom (atom-2) then at this end there will be inversion.

6. Count the number of $(4q + 2)s$ and $(4r)a$ components.

$$(4q + 2) \rightarrow \sigma^2 \rightarrow \sigma^2 s$$
$$(4r) \rightarrow \pi^4 \rightarrow \pi^4 s$$

Number of $(4q + 2)s$ component = 1

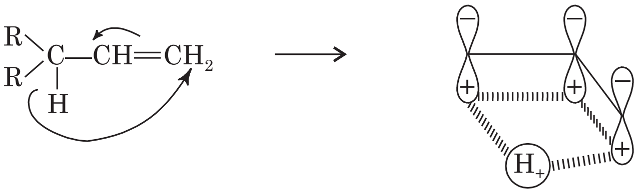
Number of $(4r)a$ component = 0

Total = 1 (odd) ; thermally allowed.

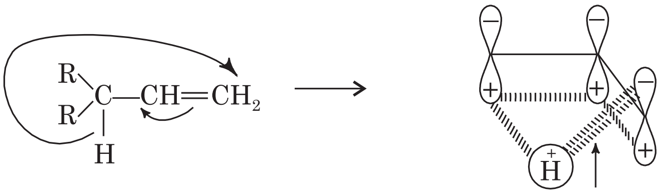
4.7 HÜCKEL-MOBIUS METHOD IN SIGMATROPIC REARRANGEMENTS

According to Hückel-Mobius rule thermal sigmatropic rearrangements take place via aromatic transition state whereas photochemical sigmatropic rearrangements proceed via antiaromatic transition state. Consider the following two rearrangements:

(i) **[1, 3] Sigmatropic Rearrangement**

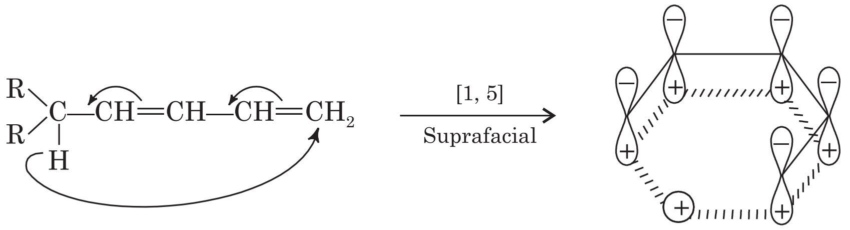


Suprafacial [1, 3], 4 electrons, zero node Hückel system, anti aromatic, *h*ν allowed

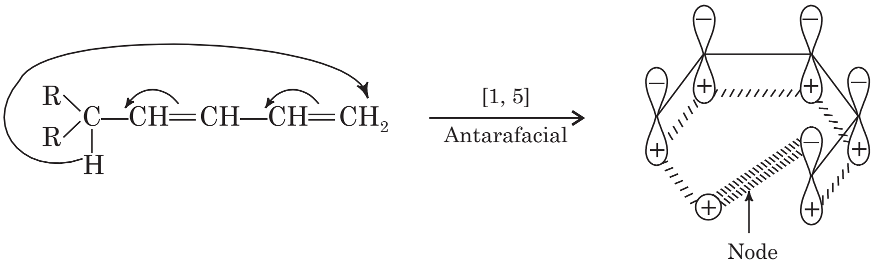


Antarafacial, 4 electrons, 1 node aromatic, mobius system, Δ allowed

(ii) [1, 5] Sigmatropic Rearrangement



6 Electrons, zero node, aromatic,
Hückel system, Δ allowed



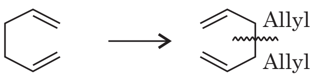
6 Electrons, one node, antiaromatic,
mobius system, $h\nu$ allowed

The selection rules for sigmatropic rearrangement of order (1, *j*) by this method are summarised in table 4.3.

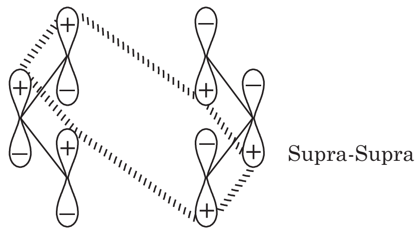
Table 4.3 Selection rules for sigmatropic rearrangement by H-M method

Number of electrons involved (1 + j)	*Number of nodes*	*Aromaticity*	*Shift mode*
$4n$	0	antiaromatic	supra, $h\nu$
$4n$	1	aromatic	antara, Δ
$4n + 2$	0	aromatic	supra, Δ
$4n + 2$	1	antiaromatic	antara, $h\nu$

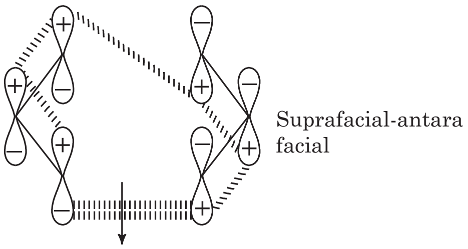
(iii) [3, 3] Sigmatropic rearrangements



The transition state for such processes is represented as two interacting allyl fragments as mentioned earlier. In this there can be two stereochemical variations-suprafacial-suprafacial (or antarafacial-antarafacial) and suprafacial-antarafacial as shown in the following transition states:



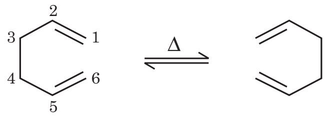
6 Electrons, zero node, aromatic, Hückel system, Δ allowed.



6 Electrons, one node, antiaromatic, mobius system, $h\nu$ allowed.

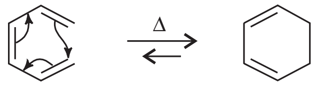
4.8 MODIFIED AND DEGENERATE COPE REARRANGEMENT

Cope rearrangement is the most general reaction of compounds having 1, 5-diene substructure



...(1)

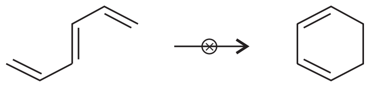
If we add a π (*pi*) bond between C-3 and C-4 then we will get *cis* 1, 3, 5-hexatriene. This compound can also be treated as 1, 5-diene substructure, therefore this compound will give Cope rearrangement.



...(2)

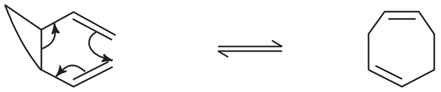
Cope rearrangement given by 1, 5-hexadiene is known as degenerate Cope rearrangement. Here degenerate means structure of reactant and product is same (Eqn. (1)). Similarly, rearrangement given by substructure of 1, 5-hexadiene, *i.e.*, 1, 3, 5-hexatriene is known as modified Cope rearrangement. In modified Cope rearrangement structure of reactant and product are not same (Eqn. (2)).

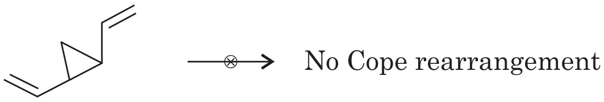
1, 3, 5-Hexatriene give Cope rearrangement only when it has *cis* geometry. In the *trans* isomer, the end of the triene system are too far apart for bond formation hence this does not give modified Cope rearrangement.



Trans-1, 3, 5-hexatriene

Similarly, *cis*-1, 2-divinylcyclopropane undergoes Cope rearrangement but *trans*-1, 2-divinylcyclopropane does not.

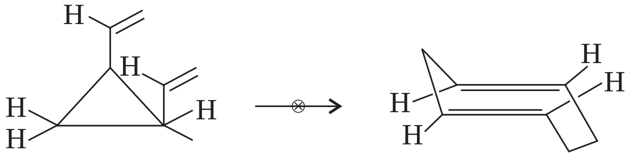

Cis-1, 2-Divinylcyclopropane 1, 4-Cycloheptadiene



Trans-1, 2-Divinylcyclopropane

These examples confirm that for Cope rearrangement both double bonds should have *cis* geometry, *i.e.,* both double bonds should be nearer to each other.

There is another stereochemical problem in this reaction. The most favourable arrangement for *cis*-1, 2-divinylcyclopropane is shown in Fig. 4.11. The two vinyl groups are directed away from the cyclopropane ring and away from the *syn* ring hydrogen. But this stable form cannot undergo Cope rearrangement at all.

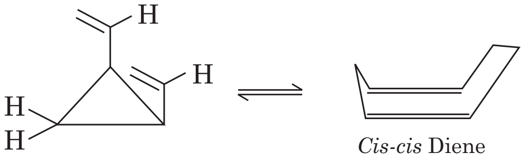


Most stable form of *cis*-1, 2-divinylcyclopropane

Trans-trans Diene (highly unstable, behaves as RI)

Fig. 4.11

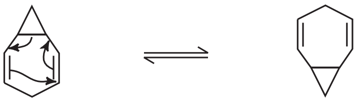
Cis-1, 2-divinylcyclopropane undergo Cope rearrangement with less favoured coiled form (Fig. 4.12). In this case geometry of two vinyl groups point back towards, the ring and are closer to the offending *syn* hydrogens.



Cis-cis Diene (stable compound)

Fig. 4.12 Less favourable, less stable coiled form

Homotropilidene undergoes degenerate Cope rearrangement rapidly.


Homotropilidene Still homotropilidene

Like 1, 2-divinylcyclopropane, the most stable extended form of homotropilidene is unable to undergo the Cope rearrangement, and it must be the higher energy coiled arrangement that is actually active in the reaction (Fig. 4.13).

Fig. 4.13 Two forms of homotropilidiene

From the above examples it has been confirmed that only those 1, 5 diene substructure give Cope rearrangement whose **geometry is *cis* and have coiled structure.**

Compounds having these characteristics undergo Cope rearrangement very rapidly even at room temperature and below room temperature.

Although such compounds undergo Cope rearrangement very rapidly, one might consider how to make the reaction even faster for the reaction to occur, an unfavourable equilibrium between more stable but unproductive extended, and the higher energy but productive coiled form must be overcome. The activation energy for the reaction includes this unfavourable equilibrium (Fig. 4.14).

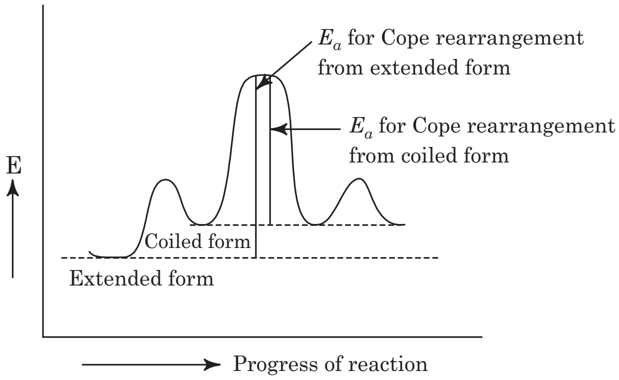


Fig. 4.14 Activation energy of reaction for two forms of homotropilidene

If this unfavourable equilibrium could be avoided in some way, and the molecule locked into a *coil form* arrangement, the activation energy would be lower (Fig. 4.14) and the reaction will occur faster.

If two methylene groups of homotropilidene are bridged then the corresponding molecule will exist only in coiled form and not in extended form. Since coiled form is responsible for Cope rearrangement, obtained compound(s) should undergo Cope rearrangement rapidly (Fig. 4.15).

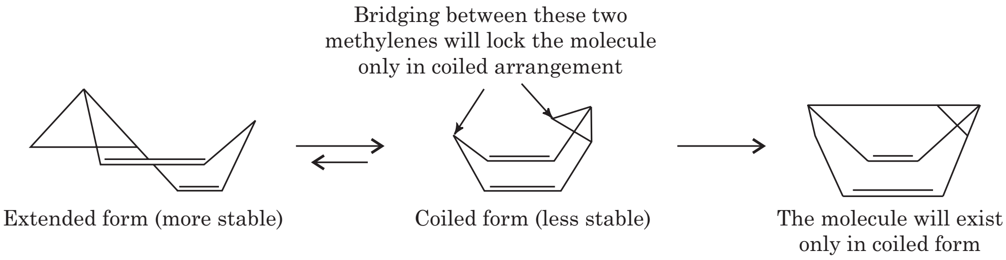
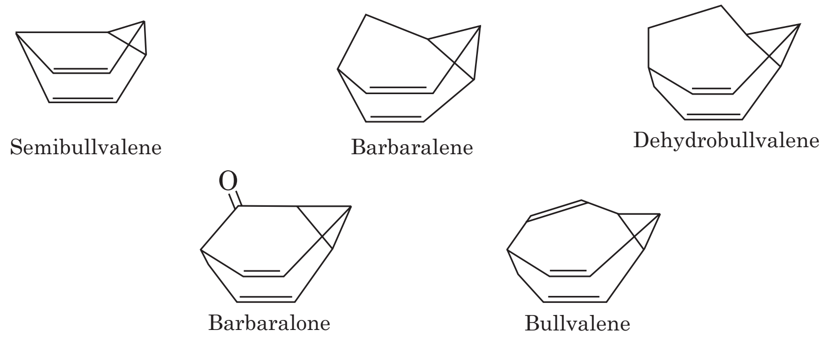


Fig. 4.15 Bridging between two methylene carbons which locks the molecule in coiled form

This modification greatly increases the rate of the Cope rearrangement as the activation energy is decreased (coiled structure, higher energy, lower activation energy, Fig. 4.14). No longer it is necessary to fight an unfavourable equilibrium in order for Cope rearrangement to occur because the molecule obtained in this way exists only in coiled form.

Many bridged homotropilidenes are now known and are given in Table 4.4.

Table 4.4 Bridged homotropilidenes



Semibullvalene

Barbaralene

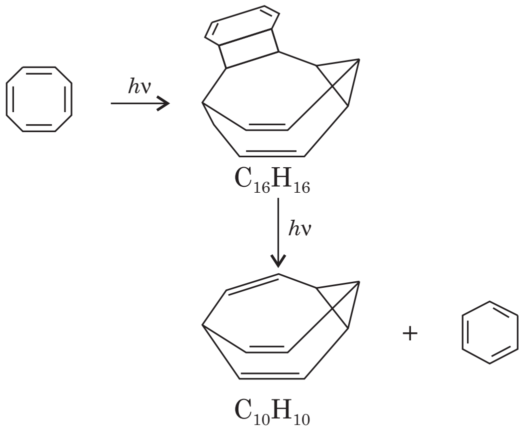
Dehydrobullvalene

Barbaralone

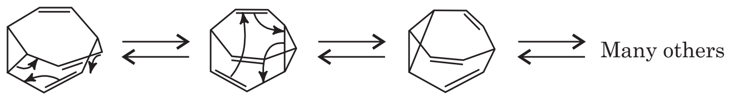
Bullvalene

4.9 FLUXIONAL MOLECULES

A number of compounds continually undergo rapid degenerate Cope rearrangement at room temperature. One such compound is bullvalene which was first prepared in 1963 by G. Schroder from cyclo-octatetraene as follows:



The [3, 3] sigmatropic rearrangements in bullvalene rapidly interconvert identical forms of the molecule.

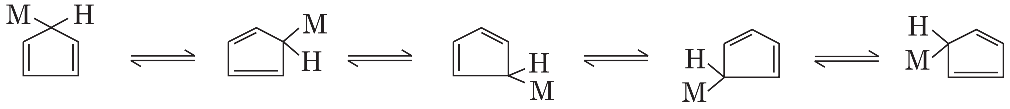


Bullvalene: Tricyclo [3, 3, 2, 0] deca 2, 7, tricyclo.

If the carbons could be individually labelled, there would be 1,209,600 different structures of bullvalene in equilibrium. Each one of these forms is interconverted into another at a rate of about 2000 times per second at room temperature.

Molecules such as bullvalene that undergo rapid bond shifts are called fluxional molecules. In fluxional molecules their atoms are in a continual state of motion associated with rapid changes in bonding. The rearrangement may involve either bond reorganisation or atom (or group) migration.

Other neutral completely fluxional organic molecules have not appeared, although the phenomenon of fluxionality appears to be rather more common in organic cations and organometallic compounds. The fluxionality of the σ (*sigma*) bonded metal cyclopentadienide involves atom migration.



Fluxionality is most readily ascertained by means of nuclear magnetic resonance spectroscopy. Conversion of one structure into other in fluxional molecule is known as *valence tautomerism* and isomers are known as *valence tautomers*.

GLOSSARY

Sigmatropic shifts: Rearrangements that formally consist of the migration of a σ (*sigma*) bond (actually the σ (*sigma*) electrons) and the group attached to this bond from one position in a chain or ring to a new position in the chain or ring. The migrating σ bond is often at an allylic position, and during the rearrangement the σ electrons are accepted into a *p*-orbital at the other terminus of the allylic system.

[1, *n*] Sigmatropic shift: A sigmatropic shift in which there is no rearrangement within the migrating group. The number 1 is to that atom in the migrating group that remains attached to the migrating σ (*sigma*) bond. The *n* indicates that the point of attachment to the chain has migrated from the first to the *n*th position along the chain.

[*m*, *n*] Sigmatropic shift ($m \neq 1$): A sigmatropic shift in which the migrating group also undergoes rearrangement. The number *m* denotes the number of the atom on the migrating group that is attached to the migrating bond after the migration. The number *n*, as *m* [1, *n*]-shift specifies the number of the atom in the chain that receives the migrating group. The numbering of atoms (*m*, *n*) on both the chain and migrating group starts at the atoms originally attached to the migrating bond.

Cope rearrangement: The thermal [3, 3]-sigmatropic shift in a 1, 5-diene resulting in its isomerisation is known as Cope rearrangement.

Claisen rearrangement: The thermally induced rearrangement of an allylphenyl ether to an *o*-allylphenol. If both *ortho* positions are occupied, the rearrangement gives the *para* isomer *via* a subsequent Cope rearrangement. Claisen rearrangement is [3, 3] sigmatropic shift. The reaction also proceeds with allylvinylether, yielding γ, δ-unsaturated carbonyl compound.

Fluxional molecules: Molecules which undergo rapid degenerate rearrangement, that is, rearrangement into indistinguishable molecules; the rearrangement may involve either bond reorganisation or atom (group) migration.

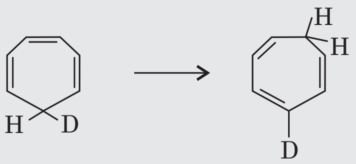
Further Reading

1. T.S. Stevens and W.E. Watts, *Selected Molecular Rearrangements,* Van Nostrand Reinhold, London, 1973, Chapter 8.
2. H.J. Hasen, *Mechanism of Molecular Migrations,* Vol. 3, Wiley Interscience, New York.
3. A.P. Marchand and R.E. Lehr, *Pericyclic Reactions*, Vol. I and II, Academic Press, New York, 1977.
4. F.A. Carey and R.J. Sundberg, *Advanced Organic Chemistry,* 4th ed., Plenum Press, New York, 2000.
5. J. Clayden, N. Greeves, S. Warren and P. Wothers, *Organic Chemistry,* 1st ed., Oxford University Press, Oxford, 2001.

Problems

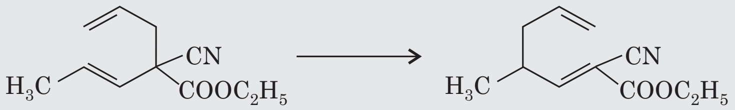
1. Which of the following sigmatropic rearrangements would proceed readily and which slowly? Explain your answers.

(*i*)



[**Hint:** This can proceed by a [1, 5] sigmatropic shift. Thus this can proceed readily.]

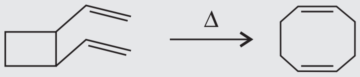
(*ii*)



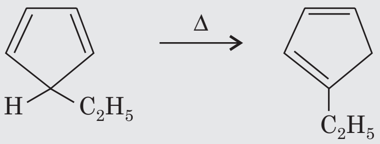
[**Hint:** This can proceed by a [3, 3] sigmatropic shift. Thus this can proceed readily.]

2. Classify each of the following sigmatropic rearrangements as [1, 3], [3, 3], etc.

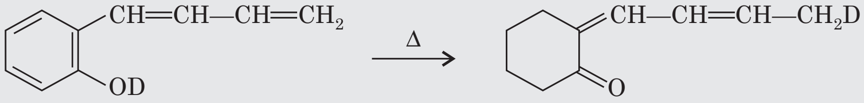
(*i*)



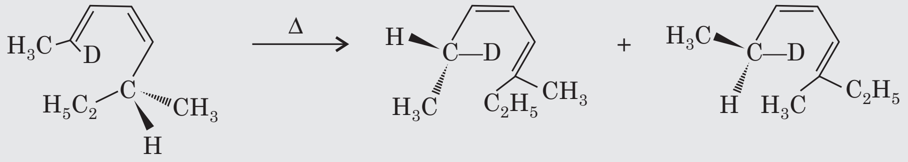
(*ii*)



(*iii*)



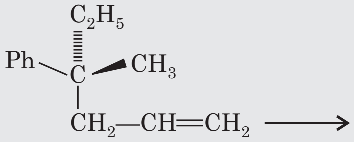
3. Explain the following observations:



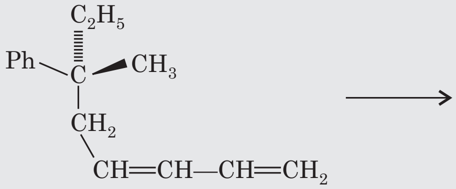
[**Hint:** [1, 5] Migration is suprafacial.]

4. Give stereochemistry at the chiral centres in the given sigmatropic rearrangements.

(*i*)



(*ii*)



[**Hint:** (*i*) [1, 3] Suprafacial migration of alkyl group proceeds with inversion of configuration at the chiral centre.

(*ii*) [1, 5] Suprafacial migration of the group proceeds with retention of configuration at the chiral centre.]

5. Explain why in the thermal [1, 3] sigmatropic rearrangement a suprafacial migration is geometrically feasible by symmetry forbidden.

6. [1, 3] Sigmatropic shift of hydrogen is thermally forbidden but photochemically allowed. Explain.

7. Explain why [1, 5] sigmatropic shift of hydrogen is thermally allowed process.

8. (*i*) Discuss sigmatropic shift of alkyl group.

(*ii*) Discuss the stereochemistry of the reaction when the group that migrates is bonded to the backbone by a chiral carbon.

9. With the help of FMO method, explain the stereochemistry of [3, 3] sigmatropic rearrangements under thermal and photochemical conditions.

10. Give reasons for the equivalence of all hydrogens in bullvalene.

11. Explain why *trans*-divinylcyclopropane is quite stable compound whereas it has not been possible to synthesise the *cis*-isomer, so far.

12. Write explanatory notes on the following:

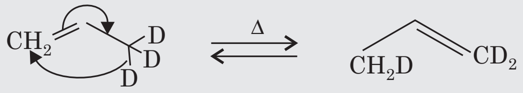
(*i*) Fluxional tautomerism.

(*ii*) Claisen rearrangement.

(*iii*) [1, 3] Sigmatropic rearrangement.

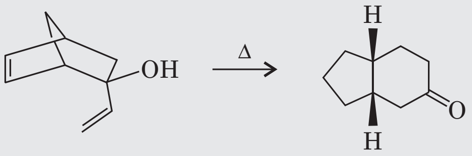
13. Using PMO method prove that Cope rearrangement occurs preferentially through a chair-like rather than a boat like transition state.

14. Do you expect the [1, 3] shift shown below to occur when propene is heated? Explain, using a molecular orbital argument.

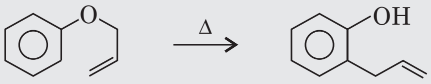


15. Provide mechanism for the reactions given below:

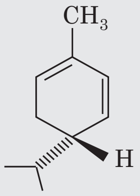
(*i*)



(*ii*)



16. *S*-(+)-α-phellandrene is an optically active compound where structure is given below. On distillation this compound loses its optical activity. Explain the reason for the loss of optical activity.

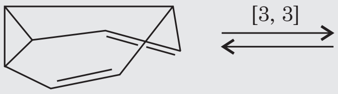


s-(+)-α-Phellandrene

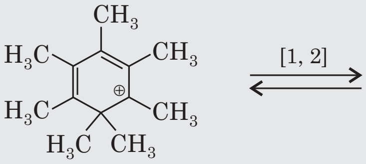
17. Carry out an orbital symmetry analysis to show that suprafacial [1, 5] carbon migration should occur with retention of configuration in the migrating group.

18. Each of the following compounds exists as a fluxional molecule, interconverted into one or more identical forms by the sigmatropic process indicated. Draw one structure in each case that demonstrates the process involved and explain why each process is an allowed pericyclic reaction.

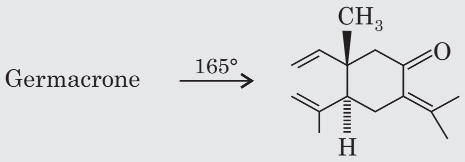
(*i*)



(*ii*)



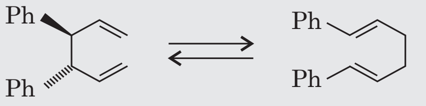
19. When the terpene germacrone is distilled under reduced pressure at 165°; it is transformed to β-elemenone by a Cope rearrangement. Give the structure of germacrone, including its stereochemistry.



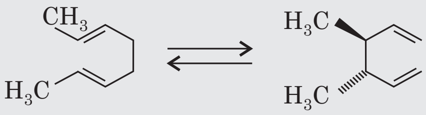
β-Elemenone

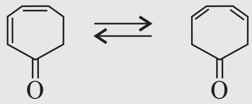
20. What do the pericyclic selection rules have to say about the position of equilibrium in each of the following reactions ? Which side of each equilibrium is favoured and why ?

(*i*)



(*ii*)





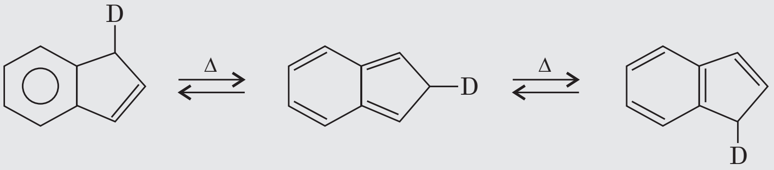
21. What do you understand from the order [*m*, *n*] of a sigmatropic rearrangement? Explain giving examples.

22. Depict the HOMO of allylic radicals with different number of carbons (*i.e.,* 3, 5, 7 and 9) in the π-framework. How are these useful in describing the transition state of a sigmatropic reaction.

23. Depict an easy way to analyse the symmetry characteristics of sigmatropic thermal rearrange-ments by taking the shift of deuterium atom on a pentadienyl system.

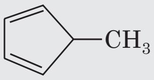
24. Why thermal [1, 3] sigmatropic migrations of hydrogens are unknown?

25. On heating 3-deuterioindene scrambling of the label to all the three positions in the five membered ring takes place. Explain.



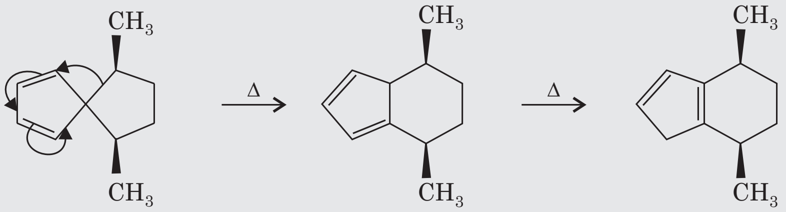
[**Hint:** This scrambling is a result of a series of [1, 5] shifts].

26. The given compound (A) shows only a singlet for the methyl group in its PMR spectrum. Explain.



[**Hint:** This compound shows [1, 5] migration of hydrogen. The migration of hydrogen takes place in the preference to the methyl group. This migration is so fast at room temperature that one see only a singlet for the methyl group.]

27. Give mechanism of the given reaction:



[**Hint:** The first product is the suprafacial sigmatropic shift of the carbon of the order of [1, 5] and is expected to occur with retention of configuration at the migrating carbon. The second step is [1, 5] shift of hydrogen.]

5

CHAPTER

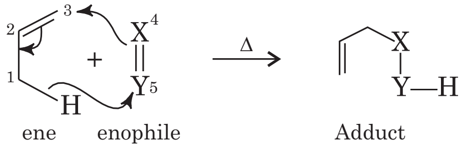
Group Transfer Reactions

A pericyclic process involving the transfer of one or more groups or atoms from one molecule to another is known as group transfer reaction. There are only a few reactions in this class. *Ene* reaction is one of the most common group transfer reaction. The other well known group transfer reaction is reduction of alkenes and alkynes by diimide.

5.1 ENE REACTIONS

Ene reaction involves the thermal reaction of an alkene (called ene) having an allylic hydrogen with a compound having multiple bond (X═Y, X≡Y), called enophile.

During the reaction, transfer of allylic hydrogen (1, 5 migration of hydrogen), shift of allylic double bond and bonding between two unsaturated termini (one terminus of ene and other terminus of enophile) takes place to form 1 : 1 adduct.

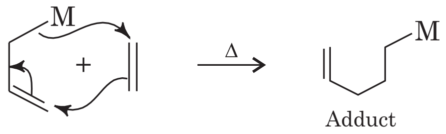


...(1)

In this reaction

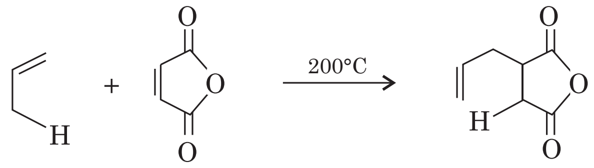
X═Y is	X≡Y is
C═C	C≡C
C═O	C≡N
C═S	
C═N	
N═O	
—N═N—	
O═O	

In ene reaction hydrogen atom of allylic carbon moves from ene to enophile. In principle atom other than hydrogen from allylic carbon can move from ene to enophile. In practice the only elements other than hydrogen commonly employed in this kind of reaction are metals like lithium, magnesium or palladium. When metal moves the reaction is known as *metalla-ene* reaction.

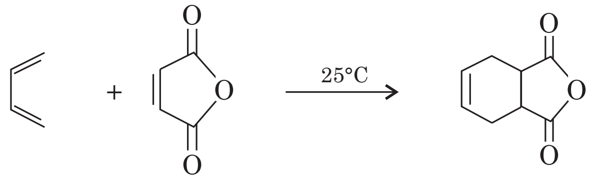


...(2)

In ene reaction there is a loss of a π (*pi*) bond and gain of two σ (*sigma*) bonds. In this reaction π (*pi*) bond of enophile is replaced by two σ (*sigma*) bonds with ene, therefore, this reaction resembles with cycloaddition reaction. This reaction also resembles with [1, 5] sigmatropic rearrangement because hydrogen migrates on atom-5 (equation-1) but reaction is neither sigmatropic nor cycloaddition reaction. This reaction is six electrons cycloaddition reaction. In this reaction hydrogen moves from ene to enophile. Due to this reason this reaction is an example of group transfer reaction. This reaction is like Diels-Alder addition. In Diels-Alder addition all six electrons are π (*pi*) electrons. In this reaction, out of six electrons, four electrons are π (*pi*) electrons but two electrons are σ (*sigma*) electrons. Thus, activation energy of this reaction is greater than the Diels-Alder reaction. Due to this reason ene reactions take place at higher temperature than Diels-Alder reaction.

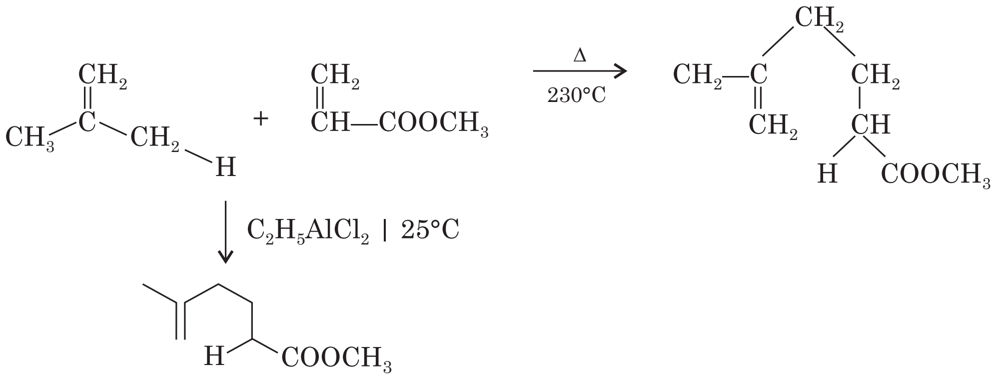


...(3)



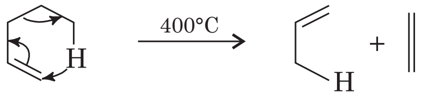
...(4)

Fortunately many ene reactions can be catalysed by Lewis acids. In the presence of Lewis acids as catalyst reaction proceeds under milder conditions. As far as catalyst is concerned the best result is obtained with alkyl aluminium halides.



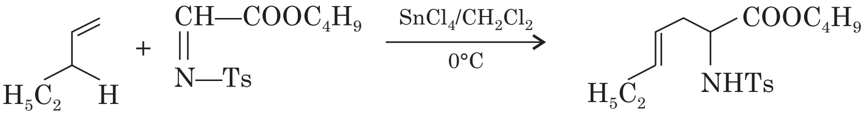
...(5)

Like Diels-Alder addition ene reaction is also reversible reaction. 1-pentene gives ethene and propene at 400°C

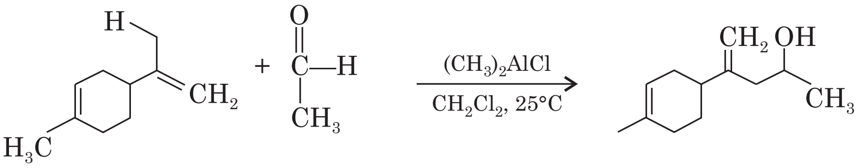


...(6)

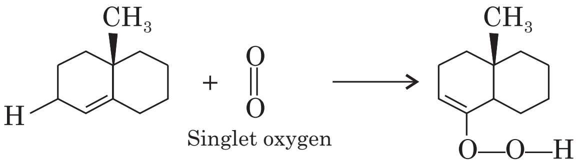
As mentioned earlier that enophile need not be alkene or alkyne derivatives heteroenophiles are also known.



...(7)

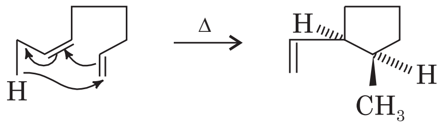


...(8)



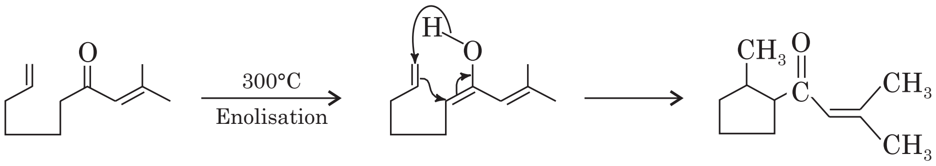
...(9)

Intramolecular ene reaction has great potential for the synthesis of cyclic compounds, particularly for the synthesis of five membered ring compounds from 1, 6-dienes.



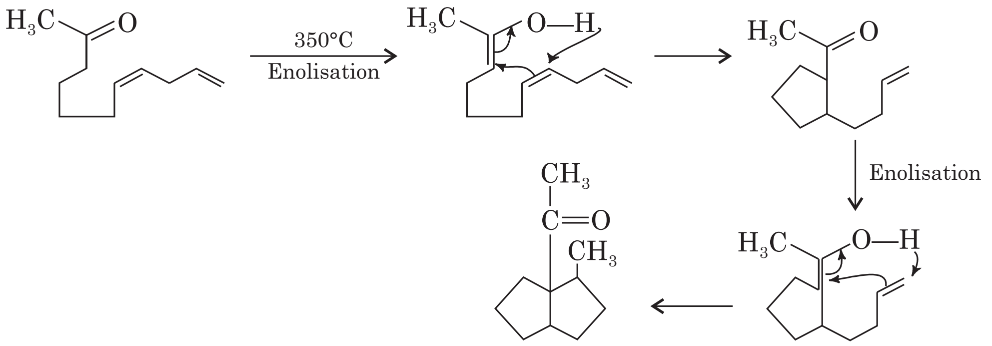
...(10)

Thermal cyclisation of 1, 8-diene-3-one provides a useful method for the preparation of cyclopentyl vinyl ketones by intramolecular ene reaction.



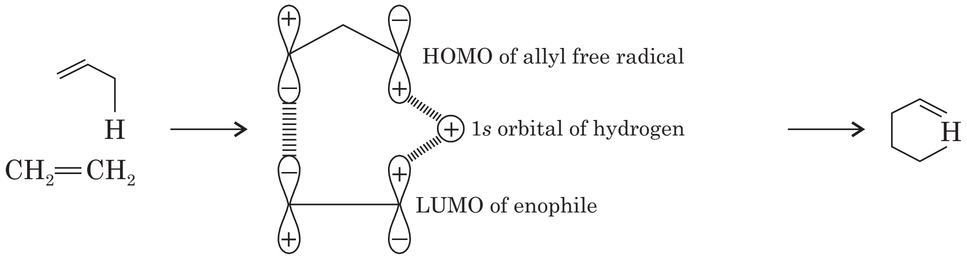
...(11)

Similarly 7, 10-alkadiene-2-one gives intramolecular ene reaction.



...(12)

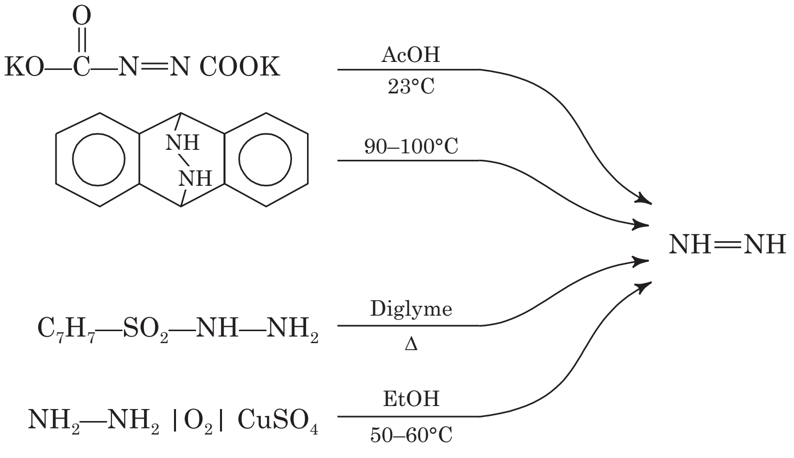
The concerted mechanism is allowed by Woodward-Hoffmann rules. The transition state involves the π (*pi*) electrons of the ene and enophile and the σ (*sigma*) electrons of the C—H bond of ene.



The ene reaction is bimolecular therefore a concerted ene reaction corresponds to the interaction of a hydrogen atom with the HOMO of an allyl radical and the LUMO of the enophile and is allowed.

5.2 GROUP TRANSFER REACTIONS GIVEN BY DIIMIDE

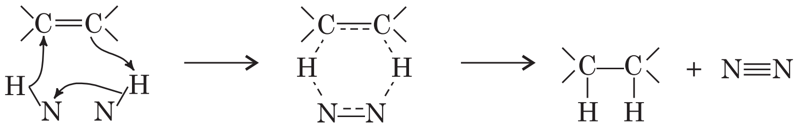
It has long been known that isolated carbon-carbon double bonds can be reduced with hydrazine in the presence of oxidising agents. The actual reducing species in these reactions is in fact the highly active species diimide, NH=NH, formed *in situ* by oxidation of hydrazine. In fact diimide is an ephemeral species which results from the decomposition with potassium azodicarboxylate, anthracene-9, 10, diimine and hydrazine and its derivatives.



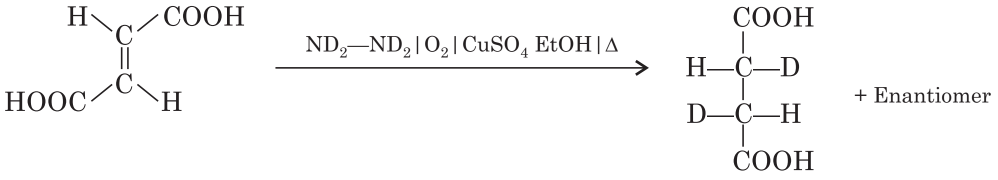
Although this species has not been isolated, its transient existence has been proven by mass spectroscopy and by its reactions in which it hydrogenates organic compounds with concomitant evolution of nitrogen (Eqn. 1)

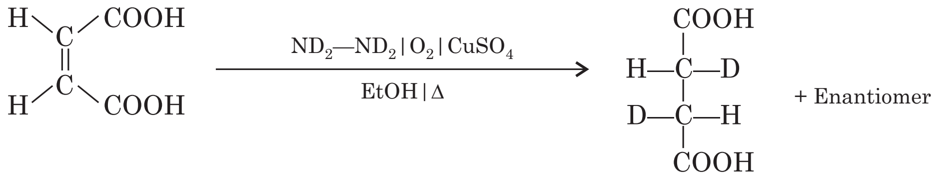
$$\rangle C{=}C\langle + NH{=}NH \longrightarrow \rangle CH{-}CH\langle + N_2 \qquad ...(1)$$

The reaction of diimide with alkenes is a concerted group transfer reaction proceeding through a six-membered transition state. It results in predominant *syn* (*cis*) addition of hydrogen and is therefore very useful for stereospecific introduction of hydrogen on to double bonds. The mechanism explains the high stereospecificity of the reaction, and couples the driving force of nitrogen formation with the addition reaction.



Concerted *cis*-transfer of hydrogen is symmetry allowed for the ground state reaction. Applications of diimide are very rare and are mainly limited to hydrogenation of carbon-carbon multiple bonds and azo compounds to hydrazo compounds.

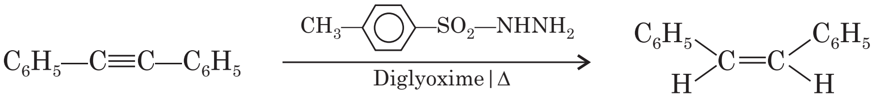




Meso form

These two reactions confirm that addition is stereospecific ***syn*** addition reaction.

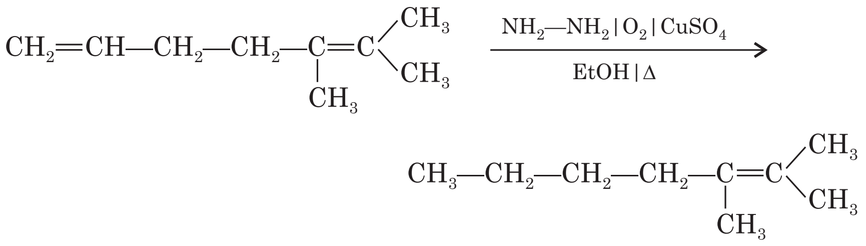
Partial reduction of alkyne into alkene by the reagent is also stereospecific



Cis-stilbene

In this reaction no ***trans*** stilbene was detected.

In sterically hindered molecules, addition takes place to the less hindered side of the double bond.



$$CH_2{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}C\begin{matrix}CH_3\\CH_3\end{matrix}\xrightarrow[EtOH\,|\,\Delta]{NH_2{-}NH_2\,|\,O_2\,|\,CuSO_4}CH_3{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$$

GLOSSARY

Ene reaction: A reaction of a double bond with an allylic system in which an allylic hydrogen and the olefinic terminus of the allylic system add across the double bond. This is very general reaction that is insensitive to the substituents involved.

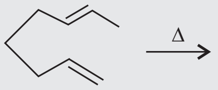
FURTHER READING

1. W. Carruthers, *Some Modern Methods of Organic Synthesis*, Cambridge University Press, 1993.
2. W. Carruthers, *Cycloaddition Reactions in Organic Synthesis,* Pergamon Press, 1990.

PROBLEMS

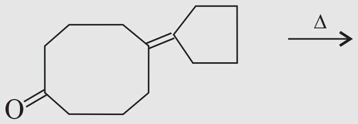
1. Define group transfer reaction and give its examples.
2. In what way ene reaction is related to [1, 5] sigmatropic shift and Diels-Alder reaction.
3. Give mechanism of ene reaction.
4. Reduction of alkene or alkyne with diimide is an example of group transfer reaction. Give mechanism and stereochemistry of the reaction.
5. What is metalla-ene reaction? What is difference between ene and metalla-ene reaction?
6. Complete the following reactions and give their mechanism:

(*a*)

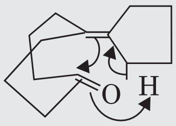


[**Hint:** This is ene reaction.]

(*b*)



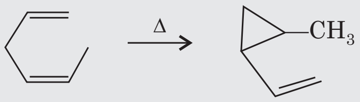
[**Hint:**



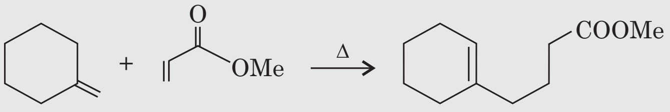
]

7. Give mechanism of the following:

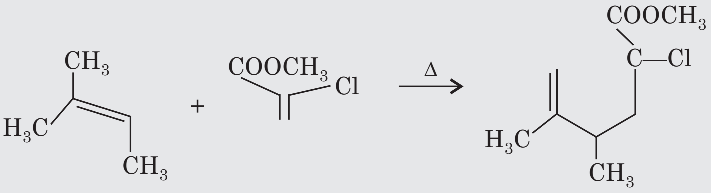
(*a*)



(*b*)



(*c*)



8. Complete the following reaction and give its mechanism:

$$CH_3—CH{=}CH_2 + SeO_2 \xrightarrow[HOH]{\Delta} HO—CH_2—CH = CH_2$$

6
CHAPTER

Introduction and Basic Principles of Photochemistry

6.1 ENERGY OF A MOLECULE

Total energy of a molecule is sum of electronic energy, vibrational energy, rotational energy and translational energy.

$$E_{Total} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$

The translational energy is not quantised whereas all other three energies are quantised and furthermore

$$E_{elec} >> E_{vib} >> E_{rot} >> E_{trans}$$

Translational energy is (only 4% of the total energy) negligible. Thus, the energy of molecule is

$$E_{Total} = E_{elec} + E_{vib} + E_{rot}$$

These energies depend on the property of the molecule that is size, shape, flexibility as well as on the type of motion. These energies are quantised that is they can change only by discrete sums ($\Delta E = h\nu$).

The various energy levels in the molecule are shown in Fig. 6.1. Suppose A and B are the two electronic states indicated by electronic quantum number n (= 1, 2, 3, 4, ...). In each electronic states there are vibrational energy levels indicated by vibrational quantum number V (= 0, 1, 2, 3, 4, ...). Again for each vibrational state (energy levels), there exist several rotational energy levels indicated by rotational quantum number J(= 0, 1, 2, 3, 4, 5, ...).

Translational energy is not quantised and changes in continuous manner.

There are two different means by which energy can be supplied to the molecules. First changing the temperature produces a continuous increase in energy. Second a quantum of energy may be absorbed by a molecule from electromagnetic radiation. These two modes of energy input give rise to *thermal chemistry* and *photochemistry*.

Thermal Energy

When thermal energy is given to the molecules, molecules move more rapidly: that is translational energy increases. A molecule can move with any velocity because translational energy is not quantised. At a given temperature there will be an energy distribution among the molecules, some molecules have higher velocity and some have lower velocity than the average velocity of the molecule. Only a few molecules will have sufficient energy (known as threshold energy) to react. At higher temperature a large fraction of molecules will have threshold energy and the rate will increase (Fig. 6.2).

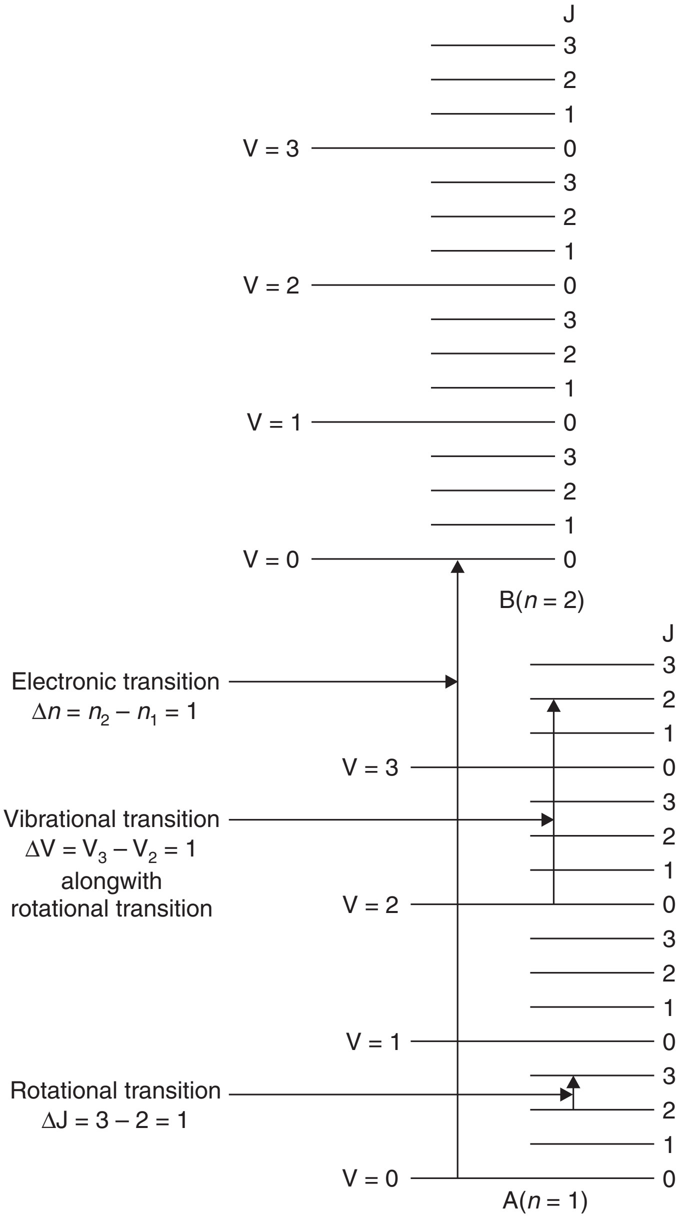


Fig. 6.1 Different energy levels of the molecule

As the temperature is raised, the molecules can acquire additional vibrational and rotational as well as translational energy. Vibrational and rotational energy are quantised, that is they can change only by discrete sums (Fig. 6.1). This can be illustrated more simply for a diatomic molecule by means of *Morse* curve (Fig. 6.3). If we imagine two atoms coming together from a distance they may eventually join to form a chemical bond and the energy of the system will decrease and will be minimum. If the internuclear distance decreases below equilibrium position (that is bond length between two atoms of the molecule) nuclear-nuclear repulsion increase rapidly and energy rises. The molecule thus finds itself in a potential well corresponding to chemical bond (Fig. 6.3).

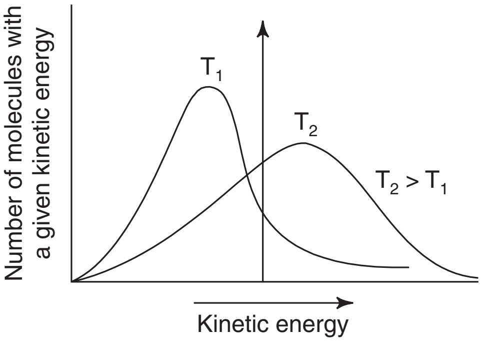


Fig. 6.2 Energy distribution in molecules at two different temperatures

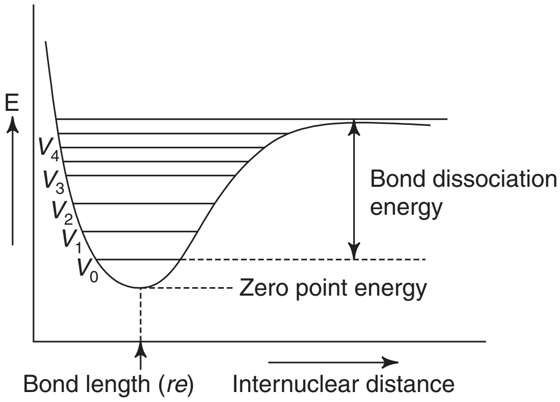


Fig. 6.3 Vibrational energy levels

Within the potential well molecule can occupy any of a number of discrete vibrational energy levels. Solution of Schrödinger wave equation leads to the result that vibrational energy levels are quantised with values

$$E = h\nu\left(V + \frac{1}{2}\right) \qquad ...(1)$$

where E is the vibrational energy and V is the vibrational quantum number.

These values are represented by equally spaced horizontal lines (Fig. 6.3). Note that the minimum vibrational energy is not zero but $\frac{1}{2}\,h\nu$.

$$E = h\nu\left(V + \frac{1}{2}\right)$$

If $V = 0$ then $E = E_0, \nu = \nu_0$

$$E_0 = h\nu_0\left(0 + \frac{1}{2}\right)$$

$$E_0 = \frac{1}{2}\,h\nu_0 \qquad ...(2)$$

This energy $\left(E_0 = \frac{1}{2}h\nu_0\right)$ is called zero point energy. This confirms that molecule can never be at rest. Thus even at absolute zero (– 273°C) when rotation stops, vibrational motion is still present.

When energy is supplied to the molecule, higher vibrational states (V_1, V_2, V_3, V_4 etc.) may become populated. Only the exact amount of energy needed to go from V_0 to V_1, V_2, V_3 or some higher energy level may be absorbed. In typical organic molecules V_1 lies from 2 to 10 kcal/mole above V_0. Molecule at room temperature have an average thermal energy content of about 0.6 kcal/mole. It is thus obvious that most molecules are present in their lowest vibrational energy level (V_0) under these conditions. As the temperature is raised, some of additional energy will go into populating higher vibrational levels. Many chemical reactions, specially those that are intramolecular involve these higher vibrational energy levels.

At still higher temperature enough vibrational energy may be absorbed to bring about rupture of bond. The minimum energy required to do this is known as bond dissociation energy and is shown in Fig. 6.3. The amount of energy required to dissociate a bond varies widely depending on the structure of the molecule and the nature of the atoms involved in the bond.

6.2 PHOTOCHEMICAL ENERGY

Another way of exciting the molecules involved absorption of electromagnetic radiation. The amount of energy that such radiation contains depends upon its wavelength according to relationship given below:

$$E = h\nu \qquad \text{...(1)}$$

$$\nu = \frac{C}{\lambda} \qquad \text{...(2)}$$

Therefore $$E = \frac{hC}{\lambda} \qquad \text{...(3)}$$

where ν = frequency of electromagnetic radiation
λ = wavelength of electromagnetic radiation
C = velocity of light
h = Planck constant

From equation (3)

$$E = \frac{2.62 \times 10^4}{\lambda} \qquad \text{...(4)}$$

This energy supplied by light of λ 254 nm equal to 113 kcal/mole (from equation (4)), an energy sufficient to rupture most chemical bonds. (Table 6.1)

Table 6.1 Energy of some covalent single bonds and the corresponding approximate wavelengths

Bond	*Energy in kcal/mole*	*λ in nm*
C—H	95	300
C—O	88	325
C—C	83	345
Cl—Cl	58	495
O—O	35	820

Table 6.2 Type of electromagnetic radiation and energy needed for different excitations

Region	*Wavelength*	*Excitation energy in kcal/mole*	*Type of excitation*
Gamma radiation X-rays, cosmic rays	< 100 nm	> 286	—
Ultraviolet			
(*i*) Vacuum	100–200 nm	286–143	Electronic
(*ii*) Quartz	200–350 nm	143–82	Electronic
Visible	350–800 nm	82–36	Electronic
Infrared			
(*i*) Near infrared	0.8–2.0 μm	36–14.3	Vibrational
(*ii*) Infrared	2–16 μm	14.3–1.8	Vibrational
(*iii*) Far infrared	16–300 μm	1.8–0.1	Vibrational
Microwave	1 cm	10^{-4}	Rotational
Radio frequency	meters	10^{-6}	Electron and nuclear spin transitions

Table 6.3 Symbols and definitions

Symbol	*Definition*
UV	Ultraviolet
IR	Infrared
Å	The unit angestron equal to 10^{-8} cm.
μm	The unit micrometer 1 μm = 10^{-6} m.
nm	The unit of nanometer 1 nm = 10^{-6} m.

6.2.1 Photochemical Excitation of the Molecule

Photochemistry begins with absorption of light in the 200–800 nm region of spectrum. In order to know what wavelength of light we should employ in a particular photochemical experiment, we must determine the UV absorption spectrum of the molecule we wish to study. Such a spectrum measures the amount of incident light absorbed by the molecule as a function of wavelength. The fraction of light absorbed $\left(\frac{I}{I_0}\right)$ is given by the *Beer's-Lambert's* law.

Lambert's law states that the fraction of the incident light absorbed by a compound is independent of the intensity of the source. Beer's law states that the absorption of light is proportional to the number of absorbing molecules. The absorption at a particular wavelength is defined by the equation

$$A = \log \frac{I_0}{I}$$

where A = absorbance

I_0 = intensity of the reference light

I = intensity of the beam coming out of the sample cell

The absorbance by a compound at a particular wavelength increases with increasing number of molecules undergoing transitions. Therefore, absorbance depends upon the electronic structure of the compound and also upon the concentration of the sample and length of the sample cell. For this reason energy absorption is reported as molar absorptivity, ε, also known as molar excitation coefficient rather than actual absorbance. Often UV spectra are reported to show ε or log ε instead of A. The log ε value is specially useful when value for ε are very large.

$$\varepsilon = \frac{A}{Cl}$$

where C = concentration of solution in mole/L

l = length of tube in cm

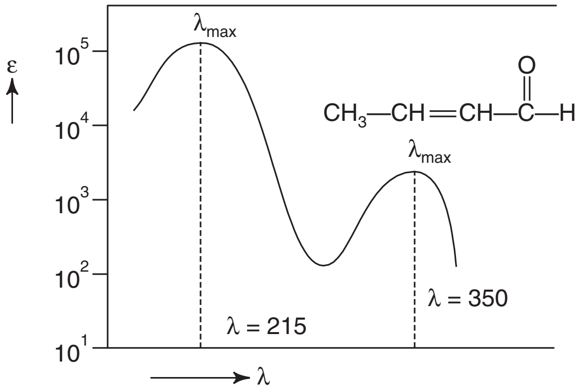


Fig. 6.4 UV spectrum of $CH_3—CH=CH—CHO$

Absorption maxima of some compounds are given in Table 6.4.

Table 6.4 General wavelength ranges for lowest energy absorption band of some classes of photochemical substrates

Substrate	λ_{max} *(nm)*
Alkenes	199 – 200
Acyclic dienes	220 – 250
Cyclic dienes	250 – 270
Styrenes	270 – 300
Ketones	270 – 280
α, β-Unsaturated ketones	310 – 330
Aromatic aldehydes and ketones	280 – 300
Aromatic compounds	250 – 280

If we wish to excite these molecules we must irradiate them with light in regions where they absorb. We must therefore match the emission of our source usually a mercury arc lamp to the absorption of the compound. Mercury arc lamp has three principle emission lines are 253.7 nm, 313 nm, 366 nm.

Filters are available which permit selection of either of these lines. For example, if system is constructed so that light must pass through borosilicate glass (Pyrex) only wavelength longer than 300 – 310 nm will reach the sample because the glass absorbs below this wavelength. Pure fused quartz which transmits down to 220 nm must be used if the 254 nm radiation is desired. Other materials have cut off points between those of quartz and pyrex. Filter solutions that absorb in specific wavelength ranges can also be used to control the energy if light reachening the sample.

6.3 ELECTRONIC TRANSITIONS

As mentioned earlier molecule of any type is not only given in electronic state but also in a given vibrational and rotational state. The difference between two vibrational levels is much smaller than difference between adjacent electronic levels, and the difference between adjacent rotational levels is smaller still. A typical situation is shown in Fig. 6.5 in the form of *Morse* potential curves for the ground state (E_0) and first excited state (E_1) of polyatomic molecule.

The excited state potential curve has minimum in it (V_0) so the molecule will not break (*i.e.,* molecule will not fly apart on excitation). The minimum in the potential curve of the excited state occurs at a larger inter nuclear distance ($r' > r$) than that of the ground state. This is reasonable since the excited state has one electron in antibonding orbital and the bonding will be weaker in the excited state. Secondly, the bond order of the molecule in excited state is less than the ground state.

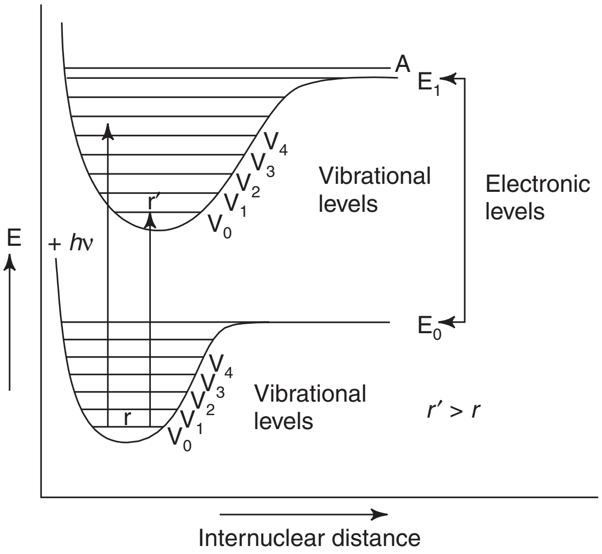


Fig. 6.5

There is series of vibrational energy levels superimposed on potential curve for each electronic state. Consider now the *Morse* curves for the ground state E_0 and first excited state E_1 (Fig. 6.5). As mentioned earlier, at room temperature we have insufficient energy to populate excited vibrational levels and most transitions will start from V_0 of the ground state E_0 (or S_0). The *Frank-Condon* principle tells us that during the electronic transition the interatomic distance of molecule does not change because the time required for electronic transition ($\approx 10^{-16}\ s$) is very-very short as compared to the time required for vibrational transitions ($\approx 10^{-13}\ s$).

Or

The most probable electronic transitions are those in which separation (internuclear distance) and kinetic energy do not change.

Thus, we have vertical excitation as shown in Fig. 6.5. Changes in molecular structure (bond angles and bond lengths) will occur as the electronically excited molecule comes to thermal equilibrium with its surrounding transition from V_0 of ground state (E_0 or S_0) may terminate in any of several vibrational levels of excited state. This is the reason for band spectra rather than sharp lines in UV spectra. The energy of electronic transition is measured from V_0 of ground state to V_0 of the excited state *i.e.,* $\Delta E = E_1(V_0) - E_0(V_0) = h\nu$ when molecule absorbs a quantum of light the electronic configuration changes to correspond to an excited state. Three general points about this process should be emphasised.

1. The excitation promotes an electron from filled orbital to an empty orbital. In most cases the promotion of electron is from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital *i.e.,* antibonding MO).

2. At the instance of excitation, only electrons are reorganised (*i.e.,* from HOMO to LUMO). The heavier nuclei retain their ground state geometry according to Frank-Condon principle.

3. The electron do not undergo spin-inversion at the instant of excitation. Inversion is forbidden by quantum-mechanical selection rules, which require that there be conservation of spin during the excitation process. Although a subsequent spin state change may occur, it is a separate step from excitation. Thus in the very short time ($10^{-16}s$) required for excitation, the molecule does not undergo changes in nuclear position or in the spin state of the promoted electron. After the excitation these changes can occur very rapidly when excited state comes in thermal equilibrium with its surrounding.

6.3.1 Types of Electronic Excitation and Molecular Orbital View of Excitation

Let us consider the different types of electronic excitations which take place on absorption of light in UV and visible region. The ground state of organic compound contains valence electrons

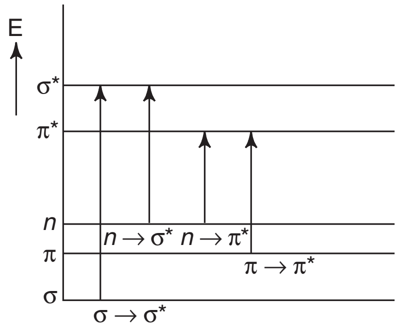


Fig. 6.6 Different types of electronic excitations

in three principle types of molecular orbitals: *Sigma* (σ) MO's, *pi* (π) MO's and filled but non-bonding (n or p) orbitals. Both σ and π MO's are formed from overlap of two atomic or hybrid orbitals. Each of these MO's therefore has an antibonding σ^* and π^* orbitals associated with it. An orbital containing nonbonding electrons or lone pair of electrons does not have an antibonding MO because it is not formed by overlap between two atomic orbitals. Electron transition involved the promotion of an electron from one of the three ground state (σ, π or n) to one of the antibonding (σ^* or π^*) MO's. The four important transitions are shown in Fig. 6.6.

The usual order of energy required for various electronic transitions is as follows:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Out of four excitations the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$are more important in organic photochemistry than the other two $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$.

Table 6.5 Types of excitation given by class of organic compounds

Type of excitation	*Type of organic compound*
(*i*) $\sigma \rightarrow \sigma^*$	Alkanes which have only σ bonds
(*ii*) $n \rightarrow \sigma^*$	Alcohols, amines, ethers thioethers etc.
(*iii*) $\pi \rightarrow \pi^*$	Alkenes, carbonyl compounds Aromatic compounds etc.
(*iv*) $n \rightarrow \sigma^*$	Carbonyl compounds, acids and acid derivatives

To understand the electronic excitation in molecular orbital terms is possible only if we consider bonding as well as antibonding MO's. The bonding and antibonding MO's of ethylene and the electronic configuration of ethylene in the ground state and excited state are shown in Fig. 6.7.

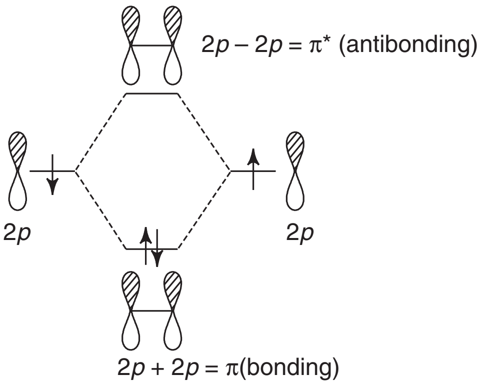


Fig. 6.7a Molecular orbital diagram of ethylene

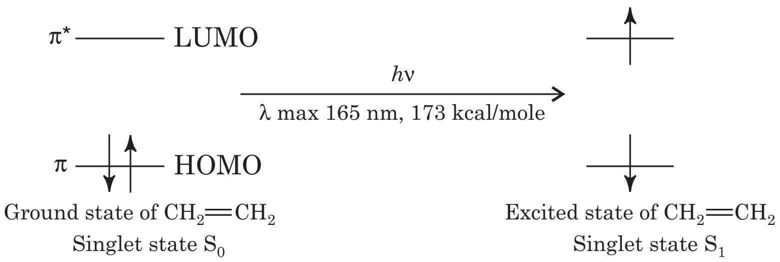


Fig. 6.7b Excitation of ethylene molecule

Absorption of UV light similarly produces electronic transition in 1, 3-butadiene, a conjugated multiple bond system. The lowest energy transition (HOMO-LUMO) occurs at 217 nm (132 kcal/mole). In this case also transition is $\pi \rightarrow \pi^*$ transition. Fig. 6.8 shows molecular orbital diagram of 1, 3-butadiene,

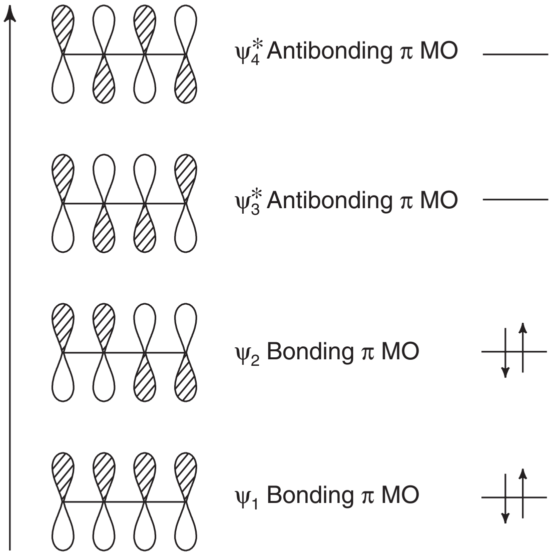


Fig. 6.8 Ground state of 1, 3-butadiene

Fig. 6.8 shows relative energy and λ_{max} of the π MO's of 1, 3-butadiene.

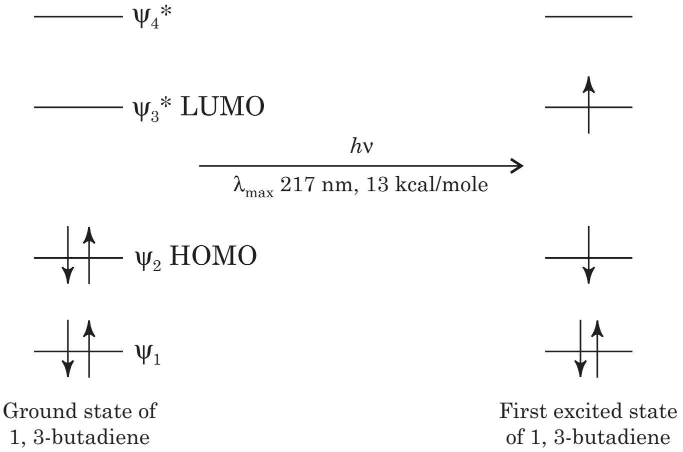


Fig. 6.9 The HOMO-LUMO transition in 1, 3-butadiene

Thus conjugation decreases energy difference between HOMO-LUMO and hence λ_{max} increases. This is general phenomenon and it may be stated as follows:

- More will be length of conjugation in the compound.

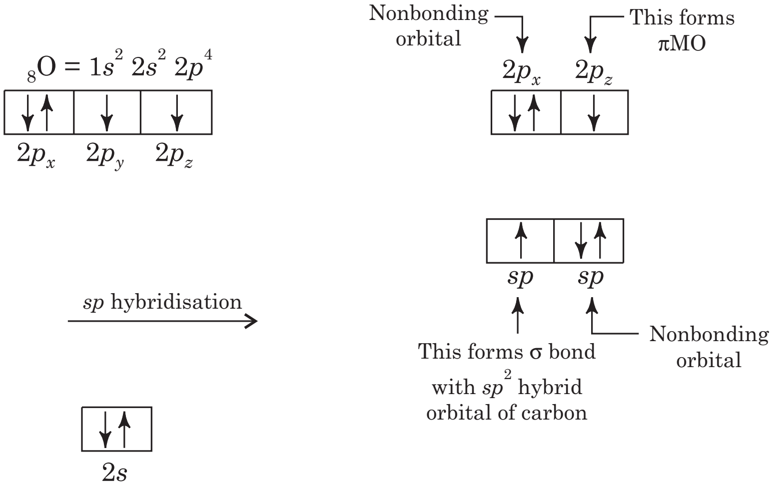
- Less will be energy difference between HOMO and LUMO.
- More will be λ_{max} of the compound.

Absorption maxima of some conjugation polyenes is given in the Table 6.6.

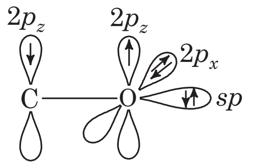
Table 6.6 UV absorption of some conjugated polyenes

Compound	λ_{max} *(nm)*
1, 3-Butadiene	217 nm
1, 3, 5-Hexatriene	245 nm
1, 3, 5, 7-Octatetraene	275 nm

The carbonyl group presents some new features of interest in terms of molecular orbital view examination. Carbonyl group is constructed from sp^2-hybrid carbon and sp-hybrid oxygen, we shall assume the σ (*sigma*) bond framework to be present, and we shall direct our attention to the non-bonding orbitals and the π (*pi*) molecular orbital. Before formation of π MO's we have $2p_z$ atomic orbitals on each carbon and oxygen. The $2p_z$ orbital on more electronegative oxygen atom is lower in energy than the $2p_z$ orbital on a carbon atom; so the oxygen atom contribute more to π than the more energetically carbon $2p$ orbital. Thus the bonding π MO will be constructed from more than 50% of oxygen $2p$ atomic orbital and less than 50% of the carbon $2p$ atomic orbital. Similarly we can see that π* will be made up of more than 50% of carbon $2p$ orbital and less than 50% of the $2p$ orbital of oxygen. The remaining orbitals ($2p_x$ and sp hybrid orbital) are doubly occupied and are non-bonding orbitals (Fig. 6.10).



Electronic configuration of oxygen



Shape of C=O group

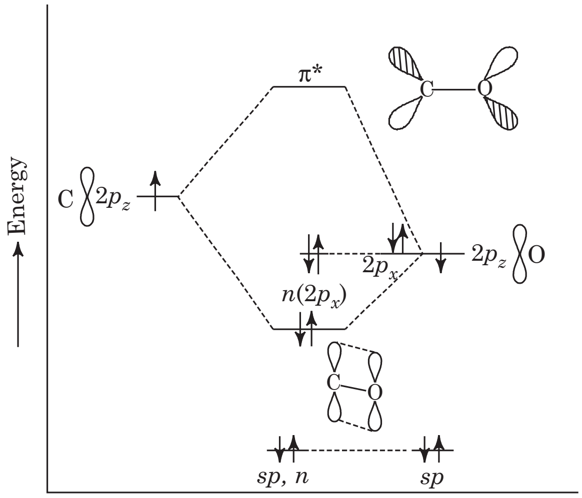


Fig. 6.10 A graphical construction of π, π* and two non-bonding orbitals of carbonyl group

The graphical construction of π, π* and two non-bonding orbitals can be shown in short as follows (Fig. 6.11):

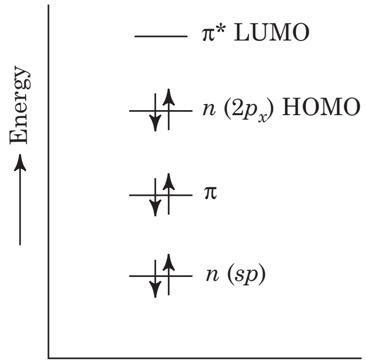


Fig. 6.11 Energy diagram of >C=O group

The non-bonding orbital, $2p_x$, is relatively high energy orbital and very important in photochemistry whereas the non-bonding orbital (*sp*) is a low energy orbital and this is not

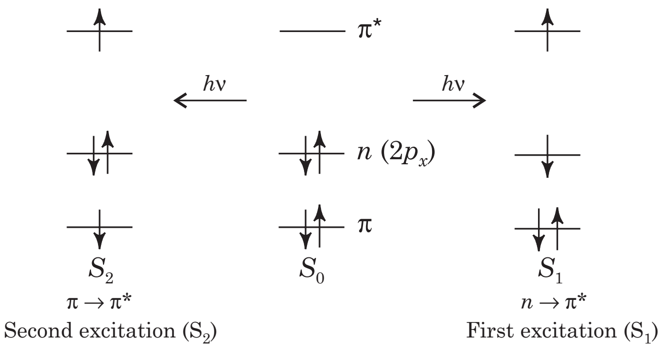
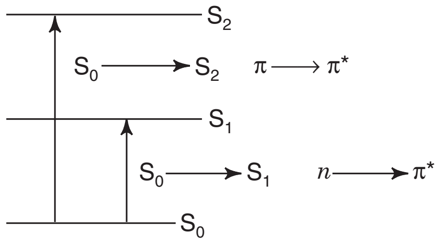


Fig. 6.12

important in photochemistry (because excitation always takes place between HOMO and LUMO). In simple energy level diagram the *n*(*sp*) orbital therefore is ignored and this for photochemistry point of view carbonyl group can be represented as in Fig. 6.12.

The $n \rightarrow \pi^*$ transition is the lowest energy transition for most ketones and this is also known as $S_0 \rightarrow S_1$ (first excitation) transition. The $\pi \rightarrow \pi^*$ is higher energy transition and this is also known as $S_0 \rightarrow S_2$ (second excitation) transition. So is the ground state whereas S_1 and S_2 are excited states. These transitions can also be represented as follows:



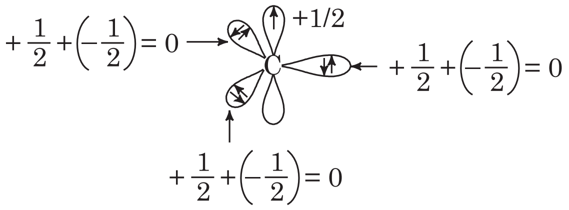
6.4 SPIN MULTIPLICITY

Spin multiplicity of any species = $2S + 1$

where S = sum of spins of the electrons

Case 1: *Suppose all electrons are paired then $S = 0$ and spin multiplicity $= 2 \times 0 + 1 = 1$. If spin multiplicity is one then state of the species is known as singlet state. For example, methyl carbocation has six electrons in its outer most orbit and all are paired hence it is in singlet state.*

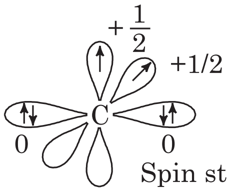
Case II: *Suppose all electrons are not paired. Take the example of methyl free radical*



Spin state = $2S + 1 = 2 \times \frac{1}{2} + 1 = 2$

Spin state of methyl free radical is doublet.

Now take the example of carbonyl group:



Sum of spin = $\frac{1}{2} + \frac{1}{2} = 1$

Spin state = $2S + 1 = 2 \times 1 + 1 = 3$

Here spin state of this species is triplet.

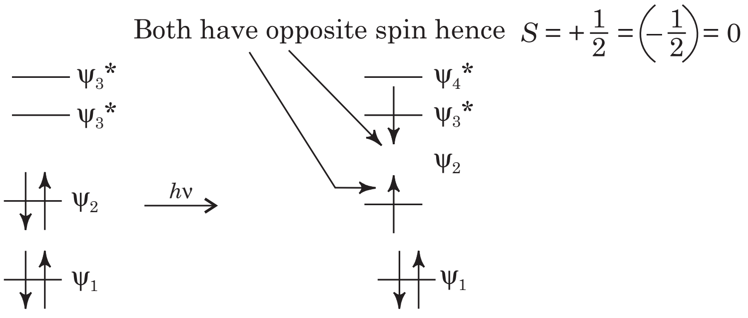
There are even number of electrons in typical organic molecules and these electrons are paired in ground state as demanded by the Pauli principle. Molecular states with all paired electrons are thus called singlet states, S_n, where $n = 0, 1, 2, 3, 4$.

Therefore, S_0 = ground state singlet

S_1 = first excited state singlet

S_2 = second excited state singlet

Absorption of light occurs without spin inversion and the initial excited state produced is a singlet excited state. In this case two electrons no longer share an orbital and the promoted electrons has the same spin as its former partner, *i.e.,* ground state.



Both have opposite spin hence $S = +\frac{1}{2} = \left(-\frac{1}{2}\right) = 0$

S_0 (Ground state) S_1 (First excited state)

Single excited state may undergo spin inversion giving a new excited state with two electrons of same spin $\left(i.e., S = +\frac{1}{2} + \left(+\frac{1}{2}\right) = 1\right)$. Molecular state with such species having $S = 1$ is called triplet states $(2S + 1 = 2 \times 1 + 1 = 3)$, T_n, where $n = 0, 1, 2, 3$.

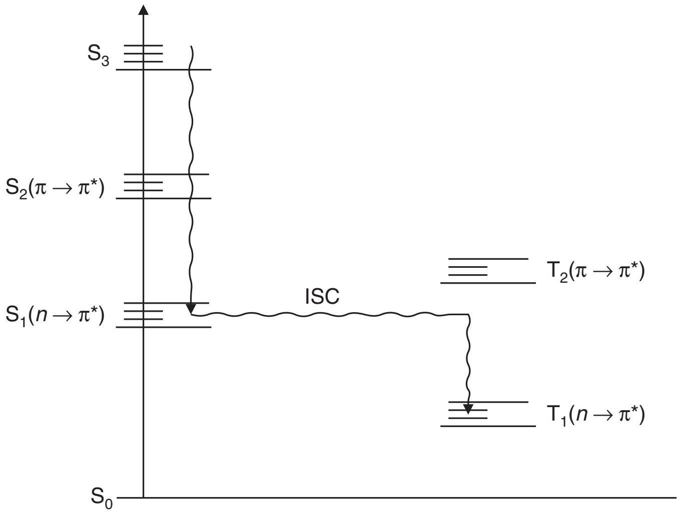
Therefore, T_0 = lowest energy state

T_1 = higher energy than T_0

T_2 = still higher energy than T_1 and T_0

The term singlet and triplet originate from the fact that singlet state does not split in a magnetic field while triplet state does as it has a magnetic moment and has three possible energy states which are distinguishable. Electronic transitions between states of same multiplicity *i.e.,* singlet-singlet and triplet-triplet are spin allowed and transitions between states of different multiplicity, *i.e.* singlet-triplet and triplet-singlet are spin forbidden.

The most important difference between the lowest excited singlet state and the lowest excited triplet state is the difference in energy of the two states. The triplet state is lower in energy as a result of the greater electronic repulsion in the excited singlet state. A systematic representation of this is given in the figure which shows an approximate energy level diagram for a carbonyl compound.



Triplet states are not readily obtained directly by absorption of a photon since such a absorption is strongly forbidden. Thus most observable spectra are singlet-singlet absorption spectra. Some triplet states can be generated indirectly by absorption of light as a result of a photophysical process referred to as **intersystem crossing** (ISC) from the initially generated singlet state (see figure). A triplet state always has an energy lower than a singlet state with the same electronic configuration but the singlet-triplet energy difference varies considerably. This energy gap is much higher for π, π* states than for *n,* π* states and so it is not usual for a molecule with a lowest energy singlet state, S_1, that is *n*π* in nature have a lowest triplet state T_1 that is *n*π*. The emphasis on the excited states of lowest energy arises because of the observation formulated by **Kasha.** According to Kasha luminescene or photochemical reaction normally occurs from the lowest energy singlet (S_1) or triplet (T_1) excited state rather than from a higher energy state (S_2 or T_2 etc.).

Fluorescence almost invariably occurs from the S_1 state and phosphorescence from the T_1 state.

6.5 NOMENCLATURE OF EXCITED STATES

A excited state of molecule can be regarded as a distinct species, different from the ground state of the same molecule and from other excited states. It is obvious that we need some method of naming excited states. One of the most common methods simply designates the original and newly occupied orbitals with or without a subscript to indicate singlet or triplet. Thus, the singlet state arising from promotion of a π to a π* orbital in 1, 3-butadiene or ethylene would be the $^1(\pi, \pi^*)$ state or the π, π* singlet state.

Another very common method can be used even in cases where one is not certain which orbitals are involved. The lowest energy excited state is called S_1, the next S_2 etc. and triplet states are similarly labelled T_1, T_2, T_3 etc. as mentioned earlier. In this notation the ground state is S_0.

Photochemistry occurs when a molecule is raised from its ground state to a higher state which can differ in multiplicity, *i.e.,* either singlet or triplet from ground state. The population of such energy levels means that molecules are in states of shorter life time than usual and have considerably more energy than the ground state from which they were formed. Thus the molecule in the excited state are considerably more reactive in the excited state. Deactivation of an excited state occurs by a **photochemical** or **photophysical** process, either monomolecularily (intramolecularly) or bimolecularily (intermolecularly). There are several paths by which deactivation can be achieved and it is these paths which will be discussed in the text. The processes are:

1. Non-radiative processes between states.
2. Radiative processes between states.
3. Loss of energy by intermolecular energy transfer.
4. Chemical reactions.

6.6 THE FATE OF THE EXCITED MOLECULE—PHYSICAL PROCESSES: JABLONSKI DIAGRAM

When a molecule has been promoted photochemically to an excited state, it does not remain there for long time. Most promotions are from the S_0 to S_1 state. Promotions to S_2 and higher singlet states (S_2, S_3, ...) take place, but in liquids and solids, these higher states usually drop very rapidly to the S_1 state because the life time of S_2, S_3 etc. is usually less than 10^{-11} to 10^{-13} sec. The energy lost when an S_2 or S_3 molecule drops to S_1 is given to the medium. Such a process is called an *energy cascade*. In a similar manner the initial excitation and the decay from higher singlet states initially populate many of the vibrational levels of S_1, but these also cascade, down to the lowest vibrational level of S_1. This cascade is known as *vibrational cascade*. All these processes will occur in about 10^{-11} to 10^{-13} sec. The thermally equilibrated low-lying singlet excited state S_1 (V_0) has a relatively long lifetime (10^{-8} sec). Therefore, in most cases, the lowest vibrational level (V_0) of the S_1 state is the only important excited singlet state. This state can undergo various physical and chemical processes. Here we will describe the physical pathways open to molecules in S_1 and excited triplet states. These pathways are shown in Jablonski diagram (Fig. 6.13).

1. A molecule in the S_1 state can cascade down through the vibrational levels of the S_0 and thus return to the ground state by giving up its energy in small increments the surrounding (*i.e.,* environment), but this is generally quite slow because the amount of energy is large between S_0 and S_1. The process of cascade is called internal conversion (IC). Because it is slow, most molecules in the S_1 state adopt other pathways.

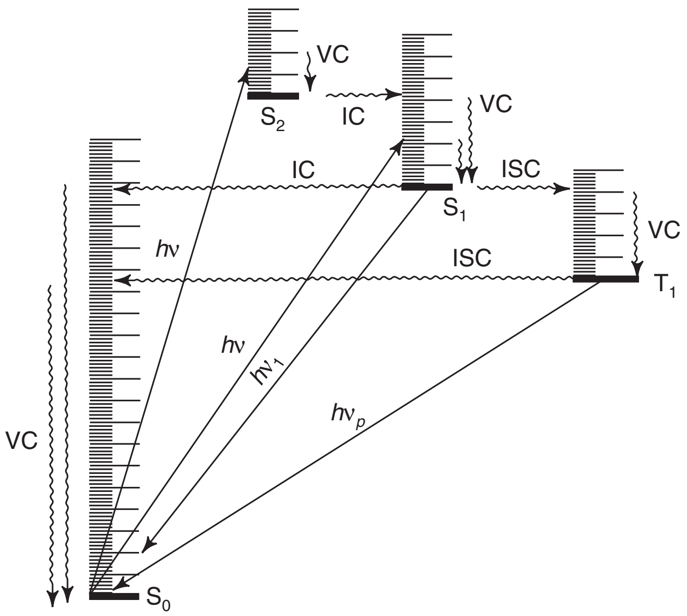


Fig. 6.13 Jablonski diagram

Note: *Internal Conversions:* Decay of S_2 to S_1 or S_1 to S_0 is known as internal conversion and this process in non-radiative and spin-allowed process. Internal conversion from S_3, S_2 to S_1 is very-very common whereas from S_1 to S_0 is not common.

2. The lifetime of S_1 state is 10^{-9} to 10^{-15} sec. A molecule in the S_1 state can drop to some low vibrational level to the S_0 (V_2, V_3, V_4 but not V_0) state all at once by giving off energy in the form of light. This process, when generally happens within 10^{-9} sec, is called *fluorescence*. This pathway is not very common either (because it is relatively slow), except for smaller molecules *e.g.,* diatomic and rigid molecules (aromatic compounds are the main examples). For compounds that show fluorescence, the fluorescence emission spectra are usually the approximate minor images of the absorption spectra. This comes about because the fluorescing molecules all drop from lowest vibrational level (V_0) of S_1 state to various vibrational levels of S_0 while excitation is from the lowest vibrational level (V_0) of S_0 to various vibrational level of S_1 (Fig. 6.14).

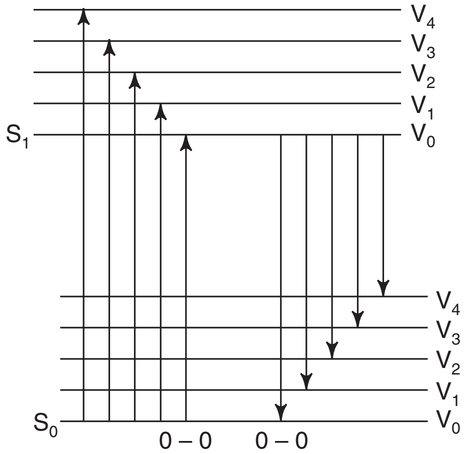


Fig. 6.14 Promotion and fluorescence between S_1 and S_0 states

The only peak in common is the one (called 0 – 0 peak) that results from transitions between V_0 (S_0) and V_0 (S_1). In solution, even the 0 – 0 peak may be non-coincidental because the two states are solvated differently.

Because of the possibility of fluorescence any chemical reactions of S_1 state must take place very fast, or fluorescence will occur before they can happen.

3. Most molecules in the S_1 state may drop to triplet state (T_1). This is slow process as a change in multiplicity (spin inversion) is formally forbidden process. However, if the singlet state S_1 is long lived, the $S_1 \rightarrow T_1$ conversion occurs by a process called *intersystem crossing* (ISC). It is important phenomenon in photochemistry. For every excited singlet state there exist a corresponding triplet state. Since transition from ground state singlet (S_0) to triplet state (T_1) is forbidden, ISC is the main source of excited triplet state. This is one way of populating the triplet state. The efficiency in ISC depends on the difference in energy between the low-lying singlet state (S_1) and triplet excited state (the $S_1 - T_1$ energy gap). When this energy difference is small the ISC is efficient. When energy difference is large, spin forbiddeness is quite important and ISC efficiency is low or zero. Generally speaking, ketones have high ISC (benzophenone has 100% intersystem crossing) efficiencies, aromatic compounds have intermediate to high ISC efficiencies and olefines have low ISC efficiencies. The presence of heavy atoms (S, Cl, Br, I, etc.) in a molecule enhances ISC efficiency.

Since a singlet state usually has a higher energy than the corresponding triplet, this means that energy must be given up. One way this to happen is for the S_1 molecule to cross to a T_1 state at a high vibrational level then for the T_1 to cascade down to its lowest vibrational level (Fig. 6.13). This cascade is very rapid (10^{-12} sec). When T_2 or higher states are populated, they too rapidly cascade to the lowest vibrational level of the T_1 state. Thus ISC is non-radiative process.

4. Lifetime of T_1 state is 10^{-5} to 10^{-3} sec. A molecule in the T_1 state may return to the S_0 state by giving up heat (ISC, non-radiative process) or light (this is called phosphorescence radiative process). ISC and phosphorescence are very slow process (10^{-3} to 10^{1} sec). This means that T_1 state generally have much longer lifetime than S_1 states (lifetime of S_1 is 10^{-9} to 10^{-15} sec, lifetime of T_1 is 10^{-5} to 10^{-3} sec). When fluorescence and phosphorescence occur in same molecule phosphorescence is found at lower frequencies than fluorescence (because of the higher difference in energy between S_1 and S_0 than between T_1 and S_0) and is longer-lived (because of longer lifetime of the T_1 state).

5. For many molecules ISC ($S_1 \rightarrow T_1$) is not very efficient. If this is the only way to produce T_1 then T_1 would be rather very-very limited.

Fortunately, triplet state can be populated by the use of donor molecule. Donor molecule is a substance whose ISC efficiency is high. Donor molecule produces T_1 in high yield by ISC and then this molecule transfer its excitation energy to the second molecule (known as acceptor).

Excited state (S_1 or T_1) of donor molecule transfer its large amount of energy to the acceptor molecule and in this process acceptor (A) species promoted to excited state and donor (D) species return to the ground state.

$$D \xrightarrow{h\nu} D^*$$

$$D^* + \mathrm{A} \rightarrow D + A^*$$

Although photons are absorbed by D, it is A which becomes excited. This phenomenon is known as *photosensitisation* and D is referred as *photosensitiser*.

The basic requirement for energy transfer is that the energy of donor molecule should be 5 kcal/mole more energy than the energy needed for excitation of acceptor molecule.

Thus there are two methods for molecule to reach an excited state, first by direct absorption of light and second by transfer of energy from excited donor molecule to the acceptor molecule.

Transfer of energy from excited singlet state produces singlet and transfer from excited triplet produces triplet. In other words, if the acceptor molecule possesses a state of same multiplicity and lower in energy than that of donor molecule, energy transfer will occur from donor to acceptor. This provides a versatile method of forming triplet by triplet-triplet energy transfer

$$\overset{\uparrow\downarrow}{D} \xrightarrow{h\nu} \overset{\uparrow\downarrow}{D}*$$

$$\overset{\downarrow\uparrow}{D}* \xrightarrow{ISC} \overset{\uparrow\uparrow}{D}*$$

$$\overset{\uparrow\uparrow}{D}* + \overset{\uparrow\downarrow}{A} \longrightarrow \overset{\uparrow\uparrow}{A}* + \overset{\uparrow\downarrow}{D}$$

$$\overset{\uparrow\uparrow}{A}* \xrightarrow[\text{Reaction}]{\text{Photochemical}} \text{Products (Sensitisation)}$$

$$\overset{\uparrow\uparrow}{D} \longrightarrow \text{Products (Quenching)}$$

*If ^{3}A gives the products of interest this is called sensitisation mechanism.

There are several ways in which energy transfer can occur but one of those phenomenon of triplet-triplet energy transfer is the most common because lifetime is maximum for triplet state.

The method of sensitisation has proved to be of enormous value as it provides a new group of potentially reactive intermediates. Aldehydes and ketones are particularly employed as sensitisor in a wide variety of photo reactions. The sensitiser should meet the following critaria:

1. It must be excited by the irradiation to be used.

2. It must be present in sufficient concentration and absorb more strongly than the other reactants under the conditions of the experiment so that it is the major light absorber.

3. The energy of triplet state of sensitiser (D^* or $^3D^*$ or ^{3}Sens*) must be greater than that of the reactant. If this condition is not met, the energy transfer becomes endothermic.

4. It must be able to transfer energy to the desired reactant.

5. The sensitiser should possess high ISC, absorb at lower wavelength and does not interfere with the analytical procedure.

Several photosensitisers in common use are given in Table 6.7.

Table 6.7 Common sensitisers and their energy in triplet state

Sensitiser	*Triplet energy (E_T) in kcal/mole*
Benzophenone	69
Acetophenone	74
Fluorenone	53
Benzene	85
Naphthalene	61
Biacetyl	56
Benzil	53

Several useful features of using a photosensitiser are that

(*i*) The reaction proceeding via singlet state can be avoided and the quantum yield of the products increased.

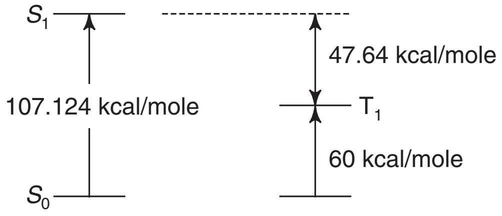
(*ii*) Substances which are unable to absorb light of conveniently longer wavelengths may often be sensitised by additives which do. In terms of energetics, it implies that common compounds whose upper singlet (S_1) and (T_1) are widely separated, thereby making ISC difficult may be excited to their triplet states by sensitiser with appropriate intermediate energy levels.

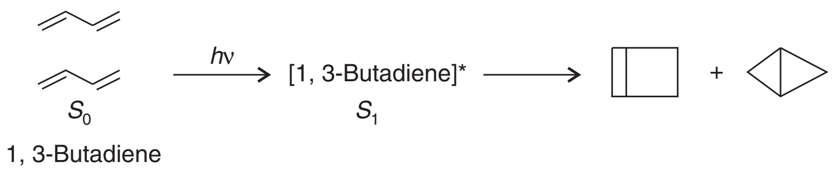
Different physical processes undergone by excited molecules are given in Table 6.8.

Table 6.8 Physical processes undergone by excited molecules

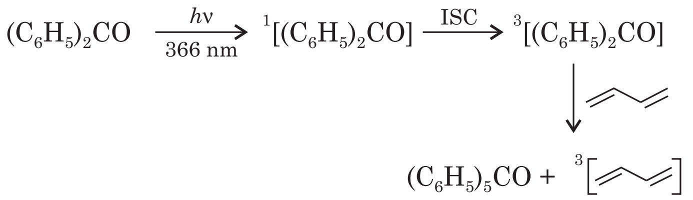
$S_0 + h\nu \longrightarrow S_1^V$	Excitation
$S_1^V \rightsquigarrow S_1 + \text{Heat}$	Vibrational relaxation
$S_1 \longrightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightsquigarrow S_0 + \text{Heat}$	Internal conversion, IC
$S_1 \rightsquigarrow T_1^v$	Intersystem crossing, ISC
$T_1^v \rightsquigarrow T_1 + \text{Heat}$	Vibrational relaxation or Vibrational cascade
$T_1 \rightsquigarrow S_0 + \text{Heat}$	ISC
$S_1 + A(S_0) \longrightarrow S_0 + A(S_1)$	Singlet-singlet transfer (photosensitisation)
$T_1 + A(S_0) \longrightarrow S_0 + A(T_1)$	Triplet-triplet transfer (photosensitisation)
The subscript V indicates	Vibrationally excited state

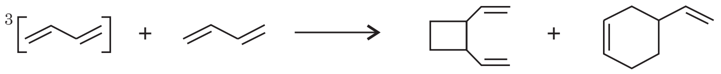
Let us consider now a specific example which illustrates the use of sensitisation in photochemistry. Direct irradiation of 1, 3-butadiene in solution gives cyclobutene and bicyclobutane with minor amounts of dimers. Intersystem crossing efficiency in 1, 3-butadiene approaches zero and triplet derived products are not formed.





Triplet excited butadiene produced by energy transfer from triplet-excited benzophenone gives only dimers.





Quenching

Intermolecular interaction between a molecule in its excited state and a molecule in its ground state can lead to deactivation of the electronically excited state and the generation of the excited state of other molecule. This phenomenon is known as quenching. Thus bimolecular deactivation is known as quenching.

$$M^* + Q \longrightarrow M + Q^*$$

Quenching process is reverse to sensitisation process. In sensitisation process a molecule in the ground state is raised to its excited state by energy transfer from other excited molecule (known as sensitiser).

$$M + \text{Sens}^* \longrightarrow M^* + \text{Sens}$$

The component that accelerates quenching is known as quencher and represented by Q. There are basically two major routes of quenching: (*i*) Photochemical quenching and (*ii*) photophysical quenching. In photochemical quenching the quincher transforms the excitation energy into chemical energy and a product is formed. Photophysical quenching can be divided into (*a*) self quenching or concentration quenching and (*b*) impurity quenching.

6.7 PHOTOLYTIC CLEAVAGE

We have said that when a molecule absorbs a quantum of light, it is promoted to an excited state. Actually this is not the only possible outcome. Because the energy of visible and ultraviolet light is of the same order of magnitude as that of covalent bonds (Table 6.1), another possibility is that molecule may cleave into two parts, a process is known as photolysis. There are three situations that can lead to cleavage:

1. The excitation may bring the molecule to a vibrational level so high that it lies above right hand portion of E_1 curve (line A, Fig. 6.15). In such a case the excited molecule cleaves at its first vibration (absorbed energy is greater than bond dissociation energy).

2. Even where the promotion is to a lower vibrational level, one which lies wholly within the E_1 curve (such as V_1 or V_2), the molecule may still cleave. As Fig. 6.15 shows that equilibrium distances are greater in excited states than in ground state. Promotion of an electron takes place much faster than a single vibration. Therefore, when an electron is suddenly promoted, even to low vibrational level, the distance between the atoms is essentially unchanged and the bond finds itself in a compressed condition. This condition may be relieved by an outward surge that is sufficient to break the bond.

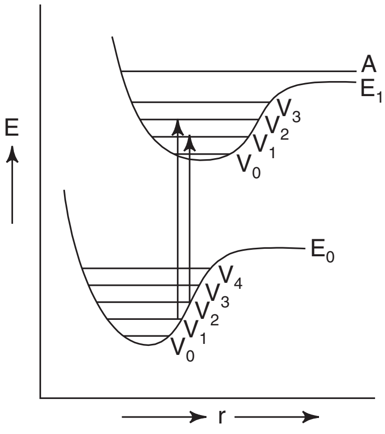


Fig. 6.15

3. In some cases the excited state is entirely dissociative (Fig. 6.16), *i.e.,* there is no minima in the *Morse* curve. In such case there is no distance where attraction outweighs repulsion and the bond must cleave.

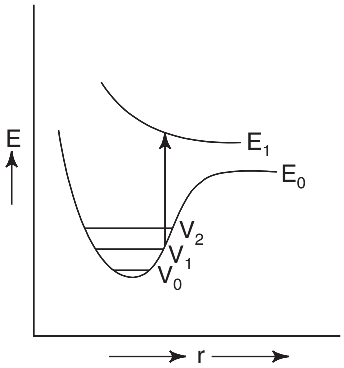


Fig. 6.16 Promotion to a dissociative state results in bond cleavage

The photolytic cleavage can break the molecule into two smaller molecules or into two free radicals. Once free radicals are produced by photolysis, they behave like free radicals produced in any other way except that they may be in excited state and this can cause differences in behaviour.

6.8 LAWS OF PHOTOCHEMISTRY

The photochemical processes are governed by the following laws:

1. First law or Grotthurs-Drapper law.
2. Second law or Einstein-Stark law of photochemical equivalence.

6.8.1 Grotthurs-Drapper Law

When light radiations fall on a substance, only the fraction of incident light which is absorbed can bring about a chemical change; reflected and transmitted light do not produce any chemical change.

The law is purely qualitative and does not give any relationship between the amount of light absorbed by the molecules and the number of molecules which have reacted.

6.8.2 Einstein's Law of Photochemical Equivalence

This law states that each molecule or atom activated by light, absorb only one quantum of light, which causes activation.

Or

Each quantum of light absorbed by a molecule, activates only one molecule in the primary step of photochemical process or briefly one molecule one quantum.

$$\underset{\substack{\text{One}\\\text{molecule}}}{AB} + \underset{\substack{\text{One}\\\text{photon}}}{h\nu} \longrightarrow \underset{\substack{\text{Activated molecule}\\\text{(excited molecule)}}}{AB^*}$$

Einstein's law of photochemical equivalence should not be interpreted to mean that one molecule will react per quantum of light absorbed, but that only one molecule is activated by each quantum of radiation.

6.9 QUANTUM YIELD OR QUANTUM EFFICIENCY

The efficiency of photochemical process is often expressed in terms of quantum yield (φ) which is defined as the number of molecules reacting per quantum of light absorbed.

Mathematically

$$\varphi = \frac{\text{Number of molecules reacting in given time}}{\text{Number of quantum of radiation absorbed in the same time}}$$

The energy E absorbed per mole of the reacting substance is called one einstein

$$E = N_A h\nu = \text{One einstein}$$

The quantum yield of the product formation

$$\varphi = \frac{\text{Number of molecules of product formed}}{\text{Number of einstein of radiation absorbed}}$$

If the law is correct then the quantum yield should be unity. This however is very rare.

The quantum yield may be as high 10^6 or as low as 10^{-2} for several photochemical reactions. The reason for low quantum yields are:

1. Excited molecules may get deactivated before they form products.
2. Collisions with excited molecules with non-excited molecules may cause the former to lose their energy.
3. The primary photochemical process may get reversed.
4. The dissociated fragments may recombine to form the original molecule.

6.9.1 The Reasons for High Quantum Yield

1. The primary process of absorption of radiation produces excited free radicals. They undergo secondary processes. Each secondary process produces again excited free radicals. This process continues unless it is checked. Thus by absorbing only one quantum of radiation, several reactant molecules undergo chemical reaction. Hence φ will be greater than unity.
2. Free radical gives chain reaction which increases quantum yield.

FURTHER READING

1. D.O. Crown and R.L. Drisko, *Elements of Organic Photochemistry,* Plenum, New York, 1976.
2. William M. Horspool, *Aspects of Organic Photochemistry,* Academic Press, New York, 1976.
3. Jan. Kopecky, *Organic Photochemistry*, VCH, New York, 1991.

PROBLEMS

1. Construct energy diagram of the carbonyl group.

2. On the basis of energy diagram show what is meaning of first and second excited states?

3. Define the following terms by the use of Jablonski diagram:
   (*i*) Energy cascade
   (*ii*) Vibrational cascade
   (*iii*) Internal conversion
   (*iv*) Intersystem crossing
   (*v*) Fluorescence
   (*vi*) Phosphorescence.

4. (*i*) What is the importance of photosensitiser in photochemistry? (*ii*) Which type of compounds can behave as photosensitiser?
   (*ii*) What criteria should be fulfilled by the compound to become sensitiser?

5. Write note on photolytic cleavage.

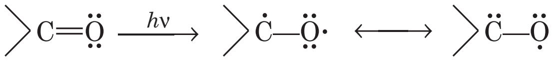
6. What types of excitations are possible in a compound containing carbonyl group on irradiation with UV light? Give details of the transition requiring lesser amount of energy.

7. Comment upon the followings:
   (*i*) Structure of carbonyl group.
   (*ii*) Singlet and triplet states.

7
CHAPTER

Photochemistry of Carbonyl Compounds

Saturated ketones exhibit four main bands in their ultraviolet absorption spectra. These bands are centered on 280, 195, 170 and 155 nm. The most important band is at 280 nm for the photochemistry of carbonyl group. This band corresponds to the $n \rightarrow \pi^*$ transition. The photochemical reactions of carbonyl group is initiated by $n \rightarrow \pi^*$ transition. Promotion of an electron will lead to either a singlet state or a triplet state. Photochemical reactions given by carbonyl group takes place either by singlet state or by triplet state or by both states.



According to the Kasha's rule, only the lowest excited states will be involved in the primary photochemical or photophysical processes of organic molecules in solution.

Carbonyl compounds give four type of reactions. These reactions include:

(*i*) α-Cleavage.
(*ii*) β-Cleavage.
(*iii*) Intramolecular and intermolecular hydrogen abstraction by carbonyl oxygen.
(*iv*) Addition of carbonyl oxygen atom to a carbon-carbon multiple bond.

In many cases the four processes are competitive and the major process followed is sensitive to structural variations in the ketones and the choice of the solvents.

7.1 α-CLEAVAGE OR NORRISH TYPE I PROCESS

Norrish type I process is given by three type of ketones:

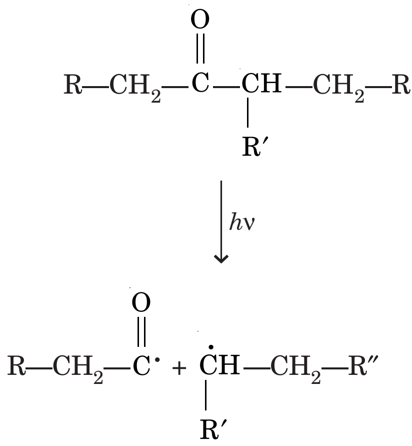
(*i*) Saturated acyclic ketones.
(*ii*) Saturated cyclic ketones.
(*iii*) β, γ-Unsaturated ketones.

7.1.1 Norrish Type I Process Given by Acyclic Saturated Ketones

Saturated carbonyl compounds undergo photoinduced decarbonylation in the gas phase. This process was first observed by R.G.W. Norrish and is known as Norrish Type I or α-cleavage process. Norrish Type I process is commonly encountered in the gas phase. The solution phase reaction of this type is uncommon.

Primary Processes

Norrish Type I process is characterised by initial cleavage of the carbonyl carbon and *alpha* carbon bond to give an **acyl** and an **alkyl** radicals. This process is known as primary photochemical process (Scheme 1).

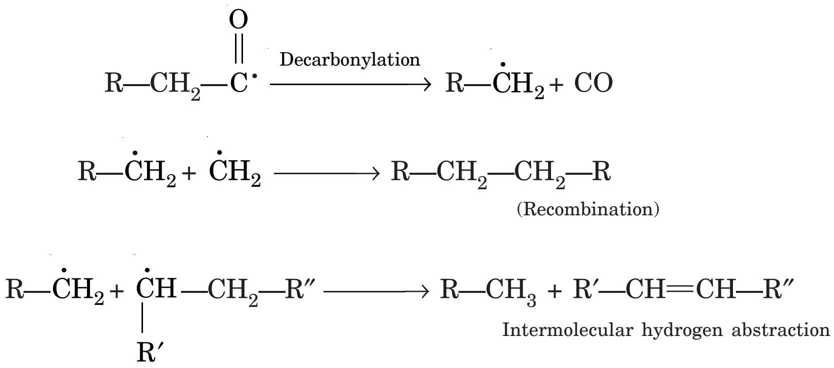


Scheme 1: Primary process

The initially formed acyl radical is stabilised by one of the secondary processes [(*a*) – (*c*)] shown in the Scheme 2. Similarly the alkyl radical can be stabilised by recombination or disproportionation (Scheme 2).

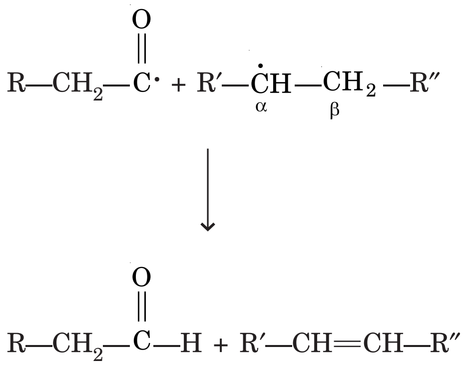
Secondary Processes

(*a*) Decarbonylation of acyl radical to give carbon monoxide and an alkyl radical. This alkyl radical can recombine to give an alkane or can undergo intermolecular hydrogen abstraction to form an alkane and an alkene [Scheme 2(*a*)].



Scheme 2 (*a*)

(*b*) Intermolecular hydrogen abstraction by the acyl radical from the alkyl radical to give an aldehyde and an alkene [Scheme 2(*b*)].

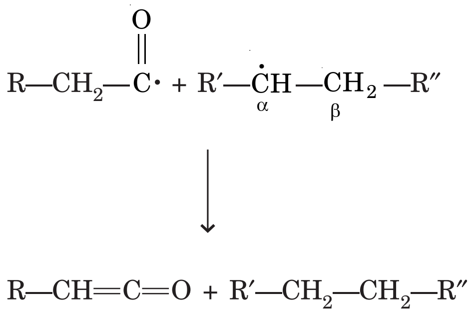


$$R{-}CH_2{-}\overset{\overset{O}{\|}}{C}\cdot + R'{-}\underset{\alpha}{\dot{C}H}{-}\underset{\beta}{CH_2}{-}R'' \longrightarrow R{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H + R'{-}CH{=}CH{-}R''$$

Scheme 2 (*b*)

This process can only be possible if alkyl radical has atleast one β-hydrogen.

(*c*) Intermolecular hydrogen abstraction by the alkyl radical from the α-carbon of the acyl radical to form a ketene and an alkane [Scheme 2 (*c*)].

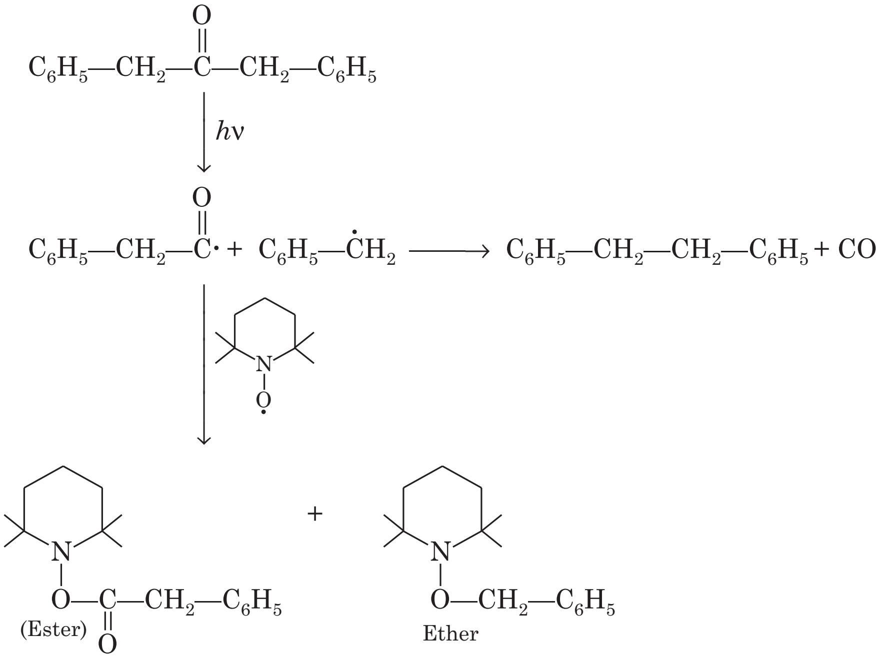


$$R{-}CH_2{-}\overset{\overset{O}{\|}}{C}\cdot + R'{-}\underset{\alpha}{\dot{C}H}{-}\underset{\beta}{CH_2}{-}R'' \longrightarrow R{-}CH{=}C{=}O + R'{-}CH_2{-}CH_2{-}R''$$

Scheme 2 (*c*)

The main reaction of saturated acyclic ketones is decarbonylation.

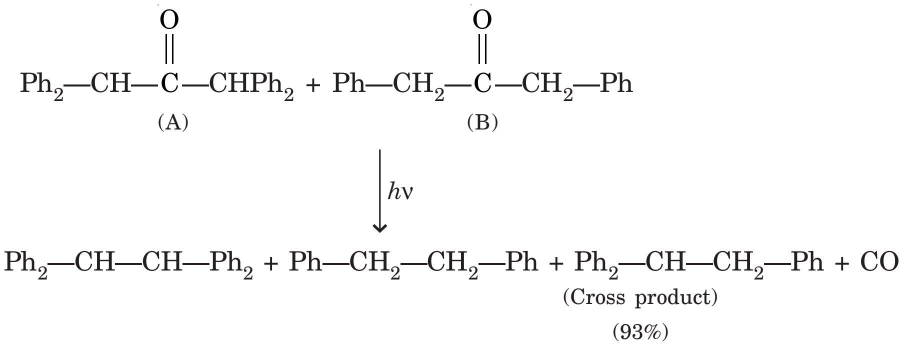
Norrish Type I process is thus a two step radical mechanism. The first step is a primary process and the second step is the secondary process. Formation of acyl and alkyl radicals can be proved by trapping of these radicals by the use of suitable trapping agents. 2, 2, 4, 4-Tetramethylpiperidine-1-oxyl was used for the trapping and the radical fragments produced by the fission of 1, 3-diphenylacetone were trapped as an ester and an ether (Scheme 3).



Scheme 3

Formation of ether and ester confirms that there should be the formation of acyl and alkyl radicals.

The formation of radical intermediates is also readily demonstrated by photolysis of a mixture of ketones (A) and (B) which give products from mixed radical combination.



$$\underset{\text{(A)}}{Ph_2\text{—}CH\text{—}\overset{O}{\overset{\|}{C}}\text{—}CHPh_2} + \underset{\text{(B)}}{Ph\text{—}CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2\text{—}Ph} \xrightarrow{h\nu} Ph_2\text{—}CH\text{—}CH\text{—}Ph_2 + Ph\text{—}CH_2\text{—}CH_2\text{—}Ph + \underset{\text{(93\%)}}{\underset{\text{(Cross product)}}{Ph_2\text{—}CH\text{—}CH_2\text{—}Ph}} + CO$$

This cross over experiment also confirmed the two steps radical mechanism.

Norrish Type I process occurs from both the excited singlet and the triplet states of $n \to \pi^*$ transition. Photolysis of ditertbutylketone results in high yield of carbon monoxide (90%) from both the excited singlet and triplet states. This clearly shows that the Norrish Type I processes occur from both the excited states. The lifetime of the singlet state is $4.5 - 5.6 \times 10^{-9}$ sec as compared with 0.11×10^{-9} sec for the excited triplet state. Since the reaction occurs from both the singlet and triplet excited states, the Type I process must occur about 100 times faster from triplet than from singlet excited state. Studies with triplet quenchers, such as 1, 3-cyclopentadiene, have also shown that Norrish Type I processes occurs from both triplet and singlet excited states.

Norrish Type I cleavage is given mostly by those ketones whose $n \to \pi^*$ state is the lowest excited states. In most of the cases, the $n \to \pi^*$ state is the lowest excited state. However, α cleavage in arylalkyl ketones and diaryl ketones is less efficient because $n \to \pi^*$ excited state is not the lowest excited state. In this case, there is a large barrier on the reaction coordinate (Fig. 7.1).

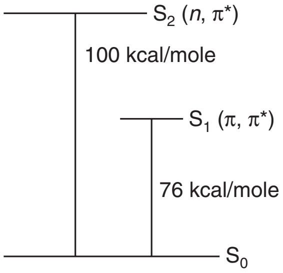
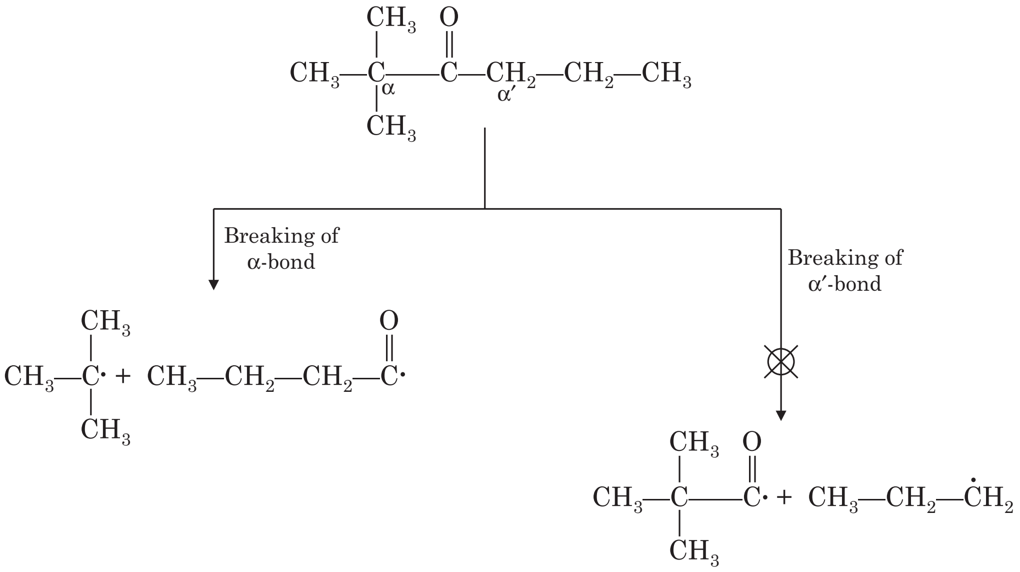
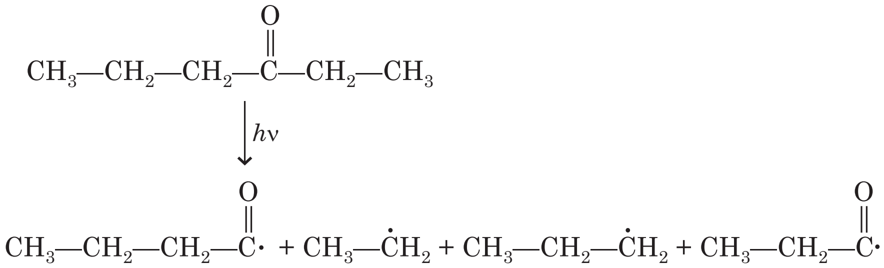


Fig. 7.1 Energy of diphenyl ketone ($C_6H_5COC_6H_5$)

In Norrish Type I reactions there is a preference for the formation of most stable alkyl radical in case of unsymmetrical ketones.



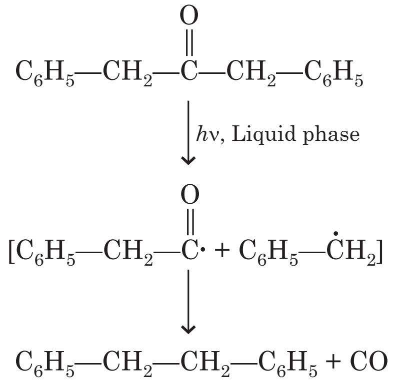
In the above case, only α-bond undergoes cleavage. If both alkyl substituents are same then there is little selectivity of bond cleavage.



$$CH_3{-}CH_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2{-}CH_3 \xrightarrow{h\nu} CH_3{-}CH_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}\cdot + CH_3{-}\dot{C}H_2 + CH_3{-}CH_2{-}\dot{C}H_2 + CH_3{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}\cdot$$

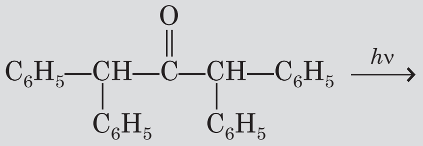
The Norrish Type I process is mostly favoured by photolysis in the vapour phase and is less pronounced for photolysis in the inert solvents. In inert solvent formation of solvent cage takes place. Formation of solvent cage facilitates recombination of the initially generated radical pair. Thus low quantum yield of products is obtained in inert solvents.

Norrish Type I process is efficient in liquid phase only if a stable radical is formed. The stable radical includes allylic, benzylic, *tert* alkyl and acyl radicals.



$$C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-C_6H_5 \xrightarrow{h\nu,\ \text{Liquid phase}} [C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}\cdot + C_6H_5-\dot{C}H_2] \longrightarrow C_6H_5-CH_2-CH_2-C_6H_5 + CO$$

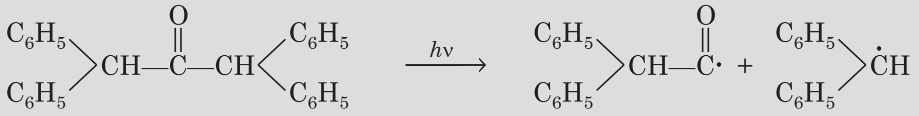
Problem 1: *Complete the following Norrish Type I reaction:*



$$C_6H_5-\underset{\underset{C_6H_5}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{CH}-C_6H_5 \xrightarrow{h\nu}$$

Solution: Compound is saturated acyclic ketone. It will give Norrish Type I process in gases as well as in solution phase.

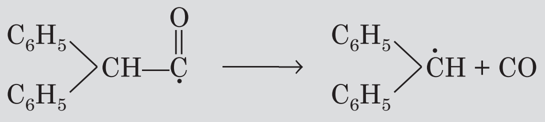
Primary process:



$$(C_6H_5)_2CH-\overset{\overset{O}{\|}}{C}-CH(C_6H_5)_2 \xrightarrow{h\nu} (C_6H_5)_2CH-\overset{\overset{O}{\|}}{C}\cdot + (C_6H_5)_2\dot{C}H$$

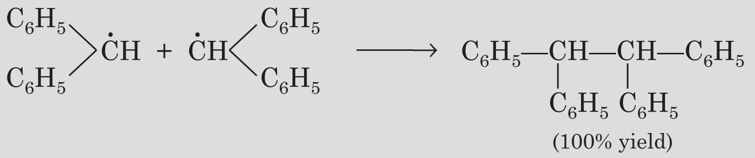
Secondary process:

(*i*) Decarbonylation



$$(C_6H_5)_2CH-\underset{\cdot}{\overset{\overset{O}{\|}}{C}} \longrightarrow (C_6H_5)_2\dot{C}H + CO$$

(*ii*) Recombination



$$(C_6H_5)_2\dot{C}H + \dot{C}H(C_6H_5)_2 \longrightarrow C_6H_5-\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{C_6H_5}{|}}{CH}-C_6H_5$$

(100% yield)

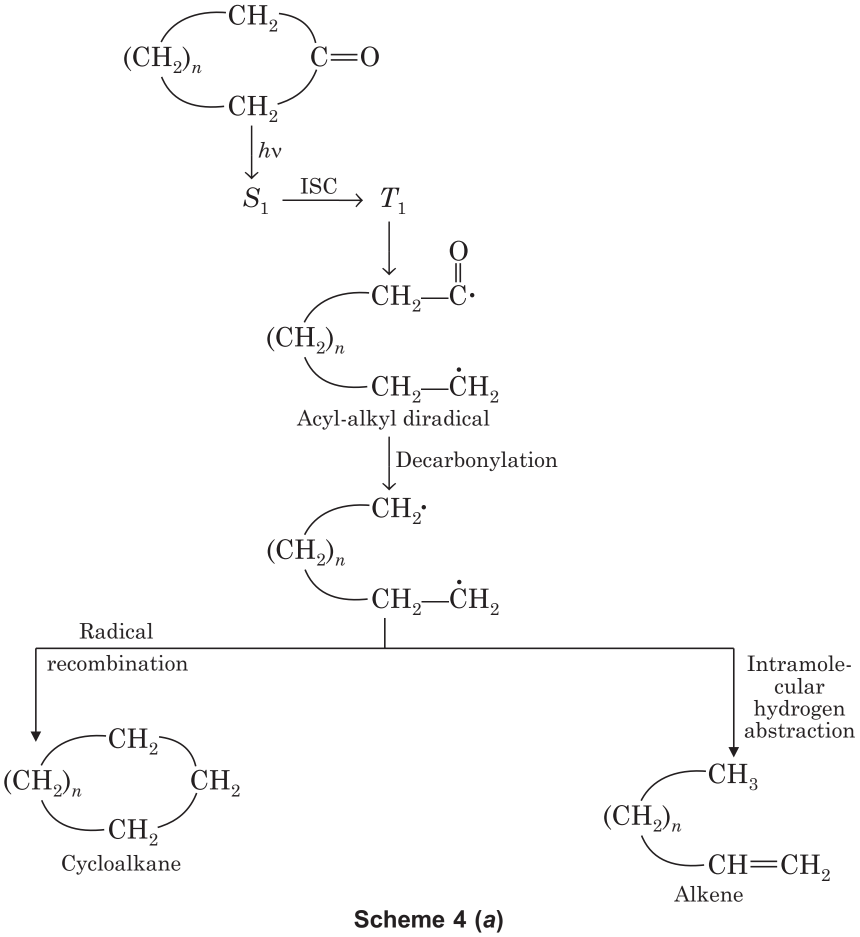
7.1.2 Norrish Type I Reaction of Saturated Cyclic Ketones

Cyclic ketones, in contrast to the acyclic ketones, show a greater tendency to undergo α-cleavage to furnish acyl-alkyl biradicals. Norrish Type I cleavage of acyclic ketones take place by singlet as well as by triplet excited state. *In cyclic ketones, the reaction takes place exclusively by the triplet state.* It is possible, however, that inter system crossing in cyclic ketones is so rapid that reaction from the singlet state would not be observed. The triplet state is atleast 100 times more reactive than the excited singlet state.

Available information indicates that the excited triplet state for Norrish Type I processes is $n \rightarrow \pi^*$ triplet state. This was demonstrated first for the irradiation of cyclopentanone in both gases and in solution phases. Under both conditions, the product is 4-pentenal. Formation of 4-pentenal takes place at 313 nm and 254 nm. The formation of the aldehyde can be quenched by 1, 3-cyclopentadiene. This quenching experiment confirms the formation of the triplet state.

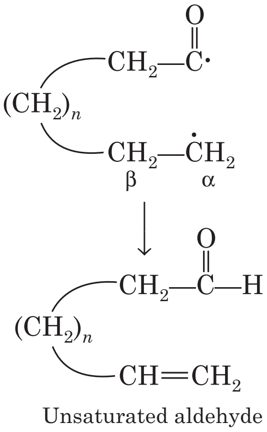
Norrish Type I process involves the initial cleavage of a carbonyl carbon-*alpha* carbon bond. Subsequent secondary processes [(*a*) to (*c*)] correspond to those observed for acyclic ketones.

(*a*) Decarbonylation of acyl-alkyl diradical to give carbon monoxide and a dialkyl radical. The dialkyl radical can recombine to give a cycloalkane or it undergoes intramolecular hydrogen abstraction to form an alkene. [Scheme 4 (*a*)].



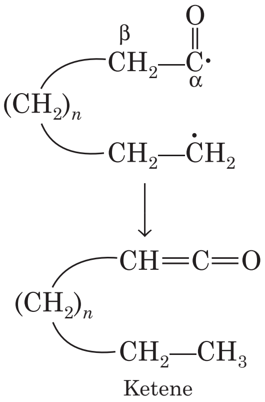
Scheme 4 (*a*)

(*b*) Intramolecular hydrogen abstraction by the acyl radical from the β-carbon of the alkyl radical to give an unsaturated aldehyde [Scheme 4 (*b*)].



Scheme 4 (*b*)

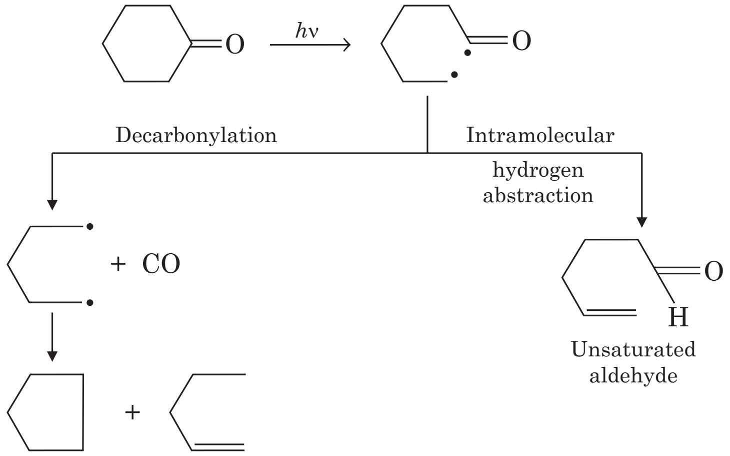
(*c*) Intramolecular β-hydrogen abstraction from the acyl radical by the alkyl radical to produce a ketene [Scheme 4 (*c*)].



Scheme 4 (*c*)

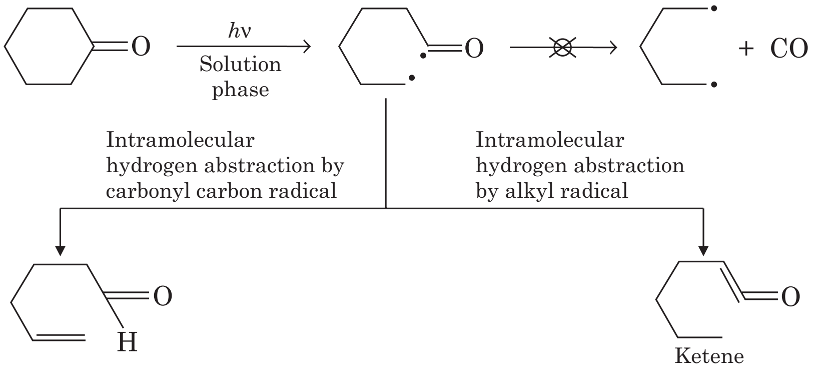
The biradical of cyclic ketones can undergo one of the two hydrogen transfer processes [(*b*) and (*c*)] *via* a cyclic transition state in which a hydrogen atom is transferred to one radical centre from the atom adjacent to other radical centre.

Photolysis of cyclic ketones in gases phase gives decarbonylation as well as intramolecular hydrogen abstraction. Intramolecular hydrogen abstraction mainly leads the formation of unsaturated aldehyde (Scheme 5).



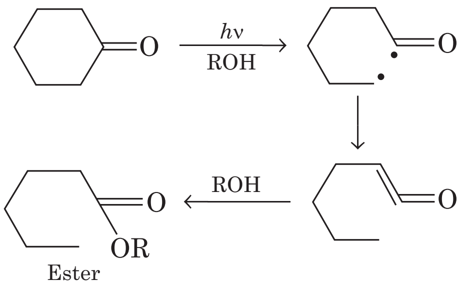
Scheme 5

In solution phase biradical pair is not usually stabilised by decarbonylation. In this case, biradical is mainly stabilised by intramolecular hydrogen atom transfer. This intramolecular hydrogen atom transfer leads to the formation of either unsaturated aldehyde or a ketene or both (Scheme 6).



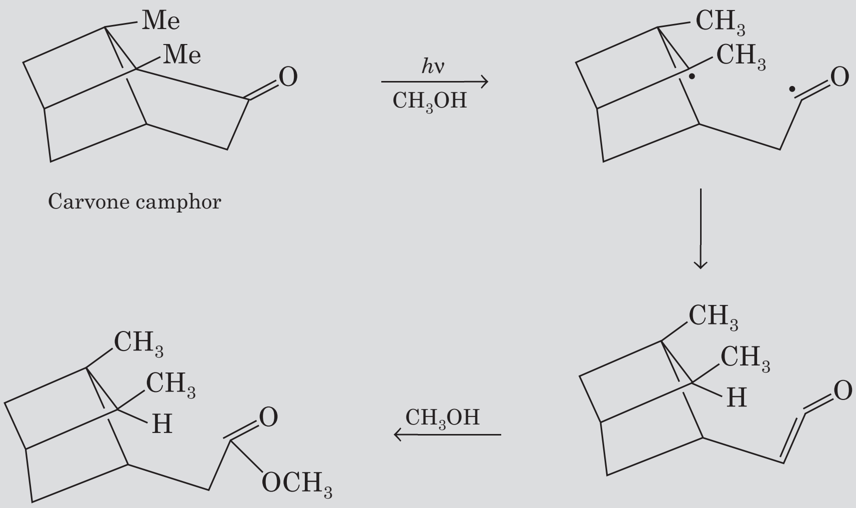
Scheme 6

When photolysis is carried out in the presence of polar protic solvent than the main species is ketene. This ketene than undergoes solvent addition to give carboxylic acid (with water) or its derivative (ester with alcohol) as the only product.



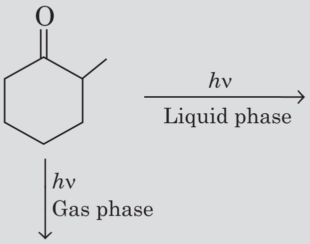
Problem 2: *What will the product of the reaction when carvone camphor is irradiated with UV light in the presence of MeOH?*

Solution: In the presence of polar protic solvent, cyclic ketone forms only ketene.

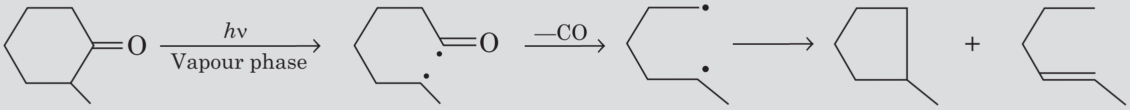


In case of unsymmetrical ketones, the α-bond that produces more stable alkyl radical cleaves preferentially.

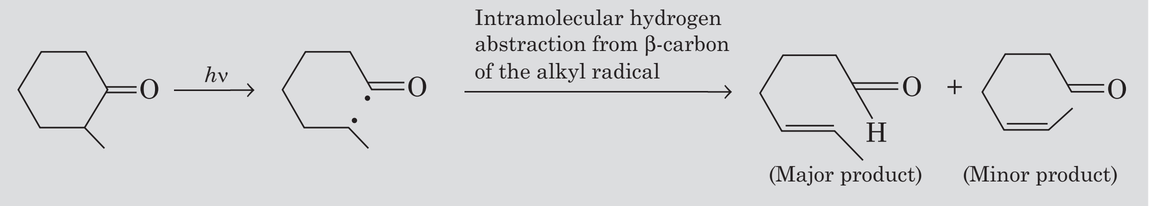
Problem 3: *Complete the following reaction:*



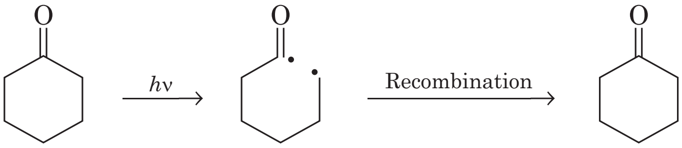
Solution: The α-bond that produces the more stable alkyl radical cleaves preferentially in unsymmetrical ketone. The vapour phase photolysis gives decarbonylation and intramolecular hydrogen abstraction.



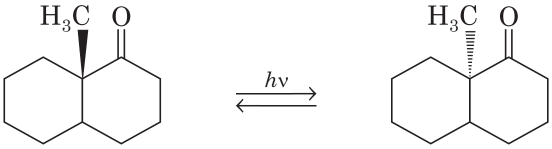
In the liquid phase, the main reaction is intramolecular hydrogen abstraction which leads the formation of unsaturated aldehydes.



According to the biradical mechanism, there is a possibility of a back recombination reaction to reform the starting material.

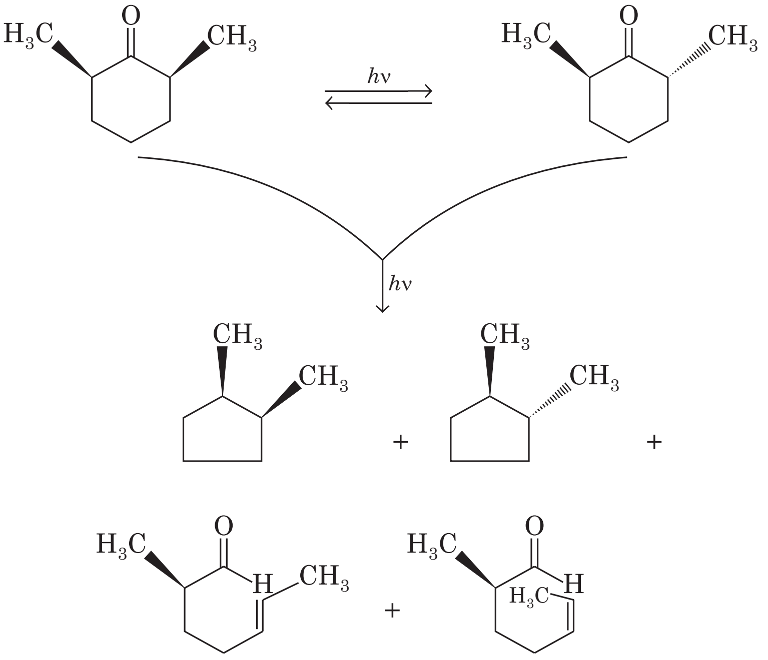


Use of suitably α-substituted cyclic ketones show that recombination reaction resulted in epimerisation at the α-carbon if α-carbon is a chiral.

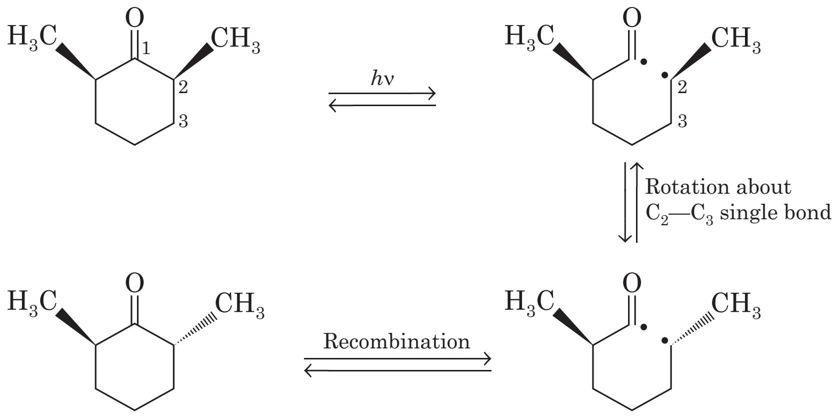


(A) Epimer of (A)

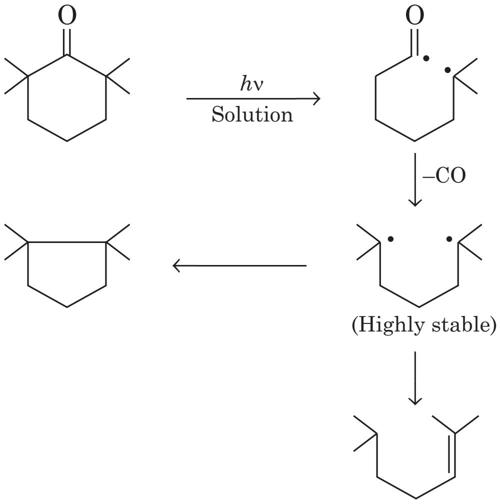
Experimently it has been found that photolysis product formation *via* route [(*a*) – (*c*)] is faster than the photochemical interconversion of the epimers. Since there is the formation of epimeric mixtures each epimer afford the same mixture of products.



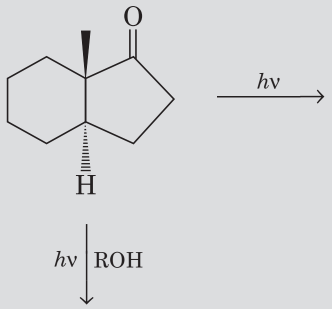
Each epimer affords the same mixture of products. This clearly indicates that the configurational integrity of the α-carbon is lost during the course of the reaction. This loss of integrity is due to the free rotation about C_2—C_3 bond in the diradical.



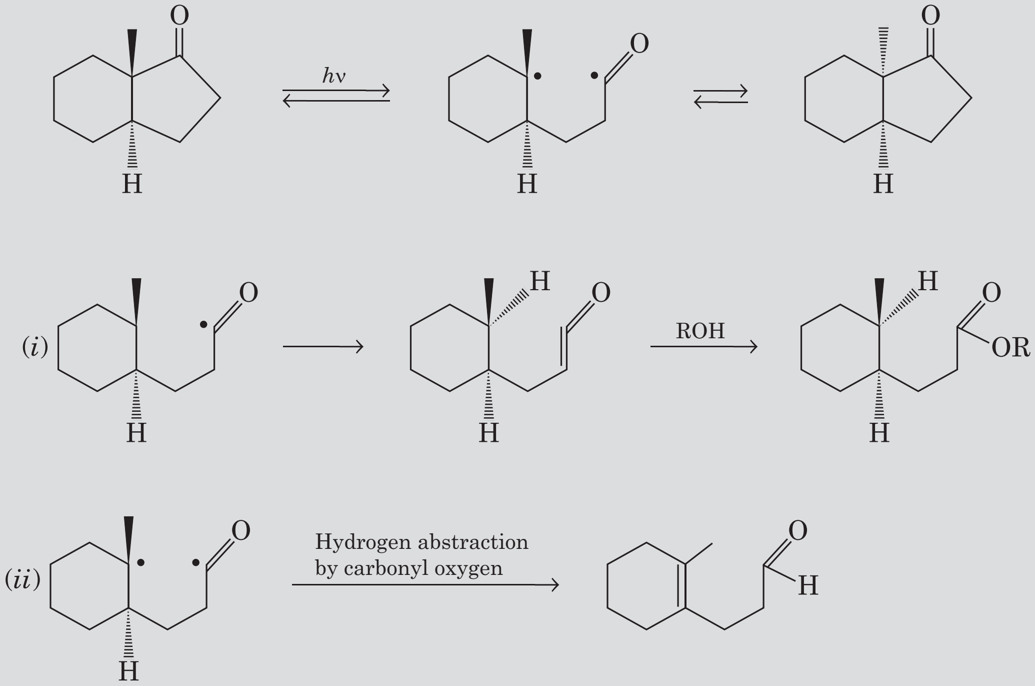
The recombination process is important even when hydrogen transfer reactions occur, but loss of carbon monoxide in solution phase photochemistry is a major reaction pathway only when the alkyl radical centres are stabilised by inductive effect, by β, γ-unsaturation or by cyclopropyl conjugation. This reflects an increase in the rate of loss of carbon monoxide from the acyl-alkyl biradical in these systems. 2, 6-Dimethyl-cyclohexanone gives carbon monoxide on photolysis in solution at room temperature. 2, 2, 6, 6-tetramethylcyclohexanone gives carbon monoxide in a yield greater than 70%, 7, 7, 9, 9-tetramethylbicyclo [4, 3, 0] non-1, 6-en-8-one gives 100% yield of carbon monoxide and hydrocarbon products.



Problem 4: *Complete the following reaction:*

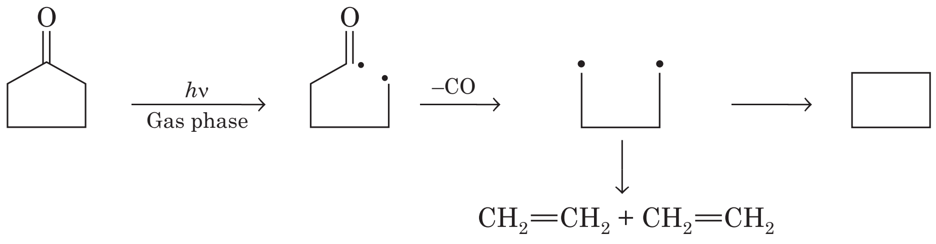


Solution:



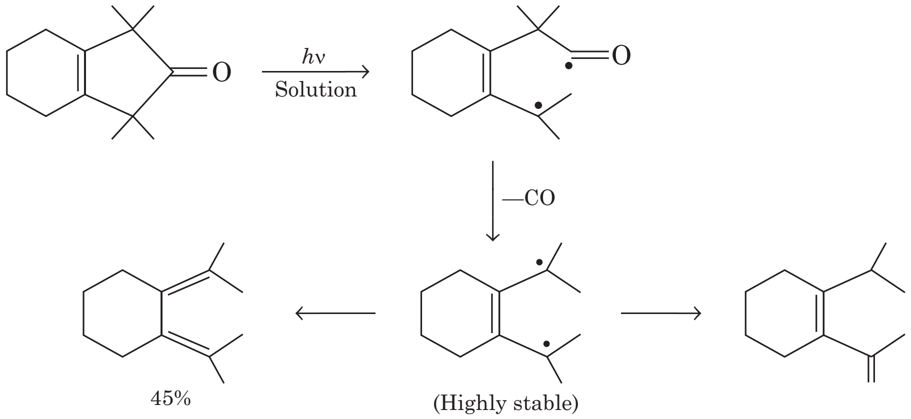
7.1.3 Norrish Type I Process Given by Cyclopentanones

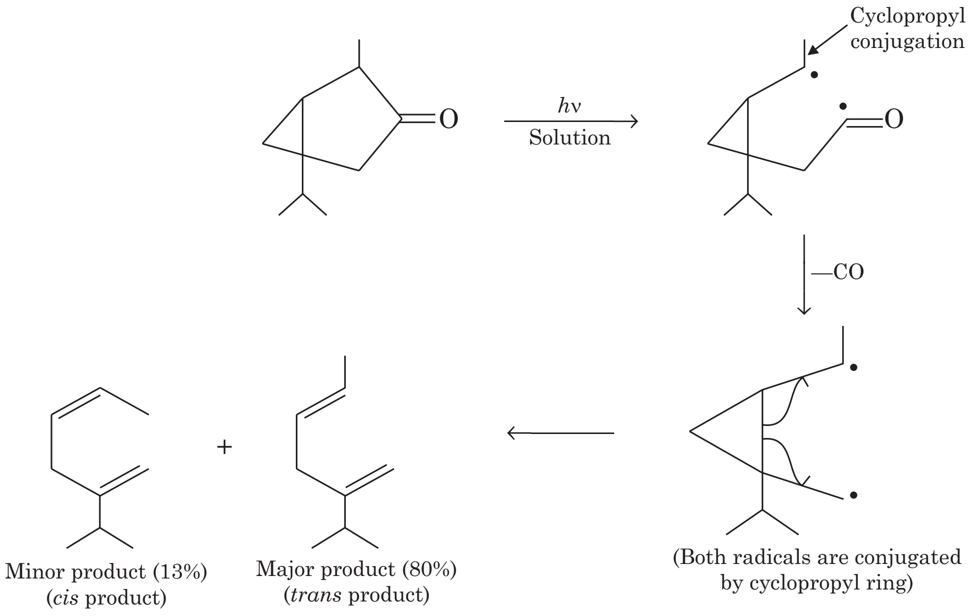
Cyclopentanone also decarbonylates on irradiation in the gas phase at 147 nm. In this case also a two step process is involved, affording a biradical which decarbonylates to another biradical, which either fragment to ethylene or undergoes bond formation to cyclobutane. Fission to ethylene is much more efficient in comparison to cyclobutane formation (Scheme 7).



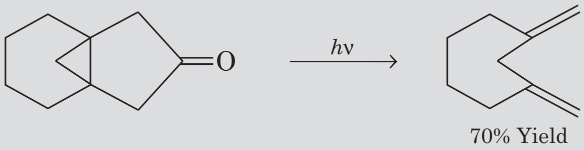
Scheme 7

In solution the loss of carbon monoxide from a cyclopentanone is a major path only when the radical centres formed are stabilised by alkyl substitution, double bond or cyclopropyl ring.

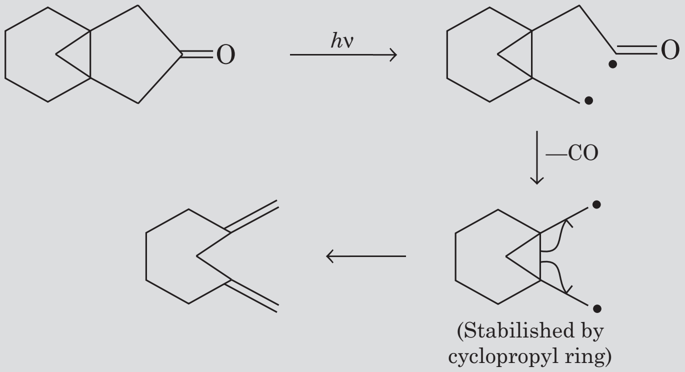




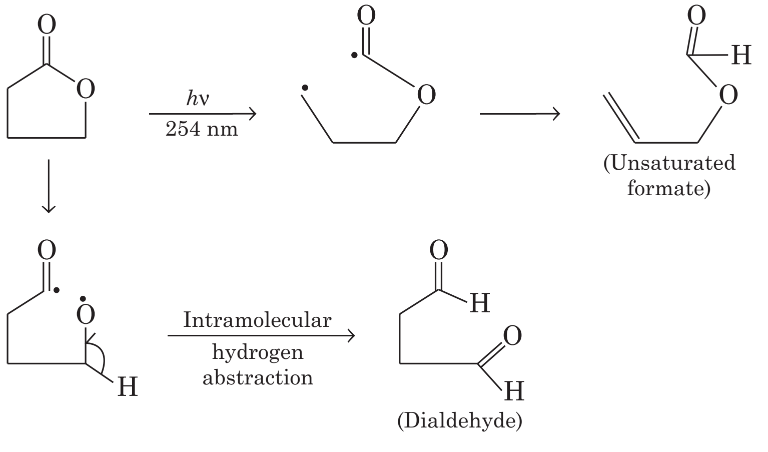
Problem 5: *Give mechanism of the following transformation:*



Solution:



α-Cleavage is not given only by cyclic ketones. Other cyclic compounds such as lactones, lactams and cyclic anhydrides undergo α-cleavage to give a biradical species on photolysis in gas or solution phase.

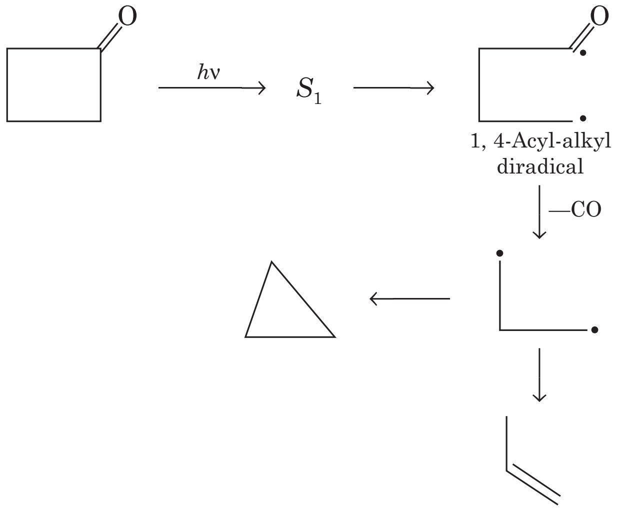


7.1.4 α-Cleavage Given by Cyclobutanones

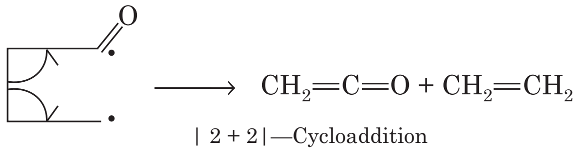
Cyclobutanone also gives α-cleavage reaction. The efficiency of α-cleavage reaction of cyclobutanone is ten times more than the cyclopentanone due to the angle strain. Angle strain and steric strain increases the efficiency of α-cleavage. The photochemistry of α-cleavage of cyclobutanone differs significantly from the photochemistry of α-cleavage of other cyclic ketones.

Unlike other ketones, cleavage occurs from S_1 ($n \rightarrow \pi^*$) and leads to the formation of a 1, 4-acyl-alkyl diradical. There are three following different pathways for stabilisation of the diradical:

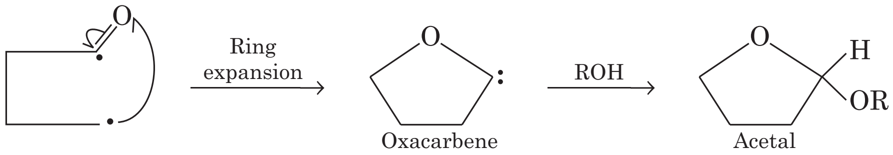
(*i*) Loss of carbon monoxide and formation of 1, 3-diradical that undergoes either recombination to cyclopropane or an hydrogen abstraction to form propene.



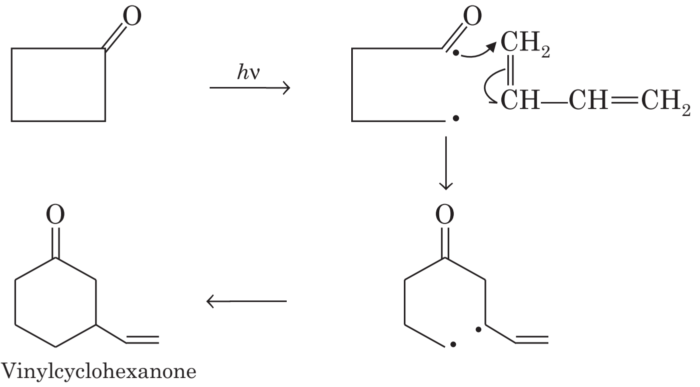
(*ii*) By a subsequent β-cleavage and formation of ethylene and ketene.



(*iii*) 1, 4-Acyl-alkyl biradical can undergo ring expansion by rebonding to oxygen to give **oxacarbene.** This carbene can be trapped by polar protic nucleophile solvents. The over all reaction is a ring expansion.

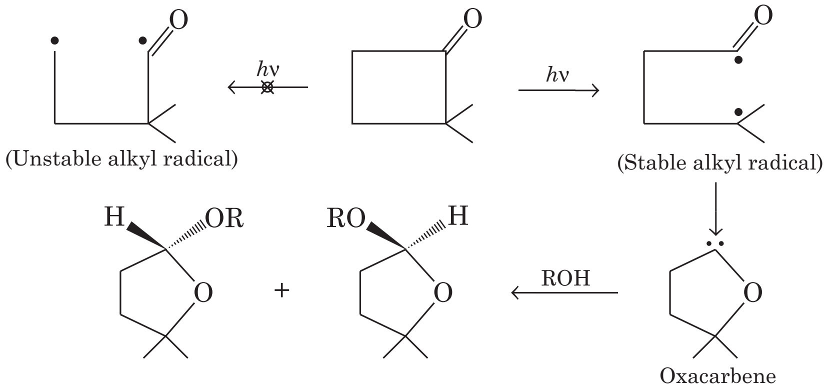


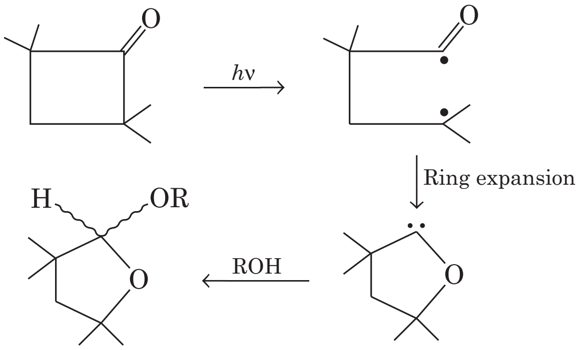
Formation of 1, 4-acyl-alkyl radical can be proved by trapping experiment. 1, 4-acyl-alkyl diradical can be trapped by 1, 3-butadiene at low temperature (–78°C) because low temperature suppress the decarbonylation and | 2 + 2 |—cycloaddition reaction. Photolysis of cyclobutanone at –78°C in the presence of trapping agent, 1, 3-butadiene gives 3-vinylcyclohexanone.



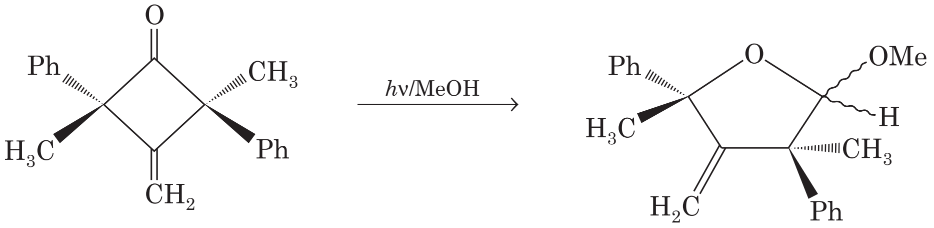
Scheme 8: Trapping of 1, 4-acyl-alkyl diradical by 1, 3-butadiene

Ring expansion of unsymmetrical cyclobutanones is highly regioselective which indicates the need for more stable alkyl radical to attack the oxygan atom of the acyl radical. Indeed alkyl substitution does increase the yield of ring expanded products. Both 2, 2-dimethyl and 2, 2, 4, 4-tetramethyl-cyclobutanone forms ring-expansion products predominantly.

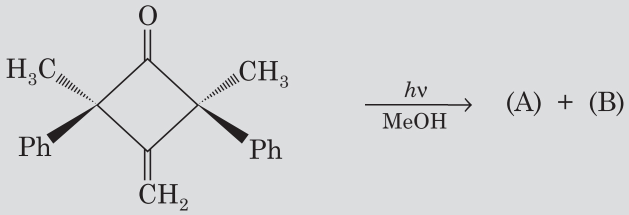




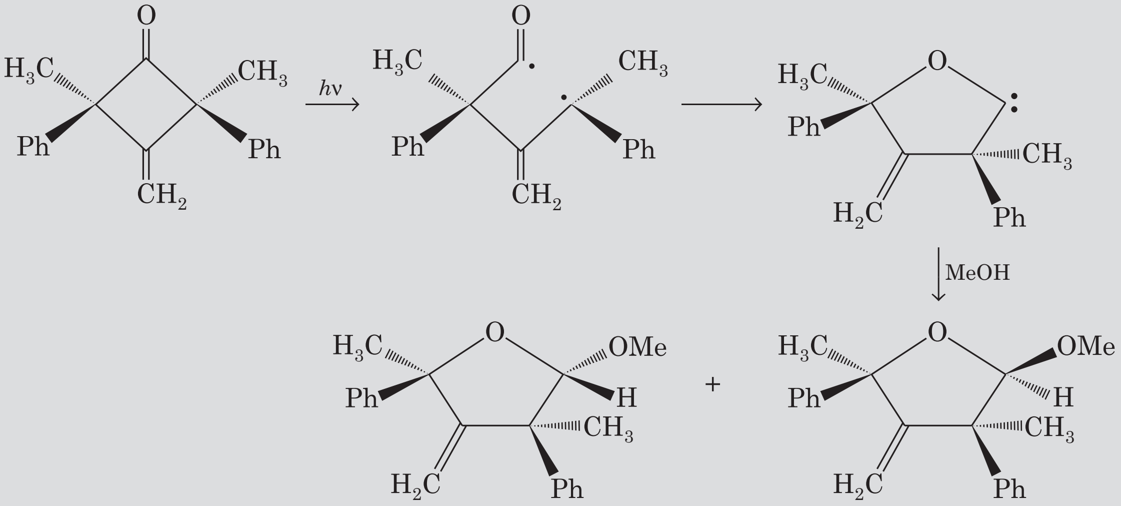
Photolysis of cyclobutanone is also stereospecific reaction. Stereochemistry at C-2 is retained during the rearrangement to the oxacarbene. Ring expansion reaction always exhibit retention of configuration in methanol.



Problem 6: *Identify (A) and (B) in this reaction:*

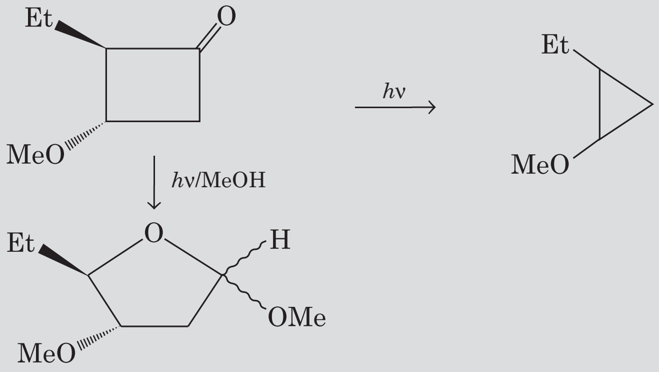


Solution:

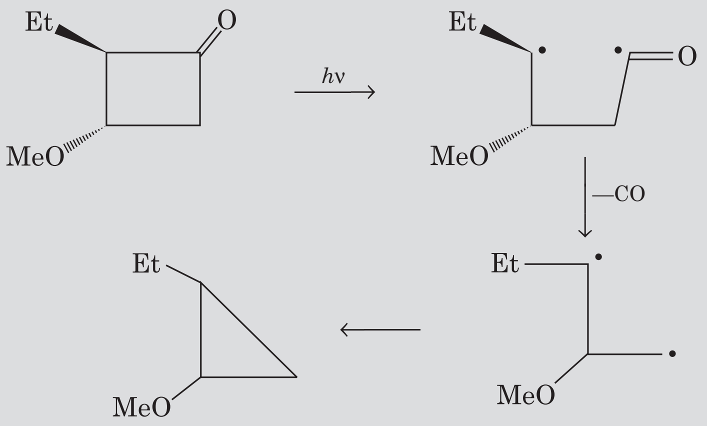


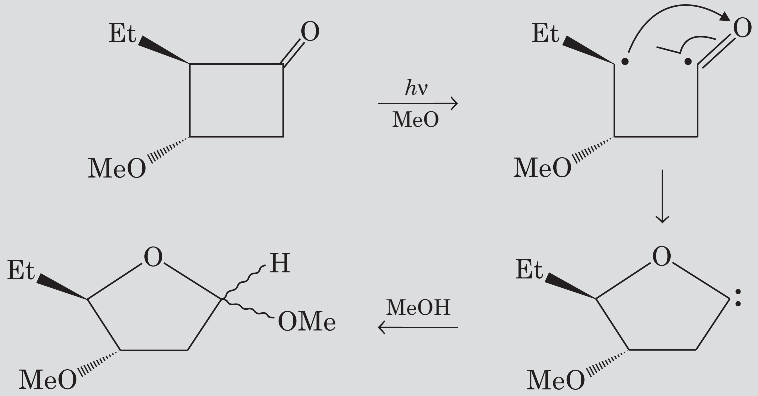
(B) (A)

Problem 7: *Give mechanism of the given reaction:*

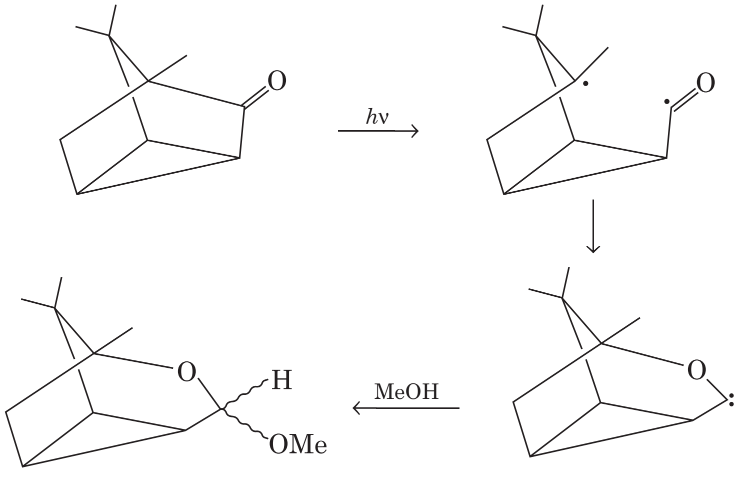


Solution:





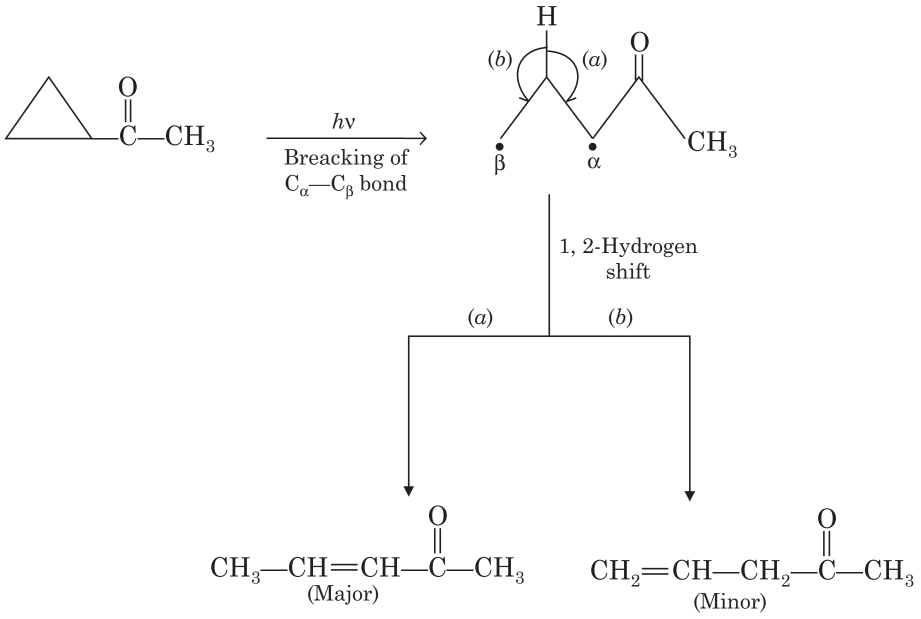
Ring expansion reaction is also possible in those cases where hydrogen transfer process are inhibited by steric factor. Certain tricyclic ketones such as *Fenchone* gives ring expansion due to the steric strain in the molecule.



7.2 β-CLEAVAGE REACTION

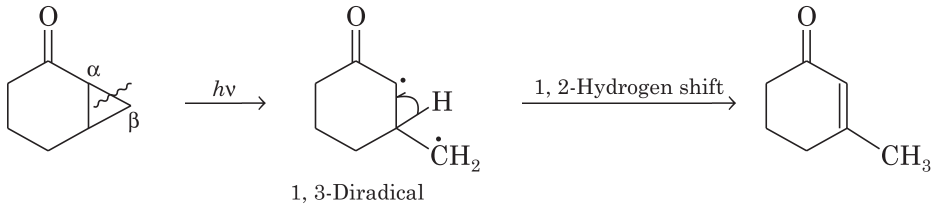
Some class of compounds have relatively weak C_{α}—C_{β} bonds which can undergo cleavage as a result of electronic excitation of the carbonyl group. Cyclopropyl ketones are one such class, and evidence for interaction between the carbonyl and cyclopropyl groups, which provides a mechanism by which energy may be transferred from the carbonyl group to the bond which is broken, is found in the UV spectrum.

The mechanism of the reaction has been shown to involve the formation of a biradical intermediate. Photolysis of acetylcyclopropane leads to cleavage of the cyclopropane ring, and this is followed by a hydrogen shift.

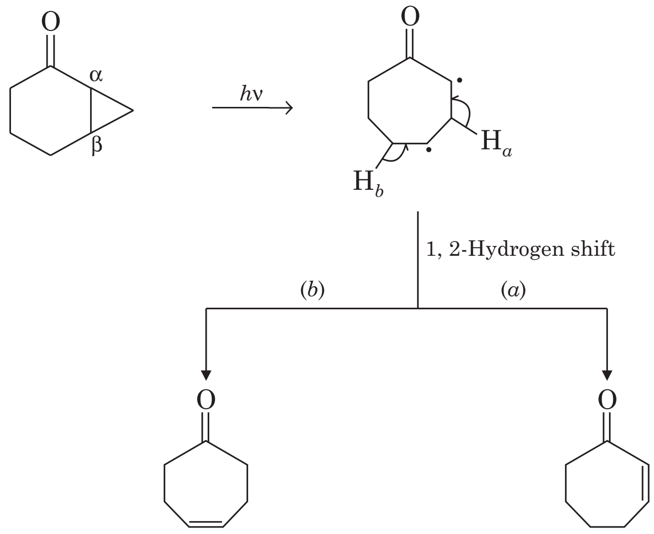


In a similar way, bicyclo [4, 1, 0] heptane-2-ones undergo cleavage of one of the cyclopropyl C—C bonds.

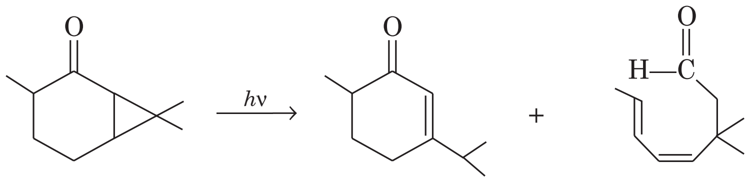
(i)



(*ii*)



In some cases the α-cleavage and β-cleavage are often in competition as shown below:

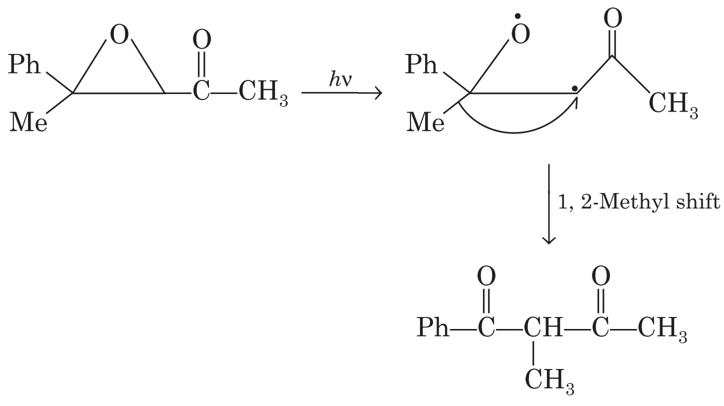


(1) (2)

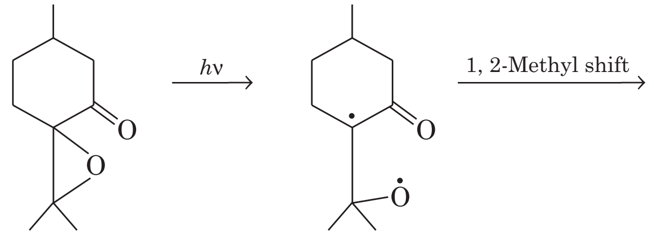
In the above case, product (1) is formed due to the β-cleavage and product (2) is formed due to the α-cleavage.

α, β-Epoxy ketones have also a relatively weak C_α—C_β bond which can be cleaved in the excited state. Epoxy ketone reacts by way of β-cleavage and alkyl migration on photolysis. Mechanistically this reaction arises from a singlet *nπ** state and result is the fission of the C—O bond. The migratory aptitudes shown within such compounds is best explained *via* the involvement of a biradical species formed by C—O bond fission. Some examples are:

(*i*)

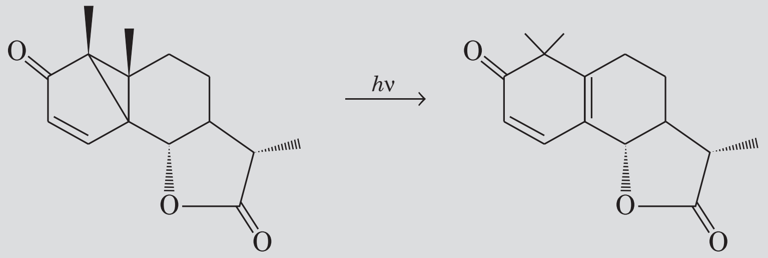


(*ii*)

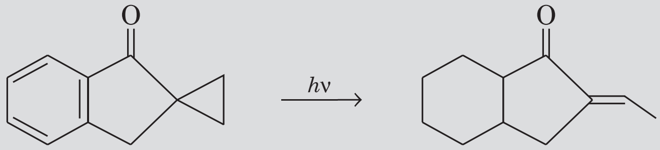


Problem 8: *Give mechanism of the given transformation:*

(*i*)

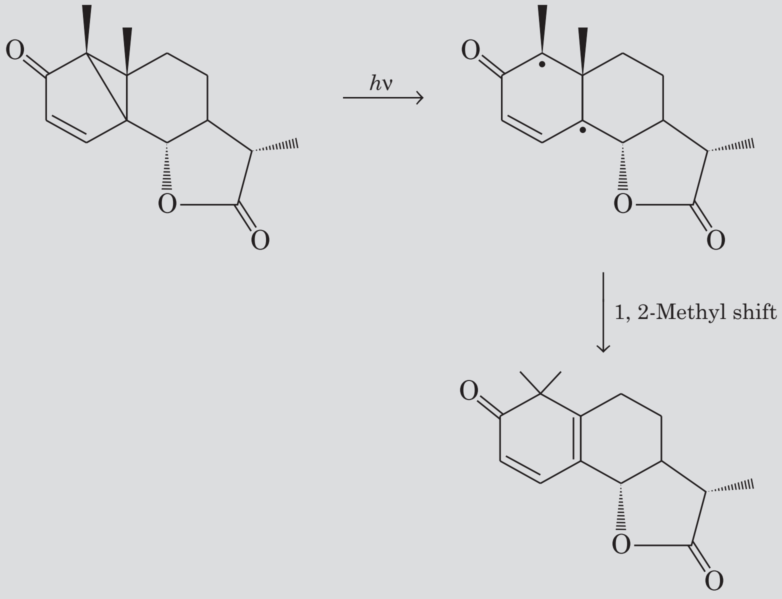


(*ii*)

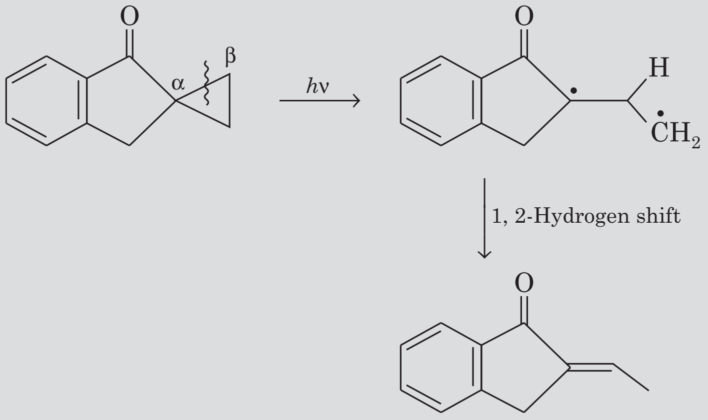


Solution: Both compounds are cyclopropyl alkyl ketone derivatives, hence both will give β-cleavage reactions.

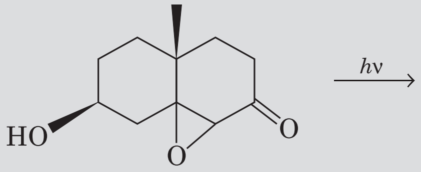
(*i*)



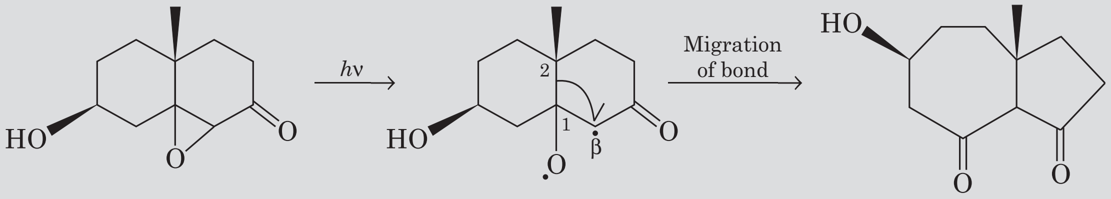
(*ii*)



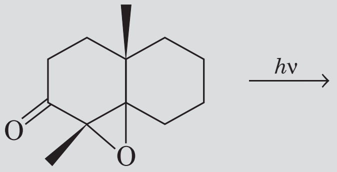
Problem 9: *Complete the given reaction:*



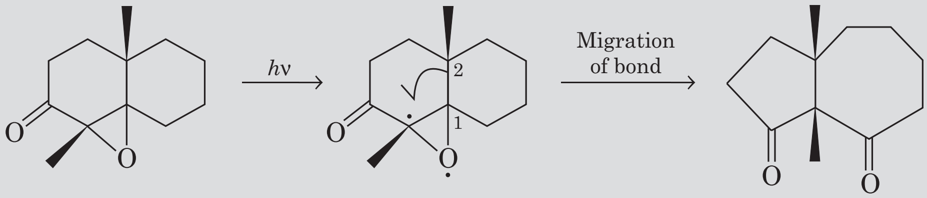
Solution:



Problem 10: *Complete the following reaction:*

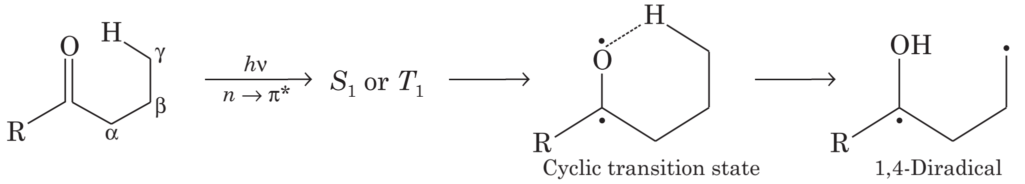


Solution:



7.3 INTRAMOLECULAR HYDROGEN ABSTRACTION (γ-HYDROGEN ABSTRACTION)

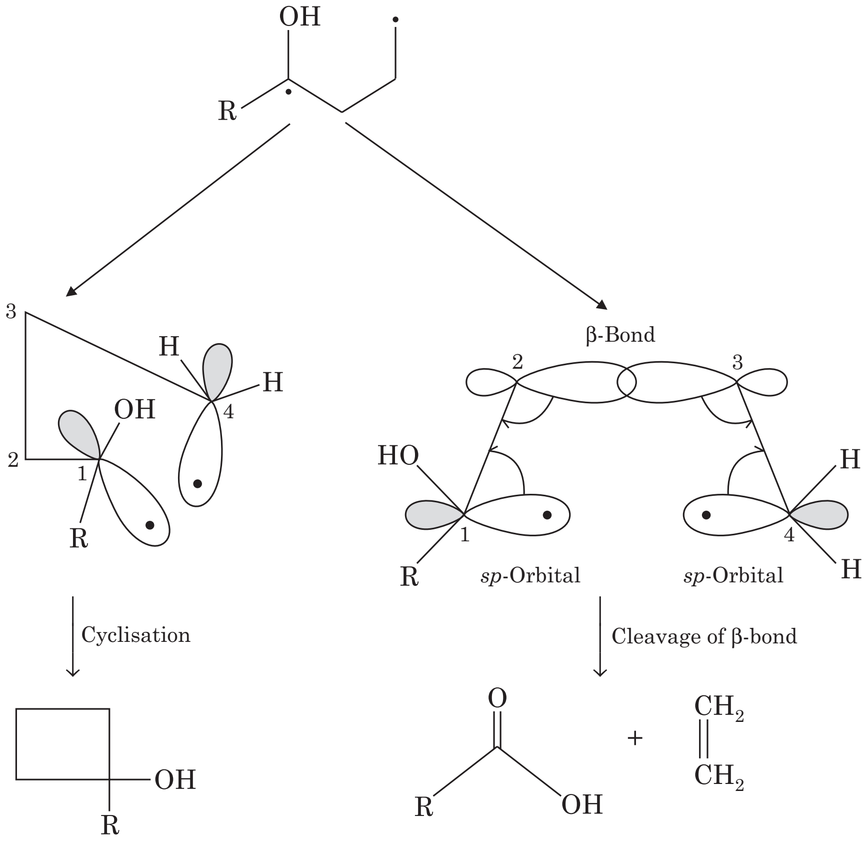
1, 3 (n, π^*) excited carbonyl compounds having an accessible hydrogen atom in the γ-position undergo a characteristic 1, 5-hydrogen atom transfer by an intramolecular cyclic process with the formation of ketyl like 1, 4-diradical.



Depending on the conformation of the initially formed 1, 4-diradical, two different pathways to stabilisation are possible:

(*i*) If only the *sp*-orbitals of the radical centres can overlap, a cyclobutanol is the product.

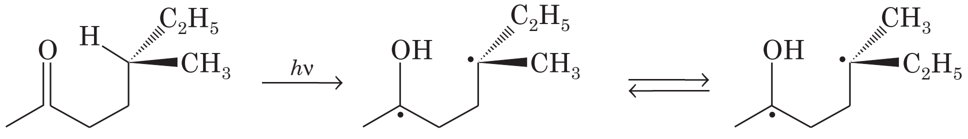
(*ii*) If the *sp*-orbitals of the radical centres are parallel to the β-bond, they participate in the formation of two double bonds (one in the enol and one in the alkene), a result of the cleavage of the β-bonds.



The second process of this reaction is known as Norrish Type II process which leads the formation of alkene and alkenol.

Although the reaction occurs from both the singlet and the triplet states of n, π^* transition, the quantum yields from the singlet state are generally lower than the triplet state. In case of aryl-alkyl ketones, the reaction occurs only with the triplet state because aromatic ketones can undergo rapid intersystem crossing. Solvents also affect the efficiency of the reaction. The singlet state reactions are unaltered in the presence of polar solvents. Polar solvents such as alcohol, on the other hand, enhance the reaction from the triplet state.

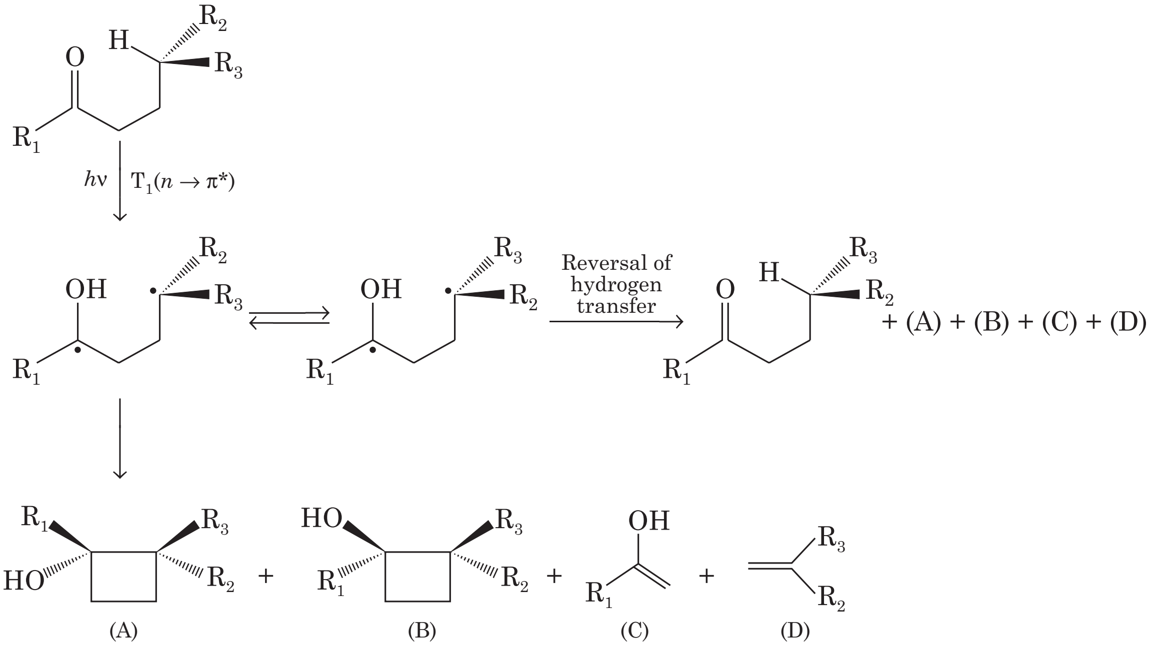
The quantum yield of the reaction is poor since radiationless deactivation from the S_1 and T_1 states and reversal of the hydrogen transfer can compete with reactions proceeding to products. The reversal process is confirmed by using the optical active ketone (1) having a chiral γ-carbon. Ketone (1) undergoes racemisation. Racemisation reaction confirmed that the reaction intermediate is 1, 4-diradical. This also confirmed the back transfer of hydrogen atom.



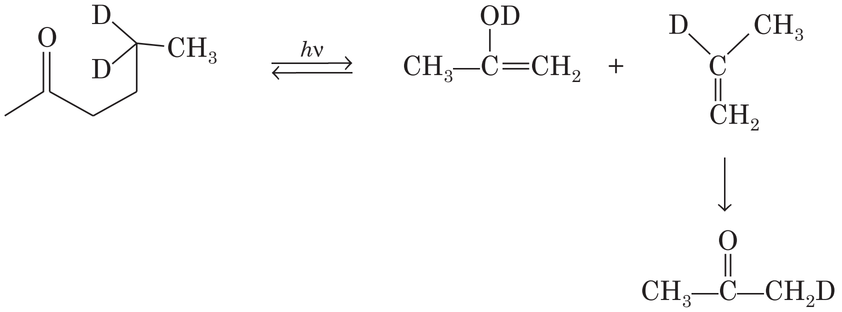
(1)

Back transfer of hydrogen atom *i.e.*, photoracemisation can be quenched by the addition of 1, 3-cyclopentadiene. This quenching experiment confirmed the formation of triplet state.

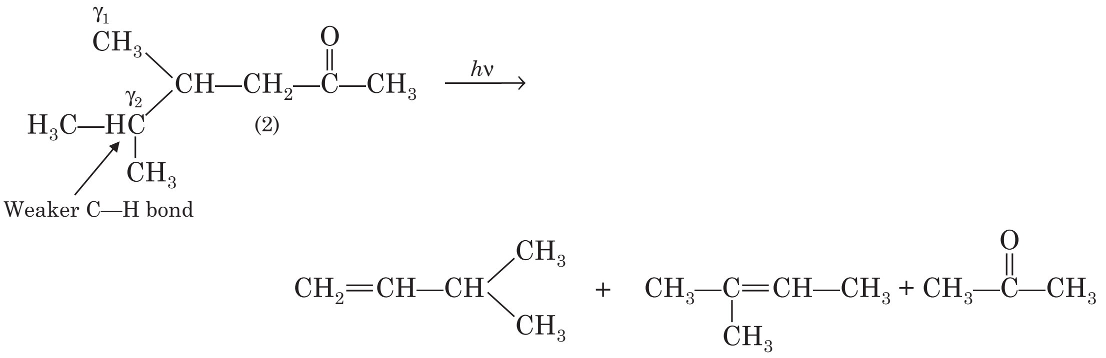
Participation of a 1, 4-diradical intermediate in the Norrish Type II reaction has been confirmed by trapping experiments and spectroscopic techniques. Formation of 1, 4-diradical has also been proven chemically. Photoracemisation of a ketone with a γ-chiral carbon atom and loss of the chirality in the product was observed.



The γ-hydrogen transfer to the oxygen atom has been shown to be intramolecular. The transfer involves a six membered cyclic transition state. 5, 5-Dideuterohexan-2-one on irradiation gives 2-deuteropropene and 1-deuteroacetone. Formation of these products confirms that the transfer of hydrogen takes place from γ-carbon and process is intramolecular.



When a molecule has two γ-carbons both having hydrogens, transfer of hydrogen in the Norrish Type II process is marked by a preference of cleavage of the weaker carbon-hydrogen bond as in case of ketone (2).

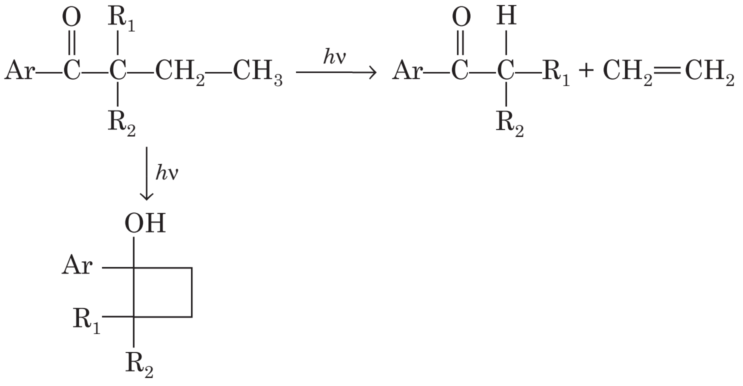


(Minor) (Major)

Intramolecular hydrogen abstraction is not possible if γ-carbon has no hydrogen.

For alkylaryl ketones the electron donating groups such as *p*-methyl and *p*-methoxy substituents decreases the rate and quantum yield for Norrish Type II cleavage. Following this trend *p*-hydroxy, *p*-amino and *p*-phenyl substituents inhibit the reaction completely. This is because in such cases energy for π → π* excitation is less than the *n* → π* excitation.

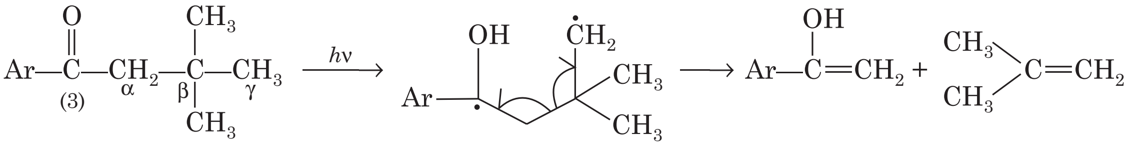
The rate of radical recombination to give cyclobutanols compared with α, β-bond cleavage is often dependent on α-substitution.



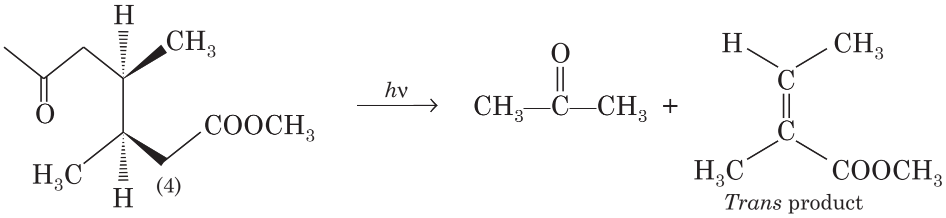
Substituents	*Cyclisation*
$R_1{=}R_2{=}H$	10%
$R_1{=}H, R_2{=}CH_3$	29%
$R_1{=}CH_3, R_2{=}CH_3$	89%

Thus substitution at α-position favours cyclisation reaction.

On the other hand substitutions at β-position favours Norrish Type II reaction. Thus ketone (3) mainly gives Norrish Type II reaction *i.e.,* elimination reaction. In other words if 1, 4-diradical is stable than this favours cyclisation reaction. If 1, 4-diradical is unstable than this favours Norrish Type II reaction.

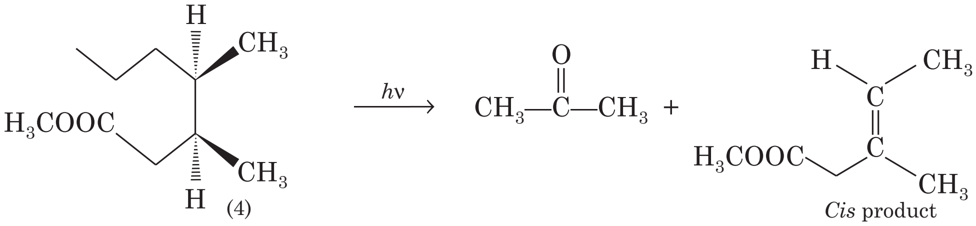


The singlet state photoelimination (Norrish Type II process) reaction occurs with a high degree of stereospecificity in *threo* and *erythro* form of ketone (4). *Threo* form of (4) gives *trans* product whereas *erythro* form gives *cis* product.



Threo form

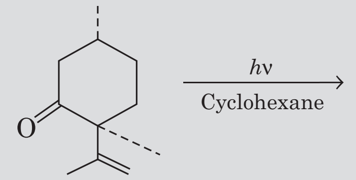
Trans product



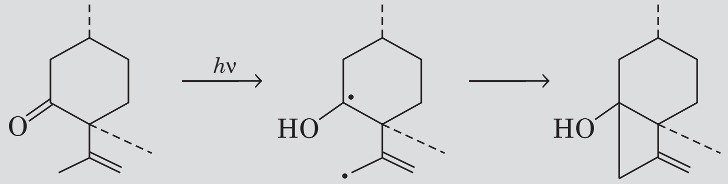
Cis product

Erythro form

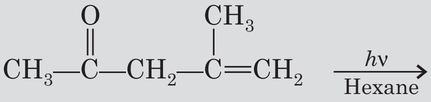
Problem 11: *Complete the following:*



Solution: Compound has hydrogen on γ-carbon which is an allylic carbon. Hence 1, 4-diradical has allylic character. This will lead the cyclisation.

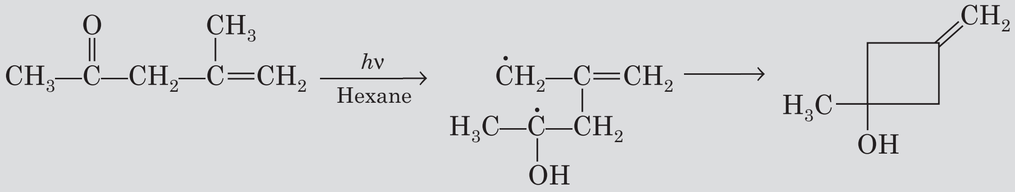


Problem 12: *Complete the following reaction:*

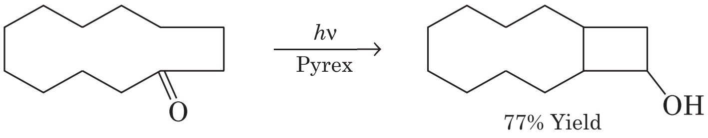


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Hexane}]{h\nu}$$

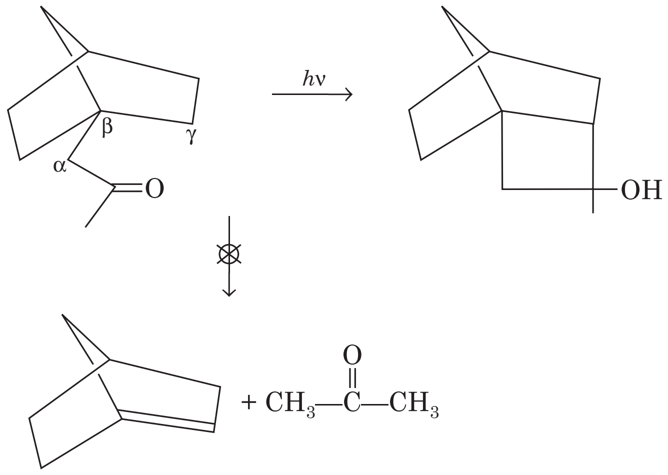
Solution: γ-Carbon is allylic carbon, hence 1, 4-diradical will be allylic free radical. Thus cyclisation will be main reaction.



Generally the yields of cyclisation product are only 10–20% of those of elimination in normal ketones. But for certain compounds cyclisation is very efficient. Some of these are systems where there are steric factors promoting cyclisation, as with *cyclododecanone*.

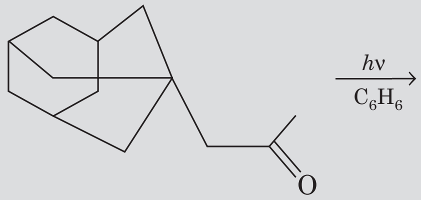


Norborane also gives only cyclisation because alkene product is highly strained (highly unstable).

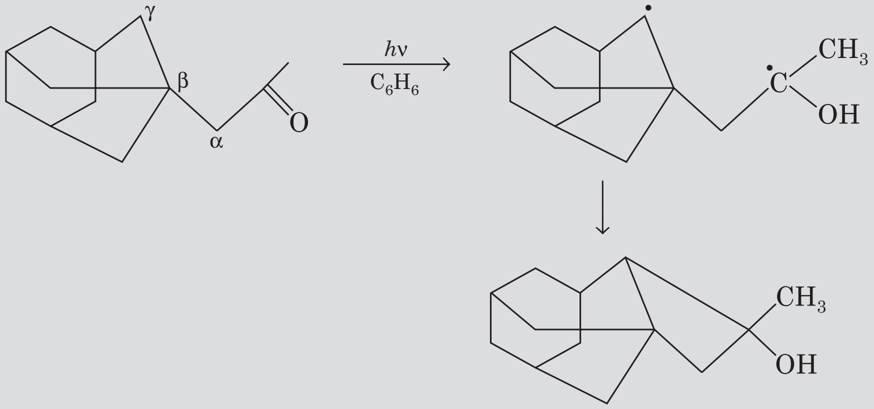


(Highly strained)

Problem 13: *Complete the following reaction:*



Solution: Compound has rigid geometry and has hydrogen on γ-carbon, hence reaction should be cyclobutanol formation.



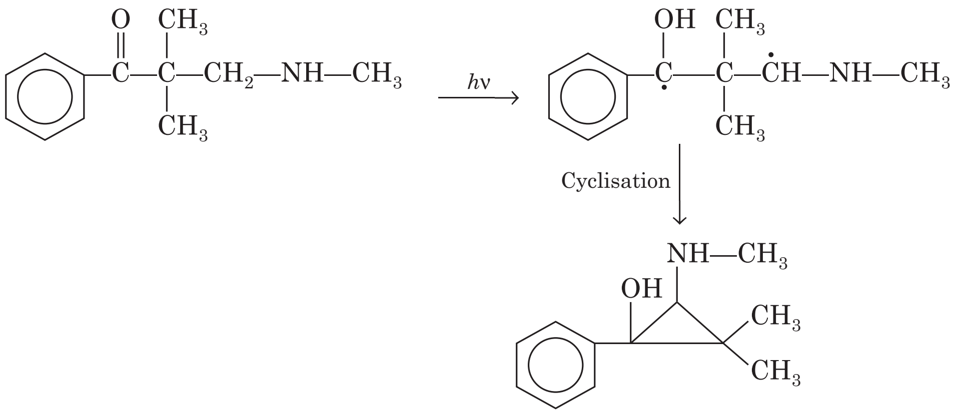
7.4 HYDROGEN ABSTRACTION FROM OTHER SITES

While the normal reaction path of Norrish Type II process involves a six-membered cyclic transition state, alternative reaction paths are fairly common. In these cases either larger or small transition states provide diradicals which cannot fragment. Alternative routes are possible when γ-carbon has no hydrogen or biradical is stabilised by hetero atoms.

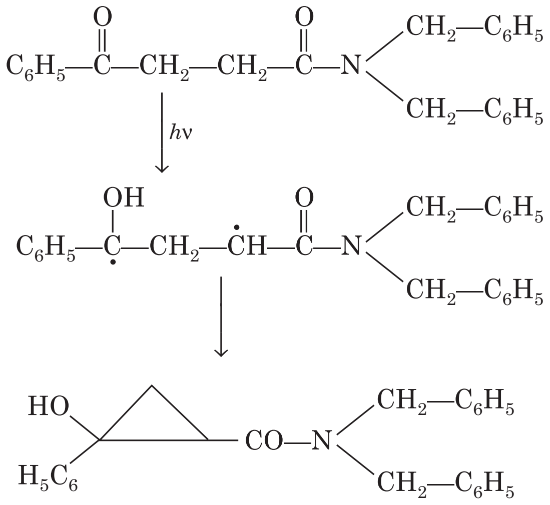
7.4.1 β-Hydrogen Abstraction

β-Hydrogen abstraction can only be possible if substrate has no γ-hydrogen and the biradical is stabilised by the presence of hetero atoms.

(*i*)

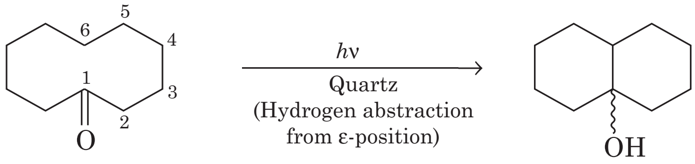


(*ii*)

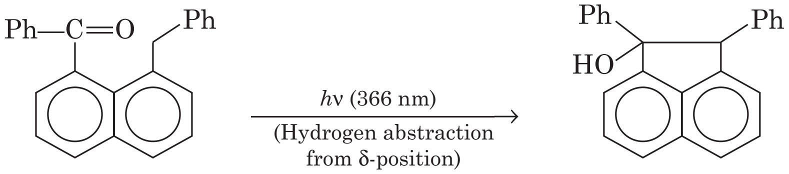


7.4.2 δ- and ε-Hydrogen Abstraction

Intramolecular γ-hydrogen abstraction by an excited carbonyl oxygen is approximately 20 times faster than δ- and ε-hydrogen abstraction. Nevertheless, the tendency of the half-occupied *n*-orbital of the carbonyl oxygen to abstract a hydrogen atom from other position is considerable. A necessary condition is the planarity of the transition state. An important example of this class is cyclodecanone. In this case intramolecular hydrogen abstraction takes place from C-6.

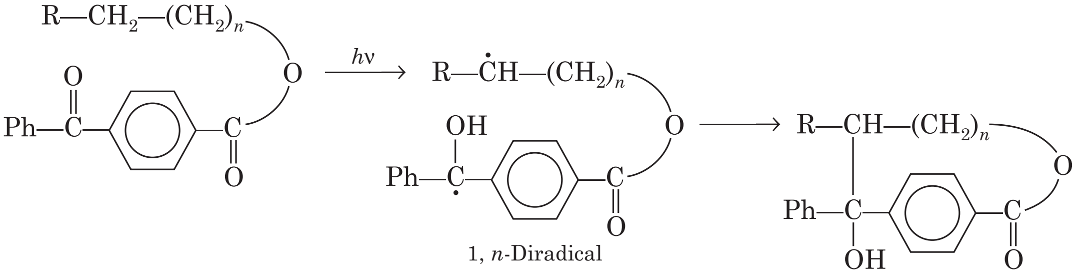


There are other systems where hydrogen abstraction through a six-membered cyclic transition state is not possible because there is no suitable placed hydrogen atom 1-(8-benzylnaphthyl)-phenyl ketone is such a compound.



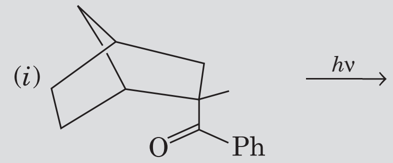
7.4.3 Hydrogen Abstraction from Distant Sites

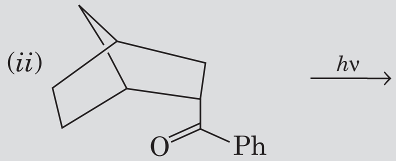
In the photolysis of alkyl esters of benzophenone-4-carboxylic acid, the planar transition state is possible only for ≥ 10, which leads to the formation of a ≥ 1, 18 biradical whose recombination produces a paracyclophane.



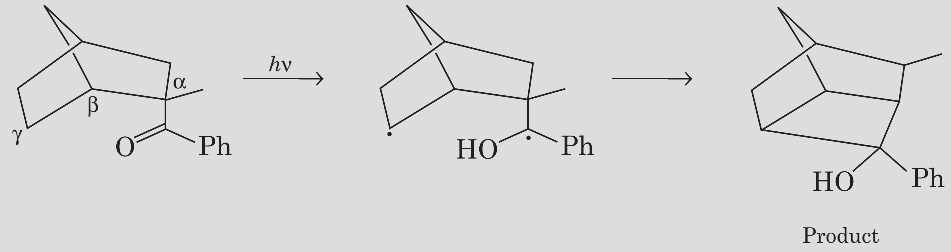
Paracyclophane

Problem 14: *Complete the following reactions:*

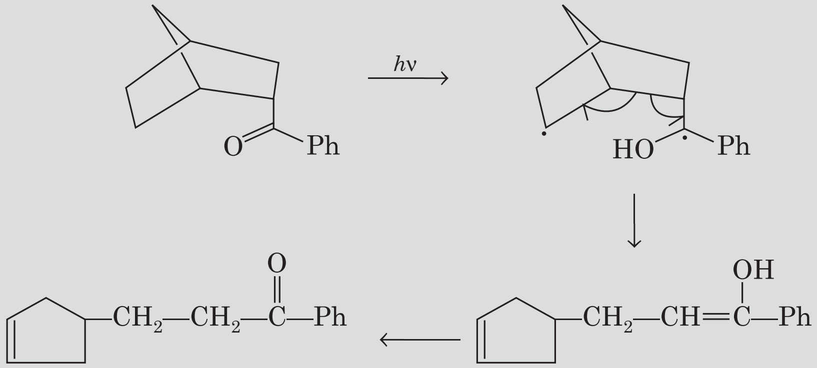




Solution: (*i*) In the compound position α is substituted and γ-position has hydrogen, hence reaction will be cyclisation.

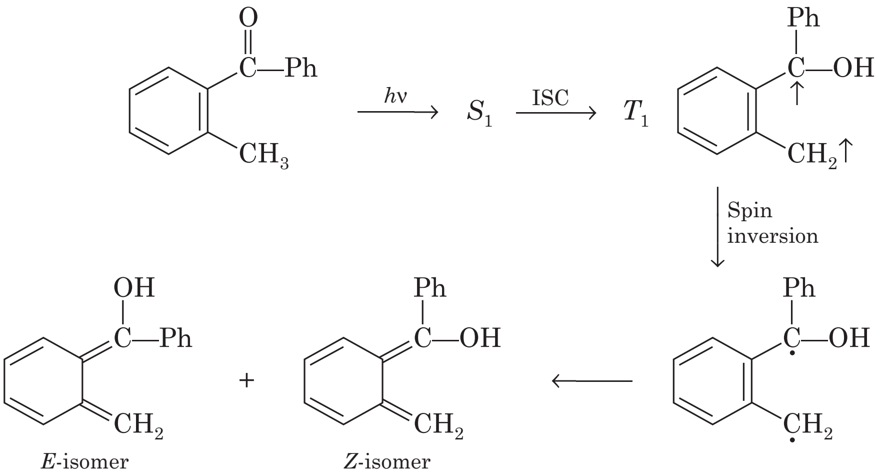


(*ii*) In the given compound, position α is not substituted hence reaction will be Norrish Type II reaction.

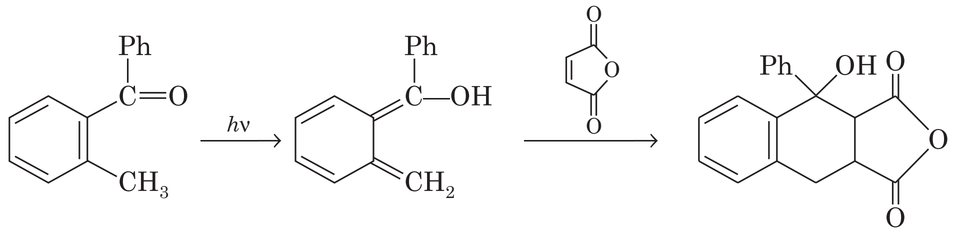


7.5 FORMATION OF PHOTOENOLS OR PHOTOENOLISATION

The formation of photoenols arises by Norrish Type II process in *ortho* substituted aryl ketones and are produced by the following mechanism:



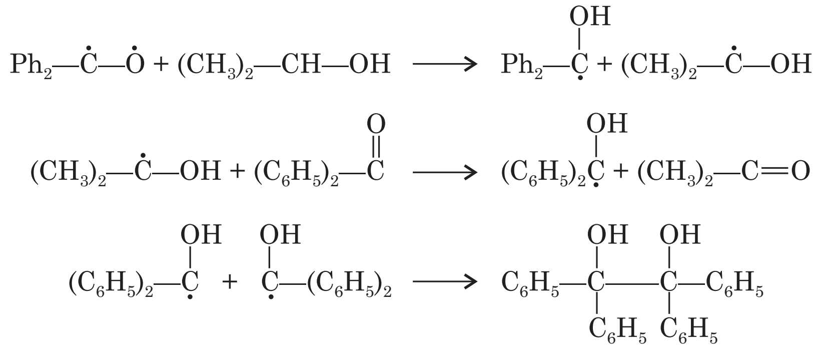
The photoenolisation can be quenched by molecular oxygen. This confirmed the formation of triplet biradical. The product of the reaction behaves as diene for Diels-Alder addition. Thus photoenols can be trapped by addition of dienophile.



7.6 INTERMOLECULAR HYDROGEN TRANSFER: INTERMOLECULAR PHOTO REDUCTION

Photo reduction of carbonyl compounds is one of the best known of photo reactions. In its initial steps the mechanism involves transfer of a hydrogen atom to the oxygen atom of the carbonyl excited state from a donor molecule which may be solvent, an added reagent or ground state molecule of reactant. Ketone undergoes photo reduction in the presence of a variety of hydrogen atom donor. Hydrogen atom donors are secondary alcohol, toluene and cumene. This reaction is bimolecular reaction.

(*i*) $(C_6H_5)_2—C{=}O \xrightarrow{h\nu} S_1(n \to \pi^*) \xrightarrow{\text{ISC}} T_1(n \to \pi^*)\ (C_6H_5)_2—\dot{C}—\dot{O}$

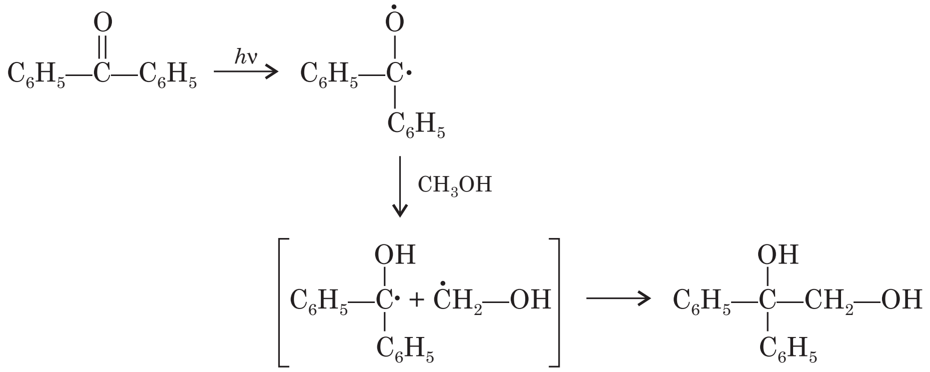


$$Ph_2—\dot{C}—\dot{O} + (CH_3)_2—CH—OH \longrightarrow Ph_2—\underset{\bullet}{\overset{OH}{\overset{|}{C}}} + (CH_3)_2—\dot{C}—OH$$

$$(CH_3)_2—\dot{C}—OH + (C_6H_5)_2—\overset{O}{\overset{\|}{C}} \longrightarrow (C_6H_5)_2\underset{\bullet}{\overset{OH}{\overset{|}{C}}} + (CH_3)_2—C{=}O$$

$$(C_6H_5)_2—\underset{\bullet}{\overset{OH}{\overset{|}{C}}} + \underset{\bullet}{\overset{OH}{\overset{|}{C}}}—(C_6H_5)_2 \longrightarrow C_6H_5—\underset{C_6H_5}{\overset{OH}{C}}—\underset{C_6H_5}{\overset{OH}{C}}—C_6H_5$$

(*ii*)



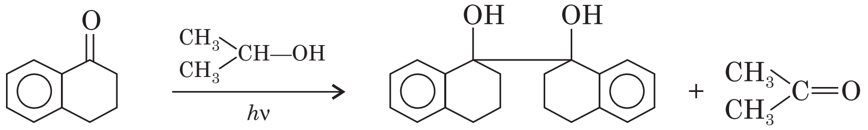
$$C_6H_5—\overset{O}{\overset{\|}{C}}—C_6H_5 \xrightarrow{h\nu} C_6H_5—\underset{C_6H_5}{\overset{\dot{O}}{C}}\cdot$$

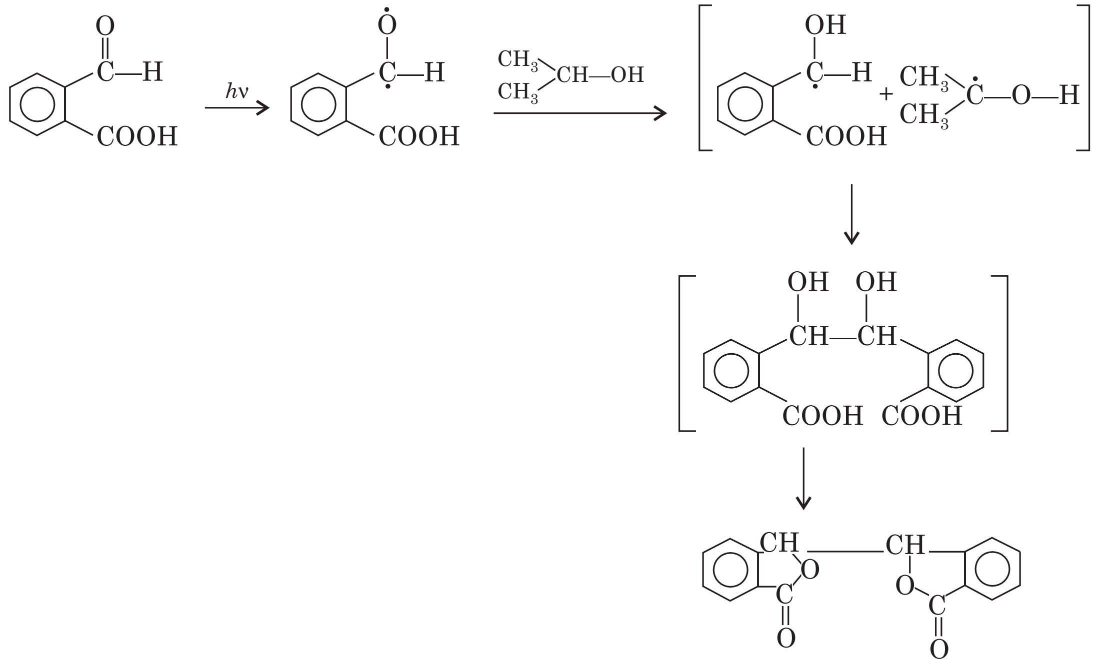
$$\Big\downarrow CH_3OH$$

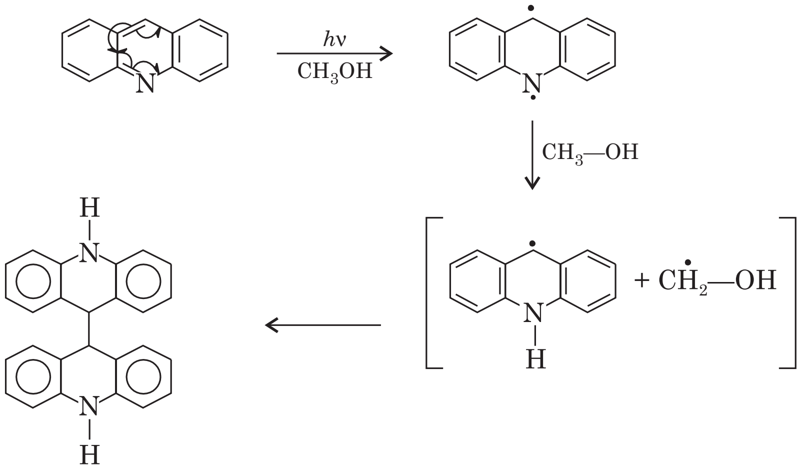
$$\left[C_6H_5—\underset{C_6H_5}{\overset{OH}{C}}\cdot + \dot{C}H_2—OH\right] \longrightarrow C_6H_5—\underset{C_6H_5}{\overset{OH}{C}}—CH_2—OH$$

The above reaction takes place when concentration of benzophenone is very small (10^{-4} m).

Other examples are:

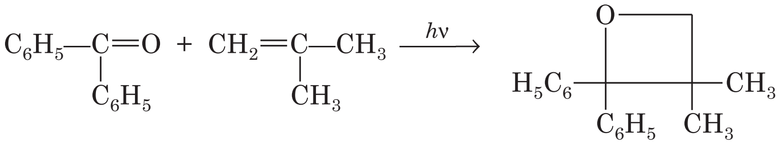






7.7 PHOTOCYCLOADDITION REACTION (PATERNO-BÜCHI REACTION)

One of the first photocycloaddition reactions to be studied was the formation of oxetanes from addition of carbonyl compounds to alkenes. This reaction is known as the Paterno-Büchi reaction. For example, benzophenone with isobutene gives a high yield of an oxetane.

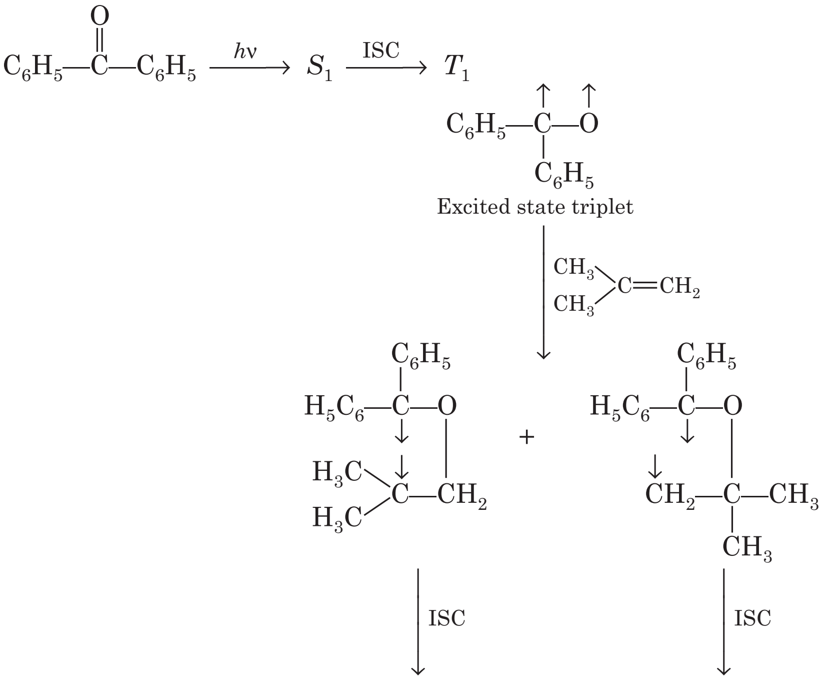


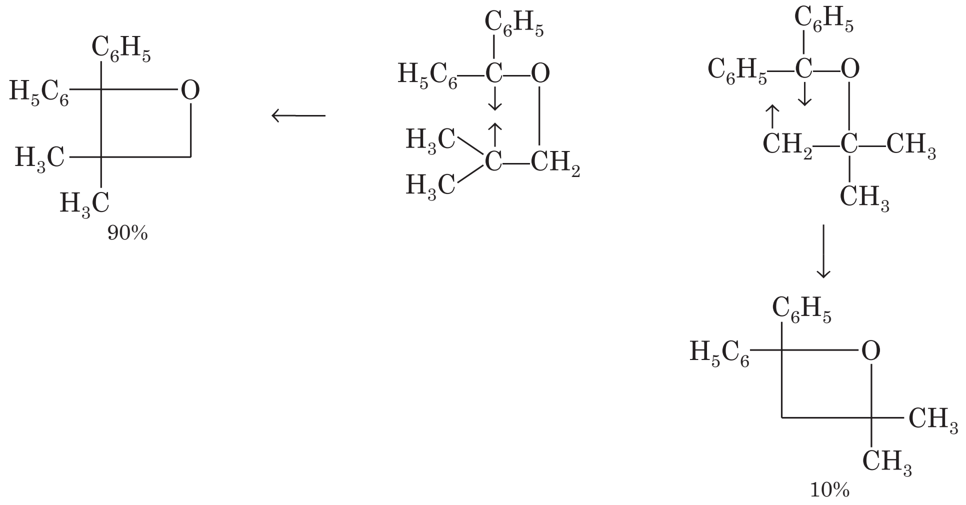
90% Yield

Paterno-Büchi reaction can be studied under two categories and the categories depend on the nature of alkenes.

7.7.1 Addition to Electron-Rich Alkenes

Mechanistic studies have shown that the reaction pathway varies according to the type of carbonyl compound and alkenes involved. Addition of simple aliphatic or aromatic ketones to electron rich alkenes involves attack on ground state alkene by the $n \rightarrow \pi^*$ triplet state of the carbonyl compound in a non-concerted manner, giving rise to all possible isomers of the oxitane. The reaction is non-concerted because the reactive excited state is a triplet state. The initial adduct of this reaction is a triplet 1, 4-diradical, which must undergo spin inversion before product formation is complete. Stereospecificity is lost if the intermediate 1, 4-diradical undergoes bond rotation faster than ring closure (Scheme 8).





Scheme 9

Although the reaction is not stereospecific, there is a preference for one orientation of addition, which can be rationalised in terms of initial attack on the alkene by the oxygen atom of the excited carbonyl group to give a biradical intermediate. The existance of biradicals has been confirmed by picosecond spectroscopy. The more energetically stable of the two possible biradicals is formed more readily. Thus reaction is regioselective reaction. The consideration of biradical stability is certainly applicable to the prediction of the major product of the cycloaddition (see Scheme 9).

Two important rules for the successful synthesis of oxitanes have been put forward. These rules are as follows:

(*i*) Only carbonyl compounds with a low-lying $n \to \pi^*$ state will form oxitanes.

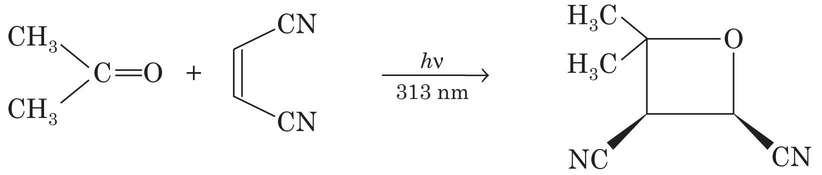
(*ii*) The energy of the carbonyl excited state must be less than that of the alkene to prevent energy transfer from the carbonyl excited state to the alkene.

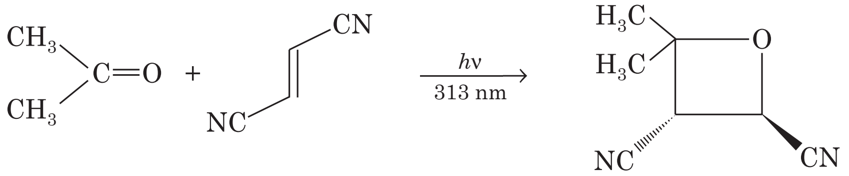
As far as the addition of aromatic carbonyl compounds is concerned only the triplet state is reactive (because inter system crossing is very efficient in case of aromatic ketones) and consequently a triplet biradical intermediate is produced.

The reaction of alkyl ketones can be complicated by the less efficient inter system crossing thus permitting reaction of both the singlet and the triplet state. Both singlet and triplet state show equal reactivity for the reaction. The singlet state reaction obtained at high concentration of the alkene. On the otherhand triplet state reaction obtained at low concentration of the alkene.

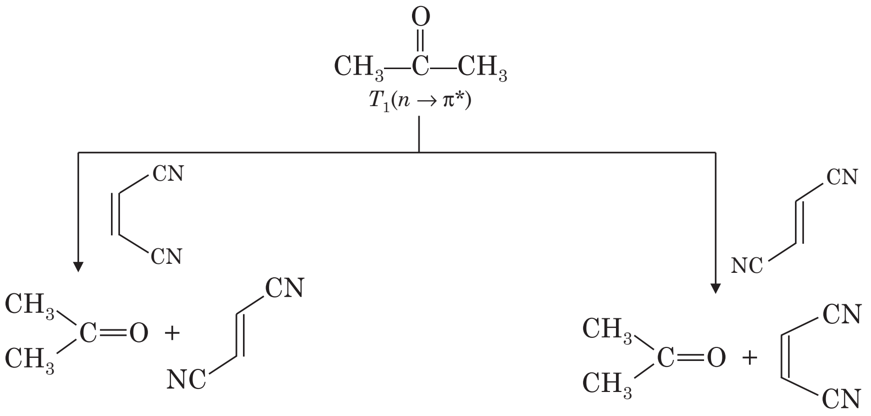
7.7.2 Addition to Electron Deficient Alkenes

Photocycloaddition of aliphatic ketones to electron-deficient alkenes, particularly dicyanoethene, involves addition of singlet state ($n \to \pi^*$) excited ketone to ground state alkene. The reaction is stereospecific and the stereochemistry of the alkene is retained in the product oxitane.



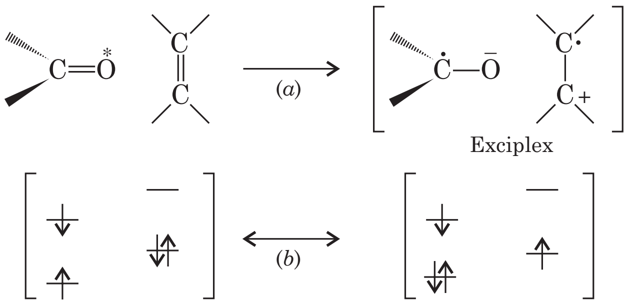


The course of the photocycloaddition of electron-deficient alkenes to ketones follows certain rules. While oxitanes are formed only from $S_1(n, \pi^*)$ state, the $T_1(n, \pi^*)$ state stereospecifically sensitises the *cis-trans* isomerisation of electron-deficient alkenes and does not lead to oxitanes.



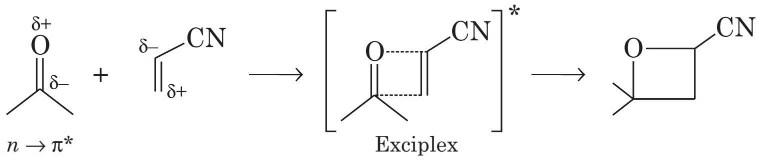
Stereospecificity of the oxitane formation with electron-deficient alkenes can be explained as follows:

It is suggested that in case of electron-deficient alkenes, oxitane formation takes place *via* formation of exciplex. Exciplex formation takes place between the singlet excited state of ketone and ground state of alkene. Exciplex is stabilised by charge transfer as well as energy transfer between the constituent molecules.



(*a*) Formation of an exciplex between a carbonyl excited state and an olefin ground state
(*b*) Charge transfer interaction in the formation of the carbonyl-olefin exciplex.

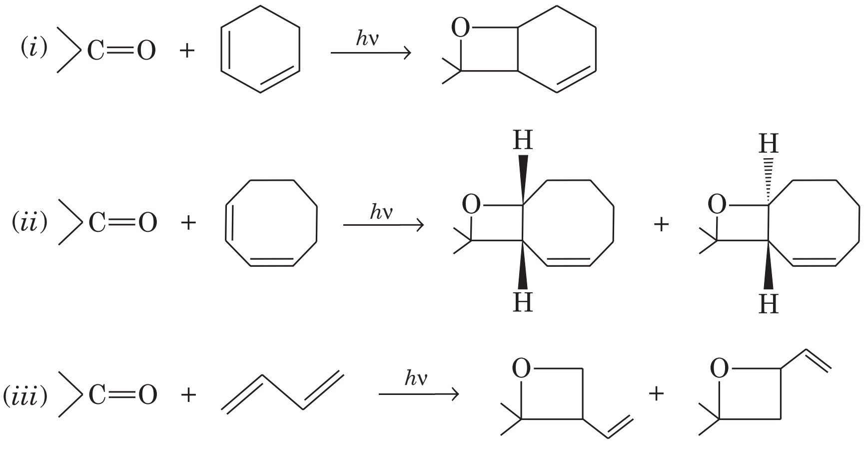
The exciplex (*i.e.,* excited state cyclic complex) has considerable charge-transfer and the stereospecific formation of products is accounted for if both new bonds are formed simultaneously in the complex, or if the second is formed after the first at a rate faster than the rate of bond rotation. There is again a preference for one orientation of addition, but this is opposite to that expected on the basis of the most stable biradical intermediate. The preference reflects the preferred orientation in the exciplex which is governed by charge densities as illustrated.



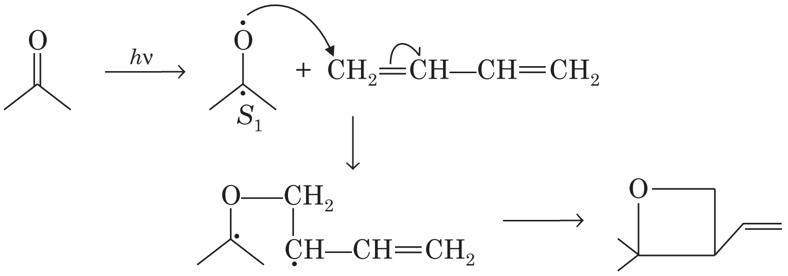
7.7.3 Oxitane Formation with Dienes and Alkynes

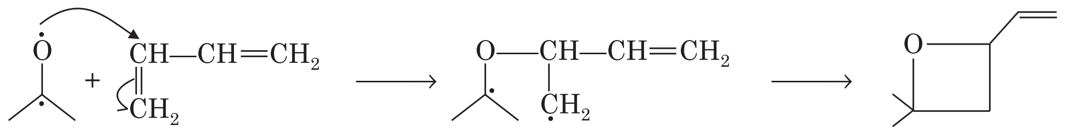
(A) With Dienes

Addition of carbonyl compounds to conjugated dienes is also feasible. The E_T of dienes is usually less than that of carbonyl compounds. However, the formation of oxetanes competes successfully with excitation energy transfer because dienes quench the T_1 ($n \rightarrow \pi^*$) state. Thus formation of oxetanes occurs from the S_1 ($n \rightarrow \pi^*$) state of the carbonyl compounds. Therefore, dienes give stereospecific reactions with dienes. Examples are as follows:



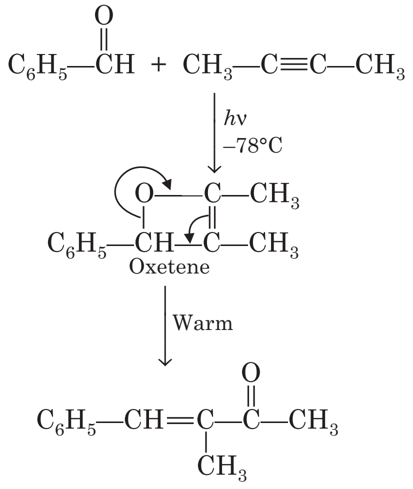
The third reaction takes place as follows:



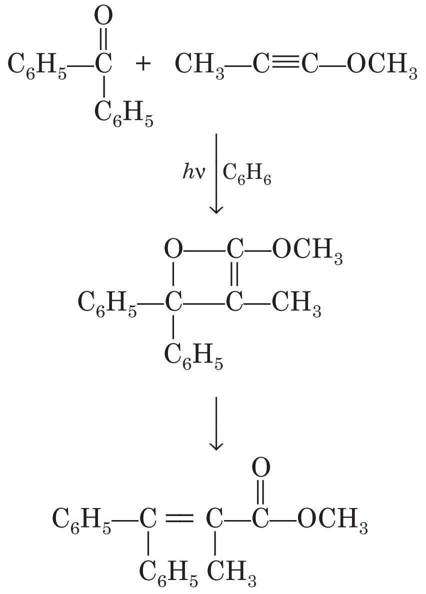


(B) With Alkynes

Carbonyl compounds undergo photochemical cycloaddition reaction to alkynes to give oxetenes which are usually not isolated but isomerises to α, β-unsaturated carbonyl compounds in a subsequent thermal reaction.



α, β-Unsaturated carbonyl compound

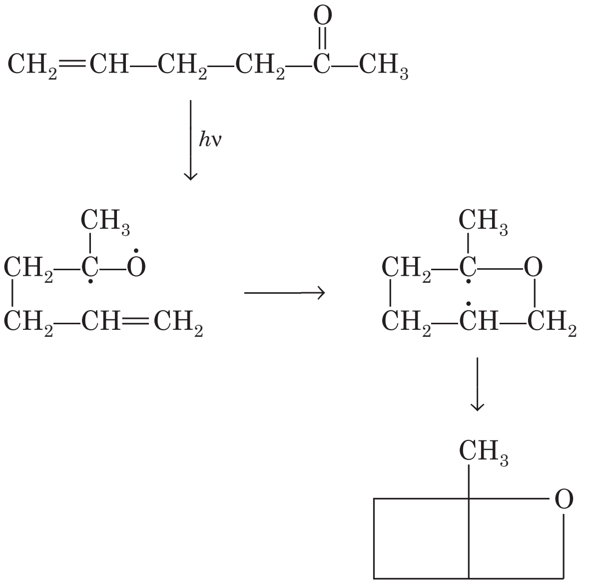


7.7.4 Intramolecular Paterno-Büchi Reaction

Intramolecular Paterno-Büchi reaction is mainly given by γ–δ-enones. The efficiency of these reactions can be attributed to the rapid rate of intraction between the excited C═O group and the ground C═C group. This combination of substrates allows the formation of one regioisomer. Thus yields are high and there is usually no byproduct(*s*). This reaction is highly efficient and versatile method for the synthesis of variety of compounds that are difficult or impossible to prepare by other methods.

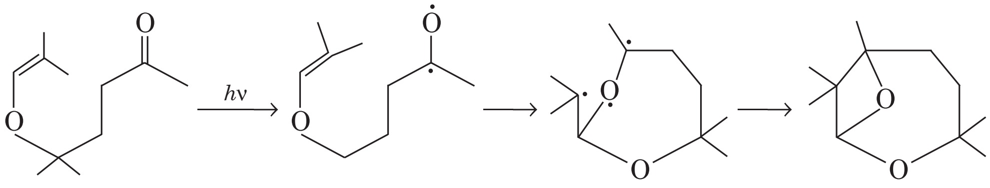
Some examples are as follows:

(*i*)

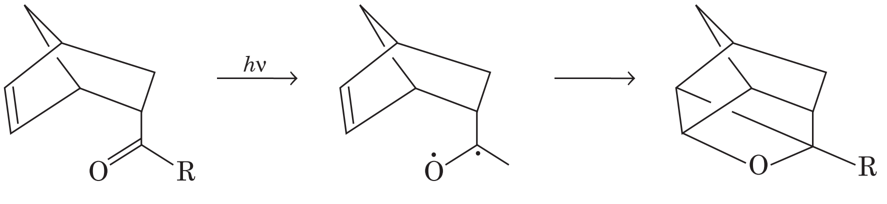


$$CH_2{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

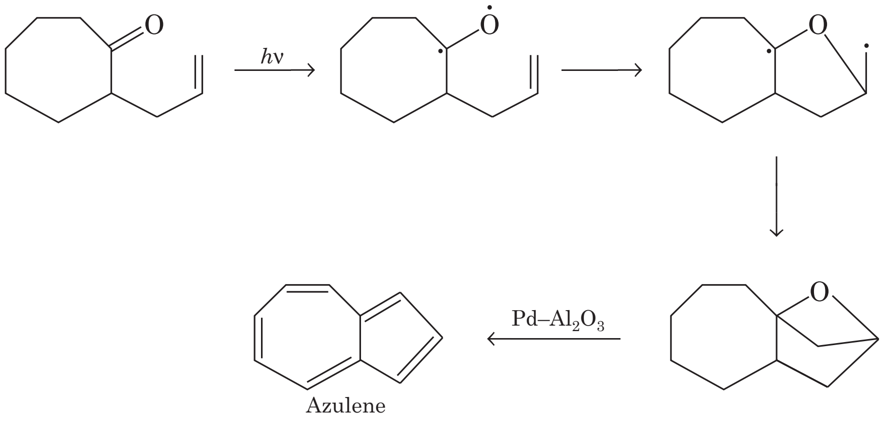
(*ii*)



(*iii*)



One of the most important reaction of this class is the preparation of azulene as follows:

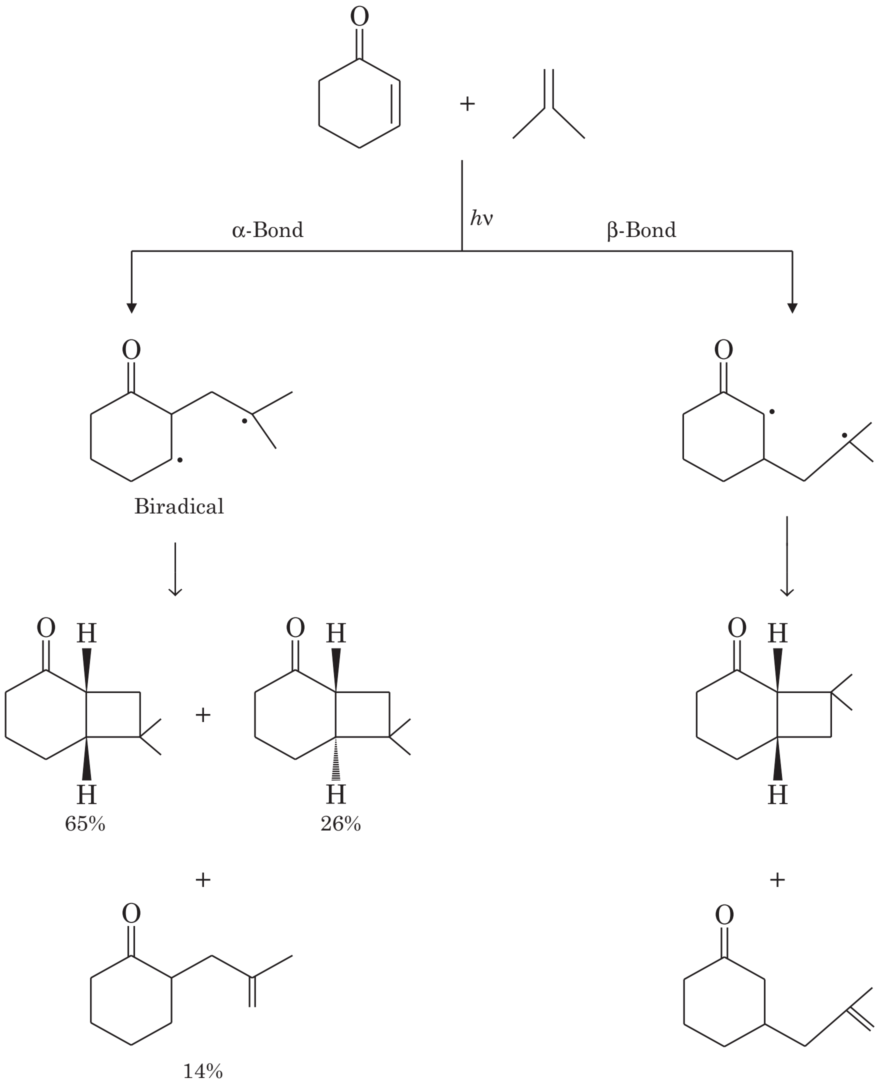


7.8 | 2 + 2 | CYCLOADDITION REACTION OF ENONES WITH ALKENES

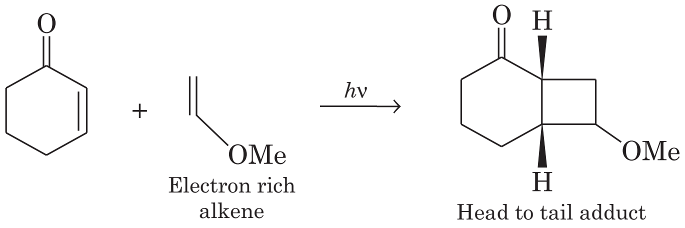
Perhaps the most useful reaction of α, β-unsaturated enones is the | 2 + 2 | photocycloaddition reaction with alkenes which affords cyclobutane derivatives. A simplified mechanism is given below:

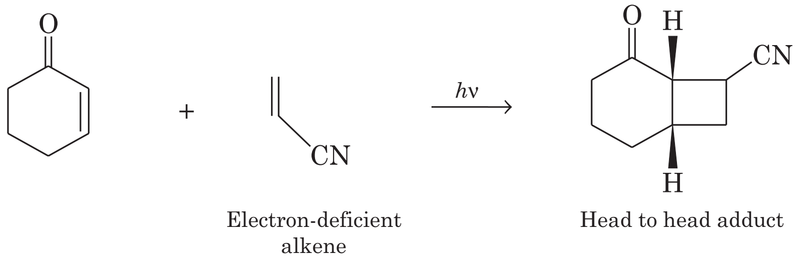
$$\begin{tikzcd}
\text{Alkene} + \text{Enone} \arrow[r, shift left, "h\nu"] & {[}\text{Enone}{]}^{1} \arrow[l, shift left] \arrow[d, "\text{ISC}"] \\
 & {[}\text{Enone}{]}^{3} \arrow[d, "\text{Alkene}"] \\
\text{Biradical} \arrow[uu] \arrow[d] & {[}\text{Exciplex}{]}^{3} \arrow[l] \\
\text{Product} &
\end{tikzcd}$$

The biradical can be formed by bonding at the α-carbon or the β-carbon of the enone to the alkene.



The reaction is regioselective with respect to unsymmetrical alkenes. Electron rich alkenes give head to tail adduct whereas electron-deficient alkenes form head to head adduct.





GLOSSARY

Excimer: A complex that is formed by the association of a ground state molecule with the excited state of the same molecule is known as excimer. An excimer reverts into its constituents upon demotion to the ground state.

Exciplex: A complex that is formed by the association of ground state molecule with the excited state of a different molecule is known as exciplex. Thus exciplex is a heteroexcimer.

Norrish Type I Cleavage: A reaction originating from the carbonyl n, π^* state and proceeding through the homolytic cleavage of the carbonyl alkyl groups (*i.e.,* α-bond) as the primary photochemical process. Norrish Type I process finds synthetic utility in the ring cleavage of cyclic ketones.

Norrish Type II Cleavage: A reaction originating from the carbonyl n, π^* state and proceeding through a six-centered fragmentation initiated by γ-hydrogen abstraction. The product of the fragmentation are an olefin and an enol which tautomerises to the carbonyl compound.

A similar reaction occurs in the mass spectral fragmentation of carbonyl compounds, where it is identified as the McLafferty cleavage.

Paterno-Büchi Reaction: The cycloaddition reaction between an electronically excited carbonyl group and a ground state olefin to yield an oxetane. This is the only good method for synthesising four-membered ether rings.

FURTHER READING

1. A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry,* CRC Press, Boca Raton, Florida, 1991.
2. W. Horspool and D. Armester, *Organic Photochemistry, A Comprehensive Treatment,* Ellis Horwood/Pentice Hall, 1992.
3. M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules,* VCH, New York, 1995.
4. J.M. Coxon, B. Halton, *Organic Photochemistry,* Cambridge University Press, Cambridge, 1974.
5. P. de Mayo, ed. *Rearrangements in Ground and Excited States,* Vol. 3, Academic Press, New York, 1980.

PROBLEMS

1. Absorption of photon by organic molecules leads two possible effects, primary and secondary. Mention (with example) the primary and secondary effects given by the molecule.

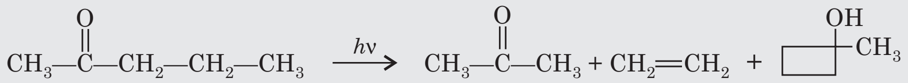
2. Ketones mainly give four types of photochemical reactions. Give name of the reactions with one example each.

3. Give mechanism of the Norrish Type I process. How many types of carbonyl compounds give this reaction? Give one example for each compound.

4. Give mechanism of Norrish Type II reaction. Explain why cyclopropyl ketones are the most common class of compound for β-cleavage reactions?

5. (*i*) Give mechanism of intramolecular hydrogen abstraction reaction given by carbonyl compounds.

(*ii*) Give mechanism of the given reaction:



6. Give mechanism of photo-enolisation. Explain why aromatic carbonyl compounds with an alkyl group at *ortho* position undergo rapid and reversible photo-enolisation reaction?

[**Hint:** Photo-enolisation takes place by way of hydrogen abstraction from the methyl group present at *ortho* position through a six-membered cyclic transition state].

7. Discuss the mechanism of the photo reduction of benzophenone leading to the formation of benzpinacol.

8. Gas phase irradiation of 2-pentanone produces acetone, ethylene in about 88% yield along with 12% 1-methylocyclobutanol. Account for the formation of these three photochemical products.

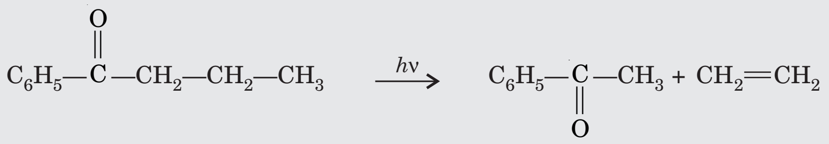
[**Hint:** Compound gives Norrish Type II reaction and intramolecular hydrogen abstraction by carbonyl oxygen].

9. What is Paterno-Büchi reaction? Discuss its mechanism along with the stereochemical consequences.

10. Write note on photodimerisation of α, β-unsaturated ketones.

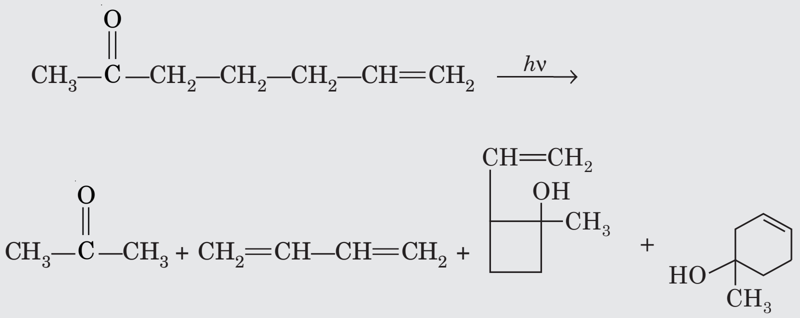
11. Suggest mechanism for the following photoreactions:

(*i*)

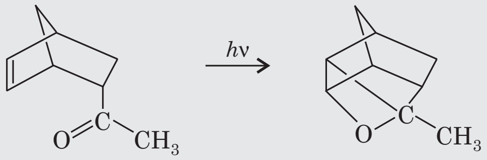


$$C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{h\nu} C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + CH_2{=}CH_2$$

(*ii*)

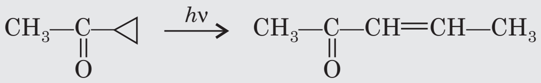


(*iii*)



[**Hint:** Paterno-Büchi reaction].

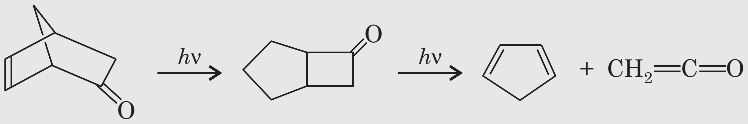
(*iv*)



$CH_3-\underset{\underset{O}{\|}}{C}-\triangleleft \xrightarrow{h\nu} CH_3-\underset{\underset{O}{\|}}{C}-CH{=}CH-CH_3$

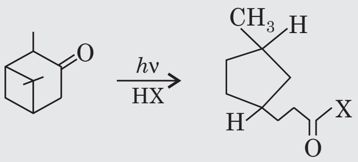
[**Hint:** Norrish Type II reaction].

(*v*)

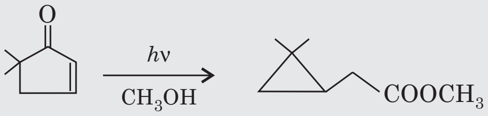


12. Suggest mechanism for the following photoreactions:

(*i*)



(*ii*)



[**Hint:** Formation of ketene derivative *via* α-cleavage followed by addition of HX in I and CH_3OH in II].

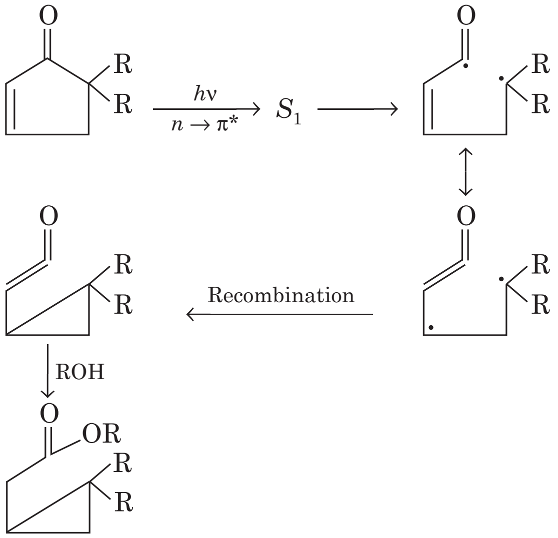
8

CHAPTER

Photo Rearrangements

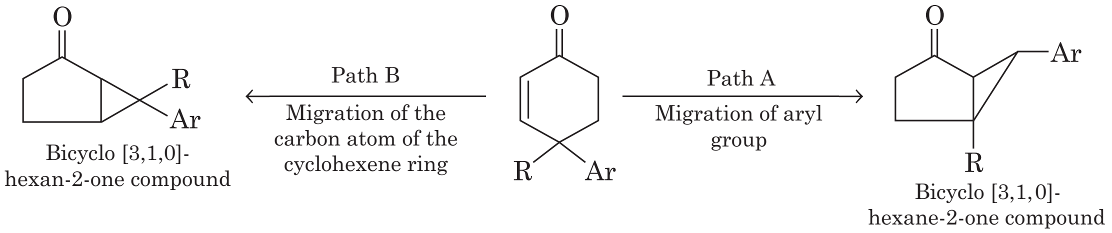
8.1 PHOTO REARRANGEMENT OF CYCLOPENTENONE

Cyclopentenone mainly gives α-cleavage reaction and | 2 + 2 | cycloaddition reactions. 5, 5-Disubstituted derivatives undergo rearrangement reaction to the cyclopropyl ketone. The rearrangement arises from the $n \rightarrow \pi^*$ singlet state and has to be carried out in dilute solution to prevent dimerisation. The substrate first undergoes Norrish Type I cleavage leading to the formation of a diradical. Recombination of this diradical leads to the formation of ketene. Ketene reacts with protic nucleophilic solvent to give adduct.



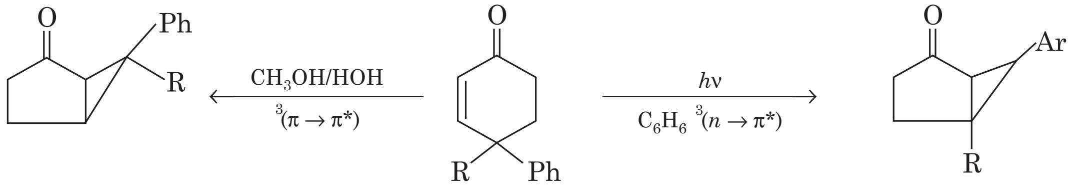
8.2 CYCLOHEXANONE REARRANGEMENTS

α, β-Unsaturated cyclohexanones give two type of rearrangements. These rearrangements are possible when bimolecular reactions (cycloadditions and dimerisations) are suppresed by the use of dilute solutions. The two prominent rearrangements are the di-π-methane type rearrangement (path A) and the lumiketone rearrangement (path B). The rearrangements are carried out mainly in the presence of *tert*-butyl alcohol.



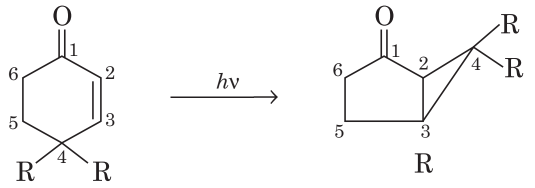
Di-π-methane type rearrangement arises by 1, 2-migration of an aryl group. Lumiketone rearrangement arises without the migration of a group. In this case the carbon atom of the cyclohexene ring migrates. Migration of aryl group of position-4 leads the formation of bicyclo [3, 1, 0] hexen-2-one (lumiketone). Similarly migration of carbon atom of the ring (*i.e.,* migration of C-5 ring carbon atom) leads skeletal change. This skeletal change also gives bicyclo [3, 1, 0]-hexen-2-one derivative.

Both type of rearrangements can be sensitised using propiophenone or quenched using naphthalene. This shows that both reactions proceed via triplet excited species. The rearrangement with ring migration occurs from a (π, π*) triplet excited state, whereas rearrangement with aryl migration occurs from an (*n*, π*) triplet excited state. This is supported by the observation that a 4-alkyl-4-aryl cyclohexenone undergoes rearrangement with aryl migration in benzene (*i.e.*, non polar solvent) but with ring migration in aqueous methanol (polar protic solvent).

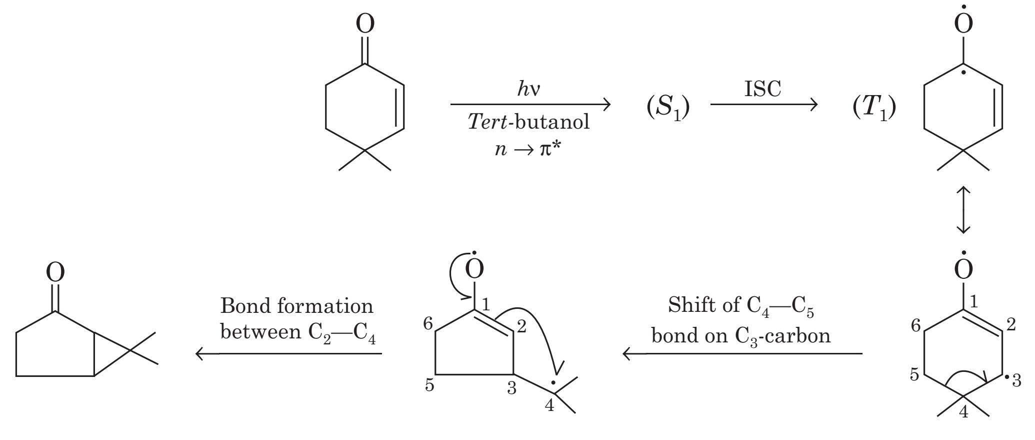


8.2.1 Lumiketone Rearrangement

Lumiketone rearrangement is mainly given by 4, 4-dialkyl cyclohexenones which involves the shift of the C_4—C_5 bond to C-3 and formation of a new C_2—C_4 bond.

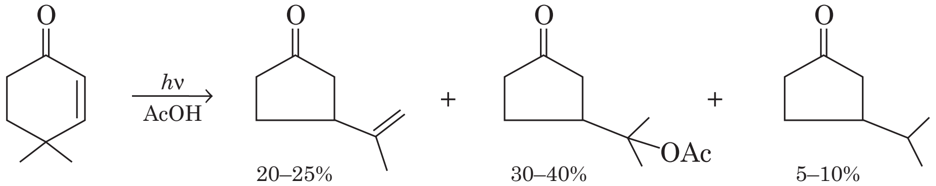


The mechanism favoured by some workers involves a radical path shown in Scheme 1 for the transformation of 4, 4-dimethyl-2-cyclohexenone into 6, 6-dimethyl bicyclo [3, 1, 0]-hexan-2-one, on photolysis in *tert*-butanol.



Scheme 1

As far as this molecular transformation is concerned, change of solvent to acetic acid has profound effect on the products formed. Irradiation of enone in acetic acid gives mainly the ketoacetate as well as rearrangement and elimination products.



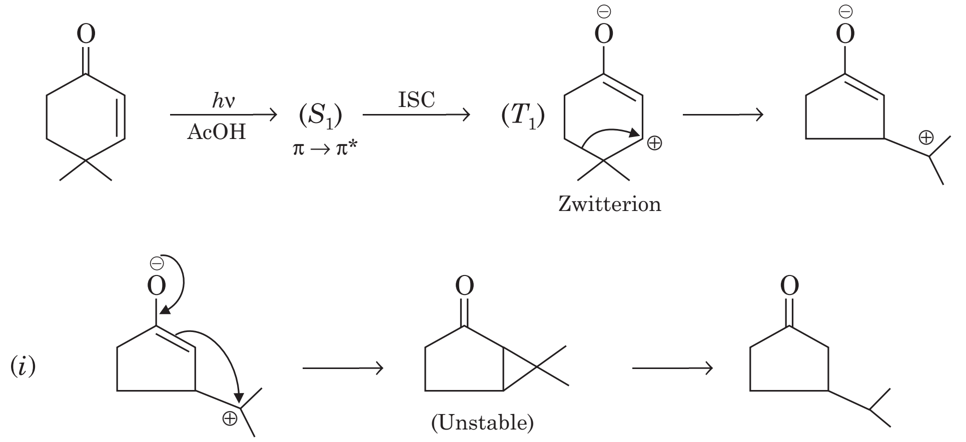
20–25%
(1)

30–40%
(2)

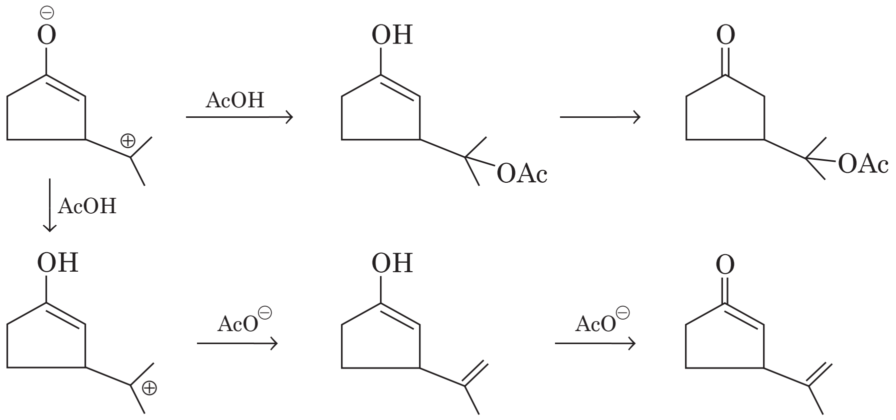
5–10%
(3)

Lumiketone is not isolated from the reaction mixture because it is unstable to light in the presence of acetic acid and is readily converted into 2-isopropylcyclopent-2-en-1-one.

It is proposed that an $n \rightarrow \pi^*$ state favours radical intermediate in *tert*-butanol or in non-polar solvent (Scheme 1) and $\pi \rightarrow \pi^*$ state predominantly favours Zwitterion intermediate in acetic acid (Scheme 2).



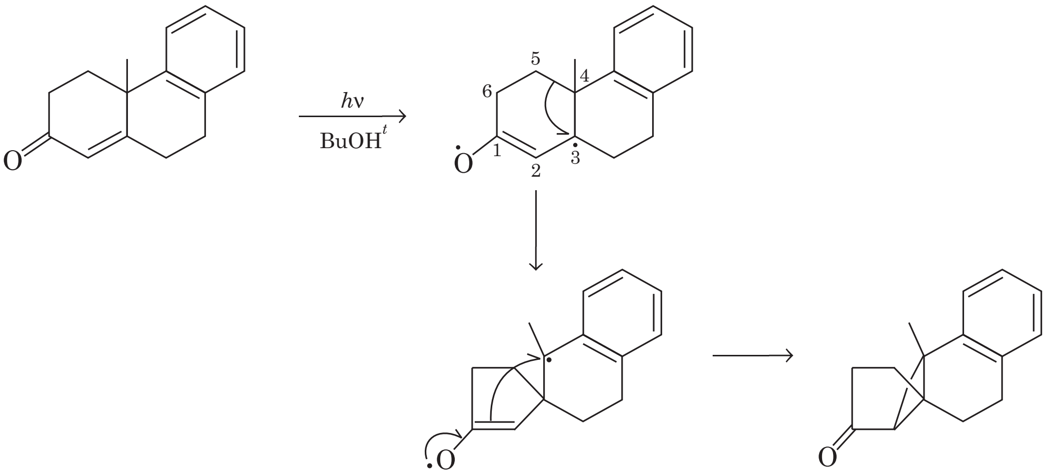
(*ii*)



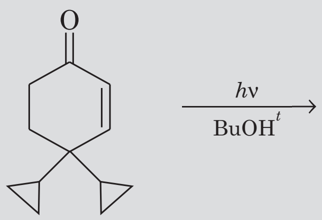
Scheme 2

This rearrangement is stereospecific. Optical activity at C-4 is atleast partially retained in the product in some cases. This suggests that the bond-forming steps in the reaction sequence occur at the same time as, or very shortly after, the bond breaking steps.

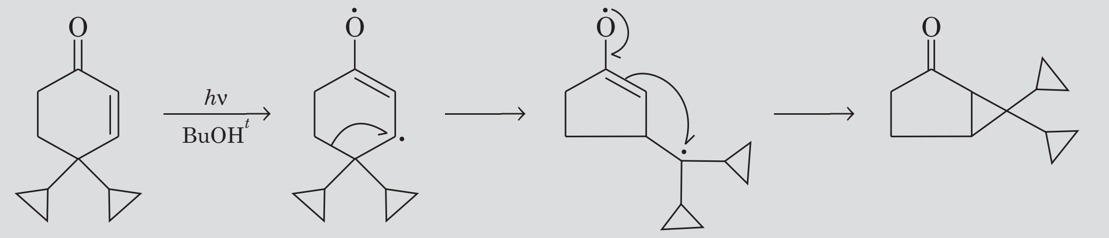
This reaction is quite general and also proceeds in the case of some 4-alkyl-4-arylcyclohexenones.



Problem 1: *Complete the following reaction:*



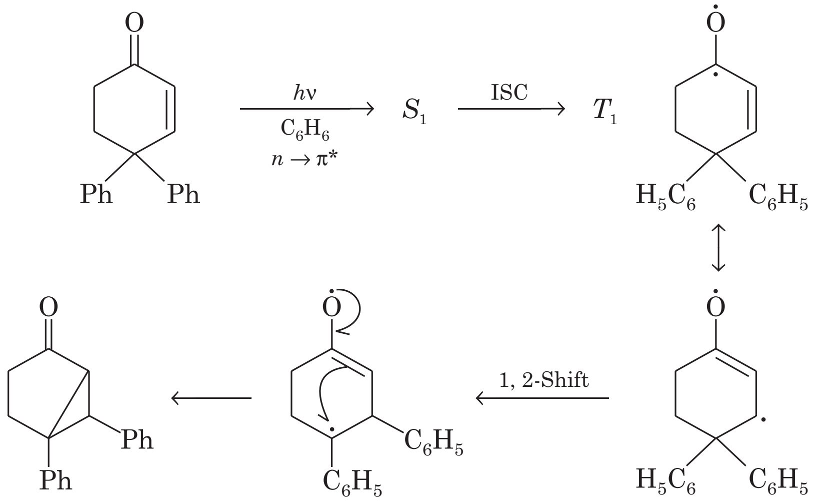
Solution:



8.2.2 Di-π-Methane Type Rearrangement

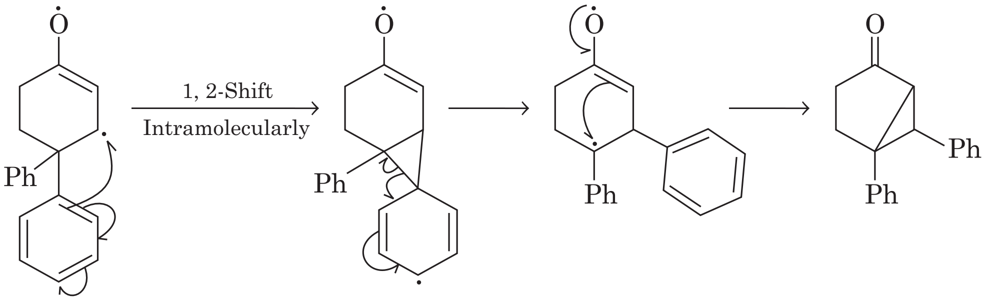
Di-π-methane type rearrangement is given by 4, 4-diarylcyclohexenones. This rearrangement is generally carried out in the presence of polar solvents. The rearrangement with aryl migration occurs from an $n \rightarrow \pi^*$ triplet excited state in the presence of *tert*-butanol. 4, 4-Diarylcyclohexenones undergo this rearrangement which involves the migration of aryl group from C-4 to C-3 position and formation of a new $C_2—C_4$ bond. The rearrangement is totally analogous to the Di-π-methane rearrangement except that the enone rearrangement can be brought about by $n \rightarrow \pi^*$ excitation which is not possible in the 1, 4-dienes.

The mechanism of this reaction involves a radical path shown in Scheme 3.



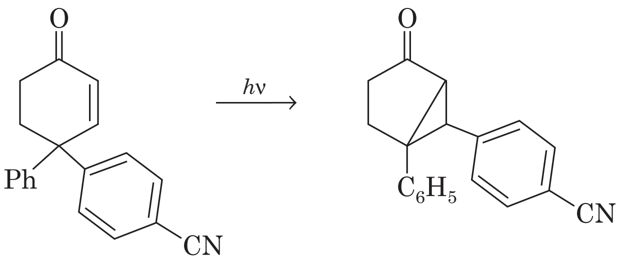
Scheme 3

1, 2-Shift in Scheme 3 takes place intramolecularly as follows in Scheme 4.

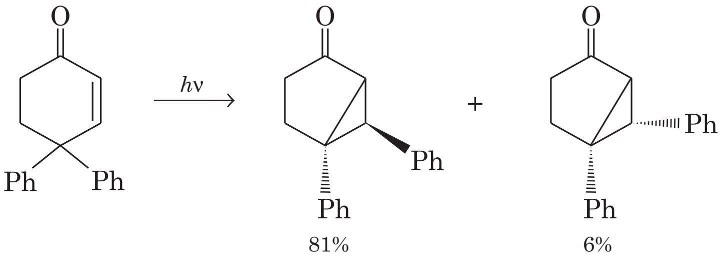


Scheme 4

In compounds in which the two aryl groups are substituted differently, it is found that substituents which stabilise radical character favours migration. Thus, the *p*-cyanophenyl substituent migrates in preference to the phenyl substituent.

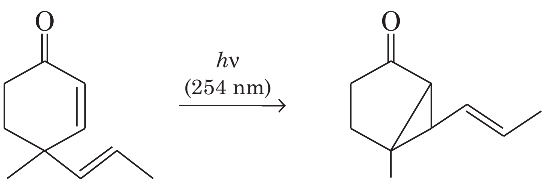


One of the most important feature of the rearrangement is the remarkable stereospecificity of the process with a 140 : 1 preference for the formation of the *trans* isomer rather than *cis*.



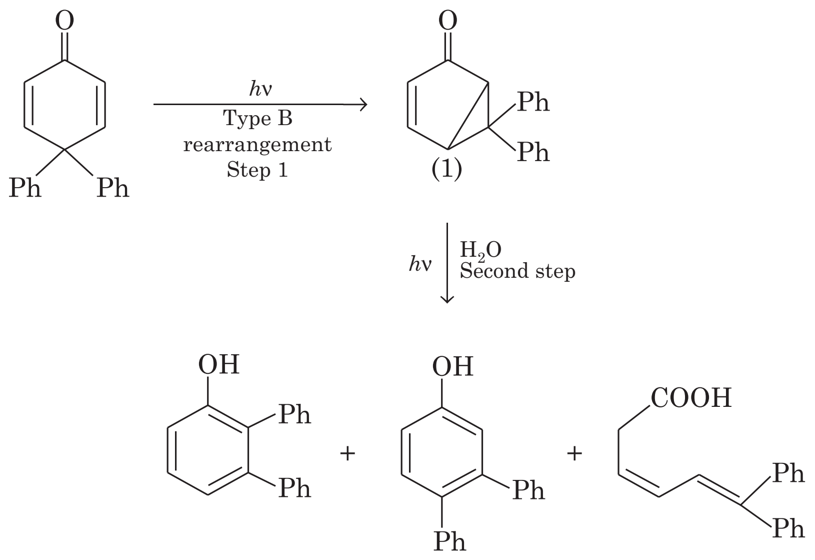
In some cases rearrangement takes place *via* formation of zwitterion intermediate particularly in the presence of *tert*-butanol.

This type of rearrangement is also given by C-4 vinyl substituted enones in which migration of vinyl group takes place.



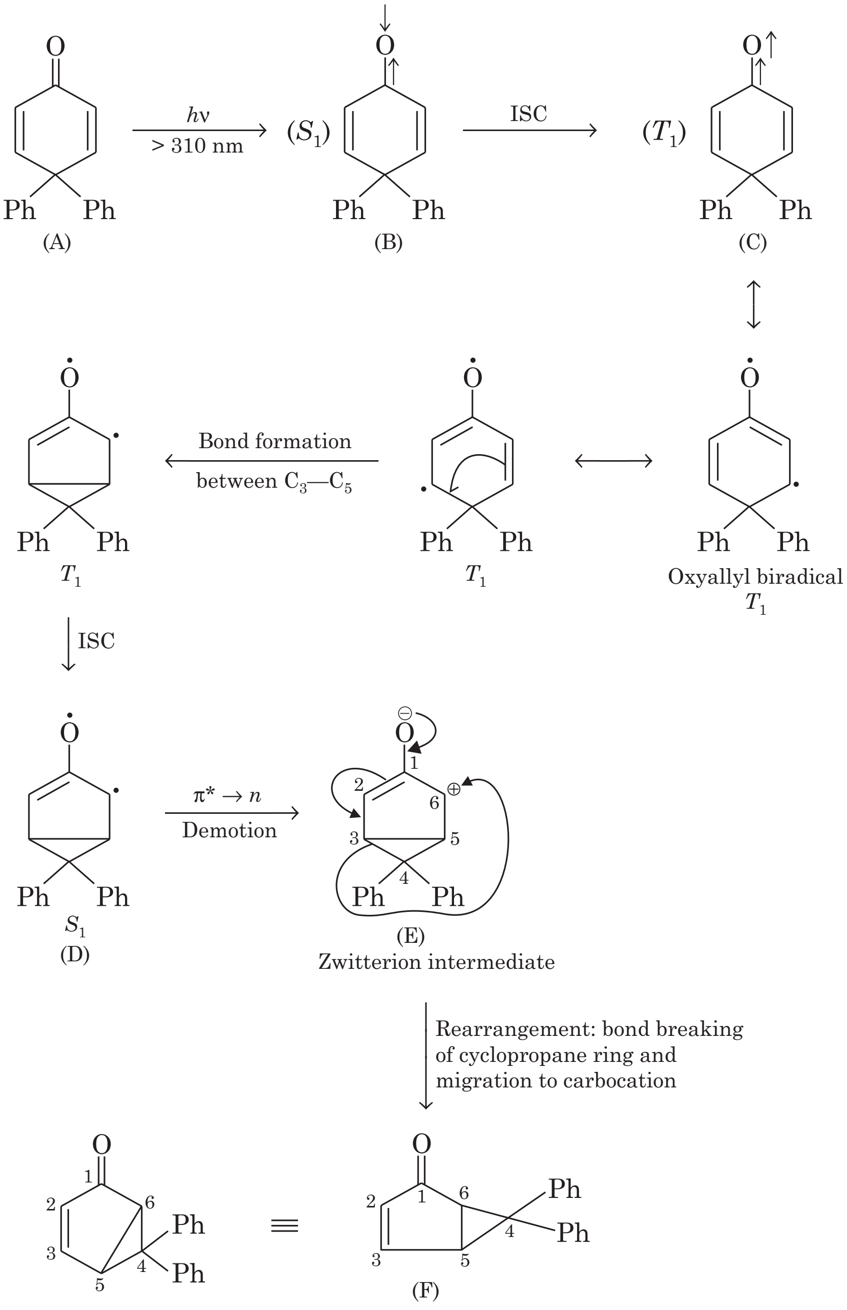
8.3 REARRANGEMENT OF DIENONES

One of the most important dienones is the cross-conjugated dienones for photochemical rearrangements. 4, 4-Disubstituted cross-conjugated dienone gives Type B rearrangement. In the Type B rearrangement of cross-conjugated 4, 4-disubstituted-2, 5-cyclohexadienones, the first photochemical step occurs with a high quantum yield (ϕ = 0.85).



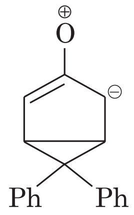
The efficiency of the second step is substantially lower (ϕ = 0.013). The formation of bicyclo [3, 1, 0]-hex-3-en-2-one is formally analogous to a 1, 2-acyl shift and occurs from the T_1 ($n \rightarrow \pi^*$) state. In all reported cases reaction proceeds from the $n \rightarrow \pi^*$ triplet state. The unsaturated acid arises from the S_1 state of the bicycloenone (1). The phenols are produced from the T_1 state of the bicycloenone (1).

Zimmerman found that 4, 4-diarylcyclohexa-2, 5-dienones undergo a rearrangement with velocity four times more than the 4, 4-dialkyl-2-cyclohexenone. The reactive excited state is the $n \rightarrow \pi^*$ triplet state of the dienone. The reaction is thought to involve C-3,-C-5 bond formation in the excited state followed by inter system crossing and electron deactivation to give Zwitterion intermediate. This Zwitterion intermediate is then rearranges to the observed bicyclic product. The electron deactivation process is known as demotion. The reaction takes place in the presence of sensitiser. The reaction is quenched by the quencher. In this reaction photophosphorescence phenomenon is observed. These results confirm that excited state is triplet and demotion process ($\pi^* \rightarrow n$) takes place during the course of the reaction. According to the Zimmerman, the mechanism can be represented as follows (Scheme 5):

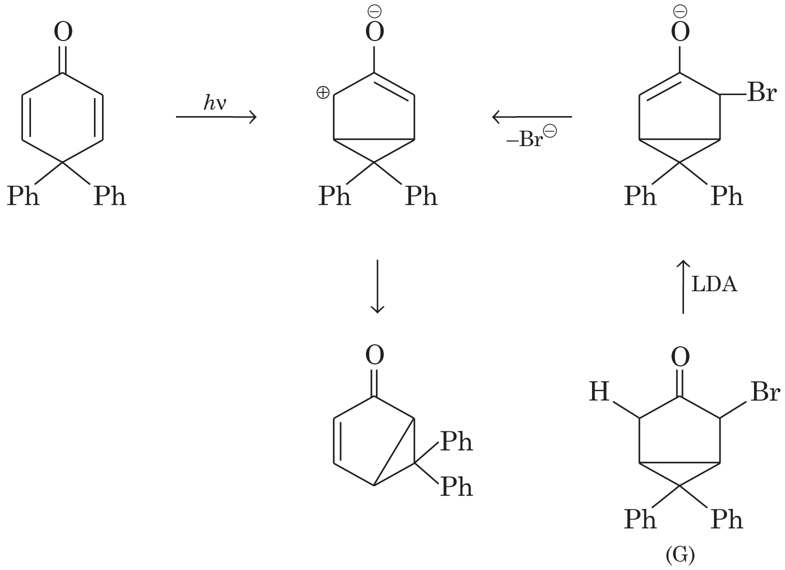

hν
> 310 nm
(S1)
ISC
(T1)
(A)
(B)
(C)
Bond formation
between C3—C5
T1
T1
Oxyallyl biradical
T1
ISC
S1
(D)
π* → n
Demotion
(E)
Zwitterion intermediate
Rearrangement: bond breaking
of cyclopropane ring and
migration to carbocation
(F)
Ph

Scheme 5

The necessity of $\pi^* \rightarrow n$ electron demotion step arises because the π (*pi*) system in the $n \rightarrow \pi^*$ state is electron rich but the observed rearrangements are characteristic of migrations to electron deficient centres. If demotion step will not take place then Zwitterion has the following structure:

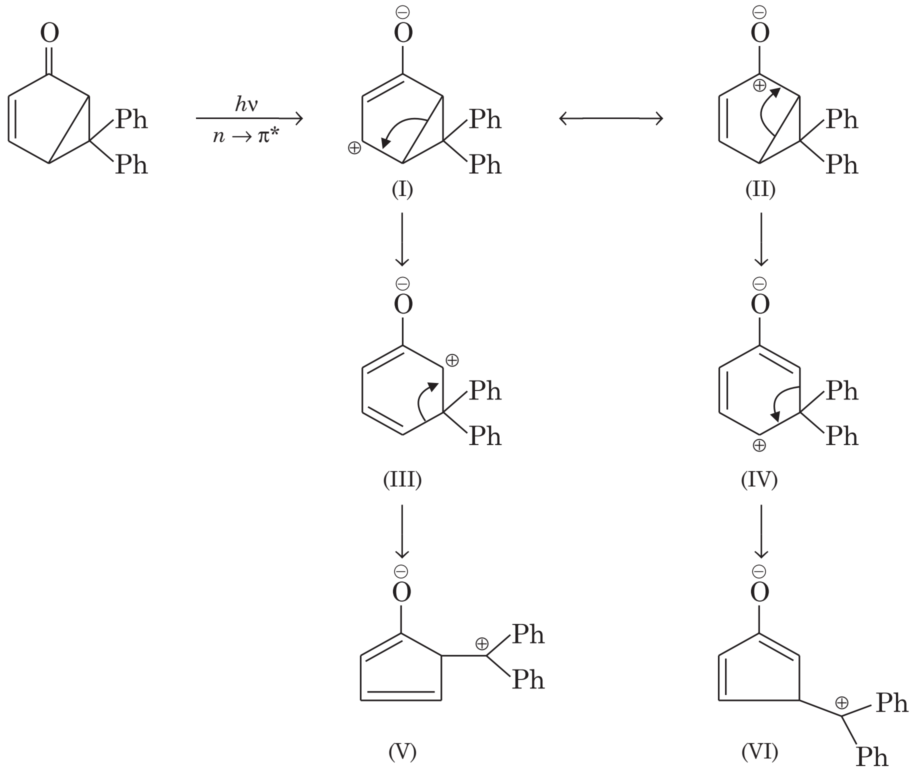


Thus reactive ground state Zwitterion (E) is an intermediate of the rearrangement and this Zwitterion rearranges to the observed product. Conformation of the participation of Zwitterion intermediate in the rearrangement is provided by the thermal preparation of the photoproduct by the reaction of the 2-bromoketone (G) (Scheme 6):



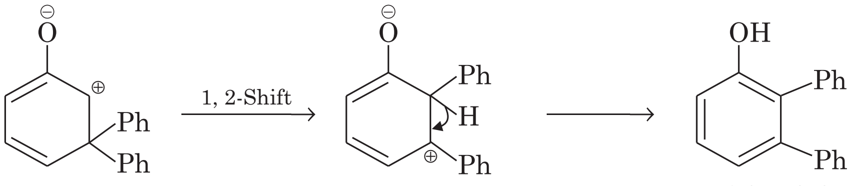
Scheme 6

Returning now to the example under discussion, we see that the product of the rearrangement can itself react further since it still have enone system capable of undergoing excitation. The following six structures represented the various states of electron distribution.

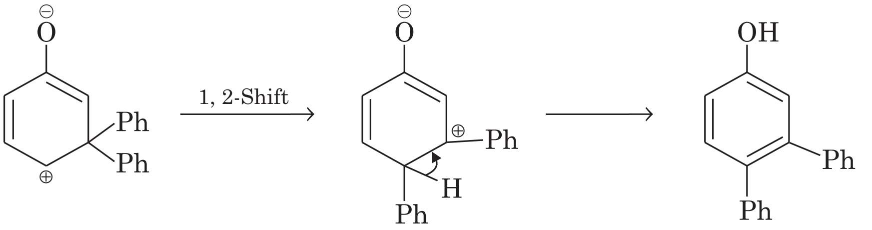


Among these (I) and (II) were proposed to be precursors in the formation of the starting material itself and they should now lead to new products.

(III) and (IV) can undergo phenyl migration leading respectively to 2, 3 and 3, 4-diphenyl phenols. Both of these phenols have been isolated from the reaction mixture.



2, 3-Diphenyl phenol

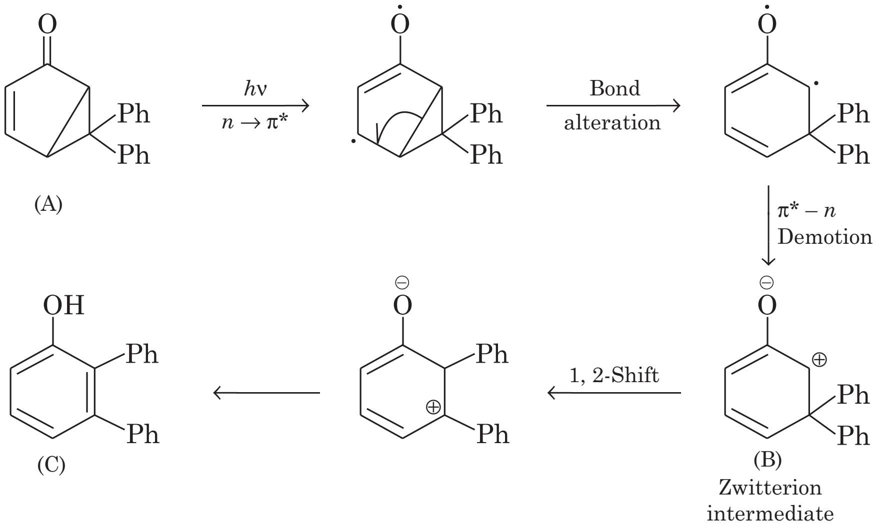


3, 4-Diphenyl phenol

When photolysis is carried out in aqueous dioxane, 2, 3-diphenylphenol is the major product and 3, 4-diphenyl phenol is the minor product. In the presence of acetic acid equal amounts of 2, 3- and 3, 4-disphenylphenols are obtained. One possible reason for this difference is the better electron delocalisation with (III) than with (IV) in the dioxane. In acetic acid protonation of oxygen occurs and delocalisation is less significant factor.

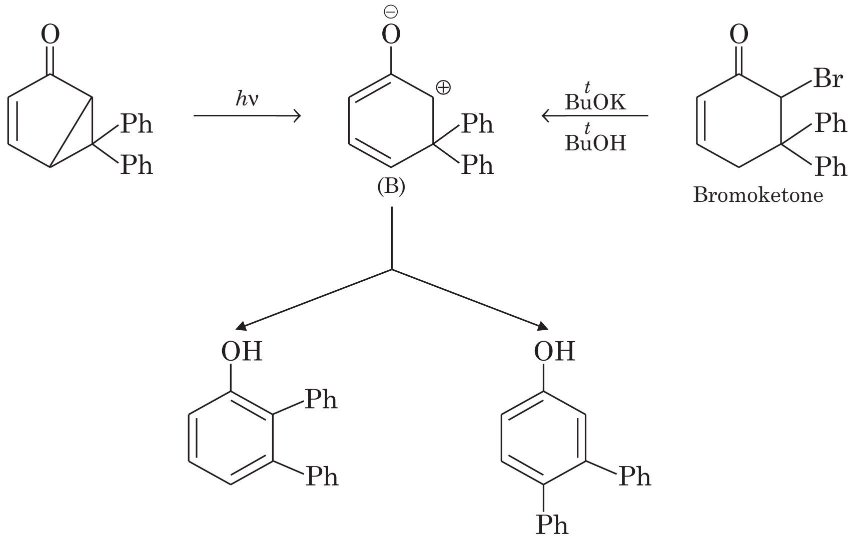
Structure (V) can rearrange to a ketene and forms an acid in aqueous medium but (VI) cannot.

In terms of mechanism given by Zimmerman, the various steps can be represented in Scheme 7.

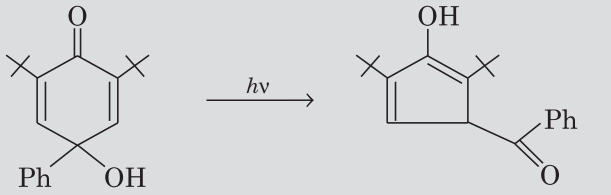


Scheme 7

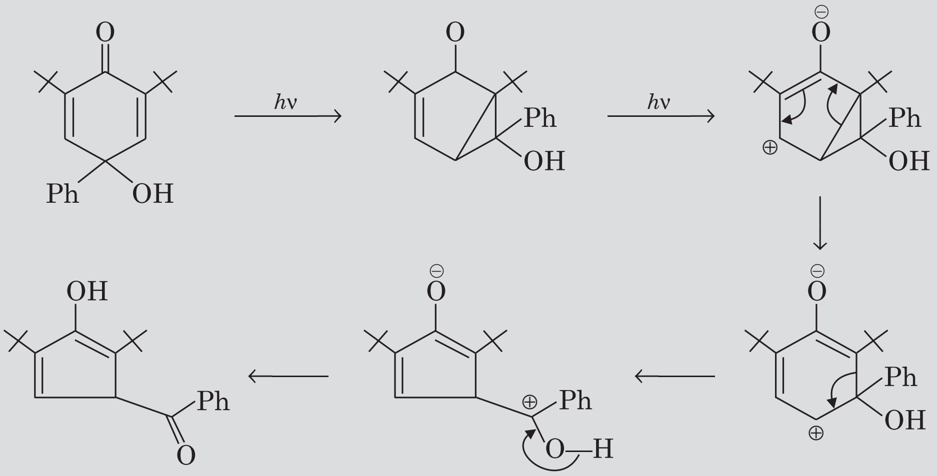
The evidence for the Zwitterion (B) being an intermediate in the reaction follows from the rearrangement of independently generated Zwitterion by non-photochemical means to the same product (C).



Problem 2: *Give mechanism of the given reaction:*



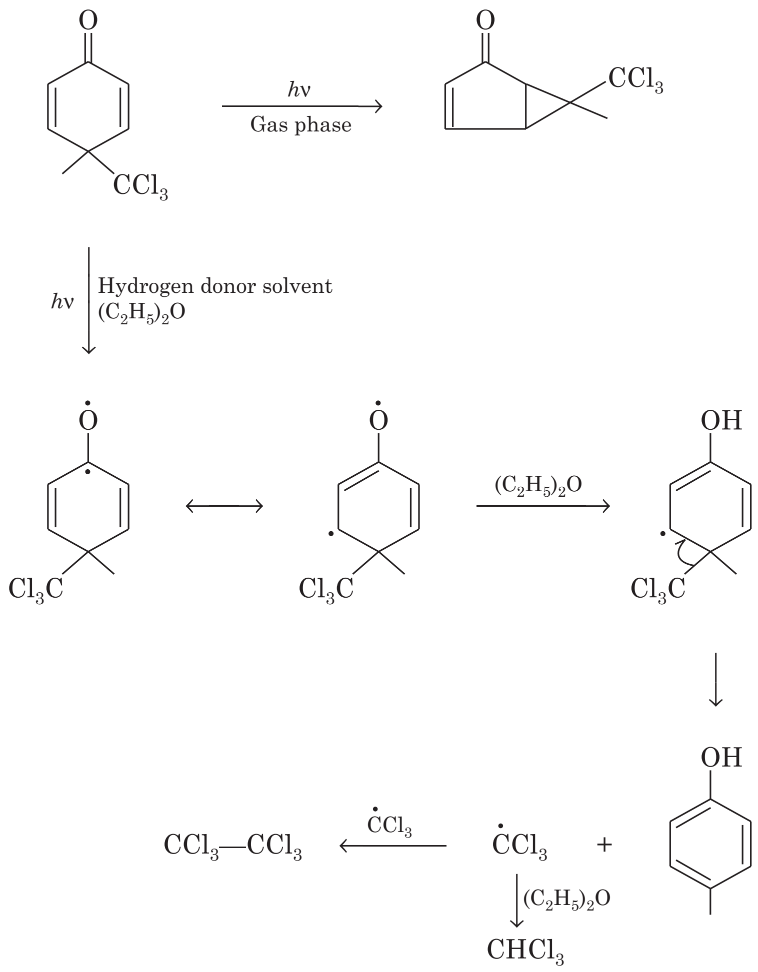
Solution:



Cross-conjugated dienone in the gas phase undergoes rearrangement by $n \rightarrow \pi^*$ excitation.

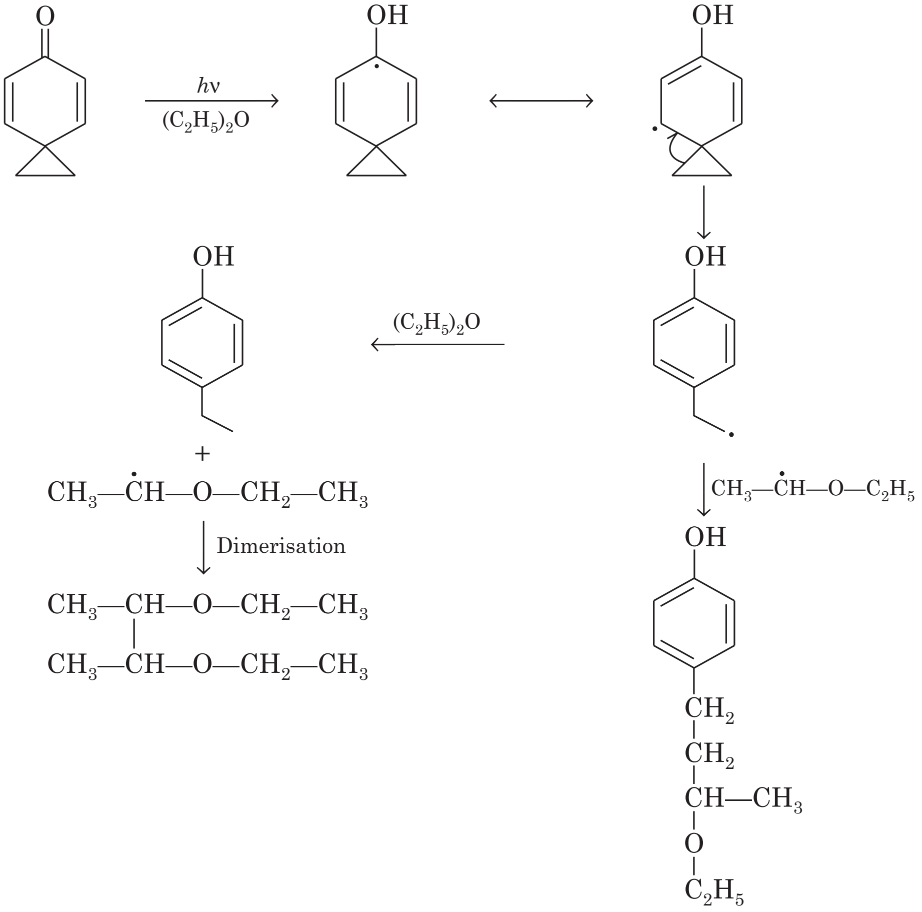
Rearrangement of 4, 4-disubstituted-2, 5-cyclohexadienones undergo rearrangement *via* formation of Zwitterion reaction intermediate in the solution. The rearrangement of these substrates in the gas phase occur *via* formation of biradical intermediates. The rearrangement in gas phase closely resembles the di-π-methane rearrangement.

A cyclohexan-2, 5-dienone with a good leaving group on C-4 undergoes a different reaction in solvents with a readily abstracted hydrogen atom. Intermolecular hydrogen abstraction followed by the elimination of the group from C 4 leads a phenolic product (Scheme 8).

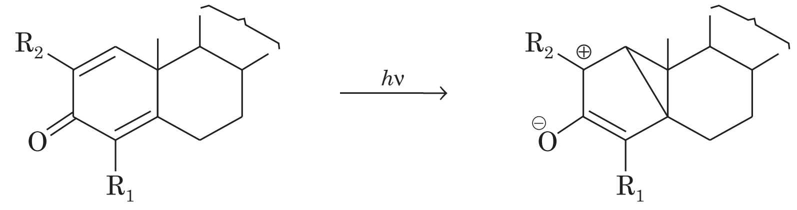


Scheme 8

Radical intermediates are also involved in the photochemical reaction of the spirocyclopropyldienone. This also gives phenolic products in the solvent which is a good source of hydrogen atom.

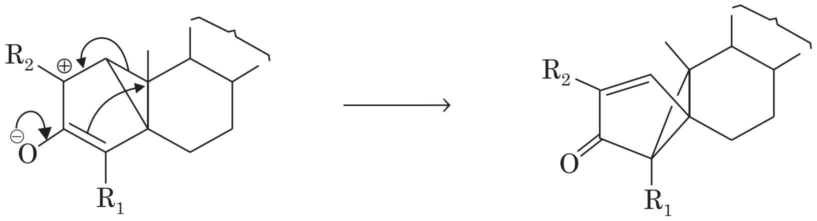


Natural products particularly terpenoids and steroids having cross-conjugated ketone system undergo dienone rearrangement *via* formation of Zwitterion intermediate.



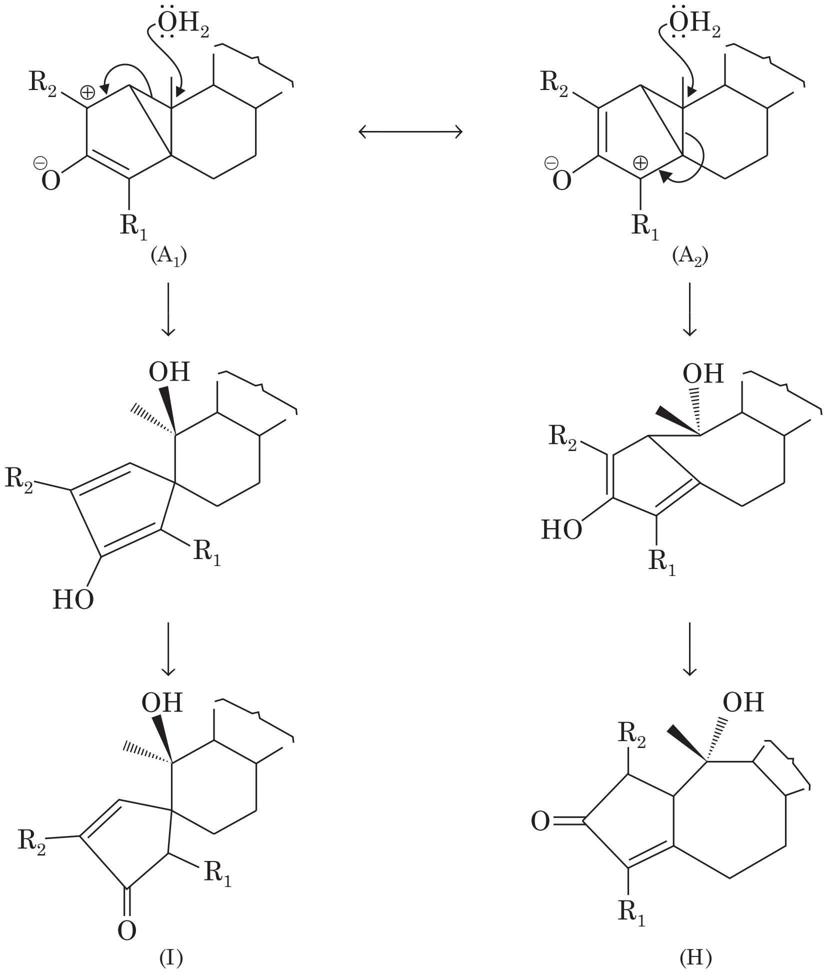
Zwitterion intermediate

In the presence of dioxane Zwitterion converts into lumiketone.



Lumiketone

Zwitterion intermediate gives two isomeric ketones (H) and (I) in acetic acid medium (45% CH_3COOH).



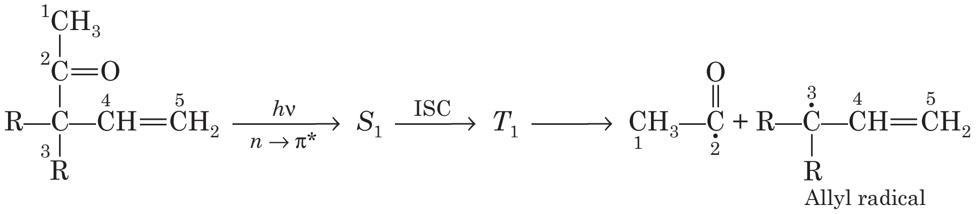
Stability of intermediate cation (A_1) and (A_2) determines the reaction path in acidic medium. When R_1 is electron donating group and R_2 is H then major product is fused ring ketone (H). Similarly if R_2 is electron donating group and R_1 = H than major product is spiran ketone (I).

8.4 PHOTO REARRANGEMENTS OF β, γ-UNSATURATED KETONES

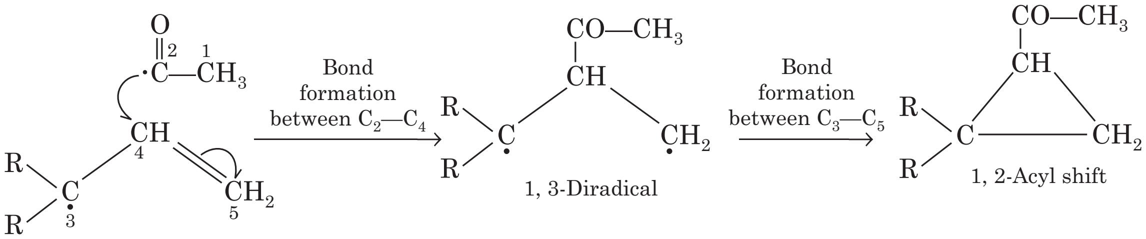
β, γ-unsaturation in a carbonyl compound promotes α-cleavage because of allylic stabilisation of the radical produced. β, γ-Unsaturated ketones, in addition to undergoing normal photochemical reactions of saturated ketones, undergo rearrangement reactions. Their irradiation induces non-concerted sigmatropic reactions that are directed by the electronic configuration and multiplicity of the excited state. The rearrangements are 1, 2-acyl shifts (oxa-di-π-methane rearrangements) which occur from the lowest triplet state of $n \rightarrow \pi^*$ transition and 1, 3-acyl, shifts which occur from direct irradiation from the S_1 or T_2 ($n \rightarrow \pi^*$) state with formation of an acyl-alkyl radical pair. It has been suggested that, while at higher temperature the radical pair is formed predominantely from the S_1 state, at lower temperature the T_2 state is involved. Although both rearrangements involve biradical or biradical pair intermediates, they are generally stereospecific.

8.4.1 Mechanism of 1, 2-Acyl Shift

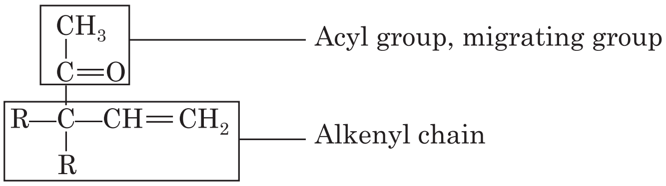
In this rearrangement the primary step is the α-cleavage which leads the formation of acyl radical and allyl radical.



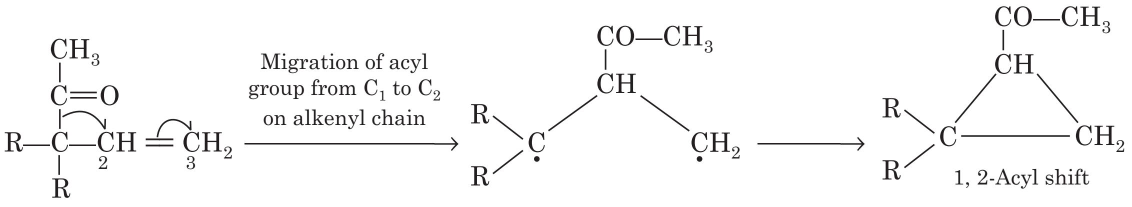
In the next step C_2—C_4 bond formation takes place between acyl radical and allyl radical which leads to the formation of 1, 3-diradical.



For 1, 2-acyl shift the substrate can be divided into two parts, the alkenyl chain and the acyl group which is migrating group.



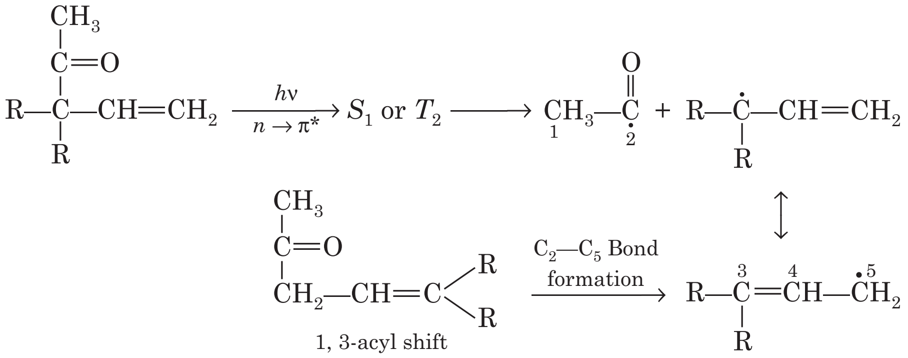
1, 2-Acyl shift in short can be represented as follows:



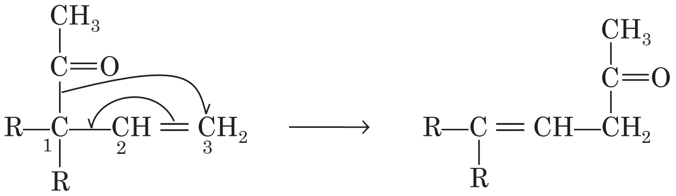
Since acyl group migrates from carbon-1 to carbon-2 of the alkenyl chain, the rearrangement due to this reason is known as 1, 2-acyl shift. 1, 2-Acyl shift given by β, γ-unsaturated ketones is known as oxa-di-π-methane rearrangement. 1, 2-acyl shift leads the formation of cyclopropane derivative.

8.4.2 Mechanism of 1, 3-Acyl Shift

In this rearrangement too the primary step is α-cleavage which leads the formation of acyl radical and allyl radical.

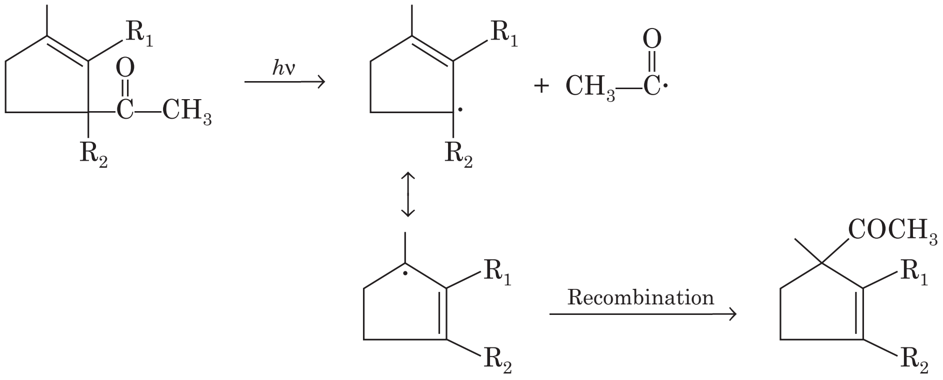


1, 3-acyl shift in short can be represented as follows:

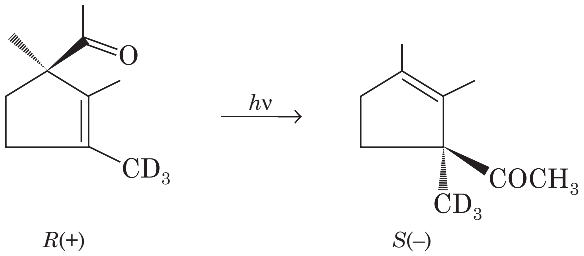


In this rearrangement migrating group migrates from C-1 to C-3 of the alkenyl chain. Due to this reason, the rearrangement is known as **1, 3-acyl shift.** 1, 3-acyl shift leads isomerisation.

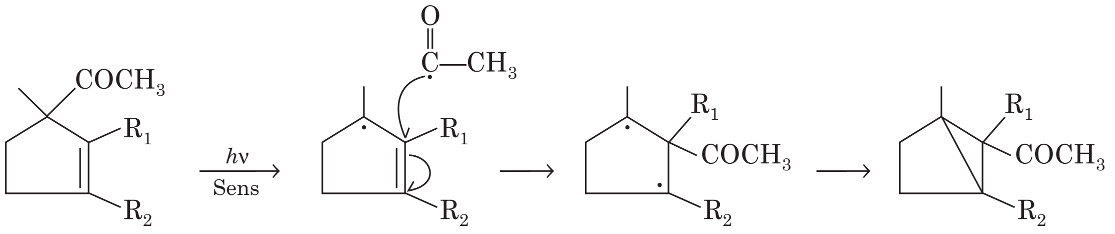
2-cyclopentyl methyl ketones were the first examples of the rearrangement of β, γ-enones. Photo CIDNP and radical trapping experiments indicate that the 1, 3-acyl shift is a radical process that proceeds predominantly *via* cage radical pair which also leads to α-cleavage products.



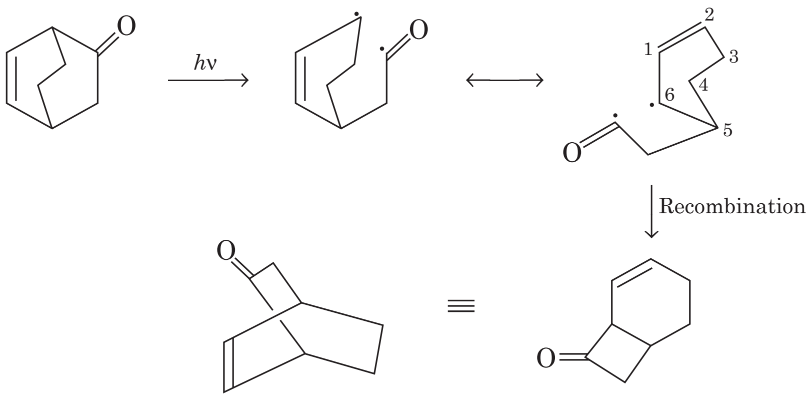
The stereospecificity of this reaction was shown by the following examples:

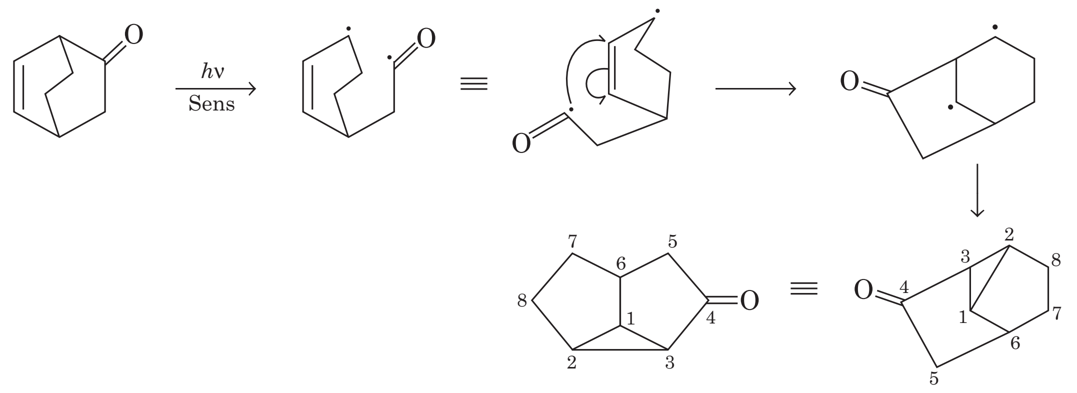


2-Cyclopentylmethyl ketones give 1, 2-acyl shift in the presence of triplet sensitiser.



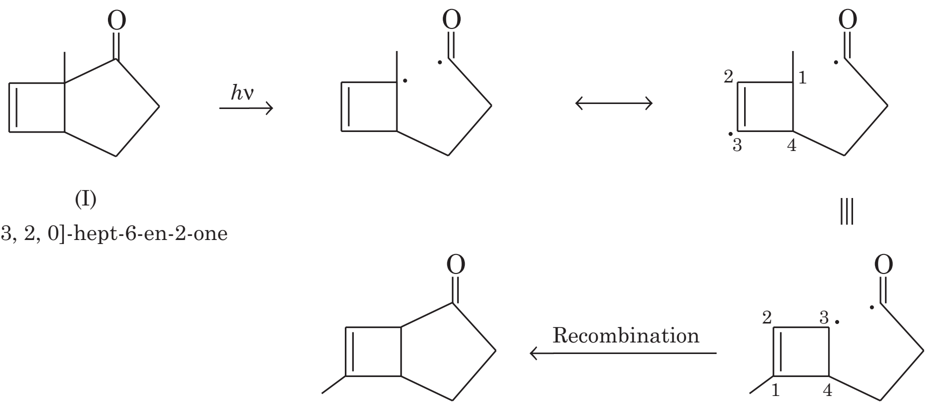
Similarly bicyclo [2, 2, 2] octenone gives 1, 3-acyl shift by direct irradiation. In the presence of triplet sensitiser it gives 1, 2-acyl shift.





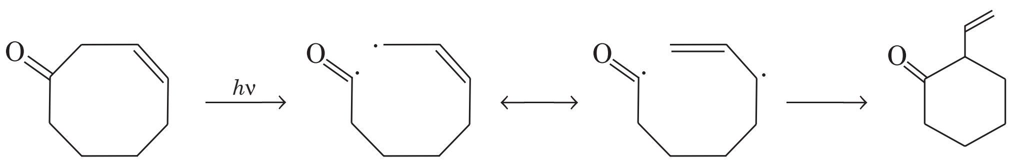
Cyclic β, γ-unsaturated ketones undergo both 1, 2 and 1, 3-acyl shifts. 1, 2-acyl shift leads to a cyclopropane derivative, while a 1, 3-shift leads isomerisation. Ring contraction and/or isomerisation is main character of 1, 3-acyl shift.

Bicyclic ketone (I) gives isomerisation by 1, 3-shift.



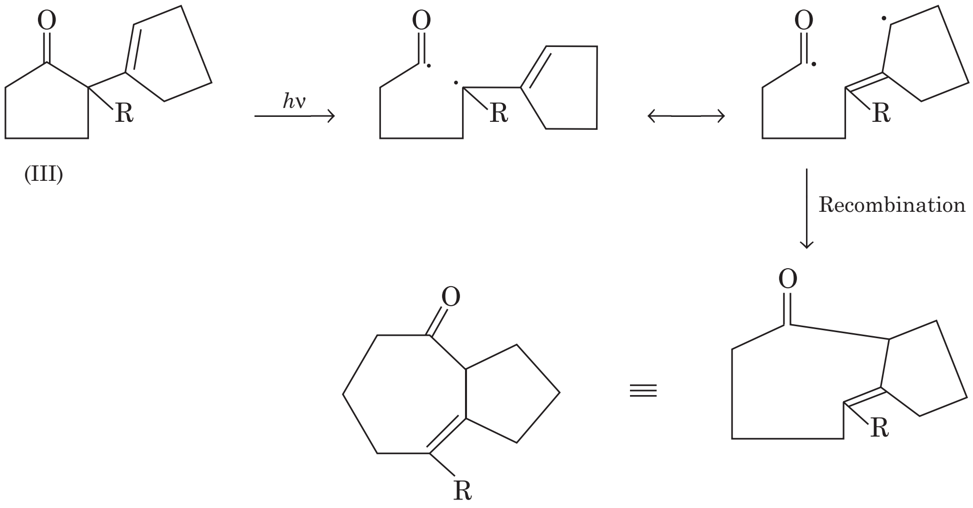
(I)
Bicyclo [3, 2, 0]-hept-6-en-2-one

On the other-hand compound (II) gives isomerisation as well as ring contraction reaction.



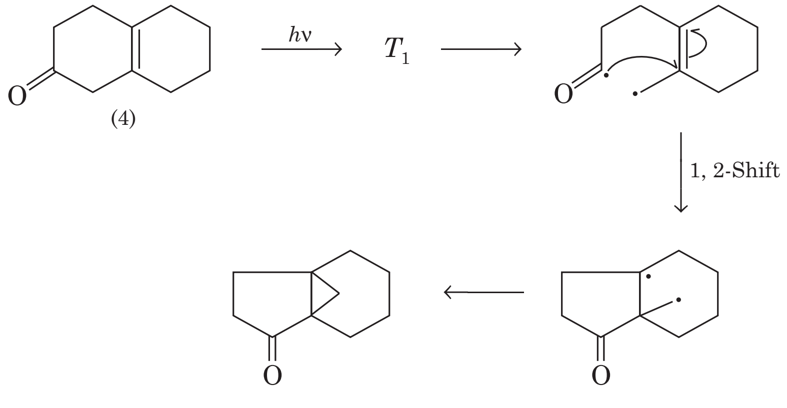
Cycloocta-3-enone
(II)

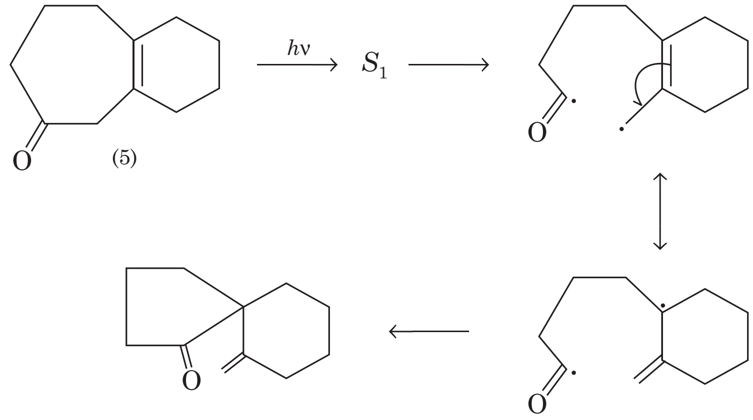
1, 3-Shift mainly results isomerisation and/or ring contraction. Sometimes it can also result in ring expansion. Compound (III) gives ring expansion 1, 3-shift.



(III)

The photolysis of homologous enones (4) and (5) are remarkable. Compound (4) gives only 1, 2-acyl shift whereas compound (5) gives only 1, 3-acyl shift.





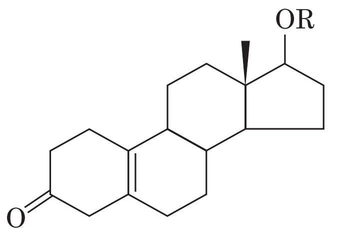
The above example shows that oxa-di-π-methane (ODPM) rearrangement is generally much more efficient in rigid than in non-rigid systems. Similarly 1, 3-acyl shift is generally much more efficient in non-rigid systems.

Since enone (4) has a much more rigid structure than enone (5), the plane of the carbonyl group and the double bond in (4) are separated. As a result, α-cleavage in the S_1 state does not compete efficiently with intersystem crossing to T_1, from which α-cleavage occurs with the formation of a triplet biradical. Thus 1, 2-acyl shift occurs.

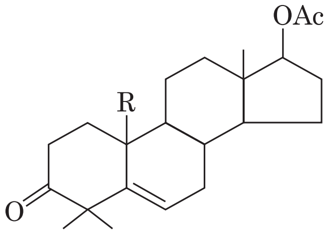
Enone (5) is a flexible molecule. Thus the overlap of carbonyl group and the double bond in enone (5) increases the efficiency of the α-cleavage. Thus it competes successfully with intersystem crossing from the S_1 state.

Generally seven membered enones (such as 5) in which double bond is present between fused carbons are flexible and gives 1, 3-acyl shift. On the other hand six-membered ring enones (such as 4) in which double bond is present between fused ring carbons are rigid and gives 1, 2-acyl shift. Other type of enones give 1, 2 as well as 1, 3-acyl shifts.

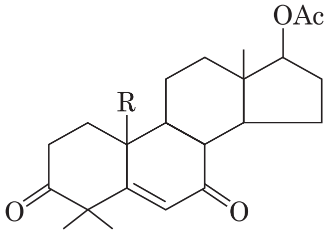
Some of the enones which gives only 1, 2-acyl shifts are as follows:



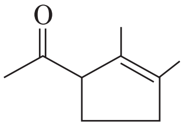
(A)



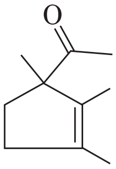
(B)



(C)

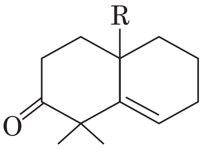


(D)

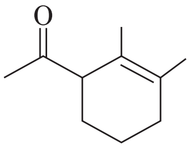


(E)

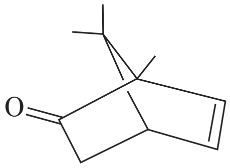
Examples of enones which gives 1, 3-acyl shifts are as follows:



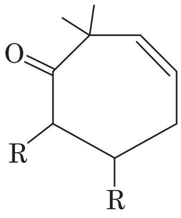
(F)



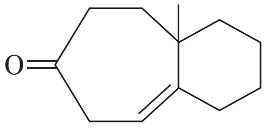
(G)



(H)

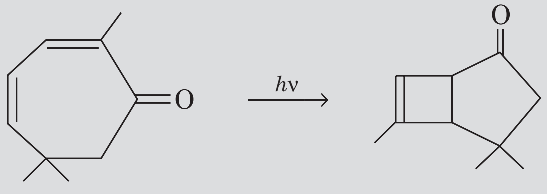


(I)



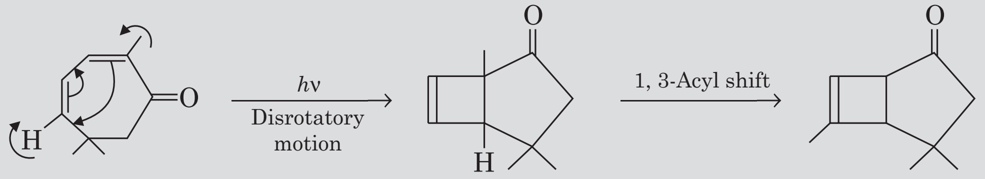
(J)

Problem 3: *Give mechanism of the given transformation:*



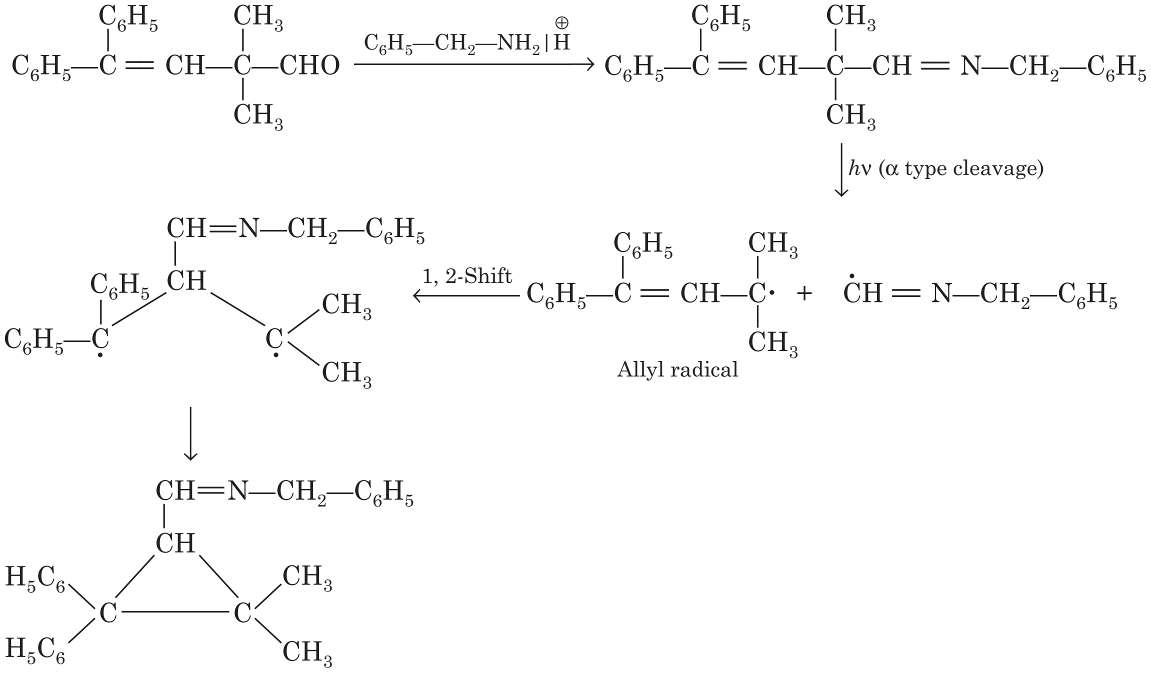
Eucarvone

Solution: Substrate can be treated as 1, 3-butadiene derivative. In the first step this will give electrocyclic ring closure reaction.



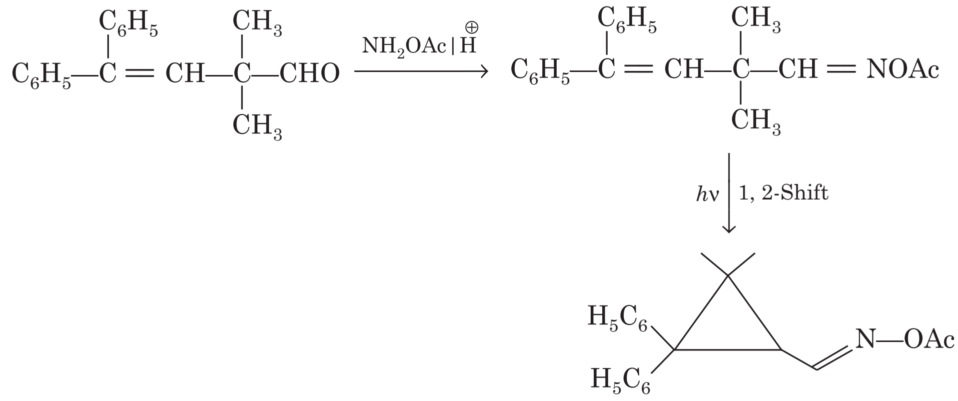
8.5 Aza-Di-π-METHANE REARRANGEMENT

1, 2-Acyl shift is given only by β, γ-unsaturated ketones. This rearrangement is not given by aldehydes. The failure of aldehydes to undergo 1, 2-acyl shift (*i.e.,* oxa-di-π-methane rearrangement) can be overcome by conversion of the aldehyde to an imine. Thus when aldehyde is converted to the imine and irradiated under sensitised conditions, the normal cyclopropane forming process takes place. The formation of the cyclopropane by this path is known as aza-di-π-methane rearrangement (Scheme 9).



Scheme 9

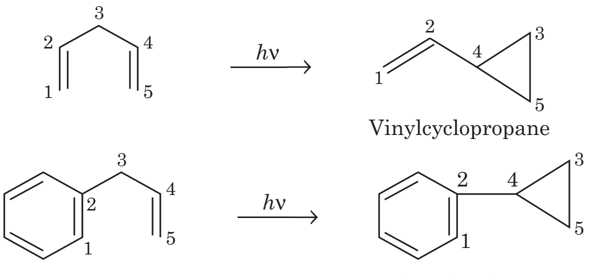
A similar path has also been shown to be involved with the oxime acetate.



$$C_6H_5—\overset{\overset{C_6H_5}{|}}{C}=CH—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO \xrightarrow{NH_2OAc \mid \overset{\oplus}{H}} C_6H_5—\overset{\overset{C_6H_5}{|}}{C}=CH—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH=NOAc$$

8.6 Di-π-METHANE (DPM) REARRANGEMENT

The most remarkable photochemical reaction of nonconjugated dienes is the di-π-methane rearrangement. This rearrangement is given by dienes having π (*pi*) system separated by an sp^3 hydridised carbon atom *i.e.,* 1, 4-pentadienes. The rearrangement is also given by 3-phenylalkenes in which one of the double bonds is replaced by benzene ring. di-π-methane rearrangement is also known as Zimmerman rearrangement or Zimmerman di-π-methane rearrangement. Irradiation of the substrate induces rearrangement to a vinylcyclopropane or phenylcyclopropane derivative.

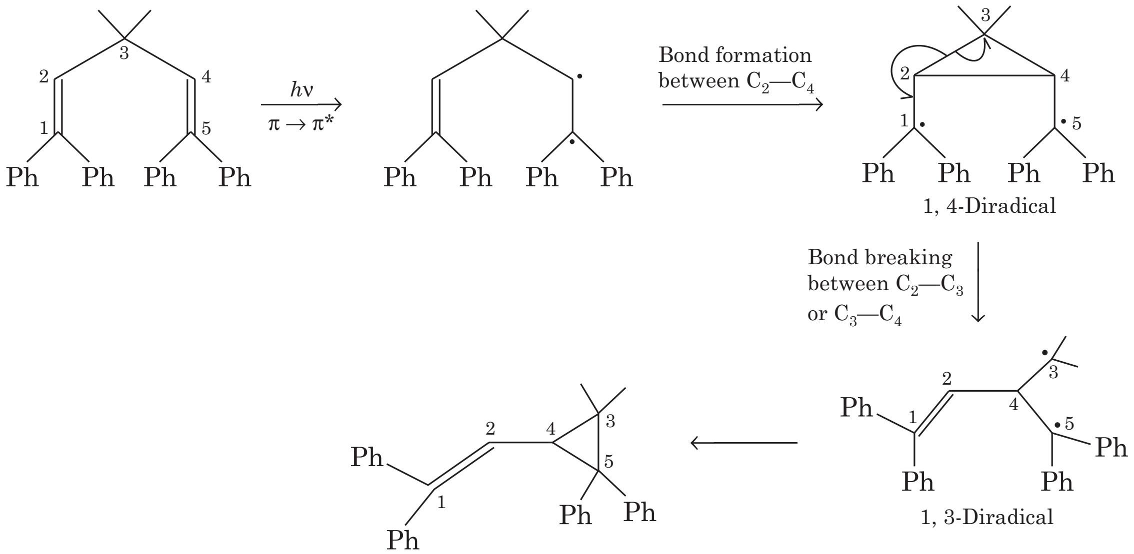


Vinylcyclopropane

Phenylcyclopropane

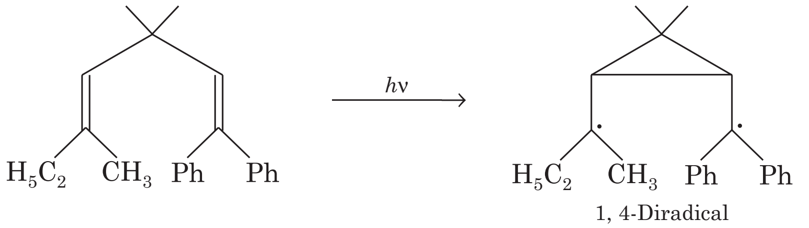
This rearrangement is found in both cyclic and acyclic dienes. The rearrangement of monocyclic and acyclic dienes occurs *solely from the singlet state*. Sensitised reaction of these substrates lead *cis-trans* isomerisation or | 2 + 2 | cycloaddition.

Experimental results show that di-π-methane rearrangement is concerted process, obeys the Woodward-Hoffmann rules, retains configuration on atom-1 and -5 (a result of disrotatory ring closure between C-3 and C-5), and inverts it on atom-3 (conrotatory mode). In actual practice the reaction is represented as one involving a 1, 4 and 1, 3-diradical intermediates in case of 1, 4-pentadiene since it is easier to follow the various steps necessary for the rearrangement (Scheme 10).

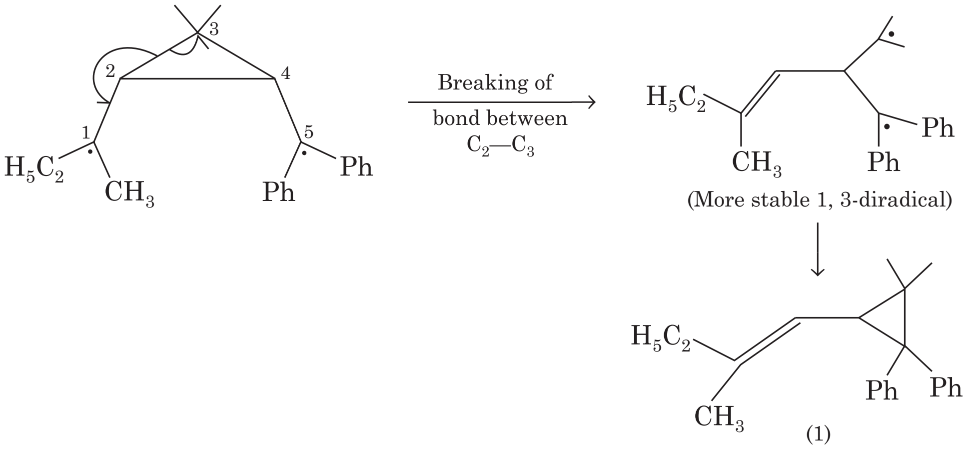


Scheme 10

Thus the di-π-methane rearrangement involves a rearrangement of the pentadiene skeleton with no alkyl or aryl group migration. Nevertheless, the reaction path that would involve the more stable diradical is always followed (Scheme 11).

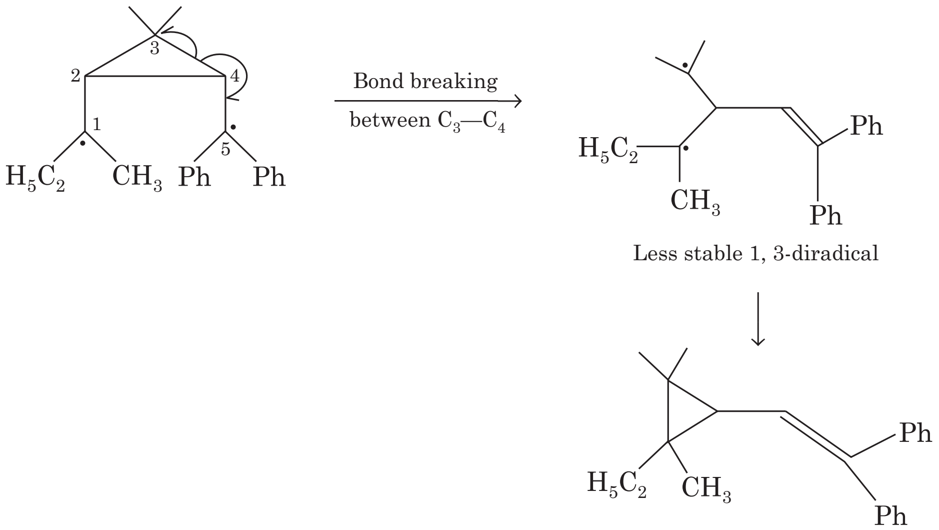


Route-*a*



(1)
(Sole product)

Route-*b*

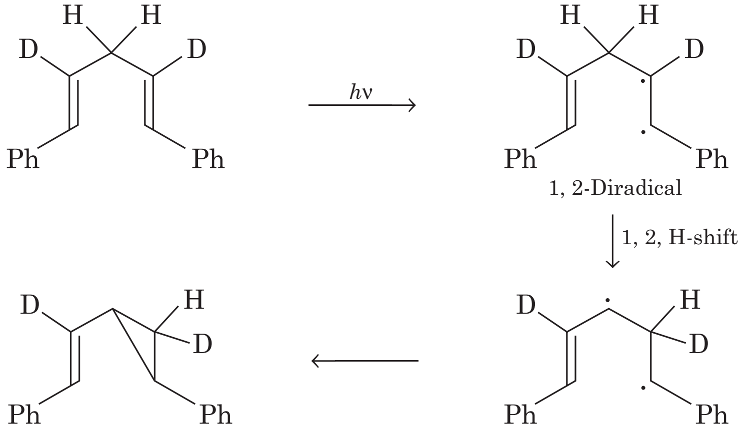


(2)
(Not observed)

Scheme 11

Formation of only one product (1) shows that there is retention of configuration at carbon-1. Thus *cis-trans* isomerisation of the bond C_1—C_2 must be slow by comparison with formation of cyclopropane derivative. Similarly formation of product (1) but not the (2) shows that *less stable radical participates in the three membered ring opening which gives more stable 1, 3-diradical.*

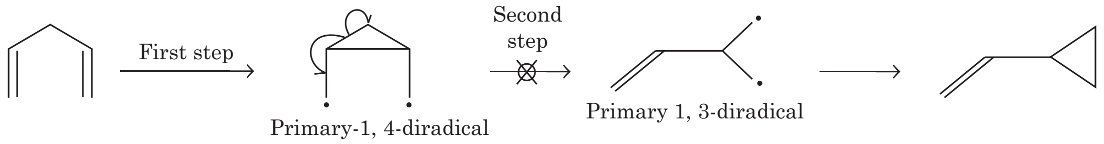
The di-π-methane rearrangement has been studied in a sufficient number of cases to develope some of the patterns regarding the substituent effects. When the central sp^3 carbon (C_3—carbon) is unsubstituted, the *di*-π-methane rearrangement mechanism becomes less favourable by mechanism given in Schemes 10 and 11. In such cases the route is the 1, 2-shift and closure to a three membered ring. The case of 1, 5-diphenyl 2, 4-didentero-1, 4-pentadiene is illustrative (Scheme 12).



Scheme 12

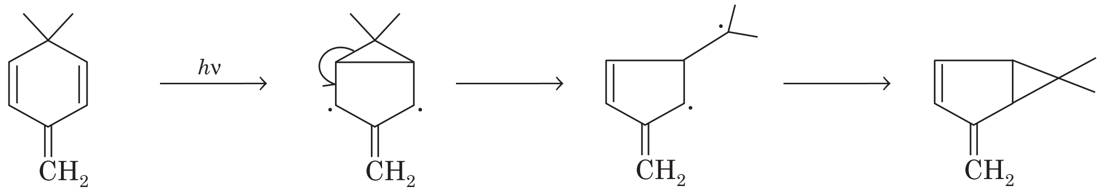
The driving force for 1, 2-migration may be the fact that a more stable allylic radical results.

The resistance of the unsubstituted system at carbon-3 to the di-π-methane rearrangement probably occurs of the second step of the rearrangement which leads the formation of primary alkyl radical which is energetically unfavourable.



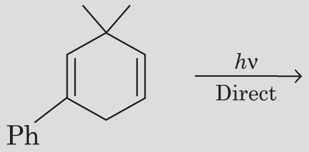
Thus substituents on the central carbon and terminal vinylic carbons are essential for the occurrence of the di-π-methane rearrangements.

Monocyclic dienes also give this rearrangement. One of the most common example of monocyclic 1, 4-diene is compound (1).

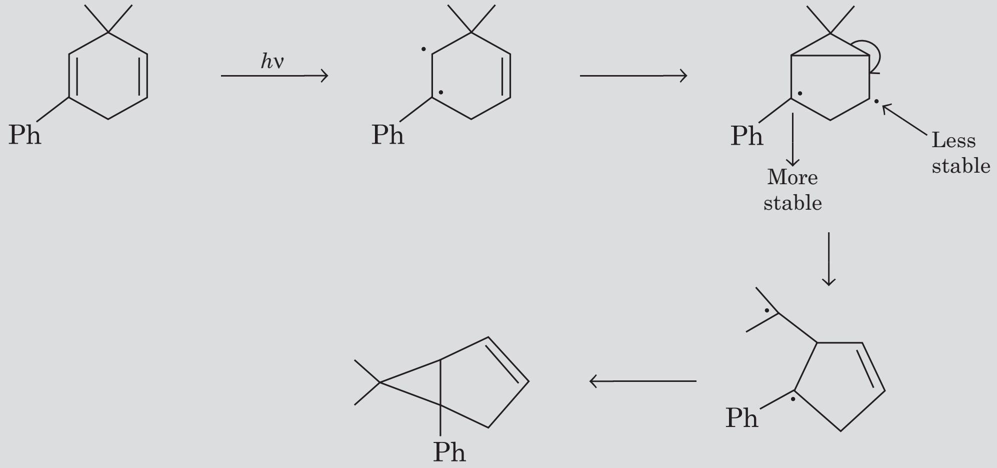


(1)

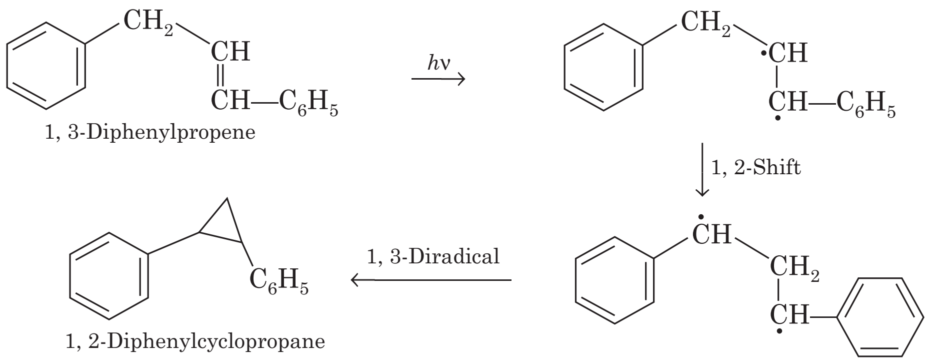
Problem 4: *Complete the following reaction:*



Solution:



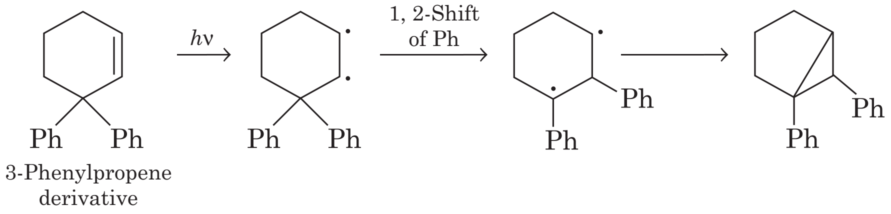
A variant of the di-π-methane rearrangement involves an aryl-vinyl interaction as in the conversion of the propene derivatives (3-phenyl propenes, 1-phenyl propenes, and 1, 3-diphenylpropenes) into cyclopropanes. In such cases rearrangement occurs *via* 1, 2-shift (Scheme 13).



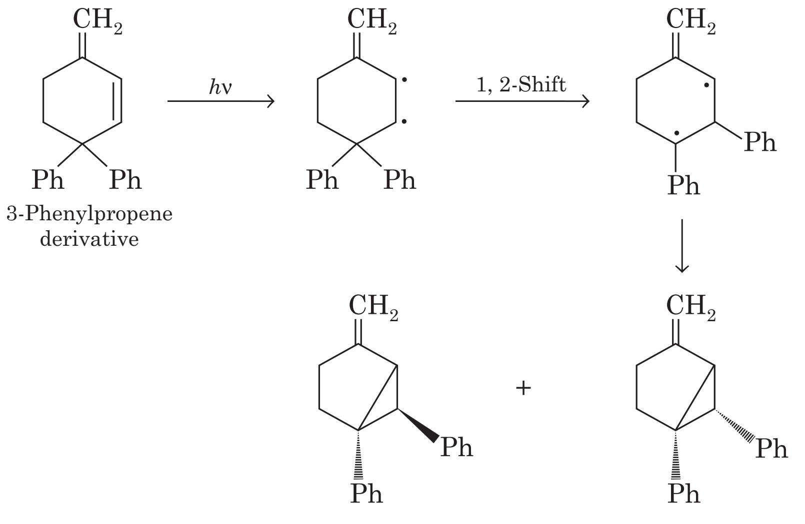
Scheme 13

Examples of this category are as follows:

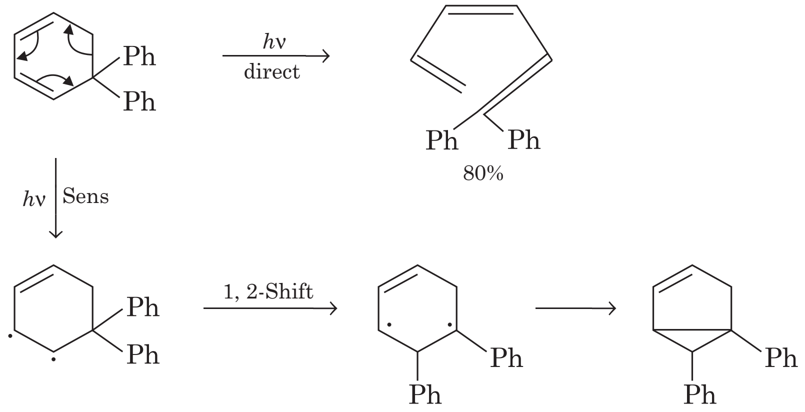
(*i*)



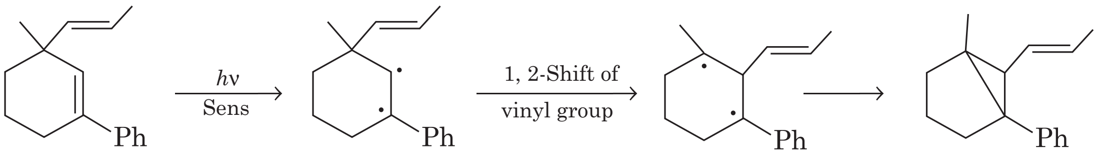
(*ii*)



Phenyl substituted propenes gives di-π-methane rearrangement by singlet state. Exceptions of this generalisation are found in the systems such as 5, 5-diphenyl-1, 3-cyclohexadiene for which direct irradiation causes electrocyclic ring opening, and triplet sensitisation leads to a di-π-methane rearrangement.

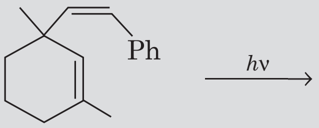


1-Phenyl-3-allyl-3-methylcyclohexene gives di-π-methane rearrangement in the presence of sensitisers.

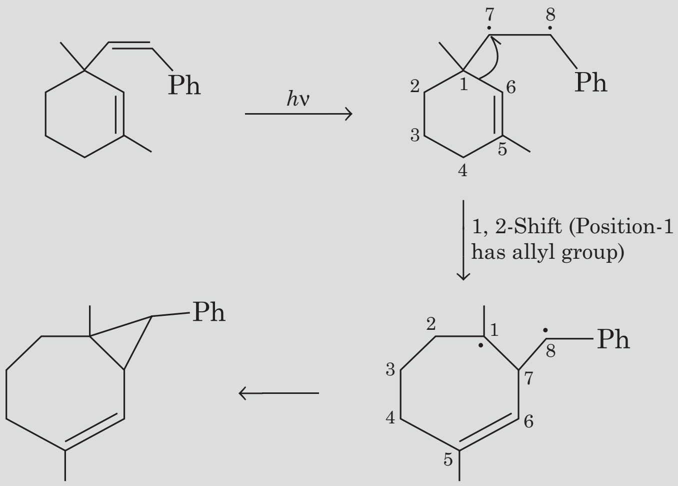


In the above case vinyl group migrates because migrating power of vinyl group is more than the phenyl group.

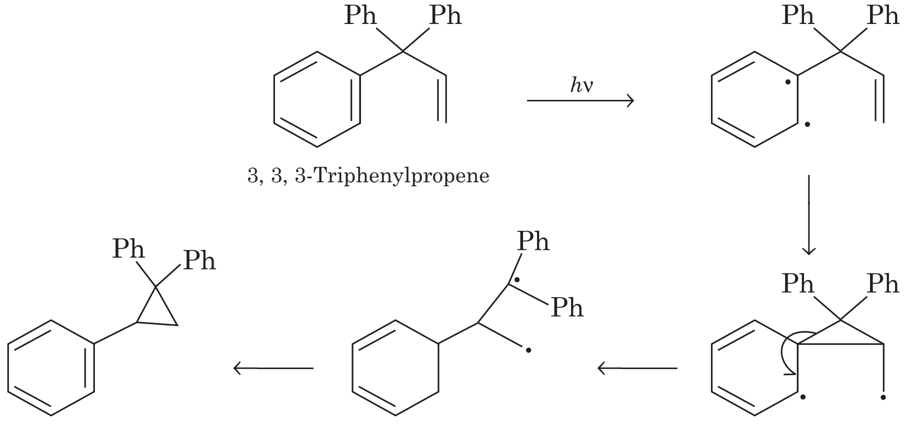
Problem 5: *Complete the following:*



Solution: Compound is 1-phenylpropene derivative hence it will give di-π-methane rearrangement.

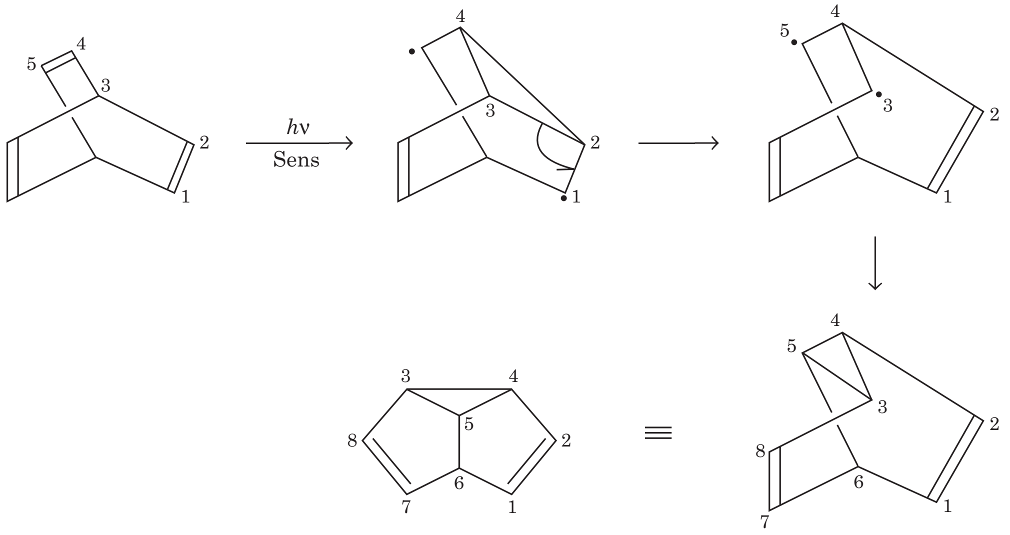


3-Phenyl propene where position-1 is not substituted behaves as 1, 4-diene. In such cases phenyl ring is part of the 1, 4-diene system.



In such cases regioselectivity operates in such a way as to regenerate the aromatic system in the three membered ring opening process.

Unlike linear and monocyclic 1, 4-dienes, polycyclic dienes undergo the di-π-methane rearrangement from the T_1 state. Barrelene was one of the first examples. A variety of barrelene derivatives have been photolysed in the presence of sensitiser.

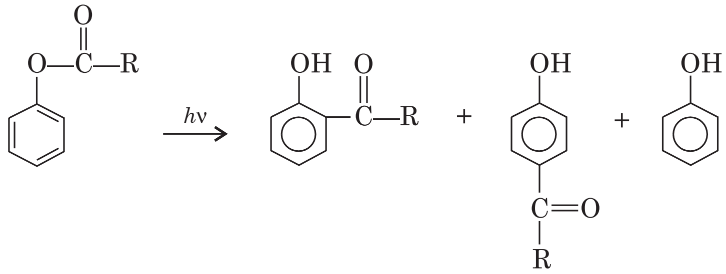


8.7 REARRANGEMENTS IN AROMATIC COMPOUNDS

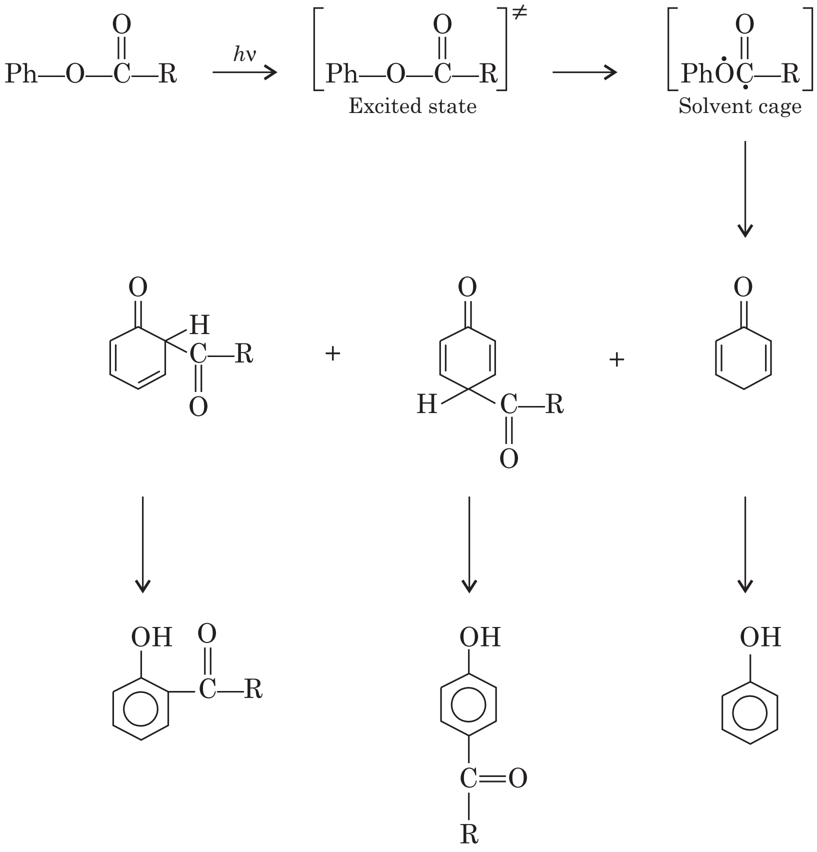
Variety of aromatic compounds, aryl esters, aryl ethers, anilides etc., undergo photochemical rearrangements. In these rearrangements acyl and alkyl groups migrates to *ortho* and *para* positions on photolysis.

Photo-Fries Rearrangement

The most extensively investigated photo rearrangement is Photo-Fries rearrangement

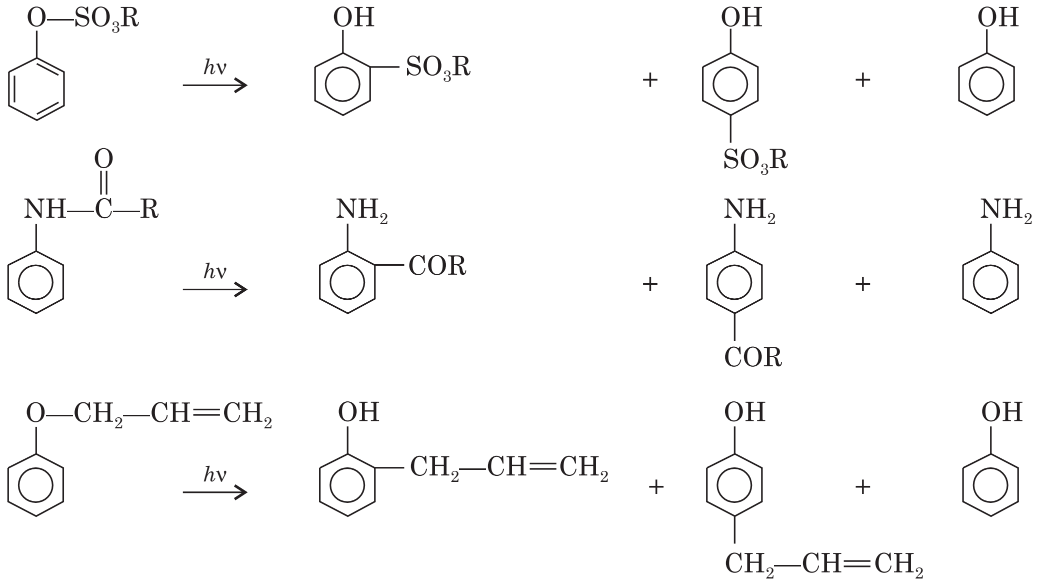


This rearrangement is an intramolecular rearrangement. In this rearrangement substrate undergoes dissociation into phenoxy and acyl radicals which combine within the solvent cage to give intermediates which on aromatisation (or enolisation) give the product. The phenol is produced by phenoxy radicals which escape from the solvent cage.



When this reaction is carried out in gaseous phase only phenol is obtained. This confirms the formation of solvent cage.

Similar rearrangements are also obtained from the following compounds:



GLOSSARY

Photo-Fries Reaction: The formation of a mixture of *o*-and *p*-acylphenols upon photolysis of phenol ester in solution.

Di-π-Methane Rearrangement: Molecules having the *di*-π-methane moiety, *i.e.,* having two π-systems bonded to a single sp^3 carbon atom undergo a general liquid phase photochemical transformation to vinylcyclopropane, called the di-π-methane rearrangement.

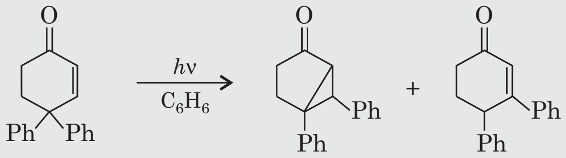
Oxa-Di-π-methane rearrangement: Di-π-methane rearrangement given by β, γ unsaturated ketone is known as oxa-di-π-methane rearrangement.

FURTHER READING

1. J.M. Coxon and B. Halton, *Organic Photochemistry,* Cambridge University Press, London, 1974.
2. P. de Mayo, ed. *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980.
3. W. Horspool and D. Arester, *Organic Photochemistry, A Comprehensive Treatment,* Ellis, Horwood/Prentice Hall, 1992.
4. J. Kopecky, *Organic Photochemistry, A Visual Approach,* VCH, Weinhim, Germany, 1992.
5. J. Kargan, *Organic, Photochemistry, Principles and Applications,* Academic Press, 1993.

PROBLEMS

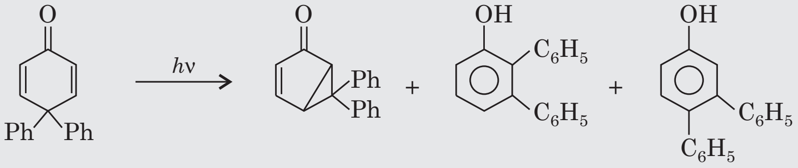
1. Irradiation of 4, 4-diphenyl cyclohexenone (A) yields a mixture of two products (B) and (C).



(A) (B) (C)

Propose a suitable mechanism for this transformation.

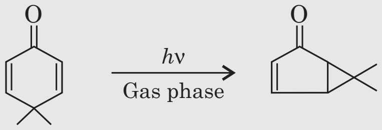
2. Discuss the mechanism of Lumiketone rearrangement reaction.
3. Discuss Zimmerman mechanism for the rearrangement given by 2, 5-dienones.
4. Irradiation of 4, 4-diphenyl-2, 5-dienone yields a mixture of three products, (A), (B) and (C).

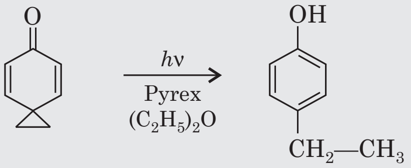


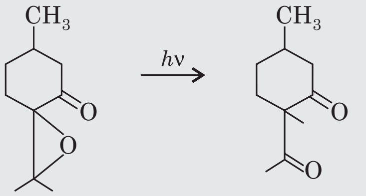
(A) (B) (C)

Propose a suitable mechanism for this transformation.

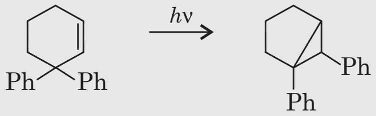
5. Suggest mechanism for the following photo rearrangements:

(i)


(ii)


(iii)


6. Discuss di-π methane rearrangement and give its mechanism.
7. Suggest mechanism for the given reaction

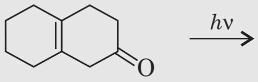
(i)


(ii) $C_6H_5—CH_2—CH{=}CH—C_6H_5 \xrightarrow{h\nu}$

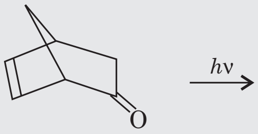

8. β, γ-Unsaturated ketones on irradiation undergo rearrangement reaction. Give name and mechanism of the rearrangement.

9. The given compounds give oxa-di-π methane rearrangement. Give product in each case.

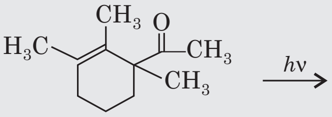
(*i*)



(*ii*)



(*iii*)



10. Di-π-methane rearrangement is given by three types of compounds.

(*i*) Give structures of those compounds, and

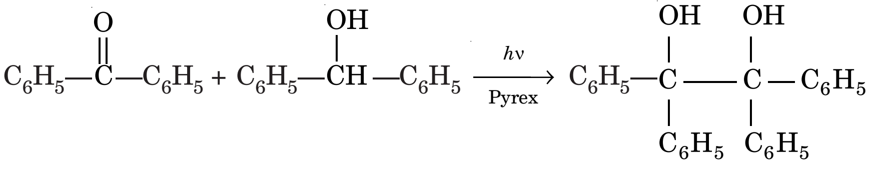
(*ii*) Give mechanism in each case.

9
CHAPTER

Photo Reduction and Photo Oxidation

9.1 PHOTO REDUCTION OF CARBONYL COMPOUNDS

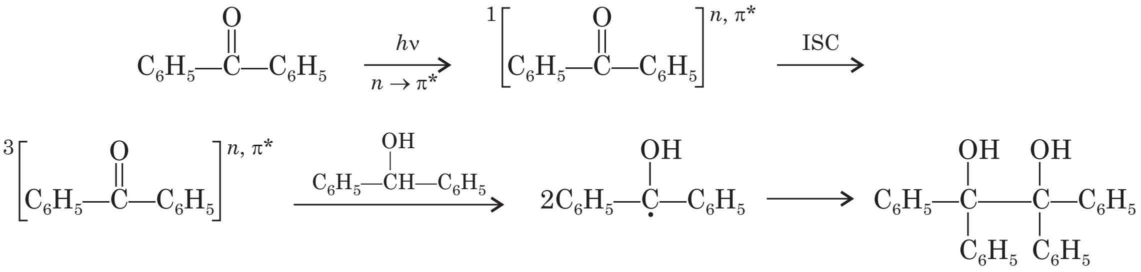
Photo reduction of carbonyl compounds is one of the most thoroughly investigated photochemical processes. In fact, one can carry out the reduction of benzophenone in benzene in a pyrex tube by exposing it to sunlight for few days. The reduction takes place in the presence of benzhydrol.



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + C_6H_5-\overset{\overset{\displaystyle OH}{|}}{CH}-C_6H_5 \xrightarrow[\text{Pyrex}]{h\nu} C_6H_5-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5$$

Benzpinacol

The first step is excitation of the benzophenone to the $^1[n, \pi^*]$ state which intersystem crosses to the $^3[n, \pi^*]$ state. Hydrogen abstraction from alcohol gives two diphenyl hydroxy methyl radicals which combine to form benzpinacol.

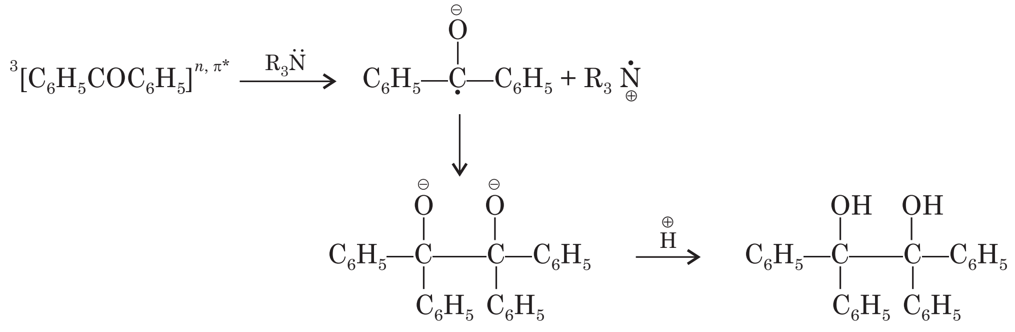


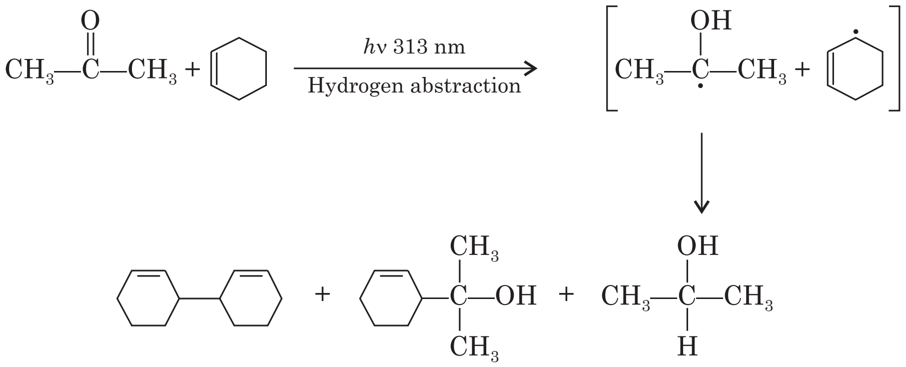
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow[n \to \pi^*]{h\nu} {}^1\left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\right]^{n,\,\pi^*} \xrightarrow{\text{ISC}}$$

$$^3\left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\right]^{n,\,\pi^*} \xrightarrow{C_6H_5-\overset{\overset{\displaystyle OH}{|}}{CH}-C_6H_5} 2C_6H_5-\overset{\overset{\displaystyle OH}{|}}{\dot{C}}-C_6H_5 \longrightarrow C_6H_5-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5$$

Ketones undergo photo reduction in the presence of a variety of hydrogen atom donors other than secondary alcohols. The effect of substituents in the aryl ring can be quite dramatic because of the changes in the electronic configuration of the low-lying triplet state. Hydrogen atom abstraction is much more efficient for n, π^* than π, π^* for ketones.

Excited ketones can be reduced by tertiary amines. The key reaction in this case is electron transfer from the amine to the ketone producing ketyl radical and the cation radical from the amine.

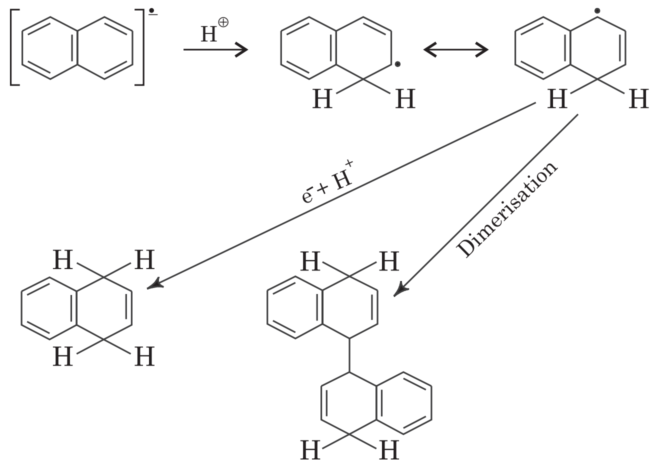




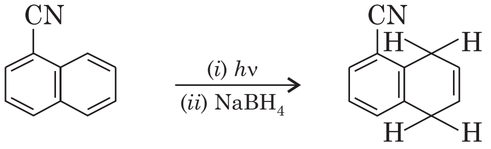
9.2 PHOTO REDUCTION OF AROMATIC HYDROCARBONS

Many excited aromatic hydrocarbons like benzene, biphenyl, naphthalene, methoxy derivative of naphthalene and anthracene react with amine to give reduction products and aminated products. The reaction is initiated by the transfer of an electron from nitrogen lone pair orbital to the half filled highest bonding molecular orbital of the excited aromatic compound.

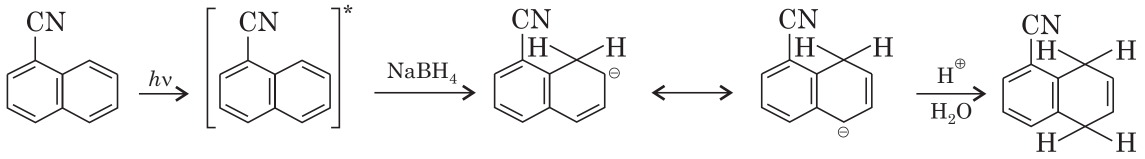
$$ArH^* + R_3\ddot{N} \longrightarrow [Ar\dot{H}]^{-} + R_3\underset{\bullet}{\overset{+}{N}}$$



Excited aromatics are also reduced by transfer of hydride ion by metal hydride or by transfer of hydrogen atom by metal hydride.



Reaction takes place as follows:



9.3 PHOTOCHEMICAL OXIDATIONS

Incorporation of oxygen in the presence of UV light is known as photochemical oxidation. There are two mechanisms by which oxygen is incorporated in photochemical oxidation reactions.

The first is the *Backstrom mechanism* which is also known as photosensitisation oxidation mechanism. Its main characteristic is abstraction of hydrogen by the sensitiser (Sens) in its excited triplet state followed by addition of oxygen to the newly created radical. This type of photooxygenation is known as type I photooxygenation.

$$\text{Sens} + h\nu \longrightarrow \overset{\uparrow\uparrow}{\text{Sens}}$$

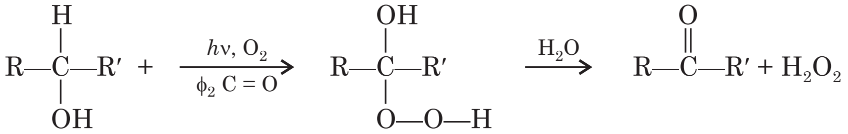
$$\overset{\uparrow\uparrow}{\text{Sens}} + \text{A}-\text{H} \longrightarrow \text{Sens}-\dot{\text{H}} + \dot{\text{A}}$$

$$\dot{\text{A}} + \text{O}_2 \longrightarrow \text{A}—\text{O}—\dot{\text{O}}$$

$$\text{A}—\text{O}—\dot{\text{O}} + \text{AH} \longrightarrow \text{A}—\text{O}—\text{O}—\text{H} + \dot{\text{A}}$$

$$\text{A}—\text{O}—\dot{\text{O}} + \text{Sens}—\dot{\text{H}} \longrightarrow \text{A}—\text{O}—\text{O}—\text{H} + \text{Sens}$$

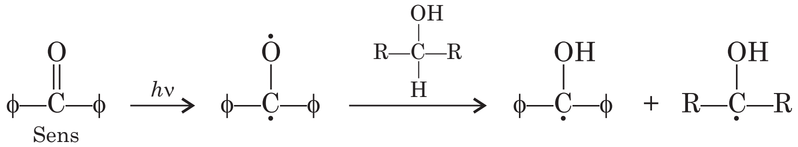
Example of photosensitised reactions that take place by this mechanism are found among the oxidation of secondary alcohols to hydroxy hydroperoxides which in aqueous medium decomposes to form ketones and hydrogen peroxide.



$$\text{R}—\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}—\text{R}' + \xrightarrow[\phi_2\,\text{C}=\text{O}]{h\nu,\ \text{O}_2} \text{R}—\underset{\text{O—O—H}}{\overset{\text{OH}}{\text{C}}}—\text{R}' \xrightarrow{\text{H}_2\text{O}} \text{R}—\overset{\text{O}}{\overset{\|}{\text{C}}}—\text{R}' + \text{H}_2\text{O}_2$$

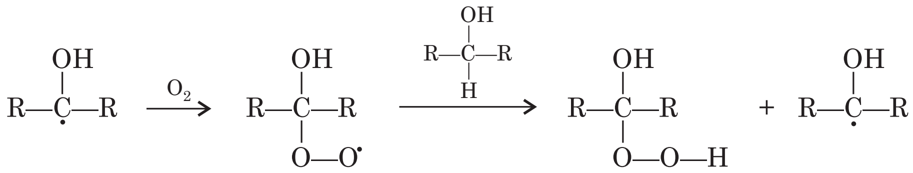
Mechanisms:

(i)



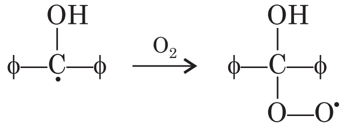
$$\underset{\text{Sens}}{\phi—\overset{\text{O}}{\overset{\|}{\text{C}}}—\phi} \xrightarrow{h\nu} \phi—\underset{\bullet}{\overset{\dot{\text{O}}}{\overset{|}{\text{C}}}}—\phi \xrightarrow{\text{R}—\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}—\text{R}} \phi—\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{C}}}}—\phi + \text{R}—\underset{\bullet}{\overset{\text{OH}}{\overset{|}{\text{C}}}}—\text{R}$$

(*ii*)



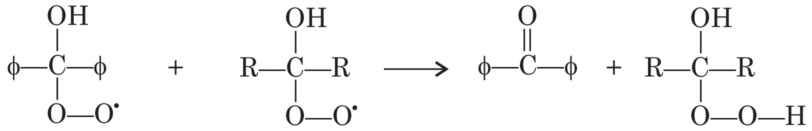
$$\mathrm{R}-\underset{\bullet}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{R} \xrightarrow{O_2} \mathrm{R}-\overset{\mathrm{OH}}{\underset{\mathrm{O-O^{\bullet}}}{\mathrm{C}}}-\mathrm{R} \xrightarrow{\mathrm{R}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{R}} \mathrm{R}-\overset{\mathrm{OH}}{\underset{\mathrm{O-O-H}}{\mathrm{C}}}-\mathrm{R} + \mathrm{R}-\underset{\bullet}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{R}$$

(*iii*)



$$\phi-\underset{\bullet}{\overset{\mathrm{OH}}{\mathrm{C}}}-\phi \xrightarrow{O_2} \phi-\overset{\mathrm{OH}}{\underset{\mathrm{O-O^{\bullet}}}{\mathrm{C}}}-\phi$$

(*iv*)



$$\phi-\overset{\mathrm{OH}}{\underset{\mathrm{O-O^{\bullet}}}{\mathrm{C}}}-\phi + \mathrm{R}-\overset{\mathrm{OH}}{\underset{\mathrm{O-O^{\bullet}}}{\mathrm{C}}}-\mathrm{R} \longrightarrow \phi-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\phi + \mathrm{R}-\overset{\mathrm{OH}}{\underset{\mathrm{O-O-H}}{\mathrm{C}}}-\mathrm{R}$$

The second mechanism known as *photosensitised oxygen transfer* involves the direct combination of the substrate with oxygen. There are two proposals regarding the state of oxygen involved. This type of photooxygenation is known as type II photooxygenation.

Schenck's favours an oxygen-transfer step in which the triplet sensitiser forms an adduct with triplet oxygen.

$$\mathrm{Sens}^{\bullet} \xrightarrow{h\nu} {}^{3}\mathrm{Sens}$$
$${}^{3}\mathrm{Sens} + O_2 \longrightarrow \dot{\mathrm{S}}\mathrm{ens}-\mathrm{O}-\dot{\mathrm{O}}$$
$$\mathrm{A} + \dot{\mathrm{S}}\mathrm{ens}-\mathrm{O}-\dot{\mathrm{O}} \longrightarrow \mathrm{AO_2} + \mathrm{Sens}$$

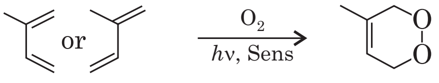
Foote favours the idea of singlet oxygen being the sole agent in the transfer step:

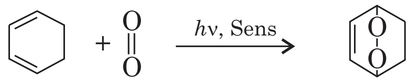
$$\mathrm{Sens} \xrightarrow{h\nu} {}^{3}\mathrm{Sens}^{*}$$
$$O_2\ (\mathrm{Triplet}) + \mathrm{Sens}^{*}\ (\mathrm{Triplet}) \longrightarrow O_2\ (\mathrm{Singlet}) + \mathrm{Sens}$$
$$\mathrm{A} + O_2\ (\mathrm{Singlet}) \longrightarrow \mathrm{AO_2}$$

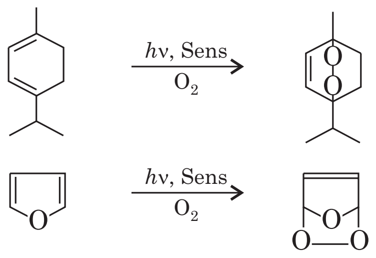
9.4 PHOTO OXIDATION OF ALKENES AND POLYENES

Alkenes, dienes and polyenes are attacked by singlet oxygen. The singlet oxygen may be generated by thermal methods (*e.g.,* by the reaction of hydrogen peroxide with sodium hypochlorite), by excitation of ground state oxygen (triplet oxygen) in a microwave discharge or by the use of visible radiation and photochemical sensitiser such as methylene blue, Rose Bengal, chlorophyll, riboflavin, fluorescein or halo fluorescein.

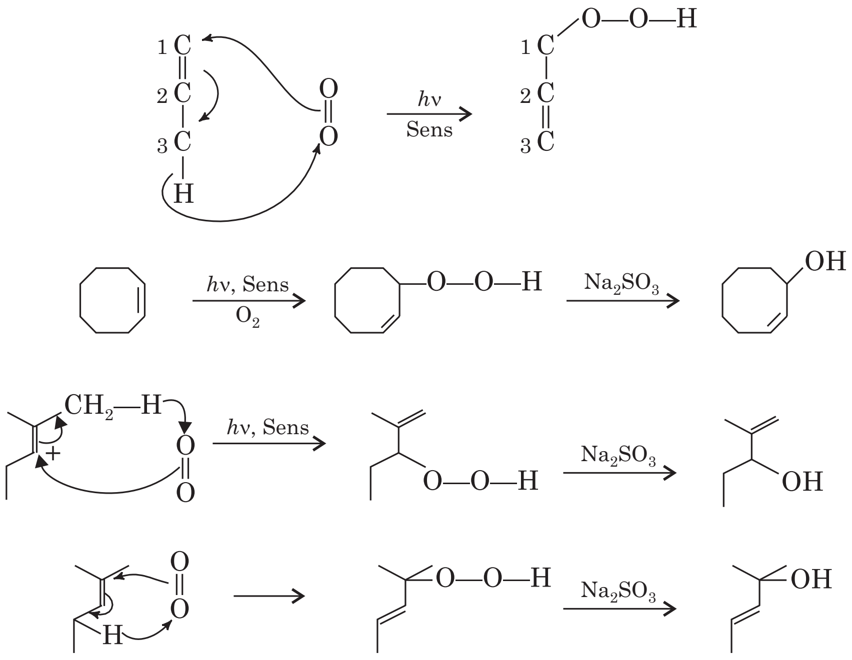
Acyclic or cyclic conjugated dienes gives 1, 4-cycloaddition reaction with singlet oxygen to form six-membered cyclic adduct, *i.e.,* cyclic peroxide.



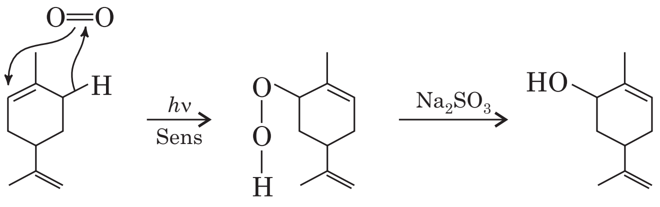




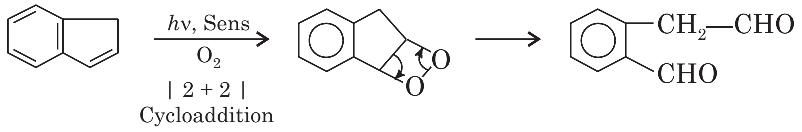
The formation of hydroperoxides in photosensitised oxygen-transfer reactions that follow the Schenck type of mechanism occurs only when hydrogen is present on allylic carbon. The reaction has, moreover, some definite steric and electronic requirements. Oxygen always becomes attached to one of the double bonded carbon, which then shifts into the allylic position. The reaction is like ene reaction.

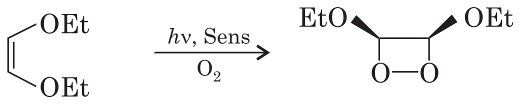


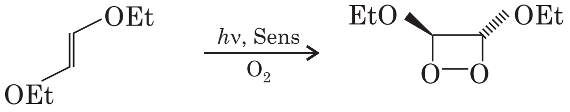
The above reactions do not proceed through free radicals. The oxidation with singlet oxygen occurs by concerted mechanism like the ene reaction.



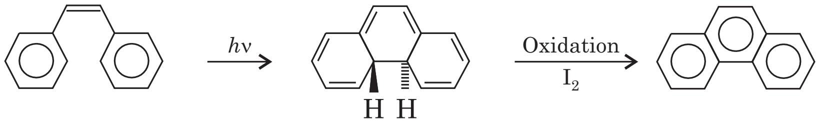
Some substituted alkenes behave differently with singlet oxygen and form a dioxetane in a cycloaddition reaction. Some dioxetanes are stable but others readily decompose to two carbonyl compounds. Electron rich alkenes undergo this reaction and reaction is stereospecific.



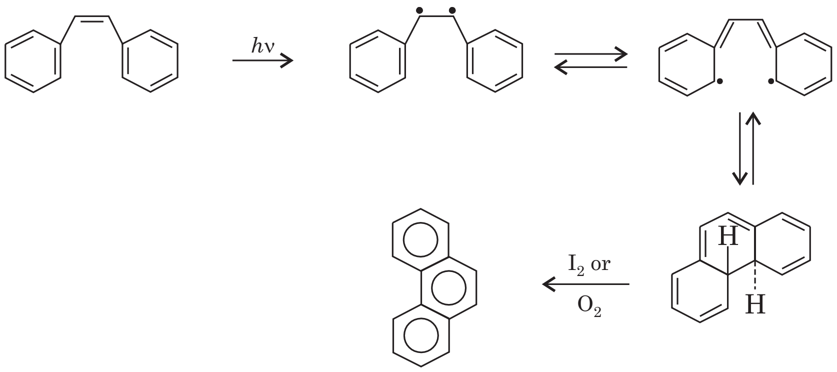




The oxidative cyclisation of conjugated trienes to form aromatic system is one of the more extensively studied photochemical oxidations. The conversion of *cis*-stilbene to phenanthrene is a main example of such a ring closure. The reaction takes place in the presence of hydrogen acceptors (O_2, I_2, $FeCl_3$).



Mechanism of the reaction is as follows:



GLOSSARY

Photooxygenation: The light initiated reaction of triplet oxygen with radicals (Type I photooxygenation), or of singlet oxygen with olefinic moieties (Type II photooxygenation) is known as photooxygenation.

Photoreduction: The light initiated reduction of a variety of functional groups in the presence of an electron donor or a hydrogen atom donor is known as photoreduction.

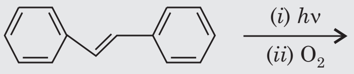
FURTHER READING

1. L. Salum, *Electrons in Chemical Reactions,* John Wiley and Sons, New York, 1982.
2. N.J. Turno, *Molecular Photochemistry*, W.A.10 Benjamin, New York, 1965.
3. J. Kopecky, *Organic Photochemistry; A Visual Approach,* VCH, Weinhim, Germany, 1992.
4. J.M. Coxon and B. Halton, O*rganic Photochemistry,* Cambridge University Press, London, 1974.

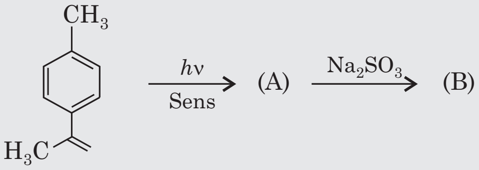
PROBLEMS

1. Give mechanism of photoreduction of aromatic hydrocarbons.
2. Give mechanism of photoreduction of carbonyl compounds.
3. (*i*) Define photochemical oxidation.
   (*ii*) Alcohol undergoes photooxidation by two types of mechanism namely photosensitisation oxidation mechanism and photosensitised oxygen transfer mechanism. Sketch these two mechanisms for secondary alcohol.
4. Write note on photooxidation of alkenes and polyenes by singlet oxygen.
5. Complete the following photooxidation reaction.

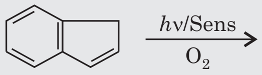
(*i*)



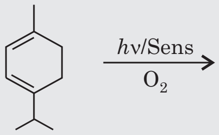
(*ii*)



(*iii*)



(*iv*)



10

CHAPTER

Photochemistry of Alkenes, Dienes and Aromatic Compounds

10.1 PHOTOCHEMISTRY OF ALKENES

Electronic absorption spectra of simple alkenes consist of an intense broad band from 140 nm to 190 nm (for ethylene) with absorption threshold of 200 nm (for ethylene) to 240 nm (for 2, 3-dimethyl-2-butene). The diffuse bands in the spectrum of ethylene are attributed to a $\pi \rightarrow \pi^*$ transition. The absorption at 174 nm for ethylene is the first singlet Rydberg transition. This Rydberg transition is due to the $2p\pi \rightarrow 3s$ excitation.

The excited states of alkenes are complex because the different electronic states have different electronic configuration. Although the nature of most electronic states of alkenes is not known in detail, some are well understood. Alkenes have two low-lying excited singlet states: The $^1[2p\pi, 3s]$ Rydberg state and the $^1[\pi, \pi^*]$ valence state. Calculation indicates that there is apparently an additional state, *i.e.,* the $(2p\pi, 3p)$ Rydberg state. The lowest triplet state is practically pure $^3(\pi, \pi^*)$ and T_2 is essentially a pure Rydberg $^3[2p\pi, 3s]$ state (Fig. 1)

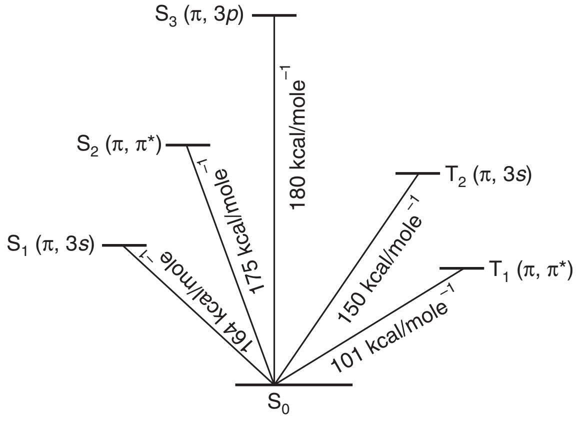


Fig. 10.1 Different electronic states of ethylene

The singlet-triplet splitting (S-T splitting) is generally large for alkenes (ethylene 70 kcal/mole^{-1}). As a result, ISC is slow and inefficient. Therefore, direct irradiation of alkenes induces singlet excited state reactions, and sensitisation is required for triplet state reactions.

Excitation of a planar alkene like ethylene results initially in the formation of planar excited state molecule according to the Franck-Condon principle. The initially formed planar excited state π, π* species, wherever as a singlet or a triplet relaxes by rotation of the terminal group—methylene in the case of ethylene—through 90° around the central bond to give the lowest energy conformation possible. Thus the molecule can rotate from the planar configuration, produced by the Frank-Condon excitation, to reach an energy minimum. This energy minimum is arrived at by rotation about the central bond so that the methylene groups are at right angles to each other so relieving the unfavourable interactions between the singly-filled orbitals on the carbon atoms. (Fig. 10.2)

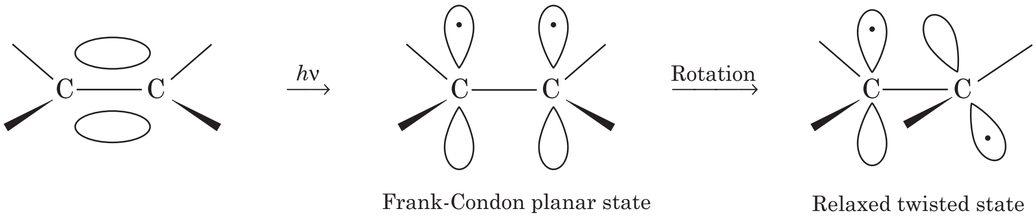


Fig. 10.2 Formation of relaxed twisted state (orthogonal state)

Spectroscopic evidence has been obtained which shows that there is additional distortion of the methylene groups from planarity as the carbon atoms tend towards tetrahedral (sp^3) hybridisation. In this energy minimum there is essentially no π (*pi*) bond, the electronic interaction is at a minimum and the terminal carbon atoms are orthogonal.

Several modes of reactions can be predicted from the excited state olefin from this orthogonal model. These are *cis-trans* isomerisation by rotation about central bond, hydrogen abstraction by the half-filled orbitals on carbon, addition to other alkenes and rearrangement.

The most facile photochemical process of alkenes is *cis-trans* isomerisation.

10.2 *Cis-Trans* ISOMERISATION OF ALKENES

The most commonly observed photochemical reaction of alkenes in solution in *cis-trans* isomerisation which can occur by both direct and sensitised irradiation. This isomerisation reaction is usually associated with π, π* excited states.

10.2.1 *Cis-Trans* Isomerisation of Alkenes by Direct Irradiation

Direct irradiation for the simplest alkenes (whose λ_{max} is below 200 nm) is difficult to achieve as a result of the high energy absorptions. However, with more substituted alkenes the UV absorptions are pushed above 200 nm and so direct excitation can be more readily achieved.

The most common substrate for isomerisation is the **stilbenes.** The irradiation of either *cis-* or *trans-* stilbene at 313 nm results in the formation of 93% *cis-* and 7% *trans-* stilbenes. No matter how long, within reason, the irradiation is continued the ratio of products does not alter and such a state is referred to as a **photostationary** state. The composition of the photostationary state is determined by the excitation co-efficient of the two isomers at the exciting wavelength. For most alkenes (ε_{max}) *trans* is greater than (ε_{max}) *cis*. Therefore, in an equilibrium mixture more molecules of *trans* than *cis* isomer will reach the excited singlet state, followed by rapid relaxation to S_0. At photostationary state the rate of *cis* → *trans* and *trans* → *cis* isomerisation becomes equal, no change in the composition of the reaction mixture occurs upon further irradiation.

The energy of a $\pi \rightarrow \pi^*$ excited species is a function of the angle twist about the carbon-carbon σ (*sigma*) bond, as mentioned earlier, and *trans*-to *cis*- isomerisation is believed to be effected by distortion of the *trans*- excited state initially produced, to an excited state common to both *cis*- and *trans* isomers. This excited state is termed as a phantom state.

The mechanism by which the *cis-trans* isomerisation occurs, in terms of the sample model involves the excitation of an electron to a planar excited state which subsequently relaxes to the twisted state. A simple representation is given in the figure 10.3. A small activation energy of 2 kcal/mole is required to twist the planar *trans* singlet to the twisted singlet state. Decay from this twisted state can give either *cis* or *trans* stilbene.

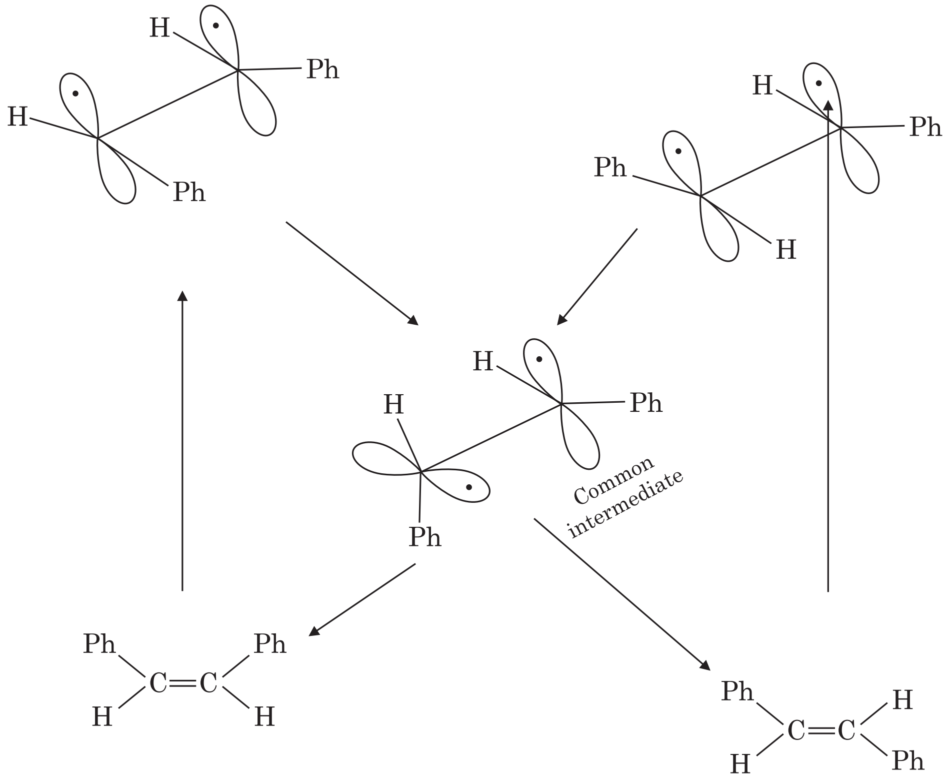
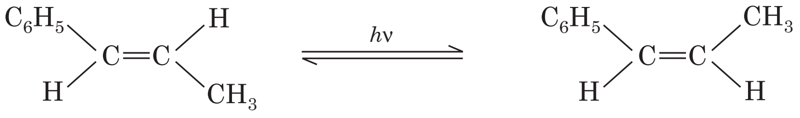
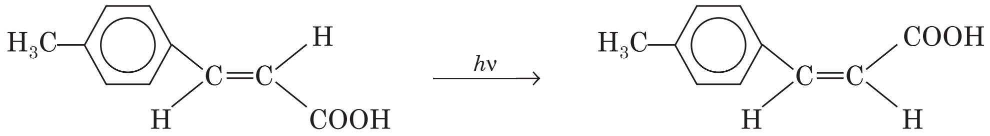


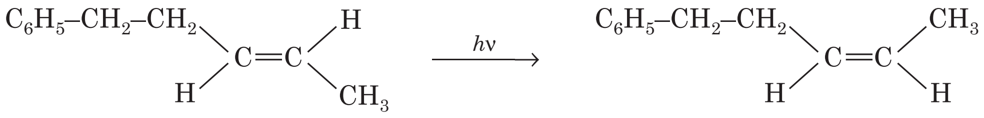
Fig. 10.3

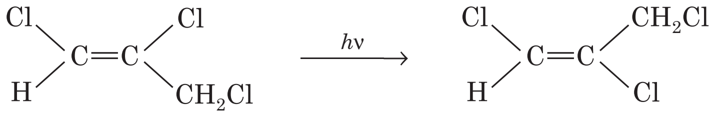
However, as mentioned earlier the *trans* form absorbs more light at the exciting wavelength (ε_{max} *trans* = 16300) than does the *cis* form (ε_{max} *cis* = 2880) and consequently the *trans* isomer is converted almost completely into the *cis*.

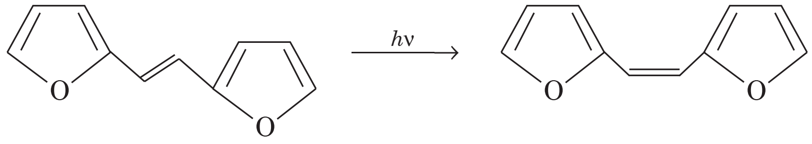
The synthetic utility value of *trans-cis* isomerisation lies in the fact that the more stable alkene can be readily converted into the less stable alkene. Some examples of the result of direct irradiation of alkenes are shown below:







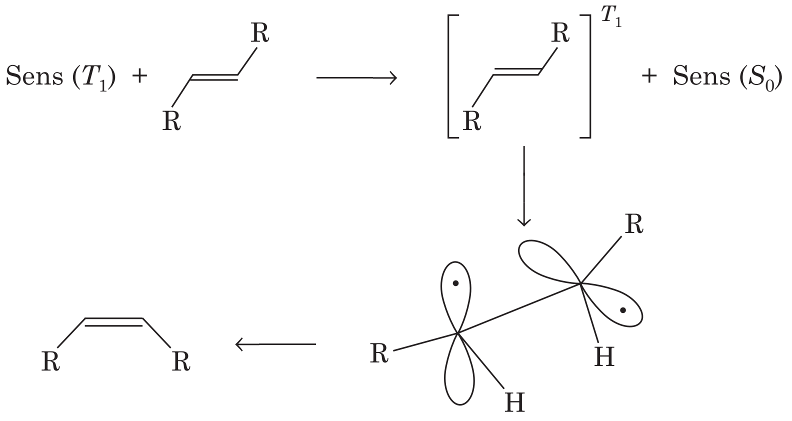




10.2.2 Sensitised *Cis-Trans* Isomerisation

Sensitised *cis-trans* isomerisation of an alkene can be brought about by the use of a triplet sensitiser such as ketone. The sensitised isomerisation of stilbene is a typical example. The composition of the photostationary state of the sensitised isomerisation varies with the energy of the sensitiser employed. In this process if the donor species fulfils the conditions for effective sensitisation and its triplet energy is greater than that of either of the geometrical isomers then triplet energy transfer to both *cis* and *trans* isomers and isomerisation takes place. The initially formed *cis* and *trans* triplet excited species undergo distortion to a common phantom triplet which, on collapsing to the ground state (S_0) affords a mixture of isomers. Because the sensitiser can excite both isomers, the proportion of *cis-trans* isomer in the photostationary state from a sensitised reaction is lower than that obtained from direct irradiation. This is in contrast to the unsensitised isomerisation. Sensitisers of high energy give photostationary state with approximately the same composition of isomers (55% *cis*), while direct photolysis results in a higher proportion of *cis* isomer (93%) in case of stilbene. As the sensitiser energy is reduced anomalous results are observed.

$$\text{Sens } (S_0) \xrightarrow{h\nu} \text{Sens } (S_1) \xrightarrow{\text{ISC}} \text{Sens } (T_1)$$



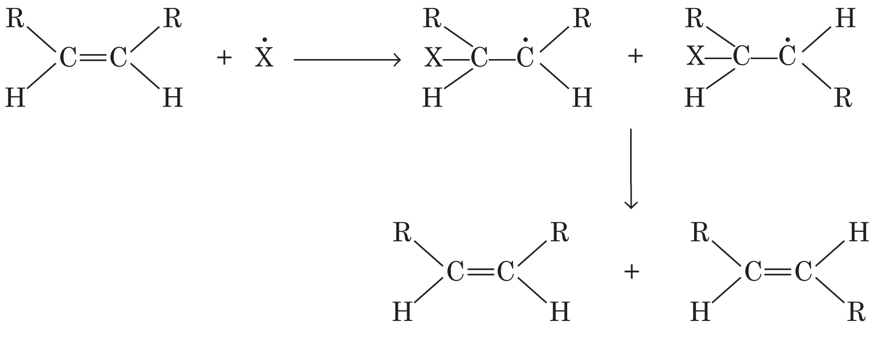
The composition of photostationary state depends very much on the triplet energy sensitiser. With sensitiser having triplet energy above 60 kcal/mole, *cis-trans* ratio is stightly more than one but a range of sensitiser having triplet energy of 52 to 58 kcal/mole offered much higher *cis-trans* ratio in the photostationary state. The higher *cis-trans* ratio in this region results from the fact that energy required for excitation of *trans* isomer is less than for excitation of *cis* isomer.

The sensitiser having triplet energies in the range of 52 to 58 kcal/mole, selectively excites the *trans* isomer. Since the rate of *trans-cis* conversion is increased, the composition of the photostationary state is then enriched in *cis* isomer.

Sometimes photochemical *cis-trans* isomerisation may also take place in the presence of halogens. It appears that under these conditions there is a photochemical product of halogen atoms which adds to the alkene yielding a radical. Elimination of halogen from this radical yields a constant ratio of *cis* and *trans* isomers.

(*i*) $X_2 \xrightarrow{hv} \dot{X} + \dot{X}$

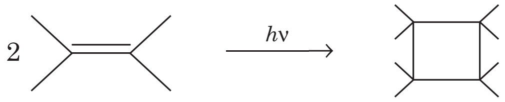
(*ii*)



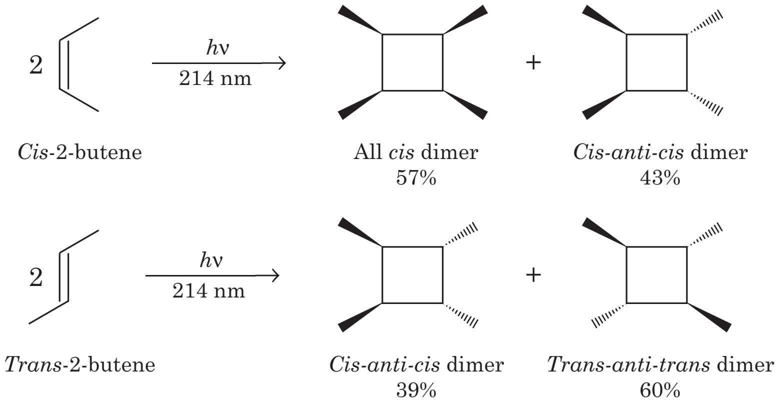
10.3 DIMERISATION OF ALKENES

Reactions competing with *cis-trans* isomerisation at increased concentrations of the alkene(s) are photocycloaddition reactions. An alkene in its S_1 or T_1 state reacts with either the same (photodimerisation) or a different (photocycloaddition) alkene in the ground state to produce a cyclobutane derivative.

Although the dimerisation of simple alkenes (whose λ_{max} is equal or less than 200 nm) is technically difficult, increase alkyl substitution of ethene causes a bathochromic shift of the absorption band, so that direct irradiation (λ abs = 224 nm) of neat 2, 3-dimethyl-2-butene gives the corresponding dimers.

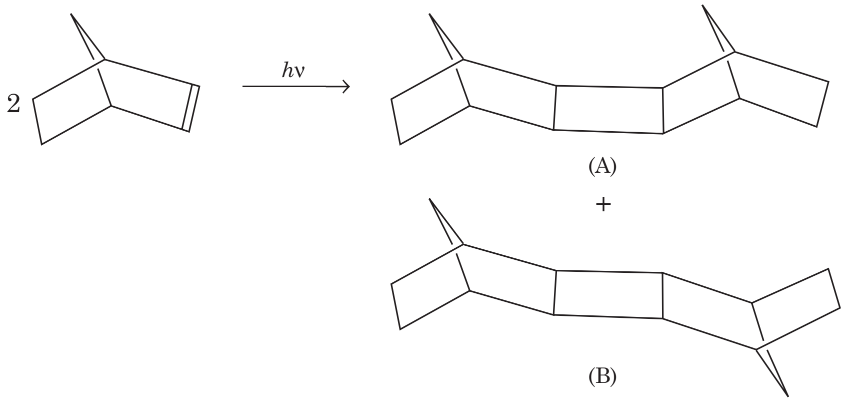


The dimerisation reaction is stereospecific and this is demonstrated by the irradiation of *cis*-2-butene which yields all *cis* dimer and the *cis-anti-cis* dimer while the *trans*-2-butene affords the *cis-anti-cis* dimer and the *trans-anti-trans* dimer (Scheme 1).



Scheme 1

Cyclohexene also dimerises, yielding a mixture of dimeric products while norbornene affords two dimers (A) and (B) in a ratio of 1 : > 10 (Scheme 2)

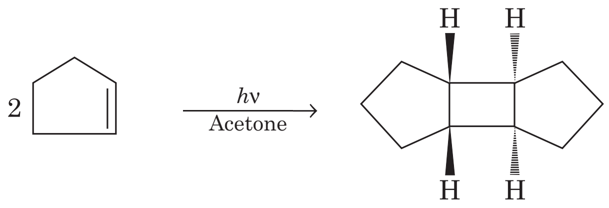


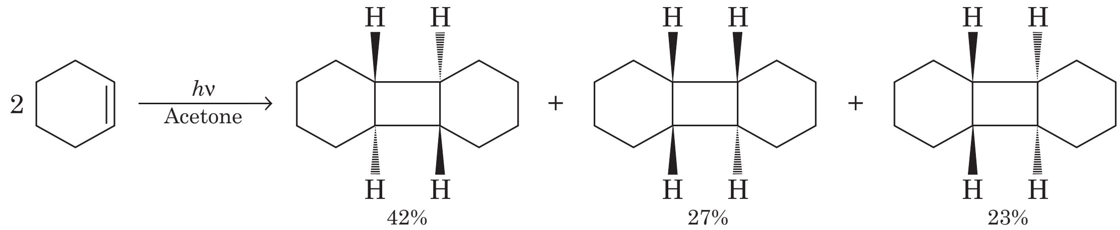
Scheme 2

Photosensitised dimerisation (triplet state dimerisation) occurs easily with cycloalkenes, particularly with small ring alkenes because they cannot undergo *cis-trans* isomerisation.

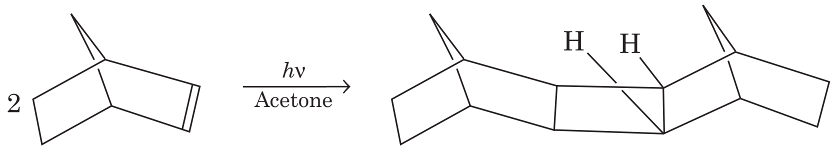
Dimerisation appears to favour the formation of *cis-trans-cis* arrangement of rings in the dimer. Example of dimerisation of cyclopropenes, cyclobutenes, cyclopentenes and cyclohexenes have been reported.

The dimerisation of alkenes and cycloalkenes is best sensitised by aliphatic ketones. Oxitane are formed from aromatic ketones.

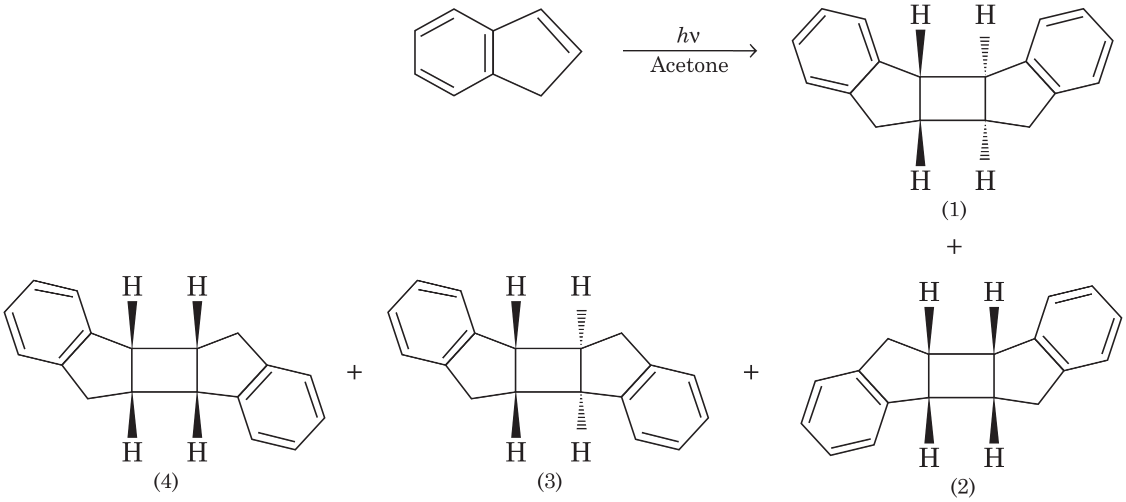




Norbornene can also be made to dimerise on sensitisation and that is preferred for the formation of the *exo-trans-endo* dimer.

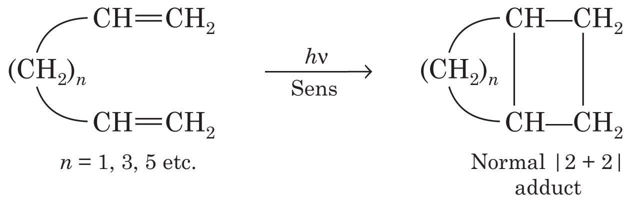


Four dimers that differ in regio and stereochemistry are formed by photodimerisation of indene. The ratio of dimers depends on the irradiation conditions. The triplet sensitised dimerisation, as a step wise bond formation process, generally produces the thermodynamically more stable *exo* products from the more stable 1, 4-biradical intermediate (head-to-head).

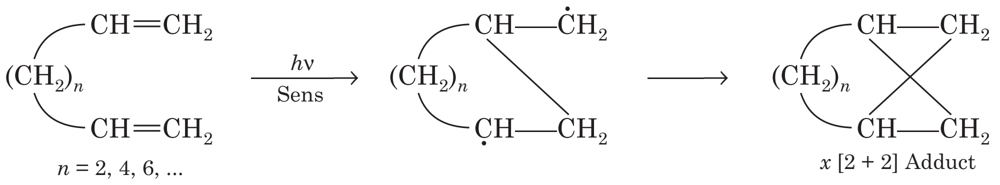


10.3.1 Intramolecular Dimerisation

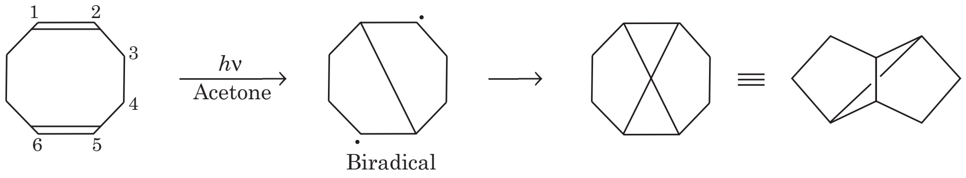
The photochemistry of nonconjugated dienes with isolated double bonds resembles with simple alkenes. Such type of alkenes give intramolecular | 2 + 2 | cycloaddition reactions to give bicyclic products. The products of sensitised intramolecular cycloadditions depend on the number of —CH_2— groups between the two double bonds. If the number of intervening groups is odd, *e.g.,* 1, 4-pentadiene or 1, 6-pentadiene, the major product results from a normal | 2 + 2 | cycloaddition.



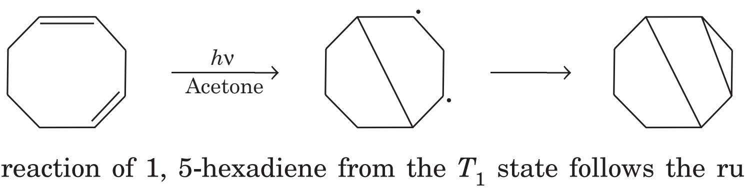
If the number *n* is even *e.g.,* 1, 5-hexadiene, the major product is formed *via* a "**cross**", *i.e., x* [2 + 2] cycloaddition to form two crossed σ (*sigma*) bonds.



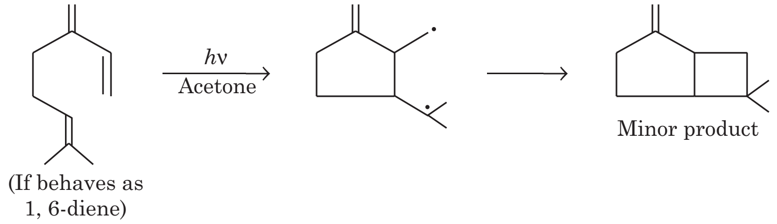
This feature is even more prominent in cyclic dienes, *e.g., n* = *m* = 2 (1, 5-cyclooctadiene) in which *x* [2 + 2] cycloadduct is the only product.

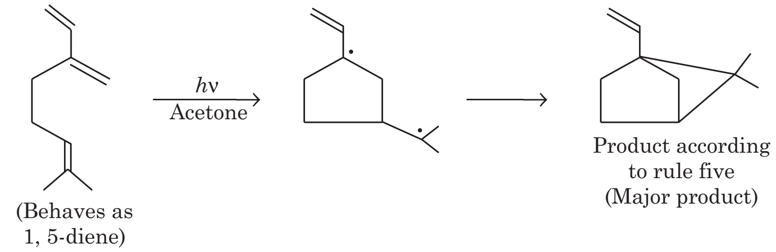


If *n* = 1 and *m* = 3 or *vice-versa* (*i.e.*, 1, 4-cyclooctadiene), the normal | 2 + 2 | cycloadduct is formed.

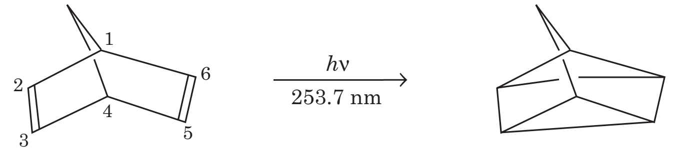


The photoreaction of 1, 5-hexadiene from the T_1 state follows the rule of **five** which states that if triplet cyclisation can lead to rings of different sizes, the one formed by 1, 5 addition is preferred kinetically. If there is several possibilities for 1, 5 addition leading to different biradicals, the most stable one is formed.

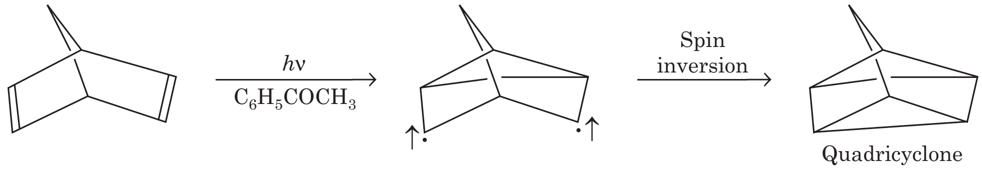




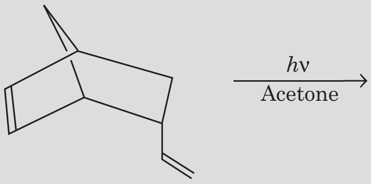
Intramolecular | 2 + 2 | cycloadditions can produce cage structures which are molecules of theoretical interest with respect to strain and bond angles. Norbornadiene (A) is a typical example of such reaction. The UV spectrum of the compound exhibits absorptions at 205 nm, 214 nm and 220 nm and a shoulder at 230 nm in ethanol. Such a spectrum is not expected for a non-conjugated diene. Molecular model also indicates that bonding is feasible between C-2 and C-6 and between C-3 and C-5 without too much strain. Due to these reasons compound (A) undergoes | 2 + 2 | cycloaddition by direct irradiation and in the presence of sensitiser.



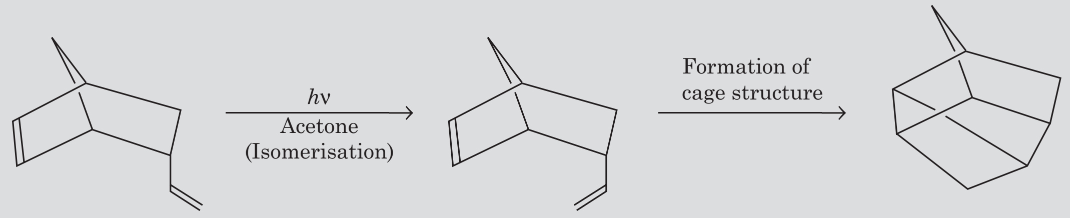
In the presence of sensitiser product formation takes place by triplet state.



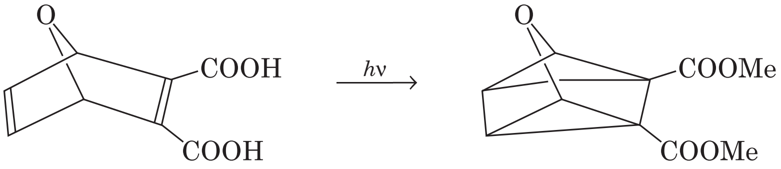
Problem 1: *Complete the following cycloaddition reaction:*

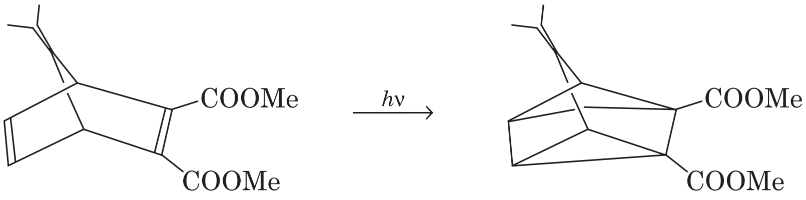


Solution:



The | 2 + 2 | cycloaddition reaction of norbornadiene in the presence of sensitiser is a reversible reaction. The introduction of groups other than —CH_2— at C-7 position does not change the relationship between isolated double bonds. In such type of compounds the reaction is not reversible. The reaction is brought about by direct irradiation or sensitised irradiation.





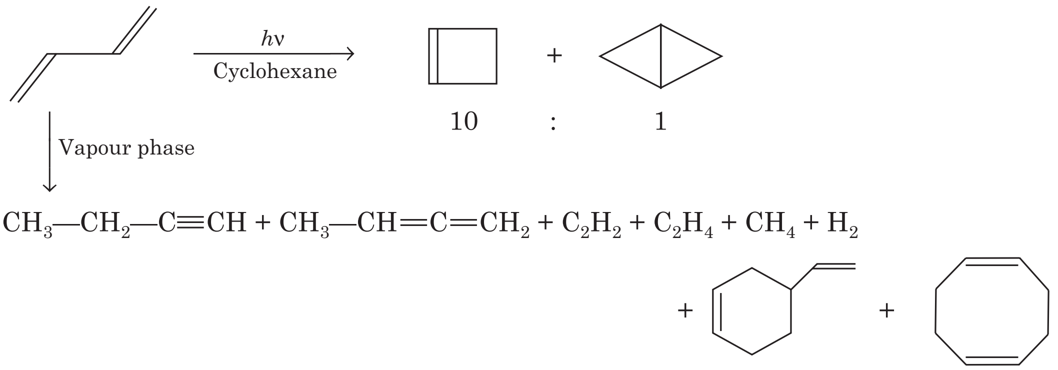
10.4 PHOTOCHEMISTRY OF CONJUGATED DIENES

Conjugated dienes can give the following type of photochemical reactions:

(*i*) *Cis-trans* isomerisation
(*ii*) Sigmatropic shift
(*iii*) Disrotatory electrocyclic ring closure
(*iv*) Intramolecular *x* [2 + 2] cycloaddition

The above photochemical reactions of conjugated dienes depend to a large extend on the excited state population, and on the phase in which reaction is performed. Singlet excitation generally leads to intramolecular process (*i.e.*, disrotatory electrocyclic ring closure and sigmatropic rearrangement) whereas dimerisation and addition reactions are more common from the triplet excited state. Reaction in the gas phase at low pressure often leads to greater fragmentation than in solution.

The solution phase photolysis of butadiene leads to cyclobutene and bicyclobutane, whereas in the vapour phase (gas phase) 1-butyne, methylallene, acetylene, ethylene, methane, hydrogen and polymeric materials are produced.



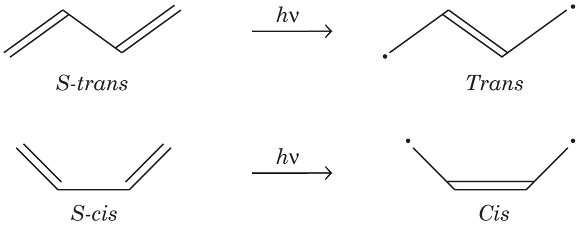
$CH_3—CH_2—C≡CH + CH_3—CH=C=CH_2 + C_2H_2 + C_2H_4 + CH_4 + H_2$

10.4.1 Photochemistry of Conjugated Dienes in Solution

Intramolecular x[2 + 2] Cycloaddition Reaction

1, 3-Butadiene exists in solution as a rapidly equilibrating mixture of *S-transoid* (95%) and *S-cisoid* (5%) conformers.

Irradiation of butadiene promotes an electron from HOMO to LUMO ($\psi_2 \rightarrow \psi_3^*$) which results in the increased bonding between C-2 and C-3 at the expense of C-1 and C-2 and C-3 and C-4. Thus the lower excited states of *S-trans* and *S-cis* butadiene should exhibit still larger energy barriers to rotation about the $C_2—C_3$ bond because of its double bond character. Thus conformational character of butadienes are retained in the excited states.



The exact energies of the S_1 states are not known, but *cisoid* S_1 probably lies below *transoid* S_1. There is large energy gap between S_1 and T_1. Also inter system crossing does not take place in this case. The energy gap between S_1 and T_1 accounts for the fact that inter system crossing does not occur. Direct irradiation of 1, 3-butadiene in solution thus gives rise to chemistry only from the S_1 state.

The energy of the excited states of butadienes are shown in the Fig. 10.4.

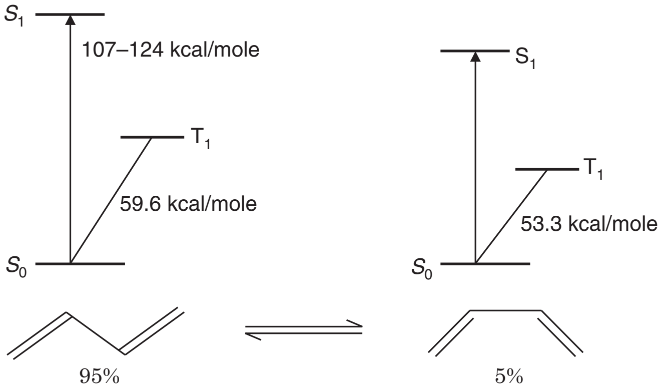
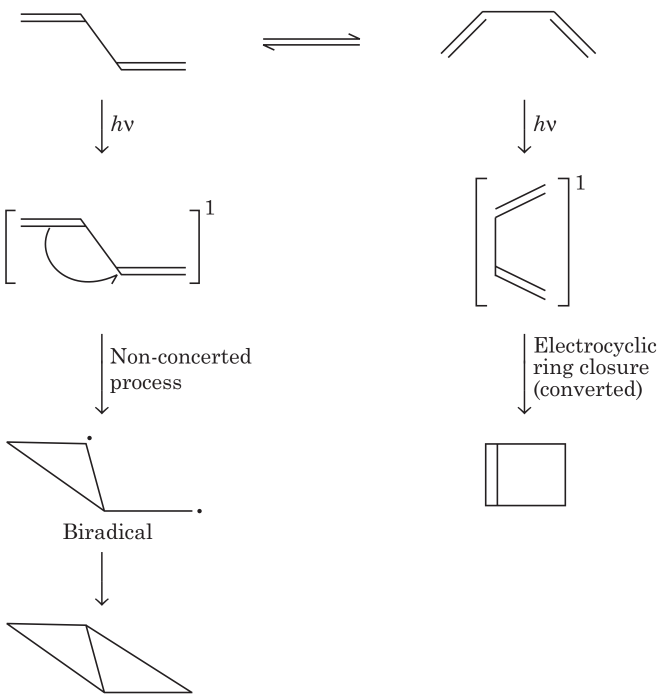
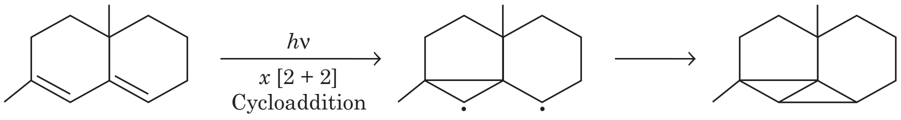


Fig. 10.4

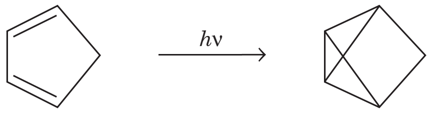
Irradiation of butadiene in cyclohexane produces cyclobutene from an electrocyclic reaction of the *S-cis* isomer, and bicyclo [1, 1, 0]-butane, the product of an intramolecular *x* [2 + 2] cycloaddition of the *S-trans* isomer, in a ratio of 6 : 1.



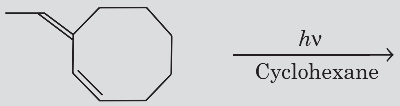
Bicyclobutane formation is particularly important in systems that contain a rigid-*S-trans* diene geometry.



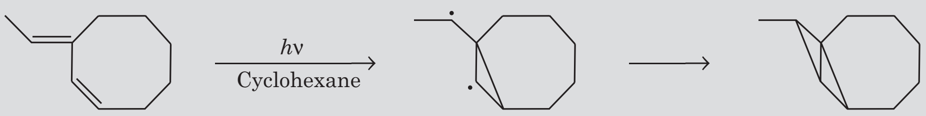
However *x* [2 + 2] cycloaddition also occurs with *cis* fused dienes particularly in case of cyclopentadiene.



Problem 2: *Complete the following reaction:*

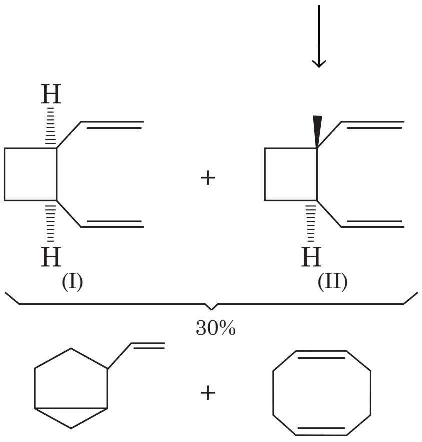


Solution: Compound is *S-trans* diene hence cyclobutane formation will takes place *via* *x*[2 + 2} cycloaddition reaction.



If a concentrated solution of 1, 3-butadiene is irradiated, some dimer formation can be detected (maximum yield 10%). We expect dimer formation to be concentration dependent, since it involves the bimolecular reaction of an excited butadiene with a ground state butadiene. The ring closure reactions (*i.e.,* formation of cyclobutene and bicyclobutane), on the other hand, are unimolecular. Thus dimerisation can only be possible on high concentration of 1, 3-butadiene. Dimerisation gives four different dimers:

$$\underset{\text{Excited state, } S_1}{{}^1[CH_2{=}CH{-}CH{=}CH_2]} + \underset{\text{Ground state, } S_0}{CH_2{=}CH{-}CH{=}CH_2}$$

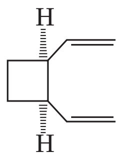
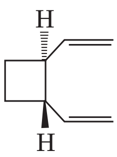
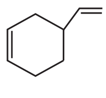


(I) (II) 30%

(III) 50% (IV) 8%

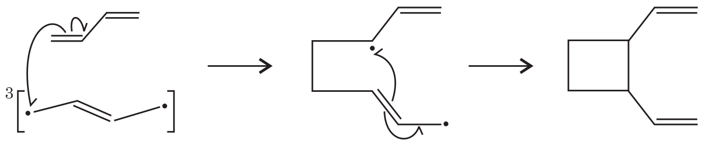
When batadiene is treated in the presence of sensitiser, the product formation takes place by triplet state.

The chemistry of the T_1 state of 1, 3-butadiene is quite different from that of the S_1 state. A mixture of dimers is formed in very good yield (≈ 75%) and neither cyclobutene nor bicyclobutane can be detected in the sensitised reaction (triplet reaction). The dimer mixture obtained from triplet also differ significantly from that given by singlet. The dimer composition in triplet state depends upon the energy of the sensitiser used to populate T_1. The results for the two sensitiser, acetophenone and benzil are given below:

Sensitiser	*E_T (kcal/mole)*	*% Composition of dimers*		
				
$C_6H_5COCH_3$	74	82	14	4
$C_6H_5COCOC_6H_5$	57	49	8	43

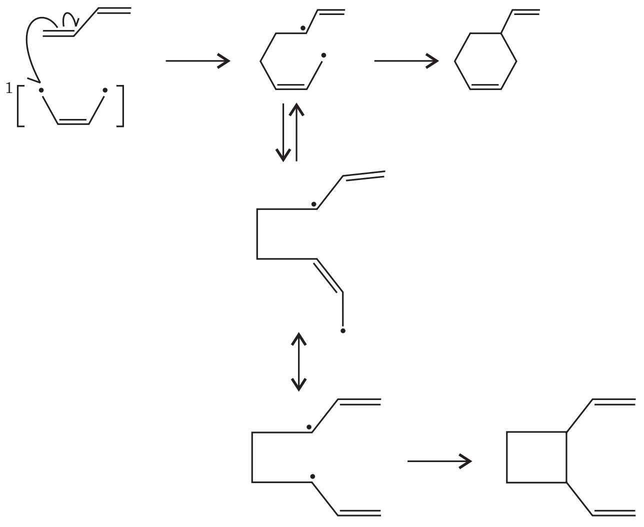
The origin of this remarkable change in product composition lies in the relative energies of the sensitiser. Acetophenone, with E_T = 74 kcal/mole, is sufficiently energic to transfer energy to either *s-cis* or *s-trans* butadiene. Since the *s-tarns* form predominates by a large margin, and since energy transfer occurs at nearly every collision, the dimer composition from the acetophenone sensitised experiment must represent primarily the reaction of *s-trans*-T_1. Benzil (E_T = 54 kcal/mole), on the other hand, is energetic enough to transfer energy to *s-cis* butadiene but not *s-trans* butadiene. Thus the dimer composition from the benzil-sensitised experiment must represent primarily the reaction of *s-cis*-T_1. If a sensitiser with a triplet energy of less than 54 kcal/mole were used, no dimer formation would be observed.

Thus when acetophenone is the sensitiser, *s-trans*-T_1 is the reacting species which reacts with *s-trans* ground state to give dimer.



Cis and *trans*

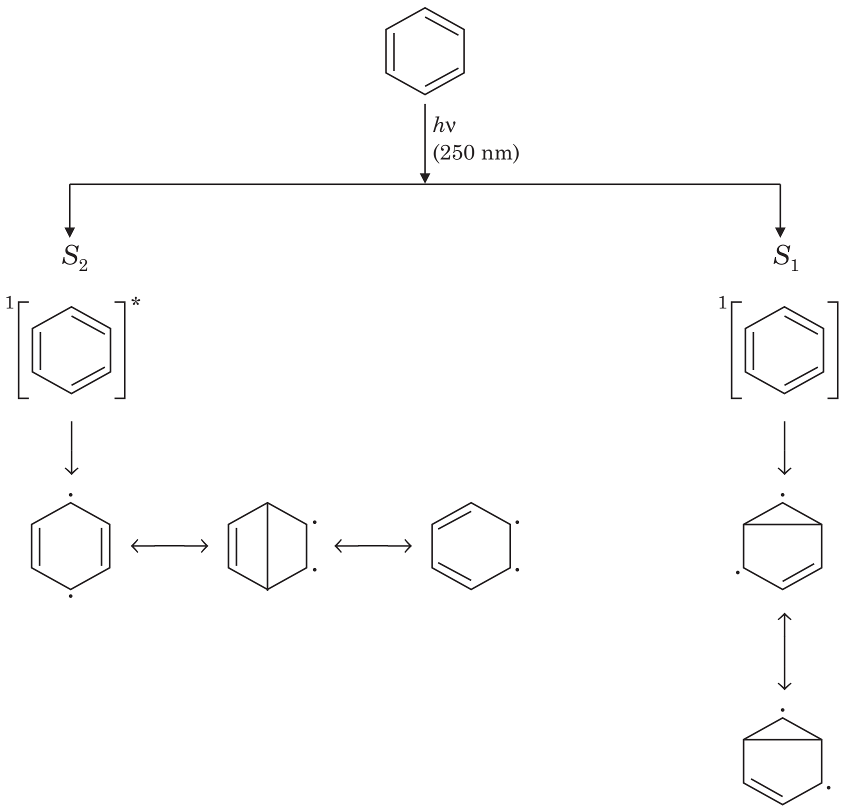
In benzil sensitised reaction, *s-cis*-T_1 adds to *s*-trans ground state butadiene.



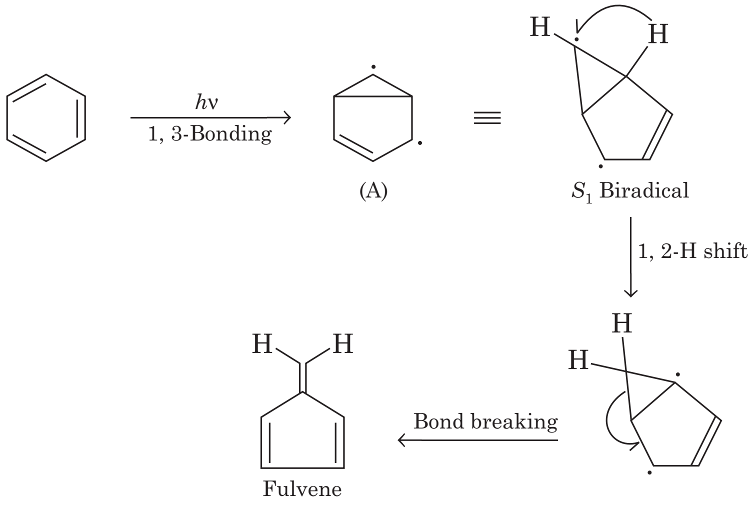
Cis and *trans*

10.5 PHOTOISOMERISATION OF BENZENE AND SUBSTITUTED BENZENE

Benzene and substituted benzene undergoes valence isomerisation by irradiation. Selective excitation into S_1 gives preferentially *meta* and *ortho* product while excitation into S_2 gives *para* bonded products by valence isomerisation. These processes are described by biradical intermediate for case of visualisation.

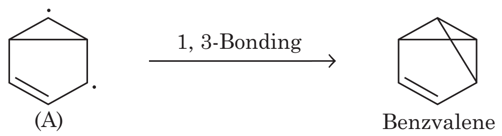


Irradiation of liquid benzene under nitrogen at 254 nm causes excitation to S_1 state and the products, benzvalene and fulvene are formed *via* 1, 3-biradical.

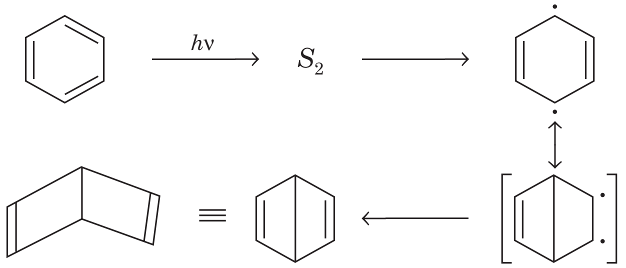


The formation of fulvene can now be considered to arise by reaction of the biradical (A) by a 1, 2-hydrogen migration and bond breaking.

Formation of benzvalene can take place as follows:

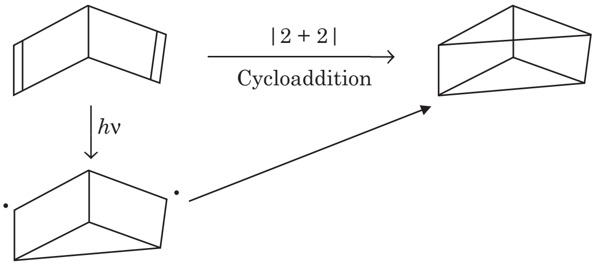


Dewar benzene is formed *via* S_2 state upon short wavelength irradiation (205 nm).



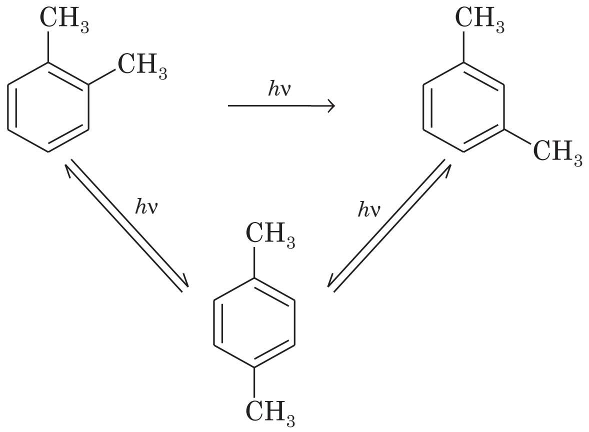
Dewar benzene

It has been confirmed that Dewar benzene is converted into prismane either by concerted path or by formation of a biradical.



All these strained intermediates are thermally labile and ultimately isomerises into benzenoid compounds.

Monocyclic aromatic compounds undergo remarkable photochemical rearrangements. For example, *o*-xylene on irradiation gives mixture of *o, m* and *p*-xylenes.



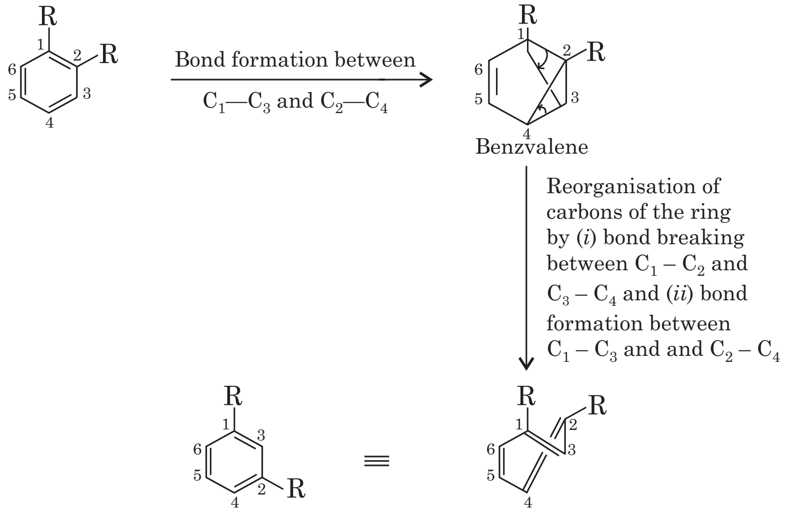
Conversion of *o*-xylene into *m*-xylene and *m*-xylene into *p*-xylene is due to 1, 2-alkyl group shift. Similarly conversion of *o*-xylene into *p*-xylene and *vice-versa* is due to the 1, 3-alkyl group shift.

1, 2-Alkyl group shift takes place by benzvalene as well as prismane intermediates whereas 1, 3-alkyl group shift takes place only by prismane intermediate.

10.5.1 1, 2-Alkyl Shift

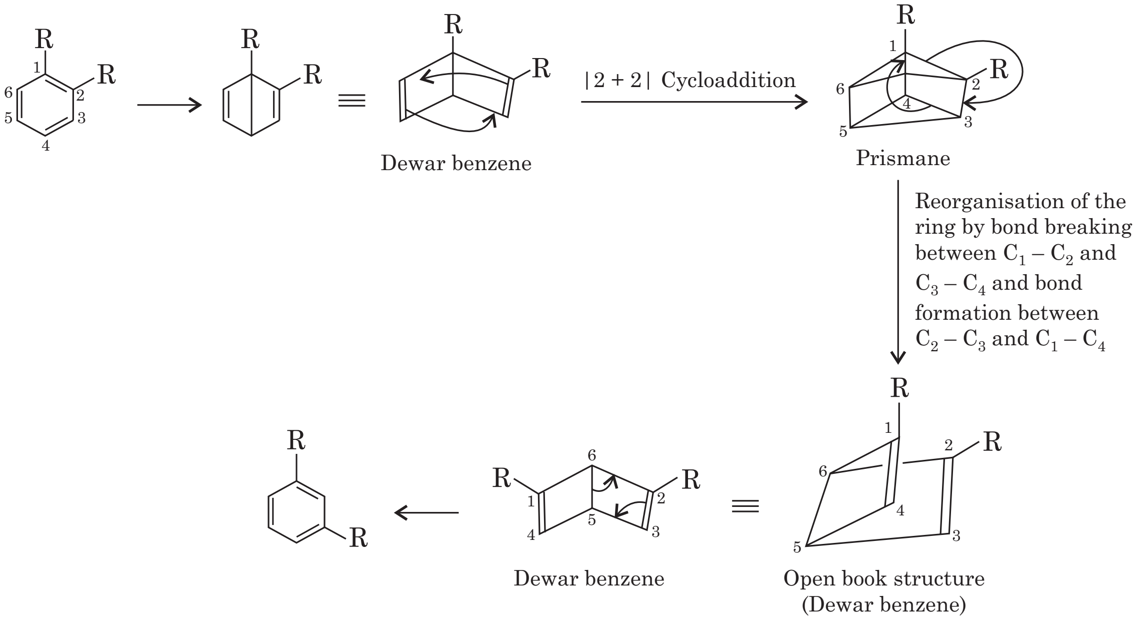
1, 2-Alkyl group shift (rearrangement of the atoms in the benzene ring) takes place *via* formation of benzvalene and prismane as reaction intermediate.

(*A*) Mechanism of 1, 2-shift via benzvalene intermediate



Reorganisation of carbons of the ring by (*i*) bond breaking between $C_1 - C_2$ and $C_3 - C_4$ and (*ii*) bond formation between $C_1 - C_3$ and and $C_2 - C_4$

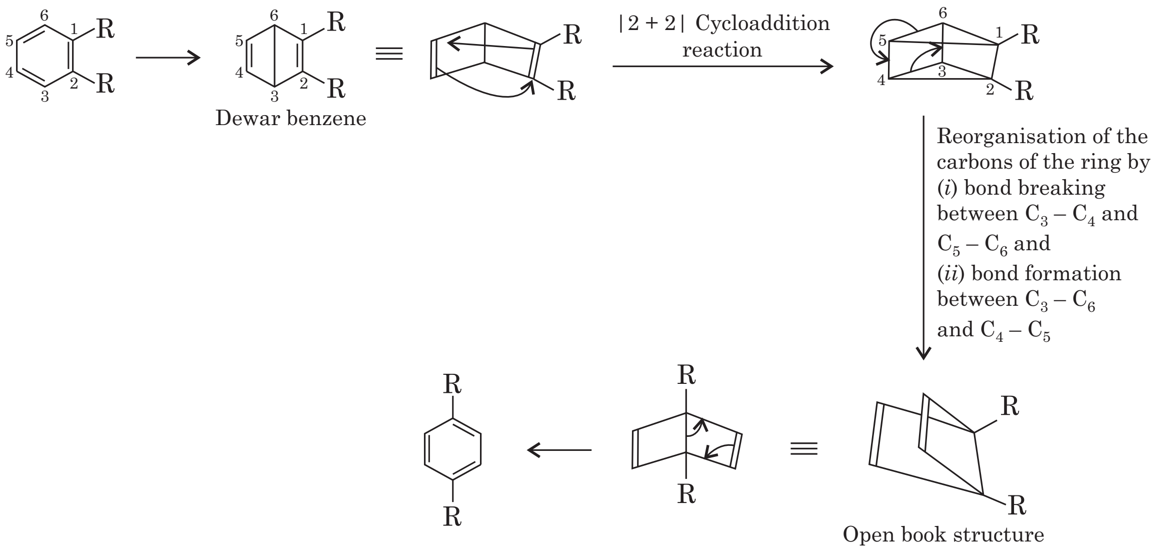
(*B*) Mechanism of 1, 2-alkyl group shift via prismane intermediate



Reorganisation of the ring by bond breaking between $C_1 - C_2$ and $C_3 - C_4$ and bond formation between $C_2 - C_3$ and $C_1 - C_4$

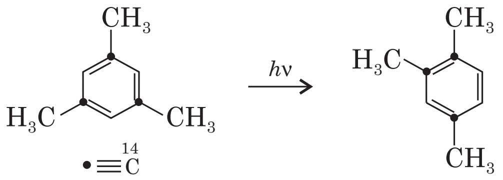
10.5.2 Mechanism of 1, 3-Alkyl Group Shift

1, 3-Alkyl group shift takes place only via formation of prismane as reaction intermediate.

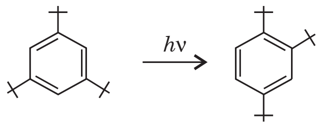


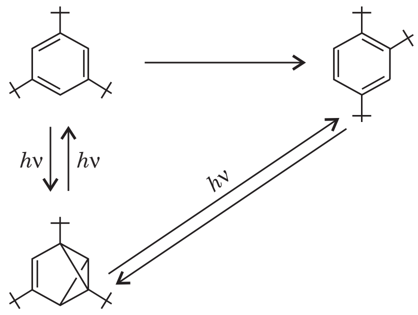
Reorganisation of the carbons of the ring by (*i*) bond breaking between $C_3 - C_4$ and $C_5 - C_6$ and (*ii*) bond formation between $C_3 - C_6$ and $C_4 - C_5$

The photo isomerisation of 1, 3, 5-trimethylbenzene to 1, 2, 4-trimethylbenzene is also due to 1, 2-alkyl group shift. This has been confirmed by isotopic labelling experiments.



Similarly, 1, 3, 5 tri-*t*-butylbenzene and 1, 2, 4-tri-*t*-butylbenzene are interconvertible to each other by 1, 2-alkyl group shift. In this case interconversion takes place via benzvalene as reaction intermediate.





10.6 PHOTOADDITION OF ALKENES TO AROMATIC BENZENOID COMPOUNDS

Benzene and its derivatives in the S_1 state undergo cycloaddition reactions with various π(*pi*) systems, specially alkenes, alkynes and dienes. The T_1 state of aromatic compounds does not give cycloaddition reactions because the T_1 state of aromatic compounds is quenched by the transfer of excitation energy to the alkene. Under certain structural and electronic circumstances a reverse model, *i.e.*, S_1 alkene + S_0 arene prevails. Three different modes of cycloaddition reactions have been observed: 1, 2 or *ortho*, 1, 3 or *meta* and 1, 4 or *para*. The 1, 4-addition is the least efficient cycloaddition reaction. These reactions occur either bimolecularly or intramolecularly. Thus there are atleast four broad mechanistic pathways possible for these reactions. These are as follows:

(*i*) Interaction of excited aromatic with ground state alkene.

(*ii*) Interaction of excited alkene with ground state aromatic.

(*iii*) Formation of biradical intermediate from excited aromatic and reaction of the biradical with alkene to give product.

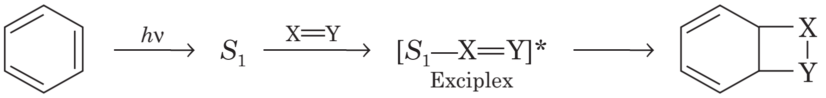
(*iv*) Involvement of dipolar entities such as

(aromatic $\overset{\bullet}{+}$ ...... olefin $\overset{\bullet}{-}$) or

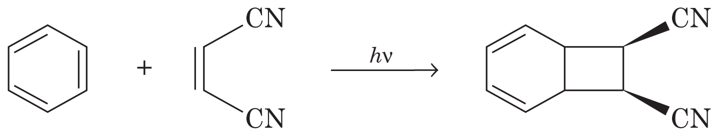
(aromatic $\overset{\bullet}{-}$ ...... olefin $\overset{\bullet}{+}$), obtained either by excitation of charge-transfer complexes pre-existing in the ground state or by electron transfer in an exciplex.

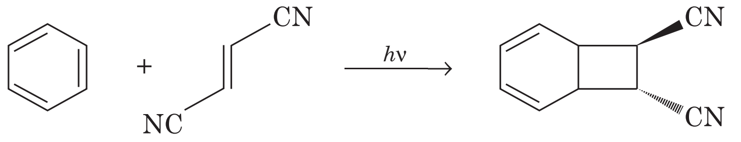
10.6.1 1, 2-Cycloaddition Reactions

Electron poor alkenes (alkenes having electron withdrawing groups) give 1, 2-addition reaction with arenes in addition to some 1, 4 products. The *para* product is the secondary product. The formation of the *ortho* product is generally favoured by donor-acceptor interaction. The more polar the interactions (charge-transfer) in the exciplex, the longer the proportion of *ortho* and *para* cycloadditions.

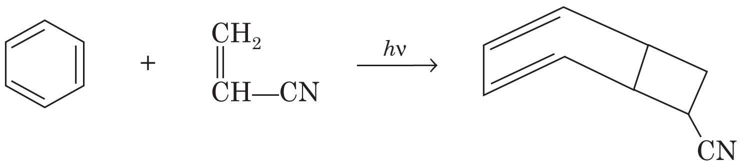


The 1, 2-cycloaddition reactions are concerted reactions. The photocycloaddition of *cis* and *trans*-2-butene to benzene in the liquid phase gives the 1, 2-adduct stereospecifically showing that the reaction is concerted reaction. This also confirmed that the product formation is taking place *via* formation of exciplex.

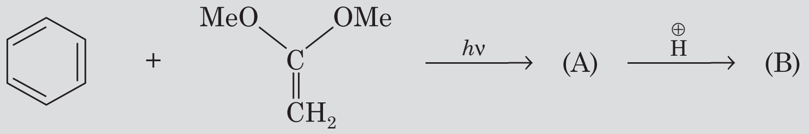




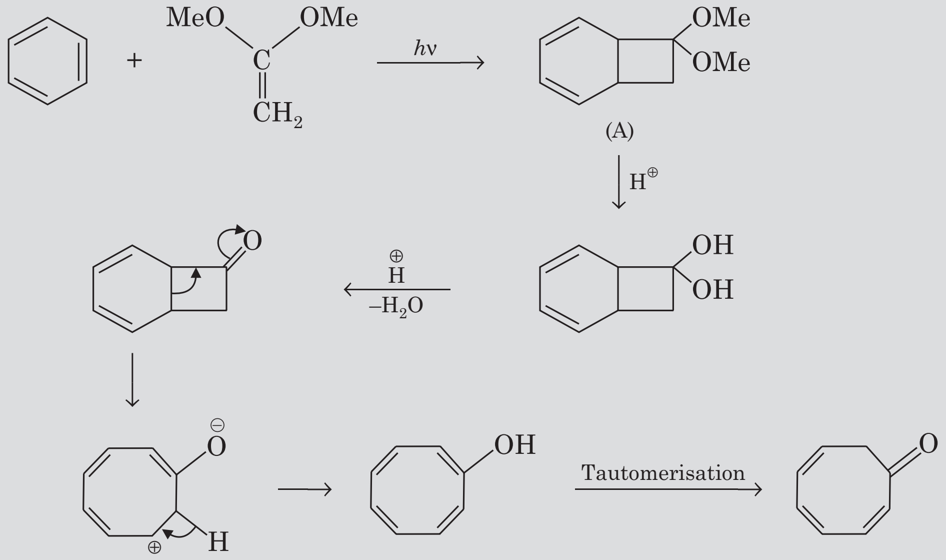
Thus benzene and its derivatives generally forms charge transfer complexes (exciplexes) with dienophiles, and, upon irradiation, gives *ortho*-cycloaddition adducts. The adduct is usually with *exo* orientation.



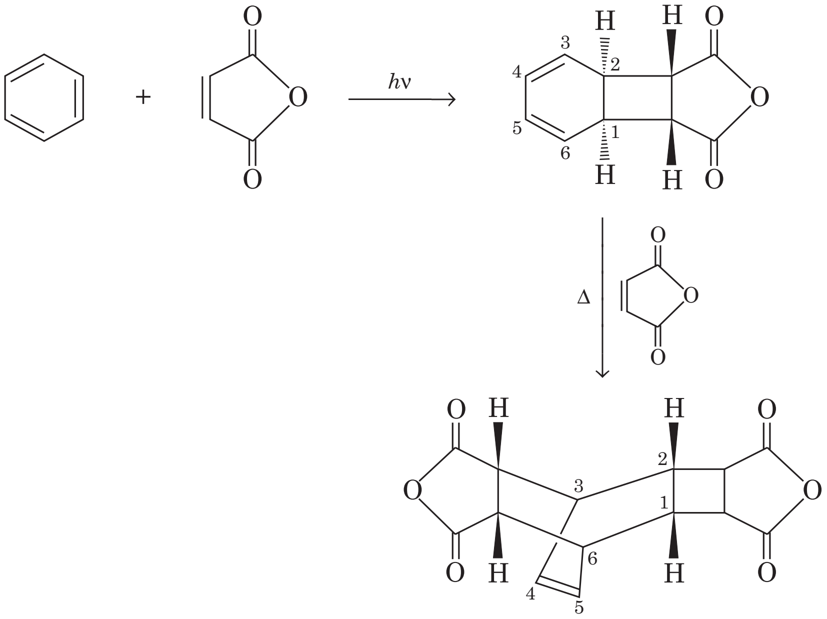
Problem 3: *Complete the following sequence of reaction:*



Solution:

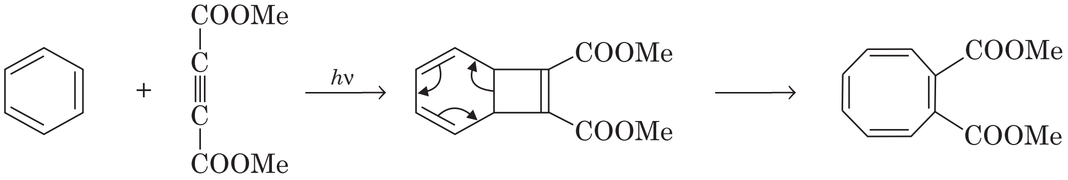


Irradiation of benzene in the presence of maleic anhydride yields an *exo* 1, 2-cycloadduct. The product formation takes place *via* S_1 state of a charge transfer complex. *Exo*-1, 2-adduct is a result of a photochemical | 2 + 2 | *ortho*-cycloaddition reaction followed by a thermal | 4 + 2 | cycloaddition.

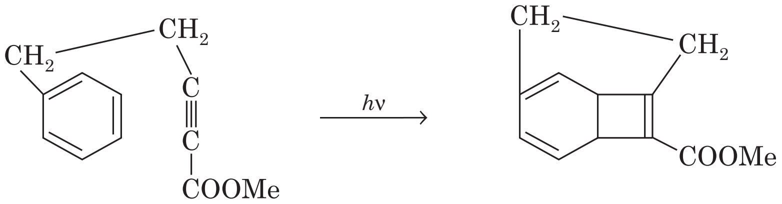


The primary products from irradiation of alkynes, specially those with electron-withdrawing groups, with benzene are the corresponding *ortho* cycloaddition products. These adducts are often unstable at ambient temperature.

These unstable adducts undergo ring opening reaction (electrocyclic ring opening) to give substituted cyclooctatetraene.



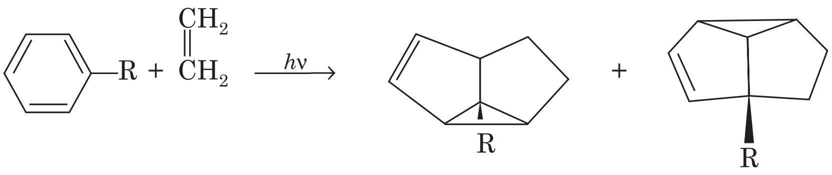
This type of cycloaddition is more efficient by an intramolecular process. This reaction is possible when alkyne moiety is linked to the arene by atleast a two carbon chain.

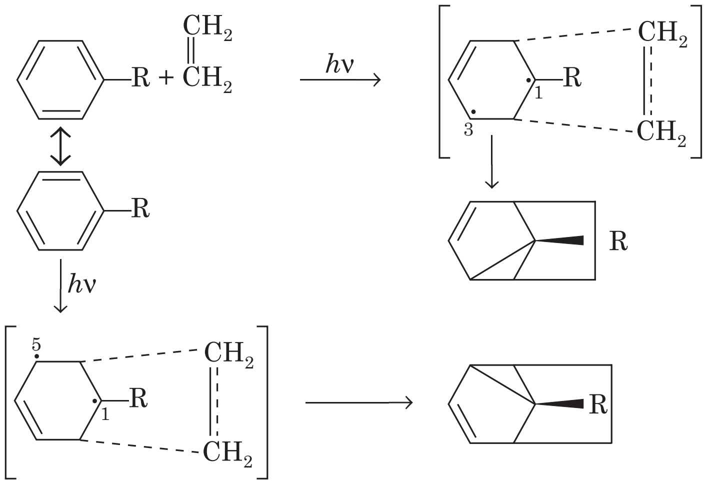


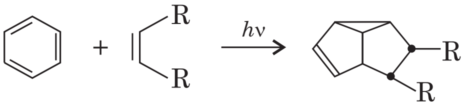
10.6.2 1, 3-Photoaddition of Benzene

This remarkable process leads to tricyclic system in which an olefinic double bond has added across the *meta*-positions of a benzene ring.

The hypothetical presentation for 1, 3 addition can be shown as follows:

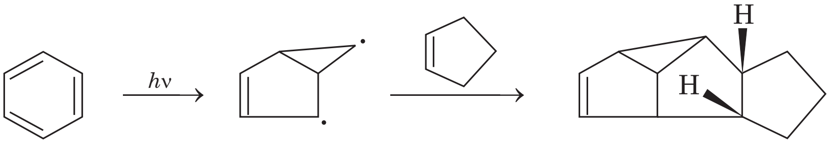






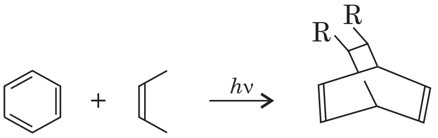
The reaction seems to be restricted to double bonds bearing only alkyl substituents such as 2-butene, norbornene, allene and cyclobutene. It occurs with 254 nm light in both gas phase and liquid phase. It is stereospecific and it involves singlet excited benzene. It is known that neither fulvene nor benzvalene is a precursor. Product formation takes place via formation of prefulvene biradical.

In 1, 3-cycloaddition reaction, *endo* product is the major product.

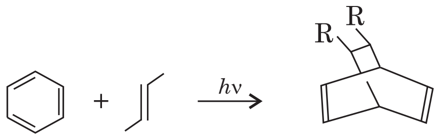


10.6.3 1, 4-Photoaddition of Benzenes

In this reaction olefinic double bond has added across the *para*-positions of a benzene ring.



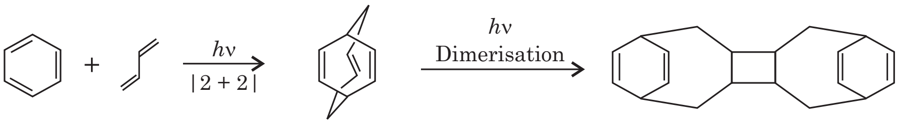
The reaction is concerted and therefore stereospecific and it involves singlet excited state benzene. The reaction is similar to Diels-Alder reaction because benzene behaves as diene in this case.



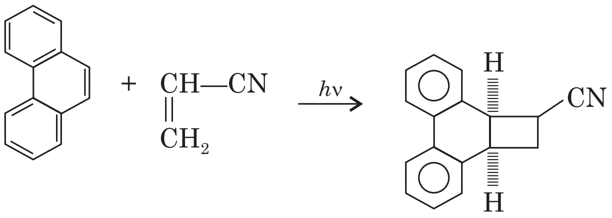
1, 4-Adduct

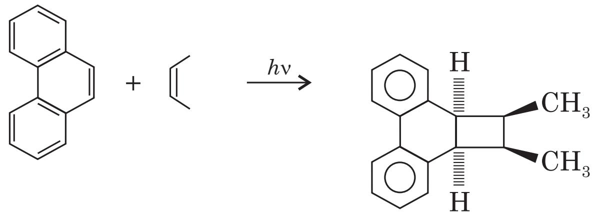
Butadiene also gives [4 + 4] cycloaddition reaction with benzene and reaction is stereospecific.

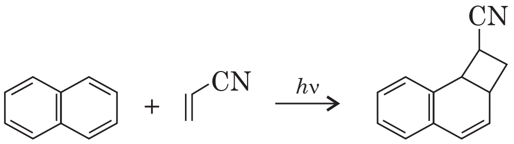
Cis

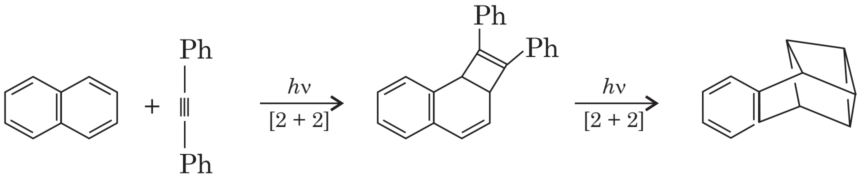


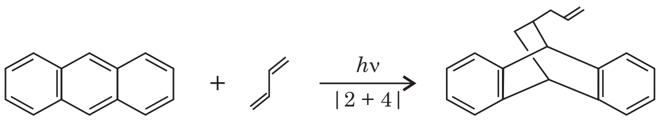
The photoaddition of olefinic systems is not restricted to benzene and its simple homologues. Analogous process occur with condensed aromatics such as naphthalene, phenanthrene or anthracene. In the case of anthracene the cycloaddition is [4 + 2] while in case of phenanthrene and naphthalene it is [2 + 2].





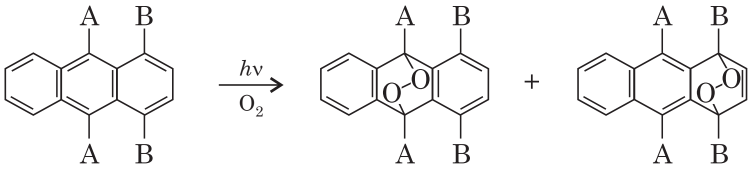


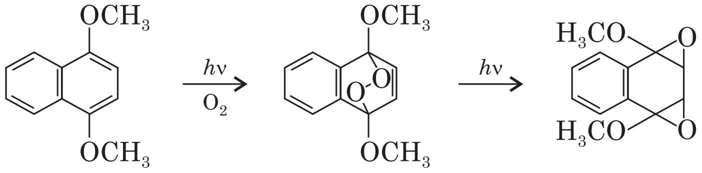




10.7 ADDITION OF OXYGEN

Polynuclear aromatic hydrocarbons such as naphthalene and anthracene from transannular peroxides when excited in the presence of oxygen, and the point of attack is substituent dependent.





Mechanistic studies indicate that the triplet excited state of the hydrocarbon excites oxygen by energy transfer, into its $1\Delta g$ state, and the singlet oxygen so produced adds thermally to the ground state hydrocarbon. Thus reaction is [4 + 2] cycloaddition reaction.

10.8 AROMATIC PHOTOSUBSTITUTION

Light-induced substitution in the aromatic compounds can occur either on a ring carbon atom or on an atom of a substituent. These substitution reactions can proceed by heterolytic or radical mechanism. The most common reactions are the heterolytic substitutions which can be classified into two categories:

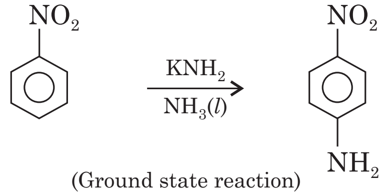
(*i*) Type A: In these reactions the orientation rules are different from those obtaining in the ground state.

(*ii*) Type B: In these reactions the orientation rules are the same as in the ground state but the process is accelerated by light absorption.

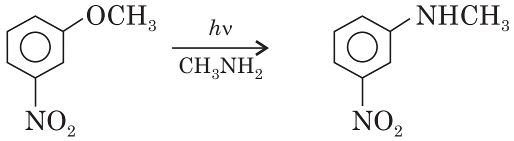
All these reactions seem to be functions of the lowest singlet excited state, and many proceed in high quantum yield.

10.8.1 Type A Reactions

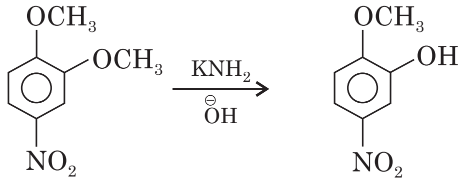
(*i*) ***Photonucleophilic Substitution:*** Nitro group is activating group and *ortho* and *para* directing group for nucleophilic substitution reactions in the ground state. In the presence of light (*i.e.,* in the excited state) the nitro group is *m*-directing group.



(Ground state reaction)

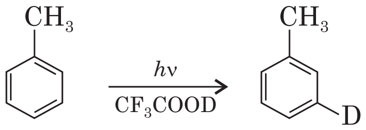


(Reaction in excited state)

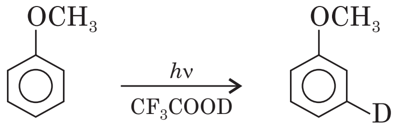


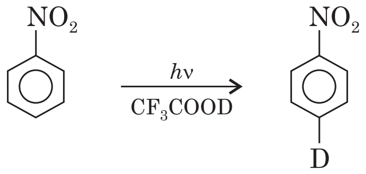
In many cases the cyano group behaves similarly, and analogous reactions are found with substituted naphthalenes.

(*ii*) ***Photoelectrophilic Substitution:*** On irradiation in the presence of CF_3COOD, toluene gives mainly *m*-deuterio toluene instead of *o*-and *p*-derivatives.



Anisole also gives *m*-derivative whereas nitrobenzene gives *p*-derivative.





Notice that the observed orientation differs from that expected in the ground state, the nitro group activates the *p*-position and the methoxy group activates the *m*-position.

Orientation rules for nucleophilic and electrophilic substitution reactions may be obtained from simple considerations of the changes in electron density on making the transition $S_0 \rightarrow S_1$. For simplicity consider benzyl carbocation as model for benzene substituted with electron-withdrawing group and benzyl carbanion with electron-donating group.

The seven π molecular orbitals of benzyl system are related to those of benzene itself and take the form of Fig. 10.1; where the number are the electron densities at the carbon atoms. The ψ_4 is the non-bonding molecular orbital, and the pairs ψ_2, ψ_3 and ψ_4, ψ_5 are no longer degenerate.

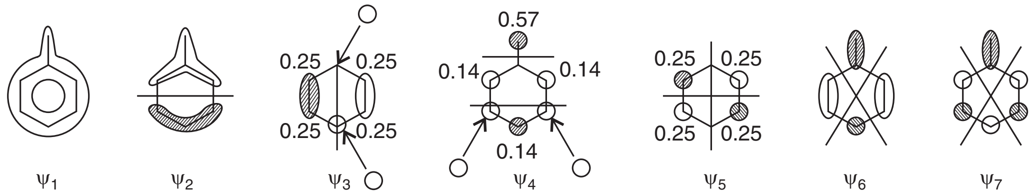


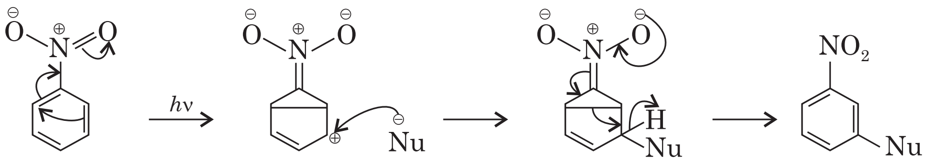
Fig. 10.6 The π molecular orbitals of benzyl systems in schematic form

Consider first the ground state benzyl cation. The six electrons are accommodated in ψ_1, ψ_2 and ψ_3. The HOMO in this case is ψ_3. Hence the $S_0 \rightarrow S_1$ state corresponds to $\psi_3 \rightarrow \psi_4$ transition. In ψ_3 the electron density in the α-position is zero and in ψ_4 it is 0.57. Thus the transition induces a very large increase in the charge density at the α-position. Similarly, one finds that excitation leads to the *o*-and particularly the *m*-position becoming more positive (electron deficient) and the *p*-position becoming somewhat more negative (electron rich). The results are reverse in case of benzyl carbanion (Table 10.1).

Table 10.1 Change in electron densities at different positions in benzyl carbocation and benzyl carbanion on excitation

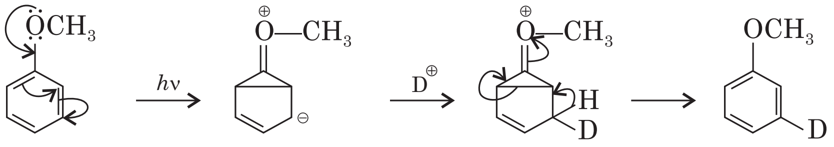
Position	*Change in electron density on excitation*	
	Benzyl carbocation	*Benzyl carbanion*
α	– –	+ +
o	+	–
m	+ +	– –
p	–	+

If one assumes that the rate of photosubstitution is correlated with the charge density at the point of attack, there is an immediate explanation of the observed result—an electron withdrawing substituent decreases electron density at *m*-position hence it is *m*-directing group for nucleophilic substitution reaction. In valence bond terms this can be explained as follows:



Mechanism of photonucleophilic substitution

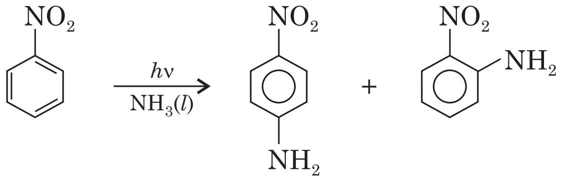
Similarly electron donating group increases electron density at *m*-position therefore, such groups are *m*-director for electrophilic substitution reactions.



Mechanism of photoelectrophilic substitution

10.8.2 Type B Substitutions

These reactions takes place on irradiation but have orientation rules characteristic of the ground state. In nucleophilic substitution reactions, nucleophile is always neutral. The detailed mechanism of Type B reactions is not yet clear.

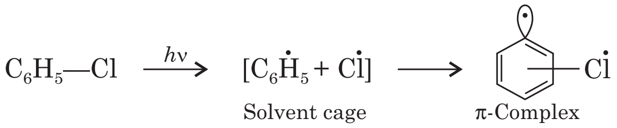


10.8.3 Radical Substitutions

Haloaromatic compounds on irradiation undergo homolysis in ground state to produce radicals which then give rise to products by well-established thermal pathway.

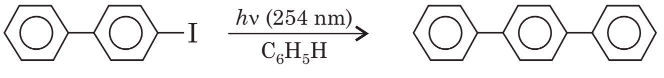
$$Ar + X \xrightarrow{h\nu} A\dot{r} + \dot{X}$$

However, when chlorobenzene is excited in the liquid phase, the $P\dot{h}$ and $C\dot{l}$ radicals seems to recombine within the solvent cage generating transient π-chlorobenzene, and isomer of chlorobenzene in which the chlorine atom forms a π complex with phenyl radical.

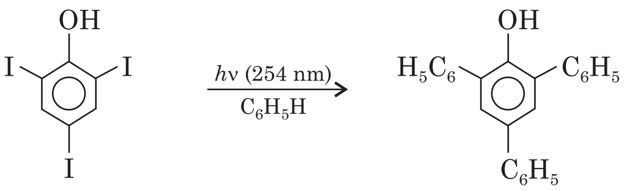


Halogen atom of π complex is more selective than halogen free radical.

The light-induced homolysis of aryl-halogen bonds has important synthetic implications. Irradiation of lodinated aromatics in benzene often gives the phenylated aromatic in high yield.

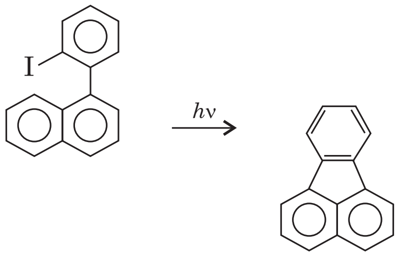


90% Yield

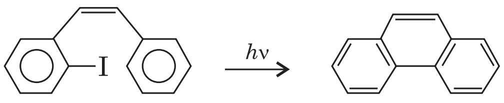


75% Yield

Intermolecular reactions of this type can be used for the preparation of polynuclear aromatic compounds.



Fluoranthene
22% yield



Phenanthrene
90% yield

Similar reaction is also given by iodoacetylenes.

$$C_6H_5\text{—}C \equiv C\text{—}I \xrightarrow[C_6H_6]{h\nu} C_6H_5\text{—}C \equiv C\text{—}C_6H_5$$

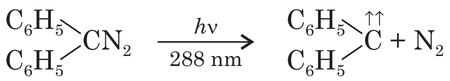
75% Yield

10.9 PHOTOCHEMISTRY OF DIAZO COMPOUNDS

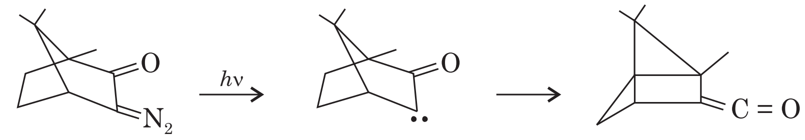
Diazoalkanes exibit a weak absorption band in the visible region (400–500 nm) which is attributed to a $n \rightarrow \pi^*$ transition.

$$R_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N} \longleftrightarrow R_2\overset{\ominus}{C}\text{—}\overset{\oplus}{N}{\equiv}\ddot{N} \longleftrightarrow R_2\overset{\oplus}{C}\text{—}\ddot{N}{=}\overset{\ominus}{N}$$

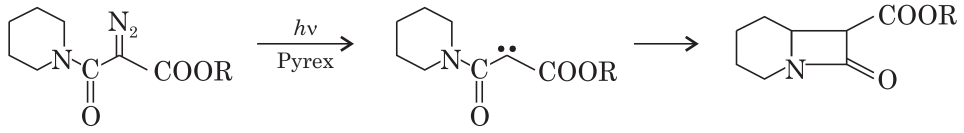
The corresponding excited states fragment readily to give molecular nitrogen and a carbene and this is a widely used method for the generation of these divalent carbon species. Direct irradiation leads initially to a singlet state of the diazo compound and hence to a *singlet carbene*, although collisional deactivation give *triplet carbene* before further reaction occurs. It may be important for those carbenes whose triplet state is lower in energy than the singlet state, especially at higher pressure in the vapour phase or in solution. Triplet sensitised decomposition of diazoalkanes gives rise directly to triplet carbene by way of the triplet excited state. These processes provide a valuable route to carbene and are employed for intramolecular reaction as in the ring contraction of cyclic diazoketones and in β-lactam formation from α-diazoamides.



$$(C_6H_5)_2CN_2 \xrightarrow[288\text{ nm}]{h\nu} (C_6H_5)_2\overset{\uparrow\uparrow}{C} + N_2$$



Cyclic diazoketone



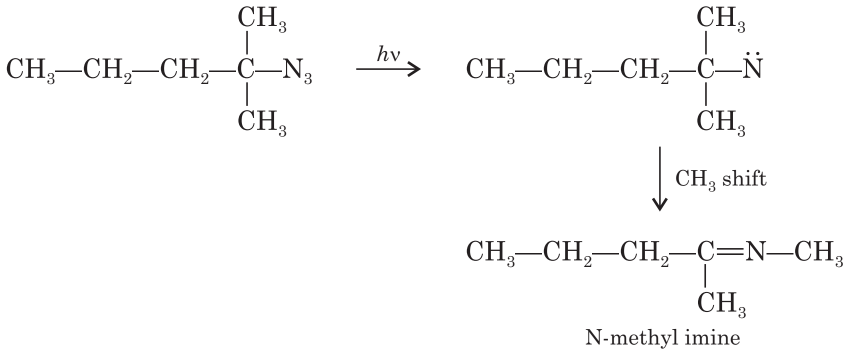
10.10 PHOTOCHEMISTRY OF AZIDES

Azides are similar to diazoalkanes. It also gives molecular nitrogen and nitrene in excited state.

Aliphatic azides give aliphatic nitrene. Aliphatic nitrenes normally give imine by a hydrogen shift.

$$CH_3—CH_2—CH_2—N_3 \xrightarrow{h\nu} CH_3—CH_2—CH_2—\ddot{N} \xrightarrow{\text{Hydrogen shift}} \underset{\text{Imine}}{CH_3—CH_2—CH{=}NH}$$

If α-carbon has no hydrogen then in that case alkyl shift takes place.

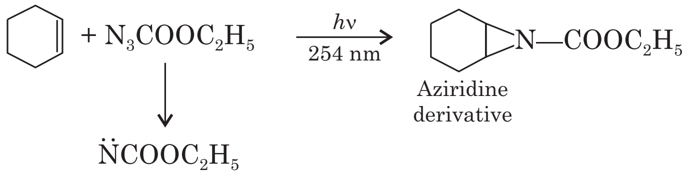


$$CH_3—CH_2—CH_2—\underset{CH_3}{\overset{CH_3}{C}}—N_3 \xrightarrow{h\nu} CH_3—CH_2—CH_2—\underset{CH_3}{\overset{CH_3}{C}}—\ddot{N} \xrightarrow{CH_3\ \text{shift}} \underset{\text{N-methyl imine}}{CH_3—CH_2—CH_2—\underset{CH_3}{C}{=}N—CH_3}$$

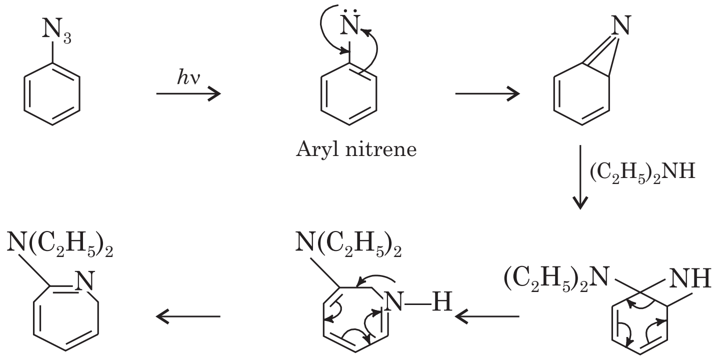
Intermolecular hydrogen abstraction from solvent can also occur to give an amine.

$$CH_3—CH_2—CH_2—\ddot{N} \xrightarrow{\text{Ether}} CH_3—CH_2—CH_2—NH_2$$

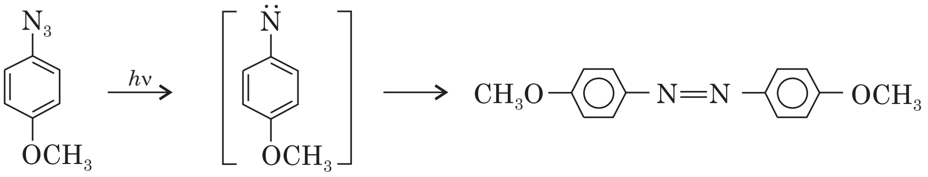
Singlet state nitrene gives addition reaction with olefines like carbenes to give aziridine.



Singlet state vinyl or aryl nitrenes undergo intramolecular cycloaddition to form a 1-azirine. In the aromatic systems this can lead to ring-expansion with eventual formation of a 6H-azepine when a nucleophile is present. In the absence of nucleophile an azo compound may be formed.



In the absence of nucleophile aryl nitrene undergoes coupling reaction to give azo compound.



GLOSSARY

Photocycloaddition: A light-initiated reactions in which the termini of two multiple bond systems become joined through σ bonds. The most common example of this type of reactions is the formation of a cyclobutane ring from two ethylene moieties.

Rydberg Transition: Any transition or absorption process in which electron is promoted to an orbital with a larger principal quantum number *n* than that of the initial orbital is known as Rydberg transition. In ethylene the 2pπ-3*S* transition is a Rydberg transition.

FURTHER READING

1. P. de Mayo, ed, *Rearrangements in Ground and Excited States,* vol. 3, Academic Press, New York, 1980.
2. J.M. Coxon and B. Halton, *Organic Photochemistry,* Cambridge University Press, London, 1974.
3. W. Harspool and D. Armester, *Organic Photochemistry, A Comprehensive Treatment*, Eillis Horwood/Prentice Hall, 1972.
4. J. Kagan, *Organic Photochemistry, Principles and Applications,* Academic Press, 1993.
5. A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry,* CRC Press, Boca Raton, Florida, 1991.

6. D.O. Crown and R.L. Drisko, *Elements of Organic Photochemistry,* Plenum, New York, 1976.

7. J. Kopecky, *Organic Photochemistry: A Visual Approach*, VCH, Weinhim, Germany, 1992.

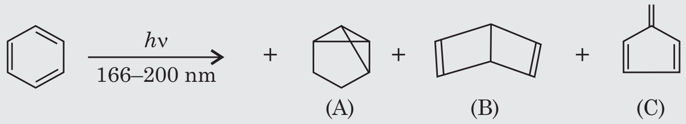
PROBLEMS

1. Discuss briefly the following:
  (*i*) *Cis-trans* isomerisation of alkenes by direct irradiation.
  (*ii*) Sensitised *cis-trans* isomerisation.

2. Alkenes give two types of photodimerisation.
  (*i*) Concerted [2 + 2] cycloaddition.
  (*ii*) Nonconcerted cycloaddition
  Give mechanism of both these reactions.

3. Discuss photochemistry of 1, 3-butadiene.

4. Irradiation of benzene yields a mixture of three products (A), (B) and (C).



Propose a suitable mechanism for this transformation.

5. Irrational of *o*-Xylene yields a mixture of *m*-and *p*-Xylenes. Propose a suitable mechanism for this transformation.

6. 1, 3, 5-Trimethylbenzene on irradiation with UV light gives 1, 2, 4-trimethylbenzene. This transformation is due to the 1, 2-alkyl group shift or 1, 3-alkyl group shift. Give mechanism for this transformation.

7. 1, 2-Alkylgroup shift in alkyl substituted benzene takes place via formation of two thermally unstable intermediates. Give mechanism for the formation of these reaction intermediates.

8. 1, 2-Dimethylbenzene on irradiation gives a mixture of 1, 3-and 1, 4-dimethylbenzene via the formation of prismane as reaction intermediate. Given structures of prismanes in both cases.

9. 1, 3-Butadiene in solution on irradiation gives chemistry only from S_1 state. Explain.

10. Discuss the mechanism of dimerisation of 1, 3-butadiene in solution in the presence of acetophenone and benzil as sensitiser.

11. Discuss the chemistry of photoaromatic nucleophilic substitution.

12. Discuss the chemistry of photoelectrophilic aromatic substitution reaction.

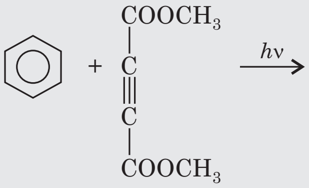
13. Explain why NO_2 is meta directing for photo induced aromatic nucleophilic substitution reactions.

14. Explain why methoxy group is meta-directing for photo induced aromatic electrophilic substitution reactions.

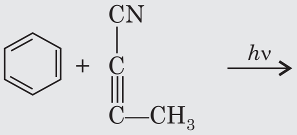
15. Discuss the chemistry of photoaddition reaction between benzene and alkenes.

16. Complete the following reactions and give their mechanism:

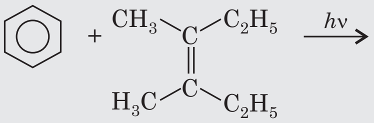
(*i*)



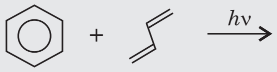
(*ii*)



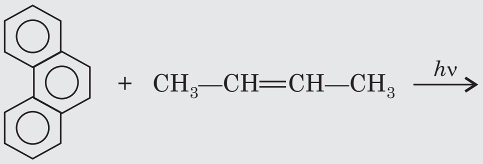
(*iii*)



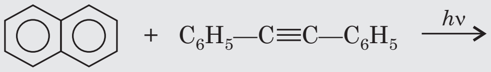
(*iv*)



(*v*)



(*vi*)



17. Discuss the photochemistry of

(*i*) Diazo compounds

(*ii*) Azides.

11
CHAPTER

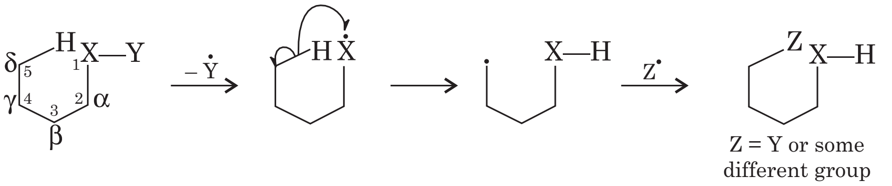
Photo Substitution Reactions at sp^3 Hybrid Carbon Having at Least One Hydrogen

11.1 INTRODUCTION

Substitution reaction at sp^3 hybrid carbon takes place when carbon has either leaving group or has at least one hydrogen. Replacement of hydrogen is possible when neighbouring group activates the carbon. Ionic attack at unactivated C—H bonds is uncommon. Free radical on the other hand, can often be obtained with enough energy to break unactivated C—H bonds. Intermolecular reactions of this type (free radical halogenation, sulphonation, nitration etc.) are of limited value because the reagents are unselective and mixture of products generally results. However, it has been found that in many molecules intramolecular free radical attack at sp^3 hybrid carbon having hydrogen can become quite specific when molecules meet certain structural and geometrical requirements. The reaction leads to the introduction of functional group at this carbon and number of reactions of this type have become of synthetic importance.

The key step in these reactions is an intramolecular abstraction of hydrogen from δ-carbon (carbon-5) resulting in the transfer of a hydrogen atom from δ-carbon to the attacking free radical in the same molecule. Transfer of hydrogen atom from δ-carbon leads to the formation of six-membered transition state which is very common in photochemistry.

The reaction can be represented as follows (equation 1):



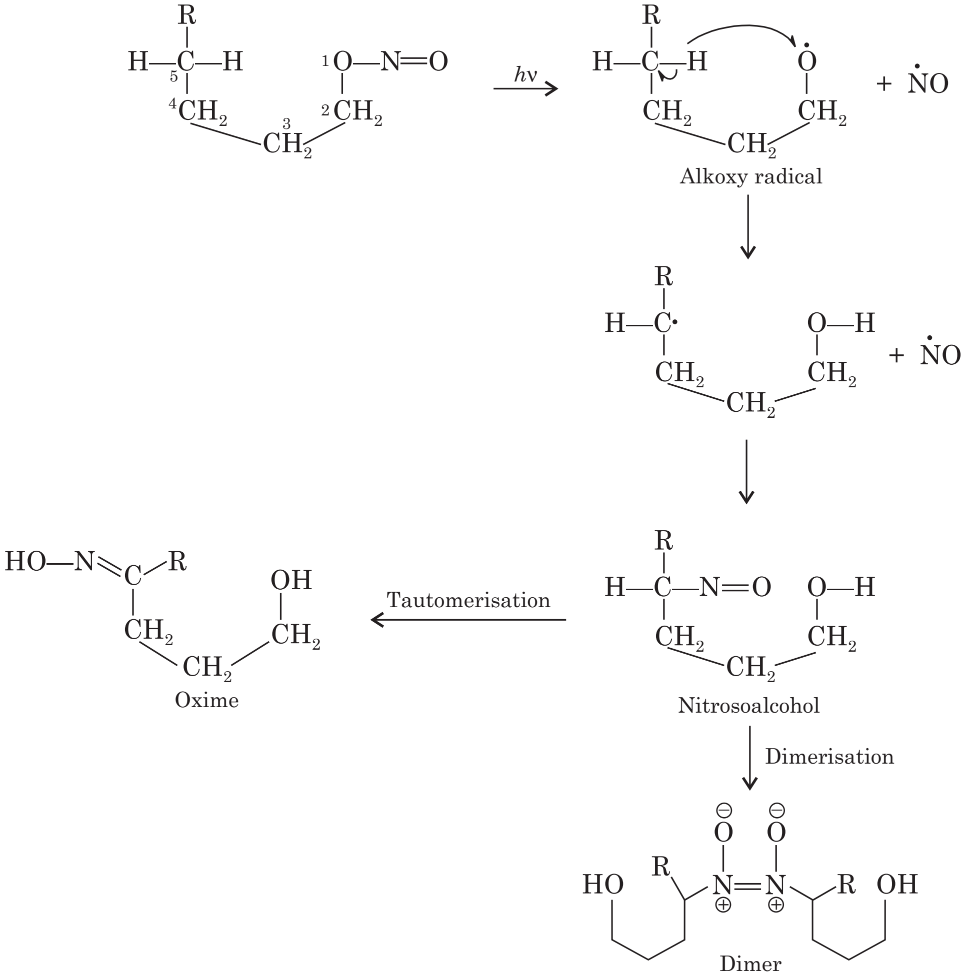
...(1)

In the above reaction X in most of the cases is either oxygen or nitrogen.

The most common reaction of this class is *Barton* reaction (when X is oxygen) and *Hoffmann-Loeffler-Freytag* reaction (when X is nitrogen).

11.2 BARTON REACTION

It has been known for many years that vapour phase photolysis or pyrolysis of organic nitrites (X = O, Y = NO) gives alkoxy radicals and nitrogen monoxide. It has been found that when the structure of the molecule is such as to bring the $-\overset{|}{\underset{|}{C}}-O-N{=}O$ group and a $-\overset{|}{\underset{|}{C}}-H$ bond into close proximity, or potentially close proximity (generally 1, 5-positions), the alkoxyl radicals produced by photolysis of the nitrites in solution have sufficient energy to bring about selective intramolecular hydrogen abstraction according to the equation (1) to give carbon radical. This carbon radical captures nitrogen monoxide to give nitrosoalcohol. This nitrosoalcohol may be isolated as dimer or may rearrange into oxime. The nitroso and oximo compounds produced may further be transformed into other functional derivatives such as carbonyl compounds, cyano compounds and amino compounds. The photolytic conversion of organic nitrites into nitroalcohols is known as *Barton reaction*. The complete reaction is as follows (Scheme 1):

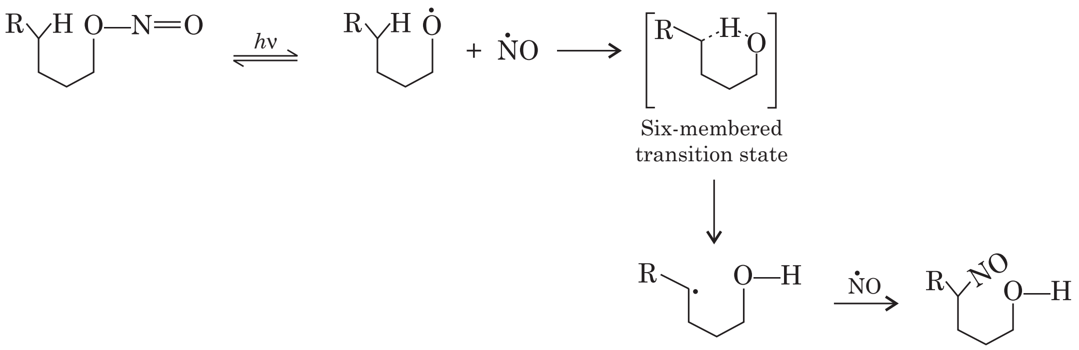


Scheme 1 Formation of nitrosoalcohol

Thus the Barton reaction is an example of the remote functionalisation of an unreactive saturated carbon atom. The reaction starts from the S_1 ($n\ \pi^*$) state (λ = 310–390 nm) with the cleavage of the R—O—NO bond (*Ediss* = 150 – 190 kJ) to produce nitric oxide and an activated alkoxy radical (Scheme 1). This is followed by abstraction of hydrogen *via* a six-membered cyclic transition state and the formation of hydroxyl group and a carbon radical that combines with nitric oxide (Scheme 1*a*). The nitroso compound dimerises or preferentially isomerises to the oxime.

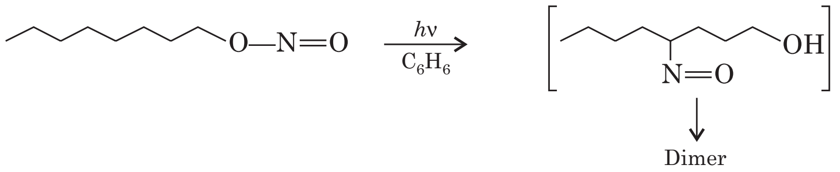
The reaction is effected by irradiation under nitrogen of a solution of the substrate in a suitable non-hydroxylic solvent with light from a high pressure mercury arc lamp. A pyrex filter is usually employed to limit the radiation of wavelength greater than 300 nm.

Quantum yield of the reaction is 0.76. This confirmed that the reaction is photochemical reaction and not the free radical chain reaction. In free radical chain reactions quantum yield is always more than one. Photolysis of nitrite ester is reversible process which has been confirmed by the use of N^{15} nitrite ester. Photolysis of nitrite ester gives an alkoxyl radical and nitrogen monoxide in reversible step which are completely dissociated from each other. The alkoxyl radical rearranges rapidly, by abstraction of hydrogen, to a carbon radical. This carbon radical can be captured by radical trapping reagents to give transfer products. The normal fate of the carbon radical in the absence of trapping reagents is to react relatively slowly with nitrogen monoxide to give nitrosoalcohol.



Scheme 1a

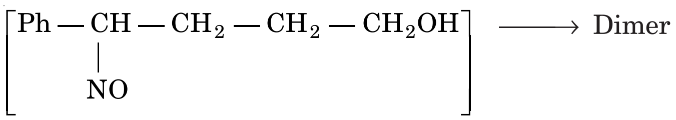
There is ample evidence to support the view that hydrogen transfer step takes place through a six-membered transition state. In practice reaction occurs at most exclusively by abstraction of a hydrogen atom from the δ-carbon. Photolysis of 1-octyl nitrite in benzene gave only dimer of 4-nitroso-1-octanol.



...(2)

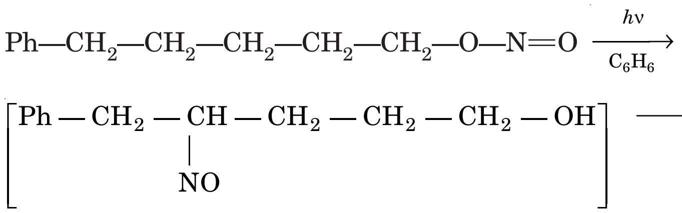
Similarly 4-phenyl-1-butylnitrite and 5-phenyl-1-pentyl nitrite are readily converted into dimer of 4-nitroso-4-phenylbutanol and 4-nitroso-5-phenylpentanol respectively.

$$\text{Ph—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—O—N=O} \xrightarrow[\text{C}_6\text{H}_6]{h\nu}$$



$$\left[\begin{array}{l}\text{Ph}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}\\ \quad\;\;\;\;\,|\\ \quad\;\;\;\text{NO}\end{array}\right] \longrightarrow \text{Dimer}$$

...(3)

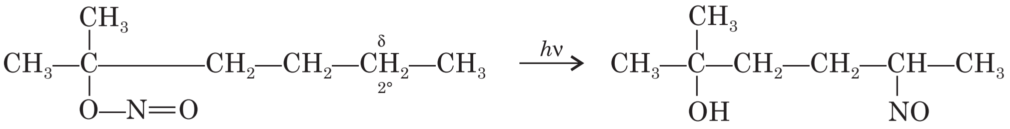


$$\mathrm{Ph{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}N{=}O} \xrightarrow[C_6H_6]{h\nu}$$

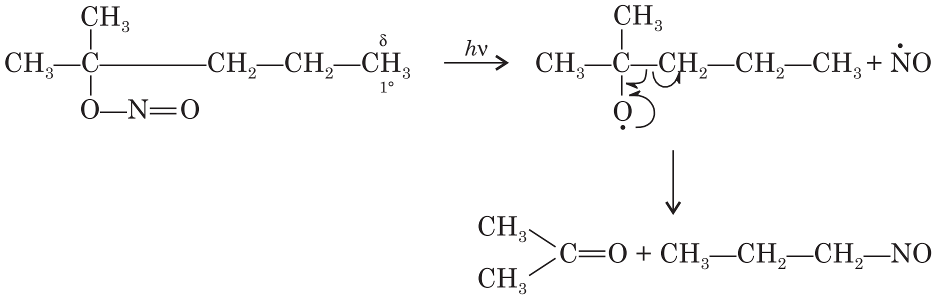
$$\left[\mathrm{Ph-CH_2-\underset{\underset{NO}{|}}{CH}-CH_2-CH_2-CH_2-OH}\right] \longrightarrow \text{Dimer} \qquad ...(4)$$

Structure of the 4-nitroso-4-phenylbutanol and 4-nitroso-5-phenylpentanol can be rationalised by assuming a six-membered cyclic transition state in the hydrogen transfer step. In case of 5-phenyl-1-pentylnitrite, none of the products is formed by abstraction of hydrogen from benzylic carbon which would require a seven membered transition state. In the same way, photolysis of 3-phenyl propyl nitrite (C_6H_5—CH_2—CH_2—CH_2—O—NO) did not yield any product corresponding to abstraction of benzylic hydrogen atom through five-membered cyclic transition state, even through abstraction of benzylic hydrogen should be highly favourable thermodynamically.

Intramolecular hydrogen abstraction by alkoxyl radicals is always accompanied to a greater or lesser extent by disproportionation, radical decomposition and intermolecular reactions. In case of alkoxyl radicals derived from tertiary nitrites the reaction follows the normal course if δ-carbon is secondary or tertiary. But if δ-carbon is primary then Barton reaction is superseded by alkoxyl decomposition.



$$\mathrm{CH_3-\underset{\underset{O-N=O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\overset{\delta}{\underset{2^\circ}{CH_2}}-CH_3} \xrightarrow{h\nu} \mathrm{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\underset{\underset{NO}{|}}{CH}-CH_3} \qquad ...(5)$$

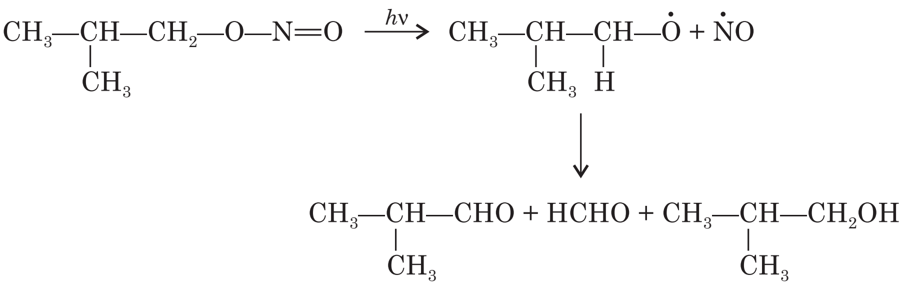


$$\mathrm{CH_3-\underset{\underset{O-N=O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\overset{\delta}{\underset{1^\circ}{CH_3}}} \xrightarrow{h\nu} \mathrm{CH_3-\underset{\underset{\dot{O}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3} + \dot{\mathrm{N}}\mathrm{O}$$

$$\downarrow \qquad ...(6)$$

$$\mathrm{(CH_3)_2C{=}O + CH_3{-}CH_2{-}CH_2{-}NO}$$

Disproportionation reactions also occur in primary and secondary nitrites having no hydrogen on δ-carbon.

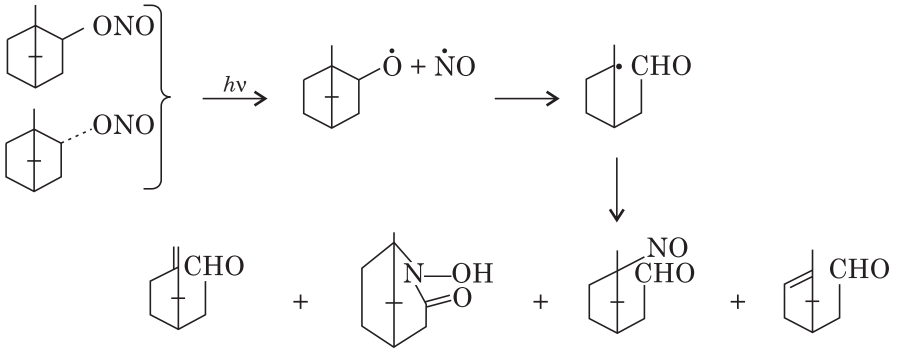


$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-N{=}O} \xrightarrow{h\nu} \mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{H}{|}}{CH}-\dot{O}} + \dot{\mathrm{N}}\mathrm{O}$$

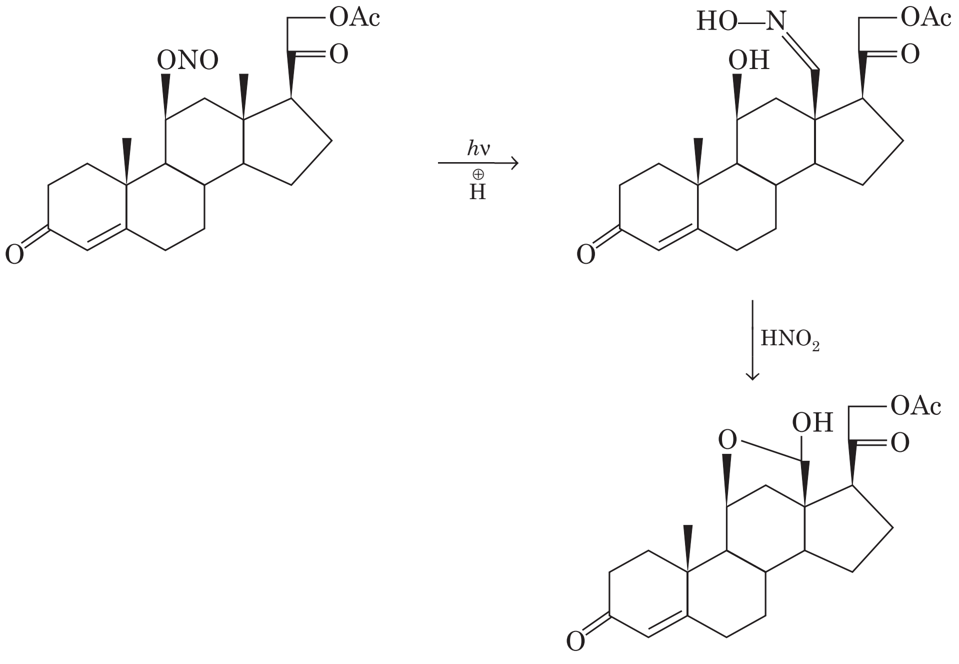
$$\downarrow$$

$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO + HCHO + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH}$$

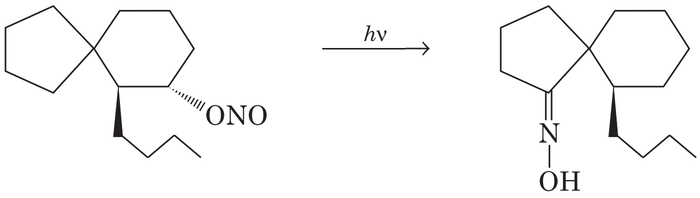
dl-Bornyl and *dl*-isobornyl also undergo disproportionation rather than Barton reaction.



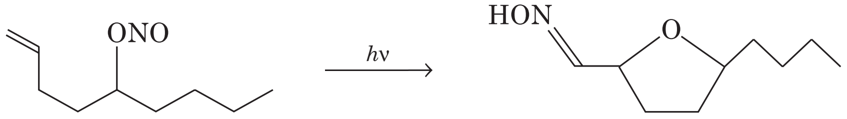
The Barton reaction is potentially useful in the synthesis of natural products, such as hormones and alkaloids. The photolysis of the 11-nitrite of corticosterone acetate has been utilised on an industrial scale in the partial synthesis of aldosterone-21-acetate.



The key step in the synthesis of the alkaloid perhydrohistorionicotoxin is the photolysis of the nitrite of a spirocyclic alcohol having three different γ-hydrogen atoms. The transition state of optimal geometry is formed between both rings of the spirocyclic molecule.

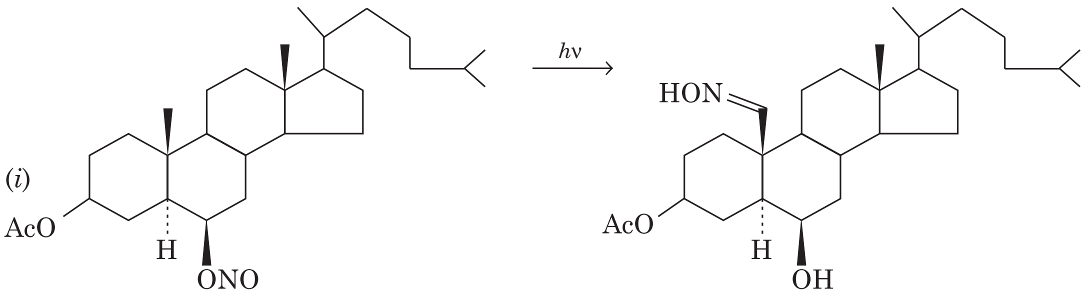


When the double bond of an alkenyl nitrite is in close proximity to the alkoxy radical formed by irradiation, the sole product is a result of its addition to the C=C bond with the formation of a cyclic ether.

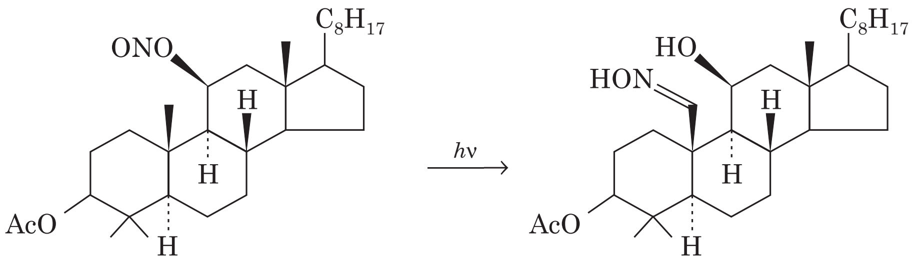


Some other examples are as follows:

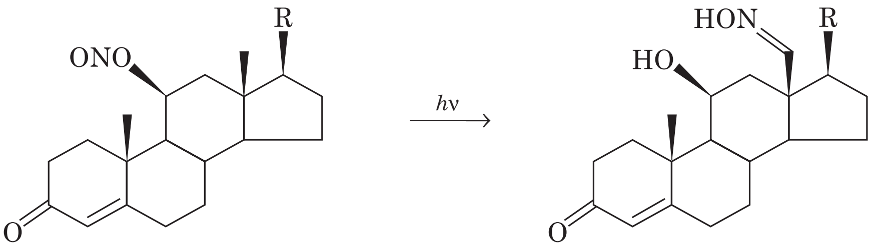
(*i*)



(*ii*)

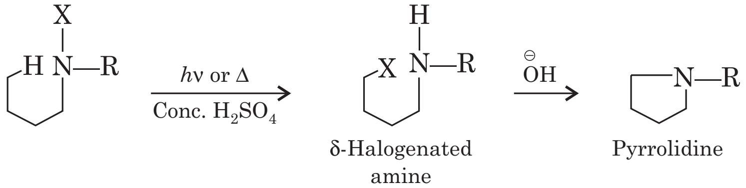


(*iii*)



11.3 THE HOFFMANN-LOEFFLER-FREYTAG REACTION

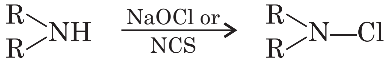
This reaction is given by N-haloamines having hydrogen on δ-carbon. The reaction is affected by warming a solution of the halogenated amine in strong acid (concentrated sulphuric acid or concentrated CF_3COOH) or by irradiation of the acid solution with ultraviolet light. The product of the reaction is the δ-halogenated amine. This product is not generally isolated in this reaction. This product on basification gives pyrrolidine and its derivatives.



...(1)

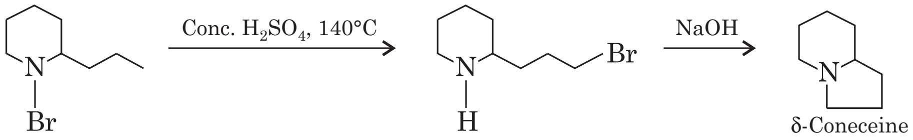
Both N-chloro and N-bromo amines are used as starting material but the N-chloroamines give better result. N-chloroamines are obtained from primary and secondary amines by the action of sodium hypochlorites or N-chlorosuccinamide (NCS).

$$R{-}NH_2 \xrightarrow[\text{NCS}]{\text{NaOCl or}} R{-}NHCl \qquad ...(2)$$



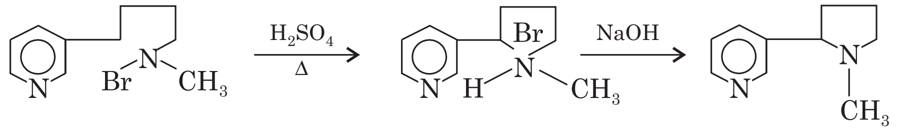
$$R_2NH \xrightarrow[\text{NCS}]{\text{NaOCl or}} R_2N{-}Cl \qquad ...(3)$$

The first example of this reaction was reported by A.W. Hoffmann equation 4.



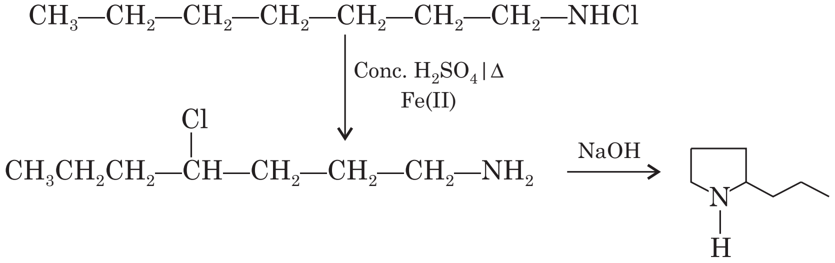
...(4)

Latter, further examples of this reaction were reported by Loeffler. One of the reactions reported by Loeffler is

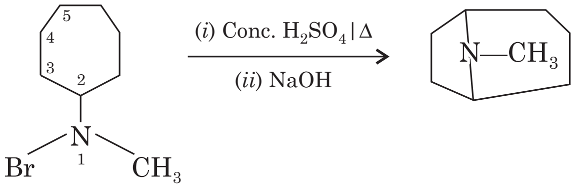


...(5)

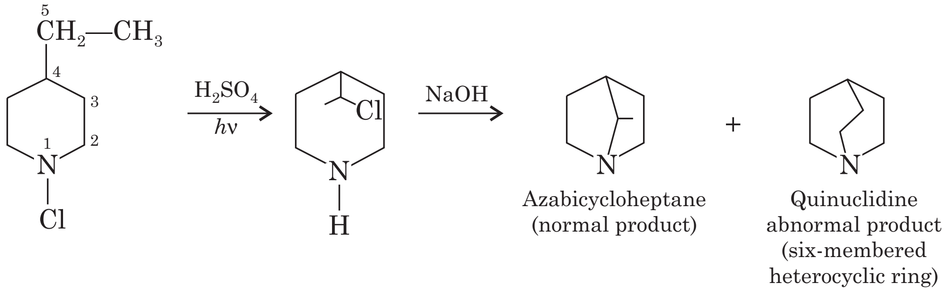
When haloamines are the derivatives of primary amines, reaction takes place in the presence of Fe(II) as initiator.



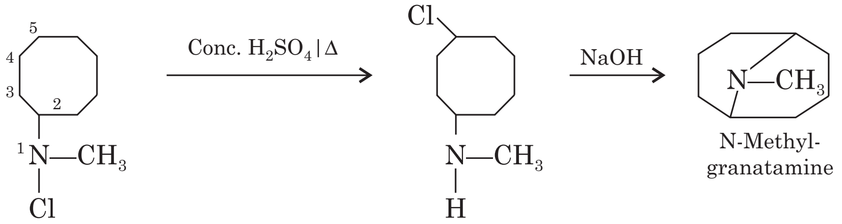
With N-halocycloalkylamines cyclisation leads to bridged-ring structures, but in these cases products may not be exclusively pyrrolidine derivatives. In some cases six-membered heterocyclic ring is formed instead of five membered heterocyclic ring. N-Bromo-N-methyl cycloheptylamine gives tropane. In this case pyrrolidine ring is formed.



Similarly N-chloro-4-ethyl piperidine gave a mixture of the azabicycloheptane and quinuclidine

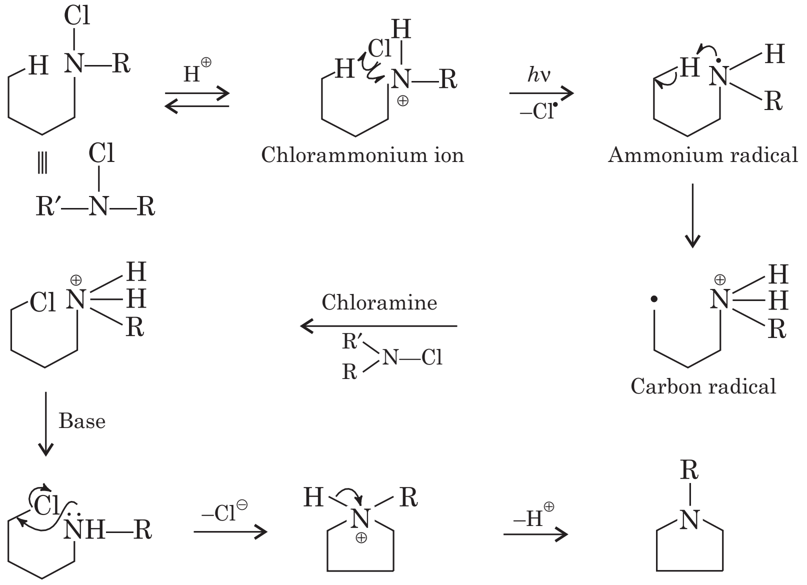


N-chloro-N-methylcyclooctylamine yields only N-methylgranatamine in which six-membered heterocyclic ring is formed.



The reason for the formation of six-membered heterocyclic ring instead of five-membered heterocyclic ring is not clearly understood.

The reaction is believed to proceed by a free radical chain process (Scheme 2).

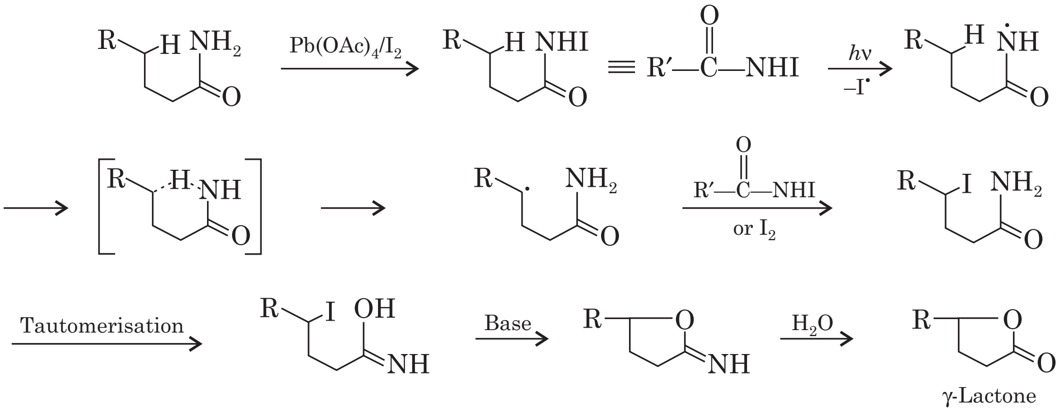


Scheme 2 Mechanism of the reaction

In acidic medium the reacting species is chlorammonium ions. This dissociates photochemically to form the ammonium radical. This ammonium radical abstracts a suitably situated hydrogen atom on the δ-carbon to give the carbon radical. This carbon radical abstract a chlorine atom from another molecule of chloramine, thus propogating the chain and at the same time forming the δ-chloroamine from which the cyclic amine is subsequently obtained (Scheme 2).

The free radical nature of the reaction is supported by the fact that reaction does not proceed in the dark at 25°C. The reaction is initiated by heat and Fe(II) and inhibited by oxygen and *p*-benzoquinone. These results also support the free radical nature of the reaction. The abstraction of hydrogen from δ-carbon is supported by the fact that in number of cases δ-chloroamines are isolated from the reaction mixture.

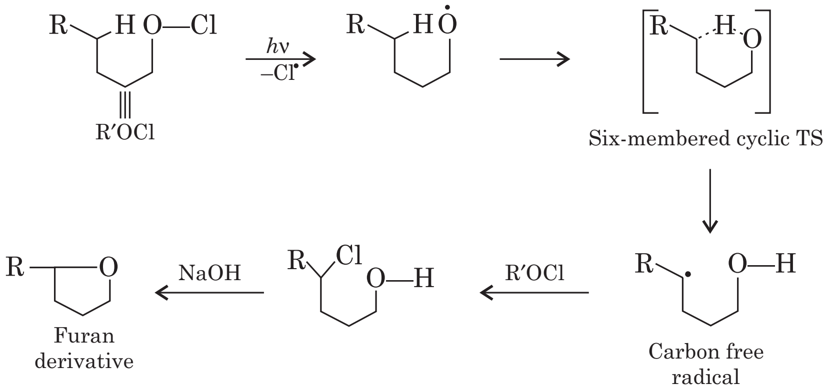
N-Haloamides also give this reaction. In this case N-halogen bond undergoes facile rupture upon photolysis. Barton has made use of this reaction to develope a useful method for the synthesis of γ-lactones. In case of amides the starting material is N-iodoamides prepared either with lead tetraacetate-iodine or by tertiary butyl hypochlorite-iodine mixture (Scheme 3).



Scheme 3 Preparation of γ-lactone from N-iodoamide having hydrogen on δ-carbon

11.4 PHOTOLYSIS OF HYPOHALITES

The photolysis of hypohalites needs little discussion, since it proceeds in a similar fashion to that of nitrite esters but reaction is free radical reaction not the concerted reaction. This reaction is free radical reaction as in case of Hoffmann-Loeffler-Freytag reaction. This reaction is given by hypohalites which have at least one hydrogen on δ-carbon. The initial products of the reaction are 1, 4-dichlorohydrins formed again by preferential abstraction of hydrogen present on δ-carbon atom of the molecule. The 1, 4-dichlorohydrins of this reaction are easily converted into tetrahydrofurans by treatment with alkali. The reaction proceeds through a six-membered cyclic transition state as in the photolysis of nitrite esters (Scheme 4).



Scheme 4

GLOSSARY

Barton Reaction: The transformation of nitrite esters to γ-oximino alcohols, via homolytic cleavage to form nitrous oxide (NO) and an alkoxy radical. The alkoxy radical may then abstract remote and unactivated hydrogen atoms from δ-carbon.

Hoffmann-Loeffler-Freytag Reaction: The homolysis of protonated N-haloamines either thermally or photochemically to form amine salts with halogenated alkyl substituents. Neutralisation of these amine salts leads to formation of cyclic amines. This reaction is particularly useful in preparing five-membered nitrogen-containing rings.

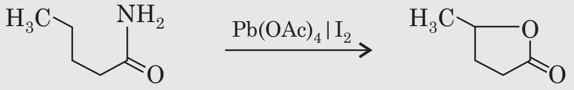
FURTHER READING

1. W. Carruthers, *Some Modern Methods in Organic Synthesis*, Cambridge University Press, Cambridge, 1987.
2. J.M. Coxon and B. Halton, *Organic Photochemistry*, Cambridge University Press, Cambridge, 1974.
3. Jan Kopecky, *Organic Photochemistry: A Visual Approach*, VCH, Weinhim, Germany, 1992.
4. William M. Horspool, *Aspects of Organic Photochemistry*, Academic Press, New York, 1976.

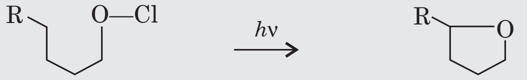
PROBLEMS

1. Give mechanism of the Barton reaction.
2. Discuss synthetic applications of Barton reaction.
3. Discuss mechanism of Hoffmann-Loeffler-Freytag reaction.
4. Discuss briefly photolysis of hypohalites.
5. Suggest mechanism for the following reactions:

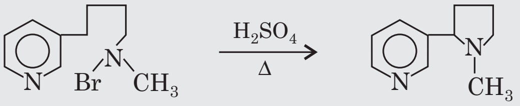
(*i*)



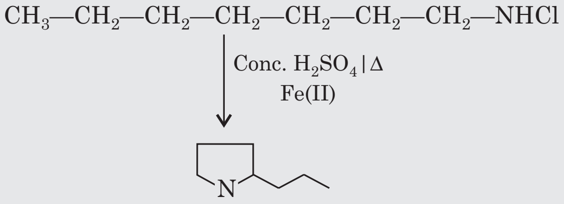
(ii)


R
O—Cl
hν
R
O

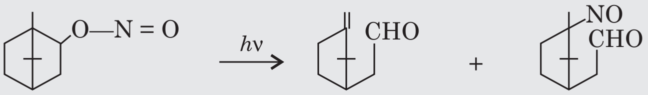
(iii)


N
N
Br
CH₃
H₂SO₄
Δ
N
N
CH₃

(iv)


CH₃—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—NHCl
Conc. H₂SO₄ | Δ
Fe(II)
N

(v)


O—N = O
hν
CHO
+
NO
CHO

12
CHAPTER

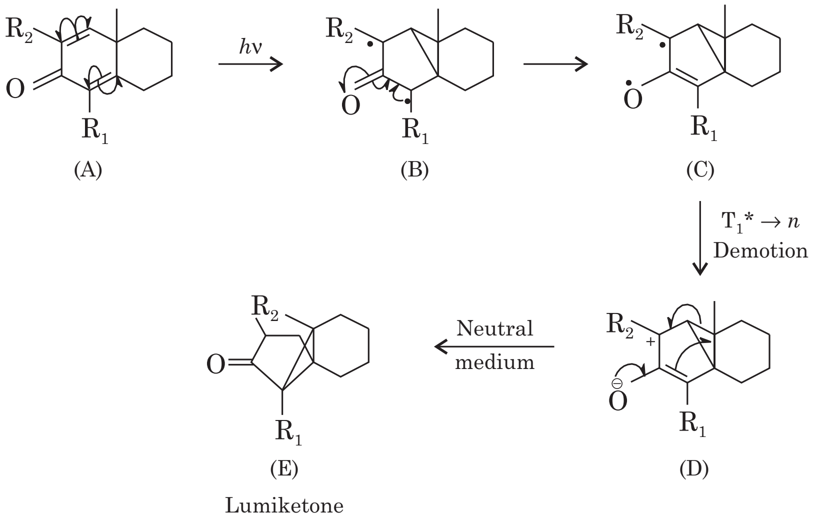
Photochemistry in Natural Products

12.1 PHOTO REARRANGEMENT OR ISOMERISATION

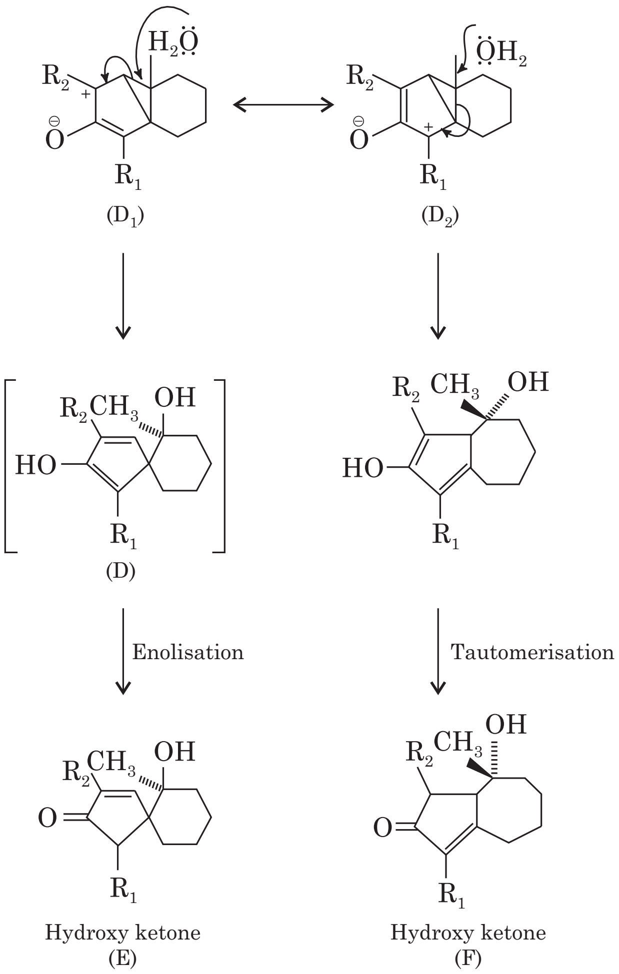
Natural products such as santonin, a molecule which offers the possibility of numerous structural and stereochemical variations, have provided excellent models for experimental and theoretical chemists to conduct studies aimed at clarifying the chemistry of excited-state molecules.

Natural products having cross conjugated ketone system (Terpenoids and steroids) undergo rearrangement (see rearrangements of Dienone) by diradical intermediate. This rearrangement takes place via an *n*, π* triplet state. This photo rearrangement shows strong solvent dependence.

General Photoisomerisation



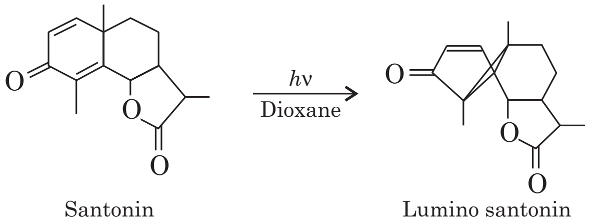
Lumiketone is obtained from (D) when medium is neutral, *i.e.*, in the presence of dioxane (D) gives two isomeric ketones (E) and (F) in acidic medium (45% CH_3COOH).



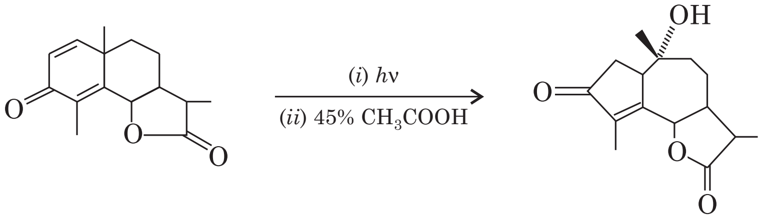
Stability of intermediate cation D_1 and D_2 determines the reaction path in acidic medium. When R_1 is +I group and R_2 = H then major product is (F) which is formed from D_2. Similarly if R_2 is +I group and R_1 = H then major product is (E) which is formed from D_1.

Photoisomerisation of Santonin in Neutral Medium

Santonin in the presence dioxane gives Luminosantonin



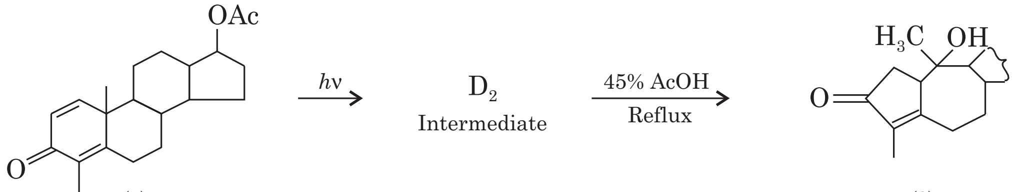
Photoisomerisation in Acidic Medium



Hydroazulenone

Conversion of santonin into hydroazulenone derivative takes place by formation of intermediate (D_2). A methyl substituent effect is observed in this case.

Steroid (1) also gives the above result in the presence of acidic medium.

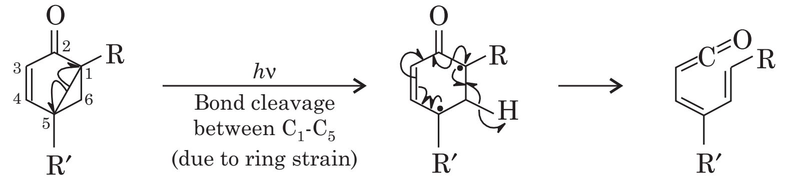


(1) (2)

12.2 PHOTOCHEMISTRY OF NATURAL PRODUCTS CONTAINING BICYCLO [3, 1, 0] HEXANE-2-ONE RESIDUE

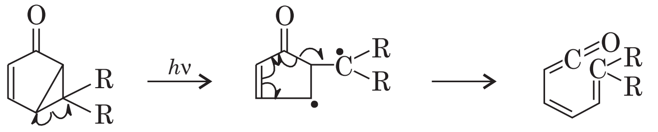
Bicyclo [3, 1, 0] hexane-2-one (1) give rise to a large number of photo chemical transformation.

(*i*) The primary process leads to the breaking of bond between C_1 and C_5 followed by C_1 and C_2. These bond cleavage give diene-ketone without skeletal rearrangement.



(1) (A) (2)

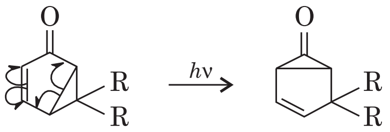
(*ii*) Breaking of bond between C_5-C_6 leads to the formation of diene-ketene with rearrangement.



(3) (4)

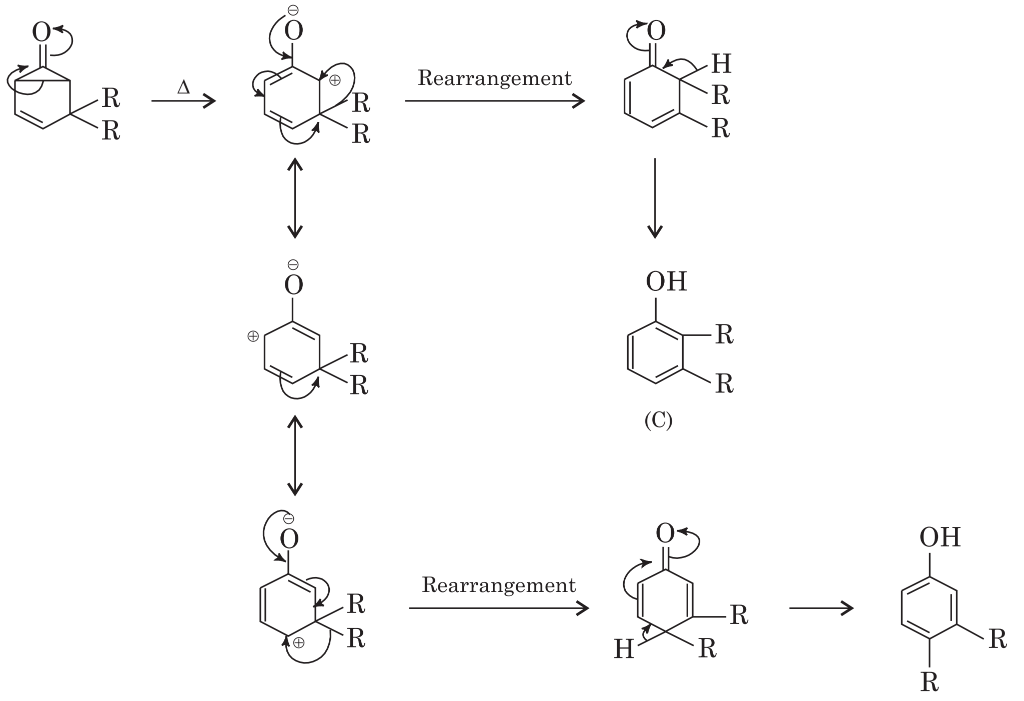
Diene ketene

(*iii*) Breaking of bond between C_1-C_5 leads to the formation of cyclopropanone derivative.



(5) (6)

This cyclopropanone derivative undergoes thermal rearrangement as follows:



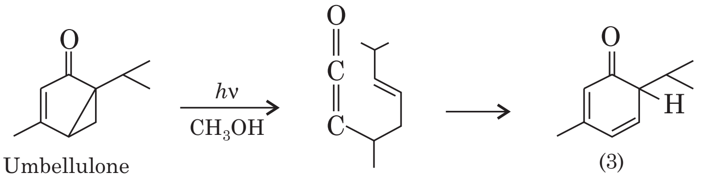
(C)

(B)

1. 1, 5 bond cleavage should be favoured by the presence of substituents on C-1 and C-5 and 5, 6 bond cleavage should be favoured by substitution on C-6.
2. Phenolic products (B) and (C) are formed by cyclopropanone intermediate (6).

Photochemistry of Umbellulone

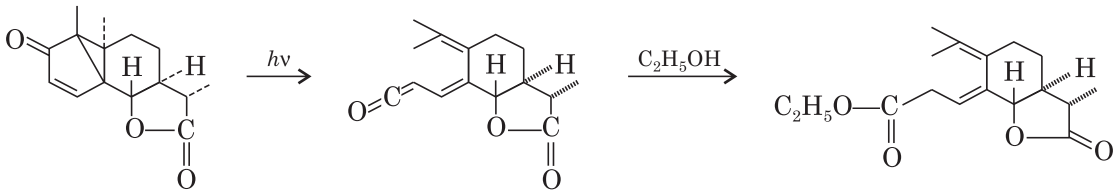
Umbellulone is a tripenoid. On irradiation with UV light in the presence of CH_3OH at room temperature it gives two isomeric compounds (2) and (3).



Umbellulone (2) (3)

Photochemistry of Lumisantonin

Lumisantonin on irradiation gives ketene (1) as a primary photo product which then converted into photosantonic acid.

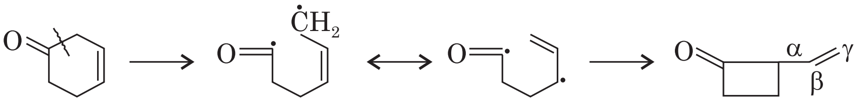


Lumisantonin (1) Photosantonic ester

12.3 PHOTOCHEMISTRY OF NATURAL PRODUCTS HAVING β, γ-UNSATURATED KETONE GROUP

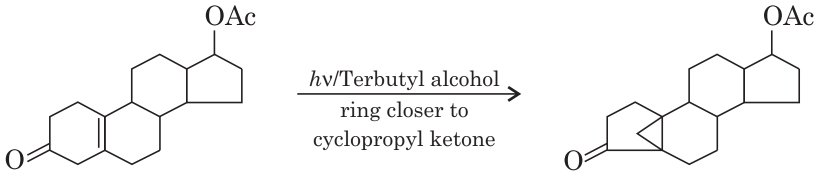
As mentioned earlier that β, γ-unsaturation promotes α-cleavage of carbonyl compound because of allylic stabilisation of the radical produced. Two modes of overall reaction are observed.

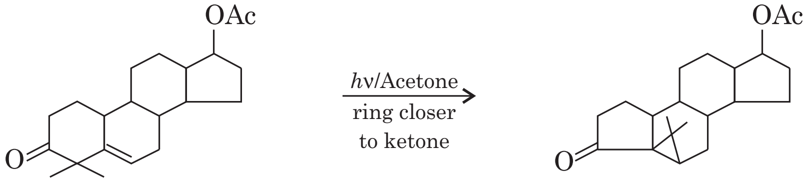
The first mode involves a 1, 3-acyl shift in the formation of an isomeric β, γ-unsaturated ketones.



The second mode of reaction involves ring closure to a cycloporpyl ketone.

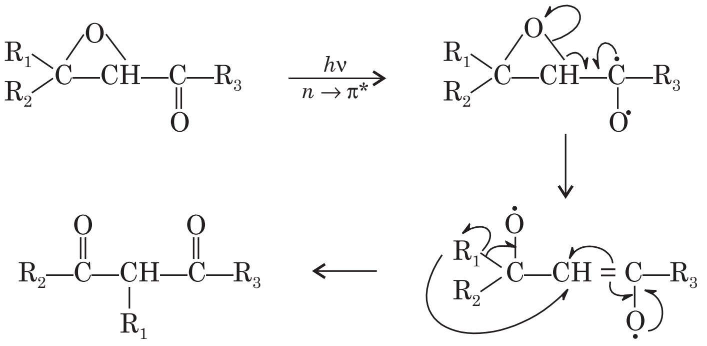
Example





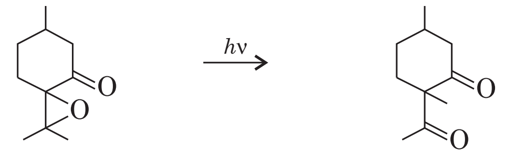
12.4 PHOTOCHEMISTRY OF NATURAL PRODUCTS HAVING EPOXY KETONE SYSTEM

As mentioned earlier that photochemical reaction of aliphatic α, β epoxy ketones give 1, 3 diketones and α-hydroxy ketones by migration of alkyl and hydrogen respectively.

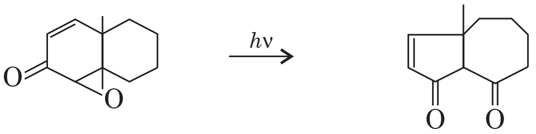


1, 3-Diketone

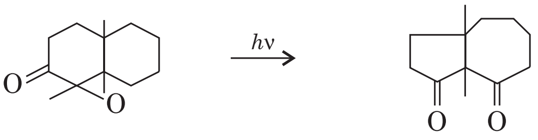
Examples



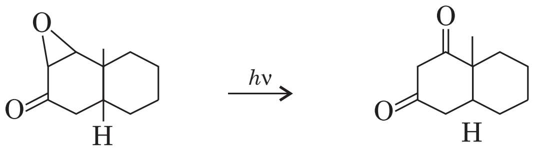
1, 3-Diketone



1, 3-Diketone



1, 3-Diketone



12.5 DYE-SENSITISED PHOTOOXYGENATIONS

Since *KAUTSKY* discovered the reactivity of singlet oxygen, dye-sensitised photooxygentation of organic compounds has been extensively investigated from synthetic and mechanistic viewpoints.

Molecular oxygen has a unique electronic configuration in that the electronic character of ground state oxygen is triplet

$$O_2 = \sigma(1s)^2\ \sigma^*(1s)^2\ \sigma(2s)^2\ \sigma^*(2s)^2\ \sigma(2px)^2\ \pi(2py)^2 = \pi(2pz)^2\ \pi^*(2py) = \pi^*(2pz)$$

It has two unpaired electrons one in $\pi^*(2py)$ and other in $\pi^*(2pz)$ hence it has triplet multiplicity $= 2s + 1 = (2 \times 1 + 1) = 3$

On the other hand, two kinds of singlet oxygen can be generated photochemically. These are ${}^1\Delta g$ and ${}^1\Sigma^+ g$ singlets.

Electronic configuration of ${}^1\Delta g$ singlet oxygen

$$\sigma(1s)^2\, \sigma^*(1s)^2\, \sigma(2s)^2\, \sigma^*(2s)^2\, \sigma(2px)^2\, \pi(2py)^2 = \pi(2py)^2\, \pi^*(2py)^2\, \underset{\text{Vacant orbital}}{\underset{\downarrow}{\pi^*(2pz)^0}}$$

Electronic configuration of ${}^1\Sigma_g^+$ singlet oxygen

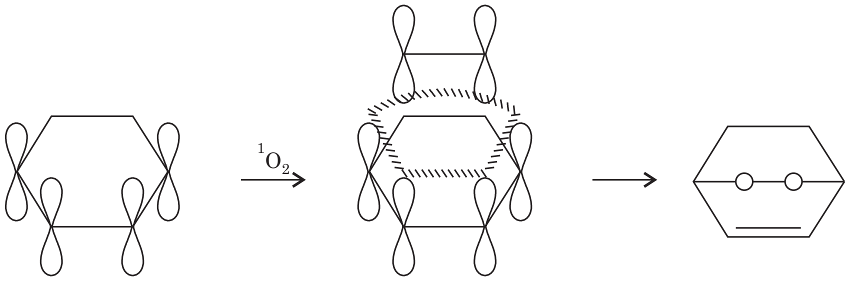
$$\sigma(1s)^2\, \sigma^*(1s)^2\, \sigma(2s)^2\, \sigma^*(2s)^2\, \sigma(2px)^2\, \sigma(2px)^2\, \pi(2py)^2 = \pi(2pz)^2\, \underset{\text{Half filled orbital}}{\underset{\Downarrow}{\pi^*(2py)\uparrow}}\, \underset{\text{Half filled orbital}}{\underset{\Downarrow}{\pi^*(2py)\downarrow}}$$

Opposite spins

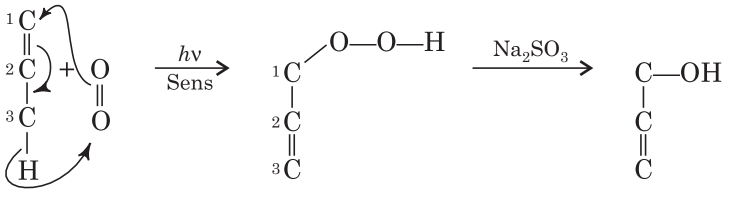
The ${}^1\Delta g$ singlet oxygen is mostly responsible for usual photooxygenation reaction.

Photooxygenation Reaction

Cisoid dienes: Singlet oxygen gives additions reactions with *cisoid* dienes and reaction proceeds in a concerted manner by formation of six-membered TS.

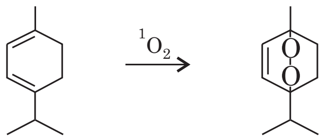


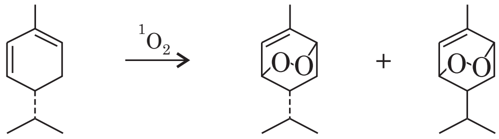
Thus dienes give 1, 4-cycloaddition reaction with singlet oxygen in concerted manner with monoalkenes. The reaction is more complex and follows the general scheme shown below:

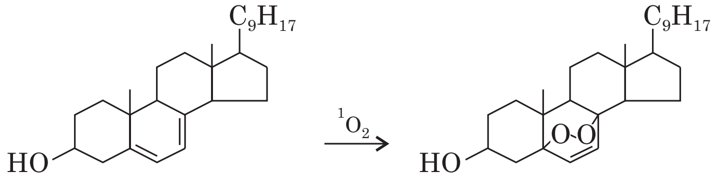


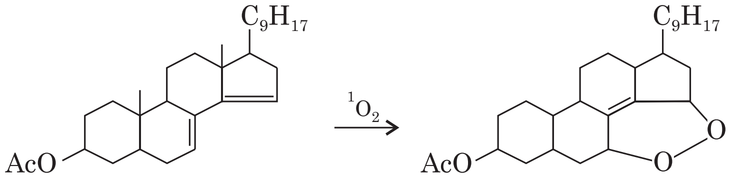
The reaction is identical to ene reaction. The obtained peroxide on reduction with Na_2SO_3 gives alcohol.

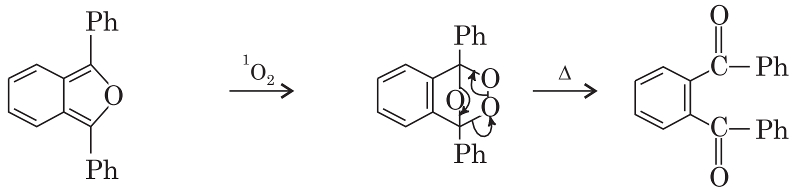
Some examples of photooxygenation of naturally occurring dienes are given below:





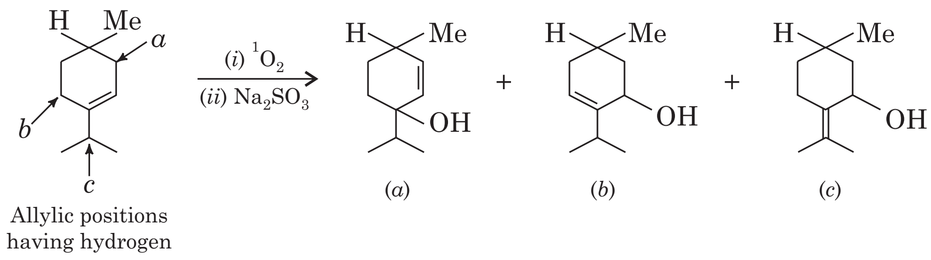


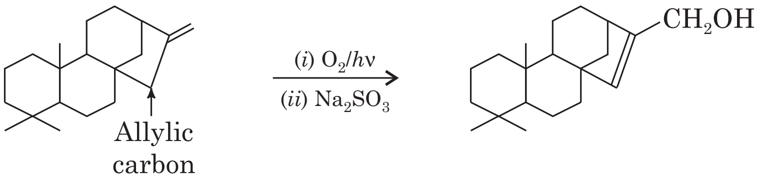


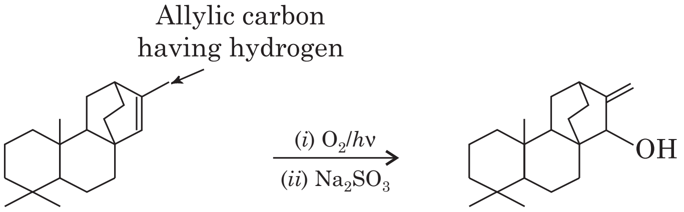


Addition with Mono-olefins

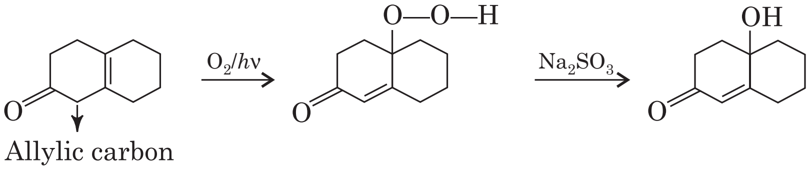
Various examples of the photooxygenation of mono-olefin are given below:





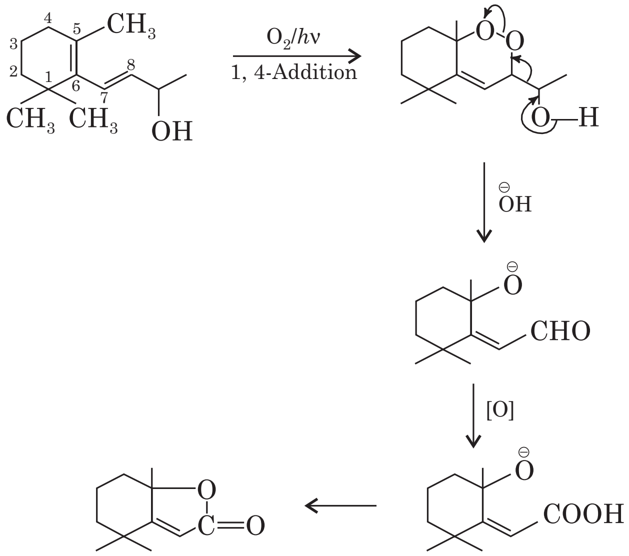


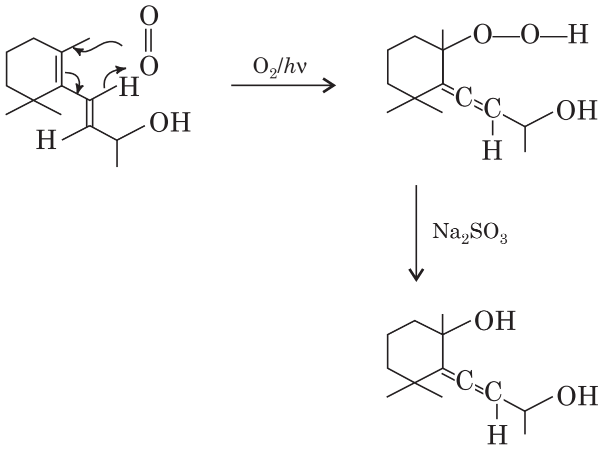
β, γ-Unsaturated ketones also gives photooxygenation in concerted manner with singlet oxygen.



Carotenoids and Related Terpenoids

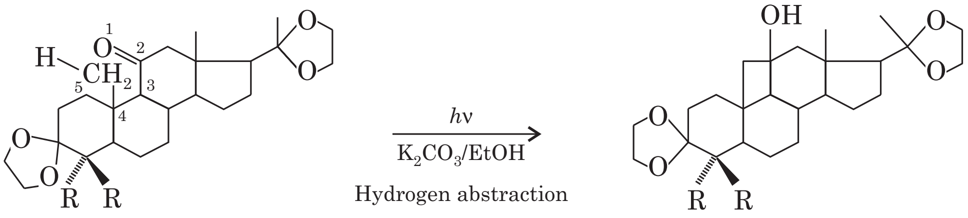
Photooxygenation of carotenoids and related terpenoids afford *ketene* derivative in addition to normal oxygenation products. This unique ketene formation is attributed to the non-planarity of the C_5, C_6 and C_7, C_8 double bonds, resulting from steric crowding of the methyl groups at C-1 and C-5. This unique photooxidation has been applied to synthesis of naturally occurring ketenic carotenoids.





12.6 PHOTOCHEMISTRY OF SATURATED KETONES

The main reactions given by saturated ketones are α-cleavage and hydrogen abstraction at δ-position.



13
CHAPTER

Photochemistry in Nature and Applied Photochemistry

Earlier Chapters of this book were related with the fundamental process of photochemistry. In this Chapter, we will study some of the ways in which photochemistry has an impact on our lives. Natural photochemical phenomena have contributed to the evolution of life and have allowed its continued existence on the Earth.

13.1 PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

Before discussing the photochemical reactions in the atmosphere, let us discuss atmospheric structure because photochemical reactions depend on atmospheric structure.

The atmosphere may be broadly divided into four regions as shown in Table 13.1.

Table 13.1

	Region	*Altitude range (km)*	*Temperature range (°C)*	*Important chemical species*
1.	Troposphere	0–11	15 to –56	N_2, O_2, CO_2, H_2O
2.	Stratosphere	11–50	–56 to –2	O_3
3.	Mesosphere	50–85	–2 to –92	$\overset{+}{O_2}, \overset{\oplus}{NO}$
4.	Thermosphere	85–500	–92 to 1200	$\overset{+}{O_2}, \overset{+}{O}, \overset{\oplus}{NO}$

Oxygen plays an important role in the troposphere whereas ozone plays a key role in the stratosphere.

Oxygen and Ozone Chemistry

The chemical activity of oxygen plays an important role in the lower atmosphere (troposphere). The stable forms of almost all elements are oxides. The atmosphere contains gases such as carbon dioxide and sulphur dioxide.

In the upper atmosphere the species of oxygen are O_2, O, $O^\bullet$, O^+, $O^\bullet_2$ and O_3. UV light causes photochemical dissociation, ionisation etc.

$$O_2 + h\nu \xrightarrow[\text{nm}]{240-260} O + O \qquad ...(1)$$

$$O_3 + h\nu \xrightarrow[\text{nm}]{308} O^\bullet + O_2 \qquad ...(2)$$

$$\mathrm{O} + h\nu \longrightarrow \mathrm{O}^{\bullet} + e \qquad \text{...(3)}$$

$$\mathrm{O_2} + h\nu \longrightarrow \mathrm{O_2}^{+} + e \qquad \text{...(4)}$$

Ozone is the important species in the stratosphere, acting as a protective radiation shield for living organism on earth. The maximum ozone concentration is around 10 ppm in the stratosphere at an altitude of 25–30 km.

Ozone is formed by a photochemical reaction, followed by a three body reaction. The photochemical reactions taking place in this region are

$$\mathrm{O_2} + h\nu\ (242\ \mathrm{nm}) \longrightarrow \mathrm{O} + \mathrm{O}$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M}\ (\mathrm{N_2}\ \text{or}\ \mathrm{O_2}) \longrightarrow \mathrm{O_3} + \mathrm{M} + \text{Heat} \qquad \text{...(5)}$$

The third body (M) absorbs the excess energy liberated by the above reaction and thereby stabilizes the O_3 molecule.

Ozone strongly absorbs ultraviolet radiations in the region 220–330 nm and thereby protects life on earth from severe radiation damage. Only small fraction of the ultraviolet light reaches the lower atmosphere and the Earth.

The mechanism of ozone removal is not well known. It is believed that ozone is eliminated by reaction with atomic oxygen, reactive hydroxyl radicals and mainly by nitric oxide.

1. $$\mathrm{O_3} + \mathrm{O} \longrightarrow \mathrm{O_2} + \mathrm{O_2} + \text{Heat}$$

2. $$\mathrm{O_3} + \mathrm{HO}^{\bullet} \longrightarrow \mathrm{O_2} + \mathrm{O}^{\bullet}\text{—O—H}$$
   $$\mathrm{O}^{\bullet}\text{—H} \longrightarrow \mathrm{HO}^{\bullet} + \mathrm{O_2}$$

3. $$\mathrm{O_3} + \mathrm{NO} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$$
   $$\mathrm{NO_2} + \mathrm{O} \longrightarrow \mathrm{NO} + \mathrm{O_2}$$

It may be noted that nitric oxide is produced in the stratosphere, below 30 km, by the reaction of nitrous oxide with excited oxygen atoms and above 30 km by ionising radiation on nitrogen

$$\mathrm{N_2O} + \mathrm{O}^{\bullet} \longrightarrow 2\mathrm{NO} \qquad \text{...(6)}$$

$$\mathrm{N_2} + h\nu \longrightarrow \mathrm{N} + \mathrm{N} \qquad \text{...(7)}$$

$$\mathrm{O_2} + \mathrm{N} \longrightarrow \mathrm{NO} + \mathrm{O} \qquad \text{...(8)}$$

Nitrogen Oxides

The nitrogen oxides in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2).

Nitrous oxide originates from microbiological processes and occurs in unpolluted air at a level of about 0.25 ppm. In the lower atmosphere it has practically no influence on chemical reactions. At higher altitudes it helps deplete the ozone layer.

$$\mathrm{N_2O} + h\nu \longrightarrow \mathrm{N_2} + \mathrm{O} \qquad \text{...(9)}$$

$$\mathrm{N_2O} + \mathrm{O} \longrightarrow \mathrm{NO} + \mathrm{NO} \qquad \text{...(10)}$$

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2} \qquad \text{...(11)}$$

Nitric oxide and nitrogen dioxide are important constituents of polluted air. These oxides, collectively designated NO_x, enter the atmosphere mainly from anthropogenic (man-made) sources, *i.e.,* combustion of fossil fuels in both stationary and mobile sources. The annual global input of NO_x is of the order of 86 million tonnes.

The photodissociation of NO_2 can yield a series of inorganic reactions:

$$\begin{aligned}
NO_2 + h\nu &\xrightarrow{< 398\text{ nm}} NO + O\\
NO_2 + h\nu &\xrightarrow{> 430\text{ nm}} NO_2\\
O + O_2 + M &\longrightarrow O_3 + M\\
NO + O_3 &\longrightarrow NO_2 + O_2\\
NO_2 + O_3 &\longrightarrow NO_3 + O_2\\
O + NO_2 + M &\longrightarrow NO_3 + M\\
NO_2 + NO_3 &\longrightarrow N_2O_5\\
NO + NO_3 &\longrightarrow 2NO_2\\
O + NO + M &\longrightarrow NO_2 + M
\end{aligned}$$

Nitrogen dioxide finally ends up as HNO_3

$$\begin{aligned}
3NO_2 + HOH &\longrightarrow 2HNO_3 + NO\\
N_2O_5 + HOH &\longrightarrow 2HNO_3
\end{aligned}$$

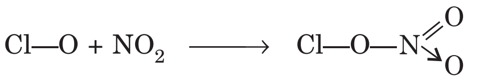
In the stratosphere, NO_2 also reacts with the hydroxyl radical to form HNO_3.

$$HO + NO_2 \longrightarrow HNO_3$$

Apart from NO_x, chlorine also plays an effective role in removing ozone in the stratosphere.

$$\dot{\text{Cl}} + O_3 \longrightarrow \text{Cl—}\dot{\text{O}} + O_2 \qquad \text{...(12)}$$

$$\text{Cl—}\dot{\text{O}} + O \longrightarrow \dot{\text{Cl}} + O_2 \qquad \text{...(13)}$$



$$\text{Cl—O} + NO_2 \longrightarrow \text{Cl—O—N}\overset{\displaystyle O}{\underset{\displaystyle O}{\lessgtr}} \qquad \text{...(14)}$$

Chlorine nitrate

The Sources of Cl• (Chlorofluorocarbons)

1. Chlorofluorocarbons are used as refrigerant aerosol spray and propellants. They are inset in the troposphere but slowly diffuse into the stratosphere where they are subjected to UV radiation at about 200 nm generating chlorine free radical. The chlorine free radical immediately reacts with ozone.

$$CFCl_3 \xrightarrow{h\nu} \dot{C}FCl_2 + \dot{\text{Cl}} \qquad \text{...(15)}$$

$$\dot{\text{Cl}} + O_3 \longrightarrow \dot{\text{Cl}}\text{O} + O_2 \qquad \text{...(16)}$$

$$\text{Cl}\dot{\text{O}} + O_2 \longrightarrow \dot{\text{Cl}} + O_2 \qquad \text{...(17)}$$

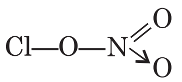
In a cyclic reaction each $\dot{\text{Cl}}\text{O}$ can initiate a series of chemical reactions which lead to destruction of up to 100,000 molecules of ozone without being destroyed itself in the process.

2. Volcanoes inject chlorine gas and HCl directly into the stratosphere. Cl_2 on exposure to UV light (300 – 400 nm) forms $\dot{\text{Cl}}$ while HCl reacts with $\text{H}\dot{\text{O}}$ to give $\text{Cl}\dot{\text{O}}$

$$\dot{\text{Cl}} + O_3 \longrightarrow \text{Cl}\dot{\text{O}} + O_2 \qquad \text{...(18)}$$

$$\text{Cl}\dot{\text{O}} + \dot{\text{O}} \longrightarrow \dot{\text{Cl}} + O_2 \qquad \text{...(19)}$$

$$\dot{Cl} + CH_4 \longrightarrow C\dot{H}_3 + HCl \qquad ...(20)$$



$$Cl\dot{O} + NO_2 \longrightarrow Cl{-}O{-}N\overset{\nearrow O}{\underset{\searrow O}{}} \qquad ...(21)$$

By reaction with CH_4, $\dot{C}l$ is trapped as HCl which is rained out in the troposphere.

Organic Compounds

Hydrocarbons and other organic compounds in the atmosphere are susceptible to oxidation through a series of steps of chemical and photochemical reactions. As a result many noxious secondary pollutant products and intermediates are produced, which belong to the category of photochemical smog.

$$CH_4 + O_2 \longrightarrow C\dot{H}_3 + H\dot{O} \qquad ...(22)$$

$$CH_4 + H\dot{O} \longrightarrow C\dot{H}_3 + H_2O \qquad ...(23)$$

$$C\dot{H}_3 + O_2 + M \longrightarrow CH_3CO\dot{O} + M \qquad ...(24)$$

Organic compounds in the atmosphere readily enter into reactions with O_3, NO_2 and free radicals such as $HO\dot{O}$, $\dot{O}H$ etc.

Natural sources, particularly trees, emit large quantity of hydrocarbons in the atmosphere. Methane is the major naturally occurring hydrocarbon emitted into the atmosphere. It is produced in considerable quantities by bacteria in the anaerobic decomposition of organic matter in water, sediments and soil.

$$2[CH_2O] \xrightarrow{\text{Bacteria}} CO_2 + CH_4 \qquad ...(25)$$

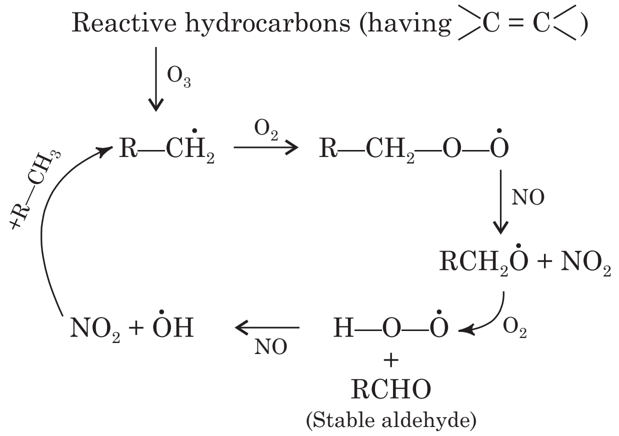
Domestic animal contribute about 85 million tones of CH_4 to the atmosphere each year, CH_4 has a mean residence time of about 3–7 years in the atmosphere.

It has been estimated that anthropogenic sources contribute about 15% of the hydrocarbons emitted to the atmosphere every year. Automobiles are the major source in this respect. About 20 different hydrocarbons were identified in the atmosphere. Among them are methane, ethane, ethene, ethyne, propane, *n*-butane, isopentane, toluene, *n*-pentane, *m*-xylene and isobutane.

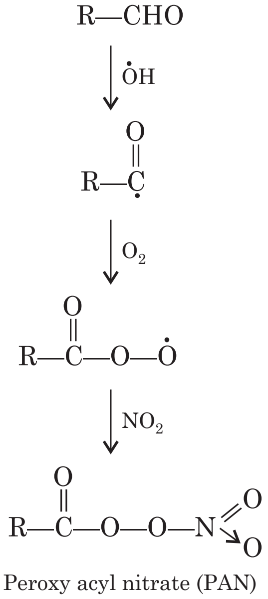
Hydrocarbons are removed from the atmosphere by several chemical and photochemical reactions. They are oxidised through a series of steps. The end products are CO_2, acids and aldehydes which are washed by rain.

Hydrocarbons do not react readily with sunlight, but they are reactive towards other substances produced photochemically. An important characteristic of atmosphere which are loaded with large quantities of automobile exhausts, trapped by an inversion layer and at the same time exposed to intense sunlight, is the formation of photochemical oxidant in the atmosphere. This gives rise to the phenomenon of *Photochemical smog*. Photochemical smog is an oxidising smog having high concentration of oxidant (*i.e.,* O_3 and NO_2).

The probable mechanism of smog-forming reactions is illustrated below (Scheme 1) :



Scheme 1 Smog formation reactions



Scheme 2 PAN formation reactions

The concentration level of O_3 and NO_2 is so high that O_3 can be virtually smelled. Moreover, a brown haze is found in the atmosphere due to the heavy load of particles. The various consequences that have been recognised so far as a result of these pollutants include damage to materials such as rubber, damaged to vegetation, reduced visibility and a tremendous increase in respiratory disorders. What might be seen as an immediate effect is eye irritation which is caused by substances such as formaldehyde, acrolein and PAN. PAN is an irritant to the respiratory system and eyes and has also been found to be highly toxic to plants, that is, it is phototoxic.

13.2 CHEMISTRY OF VISION

One of the most important areas of research in organic photochemistry is that which concerns the chemistry of vision. The eye is an extraordinary sensitive instrument. Its wavelength response is restricted to 400 to 800 nm, but its degree of sensitivity is such that a fully dark-adopted eye can clearly detect object in light so dim as to correspond to a light input over the retina of only about 10,000 quanta per second.

The gross anatomy of the vertebrate eye is the system of lens and retina. The retina is made up of two kinds of light sensitive cells known as *rods* and *cones*. The rods and cones present in the retina act as the receptors of the eye.

Rods are located primarily at the periphery of the retina. The rodes have been found to have high sensitivity and thus can function at low light intensities. Thus rods are responsible for vision in dim light. Rods, however, are colour-blind and "see" only in shades of grey. Cones are found mainly in the center of the retina and are responsible for vision in bright light. Cones also possess the pigments that are responsible for colour vision.

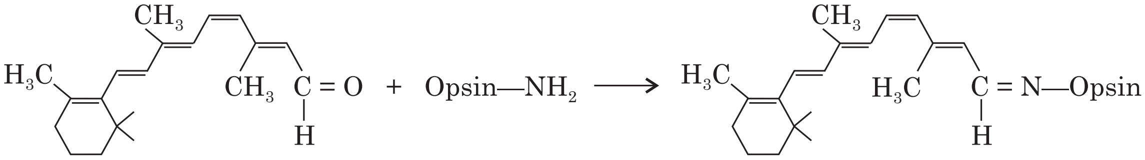
Some animals do not possess both rods and cones. The retina of pigeons contain only cones. Thus, while pigeons have colour vision, they see only in the bright light of the day. The retina of owls, on the other hand, have only rods ; owls see very well in dim light but are colour blind.

The chemical changes that occur in rods are much better understood than those in cones. For this reason we shall concern ourselves here with rod vision first.

When light strikes rod cells, it is absorbed by a compound called **rhodopsin.** This initiates a series of chemical events that ultimately results in the transmission of a nerve impulse to the brain.

Rhodopsin was discovered in 1877 by the German Physiologist Franz Boll. He noticed that the initial red-purple colour of a pigment in the retina of frogs was "bleached" by the action of light. The bleaching process led first to a yellow retina and then to a colourless one. The rhodopsin is also known as "visual purple" or *Sehpurpur* because of its colour shade. Rhodopsin has absorption maximum ≈ 500 nm. Human rhodopsin has a molecular weight of 41,000 and has 348 amino residues. It is found in membranes of the rod disks and makes up 90% of the total protein in these membranes. Rhodopsin functions when vision takes place under low light intensity, for example, at night time. It cannot distinguish different colours, since it has only one pigment whose λ_{max} is 498 nm.

The chromophore of rhodopsin is a polyunsaturated aldehyde, 11-*cis* retinal. Rhodopsin is the product of the reaction of this aldehyde and a protein called opsin (Fig. 13.1).



11-*Cis* retinal

Rhodopsin

The reaction is between the aldehyde group of 11-*cis* retinal and an α-amino group of a amino group of the chain of the protein and involves the loss of a molecule of water. Other secondary interactions involving—SH group of the protein probably also hold the *cis* retinal in place. The site on the chain of the protein is one on which *cis* retinal fits precisely (Fig. 13.1).

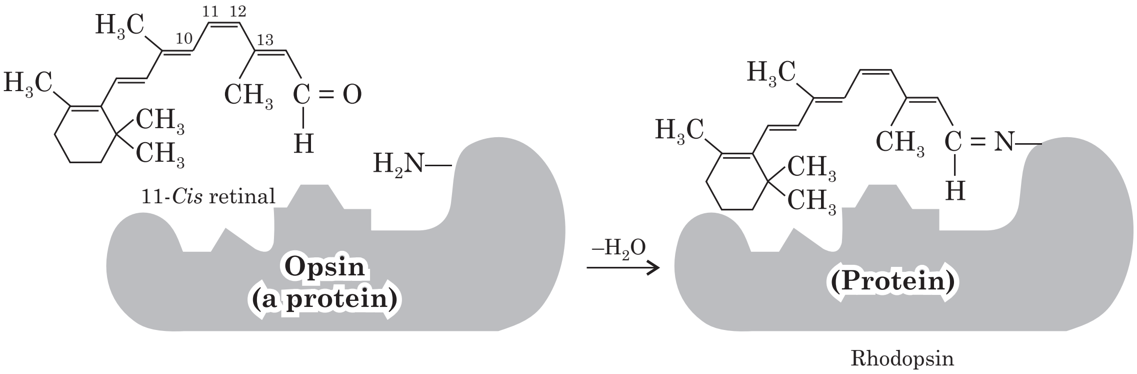


Fig. 13.1 The formation of rhodopsin from 11-*cis*-retinal and opsin

The conjugated polyunsaturated chain of 11-*cis* retinal gives rhodopsin the ability to absorb light over a broad region of the visible spectrum. Fig. 13.2 shows the absorption curve of rhodopsin in the visible region and compares it with the sensitivity curve for human rod vision. The fact that these two curves coincide provides strong evidence that rhodopsin is the light-sensitive material in rod vision (Fig. 13.2).

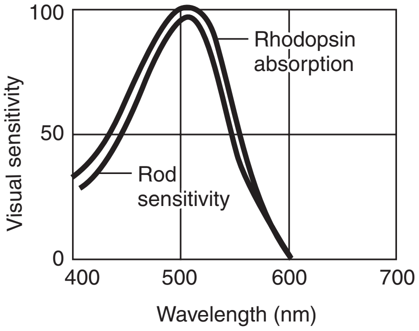


Fig. 13.2 A comparison of the visible absorption spectrum of rhodopsin and the sensitivity curve for rod vision

Irradiation of rhodopsin leads to a series of conformational changes which can be noticed by the appearance and disappearance of various intermediates of different colours. The process may be described by the Fig. 13.3.

When rhodopsin absorbs a photon of light, the 11-*cis*-retinal chromophore isomerises to the all *trans* form. The first photoproduct is an intermediate called bathorhodopsin, a compound that has about 150 kJ/mole more energy than rhodopsin. Bathorhodopsin then, through a series of steps, becomes metarhodopsin (also all *trans*). The high energy of all-*trans* chromophore of metarhodopsin II cannot fit well with the protein, it is released. The free *trans*-isomer (*i.e.,* all-*trans*-retinal) is thin enzymatically converted to *cis*-form, which instantaneously recombine with the opsin. These molecular changes produce electrical potential which is transmitted to brain within 25 million of a second after the flash of the colour (Fig. 13.4).

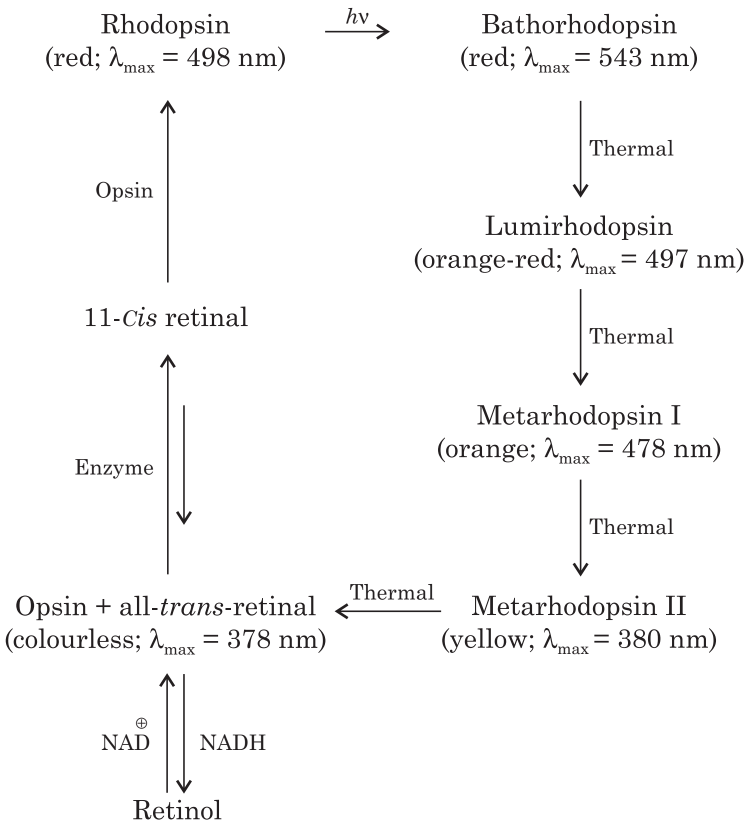
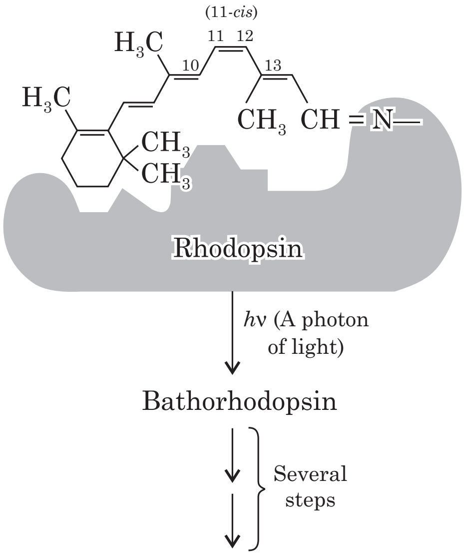


Fig. 13.3 The vision cycle of retinal opsin



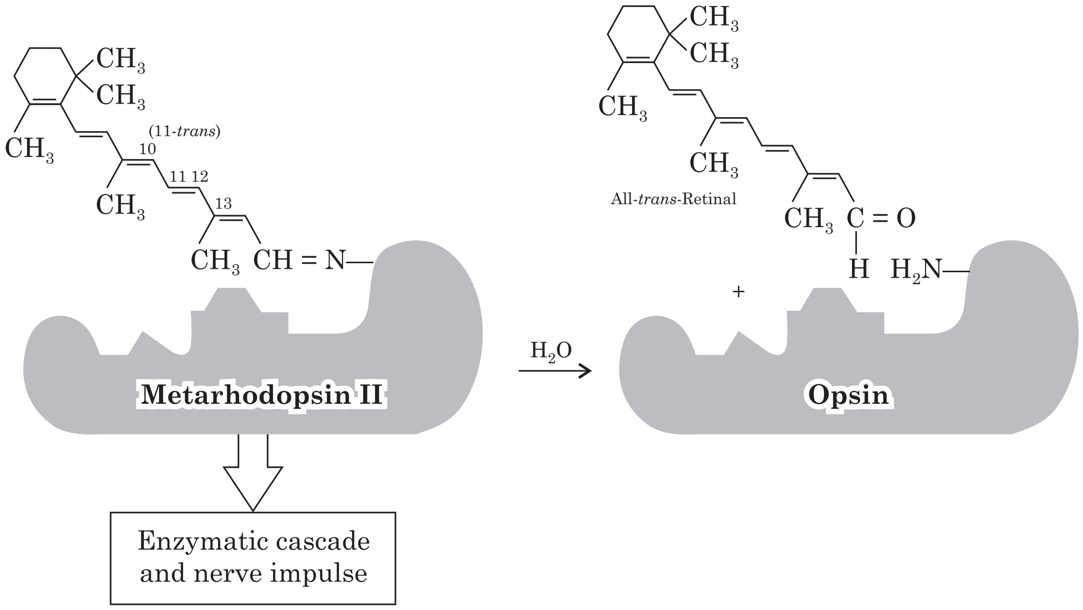
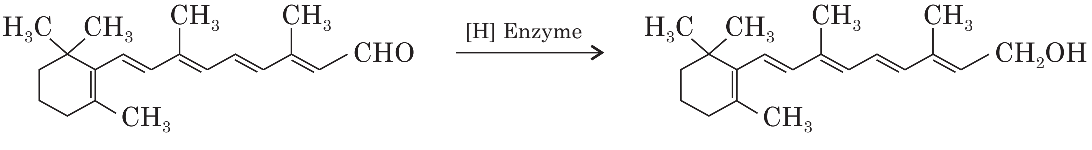


Fig. 13.4 The important chemical steps of the visual process. Absorption of a photon of light by the 11-*cis*-retinal portion of rhodopsin generates a nerve impulse as a result of an isomerization that leads, through a series of steps, to metarhodopsin II. Then hydrolysis of metarhodopsin II produces all-*trans*-retinal and opsin. This illustration greatly oversimplifies the shape of rhodopsin; the retinal portion is actually embedded in the center of a very complex protein structure

The first step to from bathorhodopsin occurs on a time-scale of tens of picoseconds and each subsequent step is $10^2 - 10^3$ times slower than its predecessor.

Rhodopsin has an absorption maximum at 498 nm. This gives rhodopsin its red-purple colour. Together, all-*trans*-retinal and opsin (*i.e.,* meta rhodopsin II) have an absorption maximum at 387 nm and thus, are yellow. The light-initiated transformation of rhodopsin to all-*trans*-retinal and opsin corresponds to the initial bleaching that Boll observed in the retina of frogs. Further bleaching to a colourless form occurs when all-*trans*-retinal is reduced enzymatically to all-*trans*-vitamin-A. This reduction converts the aldehyde group of retinal to the primary alcohol function of vitamin A (Fig. 13.5).



All-*trans*-retinal

All-*trans*-vitamin A

Fig. 13.5 Formation of vitamin A

Thus precursor of 11-*cis*-retinal is vitamin A. This is the reason why vitamin A is good for vision.

We now turn to a brief consideration of how the photochemical changes described so far become converted to an electrical impulse that stimulates the brain. There is evidence that a single quantum of radiation can stimulate a retinal rod. The absorption of one quantum does not, however, result in vision, and several quanta (between two and six) must reach the same rod within a relatively short period. Even, so, the process is remarkably efficient, and the energy of the ultimate reaction generally exceeds that absorbed by the visual pigment. The absorption of light appears to initiate a chain reaction that derives its energy from metabolism, and visual excitation is a result of 'amplification' of the light signal received at the retina. The photoreceptor is the biological equivalent of a photomultiplier, which converts photons to an electrical signal with high gain and low noise. Both photoreceptor and photomultiplier achieve high gain in a cascade of amplifying stages. Visual pigments are integral membrane proteins that reside in the photoreceptor outer segment. Photoisomerisation of retinal triggers a series of conformational changes in the attached protein that create or unveil an enzyme site. A cascade of enzymatic reactions follows, which ultimately produces a neural signal.

Rhodopsin functions when vision takes place under low light intensity, for example, at night time. It cannot distinguish different colours, since it has only one photopigment.

Colour vision is associated with the cones rather than with the rods. The photosensitive pigment in the cones is called iodopsin. The chromophore of iodopsin is also 11-*cis*-retinal. Rods contain only one colour pigment whereas cones contain three different colour pigments. Thus three type of iodopsin is present in cones. The three type of iodopsin, which contain pigments that absorb light at a maximum of 440 nm (blue), 535 nm (green) and 565 nm (red), are responsible for colour vision. Cone cells are much less sensitive to light than rod cells, so in dim lighting all objects appear in shades of grey. Thus the spectral response of the eye shifts towards the red in going from dim to bright light, as expected.

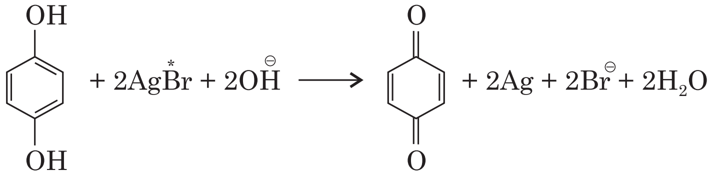
Vertebrates appear to perceive colour through the operation of a three colour system. Three different cone pigments seem to be implicated, with absorptions in the blue, the green and the red wavelength regions.

13.3 PHOTOGRAPHY

Silver halides are used as photosensitive materials for the most common form of photographic process, both for monochrome and for colour photography. A light sensitive emulsion is formed by coating microcrystalline grains of silver halide suspended in gelatin onto a suitable support, for example, film, glass plate, paper, etc. It has been seen that formation of metallic silver occurs which causes darkening of the emulsion if there happens to be a prolonged exposure to light. This phenomenon is known as *'the print-out effect'*. However, it has been found that 'a latent image' is produced in the silver halide grains by shorter exposures. For converting a latent image so produced into a visible silver deposit, a developer, which is a suitable reducing agent, is used. In actual, all developers bring about the thermodymamic reduction of silver halide.

The formation of the latent image increases the rate of the reduction of silver halides to metallic silver, rather than changing the ultimate reducibility of the emulsion itself. Unexposed emulsion, when developed, leads the formation of 'fog' (darkening). Thus we can conclude that the difference in the reduction rate for the exposed and unexposed areas governs their discrimination during development. In normal course, after the development of the exposed and unexposed areas, these areas are fixed, that is they are made permanent, by dissolving the unexposed grains of silver halides in sodium thiosulphate solution, immediately after development.

$$AgBr \xrightarrow{h\nu} \overset{*}{Ag}Br$$



...(26)

We will study the photographic sensitiser in Section 13.4. Photographic sensitiser is used in colour photography. Thus colour photography is important field where dyes have proven to be of great importance in producing images. The difference in the use of dyes is that here a larger quantity of the dye is used and this dye remain uncorporated till the final stage. In order to obtain a complete range of visible hues, a three colour 'substractive' process is used. The process involves the use of three layers of emulsion, each layer being spectrally sensitised to a different spectral region (blue, green and red) and possessing integral filter dyes, if required. The development process is arranged to form colours in each layer in *inverse* intensity to the amount of the kind of light striking it to which it is sensitised. The developed colours are complementary to the colours of the sensitising light. To make this point clear, it will be well to discuss the basic structure of ordinary colour films and the colour changes which occur on exposure, as shown in Fig. 13.6.

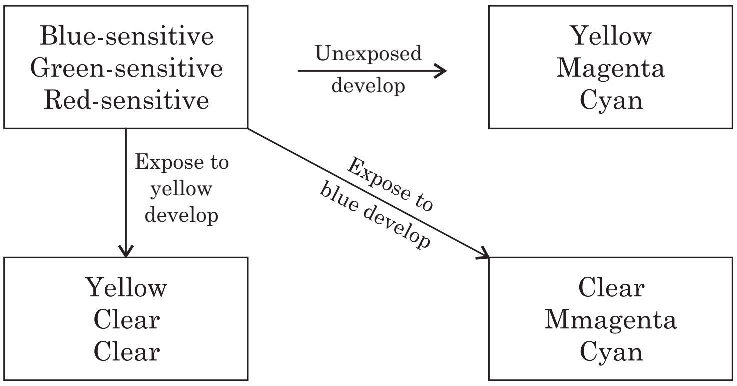


Fig. 13.6 Schematic repregentation of the layer structure of colour film and the colour changes that occur on development. The actual film also contains a filter (yellow) below the-blue-sensitive layer to remove the blue light passing through this layer (blue), an anitihalation layer below the red to prevent scattering of the light back through the emulsion, and a film base such as cellulose acetate or polyethylene glycerol-terephthalate which supports the emulsion

If unexposed film is developed intense yellow, magenta and cyan (blue-green) colour are formed in the respective layers. If white light then shines on the film, the yellow layer substracts out the blue, the magenta substracts out the green and the cyan substracts out the red. The appearance of the film is black as corresponds to no exposure to light. On the other hand, if the film is exposed to strong blue light, no yellow results in the developed film and the red and green are substracted from white light by the magenta and cyan layers so that on viewing the transparency agaist white light only blue is transmitted, as befits the colour of the original light. Similarly, exposure to strong yellow light (containing no blue) results in formation of a yellow layer with no dye in the magenta or cyan layers. This is because the green and red-sensitive emulsions are both made to be sensitive to yellow, while a blue-sensitive emulsion is insensitive to yellow.

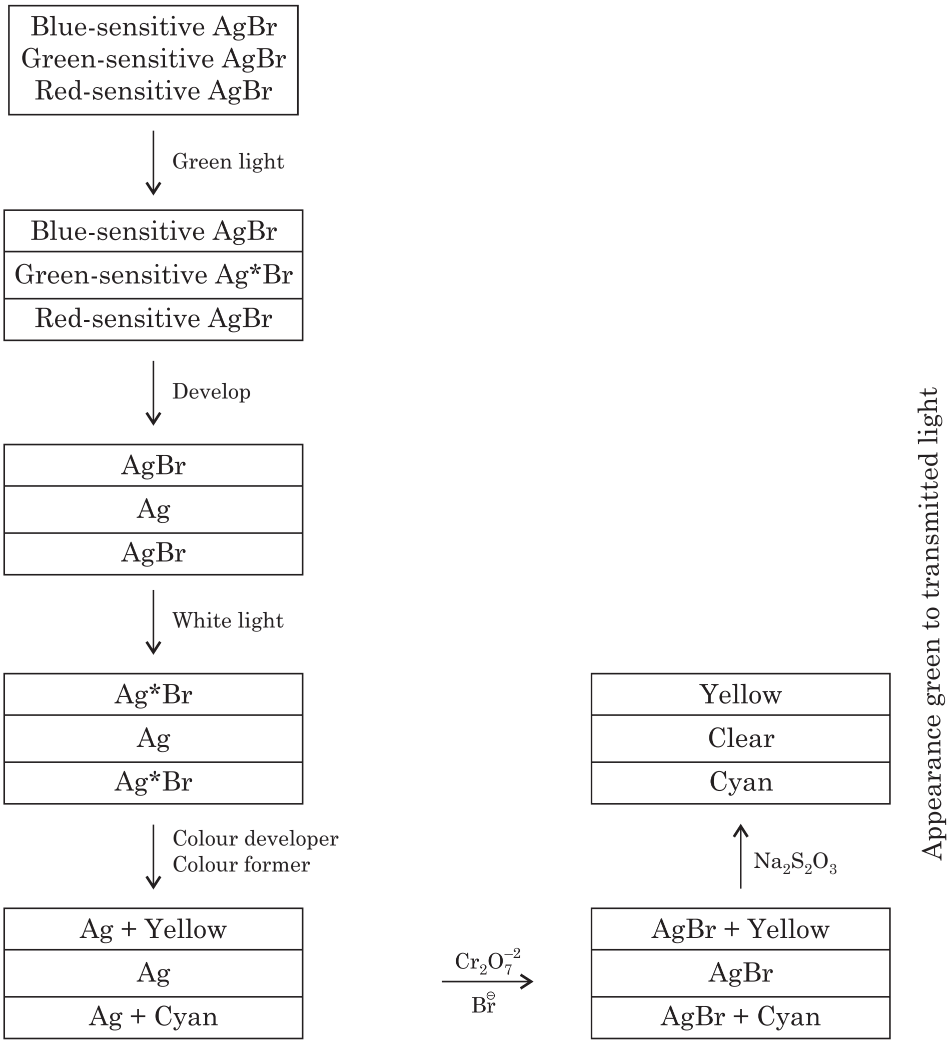
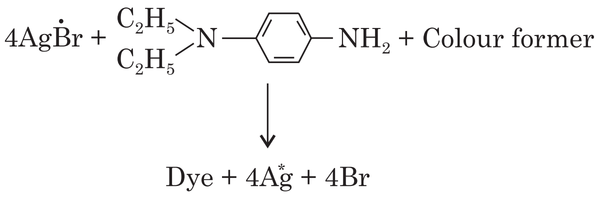


Fig. 13.7 Schematic change in the development of colour film exposed to green light

The chemistry involved in the production of the dye in colour films is highly ingenious and is achieved through the general steps shown in Fig. 13.7, which for purpose of illustration are carried through for an initial exposure to green light. The exposure activates only the green-sensitive emulsion, and development with an ordinary developer such as metal-hydroguinone produces silver metal only in the green-sensitive layer. The film now has the visual appearance of a milky negative. The developer is then washed out and the film is exposed to a strong white light which activates all the silver bromide remaining unreduced in the first step.

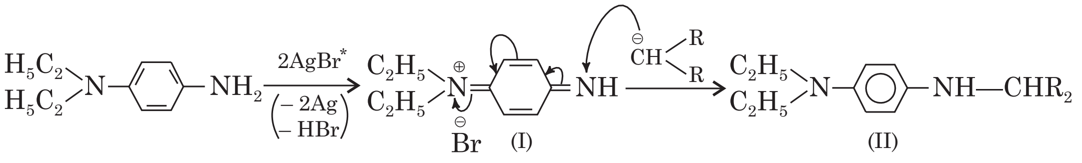
The activated silver bromide so formed is now reduced with a colour developer, usually N, N-diethyl-*p*-phenylenediamine, in the presence of a colour former. Production of dye occurs in the direct proportion to the amount of activated silver bromide present in close conformity with the following equation:



...(27)

A different colour former is used in each layer of the emulsion and, althrough the complex colour picture is formed in this step, the film is coal black because of the metallic silver produced at the same time. The silver is then oxidised to silver bromide with dichromate solution containing bromide ion and removed with thiosulphate solution. The final image thus contains no silver.

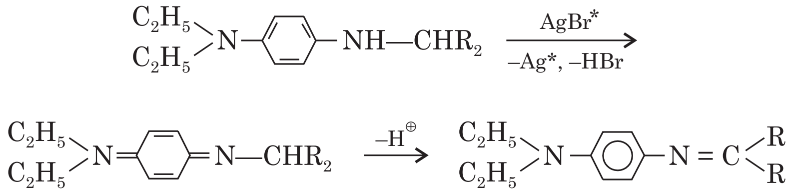
The colour forming reactions are critical to the success of the overall process and, of necessity, involve some degree of compromise between requirements for yield, reproducibility, rate, suitability of colour, and light-fastness. In the reaction of the type show in equation given below the colour former is a methylene compound R_2CH_2, where R groups have sufficient electron-attracting character to have some degree of formation of $R_2\overset{\ominus}{C}H$ in the alkaline medium used fer colour development.



...(28)

The colour developer is oxidised by the activated silver bromide produced in the third step of the Equation (28) to a quinonimmonium salt (I). This substance readily undergoes a Micheal type conjugate addition with the anion R_2CH to give a N′-substituted, N, N-diethyl phenylenediamine (II).

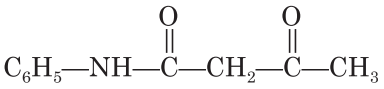
The product (II) is a photographic developer and is oxidised by activated silver bromide to a new quinonimmonium salt (III) (Equation 29).



(III) (IV)

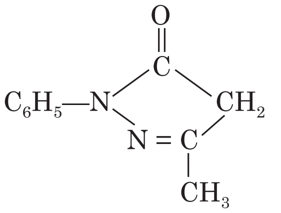
...(29)

The substance (III) has acidic hydrogen at the —CHR_2, and on loss of this hydrogen, a neutral conjugated imine (IV) results which is the actual dye. Colour is expected for these molecules because the R groups are electron-attracting, and the dimethylamino group at the other end of the conjugated system is electron-donating. Proper colour of each layer of the film depends on the nature of R_2CH_2. Illustrative colour formers that give yellow, magenta and cyan dyes with N, N-diethyl-*p*-phenylenediamine are shown below:

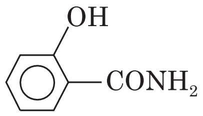


$$C_6H_5\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3$$

Acetoacetanilide
(Yellow)



1-Phenyl-3-methyl-5-pyrazolone
(Magenta)



Salicylamide
(Cyan)

In some photographic processes (for example, Agfa-colour, Ektachrome, etc.) insoluble compounds are used as colour formers and are past of the original emulsion while in other processes (as in kodachrome) soluble colour formers are diffused into the layer of the emulsion during the development process.

13.4 LIGHT-ABSORBING COMPOUNDS

Light absorbing compounds can be classified into following categories:

(A) Photosensitisers

As mentioned earlier that intersystem crossing (ISC) is very important phenomenon in photochemistry. For many molecules ISC ($S_1 \rightarrow T_1$) is not very efficient.

It is possible to excite such type of molecules (known as acceptor) by other molecule (known as donor). Donor molecule produces T_1 in high yield by ISC and than this molecule transfer its excitation energy to acceptor.

Excited state S_1 or T_1 of donor molecule transfer its large amount of energy to the acceptor molecule and in this process acceptor (A) species promoted to excited state and donor (D) species return to the ground state.

$$\text{(D)} \xrightarrow{h\nu} \text{D}^*$$
$$\text{D}^* + \text{A} \longrightarrow \text{D} + \text{A}^*$$

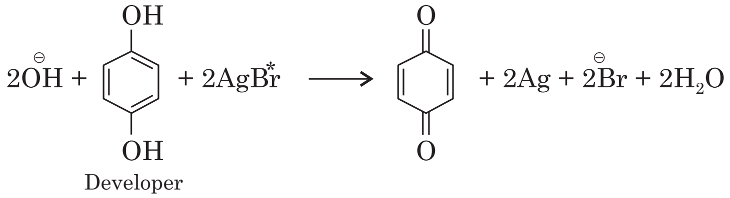
Although photons are absorbed by D, it is A which becomes excited. This phenomenon is known as photosensitisation and D is referred to as photosensitiser.

The most useful commercial sensitiser is photographic sensitisor.

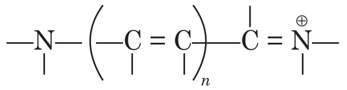
Photographic Sensitisers

A simple emulsion of silver bromide in gelatin is mainly sensitive to blue, violet or ultra violet light. As a result, a photograph made with such an emulsion represents blue and violet subjects as white and all other subject colours as gray or black. That organic dyes can act as photosensitisers for silver bromide emulsion was first discovered in 1873 and, it is possible to make photographic emulsion which are sensitive over the whole region of the visible spectrum as well as into the infrared. Since the dyes themselves absorb light of the wavelength to which they sensitise silver bromide, it appears that light activated dye molecule can transfer their energy to silver bromide and thus produce activated silver bromide capable of being reduced to suitable developing agents.

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^*$$
$$\text{Dye}^* + \text{AgBr} \longrightarrow \text{Ag}\overset{*}{\text{Br}} + \text{Dye}$$

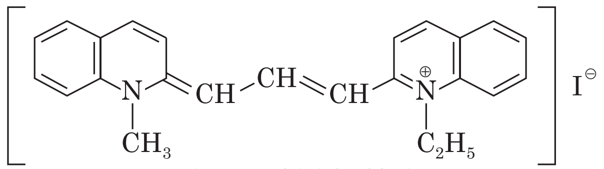


The most useful sensitising dyes are called *cyanines* and have the fallowing basic structural unit:

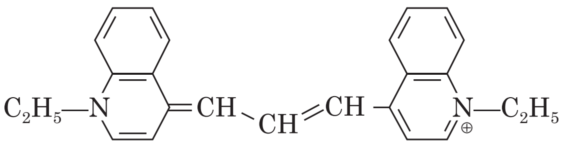


$$-\underset{|}{\text{N}}-\left(-\underset{|}{\text{C}}=\underset{|}{\text{C}}\right)_n-\overset{|}{\text{C}}=\underset{|}{\overset{\oplus}{\text{N}}}-$$

This type of system is excepted to be strongly light-absorbing by virtue of having electron-attracting and electron donating groups at the opposite ends of a conjugated system. Examples of such cyanine dyes are:



Pinacyanol (Violet-blue)



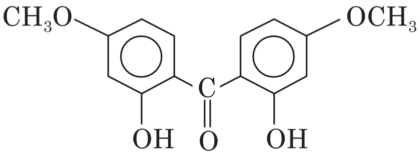
Krytocyanine (Purple-black)

Pinacyanol sensitises silver bromide emulsion is effective to red light and kryptocyanine is effective for both red and infra red radiation.

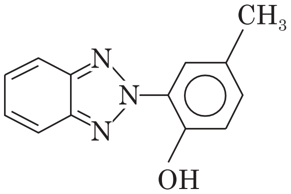
(B) Ultraviolet Screening Agents

The destructive action of ultraviolet radiation on dyes, plastics, fabrics, etc. is well known and there has been considerable research directed towards development of suitable protective agents which would act as preferential absorbers of ultraviolet light. Such substances are often called ultraviolet screening agents. A sunburn preventive agent is ultraviolet screening agent which filter out the burning but not the tanning component of sunlight. Glyceryl *p*-aminobenzoate is sunburn preventive agent which is non-toxic, nonstaining, nonvolatile and able to filter out the burning component of sunlight.

Many ultraviolet screening applications require a substance which is not itself coloured, is highly stable to light, and is an effective absorber. It is particularly to have a sharp drop in absorption coefficient at the edge of the visible coloration. These requirements are well met is many applications of *o*-hydroxy phenyl ketones, *o*-hydroxybenzophenones being particularly useful. 2-(2-Hydroxy phenyl)-benzotriazoles also possess excellent properties as screening agents.



2, 2′-Dihydroxy-4, 4′-dimethoxybenzophenone (Uvinol)



2-(2-Hydroxy-4-methylphenyl benzo [d] triazole (Tinuvin-P)

(C) Optical Bleach

A useful way of improving the appearance of white fabrics particularly cotton, which tend to yellow with continued washings, is to introduce on the fabric is a colourless substance which fluoresces blue with the ultraviolet light. Such type of substances are known as *optical bleach* or *fluorescent whitening agents*.

The principle behind the operation of an optical bleach is that the substance should absorb is the ultraviolet and radiate in the visible region, so that the washed white textile apparently reflects more light than was incident upon it. A related large-scale application is in the optical bleaching of paper.

A substance that is to be suitable as an optical bleach must satisfy following requirements:

(*i*) It must not absorb at all in the visible region, since this would lead to coloration of the fabric.

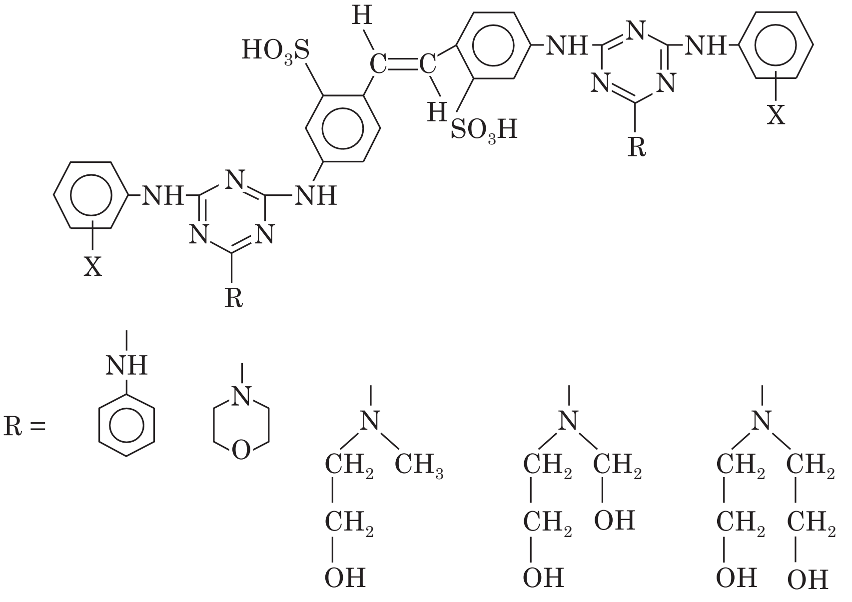
(*ii*) It must absorb strongly in the near-ultraviolet region, where there is still some intensity available from natural or artificial light sources.

(*iii*) The fluorescence must lie in the short-wavelength end of the visible region, as otherwise the fluorescence would give an apparent undesirable yellowing to white fabric.

(*iv*) The fluorescent substance must be photochemically stable, and it must not sensitise degration or oxidation of the fibre material, and

(*v*) The substance must be soluble or dispersible in the aqueous detergent solution, but must be sufficiently strongly adsorbed by the textile fibres for an appreciable concentration to build up during washing and to remain after rinsing.

Over two hundred chemically different optical brightners are commercially available and the choice for a given detergent depends on the type of textile and washing conditions for which the detergent is intended. In many cases several brightners may be added to the detergent to give a wide spectrum of activity. Almost all brightners used for cotton are derivatives of bis-triazyl-4, 4′-diamino stilbene-2, 2′-disulphonic acid (Fig. 13.8). The *trans* isomer of stilbene derivative of the above compound gives better result.



X =	H	H	H	H	SO_3Na
Code	TA	DM	DMEA	DDEA	DMDDEA

Fig. 13.8 Bis-triazinyl-4, 4′-diamino-*trans*-stillbene 2, 2′-disulphonic acid derivatives with their code names

Cotton fibres are hydrophilic fibres. Brightener of cotton fibres are also hydrophilic in character. In most of the cases brightener adsorbs on the surface of the cotton fibres by hydrogen bonding. Derivatives of 4, 4′-diamino-2, 2′-stilbene sulphonic acids are also used for cotton fibres (Fig. 13.9).

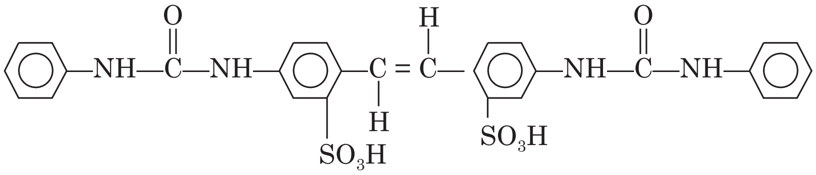
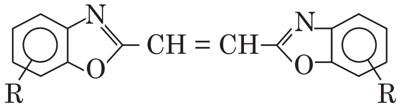


Fig. 13.9 Bis 4, 4′-(phenylureido)-2, 2′-stilbene disulphonic acid (Blankophor-B)

Brightners suitable for nylons, polyesters and acetates are the derivatives of 1, 2-dibenzoxazolylethylenes (Fig. 13.10) 2, 5-dibenzoxazoylthiophenes (Fig. 13.11) and styrlnapthoxazoles (Fig. 13.12).



R = Alkyl group

Fig. 13.10

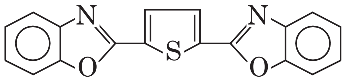
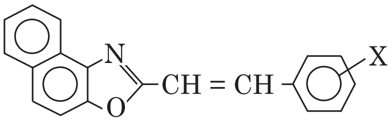


Fig. 13.11



X = Cl, H

Fig. 13.12

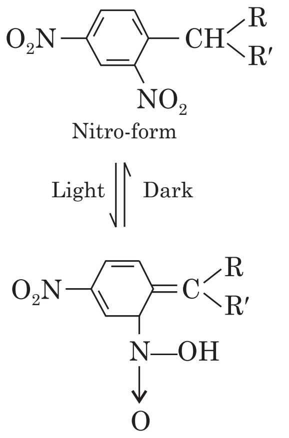
Nylon, polyester and acetates are hydrophobic fibres. Brightening of these fibres takes place possibly involving the penetration of the molecules into canals between the fibre molecules.

13.5 PHOTOCHROMISM

We have already seen, photography is an irreversible photochemical process which involves the production of an essentially permanent optical effect. Photochromism can be referred to as a reversible light induced colour change. The absorption spectrum in photochromic system is drastically altered in the presence of irradiation but when this source of irradiation is removed, original state is once again achieved by the photochromic system. The reversal can also occur by the introduction of a light of a different wavelength in some cases. Although, sometimes changes in colour for example, red to green, might occur, the most common effect that can be seen visibly in the appearance of colour in a previously colourless material.

A major shortcoming that is exhibited by substances having photochromic properties is the rapid fatigue in most of the known photochromic substances. Most of the photochromic systems exhibit reversal only a limited number of times. The best prospect of good fatigue characteristics is offered by photochromism based on isomerisation, since, with alternative systems that involve bond cleavage, a very small lack of reversibility soon leads to chemical decomposition is side reactions.

Isomerisation, dissociation and charge-transfer or redox reactions are the main chemical reactions that are responsible for the photochemical behaviour of certain substances. Although numerous substances are known to exhibit photochromic properties, one example is sufficient to explain the presence of photochromism. It has been seen that a large number of aromatic nitro compounds show photochromic isomerisation. The process actually involves the photoisomerisation of the colourless nitro form to the coloured aci-form (Fig. 13.13).



Aci-form

R = H, CH_3, C_6H_5 etc.

R′ = Electron-withdrawing group

Fig. 13.13 Photochromic isomerisation

Irradiation of chromium hexacarbonyl, $Cr(CO)_6$, in a plastic matrix leads to the formation of a deep yellow colour as a result of photodissociation. In the plastic, CO cannot escape, and recombination occurs about four hours at room temperature.

$$Cr(CO)_6 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} Cr(CO)_5 + CO$$

Both organic and inorganic charge transfer complexes or redox photochemical systems are known. A typical reversible photochemical redox reaction occurs in a mixture of mercurous iodide and silver iodide.

$$\underset{\text{Green}}{Hg_2I_2} + \underset{\text{Yellow}}{2AgI} \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} \underset{\text{Red}}{2HgI_2} + \underset{\text{Black}}{2Ag}$$

Heterolytic bond dissociation is responsible for photochromism exhibited by a large number of spiropyran derivatives (Fig. 13.14).

Some derviatives of the class of compounds known as fulgides show a particularly interesting type of photochromism. The forward photochromic reaction that is induced by light of wavelength λ*f* may be reversed by light of a different wavelength λ*r*. (Fig. 13.15). Such a system is widely used at present.

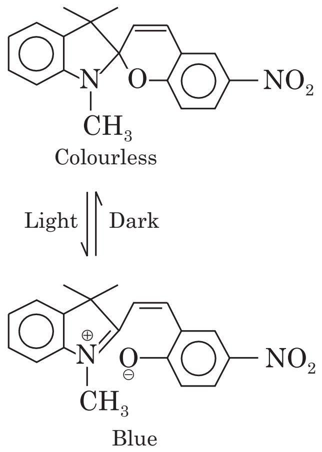


Fig. 13.14

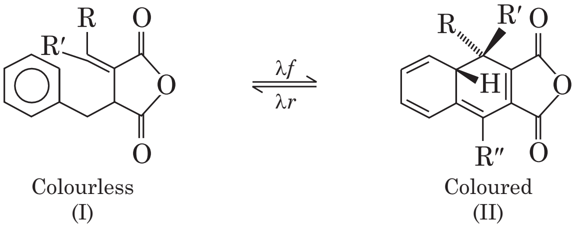


Fig. 13.15

13.6 PHOTOIMAGING

The most common of all applied photochemical processes is photography which involves the making of a more or less permanent record of light and shade. In the series of photoimaging techniques is photography which involves the capture and replication of image formation by the use of photons. Office copying and the preparation of various kinds of printing plates are some of the other large scale applications of photoimaging. If the properties (*e.g.*, the solubility) of material used to protect some underlying medium can be modified by the image, then the image can be transferred to the formely protected surface by means of subsequent treatment.

Photoresists is the name of given to such materials and these have found extensive uses in the production of printing plates, integrated circuits and printed circuit boards for the electronics industry. They may also be utilised for the manufacture of small components such as electric razor foils, camera shutter blades, etc.

Three stages that are involved in photoimaging are capture, rendition and readout. For a typical imaging system these stages can be clearly shown by the Fig. 13.16. Among the three stages, it is the image capture which is the photochemical process. The next stage, that is, image rendition consists of a series of thermal reactions. The last stage being image readout involves the development of the rendered image into a form that differentiates it physically from the unexposed background. While ordinary photography involves optical changes, solubility changes can lead to the generation of three dimensional relief patterns for printed circuits, printing plates or three dimensional topographic maps. Production of lithographic printing plates can be brought about by wettability changes. Enhanced tackiness can be used to pick up pigments to yield pigmenttoned images in printing.

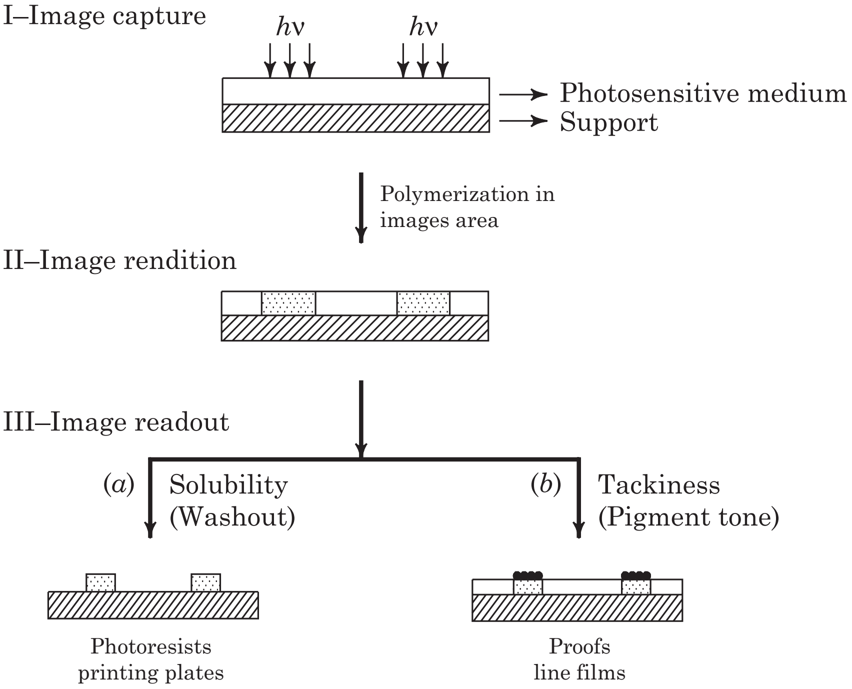


Fig. 13.16 Typical elements in photoimaging

13.7 PHOTOCHEMISTRY OF POLYMERS

Photopolymerization can be classified into two categories depending on whether each increase in relative molecular mass requires its own photochemical activation step, or whether many (thermal) polymerization steps follow the absorption of a photon. Photocrosslinking involves the formation of crosslinks between pre-existing polymer chains and it falls into the first category while the photoinitiated polymerization falls into the second.

Photopolymerisation: Imaging

There are numerous uses of photoresists. The manufacture of electronic integrated circuits is one such important application where resists are used to define the doped regions on the silicon substrate that will form resistors, capacitors, diodes and transistors of the finished circuit, together with the metal conductors joining the components and the insulating and passivating layers. The production of a complex circuit may involve several tens of successive stages of imaging, followed by eteching, doping or other processing. An accuracy as good as a few hundred nanometers is necessary at each stage. The required accuracy can be attained by means of photographic methods.

Now, since even more components are packed into a small space (very large scale integration), (VLSI) shorter wavelength X-rays or electrons or ion beams are being used instead of ultraviolet radiation. Photopolymer systems form the basis of photoresists. Refined versions of photoresists are used for the manufacture of printing plates which are in turn used in the semiconductor industry. Photocrosslinking forms the basis of a photoresist system due to the fact that cross linked polymers are generally insoluble in any solvent. The material that will be left behind after development by a solvent is that in the exposed regions, therefore the resist will be negative working. When during development, the areas exposed to light in the resist are removed, then those resists are known as positive working. Here the protective coating where the light was obscured by the transferred pattern is left behind. Thus, negative working resists leave the coating which has been exposed to light.

Now let us study one of the important photocrosslinking systems which involves the photolytic cycloaddition of pendant cinnamate groups incorporated in polymer chains.

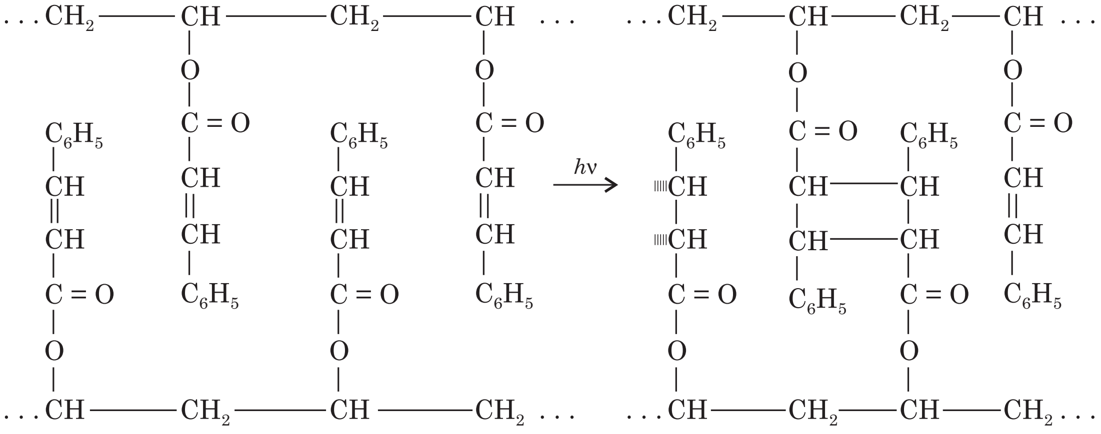


Fig. 13.17

The above reaction shows the formation of a crosslinked structure which is formed by the reaction of cinnamyl groups on irradiation of polyvinyl cinnamate. The cross linked structure so formed has been found to be insoluble in solvents. Both the singlet and the triplet excited states of the cinnamate chromophore can lead to dimerization. Dimerization of the ester can only take place in the *trans*-isomer. However, a photoisomerization reaction brings about the conversion of the *cis*-isomer into the *trans*-isomer. It has been discovered that radiations of wavelength shorter than about 320 nm can be absorbed by the cinnamates. Thus, in order to increase the sensitivity to near-*uv* and visible light by a factor of several hundred, triplet sensitizers such as 4, 4′ *bis*-(dimethylamino) benzophenone (Michler's ketone) are used.

Photopolymerisation: Curing

Due to the availability of satisfactory low temperature thermal initiators for the bulk production of thermoplastic linear polymers, photoinitiation of polymerisation is of little importance. Photopolymerisation is rather concerned with in situ polymerisation of relatively thin films of materials. In addition to the various uses of photolymerisation in imaging, it has proven to be extremely valuable is numerous applications, for example, in the drying of decorative and protective coatings on a variety of substrates and in the rapid and easily controllable hardening of resins in dentistry. Photochemical methods of curing, that is, drying or hardening processes have been found to be more advantageous as compared to other methods. For example, large quantities of solvents are used in many conventional coating techniques in order to reduce the viscosity of the primary material so as to facilitate the coating operation. These solvents find no use is the final cured coating. There may also be a necessity to bring about the heating of the entire substrate which is energy inefficient. In contrast, we find that photoinitiation of the cure works directly on the coating, leaving the substrate unaffected.

Heating operations are usually not required and the cure can be brought to completion is a fraction of second if high intensities are used.

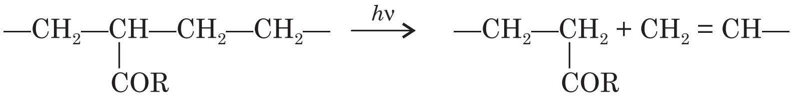
Photodegradation and Photostabilisation

Now let us briefly study two topics that deal with the durability of polymers in outdoor environment. On being exposed to visible or ultraviolet radiation, especially in the presence of atmospheric oxygen, most of the organic polymers undergo photodegradation which involves a chemical change in the polymer. This brings about a deterioration in the mechanical properties of the bulk polymer. In some contexts durability is a necessary factor, for example, in the building or automotive industries. Photostabilization is desirable in order to extend the usual lifetime of the material. On the other hand, the persistence of agricultural plastics and plastic packaging materials after disposal has gained environmental concern. Therefore, there is a deliberate effort to make the polymers light sensitive. In order to make articles such as plastic cups short lived, biodegradable plastics are used. Exposure to light reduces these articles to a fine powder, thus naturally disposing off abandoned waste.

The normal degrdation process involves a light-initiated autooxidation process. Thus, in order to bring about photostabilisation of polymers, the aim should be to reduce the rates of initiation or propagation of the chains, or to increase the rate of their termination. A decrease in the rate of initiation can be brought about by a reduction of residual impurities in the polymer while protection from oxygen would decrease the rate of propagation. However, these two methods have been found to be unpractical.

The rate of initiation can also be reduced by the prevention of the absorption of light. Photodegradation can be confined to the polymer surface by the use of highly, absorbent materials such as carbon-black. Similarly, reflecting substances such as the white oxides of zinc and titanium can also be used. In order to prevent the relatively long-lived triplets of carbonyl compounds from participating in the secondary photoinitiation steps, quenches may be used. Retardation of photodegradation can also be brought about by the use of radical scavengers such as phenols, hydroquinones and thiols which interfere with the propagation steps. *Ortho* hydroxybenzophenones have proven to be very useful as stabilizers since they operate both by screening as well as by quenching. Moreover, the hydroxybenzophenones prevent the acceleration of autoxidation by reacting chemically with hydroperoxides.

In order to obtain environmentally desirable qualities, the polymer is rendered photodegradable by a deliberate incorporation of photoactive groups into the polymer. For example, light sensitive polymers are obtained by the copolymerization of ketonic species with hydrocarbons. Photodegradation of the resulting material involves Norrish Type II scission of the polymer chain rather than a radical mediated photooxidation.



$$—CH_2—\underset{\displaystyle COR}{\underset{|}{CH}}—CH_2—CH_2— \xrightarrow{h\nu} —CH_2—\underset{\displaystyle COR}{\underset{|}{CH_2}} + CH_2 = CH—$$

Fig. 13.18

Ideally, disposable agricultural film or packaging should undergo a sharp and controllable degradation initiated by exposure to ultraviolet radiation.

PROBLEMS

1. Give a brief account of the photochemical reactions which are taking place in atmosphere.

2. Write notes on:
  (*i*) Photochemical smog
  (*ii*) PAN formation
  (*iii*) Photochemistry of chlorofluorocarbons.

3. Discuss the structural changes in the pigment of rod.

4. Discuss briefly how the photochemical changes of photo pigment become converted to an electrical impluse that stimulates the brain.

5. Discuss the chemistry of vision.

6. Discuss the chemistry of photography.

7. Write notes on:
  (*a*) photographilic sensitisers
  (*b*) ultraviolet screening agents
  (*c*) optical bleach.

8. Discuss briefly the chemistry of photochromism.

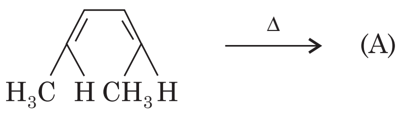
9. Write notes on photoimaging.

10. Describe briefly the following :
  (*a*) Photoimaging
  (*b*) Curing
  (*c*) Photodegradation
  (*d*) Photostabilisation.

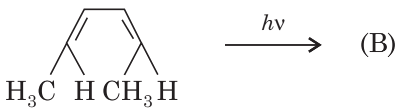
14
CHAPTER

Problems and Their Solutions

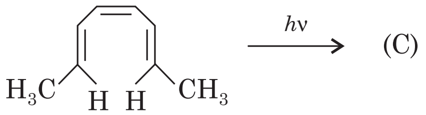
Problem 1: *Give product with its stereochemistry in the reactions given below.*

(*a*)


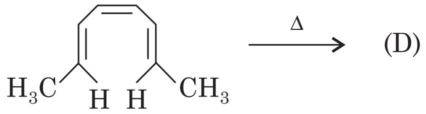
(2*E*, 4*Z*)

(*b*)


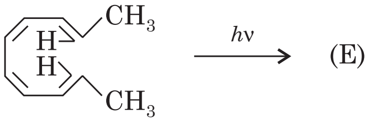
(2*E*, 4*Z*)

(*c*)


(2*E*, 4*Z*, 6*E*)

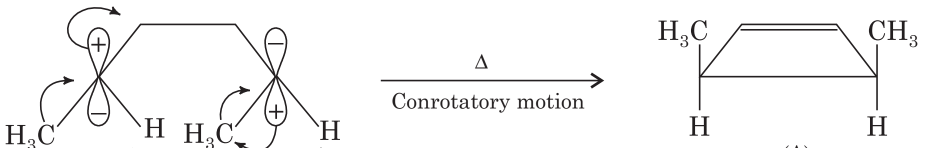
(*d*)


(2*E*, 4*Z*, 6*E*)

(*e*)


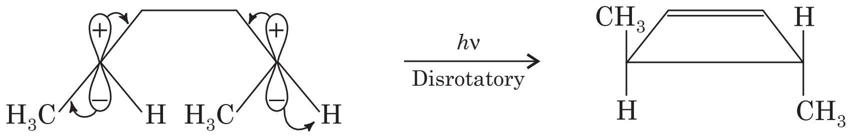
Solution: The above problems are based on electrocyclic reaction.

(*a*) The compound is 1, 3-butadiene derivative (4π component). Its HOMO under thermal condition is ψ_2 which has C_2 symmetry. Hence conrotatory motion is possible in this case.



(A)
Cis-geometry

(*b*) The compound has 4π electrons, its HOMO under photochemical process is ψ_3 having *m* symmetry. Therefore disrotatory motion is possible.

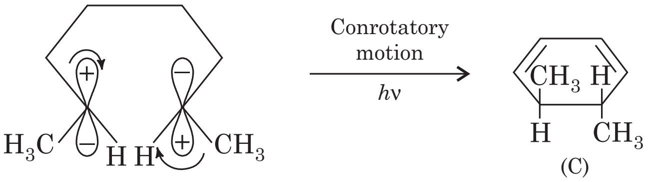


ψ_3^*
Photo (Inphase)
m-Symmetry of the π-orbitals

Trans-geometry

(B)

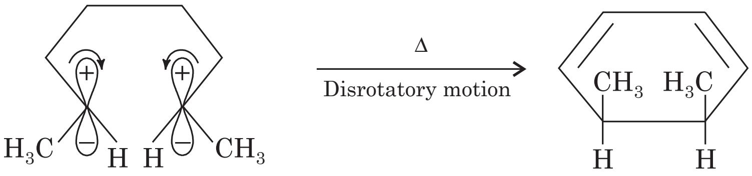
(*c*)



(C)

ψ_4^* HOMO
C_2-Symmetry,
(4*n* + 2) system

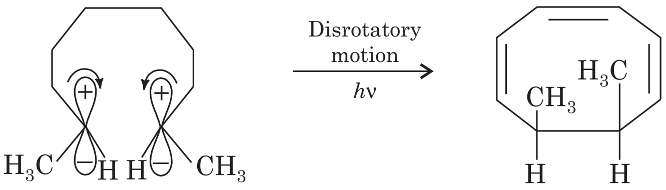
(*d*)



(D)

(4*n* + 2) π System, ψ_3
is HOMO in thermal
condition, *m*-Symmetry

(*e*)

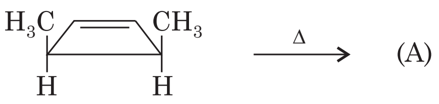


(E)

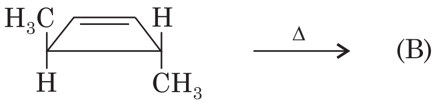
4π System, ψ_5^* is HOMO,
m-Symmetry

Problem 2: *Give product with its stereochemistry in the reactions given below:*

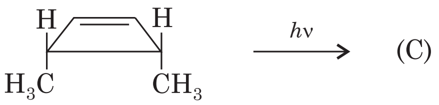
(*a*)



(*b*)

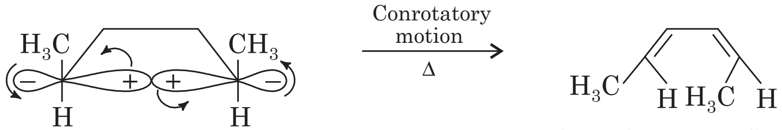


(*c*)



Solution: These problems are based on electrocyclic reaction.

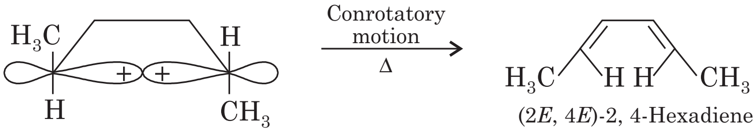
(*a*)



(2*Z*, 4*E*), 2, 4-Hexadiene
(A)

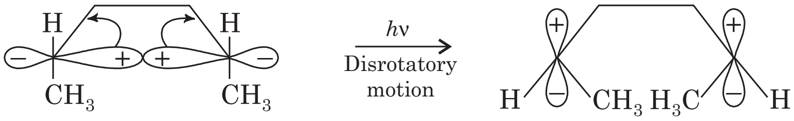
- (*i*) 4π-System.
- (*ii*) ψ_2 is HOMO in thermal condition
- (*iii*) It has C_2-Symmetry in σ bond, hence product too should have C_2-Symmetry

(*b*)

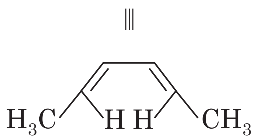


(2*E*, 4*E*)-2, 4-Hexadiene
(B)

(*c*)



‖

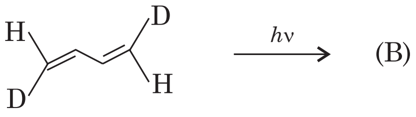


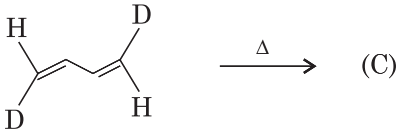
(2*E*, 4*E*) 2, 4-Hexadiene
(C)

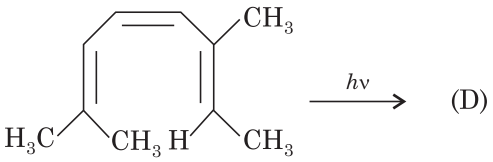
- (*i*) 4π-System.
- (*ii*) ψ_3 is HOMO in photochemical condition.
- (*iii*) It has *m*-symmetry in σ bond hence *m*-symmetry in π bond should also be present in the product. Therefore motion is disrotatory.

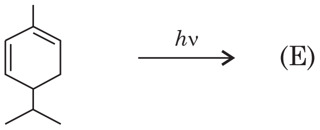
Problem 3: *Predict the product of the given reactions.*

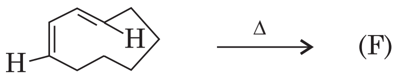
(*a*) 

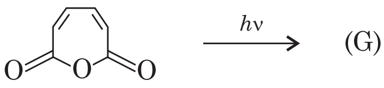
(*b*) 

(*c*) 

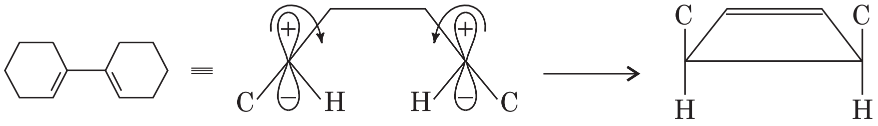
(*d*) 

(*e*) 

(*f*) 

(*g*) 

Solution: These problems are based on electrocyclic reaction.

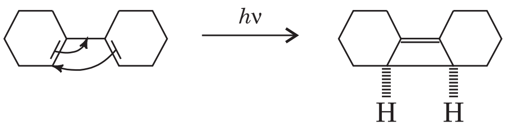
(*a*) 

(*i*) 4π-System.

(*ii*) Its HOMO is ψ_3^* in photochemical condition which has *m*-symmetry.

(*iii*) Motion is disrotatory.

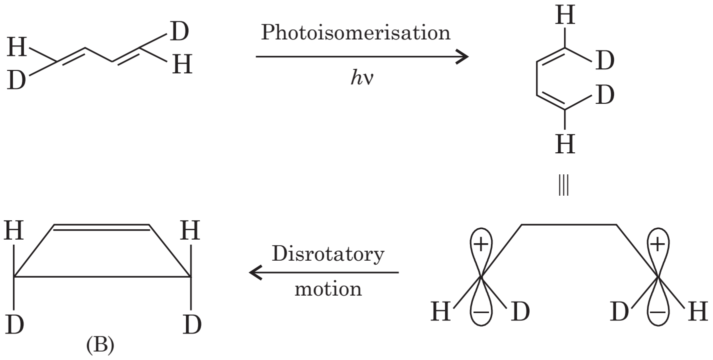
Thus in the product both hydrogens are in the same plane.



(A)

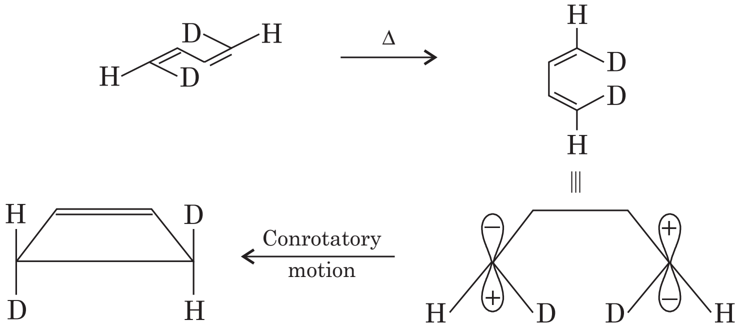
(*b*) The given diene is *trans*-diene. This undergoes photoisomerisation into *cis*-diene because cycloaddition reaction is given by *cis*-diene and not by *trans*-diene.

(*b*)



(B)

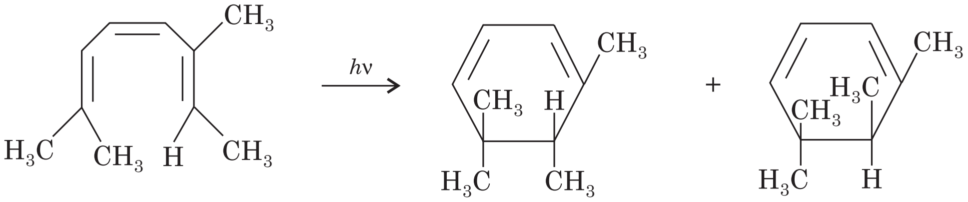
(*c*)



(C)

C_2-Symmetry

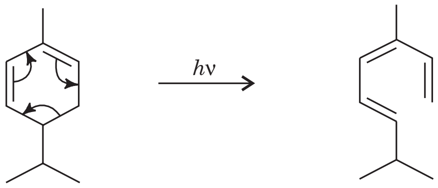
(*d*)



(4*n* + 2) π-System
Photochemical
conrotatory motion

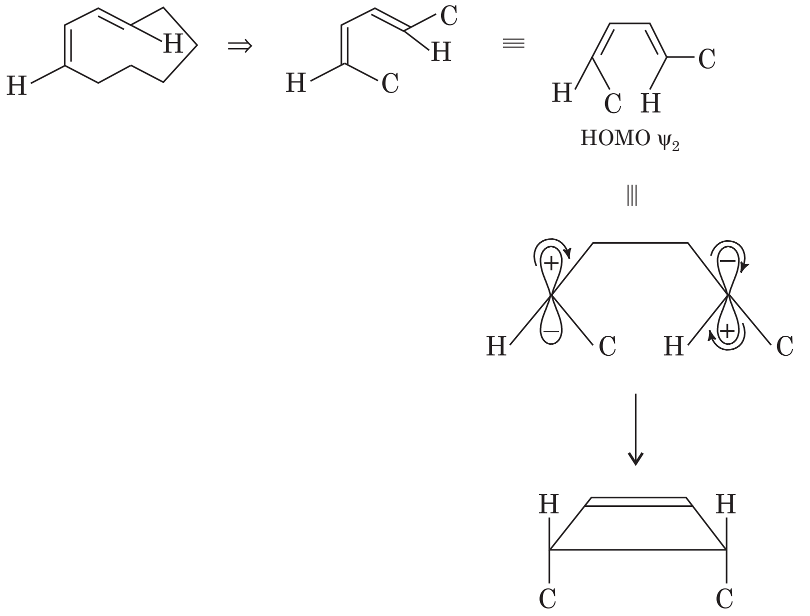
(Racemic mixture)
(D)

(*e*)

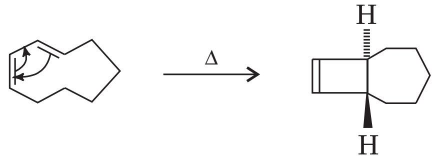


(E)
(4*n* + 2)π-System in open
chain product hence ring
opening is conrotatory

(*f*)

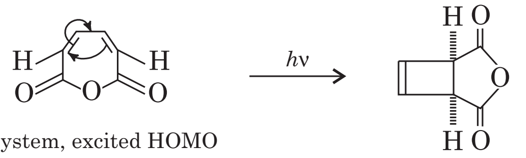


This reaction can be represented as follows:



(F)

(*g*)

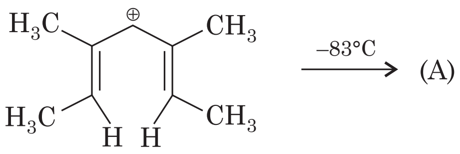


4π-System, excited HOMO
is ψ_3 which has *m*-symmetry,
motion is disrotatory.

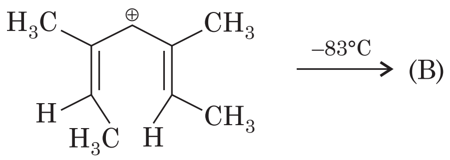
(G)

Problem 4: *Give product and stereochemistry of the product in each case.*

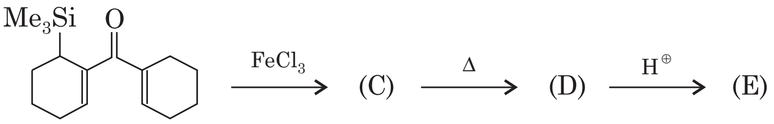
(*a*)



(*b*)

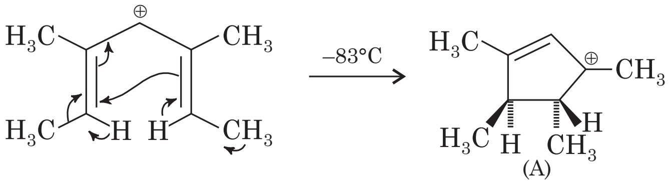


(*c*)



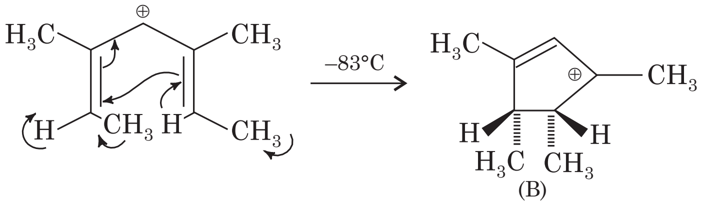
Solution: These problems are based on electrocyclic reaction.

(*a*)



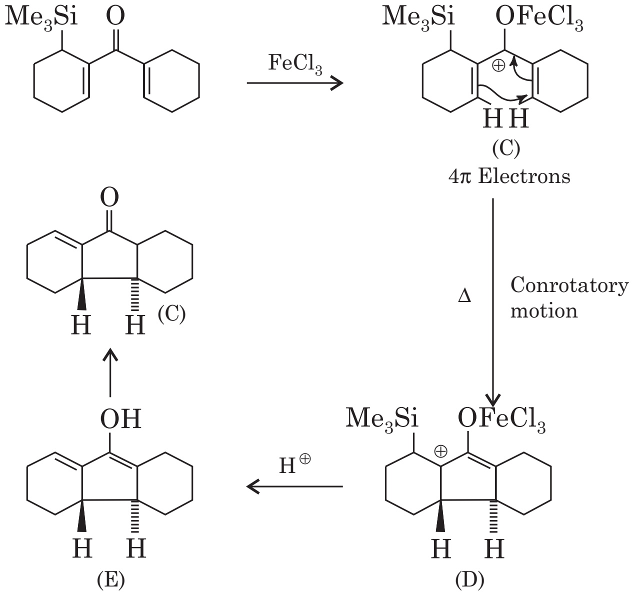
System is conjugated (+ve charge, π conjugation) having (4*n*) π electrons. HOMO in ground state is ψ_2 which has C_2 symmetry. Motion is conrotatory.

(*b*)



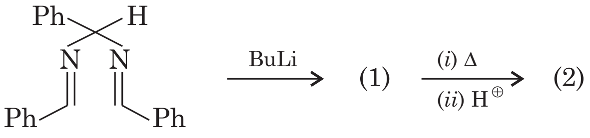
System is conjugated having (4*n*) π electrons. Its ground state HOMO is ψ_2 which has C_2 symmetry. Motion is conrotatory.

(*c*)

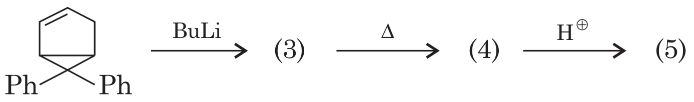


Problem 5: *Give product and stereochemistry of the product in each case.*

(*a*)

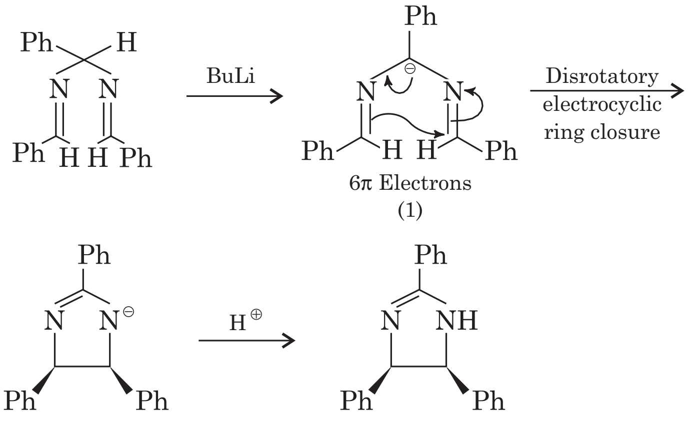


(*b*)



Solution: These problems are based on electrocyclic reaction.

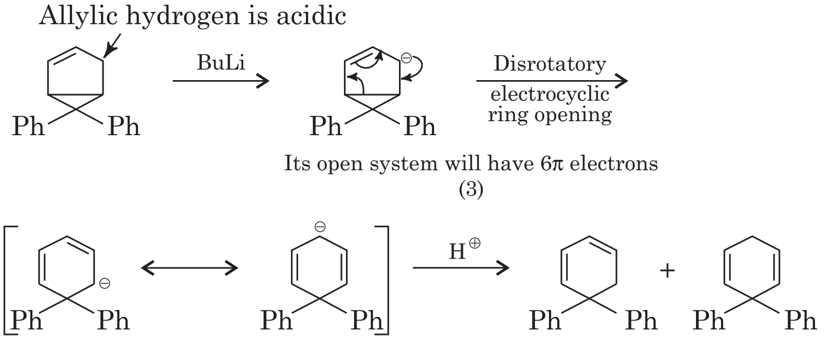
(*a*)



(1)

(2)

(*b*)



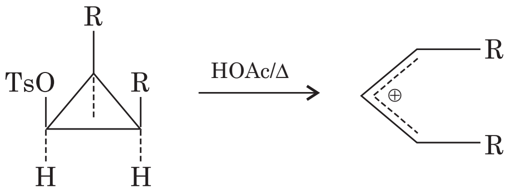
(3)

(4)

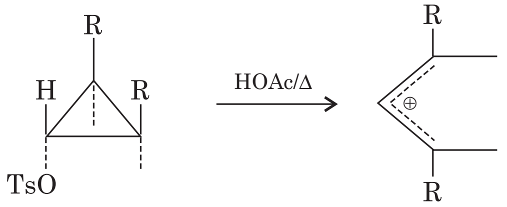
(5)

Problem 6: *State whether these reactions proceed by the conrotatory or the disrotatory mode.*

(*a*)

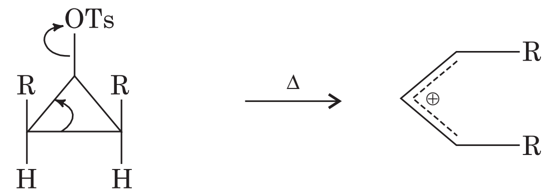


(*b*)

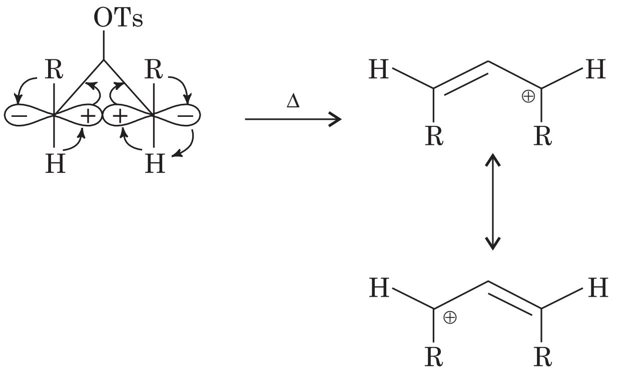


Solution: These problems are based on electrocyclic ring opening reaction

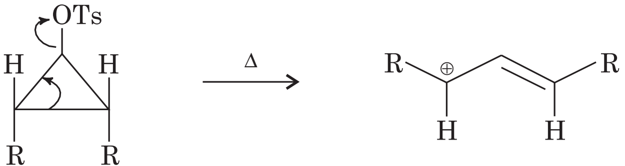
(*a*)



Its open chain system will have 2π electrons. This system will have $(4n + 2)$ π electrons. Its HOMO will be ψ_1 having mirror plane symmetry. Motion is disrotatory.

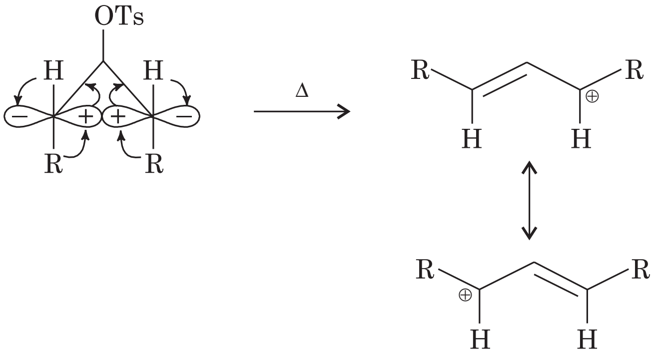


(*b*)



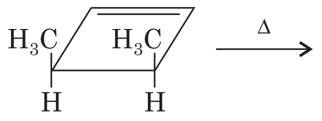
This has $(4n + 2)\pi$ conjugated electrons. Its HOMO will be ψ_1 which has mirror plane symmetry. Motion will be disrotatory.

Thus

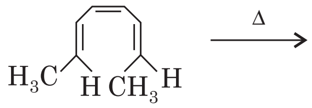


Problem 7: *Draw the structure of the chief product of each of the following thermal reactions.*

(*a*)

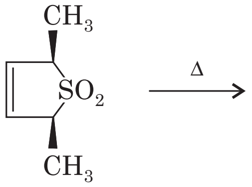


(*b*)



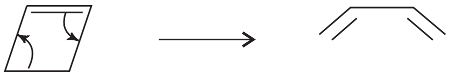
Cis/trans

(*c*)

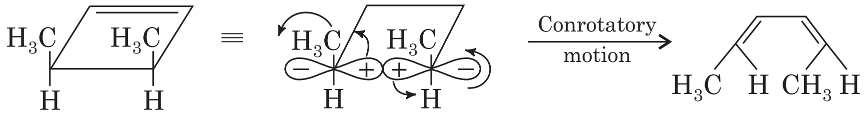


Solution: These problems are based on electrocyclic reaction.

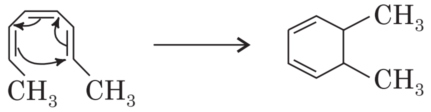
(*a*)



This system has 4π electrons. Its HOMO in thermal condition is ψ_2 which has C_2 symmetry. Thus motion will be conrotatory.

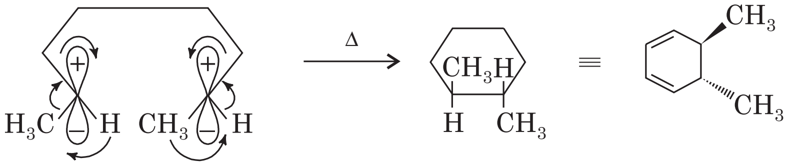


(*b*)

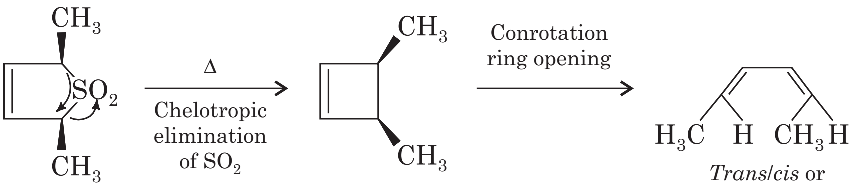


System has (4*n* + 2) π electrons

Its HOMO in thermal condition is ψ_3 which has mirror plan symmetry. Therefore motion will be disrotatory motion. Thus



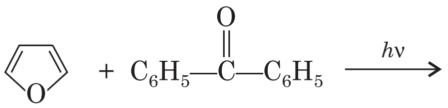
(*c*)



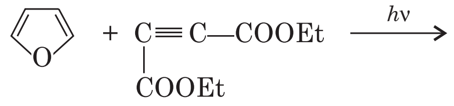
Trans/cis or (2*E*, 4*Z*)

Problem 8: *Complete the following reactions and give their mechanisms.*

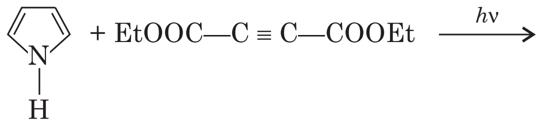
(*a*)



(*b*)

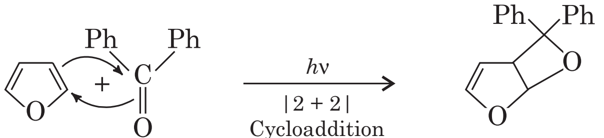


(*c*)



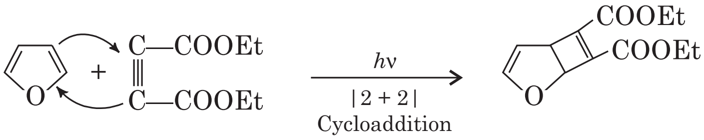
Solution: These problems are based on |2 + 2| cycloaddition reaction

(*a*)

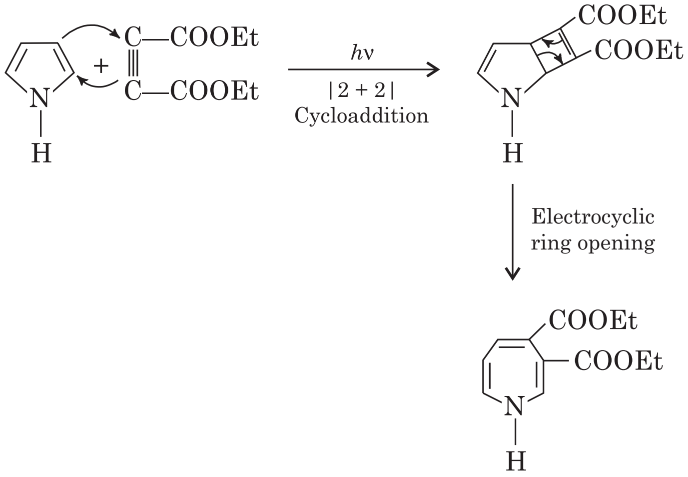


Oxetane derivative

(*b*)

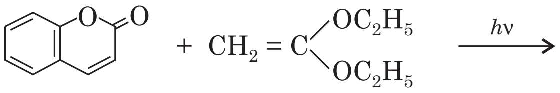


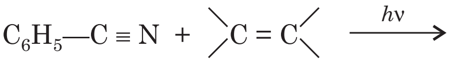
(*c*)

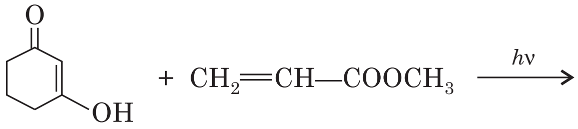


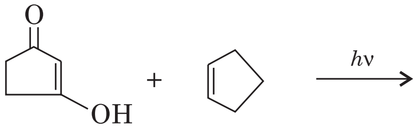
Problem 9: *Complete the following reactions:*

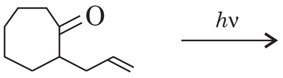
(*a*)



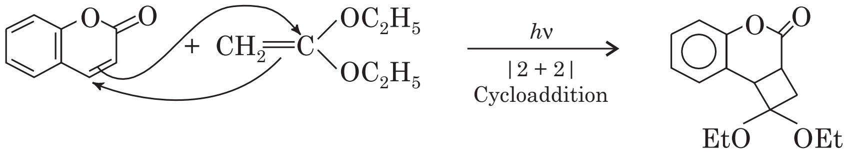
(*b*)

$C_6H_5—C\equiv N + \rangle C=C\langle \xrightarrow{h\nu}$

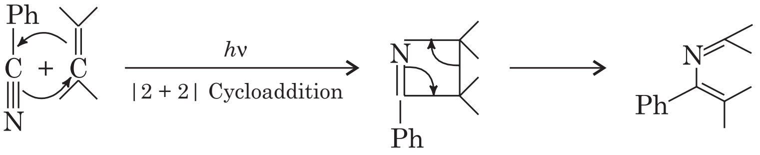
(*c*)


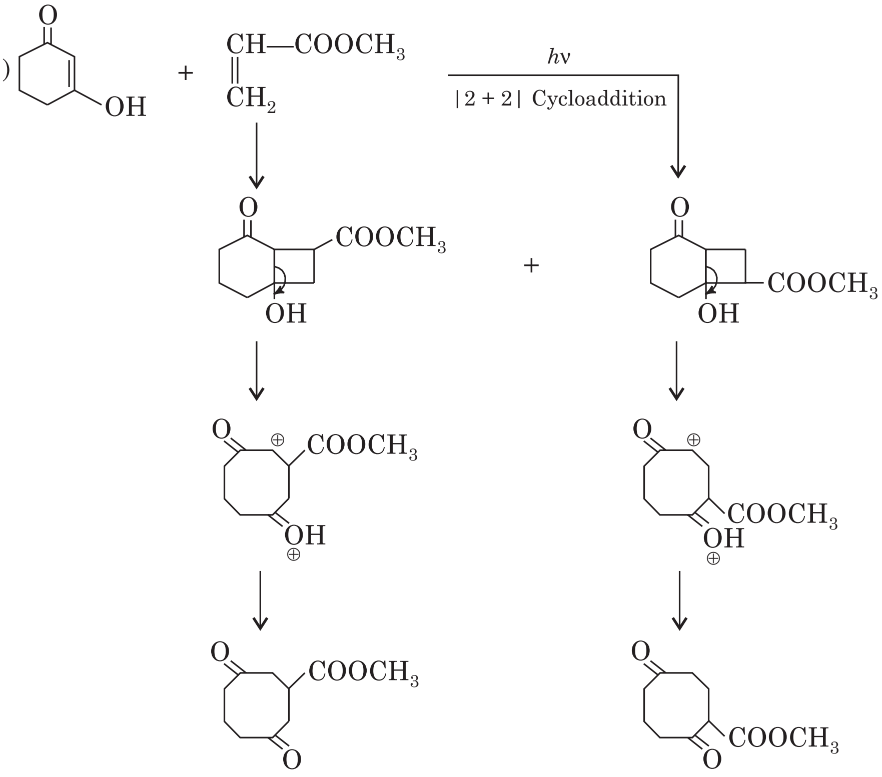
(*d*)


(*e*)


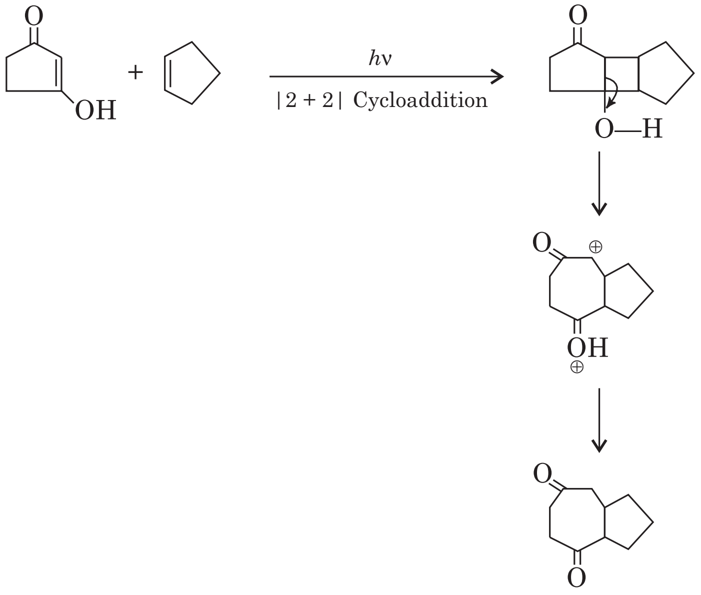
Solution: These reactions are based on |2 + 2| cycloaddition reaction.

(*a*)


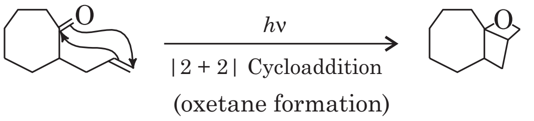
(*b*)


(*c*)


(*d*)

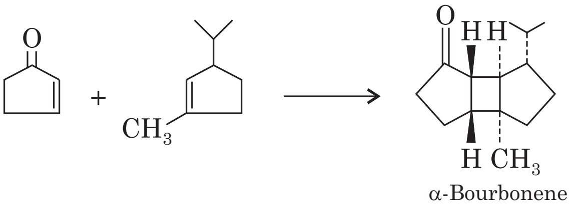


(*e*)

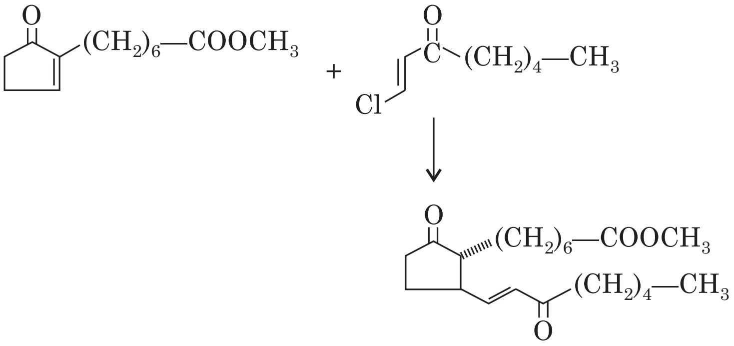


Problem 10: *How these conversions can be achieved? In these conversions atleast one step should be a photochemical reaction.*

(*a*)

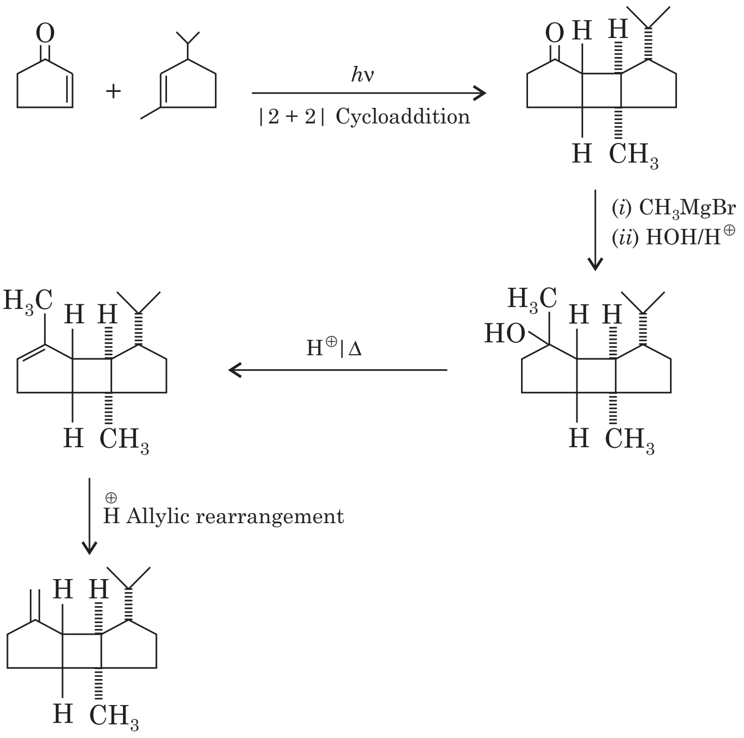


(*b*)

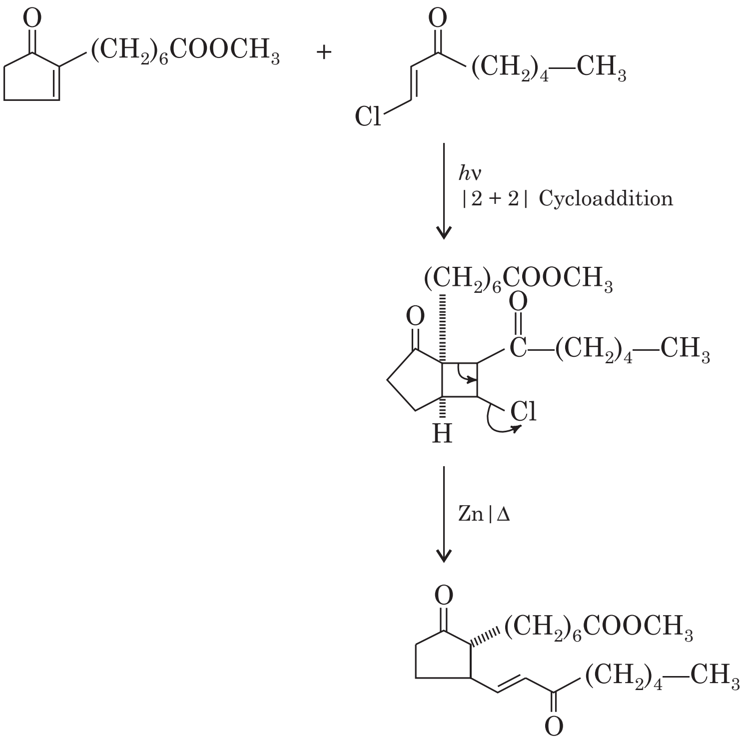


Solution:

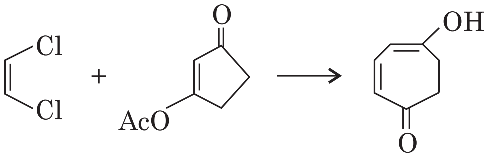
(*a*)

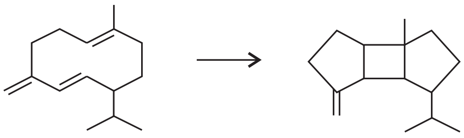

O
+
hν
|2 + 2| Cycloaddition
O H H
H CH$_3$
(*i*) CH$_3$MgBr
(*ii*) HOH/H$^\oplus$
H$_3$C
HO
H H
H CH$_3$
H$^\oplus$|Δ
H$_3$C
H H
H CH$_3$
$\overset{\oplus}{H}$ Allylic rearrangement
H H
H CH$_3$

(*b*)


O
(CH$_2$)$_6$COOCH$_3$
+
O
(CH$_2$)$_4$—CH$_3$
Cl
hν
|2 + 2| Cycloaddition
(CH$_2$)$_6$COOCH$_3$
O
O
C—(CH$_2$)$_4$—CH$_3$
Cl
H
Zn|Δ
O
(CH$_2$)$_6$COOCH$_3$
(CH$_2$)$_4$—CH$_3$
O

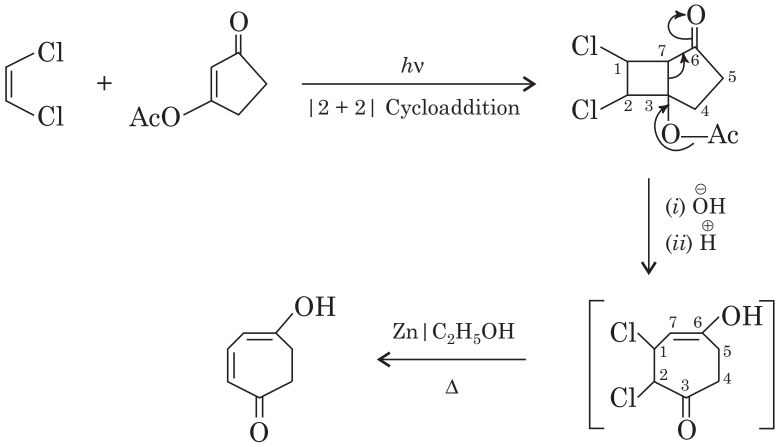
Problem 11: *How these conversions can be achieved? In these conversions atleast one step should be a photochemical reaction.*

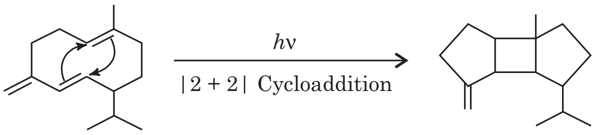
(*a*)


(*b*)


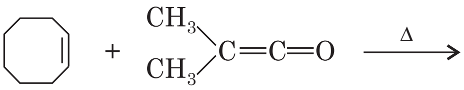
(–) β-Boubonene

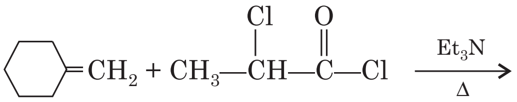
Solution:

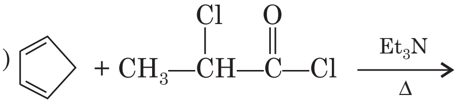
(*a*)


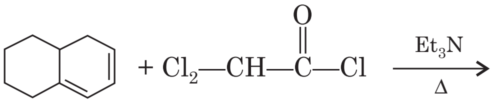
(*b*)


Problem 12: *Complete the following reactions:*

(*a*)


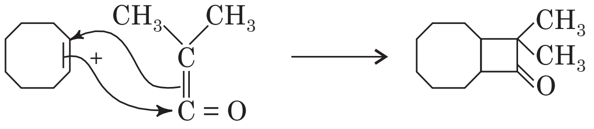
(*b*)


(*c*)


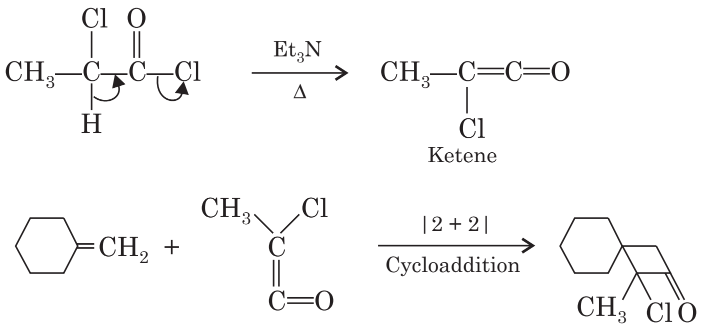
(*d*)


Solution: Ketene gives |2 + 2| cycloaddition reaction in the absence of UV light. The reaction is thermal reaction.

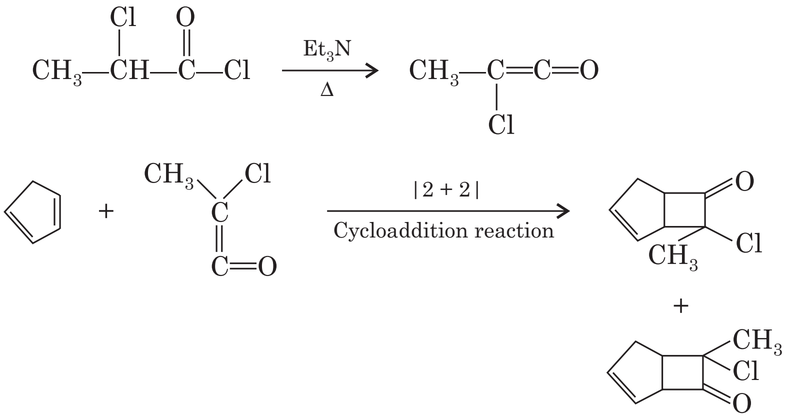
(*a*)



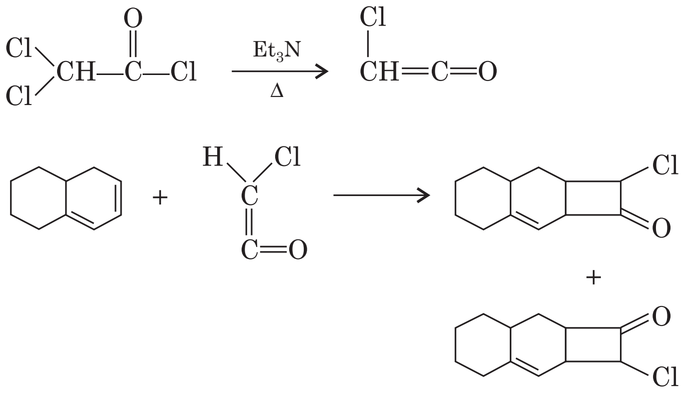
(*b*)



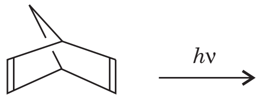
(*c*)

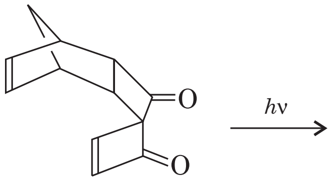


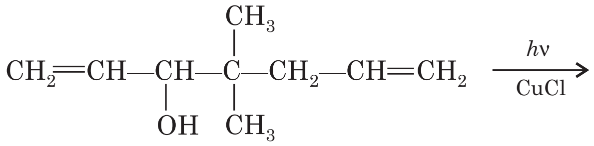
(*d*)



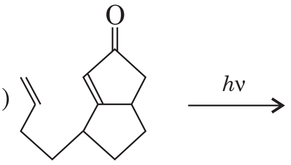
Problem 13: *Complete the following reactions:*

(*a*)


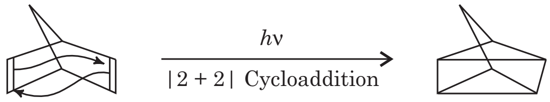
(*b*)


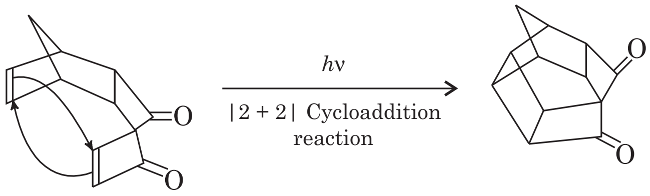
(*c*)


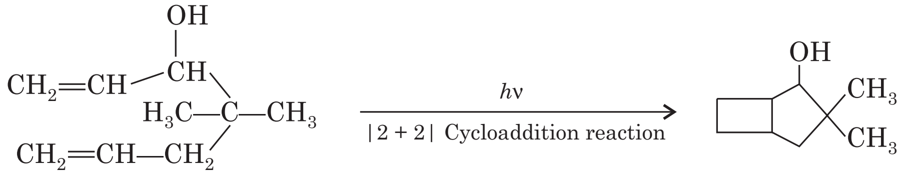
$CH_2{=}CH-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH{=}CH_2 \xrightarrow[CuCl]{h\nu}$

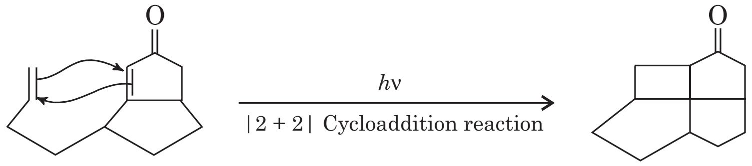
(*d*)


Solution: These problems are based on |2 + 2| cycloaddition reaction.

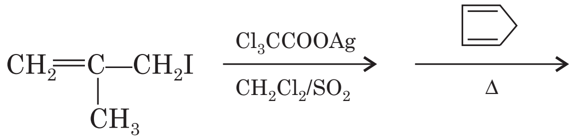
(*a*)


(*b*)


(*c*)


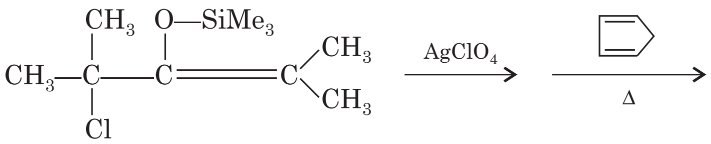
(*d*)


Problem 14: *Complete the following reactions and give product in each case.*

(*a*)


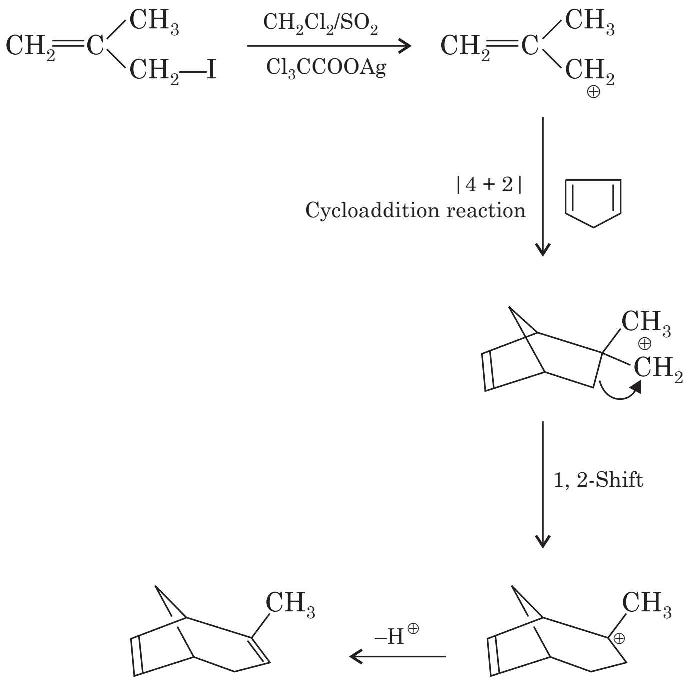
$CH_2{=}\underset{CH_3}{C}-CH_2I \xrightarrow[CH_2Cl_2/SO_2]{Cl_3CCOOAg} \xrightarrow[\Delta]{}$

(*b*)

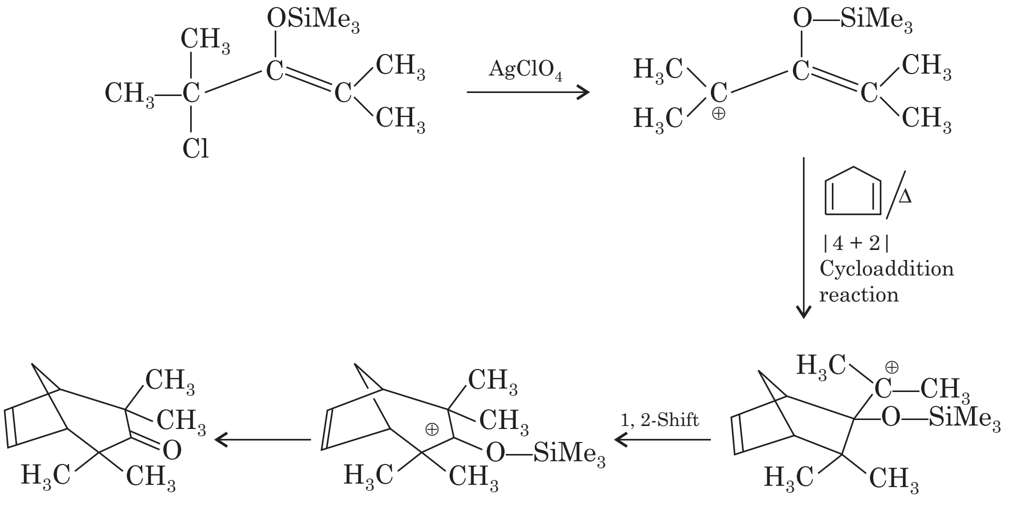


Solution: These problems are based on |4 + 2| cycloaddition reaction

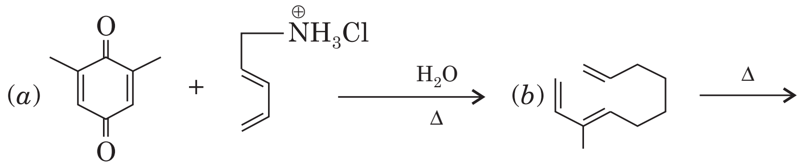
(*a*)



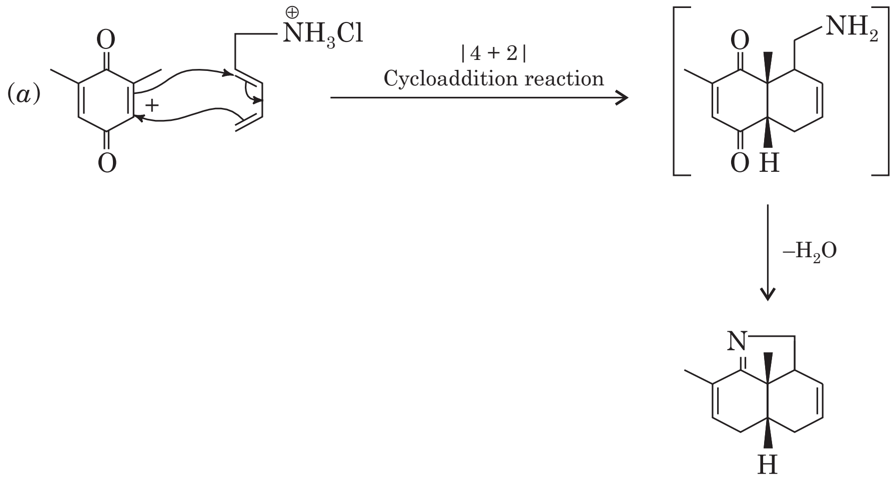
(*b*)

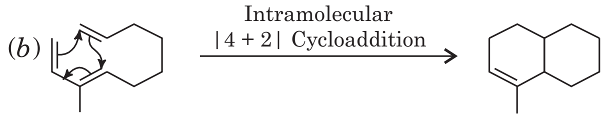


Problem 15: *Give product in the given reactions :*

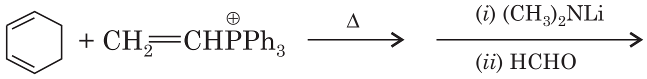


Solution:

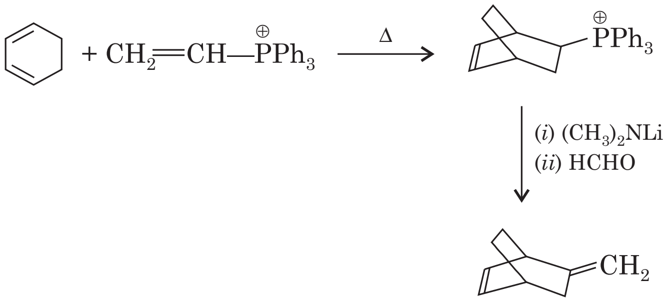




Problem 16: *Complete the given reaction and give its name (if any).*

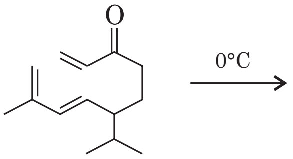


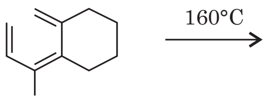
Solution:



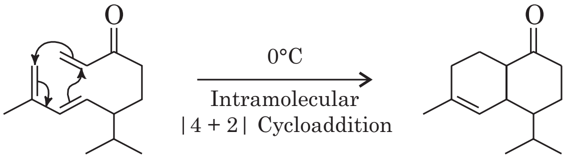
The first step is Diels-Alder addition, (|4 + 2| cycloaddition) and second step is Wittig reaction.

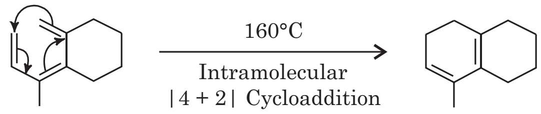
Problem 17: *Complete the following reactions and give their name (if any):*

(*a*)


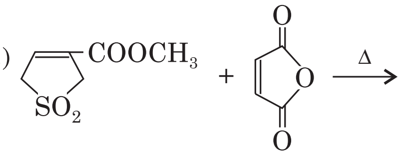
(*b*)


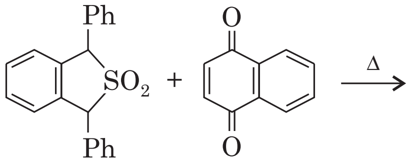
Solution: The above reactions are intramolecular Diels-Alder reactions.

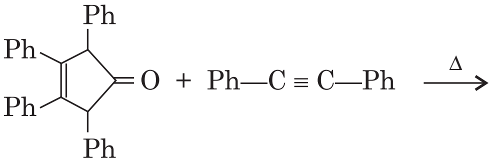
(*a*)


(*b*)


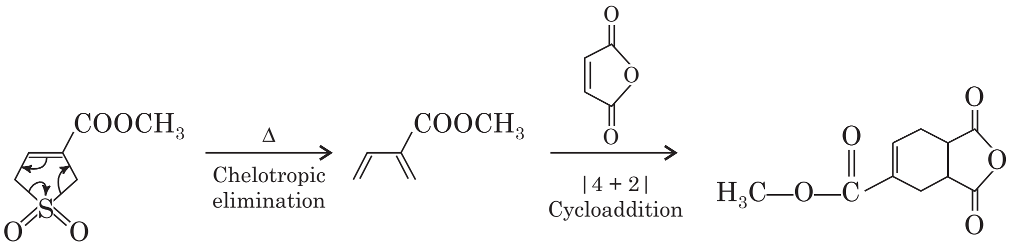
Problem 18: *Complete the following reactions:*

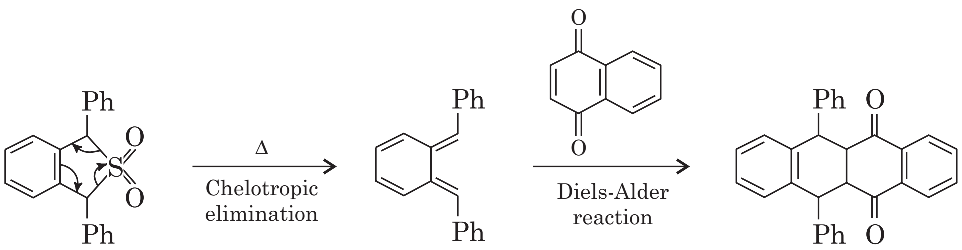
(*a*)


(*b*)


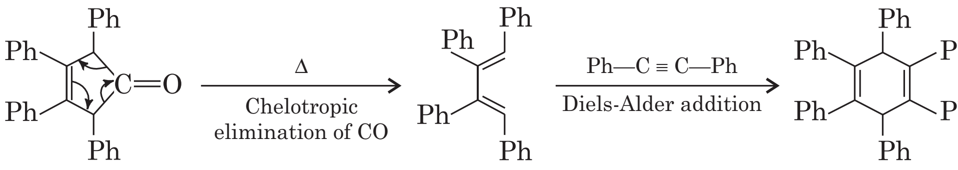
(*c*)


Solution:

(*a*)


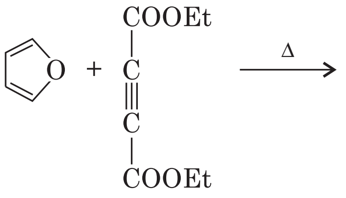
(*b*)


(*c*)

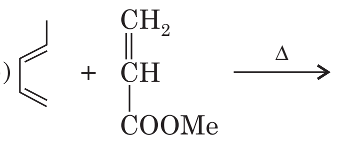


Problem 19: *Draw the structure of the chief product of each of the following thermal reactions:*

(*a*)

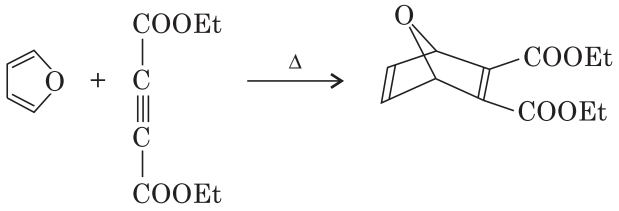


(*b*)

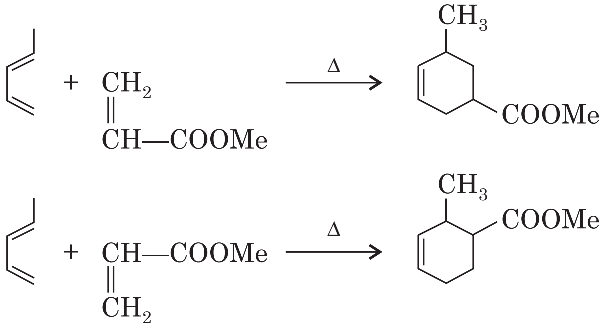


Solution: These two reactions are |4 + 2| cycloaddition reactions.

(*a*)

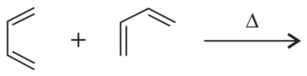


(*b*)

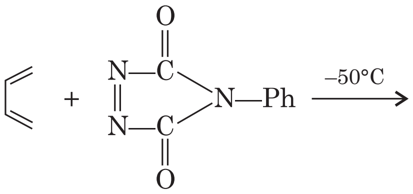


Problem 20: *Draw the structure of the chief product of each of the following thermal reactions:*

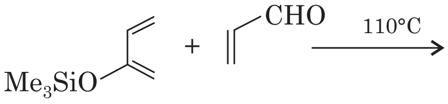
(*a*)



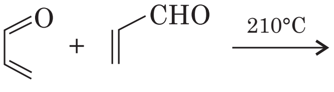
(*b*)



(*c*)



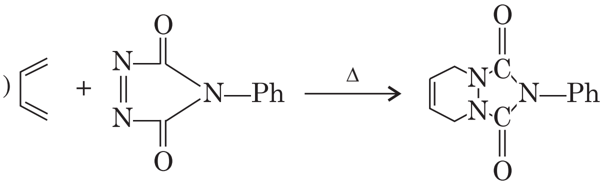
(*d*)



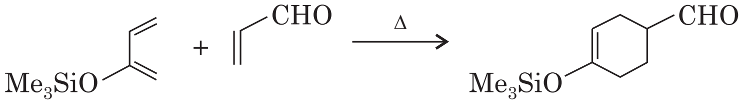
Solution: These problems are based on |4 + 2| cycloaddition reaction.

(*a*)

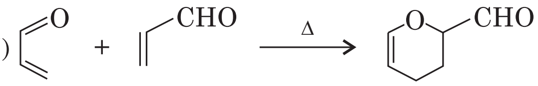
(*b*)



(*c*)

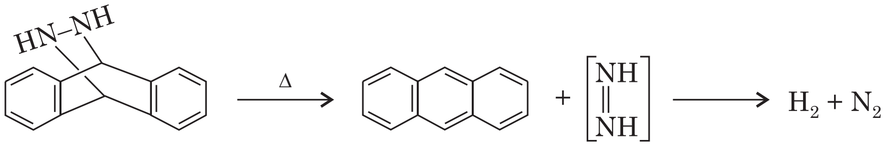


(*d*)

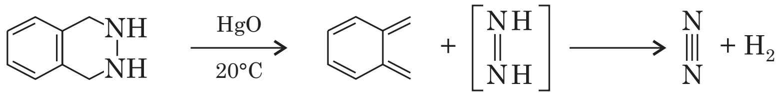


Problem 21: *Give name and mechanism of the following reactions:*

(*a*)

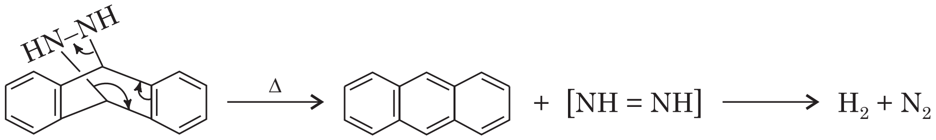


(*b*)

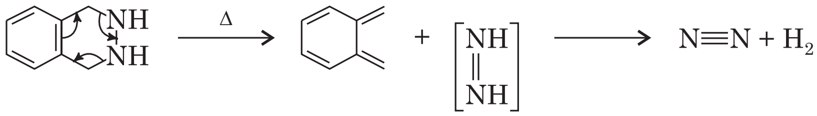


Solution: These two reactions are retro Diels-Alder reaction.

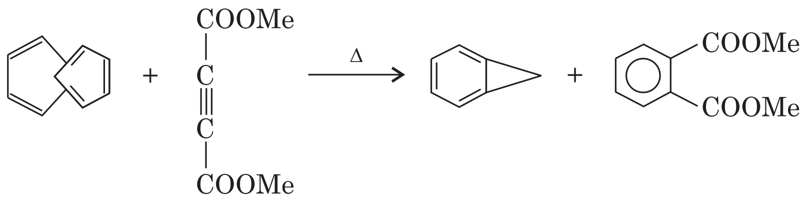
(*a*)



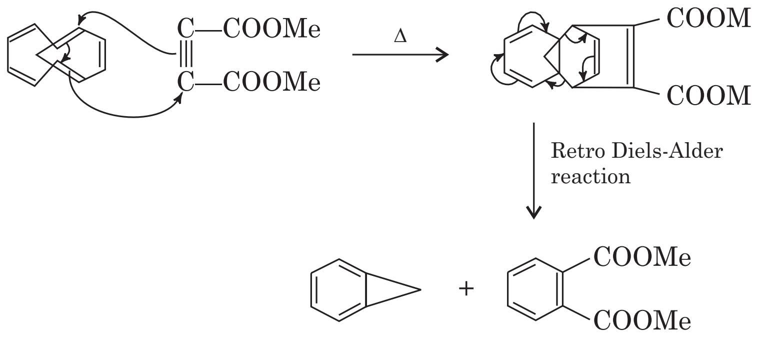
(*b*)



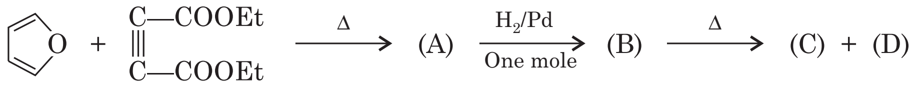
Problem 22: *Give name and mechanism of the following conversion:*



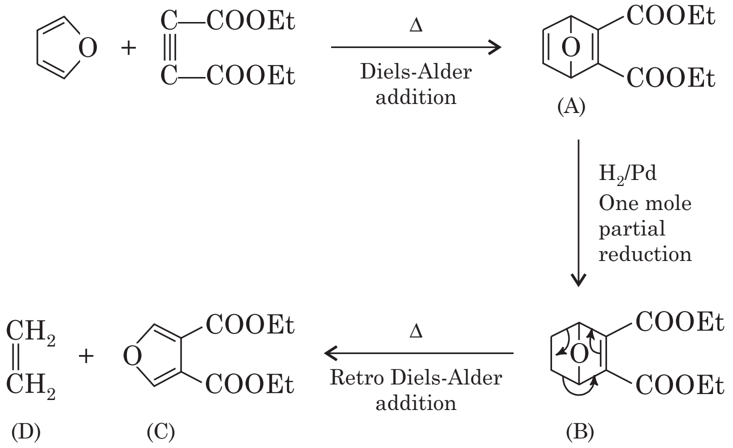
Solution: First step is Diels-Alder addition and second step is retro Diels-Alder reaction.



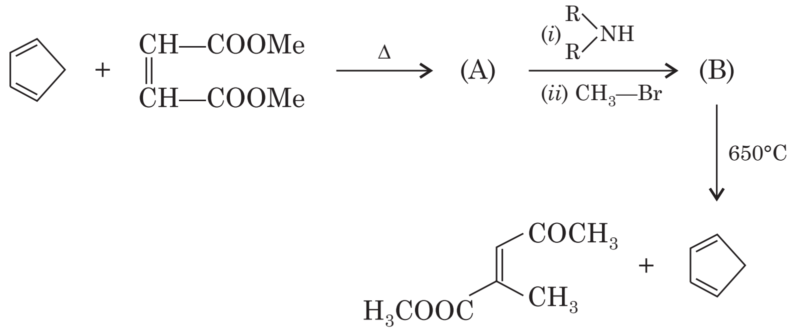
Problem 23: *Complete the given reaction and give name of the reaction at each step (where it is possible).*



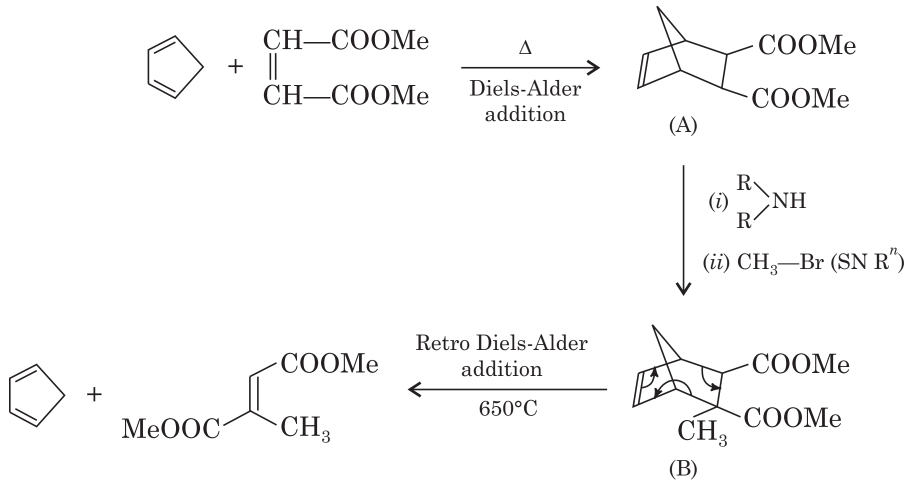
Solution:



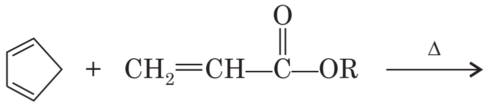
Problem 24: *Complete the given reaction:*



Solution:

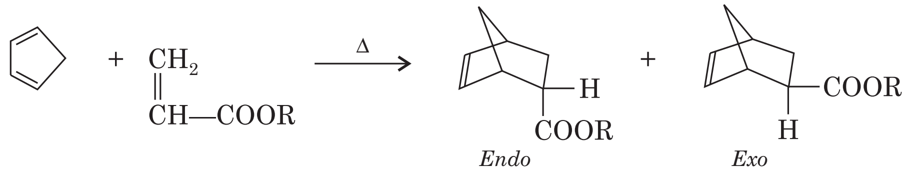


Problem 25: *Complete the given reaction. How many products will be formed and which will be major product in the given reaction?*

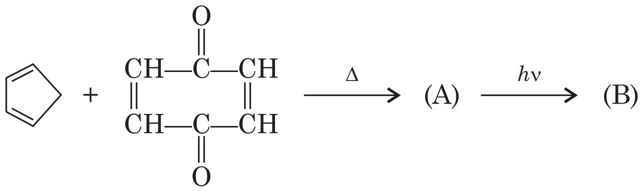


$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OR \xrightarrow{\Delta}$$

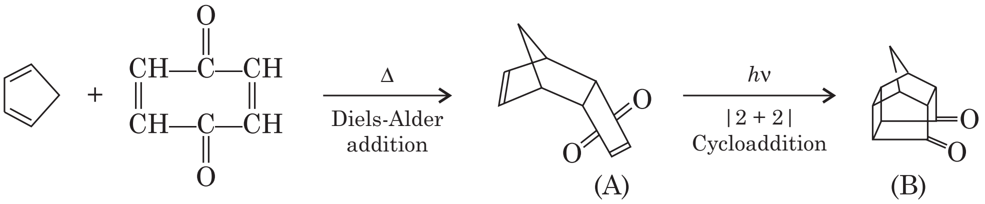
Solution: Reaction is Diels-Alder addition. Product of the reaction will be bicyclic compound. Hence two products will be formed, one is *exo* and other will be *endo*. *Endo* product will be major product because of the secondary interaction in the molecule.



Problem 26: *Complete the following sequence of reactions:*

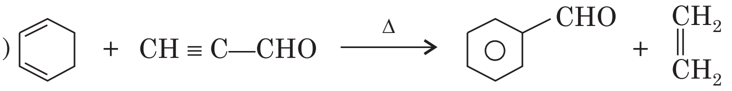


Solution:

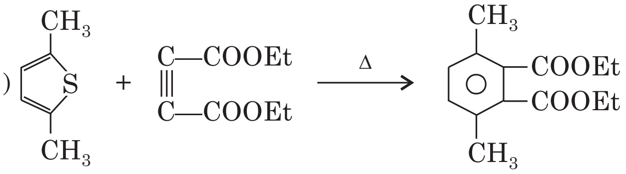


Problem 27: *Indicate how the given conversions take place?*

(*a*)

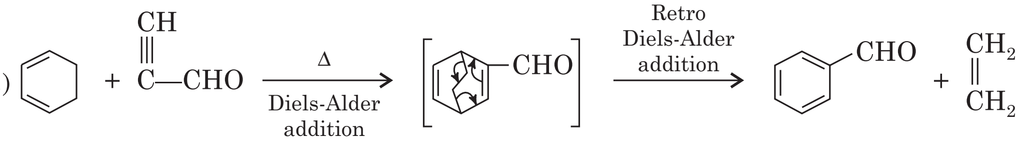


(*b*)

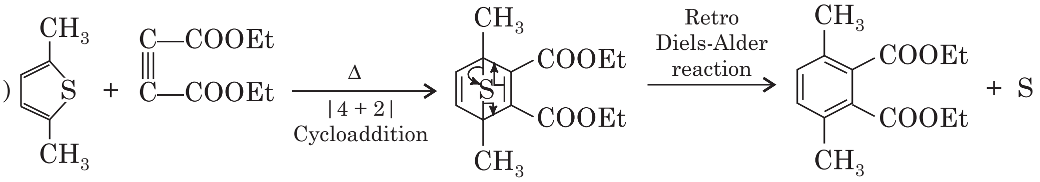


Solution:

(*a*)

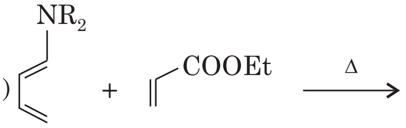


(*b*)

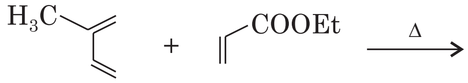


Problem 28: *Predict major product in the given thermal reactions:*

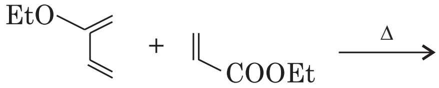
(*a*)



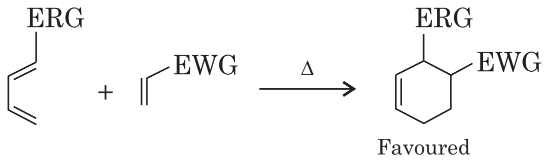
(*b*)



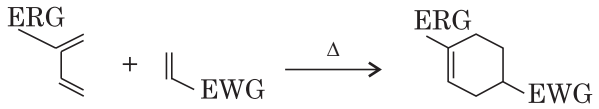
(*c*)



Solution: The above reactions are Diels-Alder addition. Both diene and the dienophile are unsymmetrically substituted. Generally there is a preference for the *ortho* and *para* orientations as follows:

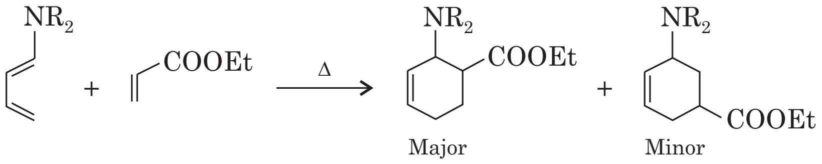


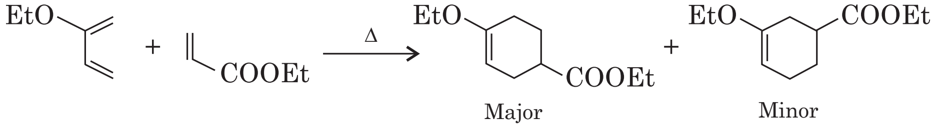
Ortho like orientation

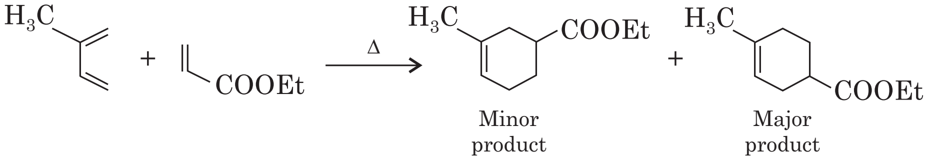


Para like orientation

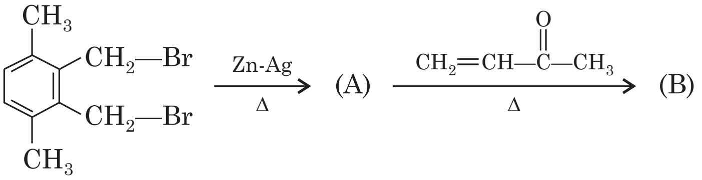
Thus

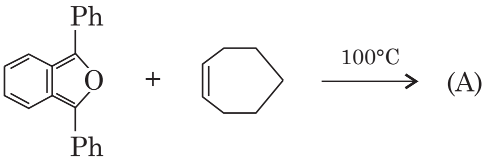
(*a*)


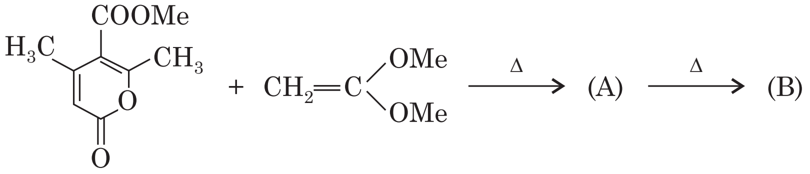
(*b*)


(*c*)


Problem 29: *Complete the following reactions:*

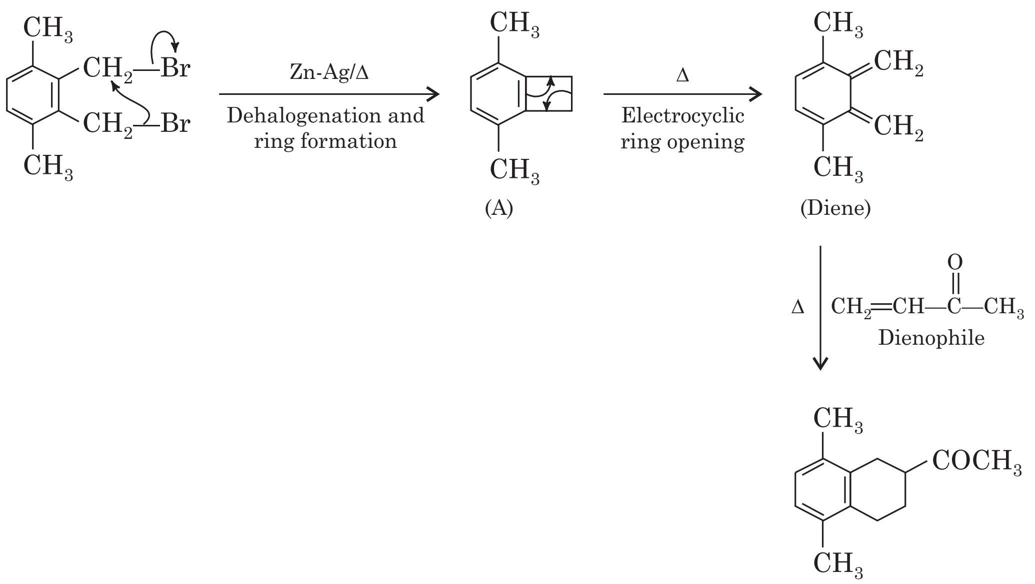
(*a*)


(*b*)


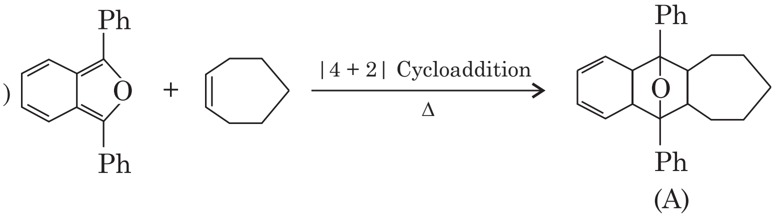
(*c*)


Solution:

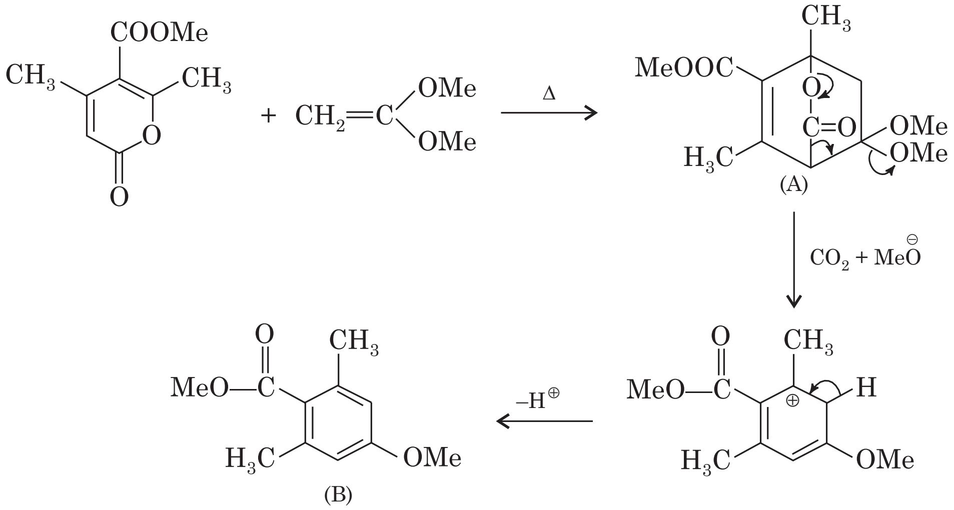
(*a*)



(*b*)

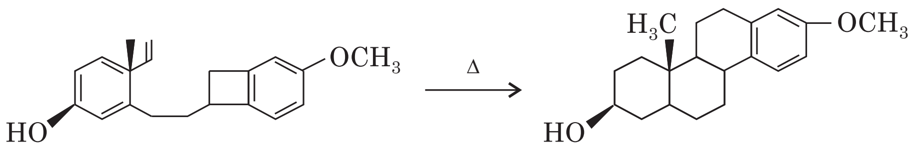


(*c*)

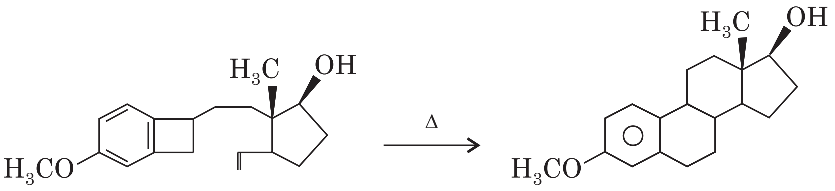


Problem 30: *Give mechanism for the following reactions:*

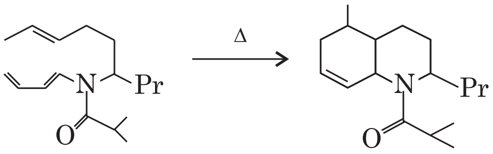
(*a*)



(*b*)

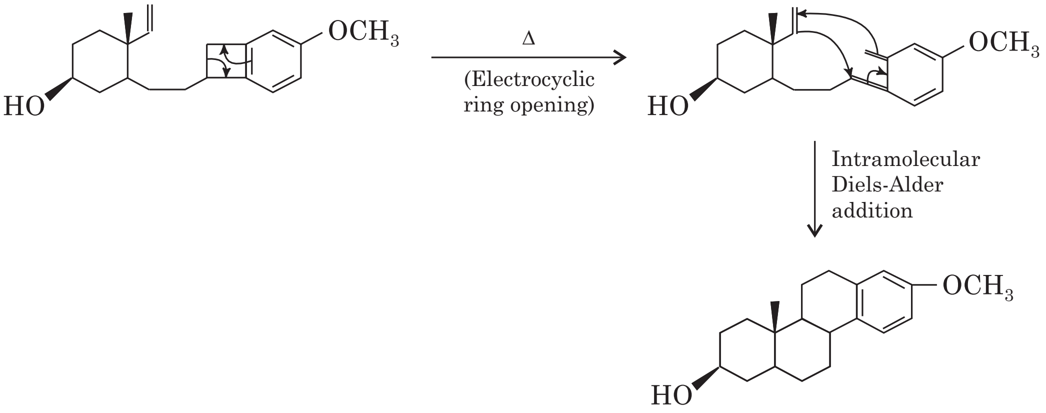


(*c*)

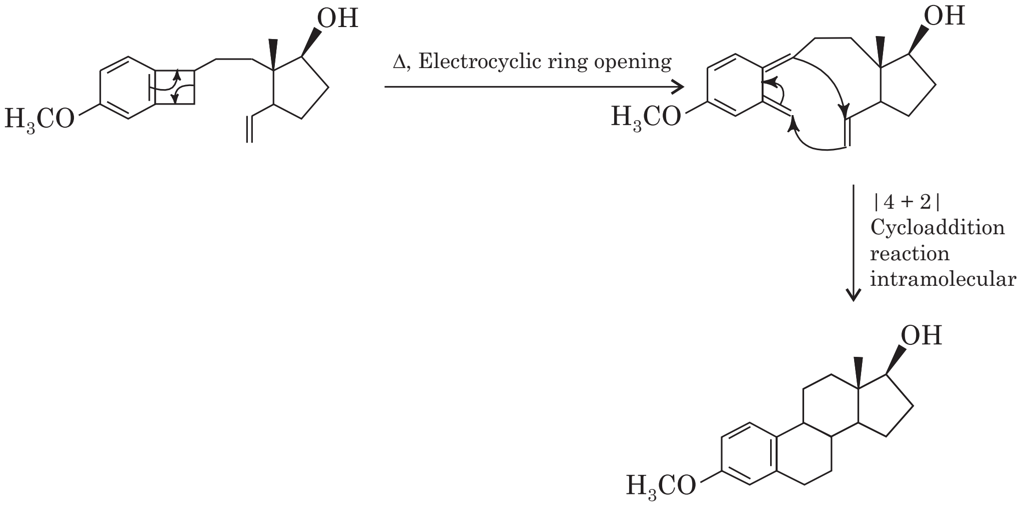


Solution:

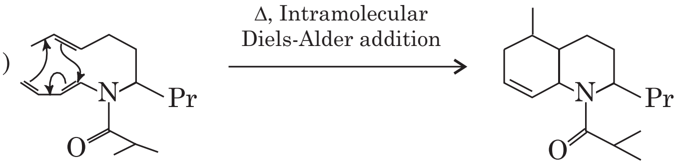
(*a*)



(*b*)



(*c*)

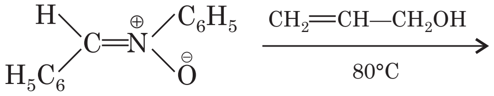


Problem 31: *Give product in the following reactions:*

(*a*) $CH_3—CHO + C_6H_5—NHOH + C_6H_5—CH{=}CH_2 \xrightarrow{80°C}$

(*b*) $CH_2{=}CH—CH{=}CH_2 + CH_2N_2 \xrightarrow{(C_2H_5)_2O}$

(*c*)

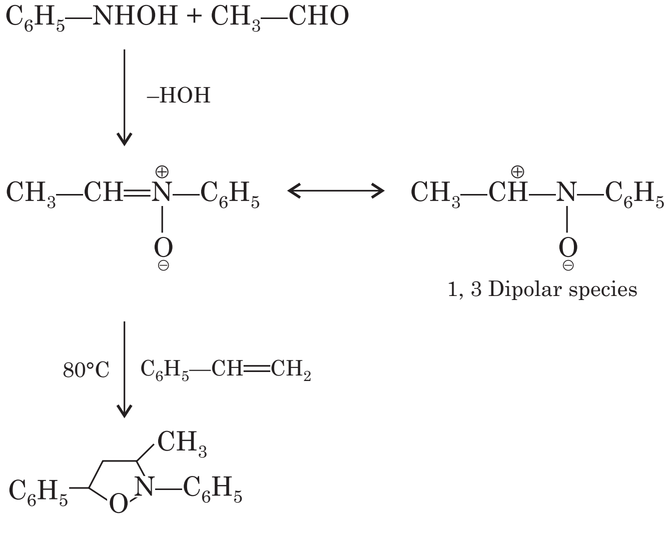


(*d*)

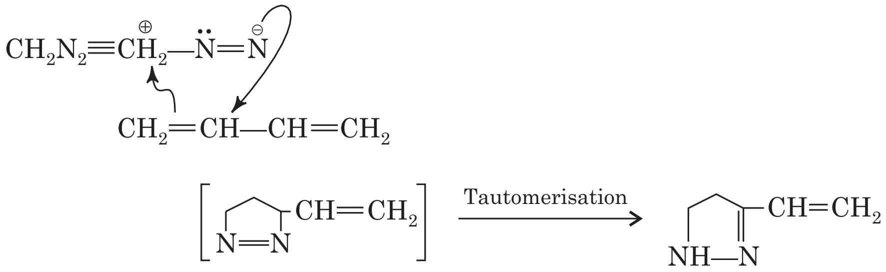
$$\begin{array}{l} CH—COOMe \\ \| \\ CH—COOMe \end{array} \xrightarrow{CH_2N_2}$$

Solution: These problems are based on 1, 3-dipolar addition reaction.

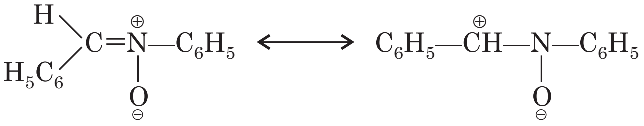
(*a*)



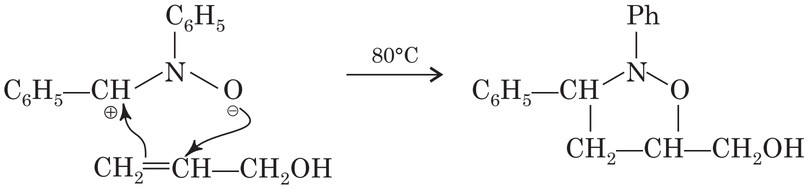
(*b*)



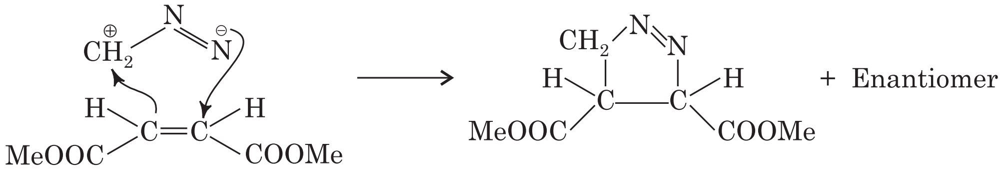
(*c*)



1, 3-Dipole

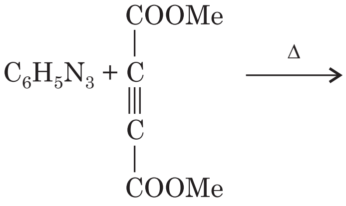


(*d*)



Problem 32: *Give product in the following reactions:*

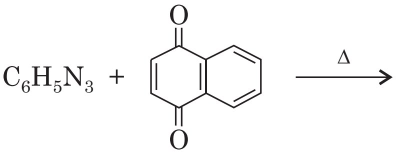
(*a*)



$$C_6H_5N_3 + MeOOC{-}C\equiv C{-}COOMe \xrightarrow{\Delta}$$

(*b*) $CH_2N_2 + CH\equiv CH \xrightarrow{\Delta}$

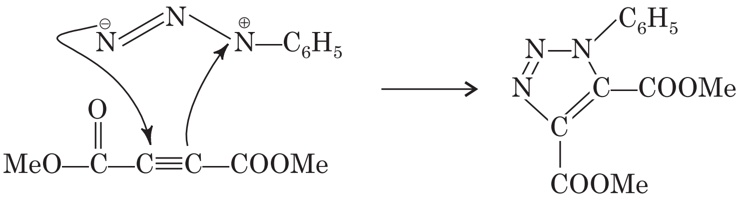
(*c*)



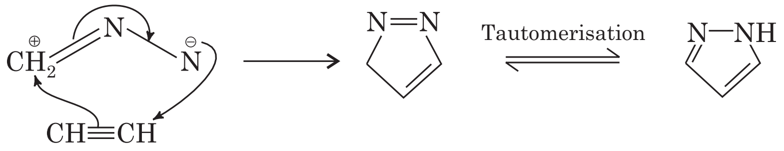
$$C_6H_5N_3 + \text{naphthoquinone} \xrightarrow{\Delta}$$

Solution: These reactions are based on 1, 3-dipolar addition.

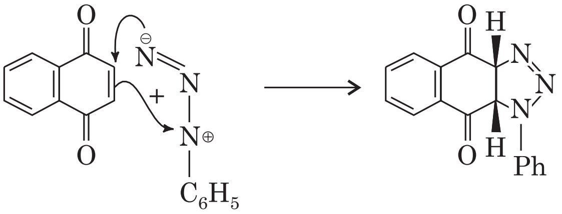
(*a*) $C_6H_5N_3 \equiv C_6H_5{-}N{=}\overset{\oplus}{N}{=}\overset{\ominus}{N} \longleftrightarrow C_6H_5{-}\overset{\oplus}{N}{-}N{=}\overset{\ominus}{N}$



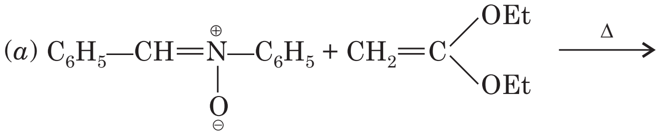
(*b*) $CH_2N_2 \equiv \overset{\oplus}{CH_2}{-}N{=}\overset{\ominus}{N} \longleftrightarrow CH_2{=}\overset{\oplus}{N}{=}\overset{\ominus}{N}$



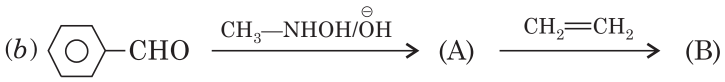
(*c*) $C_6H_5—N_3 \equiv C_6H_5—\overset{\oplus}{N}—\overset{\cdot\cdot}{N}=\overset{\ominus}{N} \longleftrightarrow C_6H_5—N=\overset{\oplus}{N}=\overset{\ominus}{N}$



Problem 33: *Give product(s) in the following reactions. Give mechanism for the reaction (b):*



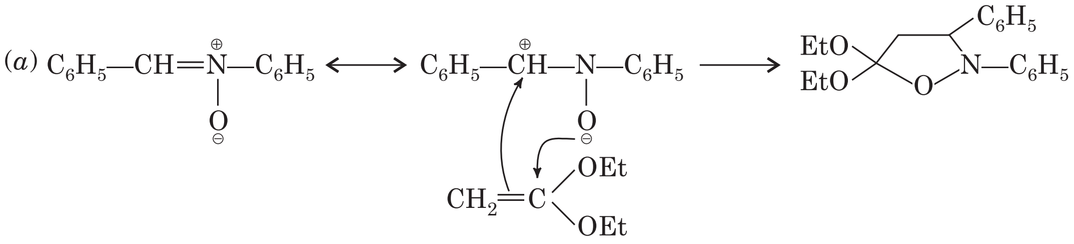
(*a*) $C_6H_5—CH=\overset{\oplus}{\underset{\underset{\ominus}{O}}{N}}—C_6H_5 + CH_2=C(OEt)_2 \xrightarrow{\Delta}$

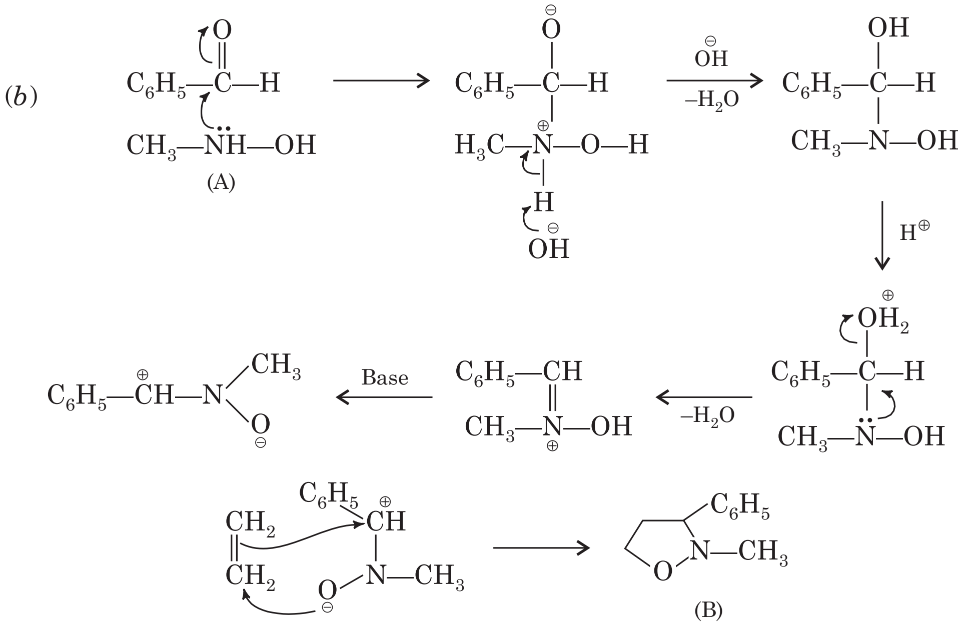


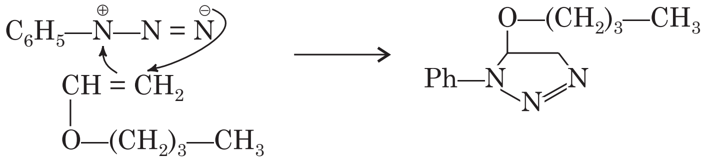
(*b*) $C_6H_5—CHO \xrightarrow{CH_3—NHOH/\overset{\ominus}{O}H} (A) \xrightarrow{CH_2=CH_2} (B)$

(*c*) $C_6H_5—N_3 + CH_3—CH_2—CH_2—CH_2—O—CH=CH_2 \xrightarrow{\Delta}$

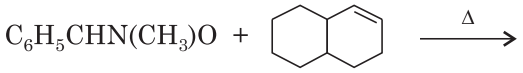
Solution: These problems are based on 1, 3-dipolar addition reaction.

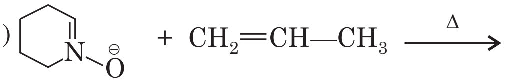




(*c*)


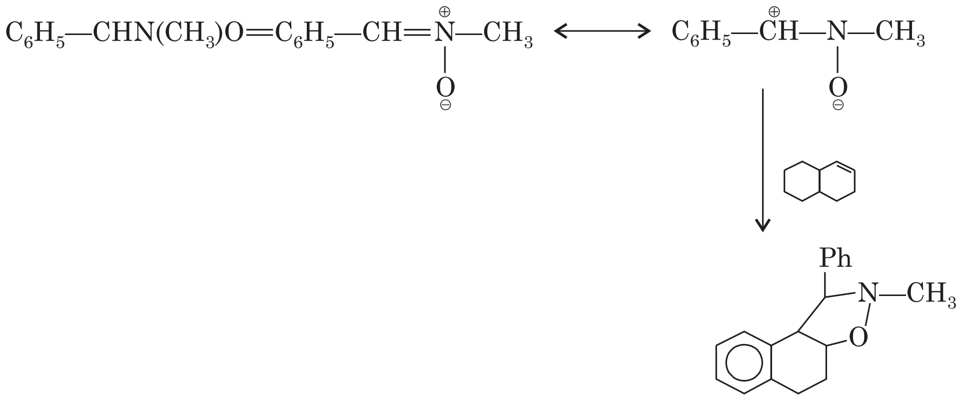
Problem 34: *Give product(s) in the following reactions:*

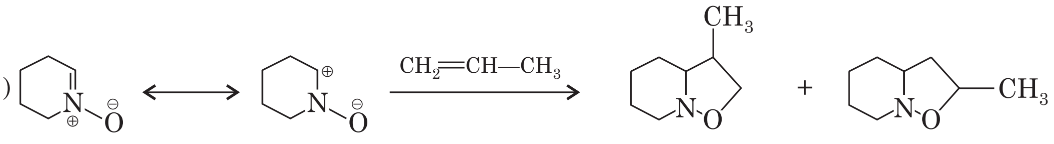
(*a*)


(*b*)


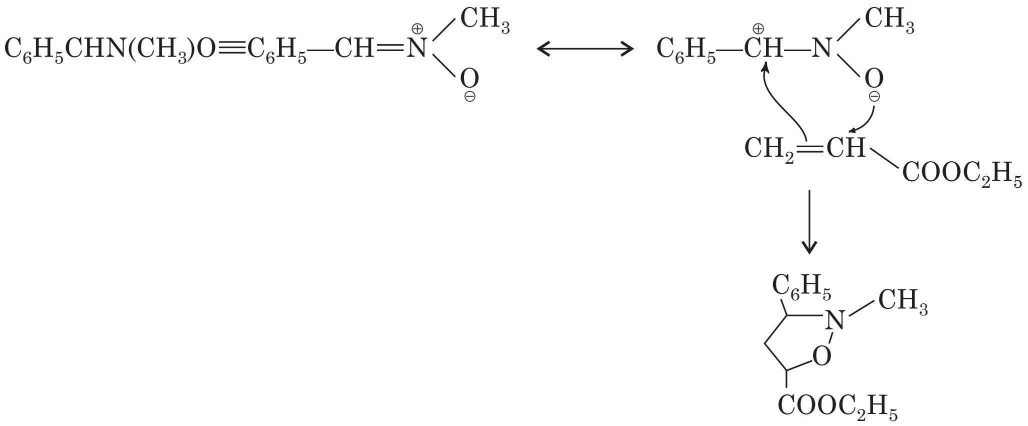
(*c*) $C_6H_5CHN(CH_3)O + CH_2{=}CH{-}COOC_2H_5 \xrightarrow{\Delta}$

Solution: These problems are based on 1,3-dipolar addition reaction.

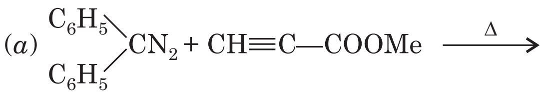
(*a*)


(*b*)


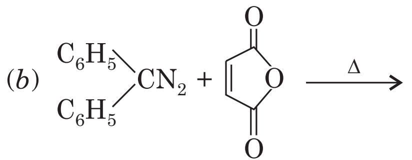
(Major product) (Minor product)

(*c*)


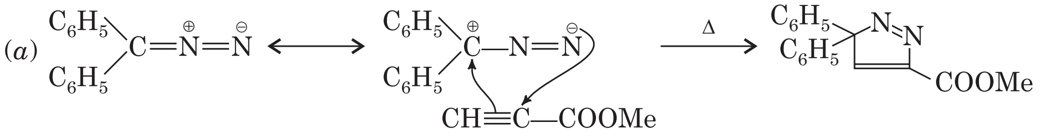
Problem 35: *Give product in each of the following reactions:*

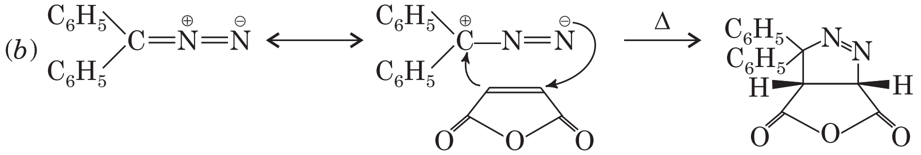


$$(C_6H_5)_2CN_2 + CH\equiv C{-}COOMe \xrightarrow{\Delta}$$

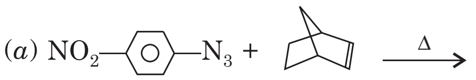


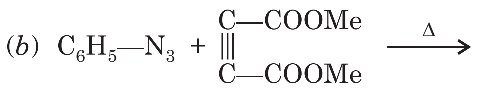
Solution: These problems are based on 1, 3-dipolar addition reaction.



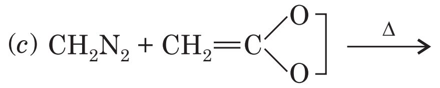


Problem 36: *Complete the following reactions:*

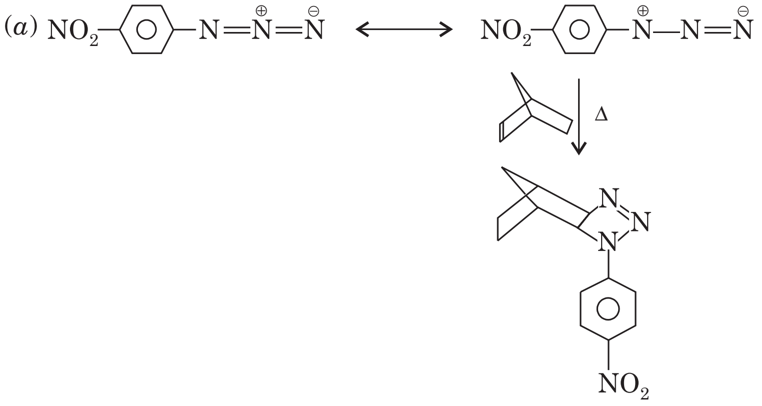


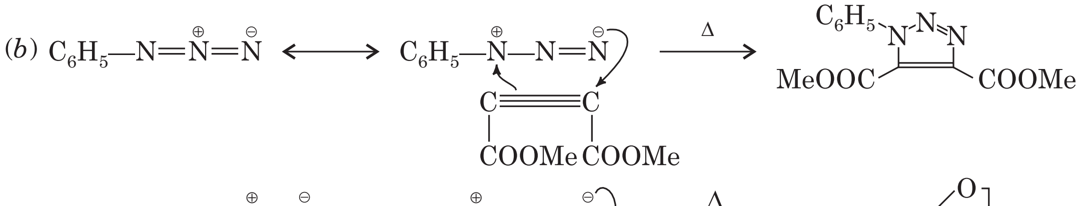


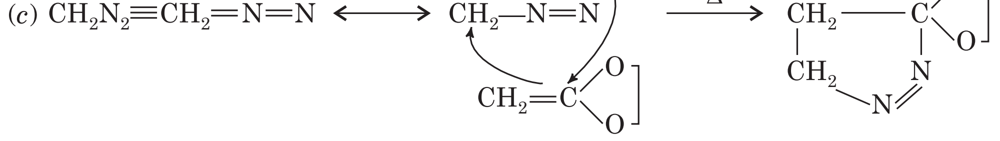
$$C_6H_5{-}N_3 + MeOOC{-}C\equiv C{-}COOMe \xrightarrow{\Delta}$$



Solution: These problems are based on 1, 3-dipolar addition reaction.

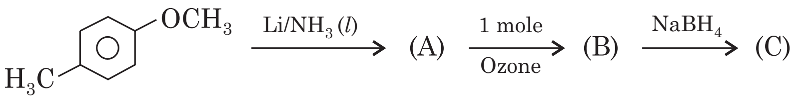




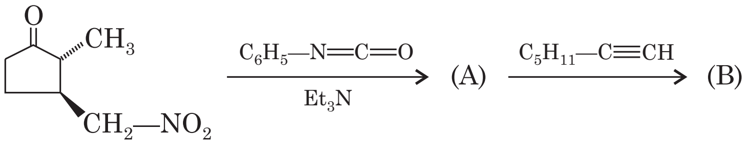


Problem 37: *Complete the following reactions and give product in each step:*

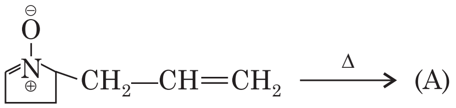
(*a*)



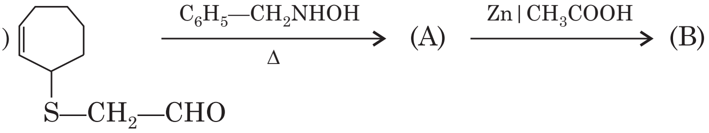
(*b*)



(*c*)

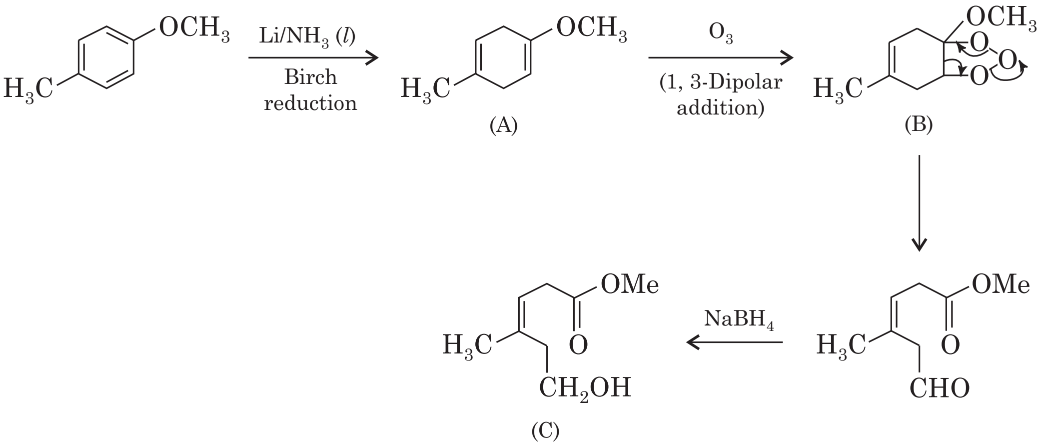


(*d*)

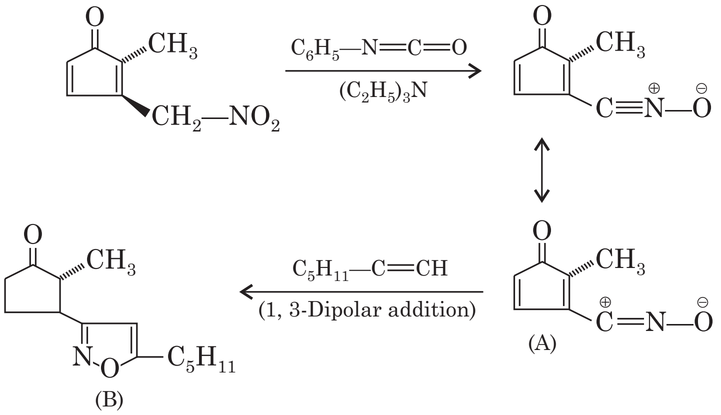


Solution:

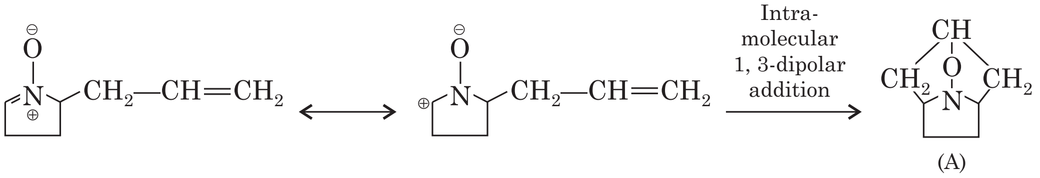
(*a*)



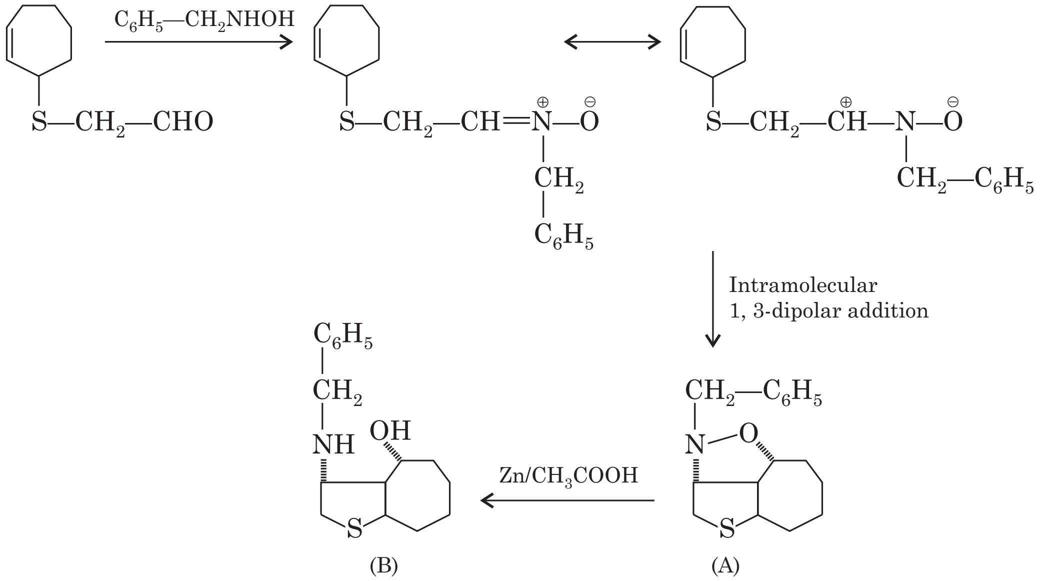
(*b*)



(c)



(d)

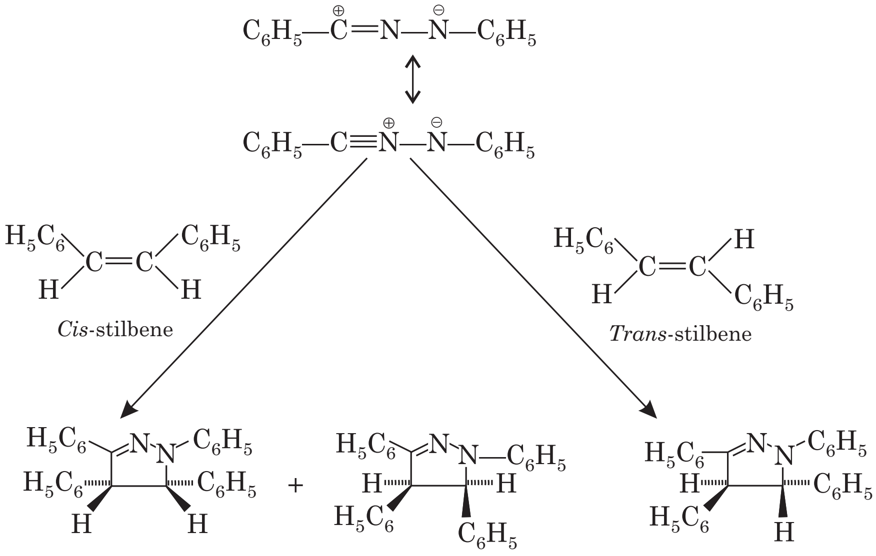


Problem 38: *What product(s) will be obtained if diphenylnitrilimine is heated with*

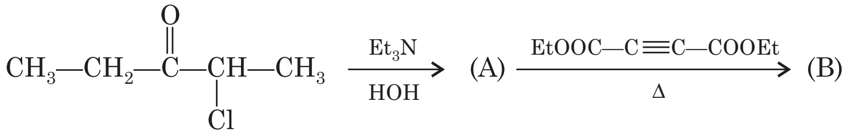
(i) cis-stilbene *(ii) trans-stilbene*

Give stereochemistry of the product in both the cases.

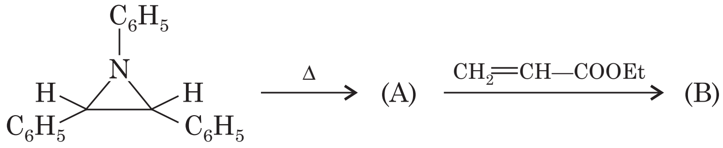
Solution:

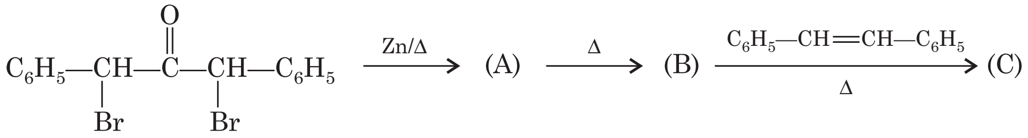


Problem 39: *Complete the following reactions and give product in each step:*

(*a*)


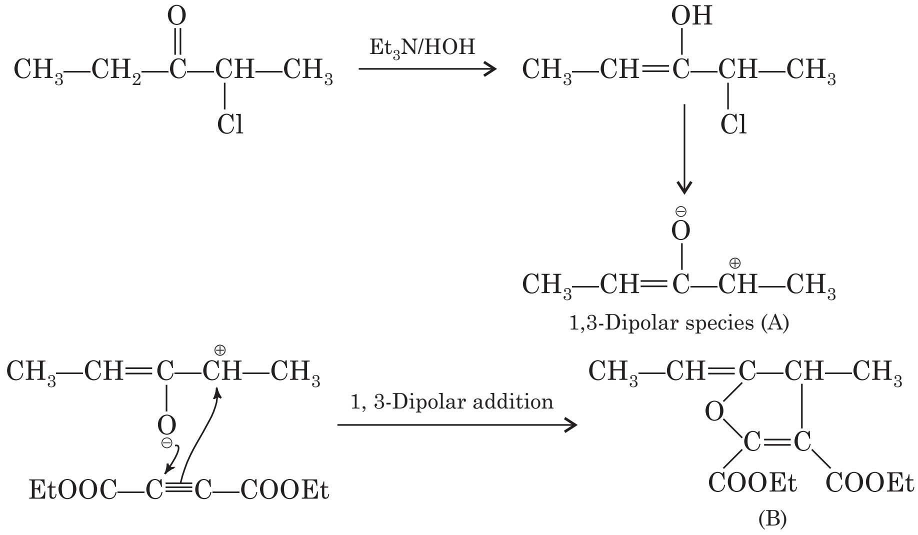
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3 \xrightarrow[HOH]{Et_3N} (A) \xrightarrow[\Delta]{EtOOC-C\equiv C-COOEt} (B)$$

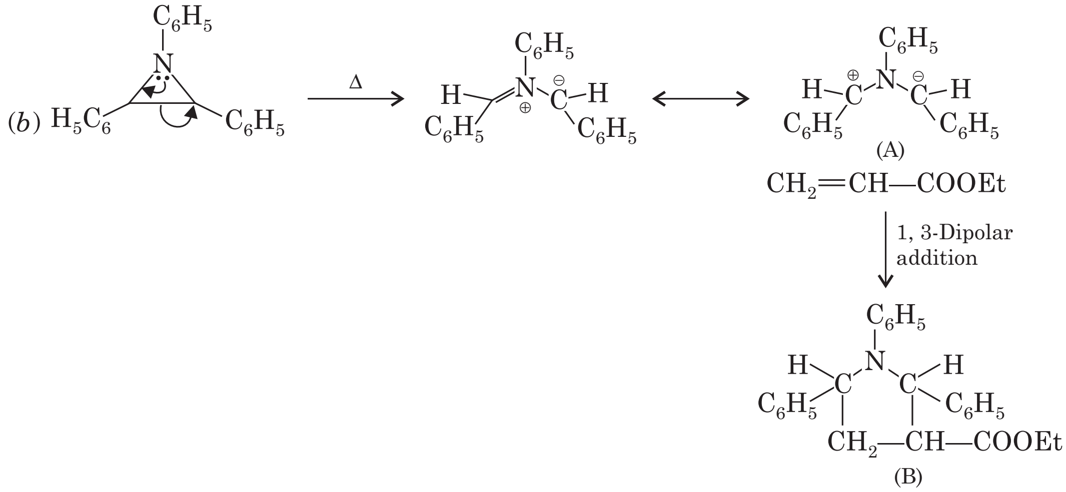
(*b*)


(*c*)


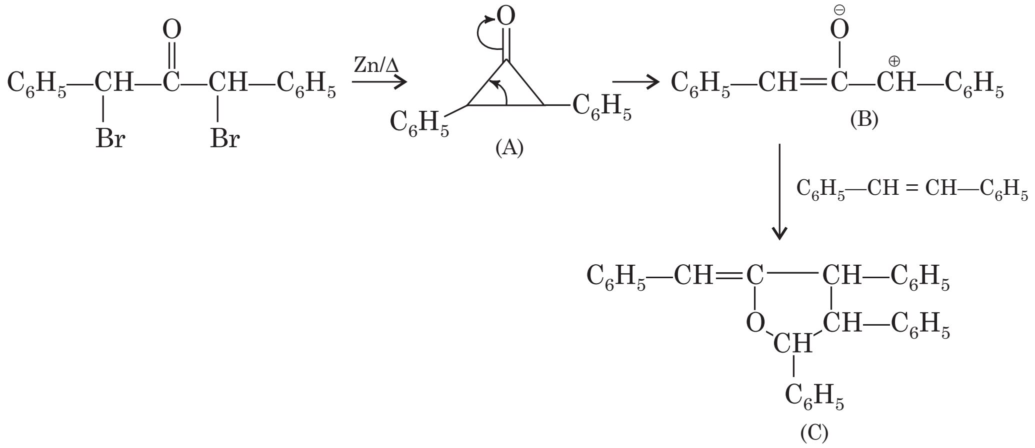
$$C_6H_5-\underset{\underset{\displaystyle Br}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Br}{|}}{CH}-C_6H_5 \xrightarrow{Zn/\Delta} (A) \xrightarrow{\Delta} (B) \xrightarrow[\Delta]{C_6H_5-CH=CH-C_6H_5} (C)$$

Solution:

(*a*)




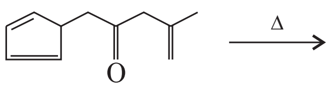
(*c*)



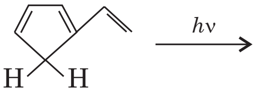
(C)

Problem 40: *Complete the following reactions:*

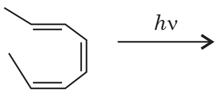
(*a*)



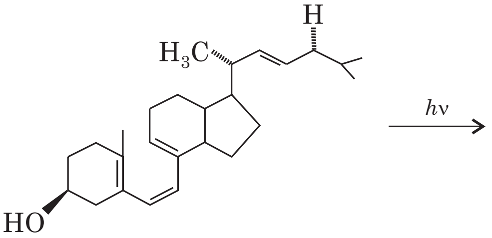
(*b*)



(*c*)

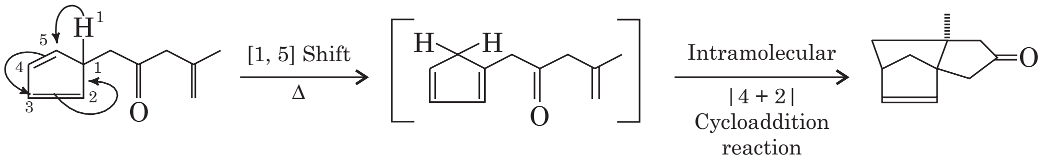


(*d*)

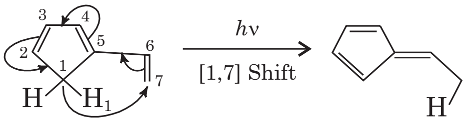


Solution: These problems are based on sigmatropic rearrangement

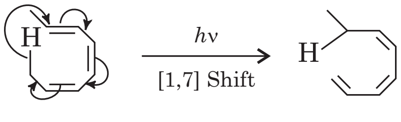
(*a*)



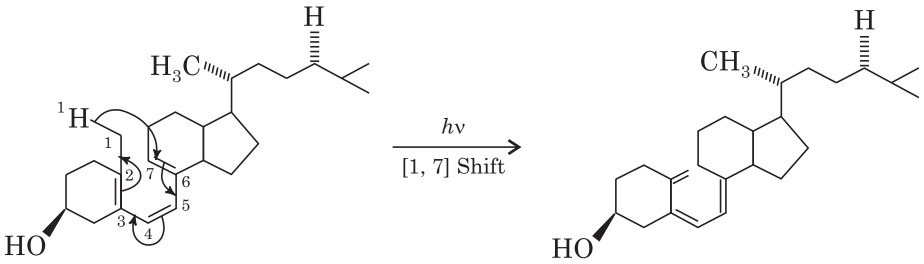
(*b*)



(*c*)



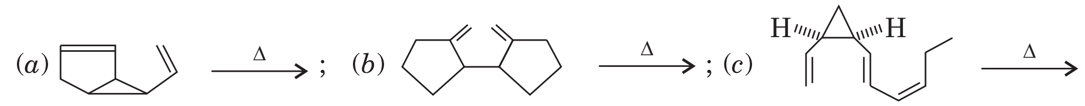
(*d*)



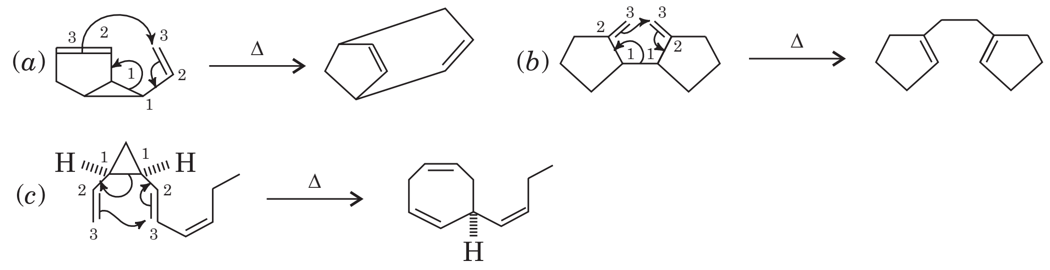
Provitamin D_2

Vitamin D_2

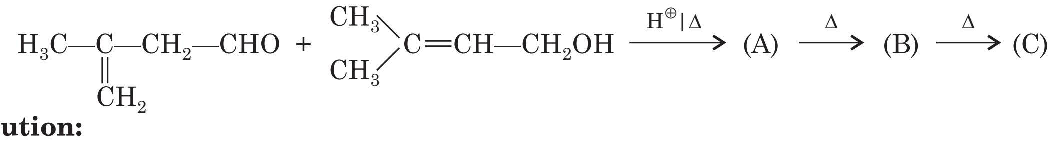
Problem 41: *Complete the following reactions, give their name and mechanism:*



Solution: These reactions are [3, 3] sigmatropic rearrangement.

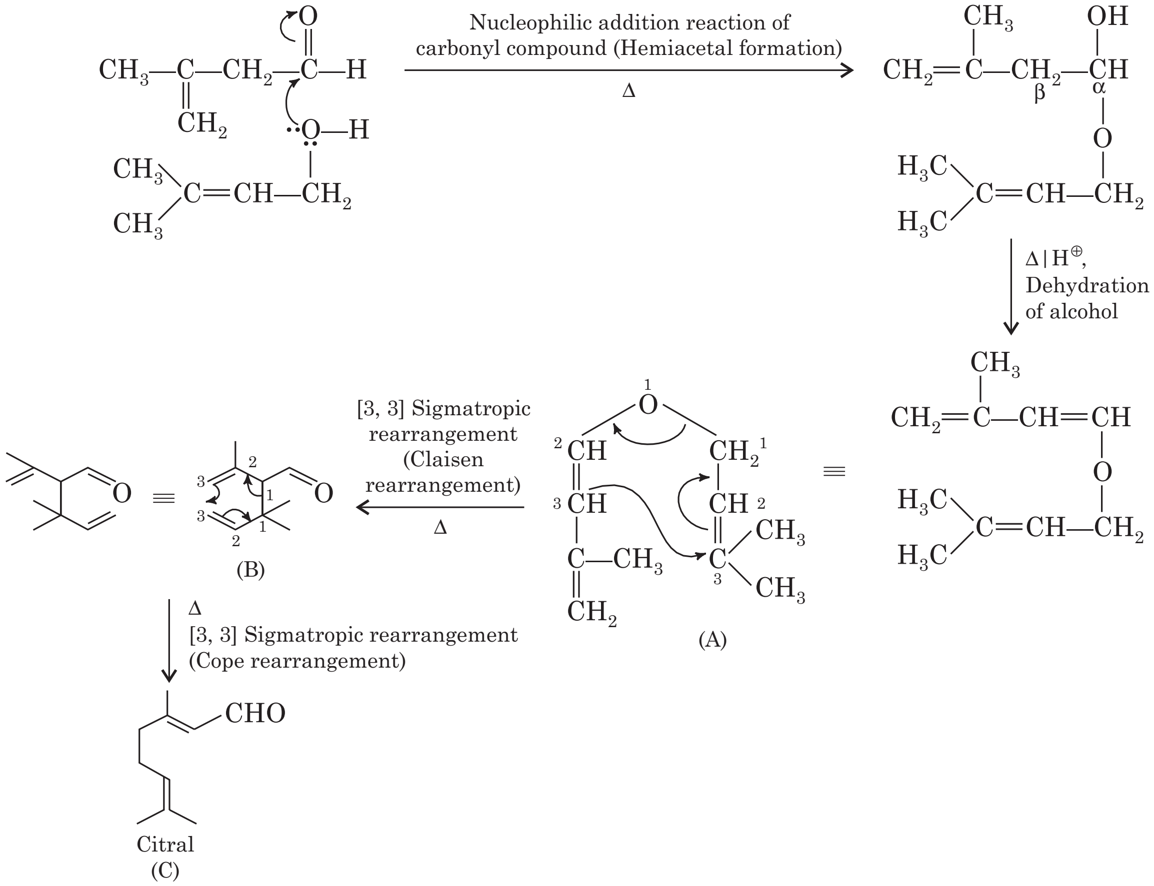


Problem 42: *Complete the following sequence of reaction and give structures of (A), (B) and (C):*

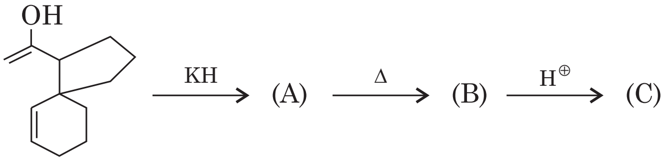


$$H_3C-\underset{\underset{CH_2}{\|}}{C}-CH_2-CHO + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH-CH_2OH \xrightarrow{H^{\oplus}|\Delta} (A) \xrightarrow{\Delta} (B) \xrightarrow{\Delta} (C)$$

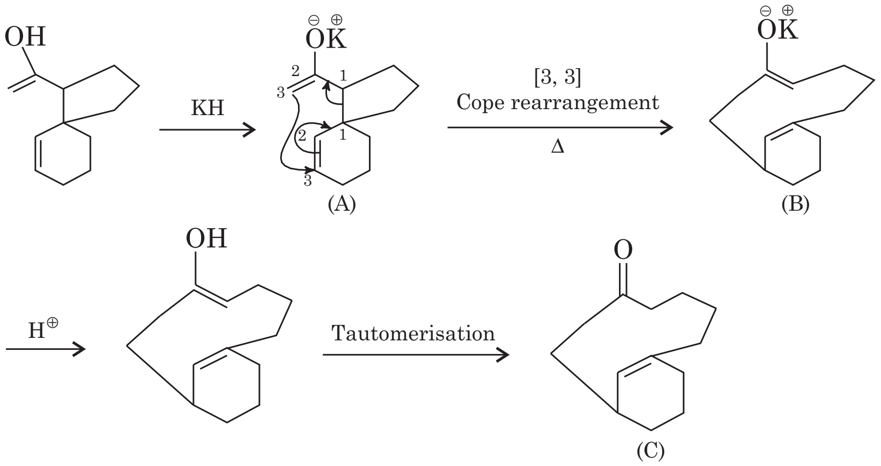
Solution:



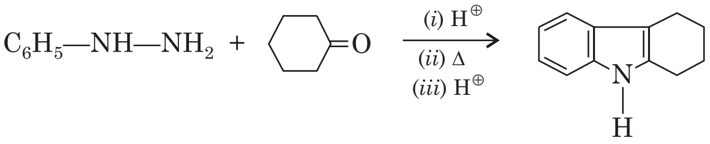
Problem 43: *Complete the following sequence of reaction and give structures of (A), (B) and (C):*



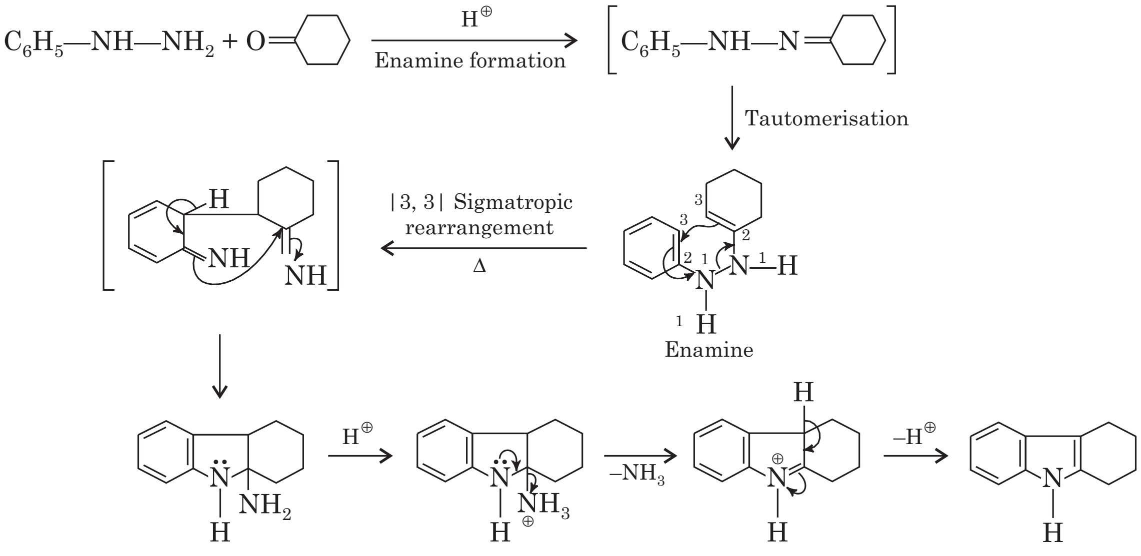
Solution:



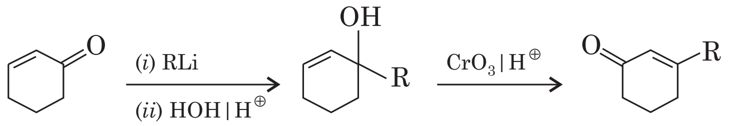
Problem 44: *Give mechanism of the following conversion and comment on the reaction:*



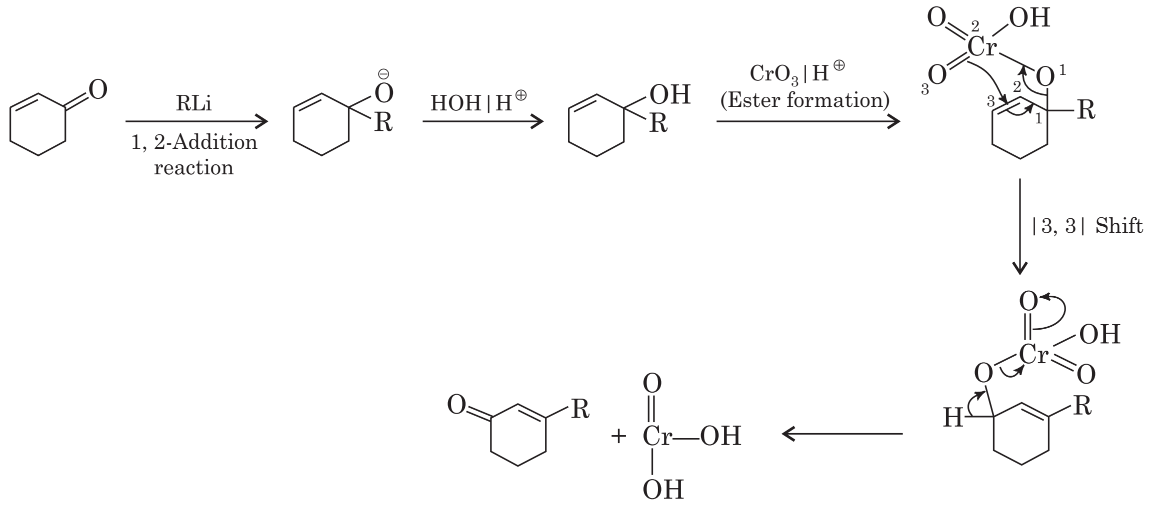
Solution:



Problem 45: *Give mechanism of the given reaction:*



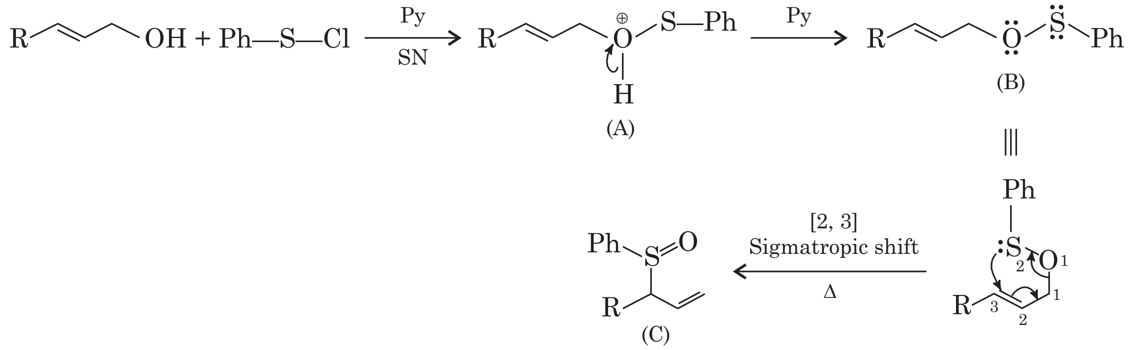
Solution:



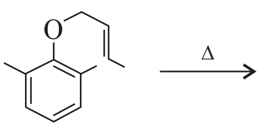
Problem 46: *Identify (A), (B) and (C) in the given reaction sequence:*

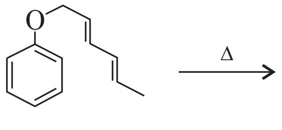
$$\mathrm{R{-}CH{=}CH{-}CH_2{-}OH} \xrightarrow[\text{Py}]{\text{Ph—S—Cl}} \text{(A)} \xrightarrow{\text{Py}} \text{(B)} \xrightarrow{\Delta} \text{(C)}$$

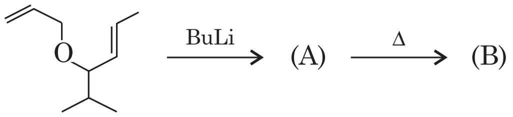
Solution:



Problem 47: *Complete the following reactions and give their names:*

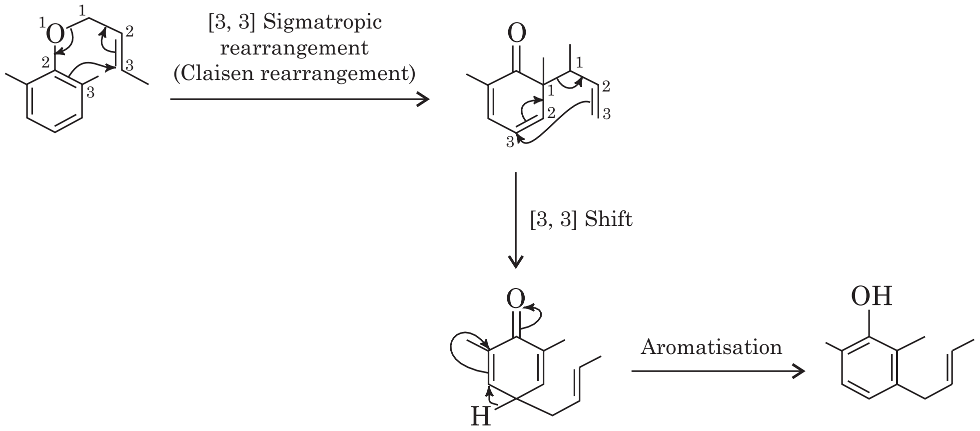
(*a*)


(*b*)


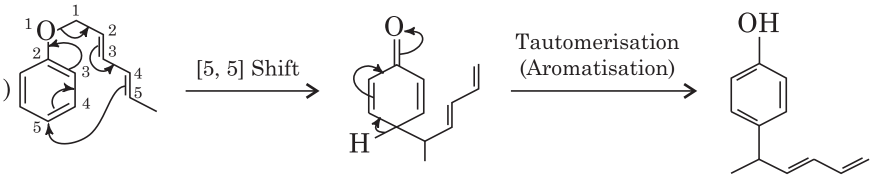
(*c*)


Solution:

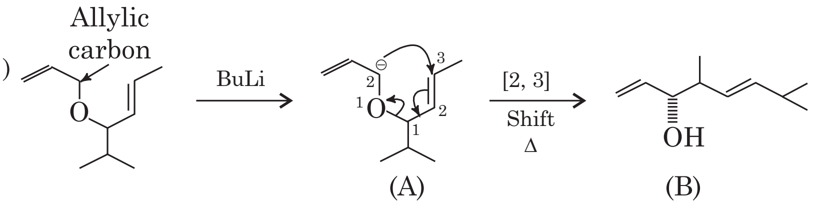
(*a*)



(*b*)

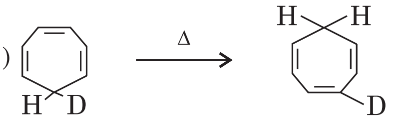


(*c*)

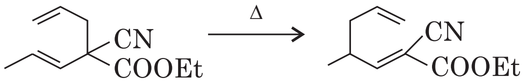


Problem 48: *Which of the following known sigmatropic rearrangements would proceed readily and which slowly? Explain your answer:*

(*a*)

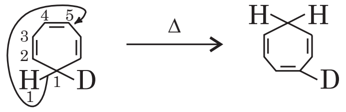


(*b*)



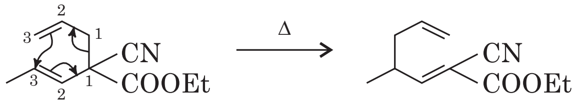
Solution:

(*a*)



The above reaction is thermal reaction. It is [1, 5] sigmatropic rearrangement which is thermally allowed. Therefore reaction will proceed readily.

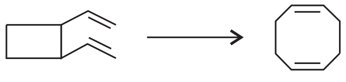
(*b*)



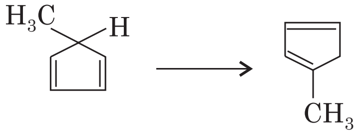
The reaction is thermal reaction. It is [3, 3] sigmatropic rearrangement or Cope rearrangement which is thermally allowed reaction. Therefore reaction will proceed readily.

Problem 49: *Classify each of the following sigmatropic rearrangements as (i, j or m, n) and indicate which will be allowed photo chemically and which will be thermally allowed:*

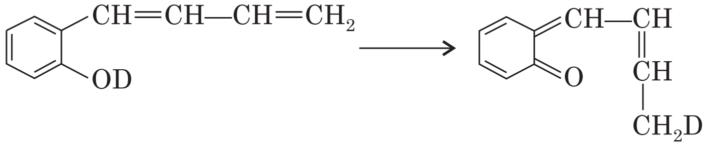
(*a*)



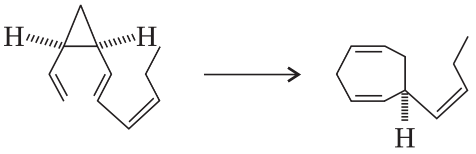
(*b*)



(*c*)

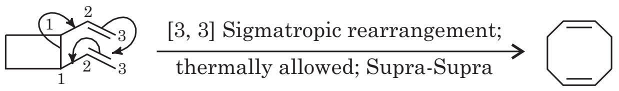


(*d*)

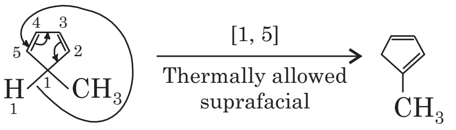


Solution:

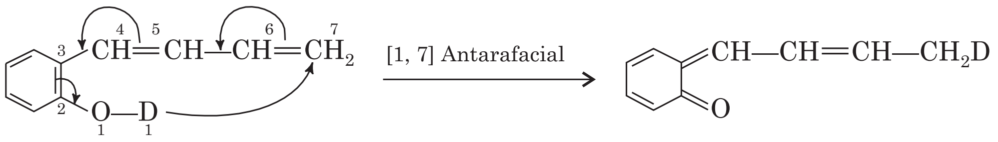
(*a*)



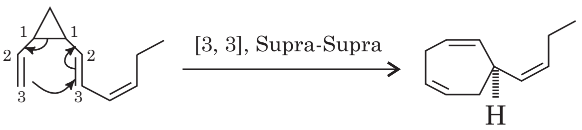
(*b*)



(*c*)

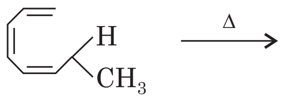


(*d*)

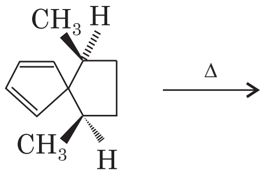


Problem 50: *Complete the following reactions and give their mechanism:*

(*a*)



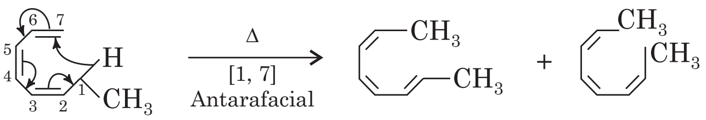
(*b*)



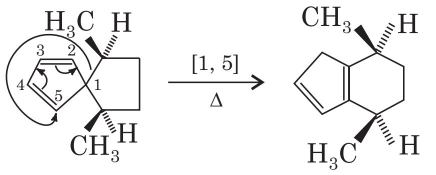
(*c*) $CH_2=CH-O-CH_2-CH=CH_2 \xrightarrow{\Delta}$

Solution:

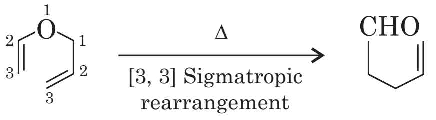
(*a*)



(*b*)

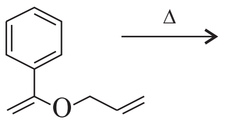


(*c*)

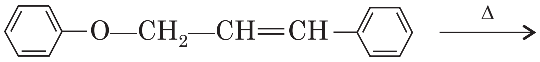


Problem 51: *Complete the following reactions and give their mechanism:*

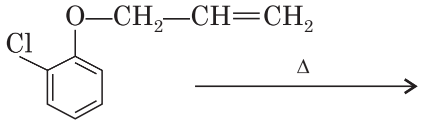
(*a*)



(*b*)

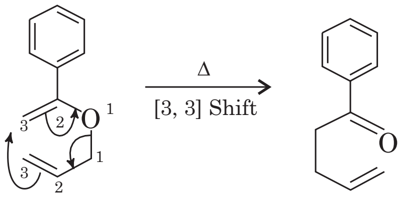


(*c*)

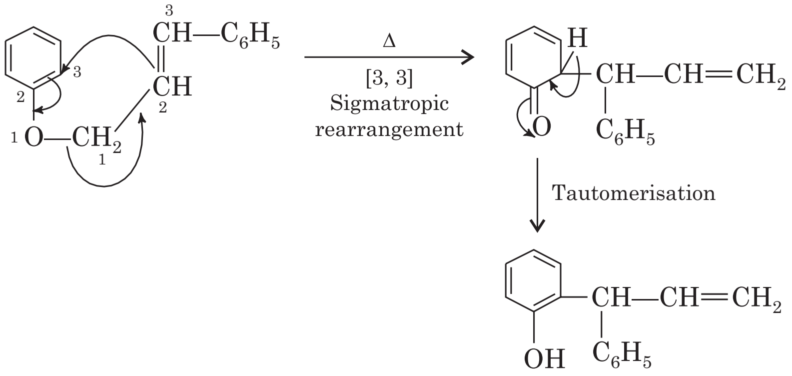


Solution:

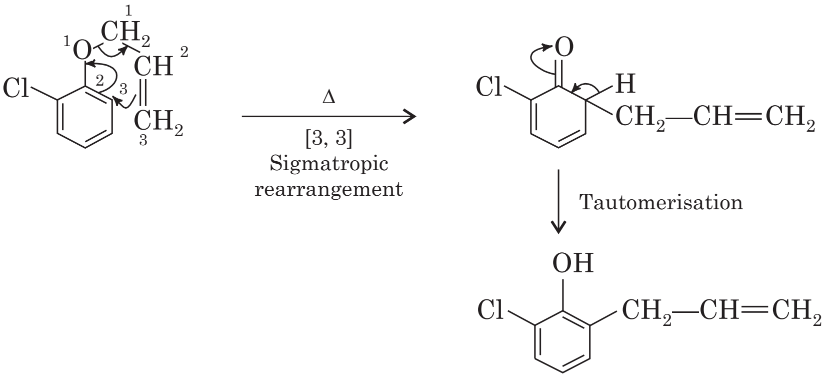
(*a*)



(*b*)

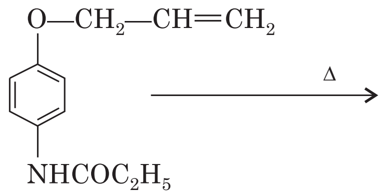


(*c*)

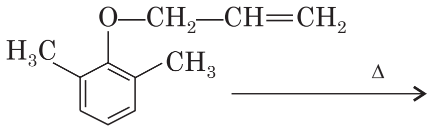


Problem 52: *Complete the following reactions and give their mechanism:*

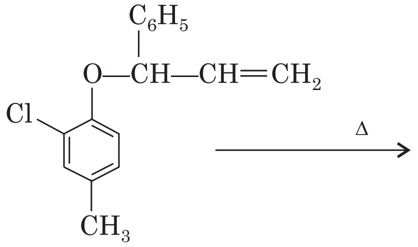
(*a*)



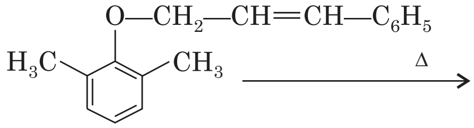
(*b*)



(*c*)

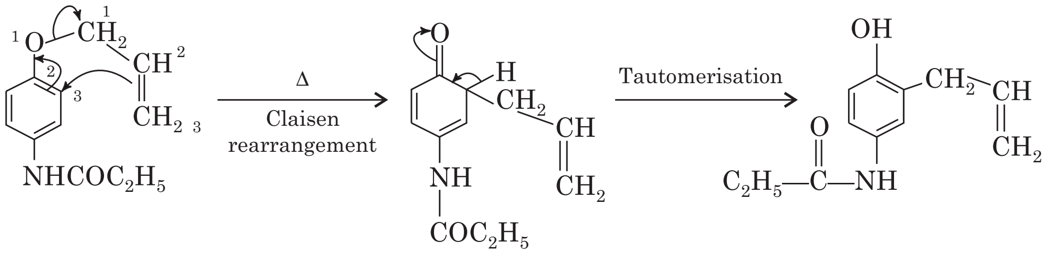


(*d*)

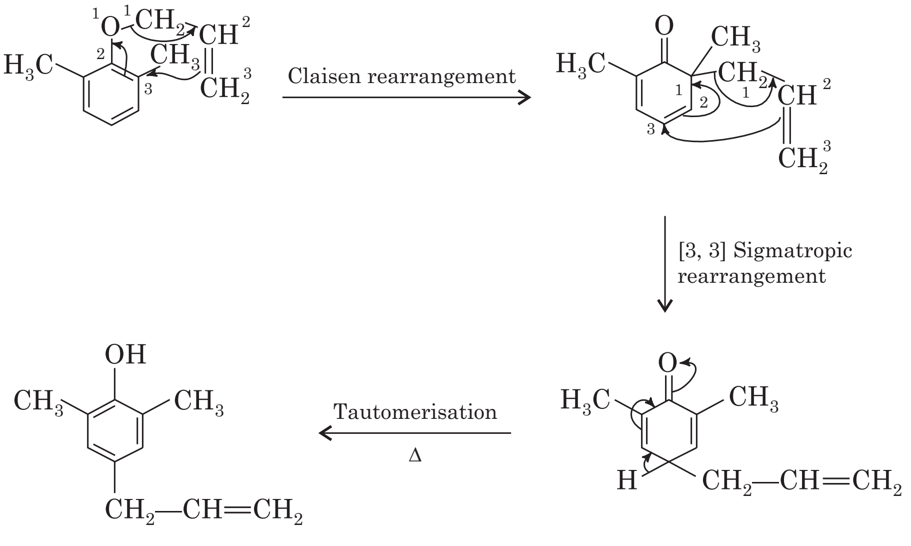


Solution:

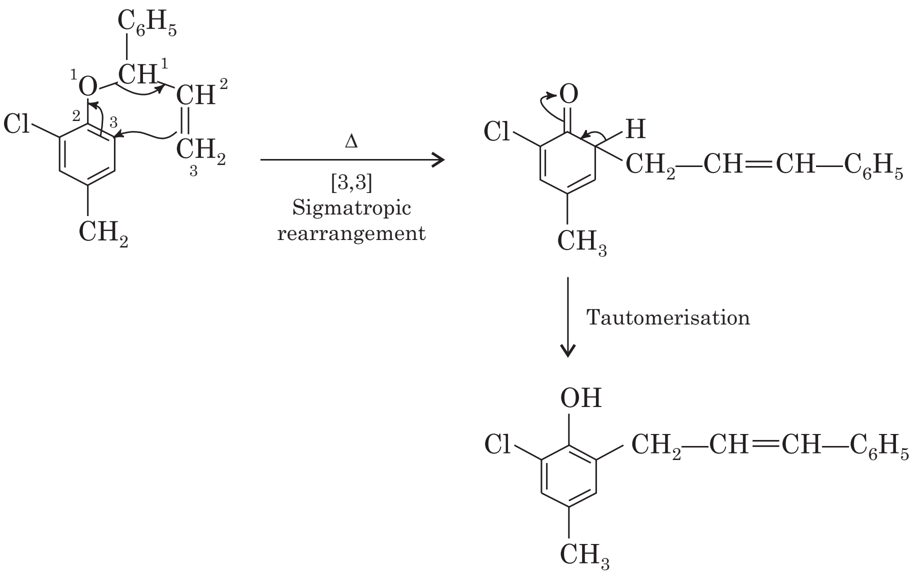
(*a*)



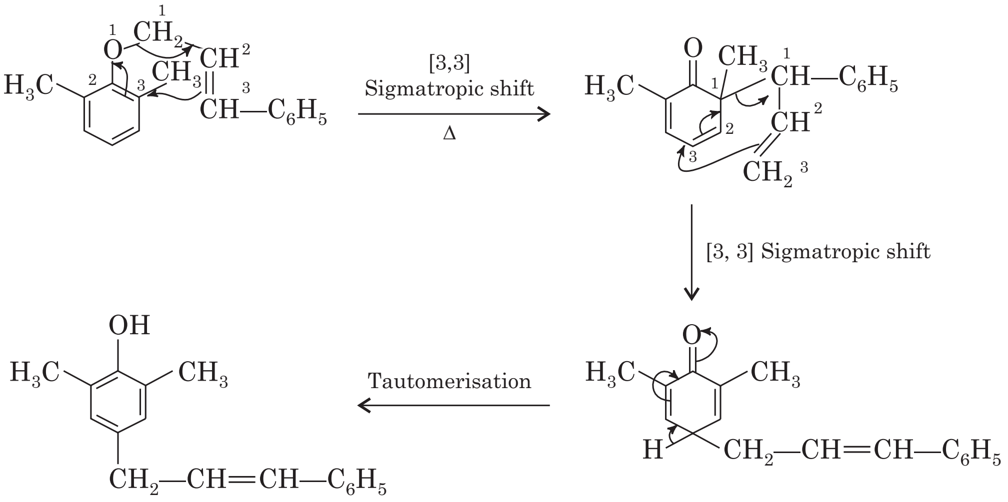
(*b*)



(*c*)

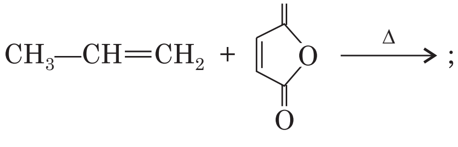


(*d*)

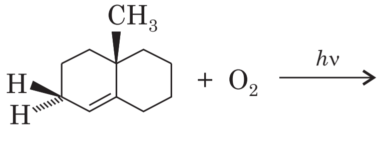


Problem 53: *Complete the following reactions:*

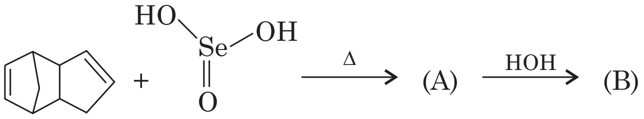
(*a*)



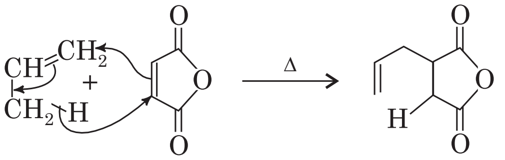
(*b*)



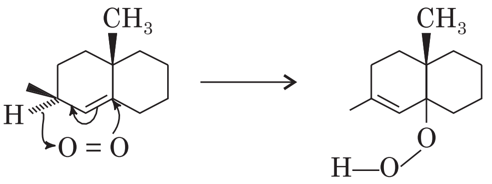
(*c*)

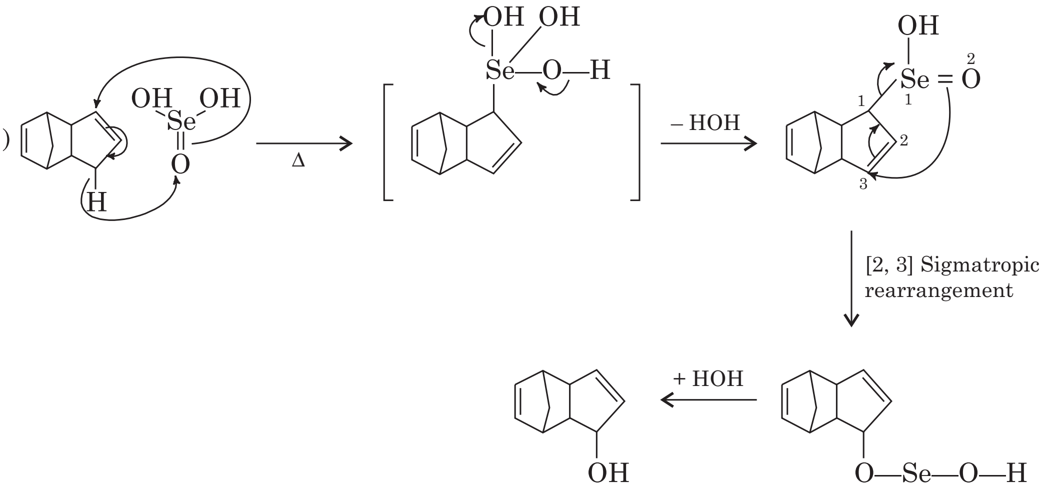


Solution: The above problems are based on ene reaction.

(*a*)


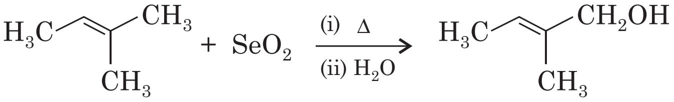
(*b*) $O_2 \xrightarrow{h\nu}$ Singlet oxygen

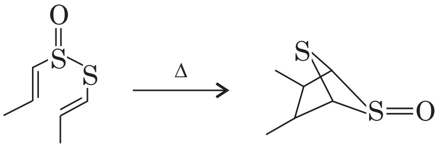


(*c*)


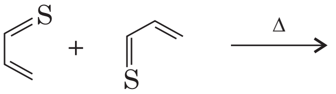
(B) (A)

Problem 54: *Give mechanism and name of given reactions:*

(*a*)


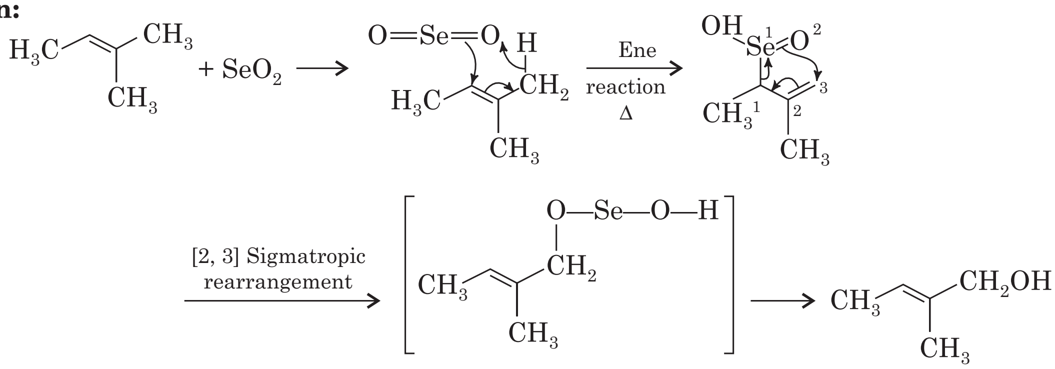
(*b*)


Zwiebelane

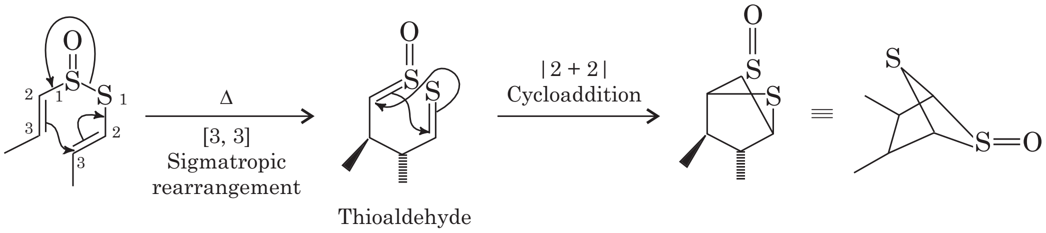
(*c*)


Solution:

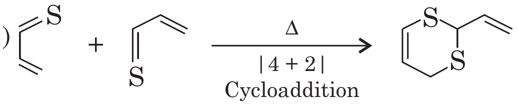
(*a*)



(*b*)

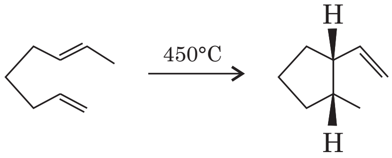


(*c*)

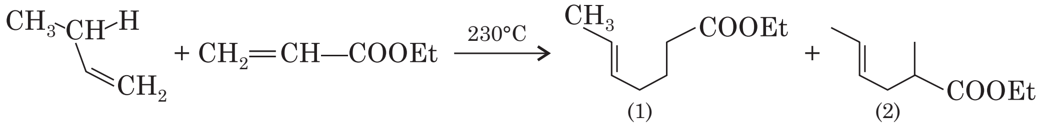


Problem 55: *Give mechanism and name of the given reactions:*

(*a*)

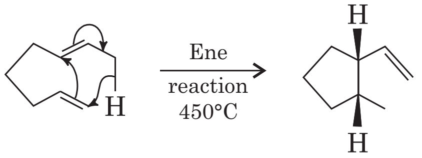


(*b*)

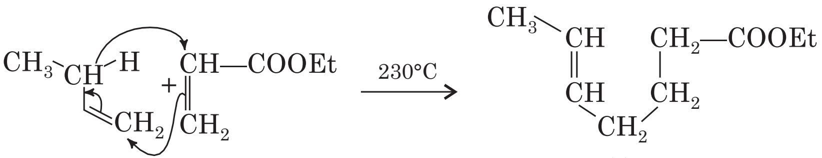


Solution:

(*a*)

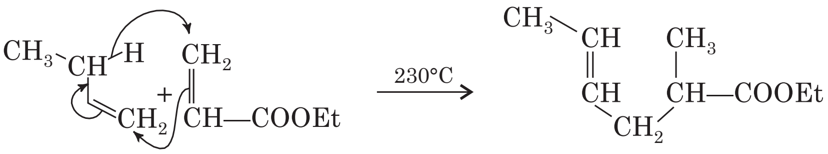


(*b*)



(1)

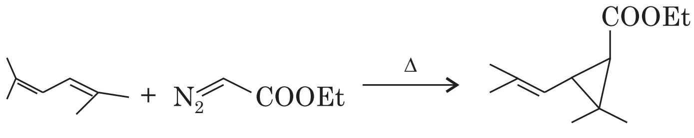
and



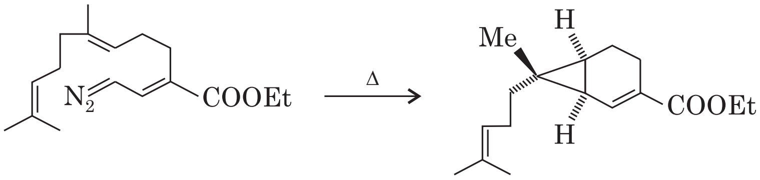
(2)

Problem 56: *Give mechanism of the given reactions:*

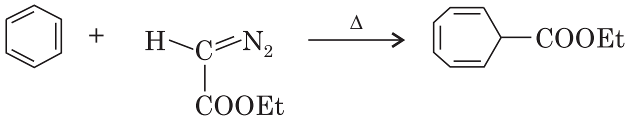
(*a*)



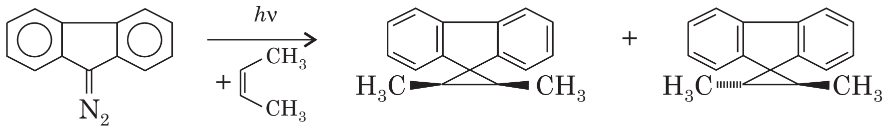
(*b*)



(*c*)

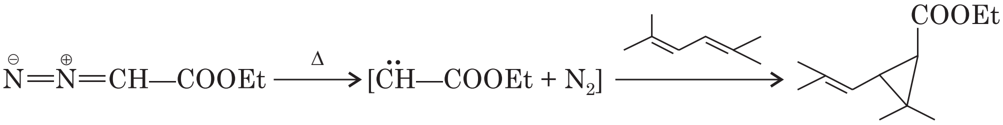


(*d*)



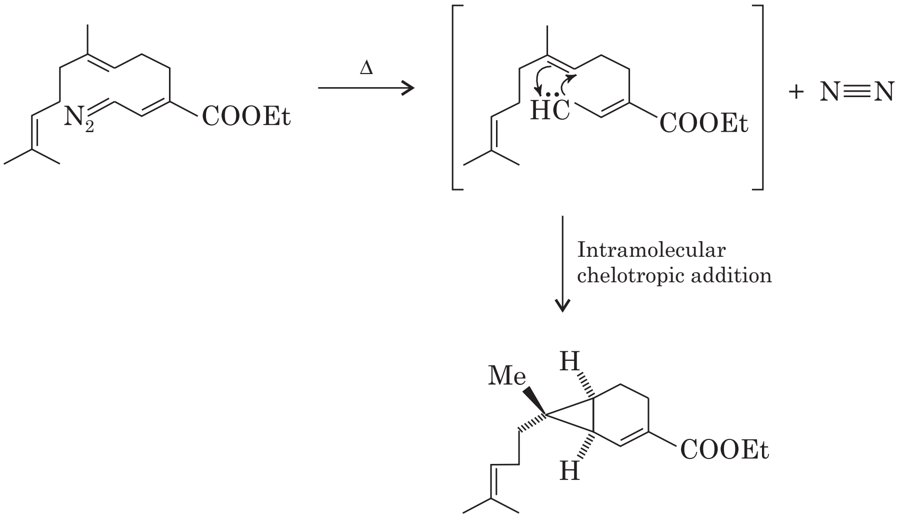
Solution: These problems are based on chelotropic addition reaction.

(*a*)

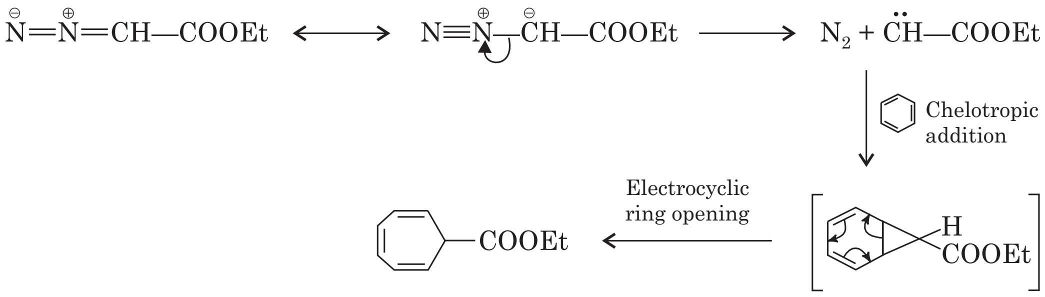


$\overset{\ominus}{N}=\overset{\oplus}{N}=CH—COOEt \xrightarrow{\Delta} [\ddot{C}H—COOEt + N_2] \longrightarrow$

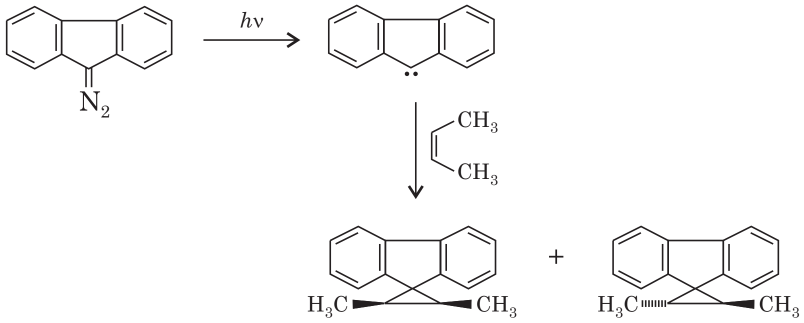
(*b*)



(*c*)

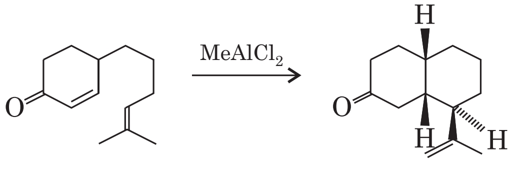


(*d*)

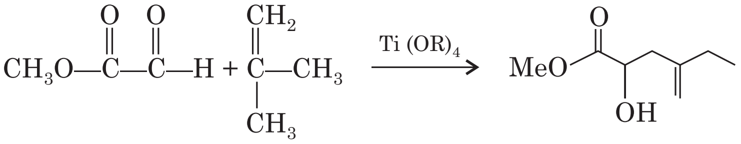


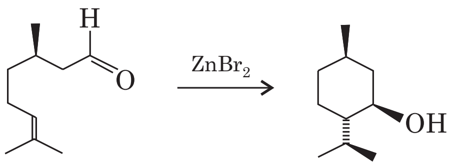
Problem 57: *Explain the formation of products in these reactions:*

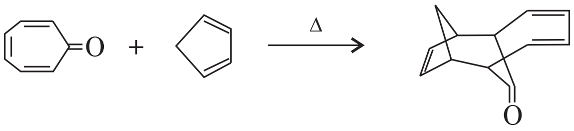
(*a*)

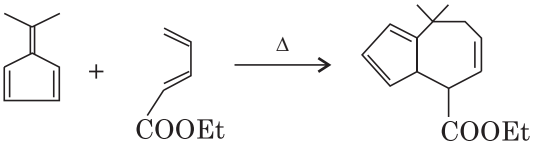


(*b*)

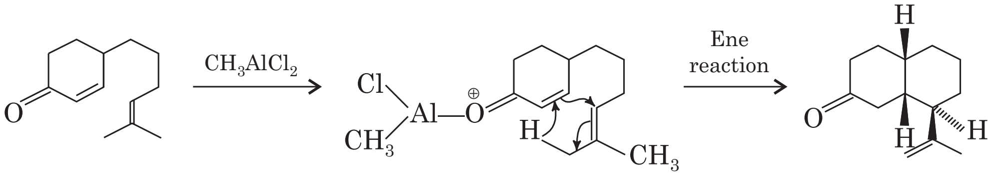


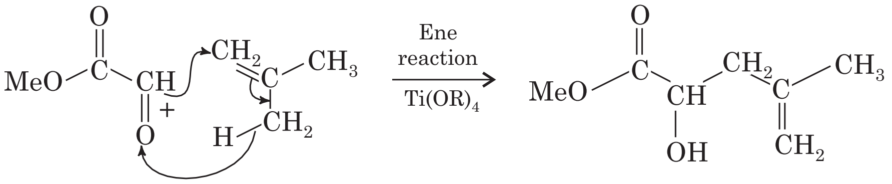
(*c*)


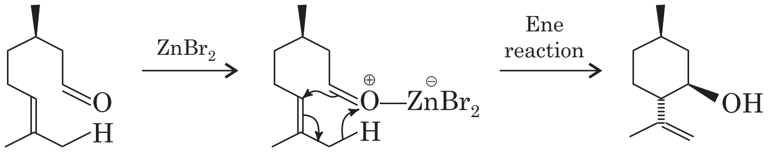
(*d*)


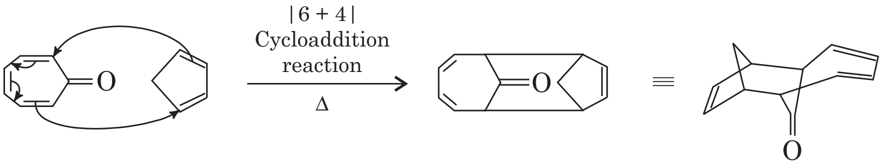
(*e*)


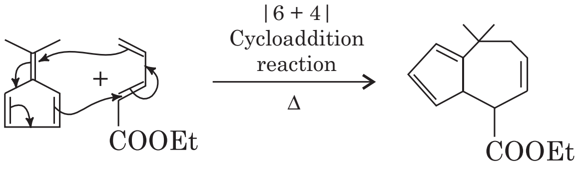
Solution:

(*a*)


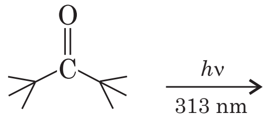
(*b*)


(*c*)


(*d*)


(*e*)


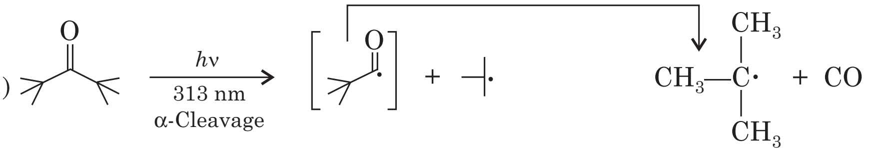
Problem 58: *Complete the following reactions and give their mechanism:*

(*a*)


(*b*) $CH_3—CHO \xrightarrow[25\text{ nm}]{h\nu}$

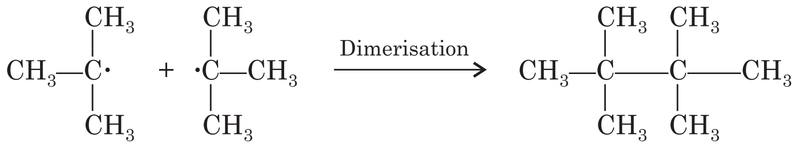
Solution:

(*a*)



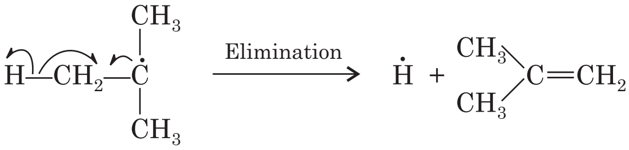
$$\mathrm{\xrightarrow[\alpha\text{-Cleavage}]{h\nu,\ 313\ nm} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot + CO}$$

(*i*)



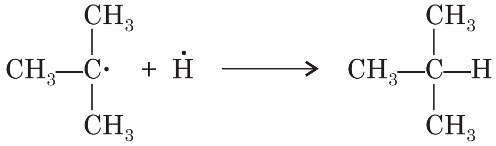
$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot + \cdot\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{\text{Dimerisation}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}$$

(*ii*)



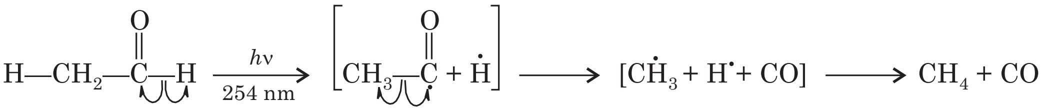
$$\mathrm{H-CH_2-\dot{\overset{CH_3}{\underset{CH_3}{C}}} \xrightarrow{\text{Elimination}} \dot{H} + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH_2}$$

(*iii*)



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot + \dot{H} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H}$$

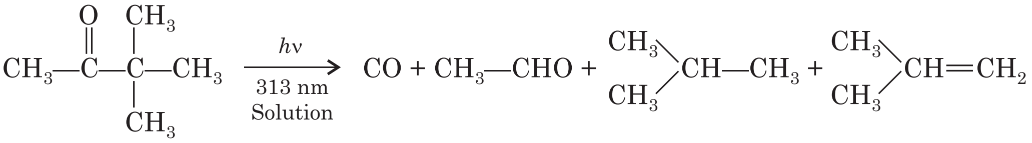
(*b*)



$$\mathrm{H-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[254\ nm]{h\nu} \left[CH_3-\overset{O}{\overset{\|}{\underset{\bullet}{C}}} + \dot{H}\right] \longrightarrow [\dot{C}H_3 + H^{\bullet} + CO] \longrightarrow CH_4 + CO}$$

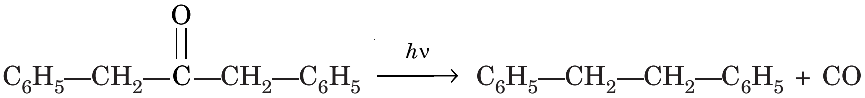
Problem 59: *Give mechanism for the following reactions:*

(*a*)



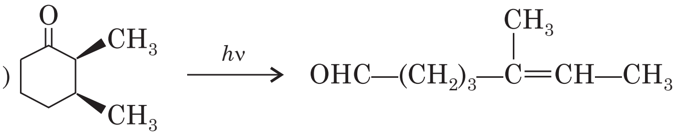
$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\substack{313\ nm\\ \text{Solution}}]{h\nu} CO + CH_3-CHO + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_3 + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{=}CH_2}$$

(*b*)



$$\mathrm{C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-C_6H_5 \xrightarrow{h\nu} C_6H_5-CH_2-CH_2-C_6H_5 + CO}$$

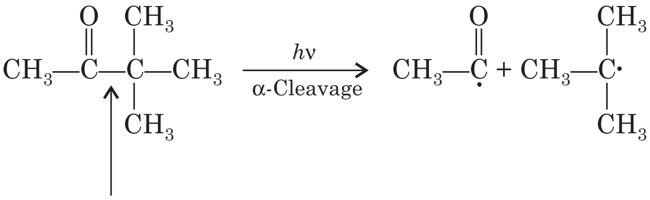
(*c*)



$$\mathrm{\xrightarrow{h\nu} OHC-(CH_2)_3-\overset{CH_3}{C}{=}CH-CH_3}$$

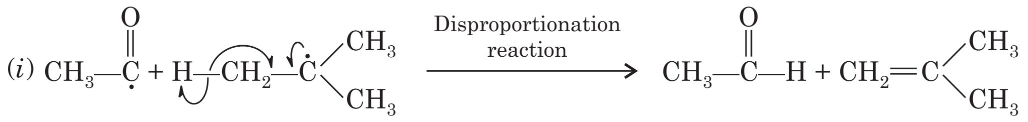
Solution:

(*a*)

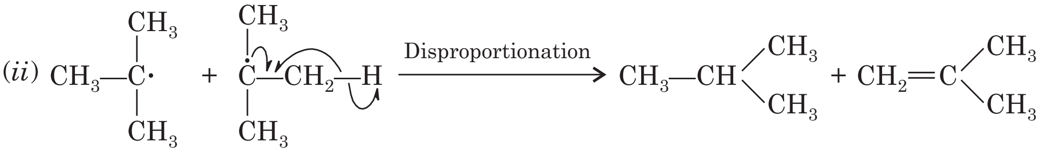


$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\alpha\text{-Cleavage}]{h\nu} CH_3-\overset{O}{\overset{\|}{\underset{\bullet}{C}}} + CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot}$$

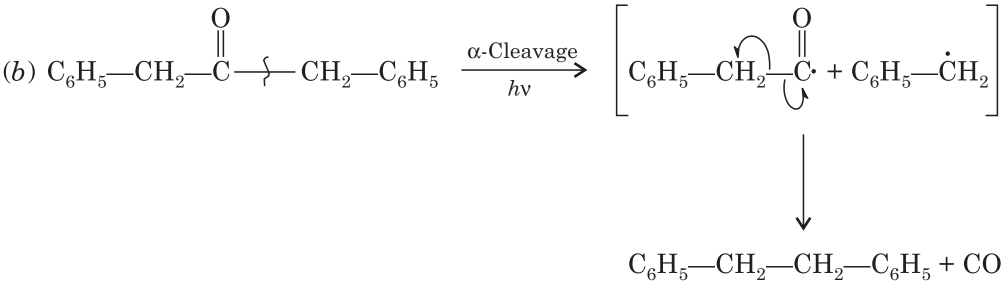
Weaker bond due to
steric hindrance



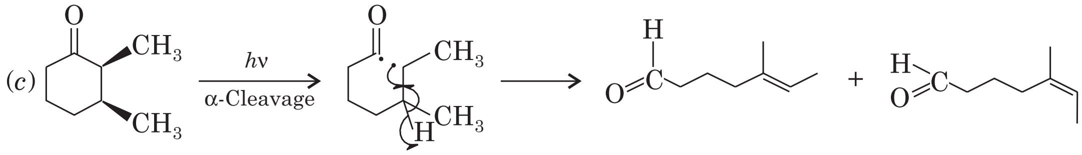
$$(i)\ CH_3-\overset{\overset{\displaystyle O}{\|}}{\dot{C}} + H-CH_2-\dot{C}\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{\text{Disproportionation reaction}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_2{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$$



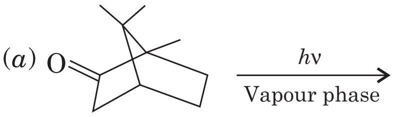
$$(ii)\ CH_3-\underset{CH_3}{\overset{CH_3}{C\cdot}} + \underset{CH_3}{\overset{CH_3}{\dot{C}}}-CH_2-H \xrightarrow{\text{Disproportionation}} CH_3-CH\begin{matrix}CH_3\\CH_3\end{matrix} + CH_2{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$$

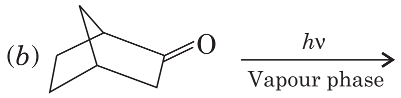


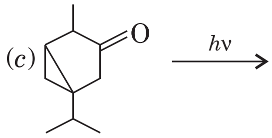
$$(b)\ C_6H_5-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-C_6H_5 \xrightarrow[h\nu]{\alpha\text{-Cleavage}} \left[C_6H_5-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\cdot + C_6H_5-\dot{C}H_2\right] \longrightarrow C_6H_5-CH_2-CH_2-C_6H_5 + CO$$

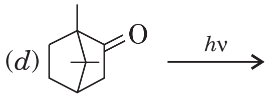


Problem 60: *Complete the following reactions and give their mechanism:*

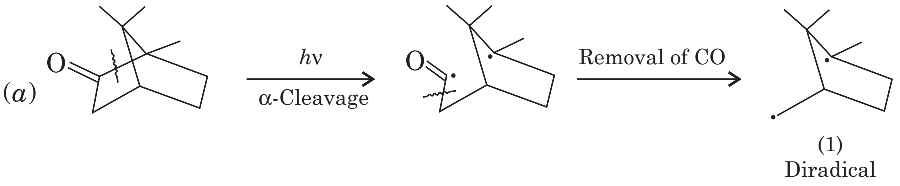


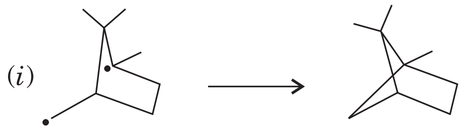


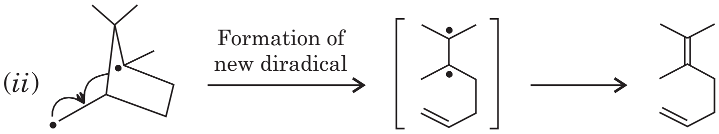




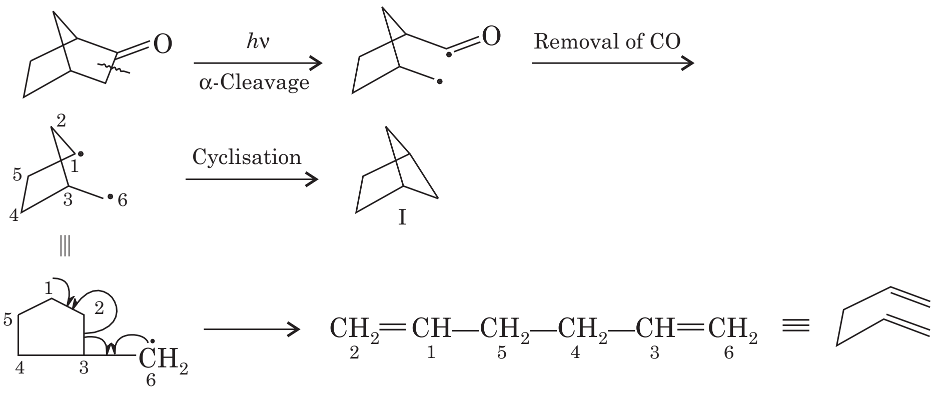
Solution:



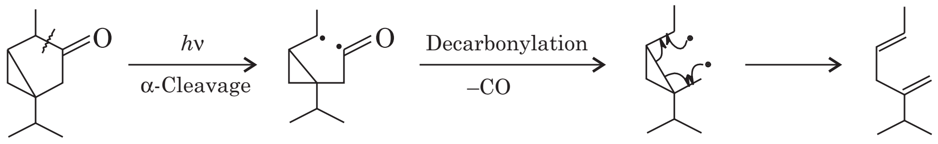




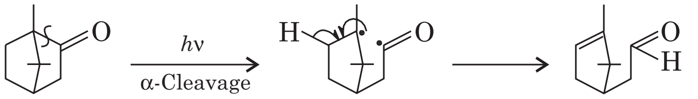
(*b*)



(*c*)

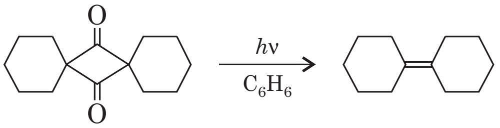


(*d*)

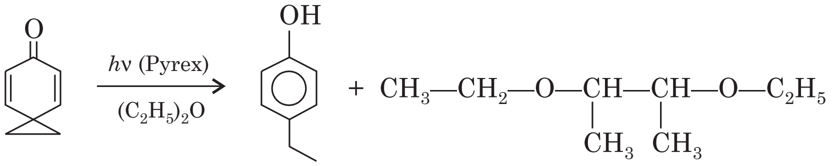


Problem 61: *Give mechanism for the given conversions:*

(*a*)

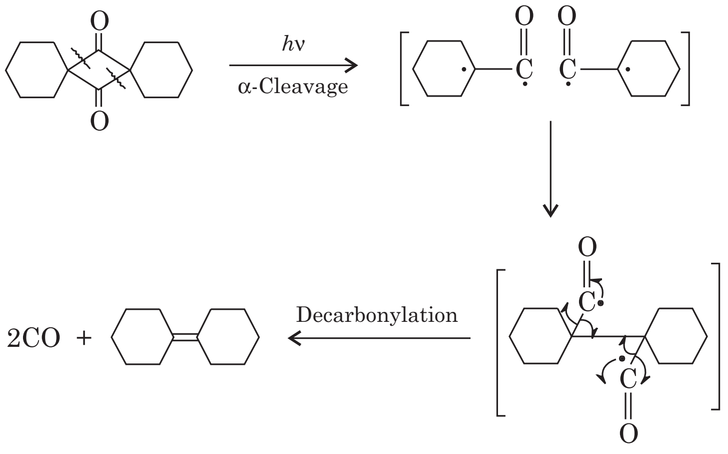


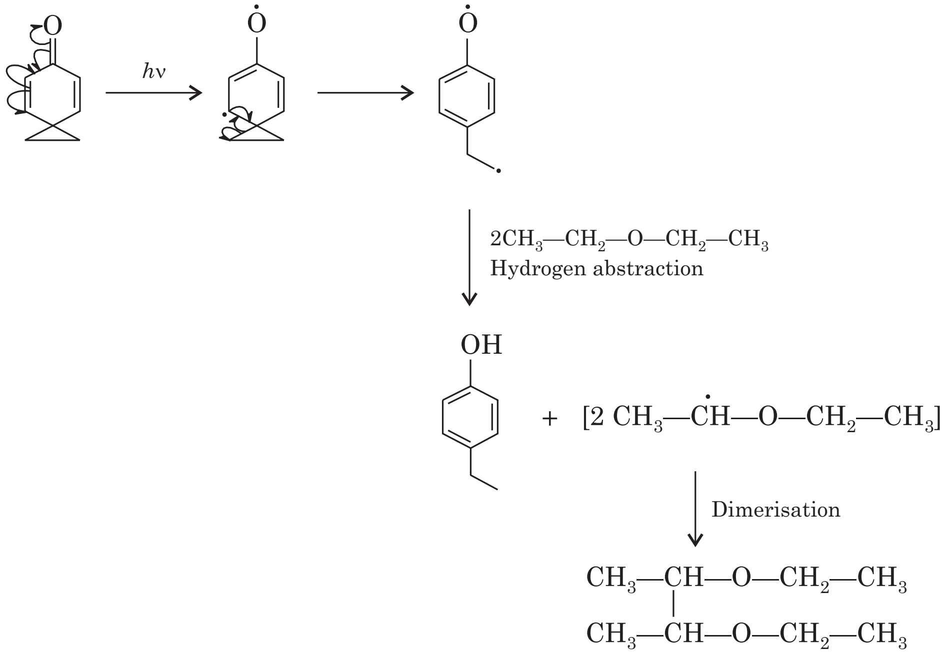
(*b*)



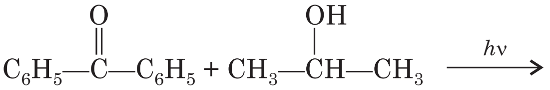
Solution:

(*a*)

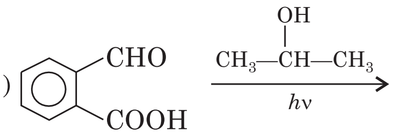


(b) 

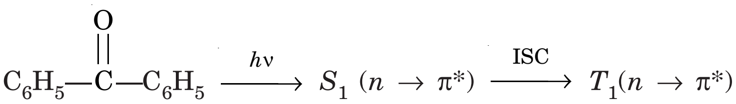
Problem 62: *Complete the following reactions and give their mechanisms:*

(a) 

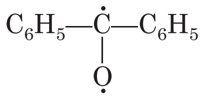
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 + CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 \xrightarrow{h\nu}$$

(b) 

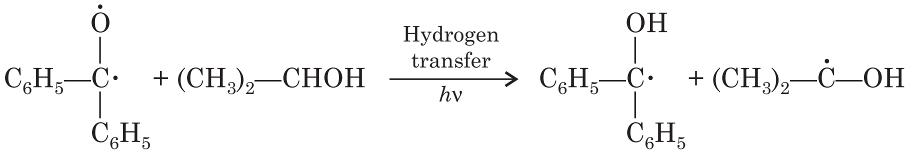
Solution: These two reactions are intermolecular photo reduction in which isopropyl alcohol works as hydrogen donor.

(a) 

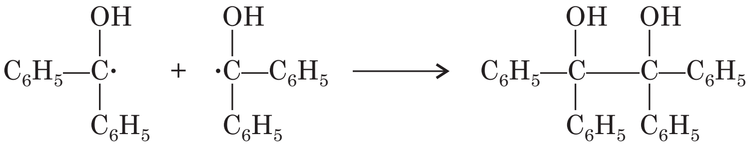
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow{h\nu} S_1\ (n \rightarrow \pi^*) \xrightarrow{\text{ISC}} T_1(n \rightarrow \pi^*)$$



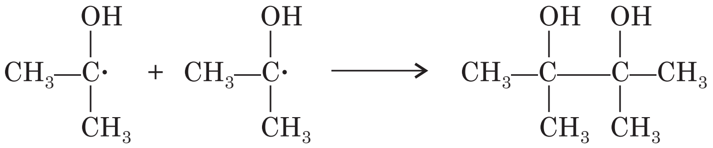
$$C_6H_5-\underset{\underset{\displaystyle \dot{O}}{|}}{\dot{C}}-C_6H_5$$



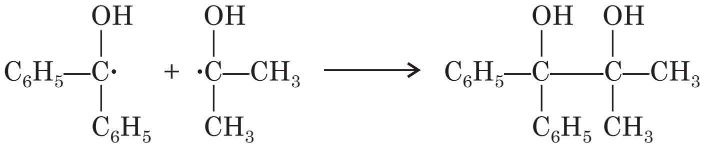
$$C_6H_5-\overset{\overset{\displaystyle \dot{O}}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}\cdot + (CH_3)_2-CHOH \xrightarrow[h\nu]{\text{Hydrogen transfer}} C_6H_5-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}\cdot + (CH_3)_2-\dot{C}-OH$$

(*i*) 

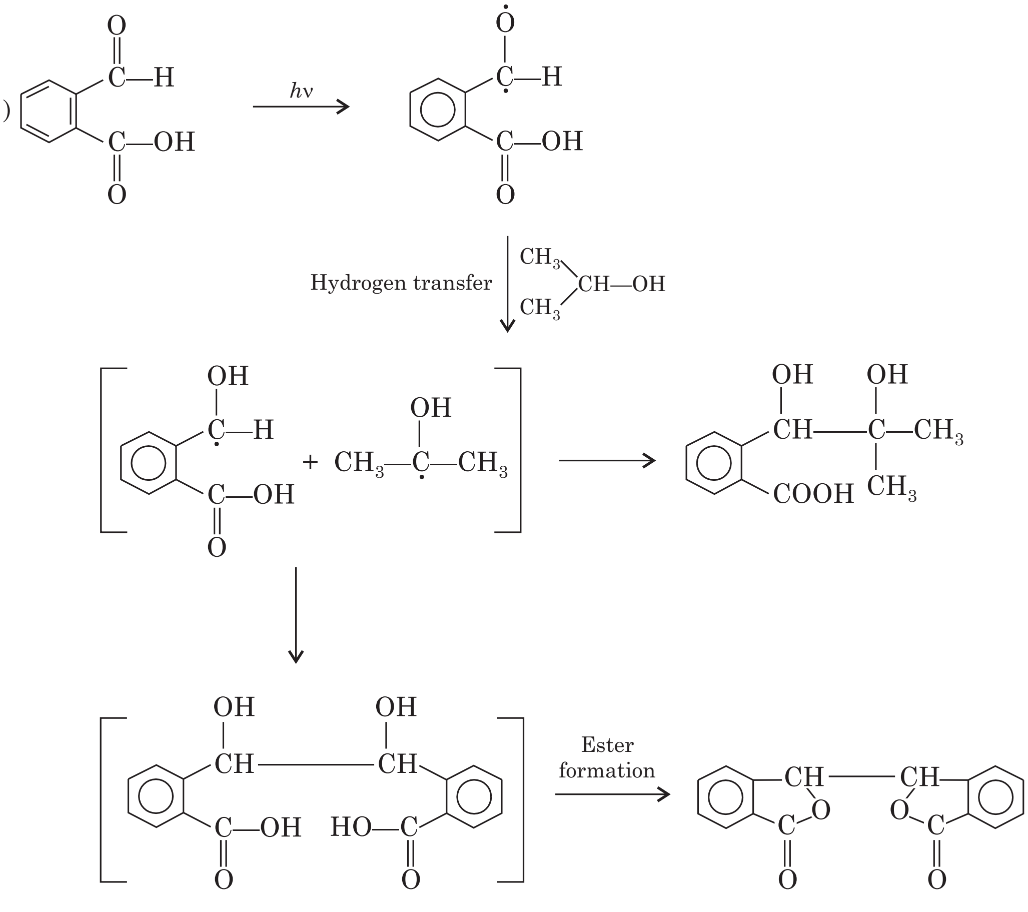
$$C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \;+\; \cdot\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-C_6H_5 \longrightarrow C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-C_6H_5$$

(*ii*) 

$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot \;+\; CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot \longrightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

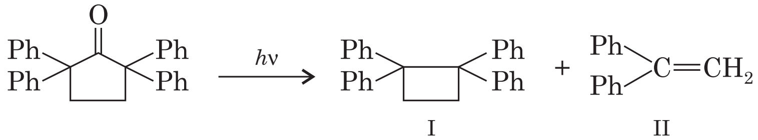
(*iii*) 

$$C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \;+\; \cdot\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \longrightarrow C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

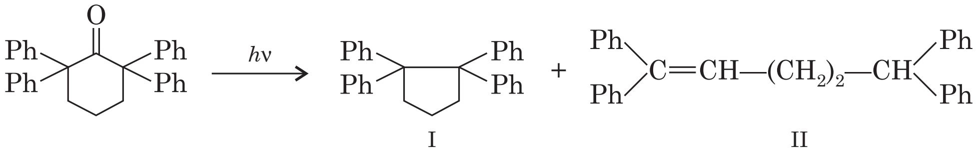
(*b*) 

Problem 63: *Provide a mechanistic rationalisation for each of the following reactions:*

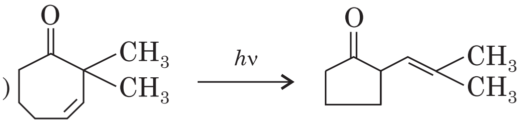
(*a*)



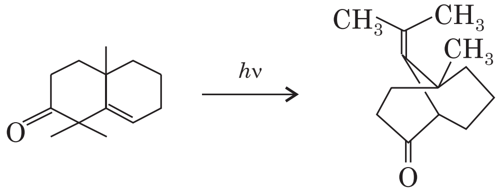
(*b*)



(*c*)

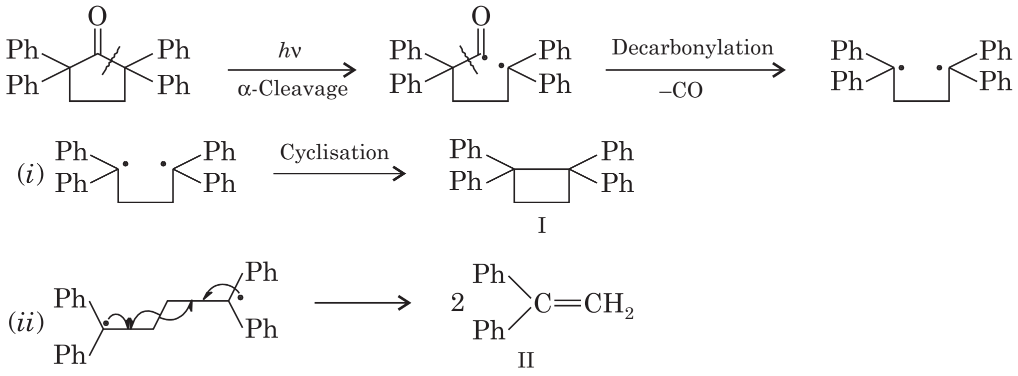


(*d*)

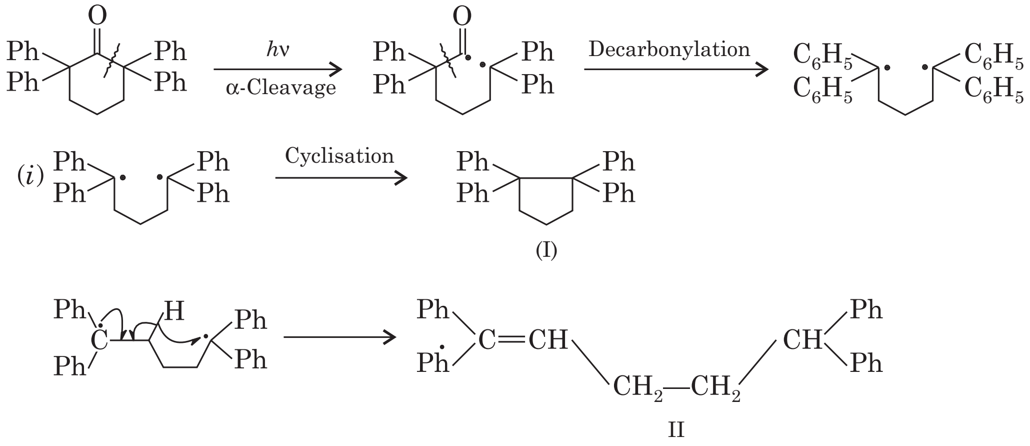


Solution:

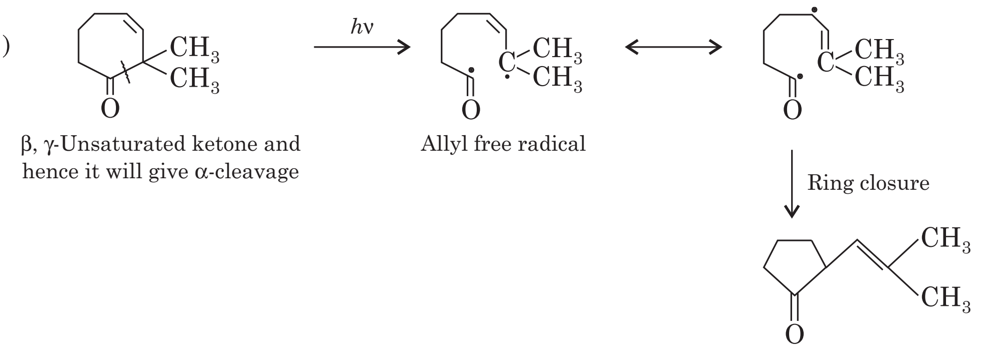
(*a*)



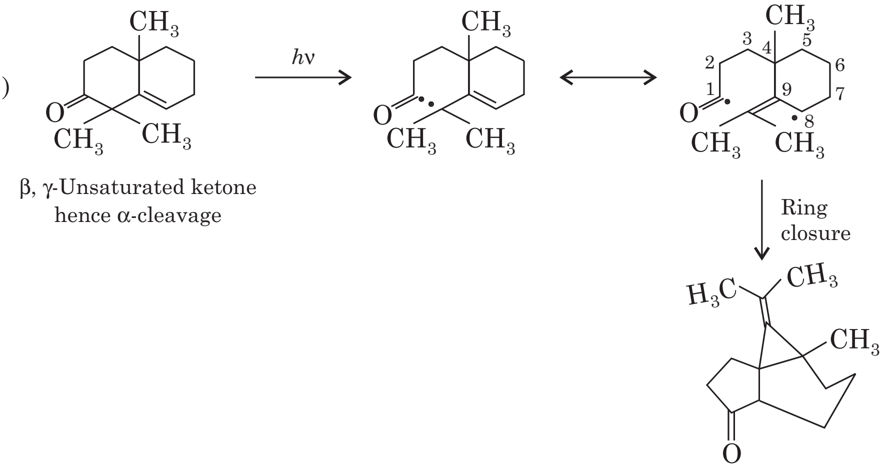
(*b*)



(*c*)

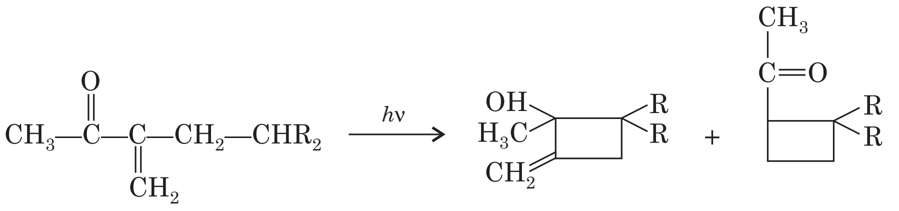


(*d*)

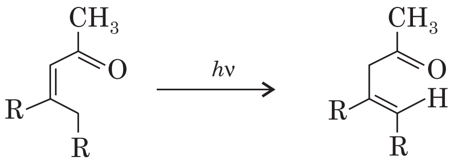


Problem 64: *Provide a mechanistic rationalisation for each of the following reactions:*

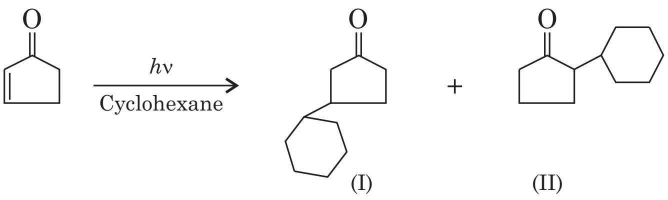
(*a*)



(*b*)

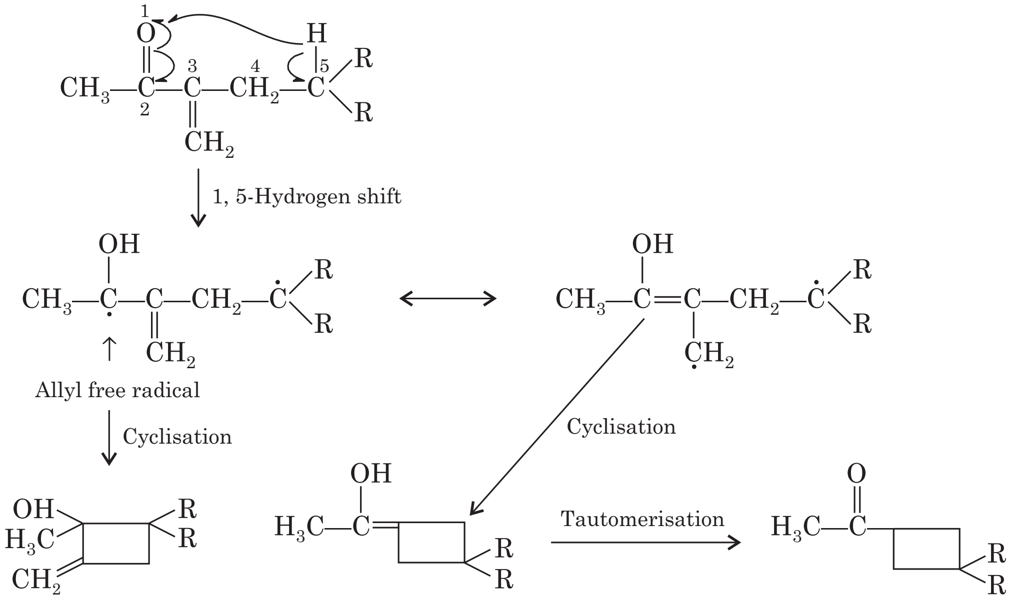


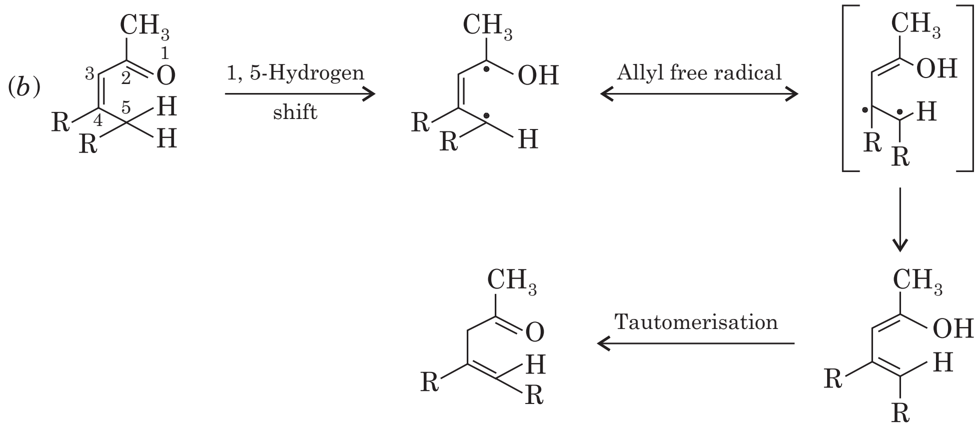
(*c*)



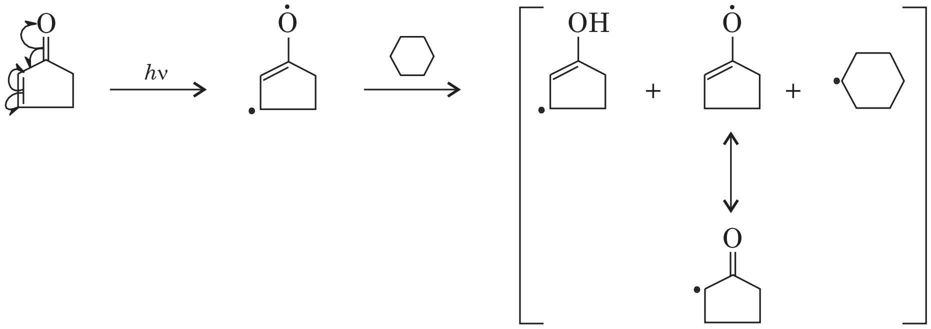
Solution:

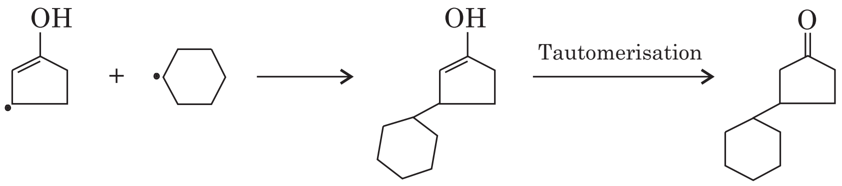
(*a*) The substrate has hydrogen on γ carbon hence intramolecular hydrogen abstraction is an important process in this reaction.

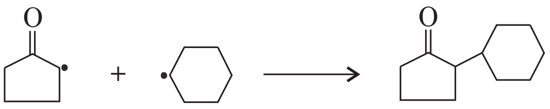




(*c*) Cyclopentenone abstracts hydrogen from hydrogen abstractor *i.e.,* cyclohexane.

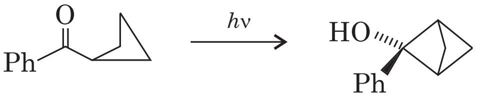


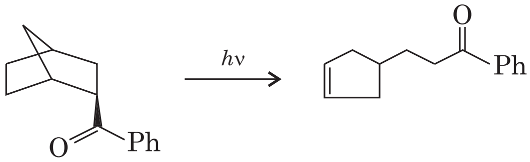
(*i*)


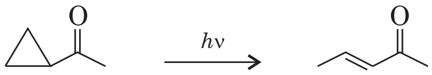
(*ii*)


(II)

Problem 65: *Provide a mechanistic rationalisation for each of the following reactions:*

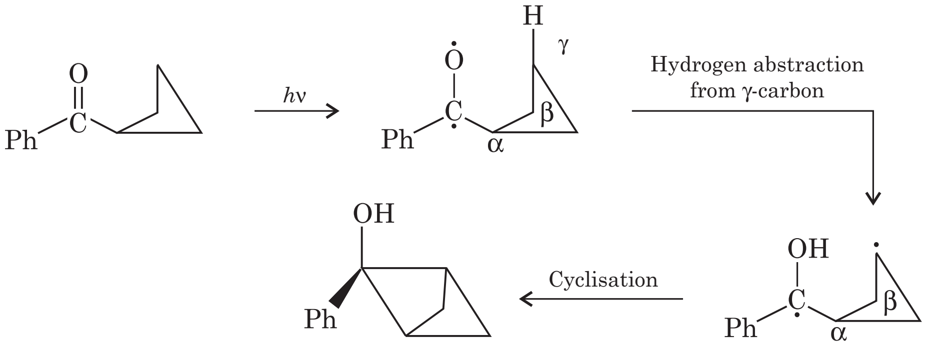
(*a*)


(*b*)


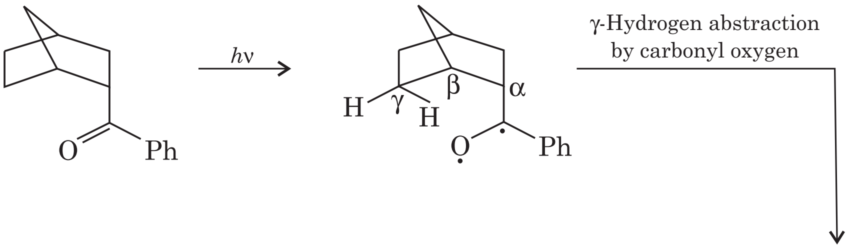
(*c*)


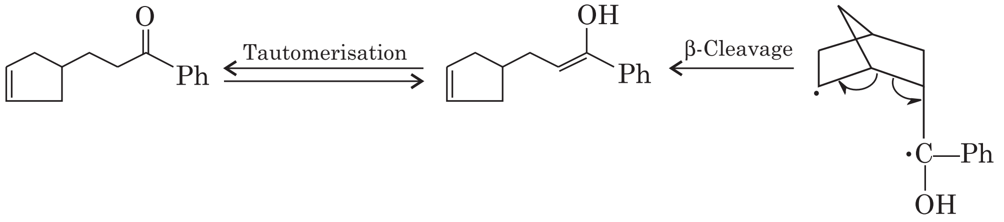
Solution:

(*a*) This compound gives Norrish Type-II reaction in which intramolecular hydrogen abstraction by the carbonyl oxygen from γ carbon takes place

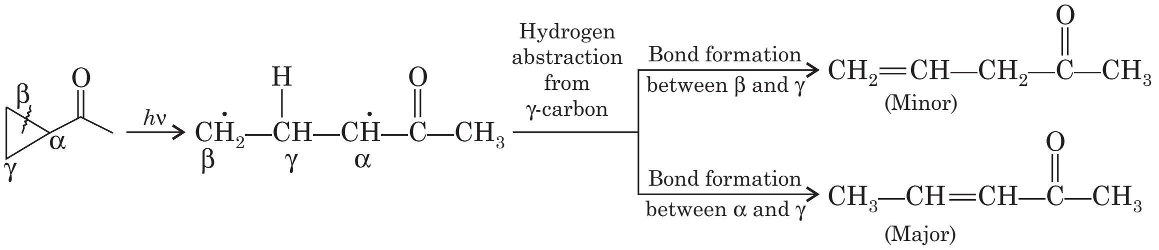


(*b*) The given reaction is an example of Norrish Type II reaction

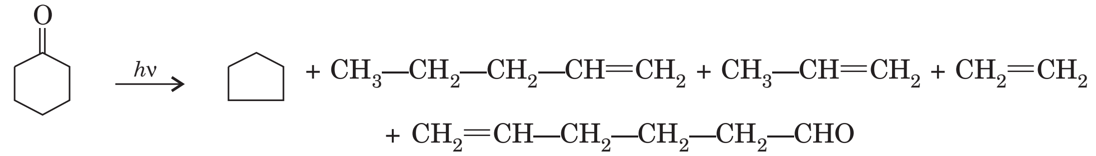




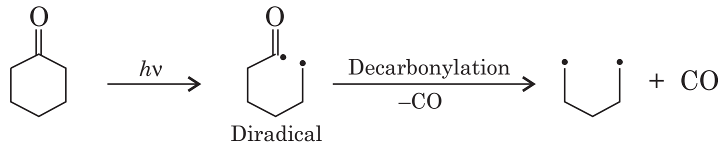
(*c*) Photolysis of acetylcyclopropane leads to breaking of the cyclopropane ring (β-cleavage) followed by hydrogen abstraction from the γ-carbon.



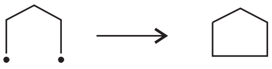
Problem 66: *Give step-wise product formation in the given reaction:*



Solution: Cyclic ketone undergoes α-cleavage to give biradical. The biradical after decarbonylation may recombine, abstract a hydrogen or undergoes secondary fission reactions to yield hydrocarbons. Abstraction of hydrogen in biradical takes place from α-carbon.



(*i*) Recombination



(*ii*) Abstraction of hydrogen atom from α-carbon

$$\dot{C}H_2—\underset{\alpha}{CH_2}—CH_2—CH_2—\dot{C}H_2$$

$$\downarrow$$

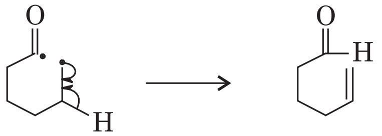
$$CH_2=CH—CH_2—CH_2—CH_3$$

(*iii*) Secondary fission reactions

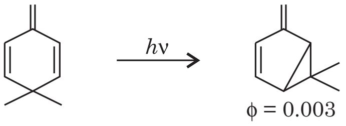
$$\dot{C}H_2—CH_2 \wr CH_2—CH_2—\dot{C}H_2$$

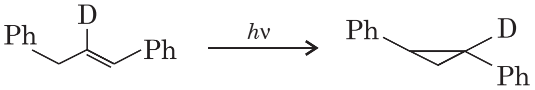
$$\downarrow$$

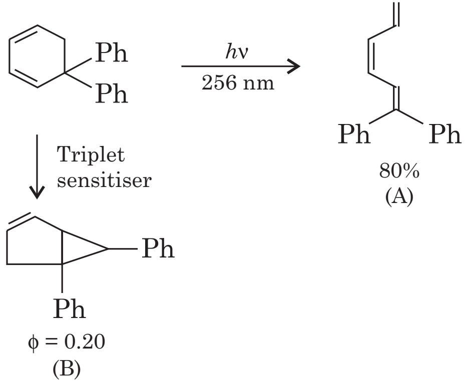
$$CH_2=CH_2 + CH_2 = CH—CH_3$$

(*iv*)


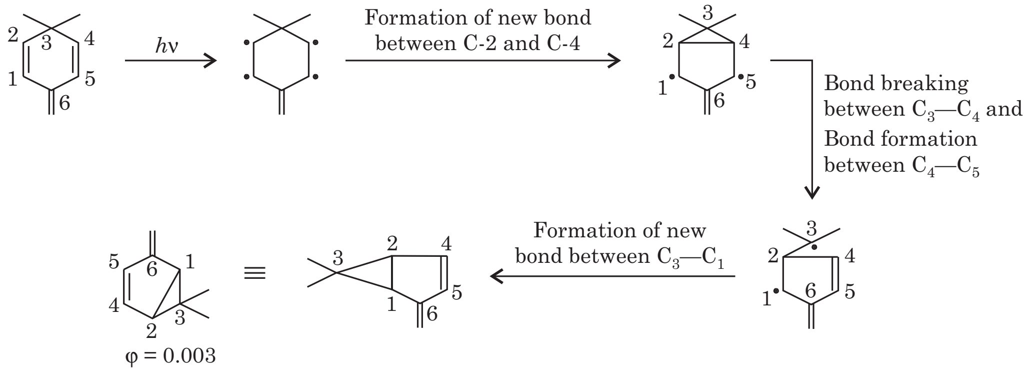
Problem 67: *Provide a mechanistic rationalisation for each of the following reactions:*

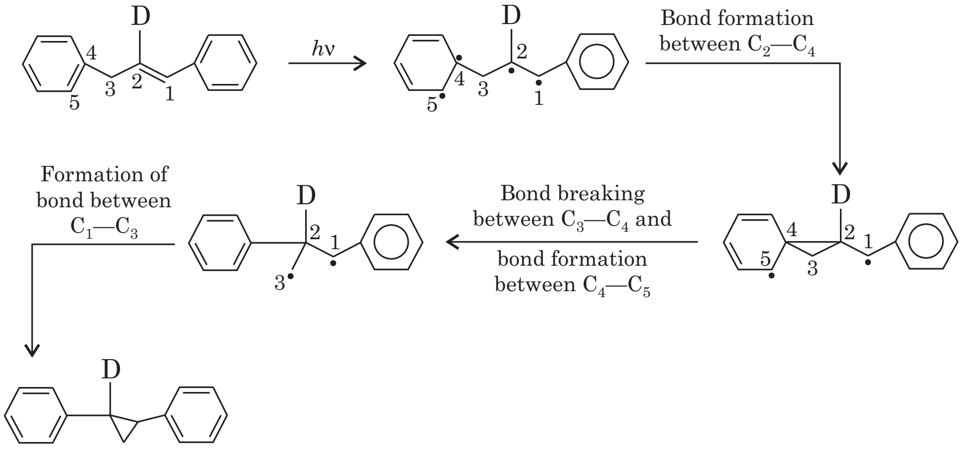
(*a*)


(*b*)


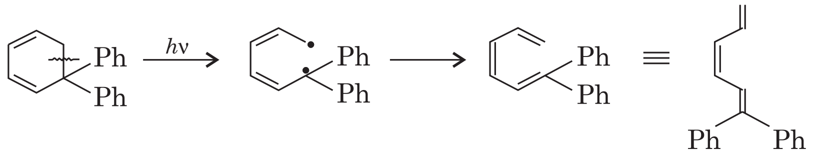
(*c*)


Solution: These problems are based on Di-π methane rearrangement.

(*a*)


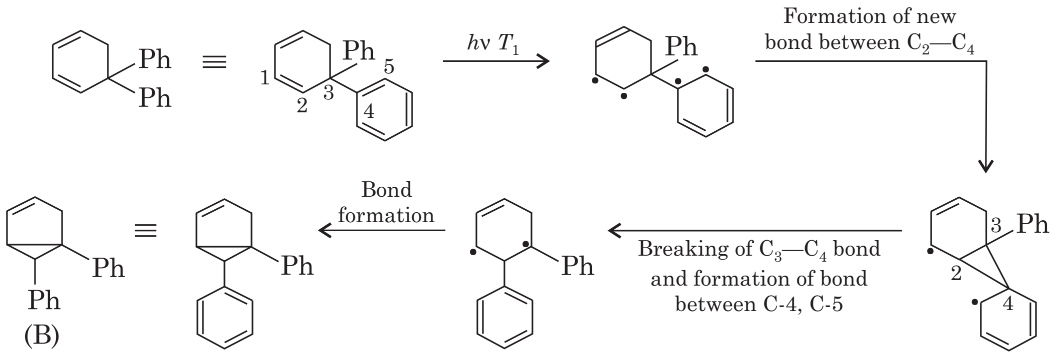
(*b*)


(*c*) In singlet state



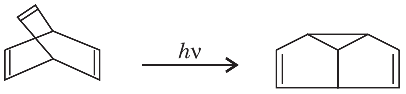
(A) 80%

Triplet sensitiser

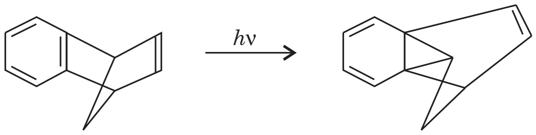


Problem 68: *Provide mechanistic rationalisation for each of the following reactions:*

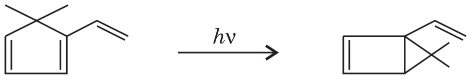
(*a*)



(*b*)

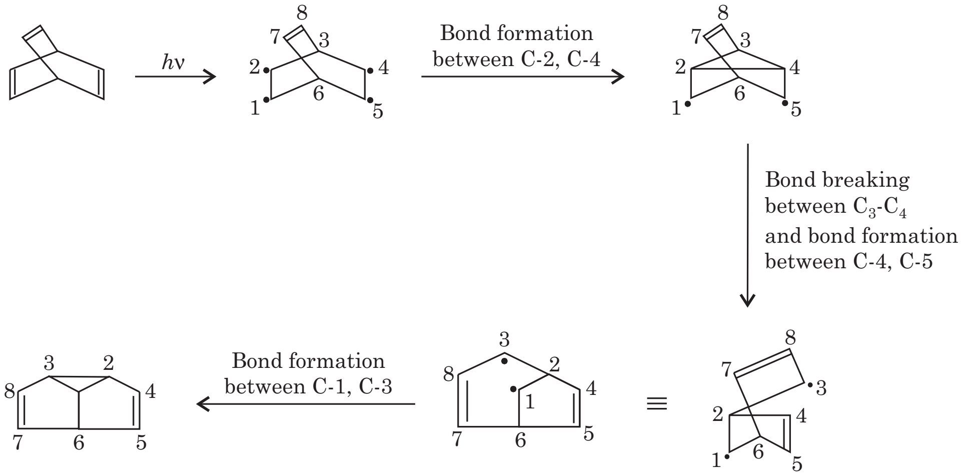


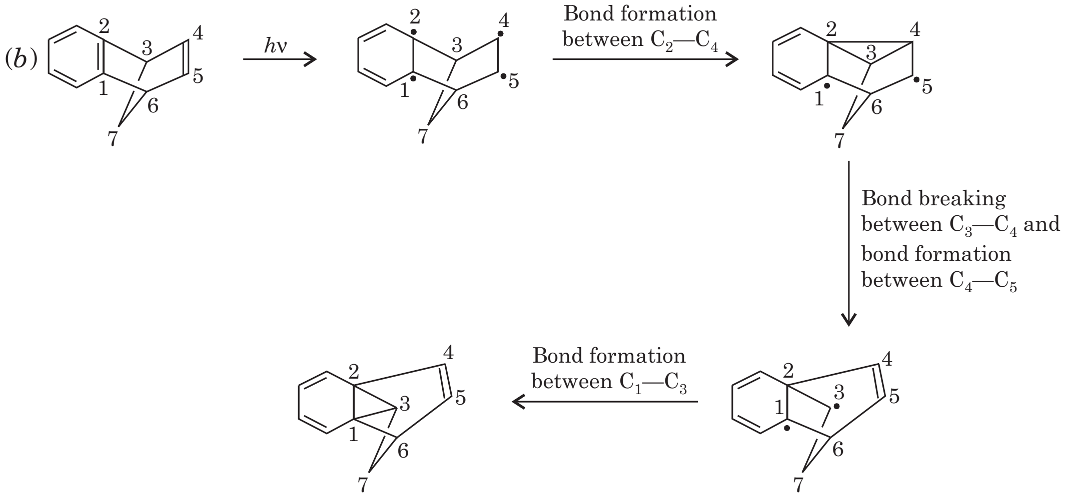
(*c*)

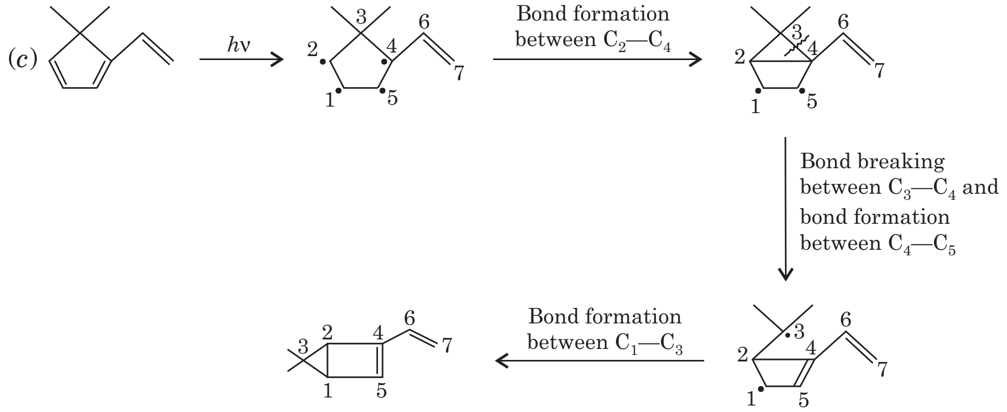


Solution: These problems are based on di-π methane rearrangement.

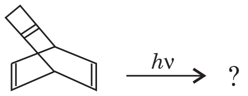
(*a*)



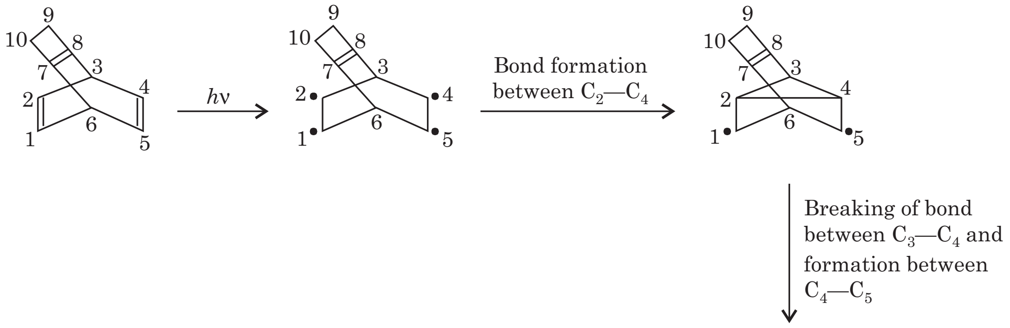


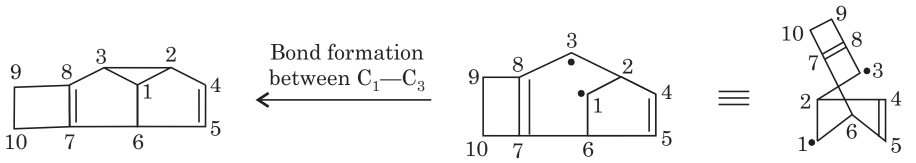


Problem 69: *Give mechanism and product of the reaction:*

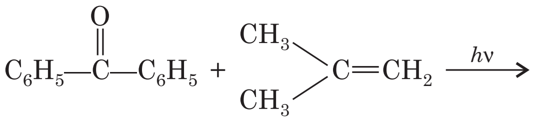


Solution: Compound can be treated as 1, 4 pentadiene derivative. Hence reaction will be di-π methane rearrangement.

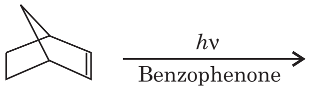


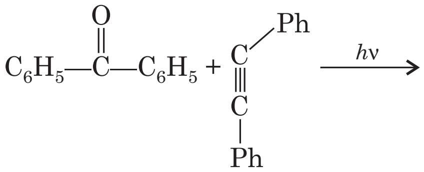


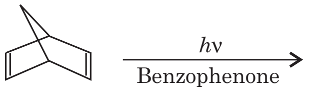
Problem 70: *Complete the following reactions:*

(*a*)


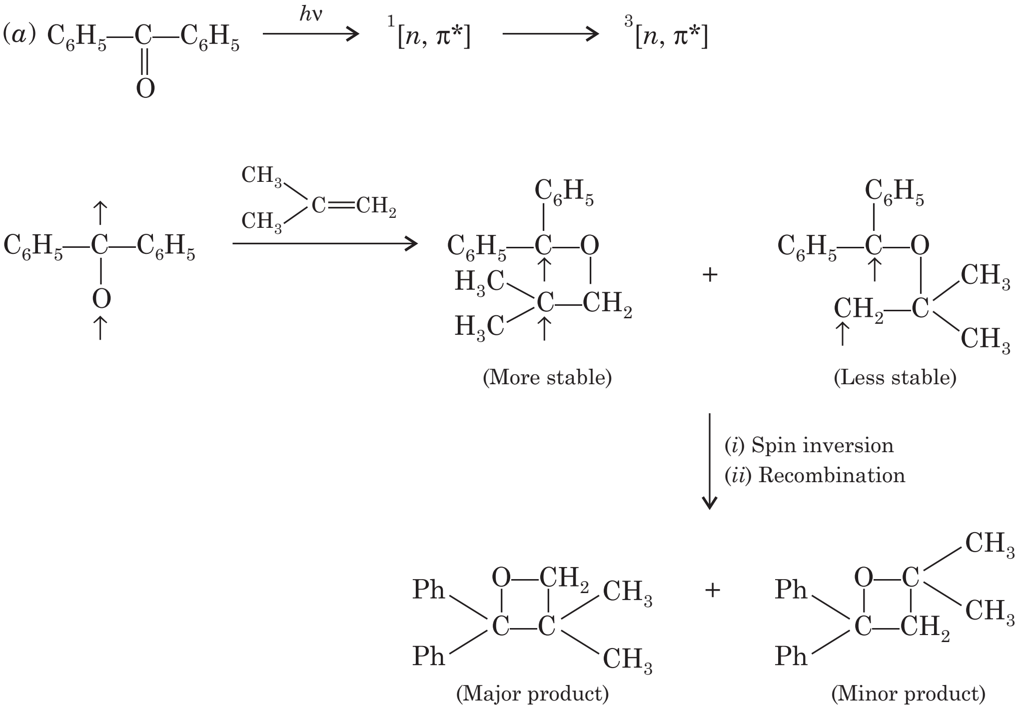
(*b*)


(*c*)


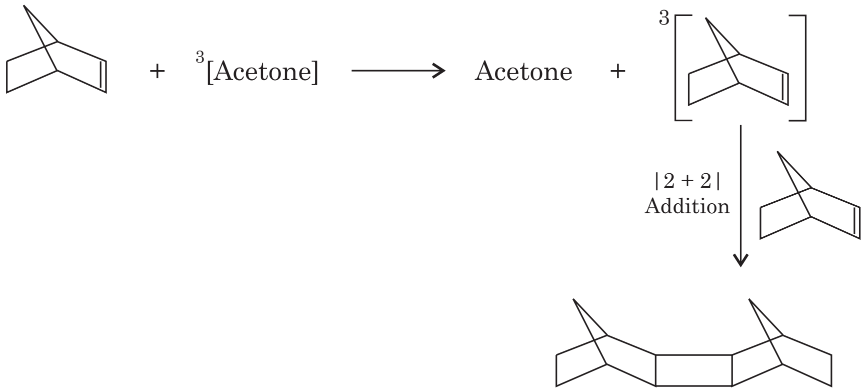
(*d*)


(*e*)


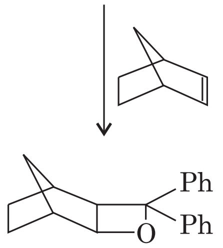
Solution: These problems are based on |2 + 2| photocycloaddition and Paterno-Büchi reaction.

(*a*)


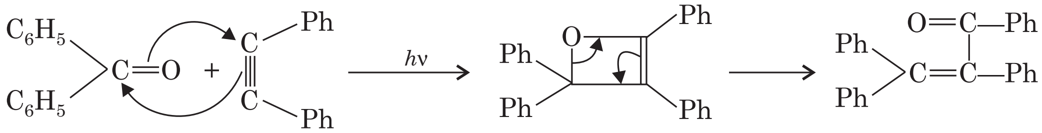
(*b*) $\text{Acetone} \xrightarrow{h\nu} {}^{1}[\text{Acetone}] \xrightarrow{h\nu} {}^{3}[\text{Acetone}]$



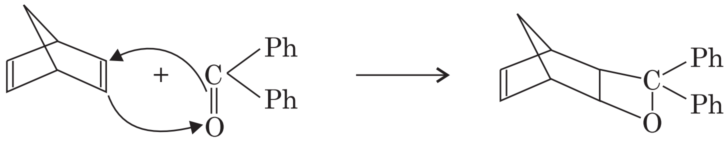
(*c*) $\text{Benzophenone} \xrightarrow{h\nu} {}^{1}[\text{Benzophenone}] \longrightarrow {}^{3}[\text{Benzophenone}]$



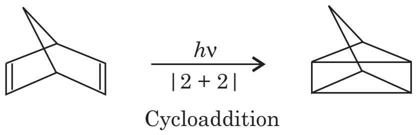
(*d*)



(*e*) (*i*)

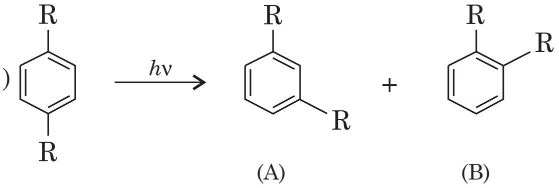


(*ii*)



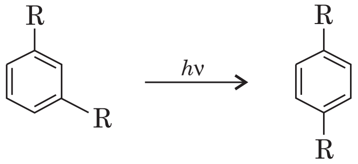
Problem 71: *Provide mechanistic rationalisation for each of the following reactions:*

(*a*)



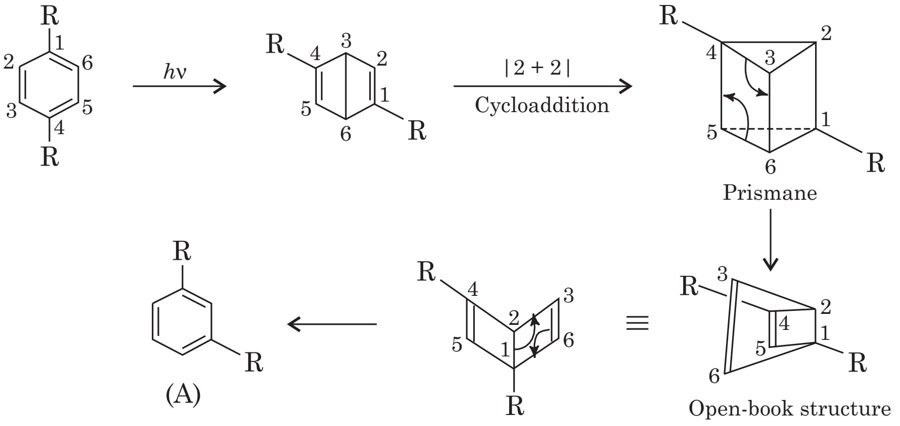
(A) (B)

(*b*)

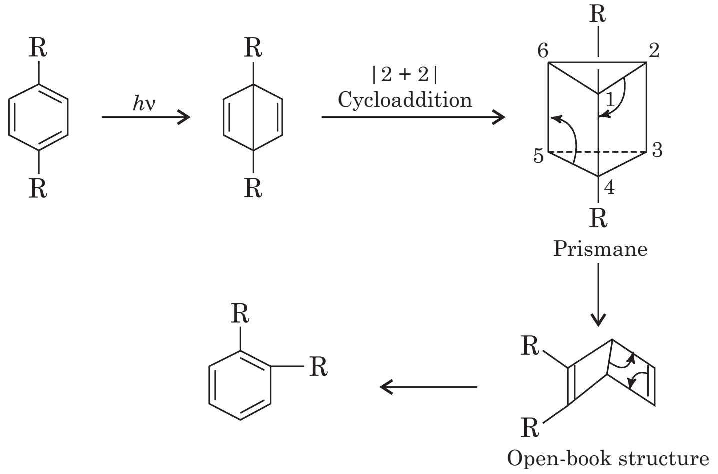


Solution: These two reactions are examples of isomerisation of disubstituted benzenes:

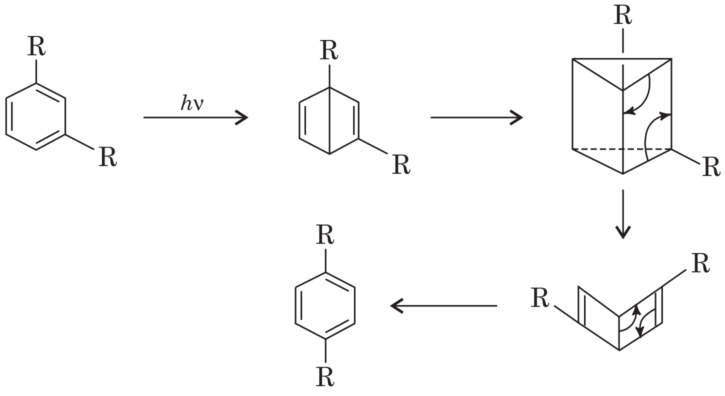
(*a*)



Formation of B

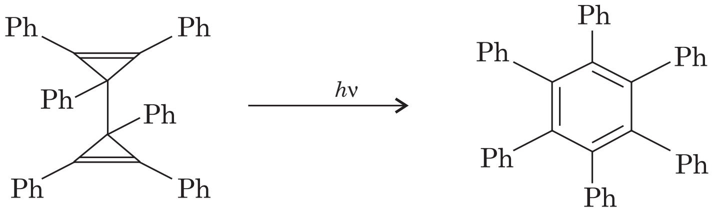


(*b*)

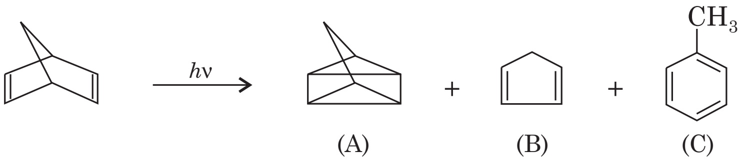


Problem 72: *Provide mechanistic rationalisation for each of the following reactions:*

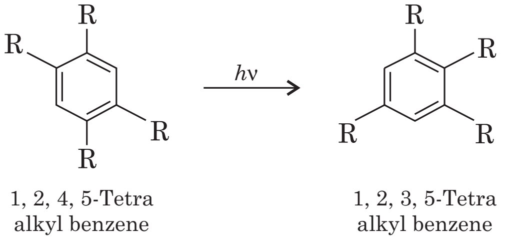
(*a*)



(*b*)

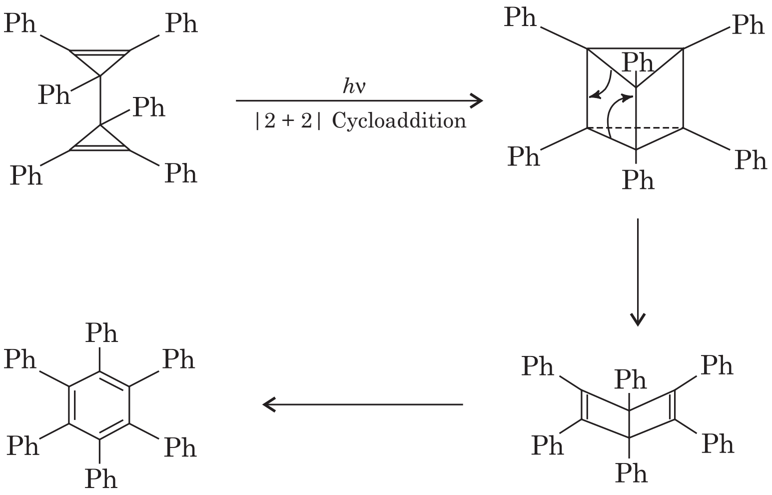


(*c*)

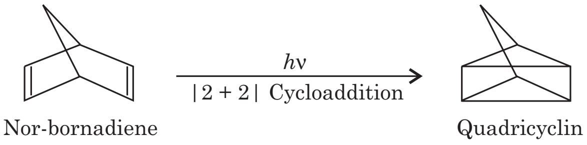


Solution:

(*a*)

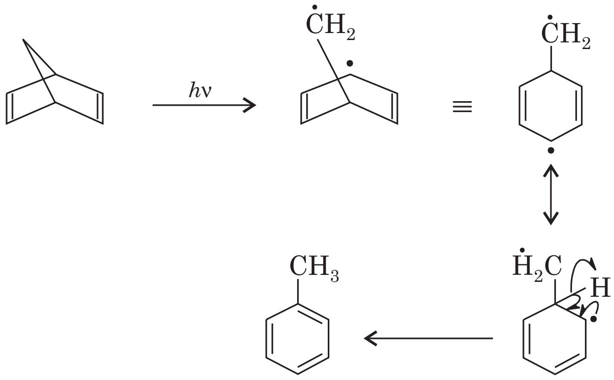


(*b*) Formation of A

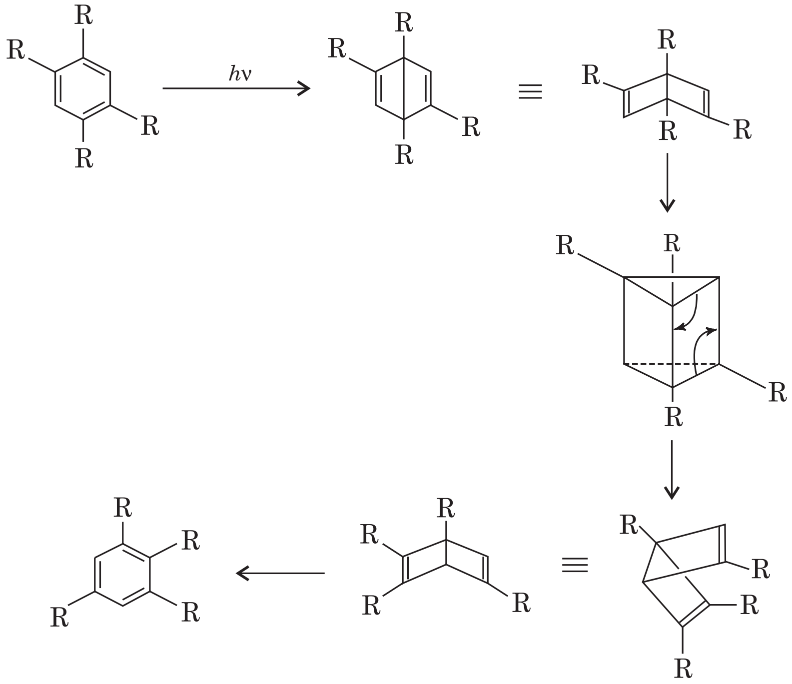


Formation of B

Formation of C

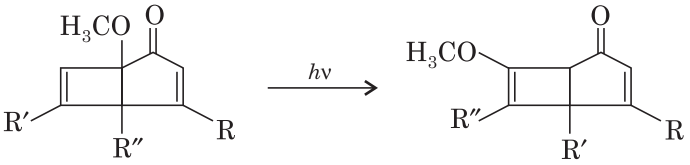


(*c*)

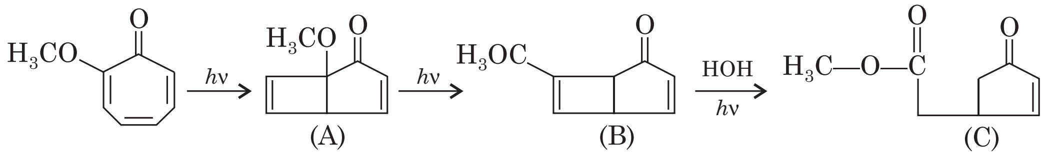


Problem 73: *Give mechanism of the given reactions:*

(*a*)

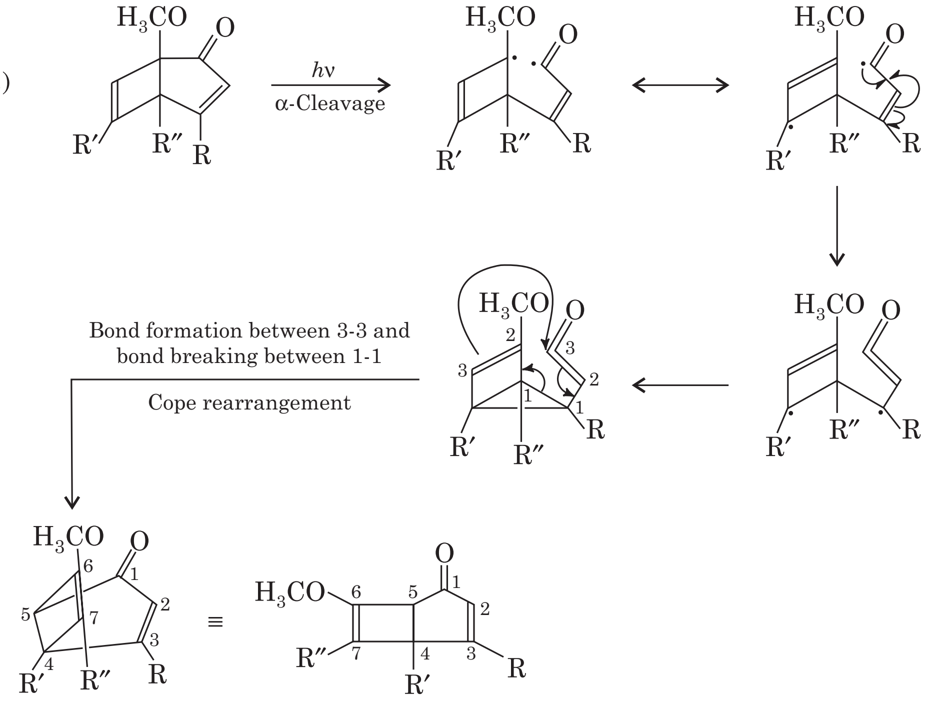


(*b*)

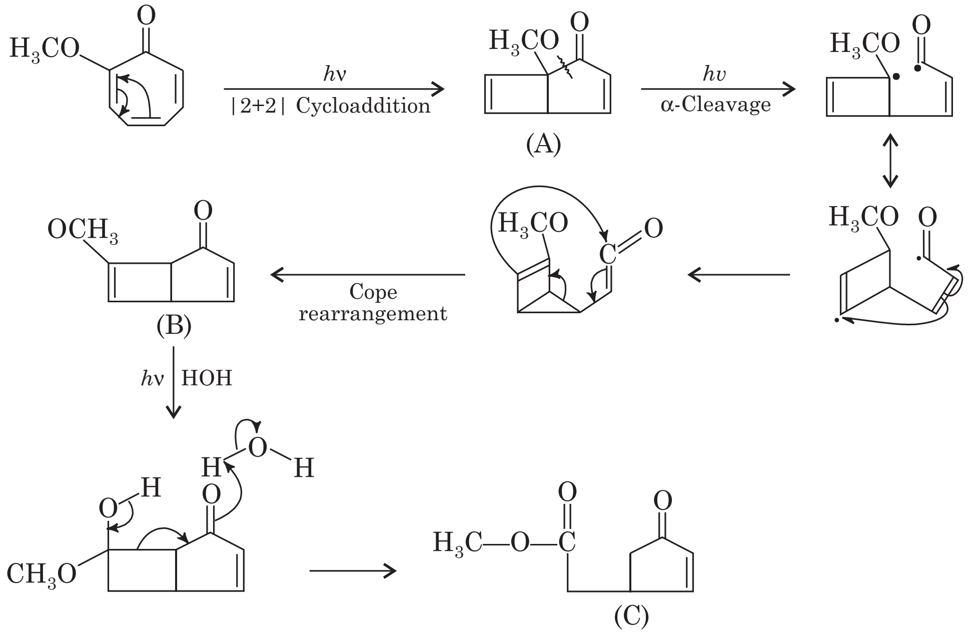


Solution:

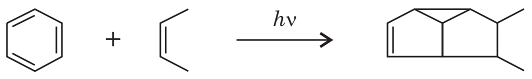
(*a*)



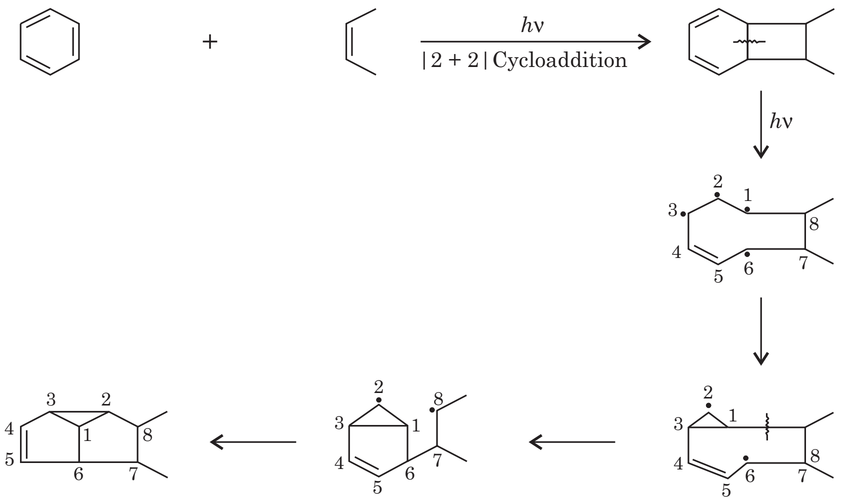
(*b*)



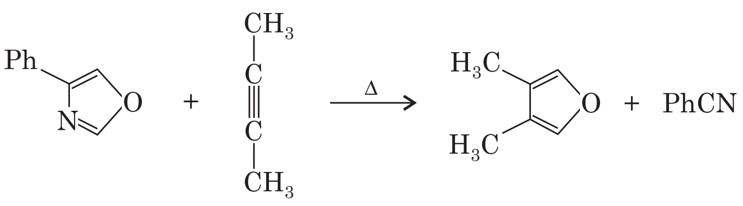
Problem 74: *Give mechanism of the given reaction:*



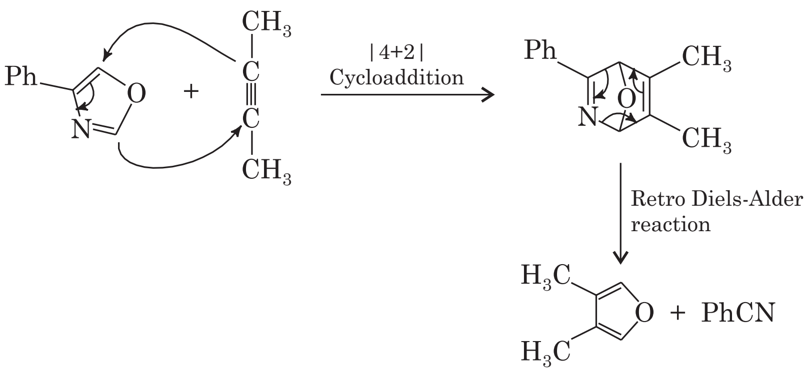
Solution:



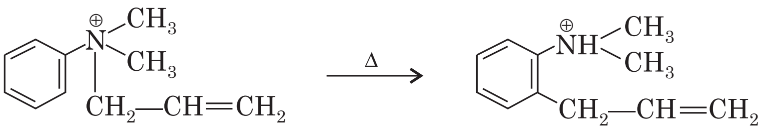
Problem 75: *Two sequential pericyclic reactions are involved in the 3,4 dimethyl furan synthesis. Identify them, and propose a mechanism for the transformation:*



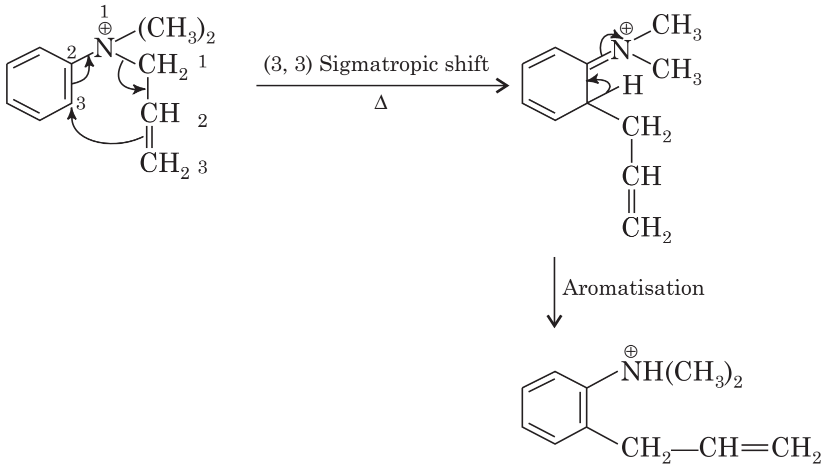
Solution:



Problem 76: *The following rearrangement of N-allyl-N, N-dimethylanilinium ion has been observed. Propose a mechanism for the reaction.*

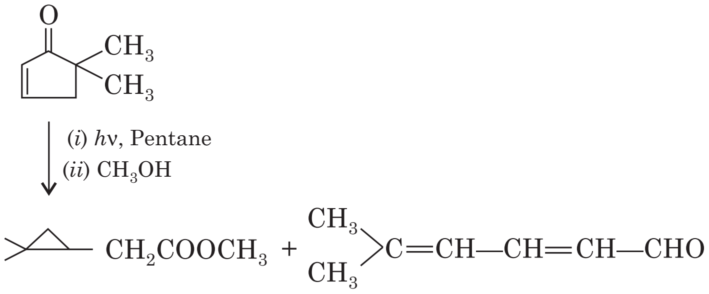


Solution:

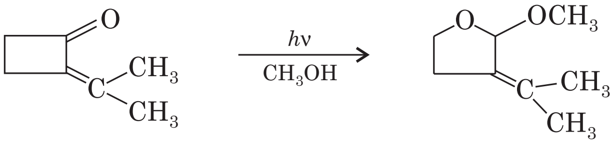


Problem 77: *Provide a mechanistic rationalisation for each of the following reactions:*

(*a*)

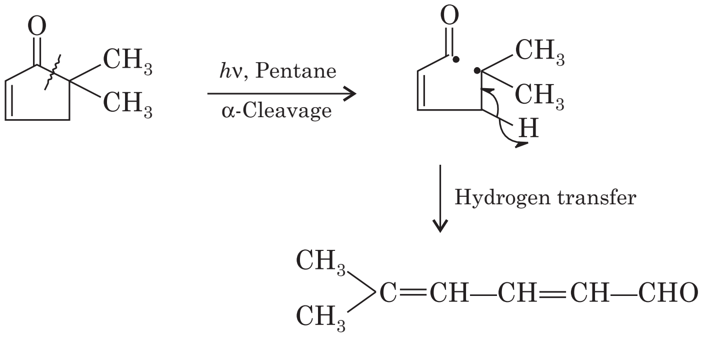


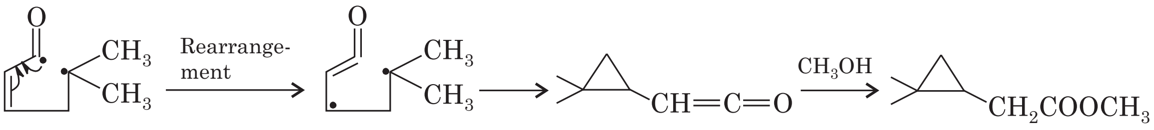
(*b*)



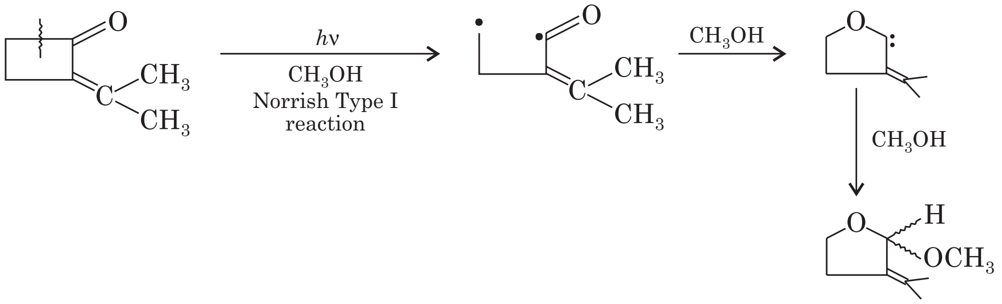
Solution:

(*a*)

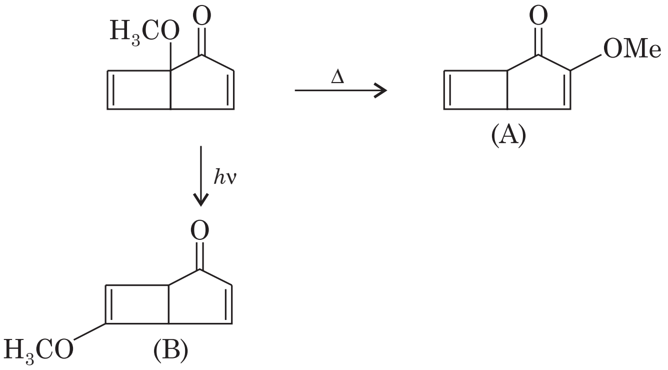




(*b*)

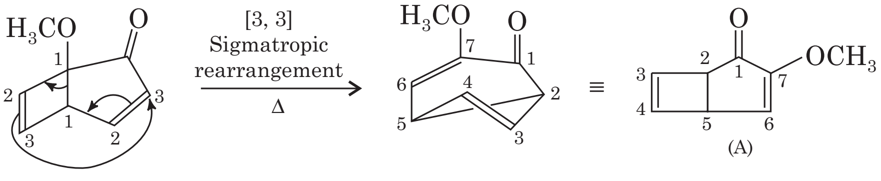


Problem 78: *Explain the following observations:*

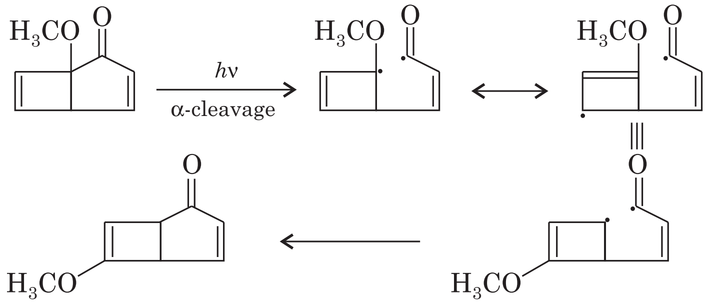


Solution:

Formation of (A)

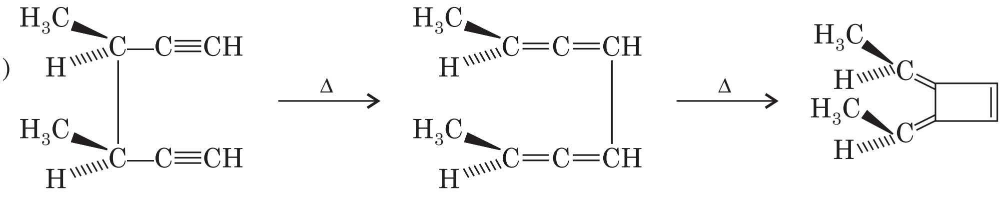


Formation of (B)

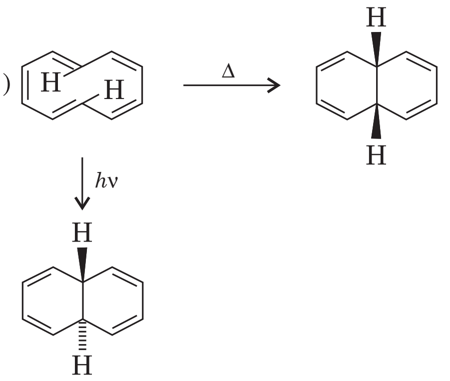


Problem 79: *Give mechanism of the following concerted reactions:*

(*a*)

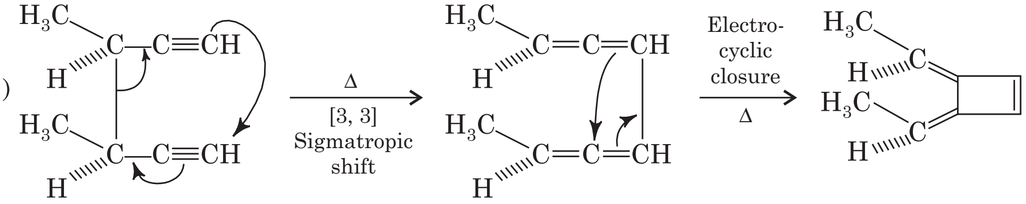


(*b*)

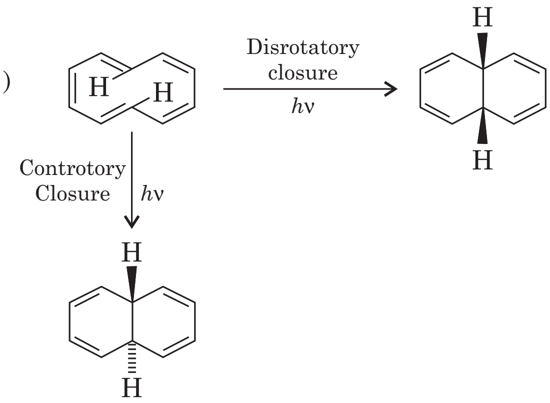


Solution:

(*a*)

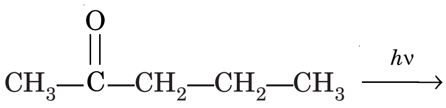


(*b*)



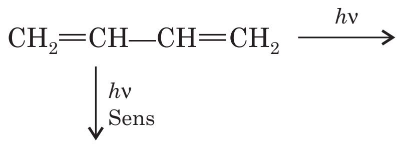
Problem 80: *Prdict the product(s) and give suitable mechanistic scheme for the following photochemical transformation:*

(*a*)



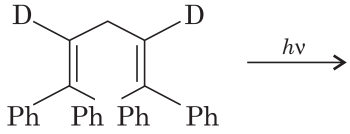
$$CH_3-\overset{\overset{\large O}{||}}{C}-CH_2-CH_2-CH_3 \xrightarrow{h\nu}$$

(*b*)

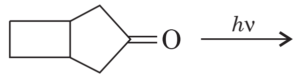


$$CH_2{=}CH-CH{=}CH_2 \xrightarrow{h\nu} \qquad \downarrow h\nu,\ \text{Sens}$$

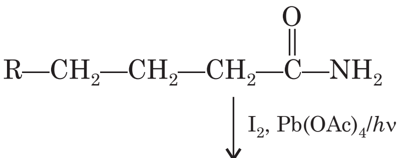
(*c*)



(*d*)

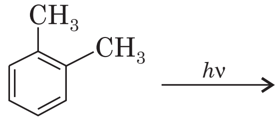


(*e*)

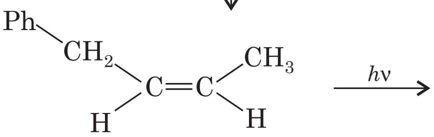


$$R-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{I_2,\ Pb(OAc)_4/h\nu}$$

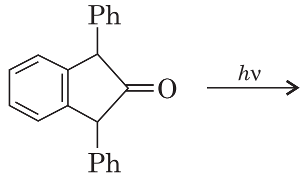
(*f*)



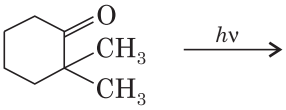
(*g*)



(*h*)

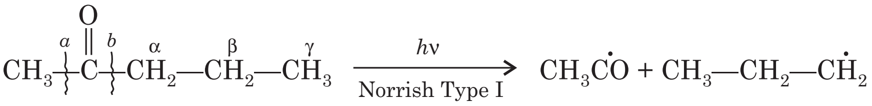


(*i*)



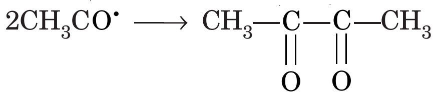
Solution:

(*a*)



$$CH_3 \overset{a}{\wr} \overset{O}{\overset{\|}{C}} \overset{b}{\wr} \overset{\alpha}{C}H_2-\overset{\beta}{C}H_2-\overset{\gamma}{C}H_3 \xrightarrow[\text{Norrish Type I}]{h\nu} CH_3\dot{C}O + CH_3-CH_2-\dot{C}H_2$$

(*i*) *Breaking of bond 'b'*



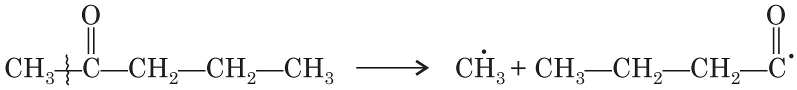
$$2CH_3CO^{\bullet} \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$$

At above 100°C temp.

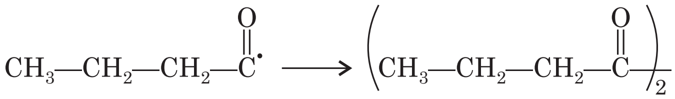
$$CH_3CO^{\bullet} \longrightarrow \dot{C}H_3 + CO$$

$$2\dot{C}H_3 \longrightarrow CH_3-CH_3$$

(*ii*) *Breaking of bond 'a'*

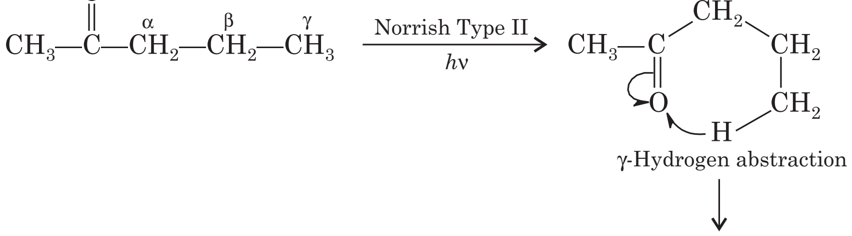


$$CH_3 \wr \overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3 \longrightarrow \dot{C}H_3 + CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}^{\bullet}$$

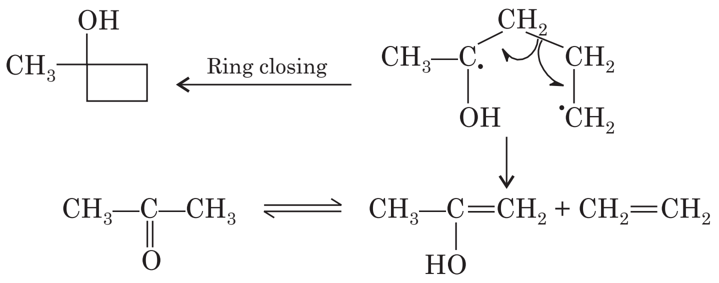


$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}^{\bullet} \longrightarrow \left(CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\right)_2$$

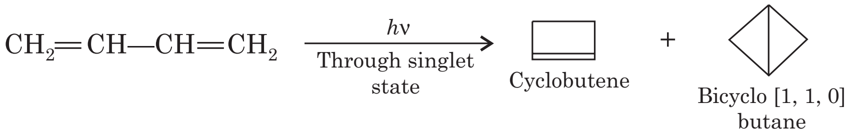
(*iii*)



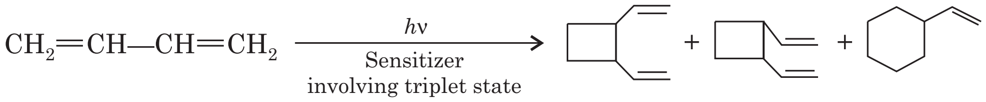
γ-Hydrogen abstraction


Ring closing

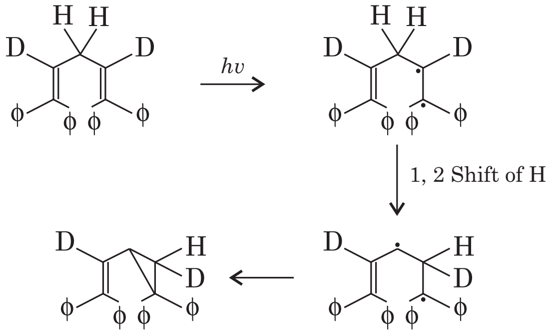
(b) (i)


hν
Through singlet state
Cyclobutene
Bicyclo [1, 1, 0] butane

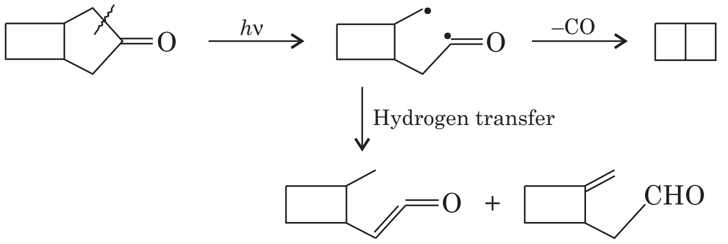
(ii)


hν
Sensitizer involving triplet state

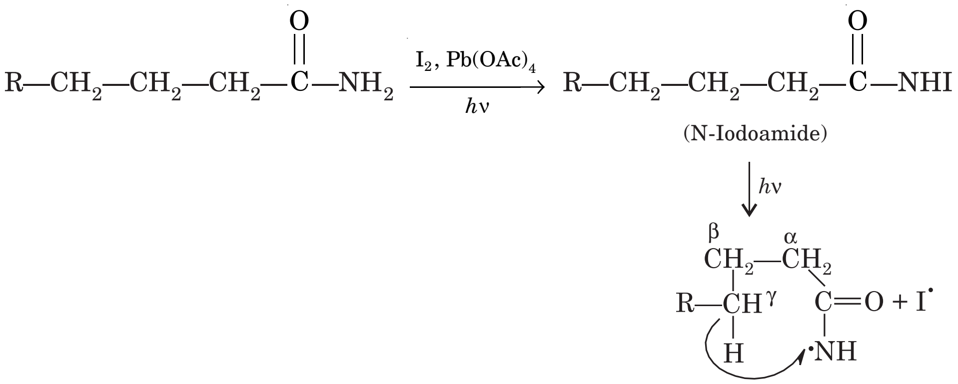
(c)

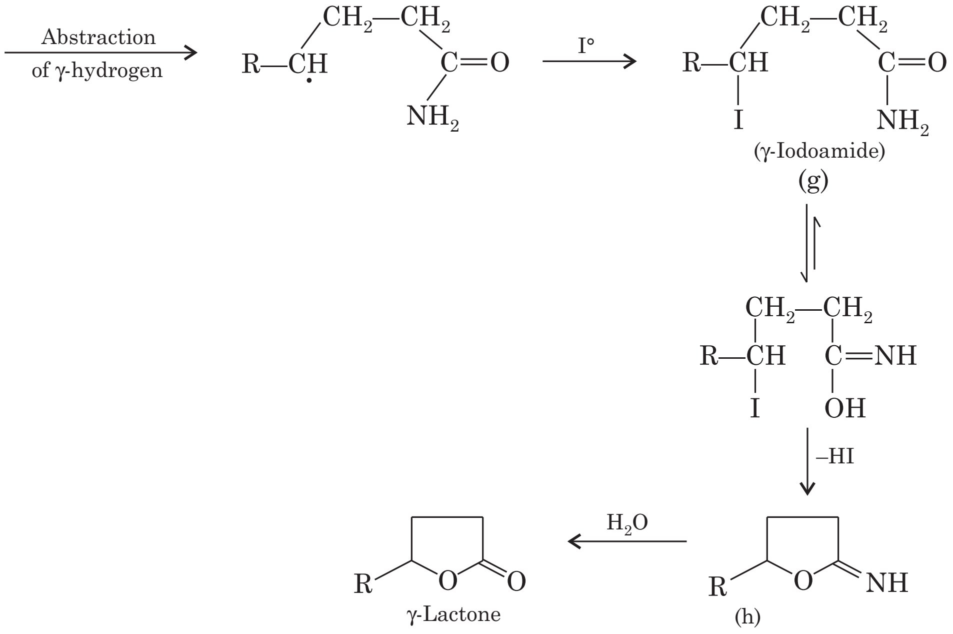

hν
1, 2 Shift of H

(d)

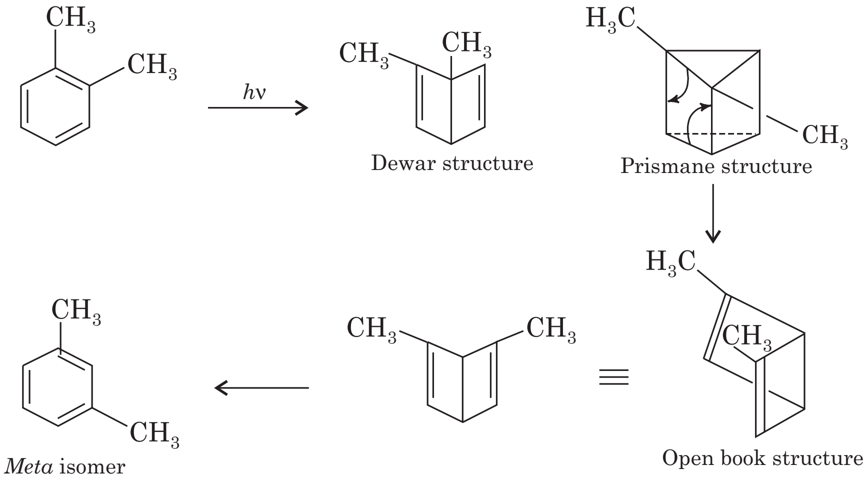

hν
–CO
Hydrogen transfer

(e)

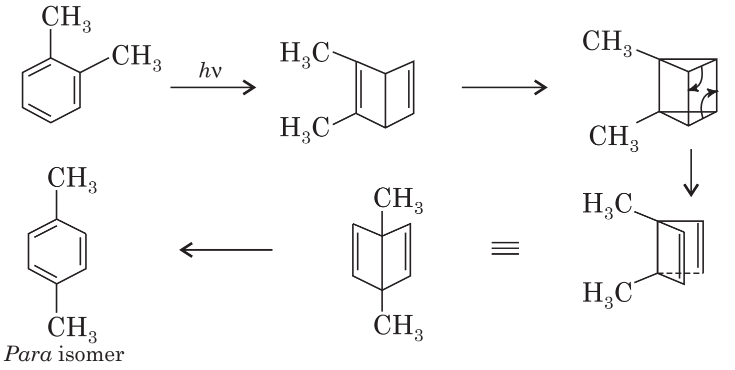

I₂, Pb(OAc)₄
hν
(N-Iodoamide)
hν
β
α
γ


Abstraction
of γ-hydrogen
R—CH
CH2—CH2
C=O
NH2
I°
R—CH
I
CH2—CH2
C=O
NH2
(γ-Iodoamide)
(g)
CH2—CH2
R—CH
I
C=NH
OH
–HI
R
O
NH
(h)
H2O
R
O
O
γ-Lactone

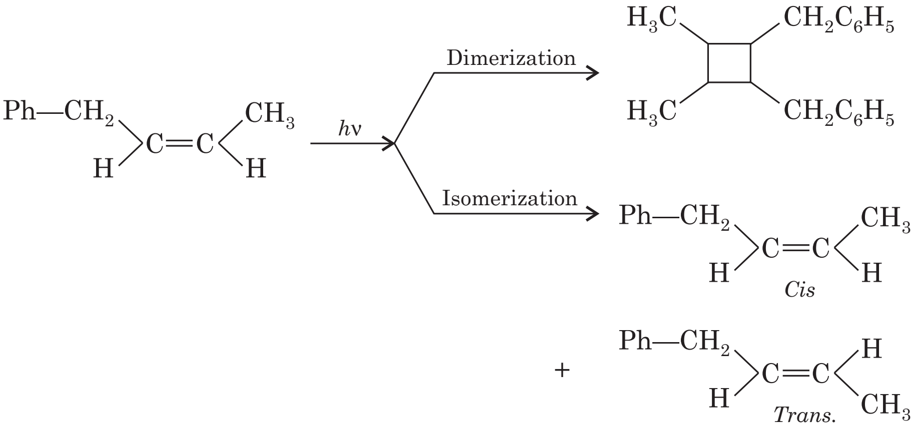
(*f*) (*i*)


CH3
CH3
hν
CH3
CH3
Dewar structure
H3C
CH3
Prismane structure
H3C
CH3
Open book structure
≡
CH3
CH3
CH3
CH3
Meta isomer

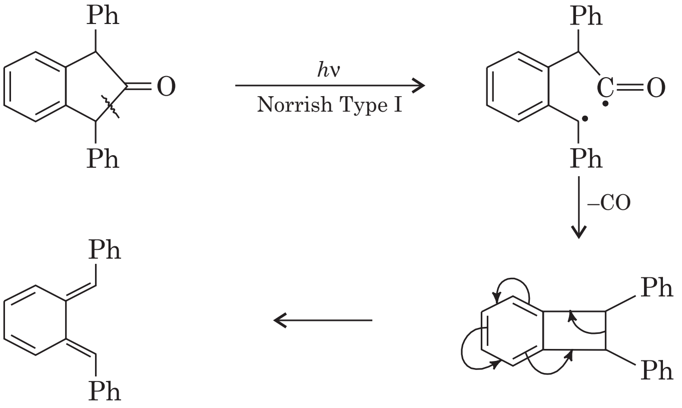
(*ii*)


CH3
CH3
hν
H3C
H3C
CH3
CH3
H3C
H3C
≡
CH3
CH3
CH3
CH3
Para isomer

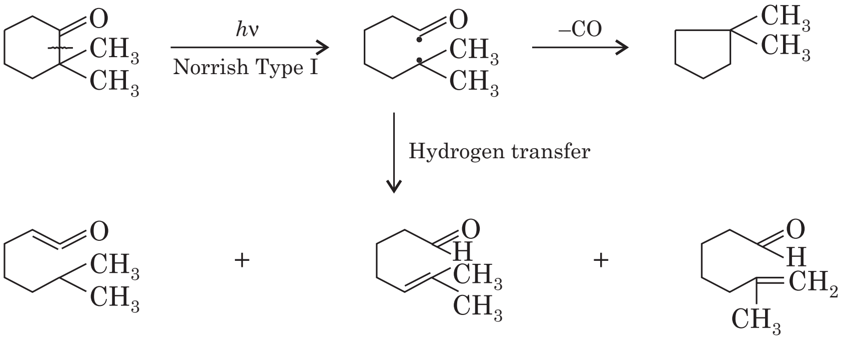
(*g*)



(*h*)

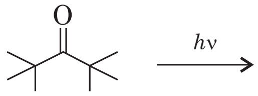


(*i*)

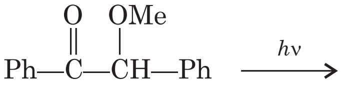


Problem 81: *Write the products formed in the following photochemical transformations:*

(*a*)

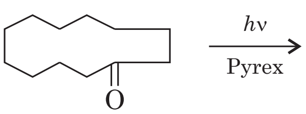


(*b*)

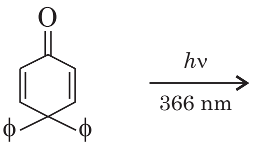


$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{OMe}{|}}{CH}-Ph} \xrightarrow{h\nu}$

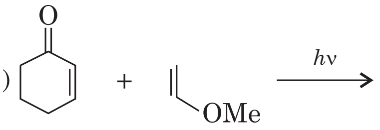
(*c*)



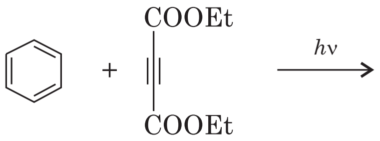
(*d*)



(*e*)

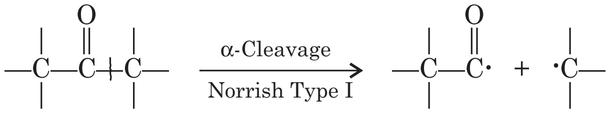


(*f*)



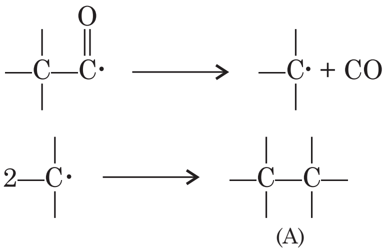
Solution:

(*a*)



$$-\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}\nmid\underset{|}{\overset{|}{C}}- \xrightarrow[\text{Norrish Type I}]{\alpha\text{-Cleavage}} -\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}\cdot + \cdot\underset{|}{\overset{|}{C}}-$$

(*i*) At temp. above 100°C decarbonylation of free radical takes place with the formation of tertiary free radical and carbon monoxide.

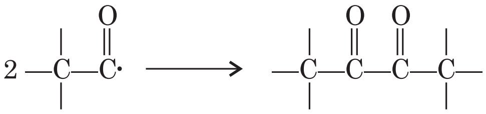


$$-\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}\cdot \longrightarrow -\underset{|}{\overset{|}{C}}\cdot + CO$$

$$2-\underset{|}{\overset{|}{C}}\cdot \longrightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$$

(A)

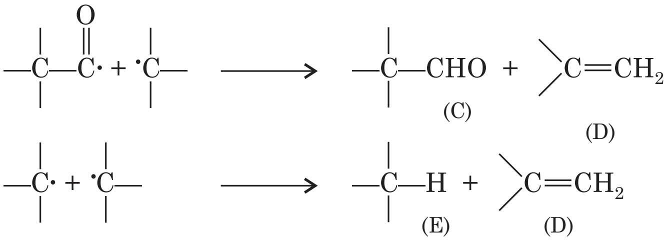
(*ii*)



$$2\,-\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}\cdot \longrightarrow -\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-$$

(B)

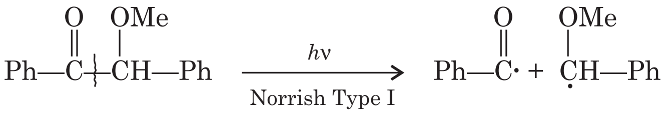
(*iii*) By hydrogen abstraction



$$-\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}\cdot + \cdot\underset{|}{\overset{|}{C}}- \longrightarrow -\underset{|}{\overset{|}{C}}-CHO + \rangle C{=}CH_2$$

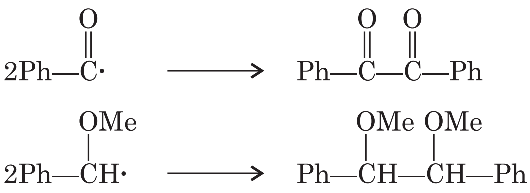
$$-\underset{|}{\overset{|}{C}}\cdot + \cdot\underset{|}{\overset{|}{C}}- \longrightarrow -\underset{|}{\overset{|}{C}}-H + \rangle C{=}CH_2$$

(*b*) (I)



$$Ph-\overset{\overset{O}{\|}}{C}\nmid\overset{\overset{OMe}{|}}{C}H-Ph \xrightarrow[\text{Norrish Type I}]{h\nu} Ph-\overset{\overset{O}{\|}}{C}\cdot + \overset{\overset{OMe}{|}}{\underset{\cdot}{C}}H-Ph$$

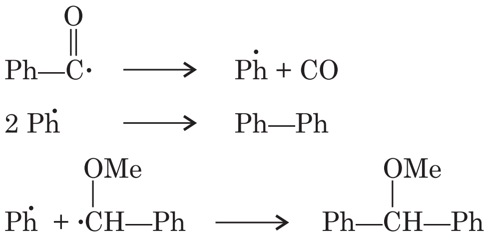
(*i*)



$$2Ph-\overset{\overset{O}{\|}}{C}\cdot \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-Ph$$

$$2Ph-\overset{\overset{OMe}{|}}{C}H\cdot \longrightarrow Ph-\overset{\overset{OMe}{|}}{C}H-\overset{\overset{OMe}{|}}{C}H-Ph$$

(*ii*) At temp. above 100°C

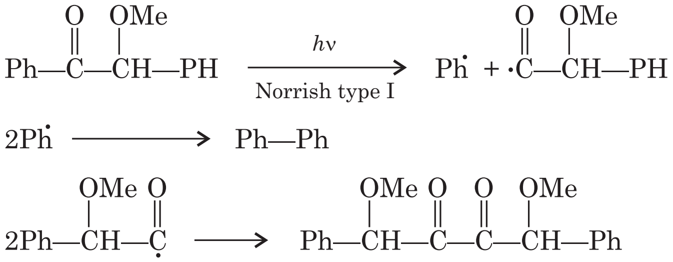


$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}\cdot} \longrightarrow \dot{\mathrm{Ph}} + \mathrm{CO}$$

$$2\,\dot{\mathrm{Ph}} \longrightarrow \mathrm{Ph{-}Ph}$$

$$\dot{\mathrm{Ph}} + \cdot\mathrm{\overset{\overset{OMe}{|}}{C}H{-}Ph} \longrightarrow \mathrm{Ph{-}\overset{\overset{OMe}{|}}{C}H{-}Ph}$$

(II)

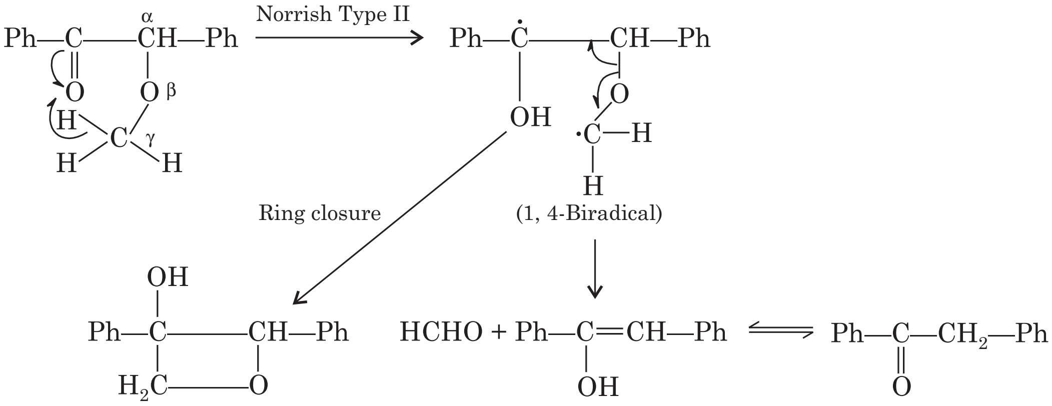


$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OMe}{|}}{C}H{-}PH} \xrightarrow[\text{Norrish type I}]{h\nu} \dot{\mathrm{Ph}} + \cdot\mathrm{\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OMe}{|}}{C}H{-}PH}$$

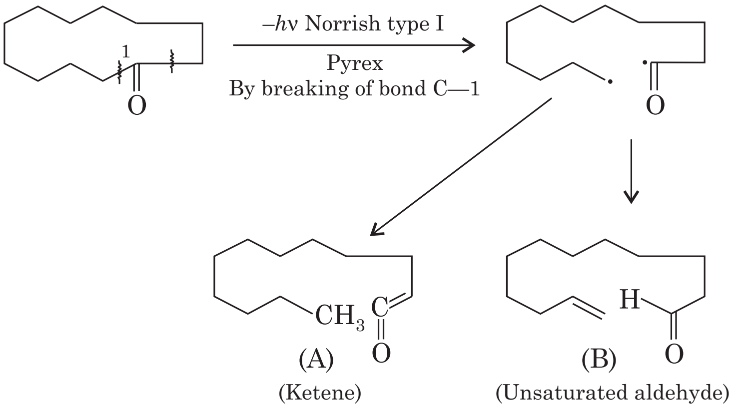
$$2\dot{\mathrm{Ph}} \longrightarrow \mathrm{Ph{-}Ph}$$

$$2\mathrm{Ph{-}\overset{\overset{OMe}{|}}{C}H{-}\underset{\cdot}{\overset{\overset{O}{\|}}{C}}} \longrightarrow \mathrm{Ph{-}\overset{\overset{OMe}{|}}{C}H{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OMe}{|}}{C}H{-}Ph}$$

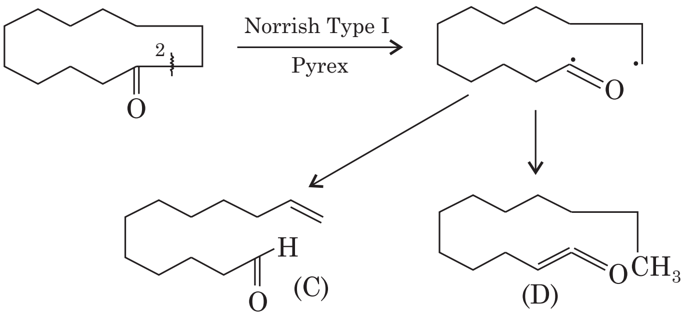
(III) Also undergoes Norrish Type II by involving γ-hydrogen abstraction.



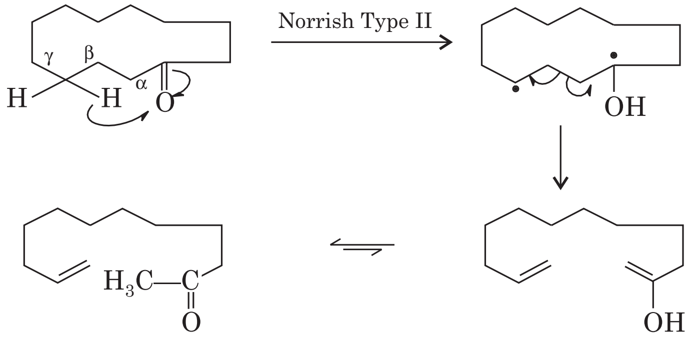
(*c*) (*i*) *Breaking of bond 1*



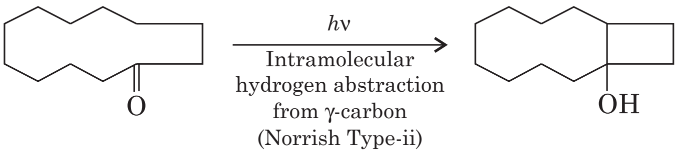
(*ii*) *Breaking of bond 2*



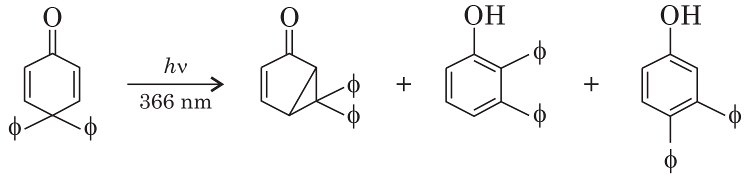
(*iii*)



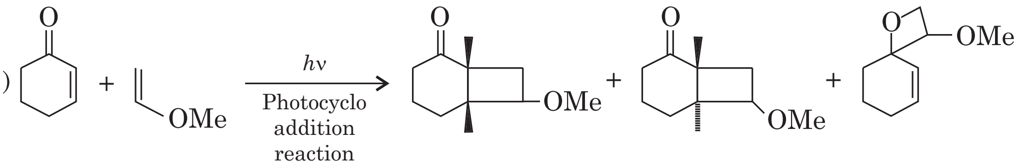
(*iv*)



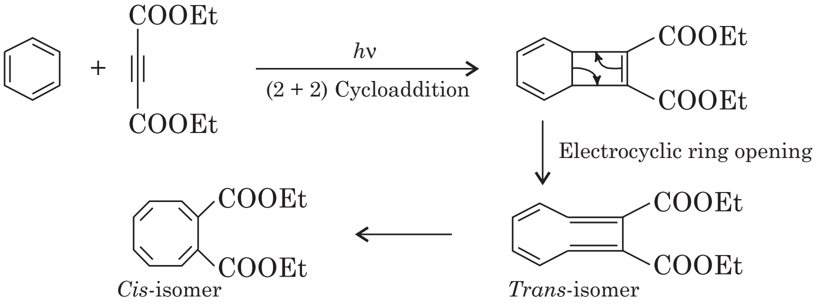
(*d*)



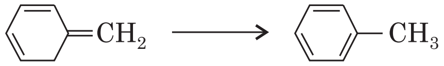
(*e*)



(*f*)

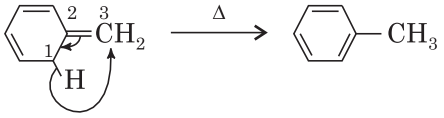


Problem 82: *The given compound (A) is extremely stable is spite of the fact that its rearrangement to toluene is energetically favoured. Explain why the rearrangement is so slow?*



(A)

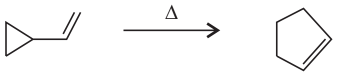
Solution:



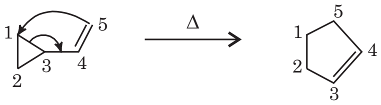
(A)

During the rearrangement 1, 3-sigmatropic shift of hydrogen is involved. The [1, 3] migration is allowed to take place only antarafacially but such a transition state would be extremely strain and geometrically not fissiable. Due to this reason process is slow.

Problem 83: *Vinyl substituted cyclopropanes undergo thermal rearrangement to yield cyclopentenes. Propose a mechanism for the reaction and identify the pericyclic process involved.*



Solution: This is degenerate Cope rearrangement. This rearrangement is given by *cis*-vinyl cyclopropanes. This rearrangement is not given by *trans* vinyl cyclopropanes. The mechanism of the transformation is as follows:



Problem 84: *What is difference between sigmatropic migration of hydrogen and alky or aryl groups?*

Solution. Hydrogen atom has its electron is a 1*s* orbital which has only one lobe. A carbone free radical (for imaginary transition state) has its odd electron in a *p*-orbital which has two lopes of opposite sign.

1, 5 Sigmatropic rearrangement

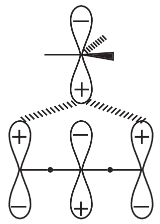
$$R—CH_2—CH{=}CH—CH = CH_2$$

$$\downarrow$$

$$R^{\bullet}$$

$$\dot{C}H_2—CH{=}CH—CH{=}CH_2$$

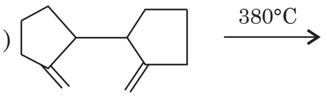
In thermal condition 1, 3-pentadiene free radical has *m*-symmetry.

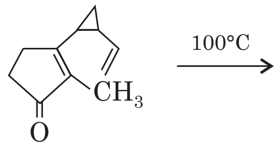


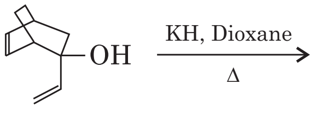
During thermal suprafacial [1, 5] process symmetry can be conserved only when the migrating carbon moves in a manner that the lobe which was originally attached to the π-system remains attached in TS.

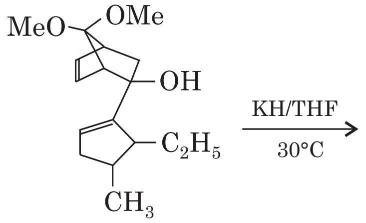
Thus a suprafacial [1, 5] thrmal rearrangement proceeds with retension of configuration at the migratory carbon.

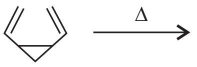
Problem 85: *Predict the product of each of the following reactions and also give name of the reactions:*

(*i*)


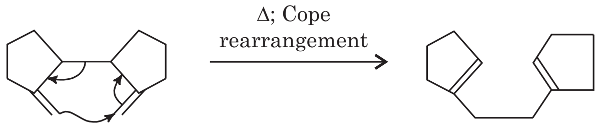
(*ii*)


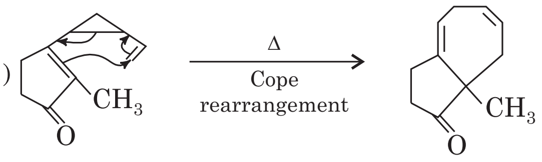
(*iii*)


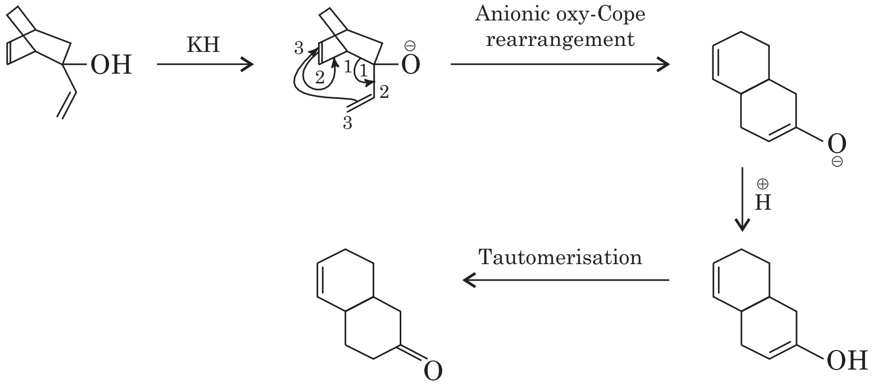
(*iv*)


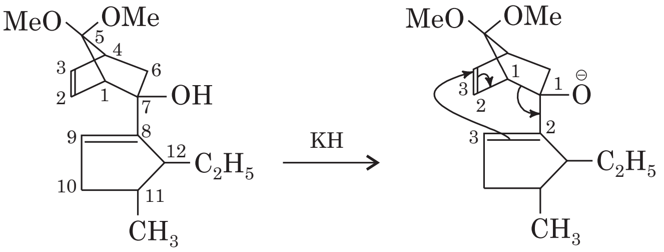
(*v*)


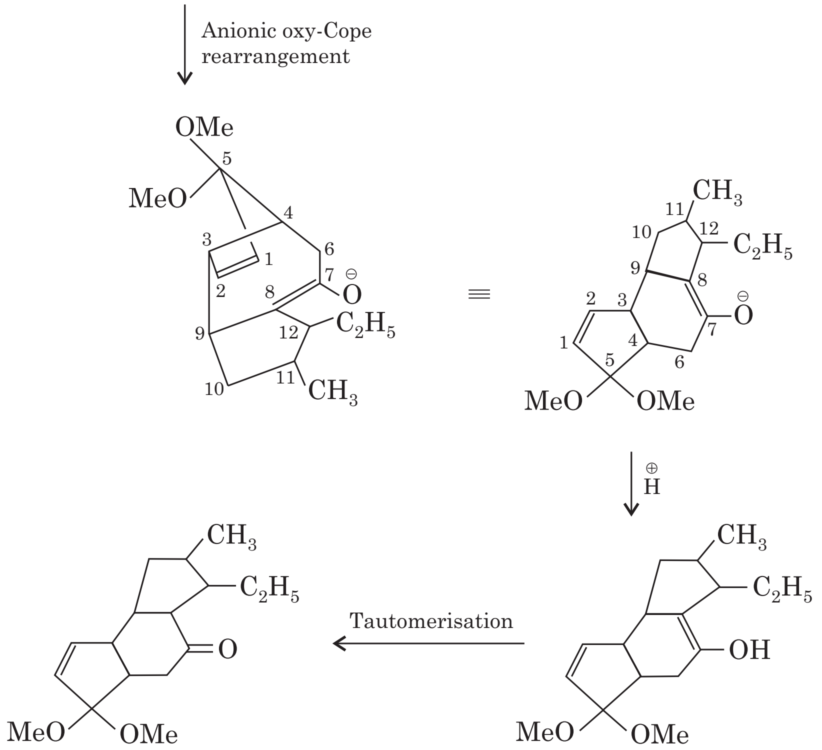
Solution: These problems are based on [3, 3] sigmatropic shift and reactions are Cope rearrangement.

(*i*)


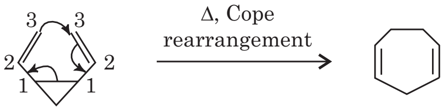
(*ii*)


(*iii*)


(*iv*)


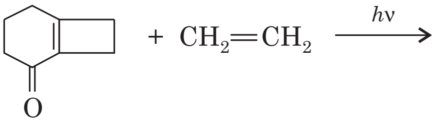


(v)

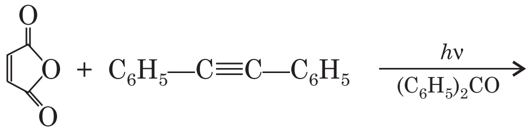


Problem 86: *Complete the following reactions:*

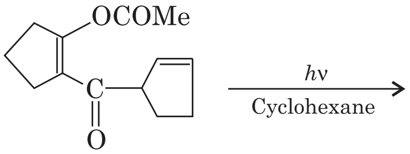
(i)



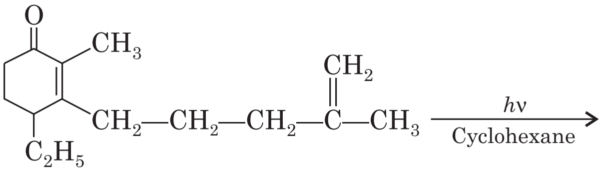
(ii)



(iii)

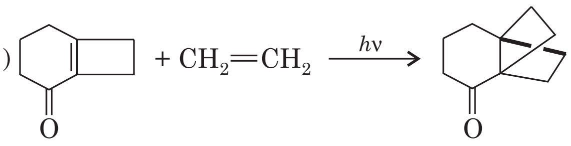


(iv)

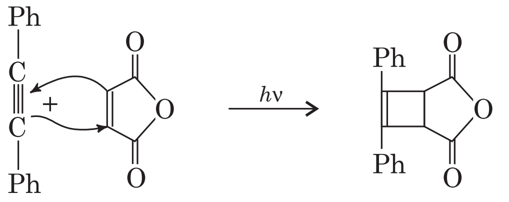


Solution: These problems are based on |2 + 2| cycloaddition reactions.

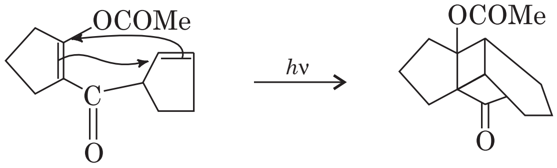
(*i*)



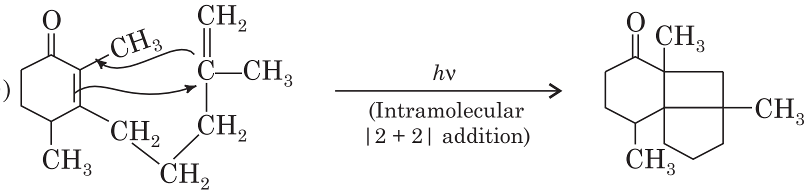
(*ii*)



(*iii*)

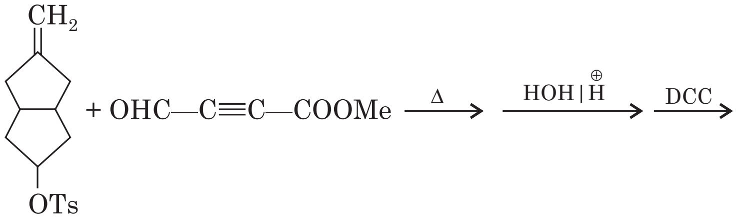


(*iv*)

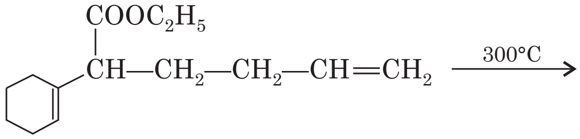


Problem 87: *Complete the following given reactions:*

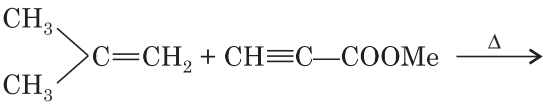
(*i*)



(*ii*)

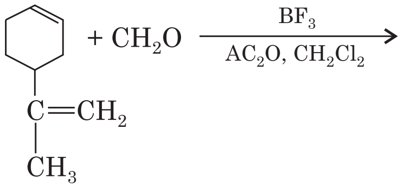


(*iii*)



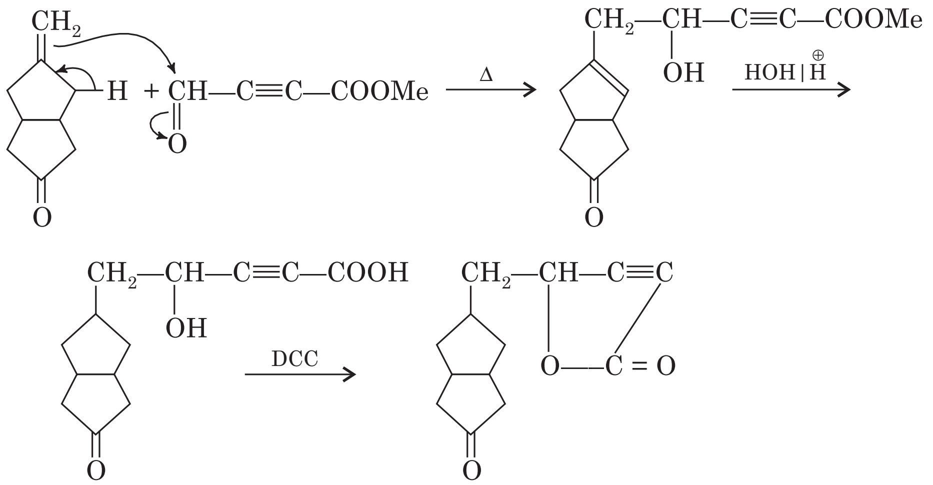
$$(CH_3)_2C{=}CH_2 + CH{\equiv}C{-}COOMe \xrightarrow{\Delta}$$

(*iv*)

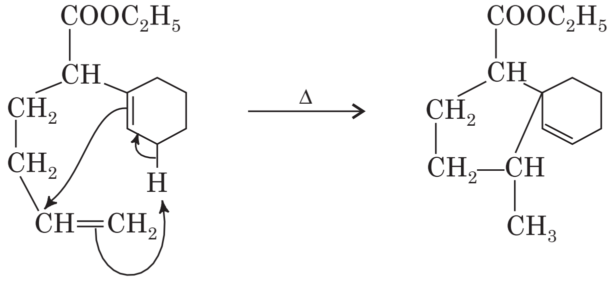


Solution: These problems are based on ene reaction.

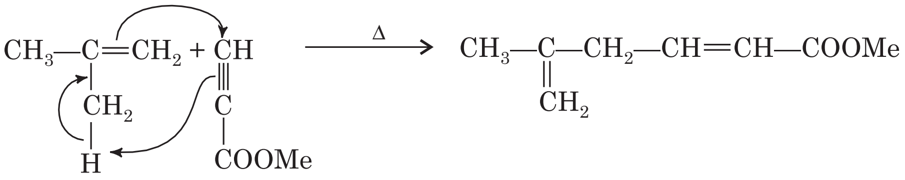
(*i*)



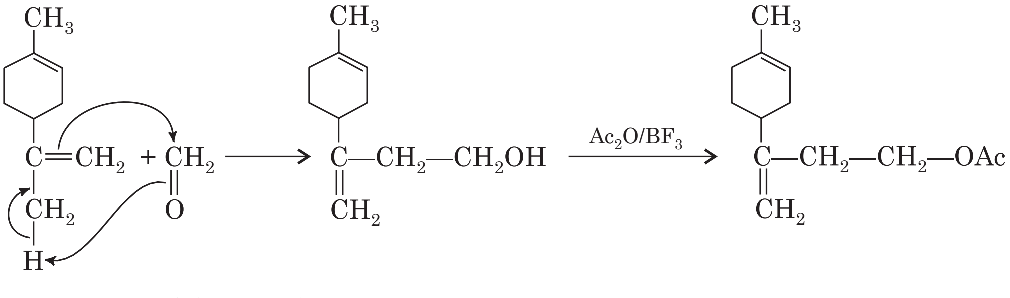
(*ii*)



(*iii*)



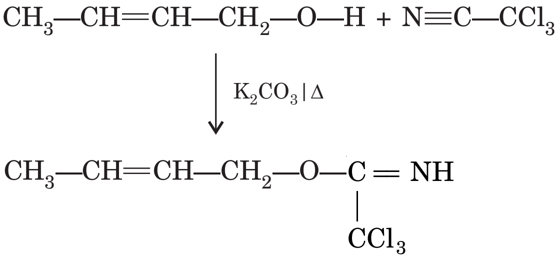
(*iv*)



Problem 88: *Identify (A) and (B) in the given reaction sequence:*

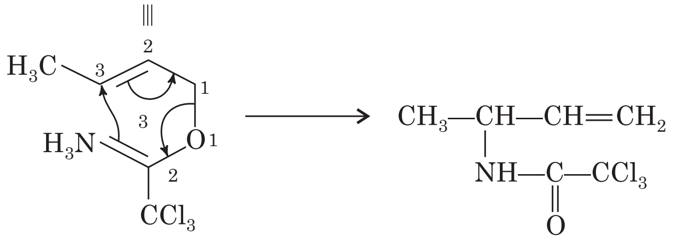
$$CH_3—CH{=}CH—CH_2OH + CCl_3—C{\equiv}N \xrightarrow[\Delta]{K_2CO_3} (A) \xrightarrow{\Delta} (B)$$

Solution: First step of the reaction is addition reaction between alcohol and cyanide to give an imine. The second step is [3, 3] sigmatropic rearrangement.



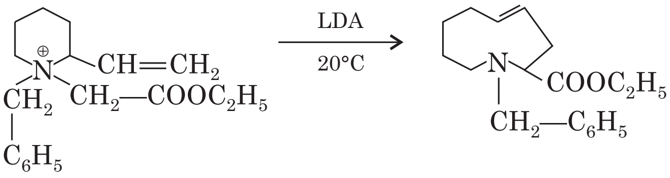
$$CH_3—CH{=}CH—CH_2—O—H + N{\equiv}C—CCl_3 \xrightarrow{K_2CO_3 \mid \Delta} CH_3—CH{=}CH—CH_2—O—\underset{\displaystyle CCl_3}{\underset{|}{C}}{=}NH$$

(A)

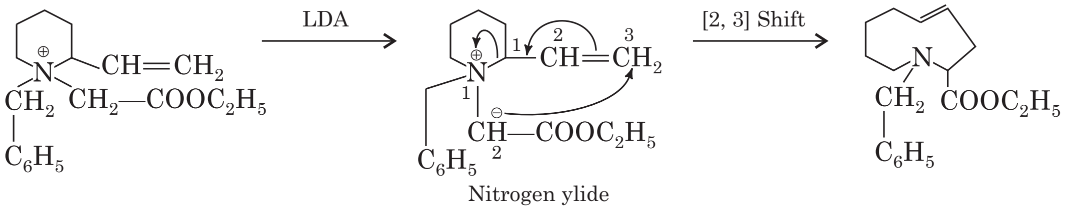


(B)

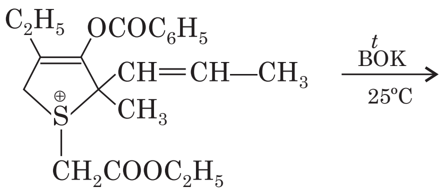
Problem 89: *Give mechanism of the given reaction:*



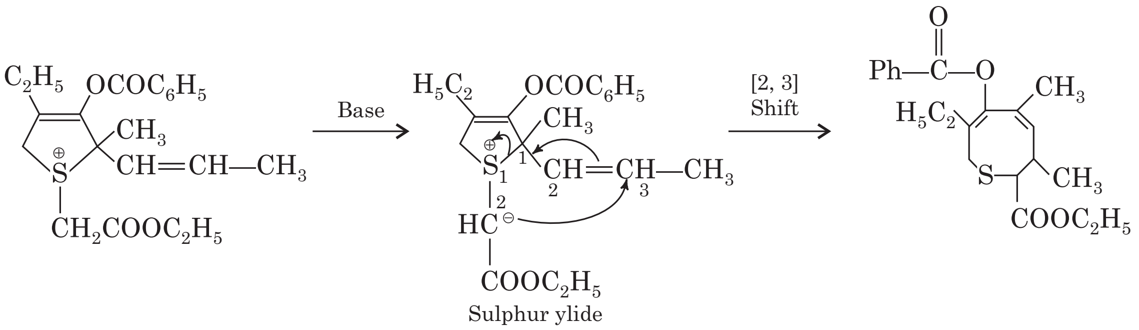
Solution: Mechanism of the reaction is as follows:



Problem 90: *Complete the given reaction and give its mechanism:*

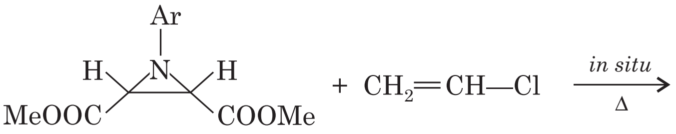


Solution:

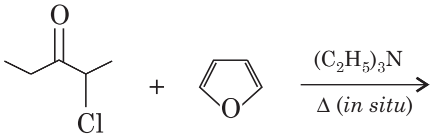


Problem 91: *Complete the given reactions:*

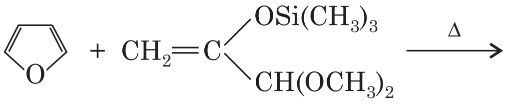
(*i*)



(*ii*)

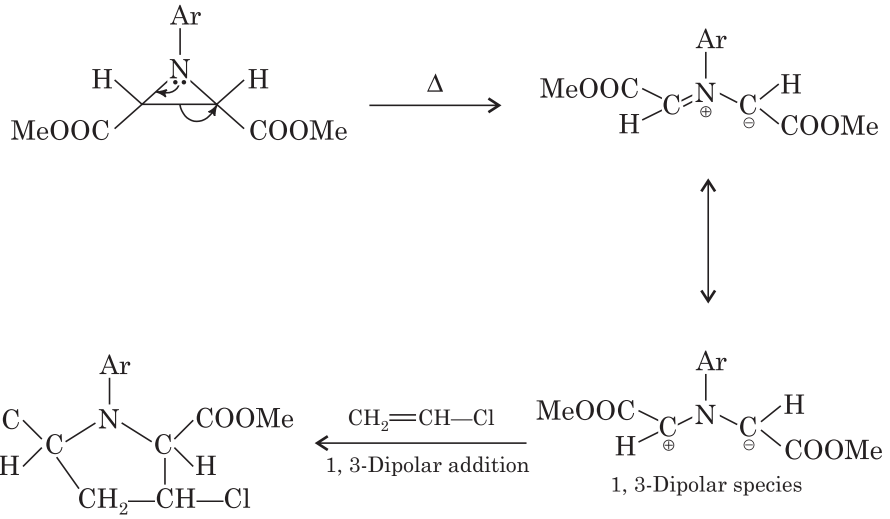


(*iii*)

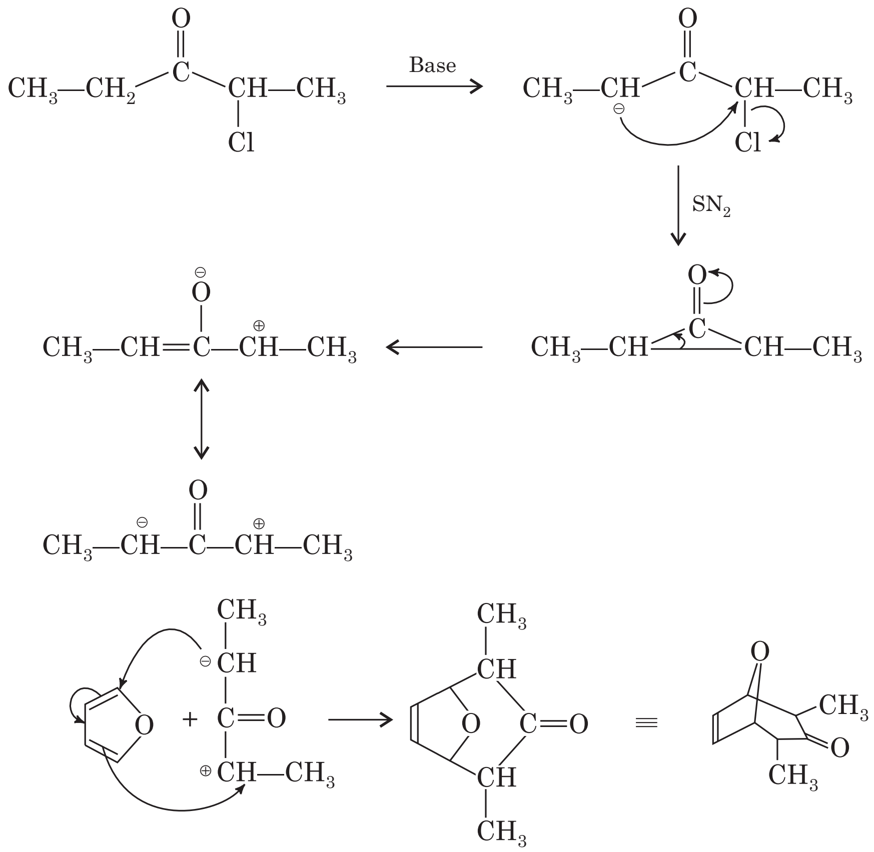


Solution: These problems are based on cycloaddition reactions

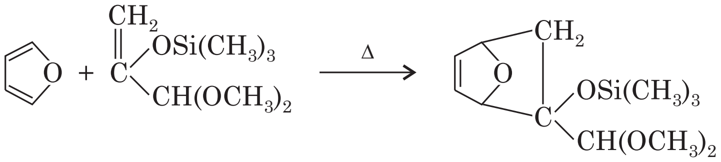
(*i*)



(*ii*)

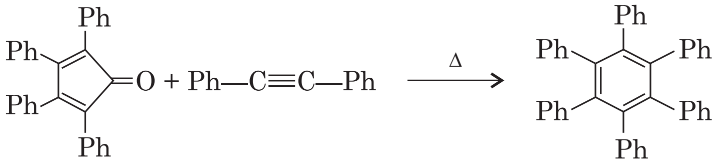


(*iii*)

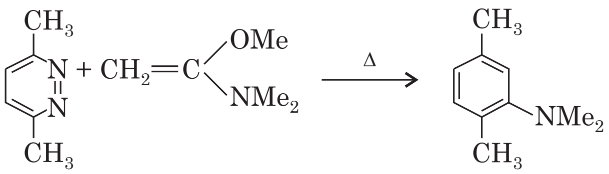


Problem 92: *Provide a mechanism for each of the following transformations:*

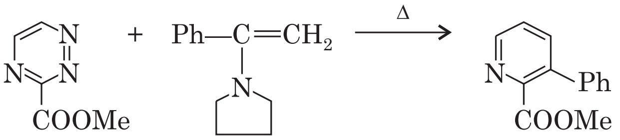
(*i*)



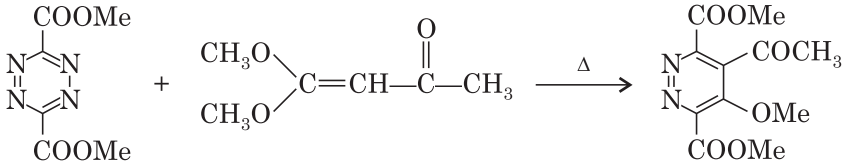
(*ii*)



(*iii*)

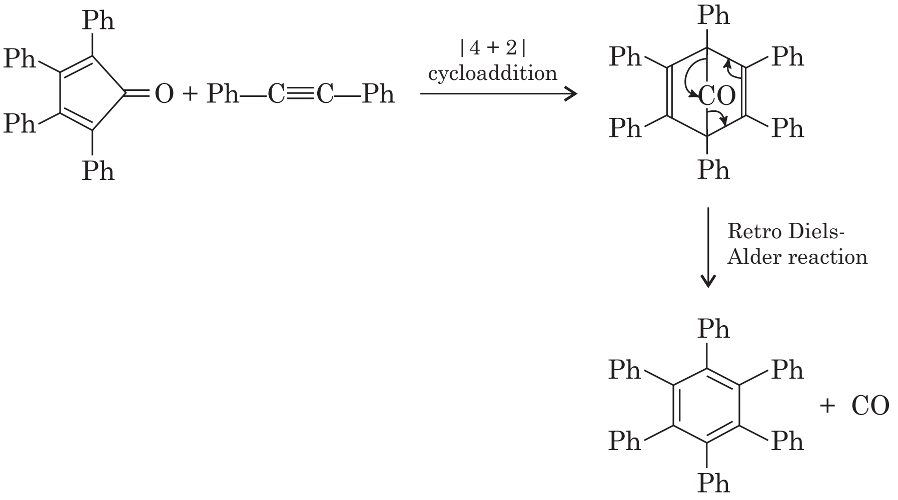


(*iv*)

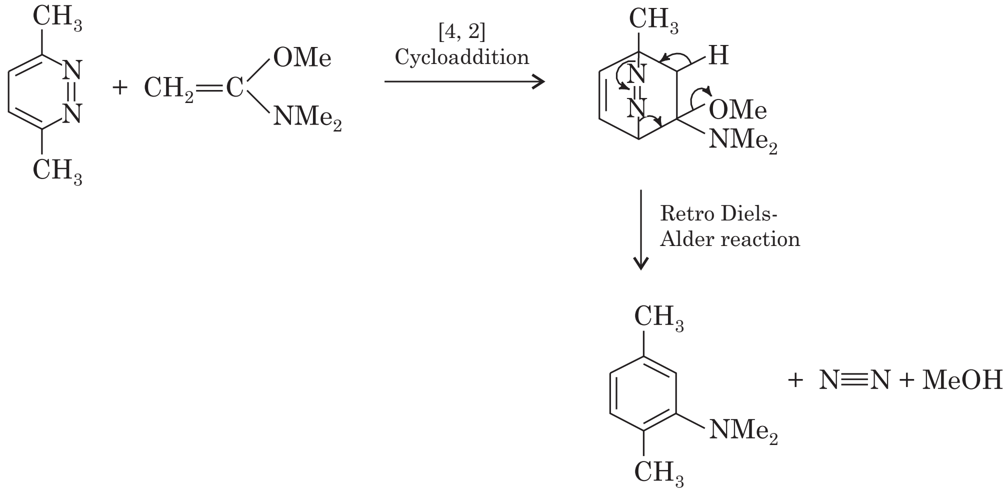


Solution:

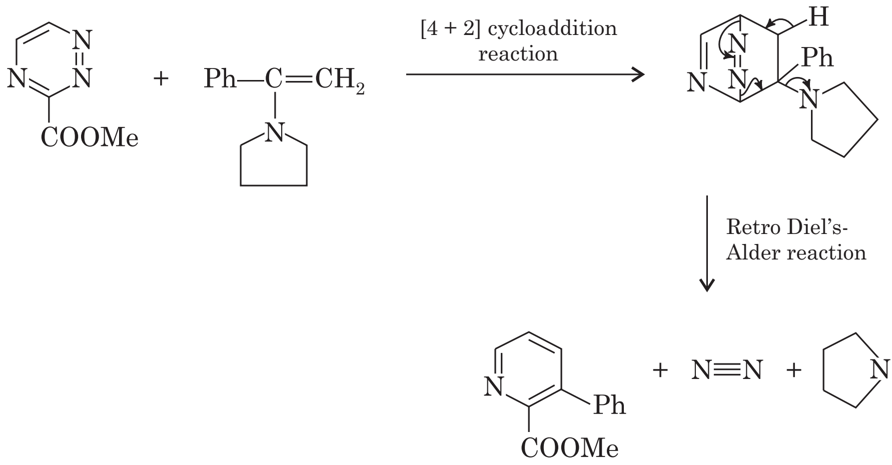
(*i*)



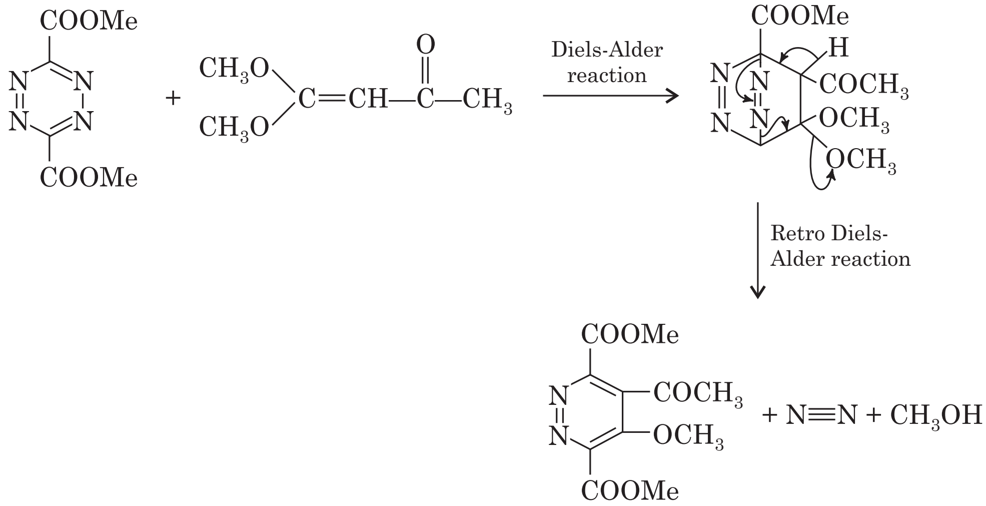
(*ii*)



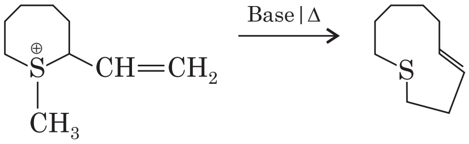
(*iii*)



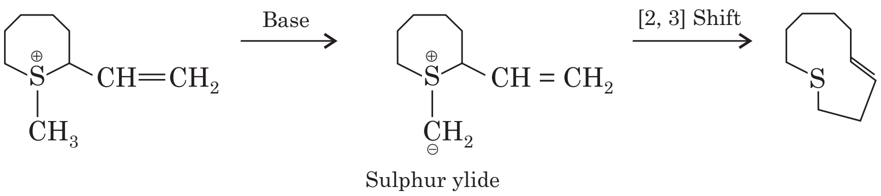
(*iv*)



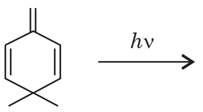
Problem 93: *Give possible mechanism for the given conversion:*

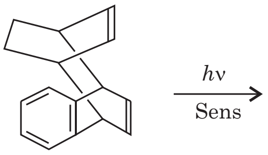


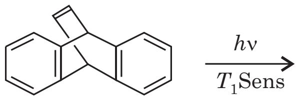
Solution: First step of the reaction is formation of sulphur ylide which undergoes [2, 3] sigmatropic rearrangement. Reaction takes place as follows:



Problem 94: *Complete the given reactions and give their mechanisms:*

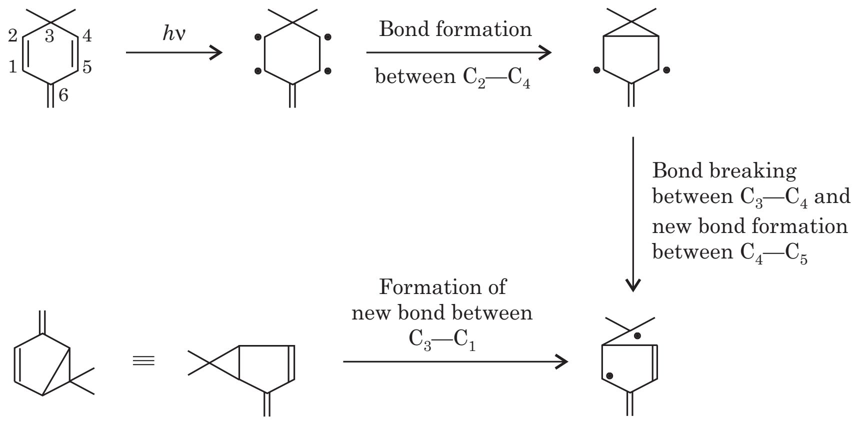
(*a*)


(*b*)


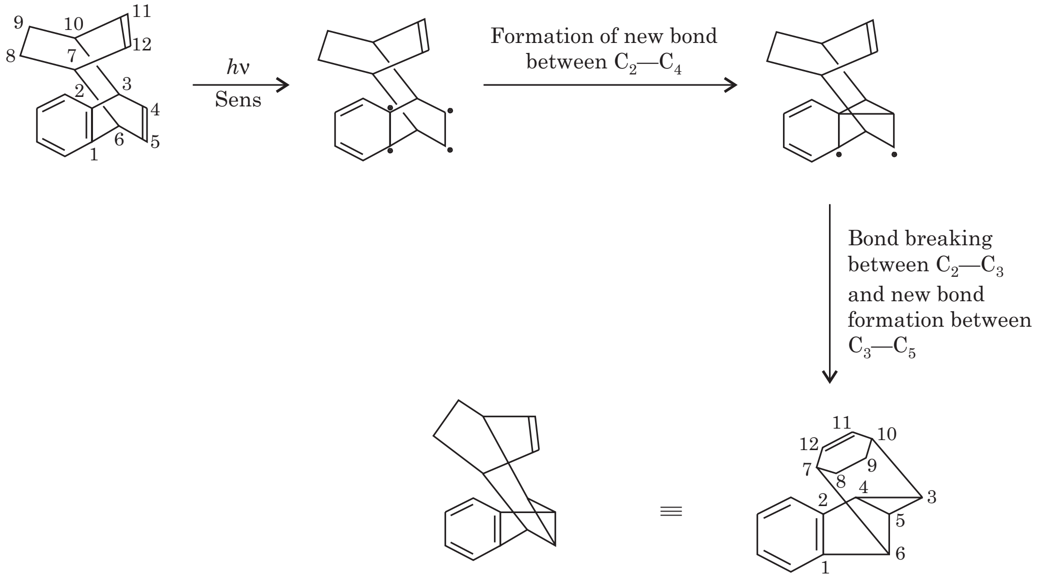
(*c*)


Solution:

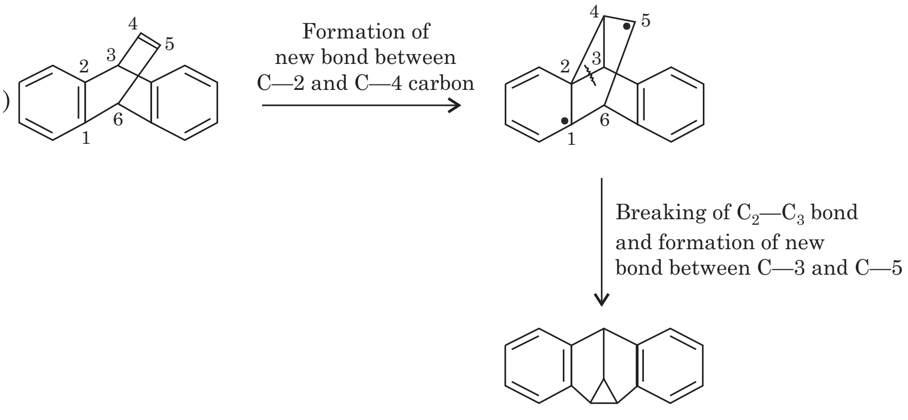
(*a*) This is an example of *Di*-π methane rearrangement which is given by 3-substituted 1, 4-diene.



(*b*) This is an example of *Di*-π methane rearrangement.

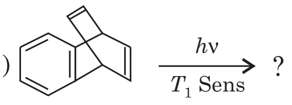


(*c*)

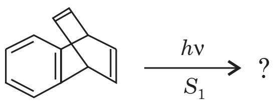


Problem 95: *Complete the following reaction:*

(*a*)

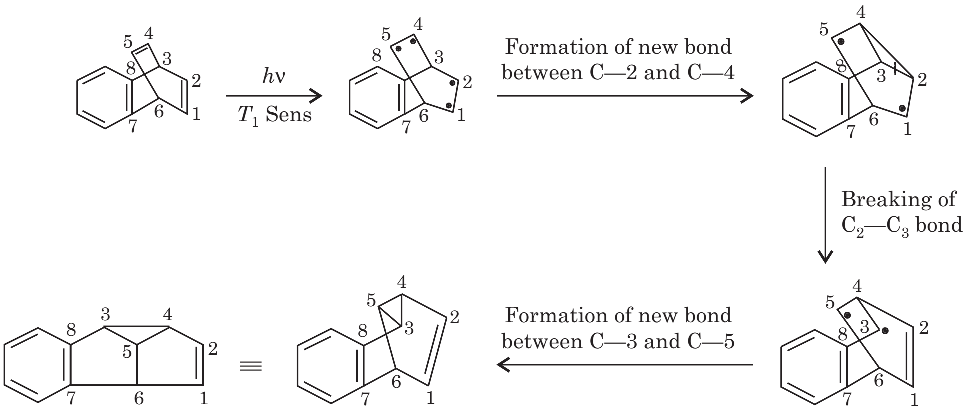


(*b*)

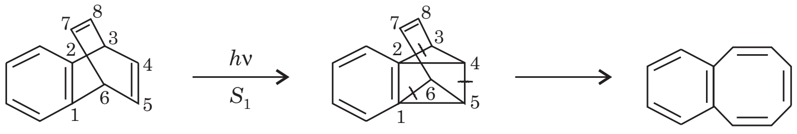


Solution:

(*a*) In presence of sensitiser this compound give *Di*-π-methane rearrangement by triplet state.



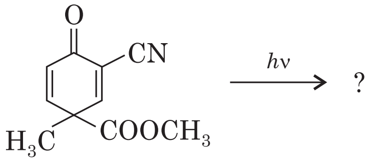
(*b*) In the absence of sensitizer this compound give bicyclic compound by singlet state.



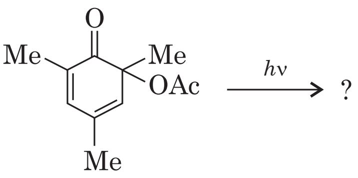
In absence of sensitized first 2 + 2 cycloaddition takes place followed by 3-bond breaks. Although this compound have 1, 4-diene system but in absence of sensitiser this does not give di-π-methane rearrangement. Instead of di-π-methane rearrangement this give 2 + 2 cycloaddition (*c.f.* – Prob. 95 – *a*).

Problem 96: *Give the product of following reactions:*

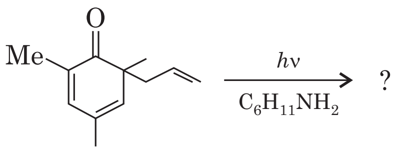
(*a*)



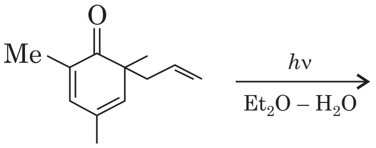
(*b*)



(*c*)

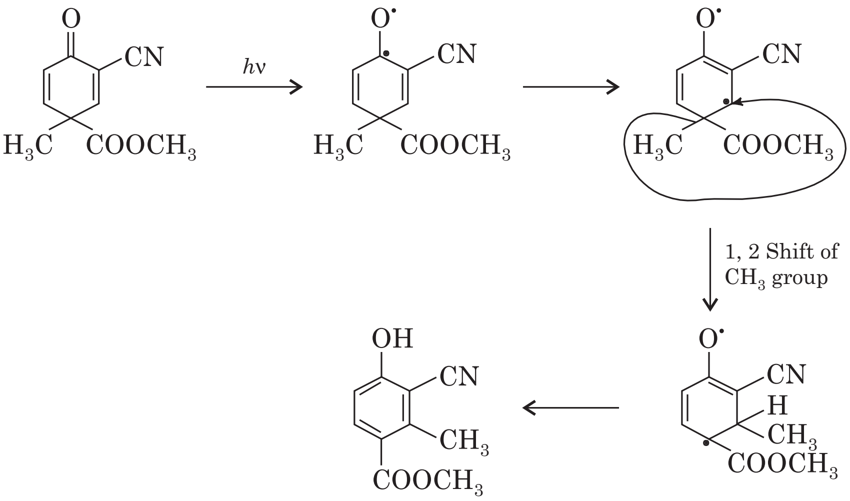


(*d*)

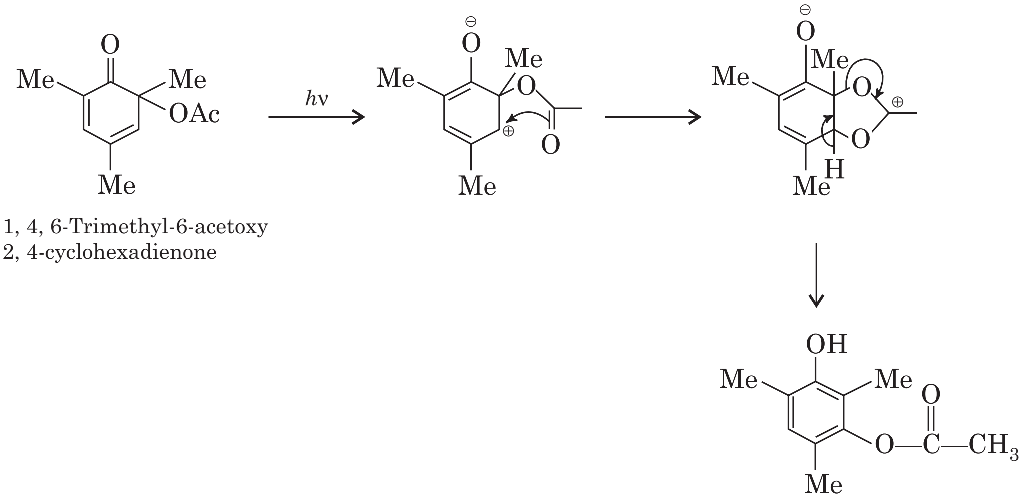


Solution:

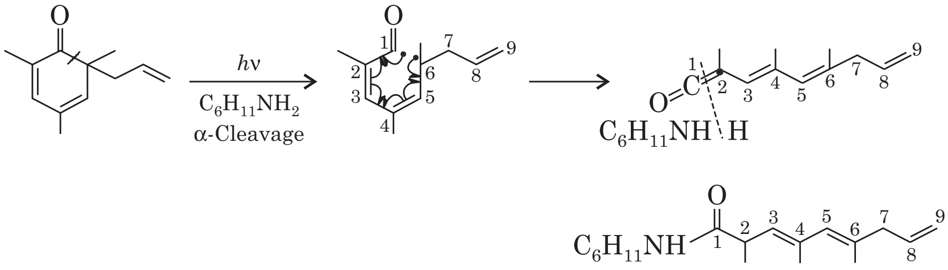
(*a*)



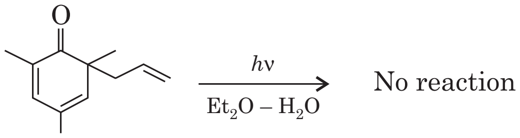
(*b*) The migration of an acetoxyl group to an adjacent carbon is a typical example of neighbouring group participation and is a characteristically *polar* process.


1, 4, 6-Trimethyl-6-acetoxy
2, 4-cyclohexadienone

(*c*) Irradiation of 2,4,6-trimethyl-6-allyl-2,4-cyclohexadienone in ether containing cyclohexoyl amine gives the expected α, β-unsaturated amide.

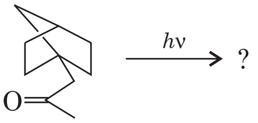


(*d*) When the above compound is irradiated in presence of mixture of ether and water there is no reaction.

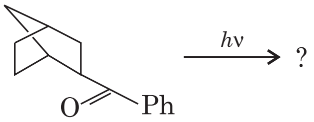


Problem 97: *Give the product of the following reactions:*

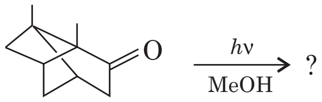
(*a*)



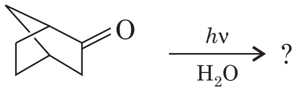
(*b*)



(*c*)

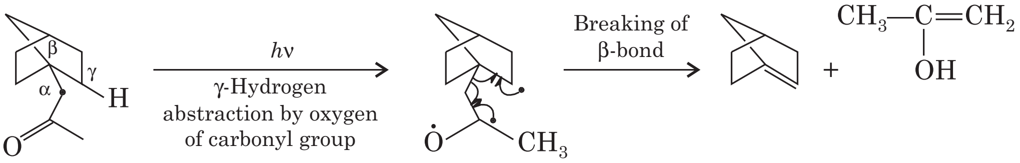


(*d*)



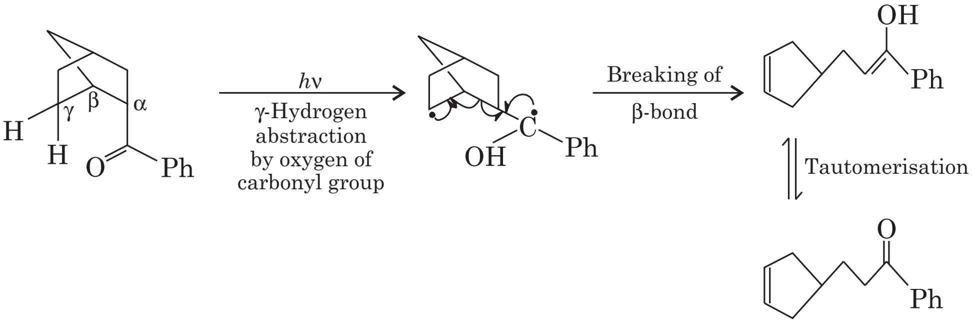
Solution:

(*a*)



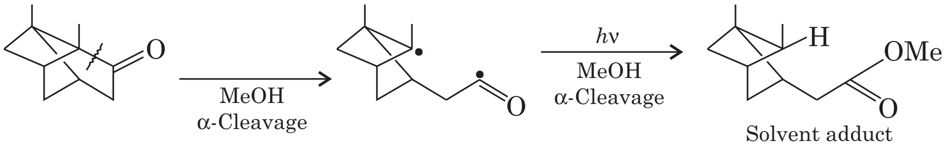
This is an example of Norish Type II reaction.

(*b*)

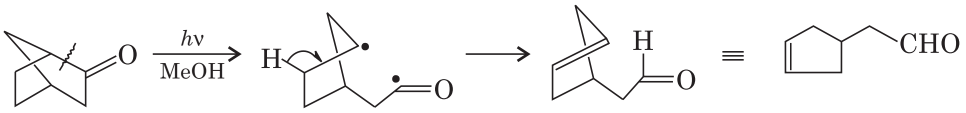


This is also an example of Norish type II reaction.

(*c*)

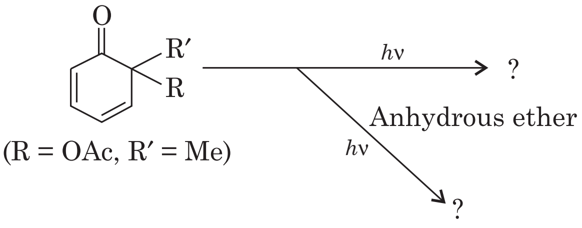


(*d*)

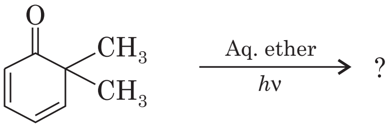


Problem 98: *Complete the following reactions:*

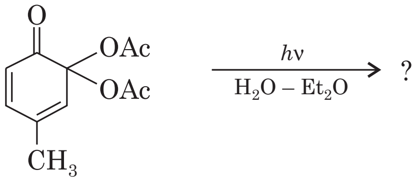
(*a*)



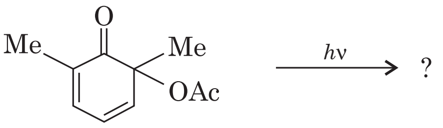
(*b*)



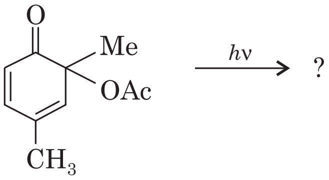
(*c*)



(*d*)

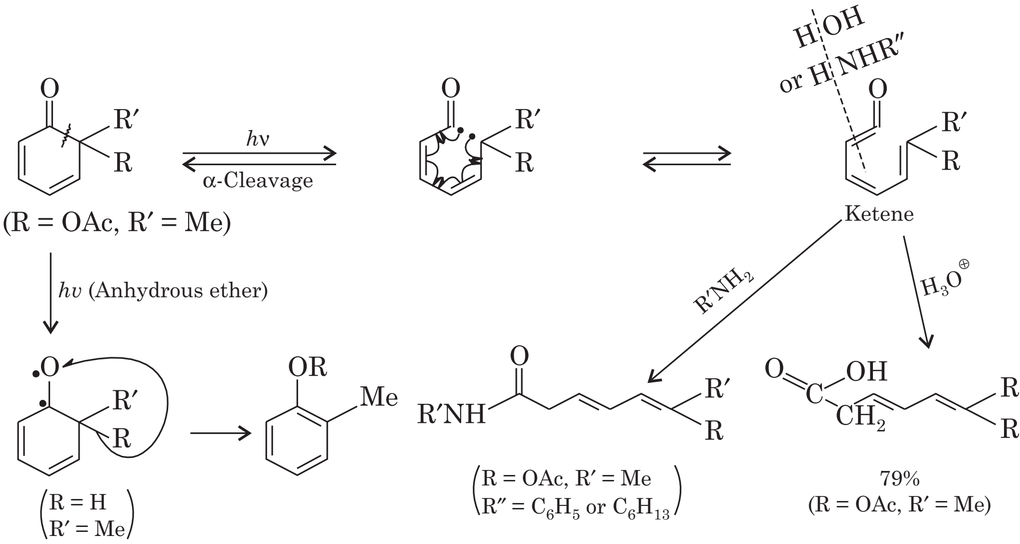


(*e*)

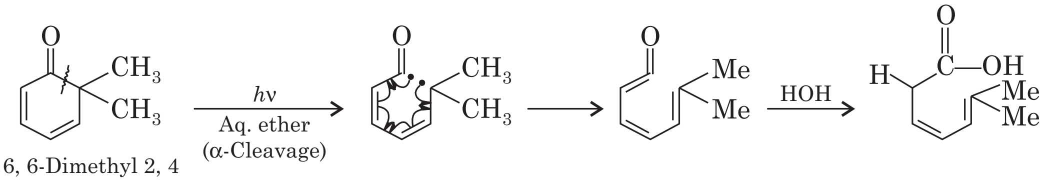


Solution:

(*a*)

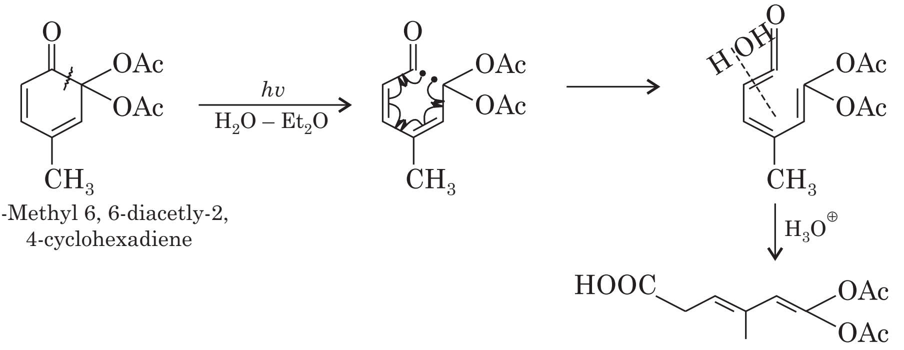


(b)



6, 6-Dimethyl 2, 4
cyclohexadiene

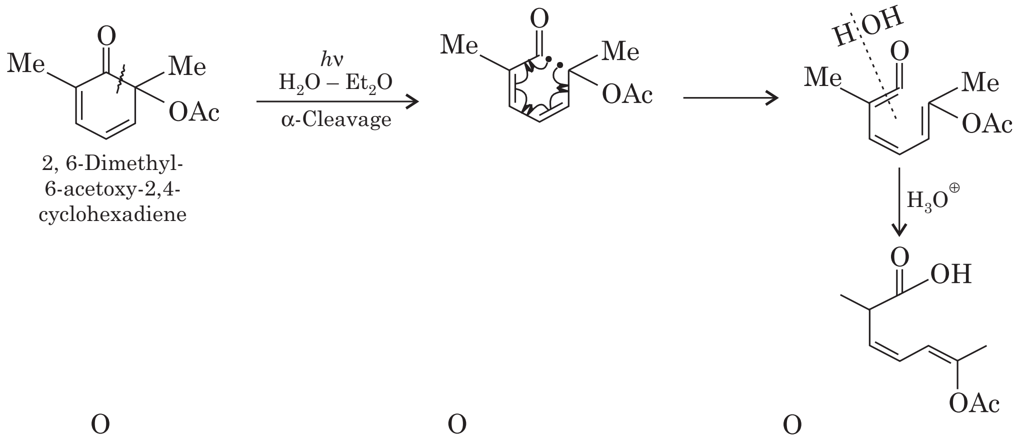
(c)



4-Methyl 6, 6-diacetly-2,
4-cyclohexadiene

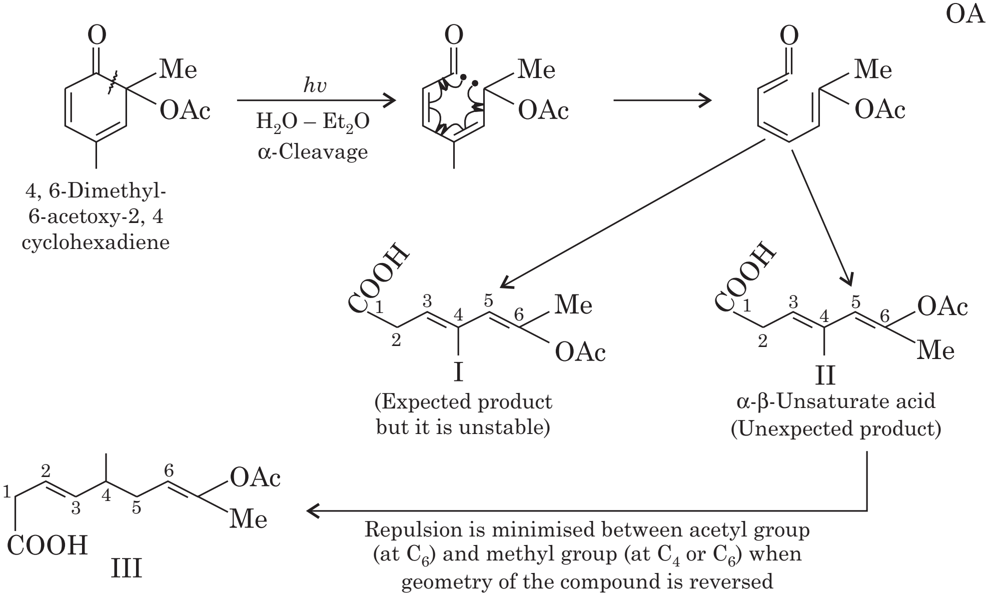
Diene acid

(d)



2, 6-Dimethyl-
6-acetoxy-2,4-
cyclohexadiene

(e)



4, 6-Dimethyl-
6-acetoxy-2, 4
cyclohexadiene

I
(Expected product
but it is unstable)

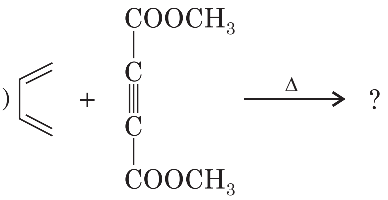
II
α-β-Unsaturate acid
(Unexpected product)

III

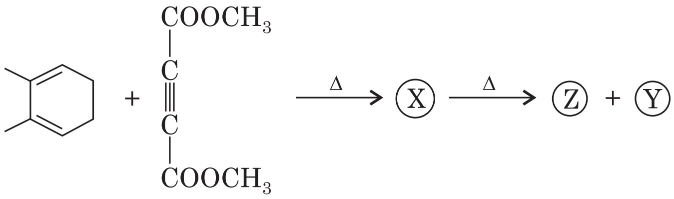
Repulsion is minimised between acetyl group
(at C_6) and methyl group (at C_4 or C_6) when
geometry of the compound is reversed

Problem 99: *Give the product of following reactions:*

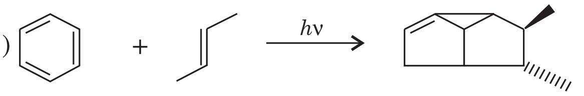
(*a*)



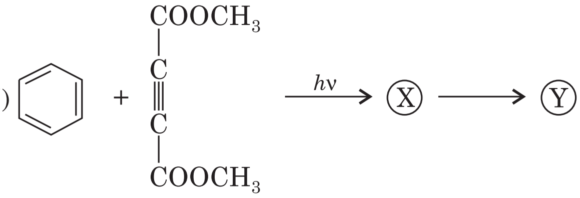
(*b*)



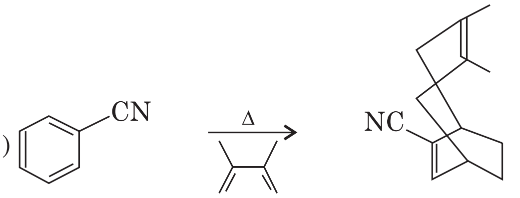
(*c*)



(*d*)

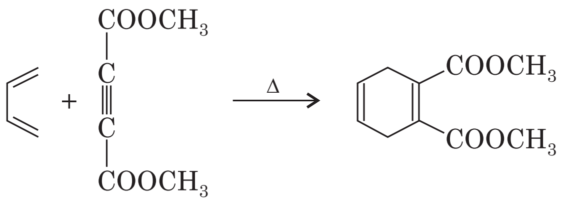


(*e*)

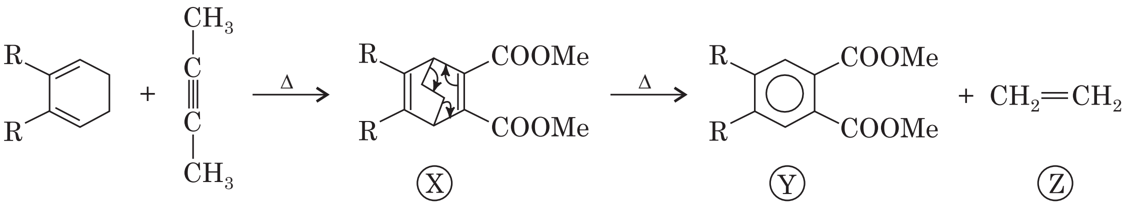


Solution:

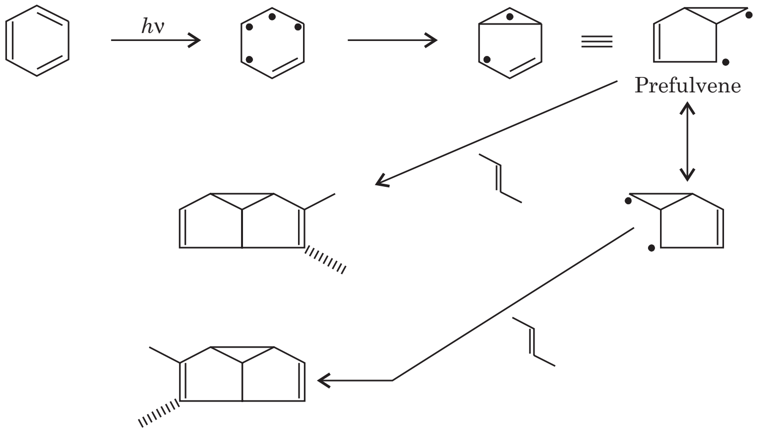
(*a*) This is | 2 + 4 | cycloaddition reaction

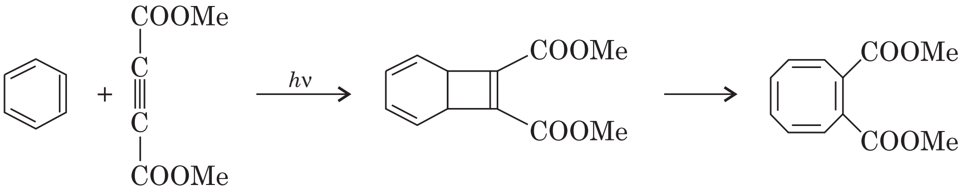


(*b*) This is also | 2 + 4 | cycloaddition reaction followed by aromatization by removal of ethylene molecule.



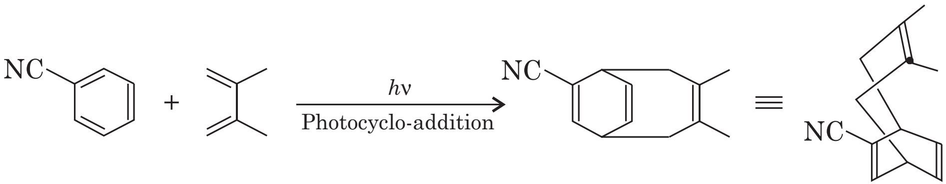
(*c*) This is example of 1, 3-photoaddition of benzene to form tricyclic system. This reaction is restricted to double bond bearing only alkyl substituent such as but-2-ene, nonbornene, alkene and cyclobutene. A biradical "Prefulvene" is precursor of this reaction.



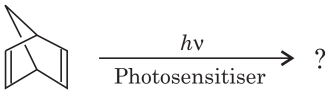
(*d*)


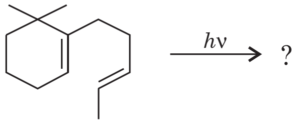
The above sequence of reactions are |2 + 2| photocycloaddition reaction followed by ring expansion.

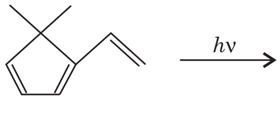
(*e*) This is special type of reaction in which |4 + 4| photocyclo addition reaction takes place.

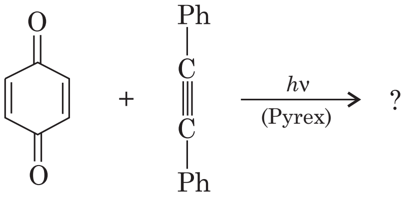


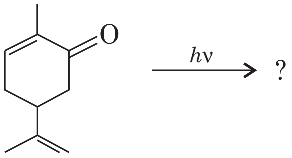
Problem 100: *Complete the following reactions:*

(*a*)


(*b*)


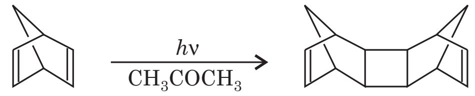
(*c*)


(*d*)


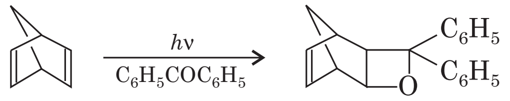
(*e*)


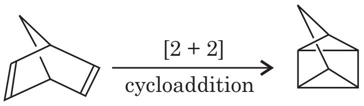
Solution:

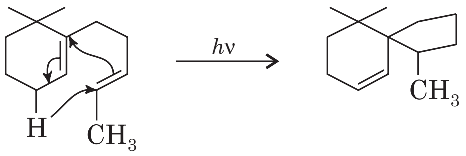
(*a*) If triplete excitation energy of ketone-acetone (sensitizer) is greater than triplet excitation of alkene, dimerisation takes place.



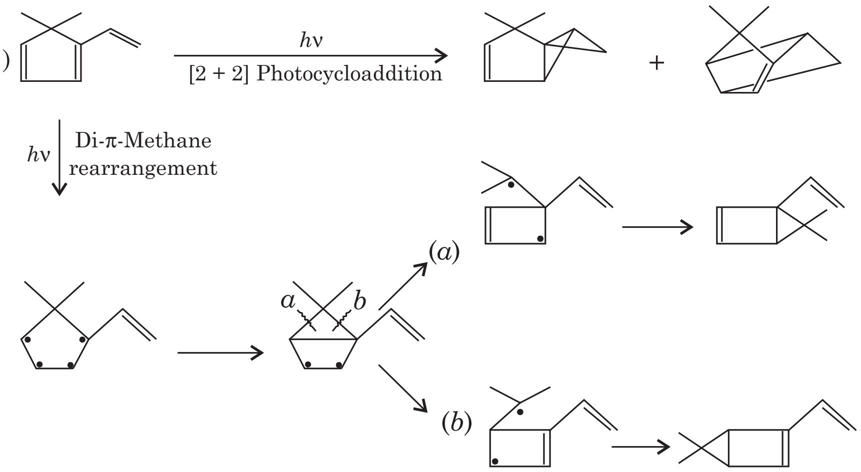
However, when ketone (sensitiser = benzopheonone) having less triplet energy than alkene, oxetane formation takes place.

(*i*)


(*ii*)


(*b*)


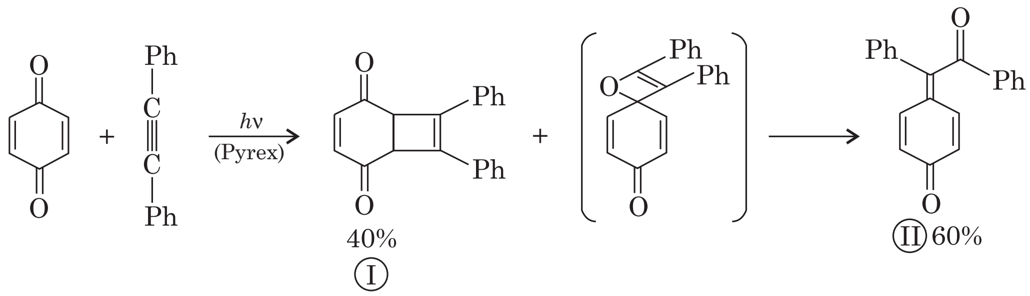
This is example of ene reaction

(*c*)


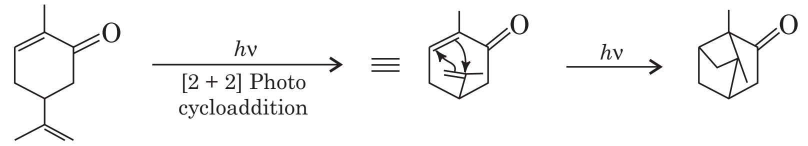
(*d*) In this example two types of [2 + 2] photocycloaddition reaction takes place.

(*i*) [2 + 2] photocycloaddition reaction between C≡C and C═C and formed Ⓘ.

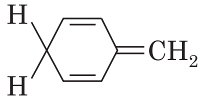
(*ii*) [2 + 2] photocycloaddition reaction between C≡C and C═O, followed by ring opening reaction to form compound (II) in 60% yield.

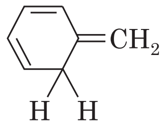


(*e*) When carvone is irradiated to photolysis [2 + 2] photocycloaddition reaction takes place.



Problem 101: *Consider the following two isomeric compounds (A) and (B) whose structures are given below:*





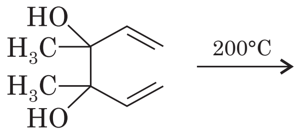
(A) (B)

Compound (A) on heating readily converts into toluene but (B) does not. Explain this observation.

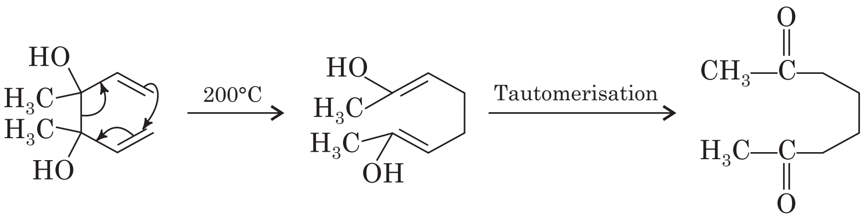
Solution: (A) gives [1, 5] sigmatropic rearrangement which is thermally allowed. Therefore reaction will proceed readily. Compound (B) can only be converted into toluene if reaction is [1, 3] sigmatropic rearrangement. [1, 3] Sigmatropic rearrangement is thermally allowed but geometrically not possible.

Hence reaction does not take place.

Problem 102: *Complete the given reaction and give its name:*



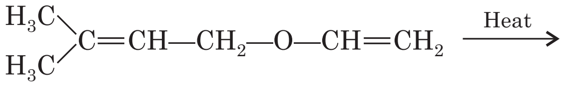
Solution: The reaction is [3,3] sigmatropic rearrangement *i.e., Cope rearrangement.*



Substrate of *Cope rearrangement* is derivative of allyl alcohol, therefore this Cope rearrangement is known as Oxy-Cope rearrangement.

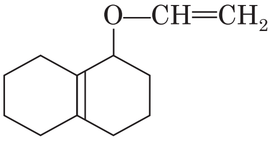
Problem 103: *Complete the following reactions:*

(*a*)



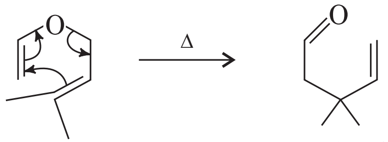
$$(H_3C)_2C{=}CH{-}CH_2{-}O{-}CH{=}CH_2 \xrightarrow{\text{Heat}}$$

(*b*)



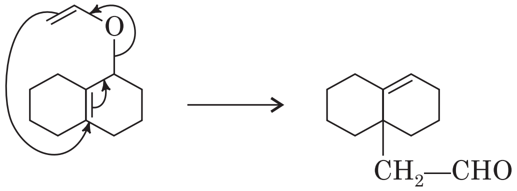
Solution:

(*a*) The substrate is allyl vinyl ether therefore reaction will be **Claisen rearrangement.**

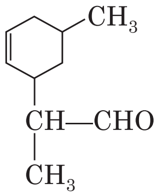


3, 3-Dimethyl-
4-pentenal

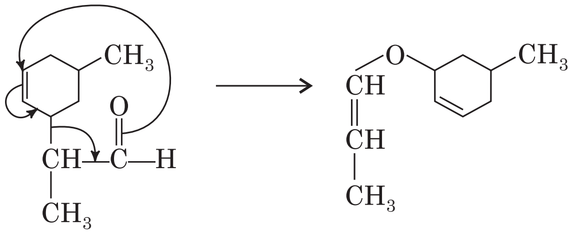
(*b*) The substrate is allyl vinyl ether therefore, the reaction is aliphatic **Claisen rearrangement.**



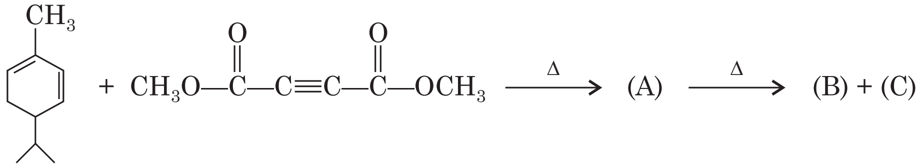
Problem 104: *What starting material would give the following compound in an aliphatic* ***Claisen rearrangement:***



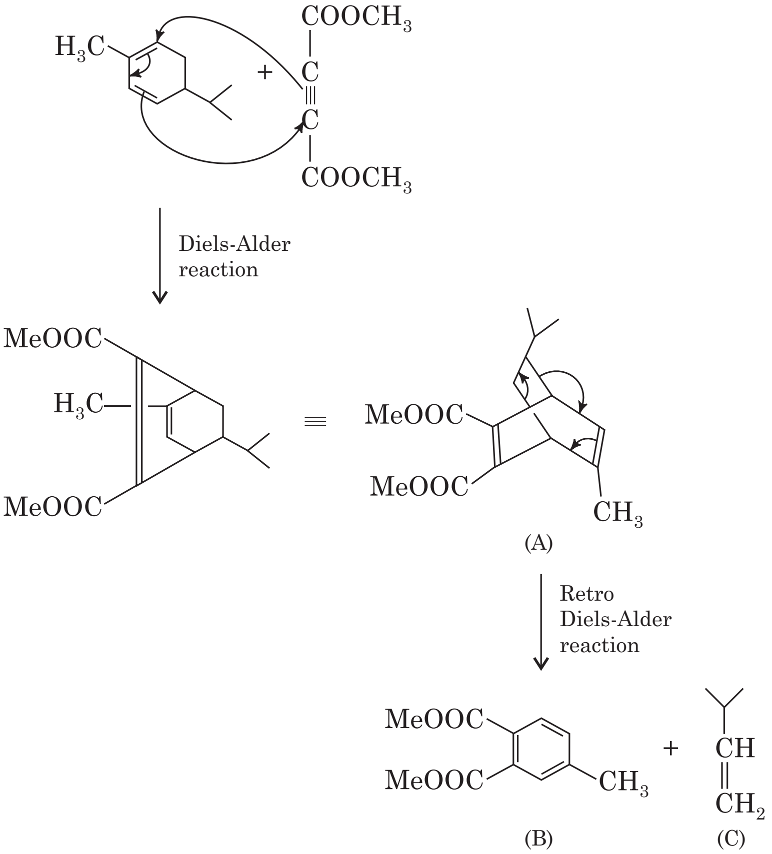
Solution: Deduce the starting material by drawing the curved arrows for the reverse of a **Claisen rearrangement:**



Problem 105: *Complete the following reaction:*

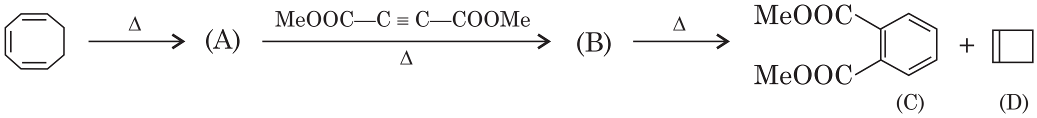


Solution: The first step is Diels-Alder addition reaction and second step is retro Diels-Alder addition.

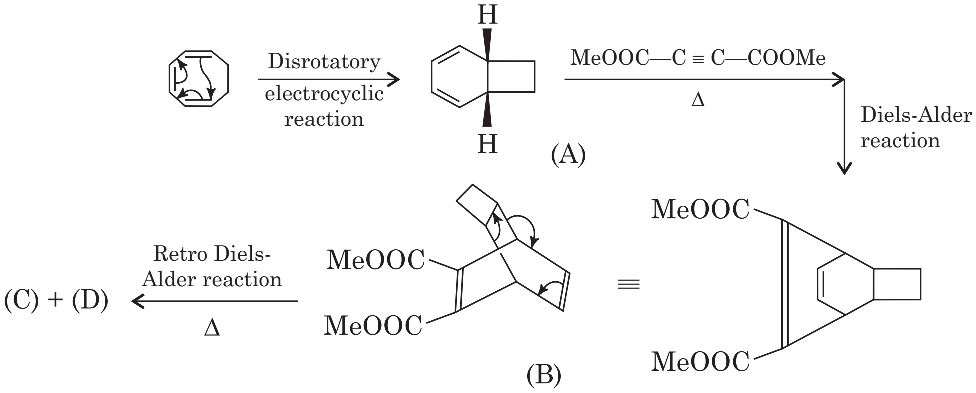


The driving force for the retro Diels-Alder reaction is formation of a product that is stabilised by aromaticity.

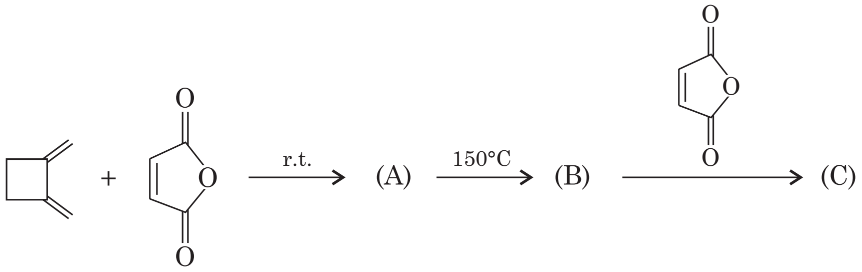
Problem 106: *Identify (A) and (B) in the given reaction sequence:*



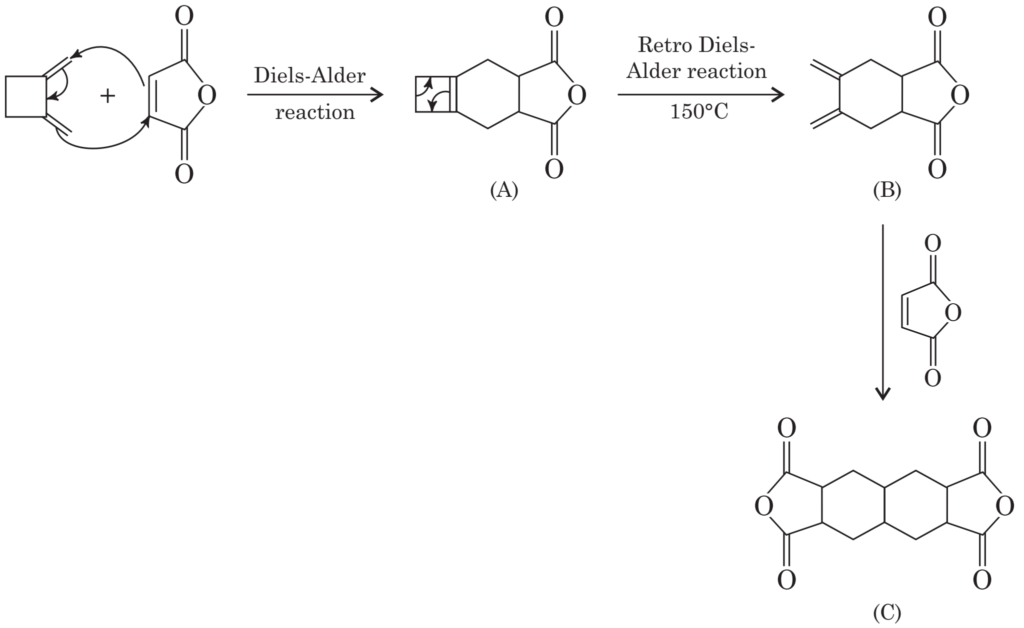
Solution:



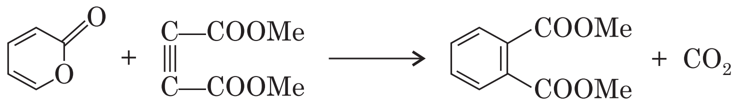
Problem 107: *Give the stereochemical structure of the products in the following reactions:*



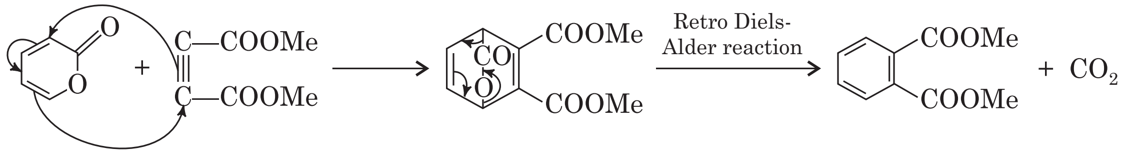
Solution:



Problem 108: *Propose a mechanism for following transformation:*

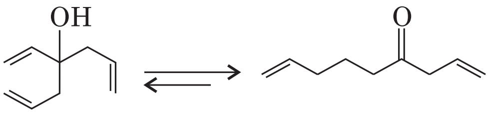


Solution:

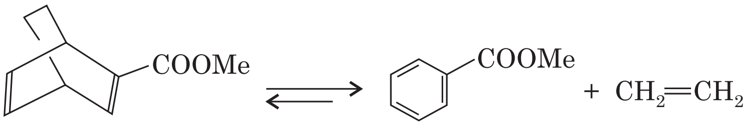


Problem 109: *What do the pericyclic selection rules have to say about the position of equilibrium in each of the following reactions ? Which side of each equilibrium is favoured and why:*

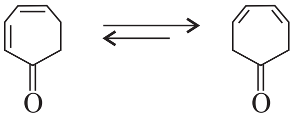
(*a*)



(*b*)



(*c*)



Solution:

(*a*) The right side of equation is favoured at equilibrium because a C = O double bond is formed at the expense of C═C double bond. C═O Double bond is stronger than C═C double bond.

(*b*) The right side of the equation is favoured at equilibrium because one product is aromatic and therefore highly stable.

(*c*) The left side of the equation is favoured at equilibrium because three double bonds are in conjugation to each other.

Index