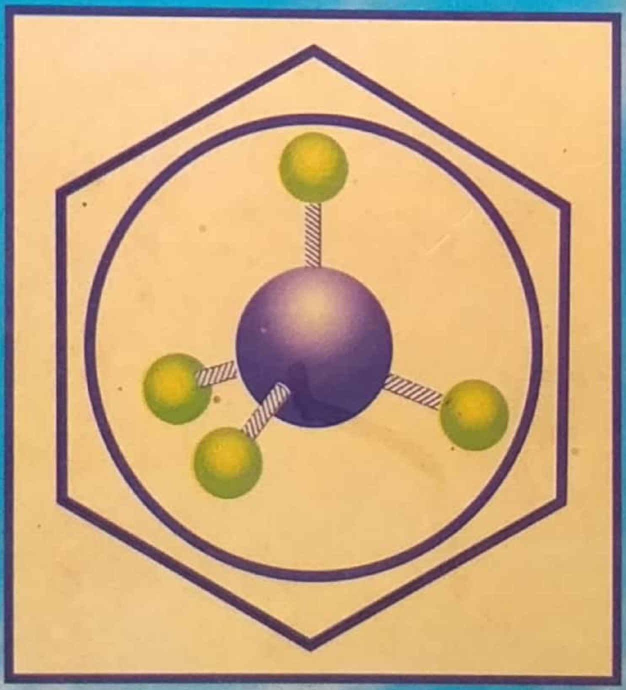
A Solution Manual
TO THE TEXTBOOK OF
ORGANIC CHEMISTRY



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CONTENTS

orbitals, whereas the energy of the nonbonding orbital is equal to the average energy of the atomic orbitals.

Orbital Hybridization

It is the process which involves mixing of different types of atomic orbitals, e.g., *s* and *p* (one or more), of an atom to form new equivalent (degenerate) atomic orbitals known as **hybrid orbitals.** The process of hybridization ends up with as many hybrid orbitals as the atomic orbitals to start with, e.g., an *s* and a *p* orbitals result in two *sp* hybrid orbitals, whereas an *s* and two *p* orbitals result in there sp^2 hybrid orbitals, and an *s* and three *p* orbitals result in four sp^3 hybrid orbitals.

Bond Angle

It is the angle subtended by two bonds at the common atom, and depends largely on the nature of hybridization of the atom, e.g., the angle between the two bonds at an *sp* hybridized carbon atom is 180°, whereas that at an sp^2 carbon atom is 120°, and at an sp^3 carbon atom is 109.5°, the angle between pure *p* orbitals is 90°.

Bond Length

It is the mean distance between the nuclei of two bonded atoms. A triple bond between two atoms is shorter than a double bond which is shorter than a single bond between the same two atoms. Furthermore, the bond length between two atoms decreases as the difference in their electronegativities increases.

Bond Energy

It is the energy required to break a bond. Generally, the bond strength increases (more energy is required to break it) as the *s* character increases. Moreover, shorter bonds are stronger bonds. Thus, the double bonds are stronger than the corresponding single bonds but not twice as strong because π overlap is less than σ overlap. This means that a σ bond is stronger than a π bond. Total energy of a molecule is approximately equal to the sum of its individual bond energies.

Covalent Bonds with Ionic Character

A covalent bond between atoms of different electronegativities has some ionic character and is polar in nature. The ionic character of a covalent bond, A—B, can be determined from the electronegativity difference between the bonded atoms A and B using the following relationship:

$$\%\ \text{ionic character} = 16(X_A - X_B) + 3.5(X_A - X_B)$$

where X_A and X_B are the electronegativities of the atoms A and B, respectively.

Inductive Effect

It is the polarization of a bond induced by an adjacent polar bond. It operates through σ bonds and decreases rapidly with distance; it is hardly felt on a bond four bonds away. The concept of inductive effect is very useful for explaining or predicting the behavior of organic compounds.

A closely related effect is the field effect which is an electrostatic effect (attractive or repulsive) acting through space, and which also decreases with the distance.

Dipole Moment

The dipole moment (μ) of a polar molecule is the product of the distance (*d*) between the centres of gravity of the positive and the negative charges, and the charge (*q*) at either centre, i.e.,

$$\mu = q \times d$$

The unit of dipole moment is Debye (D) where ID = 10^{-18} esu.cm. The dipole moment of a molecule is the vectorial sum of the individual bond moments, and usually affords information about the geometry of the molecule.

ANSWERS TO EXERCISES

1\. (a)

Electron	*n*	*l*	*m*	*s*	*orbital*
1	1	0	0	+½	*1s*
2	1	0	0	−½	*1s*
3	2	0	0	+½	*2s*
4	2	0	0	−½	*2s*
5	2	1	+1	+½	$2p_x$
6	2	1	−1	+½	$2p_y$

(b) The orbitals associated with $n = 4$ and $l = 3$ fall in the subshell *4f* which has seven differently oriented *f* orbitals each of which can accommodate two electrons. Thus, the number of different electrons (having different sets of quantum numbers) possible in this subshell is 14.

2\. The overlapping power of a directional orbital (e.g., *p* orbital) is greater than that of a non-directional orbital (e.g., *s* orbital). Furthermore, the overlapping lobe of an *sp* orbital is larger than that of an sp^2 orbital which in turn is larger than that of an sp^3 orbital. Thus, the overlapping power of various orbitals decreases in the order.

$$sp > sp^2 > sp^3 > p > s$$

3\. All angles between sp^3 orbitals are 109.5° or nearly so; the angles between sp^2 orbitals are 120°, and those between *sp* orbitals are 180°.

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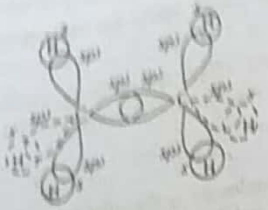

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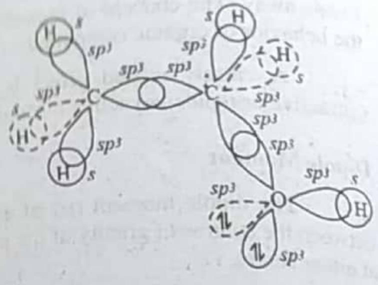

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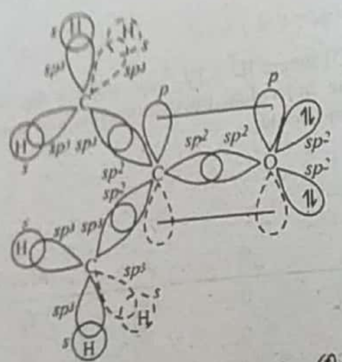

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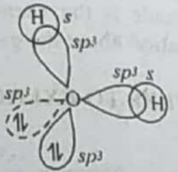

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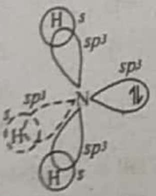

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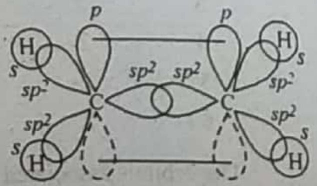

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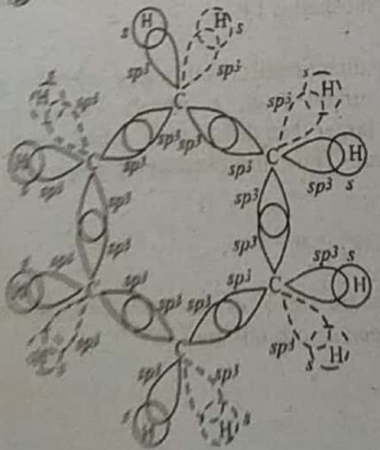

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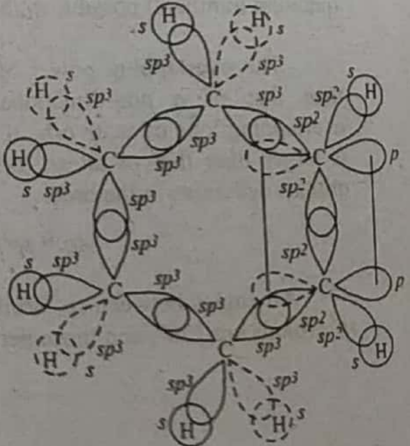

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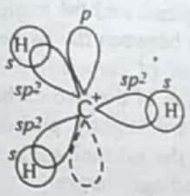

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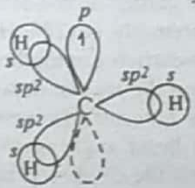

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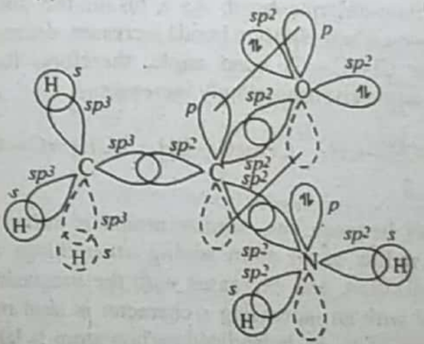

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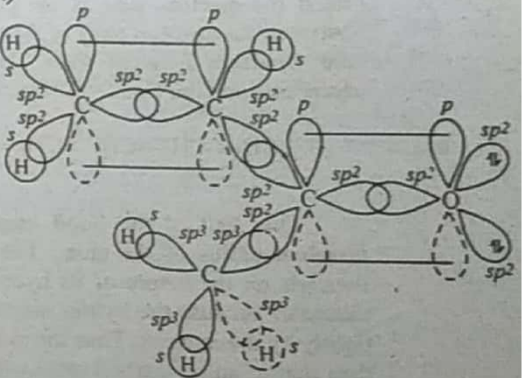

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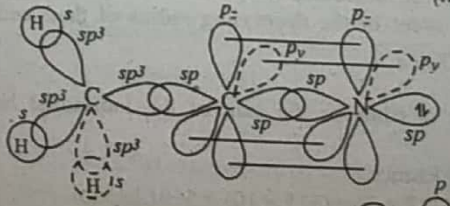

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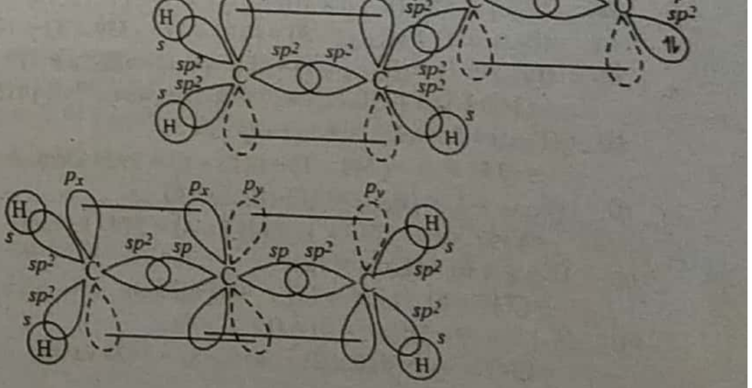


The middle carbon atom is *sp* hybridized like a carbon atom of acetylene. So, the middle carbon has the acetylenic character.

5. The carbon atoms of ethylene are sp^2 hybridized, and the angle between sp^2 orbitals normally is 120°. However, the repulsion between the two electron pairs of carbon-carbon double bond and an electron pair of carbon-hydrogen bond is greater than the repulsion between the electron pairs of the two carbon-hydrogen bonds. As a result, the carbon-hydrogen bonds are slightly pushed back. The H—C—H bond angle is, therefore, smaller than the normal angle between sp^2 orbitals, and the C—C—H bond angle is correspondingly larger.

In tetrachloroethylene, the electronegative chlorine atom attracts towards itself the electron pair of the carbon-chlorine bond. As a result, the distance between the electron pairs of the two carbon-chlorine bonds increases, decreasing the repulsion between them. The Cl—C—Cl bond angle, therefore, further decreases and the C—C—Cl bond angle correspondingly increases.

6. $\underset{1}{CH_3—CH_2—CH_3}$ $\quad$ $\underset{2}{CH_2{=}CH—CH_3}$ $\quad$ $\underset{3}{CH{\equiv}C—CH_3}$ $\quad$ $\underset{4}{CH_2{=}C{=}CH_2}$

One half of the bond length between two similar atoms is called the covalent radius of the atom. The radius of an atom among other things also depends on the nature of its hybridization, and decreases with the increasing *s* character because the hybrid orbital with an increasing *s* character is held more tightly by the nucleus. Thus the radius of an sp^3 hybridized carbon atom is larger than that of an sp^2 carbon atom which in turn is larger than that of an *sp* carbon atom. The central carbon atoms of the molecules 1, 2, 3 and 4 are sp^3, sp^2, *sp* and *sp* hybridized, respectively. The order of the decreasing radius of their central carbon atom therefore is: $1 > 2 > 3 \simeq 4$.

7. The energy of a molecule is equal to the sum of the individual bond energies. Thus,

(a) $(E_{C—H} \times 4) = 415 \times 4 = 1660$ kJ/mol.

(b) $(E_{C—C} \times 3) + (E_{C—H} \times 10) = (347 \times 3) + (415 \times 10) = 5191$ kJ/mol.

(c) $(E_{C—H} \times 1) + (E_{C—Cl} \times 3) = (415 \times 1) + (339 \times 3) = 1432$ kJ/mol.

(d) $(E_{C—C} \times 1) + (E_{C—O} \times 1) + (E_{C=O} \times 1) + (E_{O—H} \times 1) + (E_{C—H} \times 3)$
$= (347 \times 1) + (359 \times 1) + (740 \times 1) + (464 \times 1) + (415 \times 3) = 3155$ kJ/mol.

(e) $(E_{C—C} \times 2) + (E_{C=O} \times 1) + (E_{C—H} \times 6)$
$= (347 \times 2) + (740 \times 1) + (415 \times 6) = 3924$ kJ/mol.

(f) $(E_{C—C} \times 1) + (E_{C=O} \times 1) + (E_{C—H} \times 4)$
$= (347 \times 1) + (740 \times 1) + (415 \times 4) = 2747$ kJ/mol.

(g) $(E_{C—C} \times 6) + (E_{C—H} \times 12)$
$= (347 \times 6) + (415 \times 12) = 7062$ kJ/mol.

(h) $(E_{C—C} \times 4) + (E_{C=C} \times 2) + (E_{C—H} \times 8)$
$= (347 \times 4) + (610 \times 2) + (415 \times 8) = 5928$ kJ/mol.

8. Let us suppose that the bond energy of C—Cl bond $= x$ kJ/mol.
The energy of C_2H_5Cl calculated from its bond energies
$= (347 \times 1) + (415 \times 5) + (x \times 1) = 2422 + x$

This energy should be equal to the heat of formation of C_2H_5Cl which is equal to 2760 kJ/mol.

Thus, $\quad 2422 + x = 2760$

or $\quad x = 2760 - 2422 = 338$

Therefore, bond energy of C—Cl bond = 338 kJ/mol.

9. Electronegativity of an element can be determined from the equation:

$$X_A - X_B = \sqrt{\frac{\Delta}{96.5}}$$

where, X_A and X_B are the electronegativities of the more and the less electronegative elements, respectively, and Δ is the difference between the energy of a bond between two unlike atoms, say A—B, and the geometric mean of the energies of bonds A—A and B—B. The electronegativity of fluorine is given (4.0), and the bond energies of the bonds C—F, C—C and F—F are available in Table 1.6.

Let us first calculate the electronegativity of C.
Geometric mean of the C—C and F—F bond energies
$= \sqrt{E_{C—C} \times E_{F—F}} = \sqrt{347 \times 157} = 233.4$
Bond energy of the C—F bond $= 485.0$
So, $\quad \Delta = 485.0 - 233.4 = 251.6$

Now the electronegativity of C, $X_C = X_F - \sqrt{\frac{251.6}{96.5}}$
$= 4.0 - 1.6 = 2.4$

The electronegativity of C given in Table 1.8 is 2.5.

Similarly, for H,

$$\Delta = E_{H—F} - \sqrt{E_{H—H} \times E_{F—F}} = 568 - \sqrt{436 \times 157} = 568 - 261.6 = 306.4$$

and the electronegativity of H, $X_H = X_F - \sqrt{\frac{306.4}{96.5}} = 4.0 - 1.8 = 2.2$

The electronegativity of H given in Table 1.8 is 2.1.

Once the electronegativity of C or H has been determined relative to fluorine, the electronegativities of other elements can be determined from the electronegativity of C or H, which will be considered as relative to fluorine.

Thus, for O,

$$\Delta = E_{C—O} - \sqrt{E_{C—C} \times E_{O—O}} = 359 - \sqrt{347 \times 146} = 359 - 225 = 134$$

and the electronegativity of O, $X_O = \sqrt{\frac{134}{96.5}} + X_C = 1.2 + 2.4 = 3.6.$

The electronegativity of O given in Table 1.8 is 3.5.

For N,

$$\Delta = E_{C—N} - \sqrt{E_{C—C} \times E_{N—N}} = 305 - \sqrt{347 \times 163} = 305 - 238 = 67$$

and the electronegativity of N, $X_N = \sqrt{\frac{67}{96.5}} + X_C = 0.8 + 2.4 = 3.2.$

The electronegativity of N given in Table 1.8 is 3.0.

For Cl,

$$\Delta = E_{C-Cl} - \sqrt{E_{C-C} \times E_{Cl-Cl}} = 339 - \sqrt{347 \times 243} = 339 - 290 = 49$$

and the electronegativity of Cl, $X_{Cl} = \sqrt{\frac{49}{96.5}} + X_C = 0.5 + 2.4 = 2.9.$

The electronegativity of Cl given in Table 1.8 is 3.0.

For S,

$$\Delta = E_{H-S} - \sqrt{E_{H-H} \times E_{S-S}} = 339 - \sqrt{436 \times 226} = 339 - 314 = 25$$

and the electronegativity of S, $X_S = \sqrt{\frac{25}{96.5}} + X_H = 0.5 + 2.2 = 2.7.$

The electronegativity of S given in Tale 1.8 is 2.5.

10. The electronegativity difference between H and Cl ($X_{Cl} - X_H$) can be calculated from the following equation:

$$X_{Cl} - X_H = \sqrt{\frac{\Delta}{96.5}}$$

Here, $\Delta = E_{H-Cl} - \sqrt{E_{H-H} \times E_{Cl-Cl}} = 431 - \sqrt{436 \times 243}$
$= 431 - 325.5 = 105.5$

and $X_{Cl} - X_H = \sqrt{\frac{\Delta}{96.5}} = \sqrt{\frac{105.5}{96.5}} = 1.0$

The electronegativity difference from the Table 1.8 is 3.0 − 2.1 = 0.9.

11. The dipole moment, μ, of a diatomic polar molecule = $q \times d$, where q is the charge on any atom (both atoms have equal charge) and d is the distance between the two atoms (which is equal to the bond length). In a diatomic molecule the value of q depends on the difference in electronegativities of the two atoms. Greater the difference between the electronegativities of the two atoms, greater the charge on any of the atoms.

In the given hydrogen halides, F is the most electronegative, while I is the least electronegative; the order being: F > Cl > Br > I. Therefore, the value of q is maximum on F and minimum on I. Since μ is the product of q and d, the net result is that μ decreases in the order: HF > HCl > HBr > HI, although the order of the bond length is: HI > HBr > HCl > HF. This is shown in the following Table:

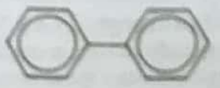
HX	*q*	×	*d*	=	μ
HF	1.91×10^{-10} esu	×	0.92×10^{-8} cm	=	1.75 D
HCl	0.81×10^{-10} esu	×	1.28×10^{-8} cm	=	1.03 D
HBr	0.55×10^{-10} esu	×	1.42×10^{-8} cm	=	0.78 D
HI	0.23×10^{-10} esu	×	1.62×10^{-8} cm	=	0.38 D

12. The dipole moment of a molecule as a whole is the vectorial sum of the individual bond moments which may augment or oppose each other depending

on the geometry of the molecule. The following molecules do not have dipole moment.

(a)

(e)



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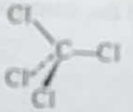
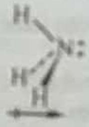


(i) O=C=O

(p)

The following molecules have dipole moment the direction of which is indicated by the arrow (⟵) beneath them.

(b)



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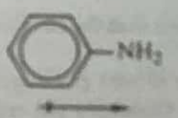

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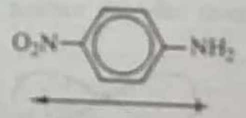

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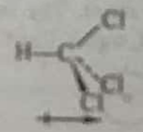

(h)

(j)

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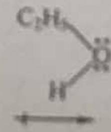

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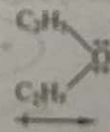

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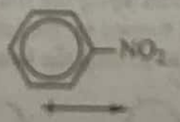

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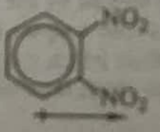

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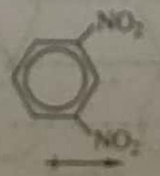


13. In a diatomic molecule involving a 'purely covalent' bond the net charge on the atoms is zero because the electronic cloud is shared equally by the two atoms, whereas in a diatomic molecule involving a 'purely ionic' bond each atom carries a charge of 4.8×10^{-10} esu (full electronic charge) with opposite signs. In a molecule having a covalent bond with some ionic character the atoms carry a charge between these two extremes, which can be calculated, as a fraction of the full electronic charge, from the dipole moment and the interatomic distance of the molecule using the following equation:

$$f = \frac{\mu}{e \times d} \qquad (q = f \times e)$$

where μ is the dipole moment of the molecule, f is the fraction of the electronic charge e, and d is the interatomic distance (bond length). For example, for H—Cl which has a dipole moment of 1.03×10^{-18} esu.cm and a bond length of 1.28×10^{-8} cm,

$$f = \frac{1.03 \times 10^{-18}}{(4.8 \times 10^{-10}) \times (1.28 \times 10^{-8})} = 0.17$$

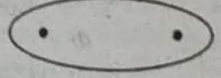
This means that the covalent bond of H—Cl has 17 % ($f \times 100$) ionic character.

14. (i) An orbital is a region in space which has high probability of finding an electron. Generally the region marked as an orbital contains more than 95% of the electronic cloud. The orbital that surrounds only one nucleus is called an **atomic orbital**, e.g., *s* orbital or *p* orbital.

s orbital

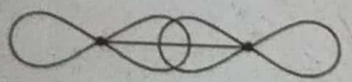
p orbital

On the other hand, when the electronic cloud extends around and encompasses two or more nuclei, the orbital is known as a **molecular orbital**, e.g., the orbital of the hydrogen molecule.

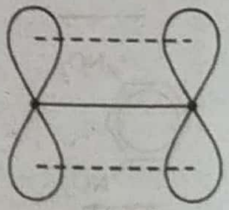


Molecular orbital of H_2

(ii) A bond formed by the overlap of atomic orbitals along the line joining the two nuclei is called a **sigma bond**, whereas a bond formed by the lateral overlap of atomic orbitals which are perpendicular to the line joining the two nuclei, and parallel to each other, is called a **pi bond**.

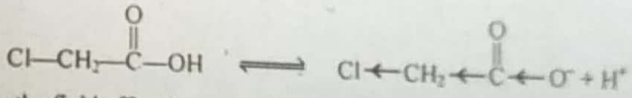


sigma bond



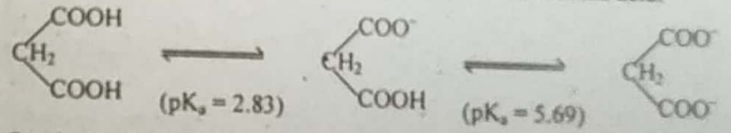
pi bond

(iii) Polarization of a bond induced by an adjacent polar bond is known as **inductive effect**. It operates through sigma bonds and decreases rapidly with distance; it is hardly felt on a bond four bonds away. The fact that chloroacetic acid is a stronger acid than acetic acid, is due to the electron-withdrawing inductive effect (–I) of chlorine which stabilizes the anion produced after the ionization of the former acid.



$$\mathrm{Cl{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH \rightleftharpoons Cl{\leftarrow}CH_2{\leftarrow}\overset{\overset{O}{\|}}{C}{\leftarrow}O^- + H^+}$$

For the field effect let us consider the ionization of malonic acid.



The first ionization is favoured by the electron-withdrawing inductive effect (–I) of the —COOH group (compare with the pK_a value of acetic acid which is 4.76), whereas the second ionization is discouraged by the electron-donating inductive effect (+I) of the —COO⁻ group. However, the difference between the first and the second ionization constants (a factor of about 10^3) is too large to be accounted for by the inductive effect alone. In fact, in addition to the (+I) of the —COO⁻ group, the ionization of the second proton leads to an unfavourable repulsion between the charges of the resulting dianion, which are close to each other in the molecule. This electrostatic effect acting through space is known as the **field effect**.

Chapter 2

Basic Concepts in Organic Chemistry

CHAPTER'S SUMMARY

Delocalized Chemical Bonding

If the electrons involved in the formation of a bond are shared by only two nuclei, the bond formed in this way is referred to as a **localized bond**. On the other hand, if the bonding electrons are shared by more than two nuclei in a molecule, the bonding is said to be **delocalized**. There are three main types of structures that show delocalization:

1. Double (or triple) bond in conjugation with another double (or triple) bond, e.g., in butadiene ($CH_2{=}CH{-}CH{=}CH_2$) and acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$).
2. Double (or triple) bond in conjugation with a *p* orbital that may be vacant, as in allylic carbocation ($CH_2{=}CH{-}\overset{+}{C}H_2$), or it may contain one or two electrons, as in allylic radical ($CH_2{=}CH{-}\dot{C}H_2$) and allylic carbanion ($CH_2{=}CH{-}\bar{C}H_2$), respectively.
3. Sigma bond in conjugation with a double (or triple) bond or a *p* orbital, e.g., in propylene ($CH_3{-}CH{=}CH_2$).

In a delocalized system, the number of molecular orbitals is the same as the number of the component atomic orbitals from which they are formed. Some of them are bonding and some are antibonding, while some may be nonbonding.

The Concept of Resonance

When a molecule has a system of delocalized bonding, it cannot be represented by a single Lewis structure, rather it is represented as a weighted average of two or more Lewis structures which are called **canonical forms** or contributing structures, and are connected to each other with a double-headed arrow ($\longleftrightarrow$). This is known as the resonance method of describing the actual structure which is then called the **resonance hybrid** of the canonical forms. The relative contribution of various canonical forms toward the resonance hybrid corresponds to their relative stability. The greater the stability of a canonical form, the more its contribution; the resonance hybrid being more stable than any of the canonical forms. The difference in the energy of the resonance hybrid and that of the most stable canonical form is called the **resonance energy**.

While writing the various canonical forms that may possibly contribute toward the same resonance hybrid, we must observe certain rules:

1. A canonical form must be a bonafide Lewis structure, i.e., it should follow the rules of valence.
2. The positions of the atomic nuclei must be the same in all the canonical forms.
3. All atoms involved in the resonance must lie in the same plane.
4. The number of unpaired electrons must be the same in all the canonical forms.
5. Canonical forms with distorted bond angles or bond lengths will not contribute to the resonance hybrid.

Since the relative contribution of the various canonical forms depends on their relative stability, their relative stability can be evaluated from the following rules:

1. The greater the number of covalent bonds, the greater the stability.
2. Canonical forms without a charge are more stable than those with a formal charge.
3. The less the charge separation, the greater the stability.
4. Canonical form with a negative charge on a more electronegative atom is more stable than that in which the negative charge is on a less electronegative atom.
5. Equivalent canonical forms make equal contribution to the resonance hybrid.

Since the resonance hybrid is more stable than any of the canonical forms, resonance is a stabilizing phenomenon. We can compare the stability of two different resonance hybrids by applying the rule, "the greater the number of principal canonical forms contributing to a resonance hybrid and more nearly equal their contribution, the greater the stability of the resonance hybrid". The resonance energy is a quantitative measure of the resonance stabilization of a resonance hybrid.

Resonance Effect

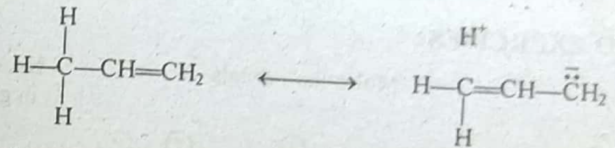
It is the decrease in electron density at one position and the corresponding increase elsewhere. It is also called **mesomeric effect**. It operates through π bonds and is felt equally at all positions. It has an appreciable influence on the physical characteristics and the chemical reactivity of organic compounds.

Steric Inhibition of Resonance

It is necessary for all the atoms involved in resonance to be in the same plane to facilitate delocalization of the π electrons. However, if the atoms are forced out of planarity, resonance is prevented or reduced. This phenomenon is called **steric inhibition of resonance**.

Hyperconjugation

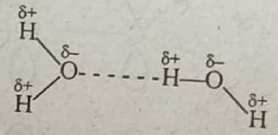
It is a phenomenon which involves delocalization of σ electrons when they are in conjugation with an unsaturated system, e.g., in propylene.



Since in some of the canonical forms there is no bond between carbon and hydrogen, this type of resonance is also called **no-bond resonance.**

Hydrogen Bonding

When in a molecule hydrogen atom is directly bonded to a highly electronegative atom like oxygen, nitrogen or fluorine, the bond is highly polar with a partial positive charge on hydrogen atom and a partial negative charge on the electronegative atom. This leads to an association between such molecules through the formation of a weak bond between the partially positively charged hydrogen atom of one molecule and the partially negatively charged electronegative atom of the other molecule.

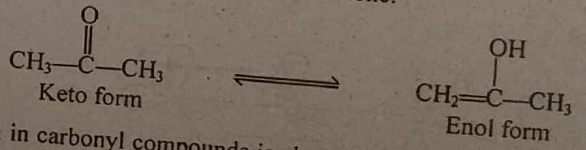


This type of weak bond is known as **hydrogen bond** which although is much weaker than ordinary covalent bonds, is much stronger than the van der Waals attractive forces. The hydrogen bond between two molecules leading to their association is known as **intermolecular hydrogen bond**. If the facility for the hydrogen bond formation is available within the same molecule, the bond formed then is known as **intramolecular hydrogen bond**. The intramolecular hydrogen bonding results in the formation of a ring, and is also known as **chelation**.

Hydrogen bonding, whether intermolecular or intramolecular, is important because of its effect on the properties of compounds such as boiling point, solubility, etc.

Tautomerism

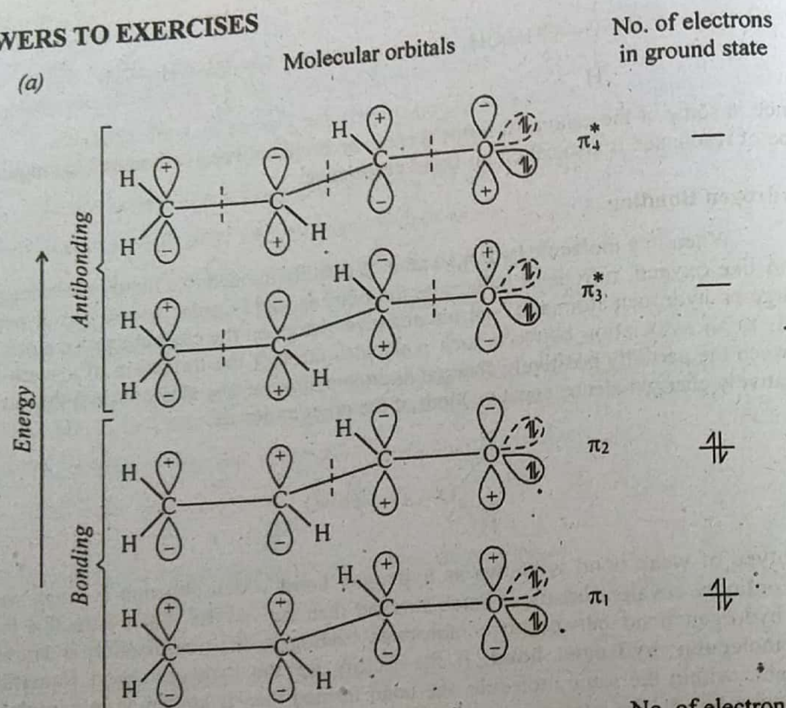
If two isomers differ in the placement of proton on one atom or another (mostly hetero atoms such as oxygen or nitrogen) with the corresponding adjustment of a double bond, the phenomenon is referred to as **tautomerism** and the isomers are known as tautomers, e.g., the keto and the enol forms of acetone.



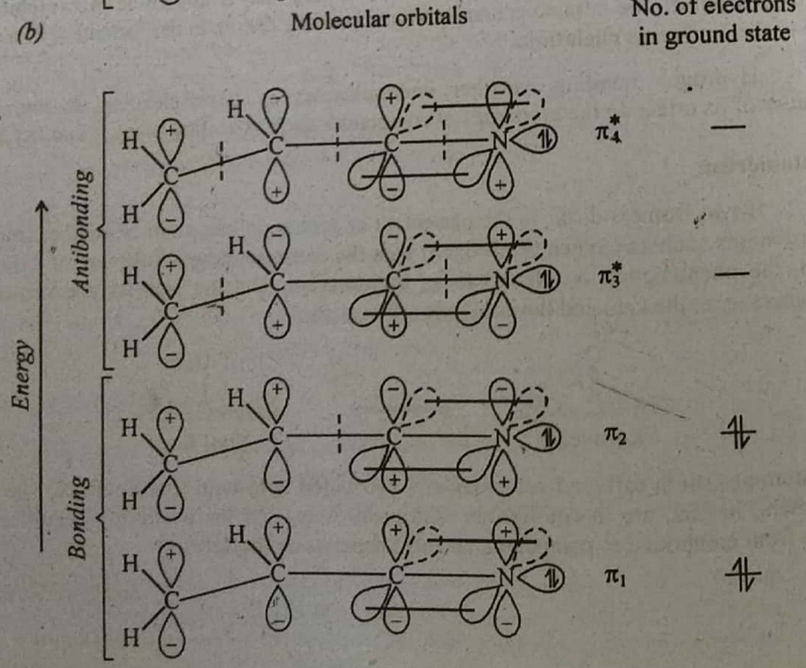
The tautomerism in carbonyl compounds is also called **keto-enol tautomerism**. The two tautomers, in fact, are in equilibrium with each other, and the position of equilibrium varies from compound to compound, and also depends on the solvent.

ANSWERS TO EXERCISES

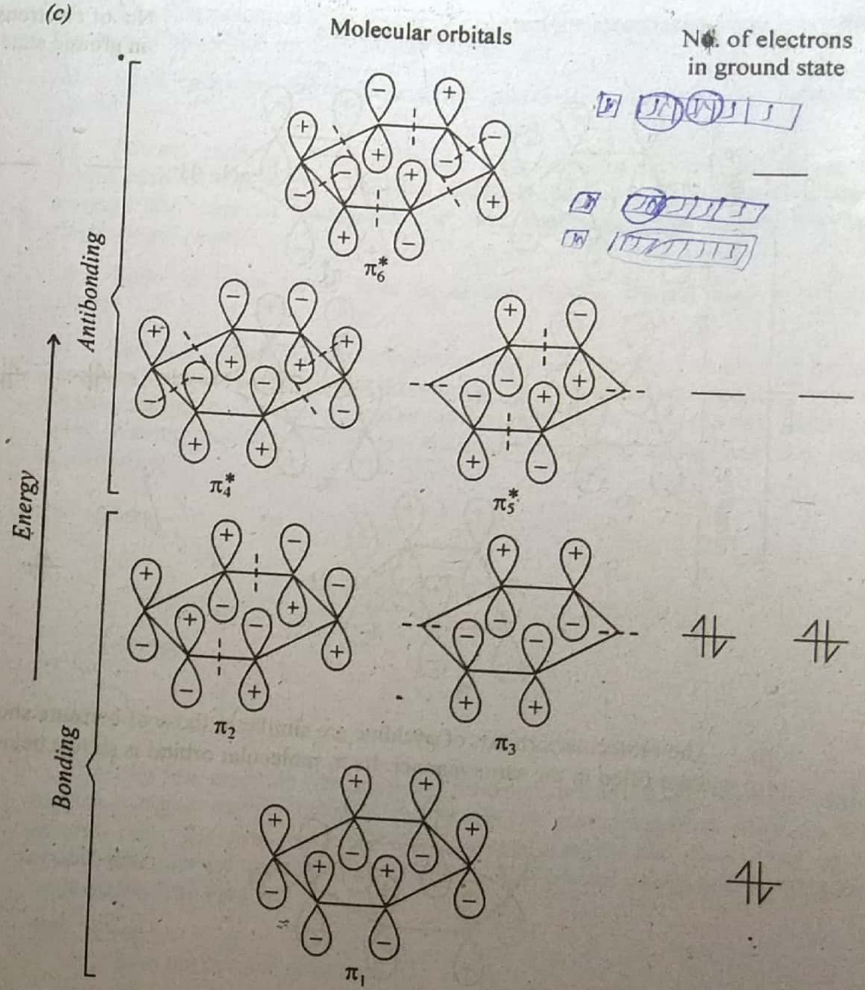
1. (a)



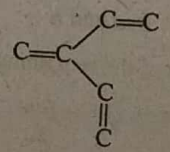
(b)



(c)

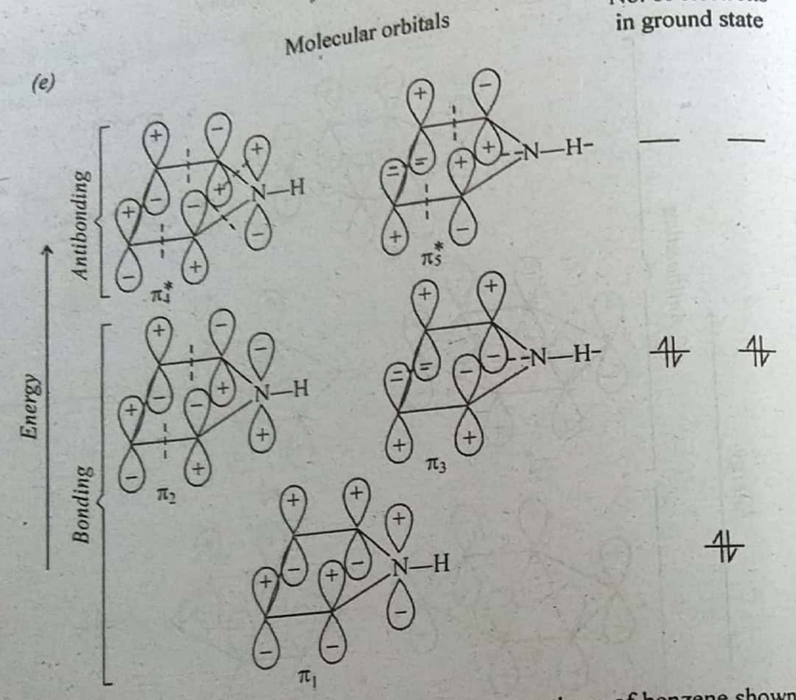


(d) It is a case of cross-conjugation:

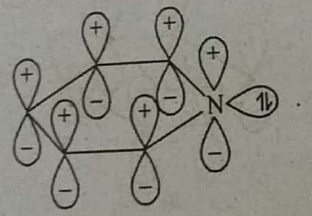


Since the benzene ring has a stable cyclic system of six delocalized π electrons of its own, it needs not to conjugate with the vinylic π bond. The molecular orbitals of the ring system are similar to those shown in (c).

(e)



(f) The molecular orbitals of pyridine are similar to those of benzene shown in (c) and are filled in the same manner. Its π_1 molecular orbital is shown below:



2 The following pairs of structures are the canonical forms of their same respective resonance hybrids:

b, *d* and *h*

The mutual relationship of the remaining pairs of structures is as under:

(a)	Identical	(c)	Tautomers
(e)	Positional isomers	(f)	Different compounds
(g)	Positional isomers		

3. The relative contribution of the canonical forms toward their resonance hybrid corresponds to their stability.

(a) The first canonical form contributes toward the resonance hybrid more than the second one which involves charge separation.

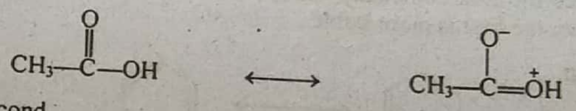
(b) Both canonical forms have equal contribution toward their resonance hybrid.

(c) Second canonical form has greater contribution toward the resonance hybrid because it carries the negative charge on the more electronegative atom, whereas the negative charge in the first canonical form is on the less electronegative atom.

(d) Both canonical forms have equal contribution toward their resonance hybrid.

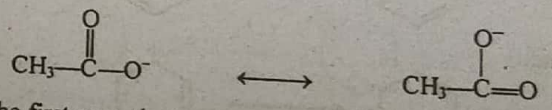
(e) The first canonical form has greater number of covalent bonds and has no charge separation. It therefore contributes the most toward the resonance hybrid. The remaining two involve charge separation, and out of them the last canonical form, having positive charge on the electronegative atom, has the least contribution.

4. (a) First,



$CH_3-\overset{\overset{O}{\|}}{C}-OH \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=\overset{+}{O}H$

Second,



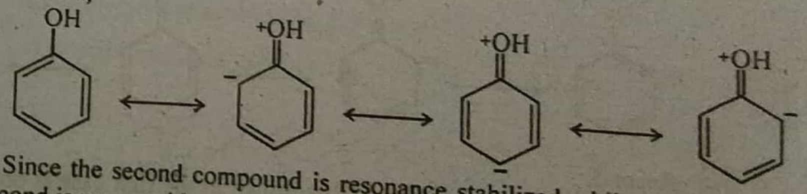
$CH_3-\overset{\overset{O}{\|}}{C}-O^- \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=O$

In the first case, the two canonical forms are not equivalent, and one of the canonical forms carries positive charge on the electronegative atom. In the second case, the two canonical forms are equivalent and thus have equal contribution toward their resonance hybrid. The second compound is therefore more stable than the first.

(b) First,

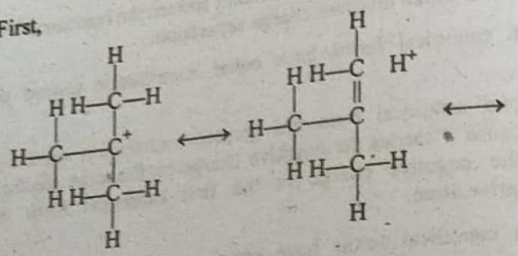
It does not involve resonance.

Second,



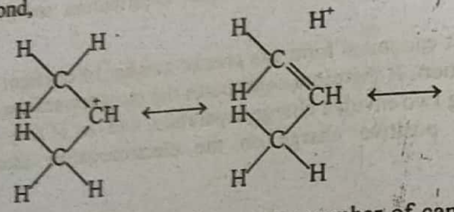
Since the second compound is resonance stabilized while the first is not, the second is more stable.

(c) First,



8 more such canonical forms

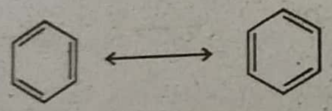
Second,



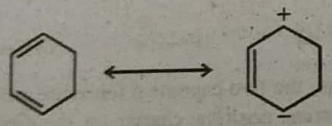
5 more such canonical forms

Since the first compound has greater number of canonical forms than the second one, the first is more stable.

(d) First,

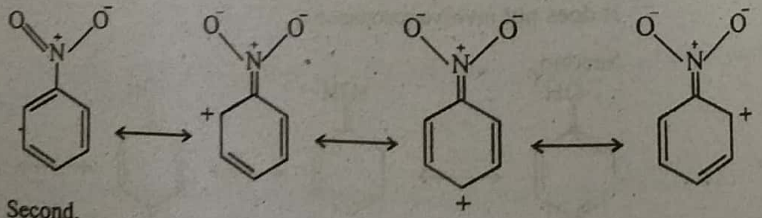


Second,



The first compound has equivalent canonical forms, while the second has non-equivalent canonical forms, one of which involves charge separation. First is, therefore, more stable than the second.

(e) First,

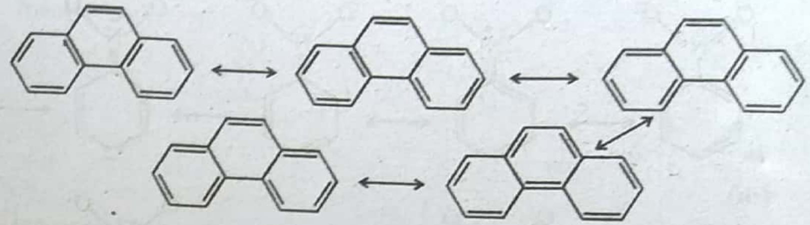


Second,

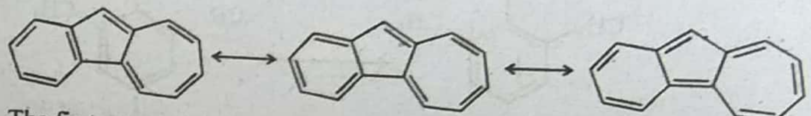
The delocalization similar to that shown in the first case is not possible in this case because the nitro group is pushed out of planarity by the two ortho methyl groups (steric inhibition of resonance).

Since the first compound is resonance stabilized while the second is not, the first is more stable.

(f) First,

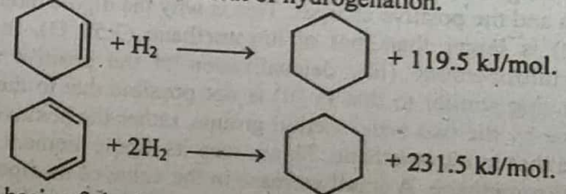


Second,



The first compound has greater number of canonical forms than the second one. It is, therefore, more stable.

5. When cyclohexene and cyclohexadiene are hydrogenated, heat is evolved, as shown below, which is called heat of hydrogenation.

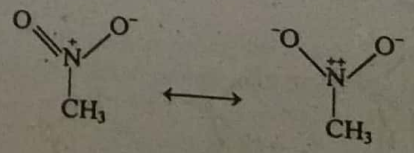


On the basis of the heat of hydrogenation of cyclohexene which contains one double bond, the heat of hydrogenation expected for cyclohexadiene should be twice the value for cyclohexene because it has two double bonds in the same ring, i.e., it should be 119.5 × 2 = 239 kJ/mol. The experimentally determined (actual) value of the heat of hydrogenation of cyclohexadiene is 231.5 kJ/mol, i.e., 7.5 kJ/mol (239 – 231.5) less than the value calculated from the most stable canonical form of cyclohexadiene. Therefore, the resonance energy of cyclohexadiene is 7.5 kJ/mol.

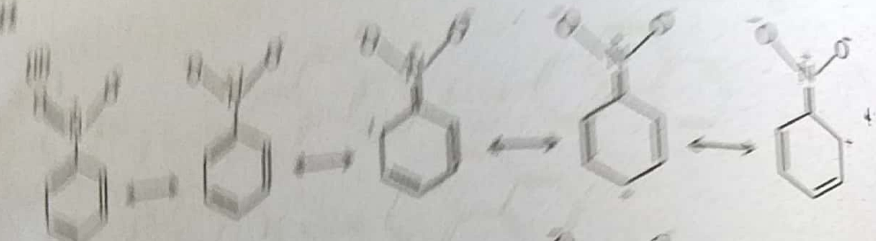
6. Dipole moment of a molecule, $\mu = q \times d$

Let us now consider the structures of the three molecules.

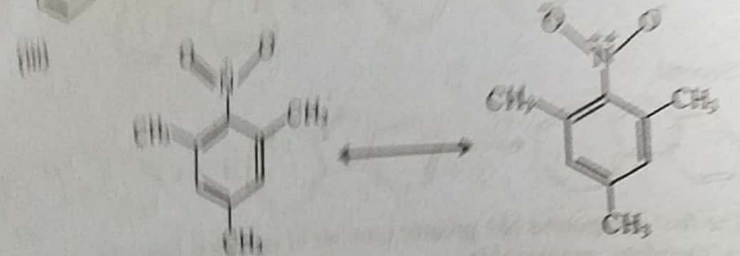
(i)



(ii)



(iii)



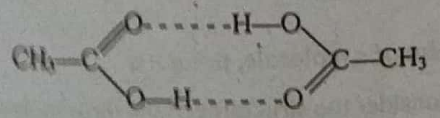
We see that in nitromethane (i), the positive charge is confined to N, whereas in nitrobenzene (ii), the positive charge is delocalized over to the benzene ring increasing the distance, *d*, between the centres of gravity of the negative and the positive charges. This is why the dipole moment of nitrobenzene ([illegible] D) is larger than that of nitromethane (3.50 D). In the case of 2,4,6-trimethylnitrobenzene (iii), delocalization of the positive charge over to the benzene ring similar to that in (ii) is not possible due to the steric inhibition of resonance by the two ortho methyl groups, rather the positive charge is confined to N like that in nitromethane. This is why its dipole moment (3.65 D) is closer to that of nitromethane. A small increase in the value of its dipole moment is due to the electron-donating inductive effect (+I) of the methyl groups which causes slight delocalization of the positive charge.

The following compounds do not involve hydrogen bonding:

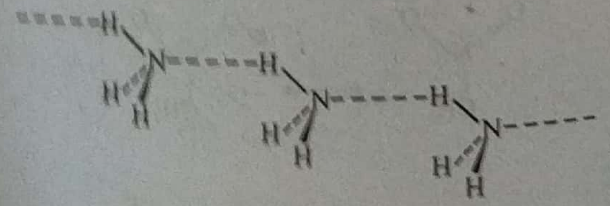
b, *d*, *f* and *g*

The hydrogen bonding formed by the other compounds is shown below:

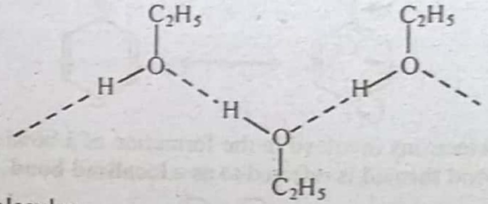
(a) Intermolecular (a dimer):



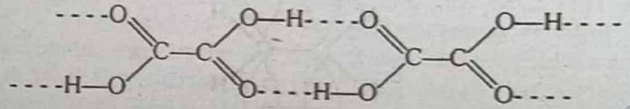
(c) Intermolecular:



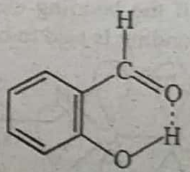
(e) Intermolecular:



(h) Intermolecular:

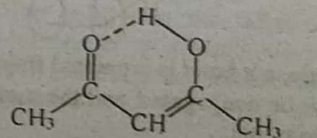


(i) Intramolecular:

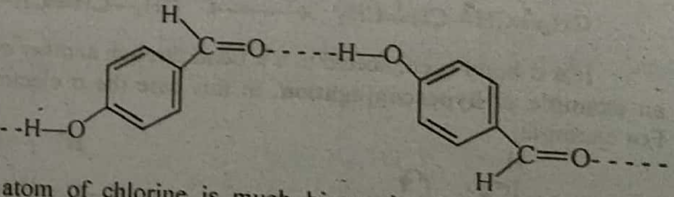


COOH
|
COOH

(j) Intramolecular in the enolic form:



(k) Intermolecular:

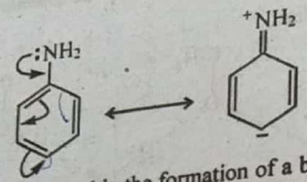


8. The atom of chlorine is much bigger in size as compared to that of nitrogen. The δ– charge is therefore spread over a large volume and is not in a position to form the hydrogen bond, whereas the δ– charge on nitrogen is confined to a smaller volume suitable for H-bond formation.

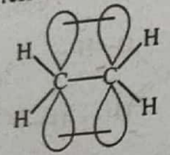
9. (i) **Inductive effect** is the polarization of a bond induced by an adjacent polar bond. It operates through σ bonds and decreases rapidly with distance. For example,

$$\overset{\delta\delta+}{CH_3}\longrightarrow\overset{\delta+}{CH_2}\longrightarrow\overset{\delta-}{Cl}$$

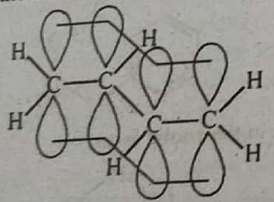
Resonance effect is the decrease in electron density at one position and the corresponding increase elsewhere. It operates through π bonds and is felt equally at all positions. For example,



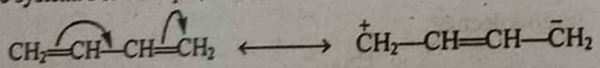
(ii) If the electrons involved in the formation of a bond are shared by only two nuclei, the bond formed is referred to as a **localized bond**. For example,



On the other hand, if the bonding electrons are shared by more than two nuclei in a molecule, the bonding is said to be **delocalized**. For example,

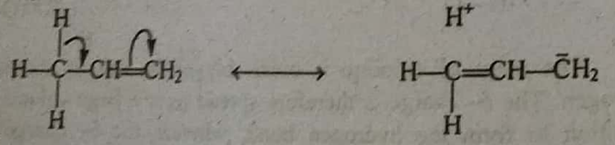


(iii) If in a molecule, a π bond is separated from another π bond by one σ bond, the system is said to be **conjugated** and the π electrons are delocalized over the whole system. For example,



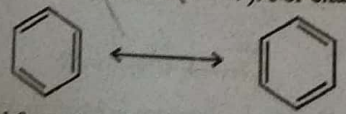
$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH-\bar{C}H_2$

If a σ bond is connected to a π bond through another σ bond, this provides an example of **hyperconjugation**. In this case the σ electrons are delocalized. For example,



$H-\underset{H}{\overset{H}{C}}-CH=CH_2 \longleftrightarrow H-\underset{H}{\overset{H^+}{C}}=CH-\bar{C}H_2$

(iv) **Resonance** is a phenomenon in which a compound cannot be described correctly by a single Lewis structure, rather it is described as a weighted average of more than one Lewis structures called canonical forms which are connected to each other by a double-headed arrow (⟷). For example,



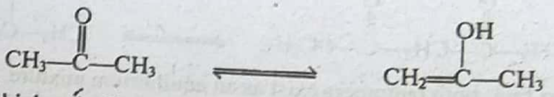
The canonical forms have to fulfil certain conditions, the most important of which is that the position of the atomic nuclei should not change.

$CH_2=CH-CH=CH_2$

$CH_3-CH=CH_2$

$\overset{+}{C}H_2=CH-\overset{-}{C}H_2$

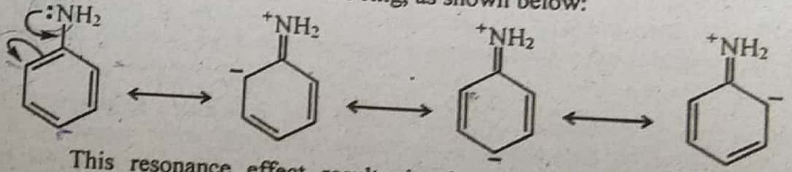
Tautomerism is a phenomenon in which two isomers (called tautomers) differ in the position of a proton which shifts from one atom to another (mostly heteroatom such as oxygen or nitrogen) with the corresponding adjustment of a double bond. The two tautomers exist as an equilibrium mixture, as shown below:



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_2=\overset{OH}{\overset{|}{C}}-CH_3$

10. (i) The higher boiling point of ethanol than that of diethyl ether has been attributed to an association of the ethanol molecules through intermolecular hydrogen bonding, shown in Ex. 7(e). Extra energy (higher temperature) is required to break this association to volatilize ethanol. This type of association is not possible in diethyl ether which, therefore, volatilizes immediately.

(ii) In aniline, the electron pair of N, which should be responsible for its basicity is delocalized over to the ring, as shown below:



This resonance effect results in the decrease in electron density on nitrogen, and thus in the decrease of its strength as a base. On the other hand, the electron pair of N in methylamine is not delocalized, and the whole electron density is available for protonation.

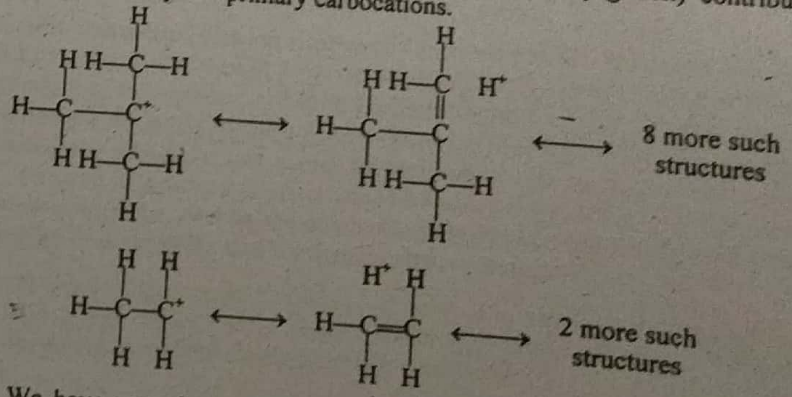
$CH_3-\ddot{N}H_2$

$CH_2=CH_2=CH_2$

This is why methylamine is more basic than aniline.

1,2.

(iii) Let us consider the no-bond resonance (hyperconjugation) contributing structures of tertiary and primary carbocations.



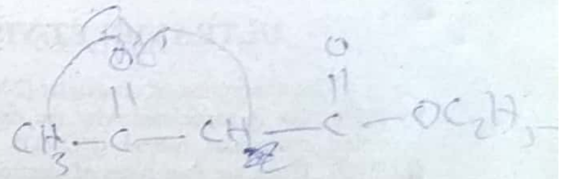
We have seen that a tertiary carbocation has ten resonance contributing structures, whereas a primary carbocation has only four such structures. We know that greater the number of resonance contributing structures, greater the stability. Thus, a tertiary carbocation is more stable than a primary carbocation.

(iv) Acetoacetic ester (a keto form) tautomerizes to its enolic form:

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

In fact, both tautomers exist as an equilibrium mixture. The enolic form has the enolic group ($\gt C=\overset{OH}{\overset{|}{C}}-$) similar to that present in phenol. Due to the presence of this group it behaves like phenol and gives ferric chloride test.

بسم الله الرحمن الرحیم



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Chapter 3

Spectroscopy

CHAPTER'S SUMMARY

Capter Supurmary is given as under

Spectroscopy is an analytical technique that is based on the absorption of electromagnetic radiation by a substance as a consequence of the interaction of the radiation with the substance.

Electromagnetic radiation is a form of energy, commonly known as *radiant energy*. It possesses some properties which are characteristic of waves and other properties which are characteristic of *particle-like discrete packets of energy*, called **photons**. A radiation can be characterized in terms of wavelength, frequency, wavenumber or energy which are interconvertible as follows:

$$E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

The whole electromagnetic spectrum covers a wide range of wavelengths and can be divided into several regions, each region being defined by the limits of any of the four parameters, i.e., wavelegnth, frequency, wavenumber or energy.

If an electromagnetic radiation is directed on to a molecule, it will be absorbed by the molecule, and the molecule will jump from a lower energy level to a higher energy level. The frequency of the absorbed radiation is related to the energy difference between the two concerned energy levels by the equation $\Delta E = h\nu$. Measurement of the absorbed radiation is called **spectroscopy**, and a plot of *absorbance (A)* against wavelength or wavenumber, is known as **absorption spectrum**. The wavelength or the wavenumber of the absorbed radiation can be used for the qualitative analysis of a sample, and the extent to which absorption occurs can be used for the quantitative analysis.

Different types of molecular transitions (electronic or vibrational) from a lower energy level to a higher energy level require different amount of energy which is available in different regions of the electromagnetic spectrum.

ULTRAVIOLET/VISIBLE SPECTROSCOPY

The absorption of ultraviolet (200–400 nm) and visible (400–800 nm) radiations by molecules is associated with the excitation of valency electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). There are four types of electronic transitions which in the decreasing order of energy requirements are:

$$\sigma\rightarrow\sigma^* > n\rightarrow\sigma^* > \pi\rightarrow\pi^* > n\rightarrow\pi^*$$

An absorption band has two characteristics i.e., its position (wavelength) and its intensity. The intensity is expressed as *molar absorptivity* (ε) which is measured as *absorbance* (A). The absorbance and the molar absorptivity are related by the **Beer-Lambert law** as follows:

$$A = \varepsilon cl$$

The Beer-Lambert law makes UV/VIS spectroscopy very useful for quantitative analysis.

A double-beam UV/VIS spectrophotometer is commonly used to measure the amount of radiation absorbed by the sample (used in the form of a very dilute solution in a transparent solvent) by comparing the intensity of the beam passing through the sample with the intensity of the reference beam at each wavelength of the UV/VIS region, and the result is obtained as a plot of absorbance against wavelength in the form of an *absorption spectrum*.

Any structural feature in a molecule that is responsible for the absorption of electromagnetic radiation in the UV/VIS region is called *chromophore*. A functional group which itself is not a chromophore but when attached to a chromophore, shifts the position of the absorption to a longer wavelength, is known as *auxochrome*. A shift of the absorption position to a longer wavelength is known as *red shift* or *bathochromic effect*, while a shift of the absorption position to a shorter wavelength is called *blue shift* or *hypsochromic effect*. An increase in the intensity of absorption is called *hyperchromic effect*, whereas a decrease in the absorption intensity is called *hypochromic effect*.

Conjugation of an auxochrome with a chromophore or a chromophore with another chromophore shifts the absorption position to a longer wavelength, and this shift increases progressively with the increase in conjugation. In fact, the importance of UV/VIS spectroscopy lies in its ability to determine the presence, nature and extent of conjugation in a molecule.

The wavelength of absorption is also affected by the presence and nature of substituents on the conjugated system. Woodward and Fieser formulated certain empirical rules for the contribution of various substituents to predict the expected wavelength of absorption separately for the diene and the α,β-unsaturated carbonyl systems.

Benzene and most of the other aromatic compounds display three absorption bands. The position of these bands may be modified by the presence and the nature of the substituents in the aromatic compounds.

The UV/VIS spectroscopy can be used for structure determination, for qualitative and quantitative analysis and for kinetic measurements.

INFRARED SPECTROSCOPY

Organic molecules are in a constant state of vibration, each bond vibrating with its characteristic frequency which depends on the strength of the bond and the masses of the bonded atoms. There are two types of bond vibrations, i.e., *stretching vibration* that can be either symmetric or antisymmetric, and *bending vibration* that can be classified as rocking, scissoring, twisting or wagging.

A molecule absorbs infrared radiation and jumps from a lower vibrational energy level to a higher one such that $\Delta E = h\nu$, provided that the vibration involves a change in dipole moment. Absorptions due to stretching vibrations are more useful than those due to bending vibrations. The approximate value of a stretching vibrational frequency can be calculated by using **Hooke's law** which helps to identify the region in which an absorption is expected to occur. Some of the more important regions are summarized here:

Bonds	Absorption regions (cm^{-1})
C—H, O—H, N—H	3700–2500
C≡C, C≡N	2300–2100
C=C, C=O, C=N	1900–1600
C—C, C—O, C—N	1300–800

A plot of absorbance (A) against wavelength or wavenumber gives an *infrared spectrum* which shows a series of absorption bands whose positions are indicated either by wavelength (μm) or by wavenumber (cm^{-1}). The intensities of the IR absorption bands are usually reported in semi-quantitative terms as strong (s), medium (m), weak (w) or variable (v).

An infrared spectrum may be divided into two parts: (i) the *fingerprint region* (1600–625 cm^{-1}) which is uniquely characteristic of each compound and is mainly used to establish the identity of a compound, and (ii) the *functional group region* (4000–1600 cm^{-1}) which reveals the characteristic absorptions of various functional groups. The IR spectroscopy is mainly used to determine the presence and nature of functional groups in a molecule.

A double-beam IR spectrophotometer similar to that used in UV/VIS spectroscopy, is used to obtain an infrared spectrum. In IR spectroscopy, the sample can be used in any physical state, i.e., gas, liquid or solid, or in the solution form.

ANSWERS TO EXERCISES

1. (*a*) **Electromagnetic radiation** is the transmission of energy. In some experiments it behaves as a wave and in others it acts as a stream of massless particles called photons.

   (*b*) **Photon** is a particle-like discrete packet of energy.

   (*c*) **Wavelength** is the distance between two adjacent crests (or troughs) of the wave in the beam of an electromagnetic radiation.

2.

	Ultraviolet	Visible	Infrared
Wavelength	200–400 nm	400–800 nm	2.5–50 μm
Wavenumber (cm^{-1})	$5.0\times10^{4}-2.5\times10^{4}$	$2.5\times10^{4}-1.3\times10^{4}$	$4.0\times10^{3}-2.0\times10^{2}$
Frequency (Hz)	$1.5\times10^{15}-7.5\times10^{14}$	$7.5\times10^{14}-3.8\times10^{14}$	$1.2\times10^{14}-6.0\times10^{12}$
Energy (J)	$1.0\times10^{-18}-5.0\times10^{-19}$	$5.0\times10^{-19}-2.5\times10^{-19}$	$8.0\times10^{-20}-4.0\times10^{-21}$

3. $E = h\nu = h\dfrac{c}{\lambda} = hc\bar{\nu}$

4. $E = h\dfrac{c}{\lambda} = \dfrac{6.625\times10^{-34}\times3.0\times10^{8}\times6.02\times10^{23}}{600\times10^{-9}\times1000} = 199.4$ kJ/mol

5. An electronically excited molecule can return to the ground state in two ways: (a) It collides with the neighbouring molecules and gradually transfers its excess energy to them as kinetic energy; the sample as a whole becomes warm. (b) The excess energy is lost by emission of radiation as fluorescence or phosphorescence.

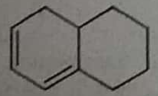
6. According to the Beer-Lambert law, $A = \varepsilon cl$.

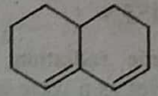
So, $\varepsilon = \dfrac{A}{c\times l} = \dfrac{0.525}{2.5\times10^{-4}\times5} = 420$

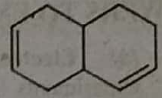
7. Conjugation causes a molecule to absorb at a longer wavelength. Therefore, $CH_3COCH{=}CH_2$ absorbs at 219 and 324 nm, while $CH_3COCH_2CH_3$ absorbs at 185 and 277 nm. In each case, the absorption at shorter wavelength is due to $\pi\rightarrow\pi^*$ transition and that at longer wavelength is due to $n\rightarrow\pi^*$ transition.

8. $a > d > c > b$

9. The three isomeric products are given below. Distinction among them can be made by measuring the λ_{max} and matching with the value predicted for each, as shown beneath them.







Predicted λ_{max}	273 nm	234 nm	< 200 nm (Undetectable)

10. (a) Below 200 nm (b) Below 200 nm
(c) 260 nm (d) 280 nm

11. A, $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$
B, $CH_2{=}CH{-}CH{=}CH{-}CH_3$

A has two isolated carbon-carbon double bonds and gives UV spectrum similar to that of 1-pentene. B has a conjugated diene system with a methyl substituent.

12.(a) A molecule must involve a net change in dipole moment during its vibrational motion in order to absorb IR radiation.

(b) H_2, O_2 and N_2 do not absorb in the infrared region because they do not involve a change in dipole moment during their vibrational motion.

13. The symmetric stretching vibration of CO_2 does not cause a change in its dipole moment, and is, therefore, infrared inactive. The antisymmetric stretching vibration causes a change in dipole moment, and is, therefore, expected to show absorption in the IR spectrum.

14. Ethylene is a symmetrical molecule and C═C stretching vibration does not involve a change in dipole moment. On the other hand, a change in dipole moment is involved in the C═C stretching vibration of the unsymmetrical propylene molecule. A change in dipole moment during vibration is a must for IR absorption.

15. According to the Hooke's law,

$$\bar{\nu}\ (\text{in cm}^{-1}) = \frac{1}{2\pi c}\times\left[\frac{f}{m_A.m_B/m_A+m_B}\right]^{1/2}$$

$$= \frac{1}{2\times3.143\times3\times10^{10}}\times\left[\frac{10\times10^{5}}{\dfrac{19.92\times10^{-24}\times26.56\times10^{-24}}{(19.92+26.56)\times10^{-24}}}\right]^{1/2} = 1573$$

So, the wavenumber, $\bar{\nu} = 1573$ cm^{-1}

and the wavelength, $\lambda = \dfrac{1}{\bar{\nu}} = \dfrac{1}{1573} = 6.357$ μm

16. The solvents most commonly used in IR spectroscopy are $CHCl_3$, CCl_4 and CS_2. Water and ethanol are not used because they dissolve the NaCl used for discs, causing fogging on their surface. They also absorb strongly in several regions of the IR spectrum.

17. The index of hydrogen deficiency suggests that the hydrocarbon C_6H_{12} is either hexene or cyclohexane. The absence of absorptions at 1650 cm^{-1} (C═C), above 3000 cm^{-1} (═C—H stretching), and at 1375 cm^{-1} (methyl C—H bending) rule out hexene. The absorptions at 2920 and 2840 cm^{-1} and at 1450 cm^{-1} are due to methylene C—H stretching and bending vibrations, respectively. The hydrocarbon is therefore cyclohexane.

18. *a*, Benzyl alcohol. The infrared spectrum shows the absorption bands for O—H and methylene C—H, and lacks the C═O absorption.

19. The symmetrical tetramethylethylene molecule does not show C═C stretching absorption, whereas 2,3-dimethyl-1-butene, the other product, being unsymmetrical, shows a C═C stretching absorption at 1640 cm^{-1}. It also shows the out-of-plane bending vibration of ═CH$_2$ at 910 cm^{-1}.

20. Acetylacetone exists as a keto-enol equilibrium mixture. In the enolic form which is about 85%, an intramolecular hydrogen bond involving O—H and C═O groups, is formed. It therefore shows a very broad O—H stretching band at 3400-2500 cm^{-1} and a broad C═C stretching band at a rather lower frequency (1600 cm^{-1}). The keto form shows the normal C═O stretching absorption at 1710 cm^{-1}.

21. *(a)* **Frequency** is the number of waves passing a fixed point on the path of a beam of radiation per second, whereas **wavenumber** is the number of waves per centimeter.

(b) **Chromophore** is a functional group in a molecule that is responsible for the absorption of UV/VIS radiation. **Auxochrome** is a functional group that itself does not absorb in the UV region above 200 nm but shifts the absorption of the attached chromophore to a longer wavelength.

(c) **Bathochromic** effect is the shift of a λ_{max} to a longer wavelength, whereas **hypsochromic** effect shifts the λ_{max} to a shorter wavelength.

(d) A vibration that causes a change in dipole moment results in the absorption of IR radiation, and is called **IR active vibration**. The vibration that does not cause a change in dipole moment will not result in the IR absorption, and is called **IR inactive vibration**.

22. *(a)* 1-Hexene shows C═C stretching band in the 1680–1620 cm^{-1} region, whereas *n*-hexane does not.

(b) 1-Butyne shows C≡C stretching band in the 2200–2100 cm^{-1} region, whereas 2-butyne, being symmetrical, does not.

(c) 2-Hexanol shows a broad band in the 3600–3200 cm^{-1} region but no absorption in the 1750–1700 cm^{-1} region. On the other hand, 2-hexanone shows an intense band in the 1750–1700 cm^{-1} region but no absorption in the 3600–3200 cm^{-1} region.

(d) In addition to an intense C═O stretching band in the 1750–1700 cm^{-1} region, CH_3CHO shows an absorption in the 2850–2700 cm^{-1} region, whereas CH_3COCH_3 does not show this band and absorbs only in the 1750–1700 cm^{-1} region.

Chapter 4

Saturated Hydrocarbons

CHAPTER'S SUMMARY

Hydrocarbons are the compounds that are composed of only carbon and hydrogen. They are divided into two broad categories, i.e., aliphatic hydrocarbons and aromatic hydrocarbons. The aliphatic hydrocarbons include the open-chain compounds and those cyclic compounds that resemble the open-chain compounds in their behaviour. They are further classified as saturated and unsaturated hydrocarbons. The saturated hydrocarbons are those compounds in which the carbon atoms are joined to each other only by single bonds, and each carbon atom is bonded to four other atoms. They include alkanes and cycloalkanes. The unsaturated hydrocarbons are those compounds which contain carbon-carbon multiple bonds. They include alkenes and alkynes. The aromatic hydrocarbons include benzene and those compounds which resemble benzene in their behaviour.

ALKANES

Alkanes are the open-chain saturated hydrocarbons which can be represented by the general formula C_nH_{2n+2}, where *n* is the number of carbon atoms. They form a homologous series in which the formula of each alkane differs from that of its neighbours by CH_2. Certain alkanes may have the same molecular formula but different arrangement of carbon atoms; these are called isomers. Whereas the prefix *n*- is used for a straight-chain hydrocarbon, the prefix *iso*- is used for a compound with two methyl groups at the end of an otherwise straight chain, and the prefix *neo*- is used to denote three methyl groups at the end of a chain.

Nomenclature

The alkanes are known either by common (or trivial) names or by IUPAC (or systematic) names. The common names are derived either from their history or from the Greek or Latin numerals indicating the number of carbon atoms in the molecules. However, the IUPAC system follows certain rules, and assigns an unambiguous name to each different compound that refers to only one structural formula.

Natural Sources of Alkanes

Alkanes are widely distributed in nature but their principal sources are natural gas and petroleum. The natural gas is a mixture of lower alkanes, consisting primarily of methane (80%) along with the small amounts of ethane, propane, butane, and higher alkanes, decreasing in the same order. Petroleum is a complex mixture of straight- and branched-chain alkanes ranging in carbon content from C_1 to C_{40}, together with small quantities of cycloalkanes and aromatic hydrocarbons. Crude petroleum is obtained from underground pockets as a viscous black liquid which is separated into various fractions by fractional distillation.

Preparation of Alkanes

Alkanes can be prepared by the following methods:

1. Catalytic hydrogenation of alkenes.

2. Reduction of alkyl halides by either dissolving metals or lithium aluminium hydride or through catalytic hydrogenolysis.

3. Hydrolysis of Grignard reagents.

4. Coupling of alkyl halides with organometallic compounds, e.g., lithium dialkylcopper.

5. Treatment of an ethereal solution of an alkyl halide with sodium metal (Wurtz reaction).

6. Coupling of alkylboranes by means of silver nitrate and sodium hydroxide.

7. Reduction of carbonyl compounds.

8. Electrolysis of a concentrated solution of potassium salt of a carboxylic acid (Kolbe reaction).

9. Decarboxylation of sodium salt of carboxylic acid by heating with soda lime.

Physical Properties of Alkanes

The physical properties of organic compounds are generally based on the size and the structure of the molecules and within a family of compounds vary fairly regularly with the molecular weights of the compounds. Generally, the physical properties of organic compounds are governed by the intermolecular forces such as dipole-dipole interaction, hydrogen bonding, van der Waals forces, etc., acting between the molecules.

As regards the alkanes, the first four members of the family are gases at room temperature, C_5 to C_{17} alkanes are liquid, whereas C_{18} and above alkanes are solid. The straight-chain alkanes generally have higher boiling points than the branched-chain alkanes of the same molecular weight, whereas the reverse is true for melting points. Alkanes, being nonpolar, are soluble in nonpolar solvents and insoluble in polar solvents, following the rule, 'like dissolves like'. All alkanes are lighter than water.

Reactions of Alkanes

Characteristically, at ordinary temperature, the alkanes are unreactive toward most reagents. However, they may be made to react with certain reagents if the right conditions are used, as shown below:

1. Halogenation. Alkanes react with halogens either on heating at 250–400°C or under the influence of light, usually to yield a mixture of halogenated alkanes.

2. Nitration. Alkanes undergo nitration on treatment with a large excess of 60% nitric acid at 400°C, in vapour phase, to yield a complex mixture of mononitroalkanes, including products of fragmentation and oxidation.

3. Sulfonation. Alkanes undergo sulfonation on treatment with oleum, to yield alkylsulfonic acids.

4. Combustion. Alkanes burn readily if ignited in the presence of air or oxygen, and are oxidized to CO_2 and H_2O with the evolution of large amount of heat. The process is called *combustion*.

5. Pyrolysis. When higher alkanes are subjected to pyrolysis (thermal decomposition) by passing them through a chamber heated to a high temperature (400–700°C), they yield a variety of smaller molecules, including lower alkanes, alkenes, and even carbon and hydrogen. The process is called *cracking*.

6. Isomerization. Alkanes undergo isomerization on treatment with $AlCl_3$ at 300°C in the presence of a small amount of HCl together with a trace of an alkene.

CYCLOALKANES

Cycloalkanes are the cyclic aliphatic saturated hydrocarbons with the general formula C_nH_{2n}. They are also known as alicyclic or carbocyclic compounds.

Nomenclature

Cycloalkanes are named by attaching the prefix *cyclo-* to the names of the alkanes having the same number of carbon atoms as the ring. They also follow the IUPAC rules for their nomenclature.

Preparation of Cycloalkanes

Many cycloalkanes are obtained from petroleum where they are known as *naphthenes*. They can also be prepared from other compounds by the following methods:

1. Dehalogenation of α,ω-dihalides.

2. Catalytic hydrogenation of cyclic alkenes.

3. Reduction of cyclic ketones.

4. Cycloaddition of an ethylenic compound to a conjugated diene (Diels-Alder

reaction), followed by catalytic hydrogenation.

5. Cycloaddition of methylene obtained by heating diiodomethane with zinc-copper couple in anhydrous ether, to an alkene (Simmons-Smith reaction).

6. Treatment of malonic ester with a dihaloalkane in the presence of sodium ethoxide (Perkin's ring closure), followed by hydrolysis and decarboxylation.

Physical Properties of Cycloalkanes

Cycloalkanes, in general, are similar to alkanes in their behaviour. However, they have relatively higher melting and boiling points than the corresponding alkanes. Cycloalkanes, like alkanes, are soluble in nonpolar solvents and insoluble in polar solvents, and are lighter than water.

Stability of Cycloalkanes

Cycloalkanes are generally less stable than the corresponding *n*-alkanes as determined from their heats of combustion. The less stability of cycloalkanes is due to the ring strain which is the result of the net effect of angle strain, torsional strain and non-bonded interaction.

Reactions of Cycloalkanes

Cycloalkanes resemble open-chain alkanes in most of their chemical properties. However, cyclopropane and cyclobutane, being under considerable ring strain, have a tendency to undergo ring-opening to yield open-chain compounds, and thus also undergo certain addition reactions similar to those of alkenes; cyclobutane is less reactive than cyclopropane.

1. **Addition reactions.** Cyclopropane and cyclobutane undergo addition reactions, such as hydrogenation, addition of halogen, addition of hydrogen halide and hydration.

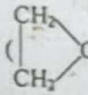
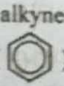
2. **Substitution reactions.** Cycloalkanes, including cyclopropane and cyclobutane, like open-chain alkanes, undergo substitution reactions, such as halogenation and sulfonation.

3. **Combustion.** Cycloalkanes undergo combustion to CO_2 and H_2O, with the evolution of heat.

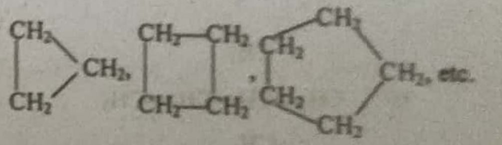
4. **Aromatization.** Cyclohexane and its derivatives may undergo dehydrogenation to yield aromatic compounds. The process is called *aromatization*.

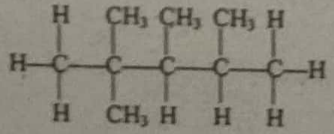
5. **Isomerization.** Cycloalkanes may undergo isomerization that may lead to open-chain compounds or to compounds of different ring size.

ANSWERS TO EXERCISES

1. Hydrocarbons are the compounds that are composed of only carbon and hydrogen. They are classified on the basis of their structure and behaviour into two main categories, i.e., aliphatic hydrocarbons and aromatic hydrocarbons. The aliphatic hydrocarbons include the open-chain compounds and those cyclic compounds that resemble the open-chain compounds in their behaviour. They are further classified as saturated and unsaturated hydrocarbons. The saturated hydrocarbons are those compounds in which the carbon atoms are joined to each other only by single bonds, and each carbon atom is bonded to four other atoms. They include alkanes, e.g., ethane ($CH_3—CH_3$), and cycloalkanes, e.g., cyclopropane (). The unsaturated hydrocarbons are those compounds which contain carbon-carbon multiple bonds. They include alkenes, e.g., ethene ($CH_2{=}CH_2$) and alkynes, e.g., ethyne ($CH{\equiv}CH$). The aromatic hydrocarbons include benzene () and those compounds that resemble benzene in their behaviour, e.g., naphthalene ().

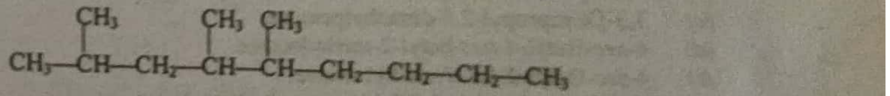
2. Homologous series is a series of those compounds all of which can be represented by the same general formula and each member of the series differs from its neighbours by the same structural unit; see, e.g., the following classes:

Class	**General formula**	**Series**
Alkanes	C_nH_{2n+2}	CH_4, C_2H_6, C_3H_8, etc.
Cycloalkanes	CH_4 2 6 3 8 C_nH_{2n} C_3H_4	
Alkyl halides	$C_nH_{2n+1}X$	CH_3X, C_2H_5X, C_3H_7X, etc.

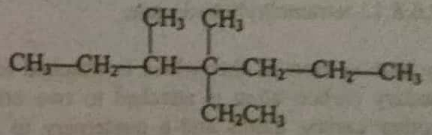
3. (a) 

$$H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

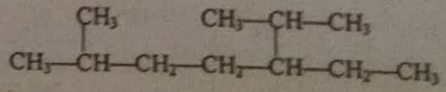
CH_2
CH_2

(b) 

$$CH_3-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_2-CH_2-CH_3$$

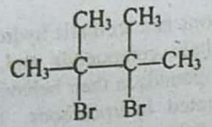
(c) 

$$CH_3-CH_2-\overset{CH_3}{CH}-\overset{CH_3}{\underset{CH_2CH_3}{C}}-CH_2-CH_2-CH_3$$

(d) 

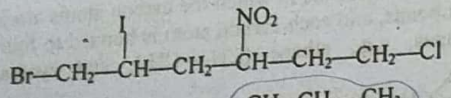
$$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3-CH-CH_3}{CH}-CH_2-CH_3$$

(e)



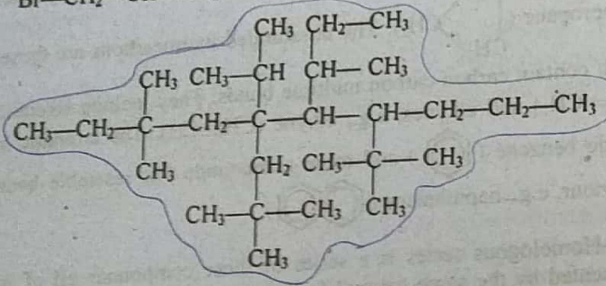
$CH_3-\overset{CH_3}{\underset{Br}{C}}-\overset{CH_3}{\underset{Br}{C}}-CH_3$

(f)

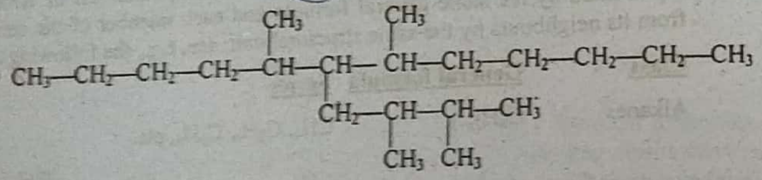


$Br-CH_2-\overset{I}{C}H-CH_2-\overset{NO_2}{C}H-CH_2-CH_2-Cl$

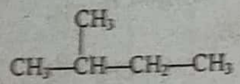
(g)



(h)

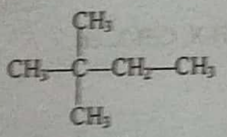


(i)



$CH_3-\overset{CH_3}{C}H-CH_2-CH_3$

(j)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

4\. (a) 3-Ethylpentane.
(b) 3-Ethyl-2,3-dimethylhexane.
(c) 3,3-Diisopropyl-2,4-dimethylpentane.
(d) 4-*sec*-Butyl-4-*tert*-butyl-2-methyloctane.
(e) 4-*sec*-Butyl-2,4,6-trimethylnonane.
(f) 7-(4-Methylheptyl)-2,6,8,12-tetramethyltetradecane.

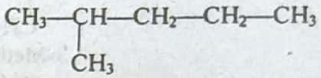
5\. (a) In alkanes, a primary carbon atom is that which is attached to only one other carbon atom, a secondary carbon atom is attached to two other carbon atoms, a tertiary to three other carbon atoms and a quaternary to four other carbon atoms.

C_6H_{14},

(i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Hexane
pri-C, two
sec-C, four

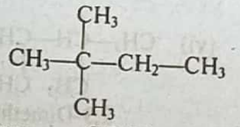
(ii)



$CH_3-\underset{CH_3}{C}H-CH_2-CH_2-CH_3$

Isohexane or 2-Methylpentane
pri-C, three
sec-C, two
tert-C, one

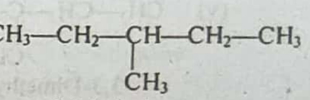
(iii)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

Neohexane or 2,2-Dimethylbutane
pri-C, four
sec-C, one
quat-C, one

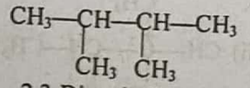
(iv)



$CH_3-CH_2-\underset{CH_3}{C}H-CH_2-CH_3$

3-Methylpentane
pri-C, three
sec-C, two
tert-C, one

(v)



$CH_3-\underset{CH_3}{C}H-\underset{CH_3}{C}H-CH_3$

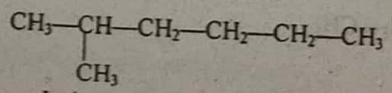
2,3-Dimethylbutane
pri-C, four
tert-C, two

C_7H_{16},

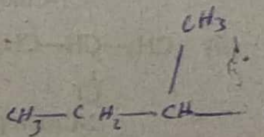
(i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ NO_2

n-Heptane
pri-C, two
sec-C, five

(ii)



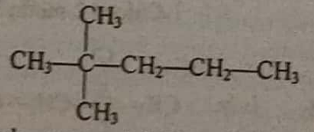
$CH_3-\underset{CH_3}{C}H-CH_2-CH_2-CH_2-CH_3$



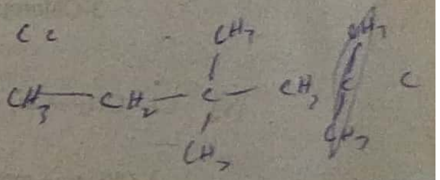
$CH_3-CH_2-\overset{CH_3}{C}H-CH_3$

Isoheptane or 2-Methylhexane
pri-C, three
sec-C, three
tert-C, one

(iii)



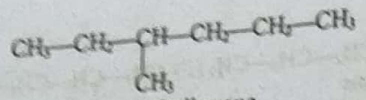
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$



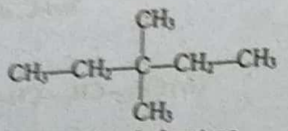
C C

$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

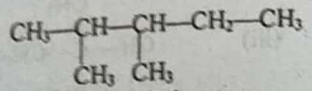
Neoheptane or 2,2-Dimethylpentane
pri-C, four
sec-C, two
quat-C, one

(iv) 
$CH_3-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-CH_2-CH_3$

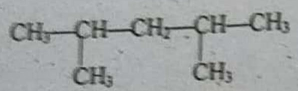
3-Methylhexane
pri-C, three
sec-C, three
tert-C, one

(v) 
$CH_3-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-CH_3$

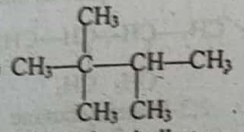
3,3-Dimethylpentane
pri-C, four
sec-C, two
quat-C, one

(vi) 
$CH_3-\underset{\underset{\textstyle CH_3}{|}}{CH}-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-CH_3$

2,3-Dimethylpentane
pri-C, four
sec-C, one
tert-C, two

(vii) 
$CH_3-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

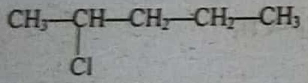
2,4-Dimethylpentane
pri-C, four
sec-C, one
tert-C, two

(viii) 
$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

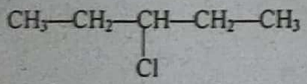
2,2,3-Trimethylbutane
pri-C, five
tert-C, one
quat-C, one

(b) $C_5H_{11}Cl$,

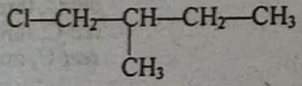
(i) $Cl-CH_2-CH_2-CH_2-CH_2-CH_3$
1-Chloropentane

(ii) 
$CH_3-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_2-CH_2-CH_3$

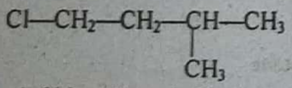
2-Chloropentane

(iii) 
$CH_3-CH_2-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_2-CH_3$

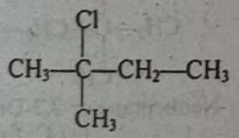
3-Chloropentane

(iv) 
$Cl-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-CH_3$

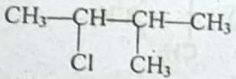
1-Chloro-2-methylbutane

(v) 
$Cl-CH_2-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

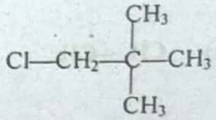
1-Chloro-3-methylbutane

(vi) 
$CH_3-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-CH_3$

2-Chloro-2-methylbutane

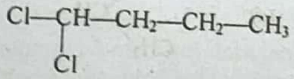
(vii) 
$CH_3-\underset{\underset{\textstyle Cl}{|}}{CH}-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

2-Chloro-3-methylbutane

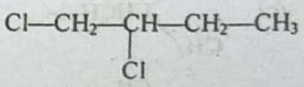
(viii) 
$Cl-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3$

1-Chloro-2,2-dimethylpropane

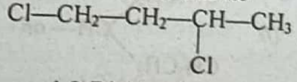
$C_4H_8Cl_2$,

(i) 
$Cl-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_2-CH_2-CH_3$

1,1-Dichlorobutane

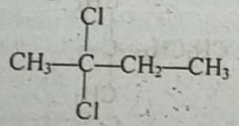
(ii) 
$Cl-CH_2-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_2-CH_3$

1,2-Dichlorobutane

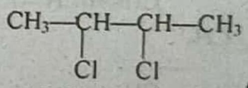
(iii) 
$Cl-CH_2-CH_2-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_3$

1,3-Dichlorobutane

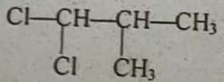
(iv) $Cl-CH_2-CH_2-CH_2-CH_2-Cl$
1,4-Dichlorobutane

(v) 
$CH_3-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{C}}-CH_2-CH_3$

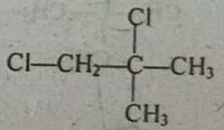
2,2-Dichlorobutane

(vi) 
$CH_3-\underset{\underset{\textstyle Cl}{|}}{CH}-\underset{\underset{\textstyle Cl}{|}}{CH}-CH_3$

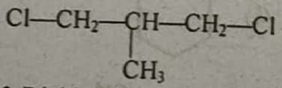
2,3-Dichlorobutane

(vii) 
$Cl-\underset{\underset{\textstyle Cl}{|}}{CH}-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

1,1-Dichloro-2-methylpropane

(viii) 
$Cl-CH_2-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3$

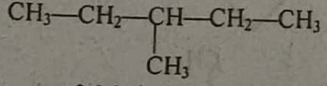
1,2-Dichloro-2-methylpropane

(ix) 
$Cl-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-Cl$

1,3-Dichloro-2-methylpropane

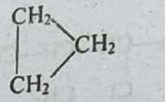
6. The correct name for the given structural formula is 3-ethyl-2,3,5-trimethylhexane *(d)*. The other names are not acceptable due to the reasons mentioned against each.

(a) The chain selected is not the longest.
(b) The chain selected does not contain the maximum number of substituents.
(c) The numerals allocated to the substituents do not give the minimum sum.
(e) The substituents are not written in alphabetical order.

7. (a) 
$CH_3-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2-CH_3$

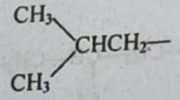
3-Methylpentane

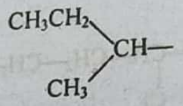
(b) (i) $CH_3—CH_3$

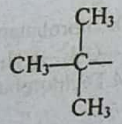
(ii) 

8. (a) $CH_3CH_2—$

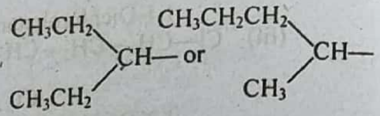
(b) $CH_3CH_2CH_2—$

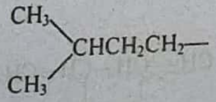
(c) 

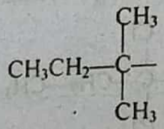
(d) 

(e) 

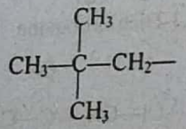
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—$

(f) 

(g) 

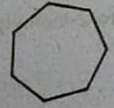
(h) 

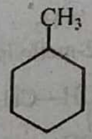
$CH_3CH_2—\overset{CH_3}{\underset{CH_3}{C}}—$

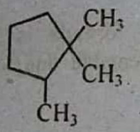
(i) 

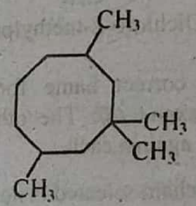
$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH_2—$

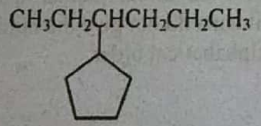
(j) $CH_3CH_2CH_2CH_2CH_2CH_2—$

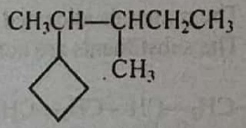
9. (a) 

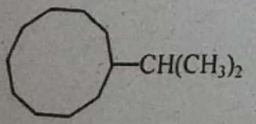
(b) 

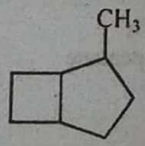
(c) 

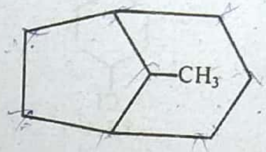
(d) 

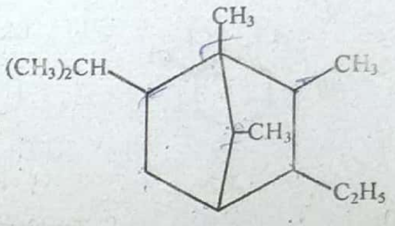
(e) 

(f) 

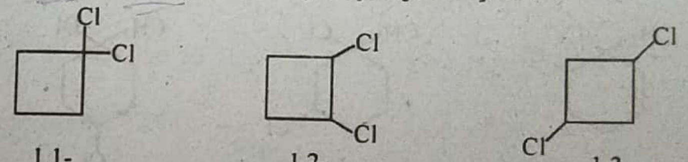
(g) 

(h) 

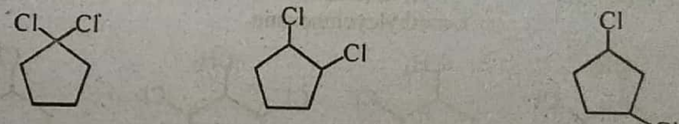
(i) 

(j) 

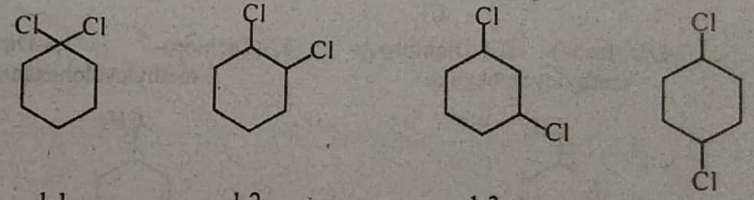
10. (a) Methylcyclopentane
(b) 1-Isopropyl-3-methylcyclohexane
(c) 3-Ethyl-1,1-dimethylcyclooctane
(d) *tert*-Butylcyclodecane
(e) 2,2-Dicyclopropylpropane
(f) 2-Chloro-1-cycloheptyl-2-methylpropane
(g) Bicyclo[4.4.0]decane
(h) 7-Methylbicyclo[2.2.1]heptane
(i) 8-Methylbicyclo[4.3.0]nonane
(j) 3-Ethyl-8-isopropyl-10-methyltricyclo[4.3.1.0]decane

11. (a) 

1,1- 1,2- 1,3-
Dichlorocyclobutane

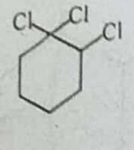
(b) 

1,1- 1,2- 1,3-
Dichlorocyclopentane

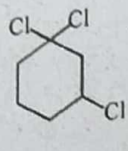
(c) 

1,1- 1,2- 1,3- 1,4-
Dichlorocyclohexane

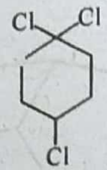
(d)



1,1,2-

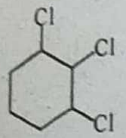


1,1,3-

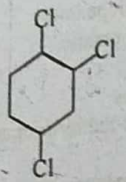


1,1,4-

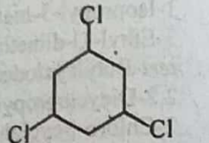
Trichlorocyclohexane



1,2,3-



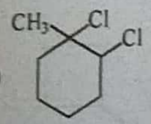
1,2,4-



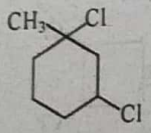
1,3,5-

Trichlorocyclohexane

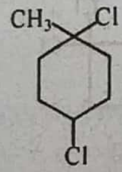
(e)



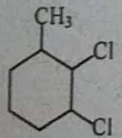
1,2-Dichloro-

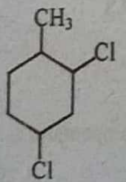


1,3-Dichloro-
1-methylcyclohexane

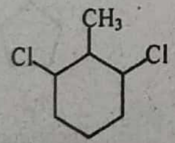


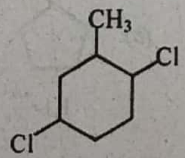
1,4-Dichloro



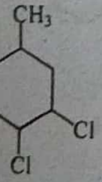


1,2-Dichloro-3- 2,4-Dichloro-1-
methylcyclohexane

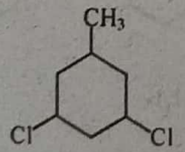




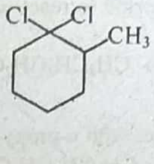
1,3-Dichloro- 1,4-Dichloro-
2-methylcyclohexane



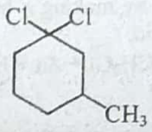
1,2-Dichloro-
4-methylcyclohexane



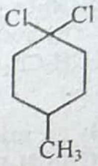
1,3-Dichloro-
5-methylcyclohexane



1,1-Dichloro-
2-methylcyclohexane



1,1-Dichloro-
3-methylcyclohexane



1,1-Dichloro-
4-methylcyclohexane

12. Petroleum is a complex mixture of straight- and branched-chain alkanes ranging in carbon content from C_1 to C_{40}, together with some quantities of cycloalkanes and aromatic hydrocarbons. Small amounts of oxygen-, nitrogen- and sulfur-containing compounds are also present in the mixture. Crude petroleum is obtained from underground pockets by drilling wells, as a viscous black liquid. It is separated into various fractions by fractional distillation. For the main fractions obtained by the fractional distillation of petroleum, see *Table 4.1* in the *Textbook*.

13. *(a)* $CH_3CH{=}CHCH_3 \xrightarrow[25°C]{H_2 + Ni} CH_3CH_2CH_2CH_3$

(b) $2C_2H_5Br + 2Na \xrightarrow[Ether]{} C_2H_5{-}C_2H_5 + 2NaBr$

(c) $C_2H_5Br + (CH_3)_2CHBr \xrightarrow[Ether]{Na} C_2H_5{-}C_2H_5 + C_2H_5{-}CH(CH_3)_2 + (CH_3)_2CH{-}CH(CH_3)_2$

(d) $(CH_3)_2CHBr \xrightarrow{Zn + HCl} CH_3CH_2CH_3$

(e) $CH_3COCH_3 \xrightarrow{Zn(Hg) + HCl} CH_3CH_2CH_3$

(f) $CH_3CH_2I \xrightarrow[Ether]{Mg} CH_3CH_2MgI \xrightarrow{H_2O} CH_3CH_3 + Mg(OH)I$

(g) $CH_3CH{=}CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2)_3B \xrightarrow[NaOH]{AgNO_3} CH_3CH_2CH_2CH_2CH_2CH_3$

14. **Methods for the preparation of *n*-hexane**

1. *n*-Hexane can be prepared by shaking a solution of hexene in ethanol under a slight pressure of hydrogen gas in the presence of a small quantity of finely divided nickel, platinum or palladium.

$$CH_3CH_2CH_2CH_2CH{=}CH_2 + H_2 \xrightarrow[25°C]{Ni} CH_3CH_2CH_2CH_2CH_2CH_3$$

2. It can be prepared by making *n*-hexyl chloride to react with zinc in the presence of hydrochloric acid.

$$CH_3CH_2CH_2CH_2CH_2CH_2Cl + Zn + HCl \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 + ZnCl_2$$

3. By the reaction of lithium di-*n*-propylcopper with *n*-propyl chloride.

$$(CH_3CH_2CH_2)_2CuLi + CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2Cu + LiCl$$

4. By the treatment of an ethereal solution of *n*-propyl bromide with sodium metal.

$$2CH_3CH_2CH_2Br + 2Na \xrightarrow[\text{Ether}]{} CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

5. By the coupling of *n*-propylborane by means of silver nitrate in the presence of sodium hydroxide. *n*-Propylborane can be obtained by the treatment of propene with diborane.

$$6CH_3CH{=}CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2CH_2)_3B \xrightarrow[\text{NaOH}]{\text{AgNO}_3} CH_3CH_2CH_2CH_2CH_2CH_3$$

6. By the reduction of hexanal or 2-hexanone with zinc amalgam and hydrochloric acid at an elevated temperature.

$$CH_3CH_2CH_2CH_2CH_2CHO \xrightarrow[200°C]{Zn(Hg) + HCl} CH_3CH_2CH_2CH_2CH_2CH_3$$

7. By the hydrolysis of *n*-hexylmagnesium bromide which can be obtained when a solution of *n*-hexyl bromide in dry ether is allowed to stand over magnesium turning.

$$CH_3(CH_2)_4CH_2Br + Mg \xrightarrow[\text{Ether}]{} CH_3(CH_2)_4CH_2MgBr \xrightarrow{H_2O} CH_3(CH_2)_4CH_3 + Mg(OH)Br$$

8. By the electrolysis of a concentrated solution of sodium or potassium salt of butanoic acid.

$$2CH_3CH_2CH_2COOK + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3CH_2CH_2CH_2CH_2CH_3 + 2CO_2 + H_2 + 2KOH$$

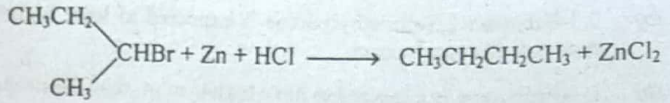
15. (*a*) $CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow[25°C]{Ni} CH_3CH_2CH_2CH_3$

(*b*) $CH_3CH{=}CHCH_3 + H_2 \xrightarrow[25°C]{Ni} CH_3CH_2CH_2CH_3$

(*c*) $2CH_3CH_2Cl + 2Na \xrightarrow[\text{Ether}]{} CH_3CH_2CH_2CH_3 + 2NaCl$

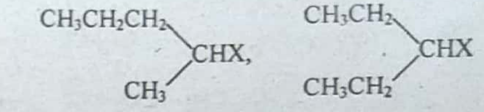
(*d*) $CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2CH_2MgBr \xrightarrow{H_2O} CH_3CH_2CH_2CH_3 + Mg(OH)Br$

(*e*)



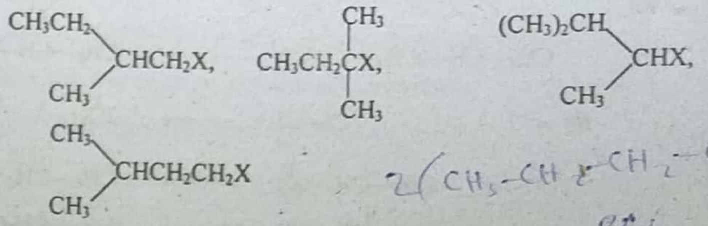
$$(CH_3CH_2)(CH_3)CHBr + Zn + HCl \longrightarrow CH_3CH_2CH_2CH_3 + ZnCl_2$$

16. (*a*) Three; $CH_3(CH_2)_3CH_2X$,



$(CH_3CH_2CH_2)(CH_3)CHX$, $(CH_3CH_2)_2CHX$

(*b*) Four;

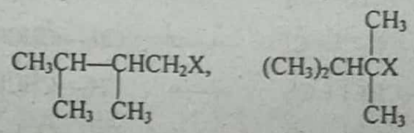


$(CH_3CH_2)(CH_3)CHCH_2X$, $CH_3CH_2C(CH_3)_2X$, $((CH_3)_2CH)(CH_3)CHX$, $(CH_3)_2CHCH_2CH_2X$

$2(CH_3-CH_2-CH_2-Cl)$

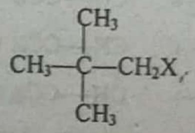
2Li

(*c*) Two;



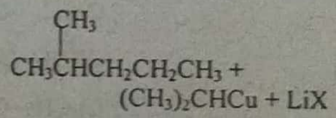
$CH_3CH(CH_3)-CH(CH_3)CH_2X$, $(CH_3)_2CHC(CH_3)_2X$

(*d*) One;



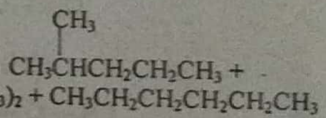
$CH_3-C(CH_3)_2-CH_2X$,

17. (i) Corey-House method,



$$[(CH_3)_2CH]_2CuLi + CH_3CH_2CH_2X \longrightarrow CH_3CH(CH_3)CH_2CH_2CH_3 + (CH_3)_2CHCu + LiX$$

(ii) Wurtz reaction,



$$(CH_3)_2CHX + CH_3CH_2CH_2X + 2Na \longrightarrow CH_3CH(CH_3)CH_2CH_2CH_3 + (CH_3)_2CHCH(CH_3)_2 + CH_3CH_2CH_2CH_2CH_2CH_3$$

In the second method we get a mixture, and thus it is not a suitable method. We should therefore prefer the Corey-House method in this case.

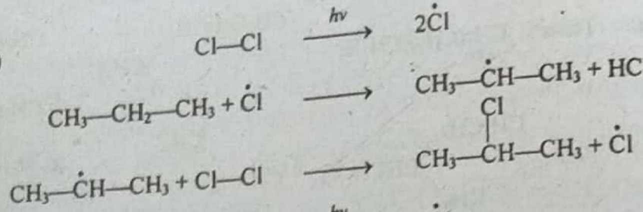
18. (a) (*a*) Hexane has higher boiling point than pentane.
(*b*) *n*-Hexane has higher boiling point than isohexane.
(*c*) 1-Chloropropane has higher b.pt. than 2-chloropropane.
(*d*) 3-Methylpentane has higher b.pt. than 2,3-dimethylbutane.

(b) 3-Methylhexane (*e*) > 3,3-dimethylpentane (*c*) > *n*-hexane (*d*) > 3-methylpentane (*b*) > *n*-pentane (*a*).

19. (a) 2,3-Dibromo-2,3-dimethylbutane is expected to have higher melting point than 3,4-dibromohexane.

(b) 1-Nitrobutane is expected to have higher m.pt. than 2-nitropropane.

20. (a)



$$Cl-Cl \xrightarrow{h\nu} 2\dot{C}l$$

$$CH_3-CH_2-CH_3 + \dot{C}l \longrightarrow CH_3-\dot{C}H-CH_3 + HCl$$

$$CH_3-\dot{C}H-CH_3 + Cl-Cl \longrightarrow CH_3-\overset{Cl}{C}H-CH_3 + \dot{C}l$$

(b)

$$Cl-Cl \xrightarrow{h\nu} 2\dot{C}l$$

$$CH_3-CH_3 + \dot{C}l \longrightarrow CH_3-\dot{C}H_2 + HCl$$

$$CH_3-\dot{C}H_2 + Cl_2 \longrightarrow CH_3-CH_2Cl + \dot{C}l$$

$$CH_3-CH_2Cl + \dot{C}l \longrightarrow CH_3-\dot{C}HCl + HCl$$

$$CH_3-\dot{C}HCl + Cl_2 \longrightarrow CH_3-CHCl_2 + \dot{C}l$$

$$CH_3-CHCl_2 + \dot{C}l \longrightarrow CH_3-\dot{C}Cl_2 + HCl$$

$$CH_3-\dot{C}Cl_2 + Cl_2 \longrightarrow CH_3-CCl_3 + \dot{C}l$$

$$CH_3-CCl_3 + \dot{C}l \longrightarrow \dot{C}H_2-CCl_3 + HCl$$

$$\dot{C}H_2-CCl_3 + Cl_2 \longrightarrow ClCH_2-CCl_3 + \dot{C}l$$

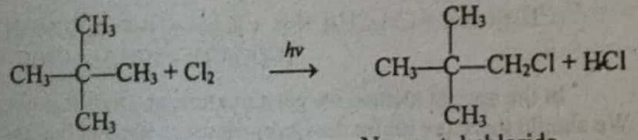
$$ClCH_2-CCl_3 + \dot{C}l \longrightarrow Cl\dot{C}H-CCl_3 + HCl$$

$$Cl\dot{C}H-CCl_3 + Cl_2 \longrightarrow Cl_2CH-CCl_3 + \dot{C}l$$

$$Cl_2CH-CCl_3 + \dot{C}l \longrightarrow Cl_2\dot{C}-CCl_3 + HCl$$

$$Cl_2\dot{C}-CCl_3 + Cl_2 \longrightarrow Cl_3C-CCl_3 + \dot{C}l$$

21.



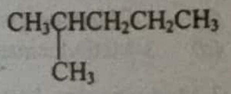
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl + HCl$$

Neopentane Neopentyl chloride

22. C_6H_{14} isomers,

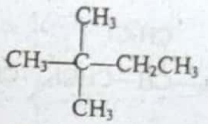
(i) $CH_3CH_2CH_2CH_2CH_2CH_3$

(ii)



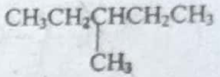
$CH_3\underset{CH_3}{C}HCH_2CH_2CH_3$

(iii)



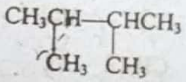
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3$

(iv)



$CH_3CH_2\underset{CH_3}{C}HCH_2CH_3$

(v)



$CH_3\underset{CH_3}{C}H-\underset{CH_3}{C}HCH_3$

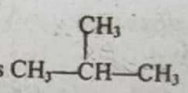
(a) The isomer (v) will give two monochloro- derivatives.

(b) The isomers (i) and (iii) will give three monochloro- derivatives.

(c) The isomer (iv) will give four monochloro- derivatives.

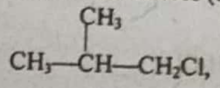
(d) The isomer (ii) will give five monochloro- derivatives.

23. The structure of isobutane is

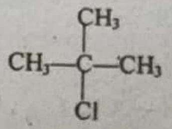


$CH_3-\overset{CH_3}{C}H-CH_3$

Monochloro- derivatives (two):

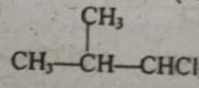


$CH_3-\overset{CH_3}{C}H-CH_2Cl,$

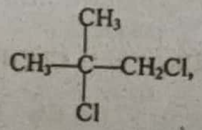


$CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_3$

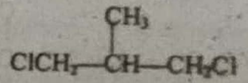
Dichloro- derivatives (three):



$CH_3-\overset{CH_3}{C}H-CHCl_2,$

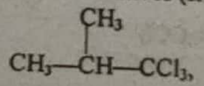


$CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2Cl,$

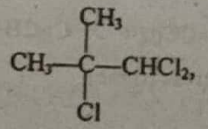


$ClCH_2-\overset{CH_3}{C}H-CH_2Cl$

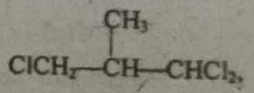
Trichloro- derivatives (five):



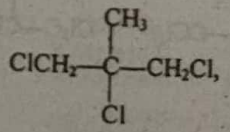
$CH_3-\overset{CH_3}{C}H-CCl_3,$



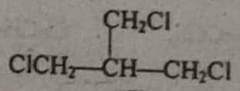
$CH_3-\overset{CH_3}{\underset{Cl}{C}}-CHCl_2,$



$ClCH_2-\overset{CH_3}{C}H-CHCl_2,$

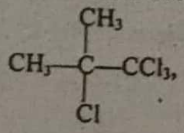


$ClCH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2Cl,$

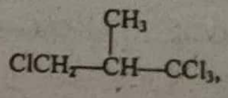


$ClCH_2-\overset{CH_2Cl}{C}H-CH_2Cl$

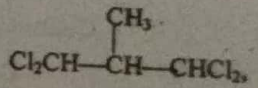
Tetrachloro- derivatives (six):



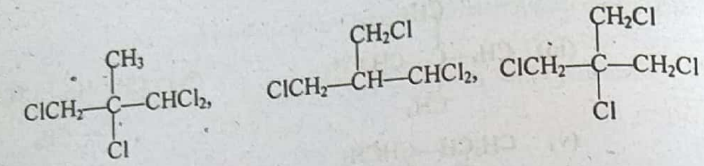
$CH_3-\overset{CH_3}{\underset{Cl}{C}}-CCl_3,$



$ClCH_2-\overset{CH_3}{C}H-CCl_3,$

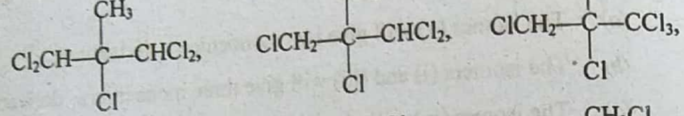


$Cl_2CH-\overset{CH_3}{C}H-CHCl_2,$

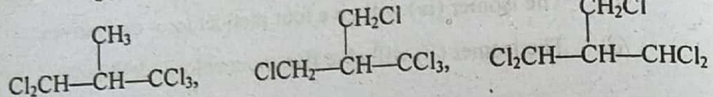


$\mathrm{ClCH_2{-}\underset{Cl}{\overset{CH_3}{C}}{-}CHCl_2}$, $\mathrm{ClCH_2{-}\overset{CH_2Cl}{CH}{-}CHCl_2}$, $\mathrm{ClCH_2{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CH_2Cl}$

Pentachloro- derivatives (six):

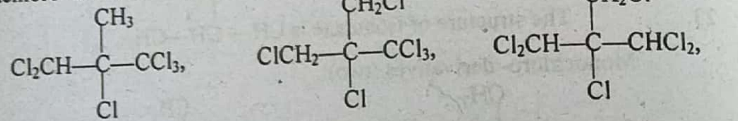


$\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CH_3}{C}}{-}CHCl_2}$, $\mathrm{ClCH_2{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CHCl_2}$, $\mathrm{ClCH_2{-}\underset{Cl}{\overset{CH_3}{C}}{-}CCl_3}$,

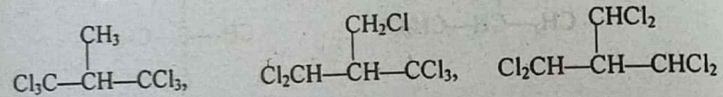


$\mathrm{Cl_2CH{-}\overset{CH_3}{CH}{-}CCl_3}$, $\mathrm{ClCH_2{-}\overset{CH_2Cl}{CH}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\overset{CH_2Cl}{CH}{-}CHCl_2}$

Hexachloro- derivatives (six):

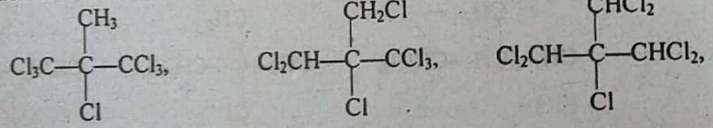


$\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CH_3}{C}}{-}CCl_3}$, $\mathrm{ClCH_2{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CHCl_2}$,

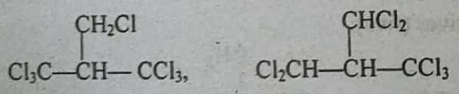


$\mathrm{Cl_3C{-}\overset{CH_3}{CH}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\overset{CH_2Cl}{CH}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\overset{CHCl_2}{CH}{-}CHCl_2}$

Heptachloro- derivatives (five):

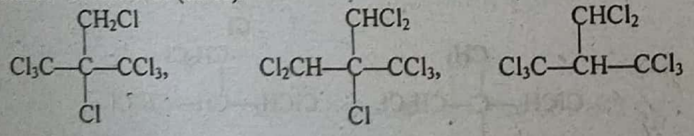


$\mathrm{Cl_3C{-}\underset{Cl}{\overset{CH_3}{C}}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CHCl_2}{C}}{-}CHCl_2}$,



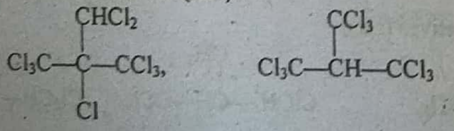
$\mathrm{Cl_3C{-}\overset{CH_2Cl}{CH}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\overset{CHCl_2}{CH}{-}CCl_3}$

Octachloro- derivatives (three):



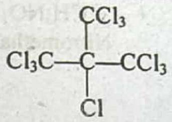
$\mathrm{Cl_3C{-}\underset{Cl}{\overset{CH_2Cl}{C}}{-}CCl_3}$, $\mathrm{Cl_2CH{-}\underset{Cl}{\overset{CHCl_2}{C}}{-}CCl_3}$, $\mathrm{Cl_3C{-}\overset{CHCl_2}{CH}{-}CCl_3}$

Nonachloro- derivatives (two):



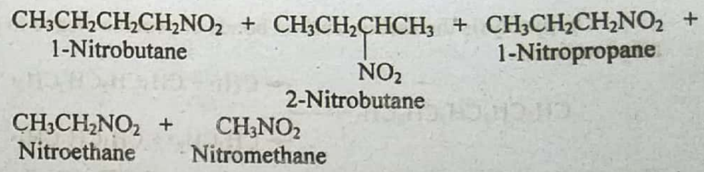
$\mathrm{Cl_3C{-}\underset{Cl}{\overset{CHCl_2}{C}}{-}CCl_3}$, $\mathrm{Cl_3C{-}\overset{CCl_3}{CH}{-}CCl_3}$

Decachloro- derivative (one):



$\mathrm{Cl_3C{-}\underset{Cl}{\overset{CCl_3}{C}}{-}CCl_3}$

24. (a)



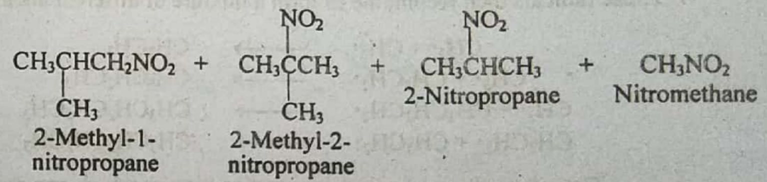
$\mathrm{CH_3CH_2CH_2CH_2NO_2}$ + $\mathrm{CH_3CH_2\underset{NO_2}{CH}CH_3}$ + $\mathrm{CH_3CH_2CH_2NO_2}$ +

1-Nitrobutane, 2-Nitrobutane, 1-Nitropropane

$\mathrm{CH_3CH_2NO_2}$ + $\mathrm{CH_3NO_2}$

Nitroethane, Nitromethane

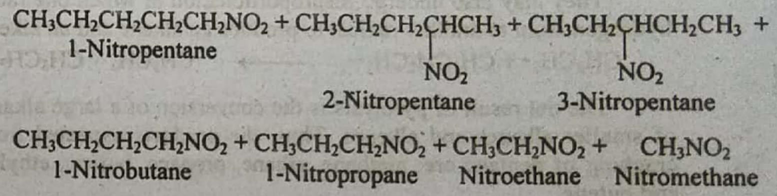
(b)



$\mathrm{CH_3\underset{CH_3}{CH}CH_2NO_2}$ + $\mathrm{CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_3}$ + $\mathrm{CH_3\overset{NO_2}{CH}CH_3}$ + $\mathrm{CH_3NO_2}$

2-Methyl-1-nitropropane, 2-Methyl-2-nitropropane, 2-Nitropropane, Nitromethane

(c)



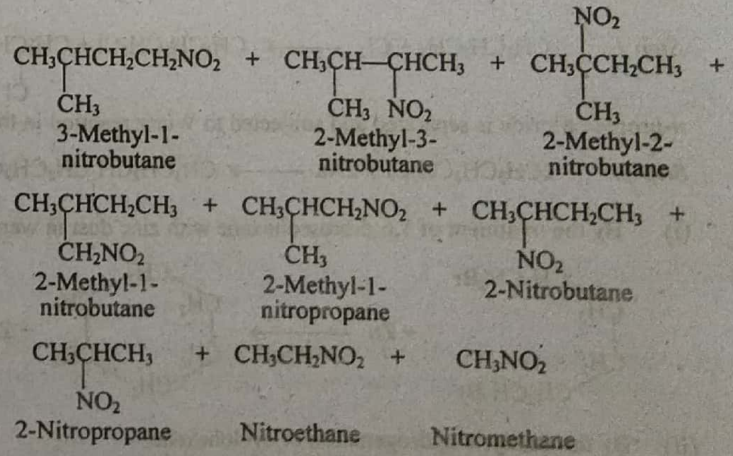
$\mathrm{CH_3CH_2CH_2CH_2CH_2NO_2}$ + $\mathrm{CH_3CH_2CH_2\underset{NO_2}{CH}CH_3}$ + $\mathrm{CH_3CH_2\underset{NO_2}{CH}CH_2CH_3}$ +

1-Nitropentane, 2-Nitropentane, 3-Nitropentane

$\mathrm{CH_3CH_2CH_2CH_2NO_2}$ + $\mathrm{CH_3CH_2CH_2NO_2}$ + $\mathrm{CH_3CH_2NO_2}$ + $\mathrm{CH_3NO_2}$

1-Nitrobutane, 1-Nitropropane, Nitroethane, Nitromethane

(d)



$\mathrm{CH_3\underset{CH_3}{CH}CH_2CH_2NO_2}$ + $\mathrm{CH_3\underset{CH_3}{CH}{-}\underset{NO_2}{CH}CH_3}$ + $\mathrm{CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_2CH_3}$ +

3-Methyl-1-nitrobutane, 2-Methyl-3-nitrobutane, 2-Methyl-2-nitrobutane

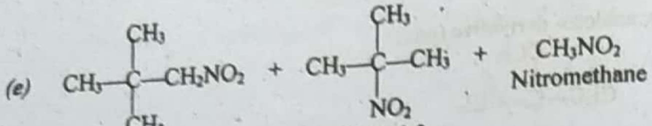
$\mathrm{CH_3\underset{CH_2NO_2}{CH}CH_2CH_3}$ + $\mathrm{CH_3\underset{CH_3}{CH}CH_2NO_2}$ + $\mathrm{CH_3\underset{NO_2}{CH}CH_2CH_3}$ +

2-Methyl-1-nitrobutane, 2-Methyl-1-nitropropane, 2-Nitrobutane

$\mathrm{CH_3\underset{NO_2}{CH}CH_3}$ + $\mathrm{CH_3CH_2NO_2}$ + $\mathrm{CH_3NO_2}$

2-Nitropropane, Nitroethane, Nitromethane

(e)



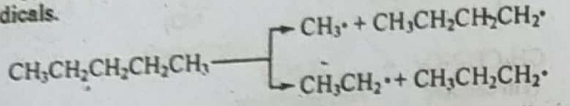
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2NO_2 + CH_3-\underset{NO_2}{\overset{CH_3}{C}}-CH_3 + CH_3NO_2$$

2,2-Dimethyl 1-nitropropane

2-Methyl-2-nitropropane

Nitromethane

25. On pyrolysis the carbon-carbon bonds of pentane cleave to produce smaller alkyl radicals.



These radicals then recombine to form a mixture of different alkanes.

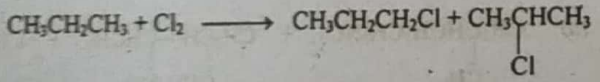
$$CH_3\cdot + CH_3\cdot \longrightarrow CH_3CH_3$$
$$CH_3\cdot + CH_3CH_2\cdot \longrightarrow CH_3CH_2CH_3$$
$$CH_3\cdot + CH_3CH_2CH_2\cdot \longrightarrow CH_3CH_2CH_2CH_3$$
$$CH_3CH_2\cdot + CH_3CH_2\cdot \longrightarrow CH_3CH_2CH_2CH_3$$

They may also undergo disproportionation in which one radical transfers a hydrogen atom to another radical to produce an alkane and an alkene.

$$CH_3CH_2\cdot + CH_3CH_2CH_2\cdot \longrightarrow CH_3CH_3 + CH_3CH{=}CH_2$$

The net result of pyrolysis is the conversion of a large alkane to a mixture of smaller alkanes and alkenes. Thus, the products expected from the thermal cracking of pentane are: methane, ethane, propane, butane, ethylene, propylene and butene.

26. *Step I.*

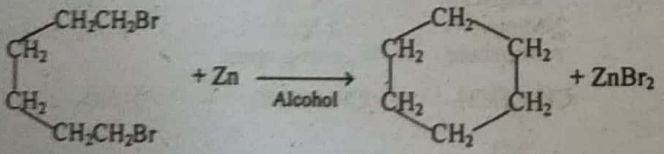


$$CH_3CH_2CH_3 + Cl_2 \longrightarrow CH_3CH_2CH_2Cl + CH_3\underset{Cl}{C}HCH_3$$

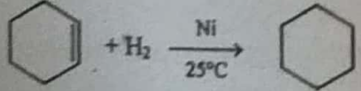
n-propyl chloride is separated and subjected to Wurtz reaction in the second step.

Step 2. $2CH_3CH_2CH_2Cl + 2Na \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaCl$

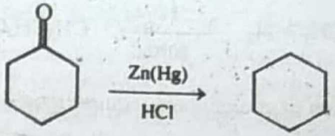
27. (i) By the treatment of 1,6-dibromohexane with zinc dust in warm alcohol.



(ii) By the catalytic hydrogenation of cyclohexene.

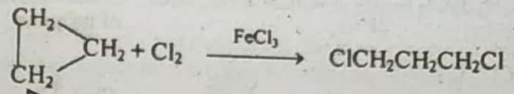


(iii) By subjecting cyclohexanone to Clemmensen reduction.

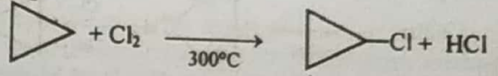


28. In a dilute solution, there is less possibility of two molecules to come close enough to undergo Wurtz reaction, and each molecule is independent to undergo Freund reaction. In a concentrated solution the molecules are closer to each other to be able to give Wurtz reaction.

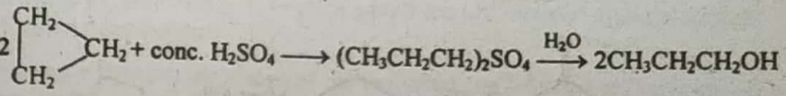
29. (a)



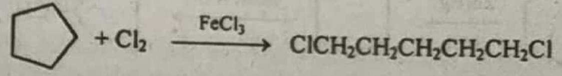
(b)



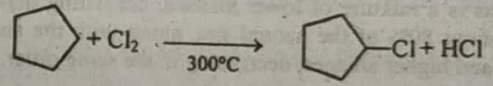
(c) 2



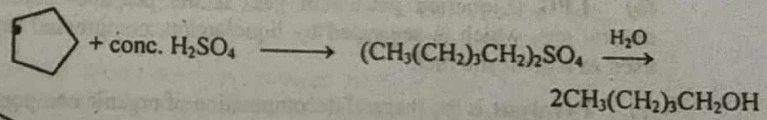
(d)



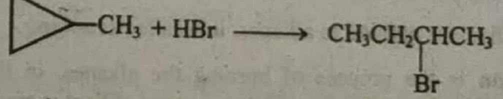
(e)



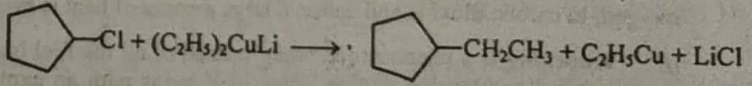
(f) 2



(g)



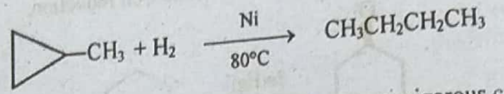
(h)



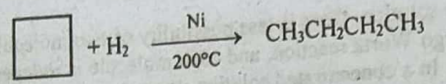
30. The three hydrocarbons can be differentiated by catalytic hydrogenation. The catalytic hydrogenation of 1-butene takes place at room temperature.

$$CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow[25°C]{Ni} CH_3CH_2CH_2CH_3$$

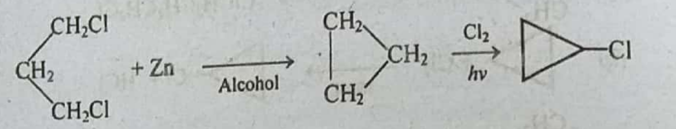
The hydrogenation of methylcyclopropane occurs at moderate temperature.



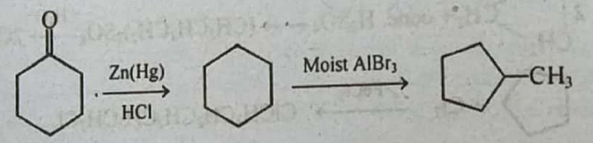
The hydrogenation of cyclobutane requires more vigorous conditions.



31. (a) $CH_3CH_2CH_3 + Cl_2 \xrightarrow[25°C]{hv} ClCH_2CH_2CH_2Cl$ + Other chloro- derivatives of propane



(b)



32. (a) **Natural gas** is a mixture of lower alkanes, consisting mainly of methane that constitutes about 80% of the natural gas, along with the small amounts of ethane, propane, and higher alkanes, decreasing in the same order.

(b) **LPG** (Liquefied petroleum gas) is the propane-butane fraction of the natural gas, which is separated by liquefaction, compressed into cylinders, and used as a domestic fuel.

(c) **Pyrolysis** is the thermal decomposition of organic compounds.

(d) When pyrolysis is applied to alkanes, it is called **cracking.**

(e) **Combustion** is the process of burning the alkanes, in the presence of oxygen, to carbon dioxide and water; a large amount of heat is evolved.

(f) **Knocking** is a phenomenon when instead of all the fuel burning smoothly in an internal combustion engine, some of it burns with an explosive violence, due to a premature ignition of the fuel.

(g) **Octane number** of a fuel is the volume percentage of isooctane in an isooctane-heptane mixture that has the knocking property similar to that of the fuel.

(h) Conversion of higher hydrocarbons into the lower ones suitable for use as motor fuel, by cracking, is known as **reforming**.

(i) Cycloalkanes are generally less stable than the corresponding open-chain alkanes, because their molecules are under strain, called the **ring strain,** due to the presence of a ring in the molecule.

(j) Any atom in a molecule normally tends to have bond angles matching to its bonding orbitals. Any deviation from these normal bond angles causes a strain in the molecule. This type of strain is called **angle strain**.

(k) Any two bonds on adjacent tetrahedral carbon atoms in a molecule, like C—H bonds of ethane, tend to be as far apart as possible to decrease repulsive interaction between the electrons of the bonds. Any decrease in the lateral distance between the bonds on two adjacent carbon atoms causes strain in the molecule. This type of strain is called **torsional strain.**

(l) When the nonbonded atoms in a molecule are close enough to cause a strain in the molecule, the strain is called **steric strain.**

(m) In cyclopropane, the tetrahedral carbon atoms cannot permit their bonding orbitals to be directed along the line joining their nuclei for bond formation. The bonds formed by the overlap of orbitals which are not directed along a straight line are called **bent bonds.**

(n) An angle between the planes of the two bonds on adjacent atoms is called **dihedral angle.**

(o) The amount of heat evolved when one mole of hydrocarbon is burnt to carbon dioxide and water, is called the **heat of combustion**.

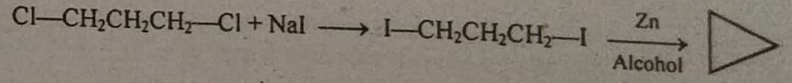
33. (a) (i), (ii) and (iii) An alkyl group at position 1 of a chain should be included in the parent chain.
(iv) Less substituted chain has been selected as the parent chain.
(v) Smaller chain has been selected as the parent chain.

(b) Since the Wurtz reaction involves an S_N2 attack by R^- of the initially formed organosodium compound on the alkyl halide, a tertiary alkyl halide is not suitable for this mechanism, rather it leads to a side reaction involving elimination.

(c) The two ends of a long chain required to synthesize a large ring are less likely to be close enough to be able to cyclise.

(d) Bromine is less reactive than chlorine, and is thus more selective in the site of attack. It mainly attacks the tertiary hydrogen atom, i.e., at position 1 of methylcyclopentane.

(e) Iodide ion converts the dichloropropane to the more reactive diiodopropane through displacement reaction.


$Cl—CH_2CH_2CH_2—Cl + NaI \longrightarrow I—CH_2CH_2CH_2—I \xrightarrow[Alcohol]{Zn}$