UNIT 14

Organic Chemistry Some Basic Principles

SYLLABUS

Tetracovalency of carbon, hybridization, (*p* and *s*) bonds, shapes of simple molecules, functional groups : –C = C–, –C ≡ C–, functional groups containing halogen, oxygen, nitrogen and sulphur.

Homologous series

Isomerism

General introduction to naming organic compounds—trivial and IUPAC nomenclature. Illustration with simple examples.

Electronic displacement in a covalent bond : inductive effect, electromeric effect, resonance and hyperconjugation.

Fission of a covalent bond : free radicals, electrophiles, nucleophiles, carbocations and carbanions.

Common types of organic reactions : substitution, addition, elimination and rearrangement reactions. Illustrations with examples.

14.1. Introduction

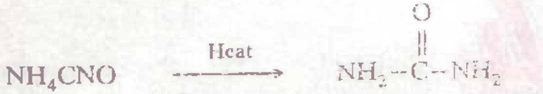
It has been known since times immemorial that minerals, plants and animals are the three major sources of naturally occurring substances. But it was only in eighteeth century that these compounds were divided into two classes, viz. Organic and Inorganic compounds mainly on the basis of their source. *Compounds like urea, sugars, oils, fats, dyes, proteins, vitamins etc., which were isolated directly or indirectly from living organisms, such as animals and plants were called* **Organic Compounds** *and the branch of chemistry which dealt with the study of these compounds was called* **Organic Chemistry**. *On the other hand, compounds like common salt, marble, alums, nitre, blue and green vitriols etc. which were isolated from non-living sources, such as rocks and minerals, were called* **Inorganic Compounds**, *and the branch of chemistry which dealt with the study of these compounds was called* **Inorganic Chemistry**.

14.1.1. Vital Force Theory

Until early nineteenth century, it was believed that organic compounds cannot be prepared in the laboratory but can only be isolated from animals and plants. On the basis of this belief, *Berzelius, a leading Swedish chemist in 1815, propounded* **Vital Force Theory**. According to this theory, *organic compounds are produced only under the influence of some mysterious force existing in the living organisms. This mysterious force was called the* **Vital Force**. Since such a mysterious force cannot be created artificially, it is impossible to synthesize organic compounds in the laboratory. This theory reigned supreme for a number of years.

However, in 1828, *Wohler*, a German chemist, made an interesting discovery. He accidentally obtained *urea*, a well known organic compound, present in the urine of man and other mammals by evaporating an aqueous solution of ammonium cyanate, a typical inorganic compound (obtained by double decomposition of ammonium chloride and potassium cyanate) :

$$NH_4Cl + KCNO \longrightarrow \underset{\text{Amm. cyanate}}{NH_4CNO} + KCl$$



$$\underset{\text{(Inorganic compound)}}{NH_4CNO} \xrightarrow[\text{Rearranges}]{\text{Heat}} \underset{\text{Urea (Organic Compound)}}{NH_2-\overset{\overset{O}{\|}}{C}-NH_2}$$

This synthesis gave a death blow to *Vital Force Theory* and clearly demonstrated that *no mysterious force was required in the formation of organic compounds in the laboratory.* The elegant synthesis of acetic acid by *Herman Kolbe* in 1845 from purely inorganic sources which had previously been obtained from biological materials, drove the last nail in the coffin of Vital Force Theory.

$$2C + H_2 \xrightarrow[\text{arc}]{\text{Electric}} \underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

Thereafter thousands and thousands of organic compounds have been synthesized in the laboratory thereby showing conclusively that like inorganic compounds, organic compounds can be easily synthesized in the laboratory.

14.1.2. Modern definition of Organic Compounds

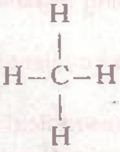
With the downfall of *Vital Force Theory*, the term organic (*pertaining to life*) lost its original significance. However, it was shown that all organic compounds whether *natural* or *synthetic* essentially contain carbon and hydrogen and occasionally a few other elements such as oxygen, nitrogen, sulphur, halogens and phosphorus. Thus, *organic chemistry* is now defined *as the chemistry of carbon compounds containing usually hydrogen and one or more additional elements like oxygen, nitrogen, sulphur, halogens, phosphorus etc. Inorganic chemistry, on the other hand, is defined as the chemistry of all elements other than carbon and their compounds.*

It should be mentioned here that some compounds of carbon such as CO, CO_2, H_2CO_3, metal carbonates, carbides, cyanides etc., which should otherwise have been included in organic chemistry are still studied under inorganic chemistry because of their greater resemblance with inorganic compounds.

Further, organic compounds made up of only carbon and hydrogen atoms are called *hydrocarbons* and all other organic compounds may be regarded to have been derived from these hydrocarbons by replacement of one or more of their hydrogen atoms by other atoms or groups. Thus, *organic chemistry may more precisely be defined as the chemistry of the hydrocarbons and their derivatives.*

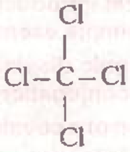
14.2. Tetravalency of Carbon

Carbon is the essential element of all organic molecules. Its electronic configuration is 2, 4. In other words, carbon has four electrons in the valence shell and thus needs four more electrons to complete its octet. Therefore, carbon is tetravelent. Further, it is very difficult for carbon to either gain or lose four electrons to achieve the nearest inert gas configuration. Consequently, carbon always combines with other atoms by mutual sharing of electrons and thus forms covalent bonds. *Since all the organic compounds contain carbon as the essential element, therefore, the nature of chemical bonding in organic compounds is always covalent.* Thus, *carbon is always* **tetracovalent,** *i.e.*, it forms four covalent bonds with other atoms as shown below :



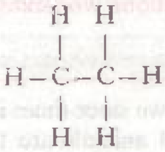
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

Methane



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

Carbon tetrachloride



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

Ethane

However, these structures do not reveal as to what is the spatial orientation of these four bonds whether they are **planar** *i.e., lie in same plane* or are **non-polar,** *i.e., lie in different planes.* The first insight into the spatial disposition of the four bonds of carbon was suggested by *van't Hoff* and *Le Bel* who in 1874 predicted that the four bonds of a carbon atom are directed towards the four corners of a *regular tetrahedron, i.e.,* the angle between any two adjacent bonds is 109° – 28′ (*tetrahedral angle*) as shown in Fig. 14.1.

This tetrahedral concept of carbon has been established beyond any doubt by electron diffraction, X-ray diffraction and spectroscopic studies.

The tetrahedral arrangement of four bonds of carbon laid the foundation of the present day fascinating field of '*Stereochemistry*'. It is because of this reason that van't Hoff was awarded the first Nobel Prize in Chemistry in 1901. He is also sometimes called '*The father of Organic Chemistry*'.

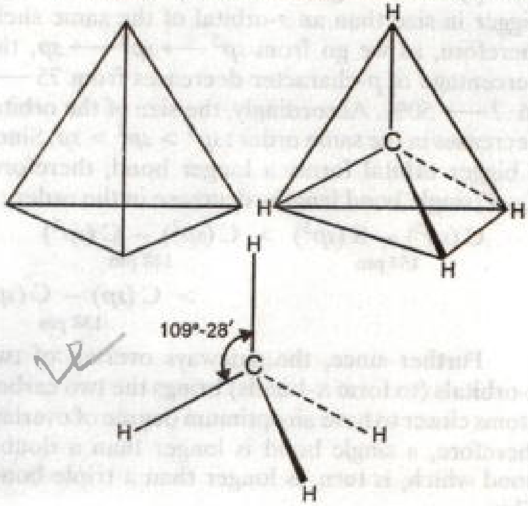


FIGURE 14.1. Vant's Hoff tetrahedral carbon atom. The wedged line is above the plane of the paper ; the normal lines lie in the plane of the paper and the dotted line lies below the plane of the paper.

PART I

HYBRIDIZATION AND SHAPES OF MOLECULES

14.3. Shapes of Simple Molecules

One of the most important aspects of organic chemistry is to understand the fundamental concepts of molecular structure since on the basis of these structures, we can easily predict the properties of organic molecules. To explain the structures of organic molecules, the electronic theory of valency and the concept of hybridization was introduced in unit 6. On the basis of sp^3-hybridization of carbon, the structures of methane (Fig. 14.2) and ethane (Fig. 14.3) molecules were predicted to be tetrahedral.

Similarly, structure of ethene ($CH_2 = CH_2$) was explained to be planar on the basis of sp^2-hybridization (Fig. 14.4) and that of ethyne ($HC \equiv HC$) to be linear on the basis of sp-hybridization as shown in FIg. 14.5.

Further the formation of ethylenic π-bond, *i.e.*, double bond was explained on the basis of sp^2-hybridization and acetylenic π-bond, *i.e.*, triple bond was explained on the basis of sp-hybridized. However, σ-bonds can be formed by overlap of atomic or hybridized orbitals.

Thus, in terms of σ- and π-bonds, a carbon-carbon double bond consists of one strong σ-bond

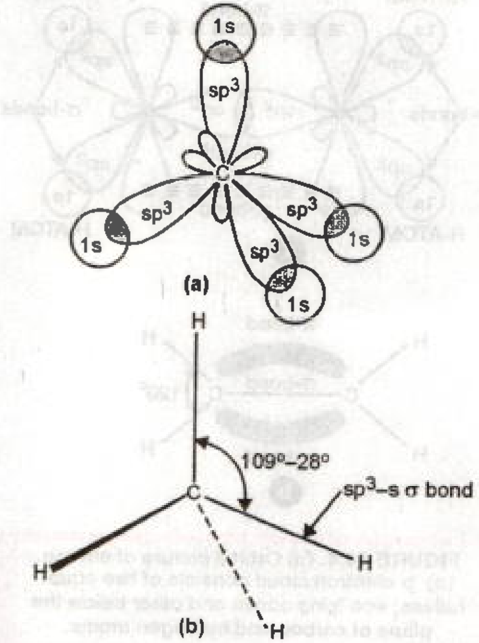


FIGURE 14.2. (a) Orbital picture of methane. (b) Bond angles and bond lengths in methane.

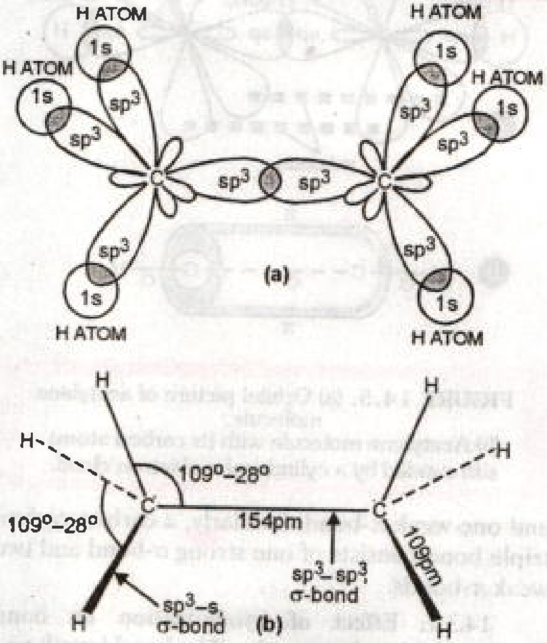


FIGURE 14.3. (a) Orbital picture of ethane. (b) Bond lengths and bond angles in ethane

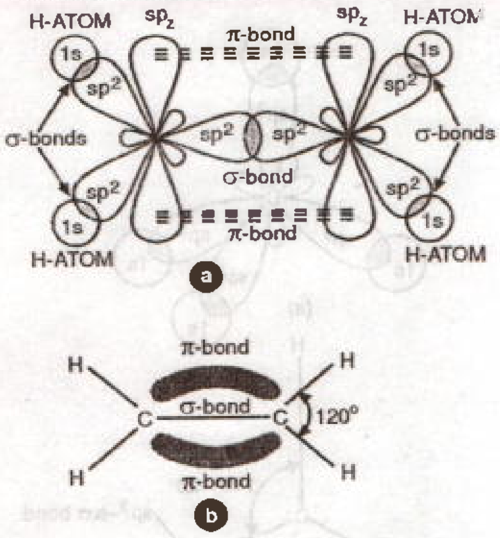


FIGURE 14.4. (a) Orbital picture of ethene. (b) p-electron cloud consists of two equal halves; one lying above and other below the plane of carbon and hydrogen atoms.

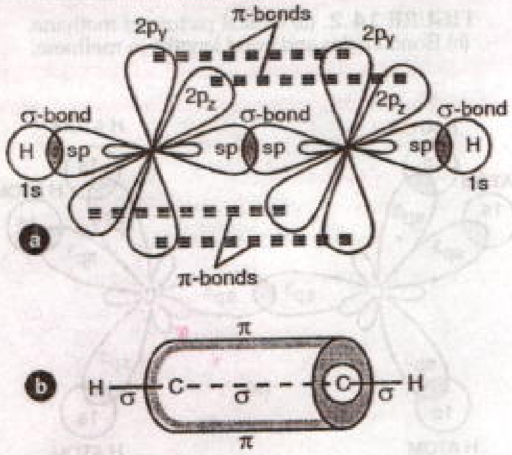


FIGURE 14.5. (a) Orbital picture of acetylene molecule.

(b) Acetylene molecule with its carbon atoms surrounded by a cylindrical π-electron cloud.

and one weak π-bond. Similarly, a carbon-carbon triple bond consists of one strong σ-bond and two weak π-bonds.

14.3.1. Effect of hybridization on bond lengths and bond strengths. The bond length and bond strength of any bond depends upon the size of the hybrid orbitals involved.

(*i*) **Bond lengths.** Since a *p*-orbital is much bigger in size than an *s*-orbital of the same shell, therefore, as we go from $sp^3 \longrightarrow sp^2 \longrightarrow sp$, the percentage of *p*-character decreases from $75 \longrightarrow 66 \cdot 7 \longrightarrow 50\%$. Accordingly, the size of the orbital decreases in the same order : $sp^3 > sp^2 > sp$. Since a bigger orbital forms a longer bond, therefore, C–C single bond lengths decrease in the order :

$$\underset{154\text{ pm}}{C(sp^3)-S(sp^3)} > \underset{148\text{ pm}}{C(sp^2)-C(sp^2)}$$
$$> \underset{138\text{ pm}}{C(sp)-C(sp)}$$

Further since, the sideways overlap of two *p*-orbitals (to form π-bonds) brings the two carbon atoms closer to have an optimum degree of overlap, therefore, a single bond is longer than a double bond which, is turn, is longer than a triple bond. Thus,

$$\underset{154\text{ pm}}{-C-C-} > \underset{134\text{ pm}}{C=C} < \underset{120\text{ pm}}{-C\equiv C-}$$

Similarly, a C–H bond may be formed by overlap of a sp^3, sp^2 or *sp*-orbital of carbon with an *s*- orbital of hydrogen, therefore, as the size of the hybrid orbital decreases, the lengths of C–H bond decrease accordingly.

$$\underset{109\text{ pm}}{C(sp^3)-H} > \underset{107 \cdot 6\text{ pm}}{C(sp^2)-H} > \underset{106\text{ pm}}{C(sp)-H}$$

(*ii*) **Bond strengths.** *Shorter the bond, greater is its strength.* Thus, the σ-bond formed by *sp*-hybridized carbon is the strongest (*i.e.* maximum bond energy) while that formed by sp^3-hybridized carbon is the weakest (*i.e.*, minimum bond dissociation energy). For example,

(*i*) $\underset{507\text{ kJ mol}^{-1}}{C(sp)-H} > \underset{443\text{ kJ mol}^{-1}}{C(sp^2)-H}$
$$> \underset{435\text{ kJ mol}^{-1}}{C(sp^3)-H}$$

(*ii*) $\underset{433\text{ kJ mol}^{-1}}{C(sp)-C(sp)} > \underset{383\text{ kJ mol}^{-1}}{C(sp^2)-C(sp^2)}$
$$> \underset{347\text{ kJ mol}^{-1}}{C(sp^3)-C(sp^3)}$$

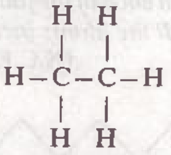
In contrast, a π-bond is formed by the sideways overlap of two *p*-orbitals. Since the extent of overlap in sideways overlap is low, a carbon-carbon π-bond is always weaker (251 kJ mol^{-1}) than a carbon-carbon σ- bond (347 kJ mol^{-1}). A carbon-carbon double bond is, however, stronger (598 kJ mol^{-1}) than a carbon-carbon single bond since it consists of a strong σ-bond and a weak π-bond. In a similar way, a carbon- carbon triple bond is still stronger (803 kJ mol^{-1}) than a carbon carbon double bond.

(*iii*) **Electronegativity.** The type of hybridization also affects the electronegativity of the atom, *i.e.*, greater the s-character of the hybrid orbitals more electronegative is the atom. Thus, a *sp*-hybridized carbon atom having hybrid orbitals with 50% *s*-character is more electronegative than a sp^2-hybridized carbon with 33·33% *s*-character and sp^3-hybridized carbon with 25% *s*-character. These small differences in electronegativity are reflected in many physical and chemical properties of the concerned molecules.

14.4. Structural Representation of Organic Compounds

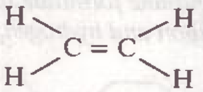
14.4.1. Complete and Condensed Formulae

The structures of organic compounds can be represented in several different ways. The most important of these is the Lewis structures. But writing these structures is quite time consuming. However, these structures can be simplied if each pair of electrons making a covalent bond is represented by *a dash* (–). Evidently *two dashes* (=) will be required to represent a double bond and three dashes (≡) to represent a triple bond. The lone pairs of electrons on the heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol may be represented by the following structural formulae.



$$\begin{array}{c} \text{H}\quad\text{H} \\ |\quad\; | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ |\quad\; | \\ \text{H}\quad\text{H} \end{array}$$

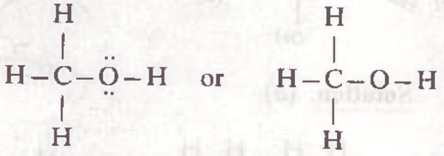
Ethane



Ethene

$\text{H}-\text{C}\equiv\text{C}-\text{H}$

Ethyne



$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\ddot{\underset{..}{\text{O}}}-\text{H} \\ | \\ \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \\ \text{H} \end{array}$$

Methanol

Such structural representations are called **complete structural formulae** or **graphic** or **displayed formulae.**

These structural formulae can be further abbreviated by omitting some or all the covalent bonds and by indicating the name of identical groups attached to an atom by a subscript. For example,

CH_3CH_3	$H_2C=CH_2$	$HC\equiv CH$	CH_3-OH
or C_2H_6	or C_2H_4	or C_2H_2	or CH_3OH
Ethane	Ethene	Ethyne	Methanol

Such structural representations are called **condensed structural formulae.**

Sometimes these structural formulae can be further condensed by enclosing the repititive structural unit within a brackets and placing an inleger as a subscript indicating the number of times the structural unit gets repeated. For example, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ can be further condensed to $CH_3(CH_2)_6COOH$.

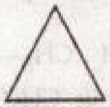
14.4.2. Bond-line Structural Formulae.

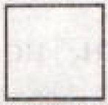
It is a simple, short and convenient method of representing organic molecules. In this method, carbon-carbon bonds are shown by lines drawn in a zig-zag fashion and carbon atoms by line ends and intersections. A single bond is represented by a single line (–), a double bond by two parallel lines (=) and a triple bond by three parallel lines (≡). Although carbon atoms are not shown but all atoms other than carbon and hydrogen atoms are shown on the zig-zag line. Further, it is assumed that each carbon on the line end or intersection is attached to required number of hydrogen atoms, *i.e.*, termini denote CH_3 groups and an unsubstituted intersection a CH_2 group. For example,

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ can by represented by the following bond-line structural formulae.

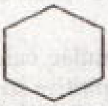
14.4.3. Polygon Formulae

There are many organic compounds, in which the carbon atoms are not joined in a chain but are joined in a ring. These are called cyclic compounds and are usually represented by polygon without showing carbon and hydrogen atoms. The corner of a polygon represents a carbon atom and the sides of a polygon denote a carbon-carbon bond. If an atom or a group of atoms other than hydrogen is attached to carbon, then that atom or a group of atoms is shown in the structure. For example,

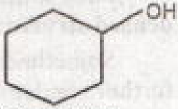

Cyclopropane


Cyclobutane


Cyclopentene


Cyclohexane

Chlorocyclohexane



Cyclohexanol

EXAMPLE 14.1. *Expand each of the following condensed formulae into their complete structural formulae* **(N.C.E.R.T.)**

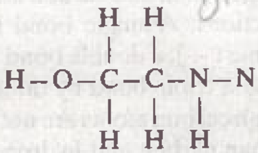
(a) $HOCH_2CH_2NH_2$

(b) $CH_3(CH_2)_3OH$

(c) $CH_3CH_2COCH_2CH_3$

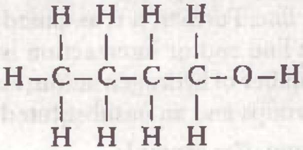
(d) $CH_3CH = CH(CH_2)_3CH_3$

Solution. (a)



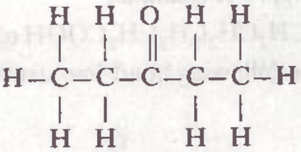
$$\begin{array}{ccccccccccc} &&&&H&&H&&&& \\ &&&&|&&|&&&& \\ H&-&O&-&C&-&C&-&N&-&N \\ &&&&|&&|&&|&& \\ &&&&H&&H&&H&& \end{array}$$

(b)



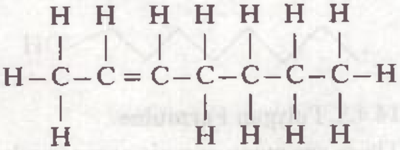
$$\begin{array}{ccccccccccccc} &&H&&H&&H&&H&&&& \\ &&|&&|&&|&&|&&&& \\ H&-&C&-&C&-&C&-&C&-&O&-&H \\ &&|&&|&&|&&|&&&& \\ &&H&&H&&H&&H&&&& \end{array}$$

(c)



$$\begin{array}{ccccccccccccc} &&H&&H&&O&&H&&H&& \\ &&|&&|&&\|&&|&&|&& \\ H&-&C&-&C&-&C&-&C&-&C&-&H \\ &&|&&|&&&&|&&|&& \\ &&H&&H&&&&H&&H&& \end{array}$$

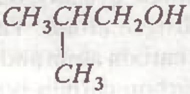
(d)



$$\begin{array}{ccccccccccccccccc} &&H&&H&&H&&H&&H&&H&&H&& \\ &&|&&|&&|&&|&&|&&|&&|&& \\ H&-&C&-&C&=&C&-&C&-&C&-&C&-&C&-&H \\ &&|&&&&&&|&&|&&|&&|&& \\ &&H&&&&&&H&&H&&H&&H&& \end{array}$$

EXAMPLE 14.2. *For each of the following compounds, write a more condensed formula and also their bond line formulae.*

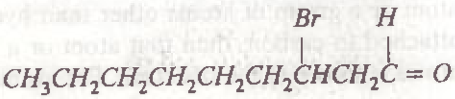
(a)



$$\begin{array}{l} CH_3CHCH_2OH \\ \quad\;\;| \\ \quad\; CH_3 \end{array}$$

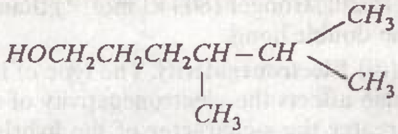
$(CH_3)_2CHCH_2OH$

(b)



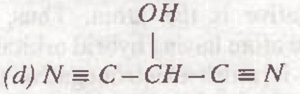
$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad Br \qquad\; H \\ \qquad\qquad\qquad\qquad\qquad\quad\; | \qquad\;\;\; | \\ CH_3CH_2CH_2CH_2CH_2CH_2CHCH_2C = O \end{array}$$

(c)



$$HOCH_2CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH\begin{array}{l} CH_3 \\ CH_3 \end{array}$$

(d)



$$N \equiv C-\overset{\displaystyle OH}{\overset{|}{CH}}-C \equiv N$$

(N.C.E.R.T.)

Solution. Condensed Formulae

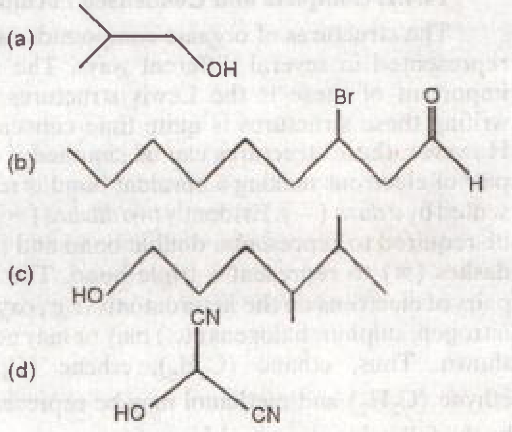
(a) $(CH_3)_2CHCH_2OH$

(b) $CH_3(CH_2)_5CHBrCH_2CHO$

(c) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$

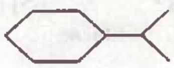
(d) $HOCH(CN)_2$

Bond-line Formulae



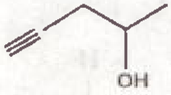
EXAMPLE 14.3. *Expand each of the following bond-line formulae to show all the atoms including carbon and hydrogen.* **(N.C.E.R.T.)**

(a)



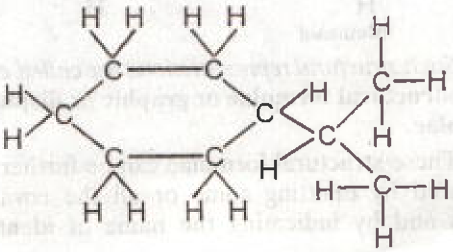
(b)

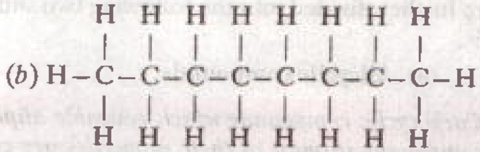
(c)



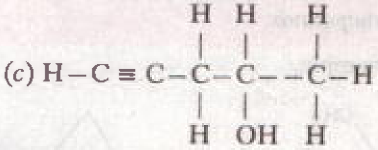
(d)

Solution. (a)



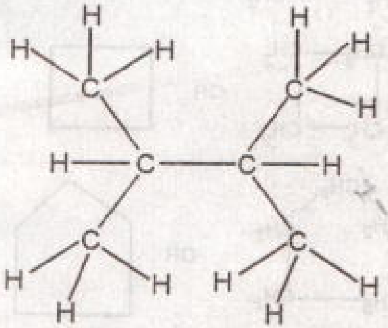


$$(b)\ H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$



$$(c)\ H-C\equiv C-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

(*d*)

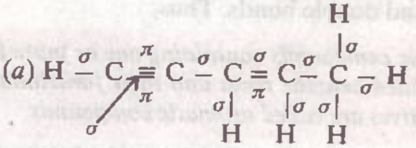


EXAMPLE 14.4. *How many σ- and π-bonds are present in each of the following molecules ?*

(*a*) $HC \equiv CCH = CHCH_3$

(*b*) $CH_2 = C = CHCH_3$ **(N.C.E.R.T.)**

Solution. Write the complete structural formulae and count the number of carbon-carbon, carbon-hydrogen *sigma*-bonds and carbon-carbon *pi*-bonds :



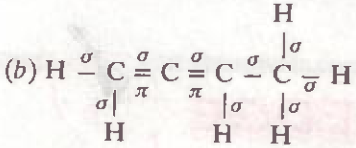
$$(a)\ H\overset{\sigma}{-}C\overset{\pi}{\underset{\pi}{\equiv}}C\overset{\sigma}{-}\underset{H}{C}\overset{\sigma}{\underset{\pi}{=}}\underset{H}{C}\overset{\sigma}{-}\underset{H}{\overset{H}{C}}\underset{\sigma}{-}H$$

No. of $\sigma_{C-C} = 4$; No. of $\sigma_{C-H} = 6$

Total no. of σ-bonds = 4 + 6 = 10

Total no. of $\pi_{C\,=\,C}$ bonds

= 2 (triple bond) + 1 (double bond) = 3



$$(b)\ H\overset{\sigma}{-}\underset{H}{C}\overset{\sigma}{\underset{\pi}{=}}C\overset{\sigma}{\underset{\pi}{=}}\underset{H}{C}\overset{\sigma}{-}\underset{H}{\overset{H}{C}}\underset{\sigma}{-}H$$

No. of $\sigma_{C-C} = 3$; No. of $\sigma_{C-H} = 6$

Total no. of σ-bonds = 3 + 6 = 9

No. of $\pi_{C\,=\,C}$ bonds = 1 × 2 (double bonds) = 2

EXAMPLE 14.5. *What is the type of hybridization of each carbon in the following compounds ?*

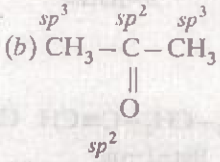
(*a*) CH_3Cl (*b*) $(CH_3)_2CO$ (*c*) CH_3CN

(*d*) $HCONH_2$ (*e*) $CH_3CH = CHCN$

(N.C.E.R.T.)

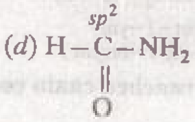
Solution. Write the partly condensed formulae of the above compounds and indicate the type of hybridization on each carbon.

(*a*) $\overset{sp^3}{CH_3}-Cl$



$$(b)\ \overset{sp^3}{CH_3}-\underset{\underset{O}{\|}}{\overset{sp^2}{C}}-\overset{sp^3}{CH_3}$$

(*c*) $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N$



$$(d)\ H-\underset{\underset{O}{\|}}{\overset{sp^2}{C}}-NH_2$$

(*e*) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv N$

EXAMPLE 14.6. *What is the shape of following compounds ?*

(*a*) $H_2C = O$ (*b*) CH_3F (*c*) $HC \equiv N$

(N.C.E.R.T.)

Solution. (*a*) In $H_2C = O$, C is sp^2-hybridized, hence formaldehyde is *trigonal planar.*

(*b*) In CH_3-F, C is sp^3- hybridized, hence methyl fluoride is *tetrahedral.*

(*c*) In $H-C\equiv N$, C is *sp*-hybridized, hence HCN is a *linear molecule.*

PART II

CLASSIFICATION AND NOMENCLATURE OF ORGANIC COMPOUNDS

14.5. Classification of Organic Compounds

The simplest organic compounds containing carbon and hydrogen only are called **hydrocarbons**. They are considered to be parent organic compounds while all other organic compounds are thought to have been derived from them by replacement of one or more of the hydrogen atoms by other atoms or groups of atoms. As the study of organic chemistry advanced, the number of organic compounds became very large. As a result, it became rather inconvenient to study the chemical behaviour of these compounds individually. Therefore, in order to simplify and systematize the study of organic chemistry, all the known organic com-

sp^3

$CH_3C=O$
CH_3 sp^2

$CH_3-C\equiv N$
SP.

sp^2

pounds have been broadly divided into two categories depending upon the nature of their carbon skeleton. These are :

I. Acyclic or open chain compounds.

II. Cyclic or closed chain compounds.

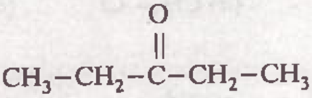
*I. **Acyclic or open chain compounds.*** These compounds contain open chains of carbon atoms in their molecules. The carbon chains may be either straight chains or branched chains. For example,

Straight chain compounds :

$CH_3-CH_2-CH_2-CH_3$ *n*-Butane

$CH_3-CH=CH-CH_3$ But-2-ene (*formerly 2-butene*)

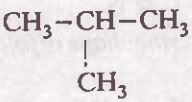
$CH_3-CH_2-C\equiv CH$ But-1-yne (*formerly 1-butyne*)



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

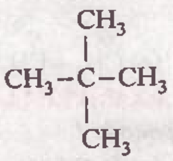
Pentan-3-one (*formerly 3-pentanone*)

Branched chain compounds :



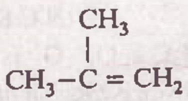
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

Isobutane



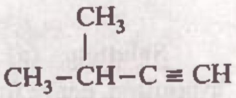
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

Neopentane



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$

Isobutylene



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-C\equiv CH$

3-Methylbut-1-yne

Open chain compounds are also called **aliphatic compounds** since the earlier compounds of this class were obtained either from animal or vegetable fats (Greek, *aliphatos* = fat).

II. Cyclic or closed chain or ring compounds. *These compounds contain one or more closed chains or rings of atoms in their molecules.* Depending upon the constitution of the ring, these are further divided into the following two categories :

1. Homocyclic or carbocyclic compounds

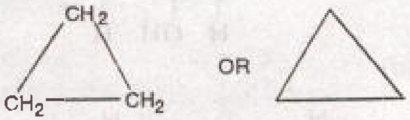
2. Heterocyclic compounds

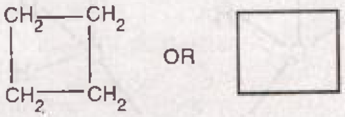
1. Homocyclic or Carbocyclic compounds. *These compounds contain rings which are made up of only one kind of atoms, i.e.* carbon atoms. These are further divided into the following two sub-classes.

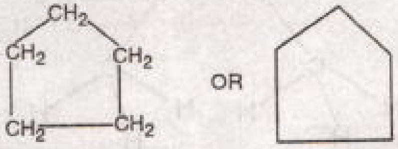
(a) Alicyclic compounds.

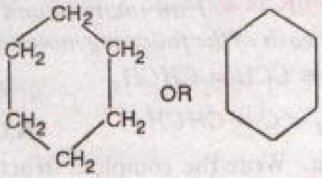
Carbocyclic compounds which resemble aliphatic compounds in most of their properties are called alicyclic compounds.

For example,









(b) Aromatic compounds. Benzene is the parent aromatic compound. It has six carbon atoms arranged in a closed chain with three alternate single and double bonds. Thus,

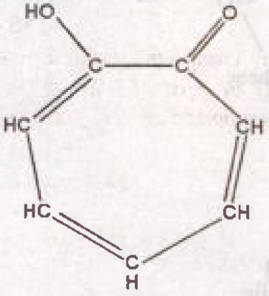
Organic compounds containing one or more fused or isolated benzene rings and their functionalized derivatives are called aromatic compounds.

These are also called **benzenoid compounds** since they resemble benzene in almost all of their properties. They are further classified as monocyclic, bicyclic, tricyclic etc. according as they contain one, two, three etc. fused benzene rings respectively in their molecules.

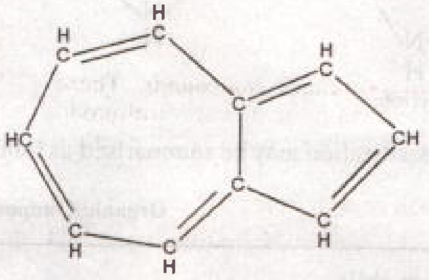
ADD TO YOUR KNOWLEDGE

Non-benzenoid aromatic compounds. There are certain aromatic compounds which do not contain benzene rings. These are called *non-benzenoid aromatic compounds.* Typical examples of such compounds are tropolone and azulene.

ADD TO YOUR KNOWLEDGE CONTD.



Tropolone

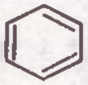


Azulene

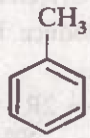
The name aromatic for this class of cyclic unsaturated compounds has been derived from the Greak word *aroma* meaning fragrant smell since most of the compounds (of this class) discovered earlier had pleasant smells. However, the term aromatic has now lost its original significance because many aromatic compounds are now known to possess unpleasant odours.

Some important examples of monocyclic, bicyclic and tricyclic aromatic compounds are :

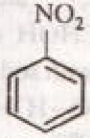
(i) *Monocyclic aromatic compounds* :



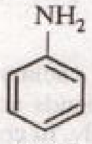
Benzene



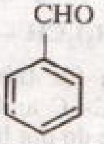
Toluene



Nitrobenzene



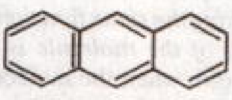
Aniline



Benzaldehyde

(ii) *Bicyclic and tricylic aromatic compounds*

Naphthalene
(*Bicyclic*)



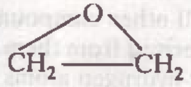
Anthracene
(*Tricyclic*)

2. Heterocyclic compounds.

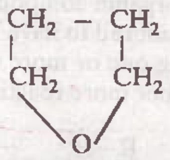
Cyclic compounds containing one or more heteroatoms* in their rings are called heterocyclic compounds.

The heteroatoms commonly found in these compounds are oxygen, nitrogen and sulphur but occasionally phosphorus, boron, silicon and some metal atoms like tin, selenium etc. may also be present. Depending upon the chemical behaviour, they are further classified into the following two categories :

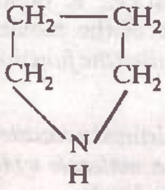
(i) Alicyclic heterocyclic compounds : *Aliphatic cyclic compounds containing one or more heteroatoms in their rings are called alicyclic heterocyclic compounds.* For example,



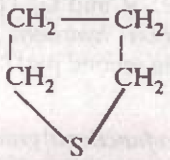
Oxirane
(*Ethylene oxide*)



Tetrahydrofuran
(THF)

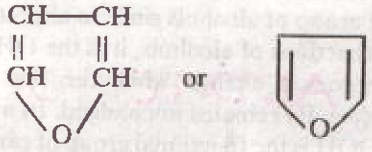


Pyrrolidine



Tetrahydrothiophene

(ii) Aromatic heterocyclic compounds : *Aromatic cyclic compounds containing one or more heteroatoms in their molecules are called* **aromatic heterocyclic compounds.** For example.



Furan

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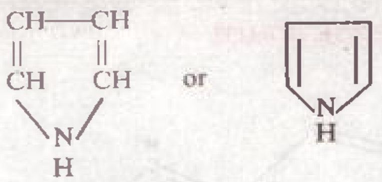
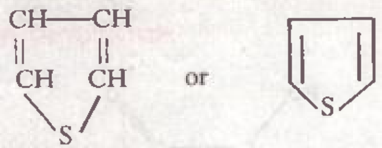
*In organic chemistry, atoms other than C and H atoms are called heteroatoms.

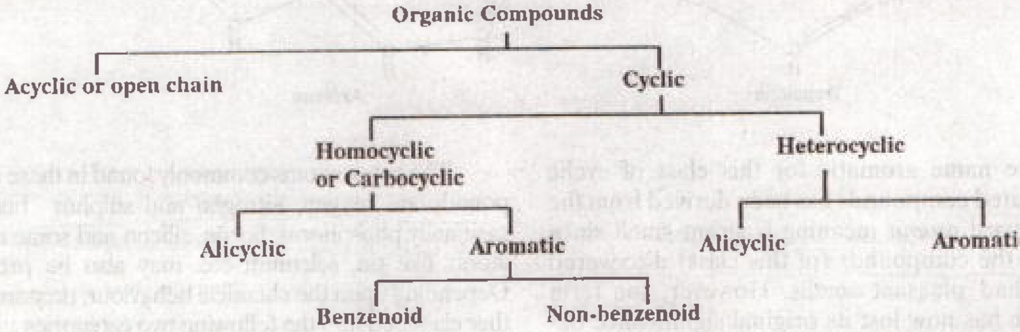


Pyrrole



Thiophene

The above classification may be summarised as follows :



14.6. Functional or Characteristic Groups

As already stated, hydrocarbons are the parent organic compounds. All other compounds are considered to have been derived from them by replacing one or more of their hydrogen atoms by some other more reactive atom or group (G)

$$\underset{\text{Hydrocarbon}}{R-H} \xrightarrow[+\,G]{-\,H} R-G$$

Thus, each organic molecule consists of two parts *i.e.*, R and G. The first part *i.e.*, 'R' denotes the *carbon- hydrogen framework* of the molecule while the second part *i.e.*, 'G' is *called the functional group.*

Thus, a functional group may be defined as an atom or a group of atoms present in a molecule which largely determines its chemical properties.

The remaining part of the molecule (*e.g.* R) mainly affects the physical properties such as melting point, boiling point, density, solubility, refractive index etc. For example, – OH (*hydroxyl*) is the functional group of alcohols since in almost all the chemical reactions of alcohols, it is the OH group that undergoes a change while the rest of the molecule (*e.g.* R) remains unchanged. In a similar way, – COOH is the functional group of carboxylic acids.

From the above discussion, it follows that the ***chemical properties of any organic compound are the properties of its functional group.*** In other words, all the organic compounds containing the same functional group show similar chemical reactions. For example, alcohols CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$ etc. all produce hydrogen when treated with sodium metal.

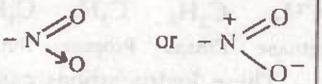
$$\underset{\text{Alcohol}}{2R-O-H} + 2Na \longrightarrow \underset{\text{Sod. alkoxide}}{2R-O^- Na^+} + H_2$$

$$\text{where } R = CH_3-,\ CH_3CH_2-,$$

$$(CH_3)_2CH- \text{ etc.}$$

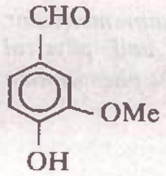
The reason for this similar chemical behaviour is that C – C and C – H bonds are very strong and hence do not break easily. In contrast, the O – H bond is weaker and hence reactive. Thus, we conclude that *any organic compound will behave in the same manner as any other organic compound having the same functional group no matter what the rest of the molecule is.* However, exceptions are known when the molecule is very large (*e.g.* group R is large) or contains two or more functional groups in close proximity to one another. In such cases, the molecule exhibits some special properties which are typical of neither one nor of the other functional group.

Some of the common functional groups present in various organic compounds are listed below :

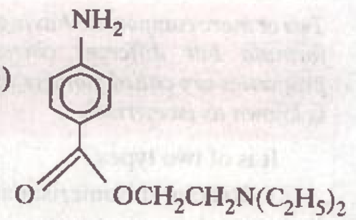
Class of organic compounds	Name of the functional group	Structure of the functional group
Alkenes	Double bond	$>C=C<$
Alkynes	Triple bond	$-C\equiv C-$
Halogen derivatives	Halogen	$-X$ (F, Cl, Br, I)
Alcohols	Hydroxy	$-OH$
Thioalcohol or Mercaptan	Thiol or Sulphhydryl or Mercapto	$-SH$
Ethers	Divalent oxygen	$-O-$
Thioether or Sulphides	Divalent sulphur	$-S-$
Aldehydes	Aldehydic (*formyl*)	$-\overset{O}{\overset{\Vert}{C}}-H$
Thioketones	Thione	$>C=S$
Ketones	Ketonic (*oxo*)	$>C=O$
Thioaldehydes	Thial	$-CH=S$
Carboxylic acids	Carboxyl	$-\overset{O}{\overset{\Vert}{C}}-OH$
Sulphonic acids	Sulphonic acid	$-\overset{O}{\overset{\Vert}{\underset{\underset{O}{\Vert}}{S}}}-OH$
Primary amines	Amino	$-NH_2$
Secondary amines	Imino	$>NH$
Tertiary amines	Tertiary N-atom	$>N-$
Alkyl cyanides or Alkanenitriles	Cyano or nitrile	$-C\equiv N$
Alkyl isocyanides or isonitriles	Isonitrile or isocyano	$-N\equiv C$
Nitroalkanes	Nitro	
Alkyl nitrites	Nitrite	$-O-N=O$

EXAMPLE 14.7. *Identify the functional groups in the following compounds :* **(N.C.E.R.T.)**

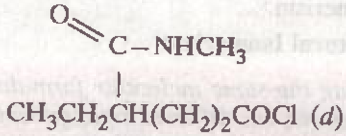
(*a*)



(*b*)

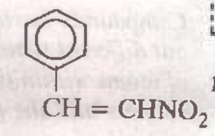


(*c*)

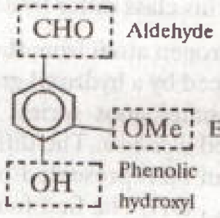


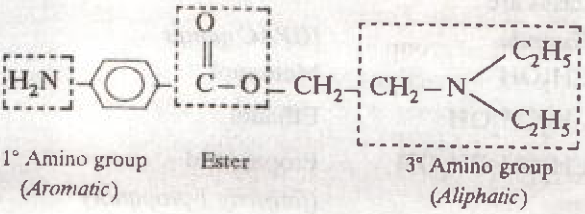
$CH_3CH_2\underset{}{\overset{\overset{O\!=\!C-NHCH_3}{|}}{C}H}(CH_2)_2COCl$

(*d*)

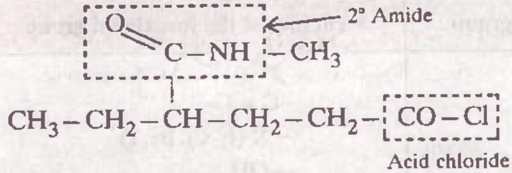


Solution. (*a*)



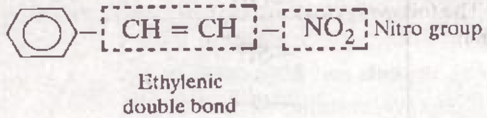


(c)



$CH_3-CH_2-\overset{\overset{O=C-NH-CH_3}{|}}{CH}-CH_2-CH_2-CO-Cl$

(d)



14.7. Homologous Series

To simplify and to systematize the study of organic chemistry, all the organic compounds have been divided into different families or groups depending upon their structure and chemical properties. Each such family or a group is called a *homologous series*.

A homologous series is defined as a family or group of structurally similar organic compounds all the members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent (or successive) members of which differ by a – CH_2 group. The individual members of such a series are called homologues and the phenomenon is called homology.

For example, alkanes constitute a homologous series. The first six members of this series are :–

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
Methane	**Ethane**	**Propane**	**Butane**	**Pentane**	**Hexane**

These hydrocarbons can be represented by the same general formula, C_nH_{2n+2} where n is the number of carbon atoms. Further, any two adjacent members of this class differ by a CH_2 group.

If a hydrogen atom from the above hydrocarbons is replaced by a hydroxyl group *i.e.* – OH, we get a new homologous series. This homologous series is called *alcohols*. The different members of this series can be represented by the general formula C_nH_{2n+1} OH. The first four members of this series are :

Formula	*IUPAC names*
CH_3OH	Methanol
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2OH$	Propan-1-ol *(formerly 1-propanol)*
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol *(formerly 1-butanol)*

Some other homologous series are alkenes, alkynes, alkyl halides, ethers, aldehydes, ketones, amines, esters and carboxylic acids etc.

Characteristics of a Homologous Series

(1) *Each homologous series can be represented by a general formula.* For example, $C_nH_{2n+1}COOH$ is the general formula of carboxylic acids.

(2) *All the members of a given homologous series possess the same functional group.* For example, the functional group of alcohols is the hydroxyl group *i.e.*, – OH group. Similarly, the functional group of aldehydes is the aldehydic group *i.e.*, – CHO and that of the ketones is the ketonic group, *i.e.*, $> C = O$.

(3) *The successive members of a homologous series differ by a CH_2 group or by $12 + 2 \times 1 = 14$ mass units.*

(4) *The individual members of a homologous series can be prepared by the general methods of preparation developed for that series.*

(5) *The physical properties such as density, melting point, boiling point of the members of a homologous series show a regular gradation with rise in molecular mass.*

(6) *The chemical properties of the members of a homologous series are similar though the first member may vary considerably from rest of the members.*

14.8. Isomerism

One of the most important characteristics of organic compounds is their ability to show isomerism.

Two or more compounds having the same molecular formula but different chemical and physical properties are called isomers and the phenomenon is known as isomerism.

It is of two types :

1. Structural isomerism and
2. Stereoisomerism.

14.8.1. Structural Isomerism

Compounds having the same molecular formula but different structures, i.e., different arrangement of atoms within the molecule are called structural isomers and the phenomenon is called structural isomerism.

It is of the following six types :

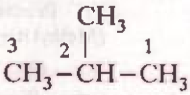
(*i*) Chain or nuclear isomerism.

Compounds having the same molecular formula but different arrangement of carbon chain within the molecule are called chain or nuclear isomers and the phenomenon is called chain or nuclear isomerism.

For example, butane and 2-methylpropane are chain isomers.

$CH_3-CH_2-CH_2-CH_3$

Butane (*n*–*Butane*)



$$\overset{3}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

2–Methylpropane (*Isobutane*)

(*ii*) Position isomerism.

Compounds which have the same structure of the carbon chain but differ only in the position of the multiple (double or triple) bond or the functional group are called position isomers and the phenomenon is called position isomerism.

For example, but-1-ene and but-2-ene are position isomers.

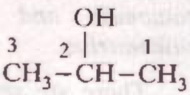
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$ $\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$

But–1–ene But–2–ene

Similarly, propan-1-ol and propan-2-ol are position isomers.

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$

Propan–1–ol
(*n*–*Propyl alcohol*)



$$\overset{3}{C}H_3-\overset{\overset{OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

Propan–2–ol
(*Isopropyl alcohol*)

(*iii*) Functional isomerism.

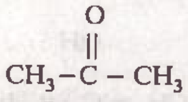
Compounds having the same molecular formula but different functional groups are called functional isomers and the phenomenon is called functional isomerism.

For example, the molecular formula, C_2H_6O represents the following two functional isomers :

CH_3-CH_2-OH CH_3-O-CH_3

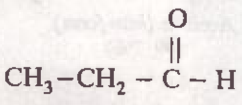
Ethanol (*Ethyl alcohol*) Methoxymethane (*Dimethyl ether*)

Similarly, the molecular formula C_3H_6O represents the following four functional isomers.



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

Propanone
(*Acetone*)



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

Propanal
(*Propionaldehyde*)

$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2OH$ $CH_2=CH-O-CH_3$

Prop–2–en–1–ol (*Allyl alcohol*) Methoxyethene (*Methyl vinyl ether*)

Further examples of Functional Isomerism

The following classes of organic compounds show functional isomerism among themselves.

(*a*) **Alcohols and Ethers**

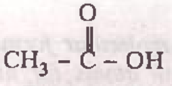
C_2H_6O represents :

CH_3-CH_2-OH and CH_3-O-CH_3

Ethanol (*Ethyl alcohol*) Methoxymethane (*Dimethyl ether*)

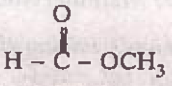
(*b*) **Carboxylic acids and esters**

$C_2H_4O_2$ represents :



$$CH_3-\overset{\overset{O}{||}}{C}-OH$$

and

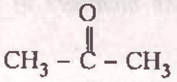


$$H-\overset{\overset{O}{||}}{C}-OCH_3$$

Ethanoic acid Methyl methanoate

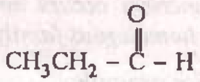
(*c*) **Aldehydes and ketones**

C_3H_6O represents :



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

and



$$CH_3CH_2-\overset{\overset{O}{||}}{C}-H$$

Propanone Propanal

(*d*) **Dienes, allenes and alkynes**

C_4H_6 represents :

$CH_2=CH-CH=CH_2$, $CH_2=C=CH-CH_3$

Buta–1, 3–diene Buta–1, 2–diene (*An allene*)

and $CH_3CH_2C\equiv CH$ or $CH_3C\equiv CCH_3$

But–1–yne But–2–yne

(*e*) **Nitroalkanes and alkyl nitrites**

$C_2H_5NO_2$ represents :

$CH_3CH_2-NO_2$ and CH_3CH_2-ONO

Nitroethane Ethyl nitrite

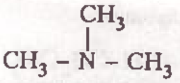
(*f*) **1°, 2° and 3°-Amines**

C_3H_9N represents :

$CH_3CH_2CH_2NH_2$, $CH_3CH_2-NH-CH_3$

Propan–1–amine (*1° Amine*) N–Methylethanamine (*2° Amine*)

and



$$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$$

N, N–Dimethylmethanamine
(*3° Amine*)

(*g*) **Cyanides and isocyanides**

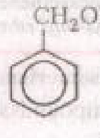
C_2H_3N represents :

$CH_3-C\equiv N$ and $CH_3-N\stackrel{\rightarrow}{\equiv}C$

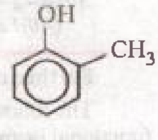
Ethanenitrile Methyl isocyanide

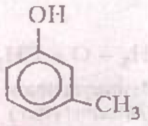
(*h*) Aromatic alcohols, phenols and ethers

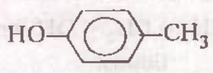
C_7H_8O represents :


Benzyl alcohol


Anisole


o-Cresol


m-Cresol


p-Cresol

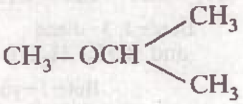
(*iv*) Metamerism.

Compounds having the same molecular formula but different number of carbon atoms (or alkyl groups) on either side of the functional group (i.e., –O–, –S–, –NH– and –CO–) are called metamers and the phenomenon is called metamerism. Metamerism occurs among the members of the same homologous family.

For example,

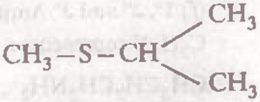
(*a*) $CH_3CH_2-O-CH_2CH_3$ is a metamer of
Ethoxyethane
(*Diethyl ether*)

$CH_3-O-CH_2CH_2CH_3$ or
1-Methoxypropane
(*Methyl n–propyl ether*)


$CH_3-OCH(CH_3)_2$
2–Methoxypropane
(*Isopropyl methyl ether*)

(*b*) $CH_3CH_2-S-CH_2CH_3$ is a metamer of
Diethyl thioether

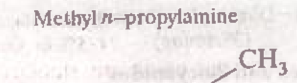
$CH_3-S-CH_2CH_2CH_3$ or
Methyl *n*–propyl thioether

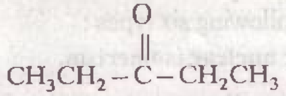

$CH_3-S-CH(CH_3)_2$
Isopropyl methyl thioether

(*c*) $CH_3CH_2-NH-CH_2CH_3$ is a metamer of
Diethylamine

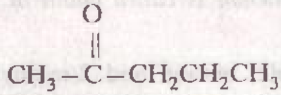
$CH_3-NH-CH_2CH_2CH_3$
Methyl *n*–propylamine

or

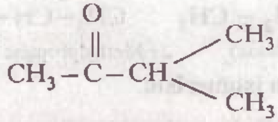

$CH_3-NH-CH(CH_3)_2$
Isopropyl methylamine


(*d*) $CH_3CH_2-CO-CH_2CH_3$
Pentan–3–one
(*Diethyl ketone*)

is a metametamer of


$CH_3-CO-CH_2CH_2CH_3$
Pentan–2–one
(Methyl *n*–propyl ketone)

or

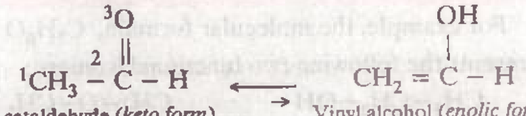

$CH_3-CO-CH(CH_3)_2$
3–Methylbutan–2–one
(*Isopropyl methyl ketone*)

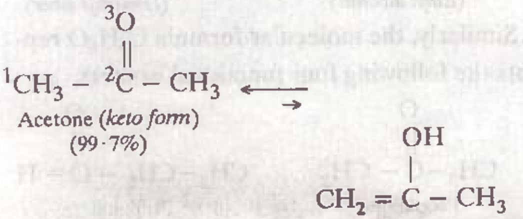
It may be noted here that metamers may also be position isomers. For example, pentan-2-one and pentan-3-one may be regarded as position isomers as well as metamers.

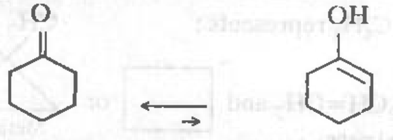
(*v*) Tautomerism.

It arises due to 1, 3-migration of a hydrogen atom from one polyvalent atom to the other within the same molecule. Isomers thus obtained which exist in dynamic equilibrium with each other are called tautomers and the phenomenon is called tautomerism.

There are several types of tautomerism but *keto-enol tautomerism* is the most important. In this type of tautomerism one form (tautomer) contains the **keto** group ($>C=O$) while the other contains the *enolic* ($>C=C-OH$) group. Two simplest examples of keto-enol tautomerism are acetaldehyde and acetone.


$$\overset{1}{C}H_3-\overset{2}{C}(=\overset{3}{O})-H \rightleftharpoons CH_2=C(OH)-H$$
Acetaldehyde (*keto form*)
(~ 100%)
Vinyl alcohol (*enolic form*)
(*Negligible amount*)


$$\overset{1}{C}H_3-\overset{2}{C}(=\overset{3}{O})-CH_3 \rightleftharpoons CH_2=C(OH)-CH_3$$
Acetone (*keto form*)
(99·7%)
Prop–1–en–2–ol (*enolic form*)
(Negligible *amount*)



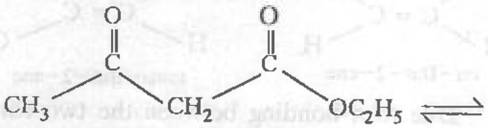
Cyclohexanone (98·8%) Cyclohex−1−en−1−ol (1·2%)

In all the monocarbonyl compounds listed above, the greater stability of the keto-form *w.r.t.* the enol form is due to the greater strength of the carbon-oxygen π-bond (364 kJ mol^{-1}) as compared to carbon-carbon π-bond (254 kJ mol^{-1}).

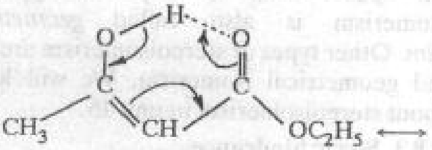
Factors affecting the relative amounts of keto and enol forms in keto-enol tautomerism.

The following three factors affect the position of equilibrium in keto-enol tautomerism.

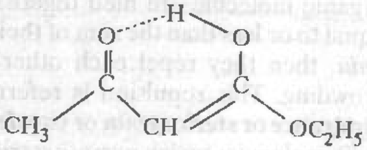
(*i*) **Stability of the enol form.** As stated above in simple aldehydes and ketones (*i.e.* acetaldehyde, acetone etc.) the amount of enolic form is negligibly small. However, if the enolic form is stabilized by intramolecular hydrogen-bonding (*chelation*), such as in 1, 3-dicarbonyl compounds, the amount of enolic form is much greater than in acetaldehyde or acetone. For example, in acetoacetic ester, the amount of enolic form is 7%.



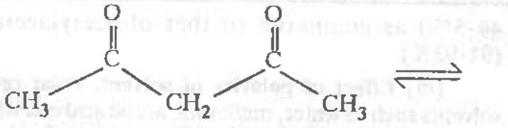
Acetoacetic ester
(1, 3−Dicarbonyl compound)
(keto form, 93%)



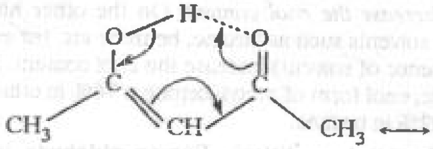
(Enol form, 7%)



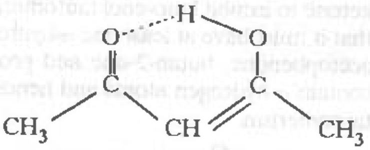
Similarly, acetylacetone (*i.e. a* 1, 3-diketone) also exhibits keto-enol tautomerism but the amount of enolic form here is much higher (76%) than even in acetoacetic ester. This is due to the reason that keto group is a *much better electron-withdrawing group than the ester group.*



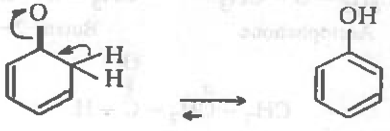
Acetylacetone *(keto form, 24%)*



(Enol form, 76%)



In contrast, the compound cyclohexa-2, 4-dien-1-one exists totally in its enol form.

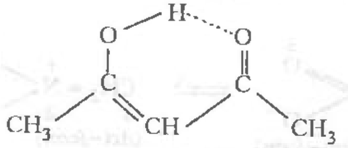


Cyclohexa−2, 4−dien−1−one *(keto−form)* Phenol *(enol form)*

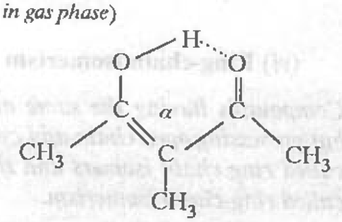
The reason being that the enol form is aromatic and is, therefore, stabilized by the resonance energy of the benzene ring (151 kJ mol^{-1}).

From the above discussion it follows, *that higher the stability of the enol form, greater is the enol content.*

(*ii*) **Steric hindrance.** Another factor which determines the enol content is the steric factor. To illustrate this, let us consider the enol content of acetylacetone and α- methylacetylacetone.



Acetylacetone
(91 −93% in gas phase)



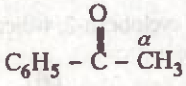
α−Methylacetylacetone
(43·5−44·5% in gas phase)

Although both the enols are stabilized by *H-bonding*, the enol form of α-methylacetylacetone is destabilized to some extent by the steric repulsion due to the presence of the α-methyl group. As a result, α-methylacetylacetone has lower enol content (43·5–

44·5%) as compared to that of acetylacetone (91·93%).

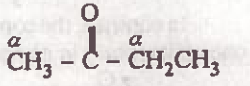
(*iii*) **Effect of polarity of solvent.** Polar protic solvents such as water, methanol, acetic acid etc. which form H-bonds with the carbonyl group of the keto-form *decrease the enol content.* On the other hand, aprotic solvents such as hexane, benzene etc. (or even the absence of solvent) increase the enol content. For example, enol form of acetylacetone is 76% in ethanol but is 92% in hexane.

Essential conditions. For an aldehyde or a ketone to exhibit keto-enol tautomerism, it is essential that it must have at least one α-hydrogen atom. Thus, acetophenone, butan-2-one and propionaldehyde all contain α-hydrogen atoms and hence show keto-enol tautomerism.



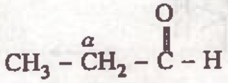
$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_3$

Acetophenone



$\overset{\alpha}{C}H_3-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_2CH_3$

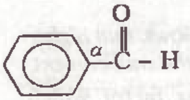
Butan−2−one



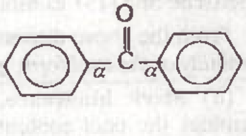
$CH_3-\overset{\alpha}{C}H_2-\overset{\overset{O}{\|}}{C}-H$

Propionaldehyde

In contrast, benzaldehyde, benzophenone etc. do not show keto-enol tautomerism because they do not contain α-hydrogen atoms.

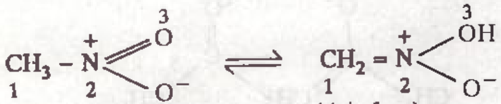


Benzaldehyde



Benzophenone

Similarly, nitro-compounds also show tautomerism.



Nitromethane (*Nitro−form*)

(*Aci−form*)

(*vi*) **Ring-chain isomerism**

Compounds having the same molecular formula but possessing open chain and cyclic structures are called ring chain isomers and the phenomenon is called ring-chain isomerism.

For example,

(*a*) C_3H_6 represents :

$CH_3CH = CH_2$ and

Propene

Cyclopropane

which are ring-chain isomers

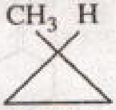
(*b*) C_4H_8 represents :

$CH_3CH_2CH=CH_2$ and

But−1−ene

Cyclobutane

or



Methyl−cyclopropane

which are ring-chain isomers.

Similarly, but-2-ene or 2-methylprop-1-ene are ring chain isomers of cyclobutane and methylcyclopropane.

(*c*) C_3H_4 represents :

$CH_3C \equiv CH$ and

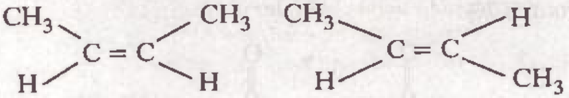
Propyne

Cyclopropene

which are also ring-chain isomers.

14.8.2. Stereoisomerism

Isomers which have the same structural formula but have different relative arrangement of atoms or groups in space are called **stereoisomers** (Greek : *stereo* = space, *meros* = part) and the *phenomenon is called* **stereoisomerism.** For example, *cis-trans* isomerism is an example of stereoisomerism.



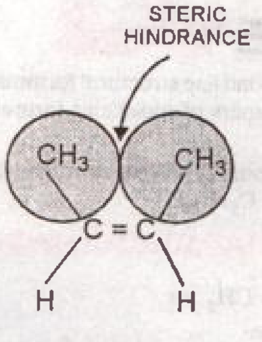
cis−But−2−ene *trans*−But−2−ene

Due to π-bonding between the two carbon atoms, the rotation around carbon-carbon double bond is prohibited and hence the geometry of the atoms or groups attached to the carbon atoms gets-fixed in space. That is why this type of stereoisomerism is also called *geometrical isomerism.* Other types of stereoisomerism are optical and geometrical isomerism. We will learn more about stereoisomerism in unit 15.

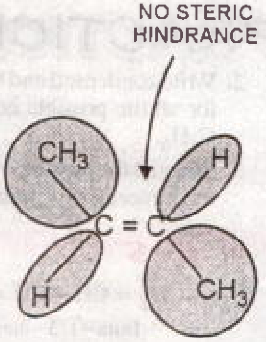
14.8.3. Steric hindrance

If two non-bonded atoms or groups in an organic molecule are hled together at a distance equal to or less than the sum of their *van der Waals' radii*, then they repel each other due to spatial crowding. This repulsion is referred to as **steric hindrance or steric strain or van der Waals' strain.** Such molecules which possess steric strain are relatively less stable as compared to those having no steric strain. For example, *cis*-but-2-ene has steric hindrance and hence is less stable as compared to *trans*-but-2-ene which has no steric hindrance.

Further as the size of the atoms/groups around a bulky atom increases, the steric hindrance increases accordingly. For example, as we move

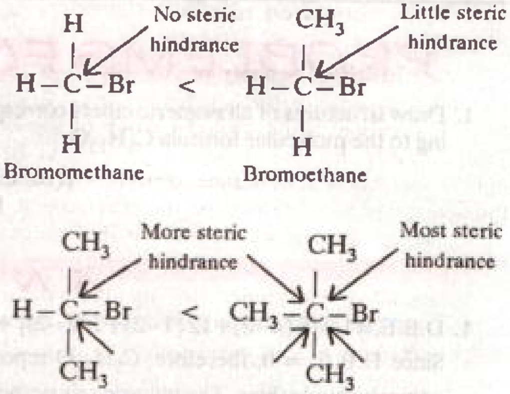


cis-But-2-ene



trans-But-2-ene

from bromomethane to bromoethane to 2-bromopropane to *tert*-butyl bromide, steric hindrance increases as shown below :



These steric effects are very important in Organic Chemistry since they influence the structure and reactivity of many organic molecules.

ADD TO YOUR KNOWLEDGE

Double bond equivalents. The problems on structural isomerism and structure determination of organic molecules can be easily solved by the **concept of double bond equivalents (D.B.E.)** *which implies the sum of double bonds and rings present in the molecule.* It is given by the relation,

$$\text{D.B.E.} = \frac{\Sigma n\,(v-2)}{2} + 1$$

where n is the number of different kinds of atoms present in the molecule and v is the valency of each atom. For example, D.B.E. of M.F.

$$C_3H_6O = \frac{3\,(4-2) + 6\,(1-2) + 1\,(2-2)}{2} + 1 = 0 + 1 = 1$$

This means that various structural isomers of C_3H_6O will contain either one double bond ($C = C$ or $C = O$) or one ring (homocyclic or heterocyclic) as discussed below under **Q.2.**

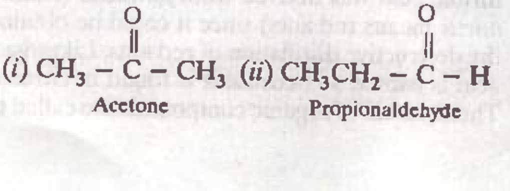
Likewise, 2 D.B.E. implies either two double bonds or one triple bond or two rings or one double bond + one ring. Similarly 4 D.B.E. implies either four double bonds or two triple bonds or two double bonds + one triple bond or three double bonds + one ring i.e., benzene ring or any other combination of rings, double and triple bonds.

EXAMPLE 14.8. *Write all the acyclic and cyclic isomers having the moleuclar formula, C_3H_6O.*

Solution. $\text{D.B.E.} = \frac{1}{2}[3\,(4-2) + 6\,(1-2) + 1\,(2-2)] + 1 = 1$

Since D.B.E. = 1, therefore, C_3H_6O may contain a $C = C$ or $C = O$ double bond or a ring. The following seven isomers are possible.

(*a*) Acyclic isomers are :



$$(i)\ CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \quad (ii)\ CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

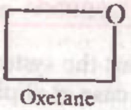
Acetone Propionaldehyde

(*iii*) $CH_2{=}CH{-}CH_2OH$ (*iv*) $CH_2{=}CH{-}OCH_3$

Prop–2–en–1–ol Methoxyethene

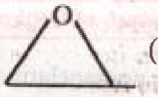
(*b*) Cyclic isomers are :

(*v*)



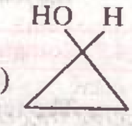
Oxetane

(*vi*)



Methyloxirane

(*vii*)



Cyclopropanol

Thus, C_3H_6O has seven isomers :

Note. While writing the structural isomers for any given molecular formula, tautomers are neglected unless otherwise asked for.

PROBLEMS FOR PRACTICE

1. Draw structures of all isomeric ethers corresponding to the molecular formula $C_5H_{12}O$. (N.C.E.R.T.)

2. Write condensed and bond line structural formulae for all the possible isomers of molecular formula C_4H_6.

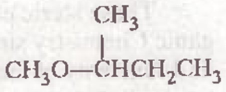
3. Draw all the possible isomeric polygon formulae for the molecular formula C_5H_{10}.

ANSWERS

1. D.B.E. = 1/2 [5 (4−2) + 12 (1−2) + 1 (2−2)] + 1 = 0.
Since D.B.E. = 0, therefore, $C_5H_{12}O$ represents only saturated ethers. The following six isomers are possible.

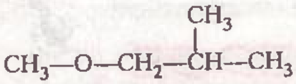
(i) $CH_3OCH_2CH_2CH_2CH_3$
1−Methoxybutane

(ii)



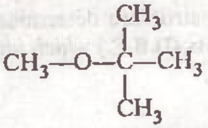
$CH_3O-\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2CH_3$
2−Methoxybutane

(iii)



$CH_3-O-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_3$
1−Methoxy−2−methylpropane

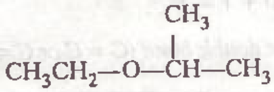
(iv)



$CH_3-O-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$
2−Methoxy−2−methylpropane

(v) $CH_3CH_2-O-CH_2CH_2CH_3$
1−Ethoxypropane

(vi)



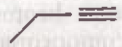
$CH_3CH_2-O-\overset{CH_3}{\overset{|}{C}}H-CH_3$
2−Ethoxypropane

2. $\text{D.B.E.} = \frac{1}{2}[4\ (4-2) + 6\ (1-2)] + 1 = 2$
Since D.B.E. = 2, therefore, C_4H_6 has either two double bonds or one triple bond or one double bond and a ring or two rings.
The following nine isomers are possible :

(i) $CH_2 = CH-CH = CH_2$ or
Buta−1, 3−diene

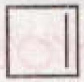
(ii) $CH_3CH_2-C \equiv CH$ or
But−1−yne

(iii) $CH_3-C \equiv C-CH_3$ or
But−2−yne



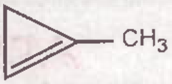
(iv) $CH_2=C=CHCH_3$
Buta−1, 2−diene

(v)



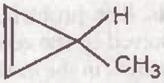
Cyclobutene

(vi)



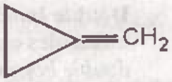
1-Methylcyclopropene

(vii)



3-Methylcycloprop-1-ene

(viii)

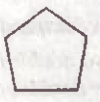


Methylenecyclopropane

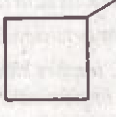
(ix)

Bicyclo[1.1.0] butane

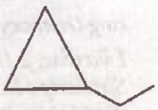
3. By polygon formulae, we mean cyclic formulae. C_5H_{10} has the following six polygon formulae :



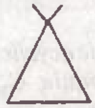
Cyclopentene



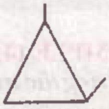
Methylcyclobutane



Ethylcyclopropane



1, 1-Dimethylcyclopropane



1, 2-Dimethylcyclopropane

14.9. Nomenclature of Organic Compounds

The term nomenclature means the system of naming of organic compounds. In case of aliphatic compounds, two systems of nomenclature are generally used : (i) *Trivial or common system* and (ii) *IUPAC system*.

(i) Trivial or common system. In the early stages of the development of organic chemistry, organic compounds were named after the source from which they were first isolated. For example, urea got its name since the compound was first obtained from the urine of mammals. Similarly, methyl alcohol was called *wood spirit* since it could be obtained by the destructive distillation of *wood*. Acetic acid got its name from *acetum* (Latin : *acetum* means vinegar) since it is present in vinegar. Similarly, the name formic acid was derived from *formicus* (Latin : *formicus* means red ants) since it could be obtained by the destructive distillation of red ants. Likewise citric acid is named so because it is found in citrus fruits. These names of organic compounds are called **trivial**

names or **common names**. Originally these names were given without any systematic basis but later on certain rules were developed to name the organic compounds by the common system. However, these rules have a number of drawbacks and thus cannot be used to name all organic compounds.

(*ii*) **IUPAC system.** Because of the unique property of catenation and isomerism, carbon forms a large number of organic compounds. Even towards the end of nineteenth century, the number of organic compounds known was so large that it became difficult to remember them by their common or trivial names. In order to systematize the nomenclature of organic compounds, IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature was first introduced in 1947. These rules underwent modifications from time to time and the most exhaustic rules for nomenclature of organic compounds were published in 1979 and later revised and updated in 1993. The rules discussed in this chapter are the latest and are based upon 1979 and 1993 editions of the IUPAC nomenclature of organic compounds.

14.10. General Rules of IUPAC System for Naming Organic Compounds

The IUPAC system is the most rational and widely used system of nomenclature in organic chemistry. *The most important feature of this system is that any given molecular structure has only one IUPAC name and any given IUPAC name denotes only one molecular structure.*

The IUPAC name of any organic compound essentially consists of three parts, *i.e.*

1. *Word root* 2. *Suffix* and 3. *Prefix.*

1. Word root. *It is the basic unit of the name. It denotes the number of carbon atoms present in the* **principal chain** (*the longest possible continuous chain of carbon atoms including the functional group and the multiple bonds*) *of the organic molecule.* For chains from one to four carbon atoms, special word roots (based upon the common names of alkanes) are used but for chains of five or more carbon atoms *Greek number* roots are used as given below :

CHAIN LENGTH	WORD ROOT	CHAIN LENGTH	WORD ROOT
C_1	Meth–	C_7	Hept (*a*)–
C_2	Eth–	C_8	Oct (*a*)–
C_3	Prop (*a*)–	C_9	Non (*a*)–
C_4	But (*a*)–	C_{10}	Dec (*a*)–
C_5	Pent (*a*)–	C_{11}	Undec (*a*)–
C_6	Hex (*a*)–	C_{12}	Dodec (*a*)–

Extra '*a*' given in parenthesis is used only if the primary suffix (explained later) to be added to the word root begins with a consonant. In general, the word root for any carbon chain is **alk**.

2. Suffix. There are two types of suffixes :

(i) Primary suffix. *A primary suffix is always added to the word root to indicate whether the carbon chain is saturated or unsaturated.* The three basic primary suffixes are given below :

TYPE OF CARBON CHAIN	PRIMARY SUFFIX	GENERAL NAME
(*a*) Saturated (containing single bonds only)	–ane	Alkane
(*b*) Unsaturated with *one double bond*	–ene	Alkene
(*c*) Unsaturated with *one triple bond*	–yne	Alkyne

If the parent carbon chain contains two, three, four or more double or triple bonds, *numerical prefixes* such as **di** (for two), **tri** (for three), **tetra** (for four) etc. are added to the primary suffix. For example,

TYPE OF CARBON CHAIN	PRIMARY SUFFIX	GENERAL NAME
(*a*) Unsaturated with *two double bonds*	–diene	Alkadiene
(*b*) Unsaturated with *two triple bonds*	–diyne	Alkadiyne

The following examples illustrate the use of word roots and primary suffixes in naming organic compounds :

ORGANIC COMPOUND	WORD ROOT	PRIMARY SUFFIX	IUPAC NAME
$CH_3CH_2CH_2CH_3$	But	ane	Butane
$CH_3CH=CH_2$	Prop	ene	Propene
$CH\equiv CH$	Eth	yne	Ethyne
$CH_2=CH-CH=CH_2$	Buta*	diene	Butadiene
$HC\equiv C-C\equiv CH$	Buta*	diyne	Butadiyne

*Extra *'a'* has been added to the word root since the primary suffix *i.e.*, diene or diyne begins with a consonant *i.e.*, *'d'* instead of a vowel as is the case in the last two examples.

(ii) Secondary suffix. *A secondary suffix is then added to the primary suffix to indicate the nature of the functional group present in the organic compound.* Secondary suffixes of some important functional groups are given below :

CLASS OF ORGANIC COMPOUNDS	FUNCTIONAL GROUP	SECONDARY SUFFIX
Alcohols	$—OH$	-ol
Aldehydes	$—CHO$	-al
Ketones	$>C=O$	-one
Carboxylic acids	$—COOH$	-oic acid
Acid amides	$—CONH_2$	-amide
Acid chlorides	$—COCl$	-oyl chloride
Esters	$—COOR$	alkyl .... oate
Nitriles	$—CN$	nitrile
Thiol	$—SH$	thiol
Amines	$—NH_2$	amine

It may be noted that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix (i.e. ane, ene, and yne) is dropped if the secondary suffix begins with a vowel but is retained if the secondary suffix begins with a consonant.

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming organic compounds.

ORGANIC COMPOUND	WORD ROOT	PRIMARY SUFFIX	SECONDARY SUFFIX	IUPAC NAME
CH_3CH_2OH	Eth	an (*e*)*	ol	Ethanol
$CH_3CH_2CH_2NH_2$	Prop	an (*e*)*	amine	Propanamine
$CH_3CH_2CH_2COOH$	But	an (*e*)*	oic acid	Butanoic acid
CH_3CH_2CN	Prop	ane	nitrile	Propanenitrile
$CH_2=CHCHO$	Prop	en (*e*)*	al	Prop-2-en-1-al
$HC\equiv CCOOH$	Prop	yn (*e*)*	oic acid	Prop-2-yn-1-oic acid

*The terminal '*e*' from the primary suffix has been dropped because the secondary suffix begins with a vowel.

It may be noted that according to 1993 recommendations of IUPAC nomenclature of Organic Compounds,

(i) locants (numericals and/or letters) are placed immediately before the part of the name to which they relate. For example,

But-2-ene	Propan-2-ol
(formerly 2-butene)	*(formerly 2-propanol)*

(ii) the locant 1 (unity) is often omitted when there is no ambiguity. For example,

$CH_3CH_3\overset{1}{C}H_2NH_2$	*Propan-1-amine is often named as Propanamine*
$Cl\overset{2}{C}H_2\overset{1}{C}H_2OH$	*2-Chloroethan-1-ol is often named as 2-Chloroethanol*
$CH_3CH_2CH_2\overset{1}{C}HO$	*Butan-1-al is often written as Butanal*

However, in this book, the numerical locant 1 is always included when another numerical locant appears in the same name. For example,

$$\overset{3}{C}H_2 = \overset{2}{C}H - \overset{1}{C}HO$$

Prop−2−en−1−al

(formerly 2−propenal)

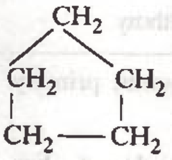
$$H\overset{3}{C} \equiv \overset{2}{C} - \overset{1}{C}O_2H$$

Prop−2−yn−1−oic acid

(formerly 2−propynoic acid)

3. Prefix. There are two types of prefixes :

(i) Primary prefix. A primary prefix is used simply to distinguish cyclic from acyclic compounds. For example, in case of *carbocyclic compounds, a primary prefix,* **cyclo** *is used immediately before the word root*. Thus,



Cyclo + **pent**
Primary prefix Word root

\+ **ane** = **Cyclopentane**
Primary suffix IUPAC name

If the prefix cyclo is not used, it simply indicates that the compound is acyclic or open chain.

(ii) Secondary prefix. In IUPAC system of nomenclature, certain groups are not considered as functional groups but instead are treated as *substitutents. These are called* **secondary prefixes** *and are added immediately before the word root (or the primary prefix in case of carbocyclic compounds) in alphabetical order to denote the side chains or substitutent groups.* The secondary prefixes for some groups which are always treated as substitutent groups (regardless of the fact whether the organic compound is monofunctional or polyfunctional) are given below :

SUBSTITUENT GROUP	SECONDARY PREFIX	SUBSTITUENT GROUP	SECONDARY PREFIX
$—F$	Fluoro	OCH_3 (OMe)	Methoxy
$—Cl$	Chloro	$-OC_2H_5$ $(-OEt)$	Ethoxy
$—Br$	Bromo		
$—I$	Iodo	$-CH_3$ $(-Me)$	Methyl
$—NO_2$	Nitro	$-C_2H_5$ $(-Et)$	Ethyl
$—NO$	Nitroso	$-CH_2CH_2CH_3$ $(n-Pr)$	*n*-Propyl
$-\overset{+}{N} \equiv N$	Diazo	$-CH(CH_3)_2$ $(-iPr)$	Isopropyl
$—OR$	Alkoxy	$-C(CH_3)_3$	*tert.*-Butyl

Besides these, other functional groups are also treated as substitutent groups in case of polyfunctional compounds as discussed later in this unit.

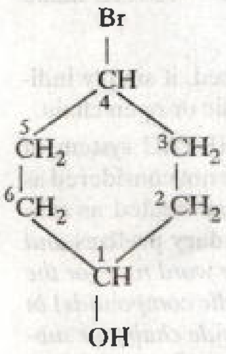
Thus, the complete IUPAC name of an organic compound consists of the following parts :

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

The following examples illustrate the use of word root, primary and secondary prefixes and suffixes in naming organic compounds :

ORGANIC COMPOUNDS	**SECONDARY PREFIX**	**WORD ROOT**	**PRIMARY SUFFIX**	**IUPAC NAME**
CH_3CH_2Br	Bromo	eth	ane	Bromoethane
CH_3NO_2	Nitro	meth	ane	Nitromethane
$C_2H_5OC_2H_5$	Ethoxy	eth	ane	Ethoxyethane

In case of carbocyclic compounds, primary prefixes are also used. For example,



4–Bromo + **cyclo** + **hex**
Secondary prefix + Primary prefix + Word root
+ **an(e)** + **1–ol**
Primary suffix + Secondary suffix
= **4–Bromo–cyclohexan–1–ol**
IUPAC name

The common and IUPAC names of some important classes of organic compounds are given below :

14.11. Nomenclature of different classes of Organic Compounds

Compounds of carbon and hydrogen are **called hydrocarbons.** These are further divided into two classes : *saturated* and *unsaturated hydrocarbons*.

1. Saturated hydrocarbons – Alkanes

Hydrocarbons in which all the carbon atoms are linked to one another by only single bonds are called saturated hydrocarbons. These may be either acyclic (open chain) or cyclic. In the IUPAC system, *saturated acyclic hydrocarbons are called* **alkanes.** Earlier, they were also called **paraffins** (Latin : *parum* = little ; *affinis* = affinity) since they are relatively inert towards most of the chemical reagents.

General formula : C_nH_{2n+2} where $n = 1, 2, 3, 4$ .... etc. *Primary suffix* : **ane.**

The IUPAC names of alkanes are obtained by adding the suffix *ane* to the word root indicating the number of carbon atoms.

For example, names of alkanes containing five or more carbon atoms are obtained by adding prefixes such as *pent* (five), *hex* (six), *hept* (seven), *oct* (eight) etc. indicating the number of carbon atoms in the molecule to the suffix '*ane*'. However, the first four alkanes (CH_4 to C_4H_{10}) have their special names *i.e. methane, ethane, propane and butane.* The name of an individual alkane is always written as one word. The molecular formulae, IUPAC and common names of some alkanes are given below :

n	**FORMULA**	**COMMON NAME**	**IUPAC NAME**
1.	CH_4	Methane	Methane
2.	CH_3CH_3	Ethane	Ethane
3.	$CH_3CH_2CH_3$	Propane	Propane
4.	$CH_3CH_2CH_2CH_3$	*n*-Butane	Butane
5.	$CH_3CH_2CH_2CH_2CH_3$	*n*-Pentane	Pentane
6.	$CH_3(CH_2)_4CH_3$	*n*-Hexane	Hexane

7.	$CH_3(CH_2)_5CH_3$	*n*-Heptane	Heptane
8.	$CH_3(CH_2)_6CH_3$	*n*-Octane	Octane
9.	$CH_3(CH_2)_7CH_3$	*n*-Nonane	Nonane
10.	$CH_3(CH_2)_8CH_3$	*n*-Decane	Decane
11.	$CH_3(CH_2)_{18}CH_3$	—	Icosane
12.	$CH_3(CH_2)_{28}CH_3$	—	Triacontane

Types of alkanes. Depending upon the structure of the carbon chain, alkanes are of the following two types :

(i) Straight chain alkanes. As the name suggests, these alkanes contain straight chains of carbon atoms in their molecules. In other words, *alkanes in which no carbon atom is linked to more than two other carbon atoms are called straight chain alkanes*

$CH_3-CH_2-CH_2-CH_3$

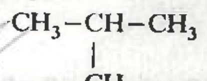
Butane (*n–Butane*)

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

Hexane (*n–Hexane*)

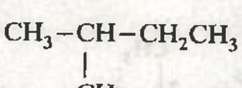
The common names of straight chain alkanes are the same as their IUPAC names except that the prefix *n-(normal)* is used in the common names (given within brackets).

(ii) Branched chain alkanes. In these alkanes, all the carbon atoms are not present in a linear sequence. In other words, *alkanes in which at least one carbon atom is linked to three or four other carbon atoms are called branched chain alkanes*. For example,



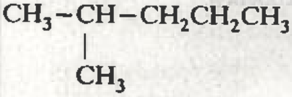
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

2–Methylpropane
(*Isobutane*)



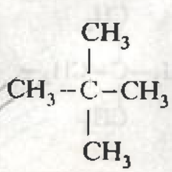
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3$

2–Methylbutane
(*Isopentane*)



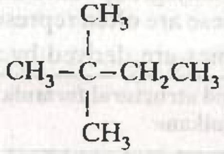
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2CH_3$

2–Methylpentane
(*Isohexane*)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

2, 2–Dimethylpropane
(*Neopentane*)



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

2, 2–Dimethylbutane
(*Neohexane*)

To distinguish the straight chain alkanes from branched chain alkanes of the same molecular formula, the prefixes *iso* and *neo* are used in the common system. The prefix *iso* is used when the second carbon of the branched chain alkane carries one methyl group while the prefix *neo* is used for those branched chain alkanes which contain *a quaternary carbon* at the end of the chain.

Types of Carbon and Hydrogen atoms in Alkanes

The carbon atoms in an alkane molecule may be classified into four types as *primary (1°), secondary (2°), tertiary (3°) and quaternary (4°)* as follows :

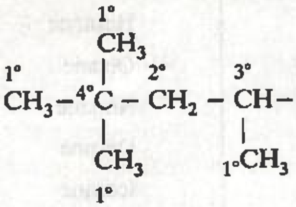
(*i*) *A carbon atom attached to one other (or no other) carbon atom is called a* **primary carbon atom** *and is designated as* **1° carbon.**

(*ii*) *A carbon atom attached to two other carbon atoms is called a* **secondary carbon atom** and is *designated* as **2° carbon.**

(*iii*) *A carbon atom attached to three other carbon atoms is called a* **tertiary carbon atom** *and is designated as* **3° carbon.**

(*iv*) *A carbon atom attached to four other carbon atoms is called a* **quaternary carbon** *atom and is designated as* **4° carbon.**

The hydrogen atoms attached to 1°, 2° and 3° carbon atoms are called primary (1°), secondary (2°) and tertiary (3°) hydrogen atoms. It may be noted here that there is nothing like quaternary hydrogen atom since a quarternary carbon does not carry any hydrogen. The following example clearly illustrates the various types of carbon and hydrogen atoms.



$$\overset{1^\circ}{CH_3}-{}^{4^\circ}\overset{\overset{1^\circ}{CH_3}}{\underset{\underset{1^\circ}{CH_3}}{C}}-\overset{2^\circ}{CH_2}-\underset{{}_{1^\circ}CH_3}{\overset{3^\circ}{CH}}-\overset{1^\circ}{CH_3}$$

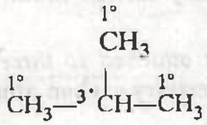
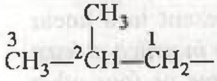
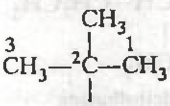
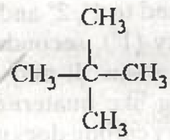
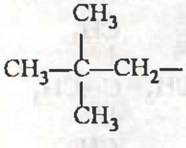
Alkyl groups. The removal of one hydrogen atom from the molecule of an alkane gives an alkyl group. Thus, alkyl groups have the general formula, C_nH_{2n+1}. These are often represented by the letter R. Their names are derived by replacing the terminal *'ane'* of the corresponding alkane by the suffix *'yl'*.

Alkane – *ane* + *yl* = **Alkyl**

In case of propane and higher alkanes, the position of the carbon atom from which the hydrogen is removed is also prefixed to the name of the alkyl group.

The IUPAC names and structural formulae of some of the alkanes and their alkyl groups are given below :

General Formula, C_nH_{2n+1} where n = 1, 2, 3, 4 .... etc.

Name and structural formula of the alkane	Corresponding alkyl group	IUPAC name (common name)
Methane CH_4	CH_3-	Methyl (*Methyl*)
Ethane, CH_3-CH_3	CH_3-CH_2-	Ethyl (*Ethyl*)
$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$	Removal of 1°H → $\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-$	1-Propyl (*n-Propyl*)
	Removal of 2°H → $CH_3-\underset{\vert}{\overset{2}{CH}}-CH_3$	2-Propyl (*Isopropyl*).
$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$	Removal of 1°H → $\overset{4}{CH_3}\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2}-$	1-Butyl (*n-Butyl*)
	Removal of 2°H → $CH_3CH_2-\underset{\vert}{CH}-CH_3$	2-Butyl (*sec-Butyl*)
 $\overset{1^\circ}{CH_3}-{}^{3^\circ}\overset{\overset{1^\circ}{CH_3}}{CH}-\overset{1^\circ}{CH_3}$	Removal of 1°H →  $\overset{3}{CH_3}-{}^{2}\overset{CH_3}{CH}-\overset{1}{CH_2}-$	2-Methyl-1-propyl (*Isobutyl*)
	Removal of 3°H →  $\overset{3}{CH_3}-{}^{2}\overset{CH_3}{\underset{\vert}{C}}-\overset{1}{CH_3}$	2-Methyl-2-propyl (*tert-Butyl*)
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ Neopentane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$	Neopentyl
$CH_3(CH_2)_8CH_3$ Decane	$CH_3(CH_2)_8CH_2-$	1-Decyl (*n-Decyl*)

2. Unsaturated hydrocarbons. *Open chain hydrocarbons which contain carbon-carbon double* ($>C=C<$) *or triple* ($-C\equiv C-$) *bonds in their molecules are called* **unsaturated hydrocarbons.** These are further classified into two types : *alkanes* and *alkynes*.

(i) Alkenes. *Unsaturated aliphatic hydrocarbons containing a carbon-carbon double bond are called* **alkenes.** They are also called **olefins** (Greek : *olefiant* = oil forming) since the lower members of this class react with chlorine to form oily products. Their general formula and suffix are given below :

General formula : C_nH_{2n} where $n = 2, 3, 4$ .... etc.

Primary suffix : = **ene**

Common names : *Alkane − ane + ylene* = **Alkylene**

IUPAC names : *Alkane − ane + ene* = **Alkene**

The positions of the double bonds are indicated by the Greek letters α, β, γ ... etc. in the common system while arabic numerals, *i.e.* 1, 2, 3, 4 etc. are used in the IUPAC system. For example,

n	FORMULA	COMMON NAME	IUPAC NAME
2	$CH_2=CH_2$	Ethylene	Ethene
3	$CH_3CH=CH_2$	Propylene	Propene
4	$CH_3CH_2\underset{2}{\overset{\beta}{C}}H=\underset{1}{\overset{\alpha}{C}}H_2$	α-Butylene	But-1-ene
4	$CH_3\overset{\beta}{C}H=\overset{\alpha}{C}HCH_3$	β-Butylene	But-2-ene

(ii) Alkynes. *Unsaturated aliphatic hydrocarbons containing a carbon-carbon triple bond are called* **alkynes** : In the common system, they are called **acetylenes** after the name of the first member of this family, *i.e.* acetylene.

General formula : C_nH_{2n-2} where $n = 2, 3, 4$, ... etc.

Primary suffix = **yne**

Common names : *Acetylene and its alkyl derivatives*

IUPAC names : *Alkane − ane + yne* = **Alkyne**

The position of the triple bond on the parent chain is designated by lowest possible arabic numerals.

The common and IUPAC names of a few simple alkynes are given below :

n	FORMULA	COMMON NAME	IUPAC NAME
2	$CH\equiv CH$	Acetylene	Ethyne
3	$CH_3—C\equiv CH$	Methylacetylene or Allylene	Propyne
4	$CH_3CH_2—\overset{2}{C}\equiv\overset{1}{C}H$	Ethylacetylene	But-1-yne
	$CH_3—\overset{2}{C}\equiv\overset{1}{C}—CH_3$	Dimethylacetylene	But-2-yne

3. Haloalkanes. *Halogen derivatives of alkanes are called* **haloalkanes.** They are further classified as *mono-, di-, tri- and tetrahaloalkanes etc.* according as they contain *one, two, three, four etc.* halogen atoms respectively in their molecules.

(a) Monohaloalkanes. *The monohalogen derivatives of alkanes are called* **alkyl halides.**

General formula : $C_nH_{2n+1}X$ where $n = 1, 2, 3$ .... etc. and X = F, Cl, Br or I.

or $R-X$ where R is any alkyl group

Functional group : X(halogen)

Secondary prefix = **Halo**

Common names. Add the word halide (fluoride, chloride, bromide, iodide) to the name of the alkyl group,

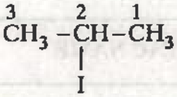
i.e., Alkyl + halide = **Alkyl halide**

IUPAC names. Add the secondary prefix *halo* to the name of the corresponding alkane.

i.e., Halo + alkane = **Haloalkane**

In case of dihalogen derivatives, the positions of both the halogen atoms are indicated.

The IUPAC and common names of some important haloalkanes are given below :

FORMULA	COMMON NAME	IUPAC NAME
$CH_3—Cl$	Methyl chloride	Chloromethane
$CH_3CH_2—Br$	Ethyl bromide	Bromoethane
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2—I$	*n*-Propyl iodide	1-Iodopropane
 $\overset{3}{C}H_3-\overset{2}{C}H(I)-\overset{1}{C}H_3$	Isopropyl iodide	2-Iodopropane

(b) Dihaloalkanes. *Alkanes containing two halogen atoms per molecule are called dihaloalkanes.*

General formula : $C_nH_{2n}X_2$ where $n = 1, 2, 3....$etc.

Common names. For purpose of naming, dihalogen derivatives of alkanes, these are divided into three categories :

(*i*) **Alkylidene dihalides.** Dihalogen derivatives of alkanes in which the two halogen atoms are attached to the same carbon atom are called **alkylidene dihalides** or simply **alkylidene halides.**

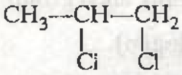
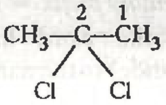
Further since the positions on the same carbon atom are called *geminal positions,* therefore, alkylidene dihalides are also called **geminal dihalides** or **simply gem-dihalides.**

(*ii*) **Alkylene dihalides.** Dihalogen derivatives of alkanes in which the two halogen atoms are attached to adjacent carbon atoms of the chain are called **alkylene dihalides** or simply **alkylene halides.** Further since positions on the adjacent carbon atoms are called *vicinal positions,* therefore, alkylene dihalides are also called **vicinal dihalides** or simply **vic- dihalides.**

(*iii*) **Polymethylene dihalides.** Dihalogen derivatives of alkanes (containing three or more carbon atoms) in which the two halogen derivatives are present on the terminal carbon atoms, *i.e.*, α, w- positions of the carbon chain are called **polymethylene dihalides.**

IUPAC names. In the IUPAC system, all types of dihalides are called **dihaloalkanes,** the positions of the halogen atoms being indicated by lowest possible arabic numerals.

The common and IUPAC names of some dihaloalkanes are given below :

FORMULA	COMMON NAME	IUPAC NAME
CH_2Cl_2	Methylene chloride	Dichloromethane
$CH_3—CHBr_2$	Ethylidene dibromide	1, 1-Dibromoethane
$BrCH_2—CH_2Br$	Ethylene dibromide	1, 2-Dibromoethane
$CH_3CH_2CHCl_2$	Propylidene dichloride	1, 1-Dichloropropane
 $CH_3—CH(Cl)—CH_2Cl$	Propylene dichloride	1, 2-Dichloropropane
 $CH_3—\overset{2}{C}Cl_2—\overset{1}{C}H_3$	Isopropylidene dichloride	2, 2-Dichloropropane
$Cl\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2Cl$	Trimethylene dichloride	1, 3- Dichloropropane

(c) Tri- and tetrahaloalkanes. The *general formula* of trihaloalkanes is $C_n H_{2n-1} X_3$ while that of tetrahaloalkanes is $C_n H_{2n-2} X_4$ where $n = 1, 2, 3$.....etc. and X = F, Cl, Br, I.

IUPAC names. In the IUPAC system, these are called **trihaloalkanes** and **tetrahaloalkanes.** The positions of the halogen atoms on the carbon chain being indicated by arabic numerals.

Common or Trivial names. There are no systematic common names for tri- and tetrahaloalkanes. However, trihalomethanes are best known by their trivial names *i.e.*, **haloforms**, tetrahalogen derivatives of methane are called **carbon tetrahalides.** While symmetrical tetrahalogen derivatives of ethane are called **acetylene tetrahalides.** The trivial and IUPAC names of some tri- and tetrahaloalkanes are given below :

FORMULA	TRIVIAL NAME	IUPAC NAME
CHF_3	Fluoroform	Trifluoromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CHI_3	Iodoform	Triiodomethane
$CH_3—CCl_3$	—	1, 1, 1- Trichloroethane
$ClCH_2—CHCl_2$	—	1, 1, 2- Trichloroethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$Br_2CH—CHBr_2$	Acetylene tetrabromide	1, 1, 2, 2-Tetrabromoethane
$ClCH_2—CCl_3$	—	1, 1, 1, 2- Tetrachloroethane

4. Alcohols or Alkanols

Alcohols are classified as *monohydric, dihydric, trihydric* and *polyhydric* according as their molecules contain *one, two, three* and *many* hydroxyl groups respectively. Since presence of two or more hydroxyl groups on the same carbon atom makes the molecule unstable, therefore, in *di, tri* and *polyhydric* alcohols, each hydroxyl group is present on a different carbon atom.

(i) Monohydric alcohols.

General formula : $C_nH_{2n+1}OH$ (where $n = 1, 2, 3$ ...) or $R-OH$ (where R is any alkyl group)

Functional group :– OH (*hydroxyl*)

Secondary suffix : **ol**

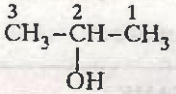
Common names. Add the word alcohol to the name of the alkyl group,

i.e., Alkyl + alcohol = **Alkyl alcohol**

IUPAC names. Replace the terminal '*e*' from the name of the corresponding alkane by the suffix '*ol*'.

i.e., Alkane – e + ol = **Alkanol**

Some imporant examples are :

FORMULA	COMMON NAME	IUPAC NAME
$CH_3—OH$	Methyl alcohol	Methanol
CH_3CH_2-OH	Ethyl alcohol	Ethanol
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2-OH$	*n*-Propyl alcohol	Propan-1-ol
 $\overset{3}{C}H_3-\underset{\displaystyle OH}{\overset{2}{C}H}-\overset{1}{C}H_3$	Isopropyl alcohol	Propan-2-ol

(ii) Dihydric alcohols :

General formula : $C_n H_{2n} (OH)_2$ where $n = 2, 3, 4$....etc.

Classification. Because of their sweet taste, dihydric alcohols are called glycols. Depending upon the relative positions of the two hydroxyl groups, they are further classified as α, β, γ..... ω

glycols etc. Thus, α-glycol is 1, 2-glycol, β-glycol is 1, 3-glycol and ω-glycol is one in which the two OH groups are attached to the terminal carbon atoms of the chain.

Common names. In the common system, α-*glycols* (also called *vic-glycols*) are named by adding the word *glycol* to the common name of the alkene from which they have been prepared by direct hydroxylation. In contrast, β-, γ- and ω-glycols are named as the corresponding *polymethylene glycols.*

IUPAC names. Add the suffix '*diol*' to the name of the alkane containing the same number of carbon atoms as the diol.

Alkane + diol = **Alkanediol**

The position of the two hydroxyl group is indicated by arabic numerals.

The common and IUPAC names of some glycols are given below :

FORMULA	COMMON NAME	IUPAC NAME
$\overset{2}{\text{HOCH}_2}\text{—}\overset{1}{\text{CH}_2\text{OH}}$	Ethylene glycol	Ethane-1, 2-diol
$\text{CH}_3\text{—}\overset{2}{\text{CHOH}}\text{—}\overset{1}{\text{CH}_2\text{OH}}$	Propylene glycol	Propane-1, 2-diol
$\overset{3}{\text{HOCH}_2}\text{—}\overset{2}{\text{CH}_2}\text{—}\overset{1}{\text{CH}_2\text{OH}}$	Trimethylene glycol	Propane-1, 3-diol

(*iii*) **Trihydric alcohols**

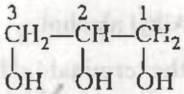
General formula : $\mathbf{C_n\ H_{2n-1}\ (OH)_3}$

Common names. There is no general rule for naming these alcohols.

IUPAC name. Add the suffix '*triol*' to the name of the alkane containing the same number of carbon atoms as the triol.

Alkane + triol = **Alkanetriol**

The position of the hydroxyl groups is indicated by arabic numerals.

FORMULA	COMMON NAME	IUPAC NAME
 $\underset{\text{OH}}{\overset{3}{\text{CH}_2}}\text{—}\underset{\text{OH}}{\overset{2}{\text{CH}}}\text{—}\underset{\text{OH}}{\overset{1}{\text{CH}_2}}$	Glycerol or Glycerine	Propane-1, 2, 3- triol

5. Ethers or Alkoxyalkanes

General formula : **R – O – R′** where R and R′ are same or different alkyl groups. If R = R′, ethers are called *simple ethers* and if R ≠ R′, then ethers are called *mixed ethers.*

Functional group : – O –

Secondary prefix : **Alkoxy**

Common names. In case of mixed ethers, add the word *ether* to the names of the alkyl groups arranged in alphabetical order. In case of simple ethers, the numerical prefix *di* is added to the name of the alkyl group followed by the word ether.

IUPAC names. In the IUPAC system, ethers are called *alkoxyalkanes*. The smaller alkyl group forms a part of the alkoxy group while the bigger alkyl group forms a part of the alkane. The names of the ethers are then derived by adding the suffix *alkoxy* to the name of the *alkane,*

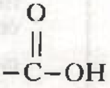
i.e., Alkoxy + alkane = **Alkoxyalkane**

Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$CH_3—O—CH_3$	Dimethyl ether	Methoxymethane
$CH_3—O—CH_2CH_3$	Ethyl methyl ether	Methoxyethane
$CH_3CH_2—O—CH_2CH_3$	Diethyl ether	Ethoxyethane

6. Monocarboxylic acids or Alkanoic acids

General formula : $C_nH_{2n+1}COOH$ where n = 0, 1, 2, 3 ..... etc. or $R-COOH$ where R = H or any alkyl group.



Functional group : $-\overset{\overset{O}{||}}{C}-OH$ (*carboxyl*)

Secondary suffix : **oic acid**

Common names. These are derived from the name of the plant or animal from which they were first isolated.

IUPAC names. Replace terminal *'e'* from the name of the corresponding alkane by the suffix *oic acid,*

i.e., Alkane – e + oic acid = **Alkanoic acid**

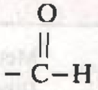
Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$H-COOH$	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3CH_2-COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2-COOH$	*n*-Butyric acid	Butanoic acid

7. Aldehydes or Alkanals

General formula : $C_nH_{2n+1}CHO$ where n = 0, 1, 2, 3 ..... etc. or $R-CHO$

where R = H or any alkyl group.



Functional group : $-\overset{\overset{O}{||}}{C}-H$ (*aldehyde*)

Secondary suffix : **al**

Common names. Replace *ic acid* from the common name of the corresponding acid which they give upon oxidation by the word *aldehyde*. For example,

Acetic acid – ic acid + aldehyde = **Acetaldehyde**

IUPAC names. Replace the terminal *'e'* from the name of the corresponding alkane by the suffix *al,*

i.e., Alkane – e + al = **Alkanal**

Some examples are :

FORMULA	COMMON NAME	IUPAC NAME
$H-CHO$	Formaldehyde	Methanal
CH_3-CHO	Acetaldehyde	Ethanal
CH_3CH_2-CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2-CHO$	*n*-Butyraldehyde	Butanal

8. Ketones or Alkanones

General formula : $C_nH_{2n+1}COC_nH_{2n+1}$ where n = 1, 2, 3 .... etc. or $R-CO-R'$ where R and R′, may be same or different alkyl groups. If $R = R'$, ketones are called *simple ketones* and if $R \neq R'$, ketones are called *mixed ketones.*

Functional group : $>C=O$ (*Ketonic*)

Secondary suffix : **one**

Common names. In case of mixed ketones, name the alkyl groups in alphabetical order and then add the word ketone. In case of simple ketones, the numerical prefix *di* is used before the name of the alkyl group,

IUPAC names. Replace terminal *'e'* from the name of the corresponding alkane by the suffix *one*

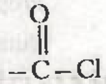
i.e. Alkane – e + one = **Alkanone**

Some examples are :

FORMULA	COMMON NAME	IUPAC NAME
$CH_3—CO—CH_3$	Dimethyl ketone or Acetone	Propanone
$CH_3—CO—CH_2CH_3$	Ethyl methyl ketone	Butan-2-one or Butanone
$\overset{1}{C}H_3—\overset{2}{C}O—\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$	Methyl *n*-propyl ketone	Pentan-2-one
$\overset{1}{C}H_3\overset{2}{C}H_2—\overset{3}{C}O—\overset{4}{C}H_2\overset{5}{C}H_3$	Diethyl ketone	Pentan-3-one

9. Acid chlorides or Acyl chlorides or Alkanoyl chlorides

General formula : RCOCl where R = H or any alkyl group

Functional group : 
$-\overset{O}{\overset{\|}{C}}-Cl$

Secondary suffix : **oyl chloride**

Common names : Replace *ic acid* from the common name of the corresponding acid by *yl chloride* For example,

Acetic acid – ic acid + yl chloride = **Acetyl chloride**

IUPAC names : Replace terminal '*e*' from the name of the corresponding alkane by the suffix *oyl chloride,*

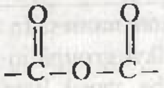
i.e., Alkane –e + oyl chloride = **Alkanoyl chloride**

Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
H—COCl (*unstable*)	Formyl chloride	Methanoyl chloride
$CH_3—COCl$	Acetyl chloride	Ethanoyl chloride
$CH_3CH_2—COCl$	Propionyl chloride	Propanoyl chloride
$CH_3CH_2CH_2—COCl$	*n*-Butyryl chloride	Butanoyl chloride

10. Acid anhydrides

General formual : **R – CO – O – CO – R′** or **$(RCO)_2O$** where R or R′ may be same or different alkyl groups.

Functional group : 
$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$

Secondary suffix : **anhydride**

Common or IUPAC names : Replace the word *acid* from the common or IUPAC name of the corresponding acid by the word *anhydride*.

Symmetrical anhydrides of substituted carboxylic acids are named by adding the prefix *bis* to the name to indicate that two identical acyl groups are present. Unsymmetrical anhydrides are named by writing the names of the two acids alphabetically before the word anhydride.

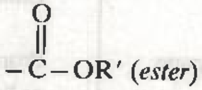
Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$(CH_3CO)_2O$	Acetic anhydride	Ethanoic anhydride
$(CH_3CH_2CO)_2O$	Propionic anhydride	Propanoic anhydride
$(ClCH_2CO)_2O$	Bis(chloroacetic anhydride)	Bis(chloroethanoic anhydride)
HCO-O-$COCH_3$	Acetic formic anhydride	Ethanoic methanoic anhydride

11. Esters

General formula : $R-COOR'$ where $R = H$ or any alkyl group while group R' is always an alkyl group.

Functional group :



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR' \text{ (ester)}$$

Secondary prefix : **alkyl**

Secondary suffix : **oate**

Common or IUPAC names : Write the name of the alkyl group before the common or IUPAC name of the parent acid with its terminal *ic acid* replaced by *oate*.

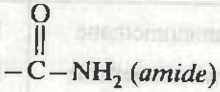
Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$H-COOCH_3$	Methyl formate	Methyl methanoate
$H-COOC_2H_5$	Ethyl formate	Ethyl methanoate
$CH_3-COOCH_3$	Methyl acetate	Methyl ethanoate
$CH_3-COOC_2H_5$	Ethyl acetate	Ethyl ethanoate

12. Acid amides or Alkanamides

General formula : **$RCONH_2$** where $R = H$ or any alkyl group

Functional group :



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \text{ (amide)}$$

Secondary suffix : **amide**

Common names : Replace *ic acid* from the common name of the corresponding acid by the **secondary suffix** ***amide***.

IUPAC names : Replace the terminal 'e' from the name of the corresponding alkane by the suffix *amide*,

i.e., *Alkane − e + amide* = **Alkanamide**

Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$H-CONH_2$	Formamide	Methanamide
CH_3-CONH_2	Acetamide	Ethanamide
$CH_3-CH_2-CONH_2$	Propionamide	Propanamide

13. Primary Amines

General formula : $R-NH_2$ where R is any alkyl group

Functional group : $-NH_2$ (*amino*)

Secondary suffix : **amine**

Common names : (*i*) Add the word *amine* to the name of the alkyl group,

i.e., *Alkyl + amine* = **Alkylamine**

(*ii*) Attach the prefix *amino* to the name of the corresponding alkane,

i.e., *Amino + alkane* = **Aminoalkane**

IUPAC names. Replace the terminal '*e*' from the name of the corresponding alkane by the secondary suffix *amine*,

i.e., *Alkane − e + amine* = **Alkanamine**

Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
CH_3-NH_2	Methylamine or Aminomethane	Methanamine
$CH_3CH_2-NH_2$	Ethylamine or Aminoethane	Ethanamine
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2-NH_2$	*n*-Propylamine or 1-Aminopropane	Propan-1-amine or Propanamine

14. Secondary amines

General formula : **R – NH – R′** where R and R′ may be same or different alkyl groups.

Functional group : > NH (*imino*)

Secondary prefix : **N-Alkyl**

Secondary suffix : **amine**

Common names : (*i*) Name the alkyl groups in alphabetical order and then add the word *amine*. In case the two alkyl groups are the same, the numerical prefix *di* is used before the name of the alkyl group.

(*ii*) Add the prefix *N-alkyl* before the name of the aminoalkane ; the smaller alkyl group forms a part of the N-alkyl group while the larger alkyl group forms a part of the alkane.

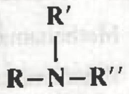
IUPAC names : Add the prefix *N-alkyl* to the name of the alkanamine corresponding to the larger alkyl group,

i.e., N-Alkyl + alkanamine = **N-Alkylalkanamine**

Some Important examples are :

FORMULA	COMMON NAME	IUPAC NAME
CH_3NHCH_3 or $(CH_3)_2NH$	Dimethylamine or N-Methylaminomethane	N-Methylmethanamine
$CH_3CH_2NHCH_3$	Ethylmethylamine or N-Methylaminoethane	N-Methylethanamine
$(CH_3CH_2)_2NH$	Diethylamine or N-Ethylaminoethane	N-Ethylethanamine

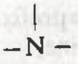
15. Tertiary amines



$$R-\underset{}{\overset{R'}{\overset{|}{N}}}-R''$$

General formula : **R–N–R″** where R, R′, R″ may be same or different alkyl groups or two of them may be same while the third may be different.

Secondary prefix : **N-alkyl, N-alkyl**



$$-\underset{|}{\overset{|}{N}}-$$

Functional group : –N– (*tertiary nitrogen atom*)

Secondary suffix : **amine**

Common names. (*i*) Name the alkyl groups in alphabetical order and add the suffix *amine*. If two or all the three alkyl groups are same, the numerical prefixes *di* and *tri* are respectively used.

(*ii*) Add the prefixes N-alkyl and N-alkyl (smaller alkyl groups) to the name of the aminoalkane corresponding to the largest alkyl group.

IUPAC names. Add the prefixes *N-alkyl* and *N-alkyl* (smaller alkyl groups) to the name of the *alkanamine* corresponding to the largest alkyl group.

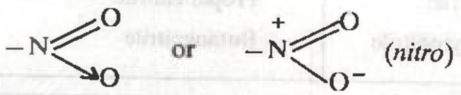
Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
$(CH_3)_3N$	Trimethylamine or N, N-Dimethylaminomethane	N, N-Dimethylmethanamine
$CH_3CH_2N(CH_3)_2$	Ethyldimethylamine or N, N-Dimethylaminoethane	N, N-Dimethylethanamine
$(CH_3CH_2)_2NCH_3$	Diethylmethylamine or N-Ethyl-N-methylaminoethane	N-Ethyl-N-methylethanamine
$(CH_3CH_2)_3N$	Triethylamine or N, N-Diethylaminoethane	N, N-Diethylethanamine

16. Nitroalkanes

General formula : $R-NO_2$ where R is any alkyl group.

Functional group :



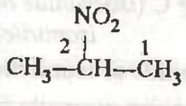
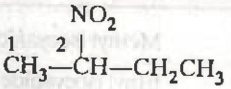
Secondary prefix : **nitro**

Common names. There are no common names for nitroalkans.

IUPAC names. Add the secondary prefix *nitro* to the name of the alkane,

i.e., *Nitro + alkane* = **Nitroalkane**

Some important examples are :

FORMULA	IUPAC NAME	FORMULA	IUPAC NAME
CH_3-NO_2	Nitromethane	 $CH_3-\overset{NO_2}{\overset{2\,\vert}{C}}H-\overset{1}{C}H_3$	2-Nitropropane
$CH_3CH_2-NO_2$	Nitroethane	$CH_3CH_2CH_2\overset{1}{C}H_2-NO_2$	1- Nitrobutane
$CH_3CH_2\overset{1}{C}H_2-NO_2$	1- Nitropropane	 $\overset{1}{C}H_3-\overset{NO_2}{\overset{2\,\vert}{C}}H-CH_2CH_3$	2- Nitrobutane

17. Alkyl nitrites

General formula : $R-O-N=O$ where R is any alkyl group

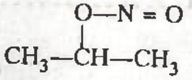
Functional group : $-O-N=O$ (*nitrite*)

Secondary suffix : **nitrite**

Common names : Add the secondary suffix *nitrite* to the name of the alkyl group

i.e., *Alkyl + nitrite* = **Alkyl nitrite**

IUPAC names. There are no IUPAC names for alkyl nitrites.

FORMULA	COMMON NAME	FORMULA	COMMON NAME
$CH_3-O-N=O$	Methyl nitrite	$CH_3CH_2CH_2-O-N=O$	*n*-Propyl nitrite
$CH_3CH_2-O-N=O$	Ethyl nitrite	 $CH_3-\overset{O-N=O}{\overset{\vert}{C}}H-CH_3$	Isopropyl nitrite

18. Alkyl cyanides or Alkanenitriles

General formula : $R-C\equiv N$ where R is any alkyl group

Functional group : $-C\equiv N$ (*cyano or nitrile*)

Secondar suffix : **nitrile**

Common names : (*i*) Add the suffix *cyanide* to the name of the alkyl group,

i.e., *Alkyl + cyanide* = **Alkyl cyanide**

(*ii*) Replace *ic acid* from the common name of the corresponding acid by the suffix *onitrile.* For example,

Acetic acid − ic acid + onitrile = **Acetonitrile**

However, in case of propionic acid, *onic acid* is replaced by *onitrile*. For example, *propionic acid onic acid + onitrile* = **Propionitrile.**

IUPAC names. Add the suffix *nitrile* to the name of the alkane containing the same number of carbon atoms as the alkyl cyanide,

i.e., *Alkane + nitrile* = **Alkanenitrile**

Some important examples are :

FORMULA	COMMON NAME	IUPAC NAME
CH_3-CN	Methyl cyanide or Acetonitrile	Ethanenitrile
CH_3CH_2-CN	Ethyl cyanide or Propionitrile	Propanenitrile
$CH_3CH_2CH_2-CN$	*n*-Propyl cyanide or *n*-Butyronitrile	Butanenitrile

19. Isocyanides or Isonitriles

General formula : $R-N \stackrel{\rightarrow}{=} C$ where R is any alkyl group

Functional group : $-N \stackrel{\rightarrow}{=} C$ (*isocyanide or isonitrile*)

Secondary suffix : **isocyanide or isonitrile**

Common names. Add the suffix *isocyanide or carbylamine* to the name of the alkyl group.

IUPAC names. There are no IUPAC names for isocyanides or isonitriles.

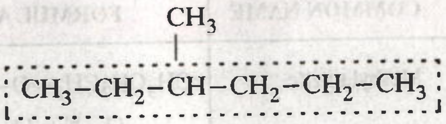
Some important examples are :

FORMULA	COMMON NAME
$CH_3-N \stackrel{\rightarrow}{=} C$	Methyl isocyanide or Methyl carbylamine or Methyl isonitrile
$CH_3CH_2-N \stackrel{\rightarrow}{=} C$	Ethyl isocyanide or Ethyl carbylamine or Ethyl isonitrile

14.11.1. Rules for IUPAC Nomenclature for Branched Chain Alkanes

The following rules are used for naming branched chain alkanes.

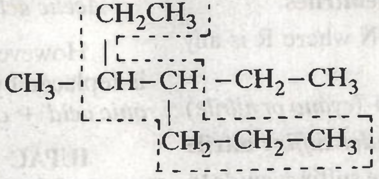
1. Longest chain rule. *Select the longest continuous chain of carbon atoms.* This is called the **parent chain** while all other carbon atoms which are not included in the parent chain are called branch chains or side chains or substituents. The branched chain alkane is then named as a derivative of the parent chain. It may be noted that the longest chain may or may not be straight but it must be continuous. For example,



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

I

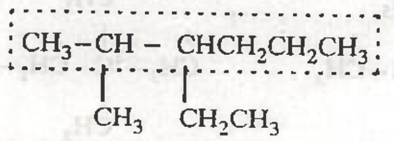
Longest chain contains *six* carbon atoms and hence (I) is named as a derivative of **hexane**



II

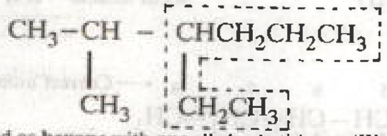
Longest chain contains *seven* carbon atoms and hence (II) is named as a derivative of **heptane**

2. Rule for larger number of side chains. *If two chains of equal lengths are possible, select the one with the larger number of side chains.* For example,



$$\underset{CH_3}{CH_3-\underset{|}{CH}}-\underset{CH_2CH_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

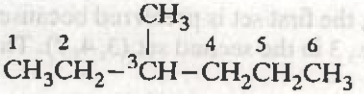
Named as hexane with *two* alkyl substituents (*Correct*)



$$\underset{CH_3}{CH_3-\underset{|}{CH}}-\underset{CH_2CH_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

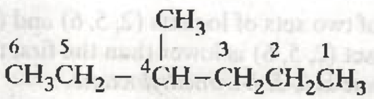
Named as hexane with *one* alkyl substituent (*Wrong*)

3. Lowest number rule. Number the carbon atoms of the parent chain as 1, 2, 3, 4 .... etc. starting from that end which gives the lowest possible number to the carbon atom carrying the substituent. For example, in structure (I), the numbering can be done in two different ways, *i.e.* **IA** and **IB**. The numbering of the carbon chain as given in the structure **IA** is *correct* since it gives a lower number, *i.e.* 3 to the substituent, *i.e.*, methyl group while the numbering as given in structure **IB** is *wrong* since it gives a higher number, *i.e.*, 4 to be substituent.



$$\overset{1}{C}H_3\overset{2}{C}H_2-{}^3\overset{CH_3}{\overset{|}{C}H}-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

IA (*Correct*)



$$\overset{6}{C}H_3\overset{5}{C}H_2-{}^4\overset{CH_3}{\overset{|}{C}H}-\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$

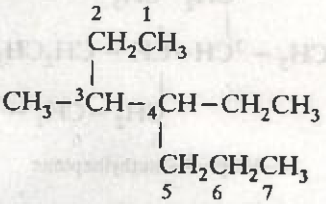
IB (*Wrong*)

The number that indicates the position of the substituent on the parent chain is called the **positional number** or the **locant**. Thus, the correct locant for the methyl side chain in structure (I) is 3.

(i) Lowest set of locants rule. When two or more substituents are present, the **lowest set of locants rule is applied.** According to this rule *when two or more different sets of locants containing the same number of terms is possible, then that set of locants is the lowest which when compared term by term with other sets, each in order of increasing magnitude, has the lowest term at the first point of difference.*

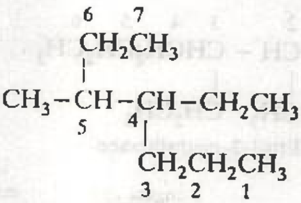
For deciding the lowest set of locants, the carbon atoms of the parent chain are numbered from all possible directions and a locant assigned to each substituent from each direction. The set of locants from each direction is then compared term by term till the first point of difference is reached. That set of locants is preferred which has a lower number at the first point of difference. That is why this rule is also sometimes called as **first point of difference rule.**

Consider, for example, the following alkanes. Each alkane can be numbered in two different ways as shown in structures **A** and **B.**



$$CH_3-{}^3\overset{\overset{2}{C}H_2\overset{1}{C}H_3}{\overset{|}{C}H}-{}_4\underset{\underset{5\ \ 6\ \ 7}{CH_2CH_2CH_3}}{\underset{|}{C}H}-CH_2CH_3$$

A (*Correct*)
Set of locants = 3, 4

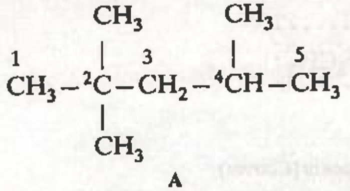


$$CH_3-\underset{5}{\overset{\overset{6\ \ 7}{CH_2CH_3}}{\overset{|}{C}H}}-\underset{\underset{3\ \ 2\ \ 1}{CH_2CH_2CH_3}}{\underset{4|}{C}H}-CH_2CH_3$$

B (*Wrong*)
Set of locants = 4, 5

Out of two sets of locants (3, 4) and (4, 5), the first set is lower and hence preferred because the first term, *i.e.*, 3 in the first set (3, 4) is lower than the first term, *i.e.*, 4 in the second set (4, 5).

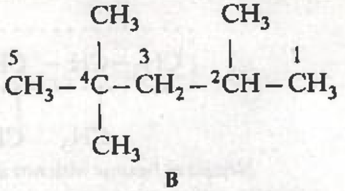
(ii)



$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

A

Set of locants = 2, 2, 4 (*correct*)

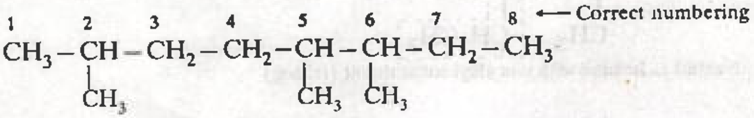


$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

B

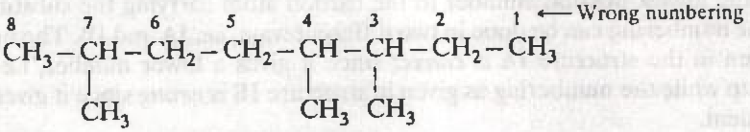
Set of locants = 2, 4, 4 (*wrong*)

(iii)



$CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_3$

Set of locants = 2, 5, 6

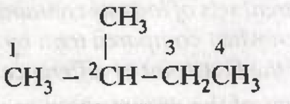


$CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_3$

Set of locants = 3, 4, 7

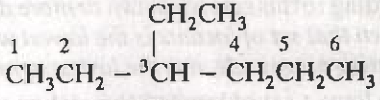
Here, out of two sets of locants (2, 5, 6) and (3, 4, 7), the first set is preferred because the first term, *i.e.* 2 in the first set (2, 5, 6) is lower than the first term, *i.e.*, 3 in the second set (3, 4, 7). Thus, the correct name of the alkane is *2, 5, 6-trimethyloctane.*

4. Name of the branched chain alkane. *Prefix the name of the substituent (i.e. the alkyl groups) to the name of the parent alkane and indicate its position (on the parent chain) by writing before it the number of the carbon atom carrying the substituent. The name of the substituent is separated from its locant by a hyphen (-). The final name of the alkane is always written as one word.* Some examples are given below for illustration.



$CH_3-CH(CH_3)-CH_2CH_3$

2–Methylbutane

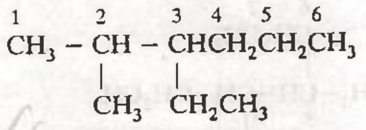


$CH_3CH_2-CH(CH_2CH_3)-CH_2CH_2CH_3$

3–Ethylhexane

5. Alphabetical order of the side chains. *When two or more alkyl groups (side chains) are present on the parent chain, each alkyl group prefixed by its positional number is arranged in alphabetical order (irrespective of its positional number) before the name of the parent alkane.* For example,

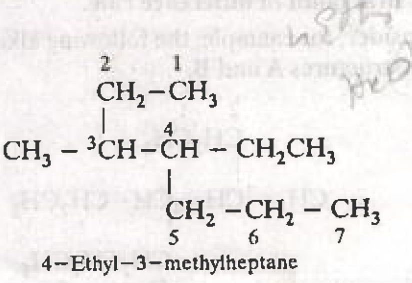
4 ethyl 3 Meth hept-an-e



$CH_3-CH(CH_3)-CH(CH_2CH_3)CH_2CH_2CH_3$

3-Ethyl-2-methylhexane

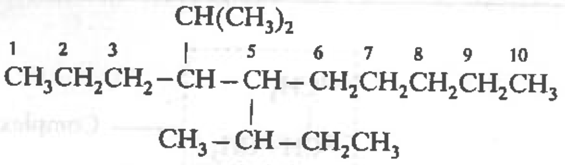
3 ethyl 2 methyl - Hex-ane.



$CH_3-CH(CH_2-CH_3)-CH(CH_2-CH_2-CH_3)-CH_2CH_3$

4–Ethyl–3–methylheptane

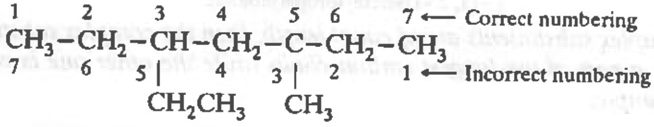
It may be noted here that while deciding the alphabetical order of the various alkyl groups, prefixes *iso* and *neo* are considered to be part of the fundamental name of the alkyl group while the prefixes *sec* and *tert* are not. For example,



$CH_3CH_2CH_2-\overset{CH(CH_3)_2}{CH}-\underset{CH_3-CH-CH_2CH_3}{CH}-CH_2CH_2CH_2CH_2CH_3$

5–*sec*–Butyl–4–isopropyldecane

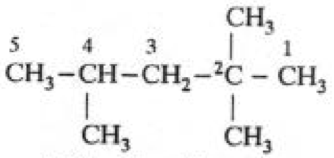
6. Numbering of different alkyl groups at equivalent positions. *If two different alkyl groups are present at equivalent positions, the numbering of the parent chain is done in such a way that the alkly group which comes first in the alphabetical order (written first in the name) gets the lower number.* For example,



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

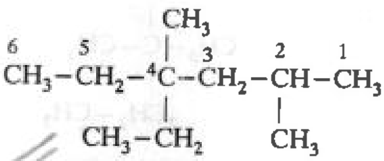
3–Ethyl–5–methylheptane

7. Naming same alkyl groups at different positions. *When the same alkyl group occurs more than once on the parent chain at different positions, the positional number of each alkyl group is separated by commas and suitable prefixes such as* **di** *(for two),* **tri** *(for three),* **tetra** *(for four) etc. are attached to the name of the alkyl group. However, the prefixes* **di, tri** *etc. are not considered while deciding the alphabetical order of the alkyl groups.*



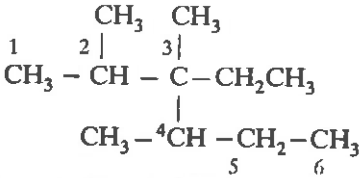
$CH_3-\underset{CH_3}{CH}-CH_2-{}^2\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

2, 2, 4–Trimethylpentane



$CH_3-CH_2-{}^4\overset{CH_3}{\underset{CH_3-CH_2}{C}}-CH_2-\underset{CH_3}{CH}-CH_3$

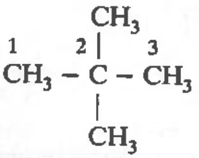
4–Ethyl–2, 4–dimethylhexane



$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3-{}^4CH-CH_2-CH_3}{C}}-CH_2CH_3$

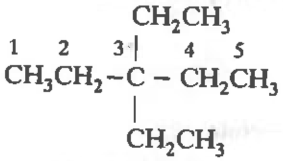
3–Ethyl–2, 3, 4–trimethylhexane

In case the same alkyl group occurs twice on the same carbon atom, its positional number is also repeated twice. For example,



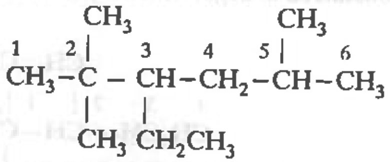
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

2, 2–Dimethylpropane



$CH_3CH_2-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-CH_2CH_3$

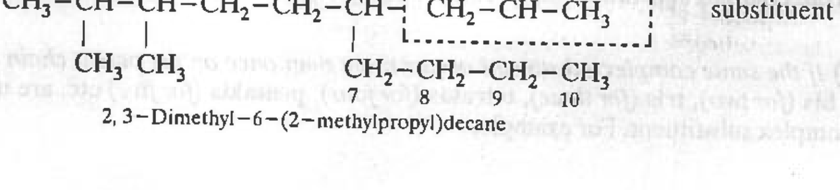
3, 3–Diethylpentane



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

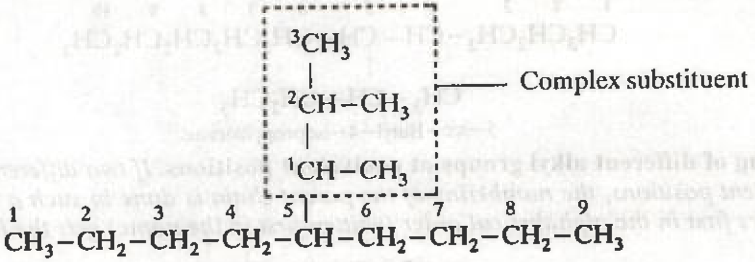
3–Ethyl–2, 2, 5–trimethylhexane

8. Numbering the complex substituent. (*a*) *In case the substituent on the parent chain is complex (i.e., it has branched chain), it is named as a substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as* 1. The name of such a substituent is always enclosed in brackets to avoid confusion with the numbers of the parent chain. For example,



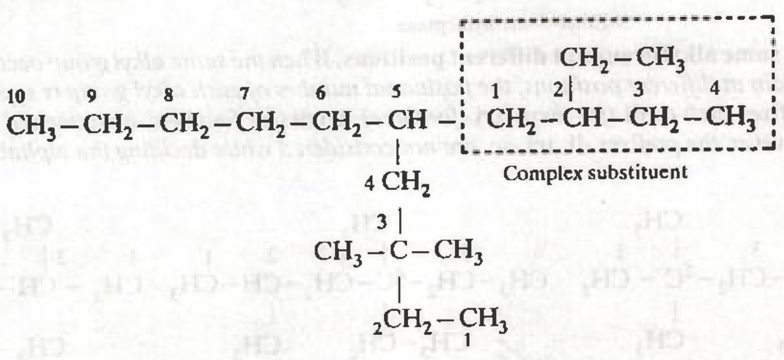
$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-CH_2-\underset{CH_2-CH_2-CH_2-CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_3$

2, 3–Dimethyl–6–(2–methylpropyl)decane



5-(1, 2-Dimethylpropyl)nonane

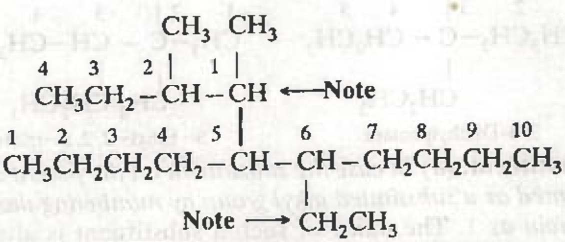
(b) If two complex substituents are of equal length, then the complex substituent with larger number of alkyl groups forms a part of the longest carbon chain while the other one is considered the real complex substituent. For example,



5-(2-Ethylbutyl)-3, 3-dimethyldecane (*Correct*)

5-(2, 2-Dimethylbutyl)-3-ethyldecane (*Incorrect*)

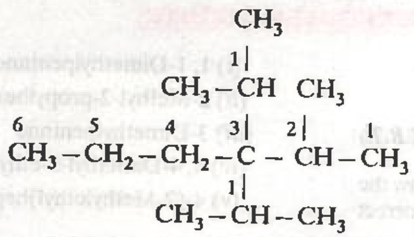
(c) While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of the complete name. For example,



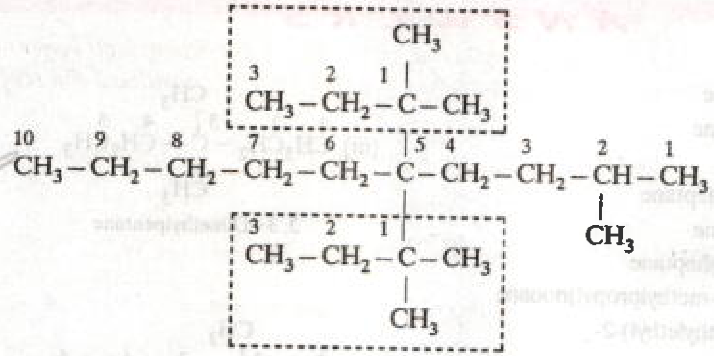
5-(1, 2-Dimethylbutyl)-6-ethyldecane

It may be noted here that the complete name of the complex substituent is *dimethylbutyl.* Since d of dimethylbutyl group comes first than e of the ethyl group in the alphabetical order, therefore, locant 5 is given to the complex substituent and 6 to the ethyl group.

(d) If the same complex substituent occurs more than once on the parent chain at different positions, prefixes **bis** *(for two),* **tris** *(for three),* **tetrakis** *(for four),* **pentakis** *(for five)* etc. are used before the name of the complex substituent. For example,



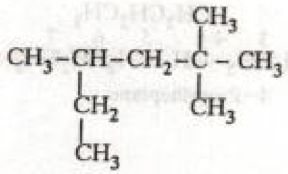
2–Methyl–3, 3–bis (1–methylethyl)hexane



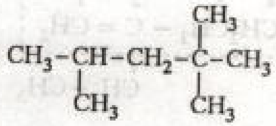
5, 5–Bis (1, 1–dimethylpropyl)–2–methyldecane

PROBLEMS FOR PRACTICE

1. Give the IUPAC names of the following alkanes :

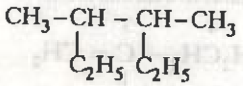
(i)


(A.I.S.B. 1992)

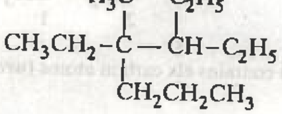
(ii)


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

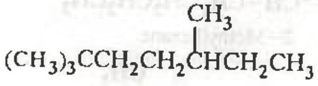
(D.S.B. 1992)

(iii)


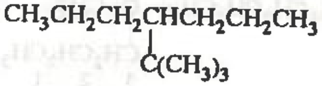
$$CH_3-\underset{C_2H_5}{CH}-\underset{C_2H_5}{CH}-CH_3$$

(iv)


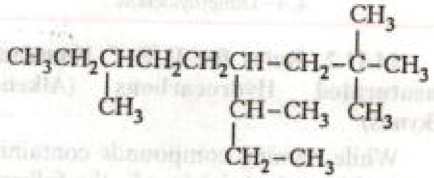
$$CH_3CH_2-\overset{H_3C}{\underset{CH_2CH_2CH_3}{C}}-\overset{C_2H_5}{CH}-C_2H_5$$

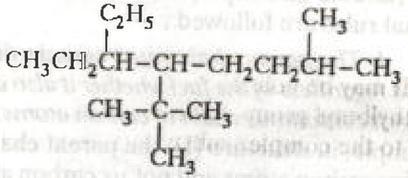
(v)


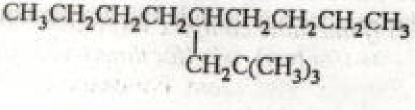
$$(CH_3)_3CCH_2CH_2\overset{CH_3}{CH}CH_2CH_3$$

(vi)


$$CH_3CH_2CH_2\underset{C(CH_3)_3}{CH}CH_2CH_2CH_3$$

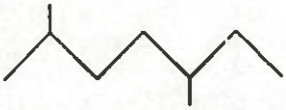
(vii)


(viii)


(ix)


$$CH_3CH_2CH_2CH_2\underset{CH_2C(CH_3)_3}{CH}CH_2CH_2CH_2CH_3$$

PRACTICE PROBLEMS CONTD.

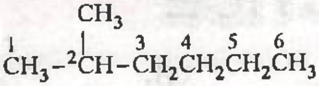
(x)  (N.C.E.R.T.)

2. What is wrong with the following names ? Draw the structures they represent and give their correct names.

(i) 1, 1-Dimethylpentane
(ii) 2-Methyl-2-propylhexane
(iii) 3-Dimethylpentane
(iv) 4, 4-Dimethyl-3-ethylpentane
(v) 4-(2-Methylethyl)heptane

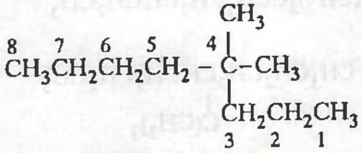
ANSWERS

1. (i) 2, 2, 4-Trimethylhexane
(ii) 2, 2, 4-Trimethylpentane
(iii) 3, 4-Dimethylhexane
(iv) 3, 4-Diethyl-4-methylheptane
(v) 2, 2, 5-Trimethylheptane
(vi) 4-(1, 1-Dimethylethyl)heptane
(vii) 2, 2, 7-Trimethyl-4-(1-methylpropyl)nonane
(viii) 6-Ethyl-5-(1, 1-dimethylethyl)-2-methyloctane
(ix) 5-(2, 2-Dimethylpropyl)nonane
(x) 2, 5-Dimethylheptane

2. (i) 

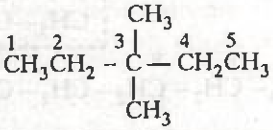
$$\overset{1}{C}H_3-\overset{2}{\underset{}{\overset{CH_3}{C}}}H-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

2−Methylhexane

(ii) 

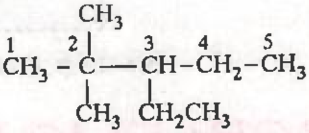
$$\overset{8}{C}H_3\overset{7}{C}H_2\overset{6}{C}H_2\overset{5}{C}H_2-\overset{4}{\underset{\displaystyle \overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3}{\overset{\displaystyle CH_3}{C}}}-CH_3$$

4, 4−Dimethyloctane

(iii) 

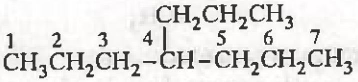
$$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{3}{\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}}-\overset{4}{C}H_2\overset{5}{C}H_3$$

3, 3−Dimethylpentane

(iv) 

$$\overset{1}{C}H_3-\overset{2}{\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}}-\underset{\displaystyle CH_2CH_3}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_3$$

3−Ethyl−2, 2−dimethylpentane

(v) 

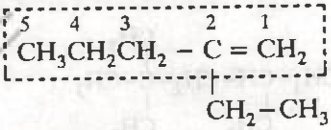
$$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2-\overset{\displaystyle CH_2CH_2CH_3}{\overset{4}{C}H}-\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_3$$

4−Propylheptane

14.11.2. Rules for IUPAC Nomenclature of Unsaturated Hydrocarbons (Alkenes and Alkynes)

While naming compounds containing multiple (double and triple) bonds, the following additional rules are followed :

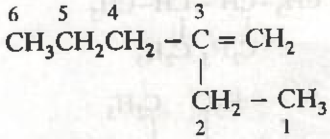
1. The parent chain must contain the multiple bond regardless of the fact whether it also denotes the longest continuous chain of carbon atoms or not. For example, in structure (I), the parent chain consists of *five* carbon atoms and not *six* carbon atoms since the latter does not include the double bond.



$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2-\underset{\displaystyle CH_2-CH_3}{\overset{2}{C}}=\overset{1}{C}H_2$$

I

Parent chain contains five carbon atoms (*correct*)



$$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2-\underset{\displaystyle \overset{2}{C}H_2-\overset{1}{C}H_3}{\overset{3}{C}}=CH_2$$

I

Parent chain contains six carbon atoms (*wrong*)

2. If both double and triple bonds are present, the numbering of the parent chain should always be done from that end which is nearer to the double or the triple bond, i.e., the **lowest set of locants rule** *for the multiple bonds must be followed.* For example,

$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}-\overset{7}{C}H_2-\overset{8}{C}H_3$$

Correct numbering, set of locants = 2, 5

$$\overset{8}{C}H_3-\overset{7}{C}H=\overset{6}{C}H-\overset{5}{C}H_2-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

Wrong numbering, set of locants = 3, 6

3. If, however, there is a choice in numbering, the double bond is always given preference over the triple bond. For example,

$$\underset{1}{\overset{5}{C}}H\equiv\underset{2}{\overset{4}{C}}-\underset{3}{\overset{3}{C}}H_2-\underset{4}{\overset{2}{C}}H=\underset{5}{\overset{1}{C}}H_2 \quad \begin{array}{l}\longleftarrow \textit{Correct numbering}\\ \longleftarrow \textit{Wrong numbering}\end{array}$$

4. If the organic compound contains only one double or the triple bond, its locant or the positional number is always placed before its suffix in accordance with 1993 recommendations for IUPAC nomenclature of organic compounds. For example,

$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$$

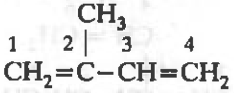
But + 2−ene = But−2−ene

If, however, both double and triple bonds are present, their locants are written before their respective suffixes, the terminal '*e*' from the suffix '*ene*' is dropped while writing the complete name of the organic compound. *It may be emphasized here that the organic compound is named as derivative of alkyne rather than alkene.* For example,

$$\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$$

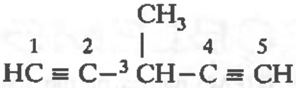
Pent + 3–en (*e*) 1–yne = Pent–3–en–1–yne

These rules are further illustrated by the following additional examples :



$$\overset{1}{C}H_2=\overset{2}{C}(CH_3)-\overset{3}{C}H=\overset{4}{C}H_2$$

2–Methylbuta–1, 3–diene



$$H\overset{1}{C}\equiv\overset{2}{C}-{}^{3}CH(CH_3)-\overset{4}{C}\equiv\overset{5}{C}H$$

3–Methylpenta–1, 4–diyne

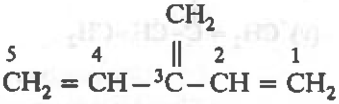
$$H\overset{6}{C}\equiv\overset{5}{C}-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$$

Hexa–1, 3–dien–5–yne

In some cases all the double and triple bonds present in the molecule cannot be included in the longest chain. In such cases the following prefixes are used for double and triple bonded groups.

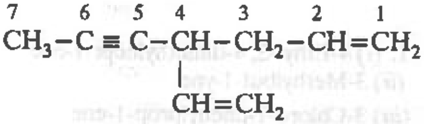
$CH_2=$	**Methylene**
$CH_3CH=$	**Ethylidene**
$CH_2=CH-$	**Vinyl or ethenyl**
$HC\equiv C-$	**Ethynyl**

For example,



$$\overset{5}{C}H_2=\overset{4}{C}H-{}^{3}C(=CH_2)-\overset{2}{C}H=\overset{1}{C}H_2$$

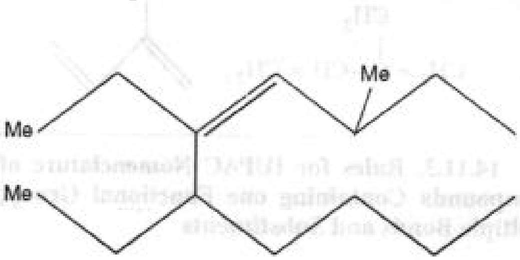
3−Metylenepenta−1, 3−diene



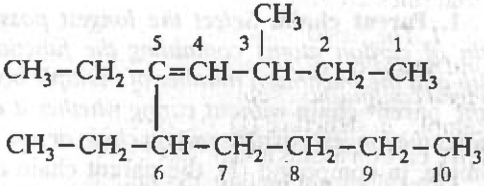
$$\overset{7}{C}H_3-\overset{6}{C}\equiv\overset{5}{C}-\overset{4}{C}H(CH=CH_2)-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$$

4−Ethenylhept−1−en−5−yne
or 4−Vinylhept−1−en−5−yne

EXAMPLE 14.9. *Give the IUPAC name of the following compound.* **(I.I.T. 1990)**



Solution. The bond line notation of the compound given in the question represents the following structure :

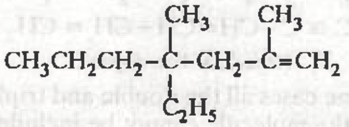


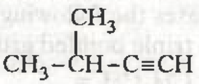
$$\begin{array}{l} CH_3-CH_2-\overset{5}{C}=\overset{4}{C}H-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}H_3 \\ \qquad\qquad\quad | \\ CH_3-CH_2-\underset{6}{C}H-\underset{7}{C}H_2-\underset{8}{C}H_2-\underset{9}{C}H_2-\underset{10}{C}H_3 \end{array}$$

5, 6–Diethyl–3–methyldec–4–ene

PROBLEMS FOR PRACTICE

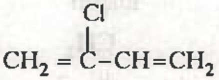
1. Give the IUPAC names of the following compounds :

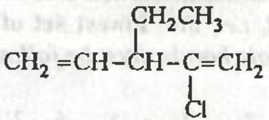
(*i*) 
$CH_3CH_2CH_2-\underset{C_2H_5}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2$

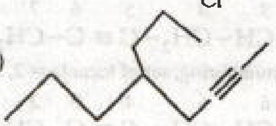
(*ii*) 
$CH_3-\overset{CH_3}{CH}-C\equiv CH$ (*D.S.B. 1992*)

(*iii*) $C_6H_5-CH=CH-CH_2Cl$

(*iv*) $CH_3CH=CH-CH_2Br$

(*v*) 
$CH_2=\overset{Cl}{C}-CH=CH_2$

(*vi*) 
$CH_2=CH-\overset{CH_2CH_3}{CH}-\underset{Cl}{C}=CH_2$ (*A.I.S.B. 1993*)

(*vii*) 

(*N.C.E.R.T.*)

2. Give the condensed and bond-line structural formulae for the following :

(*a*) 2-Methylbuta-1, 3-diene

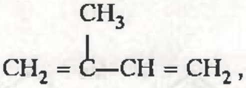
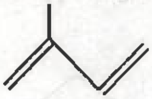
(*b*) Penta-1, 4-diene

(*c*) Hexa-1, 3, 5-triene

(*d*) 3-Ethylpenta-1, 3-diene

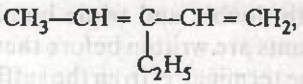
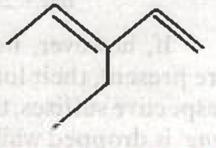
ANSWERS

1. (*i*) 4-Ethyl-2, 4-dimethylhept-1-ene
(*ii*) 3-Methylbut-1-yne
(*iii*) 3-Chloro-1-phenylprop-1-ene
(*iv*) 1-Bromobut-2-ene (*v*) 2-Chlorobuta-1, 3-diene
(*vi*) 2-Chloro-3-ethylpenta-1, 4-diene
(*vii*) 5-Propyloct-2-yne

2. (*a*) 
$CH_2=\overset{CH_3}{C}-CH=CH_2$, 

(*b*) $CH_2=CH-CH_2-CH=CH_2$, 

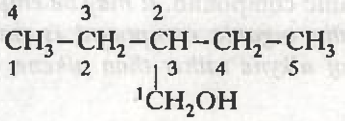
(*c*) $CH_2=CH-CH=CH-CH=CH_2$, 

(*d*) 
$CH_3-CH=\underset{C_2H_5}{C}-CH=CH_2$, 

14.11.3. Rules for IUPAC Nomenclature of Compounds Containing one Functional Group, Multiple Bonds and Substituents

While naming organic compounds containing one functional group, double and triple bonds, and substituents, the following additional rules are observed.

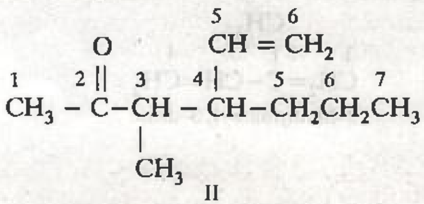
1. Parent chain. *Select the longest possible chain of carbon atoms containing the functional group and the maximum number of multiple bonds as the* **parent chain** *without caring whether it also denotes the longest possible carbon chain or not.* For example, in compound (I), the parent chain containing the functional group has **four** carbon atoms while the longest possible carbon chain has **five** carbon atoms.


$\overset{4}{\underset{1}{CH_3}}-\overset{3}{\underset{2}{CH_2}}-\overset{2}{\underset{3}{CH}}(\overset{1}{CH_2OH})-\underset{4}{CH_2}-\underset{5}{CH_3}$

I

Parent chain contains four rather than five carbon atoms.

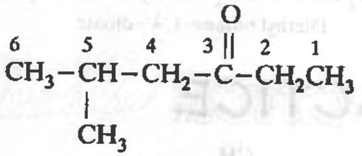
Similarly, in compound (II), the parent chain containing the functional group and the double bond has six carbon atoms while the longest possible carbon chain has seven carbon atoms.


$\overset{1}{CH_3}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\underset{CH_3}{\overset{3}{CH}}-\overset{\overset{5}{CH}=\overset{6}{CH_2}}{\underset{4}{CH}}-\overset{5}{CH_2}\overset{6}{CH_2}\overset{7}{CH_3}$

II

Parent chain contains six rather than seven carbon atoms.

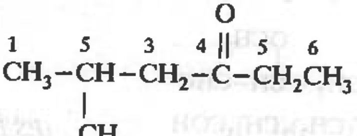
2. Lowest sum rule for the functional group. *Number the parent chain in such a way that the functional group gets the lowest possible number followed by the double and triple bonds even if it violates the lowest* **set of locants rule** *(discussed under the nomenclature of branched chain alkanes).* For example, in compound (III), the positional number for the keto group is 3 rather than 4.



$$\begin{array}{l} \qquad\qquad\qquad\quad\;\; O \\ 6 \quad\; 5 \qquad 4 \quad\; 3 \,\| \;\; 2 \quad 1 \\ CH_3-CH-CH_2-C-CH_2CH_3 \\ \qquad\;\; | \\ \qquad CH_3 \end{array}$$

III (*Correct*)

(*>C = O group gets lowest number 3*)

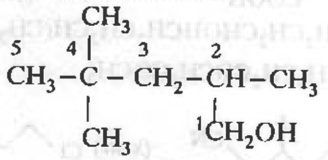


$$\begin{array}{l} \qquad\qquad\qquad\quad\;\; O \\ 1 \quad\; 5 \qquad 3 \quad\; 4 \,\| \;\; 5 \quad 6 \\ CH_3-CH-CH_2-C-CH_2CH_3 \\ \qquad\;\; | \\ \qquad CH_3 \end{array}$$

III (*Wrong*)

(*>C = O group gets number 4 which is not lowest*)

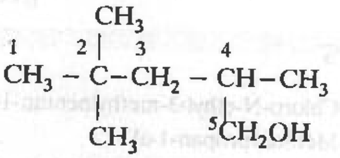
Similarly for compound (IV), correct numbering gives position 1 to the functional group and not 5 though it violates the lowest set of locants rule.



$$\begin{array}{l} \qquad\quad CH_3 \\ 5 \qquad 4 \,| \qquad 3 \qquad\quad 2 \\ CH_3-C-CH_2-CH-CH_3 \\ \qquad\;\; | \qquad\qquad\;\; | \\ \qquad CH_3 \qquad {}^1CH_2OH \end{array}$$

IV (*Correct*)

Set of locants = 2, 4, 4

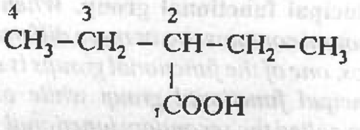


$$\begin{array}{l} \qquad\quad CH_3 \\ 1 \qquad 2 \,| \quad 3 \qquad\quad 4 \\ CH_3-C-CH_2-CH-CH_3 \\ \qquad\;\; | \qquad\qquad\;\; | \\ \qquad CH_3 \qquad {}^5CH_2OH \end{array}$$

IV (*Wrong*)

Set of locants = 2, 2, 4

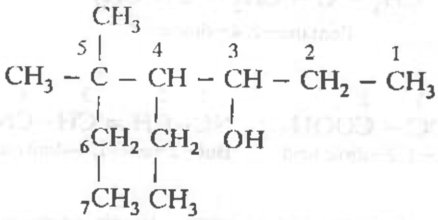
3. Numbering the chain terminating functional groups. *When a chain terminating functional group such as* $-CHO$, $-COOH$, $-COOR$, $-CONH_2$, $-COCl$, $-C\equiv N$ *etc. is present,* it is always given **number 1** and number 1 is usually omitted from the final name of the compound when there is no ambiguity. For example,



$$\begin{array}{l} 4 \qquad\quad 3 \qquad\quad 2 \\ CH_3-CH_2-CH-CH_2-CH_3 \\ \qquad\qquad\qquad\;\; | \\ \qquad\qquad\quad {}_1COOH \end{array}$$

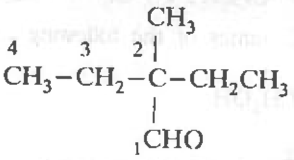
2-Ethylbutan-1-oic acid
or simply 2-Ethylbutanoic acid

However, in the following examples the numerical locant 1 is always included when another numerical locant appears in the same name.



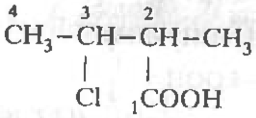
$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad 5 \,| \qquad 4 \qquad\quad 3 \qquad\quad 2 \qquad\quad 1 \\ CH_3-C-CH-CH-CH_2-CH_3 \\ \qquad\quad | \qquad\; | \qquad\;\; | \\ \qquad {}_6CH_2 \; CH_2 \;\; OH \\ \qquad\quad | \qquad\; | \\ \qquad {}_7CH_3 \; CH_3 \end{array}$$

4-Ethyl-5,5-dimethylheptan-3-ol



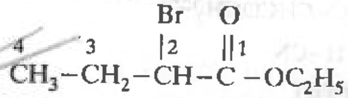
$$\begin{array}{l} \qquad\qquad\quad CH_3 \\ 4 \qquad 3 \qquad 2 \,| \\ CH_3-CH_2-C-CH_2CH_3 \\ \qquad\qquad\quad\;\; | \\ \qquad\qquad\quad {}_1CHO \end{array}$$

2-ethyl-2-methylbutan-1-al



$$\begin{array}{l} 4 \qquad 3 \qquad 2 \\ CH_3-CH-CH-CH_3 \\ \qquad\;\; | \qquad\; | \\ \qquad\; Cl \quad {}_1COOH \end{array}$$

3-Chloro-2-methylbutan-1-oic acid



$$\begin{array}{l} \qquad\qquad\qquad\quad Br \quad O \\ 4 \qquad 3 \qquad\quad |2 \quad \|1 \\ CH_3-CH_2-CH-C-OC_2H_5 \end{array}$$

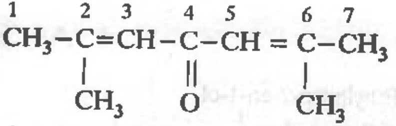
Ethyl 2-bromobutan-1-oate

$$\begin{array}{l} 4 \qquad\quad 3 \qquad\quad 2 \quad\; 1 \\ CH_3-CH=CH-CH_2OH \end{array}$$

But-2-en-1-ol

$$\begin{array}{l} 5 \qquad\quad 4 \;\; 3 \quad 2 \qquad 1 \\ CH_3-C\equiv C-CH_2-CH=O \end{array}$$

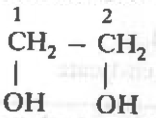
Pent-3-yn-1-al



$$\begin{array}{l} 1 \qquad\;\; 2 \quad 3 \qquad\; 4 \quad 5 \qquad\quad 6 \quad 7 \\ CH_3-C=CH-C-CH=C-CH_3 \\ \qquad\;\; | \qquad\qquad \| \qquad\qquad\; | \\ \qquad CH_3 \qquad\;\; O \qquad\qquad CH_3 \end{array}$$

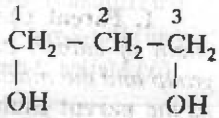
2, 6-Dimethylhepta-2, 5-dien-4-one

If a compound contains two or more like groups, the numerical prefixes *di*, *tri*, *tetra* etc. are used and the terminal *'e'* from the primary suffix is retained (not dropped) while writing the IUPAC name. For example,



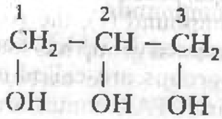
$$\begin{array}{l} 1 \qquad\quad 2 \\ CH_2-CH_2 \\ \,| \qquad\quad | \\ OH \qquad OH \end{array}$$

Ethane-1, 2-diol



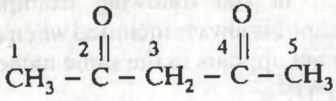
$$\begin{array}{l} \quad 1 \qquad 2 \qquad 3 \\ CH_2-CH_2-CH_2 \\ \;\; | \qquad\qquad\quad | \\ OH \qquad\qquad OH \end{array}$$

Propane-1, 3-diol



$$\begin{array}{l} \quad 1 \qquad\;\; 2 \qquad 3 \\ CH_2-CH-CH_2 \\ \;\; | \qquad\;\; | \qquad\; | \\ OH \quad OH \quad OH \end{array}$$

Propane-1, 2, 3-triol



$\overset{1}{CH_3}-\overset{O}{\overset{\|}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{O}{\overset{\|}{\overset{4}{C}}}-\overset{5}{CH_3}$

Pentane−2, 4−dione

$\overset{1}{HOOC}-\overset{2}{COOH}$

Ethane−1, 2−dioic acid

$\overset{1}{NC}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CN}$

But−2−ene−1, 4−dinitrile

$\overset{1}{HOOC}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{COOH}$

But−2−ene − 1, 4−dioic acid

$\overset{1}{OHC}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CHO}$

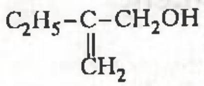
But−2−ene−1, 4 − dial

$H_5C_2OOC-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{COOC_2H_5}$

Diethyl butane−1, 4−dioate

PROBLEMS FOR PRACTICE

Give the IUPAC names of the following compounds :



(*i*) $C_2H_5-\underset{\underset{CH_2}{\|}}{C}-CH_2OH$

(*ii*) $CH_3-CH=CH-CHO$

(*iii*) $NH_2-CH_2-CH_2-CH_2-NH_2$

(*iv*) $CH_3-CH=CH-COOH$

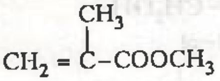
(*I.I.T. 1986*)

(*v*) $(CH_3)_2C=CHCOCH_3$

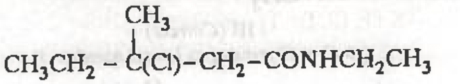
(*vi*) $CH_2=CH-CN$

(*vii*) $OCH-CHO$

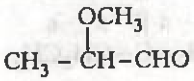
(*viii*) $HOOC-C\equiv C-COOH$



(*ix*) $CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3$

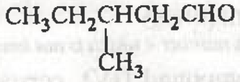


(*x*) $CH_3CH_2-\overset{\overset{CH_3}{|}}{C}(Cl)-CH_2-CONHCH_2CH_3$



(*xi*) $CH_3-\overset{\overset{OCH_3}{|}}{CH}-CHO$

(*xii*) $[(CH_3)_2CH]_3COH$ (*P.S.B. 1994*)



(*xiii*) $CH_3CH_2\underset{\underset{CH_3}{|}}{CH}CH_2CHO$

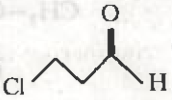
(*xiv*) $CH_3\underset{\underset{COOH}{|}}{CH}CH_2CH_3$ (*H.S.B. 1999*)

(*xv*) $CH_3CH_2CHOHCH_2CH_2CH(CH_3)CH_2CH_3$

(*xvi*) $CH_3CH_2COCH_2COCH_3$

(*xvii*)

(*xviii*)



(*N.C.E.R.T.*)

ANSWERS

(*i*) 2-Ethylprop-2-en-1-ol
(*ii*) But-2-en-1-al
(*iii*) Propane-1, 3-diamine
(*iv*) But-2--en-1-oic acid
(*v*) 4-Methylpent-3-en-2-one
(*vi*) Prop-2-en-1-nitrile
(*vii*) Ethane-1, 2-dial
(*viii*) But-2-yne-1, 4-dioic acid
(*ix*) Methyl 2-methylprop-2-en-1-oate
(*x*) 3-Chloro-N-ethyl-3-methylpentan-1-amide
(*xi*) 2-Methoxypropan-1-al
(*xii*) 2, 4-Dimethyl-3-(1-methylethyl)pentan-3-ol
(*xiii*) 3-Methylpentanal
(*xiv*) 2-Methylbutanoic acid
(*xv*) 6-Methyloctan-3-ol
(*xvi*) Hexane-2, 4-diene
(*xvii*) 3-Methylpentanenitrile
(*xviii*) 3-Chloropropanal.

14.11.4. Rules for IUPAC Nomenclature of Polyfunctional Compounds

Organic compounds which contain two or more functional groups are called *polyfunctional compounds.* Their IUPAC names are obtained as follows :

1. Principal functional group. *When an organic compound contains two or more different functional groups, one of the functional groups is selected as the* ***principal functional*** *group while all other groups (also called the secondary functional groups)* are treated as **substituents**. The choice of the principal functional group is made on the basis of the following order of preference.*

Carbodylic acids > sulphonic acids > anhydrides > esters > acid chlorides > acid amides > nitriles > aldehydes > ketones > alcohols > phenols > thiols > amines > ethers > alkenes > alkynes.

All the remaining functional groups such as *halo* (fluoro, chloro, bromo, iodo), *nitroso* (–NO), *nitro* ($-NO_2$), and *alkoxy* (–OR), R (alkyl), C_6H_5 etc. are always treated as substituent groups.

It may be noted that while writing the names of the polyfunctional compounds, the principal functional group is indicated by adding the *secondary suffix* to the word root while the secondary functional groups are indicated by adding suitable *prefixes* to the word root. The prefixes for secondary functional groups are listed below :

SECONDARY FUNCTIONAL GROUP	PREFIX	SECONDARY FUNCTIONAL GROUP	PREFIX
—X (F, Cl, Br, I)	Halo	—CHO	Formyl or alkanoyl
—OH	Hydroxy	C=O	Keto or oxo
—SH	Mercapto	—COOH	Carboxy
—OR	Alkoxy	—COOR	Alkoxycarbonyl or carbalkoxy
$—NH_2$	Amino	—COCl	Halocarbonyl or haloalkanoyl
—NHR	Alkylamino	—CN	Cyano
$—NR_2$	Dialkylamino	$—CONH_2$	Carbamoyl or Carboxamido

2. Selecting the principal chain. *While selecting the principal chain present in a polyfunctional compound care should be taken that it must contain the principal functional group and the* **maximum** *number of secondary functional groups and multiple bonds, if any.*

3. Numbering the principal chain. *The principal chain present in a polyfunctional compound must be numbered in such a way that the principal functional group gets the lowest possible number followed by double bond, triple bond and the substituents, i.e.*

Principal functional group > double bond > triple bond > substituents

4. Alphabetical order. The prefixes for the secondary functional groups and other substituents should be placed in alphabetical order before the word root as explained earlier. If, however, two groups of the same preference occupy identical positions from either end of the parent chain, the lower number must be given to the group whose prefix comes first in the alphabetical order. For example,

$$\overset{4}{\mathrm{ClCH_2}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}\mathrm{Br}$$

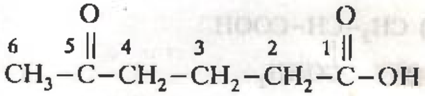
1–Bromo–4–chlorobutane (*Correct*)

$$\overset{1}{\mathrm{ClCH_2}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\mathrm{Br}$$

4–Bromo–1–chlorobutane (*Wrong*)

The rest of the rules for numerical prefixes are the same as explained earlier.

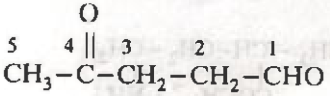
To illustrate these rules, let us consider the following examples.



$$\overset{6}{CH_3}-\overset{\overset{O}{\|}}{\overset{5}{C}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$$

5–Ketohexan–1–oic acid
or 5–Oxohexan–1–oic acid

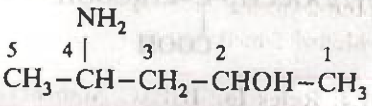
–COOH is the principal functional group while >C = O is the substituent group



$$\overset{5}{CH_3}-\overset{\overset{O}{\|}}{\overset{4}{C}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CHO}$$

4–Ketopentan–1–al
or 4–Oxopentan–1–al

–CHO is the principal functional group while >C = O is the substituent group



$$\overset{5}{CH_3}-\overset{\overset{NH_2}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CHOH}-\overset{1}{CH_3}$$

4–Aminopentan–2–ol

–OH is the principal functional group while $-NH_2$ is the substituent group

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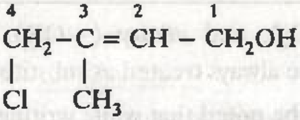
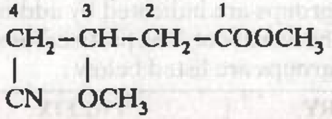
*According to 'A Guide to IUPAC' Nomenclature of Organic Compounds–Recommendations 1993 by R-Panico, W.H. Powell and Jean-Claude Richer.



$$\underset{\underset{Cl}{|}}{\overset{4}{C}H_2}-\underset{\underset{CH_3}{|}}{\overset{3}{C}}=\overset{2}{C}H-\overset{1}{C}H_2OH$$

4-Chloro-3-methylbut-2-en-1-ol

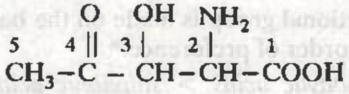
$-OH$ is the principal functional group while $-Cl$ and $-CH_3$ are substituents



$$\underset{\underset{CN}{|}}{\overset{4}{C}H_2}-\underset{\underset{OCH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}OOCH_3$$

Methyl 4-cyano-3-methoxybutan-1-oate

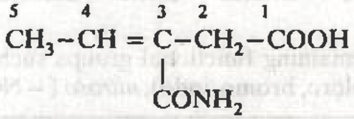
$-COOCH_3$ is the principal functional group while $-OCH_3$ and $-CN$ are the substituent groups



$$\overset{5}{C}H_3-\overset{\overset{O}{||}}{\overset{4}{C}}-\overset{\overset{OH}{|}}{\overset{3}{C}H}-\overset{\overset{NH_2}{|}}{\overset{2}{C}H}-\overset{1}{C}OOH$$

2-Amino-3-hydroxy-4-oxopentan-1-oic acid

$-COOH$ is the principal functional group while $-NH_2$, $-OH$ and $>C=O$ are the substituent groups



$$\overset{5}{C}H_3-\overset{4}{C}H=\underset{\underset{CONH_2}{|}}{\overset{3}{C}}-\overset{2}{C}H_2-\overset{1}{C}OOH$$

3-Carbamoylpen-3-en-1-oic acid

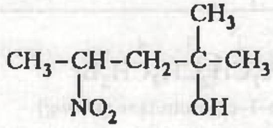
$-COOH$ is the principal functional group while $-CONH_2$ is the substituent group

PROBLEMS FOR PRACTICE

1. Give the IUPAC names for the following poly-functional compounds.

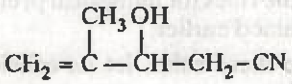
(i) $CH_3CH_2O-CH_2-CHOH-CH_3$

(ii)



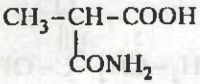
$$CH_3-\underset{\underset{NO_2}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(iii)



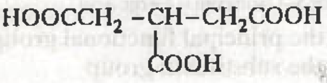
$$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{OH}{|}}{C}H-CH_2-CN$$

(iv)



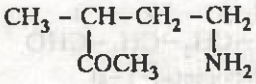
$$CH_3-\underset{\underset{CONH_2}{|}}{CH}-COOH$$

(v)



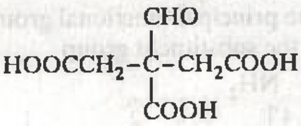
$$HOOCCH_2-\underset{\underset{COOH}{|}}{CH}-CH_2COOH$$

(vi)



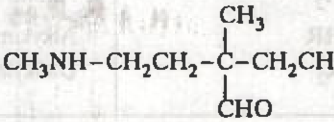
$$CH_3-\underset{\underset{COCH_3}{|}}{CH}-CH_2-\underset{\underset{NH_2}{|}}{CH_2}$$

(vii)



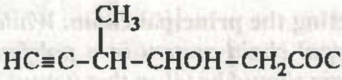
$$HOOCCH_2-\underset{\underset{COOH}{|}}{\overset{\overset{CHO}{|}}{C}}-CH_2COOH$$

(viii)



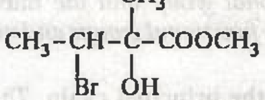
$$CH_3NH-CH_2CH_2-\underset{\underset{CHO}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$$

(ix)



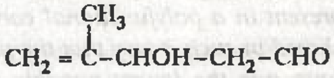
$$HC\equiv C-\overset{\overset{CH_3}{|}}{CH}-CHOH-CH_2COCl$$

(x)



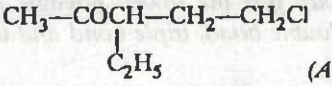
$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOCH_3$$

(xi)



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CHOH-CH_2-CHO$$

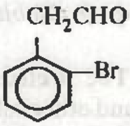
(xii)



$$CH_3-CO\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_2Cl$$

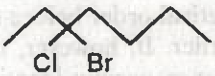
(A.I.S.B. 1999)

(xiii)



(A.I.S.B. 1999)

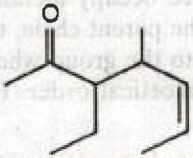
(xiv)



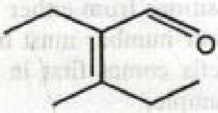
(xv) Cl_2CHCH_2OH

(N.C.E.R.T.)

(xvi)



(xvii)



ANSWERS

(i) 1-Ethoxypropan-2-ol

(ii) 2-Methyl-4-nitropentan-2-ol

(iii) 3-Hydroxy-4-methylpent-4-ene-1-nitrile

(iv) 2-Carbamoylpropanoic acid

(v) 3-Carboxy-1, 5-pentanedioic acid

(vi) 5-Amino-3-methylpentan-2-one

(*vii*) 3-carboxy-3-formylpentane-1, 5-dioic acid
(*viii*) 4-Aminomethyl-2-ethyl-2-methylbutanal
(*ix*) 3-Hydroxy-4-methylhex-5-yn-1-onyl chloride
(*x*) Methyl 3-bromo-2-hydroxy-2-methylbutan-1-oate
(*xi*) 3-Hydroxy-4-methylpent-4-en-1-al
(*xii*) 5-chloro-3-ethylpentan-2-one
(*xiii*) 2-(*o*-Bromophenyl) ethanal.
(*xiv*) 3-Bromo-3-chloroheptane
(*xv*) 2, 2-Dichloroethanol
(*xvi*) 3-Ethyl-4-methylhept-5-en-2-one
(*xvii*) 2-Ethyl-3-methylpent-2-en-1-al

14.11.5. Rules for Naming Alicyclic Compounds

The following rules are generally used.

1. *The names of alicyclic compounds are obtained by adding the prefix, 'cyclo' to the name of the corresponding straight chain hydrocarbon (alkane, alkene or alkyne).*

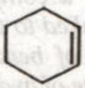

Cyclopropane


Cyclobutane

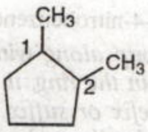

Cyclopentane

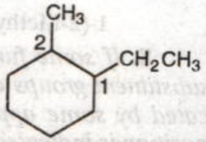

Cyclohexane

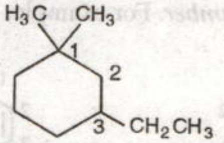

Cyclopentene


Cyclohexene

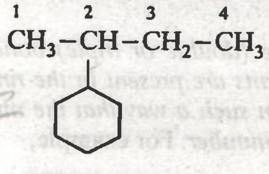
2. *If two or more alkyl groups or other substituent groups are present in the ring, their positions are indicated by arabic numerals, i.e. 1, 2, 3, 4 .... etc. While numbering the carbon atoms of the ring, the substituent which comes first in the alphabetical order is given the lowest number provided it does not violate the lowest sum rule.* For example,


1, 2 - Dimethylcyclopentane


1-Ethyl-2-methylcyclohexane

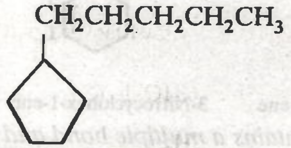

3-Ethyl-1, 1-dimethylcyclohexane

3. (*a*) *If the ring contains more or equal number of carbon atoms than the alkyl group attached to it, it is named as a derivative of cycloalkane and the alkyl group is treated as a substituent group, otherwise it is named as a derivative of alkane and the cycloalkyl group is considered as a substituent group.* For example,



$$\overset{1}{CH_3}-\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

(2-Butyl)cyclohexane



$$CH_2CH_2CH_2CH_2CH_3$$

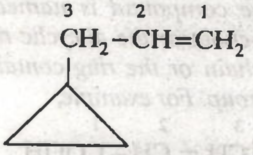
Pentylcyclopentane

$$CH_3-CH_2-CH-CH_2-CH_3$$

3-Cyclobutylpentane

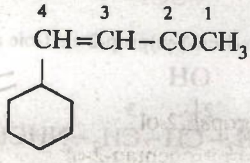
Note that parentheses are used wherever necessary to avoid confusion. Here in the first example, 2-butyl group has been enclosed in parentheses to emphasize that the locant 2 refers to the substituent on the alkane and not on the ring (*i.e.* cycloalkane).

(*b*) *If the side than contains a multiple bond or a functional group, the alicyclic ring is treated as the substituent irrespective of the size of the ring.* For example,



$$\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2}$$

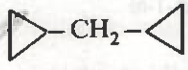
3-Cyclopropylprop-1-ene



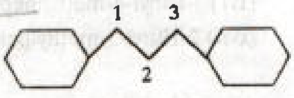
$$\overset{4}{CH}=\overset{3}{CH}-\overset{2}{C}\overset{1}{OCH_3}$$

4-Cyclohexylbut-3-en-2-one

(c) *If more than one alicyclic ring is attached to a single chain, the compound is named as a derivative of alkane irrespective of the number of carbon atoms in the ring or the chain.* For example,

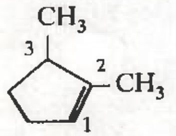


Dicyclopropylmethane

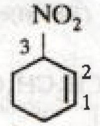


1, 3-Dicyclohexylpropane

4. ***If a multiple (double or triple) bond and some other substituents are present in the ring, the numbering is done in such a way that the multiple bond gets the lowest number.*** **For example,**

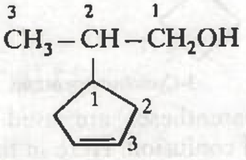


2, 3-Dimethylcyclopent-1-ene

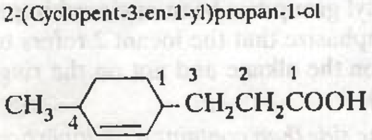


3-Nitrocyclohex-1-ene

5. *If the ring contains a multiple bond and the side chain contains a functional group, then the ring is treated as the substituent and the compound is named as a derivative of the side chain. For example,*

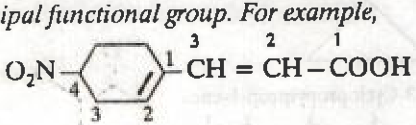


2-(Cyclopent-3-en-1-yl)propan-1-ol

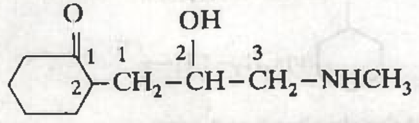


3-(4-Methylcyclohex-2-en-1-yl)propanoic acid

6. *If the ring as well as the side chain contain functional groups, the compound is named as a derivative of the side chain or the alicyclic ring according as the side chain or the ring contains the principal functional group. For example,*

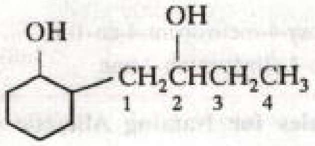


3-(4-Nitrocyclohex-1-en-1-yl)prop-2-en-1-oic acid

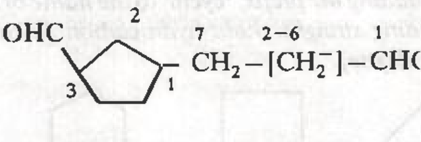


2-(3-Aminomethyl-2-hydroxypropyl) cyclohexan-1-one

If, the alicyclic ring and the side chain contain the same functional group, the compound is named as a derivative of the side chain of the ring according as the side chain or the ring contains higher number of carbon atoms. For example,

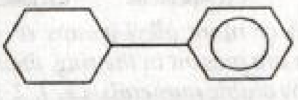


2-(2-Hydroxylbut-1-yl)cyclohexan-1-ol

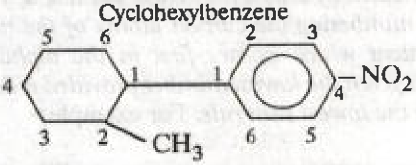


7-(3-Formylcyclopent-1-yl)heptanal

7. *If a compound contains an alicyclic ring directly linked to the benzene ring, it is named as a derivative of benzene, i.e., the compound having lowest state of hydrogenation.* For example,

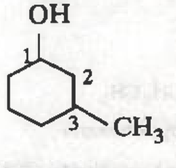


Cyclohexylbenzene

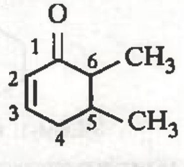


1-(2-Methylcyclohexyl)-4-nitrobenzene

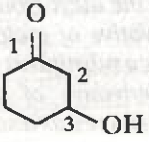
8. ***If some functional group along with other substituent groups are present in the ring, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring in such a way that the functional group gets the lowest number.*** **For example,**



3-Methylcyclohexan-1-ol



5, 6-Dimethylcyclohex-2-en-1-one



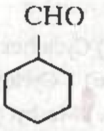
3-Hydroxycyclohexan-1-one

9. *If an alicyclic compound contains carbon containing functional groups*, the carbon atoms of the functional groups are not included in the parent name of the alicyclic system. Therefore, for such systems, the following prefixes and suffixes for the functional groups are commonly used.

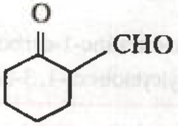
Functional group	Prefix	Suffix
—CHO	Formyl	Carbaldehyde
—COOH	Carboxy	Carboxylic acid
—COX (X = F, Cl, Br, I)	Halocarbonyl	Carbonyl halide
—COOR	Alkoxycarbonyl or Carbalkoxy	Alkyl carboxylate
—CONH$_2$	Carbamoyl	Carboxamide
—CN	Cyano	Carbonitrile

For example,

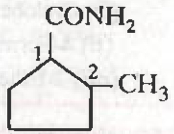
Cyclohexanecarbonitrile



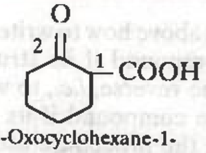
Cyclohexanecarbaldehyde



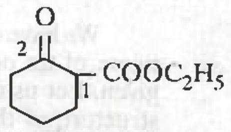
2 − Oxocyclohexane − carbaldehyde



2 − Methylcyclopentane − 1 carboxamide



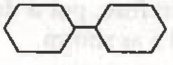
2-Oxocyclohexane-1-carboxylic acid

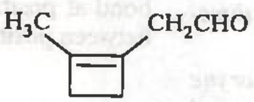


Ethyl (2-oxocyclohexane)-1-carboxylate

PROBLEMS FOR PRACTICE

1. Give the IUPAC names of the following compounds :

(*i*)


(*ii*)


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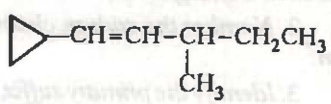

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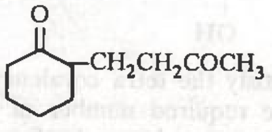

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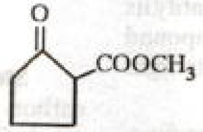

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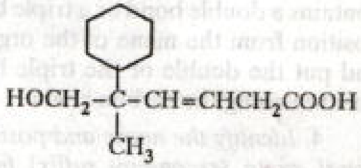

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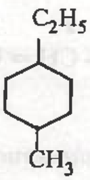

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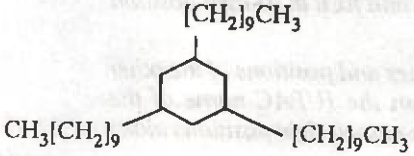

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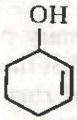

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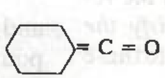

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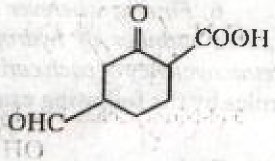

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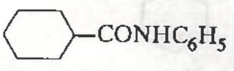

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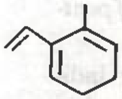

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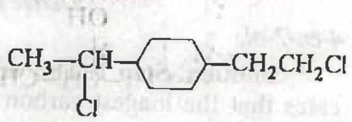


PRACTICE PROBLEMS CONTD.

(*i*) Cyclohexylcyclohexane
(*ii*) 2-(2-Methylcylobut-1-enyl)ethanal
(*iii*) 1-Cyclopropyl-3-methylpent-1-ene
(*iv*) 2-(3- Oxobutyl)cyclohexan-1-one
(*v*) Methyl (2-oxocyclopentane)-1-carboxylate
(*vi*) 5-Cyclohexyl-6 hydroxy-5-methylhex-3-en-1-oic acid
(*vii*) 1-Ethyl-4-methylcyclohexane
(*viii*) 1, 3, 5- Tris(decyl)cyclohexane
(*ix*) Cyclohex-2-en-1-ol
(*x*) Cyclohexylidenemethanone
(*xi*) 4-Formyl-2- oxocyclohexane-1-carboxylic acid
(*xii*) Cyclohexanecarboxanillide
(*xiii*) 2-Ethenyl-3-methylcyclohexa-1, 3-diene
(*xiv*) 1-(1-Chloroethyl)-4-(2-chloroethyl)cyclohexane

14.12. Writing Structural Formulae from the IUPAC Name of The Compound

We have discussed above how to write IUPAC name of an organic compound if its structure is given. Let us now do the reverse, *i.e.*, to write the structure of the organic compound if its name is given. For this purpose, the procedure used involves the following steps :

1. *Select the longest carbon chain (principal chain) from the word root of the IUPAC name of the organic compound.* For *prop* — connect three carbon atoms ; for *but* — connect four carbon atoms ; for *pent* — join five carbon atoms and so on by single bonds in a straight line.

2. *Number the carbon chain from either direction.*

3. *Identify the primary suffix, i.e. ane, ene or yne from the name of the compound.* If the compound contains a double bond or a triple bond, identify its position from the name of the organic compound and put the double or the triple bond at its right position along the carbon chain.

4. *Identify the name and position of the functional group (secondary suffix) from the IUPAC name of the compound and fix it at its right position on the carbon chain.*

5. *Identify the names and positions of the other substituents, if any, from the IUPAC name of the compound and fix them at their right positions along the carbon chain.*

6. *Finally, wherever necessary, atltach the required number of hydrogen atoms to satisfy the tetracovalency of each carbon.* Let us illustrate these rules by the following examples :

EXAMPLE 14.10. *Derive the structure of pent-4-en-2-ol.*

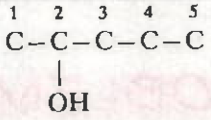
Solution. Step 1. The word root *'pent'* indicates that the longest carbon chain contains five carbon atoms.

$$C-C-C-C-C$$

Step 2. Number the carbon chain as indicated.

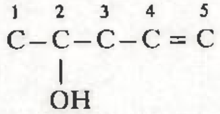
$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$

Step 3. The secondary suffix-*ol* and the numerical prefix 2 before it suggests that there is a hydroxyl group at position 2. Therefore, fix a hydroxyl group at position 2 as shown



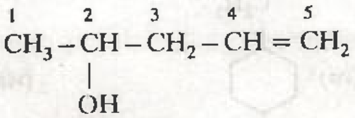
$$\overset{1}{C}-\underset{\substack{|\\ \mathrm{OH}}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$

Step 4. The primary suffix *'en'* and the numerical prefix 4 before it suggests that there is a double bond at position 4. Therefore, put a double bond between positions 4 and 5 as shown.



$$\overset{1}{C}-\underset{\substack{|\\ \mathrm{OH}}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}=\overset{5}{C}$$

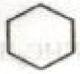
Step 5. Satisfy the tetra covalency of each carbon with the required number of hydrogen atoms. Thus, the structural formula of pent-4-en-2-ol is



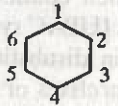
$$\overset{1}{CH_3}-\underset{\substack{|\\ \mathrm{OH}}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH}=\overset{5}{CH_2}$$

EXAMPLE 14.11. *Give the structure of the compound 3- nitrocyclohexene*

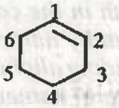
Solution. *Step 1.* The primary prefix *'cyclo'* and the word root *'hex'* means that the given compound contains a six-numbered ring. Therefore, draw a cyclohexane ring as shown :



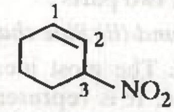
Step 2. Number the carbon atoms of the cyclohexane ring as indicated.



Step 3. The primary suffix *'en'* without any numerical prefix indicates that there is a double bond at position 1. Therefore, put a double bond between positions 1 and 2 as shown :

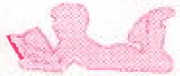


Step 4. The secondary prefix *'nitro'* and the numerical prefix 3 before it suggests that here is a nitro group at position 3. Therefore, place a nitro group at position 3.



This represents complete structure of 3-nitrocyclohexene.

PROBLEMS FOR PRACTICE



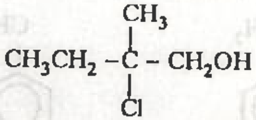
1. Draw the structures of the following compounds :
   - (*i*) 2-Chlorohexane
   - (*ii*) 6-Hydroxyheptanal
   - (*iii*) Hex-3-en-1-oic acid
   - (*iv*) 2-Chloro-2-methylbutan-1-ol
   - (*v*) 5, 5-Diethylnonan-3-ol
   - (*vi*) 1-Bromo-3-chlorocyclohex-1-ene
   - (*vii*) 1, 3-Dimethylcyclohex-1-ene
   - (*viii*) Cyclohex-2-en-1-ol.
2. Write down the structural formulae of the following: *(I.S.M. Dhanbad, 1991)*
   - (*i*) 4-Methylpent-4-en-2-one
   - (*ii*) 3-Methylbut-1-yne
   - (*iii*) 2-Ethyl-3-methylpent-1-ene.
3. Write the condensed formulae for each of the following compounds : *(I.S.M. Dhanbad 1992)*
   - (*i*) Isopropyl alcohol
   - (*ii*) Methyl *t*-butyl ether
   - (*iii*) 2-Chloro-1, 1, 1-trifluoroethane
   - (*iv*) 2-Methylbuta-1, 3-diene
   - (*v*) But-2-en-1-ol.

ANSWERS

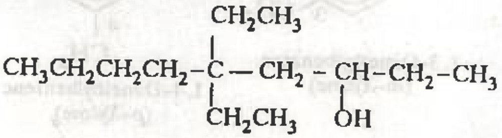
1. (*i*) $CH_3-CHCl-CH_2CH_2CH_2CH_3$

(*ii*) $CH_3-CHOH-CH_2CH_2CH_2CH_2CHO$

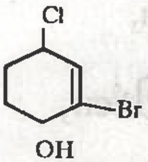
(*iii*) $CH_3CH_2CH=CHCH_2COOH$

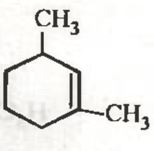
(*iv*)


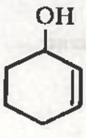
$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_2OH$$

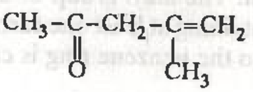
(*v*)


$$CH_3CH_2CH_2CH_2-\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{C}}-CH_2-\underset{\displaystyle OH}{CH}-CH_2-CH_3$$

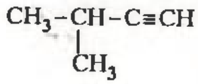
(*vi*)


(*vii*)


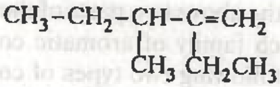
(*viii*)


2. (*i*)


$$CH_3-\underset{\displaystyle O}{\overset{\|}{C}}-CH_2-\underset{\displaystyle CH_3}{C}=CH_2$$

(*ii*)


$$CH_3-\underset{\displaystyle CH_3}{CH}-C\equiv CH$$

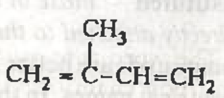
(*iii*)


$$CH_3-CH_2-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_2CH_3}{C}=CH_2$$

3. (*i*) $(CH_3)_2CHOH$

(*ii*) $CH_3-O-C(CH_3)_3$

(*iii*) F_3C-CH_2Cl

(*iv*)


$$CH_2=\overset{\displaystyle CH_3}{C}-CH=CH_2$$

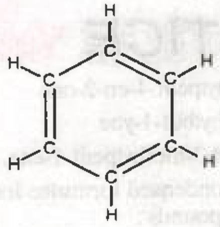
(*v*) $CH_3CH=CHCH_2OH$

14.13. Nomenclature of Simple Aromatic Compounds

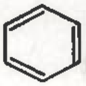
Aromatic compounds contain one or more isolated or fused benzene rings. An aromatic compound consists of two parts :

(i) Nucleus and (ii) Side chain

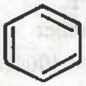
(i) Nucleus. The most ideal aromatic compound is benzene. It is represented by a regular hexagon of six carbon atoms with three alternate single and double bonds. This is called the nucleus. The ring may be represented by any of the following three ways :



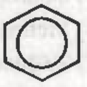
I



or



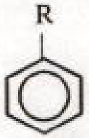
II



III

A circle inside the cyclohexane ring represents six completely delocalised π-electrons or three conjugated double bonds.

(ii) **Side chain.** The alkyl group or any other aliphatic group containing at least one carbon atom which is attached to the benzene ring is called the side chain.



In view of the above two parts of the aromatic compounds, each family of aromatic compounds consists of the following two types of compounds with quite different chemical properties.

(i) Nuclear substituted

(ii) side chain substituted

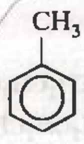
(i) Nuclear substituted – *those in which the functional group is directly attached to the benzene ring.* Most of these compounds are better known by their common and historical names. In the IUPAC system, *they are named as derivatives of benzene.* However, many of their common names have also been adopted by the IUPAC system. The positions of the substituents in disubstituted benzenes are indicated either by prefixes or by arabic numerals such as *o* (ortho) for 1, 2 ; *m* (meta) for 1, 3 and *p* (para) for 1, 4.

(ii) Side chain substituted – *those in which the functional group is present in the side chain of the benzene ring. Both in the common and IUPAC systems, these are usually named as phenyl derivatives of the corresponding aliphatic compounds (except arenes which are named as derivatives of benzene in the IUPAC system).* The positions of the substituents on the side chain including the benzene ring are indicated by Greek letters *i.e.*, α, β, γ .... in the common system, and by arabic numerals, *i.e.* 1, 2, 3 ... etc. in the IUPAC system. However, many of these compounds are better known by their common names.

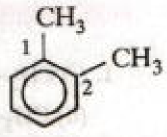
The IUPAC and common names (given in brackets) of a few important members of each family are given below. Wherever only one name is given, it implies that the common name has also been adopted by the IPUAC system.

1. **Aromatic hydrocarbons (Arenes).** *Hydrocarbons which contain both aliphatic and aromatic units are called* **arenes.**

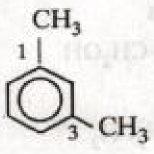
Benzene



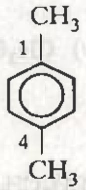
Methylbenzene
(Toluene)



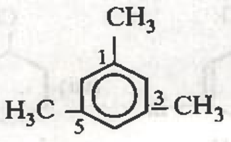
1, 2–Dimethylbenzene
(o–Xylene)



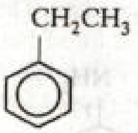
1, 3–Dimethylbenzene
(m–Xylene)



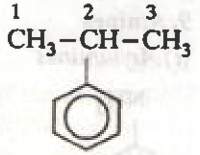
1, 4–Dimethylbenzene
(p–Xylene)



1, 3, 5–Trimethylbenzene
(Mesitylene)



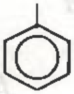
Ethylbenzene



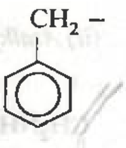
2–Propylbenzene
(*Isopropylbenzene or Cumene*)

2. Aryl groups

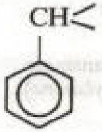
C_6H_5- or



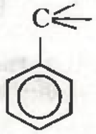
Phenyl



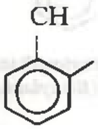
Benzyl



Benzal

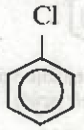


Benzo

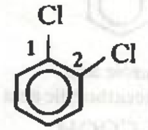


o–Tolyl

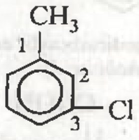
3. Halogen derivatives



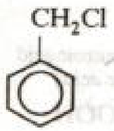
Chlorobenzene



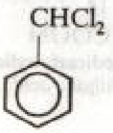
1, 2–Dichlorobenzene or *o*–Dichlorobenzene



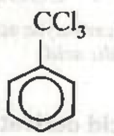
3–Chlorotoluene or
m–Chlorotoluene



Phenylchloromethane
(*Benzyl chloride*)



Phenyldichloromethane
(*Benzal dichloride*)

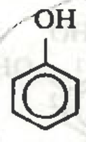


Phenyltrichloromethane
(*Benzotrichloride*)

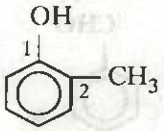
4. Hydroxy derivatives. The nuclear hydroxy derivatives are called *phenols* while the side chain substituted hydroxy derivatives are called *aromatic alcohols.*

(*i*) ***Phenols***

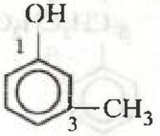
2



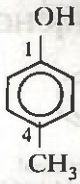
Phenol



2–Methylphenol
(*o–Cresol*)

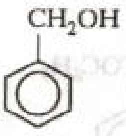


3–Methylphenol
(*m–Cresol*)

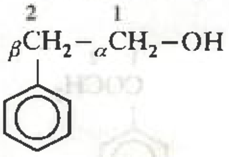


4–Methylphenol
(*p*–*Cresol*)

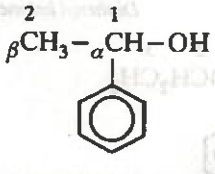
(*ii*) *Aromatic alcohols*



Phenylmethanol
(*Benzyl alcohol*)

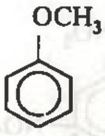


2–Phenylethan – 1 – ol
(β–Phenylethyl alcohol)

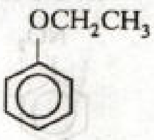


1–Phenylethan – 1 – ol
(*α–Phenylethyl alcohol*)

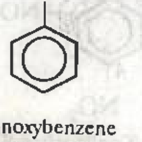
5. Aromatic ethers



Methoxybenzene
(*Anisole or Methyl phenyl ether*)

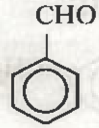


Ethoxybenzene
(*Phenetole or Ethyl phenyl ether*)

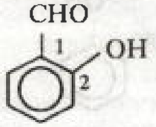


Phenoxybenzene
(*Diphenyl ether*)

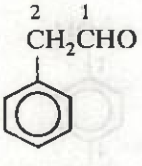
6. Aldehydes



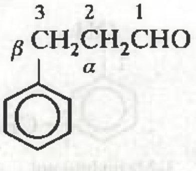
Benzaldehyde



2-Hydroxybenzaldehyde
(*Salicylaldehyde*)

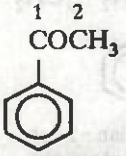


2-Phenylethanal
(*Phenylacetaldehyde*)

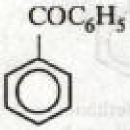


3-Phenylpropanal
(*β-Phenylpropionaldehyde*)

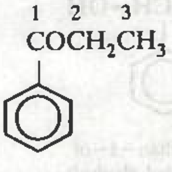
7. Ketones



1-Phenylethan-1-one
(*Acetophenone or Methyl phenyl ketone*)

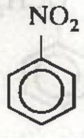


Diphenylmethanone
(*Benzophenone or Diphenyl ketone*)

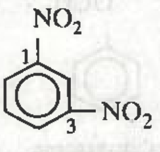


1-Phenylpropan-1-one
(*Propiophenone*)

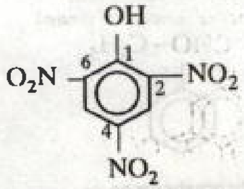
8. Nitro compounds



Nitrobenzene



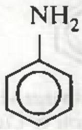
1, 3-Dinitrobenzene or *m*-Dinitrobenzene



2,4,6-Trinitrophenol
(*Picric acid*)

9. Amines

(*i*) *Arylamines*

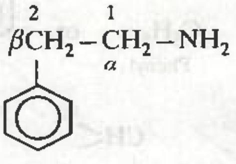


Benzenamine
(*Aniline*)

4-Methylbenzenamine
(*p-Toluidine*)

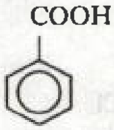
(*ii*) *Aralkylamines*

Phenylmethanamine
(*Benzylamine*)

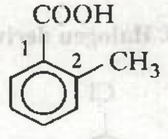


2-Phenylethanamine
(*β-Phenylethylamine*)

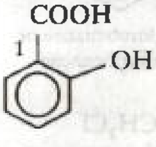
10. Carboxylic acids



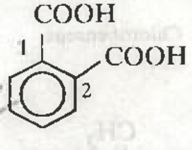
Benzoic acid
or Benzenecarboxylic acid



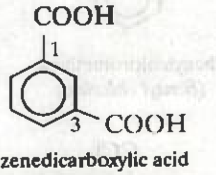
2-Methylbenzoic acid
(*o-Toluic acid*)



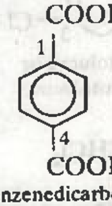
2-Hydroxybenzoic acid
(*Salicylic acid*)



1, 2-Benzenedicarboxylic acid
(*Phthalic acid*)



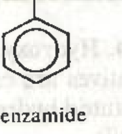
1, 3-Benzenedicarboxylic acid
(*Isophthalic acid*)



1, 4-Benzenedicarboxylic acid
(*Terephthalic acid*)

11. Acid derivatives

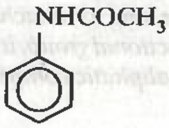
Benzoyl chloride



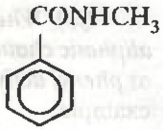
Benzamide

Methyl benzoate

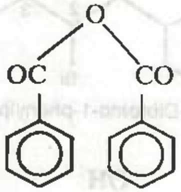
Phenyl ethanoate
(Phenyl acetate)



N−Phenylethanamide
(N−Phenylacetamide or Acetanilide)

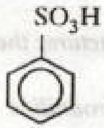


N−Methylbenzamide

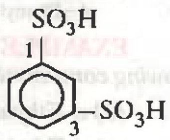


Benzoic anhydride

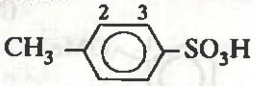
12. Sulphonic acids



Benzenesulphonic acid

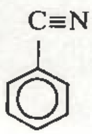


1,3−Benzenedisulphonic acid

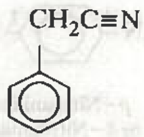


4−Toluenesulphonic acid
(p−Toluenesulphonic acid)

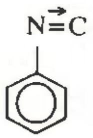
13. Cyanides and isocyanides



Benzenenitrile
(Benzonitrile or Phenyl cyanide)

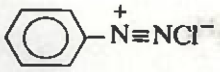


Phenylethanenitrile
(Benzyl cyanide or Phenyl acetonitrile)

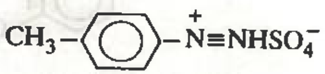


Phenylisocyanide or Phenylcarbylamine

14. Arenediazonium salts



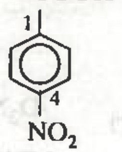
Benzenediazonium chloride



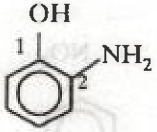
4−Toluenediazonium hydrogen sulphate
or *(p−Toluenediazonium hydrogen sulphate)*

14.14. Systematic Nomenclature for Di- and Polyfunctional Aromatic Compounds

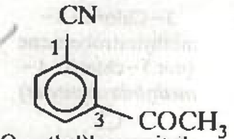
(i) When an aromatic compound contains two or more functional groups, it is named as a derivative of the compound with the principal functional group at position 1. For example,



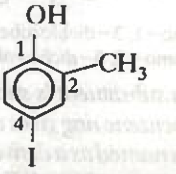
4−Nitrobenzoic acid
(COOH is the principal functional group while NO_2 is the substituent group)



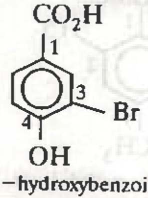
2−Aminophenol
(OH is the principal functional group while NH_2 is the substituent group)



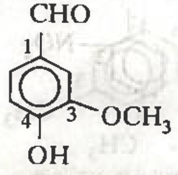
3−(1−Oxoethyl)benzonitrile
or 3−Acetylbenzonitrile
(CN is the principal functional group while $COCH_3$ is the substituent group)



4−Iodo−2−methylphenol
(OH is the principal functional group)



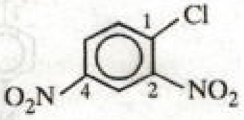
3−Bromo−4−hydroxybenzoic acid
(−COOH is the principal functional group)



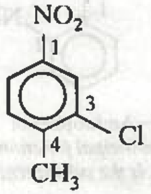
4−Hydroxy−3−methoxybenzaldehyde
(−CHO is the principal functional group)

(ii) If all the functional groups present in the benzene ring are such which are normally treated as substituent groups, the various groups are arranged in alphabetical order with the group named first in the alphabetical order getting the lowest locant provided it does not violate the lowest locant rule for all the substituents. For example,

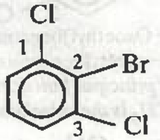
1-Bromo-
3-Chlorobenzene
(*not 1-chloro-3-bromobenzene*)



1-Chloro-2, 4-dinitrobenzene
(and not 4-chloro-1,
3-dinitrobenzene

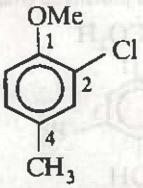


3-Chloro-4-
methylnitrobenzene
(*not* 5-chloro-4-
methylnitrobenzene)

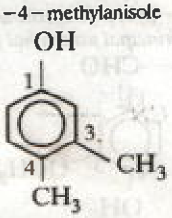


2-Bromo-1, 3-dichlorobenzene
(*not 1-bromo-2, 6-dichlorobenzene*)

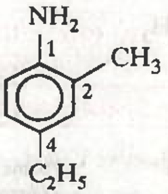
(iii) When a substituent is such which when taken together with the benzene ring gives a special name to the molecule, then it is named as a derivative of that molecule with the substituent at position 1. For example,



2-Chloro-4-methylanisole

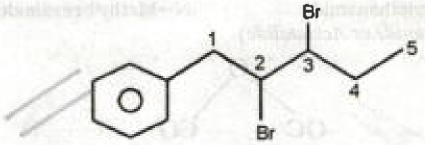


3, 4-Dimethylphenol

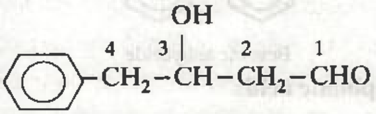


4-Ethyl-2-methylaniline

(iv) When a benzene ring is attached to an aliphatic chain having a functional group, it is named as phenyl derivative of that aliphatic compound. For example,



2, 3-Dibromo-1-phenylpentane



4-Phenyl-3-hydroxybutanal

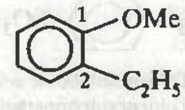
EXAMPLE 14.12. *Write the structures the following compounds :*

(a) o-Ethylanisole *(b) p-Nitroaniline*

(c) 4-Ethyl-1-fluoro-2-nitrobenzene.

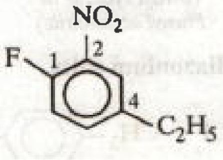
(N.C.E.R.T.)

Solution.



o-Ethylanisole
or 2-Ethylanisole

p-Nitroaniline
or 4-Nitroaniline



4-Ethyl-1-fluoro-1-
2-nitrobenzene

PART III

BASIC PRINCIPLES OF ORGANIC CHEMISTRY

14.15. Electronic Displacement Covalent Bond

14.15.1. Inductive Effect.

Whenever an electron-withdrawing atom such as *halogen i.e.* –X (or a group such as *nitro*) is attached to the end of a carbon chain, the σ-electrons of the C–X bond are attracted by or displaced towards the more electronegative halogen atom. As a result, the atom X acquires a small negative charge (*i.e.* δ^-) and C_1 acquires a small positive charge (*i.e.* δ^+) as shown below.

$$\overset{}{C_4} \longrightarrow \overset{\delta\delta\delta^+}{C_3} \longrightarrow \overset{\delta\delta^+}{C_2} \longrightarrow \overset{\delta^+}{C_1} \longrightarrow \overset{\delta^-}{X}$$

The small positive charge on C_1, in turn, attracts the σ-electrons of the $C_1 - C_2$ bond towards it. As a result, C_2 acquires a small positive charge (*i.e.*, $\delta\delta^+$), of course, smaller than that on C_1. Similarly, C_3 will acquire a small positive charge (*i.e.* $\delta\delta\delta^+$) that will still be smaller than that on C_2. *This type of displacement of σ-electrons along a saturated carbon chain whenever an electron withdrawing (or electron donating) group is present at the end of the chain is called the* **inductive effect or the I- Effect.** *This effect weakens steadily with increasing distance from the substituent (electron-withdrawing or electron-donating group) and actually dies down after three carbon atoms.* There are two types of inductive effects, *i.e.* **–I-effect** and **+ I-effect.**

(*i*) *If the substituent attached to the end of the carbon chain is* **electron-withdrawing**, the *effect is called* – **I-effect**. For example,

$$\overset{\delta\delta\delta^+}{C} \longrightarrow \overset{\delta\delta^+}{C} \longrightarrow \overset{\delta^+}{C} \longrightarrow \overset{\delta^-}{X} \quad (\textbf{–I-Effect})$$

The –I-effect of some of the atoms and groups in the decreasing order is :

$$-NO_2 > -CN > -COOH > -F$$
$$> -Cl > -Br\ -I$$

(*ii*) *If the substituent attached to the end of the carbon chain is* **electron-donating**, *the effect is called* **+ I-effect.** For example,

$$\overset{\delta\delta\delta^-}{C} \longleftarrow \overset{\delta\delta^-}{C} \longleftarrow \overset{\delta^-}{C} \longleftarrow CH_3 \ (\textbf{+ I-effect})$$

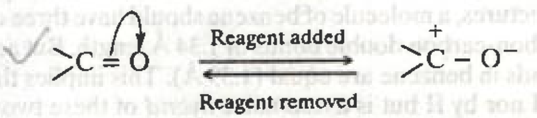
The + I-effect of some of the atoms or groups in the decreasing order is :

$$\underset{t\text{–Butyl}}{(CH_3)_3C-} > \underset{\text{Isopropyl}}{(CH_3)_2CH-} >$$
$$\underset{\text{Ethyl}}{CH_3CH_2-} > \underset{\text{Methyl}}{CH_3-} > D > H$$

Inductive effect is a *permanent effect* operating in the ground state of the organic molecules and hence is responsible for high melting point, boiling point and dipole moment of polar compounds.

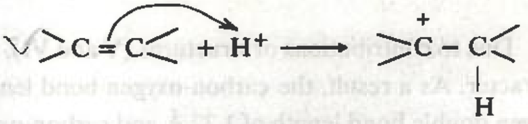
14.15.2. Electromeric Effect.

It involves the complete transfer of electrons of a multiple bond (double or triple bond) to one of the bonded atoms (usually more electronegative) in presence of an attacking reagent. It is called **E-effect.**



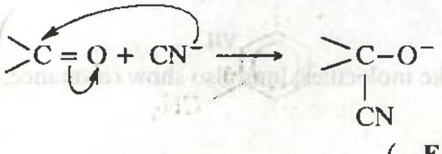
This *effect is temporary* and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position. Electromeric effect is of two types, *i.e.*, **+ E-effect** and **– E-effect.**

If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, the effect is called **+ E-effect.** *For example, addition of acids to alkenes.*



(+ E-effect)

If on the other hand, the electrons of the double bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, the effect is called **– E-effect.** For example, the addition of cyanide ion to the carbonyl group.

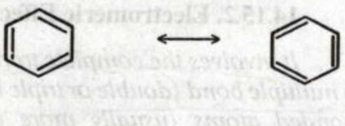


(– E-effect)

14.15.3. Resonance or Mesomerism

Sometimes it is not possible to assign a single electronic (*Lewis*) structure to a molecule which can satisfactorily explain all its properties. In such a case, it has been found that the molecule can be represented by two or more electronic structures each one of which can explain most of the properties but none of them can explain all the properties of the molecule. The real structure of the molecule lies somewhere in between all these electronic structures which, however, cannot be represented on paper. Such a molecule is said to exhibit *resonance or mesomerism.* Thus, the phenomenon of resonance is said to occur *whenever for a molecule we can write two or more Lewis structures which differ in the position of electrons but not in the relative position of atoms. The various Lewis structures are called* **canonical or resonance structures.** *The actual structure of the molecule is not represented by any of the resonance structures but is a* **resonance hybrid** *of all these Lewis structures. The various resonance structures are separated by a double headed arrow (⟷).*

Thus, in the light of resonance theory, benzene can be represented as a resonance hybrid of the following two **Kekule (Lewis) structures, I and II.**



I II

III

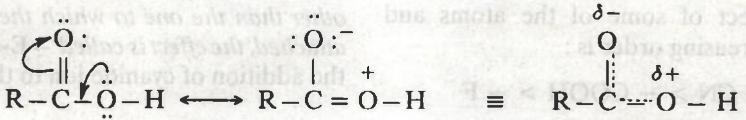
Any of these two Kekule structures, cannot explain all the properties of benzene. According to these structures, a molecule of benzene should have three carbon-carbon single bonds of 1.54 Å length and three carbon-carbon double bonds of 1.34 Å length. But actually it has been found that all the six carbon-carbon bonds in benzene are equal (1.39 Å). This implies that actual structure of benzene is neither represented by I nor by II but is a *resonance hybrid* of these two structures. In other words, any two adjacent carbon atoms in benzene are neither joined by a pure single bond nor by a pure double bond. As a result, all the carbon-carbon bond lengths are equal, *i.e.*, 1.39 Å and lie in between carbon-carbon double bond length of 1.34 Å and carbon- carbon single bond length of 1.54 Å. The resonance hybrid or the actual molecule of benzene is usually represented by the formula III. The circle inside the ring denotes completely delocalized six π-electrons.

Similarly, carbon dioxide can be written as a resonance hybrid of the following three structures (IV, V and VI) :

$$:\underset{\cdot\cdot}{\ddot{O}}=C=\ddot{O}: \longleftrightarrow {}^{-}:\underset{\cdot\cdot}{\ddot{O}}-C\equiv\overset{+}{O}: \longleftrightarrow :\overset{+}{O}\equiv C-\underset{\cdot\cdot}{\ddot{O}}:^{-}$$

Due to contributions of structures (V and VI), the carbon-oxygen bond in CO_2 has some triple bond character. As a result, the carbon-oxygen bond length (1.15 Å) in CO_2 lies in between normal carbon-oxygen double bond length of 1.22 Å and carbon-oxygen triple bond length of 1.10 Å.

Like benzene and CO_2, carboxylic acids may be regarded as a resonance hybrid of the following two structures (VII and VIII) :



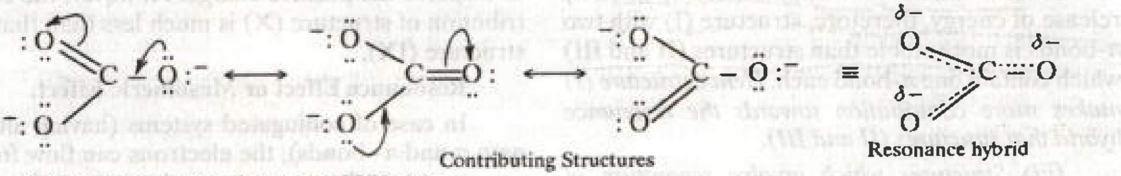
$$R-\overset{\overset{\ddot{O}:}{\|}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H \longleftrightarrow R-\overset{\overset{:\ddot{O}:^{-}}{|}}{C}=\underset{\cdot\cdot}{\overset{+}{O}}-H \equiv R-\overset{\overset{\delta-}{O}}{\vdots}\!\!\!\overset{\delta+}{C}\cdots O-H$$

Resonance hybrid

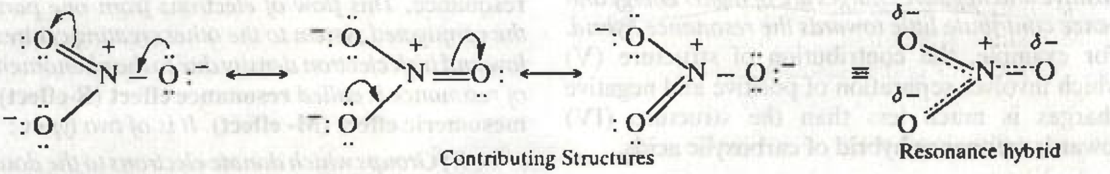
VII VIII

Like molecules, ions also show resonance. For example, CO_3^{2-}, NO_3^{-} etc.

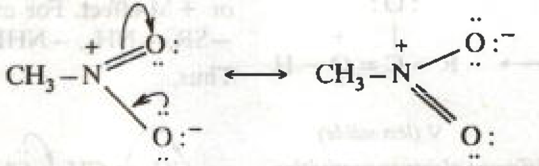
(*i*) Resonance structures of CO_3^{2-} ion :



(*ii*) Resonance structures of NO_3^- ion.



(*iii*) Resonance structurs of nitromethane



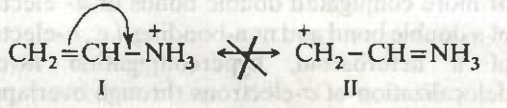
Resonance energy. A resonance hybrid (or the actual molecule) is always more stable than any of its canonical structures (hypothetical or imaginary structures). This stability is due to delocalization of electrons and is measured in terms of **resonance energy** or **delocalization energy.** *It is defined as the difference in internal energy of the resonance hybrid and the most stable canonical structure. Further, more the number of equivalent resonance structures, greater is the delocalization of electrons, higher is the resonance energy and hence more stable is the compound.* In case of benzene, this resonance energy has been determined to be 150·62 kJ (or 36 kcal) mol^{-1}.

Conditions for resonance. Some important conditions for resonance are listed below :

(*i*) *The various resonance structures should differ only in the position of electrons and not in the position of atoms or nuclei.*

(*ii*) *All the resonance structures should have the same number of unpaired electrons.*

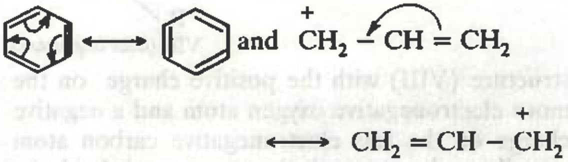
(*iii*) *In case of atoms of the second period in the periodic table, such resonance structures which violate* **octet rule** *should not be considered.* For example,



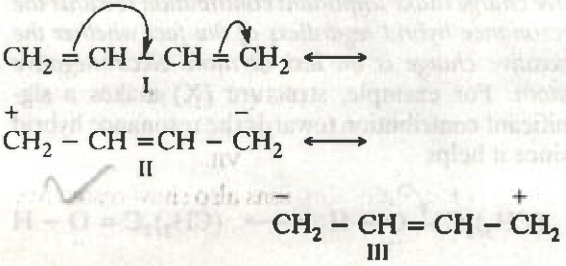
structure (II) cannot be considered as a resonance structure since it violates the octet rule because nitrogen has 10 electrons. In other words, nitrogen cannot have more than 8 electrons because it does not have *d*-orbitals.

Relative contributions of Resonance structures.

(*i*) *Structures which are indistinguishable are of equal energy and hence contribute equally towards the resonance hybrid.* For example,

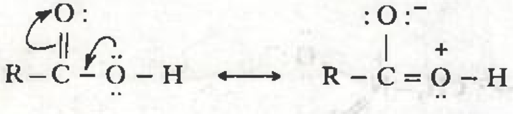


(*ii*) *Structures with greater number of covalent bonds contribute more towards the resonance hybrid.* For example, 1, 3-butadiene is a resonance hybrid of structures (I, II and III)



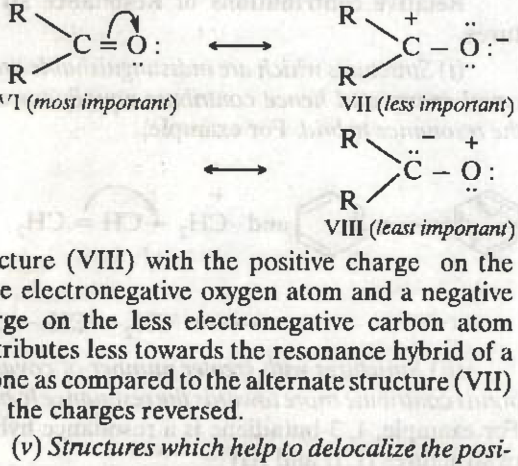
Since formation of a bond is accompanied by release of energy, therefore, structure (I) with two π-bonds is more stable than structures (II and III) which contain one π-bond each. *Hence structure (I) makes more contribution towards the resonance hybrid that structures (II and III).*

(*iii*) *Structures which involve separation of positive and negative charges are of higher energy and hence contribute little towards the resonance hybrid.* For example, the contribution of structure (V) which involves separation of positive and negative charges is much less than the structure (IV) towards resonance hybrid of carboxylic acids.



IV (*more stable*) V (*less stable*)

(*iv*) *When atoms of different electronegativities are involved, the structure with a negative charge on the more electronegative atom and positive charge on the less electronegative atom is of lower energy and hence contributes more towards the resonance hybrid than the alternate structure in which the charges are reversed.* For example,



VI (*most important*) VII (*less important*) VIII (*least important*)

structure (VIII) with the positive charge on the more electronegative oxygen atom and a negative charge on the less electronegative carbon atom contributes less towards the resonance hybrid of a ketone as compared to the alternate structure (VII) with the charges reversed.

(*v*) *Structures which help to delocalize the positive charge make important contribution towards the resonance hybrid regardless of the fact whether the positive charge is on less or more electronegative atom.* For example, structure (X) makes a significant contribution towards the resonance hybrid since it helps to disperse the positive charge. However, the contribution of structure (X) is much less than that of structure (IX).

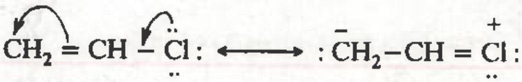
$$(CH_3)_2\overset{+}{C}-\ddot{O}-H \longleftrightarrow (CH_3)_2C=\overset{+}{O}-H$$

IX X

Resonance Effect or Mesomeric Effect.

In case of conjugated systems (having alternate σ-and π- bonds), the electrons can flow from one part of the system to the other due to resonance. *This flow of electrons from one part of the conjugated system to the other creating centres of low and high electron density due to the phenomenon of resonance is called* **resonance effect (R-effect)** or **mesomeric effect (M- effect)**. *It is of two types :*

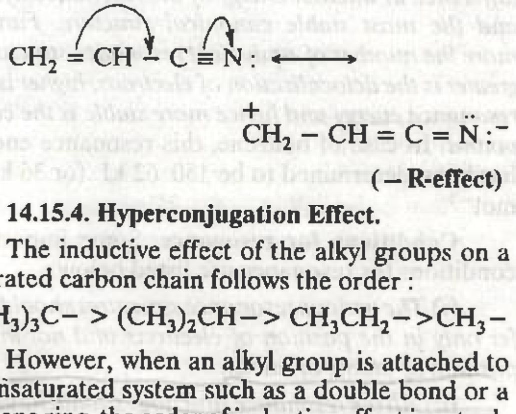
(*i*) *Groups which donate electrons to the double bond or to a conjugated system are said to have* **+R** or **+M-effect**. For example, $-OH$, $-OR$ $-SH$, $-SR$, $-NH_2$, $-NHR$, $-NR_2$, $-Cl$, $-Br$, $-I$ etc. Thus,



$$CH_2=CH-\ddot{Cl}: \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{+}{Cl}:$$

(+ R-effect)

(*ii*) *Groups which withdraw electrons from the double bond or from a conjugated system towards themselves due to resonance are said to have* **– R or – M-effect. For example, > C = O, – CHO, – COOR, – CN, – NO$_2$ etc. Thus,**



$$CH_2=CH-C\equiv N: \longleftrightarrow \overset{+}{C}H_2-CH=C=N:^-$$

(– R-effect)

14.15.4. Hyperconjugation Effect.

The inductive effect of the alkyl groups on a saturated carbon chain follows the order :

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3-$$

However, when an alkyl group is attached to an unsaturated system such as a double bond or a benzene ring, the order of inductive effect is actually reversed. This effect is called **hyperconjugation effect or Baker-Nathan effect.**

In fact, hyperconjugation effect is an extension of the resonance effect. Whereas resonance effect involves delocalization of π-electrons of two or more conjugated double bonds or π- electrons of a double bond and non-bonding, *i.e.*, *n*-electrons of a heteroatom, hyperconjugation involves delocalization of σ-electrons through overlapping of *p*-orbitals of a double bond with σ-orbital of the

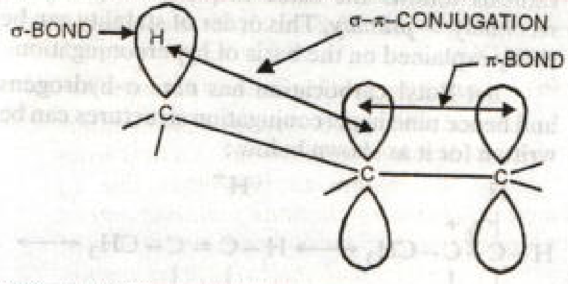
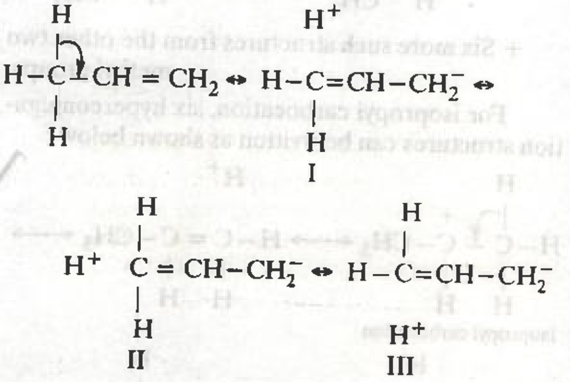


FIGURE 14.6. Orbital representation of hyperconjugation, *i.e.*, σ− π-Conjugation

adjacent single bond (*i.e.* $\sigma - \pi$, conjugation) as shown in Fig. 14.6 :

In terms of structures, hyperconjugation may be represented as follows :



$$H-\overset{H}{\underset{H}{C}}-CH=CH_2 \leftrightarrow \underset{\text{I}}{H-\overset{H^+}{\underset{H}{C}}=CH-CH_2^-} \leftrightarrow$$

$$\underset{\text{II}}{H^+\ \overset{H}{\underset{H}{C}}=CH-CH_2^-} \leftrightarrow \underset{\text{III}}{H-\overset{H}{\underset{H^+}{C}}=CH-CH_2^-}$$

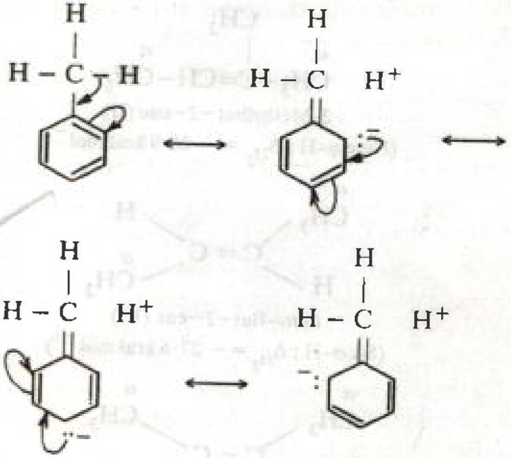
Structures I, II and III are called **hyperconjugative structures**. Since there is no bond between carbon and hydrogen atoms in these structures, hyperconjugation is also called **no bond resonance**. It may be noted that *although a free proton has been shown in the above structures, it is still bound quite firmly to the π- cloud and hence is not free to move.*

It is evident from the above structures that hyperconjugation occurs through the H-atoms present on the carbon atom next to the double bond, *i.e., α-hydrogen atoms*. Naturally more the number of such α-hydrogen atoms, more are the number of hyperconjugative structures and hence greater is the inductive effect. Clearly the number of hydrogen atoms is *three* (maximum) with methyl group, *two* with the ethyl group, *one* with the isopropyl group and *none* with the *tert*-butyl group. Thus the order of hyperconjugation effect decreases in the order :

$$CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$$

Significance of the hyperconjugation effect. Although hyperconjugation effect is a much weaker effect than resonance effect yet it is quite useful in explaining some of the physical and chemical properties of organic molecules. Some of these are :

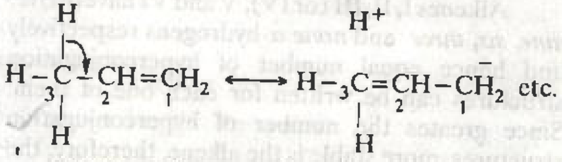
(i) Directive influence of alkyl groups. The *o*, *p*-directive influence of CH_3 and other alkyl groups can be easily explained on the basis of hyperconjugation.



(+ *Six more such structures due to two other α-hydrogen atoms*)

As a result of hyperconjugation, the electron density at *o-* and *p*-positions *w.r.t.* the CH_3 group increases and hence the electrophilic substitution (discussed in unit 16) reactions in toluene (and other alkylbenzenes) will occur at *o*-and *p*-positions *w.r.t.* the CH_3 (or the alkyl group). Thus, *alkyl groups are o, p-directing.*

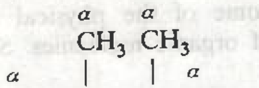
(*ii*) **Shortening of carbon-carbon single bonds adjacent to multiple bonds.**



$$H-\underset{H}{\overset{H}{\underset{3}{C}}}-\underset{2}{C}H=\underset{1}{C}H_2 \longleftrightarrow H-\overset{H^+}{\underset{H}{{}_3C}}=\underset{2}{C}H-\underset{1}{\overline{C}}H_2 \text{ etc.}$$

Because of hyperconjugation, $C_2 - C_3$ single bond in propene acquires some double bond character and hence is little shorter (1·49 Å) than the normal carbon-carbon bond length (1·54Å) in propane.

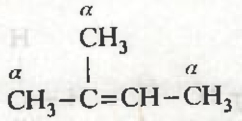
(iii) Relative stability of alkenes. Heats of hydrogenation (Δ_{H_2}) show that greater the number of alkyl groups attached to the doubly bonded carbon atoms, greater is the stability (*i.e.* lower is the heat of hydrogenation) of the alkene. Consider, for example the following alkenes :



$$\overset{\alpha}{C}H_3-\underset{\overset{|}{\underset{\alpha}{C}H_3}}{C}=\underset{\overset{|}{\underset{\alpha}{C}H_3}}{C}-\overset{\alpha}{C}H_3$$

2, 3-Dimethylbut-2-ene (I)

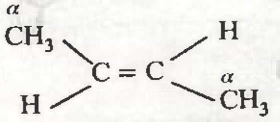
(Twelve α-H ; Δ_{H_2} = − 26·6 kcal mol^{-1})



$$\overset{\alpha}{C}H_3-\underset{\overset{|}{\underset{\alpha}{C}H_3}}{C}=CH-\overset{\alpha}{C}H_3$$

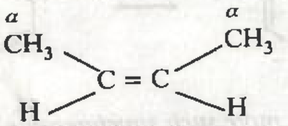
2-Methylbut-2-ene (II)

(Nine α-H ; Δ_{H_2} = − 26·9 kcal mol^{-1})



trans-But-2-ene (III)

(Six α-H ; Δ_{H_2} = − 27·6 kcal mol^{-1})



cis-But-2-ene (IV)

(Six σ-H ; Δ_{H_2} = − 28·6 kcal mol^{-1})

$$\overset{\alpha}{C}H_3-CH=CH_2$$

Propene (V)

(Three α-H ; Δ_{H_2} = − 30·1 kcal mol^{-1})

$$CH_2=CH_2$$

Ethene (VI)

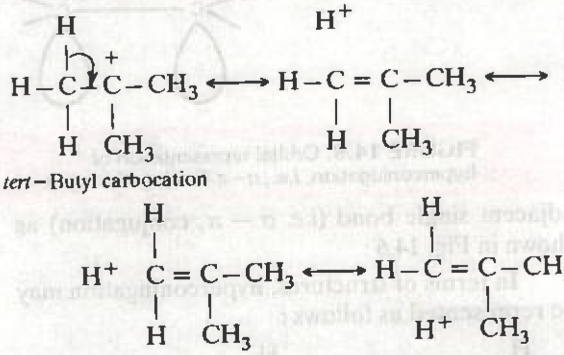
(No α-H ; Δ_{H_2} = − 32·8 kcal mol^{-1})

Alkenes I, II, III (or IV), V and VI have *twelve, nine, six, three* and *none* α-hydrogens respectively and hence equal number of hyperconjugation structures can be written for each one of them. Since greates the number of hyperconjugation structures, more stable is the alkene, therefore, the relative stability of these alkenes follows the sequence : I > II > III > IV > V > VI.

trans-But-2-ene (III) is, however, more stable than *cis*-but-2-ene (IV) in which the two methyl groups are close together and hence their electronic clouds repel each other.

(*iv*) **Stability of carbocations and free radicals.** The relative stability of carbocations and free radicals follows the same sequence : *tertiary* > *secondary* > *primary*. This order of stability can be easily explained on the basis of hyperconjugation.

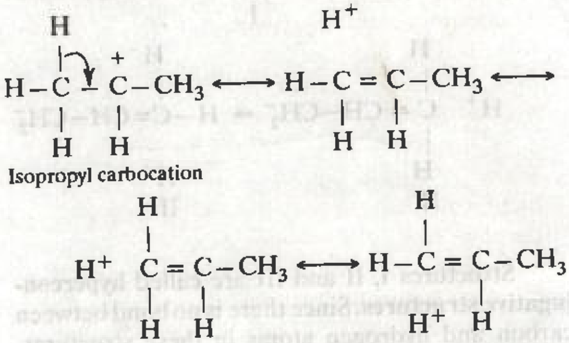
tert-Butyl carbocation has *nine* α-hydrogens and hence nine hyperconjugation structures can be written for it as shown below :



tert-Butyl carbocation

+ Six more such structures from the other two methyl groups.

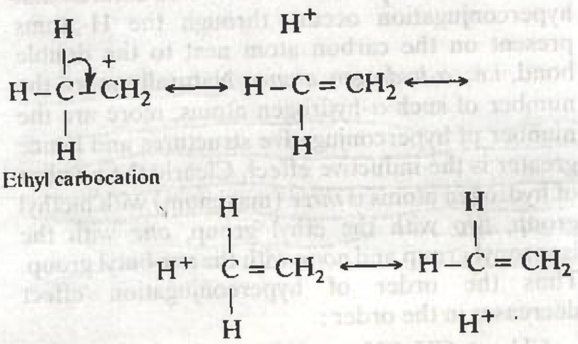
For isopropyl carbocation, six hyperconjugation structures can be written as shown below :



Isopropyl carbocation

+ three more such structures from the other methyl group

In a similar way three hyperconjugation structures can be written for ethyl arbocation as shown below :



Ethyl carbocation

However, for CH_3^+ carbocation, no hyperconjugation structure can be written. Thus, the order of stability of carbocations is

$$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+$$

Similarly, we can explain the stability of free radicals, *i.e.*,

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3.$$

14.16. Fission of a Covalent Bond

(a) Homolytic (symmetrical) fission. *If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair, it is called* **homolytic or symmetrical fission.** Homolytic fission is usually indicated by a fish arrow which denotes a one-electron displacement. For example,

$$A : B \xrightarrow{\text{Homolytic fission}} \underset{\text{Free radicals}}{\dot{A} + \dot{B}}$$

The neutral chemical species (such as A· and B·) which contain an odd or unpaired electron and which are produced by homolytic fission of covalent bonds are called **free radicals.** *Homolytic fission usually occurs in non-polar bonds and is favoured by high temperature, ultraviolet (UV) radiations and by the presence of radical initiators such as peroxides.*

(b) Heterolytic (unsymmetrical) fission. *When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond (i.e., shared pair) are taken away by one of the bonded atoms, the mode of bond cleavage is called* **heterolytic fission.** Heterolytic fission is usually indicated by a curved arrow which denotes a two-electron displacement. For example,

$$A : B \xrightarrow{\text{Heterolytic fission}} A^+ + :B^-$$

(When B is more electronegative than A)

$$A : B \xrightarrow{\text{Heterolytic fission}} A:^- + B^+$$

(When A is more electronegative than B)

As shown above, heterolytic fission results in the formation of charged species, *i.e.* cations and anions. It usually occurs in *polar covalent bonds and is favoured by polar solvents.*

14.17. Electrophiles and Nucleophiles

(a) Electrophiles *are electron loving chemical species. Their attraction for electrons is due to the presence of an electron- deficient atom in them. Electrophiles may be either positively charged or electrically neutral chemical species, i.e.,*

(*i*) *Positive electrophiles* :

H^+, H_3O^+, Cl^+, Br^+, I^+, $\overset{+}{N}O_2$, $\overset{+}{N}O$, R^+ (carbocation) etc.

(*ii*) *Neutral electrophiles* : $R\cdot$ (free radicals), $:CR_2$ (carbenes), $:\ddot{N}R$ (nitrenes), BF_3, $AlCl_3$, $FeCl_3$, $SnCl_4$ etc.

Since both positively charged and neutral electrophiles are short by a pair of electrons (free radicals are, however, short by one electron), they have a strong tendency to attract electrons from other sources and hence behave as **Lewis acids.** *Electrophiles always attack the substrate molecule at the site of highest electron-density.*

(b) Nucleophiles *are nucleus loving chemical species.* Since the nucleus of any atom is positively charged, therefore, nucleophiles must be electron rich chemical species containing at least one lone pair of electrons. They may be either negatively charged or neutral chemical species, *e.g.*,

(*i*) *Negative nucleophiles* : H^- (hydride ion), Cl^-, Br^-, I^-, R^- (carbanion), OH^-, OR^-, SR^-, NH_2^-, CN^-, $RCOO^-$ etc.

(*ii*) *Neutral nucleophiles* :

$H_2\ddot{O}$: $\ddot{N}H_3$, $R\ddot{N}H_2$, $R\ddot{O}H$, $R\ddot{S}H$, $R\ddot{O}R$ etc.

Since both negatively charged and neutral nucleophiles contain at least one unshared pair of electrons, they have a strong tendency to donate this pair of electrons to electron deficient species and hence behave as **Lewis bases.** *Nucleophiles always attack the substrate molecule at the site of lowest electron density.*

14.18. Reactive Intermediates

Most of the organic reactions occur through the involvement of certain chemical species. These are generally *short-lived* (10^{-6} seconds to a few seconds) *and highly reactive and hence cannot be isolated. These short-lived highly reactive chemical species through which the majority of the organic reactions occur are called* **reactive intermediates.** Some important examples of reactive intermenes are : *carbocations, carbanions, free-radicals, carbenes and nitrenes.*

(a) Carbocations (*earlier called as carbonium ions*). *Chemical species bearing a positive charge on carbon and carrying six electrons in its valence shell are called* **carbocations.**

These are formed by heterolytic cleavage of the covalent bonds in which the leaving group takes away with it the shared pair of electrons (of the covalent bond). For example,

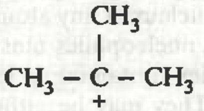
i.e., $(CH_3)_3C - Cl \longrightarrow (CH_3)_3\overset{+}{C} \;+\; Cl^-$

tert-Butyl chloride *tert*-Butyl carbocation

Classification. Carbocations are classified as primary (1°), secondary (2°) and tertiary (3°) according as the positive charge is present on a primary, secondary and a tertiary carbon atom respectively. For example,

$CH_3 - \overset{+}{C}H_2$ $\qquad$ $CH_3 - \overset{+}{C}H - CH_3$

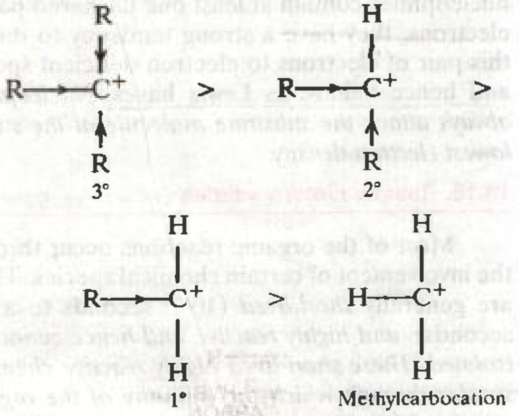
Ethyl carbocation (1°) Isopropyl carbocation (2°)



$CH_3 - \underset{+}{\overset{CH_3}{\overset{|}{C}}} - CH_3$

tert.– Butyl carbocation

Stability. The order of stability of carbocations follows the sequence : 3° > 2° > 1°. This order of stability of carbocations can be easily explained on the basis of dispersal of positive charge by the + I-effect (electron-releasing inductive effect) of the alkyl groups. Greater the number of alkyl groups on the carbon atom carrying the +ve charge, greater would be the dispersal of the charge and hence more stable would be the carbocation. Thus,



Carbocations are highly reactive chemical species since the carbon atom carrying the positive charge has only six electrons in its valence shell and thus has a strong tendency to complete its octet. Usually the order of reactivity of any chemical species is reverse that of its stability. Therefore, the order of reactivity of carbocations follows the sequence : *1° > 2° > 3°*.

Orbital Structure. *The carbocations are planar chemical species*. The carbon atom carrying the positive charge is sp^2-hybridized. The three sp^2-hybridized orbitals of this carbon form three σ-bonds with monovalent atoms or groups which lie in a plane and are inclined to one another at an angle of 120°. The unhybridized 2*p*-orbital which is perpendicular to the plane of the three σ-bonds is, however, empty (Fig. 14.7).

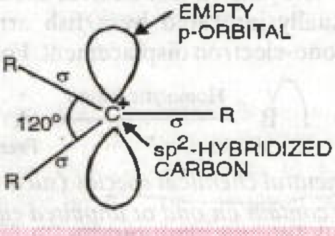


FIGURE 14.7. Orbital structure of carbocations.

(b) Carbanions. *Chemical species bearing a negative charge on carbon and possessing eight electrons in its valence shell are called* **carbanions.**

These are produced by heterolytic cleavage of covalent bonds in which the shared pair of electrons remains with the carbon atom. For example,

$HO^- + H - CH_2 - CHO \longrightarrow$

Acetaldehyde

$H_2O \;+\; :\overset{-}{C}H_2 - CHO$

Acetaldehyde carbanion

$H_2N^- + H - C \equiv C - H \longrightarrow$

Amide ion Acetylene

$^-\!:C \equiv C - H \;+ NH_3$

Acetylide ion

Classification. Like carbocations, carbanions are also classified as primary (1°), secondary (2°) and tertiary (3°) according as the negative charge is present on a primary, secondary and a tertiary carbon atom respectively. For example,

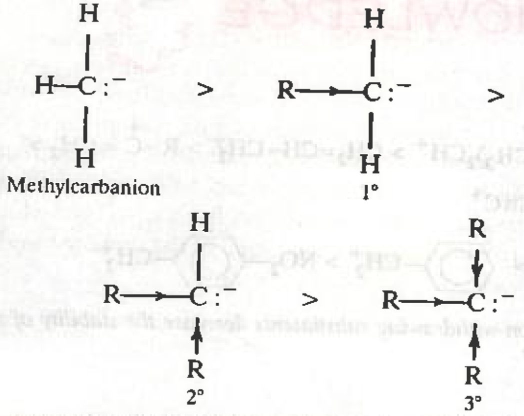
$R - CH_2^-$ $\qquad$ R_2CH^-

Primary carbanion (1°) Secondary carbanion (2°)

R_3C^-

Tertiary carbanion (3°)

Stability. The order of stability of carbanions is just opposite to that of carbocations and free radicals, *i.e.*, 1° > 2° > 3°.



This order of stability can be easily explained in terms of +I- effect of the alkyl groups. Greater the number of alkyl groups on the carbon atom carrying the negative charge, greater would be the intensity of the negative charge on carbon and hence less stable would be the carbanion.

Like carbocations and free radicals, *carbanions are also short-lived highly reactive chemical species*. The instability of carbanions is believed to be due to the presence of a formal charge on them.

Orbital structure. *The structure of simple carbanions is usually pyramidal* just like those of ammonia and amines. The carbon atom carrying the negative charge is sp^3-hybridized. Three of the four sp^3-hybridized orbitals form three σ-bonds with monovalent atoms or groups while the fourth sp^3-orbital contains the lone pair of electrons. (Fig. 14.8).

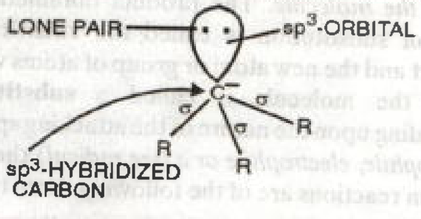
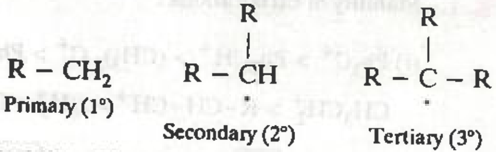


FIGURE 14.8. Orbital structure of carbanions.

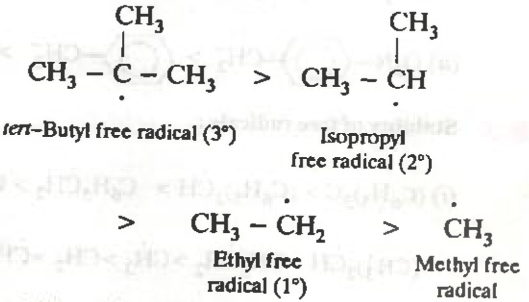
(c) Free radicals. *A free radical may be defined as an atom or a group of atoms having an odd or upaired electron*. These are generally produced by homolytic cleavage of a covalent bond. For example,

Classification. Like carbocations and carbanions, free radicals are also classified as *primary (1°), secondary (2°) and tertiary (3°)* according as the carbon atom carrying the unpaired electron is primary, secondary and tertiary respectively. For example,



$R-\dot{C}H_2$ Primary (1°) $\quad R_2\dot{C}H$ Secondary (2°) $\quad R_3\dot{C}$ Tertiary (3°)

Stability. *The order of stability of free radicals is the same as that of carbocations, i.e., 3° > 2° > 1°*. This order of stability can be easily explained on the basis of hyperconjugation. Greater the number of alkyl groups attached to the carbon atom carrying the odd electron, greater is the delocalization of the odd electron and hence more stable is the alkyl free radical. Thus,



$(CH_3)_3\dot{C}$ *tert*–Butyl free radical (3°) $>$ $(CH_3)_2\dot{C}H$ Isopropyl free radical (2°) $>$ $CH_3-\dot{C}H_2$ Ethyl free radical (1°) $>$ $\dot{C}H_3$ Methyl free radical

Like carbocations and carbanions, *free radicals are also very short-lived highly reactive chemical species because of their strong tendency of the carbon atom carrying the odd electron to acquire one more electron to complete its octet*.

Orbital structure. *Alkyl free radicals like carbocations are planar chemical species*. The only difference being that in carbocations, the unhybridized p-orbital is empty (Fig. 14.15) while in free radicals, it contains the odd electron (Fig. 14.9).

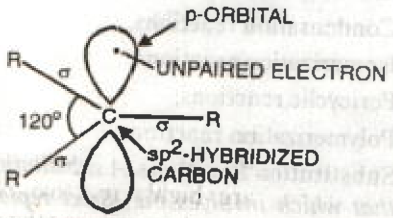


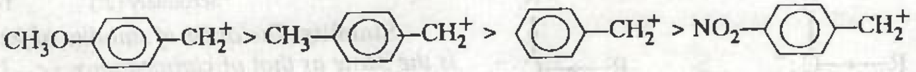
FIGURE 14.9. Orbital structure of free radicals.

ADD TO YOUR KNOWLEDGE

1. **Stability of carbocations :**

(i) $Ph_3C^+ > Ph_2CH^+ > (CH_3)_3C^+ > PhCH_2^+ > (CH_3)_2CH^+ > CH_2{=}CH{-}CH_2^+ > R{-}\overset{+}{C}{=}CH_2 >$

$CH_3CH_2^+ > R{-}CH{=}CH^+ > C_6H_5^+ > CH_3^+ > HC{\equiv}C^+$

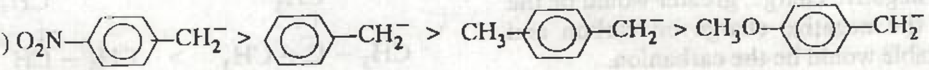
(ii) 

(electron-donating substituents increase while electron-withdrawing substituents decrease the stability of substituted benzyl carbocations)

2. **Stability of carbanions :**

(i) $HC \equiv C^- > (C_6H_5)_3C^- > (C_6H_5)_2CH^- > C_6H_5CH_2^- > CH_2{=}CH{-}CH_2^- > C_6H_5^- > CH_2{=}CH^- >$

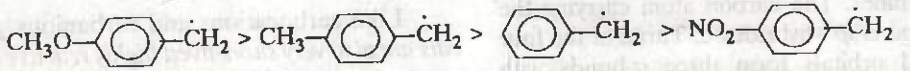
$CH_3^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$

(ii) 

3. **Stability of free radicals :**

(i) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2{=}CH{-}\dot{C}H_2 > (CH_3)_3\dot{C} >$

$(CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3 > CH_2{=}\dot{C}H > HC{\equiv}\dot{C}$

(ii) 

14.19. Common Types of Organic Reactions

All the organic reactions can be broadly classified into the following four types :

1. *Substitution reactions,*
2. *Addition reactions,*
3. *Elimination reactions and*
4. *Rearrangement reactions.*
5. Condensation reactions,
6. Isomerization reactions,
7. Pericyclic reactions,
8. Polymerization reactions.

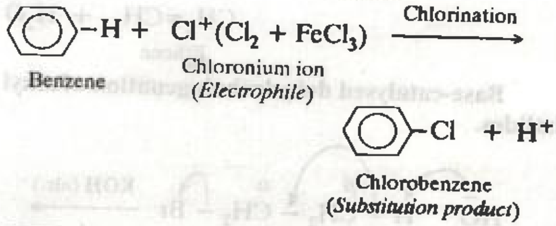
1. Substitution Reactions. *A substitution reaction is that which involves the direct replacement (displacement or substitution) of an atom or a group of atoms in an organic molecule by another atom or group of atoms without any change in the remaining part of the molecule.* The product obtained as a result of substitution is called the **substitution product** and the new atom or group of atoms which enters the molecule is called a **substituent.** Depending upon the nature of the attacking species (*nucleophile, electrophile or a free radical*) the substitution reactions are of the following three types :

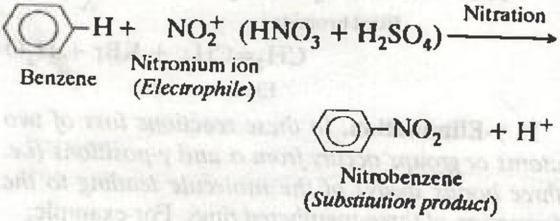
(i) Nucleophilic substitution reactions. *Substitution reactions which are brought about by nucleophiles are called nucleophilic substitution reactions.* In all these reactions, a stronger nucleophile usually displaces a weaker nucleophile. *These reactions are typical of alkyl halides.* For example, hydrolysis of an alkyl halide with an aqueous base :

$$\underset{\substack{\text{Hydroxide ion}\\(\textit{Stronger nucleophile})}}{HO^-} + \underset{\text{Alkyl halide}}{\overset{\delta+\ \ \delta-}{R-X}} \longrightarrow \underset{\substack{\text{Alcohol}\\(\textit{Substitution product})}}{R-OH}$$

$$+ \underset{\substack{\text{Halide ion}\\(\textit{Weaker nucleophile})}}{X^-} \quad (X = Cl, Br \text{ or } I)$$

(b) Electrophilic substitution reactions. *Substitution reactions which are brought about by electrophiles are called electrophilic substitution reactions. These reactions are typical of arenes and other aromatic compounds.* For example, halogenation, nitration, sulphonation and Friedel-Crafts reactions.





(iii) Free radical substitution reactions. *Substitution reactions brought about by free radicals are called free radical substitution reactions.* For example, chlorination of methane in presence of heat or diffused sunlight to give methyl chloride and hydrogen chloride

$$\underset{\text{Methane}}{CH_3-H} + Cl_2 \xrightarrow[\text{or } h\nu]{520-670\text{ K}} \underset{\text{Methyl chloride}}{CH_3-Cl} + HCl$$

The reaction occurs by a free radical mechanism which involves the following three steps :

Initiation :

$$\underset{\text{Chlorine}}{Cl-Cl} \xrightarrow[h\nu \text{ or } 520-670\text{ K}]{\text{(Homolytic fission)}} \underset{\text{Chlorine free radicals}}{2\dot{C}l}$$

Propagation :

$$CH_3-H + \cdot Cl \longrightarrow \underset{\substack{\text{Methyl free}\\\text{radical}}}{\cdot CH_3} + H-Cl$$

$$\cdot CH_3 + Cl-Cl \longrightarrow CH_3-Cl + \cdot Cl$$

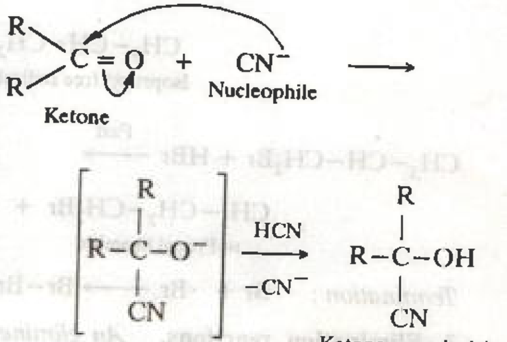
Termination : $\cdot Cl + \cdot Cl \longrightarrow Cl_2$

and $\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3-CH_3$

2. Addition reactions. *Reactions which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions. Such reactions are typical of compounds containing multiple (double and triple) bonds. Depending upon the nature of the attacking species (electrophiles, nucleophiles or free radicals), addition reactions are of the following three types :*

(i) Nucleophilic addition reactions. *Addition reactions brought about by nucleophiles are called nucleophilic addition reactions. These reactions are typical of aldehydes and ketones.* For example, base-catalysed addition of HCN to aldehydes or ketones.

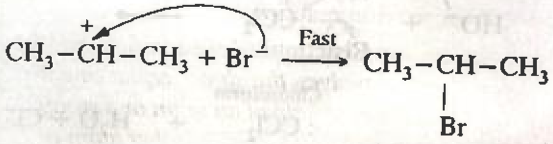
$$HO^- + HCN \longrightarrow H_2O + \underset{\text{Nucleophile}}{CN^-}$$



Ketone cyanohydrin
(*Addition product*)

(ii) Electrophilic addition reactions. *Addition reactions brought about by electrophiles are called electrophilic addition reactions. These reactions are typical of alkenes and alkynes.* For example, addition of Br_2 or HBr to propylene :

$$\underset{\text{Propylene}}{CH_3CH = CH_2} + H^+ \xrightarrow{\text{Slow}} \underset{\text{Isopropyl carbocation (2°)}}{CH_3-\overset{+}{C}H-CH_3}$$



$$CH_3-\overset{+}{C}H-CH_3 + Br^- \xrightarrow{\text{Fast}} \underset{Br}{CH_3-\underset{|}{C}H-CH_3}$$

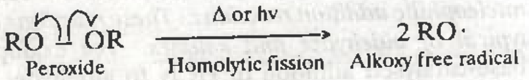
2–Bromopropane
(*Addition product*)

(iii) Free radical addition reactions. *Addition reactions brought about by free radicals are called free radical addition reactions.* For example, addition of HBr to alkenes in presence of peroxides :

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxides}} \underset{n\text{-Propyl bromide}}{CH_3-CH_2-CH_2Br}$$

The reaction occurs by the following mechanism :

Initiation :



$$\underset{\text{Peroxide}}{RO-OR} \xrightarrow[\text{Homolytic fission}]{\Delta \text{ or } h\nu} \underset{\text{Alkoxy free radical}}{2\,RO\cdot}$$

$$RO\cdot + HBr \longrightarrow ROH + \underset{\text{Bromine free radical}}{Br\cdot}$$

Propagation : $CH_3CH=CH_2 + Br\cdot \xrightarrow{\text{Slow}}$

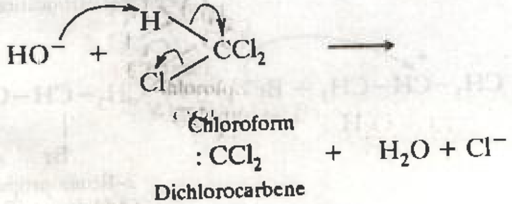
$$\underset{\text{Isopropyl free radical (2°)}}{CH_3-\dot{C}H-CH_2Br}$$

$$CH_3-\dot{C}H-CH_2Br + HBr \xrightarrow{\text{Fast}} \underset{n\text{-Propyl bromide}}{CH_3-CH_2-CH_2Br} + \cdot Br$$

Termination : $\cdot Br + \cdot Br \longrightarrow Br-Br$

3. Elimination reactions. *An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple (double or triple) bond.* Depending upon the relative positions of the atoms or groups eliminated, these reactions are classified as α (alpha), β (beta) and γ (gamma) elimination reactions.

(i) α-Elimination reactions. *In these reactions, the loss of two atoms or groups occurs from the same atom of the substrate molecule.* For example, base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene :

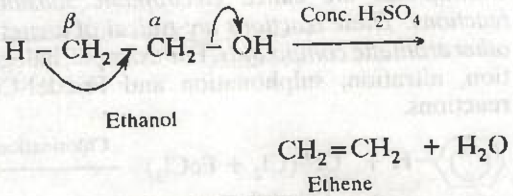


$$HO^- + \underset{\text{Chloroform}}{H-CCl_2-Cl} \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + H_2O + Cl^-$$

Dichlorocarbene is the reactive intermediate involved in *carbylamine reaction* and *Reimer-Tiemann reaction*.

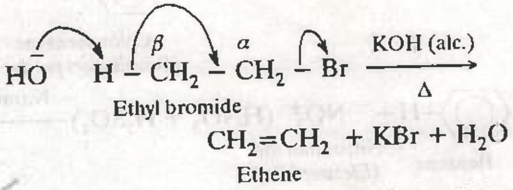
(ii) β-Elimination reactions. *In these reactions, the loss of two atoms or groups occurs from the adjacent atoms of the substrate molecule.* For example, acid-catalysed dehydration of alcohols and base-catalysed dehydrohalogenation of alkyl halides :

Acid-catalysed dehydration of alcohols.



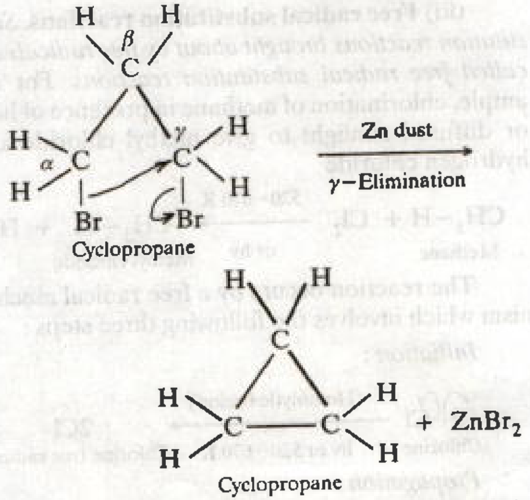
$$\underset{\text{Ethanol}}{H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-OH} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

Base-catalysed dehydrohalogenation of alkyl halides.



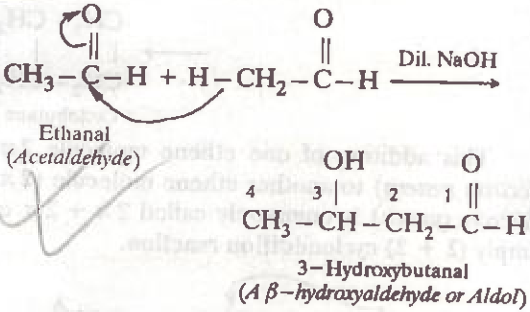
$$HO^- + \underset{\text{Ethyl bromide}}{H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-Br} \xrightarrow[\Delta]{\text{KOH (alc.)}} \underset{\text{Ethene}}{CH_2=CH_2} + KBr + H_2O$$

γ-Elimination. *In these reactions loss of two atoms or groups occurs from α and γ-positions (i.e. three bonds away) of the molecule leading to the formation of three-membered rings.* For example,



This reaction is called **Freund reaction** and is extensively used for the synthesis of three membered rings.

4. Condensation reactions. *In these reactions two or more molecules of the same or different reactants combine to form a product with or without the elimination of simple molecules such as H_2O, HCl, NH_3, ROH etc.* For example, two molecules of acetaldehyde condense in presence of dilute alkali to form 3-hydroxybutanal. Since β-hydroxyaldehydes or ketones are commonly known as aldols, therefore, this reaction is called **aldol condensation.**



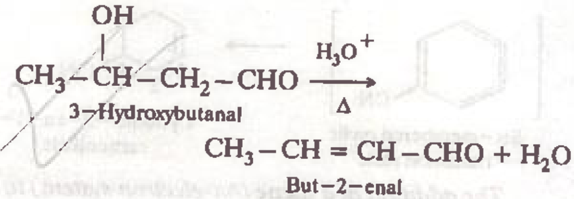
$$CH_3-\overset{O}{\overset{\|}{C}}-H + H-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Dil. NaOH}} \overset{4}{C}H_3-\overset{OH}{\overset{|}{\overset{3}{C}H}}-\overset{2}{C}H_2-\overset{O}{\overset{\|}{\overset{1}{C}}}-H$$

Ethanal (*Acetaldehyde*)

3-Hydroxybutanal (*A β-hydroxyaldehyde or Aldol*)

Aldols on heating with dilute mineral acids readily undergo dehydration to form α, β-unsaturated aldehydes or ketones.

Thus,



$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \xrightarrow[\Delta]{H_3O^+} CH_3-CH=CH-CHO+H_2O$$

3-Hydroxybutanal

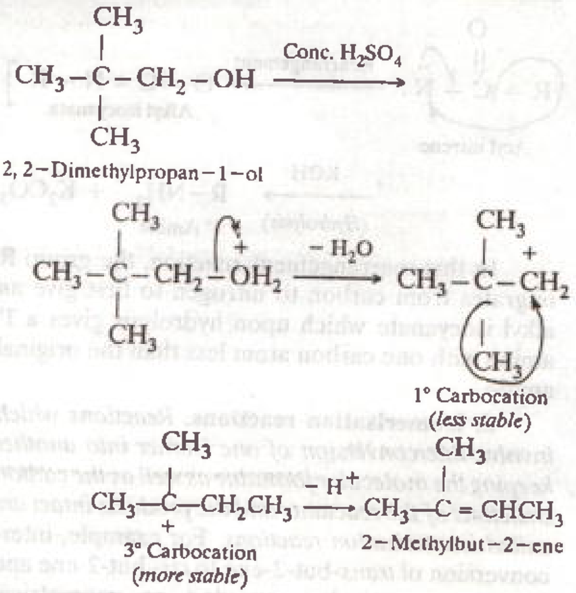
But-2-enal (*Crotonaldehyde*)

An example of a condensation reaction which occurs with the elimination of a molecule of H_2O is the reaction between benzaldehyde and aniline to form benzylideneaniline.

$$\underset{\text{Benzaldehyde}}{C_6H_5CH=O} + \underset{\text{Aniline}}{H_2NC_6H_5} \longrightarrow \underset{\text{Benzylideneaniline}}{C_6H_5CH=NC_6H_5} + H_2O$$

5. Rearrangement reactions. *Reactions involving the migration of an atom or a group from one atom to another within the same molecule are called rearrangement reactions.* For example,

(*i*) Dehydration of 2, 2-dimethylpropan-1-ol with conc. H_2SO_4, occurs through 1, 2-mgiration of the methyl group to give the rearranged product, *i e.*, 2- methylbut-2-ene



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-OH \xrightarrow{\text{Conc. } H_2SO_4}$$

2, 2-Dimethylpropan-1-ol

$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{+}{C}H_2$$

1° Carbocation (*less stable*)

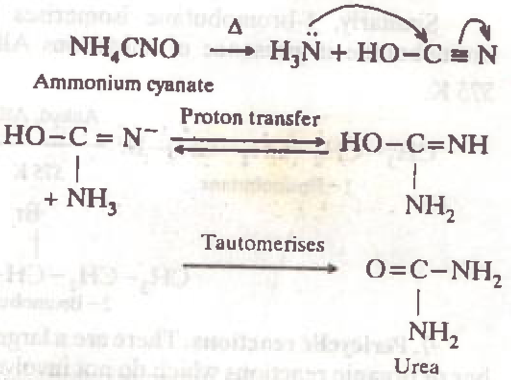
$$CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_2CH_3 \xrightarrow{-H^+} CH_3-\overset{CH_3}{\overset{|}{C}}=CHCH_3$$

3° Carbocation (*more stable*)

2-Methylbut-2-ene

(*ii*) Wohler synthesis of urea from ammonium cyanate (formed by double decomposition of a mixture of NH_4Cl and sodium cyanate) is also an example of a rearrangement reaction.

$$NH_4Cl + NaCNO \xrightarrow{\Delta} NH_4CNO + NaCl$$

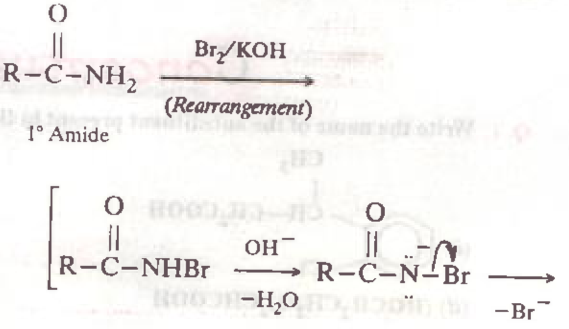


$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\Delta} H_3\ddot{N} + HO-C\equiv N$$

$$HO-\underset{+\,NH_3}{\underset{|}{C}}=N^- \xrightleftharpoons{\text{Proton transfer}} HO-\underset{NH_2}{\underset{|}{C}}=NH \xrightarrow{\text{Tautomerises}} O=\underset{NH_2}{\underset{|}{C}}-NH_2$$

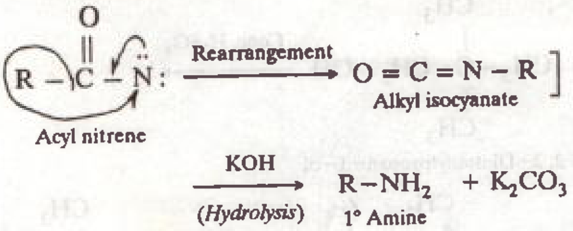
Urea

(*iii*) Hofmann bromamide reaction involving the conversion of 1° amides to 1° amines on treatment with Br_2 in presence of KOH.



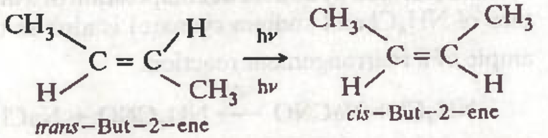
$$\underset{\text{1° Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\text{(Rearrangement)}]{Br_2/KOH}$$

$$\left[R-\overset{O}{\overset{\|}{C}}-NHBr \xrightarrow[-H_2O]{OH^-} R-\overset{O}{\overset{\|}{C}}-\overset{..}{\underset{}{N}}^{-}-Br \xrightarrow[-Br^-]{}\right.$$

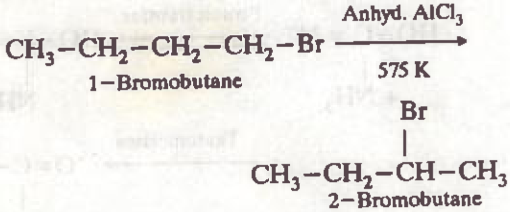


In this rearrangement reaction, the group R migrates from carbon to nitrogen to first give an alkyl isocyanate which upon hydrolysis gives a 1° amine with one carbon atom less than the original amide.

6. Isomerisation reactions. *Reactions which involve interconversion of one isomer into another keeping the molecular formulae as well as the carbon skeletons of the reactants and the products intact are called isomerization reactions.* For example, interconversion of *trans*-but-2-ene to *cis*- but-2-ene and vice versa may be regarded as geometrical isomerization reaction.

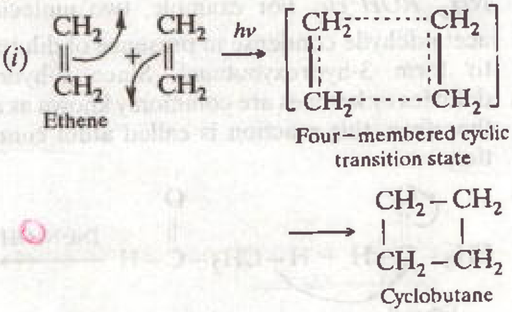


Similarly, 1-bromobutane isomerises to 2-bromobutane in presence of anhydrous $AlCl_3$ at 575 K.

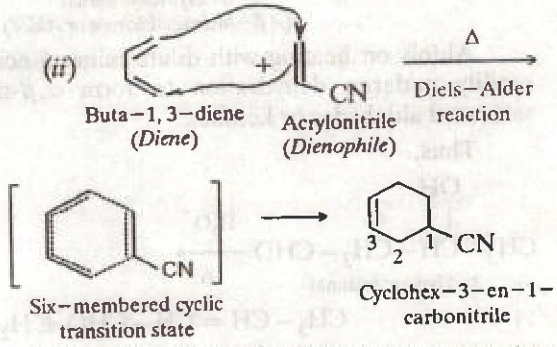


$$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow[575\ K]{Anhyd.\ AlCl_3} CH_3-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3$$

7. Pericyclic reactions. There are a large number of organic reactions which do not involve ionic or free radical intermediates. Instead these reactions occur in a single step *via* a cyclic transition state. In these reactions, bond making and bond breaking occurs simultaneously. These reactions do not require any catalyst and are initiated either by heat or light. All such reactions are called **pericyclic reactions.** For example,



This addition of one ethene molecule (2π-*electron system*) to another ethene molecule (2π-*electron system*) is commonly called $2\pi + 2\pi$ or simply **(2 + 2) cycloaddition reaction.**



The addition of a **diene** *(4π-electron system) to a* **dienophile** *(2π-electron system) to form a six-membered ring is called* **(4 + 2)cycloaddion reaction or Diels-Alder reaction.**

8. Polymerization reactions. These reactions involve the union of a large number of small molecules called **monomers** to form a molecule with high molecular weight called **polymer.** For example,

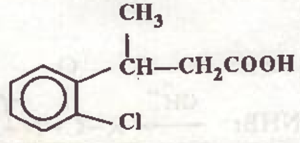
$$n\,CH_2=CH_2 \longrightarrow (CH_2-CH_2)_n$$

Ethylene (*Monomer*) Polythene (*Polymer*)

Conceptual Questions

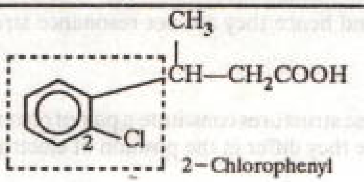
Q. 1. **Write the name of the substituent present in the following compounds :**

(i)

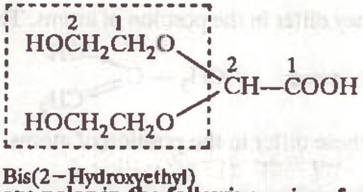


(ii) $(HOCH_2CH_2O)_2CHCOOH$

Ans. (*i*)



(*ii*)



Q. 2. **Which bond is more polar in the following pairs of molecules :**

(a) $H_3C—H$, $H_3C—Br$

(b) $H_3C—NH_2$, $H_3C—OH$

(c) $H_3C—OH$, $H_3C—SH$

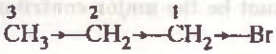
Ans. (*a*) C—Br since Br is more electronegative than H

(*b*) C—O since O is more electronegative than N

(*c*) C—O since O is more electronegative than S.

Q. 3. **In which C—C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least ?**

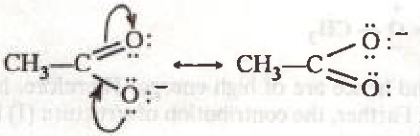
Ans. The magnitude of inductive effect decreases with distance and hence the effect is least in $C_2—C_3$ bond.



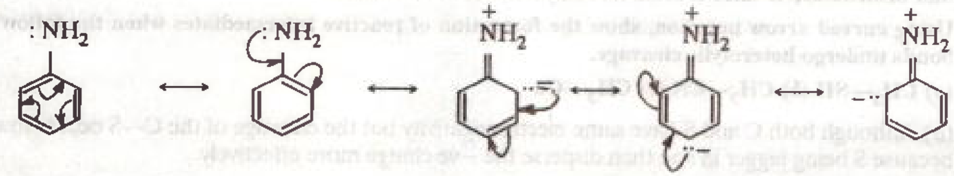
$$\overset{3}{C}H_3 \leftarrow \overset{2}{C}H_2 \leftarrow \overset{1}{C}H_2 \leftarrow Br$$

Q. 4. **Write resonance structures of (*a*) CH_3COO^- and (*b*) $C_6H_5NH_2$. Show the movement of electrons by curved arrows.**

Ans. (*a*)

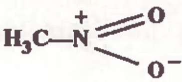


(*b*)



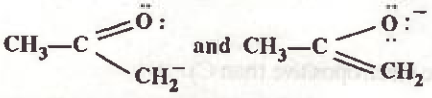
Q. 5. **Which of the following pairs of structures do not constitute resonance structures ?** (*N.C.E.R.T.*)

(*a*)

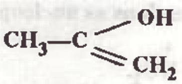


and $H_3C—O—N = O$

(*b*)

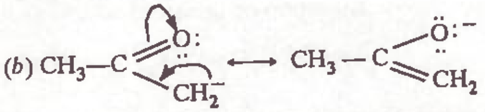


(*c*) $(CH_3)_2CO$ **and**



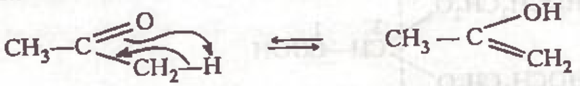
(*d*) $CH_3CH = CHCH_3$ **and** $CH_3CH_2CH = CH_2$

Ans. (*a*) The two structures differ in the position of atoms and hence they are not resonance structures. In fact, these are functional isomers

(*b*)


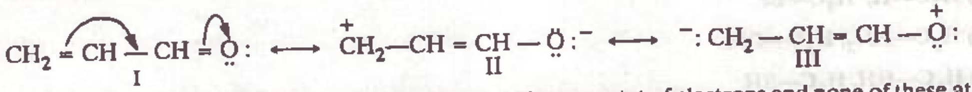
These structures constitute a pair of resonance structures since they differ in the position of electrons only.

(*c*) These are not resonance structures since they differ in the position of atoms. They are, in fact, tautomers.



(*d*) These are not resonance structures since these differ in the position of atoms. In fact, these are position isomers.

Q. 6. Write the resonance structures of $CH_2 = CH—CHO$ and arrange them in order of decreasing stability.

Ans.


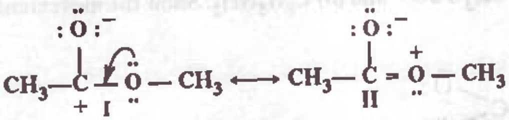
$$\underset{I}{CH_2 = CH - CH = \ddot{O}:} \longleftrightarrow \underset{II}{\overset{+}{C}H_2 - CH = CH - \ddot{O}:^-} \longleftrightarrow \underset{III}{^-:CH_2 - CH = CH - \overset{+}{O}:}$$

Structure (I) is most stable since each C and O atom has an octet of electrons and none of these atoms carries any charge.

Structures (II and III) both involve separation of charge and hence both are less stable than structure (I). However, structure (II) is more stable than structure (III) since it carries a –ve charge on the more electronegative O atom and +ve charge on the less electronegative C atom while in structure (III), the more electronegative O atom carries the +ve charge while the less electronegative C atom carries the –ve charge.

Thus, the decreasing order of stability is : I > II > III

Q. 7. Give reasons why the following two structures (I and II) cannot be the major contributors to the real structure of CH_3COOCH_3.



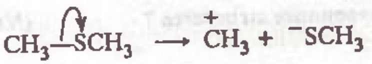
$$\underset{I}{CH_3-\overset{:\ddot{O}:^-}{\overset{|}{\overset{+}{C}}}-\ddot{O}-CH_3} \longleftrightarrow \underset{II}{CH_3-\overset{:\ddot{O}:^-}{\overset{|}{C}}=\overset{+}{\ddot{O}}-CH_3}$$

Ans. Both these structures involve separation of charge and hence are of high energy. Therefore, hence do not contribute substantially towards the resonance hybrid. Further, the contribution of structure (I) is lower than that of structure II since C atom has only a sextet of electrons.

Q. 8. Using curved arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(*a*) $CH_3—SH$ (*b*) $CH_3—CN$ (*c*) $CH_3—Cu$ *(N.C.E.R.T.)*

Ans. (*a*) Although both C and S have same electronegativity but the cleavage of the C—S occurs towards S atom because S being bigger in size than disperse the –ve charge more effectively.



$$CH_3-SCH_3 \longrightarrow \overset{+}{C}H_3 + {}^-SCH_3$$

(*b*)


$$CH_3-CN \longrightarrow \overset{+}{C}H_3 + {}^-CN$$

(∵ CN is more electronegative than CH_3)

(*c*)


$$CH_3-Cu \longrightarrow {}^-:CH_3 + Cu^+$$

(∵ Cu is more electropositive than C)

Q. 9. Giving proper justification, categorise the following molecules/ions as nucleophile or electrophile :

HS^-, BF_3, $C_2H_5O^-$, $(CH_3)_3N:$, Cl^+, $CH_3\overset{+}{C}=O$, $H_2\ddot{N}:^-$, $\overset{+}{N}O_2$. *(N.C.E.R.T.)*

Ans. (*i*) $H\ddot{\underset{..}{S}}:^-$, $C_2H_5\ddot{\underset{..}{O}}:^-$, $(CH_3)_3\ddot{N}:$, $H_2\ddot{N}:^-$

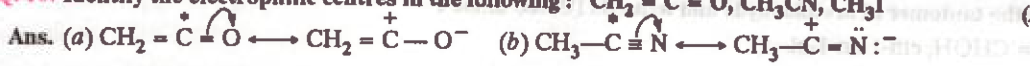
All these species have one or more lone pairs of electrons which it can easily donate to an electrophile and hence behave as nucleophiles.

(*ii*) BF_3, Cl^+, $CH_3\overset{+}{C}=O$, $\overset{+}{N}O_2$

All the positively charged species have a sextet of electrons around the +ve centres and hence can accept a pair of electrons and thus behave as electrophiles.

Similarly B has only a sextet of electrons and hence BF_3, though neutral, also acts as an electrophile.

Q. 10. Identify the electrophilic centres in the following : $CH_2=C=O$, CH_3CN, CH_3I (*N.C.E.R.T.*)



Ans. (*a*) $CH_2=\overset{*}{C}=O \longleftrightarrow CH_2=\overset{+}{C}-O^-$ (*b*) $CH_3-\overset{*}{C}\equiv N \longleftrightarrow CH_3-\overset{+}{C}=\ddot{N}:^-$

As a result of resonance, the starred carbon atom in the above molecules carry a +ve charge and hence are electrophilic centres.

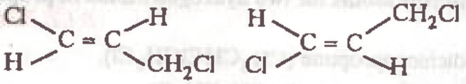
(*c*) $\overset{\delta+}{CH_3}-\overset{\delta-}{I}$

Since I being much bigger in size than C can disperse the negative charge more easily, therefore, CH_3 carries a +ve charge and hence is the electrophilic centre.

Q. 11. What is the relationship between the members of following pairs of structures ? Are they identical, structural or geometrical isomers, or resonance contributors ? (*N.C.E.R.T.*)

(*a*)

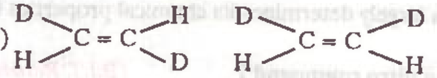
(*b*)



(*c*)

$H-\overset{+OH}{\overset{\|}{C}}-OH$ $\quad$ $H-\overset{OH}{\overset{|}{C}}=\overset{+}{O}H$

(*d*)



Ans. (*a*) Structural (actually position isomers as well as metamers) (*b*) Identical because the relationship between the H-atoms or Cl and CH_2Cl remains to be *trans* in both the structures (*c*) resonance contributors since these differ in the position of electrons but not atoms (*d*) geometrical isomerism.

Q. 12. Classify the following transformations according to the reaction type. (*N.C.E.R.T.*)

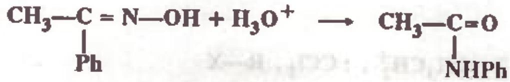
(*a*) $H_3C-CH=CH-CH_3+Br_2 \longrightarrow H_3C-CHBr-CHBr-H_3$

(*b*) $(H_3C)_2C=C(CH_3)_2+Br_2 \longrightarrow (H_3C)_2C=C(CH_3)CH_2Br+HBr$

(*c*) $H_2C=CH-CH_2CH_3 \longrightarrow H_3C-CH=CH-CH_3$

(*d*) $C_6H_5CHO+CH_3COCH_3 \longrightarrow C_6H_5CH(OH)CH_2COCH_3$

(*e*) $(CH_3)_3CCl+HO^- \longrightarrow (CH_3)_2C=CH_2$



(*f*) $CH_3-\underset{Ph}{\underset{|}{C}}=N-OH+H_3O^+ \longrightarrow CH_3-\underset{NHPh}{\underset{|}{C}}=O$

Ans. (*a*) Electrophilic addition (*b*) Free radical substitution (*c*) Isomerisation (*d*) Condensation (*e*) β-Elimination reaction (*f*) Rearrangement.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What type of hybridization is involved in (*i*) planar and (*ii*) linear molecules ?

Ans. (*i*) sp^2 (*ii*) sp.

Q. 2. What are isomers ?

Ans. Compounds having same molecular formula but different chemical and physical properties are called isomers.

Q. 3. What type of isomerism is shown by butane and isobutane ?

Ans. Chain or nuclear isomerism.

Q. 4. Write the tautomer of acetaldehyde and write its IUPAC name ?

Ans. $CH_2 = CHOH$, eth-1-en-1-ol.

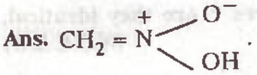
Q. 5. Write the metamer of diethyl ether. What is its IUPAC name ?

Ans. 1-Methoxypropane, $CH_3OCH_2CH_2CH_3$ or 2-methoxypropane, $CH_3—OCH(CH_3)_2$.

Q. 6. Give one example of functional isomerism.

Ans. CH_3CH_2OH and CH_3OCH_3.

Q. 7. Write the *aci*-form of nitromethane.

Ans. 

$CH_2 = \overset{+}{N}(O^-)(OH)$.

Q. 8. Draw the structure of the tautomer of phenol and write its IUPAC name.

Ans. Cyclohexa-2, 4-dien-1-one.

Q. 9. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible ? *(B.I.T. Ranchi 1992)*

Ans. Four : 1, 1-dichloropropane ($CH_3CH_2CHCl_2$), 1, 2-dichloropropane ($CH_3CHClCH_2Cl$), 2, 2-dichloropropane ($CH_3CCl_2CH_3$) and 1, 3-dichloropropane ($ClCH_2CH_2CH_2Cl$).

Q. 10. Arrange the following in increasing order of C—C bond length : C_2H_6, C_2H_4, C_2H_2. *(B.I.T. Ranchi 1994)*

Ans. $C_2H_2 < C_2H_4 < C_2H_6$.

Q. 11. What is a functional group ?

Ans. The atom or group of atoms present in a molecule which largely determines its chemical properties is called the functional group.

Q. 12. What is the functional group of (*i*) an aldehyde and (*ii*) a nitro compound ? *(B.I.T. Ranchi 1991)*

Ans. (*i*) —CHO (*ii*) $—NO_2$

Q. 13. Define homologous series.

Ans. Refer to the text.

Q. 14. What are primary and secondary suffixes as applied to IUPAC nomenclature ?

Ans. The primary suffix indicates whether the carbon chain is saturated or unsaturated while the secondary suffix indicates the functional group present in the molecule.

Q. 15. Name the alkyl groups derived from isobutane.

Ans. (*i*) $(CH_3)_2CHCH_2$- (isobutyl) and $(CH_3)_3C-$ (*t*- butyl).

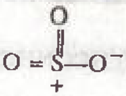
Q. 16. Give the IUPAC name of the compound : $CH_2 = CH - CH(CH_3)_2$ *(B.I.T. Ranchi 1992)*

Ans. 3-Methylbut-1-ene.

Q. 17. Select electrophiles out of the following :

H^+ , Na^+ , Cl^- , C_2H_5OH , $AlCl_3$, SO_3 , CN^- , $CH_3CH_2^+$, $:CCl_2$, R—X

Ans. H^+ , Na^+ , $AlCl_3$, SO_3 , $CH_3CH_2^+$, $:CCl_2$, R—X.

In SO_3,  $O=\overset{\overset{O}{\|}}{\underset{+}{S}}-O^-$, S atom carries a positive charge and hence acts as an electrophile. In $AlCl_3$, Al atom has *six* and in : CCl_2, C atom has *six* electrons in the valence shell and hence each one of these needs two more electrons to complete their respective octets. As a result, both $AlCl_3$ and : CCl_2 act as electrophiles. In $\overset{\delta+}{R}—\overset{\delta-}{X}$, due to greater electronegativity of X, R carries a partial positive charge and hence acts as an electrophile.

Q. 18. Select nucleophiles from the following : BF_3, NH_3, OH^-, R—X, C_2H_5OH.

Ans. $\ddot{N}H_3$, OH^-, $C_2H_5\ddot{O}H$.

Q. 19. Arrange the following :

(*i*) $-NO_2$, $-COOH$, $-F$, $-CN$, $-I$, in increasing order of –I-effect.

(*ii*) CH_3-, $D-$, $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2- in decreasing order of +I- effect.

Ans. (*i*) $-NO_2 > -CN > -COOH > -F > -I$

(*ii*) $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3- > D-$.

Q. 20. Arrange the following :

(*i*) $C_6H_5\dot{C}HCH_3$, $C_6H_5\dot{C}HCH=CH_2$, $C_6H_5CH_2\dot{C}H_2$, $C_6H_5\dot{C}(CH_3)_2$ in order of increasing stability.

(*ii*) $CH_3CH_2^+$, $C_6H_5CH_2^+$, $(CH_3)_3C^+$, $CH_2=CHCH_2^+$ in order of decreasing stability.

(*iii*) $HC\equiv C^-$, $CH_2=CH^-$, $CH_3CH_2^-$, CH_3^-, $(CH_3)_2CH^-$, $C_6H_5CH_2^-$ in order of increasing stability.

Ans. (*i*) $C_6H_5CH_2\dot{C}H_2 < C_6H_5\dot{C}HCH_3 < C_6H_5\dot{C}(CH_3)_2 < C_6H_5\dot{C}H-CH=CH_2$.

(*ii*) $(CH_3)_3C^+ > C_6H_5CH_2^+ > CH_2=CHCH_2^+ > CH_3CH_2^+$.

(*iii*) $(CH_3)_2CH^- < CH_3CH_2^- < CH_3^- < CH_2=CH^- < C_6H_5CH_2^- < HC\equiv C^-$.

Q. 21. Which is expected to be more stable, $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ and why ? (*N.C.E.R.T.*)

Ans. $O_2N \leftarrow CH_2 \leftarrow CH_2 \leftarrow O^-$ is more stable than $CH_3 \rightarrow CH_2 \rightarrow O^-$ because NO_2 group has –I-effect and hence it tends to disperse the —ve charge on the O-atom. In contrast, CH_3CH_2 has +I-effect. It, therefore, tends to intensify the –ve charge and hence destabilizes it.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec 14.1. to 14.4.

1. Explain tetravalency of carbon.

2. Why does carbon undergo hybridization prior to bond formation ?

3. Draw the orbital diagram for methane and ethane molecules indicating the hybridization involved.

4. Discuss the orbital diagram of ethene indicating the hybridization involved and the nature of the bonds formed.

5. Describe the orbital diagram of acetylene indicating the hybridization involved and the nature of bonds formed.

6. What is the effect of type of hybridization on (*i*) bond length (*ii*) bond strength.

7. Give hybridization state of each carbon in the following compounds :

(*a*) $CH_2=C=O$ (*b*) $CH_3—CH=CH_2$ (*c*) $(CH_3)_2CO$ (*d*) $CH_2=CHCN$

(*e*) $CH_3CH_2^-$ (*f*) $CH_3CH_2^+$ (*g*) $CH_3\dot{C}H_2$ (*N.C.E.R.T.*)

8. Indicate σ- and π-bonds in the following compounds :
(*a*) C_6H_6 (*b*) C_6H_{12} (*c*) CH_2Cl_2 (*d*) $CH_2 = C = CH_2$ (*e*) CH_3NO_2 (*f*) $HCONHCH_3$.
(*N.C.E.R.T.*)

9. Draw bond-line formulae for
(*a*) *tert*-butylcyclopentane, (*b*) isopropyl alcohol, (*c*) 2, 3- dimethylbutanal (*d*) heptan-4-one
(*e*) cyclohexanone. (*N.C.E.R.T.*)

10. Write condensed and bond-line structural formulae for all the possible isomers of molecular formula :
(*a*) C_6H_{14} (*b*) C_6H_{10} (*c*) C_8H_{10} (*d*) C_8H_{18} (*e*) C_3H_8O (*f*) $C_3H_6O_2$ (*g*) $C_4H_{10}O$ (*h*) $C_6H_{11}NO_2$.
(*N.C.E.R.T.*)

Sec. 14.5. to 14.8. **11.** What is structural isomerism ? Draw all the structural isomers of the hydrocarbon having the molecular formula, C_5H_{12}. Also give their IUPAC names.

12. Explain : (*i*) position isomerism (*ii*) functional isomerism giving one example in each case.

13. An alkane has a molecular mass of 72. Give all the possible structural isomers alongwith their IUPAC names.

Hint. The general formula of alkanes is C_nH_{2n+2}

$$\therefore \quad 12 \times n + 1 \times (2n + 2) = 72$$

$$\text{or} \quad 12n + 2n + 2 = 72 \quad \text{or} \quad n = 5$$

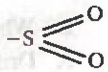
Thus, the molecular formula of the alkane is C_5H_{12}. For structural isomers and their IUPAC names, refer to the text.

14. A hydrocarbon has the molecular mass 70. Write all the possible structural isomers and give their IUPAC names.

[**Ans.** The hydrocarbon having molecular mass of 70 is C_5H_{10}. It exists in the following four structural isomers :
(*i*) $CH_3CH_2CH_2CH{=}CH_2$ (pent-1-ene),
(*ii*) $(CH_3)_2CH{-}CH{=}CH_2$ (3-methylbut-1-ene) ;
(*iii*) $CH_3CH_2CH{=}CHCH_3$ (pent-2-ene) and
(*iv*) $(CH_3)_2C{=}CHCH_3$ (2-methylbut-2-ene)]

15. Write the tautomers of (*i*) ethyl acetoacetate and acetylacetone. Explain why the latter has higher percentage of enol than the former.

16. What is a functional group ? Write the functional groups of the following :
(*i*) Thioalcohol (*ii*) Isothiocyanate (*iii*) Thiocyanate and (*iv*) Sulphonic acid.
(*v*) Sulphones (*vi*) Sulphoxides.

[**Ans.** (*i*) —SH (*ii*) $—N = C = S$ (*iii*) $—S—C \equiv N$ (*iv*) $- SO_3H$ (*v*) $> S = O$ (*vi*) ]

17. What are alicyclic compounds. Give two examples with their names.

18. What are homocyclic and heterocyclic compounds. Give one example of each type with their names.

19. What is homologous series ? Give its important characteristics. Write the first four homologues of alcohols and give their IUPAC names.

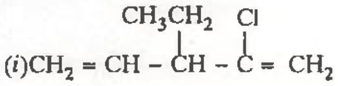
20. Give the condensed and bond-line structural formulae and identify the functional groups present, if any, for
(*a*) 2, 2, 4-Trimethylpentane (*b*) 2-Hydroxy-1, 2, 3-propanetricarboxylic acid
(*c*) Cycloocta-1, 5-diene (*d*) Hexanedial (*e*) 2-(4-Isobutylphenyl)propanoic acid
(*f*) 2-Hydroxy-1, 2-diphenylethan-1-one. (*N.C.E.R.T.*)

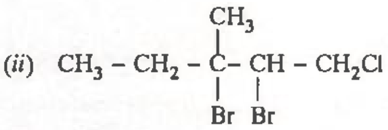
Sec.14.9. to 14.14.

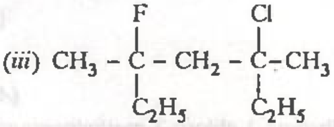
21. Explain the following terms with one example in each case, (*i*) word root (*ii*) primary and secondary suffixes and prefixes.

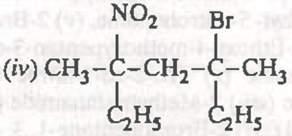
22. Draw the complete structures of bromomethane, bromoethane, 2-bromopropane and *tert*-butyl bromide. Arrange them in order of increasing steric hindrance. (*N.C.E.R.T.*)

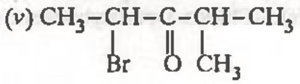
23. Give the IUPAC names of the following compounds :

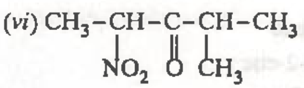
(*i*) 
$CH_2=CH-\overset{CH_3CH_2}{CH}-\overset{Cl}{C}=CH_2$ **(*A.I.S.B. 1993*)**

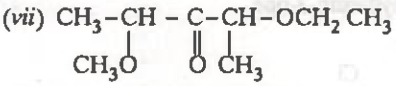
(*ii*) 
$CH_3-CH_2-\overset{CH_3}{\underset{Br}{C}}-\underset{Br}{CH}-CH_2Cl$ **(*A.I.S.B. 1994*)**

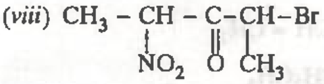
(*iii*) 
$CH_3-\overset{F}{\underset{C_2H_5}{C}}-CH_2-\overset{Cl}{\underset{C_2H_5}{C}}-CH_3$ **(*A.I.S.B. 1995*)**

(*iv*) 
$CH_3-\overset{NO_2}{\underset{C_2H_5}{C}}-CH_2-\overset{Br}{\underset{C_2H_5}{C}}-CH_3$ **(*A.I.S.B. 1995*)**

(*v*) 
$CH_3-\underset{Br}{CH}-\underset{\overset{\|}{O}}{C}-\underset{CH_3}{CH}-CH_3$ **(*D.S.B.1996*)**

(*vi*) 
$CH_3-\underset{NO_2}{CH}-\underset{\overset{\|}{O}}{C}-\underset{CH_3}{CH}-CH_3$ **(*D.S.B. 1996*)**

(*vii*) 
$CH_3-\underset{CH_3O}{CH}-\underset{\overset{\|}{O}}{C}-\underset{CH_3}{CH}-OCH_2CH_3$ **(*A.I.S.B. 1996*)**

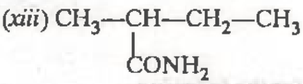
(*viii*) 
$CH_3-\underset{NO_2}{CH}-\underset{\overset{\|}{O}}{C}-\underset{CH_3}{CH}-Br$ **(*A.I.S.B. 1996*)**

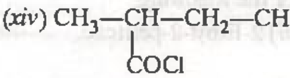
(*ix*) $CH_3CH=CHCH_2NH_2$ **(*A.I.S.B. 1997*)**

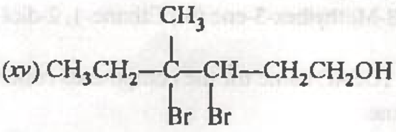
(*x*) $CH_2=CHCN$ **(*A.I.S.B. 1997*)**

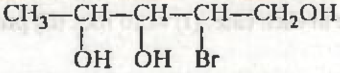
(*xi*) $CH_3CH_2CH(CHO)CH_2COOH$ **(*A.I.S.B. 2001*)**

(*xii*) 
(*D.S.B. 2001*)

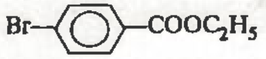
(*xiii*) 
$CH_3-\underset{CONH_2}{CH}-CH_2-CH_3$ **(*H.S.B. 2002*)**

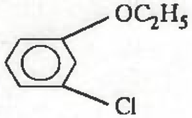
(*xiv*) 
$CH_3-\underset{COCl}{CH}-CH_2-CH_3$ **(*H.S.B. 2002*)**

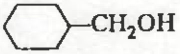
(*xv*) 
$CH_3CH_2-\overset{CH_3}{\underset{Br}{C}}-\underset{Br}{CH}-CH_2CH_2OH$ **(*D.S.B. 2002*)**

(*xvi*) 
$CH_3-\underset{OH}{CH}-\underset{OH}{CH}-\underset{Br}{CH}-CH_2OH$ *(A.I.S.B. 2002)*

(*xvii*) $CH_3-C\equiv C-CH_2-CHO$ *(A.I.S.B. 2003)*

(*xviii*)  *(A.I.S.B. 2003)*

(*xix*)  *(D.S.B. 2003)*

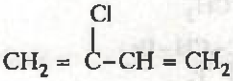
(*xx*)  *(D.S.B. 2004 S)*

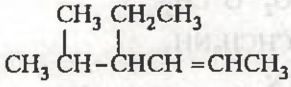
(*xxi*) $CH_3CONHC_6H_5$ *(A.I.S.B. 2004 S)*

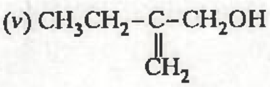
[Ans. (*i*) 2-Chloro-3-ethylpenta-1, 4-diene (*ii*) 2, 3-Dibromo-1-chloro-3-methylpentane (*iii*) 3-Chloro-5- fluoro-3, 5-dimethylheptane, (*iv*) 3-Bromo-3,5-dimethyl- 5- nitroheptane, (*v*) 2-Bromo-4-methylpentan-3-one, (*vi*) 4-Methyl-2-nitropentan-3-one (*vii*) 2-Ethoxy-4-methoxypentan-3-one (*viii*) 2-Bromo-4-nitropentan-3-one (*ix*) But-2-en-1-amine (*x*) Pro-2-en-1-nitrile (*xi*) 3-Ethyl-4-oxobutan-1-oic acid (*xii*) 4-Nitroso-N, N-dimethylaniline (*xiii*) 2-Methylbutanamide (*xiv*) 2-Methylbutanoyl chloride (*xv*) 3, 4-Dibromo-4-methylhexan-1-ol (*xvi*) 2-Bromopentane-1, 3, 4-triol (*xvii*) Pent- 3-yn-1-al (*xviii*) Ethyl 4-bromobenzoate (*xix*) 3-Chloro-1-ethoxybenzene (*xx*) Cyclohexylmethanol (*xxi*) N-Phenylethanamide]

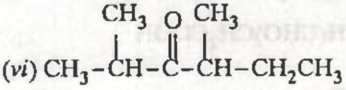
24. Write the structural formulae of the following :

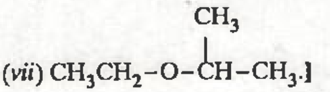
(*i*) But-3-en-1-ol
(*ii*) 2-Chlorobuta-1, 3-diene
(*iii*) 2-Aminoethan-1-ol
(*iv*) 4-Ethyl-5-methylhex-2-ene
(*v*) 2-Ethylprop-2-en-1-ol *(H.S.B. 1994)*
(*vi*) 2, 4-Dimethylhexan-3-one *(H.S.B. 1994)*
(*vii*) 2-Ethoxypropane

[**Ans.** (*i*) $CH_2=CHCH_2CH_2OH$ (*ii*) 
$CH_2=\overset{Cl}{C}-CH=CH_2$

(*iii*) $H_2NCH_2CH_2OH$ (*iv*) 
$CH_3\,\overset{CH_3}{CH}-\overset{CH_2CH_3}{CHCH}=CHCH_3$

(*v*) 
$CH_3CH_2-\underset{CH_2}{\overset{\|}{C}}-CH_2OH$

(*vi*) 
$CH_3-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{CH}-CH_2CH_3$

(*vii*) 
$CH_3CH_2-O-\overset{CH_3}{CH}-CH_3$.]

25. Pick out the error and write the correct IUPAC names for the following.

(*i*) 3-Pentyne
(*ii*) 1, 6-Hexadiene
(*iii*) 2-Ethyl-2-pentene
(*iv*) 1, 2-Dihydroxyethane
(*v*) pent- 4- en-1-yne.

[Ans. (*i*) Pent-2-yne (*ii*) Hexa-1, 5- diene (*iii*) 3-Methylhex-3-ene (*iv*) Ethane-1, 2-diol (*v*) Pent-1-en-4-yne.]

26. Which of the following represents the correct IUPAC name for the compounds concerned :

(*a*) 2, 2-Dimethylpentane or 2-Dimethylpentane

(*b*) 2, 3-Dimethylpentane or 3, 4-Dimethylpentane
(*c*) 2, 4, 7-Trimethyloctane or 2, 5, 7-Trimethyloctane
(*d*) 2-Chloro-4-methylpentane or 4-chloro-2-methylpentane
(*e*) But-3-yn-1-ol or But-4-ol-1-yne. (*N.C.E.R.T.*)

[**Ans.** (*a*) 2, 2-Dimethylpentane (*b*) 2, 3-Dimethylpentane (*c*) 2, 4, 7-Trimethyloctane (*d*) 2-Chloro-4-methylpentane (*e*) But-3-yn-1-ol.]

27. Draw formulae for the first five members of each homologous series beginning with the following compounds :
(*a*) H—COOH (*b*) CH_3COCH_3 (*c*) H—CH = CH_2 (*N.C.E.R.T.*)

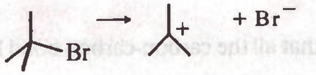
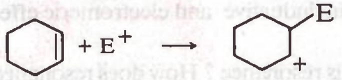
Sec.14.15. to 14.19.

28. Explain inductive and electromeric effect with examples.
29. What is resonance ? How does resonance explain that all the carbon-carbon bond lengths in benzene are equal (139 pm) ?
30. Spectroscopic measurements indicate that the two oxygen atoms of sodium acetate are equivalent. Both the C—O bonds have the same length (126 pm). Explain.
31. What is resonance effect ? What are its various types ? In what respects, does the resonance effect differ from inductive effect ?
32. Draw resonance structures for the following compounds. Show the electron shift using curved arrow notation.
(*a*) C_6H_5OH, (*b*) $C_6H_5NO_2$, (*c*) $C_6H_5CH_2^+$, (*d*) $CH_3CH = CHCHO$, (*e*) $CH_3CH = CH—CH_2^+$,
(*f*) C_6H_5CHO, (*g*) $CH_2 = CHOCH_3$. (*N.C.E.R.T.*)
33. Explain why alkyl groups act as electron donors when attached to a π-system. (*N.C.E.R.T.*)
34. Comment upon the statement : 'Usual order of inductive effects of the alkyl groups is often reversed when attached to a double bond or a benzene ring.' Name the electronic effect and illustrate your answer with suitable examples.
35. Explain hyperconjugation effect.
36. How does hyperconjugation effect explain the stability of alkenes.
37. Explain the following with one example in each case.
(*i*) Homolytic fission (*ii*) Heterolytic fission of covalent bonds.
38. What are carbocations ? Discuss their various types.
39. Give two methods of preparation of carbocations.
40. Discuss the configuration of carbocations.
41. How can inductive and hyperconjugation effects explain the stability of primary, secondary and tertiary carbocations.
42. What are electrophiles and nucleophiles ? Explain with examples. (*N.C.E.R.T.*)
43. Classify the reagents shown in the bold in the following equations as nucleophiles or electrophiles. Use curved arrow notation to show the electron movement.
(*a*) $CH_3COOH + \mathbf{OH^-} \longrightarrow CH_3COO^- + H_2O$ (*b*) $CH_3COCH_3 + \mathbf{NC^-} \longrightarrow CH_3C(CN)OHCH_3$
(*c*) $C_6H_6 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$ (*N.C.E.R.T.*)
[**Ans.** (*a*) nucleophile (*b*) nucleophile (*c*) electrophile]
44. What are reactive intermediates ? How are they generated by bond fission ? (*N.C.E.R.T.*)
45. What are free radicals ? Discuss their configuration.
46. How can hyperconjugation effect and inductive effect explain the stability of primary, secondary and tertiary free radicals.
47. What are carbanions ? Discuss their configuration.
48. Give two methods of preparation of carbanions.
49. Discuss the stability of carbanions on the basis of inductive effects.

50. Explain the following reactions :
(*i*) Substitution (*ii*) Addition (*iii*) Elimination (*iv*) Rearrangement (*v*) Isomerization
(*vi*) Condensation (*vii*) Pericyclic.

51. For the following bond cleavages, use curved arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate products as free radical, carbocation and carbanion

(*a*) $CH_3O{-}OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$ (*b*) $>C=O + OH^- \longrightarrow >\underset{-}{C}=O + H_2O$

(*c*) 
(*d*)  (*N.C.E.R.T.*)

[**Ans.** (*a*) Free radical (*b*) Carbanion (*d*) Carbocation]

52. Classify the following reactions in one of the reaction type studied.
(*a*) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$
(*b*) $(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2CCl{-}CH_3$
(*c*) $(CH_3)_3C{-}CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3$
(*d*) $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O.$ (*N.C.E.R.T.*)

[**Ans.** (*a*) nucleophilic substitution (*b*) electrophilic addition (*c*) nucleophilic substitution with rearrangement (*d*) β- elimination reaction]

Long Answer Questions CARRYING 5 or more MARKS

Sec 14.1. to 14.4. **1.** Explain the term hybridization. Why does carbon undergo hybridization ? Explain the different types of hybridizations carbon atom can undergo ?

2. In terms of hybridization of carbon atom, discuss briefly the shapes of methane, ethane, ethene and ethyne.

3. Discuss classification of hydrocarbons into various types and illustrate each class by taking two examples.

Sec. 14.5. to 14.8. **4.** Explain the following giving examples :
(*i*) Functional group (*ii*) Homologous series and its characteristics.

5. What is mean by isomerism ? Discuss its various types giving at least one example in each case.

6. Define tautomerism. Discuss briefly keto-enol tautomerism in aldehydes and ketones. Also discuss the conditions under which enol form predominates.

Sec.14.15. to 14.19. **7.** Give a brief account of the various types of electronic effects in a covalent molecule.

8. Define and explain the term resonance with suitable examples. Comment upon the relative contributions of various resonance structures.

9. What is hyperconjugation effect ? How dies it differ from resonance effect. Briefly discuss the significance of hyperconjugation effect.

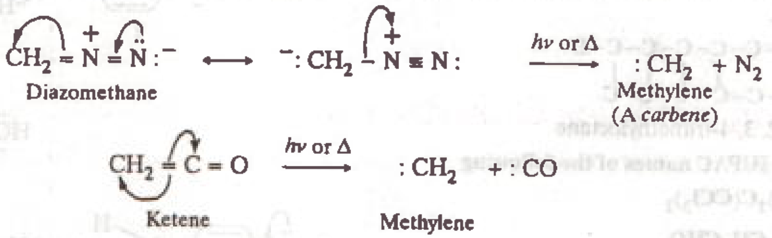
10. How are free radicals, carbocations and carbanions produced ? Discuss their relative stabilities.

11. Give an account of common types of organic reactions with suitable examples.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Carbenes. *Neutral divalent carbon species in which the carbon is bonded to two monovalent atoms or groups and also contains two non-bonding electrons are called* **carbenes.** These are generally produced either by photolysis (irradiation with UV light) or thermolysis or pyrolysis (action of heat) of diazoalkanes or ketenes. Thus,



Like carbocations, carbenes are short-lived highly reactive chemical species since the central carbon atom has only six electrons in its valence shell and thus has a strong tendency to complete its octet by gaining two more electrons. *Carbenes, thus, behave as Lewis acids or electrophiles.*

Orbital Structure. There are two types of carbenes, *i.e., singlet and triplet*. In singlet carbenes, the central carbon atom is sp^2-hybridized. Two of the sp^2-hybridized orbitals form two σ-bonds with two monovalent atoms or groups while the third sp^2- hybridized orbital contains two non-bonding electrons. The unhybridized p-orbital is, however, empty (Fig. 14.10). *Thus, a singlet carbene has a bent structure.*

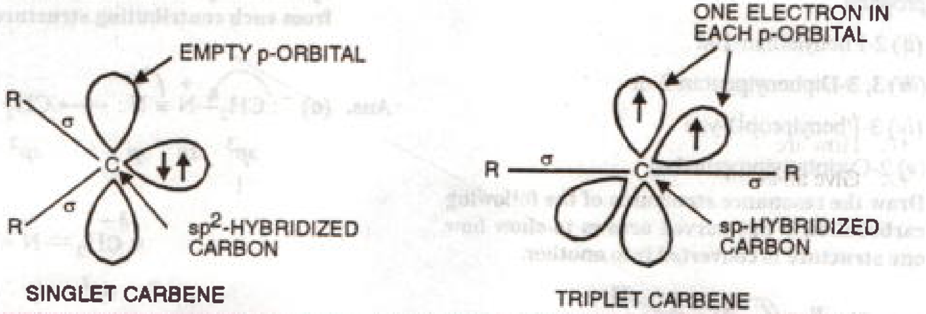


FIGURE 14.10. Orbital structure of singlet and triplet carbenes.

ADDITIONAL USEFUL INFORMATION *contd.*

In triplet carbenes, the central carbon is *sp*- hybridized ; the two *sp*-hybridized ; orbitals form two σ-bonds with two monovalent atoms or groups while the two unhybridized *p*-orbitals are perpendicular to each other and contain has one electron each. Thus, *a triplet carbene has a linear structure and behaves as a diradical* (Fig. 14.17). Further, it may be noted that a *triplet*-carbene is always more stable than a singlet carbene.

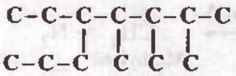
2. Nitrenes. *Neutral monovalent nitrogen species in which nitrogen has two unshared pairs of electrons and is bonded to only one monovalent atom or group are called* **nitrenes**. These are usually produced by thermolysis of azides. For example,

$$\underset{\text{Alkyl azide}}{R-\underset{..}{N}=\overset{+}{N}=\overset{..}{N}:^{-} \longleftrightarrow R-\underset{..}{\overset{-..}{N}}-\overset{+}{N}\equiv N:} \xrightarrow{\Delta} \underset{\text{Alkyl nitrene}}{R-\ddot{N}:} + :N\equiv N:$$

C.B.S.E.-P.M.T. (MAINS) SPECIAL

Common with I.I.T.

Give the IUPAC name of the saturated hydrocarbon having the following carbon skeleton.

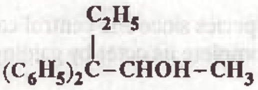


Ans. 5-Ethyl-2, 3, 4-trimethyloctane

Q. 2. **Give the IUPAC names of the following**

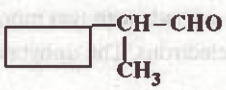
(*i*) $(CH_3)_2C(CCl_3)_2$

(*ii*) $C_6H_5CH_2CHO$

(*iii*) 

$(C_6H_5)_2\overset{C_2H_5}{\overset{|}{C}}-CHOH-CH_3$

(*iv*) $C_6H_5-CH_2-C\equiv CH$

(*v*) 

Ans. (*i*) 1, 1, 1, 3, 3, 3-Hexachloro-2, 2-dimethylpropane

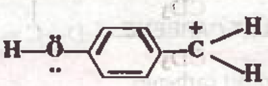
(*ii*) 2-Phenylethan-1-al

(*iii*) 3, 3-Diphenylpentan-2-ol

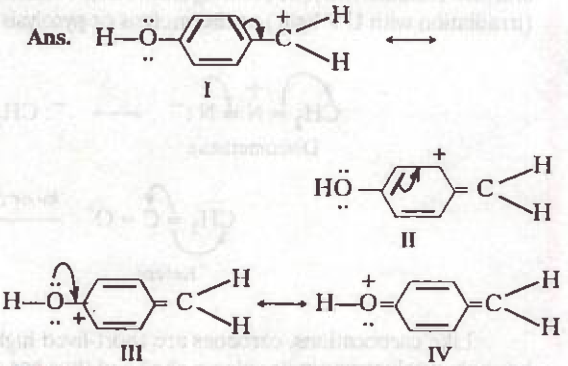
(*iv*) 3-Phenylprop-1-yne

(*v*) 2-Cyclobutylpropan-1-al

Q. 3. **Draw the resonance structures of the following carbocation ? Use curved arrows to show how one structure is converted into another.**



Ans.



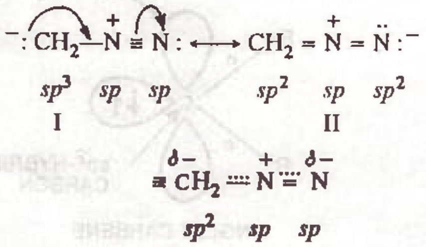
Q. 4.

(a) Write the resonance structures of diazomethane (CH_2N_2).

(b) Give the hybridized state of carbon and each N in each structure.

(c) How does the H—C—H bond angle in the hybrid compare with the bond angles predicted from each contributing structure.

Ans. (*a*)



(Resonance hybrid)

(*b*) The hybrid state of carbon and each N is shown in the structures above.

(*c*) The HCH angle in (I) is expected to be 109° – 28′ while in (II), it is expected to be 120°. Since the hybrid is blend of I and II, therefore, the actual HCH angle has some intermediate value.

Q. 5. Explain why each of the following are not resonance forms :

(i) singlet and triplet methylene

(ii) $H_2\ddot{N}—O—H$ and $H_2\overset{+}{\ddot{N}} = O—H$

Ans. (*i*) Contributing structures must have same number of paired electrons. Since singlet methylene has two paired electrons while triplet methylene has two unpaired electrons, therefore, they cannot be regarded as resonance forms.

(*ii*) $\underset{\text{I}}{H_2\ddot{N}—\underset{..}{\ddot{O}}—H} \not\leftrightarrow \underset{\text{II}}{H_2\ddot{N} = \underset{..}{\overset{+}{O}}—H}$

In structure (II), N has 10 electrons, it cannot be regarded as a resonance structure of I.

Q. 6. With proper justification, arrange the following in order of increasing stability

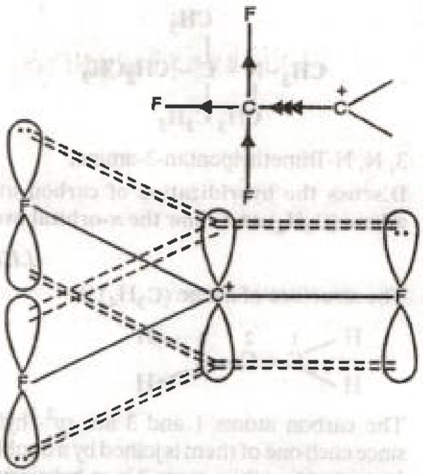
$CH_3CH_2^-$, $CH \equiv C^-$, $CH_2 = CH^-$.

Ans. In acetylide ion $CH \equiv C^-$, the carbon atom carrying the –ve charge is *sp*-hybridized and has 50% *s*-character ; in $CH_2 = CH^-$ ion, the carbon atom is sp^2- hybridized and has 33·3% *s*-character while in $CH_3CH_2^-$ ion, the carbon atom bearing the –ve charge is sp^3-hybridized and has 25% *s*-character.

Since *s*-electrons, on the average, are closer to the nucleus than *p*-electrons, therefore, a carbon atom with greater *s*-character can accommodate or stabilize the negative charge better than a carbon atom with smaller *s*- character. In other words, the stability of the carbanion increases as the *s*-character of the carbon atom carrying the negative charge increases. Now since the *s*-character of the carbon decreases as we move from *sp* to sp^2 to sp^3-carbon, therefore, the relative stabilities of the three carbanions follows the sequence: $CH \equiv C^- > CH_2 = CH^- > CH_3CH_2^-$.

Q. 7. The carbocation F_3C^+ is more stable than carbocation, $F_3C—\overset{+}{C}<$. Explain.

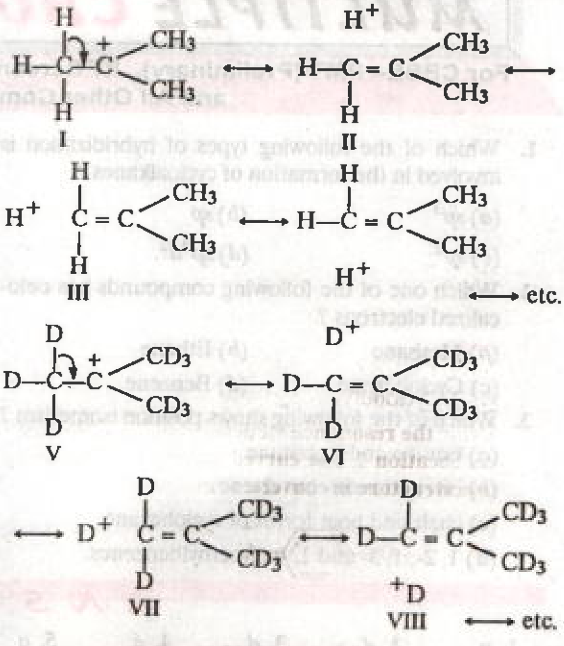
Ans. In case of carbocation, $F_3C—\overset{+}{C}<$, the strongly electron-withdrawing F_3C withdraws electrons of the C—C bond towards itself thereby intensifying the positive charge and thus destabilizing the carbocation, $F_3C—\overset{+}{C}$ relative to F_3C^+. On the other hand, in carbocation F_3C^+ lone pair of electrons on each of the three F-atoms overlap with the empty *p*-orbital of the carbon atom carrying the positive charge thereby dispersing the positive charge and thus stabilizing the carbocation, F_3C^+ relative to $F_3C—C$.



Q. 8. Which of the following carbocations is more stable and why ?

(i) $(CH_3)_3C^+$ and (ii) $(CD_3)_3C^+$

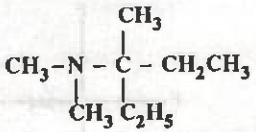
Ans. Both carbocations (*i*) and (*ii*) are stabilized by hyperconjugation as shown below :



Due to stronger C—D bond, contribution of structures (V-VIII) towards stability of carbocation, $(CD_3)_3C^+$ is less than those of structures (I-IV) for carbocation, $(CH_3)_3C^+$, therefore, carbocation (*i*) is more stable than carbocation (*ii*) *This effect is also sometimes called as β-secondary isotone effect.*

Q. 9. **Give the IUPAC name for the amine.**

(I.I.T. 1993)



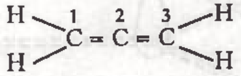
$$CH_3-\underset{\underset{CH_3}{|}}{N}-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_2CH_3$$

Ans. 3, N, N-Trimethylpentan-3-amine.

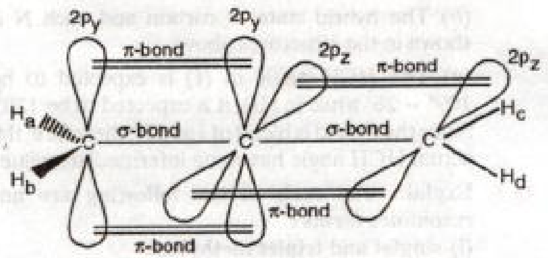
Q. 10. **Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the π-orbital overlaps.**

(I.I.T. 1999)

Ans. The structure of allene (C_3H_4) is



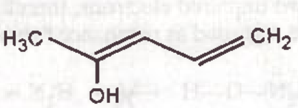
The carbon atoms 1 and 3 are sp^2- hybridized since each one of them is joined by a double bond. In contrast, carbon atom 2 is *sp*-hybridized since it has two double bonds. Thus, the two π-bonds in allene like in acetylene are perpendicular to each other as shown below :



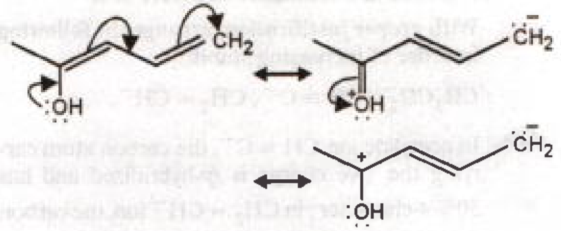
Whereas H_c and H_d lie in the plane of the paper while H_a and H_b lie in a plane perpendicular to the plane of the paper.

Q. 11. **Write resonance structures of the given compound.**

(I.I.T. 2003)



Ans. The following three resonance structures can be written for the given compound.



MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Which of the following types of hybridization is involved in the formation of cycloalkanes ?
   (*a*) sp^3 (*b*) *sp*
   (*c*) sp^2 (*d*) sp^3d^2.

2. Which one of the following compounds has delocalized electrons ?
   (*a*) Methane (*b*) Ethane
   (*c*) Cyclohexane (*d*) Benzene.

3. Which of the following shows position isomerism ?
   (*a*) butane and isobutane
   (*b*) *cis*- and *trans*- but-2-ene
   (*c*) chair and boat forms of cyclohexane
   (*d*) 1, 2-, 1, 3- and 1, 4-dimethylbenzenes.

4. The state of hybridization of the asterisked carbon in $CH_3CH = \overset{*}{C} = CH_2$ is :
   (*a*) *sp* (*b*) sp^2
   (*c*) sp^3 (*d*) none of these.

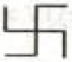
5. Which of the following are isomers ?
   (*a*) Ethyl alcohol and dimethyl ether
   (*b*) Methyl alcohol and dimethyl ether
   (*c*) Acetone and acetaldehyde
   (*d*) Propionic acid and propanone.

6. Which of the following represents a homologous series ?
   (*a*) ethane, ethylene, ethyne

ANSWERS

1. *a* **2.** *d* **3.** *d* **4.** *a* **5.** *a*

(*b*) methane, methanol, methanal
(*c*) methane, ethane, propane
(*d*) 1-hexene, 2-hexene, 3-hexene.

7. The IUPAC for the hydrocarbon represented by the Swastik sign is 
(*a*) Neononane (*b*) Tetraethylcarbon
(*c*) 2-Ethylpentane (*d*) 3, 3-Diethylpentane.

8. The members of a homologous series have
(*a*) Different general formulae
(*b*) Different molecular weights
(*c*) Different methods of preparation
(*d*) Different chemical properties.

9. For the compound,
$CH_3—CHCl—CHCl—CH_2CH_2CH_2CH_2CH_2Cl$,
the correct set of locants is
(*a*) 1, 1, 2, 7 (*b*) 1, 6, 7, 7
(*c*) 1, 6, 7 (*d*) 2, 3, 8

10. The common and IUPAC names for the group, $(CH_3)_2CHCH_2$— respectively are
(*a*) Isobutyl, 2-methylpropyl
(*b*) Isobutyl, 1-methylpropyl
(*c*) *tert*-Butyl, 1, 1-dimenthylethyl
(*d*) *sec*-Butyl, 2-methylpropyl

11. The IUPAC for the compound


—CH(CH$_3$)$_2$ is

(*a*) 2-Cyclopentylpropane
(*b*) 1, 1-Dimethyl-1-cyclopentylmethane
(*c*) (1-Methylethyl)cyclopentane
(*d*) 1-Cyclopentylpropane

12. Which of the following species is an electrophile ?
(*a*) H_2O (*b*) NH_3
(*c*) C_2H_5OH (*d*) SO_3

13. Which of the following species is a nucleophile ?
(*a*) $\overset{+}{NO_2}$ (*b*) $:NO_2^-$
(*c*) $:CX_2$ (*d*) $\bullet CH_3$

14. Which of the following series contains only electrophiles ?
(*a*) H_2O, SO_3, H_3O^+ (*b*) NH_3 ; $H_2O, AlCl_3$
(*c*) $AlCl_3, SO_3, \overset{+}{NO_2}$ (*d*) $H_2O, \overset{+}{Cl}, NH_3$

15. Out of the following, the one containing only nucleophiles is
(*a*) NH_3, CN^-, CH_3OH (*b*) $AlCl_3, BF_3, NH_3$
(*c*) $AlCl_3, NH_2^-, H_2O$ (*d*) $RNH_2, : CX_2, H^-$

16. The C—C bond length in propene is little shorter (1·49 Å) than the C—C bond length (1·54 Å) in ethane. This is due to
(*a*) +I-effect of CH_3 group
(*b*) Mesomeric effect (*c*) Electromeric effect
(*d*) Hyperconjugation effect.

17. The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane will be about
(*a*) 120° and 109·5° (*b*) 90° and 109·5°
(*c*) 109·5° and 90° (*d*) 109·5° and 120°
(I.I.T. 1988)

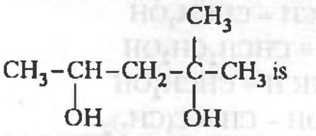
18. The compound with an isopropyl group is
(*a*) 2, 2, 3, 3-Tetramethylpentane
(*b*) 2, 2-Dimethylpentane
(*c*) 2, 2, 3, Trimethylpentane
(*d*) 2-Methylpentane. *(I.I.T. 1989)*

19. The number of isomers of C_6H_{14} is :
(*a*) 4 (*b*) 5
(*c*) 6 (*d*) 7.
(M.L.N.R. Allahabad 1990)

20. The C—H bond distance is longest in
(*a*) C_2H_2 (*b*) C_2H_4
(*c*) C_2H_6 (*d*) $C_2H_2Br_2$
(I.I.T. 1989 ; M.L.N.R. Allahabad 1990)

21. How many acyclic isomers are possible for $C_4H_{10}O$?
(*a*) 7 (*b*) 4
(*c*) 5 (*d*) 6.
(M.L.N.R. Allahabad 1992)

22. The IUPAC name for


$CH_3-\underset{OH}{CH}-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$ is

(*a*) 1, 1-Dimethyl-1-3-butanediol
(*b*) 4-Methyl-2, 4-pentanediol
(*c*) 2-Methyl-2, 4-pentanediol
(*d*) 1, 3, 3-Trimethyl-1, 3-propanediol.
(M.L.N.R. Allahabad 1992)

ANSWERS

6. *c*	**7.** *d*	**8.** *b*	**9.** *c*	**10.** *a*	**11.** *c*	**12.** *d*	**13.** *b*	**14.** *c*	**15.** *a*
16. *d*	**17.** *a*	**18.** *d*	**19.** *b*	**20.** *c*	**21.** *a*	**22.** *c*			

23. The most stable free radical among the following is

(*a*) $C_6H_5CH_2\dot{C}H_2$ (*b*) $C_6H_5\dot{C}HCH_3$

(*c*) $CH_3\dot{C}H_2$ (*d*) $CH_3\dot{C}HCH_3$

(G.A.T.E. 1992)

24. Which of the following has a bond formed by overlap of $sp - sp^3$ hybrid orbitals ?

(*a*) $CH_3-C\equiv C-H$

(*b*) $CH_3-CH=CH-CH_3$

(*c*) $CH_2=CH-CH=CH_2$

(*d*) $HC\equiv CH$. *(M.L.N.R. Allahabad 1993)*

25. What is the decreasing order of stability of the ions ?

I. $CH_3—\overset{+}{C}H—CH_3$ II. $CH_3—\overset{+}{C}H—OCH_3$

III. $CH_3—\overset{+}{C}H—COCH_3$

(*a*) I > II > III (*b*) II > III > I

(*c*) III > I > II (*d*) II > I > III

(I.I.T. 1993)

26. The maximum number of carbon atoms arranged linearly in the molecule,

$CH_3-C\equiv C-CH=CH_2$ is

(*a*) 5 (*b*) 4

(*c*) 3 (*d*) 2.

(I.S.M. Dhanbad 1994)

27. Which of the following molecular formulae belongs to the alkyne series ?

(*a*) C_7H_{14} (*b*) $C_{10}H_{22}$

(*c*) C_9H_{16} (*d*) $C_{16}H_{32}$.

(C.B.S.E. P.M.T. 1994)

28. The structure of 4-methyl-2-penten-1-ol is

(*a*) $CH_3CH_2CH=CHCH_2OH$

(*b*) $(CH_3)_2C=CHCH_2CH_2OH$

(*c*) $(CH_3)_2CHCH=CHCH_2OH$

(*d*) $CH_3CHOH-CH=C(CH_3)_2$

(C.B.S.E. P.M.T. 1994)

29. The order of decreasing stability of the carbanions is :

$(CH_3)_3C^-$ (I) ; $(CH_3)_2CH^-$ (II) ; $CH_3CH_2^-$ (III) ; $C_6H_5CH_2^-$ (IV) is

(*a*) I > II > III > IV (*b*) IV > III > II > I

(*c*) IV > I > II > III (*d*) I > II > IV > III

(Haryana C.E.E.T. 1996)

30. The number and type of bonds between two carbon atoms in CaC_2 are :

(*a*) one sigma (σ) and one pi (π) bonds

(*b*) one sigma (σ) and two pi (π) bonds

(*c*) one sigma (σ) and one and a half pi (π) bonds

(*d*) one sigma (σ) bond *(I.I.T. 1996)*

31. The cylindrical shape of an alkyne is due to

(*a*) three sigma carbon-carbon bonds

(*b*) three π-carbon-carbon bonds

(*c*) two sigma carbon-carbon and one π-carbon-carbon bond

(*d*) one sigma carbon-carbon and two π-carbon-carbon bonds *(C.B.S.E. P.M.T. 1997)*

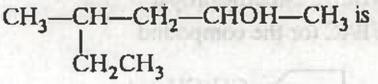
32. Number of isomers of C_4H_9- is

(*a*) 2 (*b*) 3

(*c*) 4 (*d*) None of these.

(A.F.M.C. 1997)

33. IUPAC name of the compound



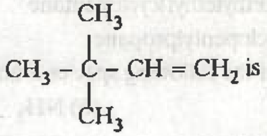
$CH_3—\underset{\large CH_2CH_3}{\underset{|}{CH}}—CH_2—CHOH—CH_3$ is

(*a*) 4-Methyl-3-hexanol (*b*) Heptanol

(*c*) 4-Methyl-2-hexanol (*d*) None of these.

(A.F.M.C. 1997)

34. The IUPAC name of the compound having the formula



$CH_3-\overset{\large CH_3}{\overset{|}{\underset{\large CH_3}{\underset{|}{C}}}}-CH=CH_2$ is

(*a*) 3, 3, 3-Trimethylpropene

(*b*) 1, 1, 1-Trimethyl-2-pentene

(*c*) 3, 3-Dimethyl-1-butene

(*d*) 2, 2-Dimethyl-3-butene.

(I.I.T. 1984 ; A.I.I.M.S. 1997)

35. The enolic form of acetone contains :

(*a*) 9 sigma bonds, 1 pi bond and two lone pairs

(*b*) 8 sigma bonds, 2 pi bonds and two lone pairs

(*c*) 10 sigma bonds, 1 pi bond and one lone pair

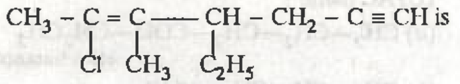
(*d*) 9 sigma bonds, 2 pi bonds and one lone pair

(I.I.T. 1990 ; A.I.I.M.S. 1997)

ANSWERS

23. *b* **24.** *a* **25.** *d* **26.** *b* **27.** *c* **28.** *c* **29.** *b* **30.** *b* **31.** *d* **32.** *c*
33. *c* **34.** *c* **35.** *a*

36. The IUPAC name of

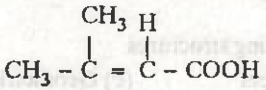


$CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-C\equiv CH$ is

(*a*) 6-Chloro-4-ethyl-5-methylhept-5-en-1-yne
(*b*) 6-Chloro-4-ethyl-5-methylhept-1-yn-5-ene
(*c*) 2-Chloro-4-ethyl-3-methylhep-2-en-6-yne
(*d*) 2-Chloro-4-ethyl-3-methylhep-6-yn-2-ene.
(M.P.C.E.E. 1998)

37. The correct IUPAC name of the compound with molecular formula, $(CH_3)_3C-CH_3$ is
(*a*) Pentane (*b*) 1, 1, 1-Trimethylethane
(*c*) 2, 2-Dimethylpropane
(*d*) Neopentane. *(Haryana C.E.E.T. 1998)*

38. The IUPAC name for the formula



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-COOH$

(*a*) 2-Methyl-2-butenoic acid
(*b*) 3-Methyl-3-butenoic acid
(*c*) 3-Methyl-2-butenoic acid
(*d*) 2-Methyl-3-butenoic acid. *(Pb. P.M.T. 1998)*

39. The IUPAC name of the compound having the formula, Cl_3CCH_2CHO is
(*a*) 3, 3, 3-Trichloropropanal
(*b*) 1, 1, 1-Trichloropropanal
(*c*) 2, 2, 2-Trichloropropanal
(*d*) Chloral. *(M.P. P.M.T. 1998)*

40. Which of the following is correct regarding the —I-effect of the substituents ?
(*a*) $-NR_2 < -OR < -F$
(*b*) $-NR_2 > -OR < -F$
(*c*) $-NR_2 < -OR > -F$
(*d*) $-NR_2 > -OR > -F$ *(C.B.S.E. P.M.T. 1998)*

41. Which of the following is an electrophile ?
(*a*) H_2O (*b*) NH_3
(*c*) $AlCl_3$ (*d*) $C_2H_5NH_2$
(I.M.S. B.H.U. 1998)

42. Which of the following carbon atoms is likely to possess tetrahedral geometry ?

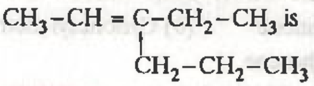
$$\overset{4}{H_2C}=\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{COOH}$$

(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4 *(C.P.M.T. 1999)*

43. Bond length of ethane (I), ethene (II), acetylene (III) and benzene (IV) follows the order
(*a*) I > II > III > IV (*b*) I > II > IV > III
(*c*) I > IV > II > III (*d*) III > IV > II > I
(C.P.M.T. 1999)

44. The compounds $CH_3-O-C_3H_7$ and $C_2H_5-O-C_2H_5$ exhibit
(*a*) optical isomerism (*b*) *cis-trans* isomerism
(*c*) metamerism (*d*) chain isomerism
(A.F.M.C. 1999)

45. The IUPAC name of the following compound



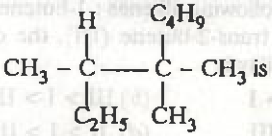
$CH_3-CH=\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{|}{C}}-CH_2-CH_3$ is

(*a*) 3-Ethyl-2-hexene (*b*) 3-Propyl-2-hexene
(*c*) 3-Propyl-3-hexene (*d*) 4-Ethyl-4-hexene.
(C.P.M.T. 1999)

46. In the compound, $CH_2=CH-CH_2-CH_2-C\equiv CH$, the C_2-C_3 bond is of the type.
(*a*) $sp-sp^2$ (*b*) sp^3-sp^3
(*c*) $sp-sp^3$ (*d*) sp^2-sp^3 *(I.I.T. 1999)*

47. The number of possible alkynes with molecular formula C_5H_8 is
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5 *(M.P. P.M.T. 2000)*

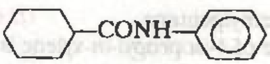
48. The IUPAC name of



$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}}-\overset{\displaystyle C_4H_9}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_3$ is

(*a*) 2-Butyl-2-methyl-2-ethylbutane
(*b*) 2-Ethyl-3, 3-dimethylheptane
(*c*) 3, 4, 4-Trimethylheptane
(*d*) 3, 4, 4-Trimethyloctane.
(B.H.U. 1998, Karnataka C.E.T. 2000)

49. The IUPAC name of



is

(*a*) N-Cyclohexylbenzamide
(*b*) N-Phenyl-N-cyclohexylmethanamide
(*c*) N-Phenylcyclohexanecarboxamide
(*d*) N-Cyclohexyl-N-phenylmethanamide.
(D.C.E. 2000)

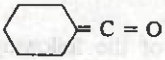
ANSWERS

36. *a* 37. *c* 38. *c* 39. *a* 40. *a* 41. *c* 42. *b* 43. *c* 44. *c* 45. *a*
46. *d* 47. *b* 48. *d* 49. *c*

50. IUPAC name of acraldehyde is
(*a*) Prop-2-en-1-al (*b*) Propenyl aldehyde
(*c*) But-2-en-1-al (*d*) Propenal.
(M.P.P.M.T. 2000)

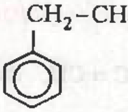
51. The IUPAC name of $CH_3CH = CHCOOC_2H_5$ is
(*a*) Ethyl but-1-enoate (*b*) Ethyl but-2-enoate
(*c*) Ethyl prop-2-enoate (*d*) None of these.
(Haryana C.E.E.T. 2000)

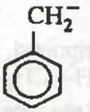
52. The IUPAC name of



is
(*a*) Cyclohexanone (*b*) Cyclohexyl methanone
(*c*) Oxycyclohexene
(*d*) Cyclohexylidenemethanone. *(D.C.E. 2000)*

53. The most stable carbanion among the following is

(*a*)


(*b*)


(*c*)


(*d*)


(D.C.E. 2000)

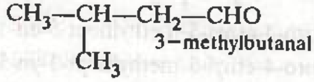
54. Among the following alkenes : 1-butene (I), cis-2-butene (II), trans-2-butene (III), the decreasing order of stability is
(*a*) III > II > I (*b*) III > I > II
(*c*) I > II > III (*d*) II > I > III.
(C.B.S.E. 2000)

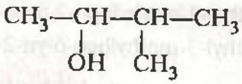
55. The compound which contains all the four 1°, 2°, 3°, 4° carbon atoms is
(*a*) 2, 3-Dimethylpentane
(*b*) 3-Chloro-2, 3-dimethylpentane
(*c*) 2, 3, 4-Trimethylpentane
(*d*) 3, 3-Dimethylpentane *(D.C.E. 2000)*

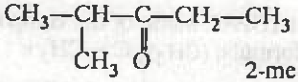
56. IUPAC name of 4-isopropyl-*m*-xylene is
(*a*) 1-Isopropyl-2, 4-dimethylbenzene
(*b*) 4-Isopropyl-*m*-xylene
(*c*) 1-Isopropyl-3, 5-dimethylbenzene
(*d*) 4-Isopropyl-3, 5-dimethylbezene.
(D.P.M.T. 2002)

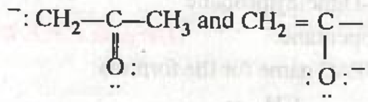
57. Which of the following compound has wrong IUPAC name ?

(*a*) $CH_3—CH_2—CH_2—COO—CH_2CH_3$
ethyl butanoate

(*b*)

$CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—CHO$
3−methylbutanal

(*c*)

$CH_3—\underset{OH}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_3$ 2-methyl-3-butanol

(*d*)

$CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{O}{\underset{\|}{C}}—CH_2—CH_3$
2-methyl-3-pentanone
(A.I.E.E.E. 2002)

58.

$^-:CH_2—\underset{\ddot{O}:}{\underset{\|}{C}}—CH_3$ and $CH_2 = \underset{:\ddot{O}:^-}{\underset{|}{C}}— CH_3$ are

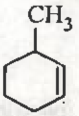
(*a*) Resonating structures
(*b*) Tautomers (*c*) Geometrical isomers
(*d*) Optical isomers *(C.B.S.E. P.M.T. 2002)*

59. The arrangement of $(CH_3)_3C—$, $(CH_3)_2CH—$, $CH_3CH_2—$ when attached to benzene or unsaturated group in increasing order of inductive effect is
(*a*) $(CH_3)_3C— < (CH_3)_2CH— < CH_3CH_2—$
(*b*) $CH_3CH_2— < (CH_3)_2CH— < (CH_3)_3C—$
(*c*) $(CH_3)_2CH— < (CH_3)_3C— < CH_3CH_2—$
(*d*) $(CH_3)_3C— < CH_3CH_2— < (CH_3)_2CH—$
(A.I.E.E.E. 2002)

60. The reaction,

$$(CH_3)_3C—Br \xrightarrow{H_2O} (CH_3)_3C—OH \text{ is}$$

(*a*) elimination reaction
(*b*) substitution reaction
(*c*) free radical reaction
(*d*) addition reaction. *(A.I.E.E.E. 2002)*

61. The IUPAC name of


is

(*a*) 3-methylcyclohexene
(*b*) 1-methylcyclohex-2-ene
(*c*) 6-methylcyclohexene
(*d*) 1-methylcyclohex-5-ene *(A.I.I.M.S. 2003)*

ANSWERS

50. *a* **51.** *b* **52.** *d* **53.** *d* **54.** *a* **55.** *b* **56.** *a* **57.** *c* **58.** *a* **59.** *a*
60. *b* **61.** *a*

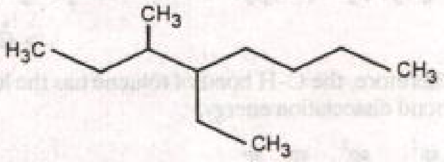
62. The IUPAC name of $CH_3COCH(CH_3)_2$ is
(*a*) 3-methyl-2-butanone
(*b*) Isopropyl methyl ketone
(*c*) 2-methyl-3-butanone
(*d*) 4-methyl isopropyl ketone *(A.I.E.E.E. 2003)*

63. Which of the following is a dehydrohalogenation reaction ?
(*a*) $C_2H_5Cl + aq.\ KOH \longrightarrow CH_2 = CH_2 + KCl + H_2O$
(*b*) $BrCH_2{-}CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$
(*c*) $CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$
(*d*) Both (*a*) and (*b*) *(M.G.I.M.S. Wardha 2003)*

64. Which of the following compounds possesses the C–H bond with the lowest bond dissociation energy ?
(*a*) Toluene (*b*) Benzene
(*c*) *n*-Pentane (*d*) 2, 2-Dimethylpropane *(A.I.I.M.S. 2003)*

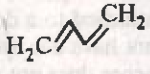
65. The general formula $C_n H_{2n} O_2$ could be for open chain
(*a*) dialdehydes (*b*) diketones
(*c*) carboxylic acids (*d*) diols *(A.I.E.E.E. 2003)*

66. Name of the compound given below is



(*a*) 4-ethyl-3-methyloctane
(*b*) 3-methyl-4-ethyloctane
(*c*) 2, 3-diethylheptane
(*d*) 5-ethyl-6-methyloctane *(C.B.S.E. P.M.T. 2003)*

67. Which of the following represents the given mode of hybridization $sp^2{-}sp^2{-}sp{-}sp$ from left to right ?
(*a*) $H_2C{=}CH{-}C{\equiv}N$ (*b*) $HC{\equiv}C{-}C{\equiv}CH$
(*c*) $H_2C{=}C{=}C{=}CH_2$ (*d*)

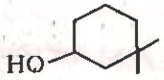


(I.I.T. 2003)

68. Which of the following is the most stable cation ?
(*a*) $F_3C{-}CH_2^+$ (*b*) $(CH_3)_2CH^+$
(*c*) CH_3^+ (*d*) CF_3^+ *(J & K C.E.T. 2004)*

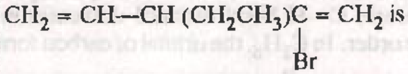
69. A molecule of urea can show
(*a*) Chain isomerism (*b*) Position isomerism
(*c*) Geometrical isomerism
(*d*) Optical isomerism
(*e*) Tautomerism *(Kerala M.E.E. 2004)*

70. The IUPAC name of the compound



is
(*a*) 1, 1-dimethyl-3-cyclohexanol
(*b*) 1, 1-dimethyl-3-hydroxycylohexane
(*c*) 3, 3-dimethyl-1-cyclohexanol
(*d*) 3, 3-dimethyl-1-hydroxycyclohexane *(A.I.E.E.E. 2004)*

71. IUPAC name of



$CH_2 = CH{-}CH\,(CH_2CH_3)\underset{\mid\atop Br}{C} = CH_2$ is
(*a*) 4-bromo-3-ethyl-1, 4-pentadiene
(*b*) 2-bromo-3-ethyl-1, 4-pentadiene
(*c*) 2-bromo-3-ethyl-1, 5-pentadiene
(*d*) none of these *(Orissa J.E.E. 2004)*

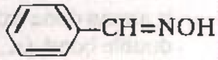
72. The IUPAC name of $CH_3CH_2C(Br) = CHCl$ is
(*a*) 4-Chloro-3-bromobutene-3
(*b*) 2-Bromo-1-chlorobutane
(*c*) 2-Bromo-1-chloroebutene-1
(*d*) 2-Bromo-2-ethyl-3-chloropropene *(C.P.M.T. 2004)*

73. The IUPAC name of the following compound

is
(*a*) Propionic anhydride
(*b*) Dipropanoic anhydride
(*c*) Ethoxypropanoic acid
(*d*) Propanoic anhydride *(J & K C.E.T. 2004)*

74. Tautomerism is not exhibited by
(*a*)

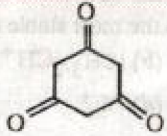
(*b*)



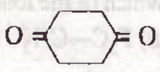
ANSWERS

62. *a* 63. *a* 64. *a* 65. *c* 66. *a* 67. *a* 68. *a* 69. *e* 70. *c* 71. *b*
72. *c* 73. *d*

(*c*)



(*d*)



(J & K C.E.T. 2004)

75. Identify the *correct* statement from below concerning the structure of $CH_2 = C = CH_2$

(*a*) The molecule is planar

(*b*) One of the three carbon atoms is in an sp^3-hybridized state

(*c*) The molecule is non-planar with the two CH_2 groups being in planar perpendicular to each other

(*d*) All the carbon atoms are *sp*-hybridized.

(*e*) The molecule is bent with the —C—C—C— angle being 120° *(Kerala E.E.E. 2004)*

76. Orbital interaction between the sigma bonds of a substituent group and the neighbouring pi-orbital is known as

(*a*) hyperconjugation

(*b*) inductive effect

(*c*) steric effect

(*d*) dipole-dipole interactions

(*e*) electric quadrruple interactions

(Kerala M.E.E. 2004)

HINTS/EXPLANATIONS to Multiple Choice Questions

4. *sp* ; the asterisked carbon forms two π-bonds and hence it is *sp*-hybridized.

17. The ClCCl in tetrachlorethene is 120° while in CCl_4 it is 109°—28′.

20. As the size of the hybrid orbital of carbon forming C—H bond decreases in the order $sp^3 > sp^2 > sp$, therefore, C—H bond distance decreases in the same order. In C_2H_6, the orbital of carbon forming C—H bond is sp^3 and hence C—H bond distance is the longest.

21. Seven out of which four are alcohols :

(*i*) $CH_3CH_2CH_2CH_2OH$, (*ii*) $(CH_3)_2CHCH_2OH$,

(*iii*) $CH_3CH_2CHOHCH_3$,

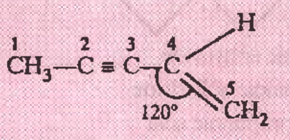
(*iv*) $(CH_3)_3COH$ and three are ethers,

(*v*) $CH_3CH_2OCH_2CH_3$,

(*vi*) $CH_3OCH_2CH_2CH_3$ and

(*vii*) $CH_3OCH(CH_3)_2$.

26. Only carbon atoms marked as 1, 2, 3 and 4 lie along a line while the fifth one is inclined to this line at angle of 120° as shown :



46. When both double and triple bonds are present in a molecule and if there is a choice, the numbering is always done from that end which is nearer to the double bond, *i.e.*,

$\overset{1}{C}H_2 = \overset{2}{C}H—\overset{3}{C}H_2—\overset{4}{C}H_2—\overset{5}{C} \equiv \overset{6}{C}H$. Thus, the $C_2—C_3$ bond is of the type $sp^2 - sp^3$.

47. Three. These are $CH_3CH_2CH_2C \equiv CH$, $(CH_3)_2CH - C \equiv CH$ and $CH_3CH_2C \equiv CCH_3$.

64. More stable the free radical formed upon homolytic fission of C–H bond, lesser is the bond dissociation energy. Since the stability of the radicals formed from toluene, benzene, *n*- pentane, 2, 2-dimethylpropane follows the order :

$$C_6H_5\dot{C}H_2 > (CH_3)_3\dot{C} > CH_3\dot{C}HCH_2CH_2CH_3 > \dot{C}_6H_5,$$

therefore, the C–H bond of toluene has the lowest bond dissociation energy.

67. $H_2\overset{sp^2}{C} = \overset{sp^2}{C}H - \overset{sp}{C} \equiv \overset{sp}{N}$

68. Carbocations are stabilized by +I-effect of CH_3 groups and destablized by —I-effectof F atoms. Therefore, $(CH_3)_2\overset{+}{C}H$ is the most stable carbocation.

74. Essential condition for tautomerism in the presence of an α-hydrogen on a saturated carbon attached to C = O, NO, NO_2 etc. or should have a H-atom present on a heteroatom (O, N, S etc.) attached to a double bond. Thus, option (*a*) does not have a α-hydrogen on a saturated carbon and hence does not exhibit tautomerism.

ANSWERS

74. *a* **75.** *c* **76.** *a*

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) If both Assertion and Reason are true and the Reason is the correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but reason is not a correct explanation of the 'Assertion'.

(*c*) If Assertion is true but Reason is false.

(*d*) If Assertion is false but Reason is true.

(*e*) If both Assertion and Reason are false.

	Assertion	**Reason**
1.	C_4H_6 represents a bicycloalkane.	The general formula for bicycloalkanes is C_nH_{2n}.
2.	But-1-ene and 2-methylprop-1-ene are position isomers.	Position isomers have same molecular formula but differ in the position of the functional group.
3.	All the carbon atoms of but-2-ene lie in one plane.	All the carbon atoms in but-2-ene are sp^2-hybridized.
4.	Alkanes having more than three carbon atoms exhibit chain isomerism.	All carbon atoms in alkanes are sp-hybridized. *(A.I.I.M.S. 1994)*
5.	Metamers can also be chain or position isomers.	The term tautomerism was introduced by Laar to explain the chemical reactivity of a substance according to two possible structures. *(A.I.I.M.S. 1999)*
6.	In $CH_2 = C = CH_2$ all the carbon atoms are sp^2-hybridized.	All the carbon atoms are linked to each other by a double bond.
7.	Butane and 2-methylbutane are homologues.	Butane is a straight chain alkane while 2-methylbutane is a branched chain alkane.

True/False Statements

Which of the following statements are true and which are false ? Rewrite the false statements correctly.

1. 2, 2-Dimethylbutane and 2-methylbutane are chain isomers of hexane.
2. Acetylene is a tetrahedral molecule.
3. In benzene, carbon uses all the three *p*-orbitals for hybridization. *(I.I.T. 1987)*
4. The members of a homologous series can be represented by a general formula.
5. Propanoic acid and methyl ethanoate are isomers.
6. Inductive effect involves displacement of σ-electrons.
7. Electromeric effect is a permanent effect.
8. Simple carbanions are isoelectronic and isostructural with ammonia.
9. Free radicals are produced by heterolyic fission of covalent bonds.
10. Carbocations are planar species.

Fill In The Blanks

1. An atom or a group of atoms present in a molecule which largely determines its chemical properties is called the .... group.
2. The consecutive members of a homologous series differ by a ..... group.
3. The IUPAC name of succinic acid is.... *(I.I.T. 1994)*
4. In methane, carbon exhibits .... hybridization and the four hybrid orbitals are inclined at angle of ....
5. Chain isomerism arises due to different arrangements of the ....
6. Resonance energy is a measure of extra stability conferred on the molecule due to .... of electrons.
7. Lewis structures which differ in the position of electrons and not in the position of atoms are called ....
8. The real structure of benzene is a .... of two ...... structures.

9. The three isomers of xylene are called ..., ..., and ....

10. Carbon-carbon bond length in benzene is....which is intermediate between carbon-carbon single bond length of .... and carbon-carbon double bond length of ....

11. $CH_3CH_2^+$ is......stable than CH_3^+ while $CH_3CH_2^-$ is......stable than CH_3^-.

12. BF_3 is an......while NH_3 is a...... .

13. Hyperconjugation involves......conjugation while resonance involves......and......conjugation.

14. Cyanide has.....effect while methyl group has.... effect.

15. The products obtained by homolytic fission of covalent bond are called...... .

16. Heterolysis of benzyl chloride produces.....and...... .

17. Electromeric effect is a......effect in which......of electrons takes place from one atom to the other joined by a......bond.

Matching Type Questions

Match entries in **Column I** with those in **Column II**

Column I	**Column II**
1. Homologues	(*a*) Benzene
2. Isomers	(*b*) $SnCl_4$
3. sp^2-Hybridization	(*c*) $\sigma-\pi$ conjugation.
4. Hyperconjugation	(*d*) Homolysis
5. Electrophile	(*e*) Methanol and ethanol
6. Carbanion	(*f*) Butane and isobutane
7. Free radicals	(*g*) Pyramidal

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*c*) 2. (*d*) 3. (*c*) 4. (*c*) 5. (*b*) 6. (*d*) 7. (*b*).

TRUE/FALSE STATEMENTS

1. False, 2, 2-Dimethylbutane and 2, 3-dimethylbutane are chain isomers. 2. False, acetylene is a linear molecule. 3. False, in benzene carbon uses only two of the three *p*-orbitals for hybridization. 4. True 5. True 6. True 7. False, temporary effect 8. True 9. False, homolytic fission 10. True.

FILL IN THE BLANKS

1. Functional 2. CH_2 3. Butane-1, 4-dioic acid 4. sp^3, 109°—28′ 5. Carbon chain 6. delocalization 7. canonical or resonating structures 8. resonance hybrid, kekule 9. *o*-, *m*- and *p*-dimethylbenzenes 10. 139 *pm*, 154 *pm*, 134 *pm* 11. more, less 12. electrophile, nucleophile 13. $\sigma-\pi$, $\pi-\pi$ and $n-\pi$ 14. —I-effect, + I-effect 15. free radicals 16. benzyl carbocation, chloride ion 17. temporary, complete transfer, multiple.

MATCHING TYPE QUESTIONS

1.—(*e*), 2.—(*f*), 3.—(*a*), 4.—(*c*), 5.—(*b*), 6.—(*g*), 7.—(*d*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

1. *Correct reason* : The general formula for bicycloalkanes is C_nH_{2n-2}.

3. *Correct reason* : Only the carbon atoms of the double bond in but-2-ene are sp^2-hybridized.

4. *Correct reason* : There are more than one way in which more than these carbon atoms can be connected.

5. *Correct explanation* : Due to different number of carbon atoms and their arrangement on either side of the functional group, metamers can also be chain isomers or position isomers.

6. *Correct assertion.* In $CH_2 = C = CH_2$, central carbon atom is *sp*-hybridized while the terminal ones are sp^2-hybridized.

   Correct reason. The central carbon atom is linked to two σ-bonds and two π-bonds.

7. *Correct explanation.* They differ by a CH_2 group.