11A

GENERAL ORGANIC CHEMISTRY

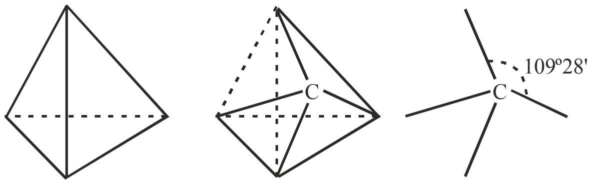
STRUCTURE AND SHAPES OF ORGANIC MOLECULES

Tetravalency of carbon :

(i) The atomic number of carbon is 6 and it has four electrons in its valence shell. In order to acquire stable inert gas configuration, it can share its electrons with the electrons of other to form four covalent bonds. Thus, carbon has a covalency of four or is tetracovalent.

(ii) In 1874, Vant Hoff and Le Bel predicted that the four bonds of carbon in methane and other saturated compounds do not lie in a plane but are directed towards the four corners of a regular tetrahedral.

(iii) It is because of this reason that Van't Hoff was awarded the first Noble Prize in Chemistry in 1901.



A Regular Tetrahedron with 4similar Faces

Space Model of Carbon Atom

The Normal Direction of Valencies

Figure : Tetrahedral representation of carbon valencies

Types of bonds :

(i) **Sigma bond :**

(a) A carbon–carbon, σ–bond can be formed by overlap of two sp^3, sp^2 or sp–hybridized orbitals of carbon atoms. Alkanes and cycloalkanes contain only sp^3–sp^3 C—C, σ–bonds, alkenes contains sp^2–sp^2, C—C σ–bonds while alkynes contain sp—sp, C—C, σ–bonds .

(b) In a similar way, carbon can form sigma bonds with hydrogen atoms, while alkanes contain only sp^3–s, C – H, σ–bonds, alkenes contain sp^2–s, C–H, σ–bonds and alkynes contain sp–s, C–H, σ–bonds

(ii) **Pi–bond :**

(a) A pi–bond is formed by sideways or lateral overlap of two p–orbitals, Thus, alkenes contain one sp^2 — sp^2, C – C, σ–bond and one π–bond.

(b) In alkynes, the carbon atoms are sp–hybridized. Therefore, alkynes contain one sp–sp, C – C, σ–bond and two π–bonds which are mutually perpendicular to each other.

(c) The two carbon atoms and two hydrogen atoms of acetylene molecule lie along a line with C – C bond angle of 180°.

Formation of organic molecules :

(i) The types of hybridizations encountered in organic compounds are sp^3 (involved in saturated organic compounds containing only single covalent bonds, eg. methane), sp^2 (involved in organic compounds having carbon linked by double bonds, e.g. ethylene) and sp (involved in organic compounds having carbon linked by a triple bond.

(ii) The bond angles and geometry associated with the three types of hybridization are :

	sp^3	sp^2	sp
Angle :	109°28'	120°	180°
Geometry :	Tetrahedral	Trigonal	Linear
Bond :	Four σ	Three σ One π,	Two σ Two π
Example:	Alkane, Cycloalkane and in saturated part of all organic molecules	Alkenes and other compoounds containing C = C, C = O, C=N * C=S	Alkynes and all other compounds containing C≡C & C≡N

(iii) **Effect of hybridization on bond length and bond strengths.**

(a) **Bond lengths :** Since a p–orbital is much bigger in size than a s–orbital of the same shell, therefore, as we go from $sp^3 \rightarrow sp^2 \rightarrow sp$, the percentage of p–character decreases from 75 → 66.7 → 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:

$$\underset{1.54\text{ Å}}{C(sp^3)-C(sp^3)} > \underset{1.34\text{Å}}{C(sp^2)-C(sp^2)} > \underset{1.20\text{ Å}}{C(sp)-C(sp)}$$

(b) **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,

$$\underset{121\text{ kcal mol}^{-1}}{C(sp)-H} > \underset{106\text{ kcal mol}^{-1}}{C(sp^2)\text{–}H} > \underset{98.6\text{ kcal mol}^{-1}}{C(sp^3)\text{–}H}$$

$$\underset{200\text{ kcal mol}^{-1}}{C(sp)-C(sp)} > \underset{142\text{ kcal mol}^{-1}}{C(sp^2)-C(sp^2)} > \underset{80\text{-}85\text{ kcal mol}^{-1}}{C(sp^3)-C(sp^3)}$$

Since the extent of overlap in sideways overlap is low, a carbon–carbon π–bond is always weaker than a carbon–carbon σ–bond. A carbon–carbon double bond is, however, stronger than a carbon–carbon single bond since it consists σ–bond and a weak π–bond. In a similar way, a carbon–carbon triple bond is still stronger than carbon–carbon double bond.

Types of carbon and hydrogen atoms :

There are four types of carbon atoms :

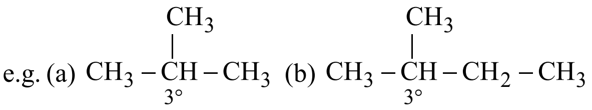
* A primary (1°) carbon atom is bonded to either one more carbon atom or to more.

eg. (a) $\overset{1^\circ}{CH_3}-\overset{1^\circ}{CH_3}$ (b) $\overset{1^\circ}{CH_3}-CH_2-\overset{1^\circ}{CH_3}$

* A secondary (2°) carbon atom is bonded to two other carbon atoms.

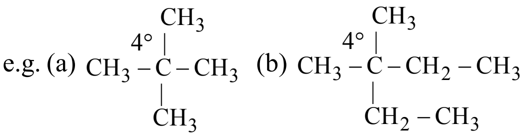
e.g. (a) $CH_3-\overset{2^\circ}{CH_2}-CH_3$ (b) $CH_3-\overset{2^\circ}{CH_2}-\overset{2^\circ}{CH_2}-CH_3$

* A tertiary (3°) carbon atom is bonded to three other carbon atoms.



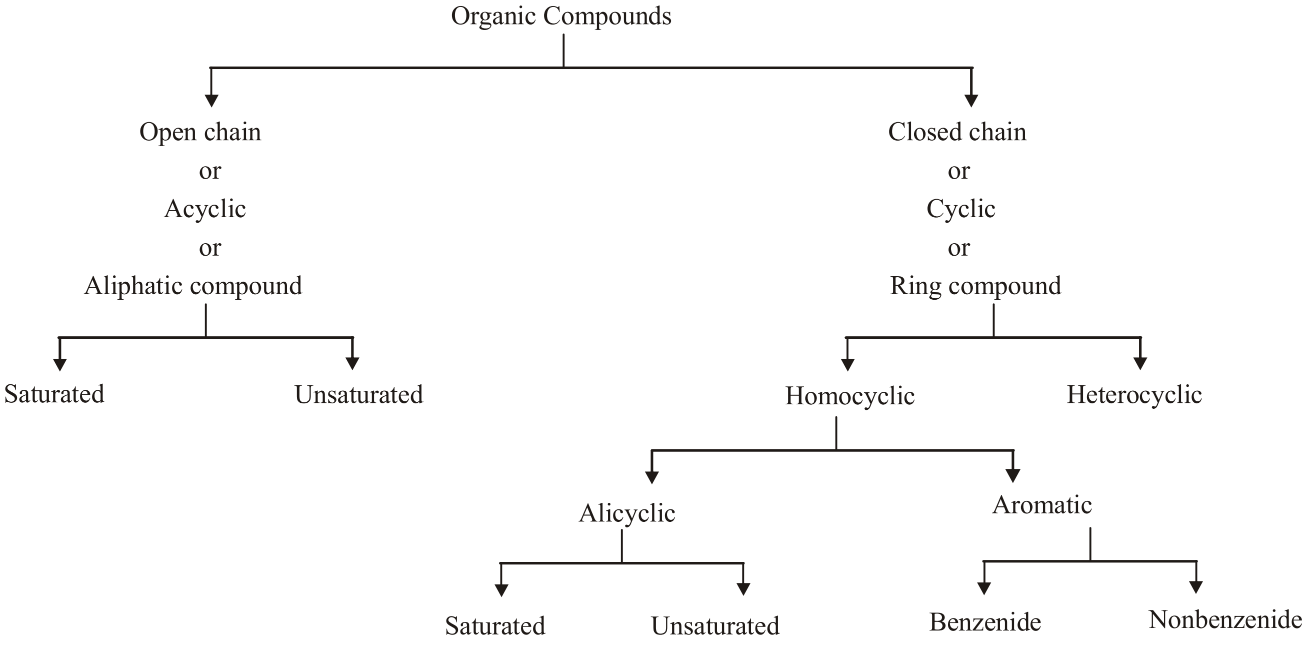
e.g. (a) $CH_3-\underset{3^\circ}{\overset{CH_3 \atop |}{CH}}-CH_3$ (b) $CH_3-\underset{3^\circ}{\overset{CH_3 \atop |}{CH}}-CH_2-CH_3$

* A quaternary (4°) carbon atom is bonded to four other carbon atoms.



e.g. (a) $CH_3-\underset{| \atop CH_3}{\overset{CH_3 \atop 4^\circ\,|}{C}}-CH_3$ (b) $CH_3-\underset{| \atop CH_2-CH_3}{\overset{CH_3 \atop 4^\circ\,|}{C}}-CH_2-CH_3$

CLASSIFICATION OF ORGANIC COMPOUNDS



Aliphatic or open chain compounds :

Those compounds in which first and last carbon atoms are not connected with each other. Branched or unbranched chains are possible in these compounds.

(i) Saturated hydrocarbons :

(a) In such type, adjacent carbons are attached with single bonds. **Ex.** $CH_3-CH_2-CH_3$

(b) General formula of these compounds is C_nH_{2n+2}.

(c) These are also called as paraffins (little reactivity) because these are less reactive due to absence of π- bonds.

(ii) Unsaturated Hydrocarbons :

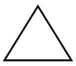
(a) There will be a double bond or a triple bond between any two carbons atoms.
$CH_2=CH-CH_3$ (Propene), $CH\equiv C-CH_3$ (Propyne)

(b) General formula is C_nH_{2n} and C_nH_{2n-2}.

(c) Alkenes are also called as olefins because they reacts with halogens to form oily substances olefins (Oleum + fines i.e. Oil forming).

(d) Due to presence of π bonds these are more reactive.

Cyclic or closed compound :

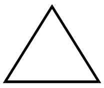
In these compounds first and last carbons are attached with each other. **Ex.**  cyclopropane.

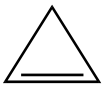
(i) Homocyclic compounds :

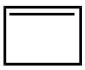
These are the compounds in which the complete ring is formed by carbon atoms only. These are also of two types-

(a) Alicyclic compounds :

These are the compounds having the properties like aliphatic compounds. These may be saturated or unsaturated like aliphatic compounds.


Cyclopropane,

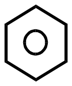

Cyclopropene

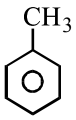

Cyclobutene

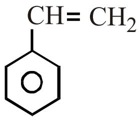
(b) Aromatic compounds : These compounds consist of at least one benzene ring i.e. a six-membered carbocyclic ring having alternate single and double bonds.

These compounds have some fragrant odour and hence, named as aromatic (greek word aroma means sweet smell)

Ex.


Benzene

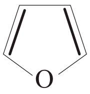

Toluene

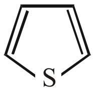

Styrene

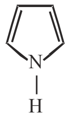
(ii) Heterocyclic compounds :

These are cyclic compounds having ring or rings built up of more than one kind of atoms.

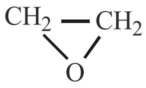
(a) Aromatic hetero cyclic compound :


Furane

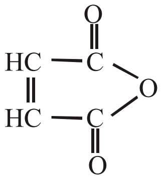

Thiophene


Pyrrole

(b) Aliphatic hetero cyclic compound :


Oxirane
or Epoxyethane
or Ethylene oxide
or dimethylene oxide
or Oxo cyclo propane

&


Maleic anhydride

GROUPS

Atom or a group of atoms which possess any 'charge' on it or any 'free valency' are called as Groups.

(i) Normal group :

(a) It is represented by 'n'.

(b) Straight chain of carbon atom is known as normal group.

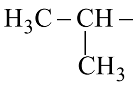
(c) Free bond will come either on Ist carbon atom or on last carbon atom.

n – butyl $C-C-C-C-$

n – propyl $C-C-C-$

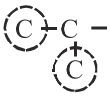
(ii) Iso group :

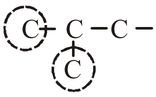
(a) It is represented by following structure :

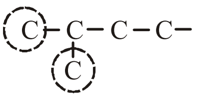


$H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}H}-$

(b) When two methyl groups are attached to the same carbon atom, group is named as iso ;

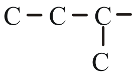

– Iso propyl ;


– Isobutyl


Isopentyl

(iii) Secondary group :

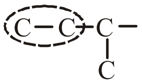
(a) t is represented by following structure –



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

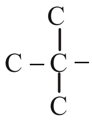
(b) When ethyl and methyl groups attached to the terminal carbon atom, group is named as secondary-

Ex.


secondary butyl

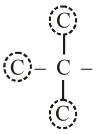
(iv) Tertiary group :

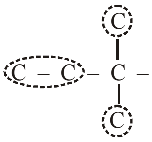
(a) It is represented by following structure :



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

(b) When three alkyl groups (similar or dissimilar) are attached to the same carbon atom, group is named as tertiary.

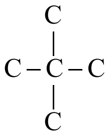

Tertiary butyl ;


Tertiary pentyl

(v) Neo group :

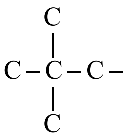
(a) When a carbon atom is attached to other four carbon atom group is named as neo group.

(b) It is represented by following structure :



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

e.g.



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

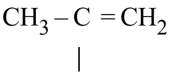
Neo pentyl

(vi) Alkyl group : When a hydrogen is removed from saturated hydrocarbon then alkyl group is formed. It is represented by R and its general formula is C_nH_{2n+1}. A bond is vacant on alkyl group on which any functional group may come.

$CH_4 \xrightarrow[-H]{} CH_3$ – Methyl

$CH_3-CH_3 \xrightarrow[-H]{} CH_3-CH_2$ – Ethyl

(vii) Alkenyl group :

$CH_2=CH-$	Vinyl (ethenyl)
$CH_2=CH-CH_2-$	Allyl (2-Propenyl)
$CH_3-CH=CH-$	Propenyl (1-propenyl)
 $CH_3-\underset{|}{C}=CH_2$	Isopropenyl

(viii) Alkynyl group :

$CH\equiv C-$	Acetynyl (Ethynyl)
$CH\equiv C-CH_2-$	Propargyl (2-propynyl)
& $CH_3-C\equiv C-$	Propynyl (1-propynyl)

HOMOLOGOUS SERIES

When structurally similar organic compounds are arranged in the order of increasing molecular weight, then the series of compounds so obtained is called a homologous series.

Characteristics of Homologous Series :

1. All the members of a homologous series can be represented by only one general formula.

2. The members of a homologous series differ in their molecular weight by 14 or its multiple and their molecular formulae by CH_2 or its multiple.

3. Physical properties of the members of a homologous series normally exhibit a regular gradual change.

4. The members of a homologous series normally exhibit similar chemical properties.

5. The members of a homologous series can be synthesised by some general methods of preparation.

6. Homologous cannot be isomers due to difference in their molecular formulae. Therefore, two or more than two isomers can never be included in the same homologous series.

Series	**Member**	**General formula**
Alkane –	CH_4, C_2H_6 etc.	C_nH_{2n+2}
Alkene –	C_2H_4, C_3H_6 etc.	C_nH_{2n}
Alkyne –	C_2H_2, C_3H_4 etc.	C_nH_{2n-2}
Alkanol –	CH_3OH, C_2H_5OH etc.	$C_nH_{2n+1}OH$
Alkanol –	$HCHO$, CH_3CHO etc.	$C_nH_{2n}O$
Alkanoic acid –	$HCOOH$, CH_3COOH etc.	$C_nH_{2n}O_2$

Alkylamines (1° or primary amines), **Dialkylamines** (2° or secondary amines) and Trialkylamines (3° or tertiary amines constitute different homologous series.

NOMENCLATURE OF ORGANIC COMPOUNDS

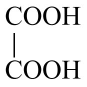
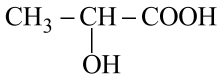
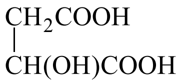
(i) Common Names or Trivial System

(ii) Derived System

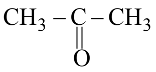
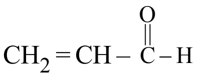
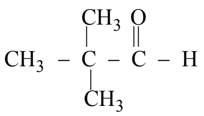
(iii) IUPAC system or Geneva System

COMMON OR TRIVIAL SYSTEM

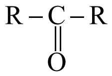
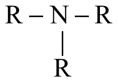
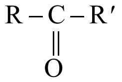
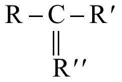
Initially organic compounds are named on the basis of source from which they were obtained.

S. No.	Organic Compound	Trivial Name	Source
1.	CH_3OH	Wood spirit or Methyl spirit	Obtained by destructive distillation of wood.
2.	C_2H_5OH	Grain Alcohol	Obtained by fermentation of Barley
3.	NH_2CONH_2	Urea	Obtained from urine
4.	CH_4	Marsh gas (fire damp)	It was produced in marsh places.
5.	CH_3COOH	Vinegar	Obtained from acetum i.e. Vinegar
6.	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Obtained from oxalis plant
7.	$HCOOH$	Formic acid [Red ant]	Obtained from formicus
8.	 $CH_3-\underset{\vert \atop OH}{CH}-COOH$	Lactic acid	Lactum = milk
9.	 $\begin{array}{l}CH_2COOH\\ \vert\\ CH(OH)COOH\end{array}$	Malic acid	Apple (Malum)
10.	$CH_3CH_2CH_2COOH$	Butyric acid	Obtained from butter

Some typical compounds in which common and trivial names are also differ.

S. No.	Compound	Trivial Name	Common Name
1.	CH_4	Marsh gas	Methane
2.	CH_3OH	Woodspirit	Methyl alcohol
3.	CH_3COOH	Vinegar	Acetic acid
4.	 $CH_3-\underset{\Vert \atop O}{C}-CH_3$	Acetone	Dimethyl ketone
5.	 $CH_2=CH-\overset{O \atop \Vert}{C}-H$	Acrolein	Acryl Aldehyde
6.	 $CH_3-\overset{CH_3 \atop \vert}{\underset{\vert \atop CH_3}{C}}-\overset{O \atop \Vert}{C}-H$	Pyvaldehyde	Tertiary valeraldehyde

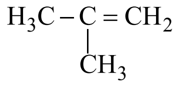
(Common – Names R is termed as alkyl -) :

S. No.	Compound	Name
1.	$R-X$	Alkyl halide
2.	$R-OH$	Alkyl alcohol
3.	$R-SH$	Alkyl thio alcohol
4.	$R-NH_2$	Alkyl amine
5.	$R-O-R$	Dialkyl ether
6.	$R-S-R$	Dialkyl thioether
7.	 $R-\underset{\underset{O}{\|}}{C}-R$	Dialkyl ketone
8.	$R-NH-R$	Dialkyl amine
9.	 $R-\underset{\underset{R}{\mid}}{N}-R$	Trialkyl amine
10.	$R-O-R'$	Alkyl alkyl' ether
11.	 $R-\underset{\underset{O}{\|}}{C}-R'$	Alkyl alkyl' ketone
12.	$R-S-R'$	Alkyl alkyl' thio ether
13.	$R-NH-R'$	Alkyl alkyl' amine
14.	 $R-\underset{\underset{R''}{\|}}{C}-R'$	Alkyl alkyl' alkyl" amine

Position of double bond :

In an unsaturated hydrocarbon if the position of double is on 1st or last carbon then it's perfix will be α (alpha) if it is on 2nd carbon it is termed as β (Beta) and the γ (gamma) and δ (delta) and so on.

Ex. $H_2C=CH-CH_2-CH_3$ α – butylene
$H_3C-CH=CH-CH_3$ β – butylene
$H_3C-CH_2-CH=CH_2$ α – butylene
$H_2C=CH-CH_3$ or $H_3C-CH=CH_2$
(Both are same positions, propylene)

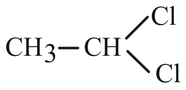

$H_3C-\underset{\underset{CH_3}{\mid}}{C}=CH_2$ Isobutylene

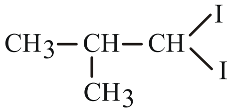
$CH_3-CH_2-CH=CH-CH_2-CH_3$ γ – hexylene
$CH_3-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_3$ δ – octylene

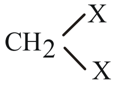
Common – Naming of dihalides :

(a) When two same halogen atoms are attached to the same carbon such compounds are called Gemdihalides.

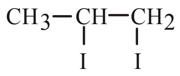
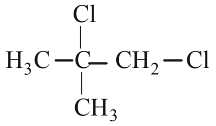
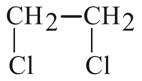
(b) Common names of such compounds are alkylidene halides.

Ex. 
$CH_3-CH\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ Ethylidene chloride


$CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CH\begin{smallmatrix}I\\I\end{smallmatrix}$ Isobutylidene Iodide

Exception :  $CH_2\begin{smallmatrix}X\\X\end{smallmatrix}$
Methylidene halide (wrong)
Methylene halide (right)

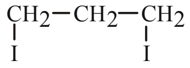
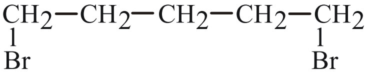
(c) When two same halogen atoms are attached to adjacent carbon, these are called as vicinal dihalides common names of such compounds are alkylene halide.

Ex.  $CH_3-\underset{\underset{I}{\mid}}{CH}-\underset{\underset{I}{\mid}}{CH_2}$  $H_3C-\overset{\overset{Cl}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-CH_2-Cl$  $\underset{\underset{Cl}{\mid}}{CH_2}-\underset{\underset{Cl}{\mid}}{CH_2}$

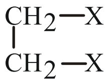
Propylene Iodide Isobutylene chloride Ethylene chloride

(d) When two same halogen atoms are attached at the two ends of a carbon chain its common naming will be polymethylene halide. **'poly'** word indicates the number of $-CH_2-$ groups.

$-CH_2-$	2	3	4	5	6
Poly	di	tri	tetra	penta	hexahexa

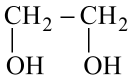
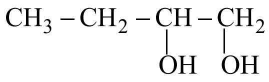
Ex.  $\underset{\underset{I}{\mid}}{CH_2}-CH_2-\underset{\underset{I}{\mid}}{CH_2}$  $\underset{\underset{Br}{\mid}}{CH_2}-CH_2-CH_2-CH_2-\underset{\underset{Br}{\mid}}{CH_2}$

Trimethylene Iodide Pentamethylene Bromide

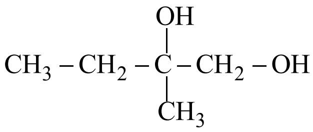
Exception :  $\begin{matrix}CH_2-X\\ \mid\\ CH_2-X\end{matrix}$
dimethylene halide (wrong)
ethylene halide (right)

Common – Naming of di-hydroxy compounds :

(a) When two – OH groups are attached to adjacent carbon's they are termed as alkylene glycol.

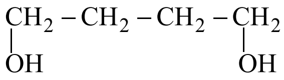
Ex.  $\underset{\underset{OH}{\mid}}{CH_2}-\underset{\underset{OH}{\mid}}{CH_2}$  $CH_3-CH_2-\underset{\underset{OH}{\mid}}{CH}-\underset{\underset{OH}{\mid}}{CH_2}$

Ethylene glycol Butylene glycol

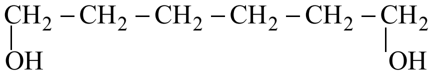

$CH_3-CH_2-\overset{\overset{OH}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-CH_2-OH$

Active amylene glycol

(b) When two – OH group are attached at the two ends of a carbon chain, these compounds are named as polymethylene glycol. Poly → Number of CH_2 groups.

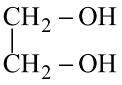
Ex.  $\underset{\underset{OH}{\mid}}{CH_2}-CH_2-CH_2-\underset{\underset{OH}{\mid}}{CH_2}$

Tetra methylene glycol


$\underset{\underset{OH}{\mid}}{CH_2}-CH_2-CH_2-CH_2-CH_2-\underset{\underset{OH}{\mid}}{CH_2}$

Hexamethylene glycol

Exception :

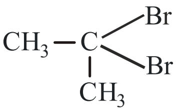
 $\begin{matrix}CH_2-OH\\ \mid\\ CH_2-OH\end{matrix}$
dimethylene glycol (wrong)
ethylene glycol (right)

Example 1 :

Make the structure of following organic compounds –

1. Isopropylidene Bromide
2. Active amylene Iodide
3. Isobutylene glycol
4. Isobutylene
5. Trimethylene glycol

Sol. 1.



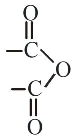
2. $CH_3-\overset{I}{\underset{CH_2}{C}}-CH_2-I$ $\quad CH_3$

3. $CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-OH$

4. $H_3C-\underset{CH_3}{C}=CH_2$

5. $\underset{OH}{CH_2}-CH_2-\underset{OH}{CH_2}$

Common – Naming of the functional group having carbon :

Functional group	Suffix
$-\overset{O}{\overset{\|}{C}}-H$	-aldehyde
$-\overset{O}{\overset{\|}{C}}-OH$	-ic Acid
$-\overset{O}{\overset{\|}{C}}-X$	-yl halide
$-\overset{O}{\overset{\|}{C}}-NH_2$	-amide
$-C\equiv N$	-o-nitrile
$-N\overset{\to}{\equiv}C$	-oisonitrile
$-\overset{O}{\overset{\|}{C}}-O-R$	-ate
	-ic anhydride

No. of Carbon		Prefix
1 Carbon	→	Form-
2 Carbon	→	Acet-
3 Carbon	→	Propion-
4 Carbon	→	Butyr → Normal → Iso
5 Carbon	→	Valer → Normal – → Iso – → Secondary – → Tertiary –
3 C + (=) double bond	→	Acryl-
4 C + double bond	→	Croton-

Ex. $H-\overset{O}{\overset{\|}{C}}-H$ $\qquad CH_3-\overset{O}{\overset{\|}{C}}-O-H$

Formaldehyde $\qquad$ Acetic Acid

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

Propionyl chloride $\qquad$ Acetaldehyde

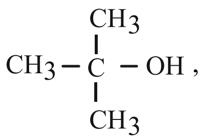
DERIVED SYSTEM

According to this system name to any compound is given according to the parent name of the homologous series. This system is reserved for the following nine homologous series.

S. No.	Name of Homologous	Derived Name	Structure of group
1.	Alkane	Methane	$-\overset{\|}{\underset{\|}{C}}-$
2.	Alkene	Ethylene	$>C=C<$
3.	Alkyne	Acetylene	$-C\equiv C-$
4.	Alkanol	Carbinol	$-\overset{\|}{\underset{\|}{C}}-OH$
5.	Alkanal	Acetalddehyde	$-\overset{\|}{\underset{\|}{C}}-CHO$
6.	Alkanoic acid	Acetic acid	$-\overset{\|}{\underset{\|}{C}}-COOH$
7.	Alkanoyl halide	Acetyl halide	$-\overset{\|}{\underset{\|}{C}}-COX$
8.	Alkanamide	Acetamide	$-\overset{\|}{\underset{\|}{C}}-CONH_2$
9.	Alkanone	Acetone	$-\overset{\|}{\underset{\|}{C}}-\underset{\underset{O}{\|}}{C}-\overset{\|}{\underset{\|}{C}}-$

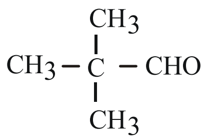
Ex. $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$, $\qquad CH_3-C\equiv C-CH_3$

Tetra methyl Methane $\qquad$ Dimethyl Acetylene



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

Trimethyl Carbinol



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

Trimethyl Acetalddehyde

I.U.P.A.C SYSTEM OR GENEVA SYSTEM

(International Union of Pure & Applied Chemistry)

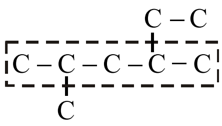
This system is based on the total number of carbons in the selected carbon chain in any organic compound. Following prefix are used in this system.

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	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)

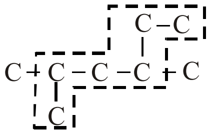
Rules for IUPAC Nomenclature :

1. **Longest chain rule :** According to it, in any organic compound the longest carbon chain is selected through all the possible chains.

Ex.



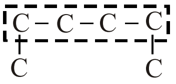
5C – chain (wrong)



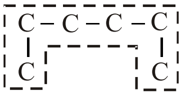
6C – chain (right)

2. **Side chains :** Those alkyl groups which are not included in the longest chains are called side chains. These never comes on first or last carbon (except in the naming of alkyl groups)

Ex.

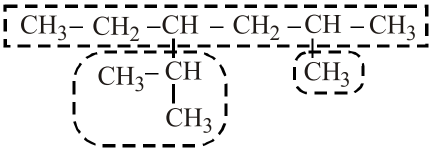


2-side chains (wrong)

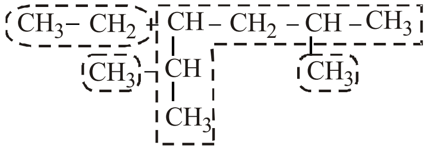


(Correct)

3. If there are the possibilities of longest chain more than one, the chain which possess more than one side chain is selected.



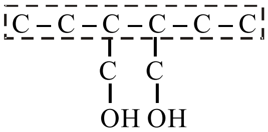
2 side chains (wrong)



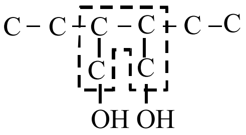
3-side chains (correct)

4. The carbon which is attached with functional group must be included in the chain selected irrespective of the length of the chain.

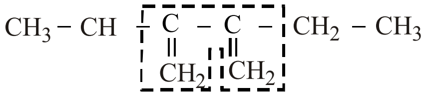
Ex.



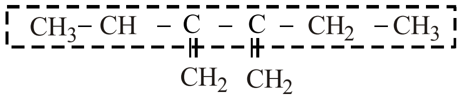
6C-Chain (wrong)



4C-Chain (right)



(correct)

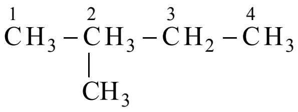


(wrong)

Numbering :

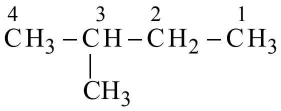
1. **For saturated hydrocarbons :**

(i) Numbering is done from the end from which side chain is nearest.



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

(Right)

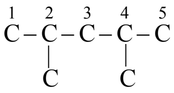


$$\overset{4}{C}H_3-\underset{CH_3}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

(Wrong)

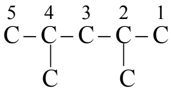
(ii) If side chains are at same carbon from both sides, following rules are adopted -

* For same side chains numbering may be given from any end.



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

(Right)

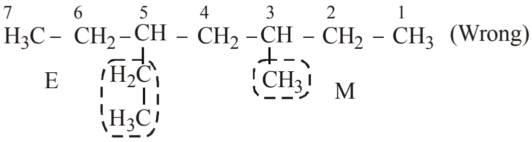


$$\overset{5}{C}-\underset{C}{\overset{4}{C}}-\overset{3}{C}-\underset{C}{\overset{2}{C}}-\overset{1}{C}$$

(Right)

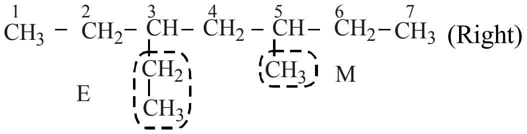
* If side chains are different numbering is given in alphabetically preference order.

Ex.



$$\overset{7}{H_3C}-\overset{6}{CH_2}-\underset{\underset{H_3C}{H_2C}}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

(Wrong)

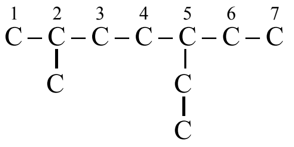


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\underset{CH_3}{CH_2}}{\overset{3}{CH}}-\overset{4}{CH_2}-\underset{CH_3}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

(Right)

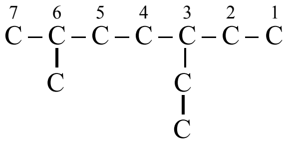
* Numbering is given from the end from which side chain is nearest.

Ex.



$$\overset{1}{C}-\underset{\substack{|\\C}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\underset{\substack{|\\C\\|\\C}}{\overset{5}{C}}-\overset{6}{C}-\overset{7}{C}$$

(Right)



$$\overset{7}{C}-\underset{\substack{|\\C}}{\overset{6}{C}}-\overset{5}{C}-\overset{4}{C}-\underset{\substack{|\\C\\|\\C}}{\overset{3}{C}}-\overset{2}{C}-\overset{1}{C}$$

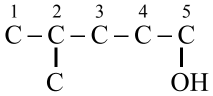
(Wrong)

2. For compounds having functional groups :

(i) Numbering is given from the end from which functional group is closest.

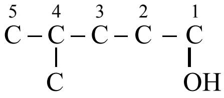
(ii) If the functional group is situated at same carbon from both sides, follow the rules of saturated hydrocarbons.

Ex.



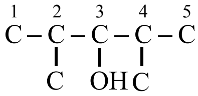
$$\overset{1}{C}-\underset{\substack{|\\C}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\underset{\substack{|\\OH}}{\overset{5}{C}}$$

(Wrong)



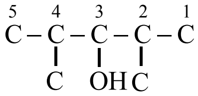
$$\overset{5}{C}-\underset{\substack{|\\C}}{\overset{4}{C}}-\overset{3}{C}-\overset{2}{C}-\underset{\substack{|\\OH}}{\overset{1}{C}}$$

(Right)



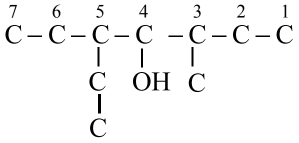
$$\overset{1}{C}-\underset{\substack{|\\C}}{\overset{2}{C}}-\underset{\substack{|\\OH}}{\overset{3}{C}}-\underset{\substack{|\\C}}{\overset{4}{C}}-\overset{5}{C}$$

(Right)



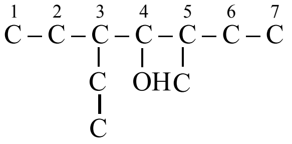
$$\overset{5}{C}-\underset{\substack{|\\C}}{\overset{4}{C}}-\underset{\substack{|\\OH}}{\overset{3}{C}}-\underset{\substack{|\\C}}{\overset{2}{C}}-\overset{1}{C}$$

(Right)



$$\overset{7}{C}-\overset{6}{C}-\underset{\substack{|\\C\\|\\C}}{\overset{5}{C}}-\underset{\substack{|\\OH}}{\overset{4}{C}}-\underset{\substack{|\\C}}{\overset{3}{C}}-\overset{2}{C}-\overset{1}{C}$$

(Wrong)



$$\overset{1}{C}-\overset{2}{C}-\underset{\substack{|\\C\\|\\C}}{\overset{3}{C}}-\underset{\substack{|\\OH}}{\overset{4}{C}}-\underset{\substack{|\\C}}{\overset{5}{C}}-\overset{6}{C}-\overset{7}{C}$$

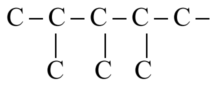
(Right)

Important Points :

* Initially write the number of that carbon on which the side chain is attached, then write it in alkyl group.

* If there are more than one side chains (same) initially write the numbers altogether using symbol (,) in between them, after last number use the symbol hyphen (-). Write the numbers in increasing order.

Ex.

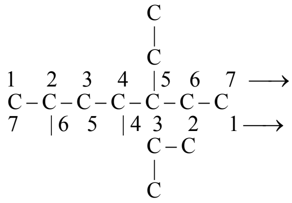


$$C-\underset{\substack{|\\C}}{C}-\underset{\substack{|\\C}}{C}-\underset{\substack{|\\C}}{C}-C-$$

2, 3, 4-trimethyl pentane

* IUPAC name is written according to english alphabets (strictly).

Ex.

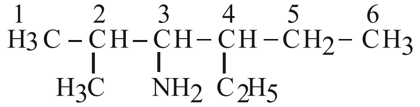


2-methyl-4-Isopropyl-5-ethyl heptane (wrong)

5-ethyl-4-Isopropyl-2-methyl heptane (right)

* Capital word is used for first substitute.

Ex.



$$\overset{1}{H_3C}-\underset{\substack{|\\H_3C}}{\overset{2}{CH}}-\underset{\substack{|\\NH_2}}{\overset{3}{CH}}-\underset{\substack{|\\C_2H_5}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

3-Amino-4-ethyl-2-methyl hexane. (more correct)

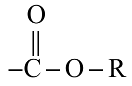
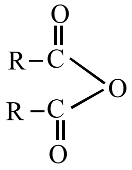
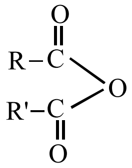
IUPAC Nomenclature of single, double and triple bonds :

S. No.	Hydrocarbon Bond	Name
1.	(–)	Alkane
2.	(=)	Alkene-(no.)
3.	(≡)	Alkyne-(no.)
4.	2 (=)	Alkadiene-(no.), (no.)
5.	2 (≡)	Alkadiyne-(no.), (no.)
6.	(=) + (≡)	(no.) Alken yne-(no.)

no = Number of carbon atom from where multiple bond attached.

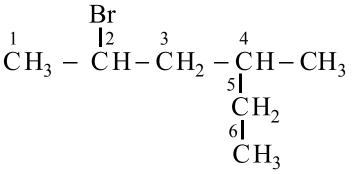
Chart Showing IUPAC Names for uni functional group :

S. No.	Functional group	IUPAC names
1.	—X	no.-Halo alkane
2.	—O—	no. - Alkoxy alkane
3.	2	Alkanamine - no.
4.	$-N \overset{\rightarrow}{\equiv} C$	Alkane isonitrile - no.
5.	—OH	Alkanol - no.
6.	—SH	Alkane thiol - no.
7.	$-\underset{\underset{O}{\|}}{C}-$	Alkanone - no.
8.	$-\underset{\underset{O}{\|}}{C}-H$	Alkanal
9.	$-\underset{\underset{O}{\|}}{C}-OH$	Alkanoic acid
10.	$-\underset{\underset{O}{\|}}{C}-Cl$	Alkanoyal chloride
11.	$-\underset{\underset{O}{\|}}{C}-NH_2$	Alkanamide
12.	—C≡N	Alkane nitrile

13.	 $-\overset{O}{\overset{\|}{C}}-O-R$	Alkyl alkanoate
14.		Alkanoic anhydride
15.		Alkanoic alkanoic' anhydride

no = Number of carbon atom from where functional group is attached or number of carbon of functional group.

Example 2 : Suggest the IUPAC name of the compound–

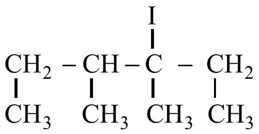

$\overset{1}{C}H_3-\overset{2}{C}H(Br)-\overset{3}{C}H_2-\overset{4}{C}H(\overset{5}{C}H_2-\overset{6}{C}H_3)-CH_3$

Sol. 2-Bromo-4-methyl hexane

Example 3 :

The correct name of the following compound will be- 3-iodo-1, 2, 3, 4-tetra methyl butane.

Sol.


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

3-Iodo-3, 4-dimethyl hexane

Nomenclature of ether :

The small alkyl group attached with oxygen is written as alkoxy in which oxygen is included and the longest chain of remaining carbons is selected.

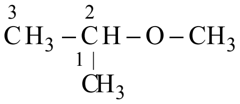
—O—, no. — alkoxy alkane

Ex. 1. $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-O-CH_3$

1-Methoxy propane

2. $CH_3-O-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_3$

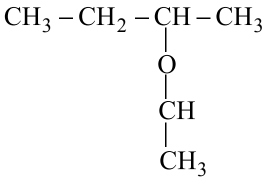
1-Methyoxy propane

3. 
$\overset{3}{C}H_3-\overset{2}{C}H(\overset{1}{C}H_3)-O-CH_3$ (2-Methoxy propane)

Example 4 :

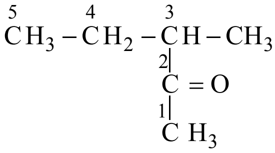
Write the correct IUPAC name of the compound 3-ethoxy butane.

Sol.

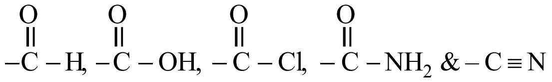

$CH_3-CH_2-CH(-O-CH-CH_3)-CH_3$ (2-ethoxy butane)

Nomenclature of keto group :

The carbon of a ketone is included in longest chain it never comes on first or last positions, whereas – CHO (Aldehyde group) comes at first and last position only.

Ex. 
$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H(-CH_3)-\overset{2}{C}(=O)-\overset{1}{C}H_3$ (3-Methyl-2-pentanone)

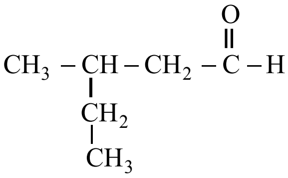
Note :

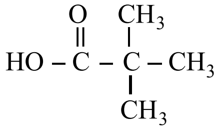

$-\overset{O}{\overset{\|}{C}}-H,\ -\overset{O}{\overset{\|}{C}}-OH,\ -\overset{O}{\overset{\|}{C}}-Cl,\ -\overset{O}{\overset{\|}{C}}-NH_2\ \&-C\equiv N$

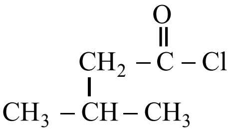
are the groups of which carbons are also included in the longest chain. If these are alone in a compounds they comes on first carbon, if double, comes on first and last positions.

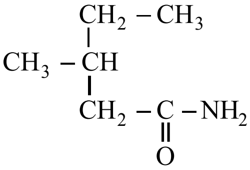
Example 5 :

Write the IUPAC names of the following :

1. 
$CH_3-CH(CH_2-CH_3)-CH_2-C(=O)-H$

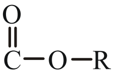
2. 
$HO-C(=O)-C(CH_3)(CH_3)-CH_3$

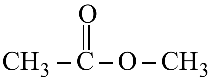
3. 
$CH_3-CH(CH_3)-CH_2-C(=O)-Cl$

4. 
$CH_3-CH(CH_2-CH_3)-CH_2-C(=O)-NH_2$

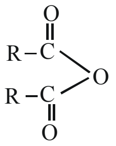
Sol. **1.** 3-Methyl pentanal
2. 2, 2-Dimethyl propanoic acid
3. 3-Methyl butanoyl chloride
4. 3-Methyl pentanamide

Nomenclature of ester :


$\overset{O}{\overset{\|}{C}}-O-R$ Alkyl alkanoate

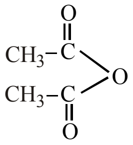
Ex. 
$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$ Methyl ethanoate

Nomenclature of anhydride :



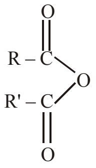
$\frac{\text{Total C}}{2}$ = Substract = number of C atom

= Alkanoic anhydride



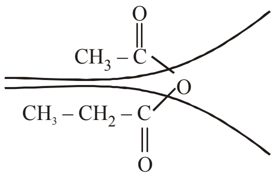
$\frac{4}{2}$ = 2 Ethanoic Anhydride

If R ≠ R'

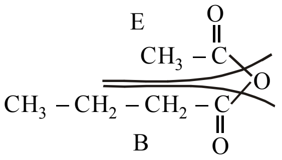


$\frac{\text{Total C}}{2}$ (wrong)

IUPAC name – alkanoic alkanoic' anhydride



Ethanoic propanoic anhydride



Butanoic ethanoic anhydride

Rules for IUPAC names for the compound having poly functional groups :

When an organic compound contains two or more different functional groups is selected as the principal functional group while other groups are treated as substitutes.

Numbering the principal chain order is

IUPAC names for the compounds having two similar functions :

S. No.	Functional group	IUPAC Name
1.	$2-X$	no., no. - di halo alkane
2.	$2-O$	no., no., - di alkoxy alkane
3.	$-NH_2$	Alkane di amine - no., no.*
4.	$2-N \stackrel{\rightarrow}{=} C$	Alkane di isonitrile - no., no.
5.	$2-OH$	Alkane diol - no., no.
6.	$2-SH$	Alkane di thiol - no., no.
7.	$2-\underset{\overset{\|}{O}}{C}-$	Alkane dione - no., no.*
8.	$2-\underset{\overset{\|}{O}}{C}-H$	Alkane dial
9.	$2-\underset{\overset{\|}{O}}{C}-OH$	Alkane dioic acid
10.	$2-\underset{\overset{\|}{O}}{C}-Cl$	Alkane dioyl chloride
11.	$2-\underset{\overset{\|}{O}}{C}-NH_2$	Alkane di amide
12.	$2-C\equiv N$	Alkane di nitrile

[Principal functional group > double bond > triple bond > substituents]

The longest possible chain of carbon atoms containing the functional group the maximum number of multiple bonds is selected as parent chain.

The priority order of the functional groups is as under :

S. No.	Name	Formula	Functional group Prefix	Suffix
1.	Carboxylic acid	$-(C)OOH$ $-COOH$ (no count)	Carboxy -Carboxylic acid	–oic acid
2.	Suphonic acid	$-SO_3H$	Sulpho	–Sulphonic acid
3.	Anhydride	$-(C)\,O$ O $-(C)\,O$	—	– oic anhydride
4.	Ester	$-(C)OOR$ $-COOR$	— Alkoxy carbonyl	– oate carboxylate
5.	Acid halide	$-(C)OX$ $-COX$	— Haloformyl	– oyl halide – carbonyl halide
6.	Acid amide	$-(C)ONH_2$ $-CONH_2$	— Carbamoyl	– amide carboxyamide
7.	Cyanide	$-(C)\equiv N$ $-C\equiv N$	— Cyano	– nitrile carbonitrile
8.	Iso cyanide	$-N \stackrel{\rightarrow}{=} (C)$ $-N \stackrel{\rightarrow}{=} C$	— Carbyl amine	– iso nitrile —

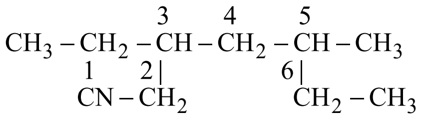
S. No.	Name	Formula	Functional group Prefix	Suffix
9.	Aldehyde	$-(C)HO$ $-CHO$	Oxo formyl	– al carbaldehyde
10.	Ketone	$-\overset{\overset{O}{\Vert}}{(C)}-$	Oxo	– one
11.	Alcohol	$-OH$	Hydroxy-	– ol
12.	Thio alcohal	$-SH$	Mercapto-	– thiol
13.	Amine	$-NH_2$	Amino-	— Amine

Note :

- * Longest chain is selected on the basis of priority and numbering is also done on priority basis.
- * Senior groups are never written as substitutes whereas juniors are written as substitutes.

Example 6 :

Write the IUPAC name of



$$\begin{array}{l} \qquad\qquad\quad 3 \qquad 4 \qquad 5 \\ CH_3-CH_2-CH-CH_2-CH-CH_3 \\ \qquad\ \ 1 \quad 2| \qquad\quad 6| \\ \qquad CN-CH_2 \qquad\ CH_2-CH_3 \end{array}$$

Sol. (1) The longest chain containing functional group is of 7 carbon atoms. Therefore, the word root is hept & the chain is numbered as shown.

(2) There is no multiple bond in it. Hence, the primary suffix is ane.

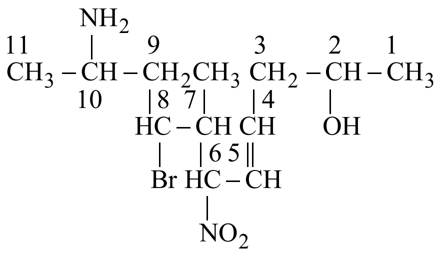
(3) The functional groups is – CN. Hence, secondary suffix is nitirle.

(4) Moreover, there is a methyl groups on carbon 5 and ethyl group on carbon 3.

(5) The IUPAC name is therefore, 3-Ethyl-5-methylheptanenitrile.

Example 7 :

Write the IUPAC name of :



$$\begin{array}{l} \qquad\ NH_2 \\ 11 \quad | \quad 9 \qquad\ 3 \quad 2 \quad 1 \\ CH_3-CH-CH_2CH_3\ CH_2-CH-CH_3 \\ \quad 10 \quad |8\ 7| \quad |4 \quad | \\ \qquad\ HC-CH\ CH \quad OH \\ \qquad\ | \quad |6\ 5\Vert \\ \qquad\ Br\ HC-CH \\ \qquad\qquad | \\ \qquad\qquad NO_2 \end{array}$$

Sol. (1) Primary suffix is ene, due to presence of double bond between C_4 and C_5.

(2) Senior functional group is alcohol hence secondary suffix is – ol.

(3) Root word is undec.

(4) Chain is numbered as shown.

(5) 6-Nitro-7-methyl-8-bromo-10-amino are prefixes. Arrange them in alphabetical order and give the name 10-Amino-8-bromo-7-methyl-6-nitroundec-4-en-2-ol.

NOMENCLATURE OF AROMATIC COMPOUNDS

(i) Nuclear substituted : Those in which the functional group is directly attached to the benzene ring. In the IUPAC system, they are named as derivatives of benzene. 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.

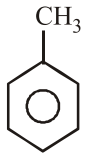
(ii) Side-chain substituted : Those in which the functional is present in the side chain of the benzene ring. Both in the common and IUPAC systems, these are usually named as phenyl derivatives of the corresponding aliphatic compounds. The positions of the substituents on the side chain including the benzene ring are indicated by Greek letters i.e., α, β, γ .... etc, 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.

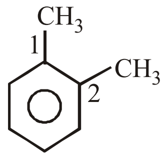
1. Aromatic hydrocarbons (Arenes) : Hydrocarbons which contain both aliphatic and aromatic units are called arenes. These are of three types :

(i) Benzene and alkylbenzenes

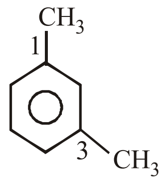
Benzene



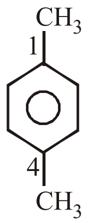
Methylbenzene
(Toluene)



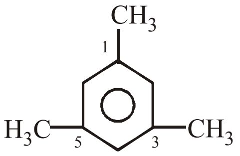
1,2-Dimethylbenzene
(o-Xylene)



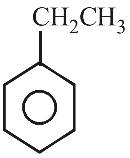
1,3-Dimethylbenzene
(m-xylene)



1,4-Dimethylbenzene
(p-xylene)

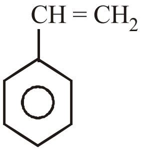


1, 3, 5-Trimethylbenzene
(Mesitylene)

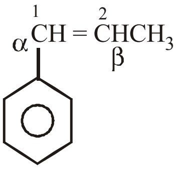


Ethylbenzene

(ii) Alkenylbenzenes

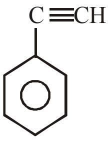


Ethenylbenzene
(Styrene, vinylbenzene
or phenylethylene)

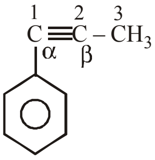


1-Propenylbenzene
(β- Methylstyrene)

(iii) Alkynylbenzene

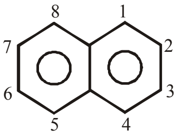


Ethynylbenzene
(Phenylacetylene)

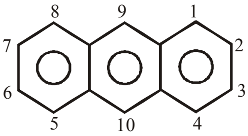


1–Propynylbenzene
(b-Methylphenylacetylene)

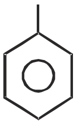
(iv) Hydrocarbons containing condensed or fused rings :



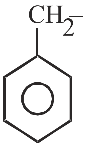
Naphthalene



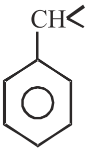
Anthracene



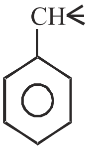
Phenyl



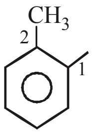
Benzyl



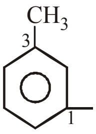
Benzal



Benzo

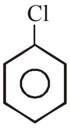


2–Tolyl or o–Tolyl

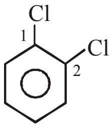


3–Tolyl or m–Tolyl

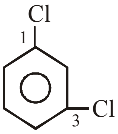
2. Halogen derivatives :



Chlorobenzene

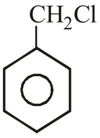


1, 2– Dichlorobenzene or
o-Dichlorobenzene

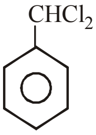


1, 3-Dichlorobenzene or
m - Dichlorobenzene

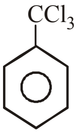
1, 4-Dichlorobenzene or
p-Dichlorobenzene



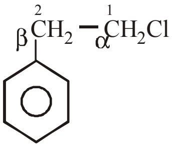
Phenylchloromethane
(Benzyl chloride)



Phenyldichloromethane
(Benzal chloride)



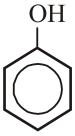
Phenyltrichloromethane
(Benzotrichloride)



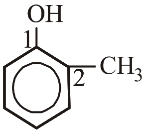
1-Chloro-2-phenylethane
(β- Phenylethyl chloride)

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

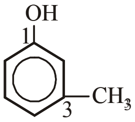
(i) Phenols — Monohydric



Phenol



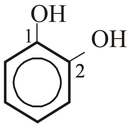
2- Methylphenol
(O-Cresol)



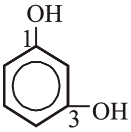
3- Methylphenol
(m-Cresol)

4- Methylphenol
(p-Cresol)

(ii) Dihydric and polyhydric phenols.

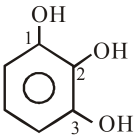


1,2-Dihydroxybenzene
(Catechol)



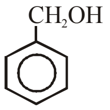
1,3 - Dihydroxybenzene
(Resorcinol)

1, 4 - Dihydroxy benzene
(Quinol)

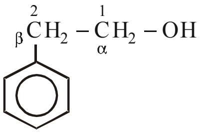


1, 2, 3 – Trihydroxybenzene
(Pyrogallo)

(iii) Aromatic alcohols

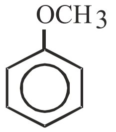


Phenylmethanol
(Benzyl alcohol)

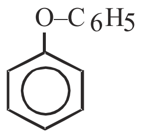


2-Phenylethanol
(β - Phenylethyl alcohol)

4. Aromatic ethers

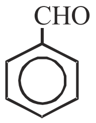


Methoxybenzene
(Anisole or Methyl phenyl ether)

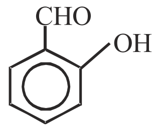


Phenoxybenzene
(Diphenyl ether)

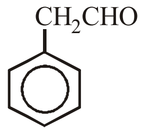
5. Aldehydes



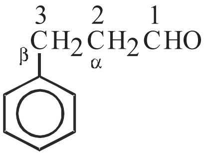
Benzaldehyde



2-Hydroxybenzaldehyde
(Salicylaldehyde)

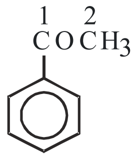


Phenylethanal
(Phenylacetaldehyde)

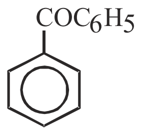


3-Phenylpropanal
(β -Phenylpropionaldehyde)

6. Ketones

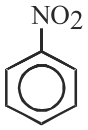


1-Phenylethanone
(Acetophenone or
Methyl phenyl ketone)

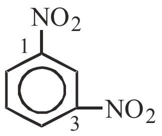


Diphenylmethanone
(Benzophenone or
Diphenyl ketone)

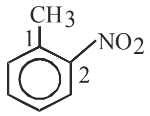
7. Nitro compounds



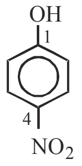
Nitrobenzene



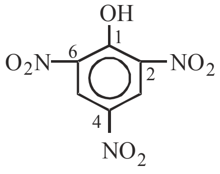
1, 3-Dinitrobenzene or
m-Dinitrobenzene



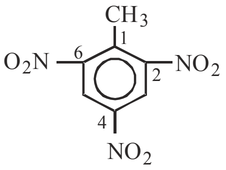
2-Nitrotoluene or
o-Nitrotoluene



4-Nitrophenol or
p-Nitrophenol



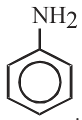
2,4,6-Trinitrophenol
(Picric acid)



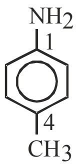
2,4,6-Trinitrotoluene (T.N.T.)

8. Amines

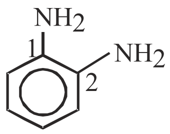
(i) Arylamines



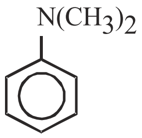
Benzenamine
(Aniline)



4-Methylbenzenamine
(p-Toluidine)

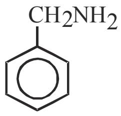


Benzene-1, 2-diamine
(o-Phenylenediamine)

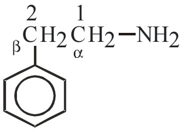


N,N-Dimethylbenzenamine
(N, N-Dimethylaniline)

(ii) Aralkylamines

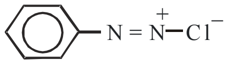


Phenylmethanamine
(Benzylamine)

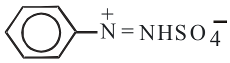


2-Phenylethanamine
(β -Phenylethylamine)

9. Arenediazonium salts

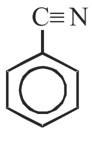


Benzenediazonium chloride

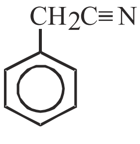


Benzenediazonium hydrogen sulphate

10. Cyanides and Isocyanides :

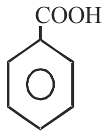


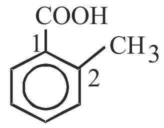
Benzonitrile or
Phenyl cyanide

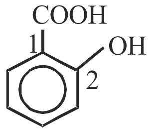


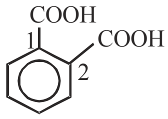
Benzyl cyanide
Phenylacetonitrile

11. Carboxylic acids :

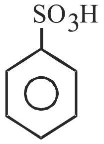

Benzoic acid
or Benzene carboxylic acid

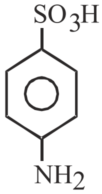

2-Methylbenzoic acid
(o-Toluic acid)


2-Hydroxybenzoic acid
(Salicylic acid)


Benzene-1, 2-dicarboxylic acid
(Phthalic acid)

12. Sulphonic acid :


Benzene sulphonic acid

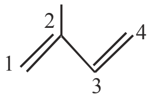

Pera amino benzene
sulphonic acid
(Sulphanilic acid)

Bond–line Notation of Organic Compounds.

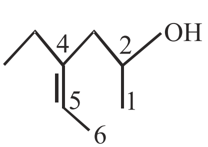
- * In this notation, bonds are represented by lines and carbon atoms by line ends and intersections.
- * It is assumed that required number of H–atoms are present wherever they are necessary to satisfy tetracovalency of carbon. For example,

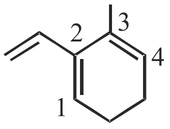
$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$ is represented as

2- Methylbuta-1,3-diene
or Isoprene


2-Methylbuta-1, 3-diene

Some other examples are :

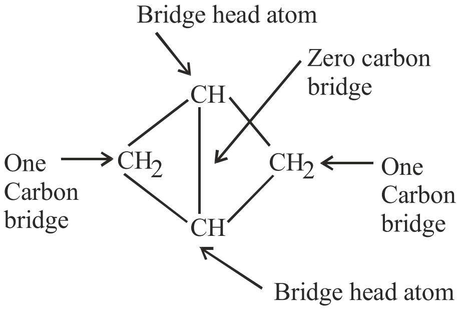

4-Ethylhex-4-en-2-ol

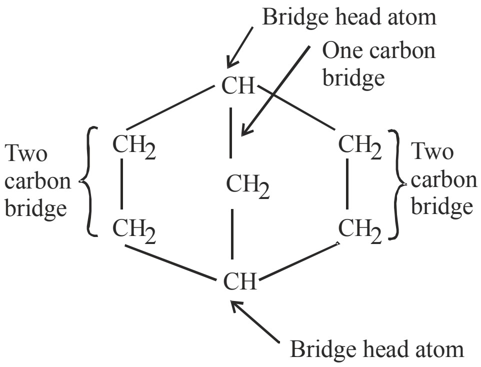

2-Ethenyl-3-methyl-
1, 3-cyclohexadiene

Nomenclature of Bicyclic Compounds :

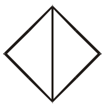
- * Many hydrocarbons and their derivatives contain two fused or bridged rings.
- * The carbon atoms common to both rings are called bridge head atoms and each bond or chain of carbon atoms connecting both the bridge head atoms is called as bridge.
- * The bridge may contain 0, 1, 2... etc. carbon atoms.

For example,

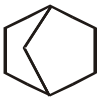




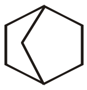
III

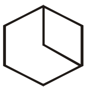


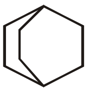
III

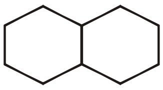


- * These bicyclic compounds are named by attaching the prefix 'bicyclo' to the name of the hydrocarbon having the same total number of carbon atoms as in the two rings.
- * The number of carbon atoms in each of the three bridges connecting the two bridge head carbon atoms is indicated by arabic numerals, i.e. 0, 1, 2,.... etc. These arabic numerals are arranged in descending order ; separated from one another by full stops and then enclosed in square brackets.
- * The complete IUPAC name of the hydrocarbon is then obtained by placing these square brackets containing the arabic numerals between the prefix bicyclo and the name of the alkane. For example,

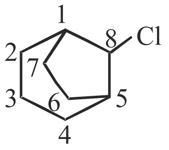

Bicyclo [2, 2, 1] heptane


Bicyclo [3, 1, 1] heptane

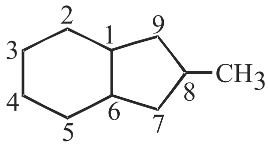

Bicyclo [2, 2, 2] octane


Bicyclo [4, 4, 0] decane
(also called decalin)

- * If a substituent is present, the bicyclic ring system is numbered. The numbering begins with one of the bridge head atoms, proceeds first along the longest bridge to the second bridge head atom, continues along the next longest bridge to the first bridge head atom and is finally completed along the shortest path. For example,



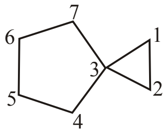
8–Chlorobicyclo [3, 2, 1] octane



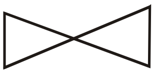
8– methylbicyclo [4, 3, 0] nonane

Nomenclature of Spiro Compounds :

- * Compounds in which one carbon atom is common to two different rings are called spiro compounds.
- * The IUPAC name for a spiro compound begins with the word spiro followed by square brackets containing the number of carbon atoms, in ascending order, in each ring connected to the common carbon atom and then by the name of the parent hydrocarbon corresponding to the total number of carbon atoms in the two rings. **Ex.**



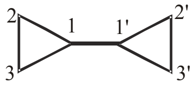
Spiro [2.4] heptane



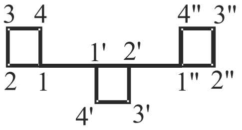
spiro[2, 2] pentane
Simplest spiro compound

- * IUPAC nomenclature of Unbranched Assemblies consisting of two or more identical hydrocarbon units joined by a Single Bond. These systems are named by placing a suitable numerical prefix such as bi for two, ter for three, quater for four, quinque for five etc. before the name of the repetitive hydrocarbon unit. Starting from either end, the carbon atoms of each repetitive hydrocarbon unit are numbered with unprimed and primed arabic numerals such as 1, 2, 3...., 1' , 2', 3' ...., 1" , 2", 3" ... etc. The points of attachment of the repetitive hydrocarbon units are indicated by placing the appropriate locants before the name,

Ex.

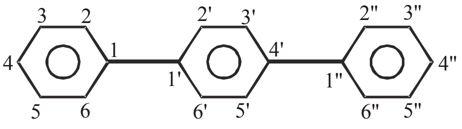


1,1'-Bicyclopropane



1, 1', 2', 1" - Tercyclobutane

- * As an exception, unbranched assemblies consisting of benzene rings are named by using appropriate prefix with the name phenyl instead of benzene. For example,



1,1',4',1"-Terphenyl

SOME IMPORTANT 1993 RECOMMENDATIONS FOR IUPAC NOMENCLATURE OF ORGANIC COMPOUNDS

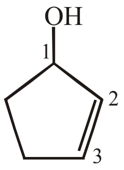
1. Locants (numerals and / or letters) are placed immediately before the part of the name to which they relate.

For example,

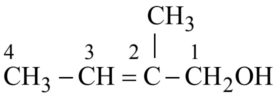
$_3CH_2CH = CH_2$ should be named as but-1-ene

$CH_3CH_2CH_2OH$ should be named as propan-1-ol.

Similarly,

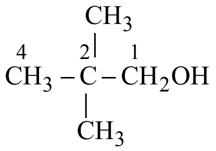


Cyclopent-2-en-1-ol



$$\overset{4}{CH_3} - \overset{3}{CH} = \overset{2}{\overset{CH_3}{C}} - \overset{1}{CH_2OH}$$

2-Methylbut-2-en-1-ol



$$\overset{4}{CH_3} - \underset{CH_3}{\overset{CH_3}{\overset{2}{C}}} - \overset{1}{CH_2OH}$$

(2,2-Dimethylpropan-1-ol)

2. The locant 1 is often omitted when there is no ambiguity.

For example,

$CH_3CH_2CH_2COOH$	CH_3CH_2CHO	$CH_3CH_2CH_2CN$
Butanoic acid	Propanal	Butanenitrile

In all the above examples locant 1 for the functional group is omitted because the position of the functional group is unambiguous. However, in the following cases the position of the functional group must be mentioned.

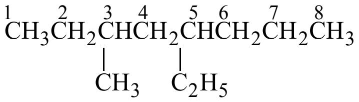
$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2NH_2$
Prepan-1-ol	Propan-1-amine

Here, we cannot write simply propanol (or propanamine) because there are two propanols : propan-1-ol and propan-2-ol.

3. **Arrangement of Prefixes :**

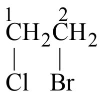
(i) Simple prefixes such as methyl, ethyl, chloro, nitro, hydroxy, etc. are arranged alphabetically.

The prefixes di, tri, etc. are however not considered for comparison. e.g.,



$$\overset{1}{C}H_3\overset{2}{C}H_2\underset{CH_3}{\overset{3}{C}H}\overset{4}{C}H_2\underset{C_2H_5}{\overset{5}{C}H}\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_3$$

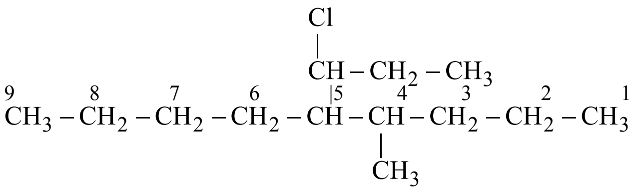
5–ethyl–3–methyl octane



$$\underset{Cl}{\overset{1}{C}H_2}\underset{Br}{\overset{2}{C}H_2}$$

1-bromo-2-chloroethane

(ii) The name of a prefix for a substituted substituent is considered to begin with the first letter of its complete name. e.g.,



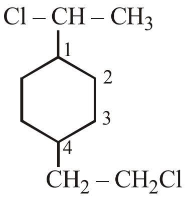
$$\overset{9}{CH_3} - \overset{8}{CH_2} - \overset{7}{CH_2} - \overset{6}{CH_2} - \overset{5}{\underset{}{CH}}\!\left(\underset{Cl}{CH} - CH_2 - CH_3\right) - \underset{CH_3}{\overset{4}{CH}} - \overset{3}{CH_2} - \overset{2}{CH_2} - \overset{1}{CH_3}$$

5-(1-chloropropyl)-4-methyloctane

For the substituted 1-chloropropyl, 'C' is taken as the first letter.

(iii) When two or more prefixes consist of identical roman letters priority for citation is given to the group which contains the lowest locant at the first point of difference.

For example,



1-(1-Chloroethyl)-4-(2-chloroethyl)cyclohexane
Here, 1-chloroethyl gets priority over 2-chloroethyl.

TRY IT YOURSELF-1

Q.1 Which of the following is the pair of homocyclic & heterocyclic compound –
(A) cyclopropane and cyclohexane
(B) cycloethane and oxyrane
(C) pyridine and thiophene
(D) cyclopentane and furane

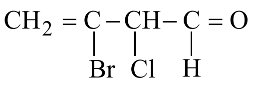
Q.2 The structure of isopropyl carbinol is –
(A) $(CH_3)_2CHOH$ (B) $CH_3–CHOH–CH_2–CH_3$
(C) $(CH_3)_2CHCH_2OH$ (D) $(CH_3)_3COH$

Q.3 The IUPAC name of the compound
$CH_3CH=CHCH=CHC\equiv CCH_3$ is –
(A) 4, 6-octadien-2-yne (B) 2, 4-octadien-6-yne
(C) 2-octyn-4, 6-diene (D) 6-octyn-2, 4-diene

Q.4 The IUPAC name of the compound
$CH_3CH_2OCOCH_2CH_2CH_3$ is –
(A) Propyl propanoate (B) Ethyl butanoate
(C) Propyl butanoate (D) Ethyl propanoate

Q.5 IUPAC name of the carbonyl chloride is
(A) Phosgene (B) Chloromethanoyl chloride
(C) Dichloroketone (D) Dichloromethanone

Q.6 The IUPAC name for

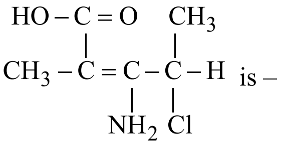


$$CH_2=\underset{Br}{\underset{|}{C}}-\underset{Cl}{\underset{|}{CH}}-\underset{H}{\underset{|}{C}}=O$$

(A) 2-chloro-3-bromo-3-butenal
(B) 2-chloro-3-bromo-3-butene carbaldehyde
(C) 3-bromo-2-chloro-3-butenal
(D) 3-bromo-2-chloro-3-butenone

Q.7 All the following IUPAC names are correct except –
(A) 1-chloro-1-ethoxypropane
(B) 1-amino-1-ethoxypropane
(C) 1-ethoxy-2-propanol
(D) 1-ethoxy-1-propanamine

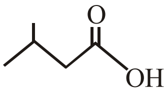
Q.8 The IUPAC name of compound

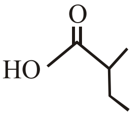


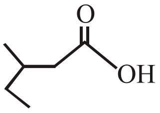
$$CH_3-\underset{NH_2}{\underset{|}{\overset{HO-C=O}{\overset{|}{C}}}}=C-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-H$$ is –

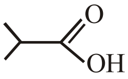
(A) 2-amino-3-chloro-2-methyl-2-pentenoic acid
(B) 3-amino-4-chloro-2-methyl-2-pentenoic acid
(C) 4-amino-3-chloro-2-methyl-2-pentenoic acid
(D) All of the above

Q.9 Write the structural formula of the compound 3-methylbutanoic acid

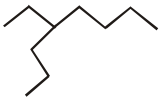
(A)


(B)


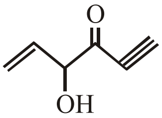
(C)


(D)


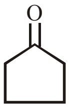
Q.10 Write the IUPAC name of compound



Q.11 Write the IUPAC name of compound



Q.12 Name the compound



ANSWERS

(1) (D) **(2)** (C) **(3)** (B)
(4) (B) **(5)** (B) **(6)** (C)
(7) (B) **(8)** (B) **(9)** (A)
(10) 4-ethyl-octane **(11)** 4-hyroxy-5-hexene-1-yne-3-one
(12) Cyclopentanone

REACTION MECHANISM

ORGANIC REACTIONS

An organic reaction is in fact a bond breaking and a new bond making process.

$$A-B+C \longrightarrow A-C+B$$

Attacking reagent + Substrate → Products.

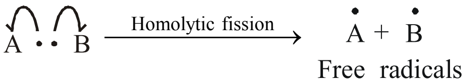
Reaction mechanism :

Substrate → Intermediate → Products
(transitory)

TYPES OF BOND FISSION

(A) Homolytic (symmetrical) fission or Homolysis :

(i) 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 or homolysis.



(ii) 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.

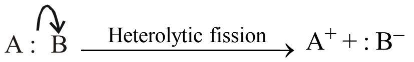
(iii) Favourable conditions :
(a) High temperature (b) Light of suitable wave length
(c) Nonpolar solvent
(d) Presence of peroxide or oxygen
(e) Ability of substrate and attacking reagent to produce free-radicals.

(B) Heterolytic (Unsymmetrical) fission or Heterolysis :

(i) 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 or heterolysis.

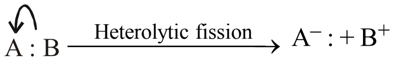
(ii) Heterolytic fission is usually indicated by a curved arrow which denotes a two–electron displacement.

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)

(iii) As shown above, heterolytic fission results in the formation of charged species, i.e. cations and anions.

(iv) Favourable conditions :

(a) Low temperature (b) Polar solvent (c) Presence of acid or base catalyst (d) Polar nature of the substrate and attacking reagent.

CLASSIFICATION OF REAGENTS

(A) Electrophiles or electrophilic reagents (E^+) :

(i) They are electron deficient species.

(ii) They are always in search of electrons.

(iii) They have a tendency to accept electron pair from another molecule (hence electro = electron, phile = love).

(iv) In a reaction, an electrophile attacks the substrate at the point of maximum electron density. Electrophiles may be neutral or positively charged.

(a) Neutral electrophiles : Centre atom has deficiency of electrons. BF_3, BCl_3, $AlCl_3$, $BeCl_2$, $FeCl_3$, SO_3, etc.

(b) Charged electrophiles :

(v) All the positive ions behave like electrophiles.

Cl^+, Br^+, I^+, NO_2^+, NO^+, H^+, H_3O^+, $\overset{+}{N}H_4$, R^+, $R-\overset{+}{C}=O$, etc.

(vi) Electrophiles are generated by heterolysis of a covalent bond.

(vii) Transitional metal cations are electrophiles Fe^{3+}, Fe^{2+}, Ag^+, Hg^{2+}, Cd^{2+}, etc.

(viii) All Lewis acids are electrophiles.

(B) Nucleophilic reagents or Nucleophiles (Nu^-) :

(i) They are electron rich species they have a tendency to donate electron pair.

(ii) They attacks the centre of minimum electron density in a chemical reaction. They are two types :–

(a) Charged Nucleophiles :

All the negative ions qualify as nucleophiles.

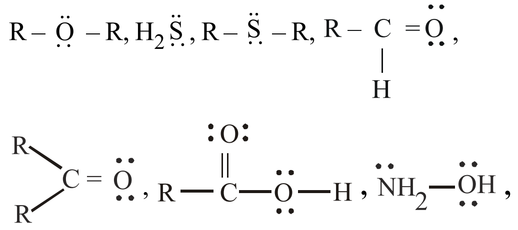
F^-, Cl^-, Br^-, I^-, OH^-, CN^-, $RCOO^-$

RO^-, R^-, $R—C\equiv C^-$, $\overset{-}{N}H_2$, $\overset{-}{S}H$, etc.

(b) Neutral Nucleophiles :

Centre atom has electron pair.

$\ddot{N}H_3$, $R—\ddot{N}H_2$, $R-\ddot{N}HR$, $R_3\ddot{N}$, $H_2\ddot{O}:$, $R-\ddot{\underset{..}{O}}-H$,



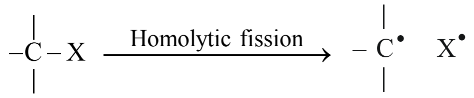
$R-\ddot{\underset{..}{O}}-R$, $H_2\ddot{\underset{..}{S}}$, $R-\ddot{\underset{..}{S}}-R$, $R-\underset{\substack{|\\H}}{C}=\ddot{\underset{..}{O}}$,

$R_2C=\ddot{\underset{..}{O}}$, $R—\overset{\substack{:O:\\ \|}}{C}—\ddot{\underset{..}{O}}—H$, $\ddot{N}H_2—\ddot{\underset{..}{O}}H$,

$NH_2-\ddot{N}H_2$, $CH_2=CH_2$, $\overset{\delta-}{R}—\overset{\delta+}{MgX}$

REACTION INTERMEDIATES

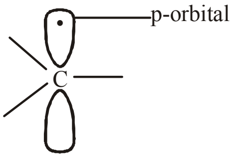
(A) FREE RADICALS



$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{Homolytic fission}} -\overset{|}{\underset{|}{C}}^{\bullet} \quad X^{\bullet}$$

If EN of C ≃ EN of X

* **Geometry, Hybridisation :– Trigonal planar (sp^2 hybrid)**



* Free radicals are electrophiles

* An atom or group of atoms possessing an odd or unpaired electron. It is electrically neutral & shows paramagnetism.

* **Types of Free Radicals :**

$\dot{C}H_3$, $CH_3\dot{C}H_2$, $(CH_3)_2\dot{C}H$, $(CH_3)_3\dot{C}$, $CH_2=CH-\dot{C}H_2$,

1° 2° 3°

$C_6H_5\dot{C}H_2$

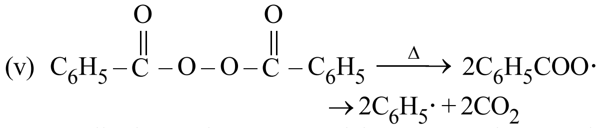
* **Formation of free radicals :**

(i) $Cl_2 \xrightarrow{h\nu} Cl\cdot + Cl\cdot$ [Homolytic fission]

(ii) $CH_3COCH_3 \xrightarrow[140°C]{h\nu} \dot{C}H_3 + CH_3\dot{C}O \rightarrow CO + \dot{C}H_3$

(iii) $(C_2H_5)_4Pb \longrightarrow Pb + 4\dot{C}_2H_5$

(iv) $CH_3-N=N-CH_3 \rightarrow N_2 + 2\dot{C}H_3$



(v) $C_6H_5-\overset{\substack{O\\ \|}}{C}-O-O-\overset{\substack{O\\ \|}}{C}-C_6H_5 \xrightarrow{\Delta} 2C_6H_5COO\cdot \rightarrow 2C_6H_5\cdot + 2CO_2$

* Free radical reactions proceed in vapour phase or in nonpolar solvents.

* Free radical reactions are frequently autocatalytic.

* **Reactions :**

(i) Chlorination of alkanes.
(ii) Pyrolysis of alkanes.
(iii) Wurtz reaction.
(iv) Anti-markownikoff rule.
(v) Kolbe electrolytic synthesis.
(vi) Polymerisation initiated by free radical.

* **Order of stability of free radicals :**
t-butyl > isopropyl > ethyl > methyl

(B) CARBONIUM ION OR CARBOCATION $\left(-\overset{|}{\underset{|}{C}}{}^{\oplus}\right)$

$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{Heterolytic fission}} -\overset{|}{\underset{|}{C}}{}^{\oplus} + :X^{\ominus}$$

If EN of X > EN of C

* **Geometry, Hybridisation :** $-\overset{|}{\underset{|}{C}}{}^{\oplus}$ planar (sp^2)

* Organic species containing positively charged carbon atom is known as carbonium ion. The positively charged carbon atom contains six electrons in its valence shell.

* **Types of carbocation :**

$$\overset{+}{C}H_3\ ,CH_3\overset{+}{C}H_2\ ,(CH_3)_2\overset{+}{C}H\ ,(CH_3)_3\overset{+}{C}$$

1° 2° 3°

* **Formation of Carbonium ion :**

(i) $(CH_3)_3C-Cl \rightarrow (CH_3)_3\overset{+}{C} + Cl^-$ [Heterolytic fission]

(ii) $CH_3OH \xrightarrow{H^+} CH_3\overset{+}{O}H_2 \xrightarrow{-H_2O} \overset{+}{C}H_3$
[Protonation]

(iii) $CH_3-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H-CH_3$
[Protonation]

* **Reactions :**
(i) Nucleophilic substitution of 3° alkyl halide.
(ii) Markownikoff reaction.
(iii) Hydrolysis of acetyl chloride.
(iv) Dehydration of alcohols.

(C) CARBANION $\left[-\overset{|}{\underset{|}{C}}:^{-\ominus}\right]$:

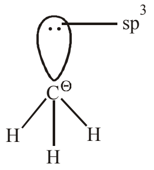
$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{Heterolytic fission}} -\overset{|}{\underset{|}{C}}:^{\ominus} + X^{\oplus}$$

If EN of C > EN of X

An organic species containing negatively charged carbon atom is called carbanion.

There are eight electrons in the valence shell of negatively charged carbon. Two electrons remain as unshared pair.

* **Geometry :**



Pyramidal

Electron pair is present in sp^3

Hybrid orbitals character, 25%

* Carbanions are nucleophile.

* **Types of carbanion ion :**

$$\overset{\ominus}{C}H_3,\ CH_3-\overset{\ominus}{C}H_2, (CH_3)_2\overset{\ominus}{C}H, (CH_3)_3\overset{\ominus}{C}$$

1° 2° 3°

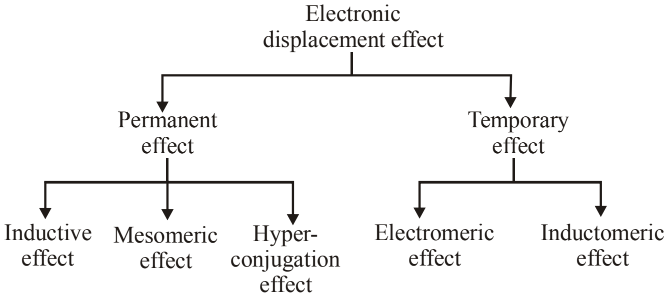
* **Formation of Carbanion :**

(i) $\overset{\ominus}{O}H + \underset{\underset{H}{|}}{CH_2}-CHO \longrightarrow \overset{\ominus}{CH_2}-CHO + H_2O$

(ii) $C_2H_5\overset{\ominus}{O} + \underset{\underset{H}{|}}{CH_2}COOC_2H_5 \longrightarrow \overset{\ominus}{CH_2}COOC_2H_5 + C_2H_5OH$

* **Reactions :**
(i) Aldol condensation (ii) Claisen condensation
(iii) Decarboxylation

ELECTRONIC DISPLACEMENT EFFECTS



INDUCTIVE EFFECT

The permanent displacement of sigma (σ) electrons along a carbon chain in a compound due to the attachment of a more electronegative or more electropositive atom or group of atoms with the terminal carbon of the chain is called inductive effect.

Assume carbon at the head of a carbon chain is attached to a more electronegative atom 'X' then

$$\overset{\delta\delta\delta\delta^+}{C_4} \rightarrow \overset{\delta\delta\delta^+}{C_3} \rightarrow \overset{\delta\delta^+}{C_2} \rightarrow \overset{\delta^+}{C_1} \rightarrow \overset{\delta^-}{X}$$

(more electronegative than carbon)

When carbon is attached to less electro negative atom 'Y' then common electron pair are push towards carbon chain that produce partially –ve charge on carbon chain.

$$\overset{\delta\delta\delta\delta^-}{C_4} \leftarrow \overset{\delta\delta\delta^-}{C_3} \leftarrow \overset{\delta\delta^-}{C_2} \leftarrow \overset{\delta^-}{C_1} \leftarrow \overset{\delta^+}{Y}$$

(Less electronegative than carbon)

Inductive effect (I–effect) is of two types.

(i) **–I effect :** Atoms or group of atoms which attract the bonded electrons more strongly than hydrogen atom, are said to have –I effect and are termed as electron attracting (–I groups). Such groups when linked with a carbon chain make it electron poor.

e.g. $-\overset{+}{N}H_3 > -NO_2 > -CN > -COOH > -F$
$> -Cl > -Br > -I > -\ddot{O}H > -\ddot{O}R > -C_6H_5 > -H$

(ii) **+I Effect :** Those atoms or group of atoms which attract the shared electron pair (bond pair) less strongly then hydrogen atom are said to have +I (electron repelling) effect. Such groups when attached with a carbon chain displace the shared σ electrons towards the chain and make it electron rich.

$(CH_3)_3C-> (CH_3)_2CH-> CH_3-CH_2-> CH_3-$

Inductive effect is represented by an arrow (→) pointing towards the more electronegative element. Inductive effect of hydrogen is zero, i.e. it neither attracts nor repels the bond pair between carbon and hydrogen.

(a) +I power of different type groups and anions :

$$-\bar{C}H_2 > -\bar{N}H > -O^- > -COO^- > \text{tertiary alkyl} > \text{secondary alkyl} > \text{primary alkyl} > -CH_3 > -H$$

+ I power in decreasing order with reference to H-atom.

(b) +I power of same type of alkyl groups:

+ I power ∝ number of C's in same type of alkyl group.

For example,

CH_3-CH_2-

$CH_3-CH_2-CH_2-$

$CH_3-CH_2-CH_2-CH_2-$

↓ + I power in increasing order

Applications of Inductive Effect

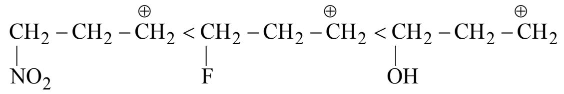
(A) Stability of carbocation :

Stability of carbocation ∝ Presence of electron releasing

$$\text{group} \propto +\text{I group} \propto \frac{1}{-\text{I group}}$$

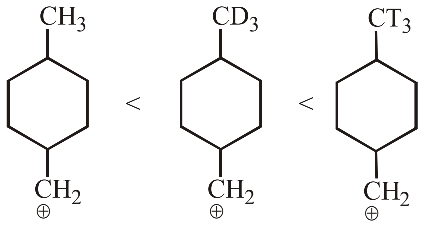
(i) $\underset{3°}{(CH_3)_3C^+} > \underset{2°}{(CH_3)_2CH^+} > \underset{1°}{CH_3CH_2^+} > CH_3^+$

(ii)



$$\underset{NO_2}{\underset{|}{CH_2}}-CH_2-\overset{\oplus}{CH_2} < \underset{F}{\underset{|}{CH_2}}-CH_2-\overset{\oplus}{CH_2} < \underset{OH}{\underset{|}{CH_2}}-CH_2-\overset{\oplus}{CH_2}$$

(iii)

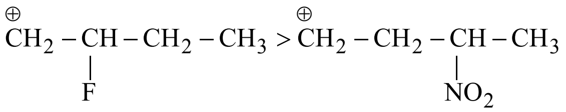


NOTE

1. DNP rule : (Distance Number Power Rule)

Example :

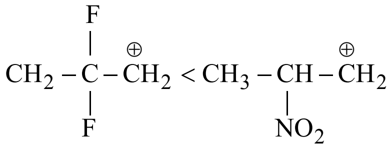
(a)



$$\overset{\oplus}{CH_2}-\underset{F}{\underset{|}{CH}}-CH_2-CH_3 > \overset{\oplus}{CH_2}-CH_2-\underset{NO_2}{\underset{|}{CH}}-CH_3$$

(Distance wins over power)

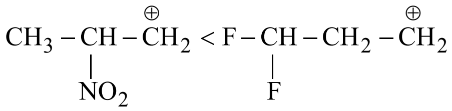
(b)



$$CH_2-\underset{F}{\underset{|}{\overset{F}{\overset{|}{C}}}}-\overset{\oplus}{CH_2} < CH_3-\underset{NO_2}{\underset{|}{CH}}-\overset{\oplus}{CH_2}$$

(Number wins over power)

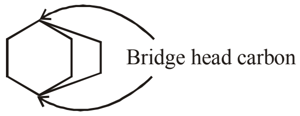
(c)



$$CH_3-\underset{NO_2}{\underset{|}{CH}}-\overset{\oplus}{CH_2} < F-\underset{F}{\underset{|}{CH}}-CH_2-\overset{\oplus}{CH_2}$$

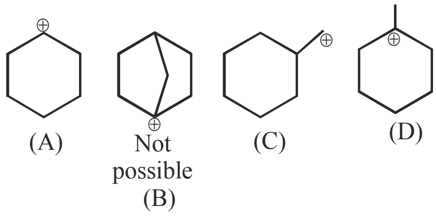
(Distance wins over power)

2. **Bredt's rule :** Formation of carbocation, free radical and π-bond at bridge head position is not possible due to angle strain.



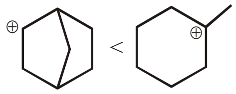
Examples :

(a)



Stability order D > A > C

(b)

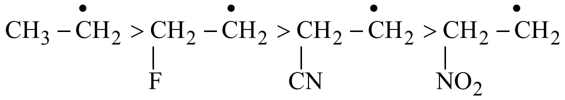


(B) Stability of free radical :

Stability of free radical ∝ Presence of electron releasing

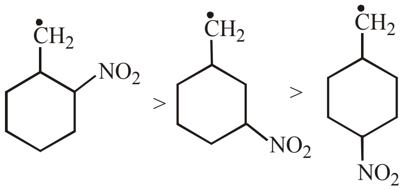
$$\text{group} \quad \propto +\text{I group} \propto \frac{1}{-\text{I group}}$$

(i)



$$CH_3-\overset{\bullet}{CH_2} > \underset{F}{\underset{|}{CH_2}}-\overset{\bullet}{CH_2} > \underset{CN}{\underset{|}{CH_2}}-\overset{\bullet}{CH_2} > \underset{NO_2}{\underset{|}{CH_2}}-\overset{\bullet}{CH_2}$$

(ii)



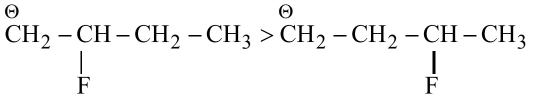
(C) Stability of Carbanion :

Stability of carbanion ∝ Presence of electron releasing

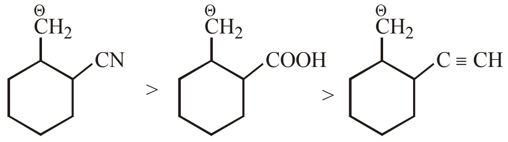
$$\text{group} \quad \propto -\text{I group} \propto \frac{1}{+\text{I group}}$$

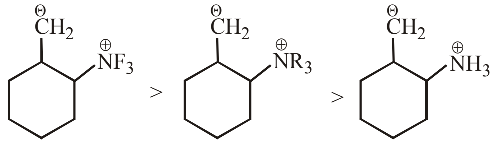
$3° < 2° < 1° < \overset{\ominus}{C}H_3$

(i) $\overset{\oplus}{C}H_2 - CH_2 \rightarrow NO_2 > \overset{\oplus}{C}H_2 - CH_2 \rightarrow F$
$> \overset{\oplus}{C}H_2 - CH_2 \rightarrow OH > \overset{\oplus}{C}H_2 - CH_2 \rightarrow NH_2$

(ii)

$\overset{\ominus}{C}H_2 - \underset{F}{\underset{|}{C}H} - CH_2 - CH_3 > \overset{\ominus}{C}H_2 - CH_2 - \underset{F}{\underset{|}{C}H} - CH_3$

$> \overset{\ominus}{C}H_2 - CH_2 - CH_2 - CH_2 - F$

(iii)


(iv)


(D) Reactivity of alkyl halides

The reactivity order of alkyl halides is –
3° or Tertiary halide (Most reactive) > 2° alkyl halide > 1° or primary halide > methyl halide (Least reactive)

(E) Acid Strength

* Strength of acid is the function of stability of acid anion.

* Acidic strength ∝ Presence of electron withdrawing group

$$\propto -I \text{ group} \propto \frac{1}{+I \text{ group}}$$

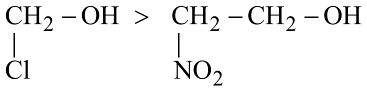
Acidic strength order :

* $HF < HCl < HBr < HI$

* $CH_4 < NH_4 < H_2O < HF$

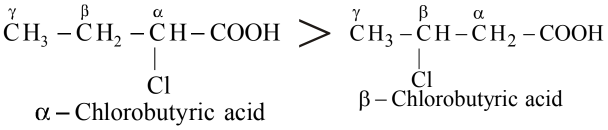
* $Cl - CH_2 - COOH < Cl_2CH - COOH < CCl_3 - COOH$

* $H{-}COOH > CH_3{-}COOH > CH_3{-}CH_2{-}COOH > CH_3{-}CH_2{-}CH_2{-}COOH$

*

$\underset{Cl}{\underset{|}{C}H_2} - OH > CH_2 - \underset{NO_2}{\underset{|}{C}H_2} - OH$

* $(CH_3)_3COH < (CH_3)_2CHOH < CH_3CH_2OH < CH_3OH$

* Halogen having stronger –I effect makes an acid stronger. In halogen substituted acids, as the halogen atom is removed further from the carboxyl group, the acid strength decreases because the influence of –I effect of the halogen atom on –COOH group goes on weakening. Thus,


$\overset{\gamma}{C}H_3 - \overset{\beta}{C}H_2 - \underset{Cl}{\underset{|}{\overset{\alpha}{C}H}} - COOH > \overset{\gamma}{C}H_3 - \underset{Cl}{\underset{|}{\overset{\beta}{C}H}} - \overset{\alpha}{C}H_2 - COOH$

α – Chlorobutyric acid β – Chlorobutyric acid

$> Cl - \overset{\gamma}{C}H_2 - \overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - COOH$
γ – chlorobutyric acid

(F) Basicity of amines :

* Strength of base ∝ + I power of group present on – NH_2

$$\propto K_b \propto \frac{1}{pK_b}$$

Whereas, a group producing –I effect [–Cl, –NO_2] tends to decrease electron density over N-atom in amines, thereby producing a base weakening effect.

$$\text{Thus, strength of base} \propto \frac{1}{-I \text{ power of group present on } -NH_2} \propto K_b$$

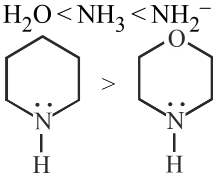
* Increasing order of basic strength of aliphatic primary amines is :

$\ddot{N}H_3 < CH_3\ddot{N}H_2 < CH_3CH_2\ddot{N}H_2 < (CH_3)_2CH\ddot{N}H_2$

* Base strength of aliphatic and aromatic amines varies as follows : $R - \ddot{N}H_2 > \ddot{N}H_3 > Ar - \ddot{N}H_2$

* $R - NH_2 < R_2NH < R_3N$

* $H_2O < NH_3 < NH_2^-$

*

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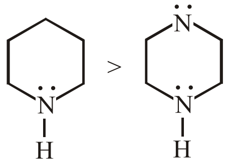

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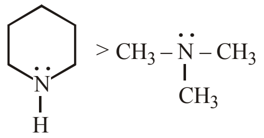


* **Order of basic strength in solvent phase :**

$R = CH_3 \rightarrow R_2NH > RNH_2 > R_3N > NH_3$

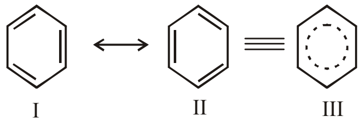
$R = C_2H_5 \rightarrow R_2NH > R_3N > RNH_2 > NH_3$

RESONANCE

(a) Sometimes, it is not possible to assign a single electronic (Lewis) structure to a molecule which can satisfactorily explain all its properties. In such cases, it has been found that the molecule can often be represented by two or more Lewis 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 structure 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.

(b) The real structure of the molecule is not represented by any of the canonical structures but is actually a resonance hybrid of all these Lewis structures. The various resonance structures are separated by a double headed arrow (↔).

(c) 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.



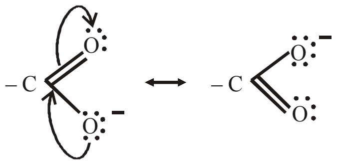
Resonance energy :

(i) A resonance hybrid (or the actual molecule) is always more stable than any of its canonical (hypothetical or imaginary) structures. This stability is due to delocalization of electrons and is measured in terms or resonance energy or delocalization energy.

(ii) 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, larger is the resonance energy and hence more stable is the compound. 150.62 kJ mol^{-1} or 36.0 kcal mol^{-1} is the resonance energy of benzene.

Types of resonance : Resonance is of two types.

(i) **Isovalent resonance :** When the different canonical forms of a molecule contain same number of bonds, the resonance is said to be isovalent. For example a carboxylate ion shows isovalent resonance.



(ii) **Heterovalent resonance :** When the number of bonds are different in different canonical forms, resonance is said to be different canonical forms, resonance is said to be heterovalent. For example, resonance in 1, 3–Butadiene :

$$\overset{\curvearrowleft}{CH_2=}CH-\overset{\curvearrowleft}{CH=}CH_2 \leftrightarrow \overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2$$

I II

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

III

Structure I has eleven bonds while structures II and III contain ten bonds each.

Conditions for Resonance :

(i) Atomic arrangement is the same in all the canonical forms.

(ii) Same number of paired or unpaired electrons must be present in each canonical form.

(iii) Canonical forms must possess same or nearly same energy.

(iv) The molecule must have a planar structure.

(v) All the canonical forms do not contribute equally towards the structure of a resonance hybrid. A more stable canonical structure contributes more to the resonance hybrid.

The contribution depends upon the following factors.

(a) Presence of isolated charges or increase in charge separation decreases the stability of a canonical form and hence its contribution in the hybrid structure.

(b) When all the structures have formal charge, that structure having negative charge on electronegative and positive charge on electro + ve element (atom) will be more stable. For example, carbonyl group is a resonance hybrid of the following structures.

$$>C=O \leftrightarrow >\overset{+}{C}-\overset{-}{O} \leftrightarrow >\overset{-}{C}-\overset{+}{O}$$

I II III

The polar structure (II) is more stable than (III) because in this structure negative charge resides on oxygen (more electronegative atom) and +ve charge is present on more electropositive carbon atom.

(c) Resonating structure having electron deficient positively charged atoms possess very high energy and hence unstable.

(d) Resonating structures with a greater number of covalent bonds is more stable.

Characteristics of resonance and resonance hybrid :

(i) A resonance hybrid is more stable than any of the canonical forms. Greater the number of resonating structures which can be written for a molecule, greater will be its stability. Thus, resonance gives extra stability to a molecule and hence decreases its reactivity. Resonance hybrid possesses lesser energy than any of the canonical forms. **Resonance energy :** It is a measure of the stability of a resonance hybrid. It may be defined as, "the difference in the energy of most stable (maximum contributing) canonical form and the resonance hybrid".

Resonance Energy = Theoretical heat of formation
– Experimental heat of formation.

Higher the resonance energy of a molecule greater is its stability.

(ii) Bond lengths between atoms in a resonance hybrid are different from those in canonical forms. For example in actual benzene molecule the carbon–carbon bond distance between adjacent atoms is equal (1.397 Å) while in the Kekule structure, it is 1.54 Å and 1.34 Å alternately.

Application of Resonance :

(i) To explain the acidic nature of hydrogen atoms in acetylene molecule.

$$H-C\equiv C-H \leftrightarrow HC\equiv \overset{-}{C}\overset{+}{H} \leftrightarrow \overset{+}{H}\overset{-}{C}\equiv CH \leftrightarrow \overset{+}{H}\overset{-}{C}\equiv \overset{-}{C}\overset{+}{H}$$

(ii) To explain the unreactivity of halogen atom in vinyl halide.

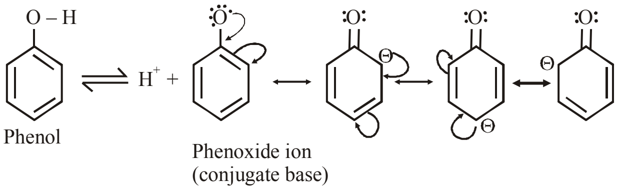
$$CH_2=CH-\ddot{C}l \leftrightarrow \overset{-}{C}H_2-CH=\overset{+}{C}l$$

(iii) To explain the reactivity of halogen atom in allyl and benzyl halides.

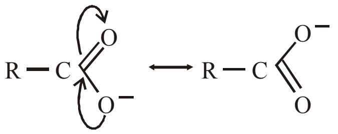
$$CH_2=CH-CH_2Cl \rightleftharpoons CH_2=CH-\overset{+}{C}H_2+\overset{-}{C}l$$

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

(iv) To explain the acidic nature of phenol. Its conjugate base (phenoxide ion) is resonance stabilized.



(v) To explain the stability of carboxylate ions.



Carboxylate ion

Bond order :

In the compounds showing resonance, bond order may be calculated as follows :

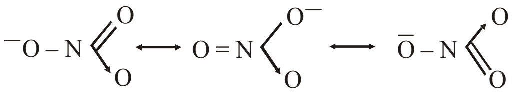
$$\text{Bond order} = \frac{\text{Total number of bonds on central atom}}{\text{Number of resonating structures}}$$

Ex.

(i) Bond order between carbon and oxygen in carbonate (CO_3^{2-}) ion : All the C — O bond distances are equal in this ion due to resonance

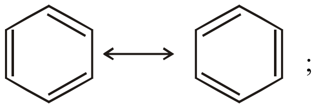
$$\text{Bond order} = \frac{2+1+1}{3} = \frac{4}{3} = 1.33$$

(ii) N — O bond order in nitrate (NO_3^-) ion :



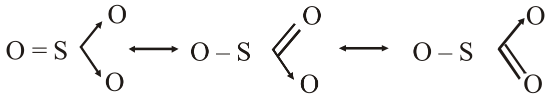
$$\text{Bond order between O and N} = \frac{2+1+1}{3} = \frac{4}{3} = 1.33$$

(iii) C — C bond order in benzene :



$$\text{C — C bond order} = \frac{2+1}{2} = \frac{3}{2} = 1.5$$

(iv) Bond order in SO_3 :



$$\text{Bond order between S and O} = \frac{2+1+1}{3} = \frac{4}{3} = 1.33$$

Example: Give the correct order of bond length of following mentioned compounds.

(i) $CH_3-CH_2\underset{a}{-}\ddot{N}H_2$

no resonance (only single bond characters)

(ii) $CH_2=CH_2\underset{b}{-}\ddot{N}H_2$

Resonance (partial double bond characters)

Bond length order a > b

MESOMERIC EFFECT

It involves π–electrons and lone pair of electrons in conjugation with each other.

It is a permanent polarization caused in a molecule due to interaction of two π–molecular orbitals or one π–molecular orbital and lone pair of electrons.

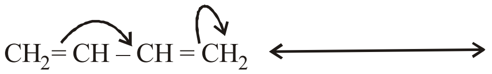
The only condition for this effect is that the π–bonds should be in conjugation with each other.

Ex. $CH_2\overset{\pi}{=}C\overset{\pi}{=}C\overset{\pi}{=}CH_2$ No mesomeric effect

Cumulative system
of double bonds

$CH_2\overset{\pi}{=}CH-CH_2-CH\overset{\pi}{=}CH_2$ No mesomeric effect

Isolated system of double bonds

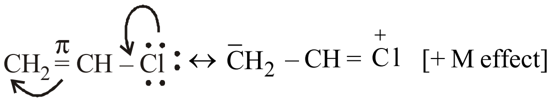


Conjugated system of double bonds, shows mesomeric effect

(π-π conjugation)

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

Mesomeric effect also arises due to π–lone pair conjugation. For example in vinyl chloride.

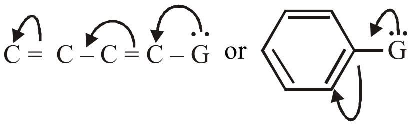


$CH_2\overset{\pi}{=}CH-\ddot{Cl}: \leftrightarrow \bar{C}H_2-CH=\overset{+}{C}l$ [+M effect]

Types of Mesomeric effect :

* **+M effect (+R) :** If the group pushes the electrons into the π electron system, the effect is said as +M effect and the group is called ERG (electron releasing group) or +M group.

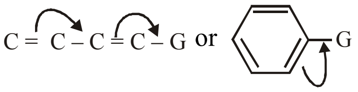
e.g.,



+M effect is shown by : – Cl, – Br, – NH_2, – NHR, – NR_2, – $NHCOCH_3$, – OH, – OR

Condition : Electron pair must be present at first atom of group.

* **– M effect (– R) :** If the π electrons are present system is pulled by the group then the effect is called – M effect and the group is called EWG group (electron withdrawing group) or – M group. e.g.,



– M effect is shown by :

– CHO, C = O, – COOH, – NO_2, – CN, – SO_3H, – SO_2Cl

Condition :

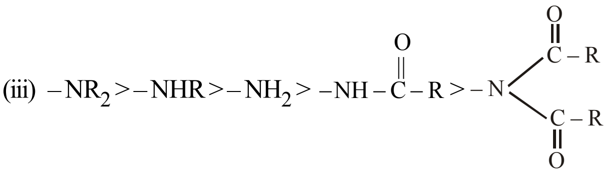
(i) Vacant orbital must be present.

(ii) Multiple bond with more electron negative second atom.

* **+M – effect order**

(i) $-\bar{C}H_2 > -\bar{N}H > -O^-$

(ii) $-\bar{N}H > -NH$



(iii) $-NR_2 > -NHR > -NH_2 > -NH-\overset{\overset{O}{\|}}{C}-R > -N\begin{matrix} C(=O)-R \\ C(=O)-R \end{matrix}$

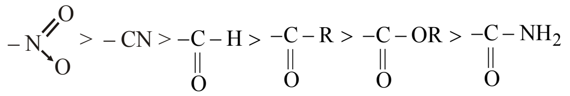
(iv) $-O^- > -OR > -\bar{O}-CH=CH_2$

(v) $-NH_2 > -OH > -F$

(vi) $-F > -Cl > -Br > -I$

* **–M – effect order**

(i) $-\overset{\oplus}{C}H_2 > -BH_2 > -\ddot{P}H_2$



(ii) $-NO_2 > -CN > -\underset{\underset{O}{\|}}{C}-H > -\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-OR > -\underset{\underset{O}{\|}}{C}-NH_2$

Note :

* Mesomeric effect works at only ortho & para position, it is absent on meta position, while inductive effect works at all three position o, m, p however intensity of effect decreases as the distance increases.

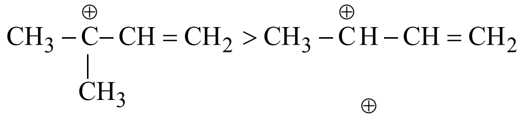
* Mesomeric effect always dominates on inductive effect except halogen (Cl, Br, I, only).

Application of Mesomeric effect:

(i) Stability of carbocation :

- Stability ∝ No. of resonating structures
- Aromatic cations are more stable than non-aromatic cations.

Stability order :

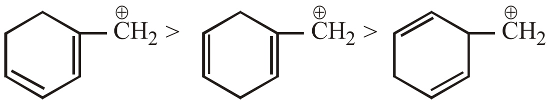


* $CH_3-\overset{\oplus}{C}(CH_3)-CH=CH_2 > CH_3-\overset{\oplus}{C}H-CH=CH_2$

$> \overset{\oplus}{C}H_2-CH=CH_2$

* $CH_2=CH-\overset{\oplus}{C}H_2 > CH_3 \rightarrow CH_2-\overset{\oplus}{C}H_2$

$> CH_2=CH-CH_2 \leftarrow \overset{\oplus}{C}H_2$

*


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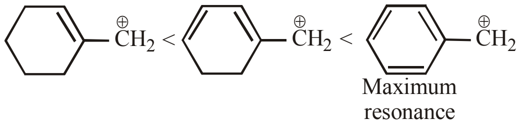

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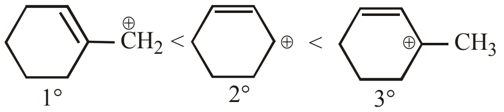
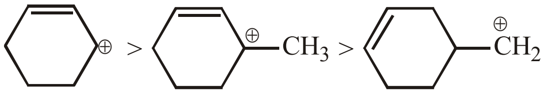


* $(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5\overset{\oplus}{C}H_2$

$> CH_2=CH-\overset{\oplus}{C}H_2 > (CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H$

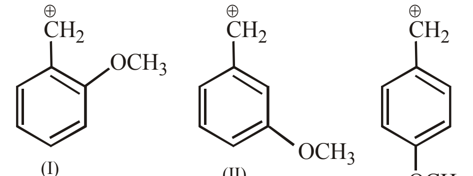
$> CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

*


* $CH_2=CH-\overset{\oplus}{C}H_2$
Allyl carbocation
Number of resonating structures = 2

$C_6H_5-\overset{\oplus}{C}H_2$
Benzyl carbocation
Number of resonating structures = 4

Hence, the benzyl carbocation is more stable than the allyl carbocation.

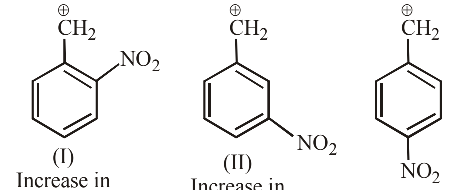
*


(I) Stabilised by +R effect destablised by –I effect –I power is maximum (due to distance)

(II) Destablised by –I effect only

(III) Stabilised by +R effect destablised by –I effect –I power is minimum (due to distance)

Stability order : III > I > II

*


(I) Increase in positive charge by –I and –R effect

(II) Increase in positive charge only by –I effect

(III) Increase in positive charge by –I and –R effect

Stability order : II > III > I

(ii) Stability of carbanion :

More resonance in carbanion, more stability of carbanion

Example : Stability order for following:

* $\underset{I}{CH_2=CH-\overset{\ominus}{C}H_2}, \underset{II}{CH_2=\overset{\ominus}{C}H}, \underset{III}{CH_3-\overset{\ominus}{C}H_2}$

Stability order : I > II > III

*

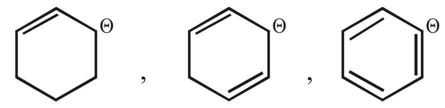
$\underset{\text{Maximum (–I)}}{\overset{\ominus}{C}H_2-OH} > \overset{\ominus}{C}H_2-CH_2-OH > \underset{\text{Minimum (–I) of OH}}{\overset{\ominus}{C}H_2-CH_2-CH_2-OH}$

*

$\underset{I}{\overset{\ominus}{C}H_2-NO_2}, \underset{II}{\overset{\ominus}{C}H_2-CH_2-NO_2}, \underset{III}{CH_3-\overset{\ominus}{C}H_2-NO_2}$

Stability order : I > III > II

*



resonance I, more resonance II, localized Θ charge III

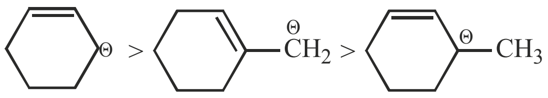
Stability order : II > I > III

* $(C_6H_5)_3\overset{\ominus}{C} > (C_6H_5)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2$

$> CH_2 = CH-\overset{\ominus}{C}H_2 > CH_2 = \overset{\ominus}{C}H$

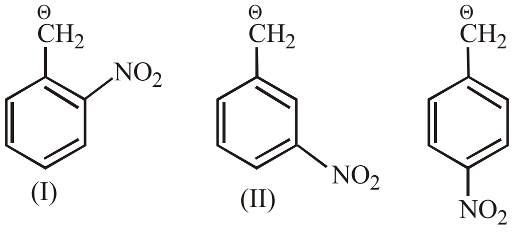
$\overset{\ominus}{C}H_3 > CH_3-\overset{\ominus}{C}H_2 > (CH_3)_2-\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

*



2° anion I, 1° anion II, 3° anion III

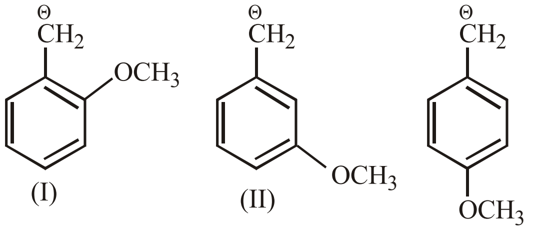
*



(I) (II) (III)

Stability order : I > III > II

*



(I) (II) (III)

Stability order : II > I > III

(iii) Stability of free radicals :

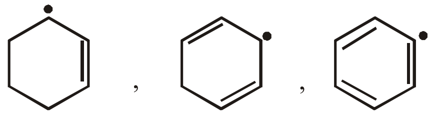
Stability ∝ No. of resonating structures

* $CH_2 = CH-\dot{C}H_2$ I less resonance $\quad CH_2 = \dot{C}H$ II no resonance

$CH_2 = CH-\dot{C}H-CH = CH_2$ III more resonance

Stability order : III > I > II

*



I resonance, II more resonance, III localized

* $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2$

$> CH_2 = CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_2)_2\dot{C}H$

$> CH_3\dot{C}H_2 > \dot{C}H_3$

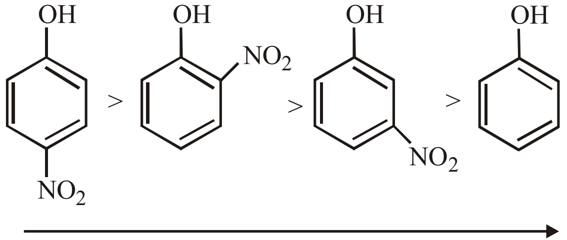
(iv) Acidic strength :

* Acidic strength ∝ Stability of conjugate base

$$\propto -M \text{ effect} \propto \frac{1}{+M} \propto -I \propto \frac{1}{+I}$$

* **Acidity of substituted phenols:**

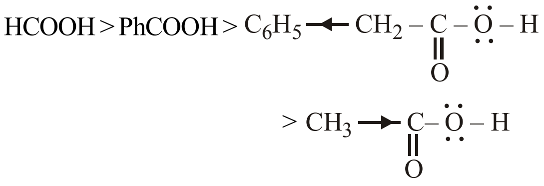
In case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative, there is intramolecular hydrogen bonding which decrease acidity. Thus order of acidity is as follows:



Acidity in decreasing order

* **Acidic strength of substituted benzoic acid :**

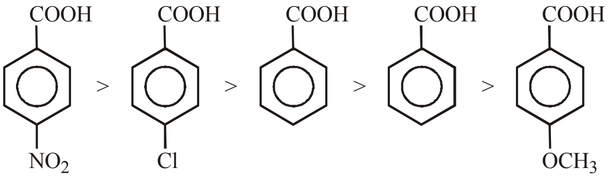
Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.



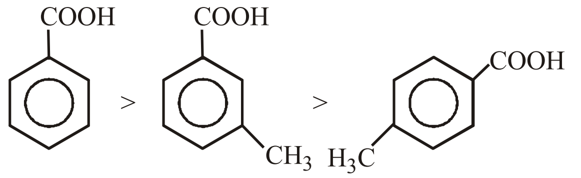
$HCOOH > PhCOOH > C_6H_5 \leftarrow CH_2-\underset{\underset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}-H > CH_3 \rightarrow \underset{\underset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}-H$

Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

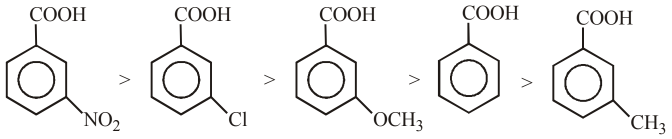
If electron donating group present at para position than it is always less acidic than benzoic acid.



Also it is less acidic then meta substituted benzoic acid.



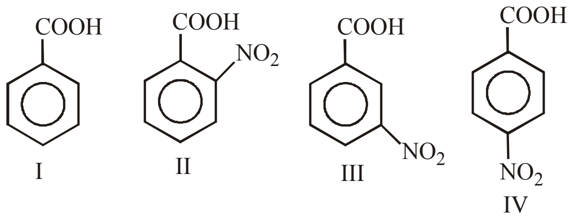
On the other hand if e$^-$ withdrawing group is present at meta position then it is more acidic than benzoic acid.



Ortho effect :

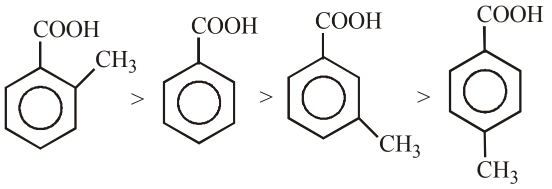
It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called ortho effect (which is combined effect of steric hindrance, crowding & electronic effect) in benzoic acid. However, exceptions are seen.

Ex. (a)

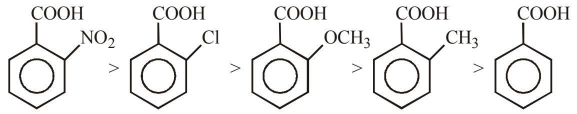


Acid strength order : II > IV > III > I

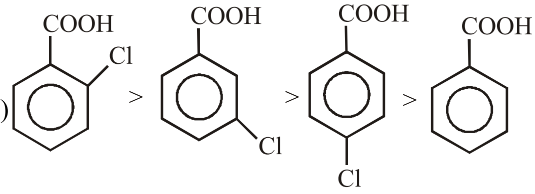
(b)



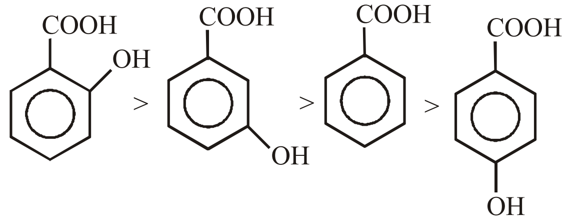
(c)



(d)

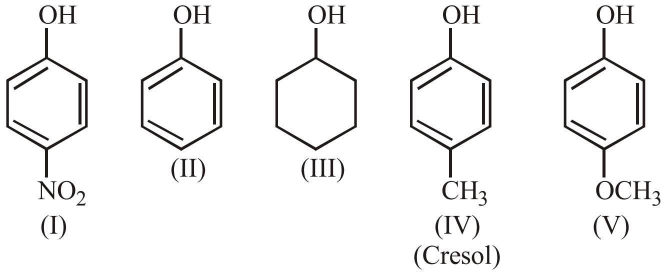


(e)



Example 8 :

Find the acid strength order.



Sol. Acid strength order: I > II > IV > V > III

Step 1 : III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).

Step 2 : Since –I,-m group will increase acid strength, Nitrophenol will be most acidic followed by phenol.

Step 3 : Amongst cresol and methoxyphenol, methoxy phenol has +m effect of – OCH_3 which increases density hence decrease acidic strength.

(v) Basic strength

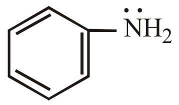
* Basic strength $\propto$ + M effect $\propto \frac{1}{-M} \propto +I \propto \frac{1}{-I}$

Basicity of aromatic amines :

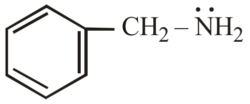
Basicity of nitrogen containing compounds $\propto$ Electron density on nitrogen.

In aromatic amines, lone pair of electrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

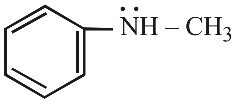
Ex. $C_6H_5NH_2$ is less basic than CH_3NH_2



Lone pair is participating in resonance
(I)



No resonance of lone pair so maximum basic
(II)



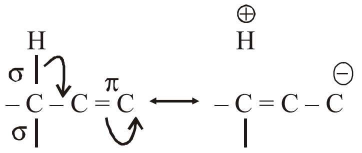
Lone pair is participating in resonance and +I of CH_3
(III)

Basic order II > III > I

HYPER CONJUGATION (BAKER - NATHAN EFFECT)

(i) It involves the delocalization of C—H sigma (σ) electrons with π–electrons of a multiple bond when they are in conjugation. Therefore, it is also called σ–π conjugation.

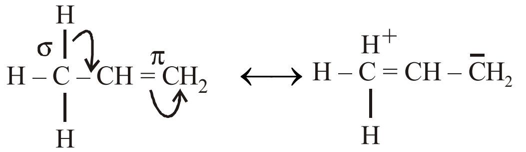
(ii) In the system $H-\overset{\alpha}{C}-C=C$, the σ electrons of C – H bond are released in the unsaturated carbon chain. This phenomenon is called hyperconjugation.



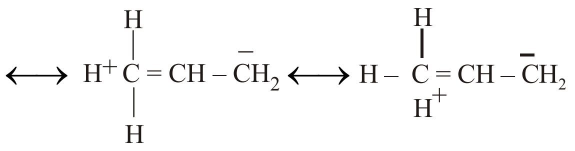
(iii) The hydrogen atom of the $H-\overset{\alpha}{C}$ bond acquires a +ve charge but remains very close to (α) carbon atom although there is not any bond between the two. Hence, the name No–bond resonance for hyperconjugation.

(iv) Greater the number of H–C bonds attached to an unsaturated system, more will be the electron release in the unsaturated carbon chain, greater will be the number of resonating structure.

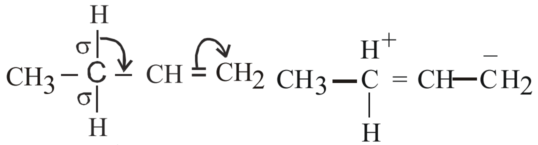
(v) For example : In propylene, there are three H—C sigma bonds in conjugation with the π bond. So, only three resonating forms can be written.



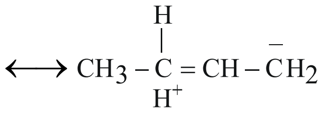
Propylene contains
3H – C hyperconjugated bond



In 1–Butene, there are two αC – H bonds in conjugation with double bond (π–electrons), So, only two canonical forms can be written.

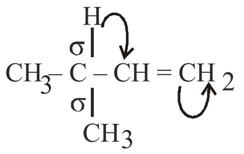


1-butene

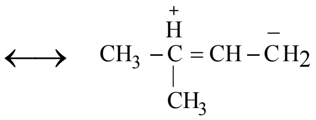


[Two C – H hyperconjugated bonds]

When an isopropyl group is attached with an olefinic system only one C – H bond is hyperconjugated.

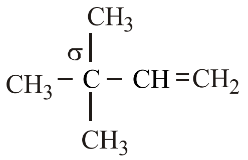


[Only one H - C hyperconjugated bond]



$$\longleftrightarrow CH_3-\overset{\overset{+}{H}}{\underset{CH_3}{C}}=CH-\bar{C}H_2$$

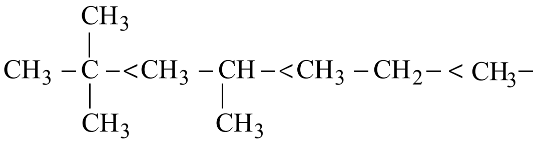
In case a tertiary butyl group is attached with an olefinic system, there is not any C – H hyperconjugated bond, hence no hyperconjugation.



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

[No hyperconjugation, no s-electron release because there is no α C – H bond]

When the alkyl groups 3°–, 2°–, 1°– and CH_3– are attached with an olefinic bond, their electron releasing tendencies are reversed.



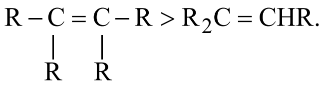
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-<CH_3-\underset{CH_3}{CH}-<CH_3-CH_2-<CH_3-$$

[t-Butyl group No electron release by hyperconjugation]

Effects of hyperconjugation :

(i) Stability of alkenes :

(a) Alkylated alkenes are more stable than others. Greater the alkylation of an alkene [greater the number of alkyl groups in an alkene] greater is its stability. Thus, the stability order is :



$$\underset{R}{R-C}=\underset{R}{C-R}>R_2C=CHR.$$

[Tetraalkyl ethylene]

$RCH=CHR>R_2C=CH_2>R-CH=CH_2>CH_2=CH_2$
Least stable

(b) Greater the number of α C – H bonds in an alkene, greater will be the number of hyperconjugated structures, hence greater will be the stability conjugated structures, hence greater will be the stability. For instance, propene is more stable than ethene.

$$\overset{\alpha}{C}H_3-CH=CH_2 > CH_2=CH_2$$

Propene	Ethene
(3C – H hyperconjugated bonds)	(No hyperconjugation)

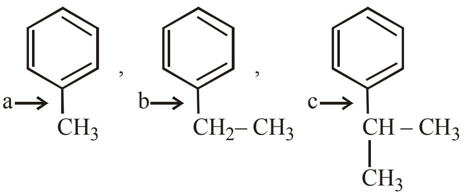
(ii) Bond length in alkenes :

More is the number of hyperconjugating structures, the more will be single bond character in carbon-carbon double bond.

The bond length between carbon-carbon double bond ∝ number of hyperconjugating structures.

Ex. (a) $CH_3-\overset{\overset{a}{\downarrow}}{CH=CH}-CH_3,\ CH_3-\overset{\overset{b}{\downarrow}}{CH=CH_2},\ \overset{\overset{c}{\downarrow}}{CH_3=CH_2}$

Bond length order : a > b > c

(b) 

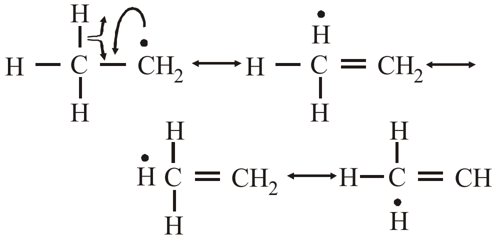
Bond length order : a > b > c

(iii) Stability of alkyl free radicals :

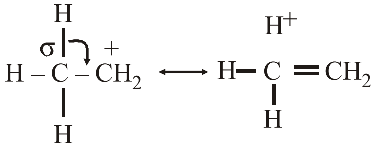
The delocalization of C – H σ electrons can also take place via the half–filled p–atomic orbital in conjugation. Thus, the relative stabilities of alkyl free radicals are in the order: t–alkyl > sec. alkyl > primary alkyl > CH_3 (methyl radical)

For example : $(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > \dot{C}H_3CH_2 > \dot{C}H_3$

Greater the number of hyperconjugative structures of an alkyl radical, higher is the stability. Ethyl radical may be regarded as a hybrid of following hyperconjugative structures :

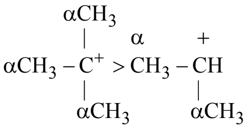


(iv) Stability of alkyl carbonium ions : C–H sigma electrons are also conjugated with a vacant p–orbital. For example, in ethyl carbonium ion.



The stability of an alkyl carbonium ion is proportional to the number of hyperconjugative structures, i.e., to the number of αC – H bonds in that carbonium ion. So, the decreasing stability order of alkyl carbonium ions is :

$t > s > p > \overset{+}{C}H_3$

Ex. 
$\alpha CH_3-\underset{\alpha CH_3}{\overset{\alpha CH_3}{C^+}} > \overset{\alpha}{CH_3}-\underset{\alpha CH_3}{\overset{+}{CH}}$

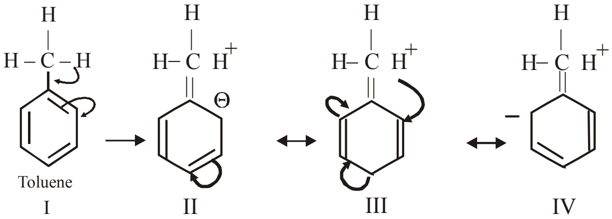
t-butyl isopropyl
(Most stable)
(Nine hyper conjugative structures)

$> \overset{\alpha}{C}H_3-\overset{+}{C}H_2 > \overset{+}{C}H_3$

Ethyl Methyl
(Least stable)

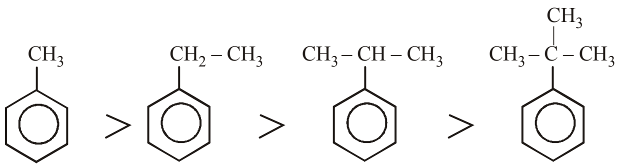
(v) Directive influence of groups :

Methyl group in toluene is an activating and ortho–para directing group. It can be explained by hyperconjugation.



The flow of electrons takes place towards the benzene ring due to hyperconjugation. Therefore, the electron density increases at both the ortho and para positions. Consequently, the benzene ring is activated and the electrophilic substitution in toluene takes place at ortho and para positions.

(vi) Stability of alkyl benzene [Stability ∝ α-H atoms]



	Methyl benzene	Ethyl benzene	Isopropyl benzene	tartery Butyl benzene
α-H %	3	2	1	0

(vii) Heat of hydrogenation (HOH) :

$R-CH=CH_2+H_2 \rightarrow R-CH_2CH_3+\Delta H$

(a) Heat evolved when 1 mole of any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation (ΔH). If alkene is more reactive towards hydrogen then it will evolve more ΔH.

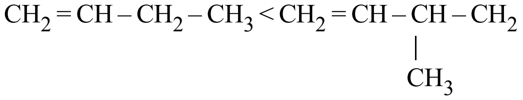
So, $\Delta H \propto \dfrac{1}{\text{stability of alkene}} \propto \dfrac{1}{\text{number of }\alpha\text{-H}}$

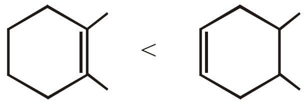
(b) $\Delta H \propto$ number of π bonds

(c) It is exothermic process (energy release)

Examples of HOH order

* $CH_2=CH-CH_2-CH_3 > CH_3-CH=CH-CH_3$

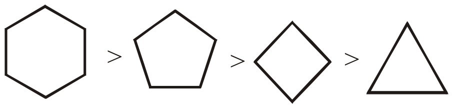
* 
$CH_2=CH-CH_2-CH_3 < CH_2=CH-\underset{CH_3}{\underset{|}{CH}}-CH_2$

* 

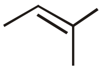
(viii) Heat of combustion (HOC) :

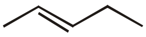
It is the energy liberated during complete combustion of organic compound.

HOC ∝ No. of carbon-atoms

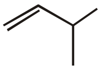
e.g., 

$$\text{HOC} \propto \frac{1}{\text{stability of hydrocarbon}}$$


(a) 9α


(b) 5α


(c) 2α


(d) 1α

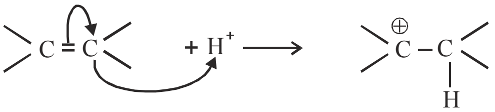
d > c > b > a

ELECTROMERIC EFFECT (E-EFFECT)

The temporary effect which operates in the organic compounds having multiple bonds i.e. double or triple bonds under the influence of an outside attacking species. As a result, one π-electron pair of the multiple bond gets completely transferred to one of the bonded atoms which is usually more electronegative.

The electromeric effect is shown by a curved arrow (↷) representing the electron transfer originating from the centre of the multiple bond and pointing towards one of the atoms which is more electronegtative.

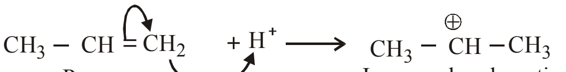
The effect can be illustrated by the attack of H^+ ion on the molecule of alkene.


Carbocation

Types of electromeric effect :

The electromeric effect is of two types i.e. + E-effect and – E-effect.

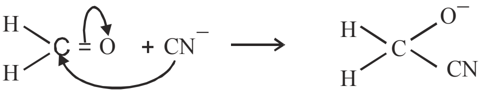
(i) **+E-effect :** If the pi-electron pair of the multiple bond is transferred to the atom to which the attacking reagent gets attached, the the effect is called +E effect. For example,


Propene Isopropyl carbocation

In this case, CH_3 group has +I (inductive) effect and the π-electron shift can take place only to the right.

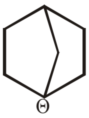
(ii) **–E-effect :** In case the pi-electron pair of the multiple bond is transferred away from the atom which gets linked to the attacking reagent, the effect is known as –E-effect.

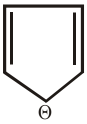
For example, attack of CN^- ion on formaldehyde,


Formaldehyde Anion

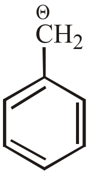
Example 9 :

Which of the following is least stable?

(A) 

(B) 

(C) $HC \equiv C^{\ominus}$

(D) 

Sol. **(A).** Is less stable due to bridgehead carbanion.

Example 10 :

$Cl - NH_2$ is less basic than methyl amine, why ?

Sol. Due to – I effect of – Cl group and $p_\pi - d_\pi$ conjugation.

Example 11 :

Phenol is more acidic than alcohols why ?

Sol.

$$Ph - OH \xrightarrow{-H^{\oplus}} Ph - O^{\ominus} \qquad R - OH \xrightarrow{-H^{\oplus}} R - O^{\ominus}$$

Stable by resonance no resonance

So, it is more acidic.

Example 12 :

Aniline is less basic than alkyl amine, why ?

Sol. Due to delocalization of lone pair. of nitrogen in aniline, aniline is less basic.

Example 13 :

Which is weakest base :

(i) $C_6H_5 - CH_2 - NH_2$
(ii) $C_6H_5 - CH_2 - NH - CH_3$
(iii) $O_2N - CH_2 - NH_2$
(iv) $CH_3 - NH - CHO$

Sol. (iv) due to resonance of lone pair.

Example 14 :

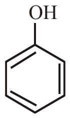
Which of the following is maximum stable

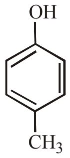
(i) Conjugated alkadiene ($CH_2 = CH - CH = CH_2$)
(ii) Isolated alkadiene ($CH_2 = CH - CH_2 - CH = CH_2$)
(iii) Cumulated alkadiene ($CH_2 = C = CH_2$)
(iv) All are equal

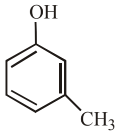
Sol. (i) Due to resonance conjugated alkadiene is maximum stable. Isolated is more stable than cumulated alkadiene due to H-effect.

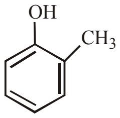
Example 15 :

Find the acid strength order.


(I)


(II)


(III)


(IV)

Sol. Acid strength order : I > III > II > IV

Step 1 : Notice that CH_3 have +Ieffect so all methylphenols (cresols) are less acidic than phenol (I).

Step 2 : Now amongst cresols p- and o- CH_3 are increasing the e^- density due to their hyper conjugation but ortho isomer has viable +I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only +I works it as least e^- density amongst the cresol.

Example 16 :

Which is correct order of stability of carbanion –

(I) $F - CH_2 - CH_2 - CH_2^{\ominus}$

(B) $O_2N - CH_2 - CH_2 - CH_2^{\ominus}$

(III) $Cl-CH_2-CH_2-CH_2^{\ominus}$

(IV) $Me_3N^{\oplus}-CH_2-CH_2-CH_2^{\ominus}$

(A) I > III > II > IV (B) IV > I > III > II

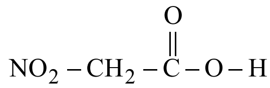
(C) IV > II > I > III (D) IV > III > I > II

Sol. **(C).** Stability of carbanion : Electron withdrawing group increases the stability of carbanion.

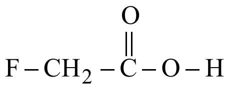
$N^{\oplus}Me_3 > NO_2 > F > Cl$

Example 17 :

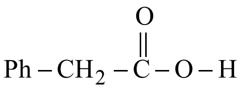
Select the least acidic compound –

(A) 

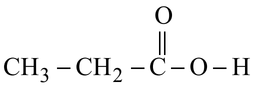
$NO_2-CH_2-\overset{\overset{O}{||}}{C}-O-H$

(B) 

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

(C) 

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

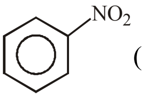
(D) 

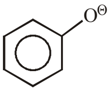
$CH_3-CH_2-\overset{\overset{O}{||}}{C}-O-H$

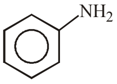
Sol. **(D).** Least acidic : Electron releasing group decreases the acidic strength in carboxylic acid. They decreases δ (+) charge on carbon.

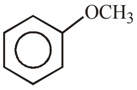
Example 18 :

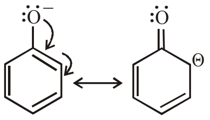
In which of the following molecules π-electrons density in ring is maximum –

(A) 

(B) 

(C) 

(D) 

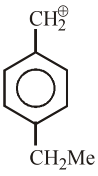
Sol. **(B).** 

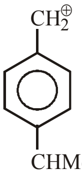
After releasing e⁻ density there is no charge on oxygen atom. (Oxygen is using their extra bank balance). So, it will be more stable.

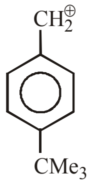
Example 19 :

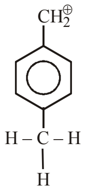
Select the most stable intermediated –

(A) 

(B) 

(C) 

(D) 

Sol. **(A).** 

This CH_3 group will show +I effect as well as hyperconjugation.

TYPES OF ORGANIC REACTIONS

(1) SUBSTITUTION OR DISPLACEMENT REACTIONS

Substitution or displacement reactions are those reactions in which an atom or group of atoms attached to a carbon atom in a substrate molecule is replaced by another atom or group of atoms.

Types of substituting reactions

(a) Free radical substituting reactions

(b) Nucleophilic substituting reactions

(c) Electrophilic substituting reactions

Examples :

(i) $CH_4 + Cl_2 \xrightarrow[\text{light}]{\text{uv}} CH_3Cl + HCl$

(Hydrogen atom is replaced by chlorine)

(ii) $CH_3CH_2Br + aq.KOH \longrightarrow CH_3CH_2OH + KBr$

Ethyl bromide Ethyl alcohol

(Bromine atom is replaced by hydroxyl group)

(iii) $CH_3OH + HBr \longrightarrow CH_3Br + H_2O$

Methyl alcohol Methyl bromide

(Hydroxyl group is replaced by bromine)

(iv) $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4(\text{conc.})} C_6H_5NO_2 + H_2O$

Benzene (conc.) Nitrobenzene

(Hydrogen is replaced by NO_2 group)

Mechanism of substitution reactions :

These reactions may follow free radical, nucleophilic or electrophilic mechanism. Some typical examples are considered to explain the three types of mechanism.

(a) Free radical substitution reactions :

Chlorination of methane : The chlorination of methane in the presence of ultraviolet light is an example of free radical substitution (HOMOLYSIS).

$$CH_4 + Cl_2 \xrightarrow[\text{light}]{\text{uv}} CH_3Cl + HCl$$

The reaction does not stop with the formation of methyl chloride (CH_3Cl) but the remaining hydrogen atoms are replaced one by one with chlorine atoms to give rise chain reaction.

$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$
$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$
$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

Mechanism : The reaction is initiated by the breaking of chlorine molecule into chlorine–free radicals in presence of UV light.

I Step : Chain initiation : $Cl_2 \xrightarrow[\text{light}]{\text{uv}} Cl^{\bullet} + Cl^{\bullet}$

II Step : Chain propagation

The chlorine–free radicals attack methane molecule.

$$CH_4 + Cl^{\bullet} \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

Each of the methyl–free radicals, in turn, reacts with chlorine molecule to form methyl chloride and at the same time chlorine–free radical is produced.

III Step : Chain termination : The chain of reactions initiated and propagated as shown above may be terminated if free radicals combine amongst themselves without giving rise to any new radicals.

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2 \ ; \ \dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

Reactivity of the halogen for free radical substitution is in the order : $F_2 > Cl_2 > Br_2 > I_2$

(b) Nucleophilic substitution :

Many substitution reactions, especially at the saturated carbon atom in aliphatic compounds such as alkyl halides, are brought about by nucleophilic reagent or nucleophiles.

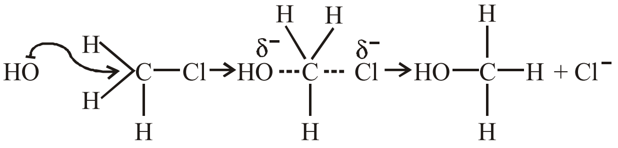
$$\underset{\text{Substrate}}{R-X} + \underset{\text{Nucleophile}}{OH^-} \longrightarrow R-OH + \underset{\text{Leaving group}}{X^-}$$

Such substitution reactions are called nucleophilic substitution reactions, i.e., S_N reactions (S stands for substitution and N for nucleophile). The nucleophilic substitution reactions are divided into two classes:

(i) S_N2 Reactions :

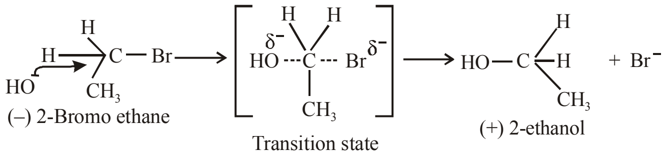
These are bimolecular reactions. When the rate of reaction depends on the concentration of both substrate and the nucleophile, the reaction is said to be S_N2, i.e., 2nd order change. Rate ∝ [Sustrate] [Nucleophile]

Hydrolysis of methyl chloride is an example of S_N2 reaction When the methyl chloride is attacked by OH^- strong nucleophile from the opposite side of the chlorine atom, a transition state (TS) results in which both OH and Cl are partially bonded to carbon atom.



Transition state Methyl Alcohol

When (—) 2–bromo ethane is allowed to react with sodium hydroxide under conditions where second order kinetics are followed, there is obtained (+) 2–ethanol.



Configuration : Hence, an S_N2 reaction proceeds with complete stereo–chemical inversion. This is also known waldon Inversion.

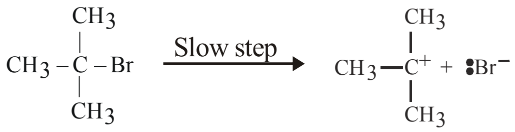
S_N2 **order :** Methyl > ethyl > isopropyl > tertiary butyl > allyl > benzyl halides

(ii) S_N1 Reactions : S_N1 stands for unimolecular reaction. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate, the reaction is of first order change and is represented as S_N1.

Rate ∝ [Substrate]

The hydrolysis of tert–butyl bromide is an example of S_N1 reaction. The reaction consists of two steps :

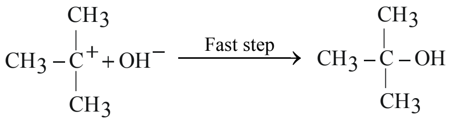
Step 1. The substrate undergoes heterolytic fission forming a carbonium ion. This is the slow process and rate determining step.



$$(CH_3)_3C-Br \xrightarrow{\text{Slow step}} (CH_3)_3C^+ + :Br^-$$

The carbonium ion is planar as the central positively charged carbon atom is sp^2 – hybridized.

Step 2. The nucleophile (OH^-) can attack the planar carbonium ion form either side to form tert–butyl alcohol and the low concentration of OH^- favours S_N1 reaction.



$$(CH_3)_3C^+ + OH^- \xrightarrow{\text{Fast step}} (CH_3)_3C-OH$$

$S_N1$reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens; i.e.,

$$\underset{\text{Tertiary}}{R_3C-X} > \underset{\text{Secondary}}{R_2CH-X} > \underset{\text{Primary}}{RCH_2-X} > \underset{\text{Methyl}}{CH_3-X}$$

Electrophilic substitution :

Electrophilic substitution involves the attack by an electrophile. It is represented as S_E (S stands for substitution and E stands for electrophile). If the order of reaction is 1, it is written as S_E1 (unimolecular) and if the order is 2, it is S_E2 (Bimolecular).

(I) S_E1 Reaction Mechanism :

Electrophilic substitution in aliphatic compounds (S_E1) are very rare : some of the important examples are :

(a) Replacement of the metal atom in an organometalic compound by hydrogen :

$$R-M + H^+ \longrightarrow R-H + M^+$$

$$CH_3CH_2Na + C_6H_6 \longrightarrow CH_3-CH_3 + C_6H_5Na$$

(b) Isotopic exchange of hydrogen for deuterium or tritium:

$$R-H + D^+ \rightleftharpoons R-D + H^+$$

$$R-H + T^+ \rightleftharpoons R-T + H^+$$

(II) S_E2 Reaction Mechanism :

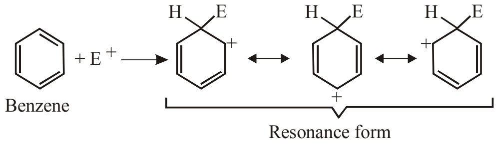
Electrophilic substitution (S_E2) is very common in benzene nucleus (aromatic compounds) in which π–electrons are highly delocalized and an electrophile can attack this region of high electron density. In all electrophilic aromatic substitution reactions, it involves

Step 1. The formation of an electrophile, E^+, i.e.,

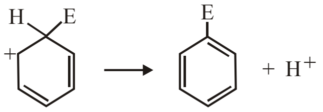
$$E-Nu \rightleftharpoons E^{\oplus} + Nu^{\ominus}$$

$$E^{\oplus} = Cl^{\oplus}, NO_2^{\oplus}, SO_3^{\oplus}, R^{\oplus}, R\overset{\oplus}{C}O$$

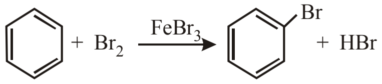
Step 2. The electrophile attacks the aromatic ring to form carbonium ion (or arenium ion) which is stabilized by resonance.



Step 3. Carbonium ion loses the proton to form substitution product.



Ex. : The bromination of benzene in the presence of $FeBr_3$ is an example of electrophilic substitution.

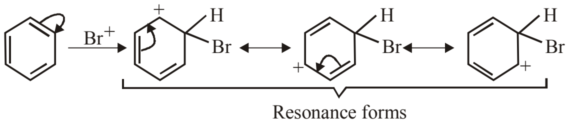


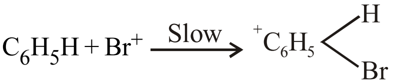
Mechanism :

Step 1. Formation of electrophile takes place.

$$Br - Br + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$$

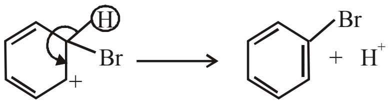
Step 2. The electrophile (Br^+) attacks the benzene ring to form a resonance stabilized carboniumion.





$$C_6H_5H + Br^+ \xrightarrow{\text{Slow}} {}^{+}C_6H_5\langle^{H}_{Br}$$

Step 3. Elimination of proton occurs and the substitution product is formed.



$$(H^+ + FeBr_4^- \longrightarrow FeBr_3 + HBr)$$

Similarly, Nitration, Sulphonation and Friedel – Crafts reaction .... etc., in benzene nucleus are the other examples of electrophilic substitution.

(2) ADDITION REACTIONS

Addition reactions are those in which the attacking reagent adds up to the substrate molecule. Such reactions are given by those compounds which possess double or triple bonds. In the process a triple bond may be converted into double bond or single bonds and a double bond is converted into single bonds. For each π–bond of the molecule two sigma bonds are formed and the hybridization state of carbon atoms changes from sp to sp^2 and sp^2 to sp^3. Types of addition reactions :

(a) Electrophilic addition reactions
(b) Nucleophilic addition reactions
(c) Free radical addition reactions

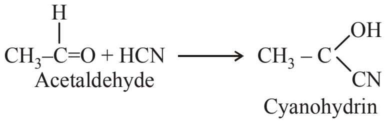
Examples :

(i) $CH \equiv CH + H_2 \xrightarrow[140°C]{Ni} CH_2 = CH_2 \xrightarrow[200°C]{H_2/Ni} CH_3 - CH_3$

Acetylene Ethylene
Ethane

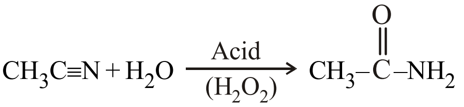
(ii) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br - CH_2Br$

Ethylene 1, 2–Dibromoethane
(Ethylene bromide)

(iii)


$$CH_3-\overset{H}{\overset{|}{C}}=O + HCN \longrightarrow CH_3 - C\langle^{OH}_{CN}$$

Acetaldehyde Cyanohydrin

(iv)


$$CH_3C \equiv N + H_2O \xrightarrow[(H_2O_2)]{Acid} CH_3-\overset{O}{\overset{||}{C}}-NH_2$$

Methyl cyanide Acetamide

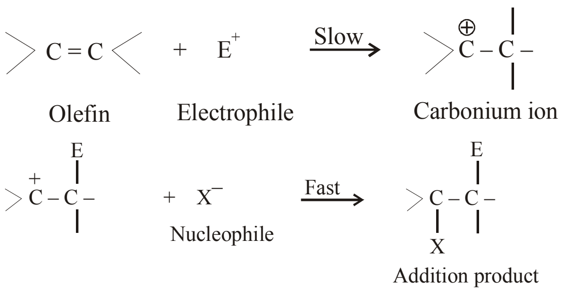
(v) $CH \equiv CH + HBr \rightarrow CH_2{=}CHBr \xrightarrow{HBr} CH_3CHBr_2$

Acetylene Vinyl bromide 1,1-Dibromoethane
(Ethylidine bromide)

Mechanism of addition reaction :

The addition reactions are the reaction of the double or triple bonds. These reactions may be initiated by electrophiles, nucleophiles or free radicals. The molecules having $>C = C<$ or $— C \equiv C —$ are readily attacked by electrophilic reagents while molecules having $>C = O$ or $- C \equiv N$ are readily attacked by nucleophilic reagents.

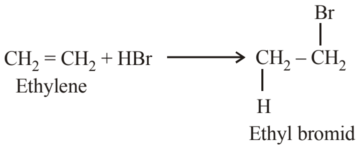
(a) Electrophilic addition reactions : In electrophilic addition reactions, an electrophile approaches the double or triple bond and in the first step forms a covalent bond with one of the carbon atoms resulting in the formation of carbonium ion which then takes up a nucleophile to result in addition product.



Trans-addition

Polar molecule attacks the dauble bond of alkene, then π electron of double bond shift to one of carbon atom due to electromeric effect.

The addition of HBr on ethylene is an example of electrophilic addition. Ethylene is a symmetrical olefin.



Mechanism :

Step 1. Hydrogen bromide gives a proton and bromide ion.

$$HBr \longrightarrow H^+ + :Br^-$$

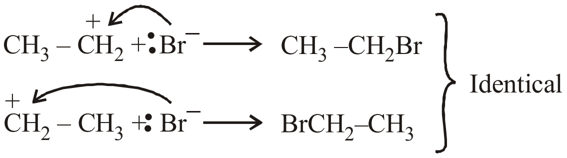
Electrophile Nucleophile

Step 2. The electrophile attacks the double bond to form a carbonium ion.

$$CH_2 = CH_2 + H^{\oplus} \longrightarrow H_2\overset{+}{C} - CH_3$$

Carbonium ion

Step 3. The nucleophile (Br^- ion) now attack the carbonium ion to form the addition product.

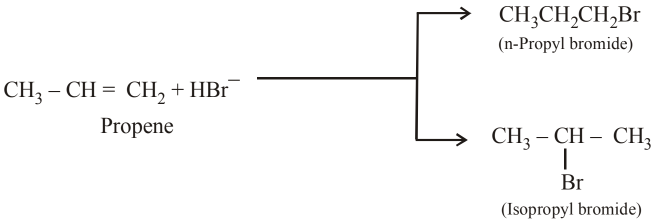


This clearly indicates that the reaction proceeds in two steps:
(a) Formation of carbonium ion (more stable) and
(b) Attack of nucleophile on the carbonium ion.

Stability of carbonium ion is in order :

Benezylic ~ 3° > allylic ~ 2° > 1° > methyl

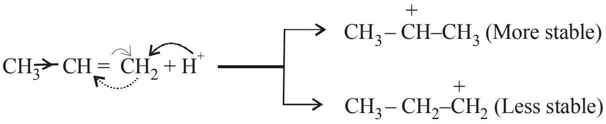
In case both alkene and the adding reagent are unsymmetrical, two products are expected.



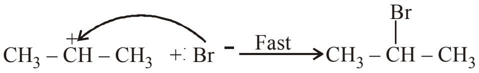
Experimentally, it is observed that isopropyl bromide is the major product. This can be explained on the basis of following mechanism. Consider the addition of HBr to propene which is unsymmetrical in nature.

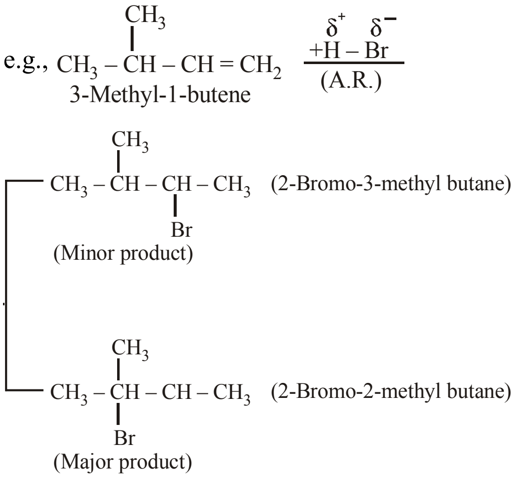
Step 1. Hydrogen bromide gives a proton (H^+) and a bromide ion (Br^-) $HBr \longrightarrow H^+ + :Br^-$

Step 2. The proton (H^+) attacks the π-bond to give a stable carbonium ion.



Step 3. The nucleophile bromide ion attack the more stable carbonium ion to give isopropyl bromide (major product).





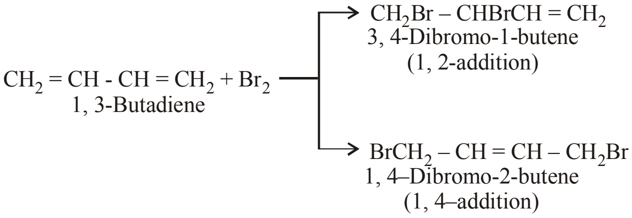
It can be explained by 1, 2–hydride shift.

Addition reactions in alkadienes :

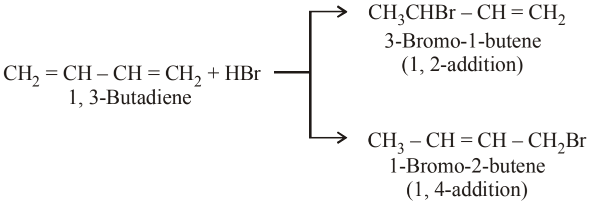
Conjugated alkadienes (1, 3–butadiene) reacts with halogens, halogen acids hydrogen and water, etc. to yield a mixture of 1, 2, and 1, 4–addition products.

Some of the important examples are :

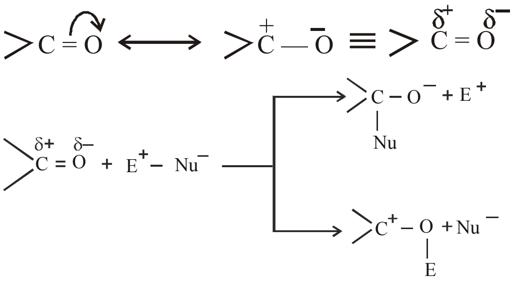
(i) Addition of halogens :



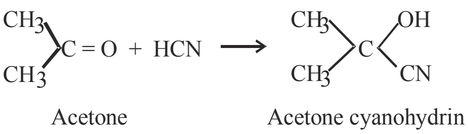
(ii) Addition of halogen acids (HBr or HCl) :



(b) Nucleophilic addition reactions : When the addition reaction occurs on account of the initial attack of nucleophile, the reaction is said to be a nucleophilic addition reaction. Due to presence of strongly π–electrons of the carbon–oxygen double bond in carbonyl group (>C = O) get shifted towards the oxygen atom and thereby such bond is highly polarised. This makes carbon atom of the carbonyl group electron deficient.



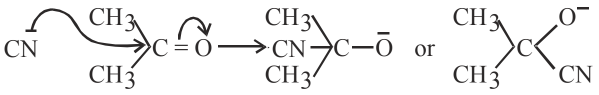
The addition of HCN to acetone (>C = O compounds) is an example of nucleophilic addition.



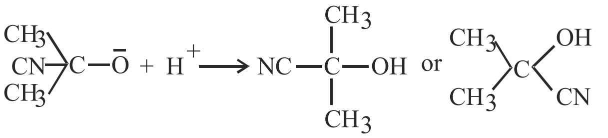
Mechanism of the reaction involves the following steps:

Step 1. HCN gives a proton (H^+) and nucleophile, a cyanide ion (CN^-). $HCN \longrightarrow H^+ + CN^-$

Step 2. The nucleophile (CN^-) attacks the positively charged carbon as to form an anion [H^+ does not attack the negatively charged oxygen as anion is more stable than cation].

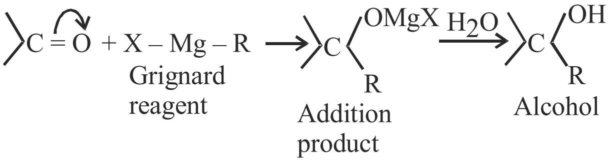


Step 3. The proton (H^+) combines with anion to form the addition product.



Other examples of nucleophilic addition reaction are :

Addition of Grignard reagent to >C = O compounds :

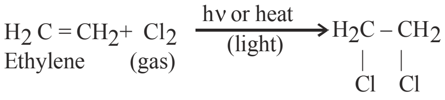


(c) **Free radical addition reaction :**

(i) This type of addition reaction takes place in vapour phase or in non–polar solvents (i.e., Cl_2, Br_2, H_2, CO_2 and CH_4 .... etc.) in presence of sunlight.

(ii) The additives are free radicals and the rate determining step suggests for addition of free radicals.

(iii) For example the photochemically catalysed addition of chlorine to ethylene may be shown as follows :



$$\underset{\text{Ethylene}}{H_2C=CH_2} + \underset{\text{(gas)}}{Cl_2} \xrightarrow[\text{(light)}]{h\nu\text{ or heat}} \underset{Cl\quad Cl}{H_2C-CH_2}$$

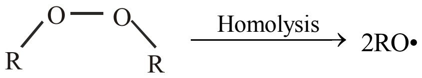
Ethylene (di) chloride

(iv) Addition of HBr on unsymmetric alkene in presence of peroxide is.

Peroxide effects : $CH_3-CH=CH_2+HBr$

$$\xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$$

Mechanism :



(i) Chain initiation : $RO\bullet + HBr \longrightarrow ROH + Br\bullet$

(ii) Chain propagation : (two steps)

$$CH_3-CH=CH_2+Br\bullet \longrightarrow \underset{2^\circ\text{ free radical}}{CH_3-\dot{C}H-CH_2Br}$$

$$CH_3-\dot{C}H-CH_2Br+HBr \longrightarrow CH_3-CH_2-CH_2Br+Br\bullet$$

(iii) Chain termination : $Br\bullet + Br\bullet$ or $2CH_3-\dot{C}H-CH_2Br$

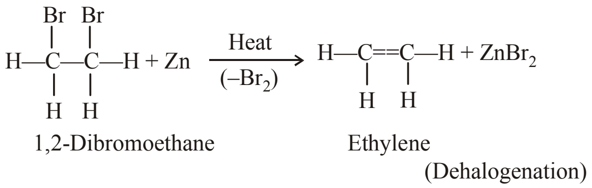
or $CH_3-\dot{C}H-CH_2Br+Br\bullet$

(3) **ELIMINATION REACTIONS**

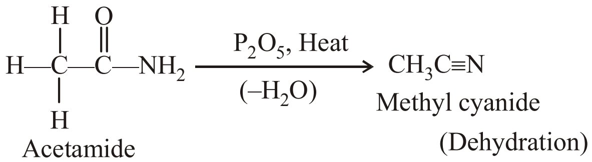
The reverse of addition reactions are termed as elimination reactions. In these reactions generally atoms or groups from two adjacent carbon atoms in the substrate molecule are removed and multiple bond is formed. In the process two sigma bonds are lost and a new π–bond is formed, i.e. state of hybridization of carbon atom changes from sp^3 to sp^2 and sp^2 to sp.

Some examples are :

(i)



(ii)



Mechanism of elimination reactions :

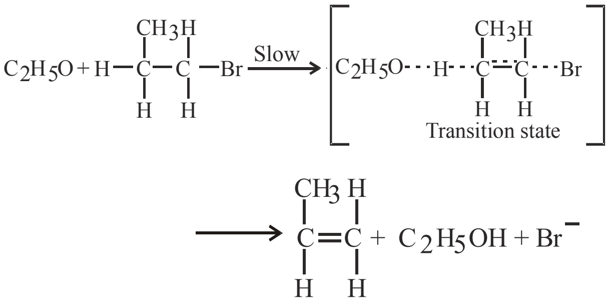
An elimination reaction, generally, involves loss of atoms or groups from adjacent carbon atoms resulting in the formation of a π–bond between these carbon atoms, so these are reverse to addition reactions. The elimination reactions are divided into two classes :

(i) E_2 reactions. E_2 stands for bimolecular elimination.

(ii) E_1 reactions. E_1 stands for unimolecular elimination.

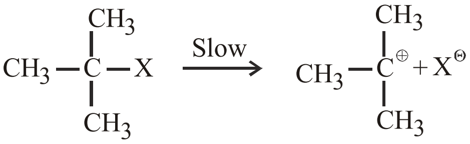
* **E_2 reactions :** The dehydrohalogenation of the alkyl halides with alcoholic alkali is an example of this type. It occurs in one step.

$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br} + C_2H_5\bar{O} \rightarrow \underset{\text{Propene}}{CH_3CH=CH_2} + Br^- + C_2H_5OH$$



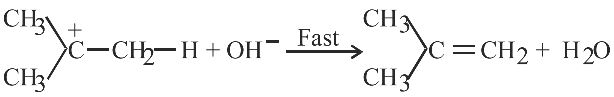
* **E_1 reactions :** These occur in two steps .

Step 1. The alkyl halide ionise to give the carbonium ion.

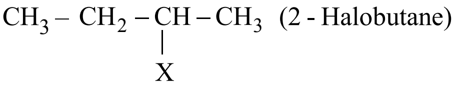


Carbonium ion

Step 2. Carbocation loss a proton from the β–carbon atom by the base (nucleophile) to form alkene.



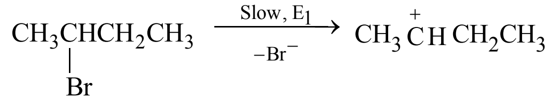
Dehydrohalogenation is removal of HX from alkyl halides with alcoholic KOH or KNH_2 or KO–ter–Bu (potassium tertiary butoxide) and an example of $\alpha-\beta$ elimination, e.g., $CH_3-CH_2X \xrightarrow[(-HX)]{\text{Alc.KOH}} H_2C=CH_2$ (Ethene)


$CH_3-CH_2-\underset{\substack{|\\X}}{CH}-CH_3$ (2 - Halobutane)

$\xrightarrow[(-HX)]{\text{Alc.KOH}} CH_3CH=CHCH_3+CH_3CH_2CH=CH_2$

2 - Butene (major) 1-Butene (minor)

The more substituted alkene is more stable (according to Saytzeff rule), hence the formation of 2–butene is preferred to 1–butene.

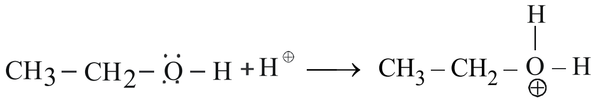
(i)

$CH_3\underset{\substack{|\\Br}}{C}HCH_2CH_3 \xrightarrow[-Br^-]{\text{Slow, } E_1} CH_3\overset{+}{C}HCH_2CH_3$

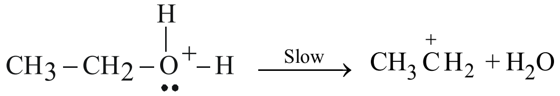
2–Bromo butane　　　Carbonium ion (2°)

(ii) $CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow[-H\ (\text{from } C_3)]{\text{Fast}} CH_3CH=CHCH_3$

2° Carbonium ion　　　2–Butene (more substituted)

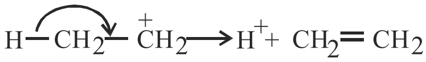
Dehydration of alcohol is another example of elimination reaction. When acids like conc. H_2SO_4 or H_3PO_4 are used as dehydrating agents, the mechanism is E_1. The proton given by acid is taken up by alcohol.


$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H+H^{\oplus} \longrightarrow CH_3-CH_2-\overset{\substack{H\\|}}{\underset{\oplus}{O}}-H$


$CH_3-CH_2-\overset{\substack{H\\|}}{\underset{\bullet\bullet}{O}}{}^{+}-H \xrightarrow{\text{Slow}} CH_3\overset{+}{C}H_2+H_2O$

Carbonium ion

The carbonium ion loses a proton to form alkene.

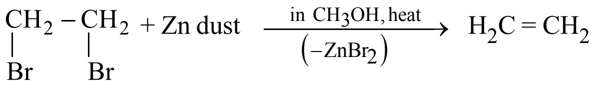

$H-CH_2-\overset{+}{C}H_2 \longrightarrow \overset{+}{H}+CH_2=CH_2$

Dehydration is removal of H_2O from alcohols, e.g.,

$CH_3CH_2OH \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_4, 170^\circ C} H_2C=CH_2$

$CH_3CH_2CH_2OH \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_4, 170^\circ C} CH_3CH=CH_2$

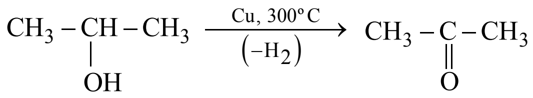
Dehalogenation : It is removal of halogens, e.g.,


$\underset{\substack{|\\Br}}{CH_2}-\underset{\substack{|\\Br}}{CH_2}+\text{Zn dust} \xrightarrow[(-ZnBr_2)]{\text{in } CH_3OH,\text{ heat}} H_2C=CH_2$

Ethylene bromide　　　Ethylene

and **Dehydrogenation :** It is removal of hydrogen, e.g.,

$CH_3CH_2OH \xrightarrow{Cu,\ 200^\circ C} CH_3CHO$

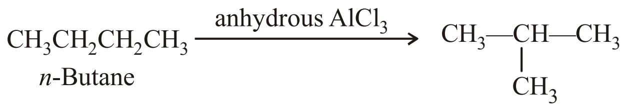

$CH_3-\underset{\substack{|\\OH}}{CH}-CH_3 \xrightarrow[(-H_2)]{Cu,\ 300^\circ C} CH_3-\underset{\substack{||\\O}}{C}-CH_3$

Isopropyl alcohol　　　Acetone

(4) REARRANGEMENT REACTIONS

The reactions which involve the migration of an atom or group from one site to another within the molecule (nothing is added from outside and nothing is eliminated) resulting in a new molecular structure are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

Some of the examples are :

(i)

$CH_3CH_2CH_2CH_3 \xrightarrow{\text{anhydrous } AlCl_3} CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_3$

n-Butane　　　Isobutane

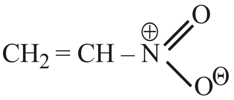
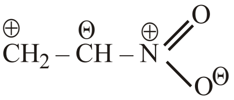
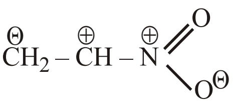
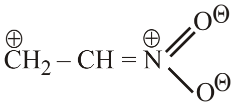
(ii) $NH_4CNO \xrightarrow{\text{Heat}} NH_2-CO-NH_2$

Ammonium cyanate　　　Urea

TRY IT YOURSELF-2

For Q.1-Q.3

Select the least stable resonating structure

Q.1 (A)

(B)

(C)

(D)


Q.2 (A) $CH_2=CH-\overset{+}{C}H-\overset{-}{C}H-NH_2$

(B) $\overset{-}{C}H_2-\overset{+}{C}H-CH=CH-NH_2$

(C) $\overset{-}{C}H_2-CH=CH-CH=\overset{+}{N}H_2$

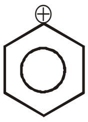
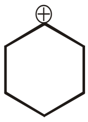
(D) $CH_2=CH-\overset{-}{C}H-CH=\overset{+}{N}H_2$

Q.3 (A) $H_2\overset{\ominus}{C}-\overset{\oplus}{C}H-CH=CH-O-CH_3$

(B) $H_2\overset{\ominus}{C}-CH=CH-CH=\overset{\oplus}{O}-CH_3$

(C) $H_2C=CH-\overset{\oplus}{C}H-\overset{\ominus}{C}H-O-CH_3$

(D) $H_2C=CH-\overset{\ominus}{C}H-CH=\overset{\oplus}{O}-CH_3$

Q.4

(I)

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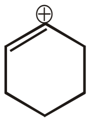

(III)

Correct order of stability of these carbocations is –

(A) I > II > III　　(B) I > III > II

(C) II > I > III　　(D) II > III > I

Q.5 Compare rotational energy barrier for indicated bond

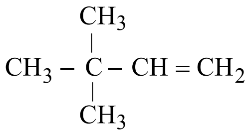
$CH_2\underset{\uparrow x}{=}CH_2$　　　$CH_2\underset{\uparrow y}{=}CH-NH_2$

$CH_2\underset{\uparrow z}{=}CH-CH_3$　　　$O_2N-CH\underset{\uparrow w}{=}CH-NH_2$

(A) x > z > y > w　　(B) w > z > y > x

(C) x > y > w > z　　(D) z > w > y > x

Q.6 Hyperconjugation phenomenon is possible in –

(A) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$ (B) $CH_2=CH_2$

(C) $C_6H_5-CH=CH_2$ (D) $CH_3-CH_2-CH=CH_2$

Q.7 The correct stability order of the following resonance structures is :

$CH_2=C=O$ (I) $H_2\overset{-}{C}-\overset{+}{C}=O$ (II)

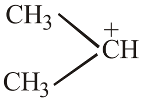
$H_2C=\overset{+}{C}-\overset{-}{O}$ (III) $H_2\overset{-}{C}-C\equiv\overset{+}{O}$ (IV)

(A) (IV) > (I) > (III) > (II) (B) (II) > (IV) > (I) > (III)
(C) (III) > (II) > (IV) > (I) (D) (I) > (IV) > (III) > (II)

Q.8 Maximum –I effect is exerted by the group
(A) C_6H_5 (B) $-OCH_3$
(C) $-Cl$ (D) $-CHO$

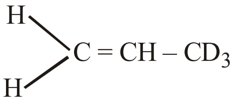
Q.9 Which of the following alkyl groups has the maximum +I effect ?
(A) $(CH_3)_2CH-$ (B) $(CH_3)_3C-$
(C) CH_3CH_2- (D) CH_3-

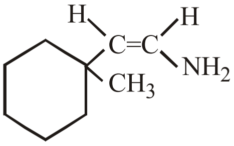
Q.10 Which of the following cannot exhibit hyperconjugation

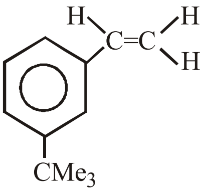
(A) $CH_3\dot{C}H_2$ (B) 

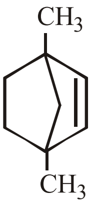
(C) $CH_3CH=CH_2$ (D) $(CH_3)_3C-\overset{+}{C}H_2$

Q.11 Hyperconjugation is possible in :

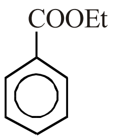
(A) 

(B) 

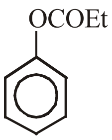
(C) 

(D) 

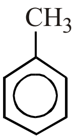
Q.12 The correct order of electron density in aromatic ring of following compounds is :



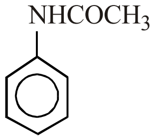
(I)



(II)



(III)



(IV)

(A) IV > III > II > I (B) I > II > III > IV
(C) IV > II > I > III (D) IV > II > III > I

Q.13 Arrange the carbanions, $(CH_3)_3\bar{C}, \bar{C}Cl_3, (CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$ in order of their decreasing stability :

(A) $(CH_3)_3\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(B) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(C) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$

(D) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

ANSWERS

(1) (C)	**(2)** (A)	**(3)** (C)
(4) (D)	**(5)** (B)	**(6)** (D)
(7) (D)	**(8)** (D)	**(9)** (B)
(10) (D)	**(11)** (A)	**(12)** (D)
(13) (B)		

PURIFICATION OF ORGANIC COMPOUNDS

Methods usually adopted for the purification of organic compounds are -

Crystallization : The method is based on the difference in the solubility of the organic compound and the impurities present in it. A saturated solution of the impure compound in a suitable solvent is prepared. Of course the temperature has to be increased for more dissolution of the organic compound. Subsequently the solution is filtered and cooled, pure crystals get separated.

Examples :

Compound and impurity	**Solvent chosen**
Benzoic acid + naphthalene	Water
Sugar + sand	Water
Sugar + Common salt	Ethanol
Iodoform + impurity	Ethanol

Sublimation : Solid $\underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}}$ Vapour

This method is used for the purification of solids which sublime from the non–volatile impurities.

Example : Camphor, naphthalene, ammonium chloride, salicylic acid, iodine, $AlCl_3$, $HgCl_2$ etc. are purified by sublimation.

Simple Distillation : Distillation implies conversion of liquid into vapour state by heating followed by condensation of the vapours by cooling. The method is suited for liquids which are stable at their boiling point.

Example : (i) Mixture of hexane (b.p. 342 K) and toluene (b.p. 384 K) **(ii)** Mixture of benzene (b.p. 353 K) and aniline (b.p. 457 K)

Fractional Distillation : Fractional distillation is a suitable process for separating two or more miscible liquids which have boiling points quite close to each other.

Example : (i) Mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338K) **(ii)** Separation of petroleum into gasoline, kerosene oil, diesel oil etc.

Differential Extraction : An aqueous solution of organic compound is taken in the separating funnel and is shaken with organic solvent which is immiscible with water but in which the organic compound is highly soluble. Organic compound is dissolved in the organic solvent which is extracted by the separating funnel. Organic compound is then recovered by evaporating the solvent in a water bath.

Example : To remove benzoic acid from aqueous solution of benzoic acid, benzene is used as the extracting solvent.

Chromatography : Chromatography may be defined as the technique of separating the components of a mixture in which separation is affected by movement of individual components through a stationary phase (fixed) under the influence of mobile phase. Different types of important chromatography are give in the table :

Chromatography	**Stationary Phase**	**Mobile Phase**
Adsorption chromatography	Solid	Liquid
Partition chromatography	Liquid	Liquid

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

* **Carbon and Hydrogen :**

Liebig's combustion method : A known weight of organic compound is heated with pure and dry cupric oxide in a steam of pure and dry oxygen From the weight of CO_2 and H_2O, the percentage of C and H can be calculated.

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$

(i) $\% \text{ of C} = \dfrac{\text{Weight of } CO_2}{\text{Weight of org. compound}} \times \dfrac{12}{44} \times 100$

(ii) $\% \text{ of H} = \dfrac{\text{Weight of } H_2O}{\text{Weight of org. compound}} \times \dfrac{2}{18} \times 100$

* **Oxygen : (i)** All the elements except oxygen present in the organic compound are estimated and the total of their percentages subtracted from 100 to get the % of oxygen.

Percentage of oxygen = 100 – (Sum of the percentages of all other elements)

(ii) Aluise's method : Organic compound containing oxygen is heated with graphite and CO formed is quantitatively converted into CO_2 on reaction with I_2O_5.

$$\text{Org. compound} \xrightarrow{\text{Pyrolysis}} \text{Oxygen}$$

$$\underset{16\,g}{O} \equiv CO \equiv \underset{44\,g}{CO_2}$$

$$\% \text{ of O} = \frac{16}{44} \times \frac{\text{mass of } CO_2}{\text{mass of org. compd.}} \times 100$$

* **Nitrogen :**

(i) Duma's method : Elemental nitrogen is converted into molecular nitrogen by a suitable chemical method and its voiume is changed to STP data.

$$C + 2H + 3CuO \rightarrow CO_2 + H_2O + 3Cu$$
$$2N + 2CuO \rightarrow N_2 + \text{oxide of nitrogen}$$
$$\text{Oxides of nitrogen} + Cu \longrightarrow N_2 + CuO$$

(ii) Kjeldahl's method : Nitrogen in organic compound is converted into NH_3 by suitable chemical method which, in turn, is absorbed by V_1mL of N_1 H_2SO_4.

$$\text{N(from organic compound)} + \text{conc. } H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$$

$$\% \text{of N} = \frac{28}{22400} \times \frac{V}{W} \times 100$$

Where, V= volume of N_2 in nitrometer (in ml) at NTP, W = Weight of substance taken;

* **Halogens :**

(i) Carius method : When an organic compound containing halogen (Cl, Br, or I) is heated in a sealed tube with fuming nitric acid in presence of silver nitrate, silver halide is formed. From the mass of silver halide formed, the percentage of the halogen can be calculated.

$$\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

$$\% \text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

$$\% \text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$$

(ii) Schiff's and Piria method : The accurately weighed organic compound (0.15 – 0.25 g) is taken in a small platinum crucible with a mixture of lime and sodium carbonate, $(CaO + Na_2CO_3)$. It is now heated strongly and then cooled and dissolved in dilute nitric acid in a beaker. The solution is then filtered and the halide is precipitated with silver nitrate solution. Halogen is now calculated as in Carius method.

* **Phosphorous :**

Carius method : The organic compound containing phosphorus is heated with fuming nitric acid. Phosphorus is oxidised to phosphoric acid. It is precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$, by the addition of magnesia mixture $(MgSO_4 + NH_4OH + NH_4Cl$. The magnesium ammonium phosphate is washed, dried and ignited when it is converted to magnesium pyrophosphate $(Mg_2P_2O_7)$.

$$2MgNH_4PO_4 \xrightarrow{\text{heat}} Mg_2P_2O_7 + 2NH_3 + H_2O$$

From the mass of magnesium pyro-phosphate, the percentage of phosphorus in the compound can be calculated.

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

* **Sulphur :**

Carius method : When an organic compound containing sulphur is heated with fuming nitric acid, sulphur is oxidised to sulphuric acid. This is precipitated as barium sulphate by adding barium chloride solution. From the amount of barium sulphate, percentage of sulphur can be calculated

$$S + HNO_3(\text{fuming}) \xrightarrow{\text{heat}} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{white ppt}}{BaSO_4} + 2HCl$$

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

USEFUL TIPS

* **Stability of reaction intermediates:**

(i) Stability of carbocation ∝ + M, + I groups.

(ii) Stability of carbon free radical ∝ + I groups.

(iii) Stability of carbanion ∝ – M, –I groups.

* **Stability of Alkene:**

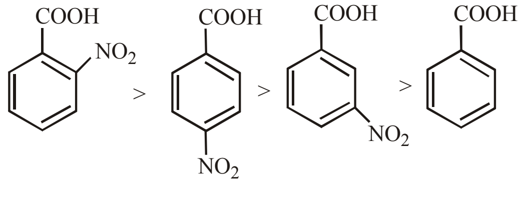
More substituted (Branched) Alkenes are more stable due to hyperconjugation

* **Acidic & Basic Strength:**

(i) Acidity (K_a) ∝ – M, –I groups.

(ii) Basicity (K_b) ∝ + M, +I groups and solvation effect in aqueous solution.

*

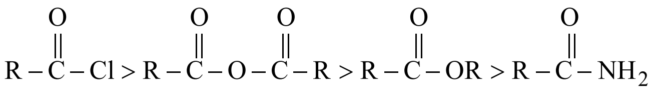


Acidity in decreasing order

* Reactivity of S_N1 ∝ Stability of carbocation

S_N1 reactivity : $3° > 2° > 1° > CH_3 - X$

* Reactivity order :



$$R-\overset{\overset{\large O}{\|}}{C}-Cl > R-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-R > R-\overset{\overset{\large O}{\|}}{C}-OR > R-\overset{\overset{\large O}{\|}}{C}-NH_2$$

* Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$

* Reactivity of H : 3°H > 2°H > 1°H

* Rate of reaction ∝ Stability of carbocation

* Rate of E1 = 3° alochol > 2° alochol > 1° alochol

Rate of reaction ∝ Stability of carbocation

* Rate of E2 reaction

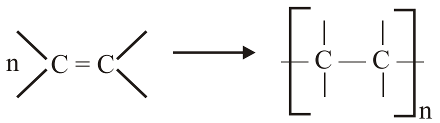
= 3° alkyl halide > 2° alkyl halide > 1° alkyl halide

* **Alkene → chloroalkane :** reagents: Cl_2

conditions: UV light ; mechanism: free radical substitution

equation: $RH + Cl_2 \rightarrow RCl + HCl$

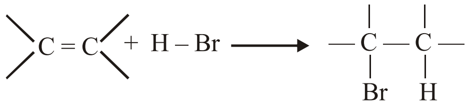
* **Alkene → polyalkene :** Conditions: low T, high p.



Type of reaction: addition polymerisation (free radical)

* **Alkene → bromoalkane :** Reagent: HX(g)

Conditions: room T ;

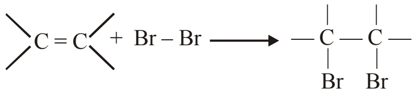


Type of reaction: electrophilic addition

* **Alkene → dibromoalkane**

Reagent: Br_2 in water or in an organic solvent

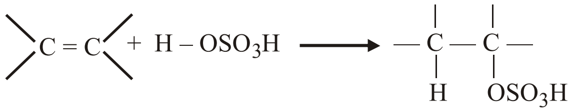
Conditions: room T



Mechanism: electrophilic addition

* **Alkene → alkylhydrogensulphate**

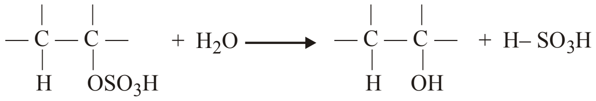
Reagent: concentrated sulphuric acid ; Conditions: cold



Mechanism: electrophilic addition

* **Alkylhydrogensulphate → alcohol**

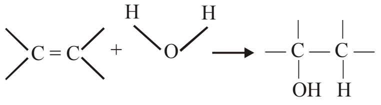
Reagent: water ; Conditions: warm



Type of reaction: hydrolysis

* **Alkene → alcohol**

Reagent: steam ; Conditions: 300°C, 60 atm, H_3PO_4 catalyst



Type of reaction: hydration

* **Haloalkane → alcohol**

Reagent: NaOH(aq) or KOH(aq)

Conditions: warm under reflux

Equation: $R - X + OH^- \rightarrow R - OH + X^-$

Type of reaction: nucleophilic substitution

* **Haloalkane → nitrile**

Reagent: KCN in aqueous ethanol

Conditions: boil under reflux

Equation : $R - X + CN^- \rightarrow R - CN + X^-$

Type of reaction: nucleophilic substitution

* **Haloalkane → Amine**

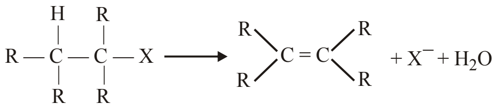
Reagent: ammonia in ethanol in a sealed tube

Conditions: heat

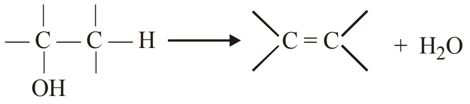
Equation: $R - X + 2NH_3 \rightarrow R - NH_2 + NH_4X$

Type of reaction: nucleophilic substitution

- **Haloalkane → alkene**
  Reagent : KOH in ethanol ; Conditions: heat



  Type of reaction: elimination
- **Primary alcohol → aldehyde**
  Reagent: potassium dichromate and dilute sulphuric acid
  Conditions: warm, distillation
  Equation: $RCH_2OH + [O] \rightarrow RCHO + H_2O$
  Type of reaction: mild oxidation
- **Secondary alcohol → ketone**
  Reagent: potassium dichromate and dilute sulphuric acid
  Conditions: heat, distillation
  Equation: $R_1CH(OH)R_2 + [O] \rightarrow R_1COR_2 + H_2O$
  Type of reaction: oxidation
- **Aldehyde → carboxylic acid**
  Reagent: potassium dichromate and dilute sulphuric acid
  Conditions: heat, reflux
  Equation: $R-CHO + [O] \rightarrow R-COOH$
  Type of reaction: oxidation
- **Alcohols→ alkenes :** Reagent: concentrated sulphuric acid
  Conditions: heat

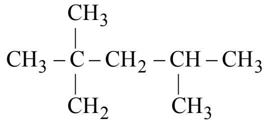


  Type of reaction: elimination
- **Glucose → ethanol :** reagent: yeast
  conditions: 35 - 55°C, no air
  equation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
  type of reaction: fermentation

ADDITIONAL EXAMPLES

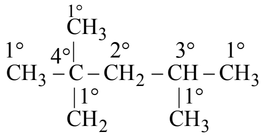
Example 1 :

How many 1°, 2°, 3° and 4° carbon atoms are present in



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

Sol.

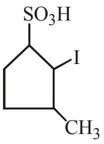


$$\overset{1°}{CH_3}-\overset{\overset{\overset{1°}{CH_3}}{|}}{\underset{\underset{CH_2}{|1°}}{\overset{4°}{C}}}-\overset{2°}{CH_2}-\underset{\underset{CH_3}{|1°}}{\overset{3°}{CH}}-\overset{1°}{CH_3}$$

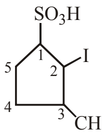
1° Carbon atoms = 5, 2° Carbon atoms = 1,
3° Carbon atoms = 1, 4° Carbon atoms = 1.

Example 2:

Write IUPAC name of



Sol.



(2-Iodo-3-methylcyclopentanesulfonic acid)

Here, Secondary prefix = 2-Iodo-3-methyl
Primary prefix = cyclo
Word root = pent
Primary suffix = ane
Secondary suffix = sulfonic acid

Example 3 :

The electron attracting species in the following is –

(1) – CN	(2) – NH_2
(3) – NHR	(4) – NHCOR

Sol. **(1).** The groups having double or triple bonds are electron attracting. Hence – CN is electron attracting and in rest of the species N-atom has lone pair of electrons.

Example 4 :

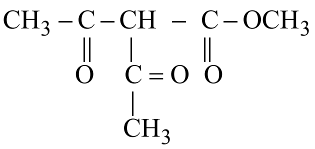
Which carbanion is less stable than the other three –

(1) $\overset{\ominus}{C}H_2-NO_2$	(2) $\overset{\ominus}{C}H_2-CHO$
(3) $\overset{\ominus}{C}H_2-CH_3$	(4) $\overset{\ominus}{C}H_3$

Sol. **(3).** Due to +I effect of CH_3 group $\overset{\ominus}{C}H_2-CH_3$ is less stable.

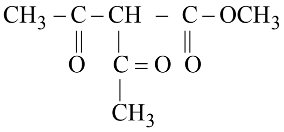
Example 5 :

Write the IUPAC name of



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OCH_3$$

Sol. The principal functional group is ester group



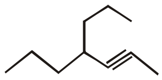
$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OCH_3$$

Methyl-2-acetyl-3-oxobutanoate

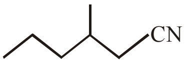
Example 6 :

Give the IUPAC names of the following compounds

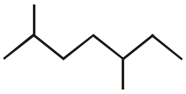
(a)



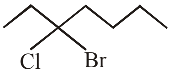
(b)



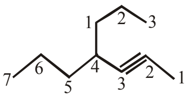
(c)



(d)

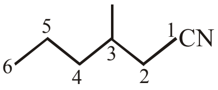


Sol. (a)

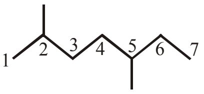


4-propylhept-2-yne

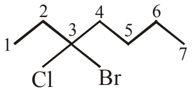
(b)



3-methylpentanenitrile

(c) 

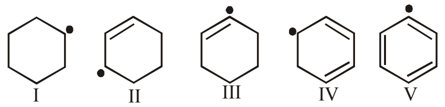
2, 5-dimethylheptane

(d) 

3-bromo-3-chloroheptane

Example 7 :

Arrange the following free radicals in increasing order of stability :



Sol. V < III < I < II < IV

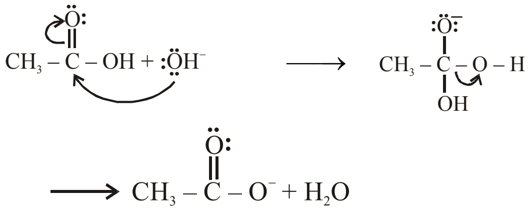
Resonance stabilized free radical is more stable.

Example 8 :

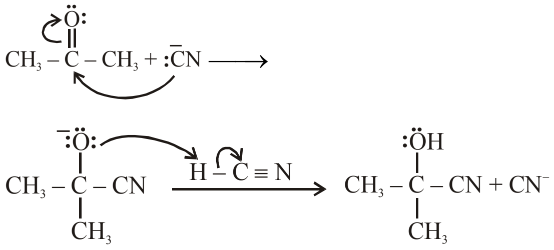
Classify the reagents shown in bold in the following equations as nucleophiles or electrophiles. Use curved arrow notation to show the electron movement.

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + {}^-\mathbf{NC} \longrightarrow CH_3C(CN)OHCH_3$

Sol. (a) 

OH⁻ is a negative nucleophile

(b) 

CN⁻ is a negative nucleophile

Example 9 :

Which order is correct regarding stability of intermediates

(I) $CH_2 = CH - \overset{\oplus}{C}H_2$ (II) $CH_2 = \overset{\oplus}{C}H$ (III) $CH \equiv \overset{\oplus}{C}$

(A) I = II = III (B) I < II < III

(C) III = II > I (D) I > II > III

Sol. **(D).** Structure Ist → Allylic C^+ (more stable)

IInd → Vinylic C^+ (less stable)

IIIrd → In 3rd option this (HC ≡ C) carbon is more electronegative and contain a positive charge make it less stable.

Example 10 :

Correct order of heat of combustion for following compounds

(P) $CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3$

(Q) $CH_2=CH-CH_2-CH_2-CH_2-CH_3$

(R) $CH_3-CH_2-CH=CH-CH_2-CH_2-CH_3$

(A) Q > R > P (B) R > P > Q

(C) P > R > Q (D) Q > P > R

Sol. **(B).** Heat of combustion ∝ No. of π bond

$$\propto \frac{1}{\text{stability of alkane}} \propto \text{No. of carbon}$$

(P) $CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3$

7 carbon atom 5α H

(Q) $CH_2=CH-CH_2-CH_2-CH_2-CH_3$

6 carbon atom

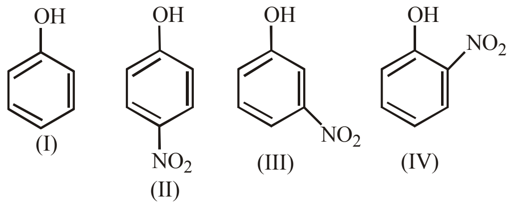
(R) $CH_3-CH_2-CH=CH-CH_2-CH_2-CH_3$

6 carbon atom 4α H

R > P > Q

Example 11 :

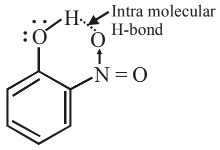
Find the acid strength order.



Sol. Acid strength order : II > IV > III > I

Step 1 : In nitrophenols –I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitro phenols.

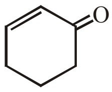
Step 2 : Only –I effect is applicable in meta nitrophenol it will be number three. Now –o, –p have both –I and –m effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho since

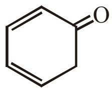


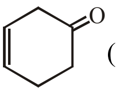
H is trapped by NO_2 group.

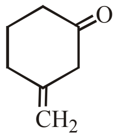
Example 12 :

Which of the following has longest C – O bond –

(A) 

(B) 

(C) 

(D) 

Sol. **(B).** In a conjugate system resonance will take place and in a double bond, single bond character increases.

11B

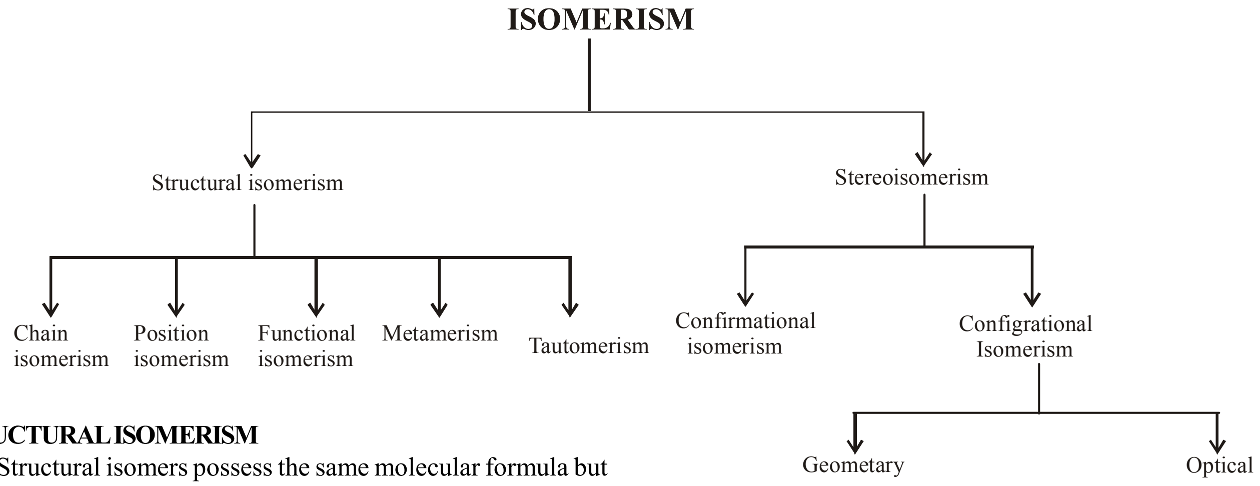
ISOMERISM

ISOMERISM :

Isomer word was first given by Berzelius.

Compounds possessing the same molecular formula but differ in physical or chemical properties are called isomers and the phenomenon is termed as isomerism.

CLASSIFICATION OR TYPES OF ISOMERISM



STRUCTURAL ISOMERISM

Structural isomers possess the same molecular formula but different connectivity of atoms. The term constitutional isomerism is a more modern term of structural isomerism. It arises because of the difference in the sequence of covalently bonded atoms in the molecule without reference to space.

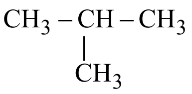
It is sub-classified into following types.

Chain Isomerism (Skeleton or Nuclear Isomerism) :

The different arrangement of carbon atoms gives rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.

(i) Butane : C_4H_{10}

$CH_3-CH_2-CH_2-CH_3$

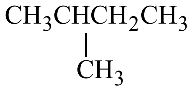

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

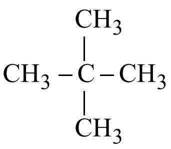
n-butane iso butane

n-butane has the chain of four carbon while isobutane has three. Hence they are chain isomers.

(ii) Pentane : C_5H_{12}

$CH_3CH_2CH_2CH_2CH_3$


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

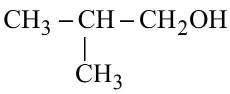

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

n-Pentane isopentane Neopentane

n-Pentane, isopentane and neopentane possess the chain of five, four and three carbons, respectively, hence they are chain isomers.

(iii) Butyl alcohol : C_4H_9OH

$CH_3-CH_2-CH_2-CH_2OH$


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

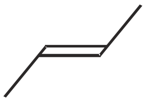
n-Butyl alcohol Isobutyl alcohol

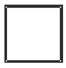
These two butyl alcohol are chain isomers.

Ring chain isomerism :

They can also be considere as functional isomers.

Ex. (i) C_4H_8

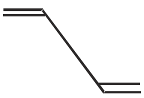

2-butene ,

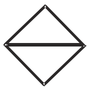

cyclobutane

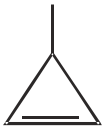
(ii) C_4H_6

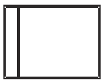

1-butyne

or


1,3-butadiene


bicyclo (1,1, 0) butane ,


3-methy cyclopropene ,

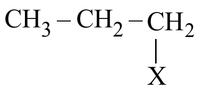

cyclobutene

Position Isomerism :

Position isomerism is shown by the compounds in which there is difference in the position of attachment of functional group, multiple bond or substituent along the same chain length of carbon atoms -

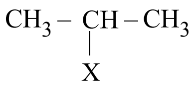
Ex. (i) Molecular formula :

C_3H_7X (X = halogen, NH_2, OH, or OR)



$CH_3-CH_2-\underset{\displaystyle X}{\underset{|}{CH_2}}$

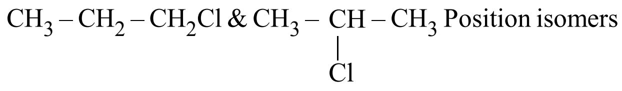
(i)



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

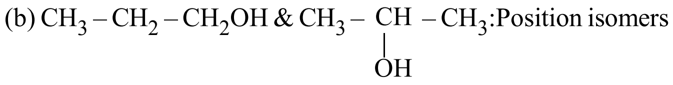
(ii)

In these structure three carbon atoms form a chain, and X is joined at the end in (i), while at the middle carbon in (ii). To be specific.



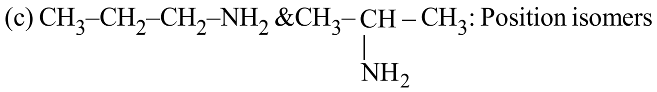
(a) $CH_3-CH_2-CH_2Cl$ & $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ Position isomers

1-Chloropropane 2-Chloropropane



(b) $CH_3-CH_2-CH_2OH$ & $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$:Position isomers

1-propanol 2-Propanol



(c) $CH_3–CH_2–CH_2–NH_2$ &$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$: Position isomers

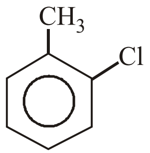
n-Propylamine Isopropylamine

(ii) Molecular formula : C_4H_8

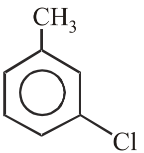
$CH_3-CH_2-CH=CH_2$ and $CH_3-CH=CH-CH_3$: Position isomers

1-Butene 2-Butene

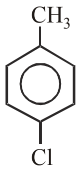
Note : In the disubstituted benzene derivatives position isomerism also exists because of the relative position occupied by the substituents on the benzene ring. Thus, Chlorotoulene, $C_6H_4(CH_3)Cl$ exist in three isomeric forms - ortho, meta and para.



o-Chlorotoluene



m-Chlorotoluene



p-Chlorotoluene

Functional Group Isomerism :

These isomers possess same molecular formula but different functional groups. Such compounds are called functional group isomers. The following pairs of families show this isomerism.

(i) Monohydric alcohol and ether
(ii) Aldehyde and ketone
(iii) Acid and ester
(iv) Cyanide and isocyanide
(v) nitroalkane and alkyl nitrite
(vi) Oxime, amide and many more
(vii) Alkene and Cycloalkane
(viii) Alkyne, Alkadiene and Cycloalkene

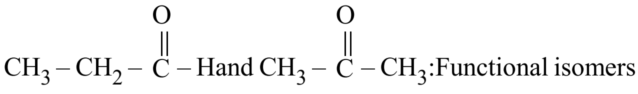
Ex. (i) Molecular formula : C_2H_6O

CH_3-CH_2-OH and CH_3-O-CH_3 : Functional isomers.

Ethyl alcohol Dimethyl ether

(Alcohol) (Ether)

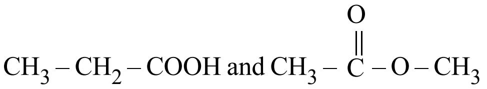
(ii) Molecular formula : C_3H_6O



$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$ and $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$:Functional isomers

Propanal Propanone
(Aldehyde) (Ketone)

(iii) Molecular formula : $C_3H_6O_2$

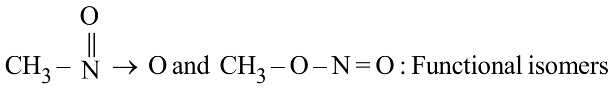


CH_3-CH_2-COOH and $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$

:Functional isomers

Propanoic acid Methyl acetate
(Acid) (Ester)

(iv) Molecular formula : CH_3NO_2



$CH_3-\overset{\overset{\displaystyle O}{\|}}{N}\rightarrow O$ and $CH_3-O-N=O$: Functional isomers

Nitromethane Methyl nitrite
(Nitro) (Nitrite)

Metamerism : This type of Isomerism is due to unequal distribution of substituents on either side of the polyvalent functional group.

Members belong to the same homologous series.

Ex.

(i) Diethyl ether and methyl propyl ether

$CH_3CH_2OCH_2CH_3$	$CH_3OCH_2CH_2CH_3$
Diethyl ether	Methyl propyl ether

(ii) Diethyl amine and methyl propylamine

$CH_3CH_2-NH-CH_2CH_3$	$CH_3CH_2CH_2-NH-CH_3$
Diethyl amine	Methyl propyl amine

Tautomerism :

(i) Tautomerism is a special type of functional group isomerism which arises due to the migration of H-atom as proton from a polyvalent atom to other polyvalent atom with reshuffling of π bond.

(ii) Such isomers are directly and readily inter convertible under ordinary conditions, and the isomers are called tautomers.

(iii) Tautomers exist in dynamic equilibrium.

(iv) They have no separate existence under ordinary conditions like other isomers mentioned above.

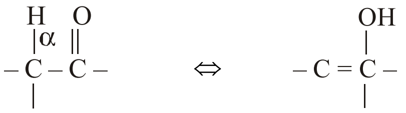
(v) The other names of tautomerism are ‘desmotroprism’ or ‘prototropy’.

Keto-Enol Tautomerism :

(i) When the tautomers exist in the two forms keto & enol then, such type of tautomerism is called keto-Enol tautomerism’.

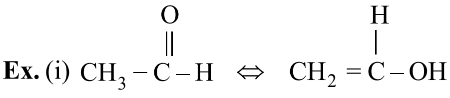
(ii) It was discovered by the scientist ‘Knorr’ in 1911 in acetoacetic ester.

(iii) The Keto means the compound has a Keto group > C = O, and the enol form has both double bond and OH (hydroxy) group Joined to the same carbon.



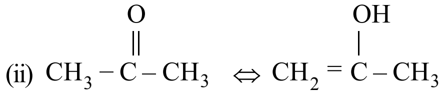
$$-\underset{|}{\overset{\overset{H}{|\alpha}}{C}}-\overset{\overset{O}{||}}{C}- \;\Leftrightarrow\; -C=\underset{|}{\overset{\overset{OH}{|}}{C}}-$$

Keto forms Enol forms



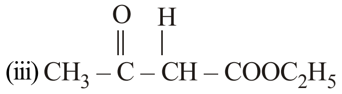
Ex. (i) $CH_3-\overset{\overset{O}{||}}{C}-H \;\Leftrightarrow\; CH_2=\overset{\overset{H}{|}}{C}-OH$

Acetaldehyde Vinyl alcohol



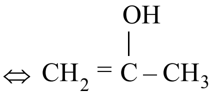
(ii) $CH_3-\overset{\overset{O}{||}}{C}-CH_3 \;\Leftrightarrow\; CH_2=\overset{\overset{OH}{|}}{C}-CH_3$

Acetone Isopropenyl alcohol



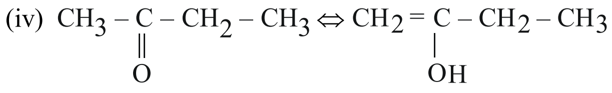
(iii) $CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{H}{|}}{CH}-COOC_2H_5$

Aceto acetic ester (AAE) Keto form



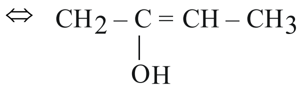
$\Leftrightarrow CH_2=\overset{\overset{OH}{|}}{C}-CH_3$

β-Hydroxy crotonic ester (Enol form)



(iv) $CH_3-\underset{\underset{O}{||}}{C}-CH_2-CH_3 \Leftrightarrow CH_2=\underset{\underset{OH}{|}}{C}-CH_2-CH_3$

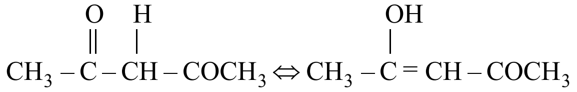
Butanone (Keto) (Enol)



$\Leftrightarrow CH_2-\underset{\underset{OH}{|}}{C}=CH-CH_3$

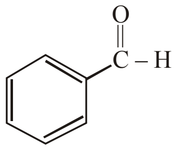
(Enol)

(v)

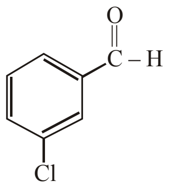


$CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{H}{|}}{CH}-COCH_3 \Leftrightarrow CH_3-\overset{\overset{OH}{|}}{C}=CH-COCH_3$

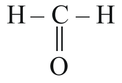
Note : In order for conversion of a keto form to its enol form it must have an α-hydrogen (i.e., hydrogen attached to the carbon adjacent to the carbonyl group). Thus benzaldehyde, m-chlorobenzaldehyde (in general, aromatic aldehydes) formaldehyde, trimethylacetaldehyde do not exist as their enol forms.



Benzaldehyde

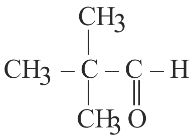


m-Chlorobenzaldehyde



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

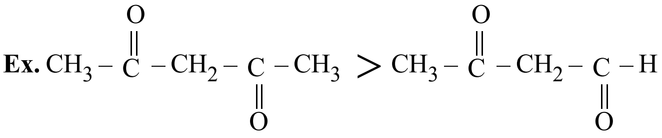
Methanal



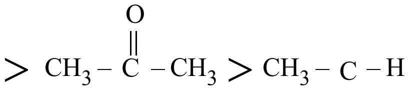
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-H$

Trimethyl-acetaldehyde

Quantity of enol ∝ no. of – CO groups ∝ no. of α – H



Ex. $CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{O}{||}}{C}-CH_3 > CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{O}{||}}{C}-H$

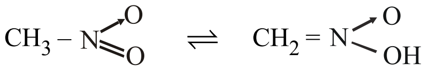


$> CH_3-\overset{\overset{O}{||}}{C}-CH_3 > CH_3-\underset{\underset{O}{||}}{C}-H$

Cyanide-iso cyanide tautomerism

$H-C\equiv N \rightleftharpoons C \equiv N-H$

Nitro-acinitro-tautomerism



$CH_3-N\overset{\nearrow O}{\underset{\searrow O}{}} \rightleftharpoons CH_2=N\overset{\nearrow O}{\underset{\searrow OH}{}}$

TRY IT YOURSELF-1

Q.1 How many chain isomers can be obtained from the alkane C_6H_{14} is –
(A) 4 (B) 5
(C) 6 (D) 7

Q.2 How many structural formula are possible for $C_5H_{11}Cl$
(A) 6 (B) 8
(C) 10 (D) 12

Q.3 What type of isomerism does exist between the following pairs of compounds
(a) Pentan-1-ol and pentan-2-ol
(b) Pentan-1-ol and 3-methylbutan-1-ol
(c) Butan-1-ol and diethylether

Q.4 Give IUPAC names of all isomeric compounds having molecular formula C_3H_8O.

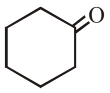
Q.5 The numbers of structural isomers of C_4H_6 is –
(A) 7 (B) 8
(C) 9 (D) 10

Q.6 How many structural isomers of C_5H_{10} are possible.
(A) 10 (B) 11
(C) 12 (D) 13

Q.7 How many structural isomer are possible when one of the hydrogen is replaced by a chlorine atom in anthracene?
(A) 3 (B) 7
(C) 4 (D) 6

Q.8 In which of the following, functional group isomerism is not possible?
(A) Alcohols (B) Aldehydes
(C) Alkyl halides (D) Cyanides

Q.9 Which of the following will not show tautomerism?
(A) HCN (B) $CH_3CH_2NO_2$
(C)



(D) CH_3OH

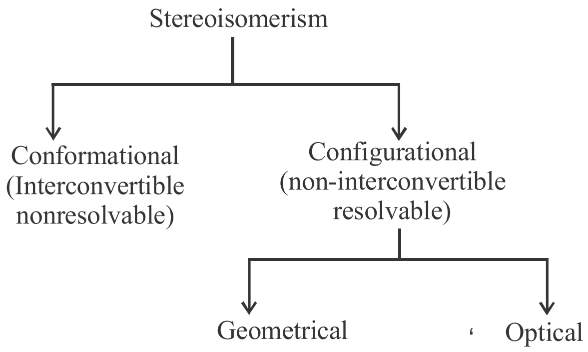
ANSWERS

(1) (B) **(2)** (B)
(3) (a) Positional isomerism, (b) Chain isomerism (c) Functional group isomerism.
(4) 1 propanol, propan-2-ol, Methoxy ethane
(5) (C) **(6)** (A) **(7)** (A)
(8) (C) **(9)** (D)

STEREO ISOMERISM

Two or more compound which have the same molecular formula and the same connectivity of atoms but different three dimensional arrangement of their constituent atom or groups are said to be stereoisomers and the phenomenon is termed as stereoisomerism.

The branch of chemistry which deals with the study of molecular structures in three dimensional space is called stereo chemistry.



CONFIGURATIONAL ISOMERISM

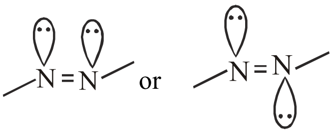
- Stereoisomer which cannot interconvert in each other at room temperature due to restricted rotation known as Geometrical isomerism.
- Stereoisomer which cannot super impose on each other due to chilarity known as optical isomerism.

GEOMETRICAL ISOMERISM

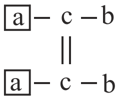
Isomerism where the isomers possess the same structural formula containing a double bond and differ only in respect of the arrangement of atoms or groups about the double bond.

Geometrical isomerism is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing the double bond. Double bond create restricted rotation.

Ex. $>C=C<$, $>C=N-$, $-N=N-$,

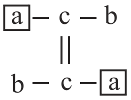


The compound having the formula abc = cab occur in two forms and exhibits geometrical isomerism.



$$\begin{array}{c}\boxed{a}-c-b\\ \|\\ \boxed{a}-c-b\end{array}$$

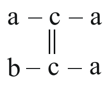
(cis form)
(Same groups lie on same side)



$$\begin{array}{c}\boxed{a}-c-b\\ \|\\ b-c-\boxed{a}\end{array}$$

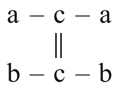
(trans form)
(Same groups lie on opposite side)

If the two atoms or groups linked to same doubly linked carbon are similar as in the molecule aac = cab, the compound does not show geometrical isomers. Here the two possible configurations are, in fact the same.



$$\begin{array}{c}a-c-a\\ \|\\ b-c-a\end{array}$$

(I)

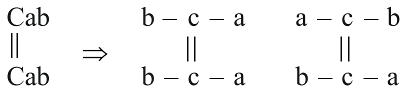


$$\begin{array}{c}a-c-a\\ \|\\ b-c-b\end{array}$$

(II)

Nomenclature of geometrical isomerism

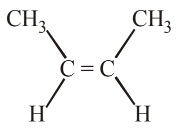
(i) Cis and trans



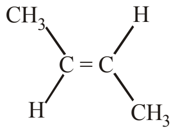
$$\begin{array}{c}Cab\\ \|\\ Cab\end{array} \Rightarrow \begin{array}{c}b-c-a\\ \|\\ b-c-a\end{array} \quad \begin{array}{c}a-c-b\\ \|\\ b-c-a\end{array}$$

cis trans

Ex. $CH_3-CH=CH-CH_3$ [2-Butene]

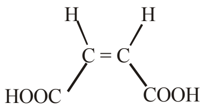


cis-2-Butene

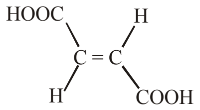


trans-2-Butene

- $CH(COOH)=CH(COOH)$ [Butenedioic acid]

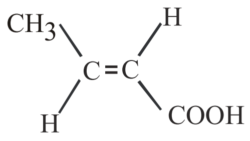


Maleic acid (cis)

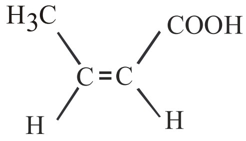


fumaric acid (trans)

- $CH_3-CH=CH\,COOH$ [2-Butenoic acid]

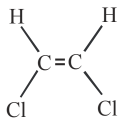


crotonic acid (trans)

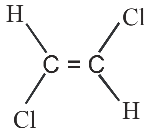


isocrotonic acid (cis)

- $CHCl=CHCl$ [1,2-Dichloroethene]



(cis)



(trans)

(ii) E-Z system of designating configuration

Cis and trans designations for geometrical Isomers are suitable when structurally similar or Identical groups are joined to the both carbon atoms.

[cis-trans] Method does not work when there are no similar groups. **Ex.** [Br ClC = CFI]

The configuration can be specified by using the notations Z and E.

The method of E, Z-system :

Find out the groups of highest priority on each carbon :–

If two high priority groups are on the same side the configuration is Z. (zusammen = together).

If the two groups of high priority are on apposite side, the configuration is E (entgegen = opposite)

(a) Naming of compound is based on priority order (atomic weight) Z

atomic number ↑ ⇒ priority ↑
atomic number ↓ ⇒ priority ↓

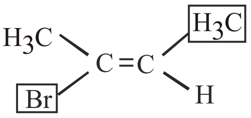
Ex. $I > Br > Cl > O > C > H$

(b) In isotopes (Use of the atomic mass) :

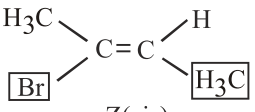
D > H

Ex. of EZ-system

(i)



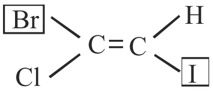
E(trans)



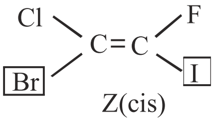
Z(cis) ;

priority is : Br > CH_3 , CH_3 > H

(ii)

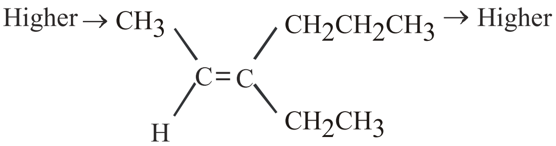


E(trans)

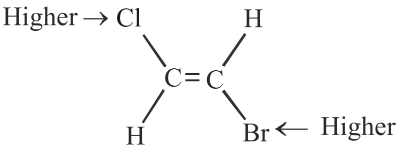


Z(cis)

(iii)

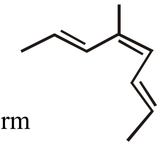


(Z)-3-ethyl-2-hexene



(E) -1-bromo-2-chloroethene

Example :

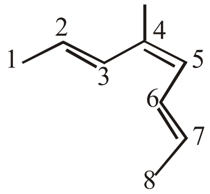


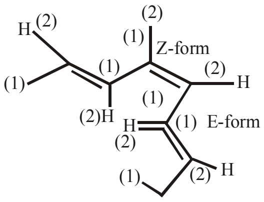
Write the IUPAC name of the compound

Sol. Higher priority groups same side ⇒ Z-form

Higher priority groups same side ⇒ E-form

2^{nd} & 6^{th} carbon is in E-form while 4^{th} carbon is in Z-formm.





IUPAC name : 2E, 4Z, 6E 4-methyl oct-2, 4, 6 triene

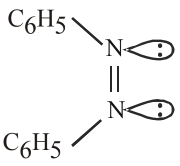
(iii) Geometrical isomerism due to – N = N– bond :

Ex. (a) $H_2N_2O_2$ (Hyponitrous acid) :

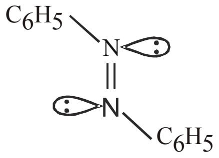
$$\begin{array}{c} N-OH \\ \| \\ N-OH \end{array} \qquad\qquad \begin{array}{r} N-OH \\ \| \\ HO-N \end{array}$$

Syn isomer Anti Isomer

(b) Azobenzene ($C_6H_5-N=N-C_6H_5$) :

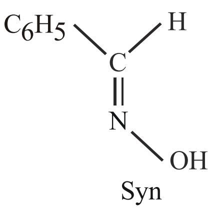


Syn

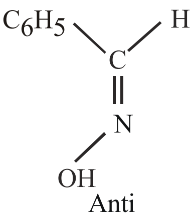


Anti

(c)



Syn



Anti

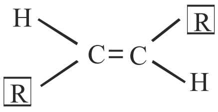
Main points :

(i) Geometrical isomerism arises due to restricted rotation about a double bond

(ii) Stability : trans > cis

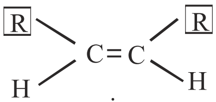
The trans isomers of alkenes are more stable than their corresponding cis isomer. In the cis isomer, the two bulkyl groups remain very close to each other. The repulsion is more pronounced hence less stable. In trans isomer the bulky groups lie on opposite side, far apart hence less repulsion more stable.

Ex.



trans

\>

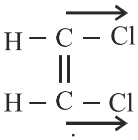


cis

(iii) Physical properties :

(a) Dipole moment(μ) : cis > trans

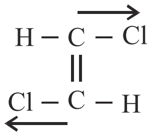
Ex.



$$\begin{array}{l} H-C-\overrightarrow{Cl} \\ \quad\ \| \\ H-C-\overrightarrow{Cl} \end{array}$$

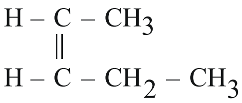
cis

\>



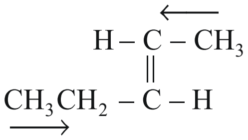
$$\begin{array}{l} \quad H-C-\overrightarrow{Cl} \\ \qquad\ \ \| \\ \overleftarrow{Cl}-C-H \end{array}$$

trans



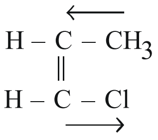
$$\begin{array}{l} H-C-CH_3 \\ \quad\ \| \\ H-C-CH_2-CH_3 \end{array}$$

\>



$$\begin{array}{r} H-C-\overleftarrow{CH_3} \\ \| \quad\ \ \\ \underrightarrow{CH_3CH_2}-C-H \end{array}$$

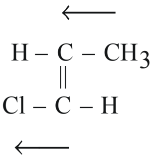
Imp. Exception : 1-chloro propene



$$\begin{array}{l} H-C-\overleftarrow{CH_3} \\ \quad\ \| \\ H-C-\underrightarrow{Cl} \end{array}$$

cis

<



$$\begin{array}{l} \quad H-C-\overleftarrow{CH_3} \\ \qquad\ \ \| \\ \underleftarrow{Cl}-C-H \end{array}$$

trans

(b) Polarity : cis > trans

μ ∝ polarity

(c) Solubility : cis > trans

Polar nature↑, solubility↑

(d) Boiling point : cis > trans

(e) Melting point : trans > cis

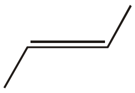
Melting point is not depends on polarity but depends on packing capacity of molecule.

Packing capacity ↑, Melting point ↑

Ex.

cis

<



trans

(f) **Separation :** cis and trans isomers can be separated by fractional distillation or fractional crystillisation.

(g) **cis and trans form can be interchange :**
The interconversion cis → trans or trans → cis is possible. On heating π-bond is broken and reforms on cooling

Ex. $\text{Maleic acid (cis)} \xrightarrow[-H_2O]{373\text{ K}} \text{Maleic anhydride}$

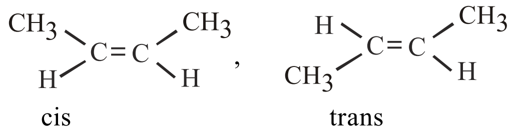
$\text{Fumaric acid (trans)} \xrightarrow{513\text{ K}} \text{Maleic acid}$

$\xrightarrow{-H_2O} \text{maleic anhydride.}$

Note: Anhydride formation in maleic acid is easier than fumaric acid.

The number of geometrical isomers for alkenes.

(a) **If alkene has one double bond :**
Then geometrical isomers is two.
Ex. 2-butene



(b) **If alkene has two or more double bond :**

(i) In structure if the terminal groups are nonsimilar. Then we can use formula. Then number of isomers = 2^n
[Where n = no. of double bond (n = odd/even)]

Ex. $CH_3-CH=CH-CH=CH-CH=CH-Br$
No. of isomers = $2^3 = 8$

(ii) In structure if the terminal groups are similar. Then we can use formula. Then number of isomers = $2^{n-1} + 2^{p-1}$
(n = double bond)
$p = n/2 \Rightarrow$ when n is even number

$p = \frac{n+1}{2} \Rightarrow$ when n is odd number

Ex. (i)$H_3C-CH=CH-CH=CH-CH=CH-CH_3$
2, 4, 6–octatriene

$n = 3, \quad p = \frac{3+1}{2}$

Number of isomers = $2^2 + 2^1 = 4 + 2 = 6$

(ii) $H_3C-CH=CH-CH=CH-CH=CH-CH=CH-CH_3$
2, 4, 6-decatetraene

$n = 4, \ p = 2^1 = 2$

Number of isomers = $2^3 + 2^1 = 4 + 2 = 6$

OPTICAL ISOMERISM

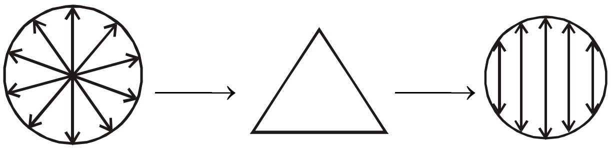
(i) The geometrical isomers differ in physical properties such as melting point, boiling point, density etc. and also in certain chemical properties.

(ii) The optical isomers will have the same chemical reactions and will be alike in all physical properties mentioned above.

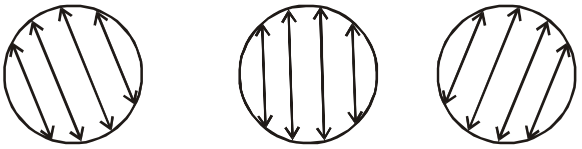
(iii) They can only be distinguished by their action on plane polarized lights this property which is often referred to as the optical activity.

Optical activity :

(i) Plane polarised light can be obtained by passing ordinary light through Nicol prism.



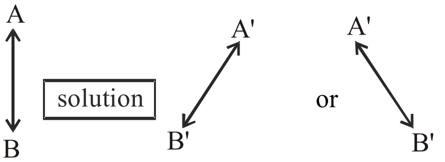
ordinary light waves vibrating in all directions — Nicol prism — Plane polarised waves vibrating in one direction



Plane rotated to the left — Plane rotated to the right

(ii) When certain organic compounds in their solutions are placed in the path of a plane polarized lights have the remarkable property of rotating its plane through a certain angle which may be either to the left or to the right if the polarized light has its vibrations in the plane AB before entering such a solution, the direction on leaving it will be changed to say A'B', the plane have been rotated through the angle as in a (fig.).

(iii) This property of a substance of rotating the plane polarized light is called optical activity and the substance possessing it is said to be optically active.



(A) The observed rotation of the plane of polarised light produced by a solution depends on.
(i) Nature of the substance
(ii) Solvent used
(iii) Concentration of solution
(iv) Length of polarimeter tube
(v) the temperature of the experiment and (t).
(vi) the wavelength of the incident light used (λ).

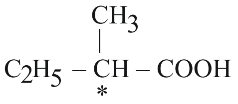
(B) For the measurement of optical rotations, a term specific rotation is introduced.
(i) This is a physical constant characteristic of a substance as much as the melting point, boiling point, density or its refractive index.
(ii) It is defined as the number of degrees of rotation observed when light is passed through 1 decimeter of its solution having concentration 1 gram per milliliter.
(iii) The specific rotation of a given substance can be calculated by using the following expression.

$$[\alpha] = \frac{\alpha_{obs}}{\ell \times c}$$

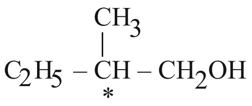
where [α] = specific rotation determined at t°C
α_{obs} = the observed angle of rotation
ℓ = length of the polarimeter tube
c = concentration of the active compound in gm/ml.
the sign attached with the angle of rotation signifies the direction of rotation. Negative sign(–) indicates that the rotation is toward the left, while positive (+) sign means that the direction of rotation is towards right.

Definition and examples of optical Isomerism :

The simple organic compounds which show optical activity are : Lactic acid $CH_3-\overset{*}{C}H(OH)-COOH$

2-Methyl butanoic acid 

$$C_2H_5-\underset{*}{\overset{CH_3}{\overset{|}{C}H}}-COOH$$

2-Methyl butanol 

$$C_2H_5-\underset{*}{\overset{CH_3}{\overset{|}{C}H}}-CH_2OH$$

All these substances are known to exist in two forms.

(1) one rotating the plane of polarised light to the left. This form is named as laevorotatory.
(Latin, laevous = left) or direction (–) form

(2) one rotating the plane of polarized light exactly to the same extent but to the right this form is named dextrorotatory (Latin Dexter - right) or direction (+) – form.

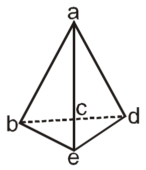
(3) An inactive form which does not rotate the plane polarized light at all. This mixture of equal amounts of (+) and (–) — forms and hence it is optically inactive.
It is named (±) - mixture or Racemic mixture.
(Latin, Racemic - mixture of equal compounds)

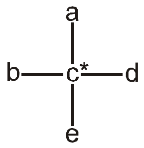
Note : Thus three lactic acids are known they are :
(a) (+) - lactic acid, (b) (–) - lactic acid and (c) (±) mixture since the (±) acid is only a mixture of (+) - and (–) forms, in reality lactic acid exists in two forms.

(a) These two acids are exactly identical in physical and chemical properties but differ in their action on the plane polarized light as they have different sign of specific rotation.

(b) Such forms of the same compound which differ only in their optical properties are called optical isomers and phenomenon is termed optical Isomerism.

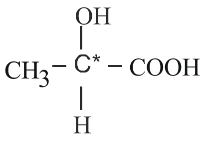
Asymmetric carbon atom :





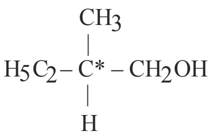
(i) A carbon atom is described as being asymmetric when four different atoms or groups are bonded to it thus an asymmetric carbon in formulas is usually indicated by on asterisk (*) placed near it.

(ii) All organic compounds containing on asymmetric carbon atom (lactic acid, amyl alcohol etc.) are optically active.



$$CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C^*}}}}-COOH$$

lactic acid
(Optically active)



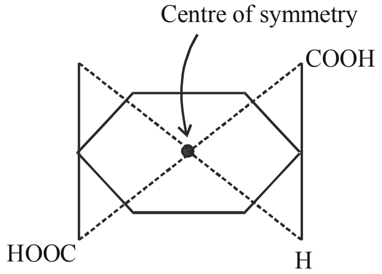
$$H_5C_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C^*}}}}-CH_2OH$$

amyl alcohol
(optically active)

Elements of symmetry : A molecule as a whole is asymmetric if it does not possess any element of symmetry such as
(i) Plane of Symmetry (ii) Centre of symmetry

(i) Plane of symmetry or mirror plane : A imaginary plane which bisect a molecule such a way that one half of the molecule is exactly the mirror image of the other half.

(ii) Centre of symmetry : A imaginary point in a molecule which divides the structures of molecule in to same parts.



trans-cyclohexane-1, 4-dicarboxylic acid

Symmetrical molecule is always optically inactive.

Chirality : This term has been recently used to describe such molecules which have no elements of symmetry, thus asymmetrical molecules are also called chiral molecules and optical activity is attributed to certain chiral centres in them.
An asymmetrical carbon is a chiral centre.
An asymmetrical object cannot be superimposed on its mirror image.

Note : Chirality is lost when the two atoms bonded to an asymmetric carbon become similar thus while lactic acid is optically active, propionic acid is not.

Chirality or molecular dissymmetry cause of optical Isomerism

(i) The necessary condition for a molecule to exhibit optical isomerism is dissymmetry or chirality.

(ii) Thus all organic compound which contain asymmetric carbon (c* abde) are chiral and exist in two tetrahedral forms.

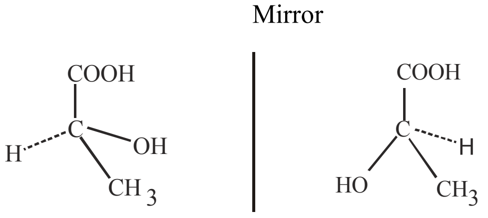
(iii) Although the two forms (I and II) have the same structure, they have different arrangements of groups a, b, d, e about the asymmetric carbon in fact, they represent asymmetric molecules they do not have a plane of symmetry, they are related to each other as an object to its mirror image and are non superimposable.

(iv) The two models or structures (I and II) actually stand for dextro or (+) and laevo or (–) isomers. Since they are related to each other as mirror images, they are commonly called

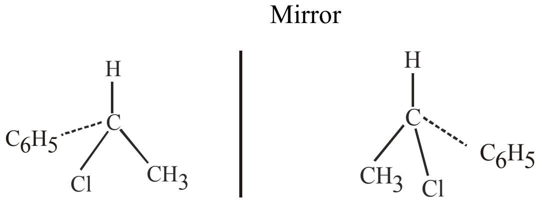
Enantiomers (Gr, enantio = opposite, morph - form) or enantiomers thus optical isomerism is now often referred to as an enatiomers.

(v) Optical isomers or enantiomers due to the presence of an asymmetric carbon atom in a compound differ only in the arrangement or configuration of groups of tetrahedral perspective.

(vi) Examples of compounds which exist as (+) and (–) enantiomers.



(I) (+) and (–) lactic acid (II)



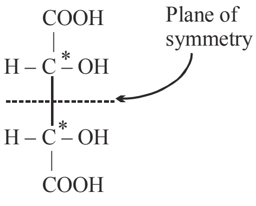
(I) (+) and (–) -1-chloro -1-phenyl ethane (II)

Criterion of enantiomerism :

(i) The compound which contain one or more asymmetric carbon atoms show enantiomerism.

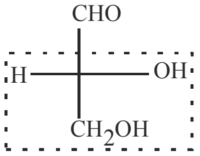
(ii) But there are some known compound which have asymmetric carbon but due to presence of plane of symmetry do not show enantiomerism.

(iii) Meso tartaric acid has two asymmetric carbons but is optically inactive.

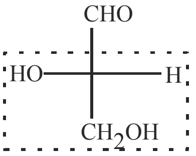


Meso tarteric acid

DL Configuration : In this system the standard chosen for assigning relative configurations was glyceraldehyde. The absolute configurations of (+) & (–) glyceraldehyde are as.



D-Glyceraldehyde
– OH on right side



L-Glyceraldehyde
– OH on left side

The other stereoisomers can be assigned D or L notation by comparison with the structural arrangements of D- and L-glyceraldehyde. For the purpose of comparison the following steps may be followed.

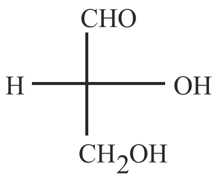
(i) The most oxidised carbon attached to the chiral center is placed on the top of vertical line

(ii) The group with carbon atom forming a part of the chain is kept at the bottom of vertical line.

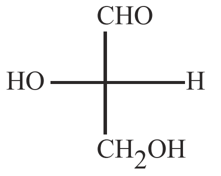
(iii) The remaining groups are assumed to be projected towards the viewer and are placed along horizontal line.

Now comparison can be made with the configurations of glyceraldehyde. For example, the two enantiomeric forms of lactic acid can be compared as follow :

Glyceraldehyde

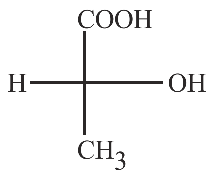


D (+)-Glyceraldehyde

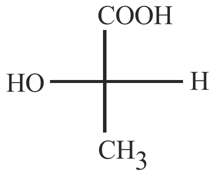


L (–)-Glyceraldehyde

Lactic acid



D (+)-Lactic acid



L (–)-Lactic acid

Note :

(a) It may be noted that the capital letters D and L do not pertains to dextro or laevo rotatory. Specific rotation of a stereoisomer is an experimentally determined property whereas D, L notations are based on comparison.

(b) D & L notation are applicable only for those stereoisomers which can be converted to or prepared from D & L glyceraldehyde.

R – S configuration (absolute configuration) :

(a) This is a newer and more systematic method of specifying absolute configuration to optically active compounds. This is totally depend on sequence rule or CIP-system (sequence rule proposed by R.S. Cahn, C.K. Ingold and V.Preiog)

(b) This system of designating configuration has been used increasingly since the early 1960 and may eventually replace the DL-system.

(c) In this system, the configuration of a stereoisomer is designated by using prefix R derived from Greek word rectus (means-right) and S derived from Greek word sinister (means-left). The procedure involves two main steps as described below.

Step 1 : Rank the groups (or atoms) which are bonded to the chirality centre in order of priority. The criterion of priority is based on certain set of rules known as sequence rules or Cahn. Ingold-Prelog (CIP) priority rules given as under.

The sequence Rules or CIP-Priority rule :

(i) The atoms or group directly bonded to the asymmetric carbon are arranged in order of decreasing atomic number and assigned priority 1, 2, 3, 4, accordingly.

Thus in chlorobromofluoromethane (CHClBrF), the substituent Br (at no = 35), Cl (at no = 17), F (at no = 9) and H (at no 1) given the order of priorities.

Br >	Cl >	F >	H
(1)	(2)	(3)	(4)

(ii) When two or more groups have identical first atoms attached to asymmetric carbon, the priority order is determined by considering the atomic numbers of the second atoms; and if the second atoms are also identical the third atoms along the chain are examined.

Let us consider the three groups

methyl $-\overset{1}{CH_2}-\overset{2}{H}$

ethyl $-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{H}$

n-propyl $-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_3}$

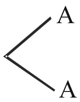
In methyl and ethyl the first atom is carbon and therefore, atomic numbers of the second atoms II (at no 1) and (at no 6) decide the priority order, ethyl > methyl. While considering ethyl and n-propyl the second atom is also identical (carbon) and hence the third atoms (H, C) give the priority order n-propyl > ethyl.

(iii) If the first atoms of the two groups have same substituents of higher atomic number, the one with more substituents takes priority.

Thus $-CHCl_2$ has a higher priority than — CH_2Cl

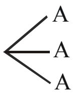
(iv) A doubly or triply bonded atom 'A' present in a group appended to asymmetric carbon, is considered equivalent to two or three singly bonded 'A' s, respectively.

Thus, $=A \Rightarrow$ A equals



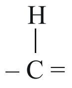
(A, A) ;

$\equiv A \Rightarrow$ A equals

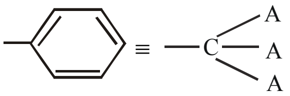


(A, A, A)

Hence between groups



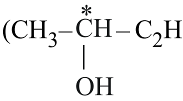
$-\overset{\overset{H}{|}}{C}=O$ (O, O, H) and $-CH_2OH$ (O, H, H), the former will have higher priority. A phenyl group is handled as if it had one of the Kekule structures.



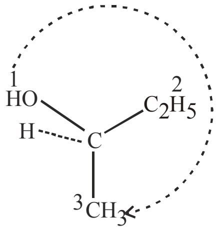
Note : It may be noted R and S system is merely a nomenclature device and has nothing to do with the sign and magnitude of optical activity. Thus the complete description of an optically active compound must include both the direction of rotation (+ or –) and the configuration of the compound (R or S). A racemic modification is an equimolecular mixture of two enantiomers and is given the prefix (RS).

Step 2. After deciding the priorities of atoms or groups around the chirality centre, the molecule is visualised in such a way that atom or group with lowest priority is directed away from the eye. Now, observe the remaining atoms or groups in decreasing order of priorities, i.e., from 1 to 2 to 3. In doing so, if movement of eye occurs in clockwise direction the configuration is specified as R. On the other hand, if eye moves in anticlockwise direction, the configuration is specified on S. Let us now, use step 1 and step 2 to specify the configurations of enantiomers of (i) 2-butanol and (ii) lactic acid.

(i) 2-Butanol

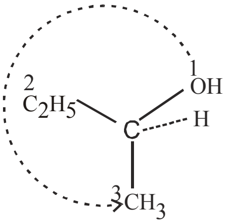


$(CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}H}-C_2H_5)$. The sequence of priority of groups around the chirality centre is OH(1), C_2H_5(2), CH_3(3), H(4). Visualising the enantiomeric forms with H directed away from the eye.



R-2-Butanol

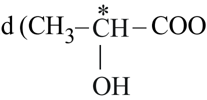
Eye moves clockwise from highest to lowest priority



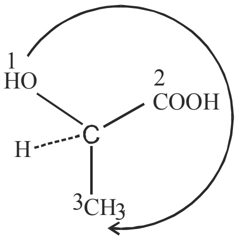
S-2-Butanol

Eye moves anticlockwise from highest to lowest priority

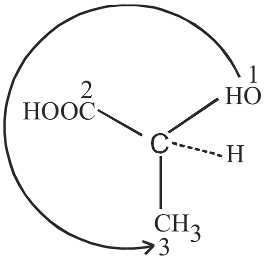
(ii) Lactic acid



$(CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}H}-COOH)$. The sequence of priority of various groups around the chirality centre is OH(1), COOH(2), CH_3(3), H(4). Visualising the formulae with H directed away from eye.



R-Lactic acid



S-Lactic acid

Eye moves clockwise

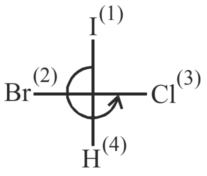
Eye moves anticlockw ise

It may be noted that the knowledge of R and S configuration does not tell us the direction in which the compound rotates the plane of polarised light because some compounds with R-configuration rotate the plane towards right whereas some compounds with R-configuration rotate the plane towards left. This implies that movement of eye towards left or right has no relationship with rotation of plane of polarised light towards left or right. The dextro or laevo rotatory nature of the compound can be judged by putting the compound in polarimeter and carrying out the experimental studies. For example, S-lactic acid and S-sodium lactate have same configuration but S-lactic acid is dextrorotatory whereas S-sodium lactate is laevo-rotatory.

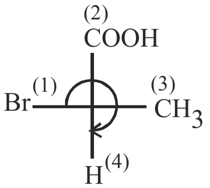
R and S Notations for the optical isomers represented by Fischer projections (by planar formulae).

Case 1 : When the atom or group of lowest priority is at the bottom :

Simply rotate the eye in decreasing order of priority and find the configuration of chiral carbon. For example,

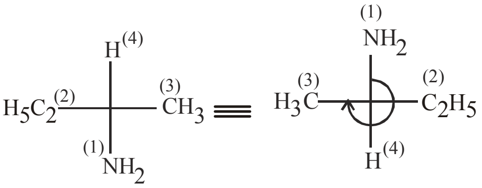


(S)-Bromochloroidomethane



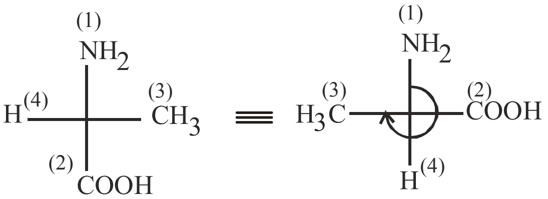
(R)-2-Bromopropanoic acid

Case 2 : When the atom or group of lowest priority is at the top. Rotate the entire molecule through an angle of 180° so that the atom or group of lowest priority is at the bottom. For example,



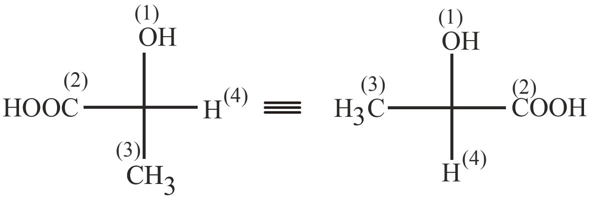
((R)-Butan-2-amine)

Case 3 : When the atom or group of lowest priority is on the left hand side. Without changing the position at the top, rotate the molecule in the anticlockwise direction so that the atom or group of lowest priority comes to the bottom. For example,



(R)-2-Aminopropanoic acid

Case 4 : When the atom or group of lowest priority is on the right hand side of the horizontal line. Without changing the position at the top, rotate the molecule in the clockwise direction so that the atom or group of minimum priority comes to the bottom. For example,



(R)-2-Hydroxypropanoic acid
(Lactic acid)

Note : R and S configuration of the stereoisomers are not linked with their dextro (+) and laevo (–) nature. This means that the stereoisomer with notation R need not be dextro and the isomer with notation S need not be laevo. However, one of them is dextro while the other is laevo.

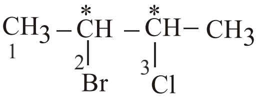
Optical Isomerism In compounds with more than one Asymmetric carbon Atom :

(i) An asymmetric carbon can produce molecular asymmetry.

(ii) Thus the molecules containing an asymmetric carbon exist in two optically active forms, (+) - isomer and (–) - isomer, and an equimolar mixture of the two, (±) - mixture, which is optically inactive.

(iii) When there are two or more asymmetric carbon atoms in a molecule, the problem is complicated considerably.

(iv) An organic compound which contains two dissimilar asymmetric carbons, can give four possible stereoisomeric form. Thus 2-bromo-3-chlorobutane may be written as



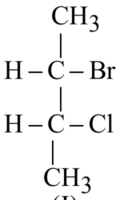
$$\underset{1}{CH_3}-\underset{\underset{Br}{|_2}}{\overset{*}{C}H}-\underset{\underset{Cl}{|_3}}{\overset{*}{C}H}-CH_3$$

(v) The two asymmetric carbons in its molecule are dissimilar in the sense that the groups attached to each of these are different.

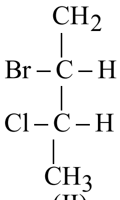
C_2 has CH_3, H, Br, $CHClCH_3$

C_3 has CH_3, H, Cl, $CHBrCH_3$

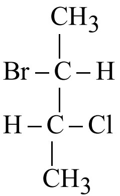
Such a substance can be represented in four configurational forms.



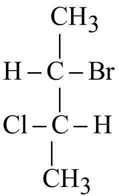
(I)



(II)



(III)



(IV)

(vi) The forms I and II are optical enatniomers (related as object and mirror image) and so are forms III and IV. These two pairs of enantiomers will give rise to two possible racemic modifications.

(vii) It may be noted that forms I (2S, 3S) and III (2S, 3R) are not mirror images or enantiomers, and yet they are optically active isomers. Similarly, the other two forms i.e., II (2R, 3R) and IV (2R, 3S) are also not enantiomers but optically active isomers.

(viii) Such stereoisomers which are optically active isomers but not mirror images, are called Diastereoismers or Diastereomers.

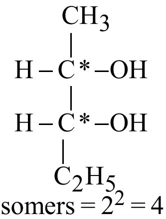
(ix) Diastereoisomers have different physical properties. Thus they have different melting points, solubilities in a given solvent, densities, and refractive indices. They also differ in specifivrotations ; they may have the same or opposite signs of rotations.

Note : Like geometrical isomers, the diastereoisomers may be separated from each other :
(i) by fractional distillation due to their difference in boiling points.
(ii) by fractional crystallisation due to their difference in solubility.
(iii) by chromatography due to their different molecular shapes and polarity.

Number of optical isomers :

Case : 1. When the molecule is unsymmetrical. (It cannot be divided into two halves)
number of d and ℓ isomers(a) = 2^n
number of meso form(m) = 0
Total number of optical isomers (a + m) = 2^n
where n is the number of chiral carbon atoms.

Ex. 2, 3-Pentane diol

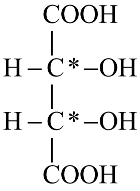


$$\begin{array}{c} CH_3 \\ | \\ H-C^*-OH \\ | \\ H-C^*-OH \\ | \\ C_2H_5 \end{array}$$

d and ℓ isomers = 2^2 = 4 meso form = 0

Case : 2. When the molecule is symmetrical.
(number of chiral carbon = even number)
number of d and ℓ forms(a) = $2^{(n-1)}$
number of meso form(m) = $2^{(n/2-1)}$
Total number (a + m) = $2^{(n-1)} = 2^{(n/2-1)}$

Ex. Tartaric acid



$$\begin{array}{c} COOH \\ | \\ H-C^*-OH \\ | \\ H-C^*-OH \\ | \\ COOH \end{array}$$

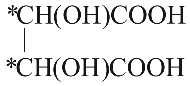
number of d and ℓ forms = $2^{(2-1)} = 2$
number of meso form = $2^{(2/2-1)} = 2^{\circ} = 1$
Total optical isomers = 3

Case : 3. When the molecule is symmetrical.
(Number of chiral carbon = odd number)
number of d and ℓ forms(a) = $2^{(n-1)} - 2^{(n/2-\frac{1}{2})}$
number of meso form (m) = $2^{(n/2-\frac{1}{2})}$
Total number of isomers (a + m) = 2^{n-1}

Ex. HOOC – CH(CH_3) – CHOH – CHBr – CHOH – CH(CH_3) – COOH
number of d and ℓ form = $2^4 - 2^2 = 12$
number of meso form = $2^2 = 4$
total optical isomers = 12 + 4 = 16

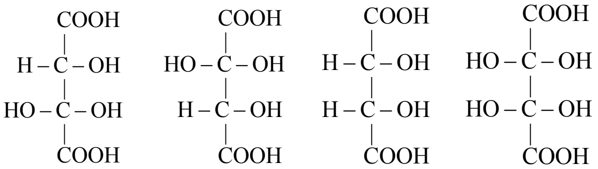
Isomerism of tartaric acid

Let us now proceed to discuss the optical isomerism of tartaric acid which contains two similar asymmetric carbon atoms, in detail. The two asymmetric carbon atoms in tartaric acid,



$$\begin{array}{l} ^*CH(OH)COOH \\ \ | \\ ^*CH(OH)COOH \end{array}$$

are attached to the groups H, OH, COOH and CH(OH)COOH. Its molecule can be represented by space models of two tetrahedra joined at corner but for the sake of convenience we will use the planed formulas. The end groups being identical, in all four arrangements are possible according as one or both H groups & OH groups are on the left or on the right.

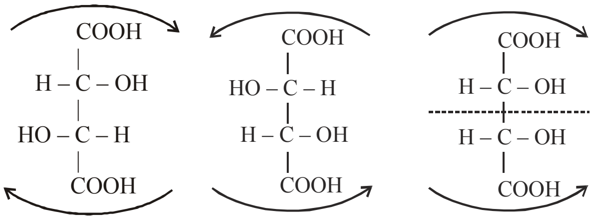


$$\begin{array}{cccc} COOH & COOH & COOH & COOH \\ | & | & | & | \\ H-C-OH & HO-C-OH & H-C-OH & HO-C-OH \\ | & | & | & | \\ HO-C-OH & H-C-OH & H-C-OH & HO-C-OH \\ | & | & | & | \\ COOH & COOH & COOH & COOH \end{array}$$

(I) (II) (III) (IV)

(v) Of these, formula IV when rotated through 180° in the plane of the paper becomes identical with formula III.

(vi) Therefore, for tartaric acid we can have only three different arrangements, viz



$$\begin{array}{ccc} COOH & COOH & COOH \\ | & | & | \\ H-C-OH & HO-C-H & H-C-OH \\ | & | & | \\ HO-C-H & H-C-OH & H-C-OH \\ | & | & | \\ COOH & COOH & COOH \end{array}$$

(I) (II) (III)

Three forms of tartaric acid

(i) structure I will rotate the plane of polarised light to the right and will represent (+) - tartaric acid.

(ii) structure II will rotate the plane of polarised light to the left and will represent (–) - tartaric acid, and

(iii) structure III will represent optically inactive tartaric acid, since the rotatory power of the upper half of the molecules is balanced by that of the lower half.

It may also be noted that formulas I and II are mirror images of each other and hence represent (+)-and (–)-isomers 'Formula III, however, has a plane of symmetry (dotted line) and hence represent an inactive isomer of tartaric acid.

In actual practice, four tartaric acids are known :

(i) (+) - Tartaric acid ;

(ii) (–) - Tartaric acid ;

(iii) Inactive Tartaric acid ; this is also known as meso - Tartaric acid or m-tartaric acid ; and

(iv) (±) Tartaric acid ; this form of tartaric acid being a mixture of equal amounts of (+) - and (–) isomers.

This is optically inactive due to internal compensation

Note : The three tartaric acids, (+), (–) -, m-, are all space isomers but m-tartaric acid is not a mirror image of either of the active forms. Hence it differs from them in melting point, density and other physical properties.

External and internal compensation

(i) If equimolecular amounts of d-and ℓ-isomers are mixed in a solvent, the solution is inactive.

(ii) The rotation of each isomer is balanced or compensated by the equal but opposite rotation of the other.

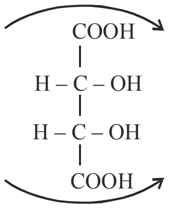
(iii) Optical inactivity having this origin is described as due to External Compensation. Such mixtures of (+) - (–)-s isomers (Racemic mixture) can be separated into the active components.

(iv) In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half.

(v) The optical inactivity so produced is said to be due to Internal Compensation.

(vi) It occurs whenever a compound containing two or more asymmetric carbon atoms has plane or point of symmetry.

(vii) Since the optical inactivity of such a compound arises with in the molecule, the question of separating into active components does not arise.

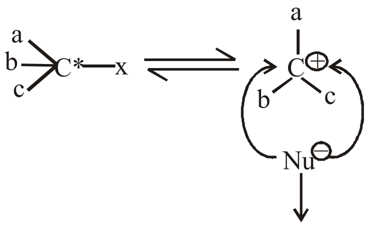


Inactivity of Meso

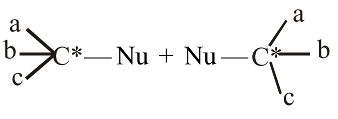
Tartaric acid by Internal Compensation

RACEMISATION

It is a process of conversion of an optically active compound in to the optically inactive racemic mixture by the application of heat/light/acid/base. **Ex. :** SN^1 Mechanism



¼Sp^2 Hybrid & Trigonal plane geometry½



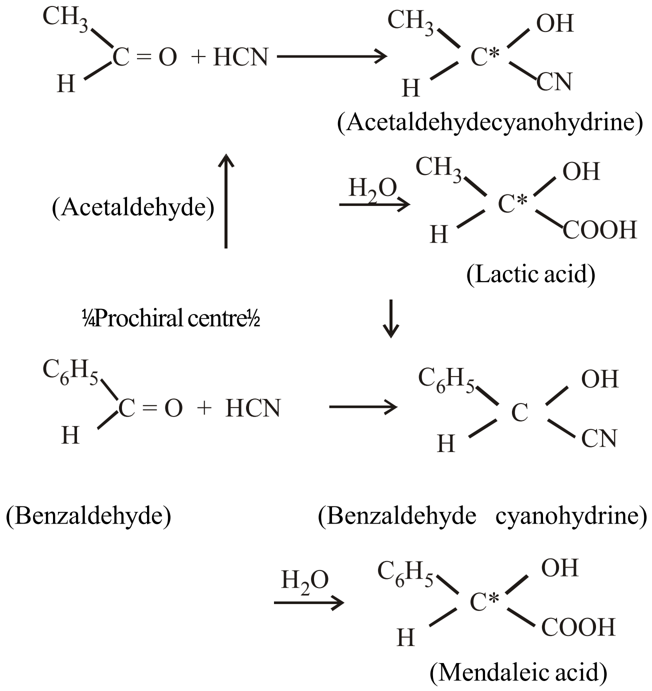
(Nu = Nucliophylic)

(dℓ mixture)

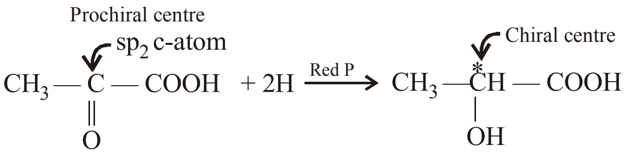
ASYMMETRIC SYNTHESIS

The synthesis of an optically active compound (Asymmetric compound) from an optically inactive compound (Symmetric compound).

Ex. : (a) Nucleophilic addition of HCN on Benzaldehyde & acetaldehyde)

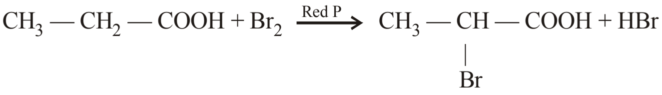


(b) Reduction of Pyruvic acid -



(Lactic acid)

(c) HVZ reaction [Hell volhard zelinsky reaction] -



$$CH_3-CH_2-COOH+Br_2\xrightarrow{\text{Red P}}CH_3-\underset{\substack{|\\Br}}{CH}-COOH+HBr$$

(Propanoic acid) ¼2–Bromo Propanoic acid½

CONFORMATION

(i) Molecules which differ from one another only by rotations about single– single bond.

(ii) It one CH_3 group of ethane is kept constant & other methyl group is permitted to rotate through C – C bond axis, an infinite no. of atomic arrangements are possible, which are called conformations.

(iii) Structure of conformers including bond length & bond angle in same configuration is also same.

(iv) Configuration is also same.

(v) Conformers can not be separated so they are not isomers, they are only different forms of same molecule.

Ethane is the best example of demonstrate conformational isomerism. In ethane molecule there is free rotation around the carbon-carbon single bond. The two orientations are :

(a) **Eclipsed confirmation :** In this orientation hydrogen atoms on one carbon are exactly eclipsing the hydrogen atoms on the other. There is minimum distance between the various hydrogen atoms. The eclipsed form has the greater energy content due to maximum repulsive interactions (less stable).

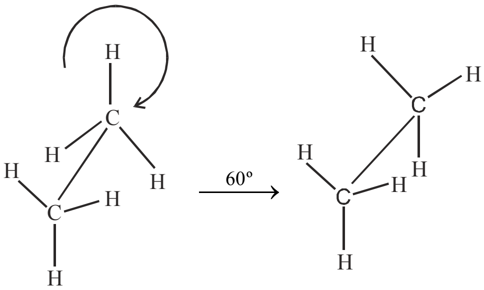
(b) **Staggered confirmation :** In this orientation the hydrogen atoms of one carbon are at maximum possible distance from that of the other. The staggered form has the less energy content due to minimum repulsive interaction. **(more stable)**

$E_{ec.} - E_{st.} = 3$ kcal/mole

The two forms of ethane are rapidly interconvertible at room temperature and are thus not separable.

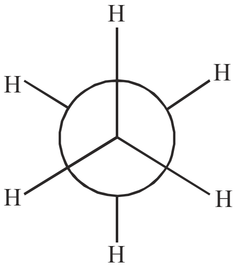
Conformers of ethane :

(i) **Sawharse projection formulae :** (3D representation)

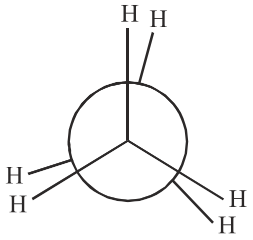


Staggered Conformation Eclipsed Conformation

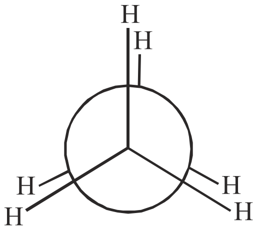
(ii) **Newman projection formulae :** (2 D representation)



Staggered



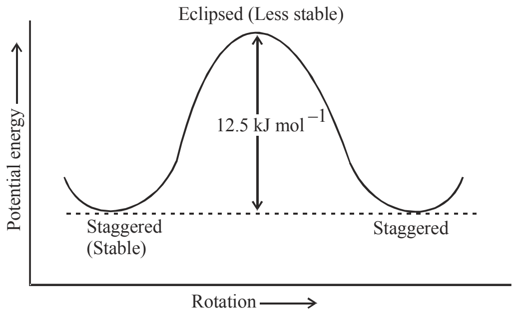
Skew



Eclisped

Note : **(a)** It many be noted that one conformation of ethane can be converted in to other by the rotation of 60° about the bond the infinite other conformations of ethane lying between the two extranes are called skew conformation.

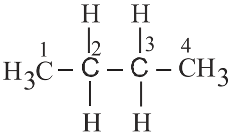
(b) Stability order & energy diagram -
Staggered > Eclipsed



Changes in energy during rotation about C – C bond in ethane.

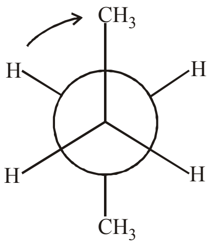
Conformations of n-Butane :

Butane molecule can be represented as derivative of ethane as given below :

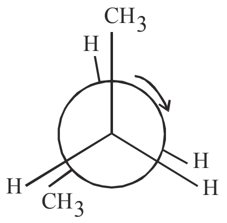


$$\overset{1}{H_3C}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}_{2}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}_{3}-\overset{4}{CH_3}$$

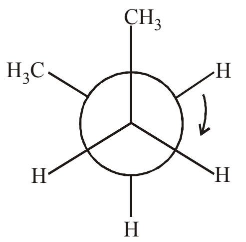
Considering the rotation around single bond between C-2 and C-3, we get many conformations of which the main conformations are.



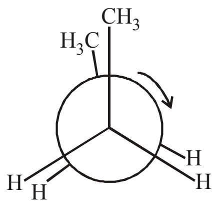
I. Staggered (Anti)



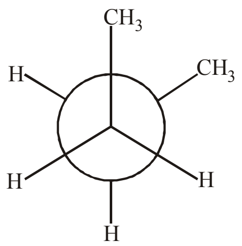
II. Eclipsed



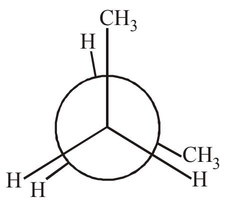
III. Staggered (Gauche)



IV. Fully Eclipsed



V. Staggered (Gauche)



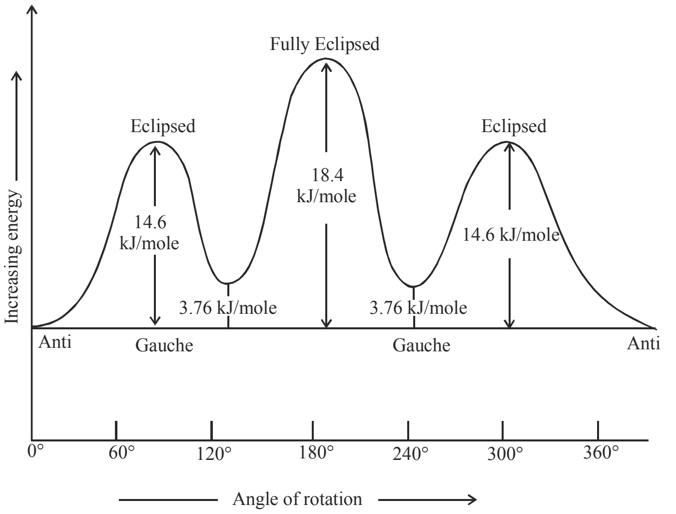
VI. Eclipsed

Conformation of n-butane :

Staggered conformation (I), in which methyl groups are as far apart as possible, is most stable due to minimum repulsion between methyl groups.

This conformation is also called anti conformation. This on rotation through 60º gives eclipsed conformation (II), in which methyl group on one carbon is overlapped by the hydrogen atom on the other carbon. Further rotation through 60º gives another staggered conformation (III) in which methyl groups or two carbons are 60º apart. This conformation, is also called Gauche conformation. Gauche conformation on further rotation through 60º gives fully eclipsed conformation (IV) in which methyl groups on two carbons are just opposite to each other. In this conformation steric strain in maximum hence this conformation is most unstable. Further rotation through 60º gives again gauche conformation (V) which is mirror image of gauche conformation (III). Conformation (V), on rotation through 60º gives conformation (VI) which is again eclipsed conformation. The order of relative stabilities various conformers of n-Butane is

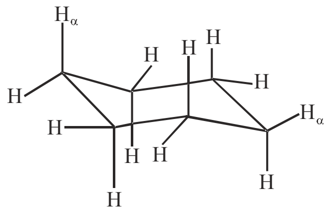
Anti staggered > Gauche > Eclipsed > Fully Eclipsed



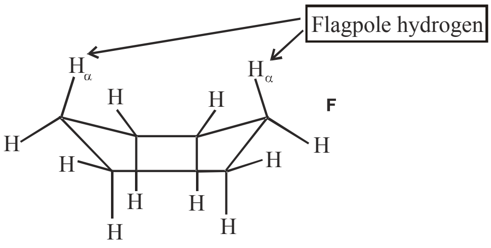
Conformations of Cyclohexane :

If cyclohexane molecule were to be planar, the c-c-c angle would have been 120º. Therefore, ring would be highly strained. Cyclohexane avoids this strain by assuming conformations in which all bond angles between carbon atoms are close to tetrahedral angle, 109º 28'. The two most important conformations of cyclohexane are the chair form and the boat form as shown in fig. Of the two, the chair form is more stable than the boat form, the energy difference being about 30 kJ mol^{-1}. However, the energy barrier between the two conformations is of about 44 kJ mol^{-1}). This is because in the boat form, may hydrogens on adjacent carbons correspond to the unfavourable eclipsed conformation of ethane. Also, the two hydrogens marked H_α also called flagpole hydrogen in the boat form are quite close and repel one another.

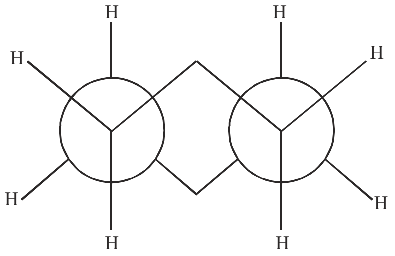
On the other hand, the chair form does not have these unfavourable interactions and all the hydrogens correspond to the more stable staggered conformation of ethane.



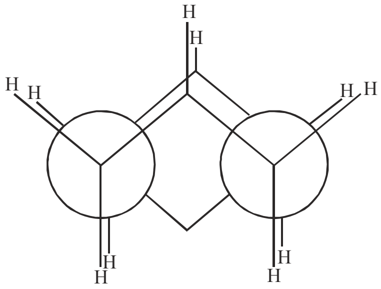
(Chair conformer



(Boat conformer)



(Chair Conformation)



(Boat Conformation)

Figure : Chair and boat conformations of cyclohexane.

NOTE

* Decreasing order of satability of conformational cyclohexane.

Chair form > Twist-boat > Boat > Half chair form

TRY IT YOURSELF-2

Q.1 Which of the following cannot be written in an isomeric form?

(A) $CH_3-CH(OH)-CH_2-CH_3$
(B) CH_3-CHO
(C) $CH_2=CH-Cl$
(D) $Cl-CH_2CH_2-Cl$

Q.2 How many minimum no. of C-atoms are required for position &geometrical isomerism in alkene?

(A) 4, 3 (B) 4, 4
(C) 3, 4 (D) 3, 3

Q.3 Which of the following does not show geometrical isomerism?

(A) 1, 2-dichloro-l-pentene (B) 1, 3-dichloro-2-pentene
(C) 1, 1-dichloro-l-pentene (D) 1, 4-dichloro-2-pentene

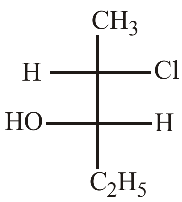
Q.4 Geometrical isomerism is possible in:
(A) isobutene
(B) acetone oxime
(C) acetophenone oxime
(D) benzophenone oxime

Q.5 The total number of isomeric optically active monochloro derivative of isopentane is:
(A) two (B) three
(C) four (D) one

Q.6 The number of optically active isomers observed in 2,3-dichlorobutane is:
(A) 0 (B) 2
(C) 3 (D) 4

Q.7 Meso-tartaric acid and d-tartaric acid are
(A) positional isomers (B) enantiomers
(C) diastereomers (D) racemic mixture

Q.8



The compound with the above configuration is called:
(A) (2S, 3S)-2-chloro-3-pentanol
(B) (2S, 3R)-2-chloro-3-pentanol
(C) (2R, 3R)-2-chloro-3-pentanol
(D) (2R, 3S)-2-chloro-3-pentanol

Q.9 What characteristic is the best common to both cis-2-butene and trans-2-butene?
(A) B.P.
(B) Dipole moment
(C) heat of hydrogenation
(D) Product of hydrogenation

Q.10 The number of optically active compounds in the isomers of C_4H_9Br is
(A) 1 (B) 2
(C) 3 (D) 4

Q.11 The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is

ANSWERS

(1) (C) **(2)** (B) **(3)** (C)
(4) (C) **(5)** (C) **(6)** (B)
(7) (C) **(8)** (A) **(9)** (D)
(10) (A) **(11)** 7

USEFUL TIPS

* Different isomerism

S.N.	Isomers	Characteristics	Conditions
1.	Chain Isomers	They have different size of main chain or side chain.	They have same nature of locants.
2.	Positional Isomers	They have different position of locants.	They should have same size of main chain and side chain and same nature of locant.
3.	Functional Isomers	Different nature of locant.	Chain and positional isomerism is not considered.
4.	Metamerism	Different nature of alkyl group along a polyvalent functional group.	They should have same nature of functional groups chain & positional isomer is ignored.
5.	Tautomerism	Different position of hydrogen atoms.	The two functional isomers remains in dynamic equilibrium to each other.

* **No. of alkane isomers as a function of no. of carbon atoms:**

No. of carbon atoms	Molecular formula	No. of isomers
1	CH_4	1
2	C_2H_6	1
3	C_3H_8	1
4	C_4H_{10}	2
5	C_5H_{12}	3
6	C_6H_{14}	5
7	C_7H_{16}	9
8	C_8H_{18}	15

* Two enantiomers have the same atoms and the same connectivity as each other, but they differ in three dimensional structure.

* Enantiomers are mirror images of each other that cannot be superimposed on each other by any rotation of the molecule as a whole or parts of the molecule.

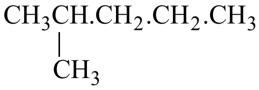
ADDITIONAL EXAMPLES

Example 1 :

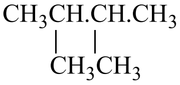
How many chain isomers can be obtained from the alkane C_6H_{14}.

Sol. 5. $CH_3CH_2CH_2CH_2CH_2CH_3$

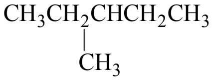
(i)


$CH_3CH(CH_3).CH_2.CH_2.CH_3$

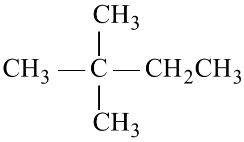
(ii)


$CH_3CH(CH_3).CH(CH_3).CH_3$

(iii)


$CH_3CH_2CH(CH_3)CH_2CH_3$

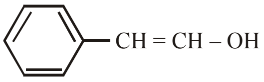
(iv)

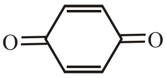

$CH_3-C(CH_3)_2-CH_2CH_3$

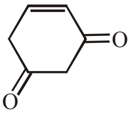
(v)

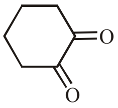
Example 2 :

Tautomerism is exhibited by –

(a) 

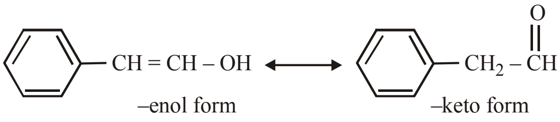
(b) 

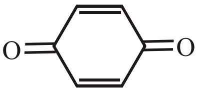
(c) 

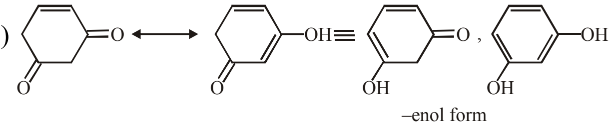
(d) 

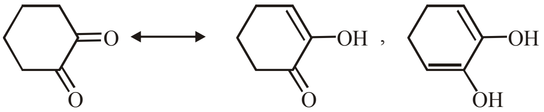
(A) All of these
(B) (b), (c), and (d)
(C) (a), (c) & (d)
(D) None of these

Sol. (C).

(a) 

(b)  cannot tautomerise

(c) 

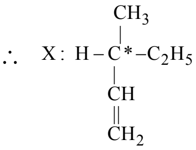
(d) 

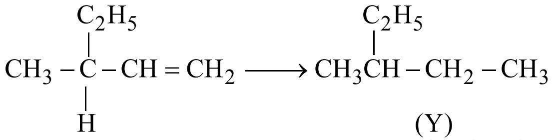
Example 3 :

C_6H_{12} (X) has chirality but on hydrogenation, (X) is converted into C_6H_{14} (Y) in which chirality disappears. Hence, (X) is –

(A) 3-methyl-1-pentene
(B) 2-methyl-2-pentene
(C) 2,3-dimethyl-2-butene
(D) 3,3-dimethyl-1-butene

Sol. (A). C_6H_{12} has chirality

$\therefore$ 
$X: H-C^*(CH_3)(C_2H_5)-CH=CH_2$ [C* = Chiral carbon]


$$CH_3-C(C_2H_5)(H)-CH=CH_2 \longrightarrow CH_3CH(C_2H_5)-CH_2-CH_3$$

(X) (Y) No more chiral molecule

Example 4 :

The least stable conformation of cyclohexane is –

(A) Boat
(B) Chair
(C) Twist boat
(D) Half chair

Sol. (D). Order of stability conformations of cyclohexane are

Chair > Twist boat > Boat > Half chair

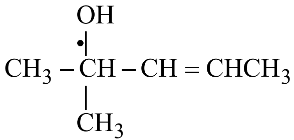
Example 5 :

The molecule 3-penten-2-ol can exhibit –

(a) Optical isomerism
(b) Geometrical isomerism
(c) Metamerism
(d) Tautomerism

The correct answer is –

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

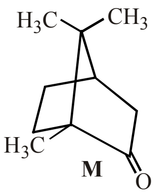
Sol. (A). 
$CH_3-\overset{\bullet}{C}H(OH)-CH=CHCH_3$

3-penten-2-ol

As given compound contains a asymmetrical carbon atom and a double bond (with sufficient conditions for geometrical isomerism). Therefore it can shown both optical and geometrical isomerism.

Example 6 :

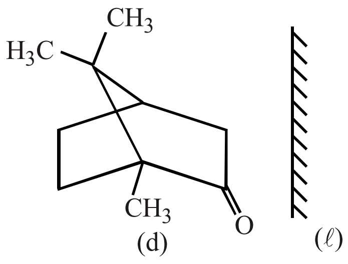
The total number of stereoisomers that can exist for M is



M

Sol. 2. Total number of stereoisomers = 2

This molecule can not show geometrical isomerism so only mirror image will be other stereoisomer.



(d + ℓ) pair

QUESTION BANK

CHAPTER 11 : ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART - 1 : SHAPES AND CLASSIFICATION OF ORGANIC COMPOUNDS

Q.1 How many 1° carbon atom will be present in a simplest hydrocarbon having two 3° & one 2° carbon atom?
(A) 3 (B) 4
(C) 5 (D) 6

Q.2 The formula C_nH_{2n-2} shows -
(A) Alkene & Alkyne (B) Alkyne & Alkadiyne
(C) Alkane & Alkadiene (D) Alkyne & Alkadiene

Q.3 In methane molecule, the hydrogen atoms around carbon are arranged as
(A) Square planar (B) Tetrahedral
(C) Triangular (D) Octahedral

Q.4 How many σ and π bonds are present in $HC \equiv C - CH = CH - CH_3$?
(A) $9\sigma, 4\pi$ (B) $10\sigma, 3\pi$
(C) $6\sigma, 6\pi$ (D) $5\sigma, 5\pi$

Q.5 What hybrid orbitals will form the following compound

$H_3C - CH = CH - CH_2 - CH_3$

(A) sp and sp^3 (B) sp^2 and sp^3
(C) sp and sp^2 (D) Only sp^3

Q.6 In compound X, all the bond angles are exactly 109°28', X is –
(A) Chloroform (B) Carbon tetrachloride
(C) Chloromethane (D) Iodoform

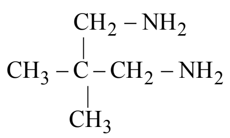
PART - 2 : NOMENCLATURE OF ORGANIC COMPOUNDS

Q.7 The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is
(A) $-CONH_2, -CHO, -SO_3H, -COOH$
(B) $-COOH, -SO_3H, -CONH_2, -CHO$
(C) $-SO_3H, -COOH, -CONH_2, -CHO$
(D) $-CHO, -COOH, -SO_3H, -CONH_2$

For Q.8-Q.19

Write the IUPAC name of the compound

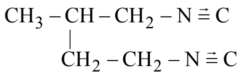
Q.8



$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2 - NH_2}{|}}{C}} - CH_2 - NH_2$$

(A) 2,3-dimethyl propane di amine-1,3
(B) 2-methyl amino-2-methyl butanamine
(C) 2,2-dimethyl propane di amine-1,3
(D) None

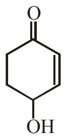
Q.9



$$CH_3 - \underset{\underset{CH_2 - CH_2 - N \equiv C}{|}}{CH} - CH_2 - N \equiv C$$

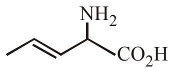
(A) 2-methyl butane di isonitrile-1,4
(B) 3-methyl butane di isonitrile-1,4
(C) 3-methyl butane di isocyanide-1,4
(D) 3-ethyl butane di isonitrile-1,4

Q.10



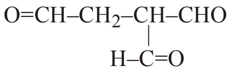
(A) 4-Hydroxy cyclo hex -2-en-1-one
(B) 5-Hydroxy cyclo hex -1-en-2-one
(C) 1-Hydroxy cyclo hex -2-en-4-one
(D) 4-Hydroxy hex -2-en-1-one

Q.11



(A) 1-amino but-2-en-1-oic acid
(B) 2-amino pent-3-en-1-oic acid
(C) 4-amino pent-2-en-5-oic acid
(D) 2-amino pent-4-en-1-oic acid

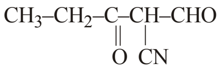
Q.12



$$O{=}CH{-}CH_2{-}\underset{\underset{H-C=O}{|}}{CH}{-}CHO$$

(A) 1,1-diformyl propanal
(B) 3- formyl butanedial
(C) 2-formyl butanedial
(D) 1,1,3-ethane tricarbaldehyde

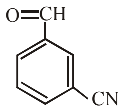
Q.13



$$CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CN}{|}}{CH}{-}CHO$$ is -

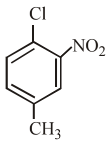
(A) 2-cyano-3-oxopentanal
(B) 2 - formyl-3-oxopentanenitrile
(C) 2-cyano-1, 3-pentanedione
(D) 1, 3-dioxo -2-cyanopentane

Q.14

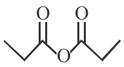


(A) 3-Aldo benzene carbonitrile
(B) 3-Aldo cyano benzene
(C) 1-cyano benzaldehyde
(D) 1-nitrile benzene-oxo

Q.15

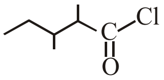


(A) 1-chloro-2- nitro-4-methylbenzene
(B) 1-chloro-4- methyl-2-nitrobenzene
(C) 2-chloro-1-nitro-5-methylbenzene
(D) m-nitro-p-chlorotoluene

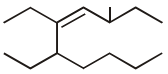
Q.16 

(A) Propionic anhydride (B)Dipropanoic anhydride
(C) Ethoxy propanoic acid (D) Propanoic anhydride

Q.17 $(CH_3)_3C-CH=CH_2$
(A) 2, 2-dimethylbut-3-ene (B)2,2-dimethylpent-4-ene
(C) 3,3-dimethylbut-1-ene (D) hex-1-ene.

Q.18 

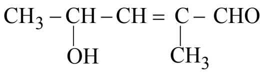
(A) 1-chloro-1-oxo-2,3-dimethylpentane
(B) 2-ethyl-3-methylbutanoyl chloride
(C) 2,3-dimethylpentanoyl chloride
(D) 3,4-dimethylpentanoyl chloride.

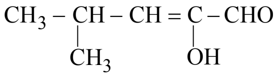
Q.19 

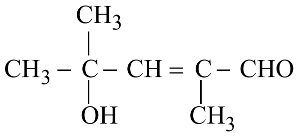
(A) 3-heptyl-5-methylhept-3-ene
(B) 5,6-diethyl-3-methyldec-4-ene
(C) 5-butyl-3-methyloct-4-ene
(D) 8-methyl-3-propylhex-3-ene

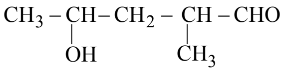
Q.20 The trivial name of the compound
$CH_2=CH-CN$ is -
(A) Vinyl cyanide (B) Cyano ethylene
(C) Acrylonitrile (D) 2 - propene nitrile

Q.21 The correct representation of
4-hydroxy-2-methylpent-2-en-1-al is

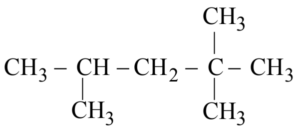
(A) 
$CH_3-\underset{OH}{\underset{|}{CH}}-CH=\underset{CH_3}{\underset{|}{C}}-CHO$

(B) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=\underset{OH}{\underset{|}{C}}-CHO$

(C) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH=\underset{CH_3}{\underset{|}{C}}-CHO$

(D) 
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO$

Q.22 How many primary, secondary, tertiary and quaternary carbon atoms are present in the following compound?


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

(A) One primary, two secondary and one tertiary.
(B) Five primary, three secondary.
(C) Five primary, one secondary, one tertiary and one quaternary.
(D) Four primary, two secondary and two quaternary.

Q.23 Which of the following is the correct IUPAC name?
(A) 3-Ethyl-4,4-dimethylheptane
(B) 4,4- Dimethyl-3-ethylheptane
(C) 5-Ethyl-4,4-dimethylheptane
(D) 4,4- Bis(methyl)-3-ethylheptane

Q.24 The IUPAC name of neo-pentane is –
(A) 2-methylbutane (B) 2,2-dimethylpropane
(C) 2-methylpropane (D) 2,2-dimethylbutane

PART - 3 : BASICS OF REACTION MECHANISM

Q.25 Heterolysis of a carbon-chlorine bond produces
(A) two free radicals (B) two carbocations
(C) one cation and one anion (D) two carbanions

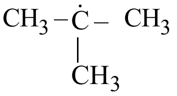
Q.26 Which type of intermediate (i) is formed during the reaction?

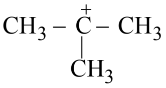
$CH_3CH_2-N{=}N{-}CH_2CH_3 \xrightarrow{Heat} (i)+N_2$

(A) Carbocation (B) Carbanion
(C) Free radical (D) Carbene

Q.27 The most stable carbanion is -
(A) methyl carbanion
(B) primary carbanion
(C) seccondary carbanion ion
(D) tertiary carbanion

Q.28 Which of the following statements is wrong ?
(A) a tertiary free radical is more stable than a secondary free radical.
(B) a secondary free radical is more stable than a primary free radical.
(C) a tertiary carbocations is more stable than a secondary carbocations.
(D) a primary carbocations is more stable than a secondary carbocations.

Q.29 Which free radical is the most stable -
(A) $C_6H_5-\dot{C}H_2$ (B) $CH_2=CH-C\dot{H}_2$
(C) $CH_3-C\dot{H}-CH_3$ (D) 
$CH_3-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$

Q.30 Which of the following is most stable carbocation.
(A) $CH_3-{}^{+}CH_2$ (B) $CH_3-{}^{+}CH-CH_3$
(C) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_3$
(D) ${}^{+}CH_3$

Q.31 Which one is the characteristic feature of a free radical
(A) presence of negative or positive charge.
(B) presence of unpaired electron.
(C) presence of even number of electrons.
(D) associated with high stability.

Q.32 Which among the following species is an ambident nucleophile :
(A) Ethene (B) Benzene
(C) Cyanide ion (D) Acetone

Q.33 A nucleophile is :
(A) electron-rich species
(B) electron-deficient species
(C) a Lewis acid
(D) Positively charged species

Q.34 Which is not a nucleophile –
(A) NH_3 (B) R – O – R
(C) BF_3 (D) HOH

Q.35 In which of the following species the central C-atom is negatively charged –
(A) Carbanion (B) Carbonium ion
(C) Carbocation (D) Free radical

Q.36 Which of the following is an electrophile –
(A) H_2O (B) SO_3
(C) NH_3 (D) ROR

Q.37 Most stable carbanion–
(A) $(CH_3)_3C^-$ (B) $(CH_3)_2CH^-$
(C) $CH_3CH_2^-$ (D) $(C_2H_5)_3C^-$

Q.38 Organic reactions, which proceed by homolytic fission are called –
(A) free radical (B) homopolar
(C) nonpolar (D) All of these

Q.39 The organic reactions which proceed through heterolytic bond cleavage are called
(A) ionic (B) heteropolar
(C) polar (D) All of these

Q.40 Most powerful leaving group in following–
(A) NH_2^- (B) OH^-
(C) CH_3^- (D) F^-

Q.41 Which of the following is an electrophilic reagent?
(A) H_2O (B) NH_3
(C) OH^- (D) NO_2^+

Q.42 Which of the following sets of groups contains only electrophiles?
(A) $NH_2^-, NO_2^+, H_2O, NH_3$
(B) F^-, OH^-, NH_3, SO_3
(C) $NO_2^+, AlCl_3, SO_3, CH_3C^+{=}O$
(D) $NH_3, BF_3, AlCl_3, H_2O$

Q43 Which among the following species is an ambidient nucleophile?
(A) H_2O (B) RCN
(C) CN^- (D) $\ddot{N}H_3$

Q.44 Free radicals can undergo
(A) rearrangement to a more stable free radical
(B) decomposition to give another free radical
(C) combination with other free radical
(D) All are correct

PART - 4 : ELECTRONIC DISPLACEMENT EFFECTS

Q.45 Electromeric effect -
(A) comes into play at the demand of attacking reagent.
(B) involves displacement of electrons in a sigma bond.
(C) comes into play in the molecule when at least one atom has unshared pair of electrons.
(D) involves the distortion of the electron cloud.

Q.46 M effect of $-CCl_3$ can be explained on the basis of
(A) –I effect (B) + R effect
(C) negative hyper conjugative effect (D) None

Q.47 Which of the alkyl groups has the maximum + I effect
(A) CH_3- (B) $(CH_3)_2CH-$
(C) $(CH_3)_3C-$ (D) $CH_3\,CH_2-$

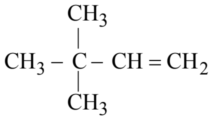
Q.48 The increasing order of electron donating inductive effect of alkyl groups is
(A) $-H < -CH_3 < -C_2H_5 < -C_3H_7$
(B) $-H > -CH_3 > -C_2H_5 > -C_3H_7$
(C) $-H < -C_2H_5 < -CH_3 < -C_3H_7$
(D) $-H > -C_2H_5 > -CH_3 > -C_3H_7$

Q.49 Inductive effect involves –
(A) displacement of σ-electrons resulting in polarisation.
(B) displacement of π-electrons resulting in polarisation.
(C) delocalisation of σ-electrons
(D) delocalisation of π-electrons.

Q.50 Maximum –I effect is exerted by the group –
(A) $-C_6H_5$ (B) $-OCH_3$
(C) – Cl (D) $-NO_2$

Q.51 Electromeric effect in organic compounds is a
(A) temporary effect
(B) permanent effect
(C) another name of inductive effect
(D) none of the above

Q.52 In which of the following species hyperconjugation is possible?
(A) $CH_3-\bar{C}H_2$ (B) $C_6H_5-CH_3$
(C) $CH_2=CH_2$ (D)



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

Q.53

$\bar{C}H_2-C(=O)-CH_3$ and $CH_2=C(O^-)-CH_3$ are
(A) Resonating structures (B) Tautomers
(C) Geometrical isomers (D) Optical isomers

Q.54 Inductive effect
(A) operates through π-bonds.
(B) involves the complete transfer of electrons which results with full charge residing on the carbon.
(C) is a weak effect, since the σ-bonds are strongly held.
(D) arising by electron withdrawing character is indicated by +I effect.

Q.55 Point out the incorrect statement about resonance?
(A) Resonance structures should have equal energy.
(B) In resonance structures, the constituent atoms must be in the same position.
(C) In resonance structures, there should not be same number of electron pairs.
(D) Resonance structures should differ only in the location of electrons around the constituent atoms.

Q.56 Which one of the following acids would you expect to be the strongest?
(A) $I-CH_2COOH$ (B) $Cl-CH_2COOH$
(C) $Br-CH_2COOH$ (D) $F-CH_2COOH$

Q.57 Hyperconjugation is –
(A) σ - π conjugation.
(B) noticed due to delocalisation of σ and π bonds.
(C) no bond resonance.
(D) All the above.

Q.58 Inductive effect of which atom or group is taken as zero to compare inductive effect of other atoms?
(A) Hydrogen (B) Chlorine
(C) Carbon (D) Oxygen

Q.59 In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?
(A) $\overset{*}{C}H_3-CH_2-Cl$ (B) $\overset{*}{C}H_3-CH_2-Mg^+Cl^-$
(C) $\overset{*}{C}H_3-CH_2-Br$ (D) $\overset{*}{C}H_3-CH_2-CH_3$

PART - 5 : TYPES OF ORGANIC REACTIONS

Q.60 Conversion of CH_4 to CH_3Cl is an example of which of the following reaction
(A) Electrophilic substitution.
(B) Free radical addition.
(C) Nucleophilic substitution.
(D) Free radical substitution.

Q.61 Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.
$H_3C-HC=CH_2+H^+\rightarrow ?$
(A) 2° Carbanion (B) 1° Carbocation
(C) 2° Carbocation (D) 1° Carbanion

Q.62 Which one is electrophilic addition
(A) $CH_3-CH_3+Cl_2\rightarrow C_2H_5Cl+HCl$
(B) $CH_3CH=O+HCN\rightarrow(CH_3)_2C(OH)CN$
(C) $(CH_3)_2C=O+HCN\rightarrow CH_3CH(OH)CN$
(D) $CH_2=CH_2+Br_2\rightarrow CH_2BrCH_2Br$

Q.63 The typical reaction of olefinic bond is –
(A) Electrophilic substitution reactions
(B) Electrophilic addition reactions
(C) Nucleophilic substitution reactions
(D) Nucleophilic addition reactions

PART - 6 : ISOMERISM

Q.64 Number of isomers for C_5H_{12} –
(A) 2 (B) 3
(C) 4 (D) 5

Q.65 Aldehyde show with ketone -
(A) Chain isomers (B) Position isomers
(C) Functional isomers (D) Both A & B

Q.66 Esters are functional isomers of -
(A) Hydroxy aldehyde (B) Ketone
(C) Diketone (D) Diol

Q.67 Which compounds exhibits geometrical isomers
(A) C_2H_5Br (B) $(CH)_2(COOH)_2$
(C) CH_3CHO (D) $(CH_2)_2(COOH)_2$

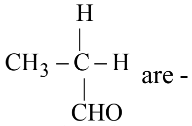
Q.68 The number of geometrical isomers of $CH_3CH=CH-CH=CH-CH=CCl$ is -
(A) 2 (B) 4
(C) 6 (D) 8

Q.69 Which of the following is an isomer of diethyl ether -
(A) $(CH_3)_3COH$ (B) $(CH_3)_2CHOH$
(C) C_3H_7OH (D) $(C_2H_5)_2CHOH$

Q.70 CH_3CHCl_2 and CH_2Cl. CH_2Cl show which type of isomerism –
(A) Functional (B) Chain
(C) Position (D) Metamerism

Q.71 Which of the following is an example of position isomerism–
(A) Isopentane and neopentane
(B) Glucose and fructose
(C) Ethanol and dimethyl ether
(D) α - Naphthol and β - naphthol

Q.72 The compounds CH_3-CH_2-COOH and



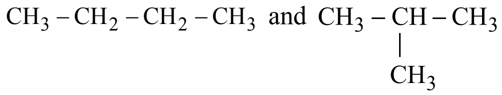
$CH_3-\underset{CHO}{\overset{H}{C}}-H$ are -
(A) Chain isomers (B) Position isomers
(C) Functional isomers (D) None

Q.73 An alkane can show structural isomerism if it has .... number of minimum carbon atoms –
(A) 1 (B) 2
(C) 3 (D) 4

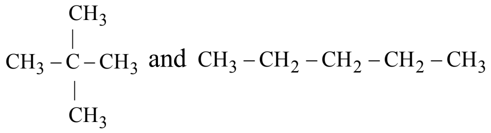
Q.74 Choose the correct statement –
(A) C_3H_8O can be represented as Propan-1-ol and Propan-2-ol.
(B) C_3H_6O can be represented as Propanone and Propanal.
(C) Both (A) and (B)
(D) None of these

Q.75 Which one of the following objects is 'achiral'
(A) Letter P (B) Letter F
(C) Ball (D) Letter I

Q.76 Which pairs is an example of position isomerism



(A) $CH_3-CH_2-CH_2-CH_3$ and $CH_3-\underset{CH_3}{CH}-CH_3$
(B) $CH_3-CH_2-CH=CH_2$ and $CH_3-CH=CH-CH_3$
(C) CH_3-CH_2OH and CH_3-O-CH_3



(D) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ and $CH_3-CH_2-CH_2-CH_2-CH_3$

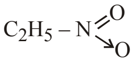
Q.77 Choose the correct statement –
(A) Metamerism arises due to different alkyl chains on either side of the functional group in the molecule.
(B) $C_4H_{10}O$ represents methoxypropane and ethoxyethane.
(C) Both (A) and (B)
(D) None of these

Q.78 An organic compound exhibits optical isomerism when
(A) Four groups linked to carbon atom are different.
(B) Three groups linked to carbon atom are different.
(C) Two groups linked to carbon atom are different.
(D) All the groups linked to carbon atom are same.

Q.79 Glucose and fructose are
(A) Optical isomers (B) Functional isomers
(C) Position isomers (D) Chain isomers

Q.80 Chirality of carbon compound is because of its
(A) Tetrahedral nature of carbon
(B) Monovalent nature of carbon
(C) Divalent nature of carbon
(D) Trivalent nature of carbon.

Q.81 Choose the pair of chain isomer
(A) CH_3CHBr_2 and CH_2BrCH_2Br
(B) 1-propanol and 2-propanol
(C) Neo-pentane and isopentane
(D) Diethyl ether and methyl-n-propyl ether

Q.82 
$C_2H_5-N\overset{O}{\underset{O}{\lessgtr}}$ and $C_2H_5-O-N=O$ are examples of –
(A) functional isomers (B) tautomers
(C) position isomers (D) metamers

Q.83 Which of the following is an isomer of ethanol?
(A) Methanol (B) Acetone
(C) Diethylether (D) Dimethylether

PART - 7 : PURIFICATION OF ORGANIC COMPOUNDS

Q.84 The substance which can be used as adsorbent in column chromatography is
(A) Na_2O (B) Na_2SO_4
(C) Al_2O_3 (D) NaCl

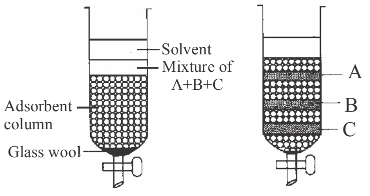
Q.85 Which process is suitable for the purification of aniline?
(A) Vacuum distillation (B) Steam distillation
(C) Fractional distillation (D) Fractional crystallisation

Q.86 Those substances can be separated by steam distillation which are –
(A) steam volatile and insoluble in water
(B) steam volatile and soluble in water
(C) steam volatile and sparingly soluble in water
(D) in liquid form in steam and solid form in water.

Q.87 The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is
(A) distillation
(B) crystallisation
(C) distillation under reduced pressure
(D) steam distillation

Q.88 In paper chromatography –
(A) mobile phase is liquid and stationary phase is solid.
(B) mobile phase is liquid and stationary phase is liquid.
(C) both phases are solids
(D) both phases are liquids.

Q.89 Given below is a column of adsorbent in which the mixture of compounds A + B + C is placed. When the solvent is poured through the column, the components are separated depending upon the degree of adsorption. Which of the given statements is correct?



(A) A is the most weakly adsorbed component hence remains near the top.
(B) A is the most strongly adsorbed component hence remains near the top.
(C) C is the most strongly adsorbed component hence is found near the bottom.
(D) B is the most strongly adsorbed component hence is found in the centre of the column.

PART - 8 : QUALITATIVE AND QUANTITATIVE ANALYSIS

Q.90 The presence of carbon in an organic compound can be shown by –
(A) heating the compound with sodium
(B) heating the compound with cupric oxide
(C) heating the compound on bunsen flame
(D) heating the compound with magnesium.

Q.91 In Kjeldahl's method of estimation of nitrogen, nitrogen is quantitatively converted to ammonium sulphate. It is then treated with standard solution of alkali. The nitrogen which is present is estimated as –
(A) N_2 gas (B) NO_2 gas
(C) NH_3 gas (D) $(NH_4)_2SO_4$ ppt.

Q.92 1.6 g of an organic compound gave 2.6g of magnesium pyrophosphate. The percentage of phosphorus in the compound is –
(A) 45.38% (B) 54.38%
(C) 37.76% (D) 19.02%

Q.93 In Kjeldahl's method, copper sulphate acts as
(A) an oxidising agent (B) a reducing agent
(C) a catalytic agent (D) a hydrolysing agent

Q.94 The blue compound formed in the positive test for nitrogen with Lassaigne solution of an organic compound is –
(A) $Na_4[Fe(CN)_5(NOS)]$ (B) $Na_3[Fe(CN)_6]$
(C) $Fe(CN)_3$ (D) $Fe_4[Fe(CN)_6]_3$

EXERCISE - 2 [LEVEL-2]

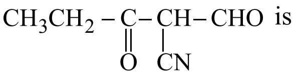
Choose one correct response for each question.

Q.1 Which of the following ions is most stable :

(A) $CH_3CH_2\overset{+}{C}H_2$ (B) $CH_3\overset{+}{C}HCH_2CH_3$

(C) $(CH_3)_3\overset{+}{C}$ (D) $(CH_3)_3C\overset{+}{C}H_2$

Q.2 The correct name of the compound



$CH_3CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CN}{|}}{CH}-CHO$ is

(A) 2-cyano-3-oxopentanal
(B) 2-formyl-3-oxopentanenitrile
(C) 2-cyano-1,3-pentadiene
(D) 1,3-dioxo-2-cyanopentane.

Q.3 Consider the following compound :

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

Carbon-carbon bond length between C_2 and C_3 will be
(A) 1.54 Å
(B) 1.3 Å
(C) Less than 1.54 and greater than 1.33 Å
(D) 1.21 Å

Q.4 Consider the following carbocations -

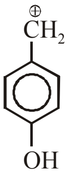
(a) $CH_3-\overset{+}{C}H_2$ (b) $CH_2=\overset{\oplus}{C}H$

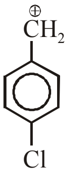
(c) $CH_2=CH-\overset{+}{C}H_2$ (d) $C_6H_5-\overset{+}{C}H_2$

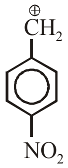
Stability of these carbocations in decreasing order is -
(A) d > c > a > b (B) d > c > b > a
(C) c > d > b > a (D) c > d > a > b

Q.5 Which carbocation is the most stable -

(A)


(B)


(C)


(D)


Q.6 Which of the following statements does not apply to free radical chain reaction :
(A) it may be initiated by ultraviolet rays.
(B) one mole of product is obtained for each mole of free radical produced in the initiation step.
(C) it is not affected by changes in polarity of solvent.
(D) it is inhibited by the presence of certain reagents.

Q.7 Which of the following statement is correct:

(A) allyl carbonium ion ($CH_2{=}CH{-}\overset{+}{C}H_2$) is more stable than propyl carbonium ion.
(B) propyl carbonium ion is more stable than allyl carbonium ion
(C) both are equally stable
(D) none of these

Q.8 Which of the following is the correct order of stability of free radicals :
(A) benzyl > allyl > 3° > 2° (B) allyl > benzyl > 3° > 2°
(C) allyl > 3° > 2° > benzyl (D) benzyl > 3° > 2° > allyl

Q.9 Which of the following resonating structures of 1-methoxy-1, 3-butadiene is least stable –

(A) $\overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{O}-CH_3$

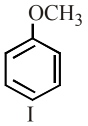
(B) $CH_2=CH_2-\overset{\ominus}{C}H-CH=\overset{\oplus}{O}-CH_3$

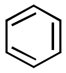
(C) $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH-O-CH_3$

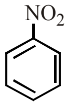
(D) $CH_2=CH-\overset{\ominus}{C}H-\overset{\oplus}{C}H-O-CH_3$

Q.10 Which one of the following is least reactive in a nucleophilic substitution reaction
(A) CH_3CH_2Cl (B) $CH_2=CHCH_2Cl$
(C) $(CH_3)_3C-Cl$ (D) $CH_2=CHCl$

Q.11 Among the following compounds (I-III) the correct order of reaction with electrophilic reagent is


I

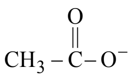

II


III

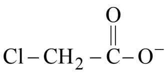
(A) II > III > I (B) III < I < II
(C) I > II > III (D) I = II > III

Q.12 Which of the following compounds are not arranged in order of decreasing reactivity towards electrophilic substitution –
(A) Fluoro benzene > chloro benzene> bromo benzene
(B) Phenol > n-propyl benzene > benzoic acid
(C) Chloro toluene > para-nitro toluene > 2-chloro-4-nitro toluene
(D) Benzoic acid > phenol > n-propyl benzene

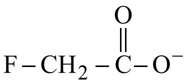
Q.13 Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?

(A)


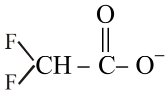
$CH_3-\overset{\overset{O}{\|}}{C}-O^-$

(B)


$Cl-CH_2-\overset{\overset{O}{\|}}{C}-O^-$

(C)


$F-CH_2-\overset{\overset{O}{\|}}{C}-O^-$

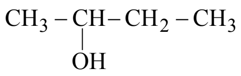
(D)


Q.14 Correct order of nucleophilicity–
(A) $CH_3^- < NH_2^- < OH^- < F^-$
(B) $F^- < OH^- < CH_3^- < NH_2^-$
(C) $OH^- < NH_2^- < F^- < CH_3^-$
(D) $F^- < OH^- < NH_2^- < CH_3^-$

Q.15 Benzoic acid is less acidic than salicylic acid because of
(A) Hydrogen bond (B) Inductive effect
(C) Resonance (D) none of these

Q.16 Freshly prepared solution of sodium nitroprusside is added to the sodium extract. Appearance of a deep violet colour indicates the presence of –
(A) nitrogen (B) sulphur
(C) both nitrogen & sulphur (D) halogen

Q.17 Given below are the structures of few compounds with molecular formula $C_4H_{10}O$. Select metamers from these structures.
(i) $CH_3-O-CH_2CH_2CH_3$
(ii) $CH_3CH_2CH_2CH_2OH$
(iii) $CH_3-CH_2-O-CH_2-CH_3$
(iv)



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$

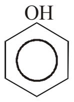
(A) (i) and (ii) (B) (ii) and (iii)
(C) (i) and (iii) (D) (ii) and (iv)

Q.18 In Duma's method 0.52 g of an organic compound on combustion gave 68.6 mL N_2 at 27°C and 756 mm pressure. What is the percentage of nitrogen in the compound?
(A) 12.22% (B) 14.93%
(C) 15.84% (D) 16.23%

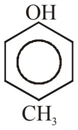
Q.19 Strongest acid out of the following–
(A) CH_3COOH (B) $ClCH_2COOH$
(C) CH_3CH_2COOH (D) $(CH_3)_2CHCOOH$

Q.20 Increasing order of acid strength among
(i) p-methoxyphenol, (ii) p-methylphenol, and
(iii) p-nitrophenol is–
(A) (iii) < (i) < (ii) (B) (ii) < (i) < (iii)
(C) (iii) < (ii) < (i) (D) (i) < (ii) < (iii)

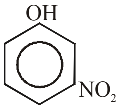
Q.21 In the following compounds–



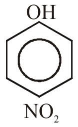
(I)



(II)



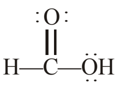
(III)



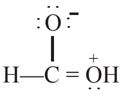
(IV)

the order of acidity is–
(A) III > IV > I > II (B) I > IV > III > II
(C) II > I > III > IV (D) IV > III > I > II

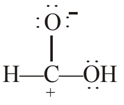
Q.22



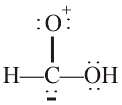
(I)



(II)



(III)



(IV)

Increasing order of stability is–
(A) I < III < II < IV (B) IV < III < II < I
(C) III < IV < II < I (D) II < IV < III < I

Q.23 The order of decreasing stability of the following carbanions is
(i) $(CH_3)_3C^-$ (ii) $(CH_3)_2CH^-$
(iii) $CH_3CH_2^-$ (iv) $C_6H_5CH_2^-$
(A) (i) > (ii) > (iii) > (iv) (B) (iv) > (iii) > (ii) > (i)
(C) (iv) > (i) > (ii) > (iii) (D) (iii) > (ii) > (i) > (iv)

Q.24 The number of geometrical isomers in case of a compound with the structure :
$CH_3-CH=CH-CH=CH-C_2H_5$ is –
(A) 4 (B) 3
(C) 2 (D) 5

Q.25 Which of the following compounds which is an optically active compound
(A) 1-butanol (B) 2-butanol
(C) 3-butanol (D) 4-heptanol

Q.26 The IUPAC name of the compound
$CH_3CH_2OCOCH_2CH_2CH_3$ is –
(A) Propyl propanoate (B) Ethyl butanoate
(C) Propyl butanoate (D) Ethyl propanoate

Q.27 Geometrical isomerism is not possible in
(A) Propene (B) 3-hexane
(C) Butenedioic acid (D) Cyclic compound

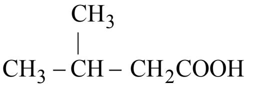
Q.28 Which compound is chiral
(A) butane
(B) 1-chloro-2-methyl butane
(C) 2-methyl butane
(D) 2-methyl propane

Q.29 Methyl acetate and propionic acid are
(A) Functional isomer (B) Structural isomer
(C) Stereoisomer (D) Geometrical isomer

Q.30 Lactic acid shows which type of isomerism –
(A) Geometrical isomerism (B) Tautomerism
(C) Optical isomerism (D) Metamerism

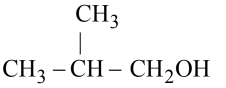
Q.31 Which compounds shows optical isomerism
(A) $CH_3CHCl-CH_2-CH_3$
(B) $CH_3-CH_2-CHCl-CH_2-CH_3$
(C) $ClCH_2-CH_2-CH_2-CH_3$
(D) $ClCH_2-CH_2-CH_3$

Q.32 Which of the following has chiral structure
(A)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2COOH$

(B) $CH_3-CH=CH-CH_3$
(C)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2OH$

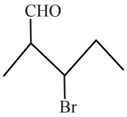
(D) $CH_3-CHOH-CH_2CH_3$

Q.33 Select the correct order of basic nature
(A) $CH_3CH_2^- > CH_2{=}CH^- > CH\equiv C^- > OH^-$
(B) $CH_3CH_2^- > CH\equiv C^- > CH_2=CH^- > OH^-$
(C) $CH_3CH_2^- > OH^- > CH\equiv C^- > CH_2=CH^-$
(D) $OH^- > CH\equiv C^- > CH_2=CH^- > CH_3CH_2^-$

Q.34 How many isomers of $C_5H_{11}OH$ will be primary alcohols
(A) 2 (B) 3
(C) 4 (D) 5

Q.35 Which of the following is an chiral compound
(A) Hexane (B) Methane
(C) n-butane (D) 2,3,4-trimethyl hexane

Q.36 Chloroacetic acid is a stronger acid than acetic acid. This can be explained using –
(A) – I effect (B) – M effect
(C) + I effect (D) + M effect

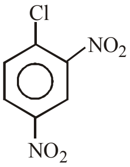
Q.37 The IUPAC name of  is

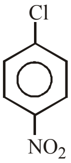
(A) 3 - bromo - 2 - methylbutanal
(B) 2 - methyl - 3 - bromohexanal
(C) 3 - bromo - 2 methypentanal
(D) 2 - methyl - 3 - bromobutanal

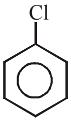
Q.38 The maximum number of possible isomers in 1-bromo-2-methyl cyclobutane is –
(A) 2 (B) 4
(C) 16 (D) 8

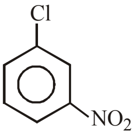
Q.39 Acetone and propanal are –
(A) Functional isomers (B) Position isomers
(C) Geometrical isomers (D) Optical isomers

Q.40 The compound that reacts fastest with sodium methoxide is –

(A) 

(B) 

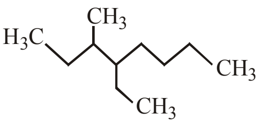
(C) 

(D) 

Q.41 Arrange the following compounds in the increasing order of their acidic strength :
i. m-nitrophenol ii. m-cresol
iii. phenol iv. m-chlorophenol
(A) iii < ii < i < iv (B) ii < iv < iii < i
(C) ii < iii < iv < i (D) ii < iii < i < iv

Q.42 Which of the following compound possesses the "C – H" bond with the lowest bond dissociation energy?
(A) Toluene (B) Benzene
(C) n-pentane (D) 2, 2-dimethyl propane

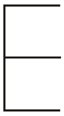
Q.43 Which type of hybridisation of each carbon is there in the compound?
$CH_3-CH=CH-CN$
(A) sp^3, sp^2, sp^2, sp (B) sp^3, sp^2, sp^2, sp^3
(C) sp^3, sp^2, sp^3, sp^3 (D) sp^3, sp^2 , sp, sp^3

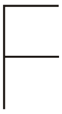
Q.44 IUPAC name of the compound


(A) 2,3-dimethylheptane
(B) 3-methyl-4-ethyloctane
(C) 5-ethyl-6-methyloctane
(D) 4-ethyl-3-methyloctane

Q.45 Which method can be applied to separate a mixture of camphor and benzoic acid?
(A) Sublimation
(B) Chemical methods
(C) Crystallisation
(D) Extraction with solvent.

Q.46 IUPAC names of the given structures are

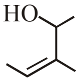
(i) 

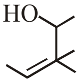
(ii) 

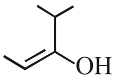
(A) (i) hexane, (ii) 3-methylbutane
(B) (i) isopentane, (ii) 2,2-dimethylbutane
(C) (i) 3–ethylbutane, (ii) isopentane
(D) (i) 3-methylpentane, (ii) 2-methylbutane.

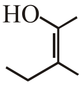
Q.47 During sodium extract preparation for Lassaigne's test both N and S present in organic compound change to–
(A) NaCN and Na_2S (B) $NaNH_2$ and Na_2SO_4
(C) NaSCN (D) $NaNO_3$ and Na_2S

Q.48 Correct representation of 3-methylpent-3-en-2-ol is –

(A) 

(B) 

(C) 

(D) 

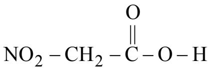
Q.49 0.46 g of an organic compound was analysed. The increase in mass of $CaCl_2$ U-tube was 0.54g and potash bulb was 0.88g. The percentage composition of the compound is –
(A) C = 52.17%, H = 13.04%, O = 34.79%
(B) C = 50%, H = 50%
(C) C = 32.19%, H = 18.01%, O = 49.8%
(D) C = 72%, H = 28%

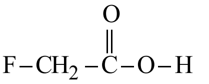
Q.50 Which of the following is the pair of homocyclic & heterocyclic compound –
(A) cyclopropane and cyclohexane
(B) cycloethane and oxyrane
(C) pyridine and thiophene
(D) cyclopentane and furane

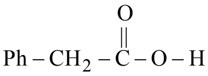
Q.51 The structure of isopropyl carbinol is –
(A) $(CH_3)_2CHOH$
(B) $CH_3–CHOH-CH_2-CH_3$
(C) $(CH_3)_2CHCH_2OH$
(D) $(CH_3)_3COH$

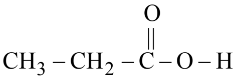
Q.52 The IUPAC name of the compound
$CH_3CH=CHCH=CHC\equiv CCH_3$ is –
(A) 4, 6-octadien-2-yne (B) 2, 4-octadien-6-yne
(C) 2-octyn-4, 6-diene (D) 6-octyn-2, 4-diene

Q.53 Select the least acidic compound –

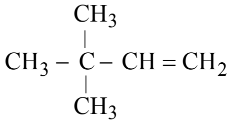
(A) 
$NO_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

(B) 
$F-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

(C) 
$Ph-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

(D) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

Q.54 Hyperconjugation phenomenon is possible in –

(A) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$

(B) $CH_2=CH_2$

(C) $C_6H_5-CH=CH_2$

(D) $CH_3-CH_2-CH=CH_2$

Q.55 The correct stability order of the following resonance structures is :

$CH_2=C=O$ (I)

$H_2\overset{-}{C}-\overset{+}{C}=O$ (II)

$H_2C=\overset{+}{C}-\overset{-}{O}$ (III)

$H_2\overset{-}{C}-C\equiv\overset{+}{O}$ (IV)

(A) (IV) > (I) > (III) > (II)

(B) (II) > (IV) > (I) > (III)

(C) (III) > (II) > (IV) > (I)

(D) (I) > (IV) > (III) > (II)

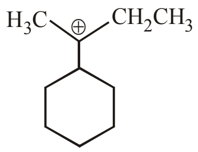
EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

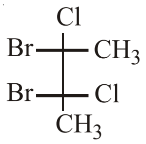
Q.1 The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is

Q.2 The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is :

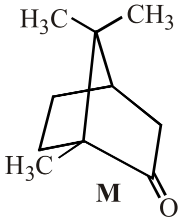
Q.3 The total number of contributing structures showing hyperconjugation (involving C – H bonds) for the following carbocation is –



Q.4 The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are) :



Q.5 The total number of stereoisomers that can exist for M is



M

Q.6 The number of isomers for the compound with molecular formula $C_2BrClFI$ is :

Q.7 The number of structural isomers for C_6H_{14} is

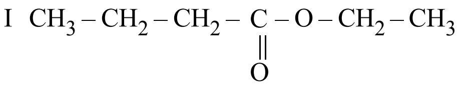
Q.8 The number of stereoisomers obtained by bromination of trans-2-butene is:

Q.9 The number of possible alkyl groups of isopentane are

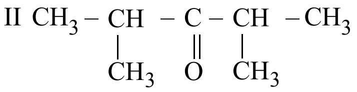
EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]

GOC

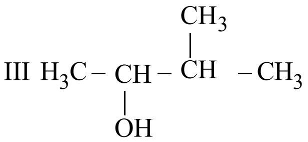
Q.1 Of the following compounds which has a wrong IUPAC name - **[AIEEE-2002]**

I 
$CH_3-CH_2-CH_2-\underset{\substack{\| \\ O}}{C}-O-CH_2-CH_3$

ethyl butanoate

II 
$CH_3-\underset{CH_3}{CH}-\underset{\substack{\| \\ O}}{C}-\underset{CH_3}{CH}-CH_3$

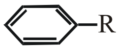
2,4 dimethyl -3- pentanone

III 
$H_3C-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_3$

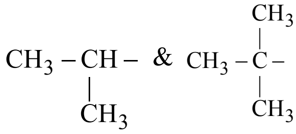
2-methyl -3- butanol

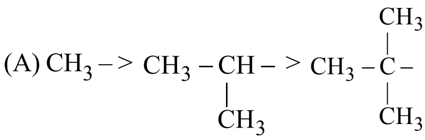
IV $CH_3-CH_2-CH_2-CHO$
butanal

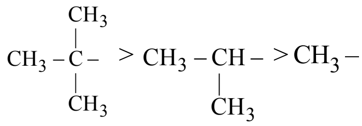
(A) I
(B) II
(C) III
(D) IV

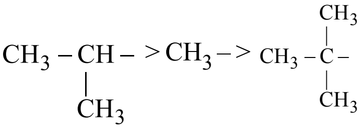
Q.2 In the following benzyl/alkyl system $R-CH=CH_2$ or  R (R is alkyl group) increasing order of inductive effect is – **[AIEEE-2002]**

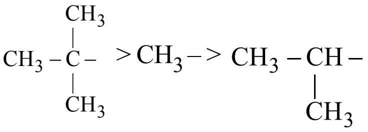
(A) $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$
(B) $(CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$
(C) $(CH_3)_2CH- > CH_3CH_2- > (CH_3)_3C-$
(D) $(CH_3)C- > CH_3CH_2- > (CH_3)_2CH-$

Q.3 When $-CH_3$,  $CH_3-\underset{CH_3}{CH}-$ & $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-$ groups are introduced on benzene ring then correct order of their inductive effect is - **[AIEEE-2002]**

(A) 
$CH_3- > CH_3-\underset{CH_3}{CH}- > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-$

(B) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}- > CH_3-\underset{CH_3}{CH}- > CH_3-$

(C) 
$CH_3-\underset{CH_3}{CH}- > CH_3- > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-$

(D) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}- > CH_3- > CH_3-\underset{CH_3}{CH}-$

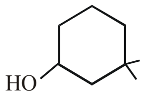
Q.4 The correct order of increasing basic no. of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is – **[AIEEE-2003]**

(A) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(B) $CH_3NH_2 < (CH_3)_2NH < NH_3$
(C) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(D) $(CH_3)_2NH < NH_3 < CH_3NH_2$

Q.5 The IUPAC name of $CH_3COCH(CH_3)_2$ is – **[AIEEE-2003]**

(A) 4-methylisopropyl ketone
(B) 3-methyl-2-butanone
(C) Isopropylmethyl ketone
(D) 2-methyl-3-butanone

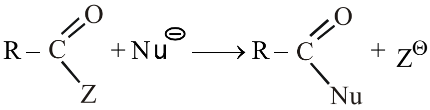
Q.6 The IUPAC name of the compound **[AIEEE-2004]**



is -

(A) 3,3 -dimethyl-1-hydroxy cyclohexane
(B) 1, 1 – dimethyl–3– hydroxy cyclohexane
(C) 3,3-dimethyl-1-cyclohexanol
(D) 1,1 - dimethyl - 3- cyclohexanol

Q.7 Rate of the reaction **[AIEEE-2004]**



is fastest when Z is -

(A) Cl
(B) NH_2
(C) OC_2H_5
(D) $OCOCH_3$

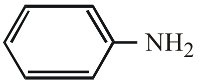
Q.8 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

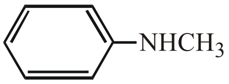
(a) PhCOOH
(b) $o-NO_2C_6H_4COOH$
(c) $p-NO_2C_6H_4COOH$
(d) $m-NO_2C_6H_4COOH$

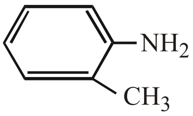
Which of the following order is correct ?

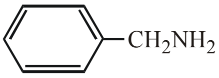
(A) a > b > c > d
(B) b > d > c > a
(C) b > d > a > c
(D) b > c > d > a

Q.9 Which of the following is the strongest base - **[AIEEE-2004]**

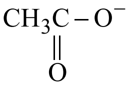
(A) 

(B) 

(C) 

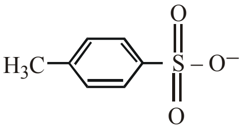
(D) 

Q.10 The decreasing order of nucleophilicity among the nucleophiles **[AIEEE-2005]**

(a) 
$CH_3\underset{\substack{\| \\ O}}{C}-O^-$

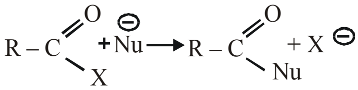
(b) CH_3O^-

(c) CN^-

(d) 

is

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

Q.11 The reaction  is fastest when X is – **[AIEEE-2005]**

(A) NH_2
(B) Cl
(C) OCOR
(D) OC_2H_5

Q.12 Amongst the following the most basic compound is– **[AIEEE-2005]**

(A) aniline
(B) benzylamine
(C) p–nitroaniline
(D) acetanilide

Q.13 The increasing order of stability of the following free radicals is – **[AIEEE 2006]**

(A) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(B) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(C) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(D) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

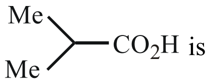
Q.14 $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is

[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O] **[AIEEE 2006]**

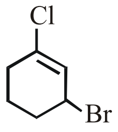
(A) D > C > B > A
(B) A > B > C > D
(C) B > D > C > A
(D) D > C > A > B

Q.15 The correct order of increasing acid strength of the compounds **[AIEEE 2006]**

(a) CH_3CO_2H
(b) $MeOCH_2CO_2H$
(c) CF_3CO_2H
(d)  is

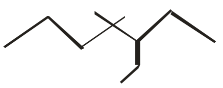
(A) d < a < c < b
(B) d < a < b < c
(C) a < d < c < b
(D) b < d < a < c

Q.16 The IUPAC name of the compound shown below is - **[AIEEE 2006]**



(A) 6-bromo-2-chlorocyclohexene
(B) 3-bromo-1-chlorocyclohexene
(C) 1-bromo-3-chlorocylohexene
(D) 2-bromo-6-chlorocycohex-1-ene

Q.17 The IUPAC name of **[AIEEE 2007]**

 is –

(A) 1, 1-diethyl-2-dimethylpentane
(B) 4, 4-dimethyl-5, 5-diethylpentane
(C) 5, 5-diethyl-4, 4-dimethylpentane
(D) 3-ethyl-4, 4 dimethylheptane

Q.18 Which one of the following is the strongest base in aqueous solution ? **[AIEEE-2007]**

(A) Trimethylamine
(B) Aniline
(C) Dimethylamine
(D) Methylamine

Q.19 Presence of a nitro group in a benzene ring- **[AIEEE 2007]**

(A) activates the ring towards electrophilic substitution
(B) renders the ring basic
(C)deactivates the ring towards nucleophilic substitution
(D)deactivates the ring towards electrophilic substitution

Q.20 The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[AIEEE 2008]**

(A) $-SO_3H, -COOH, -CONH_2, -CHO$
(B) $-CHO, -COOH, -SO_3H, -CONH_2$
(C) $-CONH_2, -CHO, -SO_3H, -COOH$
(D) $-COOH, -SO_3H, -CONH_2, -CHO$

Q.21 Arrange the carbanions, $(CH_3)_3\bar{C}, \bar{C}Cl_3, (CH_3)_2\bar{C}H, C_6H_5\bar{C}H_2$, in order of their decreasing stability- **[AIEEE 2009]**

(A) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(B) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

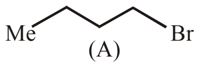
(C) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$

(D) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

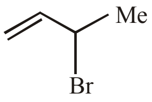
Q.22 The IUPAC name of neopentane is: **[AIEEE 2009]**

(A) 2,2–dimethylbutane
(B) 2–methylbutane
(C) 2,2-dimethylpropane
(D) 2–methylpropane

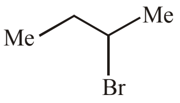
Q.23 Consider the following bromides :



(A)



(B)



(C)

The correct order of S_N1 reactivity is **[AIEEE 2010]**

(A) B > C > A
(B) B > A > C
(C) C > B > A
(D) A > B > C

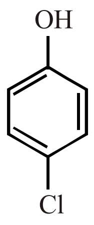
Q.24 The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is – **[AIEEE 2010]**

(A) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$
(B) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$
(C) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$
(D) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

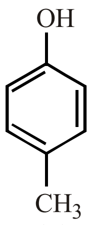
Q.25 The strongest acid amongst the following compounds is – **[AIEEE 2011]**

(A) CH_3COOH
(B) HCOOH
(C) $CH_3CH_2CH(Cl)CO_2H$
(D) $ClCH_2CH_2CH_2COOH$

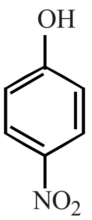
Q.26 Arrange the following compounds in order of decreasing acidity : **[JEE MAIN 2013]**



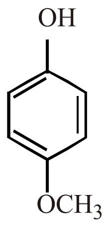
(I)



(II)



(III)

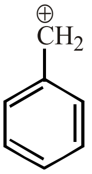


(IV)

(A) II > IV > I > III (B) I > II > III > IV
(C) III > I > II > IV (D) IV > III > I > II

Q.27 The order of stability of the following carbocations :

$CH_2=CH-\overset{\oplus}{C}H_2$ (I) ; $CH_3-CH_2-\overset{\oplus}{C}H_2$ (II) ;



is –

(III)

[JEE MAIN 2013]

(A) III > II > I (B) II > III > I
(C) I > II > III (D) III > I > II

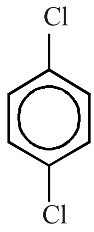
Q.28 In S_N2 reactions, the correct order of reactivity for the following compounds: **[JEE MAIN 2014]**

CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is:

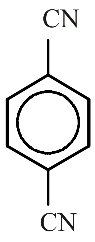
(A) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(B) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
(C) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(D) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

Q.29 For which of the following molecule significant $\mu \neq 0$? **[JEE MAIN 2014]**

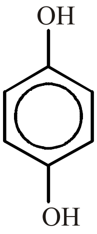
(a)



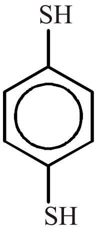
(b)



(c)



(d)

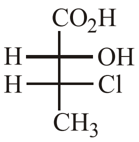


(A) Only (c) (B) (c) and (d)
(C) Only (a) (D) (a) and (b)

Q.30 The distillation technique most suited for separating glycerol from spent-lye in the soap industry is: **[JEE MAIN 2016]**

(A) Fractional distillation
(B) Steam distillation
(C) Distillation under reduced pressure
(D) Simple distillation

Q.31 The absolute configuration of

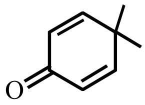


[JEE MAIN 2016]

(A) (2S, 3R) (B) (2S, 3S)
(C) (2R, 3R) (D) (2R, 3S)

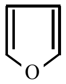
Q.32 Which of the following molecules is least resonance stabilized? **[JEE MAIN 2017]**

(A)

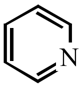


(B)

(C)

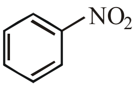


(D)

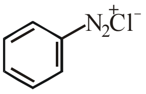


Q.33 Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation ? **[JEE MAIN 2018]**

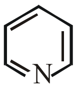
(A)



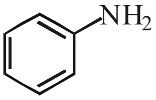
(B)



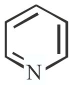
(C)



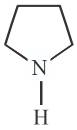
(D)



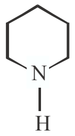
Q.34 Arrange the following amines in the decreasing order of basicity:



(I)



(II)



(III)

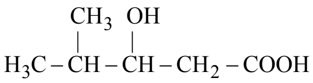
[JEE MAIN 2019 (JAN)]

(A) I > II > III (B) III > II > I
(C) I > III > II (D) III > I > II

Q.35 Which amongst the following is the strongest acid? **[JEE MAIN 2019 (JAN)]**

(A) CHI_3 (B) $CHCl_3$
(C) $CHBr_3$ (D) $CH(CN)_3$

Q.36 The IUPAC name of the following compound is :

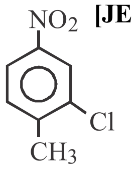


$$H_3C-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\overset{OH}{\overset{|}{C}H}-CH_2-COOH$$

[JEE MAIN 2019 (APRIL)]

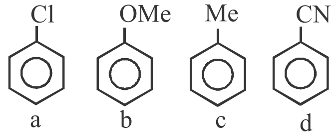
(A) 2-Methyl-3Hydroxypentan-5-oic acid
(B) 4,4-Dimethyl-3-hydroxy butanoic acid
(C) 3-Hydroxy-4 -methylpentanoic acid
(D) 4-Methyl-3-hydroxypentanoic acid

Q.37 The correct IUPAC name of the following compound is **[JEE MAIN 2019 (APRIL)]**



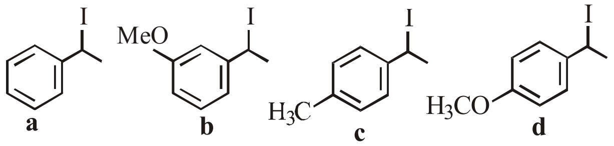
(A) 5-chloro-4-methyl-1-nitrobenzene
(B) 2-methyl-5-nitro-1-chlorobenzene
(C) 3-chloro-4-methyl-1-nitrobenzene
(D) 2-chloro-1-methyl-4-nitrobenzene

Q.38 The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is : **[JEE MAIN 2019 (APRIL)]**



(A) d < b < a < c (B) a < b < c < d
(C) d < a < c < b (D) b < c < a < d

Q.39 Increasing rate of S_N1 reaction in the following compounds is : **[JEE MAIN 2019 (APRIL)]**

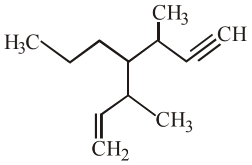


(A) a < b < c < d (B) b < a < d < c
(C) b < a < c < d (D) a < b < d < c

Q.40 An organic compound 'A' is oxidized with Na_2O_2 followed by boiling with HNO_3. The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate. Based on above observation, the element present in the given compound is : **[JEE MAIN 2019 (APRIL)]**

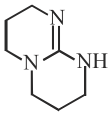
(A) Sulphur (B) Nitrogen
(C) Fluorine (D) Phosphorus

Q.41 The IUPAC name of the following compound is : **[JEE MAIN 2019 (APRIL)]**



(A) 3,5-dimethyl-4-propylhept-6-en-1-yne
(B) 3-methyl-4-(3-methylprop-1-enyl)-1-heptyne
(C) 3-methyl-4-(1-methylprop-2-ynyl)-1-heptene
(D) 3,5-dimethyl-4-propylhept-1-en-6-yne

Q.42 The increasing order of pK_b for the following compounds will be : **[JEE MAIN 2020 (JAN)]**

a. 

b. $CH_3–NH–CH_3$ c. $NH_2 – CH = NH$

(A) a > b > c (B) b > a > c
(C) c > b > a (D) b > c > a

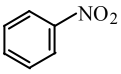
Q.43 A chromatography column, packed with silica gel as stationary phase, was used to separate a mixture of compounds consisting of (a) benzanilide (b) aniline and (c) acetophenone. When the column is eluted with a mixture of solvents, hexane : ethyl acetate (20 : 80), the sequence of obtained compounds : **[JEE MAIN 2020 (JAN)]**

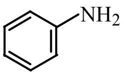
(A) (b), (c) and (a) (B) (c), (a) and (b)
(C) (a), (b) and (c) (D) (b), (a) and (c)

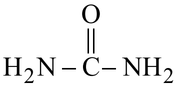
Q.44 A flask contains a mixture of isohexane and 3-methylpentane. One of the liquids boils at 63°C while the other boils at 60°C. What is the best way to seprate the two liquids and which one will be distilled out first? **[JEE MAIN 2020 (JAN)]**

(A) Simple distillation and isohexane.
(B) Fractional distillation and isohexane.
(C) Simple distillation and 3-Methylpantane.
(D) Fractional distillation and 3-Methylpantane.

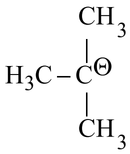
Q.45 Kjeldahl method cannot be used for : **[JEE MAIN 2020 (JAN)]**

(A) 

(B) 

(C) $CH_3–CH_2–CH_2–C≡N$ (D) 
$H_2N – \overset{\overset{\large O}{||}}{C} – NH_2$

Q.46 The increasing order of basicity for the following intermediates is (from weak to strong) **[JEE MAIN 2020 (JAN)]**

(i) 
$H_3C – \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{}^{\ominus}$

(ii) $H_2C = CH – \overset{\ominus}{C}H_2$

(iii) $HC \equiv \overset{\ominus}{C}$ (iv) $\overset{\ominus}{C}H_3$ (v) $\overset{\ominus}{C}N$

(A) (v) < (i) < (iv) < (ii) < (iii)
(B) (iii) < (i) < (ii) < (iv) < (v)
(C) (v) < (iii) < (ii) < (iv) < (i)
(D) (iii) < (iv) < (ii) < (i) < (v)

Q.47 Which of the following has the shortest C-Cl bond? **[JEE MAIN 2020 (JAN)]**

(A) $Cl–CH=CH–OCH_3$ (B) $C1–CH=CH–CH_3$
(C) $C1–CH=CH_2$ (D) $C1–CH=CH–NO_2$

Q.48 The number of sp^2 hybrid orbitals in a molecule of benzene is : **[JEE MAIN 2020 (JAN)]**

(A) 24 (B) 6
(C) 12 (D) 18

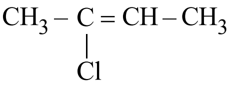
ISOMERISM

Q.1 Stereo - Isomerism includes - **[AIEEE-2002]**

(A) Geometrical isomerism only
(B) Optical isomerism only
(C) Both geometrical & optical isomerism
(D) Position & Functional isomerism

Q.2 Which of the following does not show geometrical isomerism - **[AIEEE-2002]**

(A) $CH_3 – CH = CH – CH_3$ (B) $CH_3 – CH_2 – HC = CH_2$

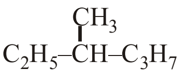
(C) 
$CH_3 – \underset{\underset{\large Cl}{|}}{C} = CH – CH_3$ (D) $ClHC=CH– CH_2 – CH_3$

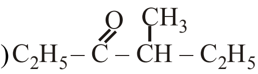
Q.3 Racemic mixture is formed by mixing two – **[AIEEE-2002]**
(A) Isomeric compounds
(B) Chiral compounds
(C) Meso compounds
(D) Enanitiomers with chiral carbon

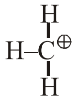
Q.4 Geometrical isomerism is not shown by – **[AIEEE-2002]**
(A) 1, 1– dichloro–1–pentene
(B) 1, 2– dichloro–1–pentene
(C) 1, 3– dichloro–2–pentene
(D) 1, 4– dichloro–2–pentene

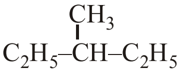
Q.5 Racemic mixture is – **[AIEEE-2002]**
(A) A mixture of chiral carbons
(B) A mixture of isomers
(C) A mixture of aldehydes and ketones
(D) A mixture of alcohols and ethers

Q.6 Among the following four structures I to IV

(i)

$C_2H_5-\overset{CH_3}{\overset{|}{C}H}-C_3H_7$

(ii)

$C_2H_5-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}H}-C_2H_5$

(iii)

$H-\overset{H}{\underset{H}{C}}{}^{\oplus}$

(iv)

$C_2H_5-\overset{CH_3}{\overset{|}{C}H}-C_2H_5$

It is true that – **[AIEEE-2003]**
(A) Only (iii) is a chiral compound
(B) Only (ii) and (iv) are chiral compounds
(C) All four are chiral compounds
(D) Only (i) and (ii) are chiral compounds

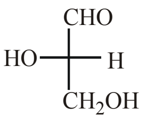
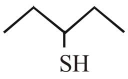
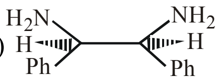
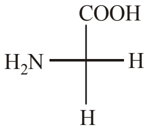
Q.7 Which of the following compounds is not chiral ?
(A) 1-chloropentane **[AIEEE-2004]**
(B) 2-chloropentane
(C) 1-chloro-2-methyl pentane
(D) 3-chloro-2-methyl pentane

Q.8 Which of the following will have a mesoisomer also
(A) 2-Chlorobutane **[AIEEE-2004]**
(B) 2, 3-Dichlorobutane
(C) 2,3-Dichloropentane
(D) 2-Hydroxypropanoic acid

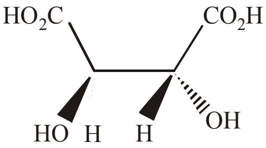
Q.9 Which types of isomerism is shown by 2,3-dichlorobutane **[AIEEE-2005]**
(A) Optical (B) Diastereo
(C) Structural (D) Geometric

Q.10 Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is **[AIEEE 2006]**
(A) Gauche, Eclipse, Anti (B) Eclipse, Anti, Gauche
(C) Anti, Gauche, Eclipse (D) Eclipse, Gauche, Anti

Q.11 Which of the following molecules is expected to rotate the plane of plane-polarised light? **[AIEEE-2007]**

(A)

(B)

(C)

(D)


Q.12 Which one of the following conformations of cyclohexane is chiral ? **[AIEEE-2007]**
(A) Twist boat (B) Rigid
(C) Chair (D) Boat

Q.13 The absolute configuration of

is **[AIEEE-2008]**
(A) R, R (B) R, S
(C) S, R (D) S, S

Q.14 The number of stereoisomers possible for a compound of the molecular formula $CH_3-CH=CH-CH(OH)-Me$ is: **[AIEEE 2009]**
(A) 6 (B) 3
(C) 2 (D) 4

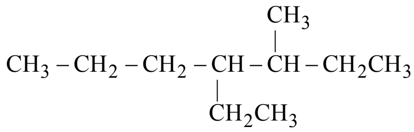
Q.15 Identify the compound that exhibits tautomerism – **[AIEEE 2011]**
(A) 2-Butene (B) Lactic acid
(C) 2-Pentanone (D) Phenol

Q.16 Which of the following compounds will exhibit geometrical isomerism? **[JEE MAIN 2015]**
(A) 3 - Phenyl - 1 - butene (B) 2 - Phenyl - 1 - butene
(C) 1, 1-Diphenyl-1 propane (D) 1 - Phenyl - 2 - butene

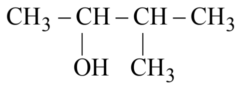
EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)

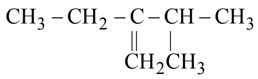
Choose one correct response for each question.

Q.1 Names of some compounds are given. Which one is not correct in IUPAC system ? **[AIPMT 2005]**

(A) 
$CH_3-CH_2-CH_2-\underset{CH_2CH_3}{CH}-\overset{CH_3}{CH}-CH_2CH_3$

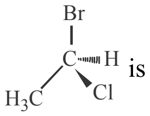
3-methyl-4-ethyl heptane

(B) 
$CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3$ 3-methyl-2-butanol

(C) 
$CH_3-CH_2-\underset{\underset{CH_2CH_3}{\|}}{C}-\underset{|}{CH}-CH_3$ 2-ethyl-3-methyl-but-1-ene

(D) $CH_3-C\equiv C-CH-(CH_3)_2$ 4-methyl-2-pentyne

Q.2 The chirality of the compound **[AIPMT 2005]**

 is

(A) R (B) S

(C) E (D) Z

Q.3 Which of the following pairs represents stereoisomerism **[AIPMT 2005]**

(A) Structural isomerism and geometrical isomerism.

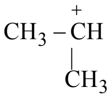
(B) Optical isomerism and geometrical isomerism.

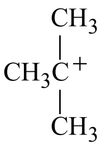
(C) Chain isomerism and Rotational isomerism.

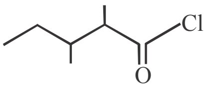
(D) Linkage isomerism and geometrical isomerism.

Q.4 Which amongst the following is the most stable corbocation – **[AIPMT 2005]**

(A) $\overset{+}{C}H_3$ (B) $CH_3\overset{+}{C}H_2$

(C) 
$CH_3-\underset{CH_3}{\overset{+}{CH}}$

(D) 
$CH_3\underset{CH_3}{\overset{CH_3}{C^+}}$

Q.5 The IUPAC name of  is – **[AIPMT 2006]**

(A) 1-chloro-1-oxo-2,3-dimethyl pentane

(B) 2-ethyl-3-methylbutanoyl chloride

(C) 2,3-dimethylpentanoyl chloride

(D) 3,4-dimethylpentanoyl chloride

Q.6 Which of the following is not chiral – **[AIPMT 2006]**

(A) 2,3-Dibromopentane (B) 3-Bromopentane

(C) 2-Hydroxypropanoic acid (D) 2-Butanol

Q.7 The general molecular formula, which represents the homologous series of alkanols is – **[AIPMT 2006]**

(A) $C_nH_{2n}O$ (B) $C_nH_{2n+1}O$

(C) $C_nH_{2n+2}O$ (D) $C_nH_{2n}O_2$

Q.8 If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that – **[AIPMT 2007]**

(A) the compound is certainly meso.

(B) there is no compound in the solvent.

(C) the compound may be a racemic mixture.

(D) the compound is certainly a chiral.

Q.9 For (i) I^-, (ii) Cl^-, (iii) Br^-, the increasing order of nucleophilicity would be – **[AIPMT 2007]**

(A) $Cl^- < Br^- < I^-$ (B) $I^- < Cl^- < Br^-$

(C) $Br^- < Cl^- < I^-$ (D) $I^- < Br^- < Cl^-$

Q.10 The order of decreasing reactivity towards an electrophilic reagent, for the following would be **[AIPMT 2007]**

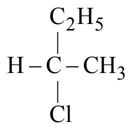
(i) benzene (ii) toluene

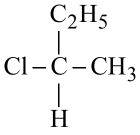
(iii) chlorobenzene (iv) phenol

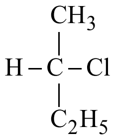
(A) (ii) > (iv) > (i) > (iii) (B) (iv) > (iii) > (ii) > (i)

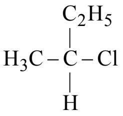
(C) (iv) > (ii) > (i) > (iii) (D) (i) > (ii) > (iii) > (iv)

Q.11 $CH_3-CHCl-CH_2-CH_3$ has a chiral centre which one of the following represents its R-configuration – **[AIPMT 2007]**

(A) 
$H-\underset{Cl}{\overset{C_2H_5}{C}}-CH_3$

(B) 
$Cl-\underset{H}{\overset{C_2H_5}{C}}-CH_3$

(C) 
$H-\underset{C_2H_5}{\overset{CH_3}{C}}-Cl$

(D) 
$H_3C-\underset{H}{\overset{C_2H_5}{C}}-Cl$

Q.12 Base strength of:

(a) $H_3C\overset{\ominus}{C}H_2$ (b) $H_2C=\overset{\ominus}{C}H$ and (c) $H-C\equiv\overset{\ominus}{C}$ is

the order of : **[AIPMT 2008]**

(A) (a) > (b) > (c) (B) (b) > (a) > (c)

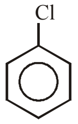
(C) (c) > (b) > (a) (D) (a) > (c) > (b)

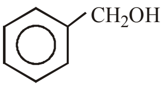
Q.13 How many stereoisomers does this molecule have ? $CH_3CH=CHCH_2CHBrCH_3$ **[AIPMT 2008]**

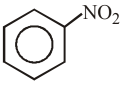
(A) 2 (B) 4

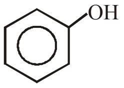
(C) 6 (D) 8

Q.14 Which one of the following is most reactive towards electrophilic attack ? **[AIPMT 2008]**

(A) 

(B) 

(C) 

(D) 

Q.15 In the hydrocarbon

$CH_3-CH=CH-CH_2-C\equiv CH$

6 5 4 3 2 1

The state of hybridization of carbons 1, 3 and 5 are in the following sequence: **[AIPMT 2008]**

(A) sp^3, sp^2, sp (B) sp^2, sp, sp^3

(C) sp, sp^3, sp^2 (D) sp, sp^2, sp^3

Q.16 The stability of carbanions in the following **AIPMT 2008]**

(a) $RC\equiv\overset{\ominus}{C}$

(b) 

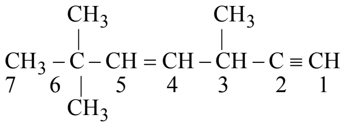
(c) $R_2C=\overset{\ominus}{C}H$ (d) $R_3C-\overset{\ominus}{C}H_2$

is the order of

(A) (a) > (c) > (b) > (d) (B) (a) > (b) > (c) > (d)

(C) (b) > (c) > (d) > (a) (D) (d) > (b) > (c) > (a)

Q.17 The state of hybridization of C_2, C_3, C_5 and C_6 of the hydrocarbon,



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

is in the following sequence – **[AIPMT 2009]**

(A) sp^3, sp^2, sp^2 and sp (B) sp, sp^2, sp^2 and sp^3

(C) sp, sp^2, sp^3 and sp^2 (D) sp, sp^3, sp^2 and sp^3

Q.18 The IUPAC name of the compound having the formula $CH\equiv C-CH=CH_2$ is: **[AIPMT 2009]**

(A) 1-butyne-3-ene (B) but-1-yne-3-ene

(C) 1-butene-3-yne (D) 3-butene-1-yne

Q.19 Which of the following reactions is an example of nucleophilic susbtitution reaction? **[AIPMT 2009]**

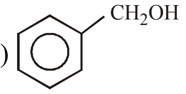
(A) $2\,RX+2\,Na\longrightarrow R-R+2\,NaX$

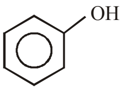
(B) $RX+H_2\longrightarrow RH+HX$

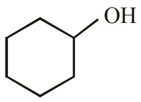
(C) $RX+Mg\longrightarrow RMgX$

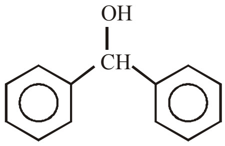
(D) $RX+KOH\longrightarrow ROH+KX$

Q.20 Which one of the following compounds has the most acidic nature? **[AIPMT (PRE) 2010]**

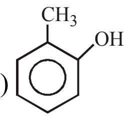
(A) 

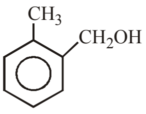
(B) 

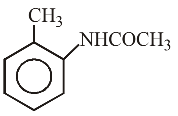
(C) 

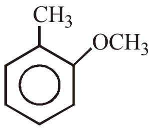
(D) 

Q.21 Which one is most reactive towards electrophilic reagent **[AIPMT (PRE) 2010, 2011]**

(A) 

(B) 

(C) 

(D) 

Q.22 Which of the following species is not electrophilic in nature? **[AIPMT (MAINS) 2010]**

(A) $\overset{\oplus}{Cl}$ (B) BH_3

(C) $H_3\overset{\oplus}{O}$ (D) $\overset{\oplus}{N}O_2$

Q.23 The IUPAC name of the compound $CH_3CH=CHC\equiv CH$ is **[AIPMT (MAINS) 2010]**

(A) Pent-4-yn-2-ene (B) Pent-3-en-1-yne

(C) Pent-2-en-4-yne (D) Pent-1-yn-3-ene

Q.24 Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear?

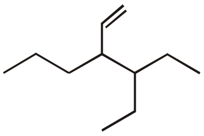
(A) $CH_3-CH_2-CH_2-CH_3$ **[AIPMT (PRE) 2011]**

(B) $CH_3-CH=CH-CH_3$

(C) $CH_3-C\equiv C-CH_3$

(D) $CH_2=CH-CH_2-C\equiv CH$

Q.25 The correct IUPAC name of the compound



[AIPMT (PRE) 2011]

(A) 3-(1-ethyl propyl) hex-1-ene

(B) 4-Ethyl-3-propyl hex-1-ene

(C) 3-Ethyl-4-ethenyl heptane

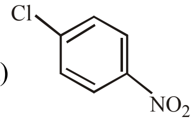
(D) 3-Ethyl-4-propyl hex-5-ene

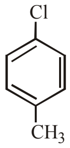
Q.26 In Dumas' method of estimation of nitrogen 0.35g of an organic compound gave 55 mL of nitrogen collected at 300K temperature and 715mm pressure. The percentage composition of nitrogen in the compound would be (Aqueous tension at 300 K = 15 mm) **[AIPMT (PRE) 2011]**

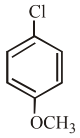
(A) 14.45 (B) 15.45

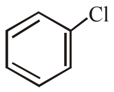
(C) 16.45 (D) 17.45

Q.27 Which of the following compounds undergoes nucleophilic substitution reaction most easily ? **[AIPMT (MAINS) 2011]**

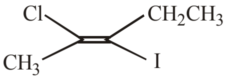
(A) 

(B) 

(C) 

(D) 

Q.28 The IUPAC name of the following compound



is **[AIPMT (MAINS) 2011]**

(A) trans-2-chloro-3-iodo-2-pentene

(B) cis-3-iodo-4-chloro-3-pentene

(C) trans-3-iodo-4-chloro-3-pentene

(D) cis-2-chloro-3-iodo-2-pentene

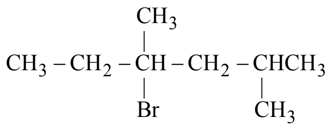
Q.29 Among the following compounds the one that is most reactive towards electrophilic nitration is : **[AIPMT (PRE) 2012]**

(A) Benzoic Acid (B) Nitrobenzene

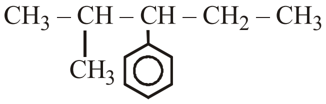
(C) Toluene (D) Benzene

Q.30 Which nomenclature is not according to IUPAC system **[AIPMT (PRE) 2012]**

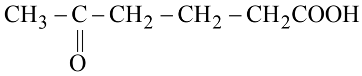
(A) $Br-CH_2-CH=CH_2$, 1-Bromoprop-2-ene

(B)

$CH_3-CH_2-\underset{Br}{\overset{CH_3}{C}}H-CH_2-\underset{CH_3}{C}HCH_3$

4-Bromo-2,4-di-methylhexane

(C)


2-Methyl-3-phenylpentane

(D)

$CH_3-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_2-CH_2-CH_2COOH$

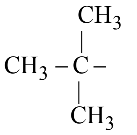
5-oxohexanoic acid

Q.31 Which of the following acids does not exhibit optical isomerism ? **[AIPMT (PRE) 2012]**

(A) Maleic acid (B) α-amino acids

(C) Lactic acid (D) Tartaric acid

Q.32 The structure of isobutyl group in an organic compound is– **[NEET 2013]**

(A)

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

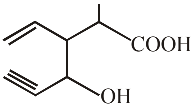
(B)

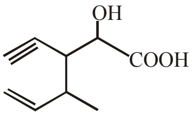

(C)

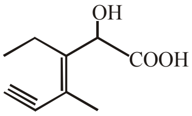
$CH_3-\underset{|}{C}H-CH_2-CH_3$

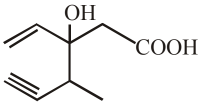
(D) $CH_3-CH_2-CH_2-CH_2-$

Q.33 Structure of the compound whose IUPAC name is 3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is – **[NEET 2013]**

(A)


(B)


(C)


(D)


Q.34 Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating? **[NEET 2013]**

(A) $-NO_2$ (B) $-C\equiv N$

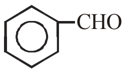
(C) $-SO_3H$ (D) $-COOH$

Q.35 In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is – **[AIPMT 2014]**

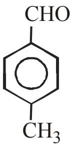
(A) 37.33 (B) 45.33

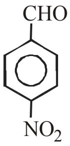
(C) 35.33 (D) 43.33

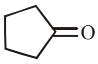
Q.36 Which one is most reactive towards Nucleophilic addition reaction? **[AIPMT 2014]**

(A)


(B)


(C)


(D)


Q.37 Treatment of cyclopentanone  with methyl lithium gives which of the following species ? **[AIPMT 2015]**

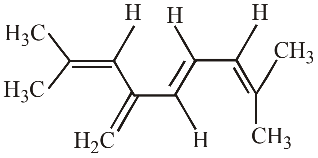
(A) Cyclopentanonyl cation

(B) Cyclopentanonyl radical

(C) Cyclopentanonyl biradical

(D) Cyclopentanonyl anion

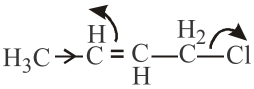
Q.38 The total number of π-bond electrons in the following structure is : **[AIPMT 2015]**

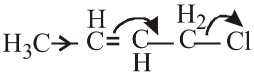


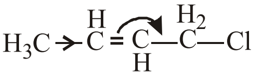
(A) 8 (B) 12

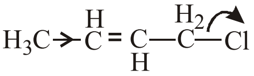
(C) 16 (D) 4

Q.39 Which of the following is the most correct electron displacement for a nucleophilic reaction to take place ? **[AIPMT 2015]**

(A)


(B)


(C)


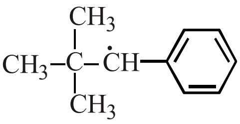
(D)


Q.40 In Duma's method for estimation of nitrogen 0.25g of an organic compound gave 40mL of nitrogen collected at 300K temperature and 725mm pressure. If the aqueous tension at 300K is 25 mm, the percentage of nitrogen in the compound is : **[AIPMT 2015]**

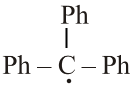
(A) 18.20 (B) 16.76

(C) 15.76 (D) 17.36

Q.41 Consider the following compound.



(I)



(II)

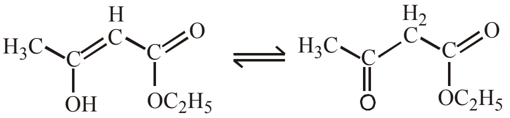
(III)

Hyperconjugation occurs in : **[AIPMT 2015]**

(A) II only (B) III only

(C) I and III (D) I only

Q.42 The enolic form of ethyl acetoacetate as shown below has :



[AIPMT 2015]

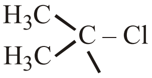
(A) 16 sigma bonds and 1 pi bond

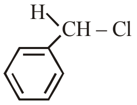
(B) 9 sigma bonds and 2 pi-bond

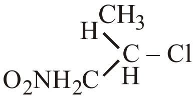
(C) 9 sigma bonds and 1 pi-bond

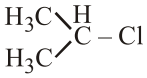
(D) 18 sigma bonds and 2 pi-bond

Q.43 In which of the following compounds, the C – Cl bond ionisation shall give most stable carbonium ion ? **[AIPMT 2015]**

(A) 

(B) 

(C) 

(D) 

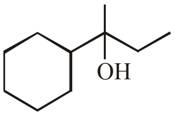
Q.44 Which of the following statements is not correct for a nucleophile ? **[RE-AIPMT 2015]**

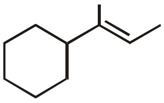
(A) Nucleophiles attack low e^- density sites.

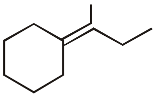
(B) Nucleophiles are not electron seeking.

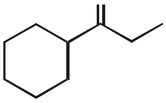
(C) Nucleophile is a Lewis acid.

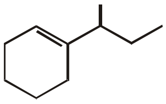
(D) Ammonia is a nucleophile.

Q.45 Which of the following is not the product of dehydration of  ? **[RE-AIPMT 2015]**

(A) 

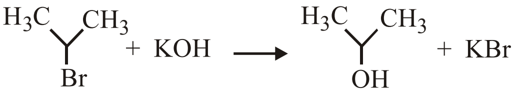
(B) 

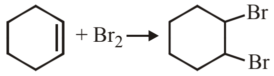
(C) 

(D) 

Q.46 For the following reactions :

(a) $CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH=CH_2 + KBr + H_2O$

(b) 

(c) 

Which of the following statements is correct? **[NEET 2016 PHASE 1]**

(A) (a) and (b) are elimination reactions and (c) is addition reaction.

(B) (a) is elimination, (b) is substitution and (c) is addition reaction.

(C) (a) is elimination, (b) and (c) are substitution reactions

(D) (a) is substitution, (b) and (c) are addition reactions.

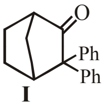
Q.47 The pair of electron in the given carbanion, $CH_3C\equiv C^{\ominus}$ is present in which of the following orbitals? **[NEET 2016 PHASE 1]**

(A) 2p (B) sp^3

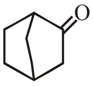
(C) sp^2 (D) sp

Q.48 Which among the given molecules can exhibit tautomerism? **[NEET 2016 PHASE 2]**

I



I



III

(A) III only (B) Both I and III

(C) Both I and II (D) Both II and III

Q.49 Which one is the correct order of acidity ? **[NEET 2017]**

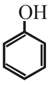
(A) $CH\equiv CH > CH_3-C\equiv CH > CH_2=CH_2 > CH_3-CH_3$

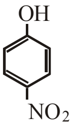
(B) $CH\equiv CH > CH_2=CH_2 > CH_3-C\equiv CH > CH_3-CH_3$

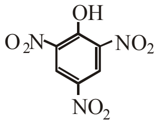
(C) $CH_3-CH_3 > CH_2=CH_2 > CH_3-C\equiv CH > CH\equiv CH$

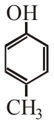
(D) $CH_2=CH_2 > CH_3-CH=CH_2 > CH_3-C\equiv CH > CH\equiv CH$

Q.50 Which one is the most acidic compound ? **[NEET 2017]**

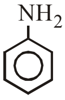
(A) 

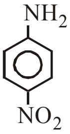
(B) 

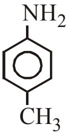
(C) 

(D) 

Q.51 The CORRECT increasing order of basic strength for the following compounds is : **[NEET 2017]**

(I) 

(II) 

(III) 

(A) III < I < II (B) III < II < I

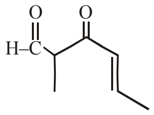
(C) II < I < III (D) II < III < I

Q.52 The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is : **[NEET 2017]**

(A) Chromatography (B) Crystallisation

(C) Steam distillation (D) Sublimation

Q.53 The IUPAC name of the compound



is – **[NEET 2017]**

(A) 5-formylhex-2-en-3-one
(B) 5-methyl-4-oxohex-2-en-5-al
(C) 3-keto-2-methylhex-5-enal
(D) 3-keto-2-methylhex-4-enal

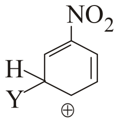
Q.54 The correct statement regarding electrophile is **[NEET 2017]**

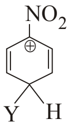
(A) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile.
(B) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile.
(C) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile.
(D) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile.

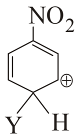
Q.55 Which of the following molecules represents the order of hybridisation sp^2, sp^2, sp, sp from left to right atoms? **[NEET 2018]**

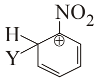
(A) $CH_2=CH-CH=CH_2$ (B) $CH_2=CH-C\equiv CH$
(C) $HC\equiv C-C\equiv CH$ (D) $CH_3-CH=CH-CH_3$

Q.56 Which of the following carbocations is expected to be most stable? **[NEET 2018]**

(A)


(B)


(C)


(D)


Q.57 Which of the following is correct with respect to – I effect of the substituents? (R = alkyl) **[NEET 2018]**

(A) $-NH_2 > -OR > -F$ (B) $-NR_2 < -OR < -F$
(C) $-NH_2 < -OR < -F$ (D) $-NR_2 > -OR > -F$

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	D	B	B	B	B	B	C	A	A	B	C	B	A	B	D	C	C	B	C	A	C	A	B	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	A	D	A	C	B	C	A	C	A	B	C	D	D	D	D	C	C	D	A	C	C	A	A	D
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	A	B	A	C	C	D	D	A	A	D	C	D	B	B	C	A	B	D	A	C	D	D	D	C	C
Q	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94						
A	B	C	A	B	A	C	A	D	C	B	A	D	D	B	B	C	A	C	D						

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	C	B	C	A	B	C	A	A	C	D	C	D	D	D	D	B	C	B	B	D	D	B	B	A	B	B	A	B	A	C
Q	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55					
A	A	D	A	C	D	A	C	B	A	C	C	A	A	D	B	D	C	A	A	D	C	B	D	D	D					

EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9
A	7	5	6	3	2	6	5	1	4

EXERCISE - 4 [GOC]

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	C	A	B	A	B	C	A	D	D	D	B	B	D	D	B	B	D	C	D	D
Q	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
A	B	C	A	D	C	C	D	D	B	C	A	A	D	D	D	C	D	C	C	D
Q	41	42	43	44	45	46	47	48												
A	D	C	B	B	A	C	D	D												

EXERCISE - 4 [ISOMERISM]

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
A	C	B	D	A	A	D	A	B	A	D	A	A	A	D	C	D

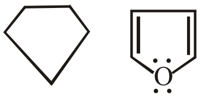
EXERCISE - 5

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

GENERAL ORGANIC CHEMISTRY

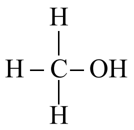
TRY IT YOURSELF-1

(1) **(D).**



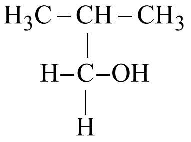
Cyclopentane and furnae is a pair of homocyclic & heterocyclic compound. In which cyclopentane is homocyclic and furane is heterocyclic.

(2) **(C).** In derived name system



$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Carbinol

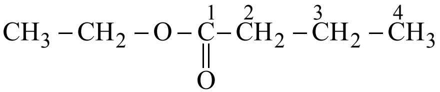


$$\begin{array}{c} H_3C-CH-CH_3 \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Isopropyl carbinol

(3) **(B).** Between double bond & triple bond double bond is preferred.

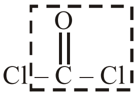
(4) **(B).** The IUPAC name of the compound $CH_3CH_2OCOCH_2CH_2CH_3$ is ethyl butanoate.



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

Ethyl butanoate

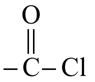
(5) **(B).** IUPAC name of the carbonyl chloride is Chloromethanoyl chloride .



$$Cl\boxed{-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$$

(Chloromethanoyl chloride)

Principal functional group is

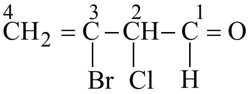


$$-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

(-oyl-chloride)

Its common name is phosgene & it is poisonous gas.

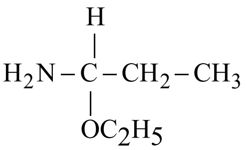
(6) **(C).**



$$\overset{4}{C}H_2=\underset{\underset{\displaystyle Br}{|}}{\overset{3}{C}}-\underset{\underset{\displaystyle Cl}{|}}{\overset{2}{C}H}-\underset{\underset{\displaystyle H}{|}}{\overset{1}{C}}=O$$

3-bromo-2-chloro-3-butenal

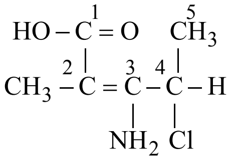
(7) **(B).** All the given IUPAC names are correct except 1-amino-1-ethoxypropane



$$H_2N-\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_2-CH_3$$

It's correct IUPAC name is ethoxy-1-amino propane

(8) **(B).** The IUPAC name of compound

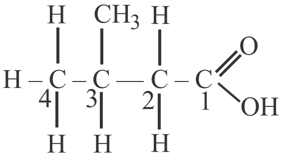


$$CH_3-\overset{\overset{\displaystyle HO-\overset{1}{C}=O}{|}}{\overset{2}{C}}=\underset{\underset{\displaystyle NH_2}{|}}{\overset{3}{C}}-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle \overset{5}{C}H_3}{|}}{\overset{4}{C}}}-H$$

is

3-amino-4-chloro-2-methyl-2-pentenoic acid
The principal functional group is carboxylic acid (–COOH)

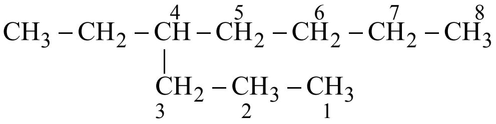
(9) **(A).**



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{\overset{4}{C}}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{\overset{3}{C}}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{\overset{2}{C}}}-\overset{1}{C}\begin{array}{l} =O \\ -OH \end{array}$$

(3-methylbutanoic acid)

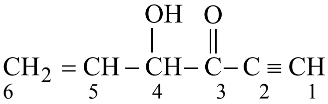
(10)



$$CH_3-CH_2-\underset{\underset{\displaystyle \underset{3}{C}H_2-\underset{2}{C}H_3-\underset{1}{C}H_3}{|}}{\overset{4}{C}H}-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_3$$

4-ethyl-octane

(11)



$$\underset{6}{CH_2}=\underset{5}{CH}-\underset{4}{\overset{\overset{\displaystyle OH}{|}}{CH}}-\underset{3}{\overset{\overset{\displaystyle O}{\|}}{C}}-\underset{2}{C}\equiv\underset{1}{CH}$$

4-hyroxy-5-hexene-1-yne-3-one

(12) Cyclopentanone

TRY IT YOURSELF-2

(1) **(C).** In option (C) two positive charges are nearer, make this structure less stable.

(2) **(A).** $CH_2=CH-\overset{\oplus}{CH}-\overset{\ominus}{CH}-\ddot{N}H_2$ Releasing group

In $\ddot{N}H_2$ group nitrogen having l.p. and increases e^- density on carbon atom, (C^-), make it unstable.

(3) **(C).** $H_2C=CH-\overset{\oplus}{C}H-\overset{\ominus}{C}H-\overset{\curvearrowleft}{\ddot{O}}CH_3$ e^- releasing group

Electron releasing group increases electron density more on C^-, make it unstable.

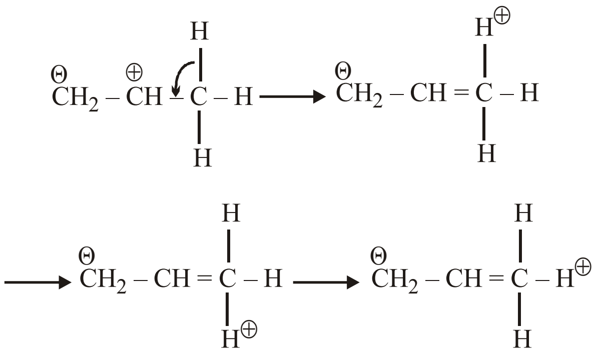
(4) **(D).** Positive charge in I & III are less stable then II as it is on double bonded carbon. Donating effect of alkyl group is making III more stable than I.

(5) **(B).**

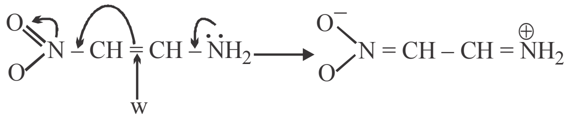
(x) $CH_2=CH_2 \rightarrow$ Pure double bond – No resonance

(y) $CH_2\underset{\uparrow y}{=}CH-NH_2 \rightarrow$ is getting involved in resonance.

(z) $\overset{\curvearrowleft}{CH_2}\underset{\uparrow z}{=}CH\overset{\curvearrowright}{-}CH_3$ z + Hyperconjugation will occur.



z will acquire single bond character, as getting involved in hyperconjugation.

(w) 

Greater extend of resonance.

(6) **(D).** $CH_3-CH_2-CH=CH_2$ has two α-hydrogen for hyperconjugation.

(7) **(D).** I is the most stable resonating structure becasue it is neutral. IV has complete octet on each atoms, II and III both have incomplete octet at 'C' atom bearing positive charge but in 'III' structure negative charge is present on more electronegative atom i.e. oxygen.

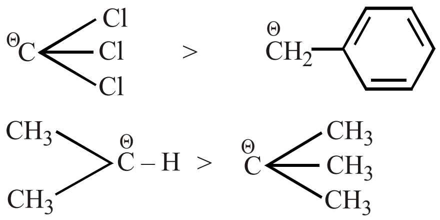
(8) **(D).** Maximum – I effect . CHO.

(9) **(B).** Order of +I $=(CH_3)_3C->(CH_3)_2CH->CH_3CH_2->-CH_3$.

(10) **(D).** Those species which more α-H then it will show maximum hyperconjugation

(11) **(A).** α-D or α-H will show hyperconjugation.

(12) **(D).** On the basis of electronic effect.

(13) **(B).** 

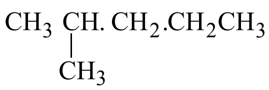
pπ-dπ back bonding effect of two CH_3

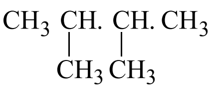
delocalisation +I +I effect of three CH_3

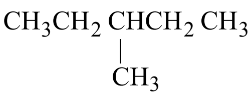
ISOMERISM

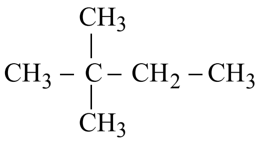
TRY IT YOURSELF-1

(1) **(B).**

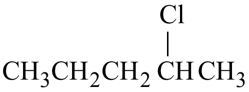
(i) $CH_3CH_2CH_2CH_2CH_2CH_3$ (ii) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CH_2CH_3$

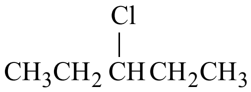
(iii) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_3$

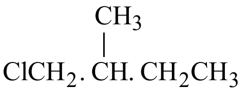
(iv) 
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_3$

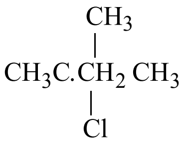
(v) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

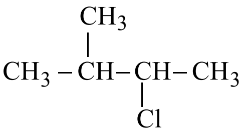
(2) **(B).**

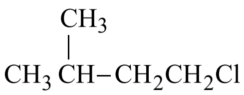
(i) $CH_3CH_2CH_2CH_2CH_2Cl$ (ii) 
$CH_3CH_2CH_2\overset{\displaystyle Cl}{\overset{|}{CH}}CH_3$

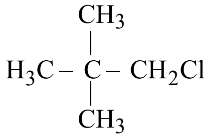
(iii) 
$CH_3CH_2\overset{\displaystyle Cl}{\overset{|}{CH}}CH_2CH_3$

(iv) 
$ClCH_2.\overset{\displaystyle CH_3}{\overset{|}{CH}}.CH_2CH_3$

(v) 
$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}.CH_2CH_3$

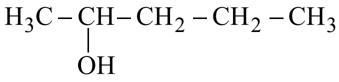
(vi) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

(vii) 
$CH_3\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2CH_2Cl$

(viii) 
$H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2Cl$

(3) (a) $H_3C-H_2C-H_2C-H_2C-H_2C-OH$

Pentan-1-ol

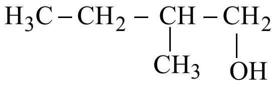

$H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

pentan-2-ol

* Positional isomerism.

(b) $H_3C-CH_2-CH_2-CH_2-CH_2-OH$

Pentan-1-ol


$H_3C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

3-methylbutan-1-ol

* Chain isomerism.

(c) $CH_3-CH_2-CH_2-CH_2-OH$

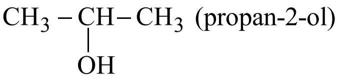
Butan-1-ol

$CH_3-CH_2-O-CH_2-CH_3$

diethylether

* Functional group isomerism.

(4) C_3H_8O : $CH_3-CH_2-CH_2-OH$ (1 propanol)


$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (propan-2-ol)

CH_3-O-CH_2-CH (Methoxy ethane)

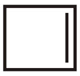
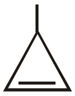
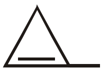
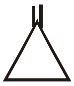
(5) **(C).** C_4H_6 :

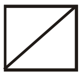
(a) Alkyne & dienes

(i) $CH_3-CH_2-C\equiv CH$, (ii) $CH_3-C\equiv C-CH_3$

(iii) $CH_2=CH-CH=CH_2$ (iv) $CH_2=C=CH-CH_3$

(b) Cyclo alkene

(i)  (ii)  (iii)  (iv) 

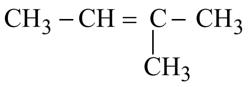
(c) Bicyclo 

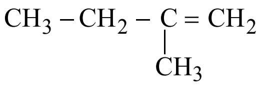
Total = 4 + 4 + 1 = 9

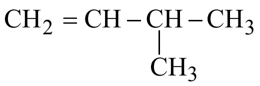
(6) **(A).** C_5H_{10}:

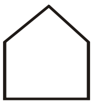
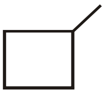
(1) $CH_3-CH_2-CH_2-CH=CH_2$

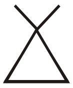
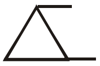
(2) $CH_3-CH=CH-CH_2-CH_3$

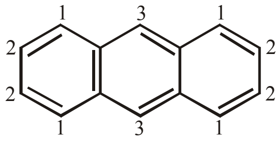
(3) 
$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$

(4) 
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

(5) 
$CH_2=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(6)  (7)  (8) 

(9)  (10) 

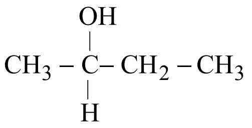
(7) **(A).** Anthracene : 

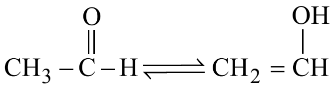
Only three types of hydrogen so only three structural isomers possible.

(8) (C)

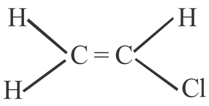
(9) (D)

TRY IT YOURSELF-2

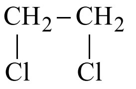
(1) **(C).** (A) 
$CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CH_2-CH_3$ exist in isomeric form.

(B) 
$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-H \rightleftharpoons CH_2=\overset{\displaystyle OH}{\overset{|}{CH}}$

exist in tautomeric form.

(C) $CH_2=CH-Cl\rightarrow$ 

not show G.I./or any isomers.

(D) 
$\underset{\displaystyle Cl}{\underset{|}{CH_2}}-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$ → exist in conformational form.

(2) **(B).** Ethene → $CH_2=CH_2$ cannot show G.I.

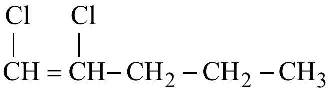
Propene → $CH_3-CH=CH_2$ cannot show G.I.

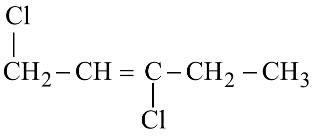
Butene → $CH_3-CH=CH-CH_3$

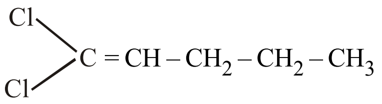
Show G.I. and it also show positional iosmerism.

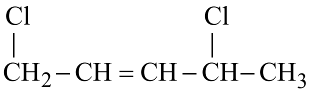
$CH_3-CH_2-CH=CH_2$ and $CH_3-CH=CH-CH_3$

(3) **(C).**

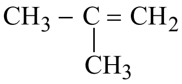
(A) 
$\overset{\displaystyle Cl}{\overset{|}{CH}}=\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_2-CH_2-CH_3$ Show G.I.

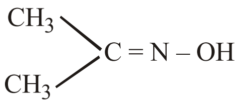
(B) 
$\overset{\displaystyle Cl}{\overset{|}{CH_2}}-CH=\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2-CH_3$ Show G.I.

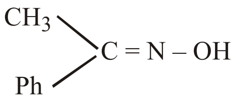
(C) 
$Cl_2C=CH-CH_2-CH_2-CH_3$: not show G.I.

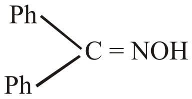
(D) 
$\overset{\displaystyle Cl}{\overset{|}{CH_2}}-CH=CH-\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_3$ Show G.I.

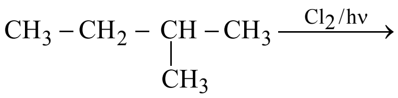
(4) **(C).**

(A) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ isobutene

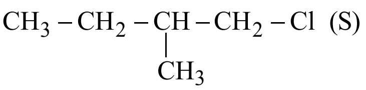
(B) 
$(CH_3)_2C=N-OH$ acetone oxime

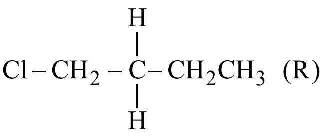
(C) 
$CH_3(Ph)C=N-OH$ acetophenone oxime, Show G.I.

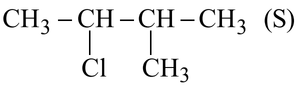
(D) 
$Ph_2C=NOH$ benzophenone oxime

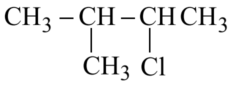
(5) **(C).** Isopentane : 
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3\xrightarrow{Cl_2/h\nu}$

Products are :

(I) 
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$ (S)

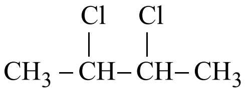
(II) 
$Cl-CH_2-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CH_2CH_3$ (R)

(III) 
$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (S)

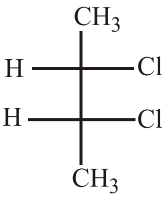
(IV)  (R)

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

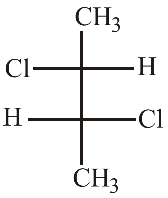
Only (I) and (III) are optically active.

(6) **(B).**  [Total optical isomers = 3]

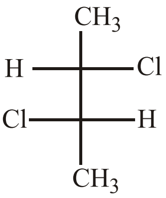
$CH_3-\overset{Cl}{CH}-\overset{Cl}{CH}-CH_3$



(i)



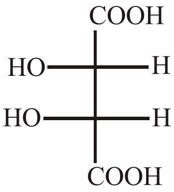
(ii)



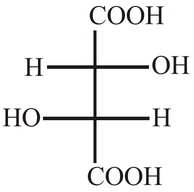
(iii)

(ii) and (iii) are optically active

(7) **(C).**



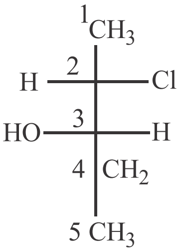
meso tartaric acid



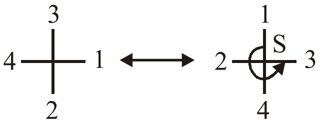
d-tartaric acid

They are diastereomers.

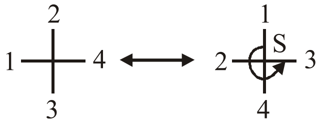
(8) **(A).**



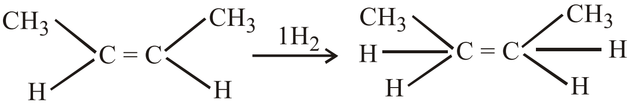
R-S configuration of 2nd carbon.

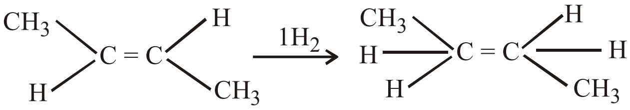


R-S configuration of 3rd carbon.



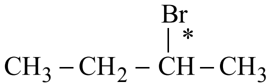
(9) **(D).** Both will give n-butane as a product.
Boiling point : cis-2-butene > trans 2-butane
Dipole moment : cis-2-butene > trans 2-butane
Heat of hydrogenation : cis-2-butene > trans 2-butane
Product same.





Same compounds

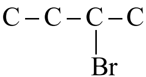
(10) **(A).** One chiral carbon containing compound always optically active.



$CH_3-CH_2-\overset{Br}{\overset{|\,*}{CH}}-CH_3$

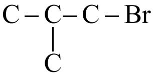
(2 – forms)

C_4H_9-Br $C-C-C-C-Br$ (inactive)



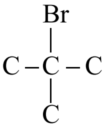
$C-C-\underset{Br}{C}-C$

(active)



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

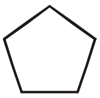
(inactive)

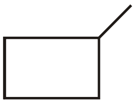


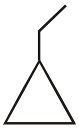
$C-\overset{Br}{\underset{C}{C}}-C$

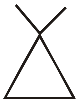
(inactive)

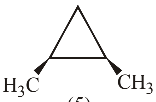
(11) **7.**


(1)

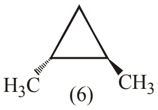

(2)


(3)

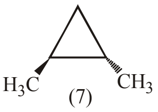

(4)



(5)
(cis, meso)



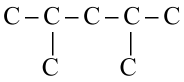
(6)



(7)

Trans (±)

CHAPTER-11 :
ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES
EXERCISE-1

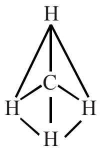
(1) **(B).** 

$$C-\underset{C}{C}-C-\underset{C}{C}-C$$

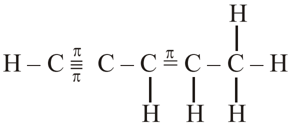
2, 4 - dimethyl pentane is the compound having 2–3° carbon & 1 – 2° carbon atom & 4-1° carbon atoms.

(2) **(D).** For Acetylene & Allene

$HC\equiv CH$ (C_2H_2) $CH_2=C=CH_2$ (C_3H_4)

(3) **(B).**  (CH_4)

Tetrahedral

(4) **(B).** 

$$H-C\overset{\pi}{\underset{\pi}{\equiv}}C-\underset{H}{C}\overset{\pi}{=}\underset{H}{C}-\underset{H}{\overset{H}{C}}-H$$

Number of σ bonds = 10,

Number of π bonds = 3

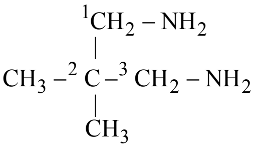
(5) **(B).** sp^2 and sp^3

$$\underset{sp^3}{CH_3}-\underset{sp^2}{CH}=\underset{sp^2}{CH}-\underset{sp^3}{CH_2}-\underset{sp^3}{CH_3}$$

(6) **(B).** In CCl_4 all bond angles are same i.e. of 109°28' the carbon is sp^3 hybridised.

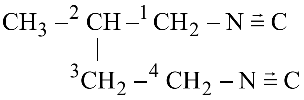
(7) **(B).** The order of preference of functional groups is as follows: $-COOH, > -SO_3H > -COOR > -COCl > -CONH_2 > -CN > -CHO$

$> \rangle C=O > -OH > -NH_2 > \rangle C=C\langle > -C\equiv C-$

(8) **(C).** 

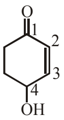
$$CH_3-^2\underset{CH_3}{\overset{^1CH_2-NH_2}{C}}-^3CH_2-NH_2$$

2,2-dimethyl propane di amine-1,3

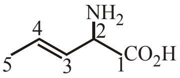
(9) **(A).** 

$$CH_3-^2\underset{^3CH_2-^4CH_2-N\equiv C}{CH}-^1CH_2-N\equiv C$$

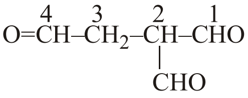
2-methyl butane di isonitrile -1,4

(10) **(A).** 

4-Hydroxy cyclo hex -2-ene-1-one

(11) **(B).** 

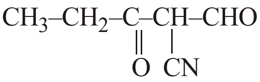
2-amino pent-3-en-1-oic acid

(12) **(C).** The IUPAC name of the given compound is 2-formyl butanedial, 

$$\overset{4}{O=CH}-\overset{3}{CH_2}-\underset{CHO}{\overset{2}{CH}}-\overset{1}{CHO}$$

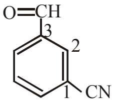
2 - formyl butanedial

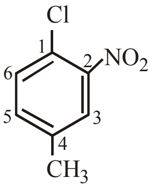
The principal functional group is – CHO.

(13) **(B).** The correct I.U.P.A.C. name of 

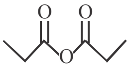
$$CH_3-CH_2-\underset{O}{\underset{\|}{C}}-\underset{CN}{CH}-CHO$$

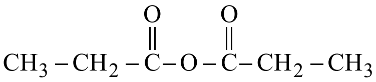
is 2-formyl -3- oxopentanenitrile Here the main functional group is -CN, which has nitrile suffix and CHO and CO are the side functional groups which are used as prefixes.

(14) **(A).**  3-Aldo benzene carbonitrile

(15) **(B).**  as ‘m’ comes before ‘n’.

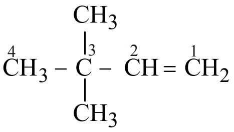
1-Chloro-4- methyl-2-nitrobenzene

(16) **(D).**  Propanoic anhydride.

or 

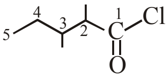
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

(The given compound is an anhydride of propanoic acid)

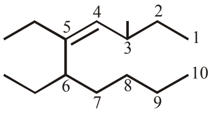
(17) **(C).** 

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

3,3-dimethylbut-1-ene

(18) **(C).** 

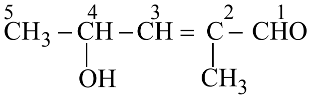
2,3-dimethylpentanoyl chloride

(19) **(B).** 

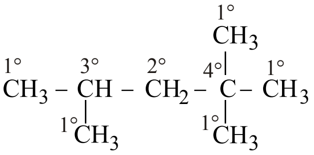
5,6-diethyl-3-methyldec-4-ene

(20) **(C).** 3C + (=) → Acryl group

Suffix of – CN group is onitrile.

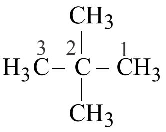
(21) **(A).** 
$$\overset{5}{C}H_3-\overset{4}{C}H(OH)-\overset{3}{C}H=\overset{2}{C}(CH_3)-\overset{1}{C}HO$$

4-Hydroxy-2-methylpent-2-en-1-al

(22) **(C).** 
$$\overset{1^\circ}{C}H_3-\overset{3^\circ}{C}H(\overset{1^\circ}{C}H_3)-\overset{2^\circ}{C}H_2-\overset{4^\circ}{C}(\overset{1^\circ}{C}H_3)(\overset{1^\circ}{C}H_3)-\overset{1^\circ}{C}H_3$$

$1^\circ - 5, 2^\circ - 1, 3^\circ - 1, 4^\circ - 1$

(23) **(A).** While writing the name of the substituents in alphabetical order, the prefixes such as di, tri, tetra, penta, hexa etc, are not considered. As 'e' of ethyl comes before, 'm' of dimethyl thus, lower locant 3 is assigned to ethyl group and is written first.

(24) **(B).** 
$$H_3\overset{3}{C}-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_3$$

neo-pentane or 2,2-dimethylpropane

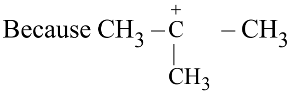
(25) **(C).** In C – Cl bond, the electron pair is carried away by Cl atom due to higher electronegativity. $C-Cl \rightarrow C^+ + Cl^-$. Hence, carbon cation and chlorine anion are formed.

(26) **(C).** $CH_3CH_2-N=N-CH_2CH_3 \xrightarrow{\text{Heat}} \underset{\text{Free radical}}{2CH_3\dot{C}H_2} + N_2$

(27) **(A).** + I group decreases the stability of carbanion.

(28) **(D).** Due to + I effect.
Order of stability of carbocations :
Primary < Secondary < Tertiary

(29) **(A).** More resonance in (A).

(30) **(C).** Because 
$$CH_3-\overset{+}{C}(CH_3)-CH_3$$
has '9' α H atoms which is maximum in all four examples.

(31) **(B).** Presence of odd electrons

(32) **(C).** Cyanide ion is an ambident nucleophile

(33) **(A).** A nucleophile is electron-rich species

(34) **(C).** BF_3 is an electrophile.

(35) **(A).** A carbanion is an anion in which carbon is tetravelent and bears a formal negative charge.

(36) **(B).** $H-\ddot{O}-H, :NH_3, R-\ddot{O}-R$ - nucleophiles SO_3 has electron deficient centre (a reagent which can accept an electron pair in a reaction, is called an electrophile)

(37) **(C).** Primary carbanion is most stable

(38) **(D).** Organic reactions, which proceed by homolytic fission are called free radical or homopolar or nonpolar reactions.

(39) **(D).** The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar reactions.

(40) **(D).** Weak base are always better leaving group.

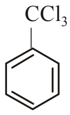
(41) **(D).** Electron deficient species act as electrophiles.

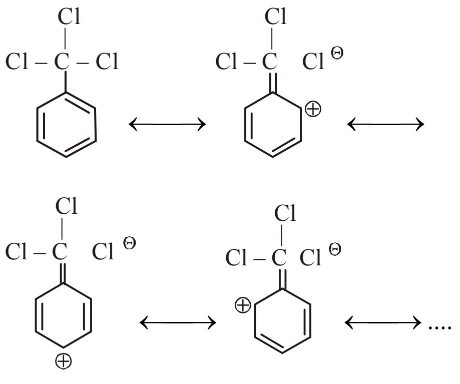
(42) **(C).** $NO_2^+, AlCl_3, SO_3$ and $CH_3C^+=O$ are electrophiles.

(43) **(C).** CN^- act as an ambidient because both C and N can act as nucleophile.

(44) **(D).** Free radicals can undergo all given types of processes.

(45) **(A).** Electromeric effect comes into play at the demand of attacking reagent

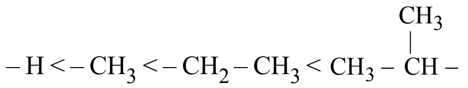
(46) **(C).** There is a negative hyperconjugative in  as -



(47) **(C).** Increasing + I effect

$$(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$$

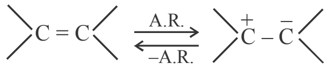
(48) **(A).** The order of +I effect of alkyl group is


$$-H < -CH_3 < -CH_2-CH_3 < CH_3-CH(CH_3)-$$

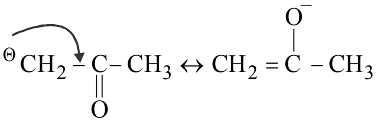
(49) **(A).** Due to displacement of σ-electrons towards more electronegative atom the bond becomes polar. The polar bond induces polarity to the adjacent bonds.

(50) **(D).** Decreasing order of –I effect
$R_3N^+ > NO_2 > CN > F > Cl > OH$
$> OCH_3 > Br > I > {}^-CH=CH_2$

(51) **(A).** It is arised on the need of attacking reagent, e.g.,



(52) **(B).** Hyperconjugation is orbital interactions between π-systems and the adjacent σ bond of substituent groups. For hyperconjugation α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

(53) **(A).** 
$${}^{\ominus}CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \leftrightarrow CH_2=\overset{\overset{O^-}{|}}{C}-CH_3$$

(54) **(C).** Inductive effect causes a state of polarization, but it is feeble as it involves the shift of strongly held σ-bonds. The concept of + I and – I effects is due to the inductive effect arising by atoms or groups which are electron releasing and electron with-drawing respectively.

(55) **(C).** The resonating structures should have same number of electron pairs.

(56) **(D).** Fluorine is most electronegative atom and exerts maximum –I effect.

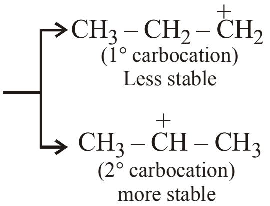
(57) **(D).** Hyperconjugation involves conjugation of σ electrons of C – H bond and π electrons of multiple bond. It is noticed due to delocalisation of σ- and π-bonds, It is also known as no-bond resonance.

(58) **(A).** Hydrogen does not exert I-effect. Its inductive effect is taken as zero. Electron releasing or electron withdrawing capability of other atoms are compared by hydrogen.

(59) **(A).** As Cl is most electronegative element among Cl, Mg, Br and C thus, it has greater –I effect and the asterisk marked carbon in $\overset{*}{C}H_3-CH_2-Cl$ is expected to have greater positive charge.

(60) **(D).** When methane gas is treated with chlorine in the presence of sunlight, one hydrogen of methane replaced by the chlorine atom and forms methyl chloride. The mechanism involved in this reaction is free radical mechanism. So it is an example of free radical substitution reaction.

(61) **(C).** $H_3C-HC=CH_2+H^+$

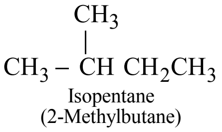


Thus, 2° Carbocation is formed.

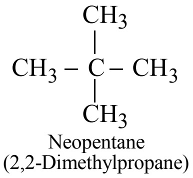
(62) **(D).** Halogenation on alkene occurs by electrophilic addition

(63) **(B).** Typical reaction of olefinic bond is electrophilic addition reactions.

(64) **(B).** C_5H_{12} represents three compounds:
$CH_3CH_2CH_2CH_2CH_3$: Pentane

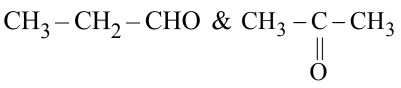

$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}\ CH_2CH_3$

Isopentane
(2-Methylbutane)

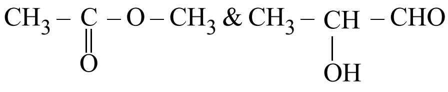

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

Neopentane
(2,2-Dimethylpropane)

(65) **(C).** Aldehyde possesses — CHO functional group while ketone — CO — group so these are functional group isomers eg.


$CH_3-CH_2-CHO\ \&\ CH_3-\underset{\underset{O}{||}}{C}-CH_3$

(66) **(A).** Ester are functional isomers of hydroxy aldehydes.


$CH_3-\underset{\underset{O}{||}}{C}-O-CH_3\ \&\ CH_3-\underset{\underset{OH}{|}}{CH}-CHO$

methyl ethenoate 2- hydroxy propanal

(67) **(B).** $(CH)_2(COOH)_2$ in fact represents
$HOOC-CH=CH-COOH$
and hence shows geometrical isomerism.

(68) **(D).** Since both the carbon atoms of each of the three double bonds are differently substituted. Therefore, $2^3=8$ geometrical isomers are possible.

(69) **(A).** Diethyl ether has 4 carbon atoms, among different alternative alochols only $(CH_3)_3COH$ has 4 carbon atoms.

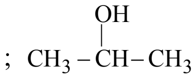
(70) **(C).** The two isomers have same functional group, but at different positions.

(71) **(D).** As the name indicates α - naphthol and β-naphthol differ in the position of the alcoholic group.

(72) **(D).** The molecular formulas are different so they do not exhibit isomerism.

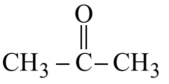
(73) **(D).** CH_4, $CH_3.CH_3$, $CH_3.CH_2.CH_3$ exist only in one structural form, while $CH_3CH_2CH_2CH_3$ can exist in more than one structural form.

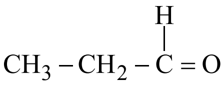
(74) **(C).** C_3H_8O can be represented as

$CH_3CH_2CH_2OH$;

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

Propan-1-ol Propan-2-ol.

C_3H_6O can be represented as


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


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

Propanone Propanal.

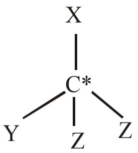
(75) **(C).** Ball is achiral where other objects are chiral because objects and their mirror images are non-super imposable


(a) (b) (d)

(76) **(B).** $\underset{\text{1–butene}}{CH_3-CH_2-CH=CH_2}$ and $\underset{\text{2–butene}}{CH_3-CH=CH-CH_3}$

(77) **(C).** Metamerism arises due to different alkyl chains on either side of the functional group in the molecule. $C_4H_{10}O$ represents methoxypropane$(CH_3OC_3H_7)$ and ethoxyethane $(C_2H_5OC_2H_5)$.

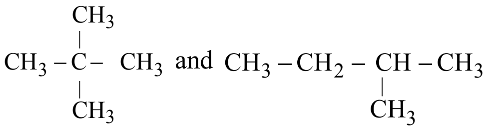
(78) **(A).** Four groups linked to carbon atom are different.



(79) **(B).** Glucose and fructose have similar molecular formula with difference of functional group, so they are functional isomers.

(80) **(A).** Chirality of carbon compound is because of its tetrahedral nature of carbon.

(81) **(C).** Neopentane and isopentane are chain isomers.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \text{ and } CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

(82) **(A).** Compounds having same molecular formula but different functional groups are called functional isomers.

(83) **(D).** CH_3CH_2OH and $CH_3–O–CH_3$ are functional isomers.

(84) **(C).** Alumina or silica gel are generally used as adsorbent in column chromatography.

(85) **(B).** Aniline is steam volatile.

(86) **(A).** Steam distillation is applied to separate substances which are steam volatile and are immiscible in water.

(87) **(D).** Steam distillation is used to separate substances which are steam volatile and are immiscible with water.

(88) **(D).** In paper chromatography stationary phase is water which is either adsorbed or chemically bound to a special type of paper called chromatographic paper and mobile phase is another liquid.

(89) **(B).** The most strongly adsorbed component is present in the band near the top while the weakly adsorbed constituent is found near the bottom.

(90) **(B).** Compound when heated with CuO reduces CuO to Cu and oxidises C to CO_2 which turns lime water milky. $C+2CuO \rightarrow 2Cu+CO_2$

$$CO_2+Ca(OH)_2 \rightarrow \underset{\text{(Milky)}}{CaCO_3}+H_2O$$

(91) **(C).** When treated with standard solution of alkali nitrogen is liberated as NH_3 which is absorbed in H_2SO_4 to get percentage of nitrogen.

(92) **(A).** $\% \text{ of P} = \frac{62}{222} \times \frac{x}{w} \times 100 = \frac{62}{222} \times \frac{2.6}{1.6} \times 100 = 45.38\%$

(93) **(C).** In Kjeldahi’s method, copper sulphate acts as catalyst only.

(94) **(D).** Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

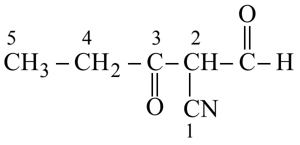
$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{x\,H_2O} \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

EXERCISE-2

(1) **(C).** Tertiary carbocation is more stable.

(2) **(B).**



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

2-formyl-3-oxopentanenitrile

(3) **(C).** $C_2 - C_3$ are at conjugated position.

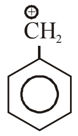
(4) **(A).** d have more resonating structure than (C)

(5) **(B).** +m effect of OH is highest, which decrease magnitude of charge thus stability increases.

(6) **(C).** It is affected by changes in polarity of solvent.

(7) **(A).** Allyl carbocation is resonance stablised.

(8) **(A).**



$CH_2=CH-\overset{+}{C}H_2$ 3° & 2°

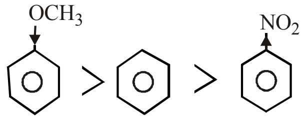
4-RS 2-RS No RS

3° is more stable than 2°.

(9) **(C).** The octet of all atoms are complete in structures (A) and (B). In structure (D) electron deficiency of positively charged carbon is duly compensated by lone pair electrons of adjacent oxygen atom while such neighbour group support is not available in structure (C).

(10) **(D).** Due to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group the lone pair must be localised again on the chlorine atom. This requires energy and so the chlorine is more firmly bound than has no conjugation occurred.

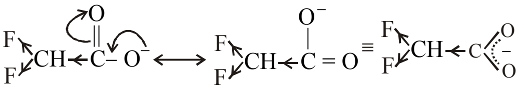
(11) **(C).** I > II > III



Methoxy group is electron releasing it increases electron density of benzene nucleus while $-NO_2$ decreases electron density of benzene.

(12) **(D).** –COOH group is a deactivating group, hence benzoic acid is less reactive towards electrophilic substitution than phenol.

(13) **(D).**



As F is most electronegative and in this structure there are two F atoms, therefore, dispersal of negative charge is maximum hence it is the most stable.

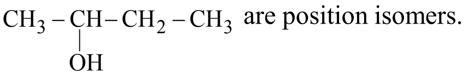
(14) **(D).** For same periods nucleophilicity ∝ Basic Strength. Thus if more electronegative atom consist of negative charge than stability increases and basic strength decreases. Thereby nucleophilicity decreases.

(15) **(D).** It is due to ortho effect.

(16) **(B).** $Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5(NO)]} \rightarrow \underset{\substack{\text{Sodium thionitroprusside} \\ \text{(Violet)}}}{Na_4[Fe(CN)_5(NOS)]}$

(17) **(C).** $CH_3-O-CH_2CH_2CH_3$ and $CH_3CH_2-O-CH_2CH_3$ are metamers.

(ii) and (iv) i.e. $CH_3CH_2CH_2CH_2OH$ and



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ are position isomers.

(18) **(B).** $V_1 = 68.6\text{ mL}, P_1 = 756\text{ mm}, T_1 = 300\text{ K}$
$V_2 = ?, P_2 = 760\text{ mm}, T_2 = 273\text{ K}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

At NTP, volume of N_2,

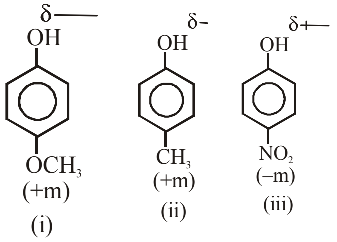
$$V_2 = \frac{P_1V_1}{T_2} \cdot \frac{T_2}{P_2} = \frac{756 \times 68.6}{300} \times \frac{273}{760} = 62.09\text{ mL}$$

% of nitrogen in organic compound

$$= \frac{28}{22400} \times \frac{V_2}{w} \times 100 = \frac{28}{22400} \times \frac{62.09}{0.52} \times 100 = 14.93\%$$

(19) **(B).** Acidic strength $\propto$ –I power of Cl group.

(20) **(D).**

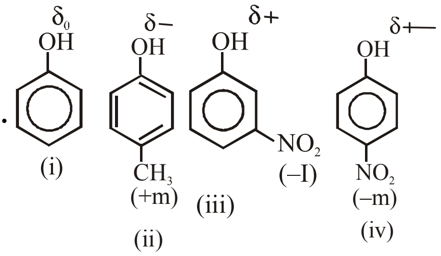


$+m(-OCH_3) > +m(-CH_3)$
$(i) < (ii) < (iii)$

$\xrightarrow{\hspace{4em}}$

↑ of acidic strength

(21) **(D).**



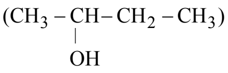
At meta position +m effect absent thus only –I effect of $-NO_2$ is taken in (iii)
$(iv) > (iii) > (i) > (ii)$

(22) **(B).** (I) → have higher no of covalent bond
(II) → have complete octet
(III) → more electronegative atom consist –ve charge.

(23) **(B).** Stability of carbanions decreases with increase in +I effect. +I effect is maximum in $(CH_3)_3C^-$, followed by $(CH_3)_2CH^-$ and $CH_3CH_2^-$.
In $C_6H_5CH_2^-$, resonance effect increases the stability. Hence, the order of stability is
$(iv) > (iii) > (ii) > (i)$.

(24) **(A).** Given alkene is unsymmetrical one and has two double bonds, the number of geometrical isomers is given by 2^n.
$(n = 2)$ therefore number of geometrical isomers will be $2^2 = 4$.

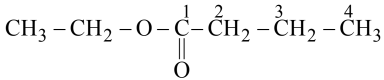
(25) **(B).** 2-butanol



$(CH_3-\underset{\large OH}{\underset{|}{CH}}-CH_2-CH_3)$

is optically active because it has asymmetric carbon atom.

(26) **(B).** The IUPAC name of the compound $CH_3CH_2OCOCH_2CH_2CH_3$ is ethyl butanoate.

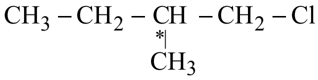


$CH_3-CH_2-O-\underset{\large O}{\underset{||}{\overset{1}{C}}}-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$

Ethyl butanoate

(27) **(A).** Geometrical isomerism is not possible in propene.

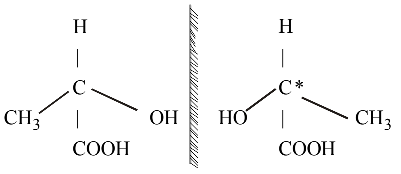
(28) **(B).**



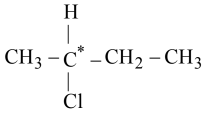
$CH_3-CH_2-\underset{CH_3}{\underset{*|}{CH}}-CH_2-Cl$

(29) **(A).** Functional isomerism

(30) **(C).** Lactic acid shows optical isomerism



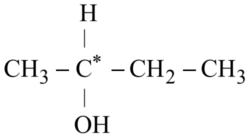
(31) **(A).**



$CH_3-\underset{Cl}{\underset{|}{\overset{H}{\overset{|}{C^*}}}}-CH_2-CH_3$

In other compounds chiral carbon is absent.

(32) **(D).**



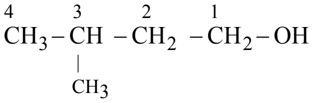
$CH_3-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C^*}}}}-CH_2-CH_3$

Chiral structure is that in which one carbon atom is attached to 4 different atoms or groups.

(33) **(A).** Order of acidic strength is
$H_2O > CH\equiv CH > CH_2=CH_2 > CH_3CH_3$
We know that a stronger acid has weak conjugate base and vice versa, thus order of basic nature of given compounds is
$CH_3-CH_2^- > CH_2=CH^- > CH\equiv C^- > OH^-$

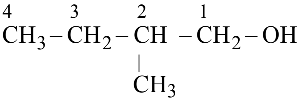
(34) **(C).** $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

Pentan-1-ol



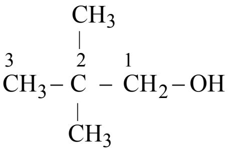
$\overset{4}{C}H_3-\underset{CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$

3–Methyl butan–l–ol



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

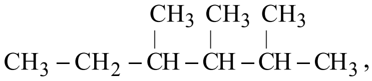
2–Methyl butan–l–ol



$\overset{3}{C}H_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{\overset{2}{C}}}}}-\overset{1}{C}H_2-OH$

2,2–Dimethyl propan–l–ol

(35) **(D).**



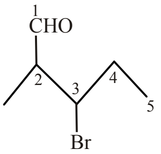
$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$,

It is a chiral compound.

(36) **(A).** – Cl group is an example for – I group.

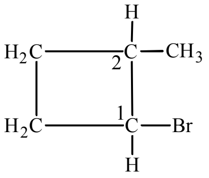
– I group stabilizes – COOH group due to their electron withdrawing nature. The release of proton becomes easier.

(37) (C).



Root word = Pent- ; Suffix (1°) = -ane ; (2°) = -al
Prefix = 3-bromo-2-methyl
IUPAC Name: 3-bromo-2-methyl pentanal

(38) (B).



Number of asymmetric c-atoms = (n) = 2
∴ Total number of optical isomers = $2^n = 2^2 = 4$

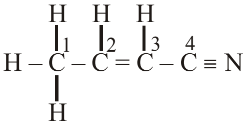
(39) (A). Acetone (CH_3COCH_3) and propanal (CH_3CH_2CHO) are functional isomers.

(40) (C). As electron withdrawing group strengthens C-Cl bond, the reaction rate decreases.

(41) (C). m-cresol has electron releasing group (CH_3). Hence it decreases the acidic strength. Both nitro and chloro are having – I effect. Hence, they show higher acidic strength.
But nitro is a stronger –I group than chloro group. Hence m-nitrophenol is more acidic than m-chlorophenol

(42) (A). Toluene has lowest bond dissociation energy as the C–H protons are involved in hyperconjugation.

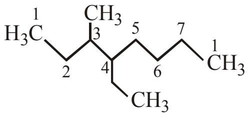
(43) (A).



$$H-\underset{H}{\overset{H}{\overset{1}{C}}}-\overset{H}{\overset{2}{C}}=\overset{H}{\overset{3}{C}}-\overset{4}{C}\equiv N$$

From left 1- sp^3, 2-sp^2, 3-sp^2, 4-sp

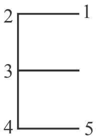
(44) (D).



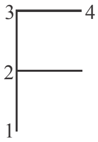
4-ethyl-3-methyloctane

(45) (B). Since both benzoic acid and camphor sublimate they can be separated by chemical methods. Benzoic acid reacts with alkalies whereas camphor does not.

(46) (D). (i)



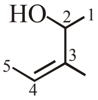
(ii)



3-methylpentane 2-methylbutane

(47) (C). $Na + C + N \rightarrow NaCN$
$Na + C + N + S \rightarrow NaSCN$

(48) (A).



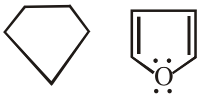
(49) (A). Mass of $H_2O = 0.54$ g
Mass of $CO_2 = 0.88$ g

$$\%\text{ of C} = \frac{12}{44}\times\frac{0.88}{0.46}\times 100 = 52.17\%$$

$$\%\text{ of H} = \frac{2}{18}\times\frac{0.54}{0.46}\times 100 = 13.04\%$$

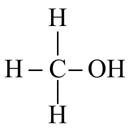
$$\%\text{ of O} = 100-(52.17+13.04) = 34.79\%$$

(50) (D).



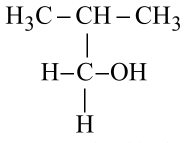
Cyclopentane and furan is a pair of homocyclic & heterocyclic compound. In which cyclopentane is homocyclic and furan is heterocyclic.

(51) (C). In derived name system



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

Carbinol



$$\underset{H}{\overset{H_3C-CH-CH_3}{H-C-OH}}$$

Isopropyl carbinol

(52) (B). Between double bond & triple bond double bond is preferred.

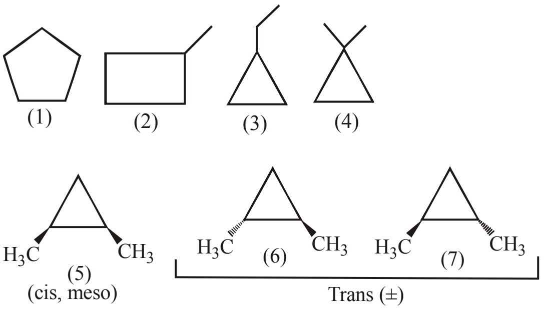
(53) (D). Least acidic : Electron releasing group decreases the acidic strength in carboxylic acid. They decreases δ(+) charge on carbon.

(54) (D). $CH_3 - CH_2 - CH = CH_2$ has two α-hydrogen for hyperconjugation.

(55) (D). I is the most stable resonating structure becasue it is neutral. IV has complete octet on each atoms, II and III both have incomplete octet at 'C' atom bearing positive charge but in 'III' structure negative charge is present on more electronegative atom i.e. oxygen.

EXERCISE-3

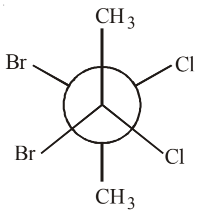
(1) 7.

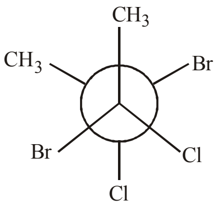


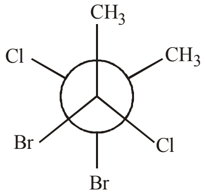
(2) 5.

(3) 6. There are total 6 hyperconjugable H-atoms in this carbocation which are contributing in the hyperconjugation.

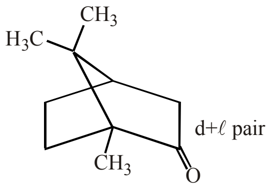
(4) **3.** Following conformers are stable with non-zero dipole moment





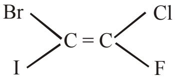


(5) **2.** Total number of stereoisomers = 2

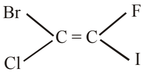


This molecule can not show geometrical isomerism so only mirror image will be other stereoisomer.

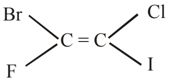
(6) **6.** Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.



(Z and E)



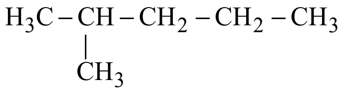
(Z and E)



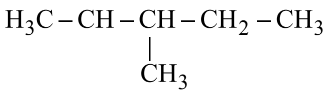
(Z and E)

(7) **5.** C_6H_{14}

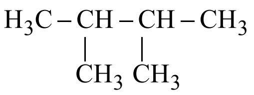
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_3$



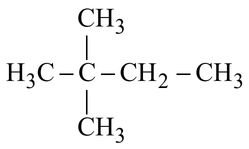
$H_3C-\underset{CH_3}{CH}-CH_2-CH_2-CH_3$



$H_3C-CH-\underset{CH_3}{CH}-CH_2-CH_3$

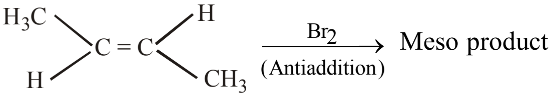


$H_3C-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$;

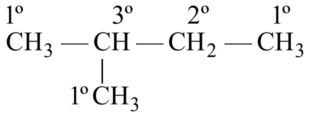


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

(8) **1.**



(9) **4.**

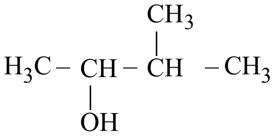


$$\overset{1^\circ}{CH_3}-\overset{3^\circ}{\underset{1^\circ CH_3}{CH}}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$$

Two carbons attached with 3° carbon atom will make one alkyl group. One carbon attached with 2° will make one alkyl group. Similarly 2° & 3° carbon will make one alkyl group each.

EXERCISE-4 [GOC]

(1) **(C).**



$H_3C-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_3$

(3-methyl -2-butanol)

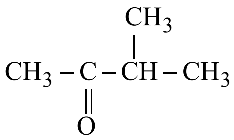
(2) **(A).** Order of + inductive effect

$-O^- > -COO^- > (CH_3)_3C > (CH_3)_2-CH > CH_3CH_2- > CH_3^-$

(3) **(B).** Inductive effect increases with no. of CH_3 group.

(4) **(A).** Group with + inductive effect increases basicity. tertiary > secondary > primary

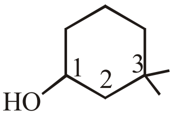
(5) **(B).**



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

3-Methyl-2-butanone

(6) **(C).**



3,3-dimethyl-1-cyclohexanol

(7) **(A).** Cl is the weakest base hence better leaving group.

(8) **(D).** In aromatic acid acidity increases due to –I group.

$o–NO_2.\ C_6H_4COOH > p–NO_2.\ C_6H_4COOH > m–NO_2\ C_6H_4COOH > phCOOH.$

(9) **(D).** Aromatic amines are weak base because of electron pair on N atom. (displacement)

(10) **(D).** If acid is weak its nucleophile is strong.

(11) **(B).** Cl is a good leaving group.

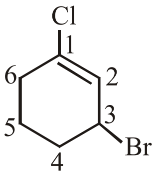
(12) **(B).** Benzyl is electron repulsive group hence increase basicity.

(13) **(D).**

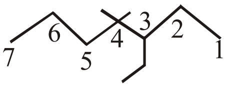
(14) **(D).** + I effect

(15) **(B).** – I effect increases acidity.
+ I effect decreases acidity.
– I effect of CF_3 is greater than Meo gorup.

(16) **(B).**



(3-bromo-1-chlorocyclohexene)

(17) **(D).** 

(3-ethyl-4, 4 dimethylheptane)

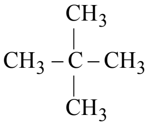
(18) **(C).** In aqueous solution basicity order dimethylamine > Methylamine > Trimethylamine > aniline
2° 1° 3°

(19) **(D).** – NO_2 group accepts electron and show – M effect.

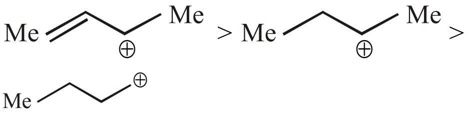
(20) **(D).** According to modern concept, the priority of groups is as follows:– COOH > – SO_3H > – $CONH_2$ > – CHO

(21) **(B).** $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

($\bar{C}Cl_3$ is stabilized due to –I effect of Cl and $p\pi - d\pi$ delocalization).

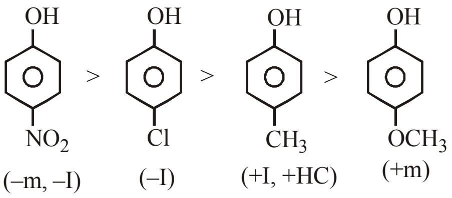
(22) **(C).** 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ 2,2-dimethylpropane

(23) **(A).** S_N1 proceeds via carbocation intermediate, the most stable one forming the product faster. Hence reactivity order for A, B, C depends on stability of carbocation created.



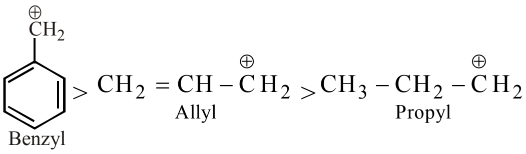
(24) **(D).** $R-COO^{(-)} < CH \equiv C^{(-)} < NH_2{}^{(-)} < R^{(-)}$

(25) **(C).** α-chlorobutyric acid is more stronger acid than others due to – I effect of Cl.

(26) **(C).** 

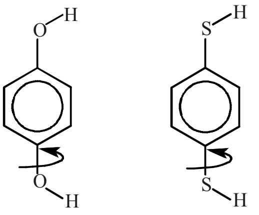
Electron releasing group decreases and electron withdrawing group increases acidic strength.

(27) **(D).** The order of stability of carbocation will be



(28) **(D).** Rate of S_N2 reaction

$$\propto \frac{1}{\text{steric over crowding in transition state}}$$

(29) **(B).** 

Due to infinite possible conformations in the above cases (of which only one has zero μ); a weighted μ will finally exist.

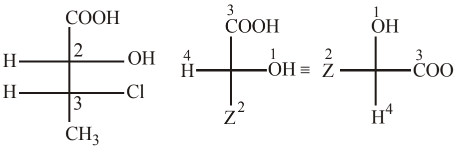
(30) **(C).** Steam distillation is preferred for separation of substances which are steam volatile and are immiscible with water.

Fractional distillation is used if the difference in boiling points of two liquids is not much. This technique is used to separate different fractions of crude oil in petroleum industry.

Distillation under reduced pressure is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Glycerol can be separated from spent-lye in soap industry by using this technique

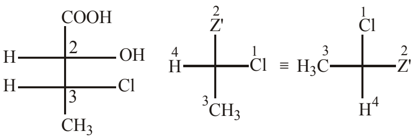
Simple distillation ⇒ This technique is used to separate volatile liquids from nonvolatile impurities or liquids having sufficient difference in their boiling points.

(31) **(A).** Order of priority of substituent of C-2 is
OH > CH(Cl)(CH_3) > COOH
(Z)

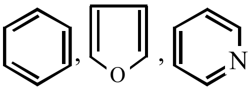


Order of priority is in anti-clockwise direction hence, its configuration is S.

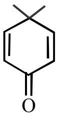
Order of priority of substituent of C-3 is
Cl > CH(OH)COOH > CH_3
(Z')



Order of priority is in clockwise direction hence, its configuration is R.

(32) **(A).** 

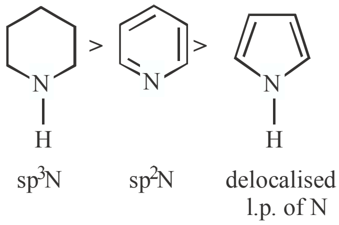
are aromatic and stabilized by according to Huckel's rule.



is non-aromatic hence least stabilized by resonance.

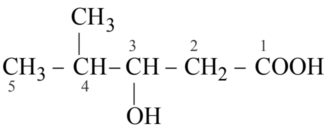
(33) **(D).** Kjeldahl method is not applicable to compounds containing nitrogen in nitro (NO_2) and azo (N = N–) groups and nitrogen present in the ring (pyridine) as nitrogen of these compounds does not change to ammonium sulphate.

(34) **(D).** Order of basic strength :



(35) **(D).** Acidic strength ∝ Stability of anion after loosing proton. CN makes anion most stable so answer is $CH(CN)_3$.

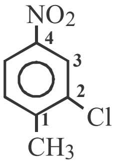
(36) **(C).**



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

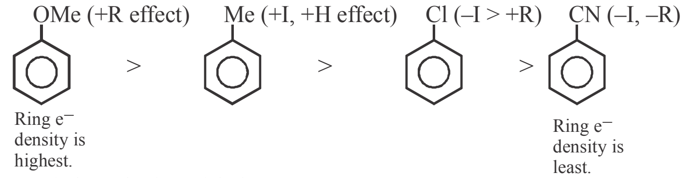
3-Hydroxy-4-methylpentanoic acid
– COOH principal functional group

(37) **(D).**



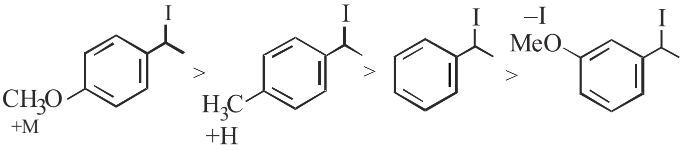
2-chloro-1-methyl-4-nitrobenzene

(38) **(C).**



(More is the e^- density at right faster is the reaction towards EAS)

(39) **(C).** Rate of S_{N^1} is directly proposional to stability of first formed carbocation so answer is



(40) **(D).** The phosphorus containing organic compound are detected by 'Lassaigne's test' by heated with an oxidizing agent (sodium peroxide).

The phosphorus present in the compound in oxidised to phosphate.

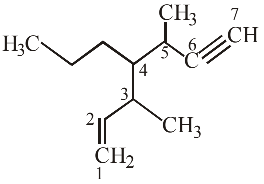
The solution is boiled with nitric acid and then treated with ammonium molybdate to produced canary yellow precipitate.

$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$
(Ammonium molybdate)

$\rightarrow (NH_4)_3PO_4.12MoO_3\downarrow + 21\ NH_4NO_3 + 12\ H_2O$
(Ammonium phosphomolybdate)
(Canary yellow precipitate)

(41) **(D).**

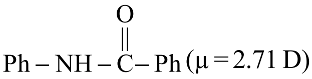


3,5-Dimethyl-4-propylhept-1-en-6-yne
Longest carbon chain, including multiple bonds, and numbering starts from double bond.

(42) **(C).** Option (a) represent Guanadine, the conjugate acid of which is resonance stabilised. The option (b) is aliphatic amine, here the 'N' is sp^3 whereas in option (c) the 'N' is sp^2, hence (b) is more basic than (c).

(43) **(B).**

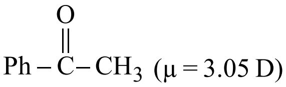
(a) Benzanilide →



$Ph-NH-\overset{\overset{O}{\|}}{C}-Ph\ (\mu = 2.71\ D)$

(b) Aniline → $Ph–NH_2\ (\mu = 1.59\ D)$

(c) Acetophenone →



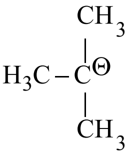
$Ph-\overset{\overset{O}{\|}}{C}-CH_3\ (\mu = 3.05\ D)$

Dipole moment : c > a > b
Hence the sequence of obtained compounds is (c), (a) and (b)

(44) **(B).** Liquid having lower boiling point comes out first in fractional distillation. Simple distillation can't be used as boiling point difference is very small.

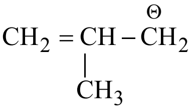
(45) **(A).** Kjeldahl method is not applicable to nitro or diazo groups present in the ring, as nitrogen atom can't be converted to ammonium sulfate under the reaction conditions.

(46) **(C).** (i)



$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\ominus}$

(ii)

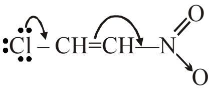


$CH_2=CH-\underset{\underset{CH_3}{|}}{CH}-\overset{\ominus}{CH_2}$

(iii) $HC\equiv\overset{\ominus}{C}$ (iv) $\overset{\ominus}{C}H_3$ (v) $\overset{\ominus}{C}\equiv N$

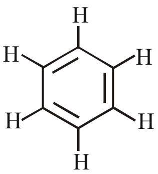
Basic strength order : (i) > (iv) > (ii) > (iii) > (v)

(47) **(D).**



Due to –M effect of $–NO_2$ and + M effect of Cl more D.B. character between C – Cl bond. So shortest bond length.

(48) **(D).**



Each carbon atom is sp^2 hybridized.
Therefore each carbon has $3sp^2$ hybrid orbitals. Hence total sp^2 hybrid orbitals are 18.

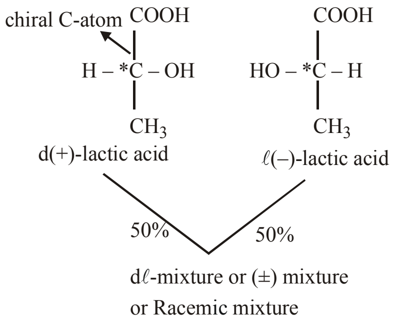
[ISOMERISM]

(1) Both geometrical and optical isomerism.

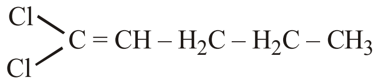
(2) **(B).** $CH_3 - CH_2 - HC = CH_2$

Two similar group are attached to the C.

(3) **(D).** Racemic mixture is a equimolar mixture of d & ℓ isomer of a compound it is optically inactive.



(4) **(A).**



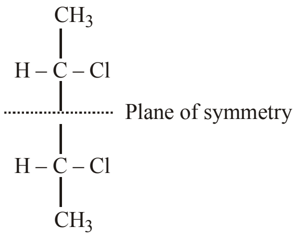
Similar group are attached to double bonded C.

(5) **(A).** Racemic mixture is formed by mixing of d and ℓ isomer in equal amount. The d & ℓ have chiral carbon atoms. So that they are optically active. But racemic mixture is optically inactive.

(6) **(D).** All four different groups are attached to the central C-atoms.

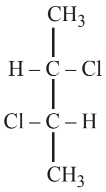
(7) **(A).** $Cl - CH_2 - CH_2CH_2 - CH_2 - CH_3$

(8) **(B).**



(meso isomer)-2,3, dichlorobutane

(9) **(A).**



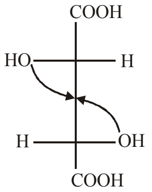
Optical

(10) **(D).** The stability depends upon the magnitude of repulsion of bond pairs. Farther the bond pair of bulky groups greater is the stability.

(11) **(A).** Chiral C atom is present in 1 but 2, 3, 4 are symmetric thus optical inactive so cannot rotate the plane of polarized light.

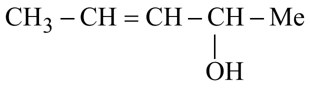
(12) **(A).**

(13) **(A).**



If H – OH horizontal line anticlockwise is denoted as – R.

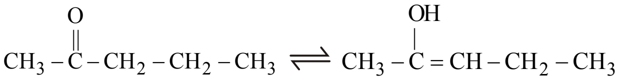
(14) **(D).**



$$CH_3 - CH = CH - \underset{\substack{|\\ OH}}{CH} - Me$$

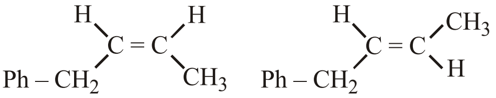
Isomer 1: cis d ; Isomer 2: cis ℓ ; Isomer 3: trans d ; Isomer 4: trans ℓ

(15) **(C).**



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

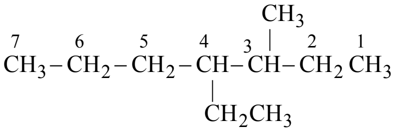
(16) **(D).** For geometrical isomerism doubly bonded carbon must be bonded to two different groups which is only satisfied by 1 - Phenyl - 2 - butene.



cis trans

EXERCISE-5

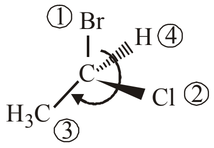
(1) **(A).** Correct IUPAC name of



$$\overset{7}{CH_3} - \overset{6}{CH_2} - \overset{5}{CH_2} - \underset{\substack{|\\ CH_2CH_3}}{\overset{4}{CH}} - \overset{\substack{CH_3\\ |}}{\overset{3}{CH}} - \overset{2}{CH_2}\,\overset{1}{CH_3}$$

is 4-ethyl-3-methyl heptane

(2) **(A).** Clockwise rotation:

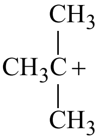


Hence configuration is R.

If the eye travel in a clockwise direction, the configuration is specified as the order of priority is : $Br > Cl > CH_3 > H$

(3) **(B).** Optical and geometrical isomerism pair up to exhibit sterioisomerism. This is because the isomers differ only in their orientation in space.

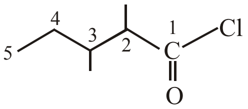
(4) **(D).** More the number of alkyl groups, the greater the dispersal of positive charge and therefore more the stability of carbocation hence



$$CH_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}+$$

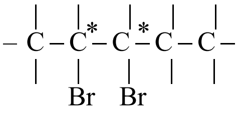
is most stable.

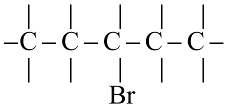
(5) **(C).**

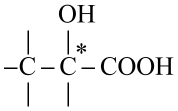


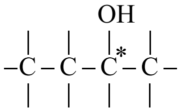
It is 2,3-dimethyl pentanoyl chloride

(6) **(B).**

(A) 
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{Br}{|}}{C^*}}-\overset{|}{\underset{\underset{Br}{|}}{C^*}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ [Chiral]

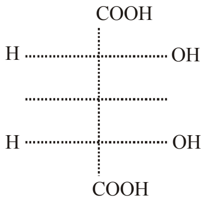
(B) 
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{Br}{|}}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ [Not chiral]

(C) 
$-\overset{|}{\underset{|}{C}}-\overset{\overset{OH}{|}}{\underset{|}{C^*}}-COOH$ [Chiral]

(D) 
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{\overset{OH}{|}}{\underset{|}{C^*}}-\overset{|}{\underset{|}{C}}-$ [Chiral]* marked are chiral carbons.

(7) **(C).** $C_nH_{2n+2}O$ $[C_nH_{2n+1}OH]$

(8) **(A).** Compounds which do not show optical activity inspite of presence of chiral carbon atoms are called meso-compounds. The absence of optical activity in these compound is due to the presence of a plane of symmetry in the molecules. eg. meso-tartaric acid is optically inactive.

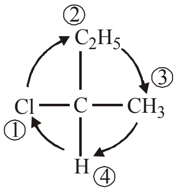


(Plane of symmetry)

(9) **(A).** Nucleophilicity increases down the periodic table. $I^- > Br^- > Cl^- > F^-$

(10) **(C).** Electrophiles have high affinity for electrons. They attack at the site where electron-density is highest. Electron withdrawing substances increases the electron density. The electron withdrawing tendency decreases in the order : $-OH > -CH_3 > -H > -Cl$ Therefore, the correct order of reactivity towards electrophile is $C_6H_5OH > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl$

(11) **(B).**



R-configuration

(12) **(A).** Higher the electron density on carbanion more is the basic strength. Weaker the acid, strongest is its conjugate base. Among alkane, alkene and alkyne, alkynes are most acidic acid and alkanes are least acidic, so the order of base strength is :

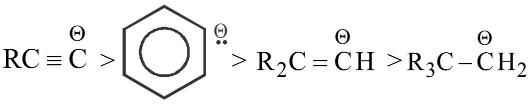
Alkane > Alkene > Alkyne.

(13) **(B).** Number of geometrical isomer = 2 (cis and trans)
Number of active optical isomer = 2 (d and ℓ)
Total 4

(14) **(D).** – OH group behaves as +R effect thereby increases the electron density and increases the electrophilic substitution.

(15) **(C).** $\underset{\underset{sp^2}{\downarrow}}{CH_3-CH}=CH-\underset{\underset{sp^3}{\downarrow}}{CH_2}-C\equiv\underset{\underset{sp}{\downarrow}}{CH}$

(16) **(B).** The carbanion with more s-character is more stable. Thus, the order of stability is


$RC\equiv\overset{\ominus}{C} > C_6H_5^{\ominus} > R_2C=\overset{\ominus}{C}H > R_3C-\overset{\ominus}{C}H_2$

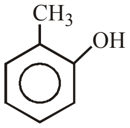
(17) **(D).** If number of σ bonds = 2, Hybridisation is sp.
If number of σ bonds = 3, Hybridisation is sp^2.
If number of σ bonds = 4, Hybridisation is sp^3.
sp, sp^3, sp^2, sp^3

(18) **(C).** IUPAC name of $\overset{4}{C}H\equiv\overset{3}{C}-\overset{2}{C}H=\overset{1}{C}H_2$ is 1-butene-3-yne.

(19) **(D).** $KOH \rightarrow K^+ + OH^-$
$RX + \underset{\text{nucleophile}}{OH^-} \rightarrow R-OH + X^-$
OH^- stronger nucleophile than halogen so, easily replace the weaker nucleophile.
Nucleophiles are either negative charge or lone pair of electrons bearing species, X^- is replaced by OH^-

(20) **(B).** Presence of electron withdrawing substituent increases the acidity while electron relasing substituent, when present, decreases the acidity. Phenyl is an electron withdrawing substituent while $-CH_3$ is an electron releasing substituent. Moreover, phenoxide ion is more resonance stabilised as compared to benzyloxide ion, thus releases proton more easily. That's why it is a strong acid among the given.

(21) **(A).** Electron withdrawing substituent deactivates the benzene nucleous towards electrophilic substitution while electron releasing substituent activates the ring towards electrophilic substitution.
Among the given, – OH has the higher electron donating tendency and thus, activates the ring more towards electrophilic substitution. Hence, is more reactive towards electrophilic reagent.



(22) **(C).** Electrophiles are electron deficient species. Among the given, $H_3O^{\oplus}$ has lone pair of electrons for donation, thus it is not electron deficient and hence, does not behave like an electrophile.

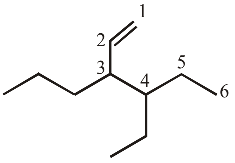
(23) **(B).** $\overset{5}{C}H_3\overset{4}{C}H = \overset{3}{C}H\overset{2}{C} \equiv \overset{1}{C}H$

Pent-3-en-1-yne

If a molecule contains both carbon-carbon double or triple bonds, the two are treated at par in seeking the lowest number combination. However, if the sum of numbers turns out to be the same starting from either of the carbon chain, then lowest number is given to the C = C double bond.

(24) **(C).** $H_3C - \underset{\underset{sp}{\uparrow}}{C} \equiv \underset{\underset{sp}{\uparrow}}{C} - CH_3$

In sp hybridised carbon bond angle is 180°.

(25) **(B).** 

4-Ethyl-3-propylhex-1-ene

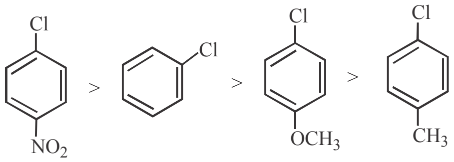
(26) **(C).** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

On calculation $V_2 = 46.09$ ml

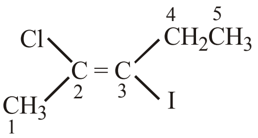
$$\% \text{ of } N = \frac{28 \times V \times 100}{22400 \times \text{mass of org. comp.}}$$

$$\% \text{ of } N = \frac{28 \times 46.09 \times 100}{22400 \times 0.35} = 16.45$$

(27) **(A).** The correct order of nucleophilic substitution reactions

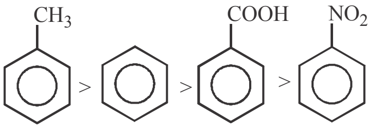


Electron withdrawing groups like $-NO_2$ facilitates nucleophilic substitution reaction in chlorobenzene.

(28) **(A).** 

Correct IUPAC name of above compound is trans-2-chloro-3-iodo-2-pentene.

(29) **(C).** As the +I effect increases reactivity towards electrophilic reactions increases and as –I or –M effect increases reactivity towards electrophilic reactions decreases. Thus, the order is

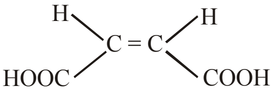


Toluene Benzene Benzoic acid Nitrobenzene

Toluene is most reactive

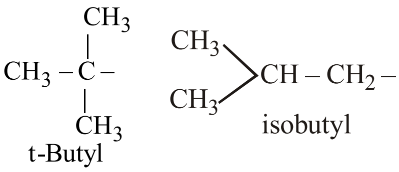
(30) **(A).** $Br - \underset{3}{C}H_2 - \underset{2}{C}H = \underset{1}{C}H_2$

The correct name is 3-Bromoprop-1-ene.

(31) **(A).** 

Maleic acid

It shows Geometrical isomerism but does not show optical isomerism.

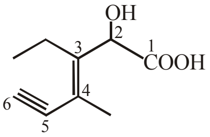
(32) **(B).** 

$CH_3 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} -$ t-Butyl

$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH - CH_2 -$ isobutyl

$CH_3 - \underset{|}{C}H - CH_2 - CH_3$ sec-butyl

$CH_3 - CH_2 - CH_2 - CH_2 -$ n-butyl

(33) **(C).** 

3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid

(34) **(A).** Deactivating power :

$-NO_2 > -C \equiv N > -SO_3H > -COOH$

(35) **(A).** $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$

10mL of 1M H_2SO_4 = 10m mol [$\because M \times V_{(mL)} = m$ mol]

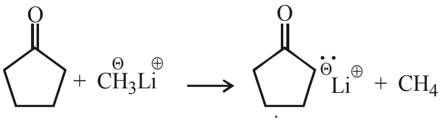
NH_3 consumed = 20m mol

Acid used for the absorption of ammonia

= 20 – 10 m mol = 10 mL of 2N (or 1 M) H_2SO_4

$$\%N = \frac{1.4 \times N \times V}{w} = \frac{1.4 \times 10 \times 2}{0.75} = 37.33\%$$

(36) **(D).** Electron withdrawing group i.e., – NO_2 favours nucleophilic attack.

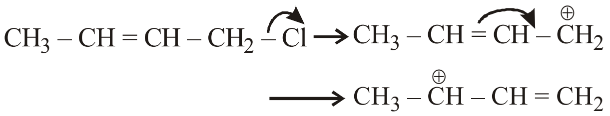
(37) **(D).** 

CH_3Li abstract is an active proton from cyclo pentanone forming methane leaving behind an intermediate lithium cyclopentanoyl anion.

(38) **(A).** π-bond electrons

= number of double bond × 2 = 4 × 2 = 8

(39) **(B).**



$$CH_3-CH=CH-CH_2-Cl \rightarrow CH_3-CH=CH-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH=CH_2$$

After leaving Cl^-, due to resonance, π bond is also transferred

(40) **(B).** Mass of organic comp. = 0.25 g

$V_1 = 40$ ml, $T_1 = 300$ K,

$P_1 = 725 - 25 = 700$ mm of Hg

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{700 \times 40 \times 273}{300 \times 760} = 33.52 \text{ ml}$$

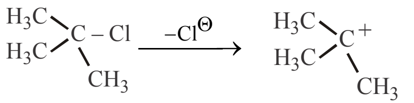
$$\%\text{ of N} = \frac{28 \times V \times 100}{22400 \times \text{mass of org. comp.}}$$

$$= \frac{28 \times 33.52 \times 100}{22400 \times 0.25} = 16.76$$

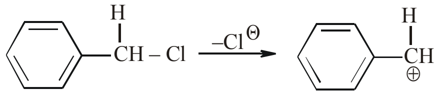
(41) **(B).** Hyperconjugation possible in  due to presence of α-H.

(42) **(D).** 18σ and 2π bonds in both keto and enol form of ethyl acetoacetate.

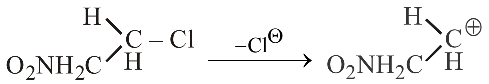
(43) **(B).**



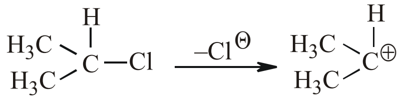
t-butyl carbonium ion



benzyl carbonium ion
[stable due to resonance]

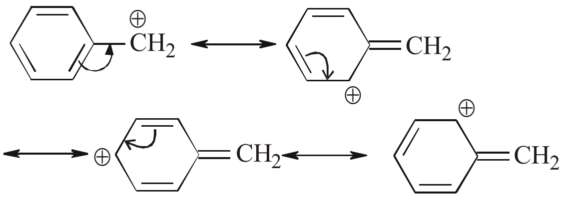


(–I effect)

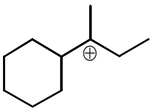


Secondary carbonium ion
[isopropyl carbonium ion]

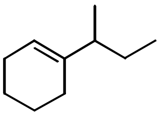
Most stable carbonium ion is benzyl carbocation due to resonance.



(44) **(C).** Nucleophiles are electron rich species so act as Lewis bases.

(45) **(D).** 

Intermediate carbocation (more stable).
No rearrangement in C^+ takes place.

 product is not possible.

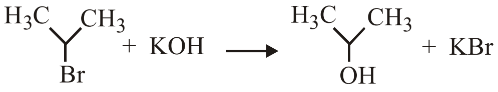
(46) **(B).**

(a) Elimination reaction :

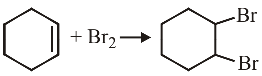
$CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH=CH_2 + KBr + H_2O$

Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.

(b) Substitution reaction :

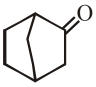
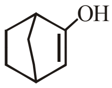


–Br group is replaced by –OH group hence, it is a substitution reaction.

(c) Addition reaction : 

Addition of Br_2 converts an unsaturated compound into a saturated compound, hence it is an addition reaction.

(47) **(D).** $CH_3\overset{sp}{C}\equiv\overset{sp}{C}^{\ominus}$. Thus pair of electrons is present in sp-hybridised orbital.

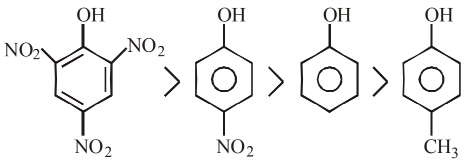
(48) **(A).** Bridge-head carbocation is unstable, therefore, tautomerism will be shown only by  and the enolic form would be  .

(49) **(A).** Correct order of acidic strength

$CH\equiv CH > CH_3-C\equiv CH > CH_2=CH_2 > CH_3-CH_3$

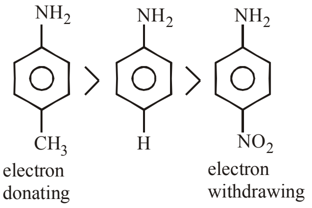
According to EN and Inductive effect.

(50) **(C).**

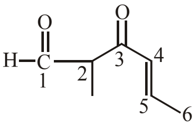


More – I, – M, more acidic

(51) **(C).** Order of Basic Strength



(52) **(C).** The ortho and para isomers can be separated by steam distillation o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitro phenol is less volatile due to intermolecular hydrogen bonding which cause association of molecule.

(53) **(D).** 

3-keto-2-methylhex-4-en-1-al

(54) **(C).** Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electron from a nucleophile.

(55) **(B).** $\overset{sp^2}{CH_2} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv \overset{sp}{CH}$

Number of orbital require in hybridization
= Number of σ-bonds around each carbon atom.

(56) **(A).** $-NO_2$ group exhibit –I effect and it decreases with increase in distance. In option (A) positive charge present on C-atom at maximum distance so –I effect reaching to it is minimum and stability is maximum.

(57) **(C).** –I effect increases on increasing electronegativity of atom. So, correct order of –I effect is
$-NH_2 < -OR < -F$.
Most appropriate Answer is option (C), however option (B) may also be correct answer.