

Chapter 23 General Organic Chemistry

Carbon is an essential element of organic compounds, it has four electrons in its outer most shell.

According to the ground state electronic configuration of carbon, it is divalent. Tetravalency of carbon can be explained by promoting one of the $2s^2$ -electrons to the unocupied $2p_{z^1}$ atomic orbital.

The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to **Le Bell and Van't Hoff** the four valencies of carbon do not lie in one plane. They are directed towards the corners of a regular tetrahedron with carbon atom at the centre and the angle between any two valencies is 109°28'.

Hybridisation in Organic Compounds

(1) The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as *hybridisation*. There are *three types* of hybridisation,

(i) *sp*³ *hybridisation* (involved in saturated organic compounds containing only single covalent bonds),

(ii) sp^2 **hybridisation** (involved in organic compounds having carbon atoms linked by double bonds) and

(iii) *sp* **hybridisation** (involved in organic compounds having carbon atoms linked by a triple bonds).

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		-	
Type of	sp ³	sp^2	sp
hydriuisation			
Number of	1 <i>s</i> and 3 <i>p</i>	1 <i>s</i> and 2 <i>p</i>	1 <i>s</i> and 1 <i>p</i>
orbitals used			
Number of	Nil	One	Two
unused			
p-orbitals			

Bond	Four -σ	Three -σ	Two -σ
		One -π	Two -π
Bond angle	109.5°	120°	180°
Geometry	Tetrahedra	Trigonal	Linear
	1	planar	
% s-character	25 or 1/4	33.33 or	50 or 1/2
		1/3	

(2) **Determination of hybridisation at different carbon atoms :** It can be done by two methods,

(i) *First method* : In this method hybridisation can be know by the number of π – bonds present on that particular atom.

Number of π - bond/s	0	1	2
Type of hybridisation	sp^3	sp^2	sp

Examples :

(ii)
$$CH_2 = C = CH_2$$

 $\downarrow \qquad \downarrow \qquad \downarrow$
 $sp^2 \qquad sp \qquad sp^2$

sp sp sp^2 sp^2

□ In diamond carbon is sp^3 hybridised and in graphite carbon is sp^2 hybridised.

(ii) Second method : (Electron pair method)

ep = bp + lp; where ep = electron pair present in hybrid orbitals , bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms attached to the central atom of the species





Number of *lp*'s can be determined as follows,

(a) If carbon has π - bonds or positive charge or odd electron, than lp on carbon will be zero.

(b) If carbon has negative charge, then lp will be equal to one.

Number of electron pairs (*ep*) tells us the type of hybridisation as follows,

ер	2	3	4	5	6
Type of	sp	sp^2	sp^3	$sp^{3}d$	sp^3d^2
hybridisation					
Example :					
(i) $CH_2 = \overset{\oplus}{\underset{\downarrow}{CH}}$		(ii)	$CH_2 =$	$\stackrel{\Theta}{\downarrow}$	
bp = 2 lp = 0			bp = lp =	: 2 : 1	
$\frac{1}{ep = 2, sp}$			ep = 3	$\overline{sp^2}$	
(iii) $CH_2 = C$	– <i>CH</i> ₃	(i	v) CH	$\equiv \overset{\Theta}{\overset{\circ}{\underset{ }}}$	
	U		bp	p=1	
L.	= 3		<u> </u>	$\frac{-1}{2}$ and	
lp	= 0		ер =	2,5p	
ep =	$3, sp^2$				
(v) $CH_3 - \bigcup_{i=1}^{\Theta} CH_{i=1}$	– <i>CH</i> ₃				
bp = 3 $lp = 1$					
ep = 4,	sp^3				

(3) Applications of hybridisation

(i) **Size of the hybrid orbitals** : Since s - orbitals are closer to the nucleus than p - orbitals, it is reasonable to expect that greater the s character of an orbital the smaller it is. Thus the decreasing order of the size of the three hybrid orbitals is opposite to that

of the decreasing order of s orbital character in the three hybrid orbitals.

$$sp^3 > sp^2 > sp$$

- (ii) Electronegativity of different orbitals
- (a) Electronegativity of *s*-orbital is maximum.

(b) Electronegativity of hybrid orbital \propto % s-character in hybrid orbitals

Orbital	sp	sp^2	sp^3	
% <i>s</i> - character	50	33.33	25	

s-character in decreasing order and electroneg ativity in decreasing order

Thus *sp*-hybrid carbon is always electronegative in character and sp^3 - hybrid carbon is electropositive in character. sp^2 -hybrid carbon can behave as electropositive (in carbocation) as well as electronegative (in carbanion) in character.



(c) Electronegativities of different hybrid and unhybrid orbitals in decreasing order is as follows

	$s > sp > sp^2 > sp^3 > p$	
% s - character	and electroneg ativity in decreasing	order.

(iii) Bond length variation in hydrocarbons

% of s orbital character

$$\propto \frac{1}{C - C \text{ bond length}} \propto \frac{1}{C - H \text{ bond length}}$$

Table	:	23.2
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Bond type (C – H)	Bond length	Bond type (C – C)	Bond length
$sp^3 - s$	1.112Å	$sp^3 - sp^3$ (al	1.54 Å
(alkanes)		kanes)	
$sp^2 - s$	1.103Å	$sp^2 - sp^2$ (al	1.34Å
(alkenes)		kenes)	
sp-s	1.08Å	<i>sp–sp</i> (alk	1.20Å
(alkynes)		ynes)	

(iv) **Bond strength in hydrocarbons** : The shorter is the bond length, the greater is the compression between atomic nuclei and hence greater is the strength of that bond.

Table : 23.3

Bond	Bond	Bond type	Bond
type (C –	energy	(C – C)	energy

<i>H</i>)	(kcal/mole)		(kcal/mole)
$sp^3 - s$	104	$sp^3 - sp^3$	80 - 90
(in		(in	
alkanes)		alkanes)	
$sp^2 - s$	106	$sp^2 - sp^2$	122 - 164
(in		(in	
alkenes)		alkenes)	
sp-s	121	sp-sp	123 - 199
(in		(in	
alkynes)		alkynes)	

(v) Acidity of hydrocarbons

(a) Hydrogen present on electronegative carbon is acidic in nature.

(b) Acidity of hydrogen is directly proportional to the electronegativity of the atom on which hydrogen is present.

Thus

pKa

H - O - H $> NH_3$ Electronegativity of the atoms

Acidity of compounds in decreasing order

(c) Acidity of hydrocarbon \propto % of *s*-character

 $CH_2 = CH_2$

44

 $CH_3 - CH_3$

50

33.33

25

25

 $CH \equiv CH$

% s-character 50

s- character and acidity in decreasing order

Acidity $\propto Ka$ and Acidity $\propto \frac{1}{pKa}(pKa = -\log Ka)$

Order of acidic nature of alkynes is,

 $HC \equiv CH > HC \equiv C - CH_3$

The relative acidic character follows the order;

 $H_2O > ROH > HC \equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$

Obviously, the basic character of their conjugate bases follows the reverse order, *i.e.*,

$$CH_3CH_2^{\tiny \text{eff}} > CH_2 = CH^{\tiny \text{eff}} > NH_2^{\tiny \text{eff}} > HC = C^{\tiny \text{eff}} > RO^{\tiny \text{eff}} > HO^{\tiny \text{eff}}$$

Steric effect

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called steric hinderance or steric effect.

(1) Tertiary alkyl halides having bulky groups form tertiary carbocation readily when hydrolysed because of the presence of the three bulky groups on the carbon having halogen.



(2) Primary alkyl halide having quaternary β carbon does not form transition state because of the steric strain around α -carbon by the β -carbon. To release the strain it converts into carbocation.



(3)Steric strain inhibits the resonance. This phenomenon is known as steric inhibitions of resonance.

Electronic displacement in covalent bonds

It is observed that most of the attacking reagents always possess either a positive or a negative charge, therefore for a reaction to take place on the covalent bond the latter must possess oppositely charged centres. This is made possible by displacement (partial or complete) of the bonding electrons. The electronic displacement in turn may be due to certain effects, some of which are permanent and others are temporary. The former effects are permanently operating in the molecule and are known as polarisation effects, while the latter are brought into play by the attacking reagent and as soon as the attacking reagent is removed, the electronic displacement disappears; such effects are known as the polarisability effects.



Inductive effect or Transmission effect

(1) When an electron withdrawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to displacement of shared electron of a covalent bond towards a more electronegative atom. This is called *inductive effect or simply as I – effect.*

$$C - C - C - C \text{ Non polar}$$

$$C^{\delta \delta \delta^{+}} \qquad C^{\delta \delta^{+}} \rightarrow C^{\delta \delta^{+}} \rightarrow C^{\delta^{+}} \rightarrow X^{\delta^{-}}$$

$$C^{\delta \delta \delta \delta^{-}} \leftarrow C^{\delta \delta \delta^{-}} \leftarrow C^{\delta \delta^{-}} \leftarrow C^{\delta^{-}} \leftarrow Y^{\delta^{+}}$$

(2) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to have-I effect whereas atoms or groups which have a greater electron releasing power are said to have +I effect.

 $\tilde{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR$ > CONH _2 > F > Cl > Br > l > OH > OR > NH_2 > C_6H_5 > H

-I power of groups in decreasing order with respect to the reference *H*

ter. alkyl > *sec.* alkyl > *pri.* alkyl > $CH_3 > H$

+ I power in decreasing order with respect to the reference *H*

+ I power ∞ number of carbon in the same type of alkyl groups

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

 $CH_2 - CH_2 - CH_2 - > CH_2 - CH_2 -$

+ *I* power in decreasing order in same type of alkyl groups

(3) Applications of Inductive effect

(i) Magnitude of positive and negative charges : Magnitude of +ve charge on cations and magnitude of -ve charge on anions can be compared by + I or - Igroups present in it.

• Magnitude of +ve charge
$$\infty \frac{1}{1 + I \text{ power of the group}} \propto -I$$
 power of the group.

• Magnitude of -ve charge $\frac{1}{1-ve} \propto +I$ power of the group.

-Ipower of the group

(ii) **Reactivity of alkyl halide :** + I effect of methyl group enhances - I effect of the halogen atom by repelling the electron towards tertiary carbon atom.

$$H_{3}C \longrightarrow \begin{pmatrix} CH_{3} & CH_{3} \\ \downarrow & \downarrow \\ CH_{3} \end{pmatrix} \xrightarrow{CH_{3}} X > H_{3}C \xrightarrow{CH_{3}} X$$

$$> CH_{2} \longrightarrow CH_{2} \longrightarrow X > CH_{2} \longrightarrow X$$

Tertiary > Secondary > Primary > Methyl

(iii) Relative strength of the acids :

(a) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have +I effect.

Thus, acidic nature is,

$HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$

+*I* effect increases, so acid strength decreases

Formic acid, having no alkyl group, is the most acidic among these acids.

(b) The group or atom having – I effect increases the acid strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is,

$$\begin{array}{c} CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH \\ Trichloro \\ acetic acid \\ \end{array} \begin{array}{c} Dichloro \\ acetic acid \\ \end{array} \begin{array}{c} Monochloro \\ acetic acid \\ \end{array} \begin{array}{c} Acetic acid \\ \end{array} \end{array}$$

(- Inductive effect increases, so acid strength increases)

(c) Strength of aliphatic carboxylic acids and benzoic acid

$$\begin{array}{ccc} R \longrightarrow COOH & C_6H_5 \longleftarrow COOH \\ \uparrow & \uparrow \\ +I \, group & -I \, group \end{array}$$

Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus,

$$HCOOH > C_6H_5COOH > RCOOH$$

Acid strength in decreasing order

Decreasing order of acids :

 $NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH$.

$$F_3C - COOH > Cl_3C - COOH > Br_3C - COOH > I_3C - COOH .$$

CH_3OH	$> CH_3 CH_2 OH$	$> (CH_3)_2 CHOH$	$> (CH_3)_3 COH$
Methyl	Ethyl	Iso-propyl	Tert-butyl
alcohol	Alcohol	alcohol	alcohol

As compared to water, phenol is more acidic (-I effect) but methyl alcohol is less acidic (+I effect).

$$\bigcup_{Phenol} OH > H - OH > CH_3 \longrightarrow OH$$

Methylalcohol

(vi) **Relative strength of the bases** (Basic nature of $-NH_2$)

The difference in base strength in various amines can be explained on the basis of inductive effect. The +Ieffect increases the electron density while -I effect decreases it. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to +I effect while $CINH_2$ is less basic due to -I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, *i.e.*, more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature".

Thus, the basic nature decreases in the order;

 $\begin{array}{c} (C_2H_5)_2NH > CH_3CH_2NH_2 > CH_3NH_2 > NH_3 > ClNH_2 \\ \begin{array}{c} \text{Diethyl} \\ \text{amine} \end{array} \\ \begin{array}{c} \text{Ethyl} \\ \text{amine} \end{array} \\ \begin{array}{c} \text{Methyl} \\ \text{amine} \end{array} \\ \begin{array}{c} \text{Ammonia} \end{array} \\ \begin{array}{c} \text{Chloro} \\ \text{amine} \end{array} \\ \end{array}$

The order of basicity is as given below;

Alkyl groups (<i>R</i> -)	Relative base strength
CH ₃	$R_2 NH > RNH_2 > R_3 N > NH_3$
C_2H_5	$R_2 NH > RNH_2 > NH_3 > R_3 N$
(<i>CH</i> ₃) ₂ <i>CH</i>	$RNH_2 > NH_3 > R_2NH > R_3N$
(<i>CH</i> ₃) ₃ <i>C</i>	$NH_3 > RNH_2 > R_2NH > R_3N$

□ The relative basic character of amines is not in total accordance with inductive effect (t > s > p) but it is in the following order: Secondary > Primary > Tertiary. The reason is the steric hindrance existing in the *t*-amines.

□ In gas phase or in aqueous solvents such as chlorobenzene etc, the solvation effect, *i.e.*, the stabilization of the conjugate acid due to *H*-bonding are absent and hence in these media the basicity of amines depends only on the +*I* effect of the alkyl group thus the basicity of amines follows the order : $3^{\circ} > 2^{\circ} > 1^{\circ} > NH_3$.

(vii) **Basicity of alcohols** : The decreasing order of base strength in alcohols is due to +I effect of alkyl groups.

$$(CH_3)_3 COH > (CH_3)_2 CHOH > CH_3 CH_2 OH > CH_3 OH (3°) (2°) (1°)$$

(viii) **Stability of carbonium ion :**+I effect tends to decrease the (+ve) charge and -I effect tends to increases the +ve charge on carbocation.

$$(CH_3)_3 C^{\oplus} > (CH_3)_2 CH^{\oplus} > CH_3 CH_2^{\oplus} > CH_3^{\oplus}$$

(ix) **Stability of carbanion :** Stability of carbanion increases with increasing – *I* effect.

$$CH_{3}^{-} > CH_{3}CH_{2}^{-} > (CH_{3})_{2}CH^{-} > (CH_{3})_{3}C^{-}$$

Resonance effect or mesomeric effect

(1) The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (*s*) of electrons from an atom to the adjacent single covalent bond is called **mesomeric effect** or simply as *M***-effect**. In case of the compound with conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.

(2) Groups which have the capacity to increase the electron density of the rest of the molecule are said to have +M effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have -M effect, e.g.,

(a) The groups which donate electrons to the double bond or to a conjugated system are said to have +M effect or +R effect.

+*M* effect groups :

$$-Cl, -Br, -I, -NH_2, -NR_2, -OH, -OR, -SH, -OCH_3, -SR$$

(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have -M effect or -R effect.

-*M* effect groups :

$$O = || \\
-NO_2, -C = N, -C, -CHO, -COOH, -SO_3H$$

(3) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to – I effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.

$$: \stackrel{\cdot}{Cl} \xrightarrow{CH} CH \stackrel{\frown}{=} CH_2 \longleftrightarrow : \stackrel{\oplus}{Cl} = CH - \stackrel{\frown}{CH}_2$$

Application of mesomeric effect : It explains,

(1) Low reactivity of aryl and vinyl halides,

(2) The acidic nature of carboxylic acids,

(3) Basic character comparison of ethylamine and aniline,

(4) The stability of some free radicals, carbocations and carbanions.

Difference between Resonance and Mesomerism : Although both resonance and mesomerism represent the same phenomenon, they differ in the following respect : Resonance involves all types of electron displacements while mesomerism is noticeable only in those cases where a multiple bond is in conjugation with a multiple bond or lone pair of electron.

Example :

(i)
$$\bigcap \qquad \bigcap \qquad \cdots \qquad \stackrel{@}{\longrightarrow} H_2C = CH - CH = CH_2 \longleftrightarrow H_2 \stackrel{@}{\longleftarrow} H_2 \stackrel{@}{C} - CH = CH - \stackrel{\oplus}{C} H_2$$

(ii)
$$R - C - O - H \longleftrightarrow R - C = O - H$$

Both (i) and (ii) are the examples of mesomerism and resonance effect. Let us consider the following example H Cl: $\longleftrightarrow HCl$. Such an electron

. .

displacement is the example of resonance only (not the mesomerism).

Hyperconjugative effect

(1) When a H-C bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the H-C bond interact or enter into conjugation with the unsaturated system. The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single H-C bonds) of the substituent groups in organic compounds is called **hyperconjugation**. The concept of hyperconjugation was developed by Baker and Nathan and is also known as Baker and Nathan effect.

In fact hyperconjugation effect is similar to resonance effect. Since there is no bond between the α -carbon atom and one of the hydrogen atoms, the hyperconjugation is also called *no-bond resonance*.

(2) Structural requirements for hyperconjugation

(i) Compound should have at least one sp^2 - hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

(ii) α -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

(iii) Hyperconjugation is of three types

(iv) Resonating structures due to hyperconjugation may be written involving "*no bond*" between the alpha carbon and hydrogen atoms.

$$H - \bigcup_{\substack{H \\ H \\ H}}^{H} CH = CH_{2} \longleftrightarrow H - \bigcup_{\substack{H \\ H \\ H}}^{\oplus} CH = CH_{2} \longleftrightarrow H - CH_{2} \longleftrightarrow H - CH_{2} \longleftrightarrow H$$

(v) Number of resonating structures due to the hyperconjugation = Number of α -hydrogens + 1.

Applications of hyperconjugation

(1) **Stability of alkenes :** Hyperconjugation explains the stability of certain alkenes over other alkenes.

Stability of alkenes ∞ Number of alpha hydrogens ∞ Number of resonating structures

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

$$CH_3 - CH - CH = CH_2$$

$$CH_3 - CH - CH = CH_2$$

$$CH_3 - CH - CH = CH_2$$

(2) **Carbon-carbon double bond length in alkenes :** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond.

(3) Stability of alkyl carbocations : Stability of alkyl carbocations \propto number of resonating structures \propto number of alpha hydrogens.

(4) **Stability of alkyl free radicals** : Stability of alkyl free radicals can be explained by hyperconjugation. Stability depends on the number of resonating structures.

(5) Electron releasing (or donating) power of R in alkyl benzene : CH_3 – (or alkyl group) is +R group,

ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.

The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α -carbon. The electron releasing power of some groups are as follows,

$$CH_{3} - > CH_{3} - CH_{2} - > \overset{CH_{3}}{\underset{CH_{3}}{\longrightarrow}} CH - > CH_{3} - \overset{CH_{3}}{\underset{CH_{3}}{\overset{|}}} CH - > CH_{3} - \overset{|}{\underset{CH_{3}}{\overset{|}}} CH_{3}$$

Increasing inductive effect

Electron donating power in decreasing order due to the hyperconjugation.

(6) **Heat of hydrogenation :** Hyperconjugation decreases the heat of hydrogenation.

(7) **Dipole moment :** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

The increase in dipole moment, when hydrogen of formaldehyde ($\mu = 2.27D$) is replaced by methyl group, *i.e.*, acetaldehyde ($\mu = 2.72D$) can be referred to hyperconjugation, which leads to development of charges.

$$\begin{array}{c} H \\ | \\ H - C = O \\ (\mu = 2.27D) \end{array}, H - \begin{array}{c} H \\ - C - CH \end{array} \xrightarrow{\frown} O \longleftrightarrow H - \begin{array}{c} H^+ \\ - C = CH - O \\ | \\ H \end{array}$$

(8) Orienting influence of alkyl group in o, p - positions and of $-CCl_3$ group in *m*-position : Orthopara directing property of methyl group in toluene is partly due to +I effect and partly due to hyperconjugation.

Reverse Hyperconjugation : The phenomenon of hyperconjugation is also observed in the system given below,

$$X = -C = C; \text{ where } X = \text{ halogen}$$

In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.



The *meta* directing influence and the deactivating effect of CX_3 group in electrophilic aromatic substitution reaction can be explained by this effect.



Inductomeric effect

Inductomeric effect is the temporary effect which enhances the inductive effect and it accounts only in the presence of an attacking reagent.

Example,



In methyl chloride the -I effect of Cl group is further increased temporarily by the approach of hydroxyl ion.

Electromeric effect

(1) The phenomenon of movement of electrons from one atom to another in multibonded atoms at the demand of attacking reagent is called electromeric effect. It is denoted as E-effect and represented by a curved arrow () showing the shifting of electron pair.

$$A \stackrel{\frown}{=} B \xrightarrow[\text{Reagent}]{\oplus} A \stackrel{\oplus}{-} B \stackrel{\oplus}{:}$$

(2) (i)When the transfer of electrons take place towards the attacking reagent, the effect is called +E effect. The addition of acids to alkenes.



$$C = C + H^{\oplus} \longrightarrow C^{+} - C$$

$$H$$

$$CH_{3} \longrightarrow CH = CH_{2} + H^{+} \rightarrow CH_{3} - CH_{3} - CH_{3} - CH_{3} + CH_{3} +$$

Since, $-CH_3$ group is electron donating, the electrons are transferred in the direction shown.

The attacking reagent is attached to that atom on which electrons have been transferred.

(ii) When the transfer of electrons takes place away from the attacking reagent, the effect is called -E effect. Example, The addition of cyanide ion to carbonyl compounds.

$$\sum C = O + CN \stackrel{\text{d}}{\longrightarrow} \sum_{\substack{i \\ CN}} C = O \stackrel{\text{d}}{\longrightarrow} C = O \stackrel{\text{d}}{\longrightarrow} C$$

The attacking reagent is not attached to that atom on which electrons have been transferred.

(3) **Direction of the shift of electron pair :** The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur in either direction.

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect.

In the case of carbonyl group, the shift is always towards oxygen, *i.e.*, more electronegative atom.

$$C = O \longrightarrow C - O:$$

In cases where inductive effect and electromeric effect simultaneously operate, usually electrometric effect predominates.

Cleavage (fission or breaking) of covalent bonds

Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways,

(1) Homolytic bond fission or Homolysis

(i) In homolysis, the covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.

$$A: B \longrightarrow A + B$$

Free radical

(ii) The factor which favours homolysis is that the difference in electronegativity between A and B is less or zero.

(iii) Homolysis takes place in gaseous phase or in the presence of non polar solvents (CCl_4, CS_2) , peroxide,

UV light, heat $(\geq 500\,^o\,C)$, electricity and free radical.

(iv) Mechanism of the reaction in which homolysis takes place is known as homolytic mechanism or free radical mechanism.

(2) Heterolytic bond fission or heterolysis

(i) In heterolysis, the covalent bond is broken in such a way that one species (*i.e.*, less electronegative) is deprived of its own electron, while the other species gains both the electrons.

$$A: B \longrightarrow A: + B \\ carbanion + carbocation$$

Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.

(ii) The factor which favours heterolysis is greater difference of electronegativities between A and B.

(iii) Mechanism of the reaction in which heterolysis takes place is known as heterolytic mechanism or ionic mechanism.

(iv) The energy required for heterolysis is always greater than that for homolysis due to electrostatic forces of attraction between ions.

Reaction Intermediates

Short lived fragments called reaction intermediates result from homolytic and heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, benzyne and nitrenes.

Table : 23.4

Characteristi	Free radical	Carbocation	Carbanion	Carbene
c				

Nature	Neutral having odd electron	Positive charge on C	Negative charge on	Neutral, divalent
			С	with 2 unshared
				electrons
Hybridisation	sp^2	sp^2	sp ³ (non-	(i) <i>sp</i> ² (singlet)
			conjugated)	(ii) <i>sp</i> (triplet)
			<i>sp</i> ² (Conjugated)	
Structure	Planar	Planar	Pyramidal/Planar	(i) Planar (singlet)
				(ii) Linear (triplet)
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	(i) Diamagnetic
				(ii) Paramagnetic
Stability		+ $+$ $+$ $+$ $+$ $ -$		(ii) Paramagnetic Triplet > singlet
Stability order	$Ph_3 \stackrel{.}{C} > Ph_2 \stackrel{.}{C} H > Ph \stackrel{.}{C} H_2 >$	$Ph_3 \stackrel{+}{C} > Ph_2 \stackrel{+}{CH} > \stackrel{+}{PhCH}_2 >$	$Ph_3C > Ph_2CH >$	(ii) Paramagnetic Triplet > singlet
Stability order	$Ph_3 C > Ph_2 CH > Ph CH_2 >$	$Ph_{3}\overset{+}{C} > Ph_{2}\overset{+}{C}H > \overset{+}{P}hCH_{2} >$ $CH_{2} = CH_{2}\overset{+}{C}H > CH_{2} >$	$Ph_{3}C > Ph_{2}CH >$	(ii) Paramagnetic Triplet > singlet
Stability order	$Ph_{3}\dot{C} > Ph_{2}\dot{C}H > Ph\dot{C}H_{2} >$ $CH_{2} = CH - \dot{C}H_{2} > 3^{o} > 2^{o} >$	$Ph_{3} \stackrel{+}{C} > Ph_{2} \stackrel{+}{C}H > \stackrel{+}{P}hCH_{2} >$ $CH_{2} = CH - \stackrel{+}{C}H_{2} >$	$Ph_{3}C > Ph_{2}CH >$ $PhCH_{2} > Ally >$	(ii) Paramagnetic Triplet > singlet
Stability order	$Ph_{3}\dot{C} > Ph_{2}\dot{CH} > Ph\dot{CH}_{2} >$ $CH_{2} = CH - \dot{CH}_{2} > 3^{o} > 2^{o} >$ $1^{o} > \dot{CH}_{2} > CH_{2} = CH$	$Ph_{3} \stackrel{+}{C} > Ph_{2} \stackrel{+}{C}H > \stackrel{+}{P}hCH_{2} > CH_{2} = CH - \stackrel{+}{C}H_{2} > 3^{o} > 2^{o} > 1^{o} > \stackrel{+}{C}H_{3}$	$Ph_{3}C > Ph_{2}CH >$ $PhCH_{2} > Ally >$ $CH_{2} > 1^{o} > 2^{o} > 3^{o}$	(ii) Paramagnetic Triplet > singlet

Benzyne

(1) 1, 2-Didehydrobenzene, C_6H_4 and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(2) It is neutral reaction intermediate derived from benzene ring by removing two substituents, of *ortho* positions, one in the form of electrophile and other in the from of nucleophile leaving behind two electrons to be distributed between two orbitals.



(3) Benzyne intermediate is aromatic in character.

(4) When halobenzene is heated with sodamide formation of benzyne takes place.



(5) (i) It behaves as dienophile and gives Diels-Alder reaction with diene.



Nitrenes (R – N :)

(1) The nitrogen analogous of carbenes are called nitrenes.

(2) There is possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.



(3) In general nitrenes obey Hunds rule and the ground state triplet with two degenerate sp-orbitals containing a single elec $\sqrt{n/r}$ ch.



(4) Nitrenes can be generated, in situ, by the following methods,

(i) By action of Br₂ in presence of a base on a 1^o
 amide (Hofmann-bromamide reaction),



(ii) By decomposition of azides in presence of heat or light.

$$R - \stackrel{-}{N} = \stackrel{-}{N} = \stackrel{-}{N} : \stackrel{-}{\longrightarrow} \stackrel{\Delta or hv}{\longrightarrow} \stackrel{-}{R} - \stackrel{-}{N} : + N \equiv N$$

Alkyhzide

(iii) Unsubstituted nitrene (H - N :) can be obtained by photolysis of (or by passing electric discharge through) NH_3, N_2H_4 or N_3H .

Attacking reagents

The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

Electrophiles or electrophilic reagents and Nucleophiles or nucleophilic reagents.

(1) **Electrophiles :** Electron deficient species or electron acceptor is an electrophile.

It can be classified into two categories :

(i) *Charged electrophiles* : Positively charged species in which central atom has incomplete octet is called charged electrophile.

$$H^{\oplus}, X^{\oplus}, R^{\oplus}, N \stackrel{\oplus}{\swarrow} O, N = O, S O_3 H$$

All cations are charged electrophiles except cations of IA, IIA group elements, Al^{+++} and $\overset{\oplus}{NH}_4$

(ii) *Neutral electrophiles* : It can be classified into three categories,

(a) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,

$$\textit{BeCl}_2,\textit{BH}_3,\textit{ZnCl}_2,\textit{AlX}_3,\textit{FeX}_3,\textit{CH}_3,\textit{CH}_2,\textit{CX}_2$$

(b) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled -d-sub-shell is neutral electrophile,

SnCl₄, SiCl₄, PCl₅, SF₆, IF₇

(c) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is called neutral electrophile.

 $\textit{BeCl}_2,\textit{BX}_3,\textit{AlX}_3,\textit{FeX}_3,\textit{SnCl}_4,\textit{PCl}_3$;

$$PCl_5$$
, NF_3 , CX_2 , CO_2 , SO_3 , CS_2 ,

 Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

Electrophiles are Lewis acids.

(2) **Nucleophiles :** Electron rich species or electron donors are called nucleophiles. Nucleophiles can be classified into three categories :

(i) *Charged nucleophiles* : Negatively charged species are called charged nucleophiles.

$$\stackrel{\text{d}}{H}, OH, R - O, CH_3, X, SH, R - S$$

(ii) **Neutral nucleophiles :** It can be classified into two categories :

(a) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.

$$\ddot{N}H_{3,}R - \ddot{N}H_{2}, R_{2}\ddot{N}H, R_{3}\ddot{N}, NH_{2} - NH_{2}$$
 (Nitrogen nucleophile)

$$H - O - H, R - O - H, R - O - R$$
(Oxygen

nucleophiles)

$$H - S - H, R - S - H, R - S - R$$
 (Sulphur nucleophiles)

$$PH_3, RPH_2, R_2PH, R_3P$$
 (Phosphorus

nucleophiles)

(b) Organic compound containing carbon, carbon multiple bond/ bonds behaves as nucleophile.

Alkenes, Alkynes, Benzene,

 $CH_2 = CH - CH = CH_2, CH_2 = CH - C \equiv CH$

(iii) *Ambident nucleophiles* : Species having two nucleophilic centres out of which, one is neutral (complete octet and has at least one lone pair of electrons) and the other is charged (negative charge) behaves as ambident nucleophile

$$\begin{array}{c} \textcircled{O} & \ddots & \textcircled{O} & \ddots \\ C \equiv N, O - N = O, O - \begin{matrix} \textcircled{O} \\ S \\ O \end{matrix} \\ O \end{matrix}$$

□ Organometallic compounds are nucleophiles.

□ Nucleophiles are Lewis bases.

Organic compounds which behave as an electrophile as well as a nucleophile : Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as electrophile as well as nucleophile :

$$O O O O O O O R - C - H, R - C - R, R - C - OH, R - C - Cl,$$

$$O O O R - C - OR, R - C - NH_2, R - C \equiv N, R - N \equiv C$$

□ During the course of chemical reaction electrophile reacts with nucleophile.

□ Strong Lewis acid is stronger electrophile $CO_2 < NO_2 < SO_3H$. Stronger is an acid, weaker is its conjugated base or weaker is the nucleophile.

Examples: $HF > H_2O > NH_3 > CH_4$

 $F^- < OH^- < NH_2^- < CH_3^-$

Increasing order of nucleophilicity.

Types of organic reactions

It is convenient to classify the numerous reactions of the various classes of organic compound into four types,

• Substitution reactions, • Addition reaction,

• Elimination reactions, • Rearrangement reactions,

Substitution reactions

Replacement of an atom or group of the substrate by any other atom or group is known as substitution reactions.

Evennles		Substituting or
Examples :	Leaving group	attacking
	\downarrow	group
$CH_3 - CH_2$	- Br+ NaOH	$\longrightarrow CH_3 - CH_2OH + NaBr$
Ethyl bromide		Ethyl alcohol

(Bromine atom is replaced by hydroxyl group)

Types of substitution reactions : On the basis of the nature of attacking species substitution reactions are classified into following three categories,

(1) Nucleophilic substitution reactions

(2) Electrophilic substitution reactions

(3) Free radical substitution reactions

(1) Nucleophilic substitution reactions

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

$$\begin{array}{c} R - X + \underset{Nucleophile}{OH} \overset{\text{@D}}{\longrightarrow} R - OH + \underset{Leaving group}{X} \overset{\text{@D}}{\longrightarrow} \end{array}$$

Such substitution reactions are called nucleophilic substitution reactions, *i.e.*, S_N reactions (*S* stands for substitution and *N* for nucleophile).

(ii) The weaker the basicity of a group of the substrate, the better is its leaving ability.

Leaving power of the group $\propto \frac{1}{\text{Basicity of the group}}$

$$Example: \xrightarrow{HI > HBr > HCl > HF}$$

Decreasing acidity



(iii) The leaving power of some nucleophilic groups are given below in decreasing order,



(iv) In these reactions leaving group of the substrate is replaced by another nucleophile. If reagent is neutral then leaving group is replaced by negative part of the reagent. Negative part of the reagent is always nucleophilic in character.

$$R - L \xrightarrow{\stackrel{+\delta}{E} - Nu}_{E - Nu} \rightarrow R - Nu + L; \quad R - L + Nu \xrightarrow{et}_{R} - Nu + L$$

(v) In S_N reactions basicity of leaving group should be less than the basicity of incoming nucleophilic group. Thus strongly basic nucleophilic group replaces weakly basic nucleophilic group of the substrate.

Example :
$$R - Cl \xrightarrow{OH^{\oplus}} R - OH + Cl$$
(A)

Basicity of OH^{eff} is more than Cl hence OH replaces Cl as Cl.

$$R - OH \xrightarrow[(HCl)]{O} R - Cl + OH \quad \dots (B)$$

Basicity of $\stackrel{\circ}{Cl}$ is less than $\stackrel{\circ}{OH}$, hence $\stackrel{\circ}{Cl}$ will not replace OH as $\stackrel{\circ}{OH}$ hence reaction (B) will not occur.

(vi) Unlike aliphatic compounds having nucleophilic group as leaving group, aromatic compounds having same group bonded directly with aromatic ring do not undergo nucleophilic substitution reaction under ordinary conditions.

The reason for this unusual reactivity is the presence of lone pair of electron or π bond on the key atom of the functional group. Another factor for the low reactivity is nucleophilic character of aromatic ring.

(vii) The S_N reactions are divided into two classes, S_{N^2} and S_{N^1} reactions.

Table : 23.5 Distinction between S_{N^2} and S_{N^1} reactions

Factors	S_{N^2} Reactions	S_{N^1} Reactions
Number of steps	One: $R: L+: Nu \to R: Nu+: L$	Two: (i) $R: L \xrightarrow{Slow} R^+ + : L^{\textcircled{T}}$
		(ii) $R^+ + : Nu^- \xrightarrow{Fast} R : Nu$
Reaction rate and order	Second order:	First order:
	Rate \propto [Substrate] [Nucleophile] or	Rate \propto [Substrate] or Rate = $K_1[RL]$
	Rate = $K_2[RL][: Nu^{C_1}]$	
Molecularity	Bimolecular	Unimolecular
TS of slow step	$ \overset{\delta^-}{: Nu C : L } $: Nu C L Nu:
Reacting nucleophile	The nucleophile attacks the carbon of	The nucleophile can attack the carbon of the
	the substrate exclusively from the	substrate both from the back and front sides
	back side.	although the back side attack predominates.
Stereochemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.
Reactivity order of alkyl	Methyl>1°>2°>3°halides.	$3^{\circ}>2^{\circ}>1^{\circ}>$ methyl halides. $(I > Br > Cl > F)$
nalides	(I > Br > Cl > F)	
Rearrangement	No rearranged product is formed (except for allylic).	Rearranged products can be formed.
Nature of nucleophiles	Favoured by strong and high	Favoured by mild and low concentration of
Delewiter	Encourad has colourate of low relarity	Forward he columns of high polority
Polarity	Favoured by solvents of low polarity.	Favoured by solvents of high polarity.
Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of $\stackrel{\oplus}{R}$).
Catalysis	Not catalysed by any catalyst (phase	Catalysed by Lewis and Bronsted acids, e.g.,
	transfer).	$\stackrel{\oplus}{Ag}$, $AlCl_3$, $ZnCl_2$ and strong HA.

(2) **Electrophilic substitutions reactions :** Electrophilic substitution involves the attack by an electrophile. It is represented as S_E (*S* stands for substitution and *E* stands for elctrophile). If the order of reaction is 1, it is written as S_{E^1} (unimolecular)and if the order is 2, it is S_{E^2} (Bimolecular).

 $^{H} \times ^{E}$

E

Substitution and *E* status for electrophile). If the order

$$S_{E^{1}} \text{ Reaction mechanism : Electrophilic substitution in all phases are:
(i) Replacement of the metal atom in an organometallic compound by hydrogen : $R - M + H \rightarrow R - H + M$
(i) Replacement of the metal atom in an organometallic compound by hydrogen : $R - M + H \rightarrow R - H + M$
e.g., $CH_3 - CH_2 - MgBr - MgBr \rightarrow CH_3 - CH_2 - H \rightarrow CH_3 - CH_3$
 $CH_3 - CH_2 - MgBr + H - Br \rightarrow CH_3 - CH_2 - H \rightarrow CH_3 - CH_3 + MgBr_2$
(ii) Decarboxylation of silver salt of carboxylic acid by means of bromine:
 $R_3C - C - OAg + Br - Br \rightarrow R_3C - C - O + Br - Br + Ag = O - O - O + Br - Br - Br + Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - Br - Ag = O - O - O + Br - D - O - O + Br - O - O - O + Br - O - O + Br - D - O - O - O + Br - D - O - O - O + Br - O - O - O - O + Br - O - O + Br - O - O - O - O + Br - O - O - O + Br - O - O - O - O + Br - O - O - O - O - O + Br - O - O - O - O - O - O - O - O -$$$

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$R - H + D \rightleftharpoons R - D + H$ $R - H + T \rightleftharpoons R - T + H$	ring to form carbonium ion (or arenium ion) which is stabilized by resonance.
	Step 3. Carbonium ion loses the proton to form substitution product.
	The bromination of benzene in the presence of $FeBr_3$ is a example of electrophilic substitution reaction.
	Similarly, Nitration, sulphonation and Friedel-Crafts reactionetc., in benzene nucleus are the other examples of electrophilic substitution reactions.

(3) **Free radical substitution reactions :** Free radical substitution reactions involves the attack by a free radical. These reactions occurs by free radical mechanism which involves Initiation, Propagation and Termination steps. *Examples*,

(i) *Chlorination of methane* : The chlorination of methane in the presence of ultraviolet light is an examples of free radical substitution.

$$CH_{4} + Cl_{2} \xrightarrow{UV} CH_{3}Cl + HCl$$

$$Methane Methylchloride$$

(ii) *Arylation of aromatic compounds* (Gomberg reaction) : The reaction of benzene diazonium halide with benzene gives diphenyl by a free radical substitution reaction.

$$C_{6}H_{5} - H + \underbrace{C_{6}H_{5}N_{2}X}_{\text{Benzene diazonium halide}} \xrightarrow{\text{Alkali}} C_{6}H_{5} - C_{6}H_{5} + N_{2} + HX$$

(iii) *Wurtz reaction*: Ethyl bromide on treatment with metallic sodium forms butane, ethane and ethylene by involving free radical mechanism.

(iv) Allylic bromination by NBS (*N*-Bromosuccinimide) : NBS is a selective brominating agent and it normally brominates the ethylenic compounds in the allylic $(CH_2 = CH - CH_2 -)$ position. This type of reaction involving substitution at the alpha carbon atom with respect to the double bond is termed Allylic substitution. It is also used for benzylic bromination. Some examples are:

$$CH_{3} - CH = CH_{2} + \bigvee_{Propene}^{CH_{2} - CO} N - Br \xrightarrow{CCI_{4}} N$$

$$Br - CH_{2} - CH = CH_{2} + \bigvee_{Ally \text{ bromide}}^{CH_{2} - CO} NH$$

$$CH_{2} - CO$$
Succinim ide

Addition reactions

These reactions are given by those compounds which have at least one π bond,

0

i.e.,
$$(> C = C <, -C \equiv C -, -C \equiv N)$$
. In such reaction there is loss of one π bond and gain of two σ bonds. Thus product of the reaction is generally more stable than the reactant. The reaction is a spontaneous reaction.

Types of addition reactions : Addition reactions can be classified into three categories on the basis of the nature of initiating species.

(1) Electrophilic additions

(2) Nucleophilic additions

(3) Free radical additions

(1) Electrophilic addition reactions

(i) Such reactions are mainly given by alkenes and alkynes.

(ii) Electrophilic addition reactions of alkenes and alkynes are generally two step reactions.

Cl

(iii) Alkenes and alkynes give electrophilic addition with those reagents which on dissociation gives electrophile as well as nucleophile.

(iv) If the reagent is a weak acid then electrophilic addition is catalysed by strong acids (Generally H_2SO_4).

(v) Unsymmetrical alkenes and alkynes give addition reactions with unsymmetrical reagents according to Markownikoff's rule.

The negative part of the addendum adds on that doubly bonded carbon of the alkene which has least number of hydrogen atom.

This rule can be used only in those alkenes which fulfil the following conditions:

(a) Alkene should be unsymmetrical.

(b) Substituent/substituents present on doubly bonded carbon/(*s*) should only be +*I* group.

(c) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl groups.

For example, the following alkenes will give addition according to the Markownikoff's rule.

$$CH_{3} - CH = CH_{2},$$

 $CH_{3} - CH = CH_{2},$
 $CH_{3} - CH = CH_{2},$
 $C_{6}H_{5} - CH = CH_{2}$
 $C_{6}H_{5} - CH = CH_{2}$

Following alkenes will not give addition reaction according to Markownikoff's rule.



(vi) Unsymmetrical alkenes having the following general structure give addition according to anti Markownikoff's rule.

 $CH_2 = CH - G$, where G is a strong -I group such

$$O$$

$$= CX_{3}, -NO_{2}, -CN, -CHO, -COR, -COOH, -C-Z$$

$$(Z = Cl, OH, OR, NH_{2})$$

Example:

as

$$CH_2 = CH - CHO + HCl \xrightarrow{\text{Anti-Markowniko ffs addition}} CH_2 - CH_2 - CH_2 - CHO$$

(vii) Mechanism of electrophilic addition reactions is as follows,



(2) **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 electronegative oxygen atom, the 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.

$$\sum C = O \qquad \leftrightarrow \qquad \sum C = O \qquad \equiv \qquad \sum C - O$$

Example : The addition of *HCN* to acetone is an example of nucleophilic addition.



The mechanism of the reaction involves the following steps:

Step 1. HCN gives a proton (\tilde{H}) and a nucleophile,

cyanide ion (\widetilde{CN}) .

$$HCN \rightarrow H^{\oplus} + CN^{\oplus}$$

Step 2. The nucleophile (CN^{eff}) attacks the positively charged carbon so as to form an anion [H^{\oplus} does not initiate the negatively charged oxygen as anion is more stable than cation].

$$\begin{array}{c} \overbrace{CN} & \overbrace{CH_3} & C \xrightarrow{CH_3} & C \xrightarrow{CH_3} & C \xrightarrow{O} & O \\ \hline & CN & \overbrace{CH_3} & C \xrightarrow{O} & O \\ \hline & CH_3 & C \\ \hline & CH_3 & C$$

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

$$CH_{3} \xrightarrow{CH_{3}} C \xrightarrow{OH} H \xrightarrow{OH} NC \xrightarrow{-C - OH} OT \xrightarrow{CH_{3}} CH_{3} \xrightarrow{OH} CH_{3}$$

In
$$C = O$$
 compounds, the addition of liquid *HCN*

gives cyanohydrin and the addendum is CN^- ion and not *HCN* directly (addition is catalysed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds).



Nucleophilic addition (A_N) reactions on carbonyl compounds will be in order:

$$H = O > H = O > H = C = O > H = C = O > H = C = O$$

Decreasing order of nucleophilic addition in some species.

 $-COCH_3 > -COCl > -COOCH_3 > -CONH_2 > -COOH$

(3) Free radical addition reactions : Those reactions which involve the initial attack by a free radical are known as free radical reactions. Addition of hydrogen bromide to alkenes (say, propylene) in the presence of peroxide (radical initiator) follows free radical mechanism. Free radical reactions generally take place in non-polar solvents such as CCl_4 , high temperature, in presence of light or a free radical producing substance like O_2 and peroxides.

Elimination reactions

Elimination reactions are formally the reverse of addition reactions and involve the removal of the two groups (Generally, one being a proton) from one or two carbon atoms of a molecule to form an unsaturated linkage or centre.

Elimination reaction is given by those compounds which have a nucleophilic group as leaving group,

i.e., X, OH, OR,
$$\overset{\oplus}{N_2}$$
, N_3 , H_3O , $\overset{\oplus}{\bigwedge}$, $\overset{R}{R}$, $\overset{R}{}$
 R , $\overset{R}{}$, $\overset{R}{}$

Elimination reactions are generally endothermic and take place on heating.

Elimination reactions are classified into two general types,

(I) α - elimination reactions or 1, 1-elimination reactions.

(II) $\beta\!\!\!\!/$ elimination reaction or 1, 2-elimination reactions.

(I) α -elimination reactions or 1,1-elimination reactions: A reaction in which both the groups or atoms are removed from the same carbon of the molecule is called α - elimination reaction. This reaction is mainly given by gem dihalides and gem trihalides having at least one α - hydrogen.

$$CHX_3 \xrightarrow{\text{Alc. } KOH/\Delta} CX_2 + X + H$$

Product of the reaction is halocarbenes or dihalocarbenes. which are key intermediates in a wide variety of chemical and photochemical reactions.

(II) *β*-elimination reactions or 1, 2-elimination reactions: Consider the following reactions,

$$CH_3 - CH_2 - CH_2 - CH_2 - L \rightarrow CH_3 - CH = CH_2 + H + L$$

A reaction in which functional group (*i.e.*, leaving group) is removed from α - carbon and other group (Generally hydrogen atom) from the β - carbon is called β - elimination reaction. In this reaction there is loss of two σ bonds and gain of one π bond. Product of the reaction is generally less stable than the reactant.

(1) **Types of** β **- elimination reactions :** In analogy with substitution reactions, β - elimination reactions are divided into three types:

(i) E_1 (Elimination unimolecular) reaction, (ii) E_2 (Elimination bimolecular) reaction and (iii) E_{1cb} (Elimination unimolecular conjugate base) reaction

(i) E_1 (Elimination unimolecular) reaction : Consider the following reaction,

$$CH_{3} \xrightarrow{C}_{-} CH_{3} \xrightarrow{C}_{2}H_{5} \xrightarrow{O/\Delta} CH_{2} = C \xrightarrow{CH_{3}} + C_{2}H_{5}OH + CI$$

(a) Reaction velocity depends only on the concentration of the substrate; thus reaction is unimolecular reaction.

Rate ∝ [Substrate]

(b) Product formation takes place by the formation of carbocation as reaction intermediate (*RI*).

(c) Since reaction intermediate is carbocation, rearrangement is possible in E_1 reaction.

(d) Reaction is carried out in the presence of polar protic solvent.

(e) The E_1 reaction occurs in two steps,

Step 1.

$$CH_{3} \xrightarrow[-]{C} CH_{3} \xrightarrow[-]{C} CH_{3} \xrightarrow[-]{\delta^{+}} CH_{3} \xrightarrow[-]{\delta^{+}}$$

Step 2.

 $\begin{array}{c}
\overset{\bullet}{B}+H \underbrace{CH_2}_{CH_3} \stackrel{\oplus}{\longrightarrow}_{CH_3} - CH_3 \rightarrow \begin{bmatrix} B - \cdots - H - \cdots - CH_2 - \cdots & C & -CH_3 \\ & & CH_3 \end{bmatrix} \\
\xrightarrow{fast} \stackrel{\oplus}{\longrightarrow}_{B}H + CH_2 = C \underbrace{CH_3}_{CH_3}$

(ii) E_2 (Elimination bimolecular) *reaction* : Consider the following reaction,

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow{Base(B)} CH_3 - CH = CH_2 + H + Br$$

(a) Reaction velocity depends only on the concentration of the substrate and the base used; thus reaction is bimolecular reaction. Rate ∞ [Substrate] [Base]

(b) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state (TS).

(c) Rearrangement does not take place in E_2 reaction but in case of allylic compound rearrangement is possible.

(d) Reaction is carried out in the presence of polar aprotic solvent.

(2) **Orientation in** β - **elimination reactions :** If substrate is unsymmetrical, then this will give more than one product. Major product of the reaction can be known by two emperical rules.

(i) **Saytzeff rule**: According to this rule, major product is the most substituted alkene *i.e.*, major $\stackrel{\oplus}{H}$ from that β -carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.

$$Cl \qquad CH_{3} \xrightarrow{\beta_{2}} (H_{3} \xrightarrow{\beta_{1}} (H_{3} \xrightarrow{-CH} (H_{3} \xrightarrow{-CH} (H_{3} \xrightarrow{-HCl} (H_{3} \xrightarrow{-HCl} (H_{3} \xrightarrow{-CH} (H_{3} \xrightarrow{-CH} (H_{3} \xrightarrow{-HCl} ($$

(ii) **Hofmann rule** : According to this rule, major product is always least substituted alkene *i.e.*, major product is formed from β - carbon which has maximum number of hydrogen. Product of the reaction in this case is known as Hofmann product.

$$CH_{3} \xrightarrow[]{} CH_{3} \xrightarrow[]{} Br \xrightarrow[]{} CH_{3} \xrightarrow[]{} CH_{3}$$

 \Box In E_1 reactions, product formation always takes place by Saytzeff rule.

□ In E_{1cb} reactions, product formation always takes place by Hofmann rule.

□ In E_2 reactions, product formation takes place by Saytzeff as well as Hofmann rule. In almost all E_2 reactions product formation take place by Saytzeff rule.

(3) Examples of β - elimination reactions

(i) **Dehydrohalogenation** is removal of *HX* from alkyl halides with alcoholic *KOH* or *KNH*₂ or ter- BuOK (Potassium tertiary butoxide) and an example of α - β elimination,

e.g.,
$$CH_3 - CH_2 X \xrightarrow{\text{Alc.KOH}} H_2 C = CH_2$$
;
 $CH_3 - CH - CH_3 \xrightarrow{\text{Alc.KOH}} CH_3 CH = CH_2$
 X
 $CH_3 - CH_2 - CH_3 \xrightarrow{\text{Alc.KOH}} CH_3 - CH = CH_2 - CH_3 + CH_3 - CH_2 - CH_3 + CH_3 - CH_3 - CH_2 - CH_3 + CH_3 - CH_2 - CH_3 + CH_3 - CH_2 - CH_3 - CH_2 - CH_3 + CH_3 - CH_2 - CH_3 - CH_2 - CH_3 + CH_3 - CH_2 - CH_3 - CH_2 - CH_3 + CH_3 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 + CH_3 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 + CH_3 - CH_3$

(ii) **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.

Dehydration is removal of H_2O from alcohols,

e.g.,

$$CH_{3} - CH_{2} - OH \xrightarrow{\text{Conc. } H_{2}SO_{4}, 170 \,^{\circ}C} \rightarrow H_{2}C = CH_{2}$$

$$CH_{3} - CH_{2} - CH_{2} - OH \xrightarrow{\text{Conc. } H_{2}SO_{4}, 170 \,^{\circ}C} \rightarrow CH_{3} - CH = CH_{2}$$

$$Propan - 1 - ol$$

$$Propene$$

□ Dehydration of alcohols is in the order: Tertiary > Secondary > Primary

□ 2° and 3° alcohol by E_1 process and 1° alcohol by E_2 process. Alcohols leading to conjugated alkenes are more easily dehydrated than the alcohols leading to non-conjugated alkenes. $CH_2 = CH - CH - CH_3$ is easily OH

dehydrated than



(iii) Dehalogenation : It is removal of halogens,

e.g.,
$$CH_2 - CH_2 + Zn \operatorname{dust} \xrightarrow{\operatorname{in CH_3OH, heat}} H_2C = CH_2$$

 $H_2C = CH_2$
 $Br Br$
Ethylene bromide

(iv) Dehydrogenation : It is removal of hydrogen,

e.g.,
$$CH_3 - CH - CH_3 \xrightarrow{Cu, 300^{\circ}C} CH_3 - C - CH_3$$

 $OH_{(-H_2)} \xrightarrow{O} OH_{(-H_2)} O_{Acetone}$

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.

It is convenient to divide rearrangement reactions into following types:

(1) **Rearrangement or migration to electron deficient atoms** (Nucleophilic rearrangement) : Those rearrangement reactions in which migrating group is nucleophilic and thus migrates to electron deficient centre which may be carbon, nitrogen and oxygen.



Bridged or non-classical carbocation

X= Nucleophilic species, Y = Electronegative group, B = Another nucleophile.

(2) **Rearrangement or migration to electron rich atoms** (Electrophilic rearrangement) : Those rearrangement reactions in which migrating group is electrophile and thus migrates to electron rich centre.

(3) **Rearrangement or migration to free radical species** (Free radical rearrangement) : Those rearrangement reactions in which the migrating group moves to a free radical centre. Free radical rearrangements are comparatively rare.

(4) **Aromatic rearrangement :** Those rearrangement reactions in which the migrating group moves to aromatic nucleus. Aromatic compounds of the type (*I*) undergo rearrangements in the manner $\begin{array}{c} X-H \\ X-Y \\ mentioned below, \end{array}$



The element *X* from which group *Y* migrates may be nitrogen or oxygen.

Isomerism

Organic compounds having same molecular formula but differing from each other at least in some physical or chemical properties or both are known as isomers (Berzelius) and the phenomenon is known as isomerism.

The difference in properties of isomers is due to the difference in the relative arrangements of various atoms or groups present in their molecules. Isomerism can be classified as follows:



Constitutional or structural isomerism

(1) **Chain, nuclear or skeleton isomerism :** This type of isomerism arises due to the difference in the nature of the carbon chain (*i.e.*, straight or branched) which forms the nucleus of the molecule.

Examples :

(i) C_4H_{10} : $CH_3 - CH_2 - CH_2 - CH_3$, $_{n-Butane}$

CH₃ Isobutane

> (ii) C_5H_{12} : (Three) $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$, *n*-Pentane

> > CH_3

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

 $\hfill\square$ Except alkynes chain isomerism is observed when the number of carbon atoms is four or more than four.

□ Chain isomers differ in the nature of carbon chain, *i.e.*, in the length of carbon chain.

□ The isomers showing chain isomerism belong to the same homologous series, *i.e.*, functional group, class of the compound (Cyclic or open) remains unchanged.

□ Chain and position isomerism cannot be possible together between two isomeric compounds. If two compounds are chain isomers then these two will not be positional isomers.

(2) **Position isomerism :** It is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain.

(ii)
$$C_3$$
 H_6 Cl_2 :
 $CH_3 - CCl_2 - CH_3$, $CH_3 - CH_2 - CH - Cl_2$,
 $2,2$ -Dichloro propane, $1,1$ -Dichloro propane
(gemdihalide)
 $CH_3 - CH - CH_2$, $CH_2 - CH_2 - CH_2$
 Cl Cl Cl Cl
 $1,2$ -Dichloro propane
(Vicdihalide)
 $(\alpha,\gamma$ -dihalide)

□ Aldehydes, carboxylic acids (and their derivatives) and cyanides do not show position isomerism.

☐ Monosubstituted alicylic compounds and aromatic compounds do not show position isomerism.

□ Structural isomers which differ in the position of the functional group are called regiomers. For example, (i) $CH_3 - CH_2 - CH_2 - OH$ (ii) $CH_3 - CH - CH_3$ | OH

(3) **Functional isomerism :** This type of isomerism is due to difference in the nature of functional group present in the isomers. The following pairs of compounds always form functional isomers with each other.

Examples :
(i) Alcohols and ethers
$$(C_n H_{2n+2}O)$$

 C_2H_6O : $CH_3 - CH_2 - OH$; $H_3C - O - CH_3$
Ethylatcohol Dimethylether
 C_3H_8O : $CH_3 - CH_2 - CH_2 - OH$; $C_2H_5 - O - CH_3$
 $n - propylatcohol$; $C_4H_{10}O$; $CH_3 - CH_2 - CH_2 - CH_2 - OH$;
 $C_2H_5 - O - C_2H_5$
Diethylether

(ii) Aldehydes, ketones and unsaturated alcohols ... etc. ($C_n H_{2n}O$)

 \sim

$$C_{3}H_{6}O: CH_{3} - CH_{2} - CHO ; CH_{3} - C - CH_{3} ;$$

Propionald ehy de ; $CH_{3} - C - CH_{3} ;$

$$CH_{2} - CH - CH_{3} ; CH_{2} = CH - CH_{2}OH$$

Ally kalcohol
I,2-Epoxy propane

(iii) Acids, esters and hydroxy carbonyl compounds ...etc. $(C_n H_{2n}O_2)$

$$C_2H_4O_2$$
: CH_3COOH ; $HCOOCH_3$
Aceticacid Methylformate

 $C_3H_6O_2$: $CH_3 - CH_2 - COOH$; CH_3COOCH_3 ; Propionic acid; Methylacetate; Methylacetate;

$$CH_{3}CHCHO ; CH_{3} - C - CH_{2} - OH$$

$$OH$$

$$(CH_{3} - C - CH_{2} - OH_{2} - OH_{$$

(iv) Alkynes and alkadienes (
$$C_n H_{2n-2}$$
)
 C_4H_6 : $CH_3 - CH_2 - C \equiv CH$; $H_2C = CH - CH = CH_2$;
 $1-Butyne$
 $CH_3 - C \equiv C - CH_3$; $H_2C = C = CH - CH_3$
 $1,2-Butadiene$

(v) Nitro alkanes and alkyl nitrites ($-NO_2$ and -O-N=O)

$$C_{2}H_{5}NO_{2}: C_{2}H_{5} - N \bigvee_{O}^{O}; C_{2}H_{5} - O - N = O$$

Nitro ethane

(vi) Amines (Primary, secondary and tertiary)





(viii) Oximes and amides

$$C_2H_5NO: CH_3 - CH = NOH; CH_3 - C - NH_2$$

Acetaldoxime Acetamide

 \sim

(4) Ring-chain isomerism : This type of isomerism is due to different modes of linking of carbon atoms, i.e., the isomers possess either open chain or closed chain sturctures.

$$C_{6}H_{12}: \qquad \begin{array}{c} H_{2} \\ H_{2}C \\ H_{2}C \\ H_{2} \\ CH_{2} \\ C$$

□ Ring – chain isomers are always functional isomers.

(5) Metamerism : This type of isomerism is due to the difference in the nature of alkyl groups attached to the polyvalent atoms or functional group. Metamers always belong to the same homologous series. Compounds like ethers, thio-ethers ketones, secondary amines, etc. show metamerism.

(i)
$$C_5H_{13}N$$
: $C_3H_7 - N \leftarrow \begin{array}{c} CH_3 \\ CH_3 \\ Dimethyl propylamine \end{array}$; $C_2H_5 - N \leftarrow \begin{array}{c} C_2H_5 \\ CH_3 \\ Diethyl methylamine \end{array}$
(ii) $C_6H_{15}N$: $C_3H_7 - NH - C_3H_7$;
 $C_2H_5 - NH - C_4H_9$
Butyl ethylamine

I If same polyvalent functional group is there in two or more organic compounds, then chain or position isomerism is not possible, there will be metamerism e.q.,

Alkenes does not show metamerism.

(6) Tautomerism

(i) The type of isomerism in which a substance exist in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism and the different forms are called tautomers (or tautomerides).

The term **tautomerism** (Greek: *tauto* = same; meros = parts) was used by Laar in 1885 to describe the phenomenon of a substance reacting chemically according to two possible structures.

(ii) It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as **Desmotropism** (Desmos = bond and tropos = turn). If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is a dyad and if the hydrogen atom travels from first to third atom in a chain, the system is a **triad**.

(a) Dyad system : Hydrocyanic acid is an example of dyad system in which hydrogen atom oscillates between carbon and nitrogen atoms. $H - C \equiv N \Rightarrow$ $C \equiv N - H$

(b) Triad system

Keto-enol system : Polyvalent atoms are oxygen and two carbon atoms.

Examples :

$$\begin{array}{ccc} O & H & OH \\ \parallel & \mid & \mid \\ -C-C & \rightleftharpoons & -C = C - \\ \mid & \mid \\ (\text{Keto}) & (\text{Enol}) \end{array}$$

Acetoacetic ester (Ethyl acetoacetate) :

$$CH_{3} - C - CH_{2}COOC_{2}H_{5} \approx CH_{3} - C - CHCOOC_{2}H_{5}$$

Keto form (92.1%) $\approx CH_{3} - C = CHCOOC_{2}H_{5}$
Enol form (7.9%)

Acetoacetic ester gives certain reactions showing the presence of keto group (Reactions with HCN,

H_2NOH , $H_2NNHC_6H_5$, etc.) and certain reactions showing the presence of enolic group (Reactions with $Na, CH_3COCl, NH_3, PCl_5, Br_2$ water and colour with neutral sta

FeCl₃, etc.).

Enolisation is in order

 $CH_{3}COCH_{3} < CH_{3}COCH_{2}COOC_{2}H_{5} < C_{6}H_{5}COCH_{2}COOC_{2}H_{5}$ $< CH_{3}COCH_{2}COCH_{3} < CH_{3}COCH_{2}CHO$

Acid catalysed conversion $CH_3 - C - CH_{\frac{H}{2} - R}$

$$CH_{3} \xrightarrow{-H \oplus CH} CH_{3} \xrightarrow{-$$

Base catalysed conversion

$$CH_{3} \xrightarrow{C} C-CH_{2} - R \xrightarrow{OH^{-}} CH_{3} \xrightarrow{C} C-CH - R$$

$$\xrightarrow{O} CH_{3} \xrightarrow{C} C-CH - R$$

(c) Triad system containing nitrogen : Examples Nitrous acid exists in 2 forms

$$H - O - N = O$$
 \longrightarrow $H - N = O$
Nitro form

Nitro acinitro system

$$CH_3 - CH_2 - N \bigotimes_{O}^{O} \xrightarrow{} CH_3 - CH = N \underset{OH}{\swarrow} O$$
nitro form(i) Aciform(ii)

(iii) Characteristics of tautomerism

(a) Tautomerism (cationotropy) is caused by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule. The change is accompanied by the necessary rearrangement of single and double bonds.

(b) It is a reversible intramolecular change.

(c) The tautomeric forms remain in dynamic equilibrium. Hence, their separation is a bit difficult. Although their separation can be done by special methods, yet they form a separate series of stable derivatives.

(d) The two tautomeric forms differ in their stability. The less stable form is called the labile form. The relative proportion of two forms varies from compound to compound and also with temperature, solvent etc. The change of one form into another is also catalysed by acids and bases.

(e) Tautomers are in dynamic equilibrium with each other and interconvertible (=).

(f) Two tautomers have different functional groups.

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(g) Tautomerism has no effect on bond length.

(h) Tautomerism has no contribution in stabilising the molecule and does not lower its energy.

(i) Tautomerism may occur in planar or nonplanar molecules.

 \Box Keto=enol tautomerism is exhibited only by such aldehydes and ketones which contain at least one α -hydrogen.

For example

CH₃CHO, CH₃CH₂CHO, CH₃COCH₂COCH₃ etc,.

□ Tautomerism is not possible in benzaldehyde (C_6H_5CHO) , benzophenone $(C_6H_5COC_6H_5)$, tri methyl acetaldehyde, $(CH_3)_3C$ – *CHO* and chloral CCl_3 – *CHO* as they do not have α – *H*.

Number of structural isomers

Molecular formula	Number of isomers		
Alkanes			
$C_4 H_{10}$	Two		
$C_5 H_{12}$	Three		
$C_{6}H_{14}$	Five		
$C_{7}H_{16}$	Nine		
$C_{8}H_{18}$	Eighteen		
$C_{9}H_{20}$	Thirty five		
$C_{10}H_{22}$	Seventy five		
Alkenes and			
cycloalkanes			
C_3H_6	Two (One alkene + one cycloalkane)		
C_4H_8	Six (Four alkene + 2 -		
	cycloalkane)		
$C_5 H_{10}$	Nine (Five alkenes + 4 – cycloalkanes)		
Alkynes			
C_3H_4	Two		
C_4H_6	Six		
Monohalides			
C_3H_7X	Two		
C_4H_9X	Four		
$C_5H_{11}X$	Eight		
Dihalides			
$C_2H_4X_2$	Two		
$C_3H_6X_2$	Four		
$C_4H_8X_2$	Nine		
$C_5 H_{10} X_2$	Twenty one		

Alcohols and ethers	
C_2H_6O	Two (One alcohol and one ether)
C_3H_8O	Three (Two alcohols and one ether)
$C_4H_{10}O$	Seven (Four alcohols and three ethers)
$C_5H_{12}O$	Fourteen (Eight alcohols and six ethers)
Aldehydes and	
ketones	
C_3H_6O	Two (One aldehyde and one ketone)
C_4H_8O	Three (Two aldehydes and one ketone)
$C_5H_{10}O$	Seven (Four aldehydes and three ketone)
Monocarboxylic acids and esters	
a a	

$C_2H_4O_2$	Two (One acid and one ester)		
$C_3H_6O_2$	Three (One acid and two esters)		
$C_4H_8O_2$	Six (Two acids and four esters)		
$C_5 H_{10} O_2$	Thirteen (Four acids and nine esters)		
Aliphatic amines			
C_2H_7N	Two (One 1°-amine and one 2°- amine)		
C_3H_9N	Four (Two 1°-amines, one 2°- amine and one 3°-amine)		
$C_4 H_{11} N$	Eight (Four 1º-amines, three 2º-		

amines and one 3°-amines)

Aromatic compounds

$C_{8}H_{10}$	Four
$C_9 H_{12}$	Nine
$C_7 H_8 O$	Five

Geometrical or cis-trans isomerism

The compounds which have same molecular formula but differ in the relative spatial arrangement of atoms or groups in space are known as geometrical isomers and the phenomenon is known as geometrical isomerism. The isomer in which same groups or atoms are on the same side of the double bond is known as *cis* form and the isomer in which same groups or atoms are on the opposite side is called *trans*-isomer.

Examples :

H - C - COOH	H - C - COOH
H - C - COOH Maleic acid (<i>cis</i>)	HOOC - C - H Fumaric acid (<i>trans</i>)
$H_3C - C - COOH$	$H_3C - C - COOH$
H - C - COOH Citraconic acid (<i>cis</i> -isomer)	HOOC - C - H Mesaconic acid(<i>trans</i> -isomer)

(1) **Conditions for geometrical isomerism :** Compound will show geometrical isomerism if it fulfils the following two conditions

(i) There should be frozen rotation about two adjacent atoms in the molecule.

(a) > C = 6 frozen rotation about carbon, carbon double bond in alkenes.



(b) \checkmark frozen rotation about carbon, carbon single bond in cycloalkanes.

(c) > C = N - frozen rotation about carbon, nitrogen double bond in oxime and imine.

(ii) Both substituents on each carbon should be different about which rotation is frozen.

If these two conditions are fulfilled, then compound will show geometrical isomerism.

□ The compounds of the following type will not show geometrical isomerism.

$$\begin{array}{cccc} a-C-a & x-C-a & a-C-a \\ \parallel & \parallel & \parallel \\ x-C-y & a-C-a & x-C-x \end{array}$$

(2) Distinction between cis- and trans- isomers

(i) **By cyclization method :** Generally, the *cis*isomer (*e.g.* maleic acid) cyclises on heating to form the corresponding anhydride while the *trans*-isomer does not form its anhydride.

$$\begin{array}{c} H - C - COOH \\ \parallel \\ H - C - COOH \\ Maleic acid(cis) \end{array} \xrightarrow{Heat} \begin{array}{c} H - C - CO \\ \parallel \\ H - C - COOH \\ Maleic anhy dride \end{array} O$$

□ Note that the two reacting groups (*-COOH*) are near to each other.

$$\begin{array}{c} H - C - COOH \\ || \\ HOOC - C - H \\ Fimaric acid (trans) \end{array}$$
 No anhy dride

□ Note that the two reacting groups (*-COOH*) are quite apart from each other, hence cyclisation is not possible.

(ii) **By hydroxylation** (Oxidation by means of $KMnO_4, OsO_4$ or H_2O_2 in presence of OsO_4): Oxidation (Hydroxylation) of alkenes by means of these reagents proceeds in the *cis*-manner. Thus the two geometrical

isomers of an alkene leads to different products by these reagents. For example,



(iii) **By studying their dipole moments :** The *cis*isomer of a symmetrical alkene (Alkenes in which both the carbon atoms have similar groups) has a definite dipole moment, while the *trans*-isomer has either zero dipole moment or less dipole moment than the *cis*isomer. For example, 1,2-dichloroethylene and butene-2.

H - C - Cl	H - C - Cl	$H - C - CH_3$	$H - C - CH_3$
		5	
H-C-Cl	Cl-C-H	$H - C - CH_3$	$CH_3 - C - H$
cis-Dichloroethy lene	trans-Dichloroethy lene	cis-Butene -2	trans-Butene -2
$(\mu = 1.9D)$	$(\mu = 0.0D)$		$(\mu = 0.0D)$

In *trans*-isomer of the symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

In case of unsymmetrical alkenes, the *cis*-isomer has higher dipole moment than the corresponding *trans*-isomer.

For Example,

$$H_3C-C-Cl$$
 CH_3-C-Cl
 \parallel \parallel
 CH_3-CH_2-C-Cl $Cl-Cl-CH_2CH_3$
 $cis-2,3-Dichloropentene-2$ $(Less dipolemoment)$

Similar is the case with hexene-2.

$$H_{3}C \xrightarrow{H_{2}C} C = C \underbrace{CH_{2}CH_{2} - CH_{3}}_{H_{cis-Hexene-2(more polar)}}$$

$$H \xrightarrow{C} C = C \underbrace{CH_{2}CH_{2} - CH_{3}}_{H_{cH_{3}}}$$

$$H \xrightarrow{C} C = C \underbrace{CH_{2}CH_{2} - CH_{3}}_{H_{rans-Hexene-2(Less polar)}}$$

(iv) **By studying other physical properties:** (a) The *cis*-isomer of a compound has higher boiling point due to higher polarity, higher density and higher refractive index than the corresponding *trans*-isomer (*Auwers-skita rule*).

$$\begin{array}{cccc} CH_{3}-C-H & CH_{3}-C-H \\ CH_{3}-C-H & H-C-CH_{3} \\ cis^{-2-Butene} & 1^{\circ}C \\ h.p. & -139^{\circ}C & -106^{\circ}C \\ \end{array}$$

(b) The *trans*-isomer has higher melting point than the *cis*-isomer due to symmetrical nature and more close packing of the *trans*-isomer.

(v) *Stability* : *Trans*-isomer is more stable than *cis*-isomer due to symmetrical structure.

☐ Terminal alkenes such as propene, 1-butene and 2-methyl propene do not show geometrical isomerism.

□ *Cis-trans* isomers are configurational isomers but not mirror images, hence *cis* and *trans* isomers are always *diastereomers*.

□ Non-terminal alkenes with the same atoms or groups either on one or both the carbon atoms of the double bond such as 2-methyl-2-butene, 2,3-dimethyl – 2 – butene etc. do not show geometrical isomerism.

(3) *E* and *Z* system of nomenclature : '*Cis*' and '*Trans*' designations cannot be used if four different atoms or groups are attached to the carbon atoms of a double bond.

$$a > C = C < d e$$

In such cases, *E* and *Z* system of nomenclature is used. This system is based on a priority system developed by *Cahn, Ingold* and *Prelog*.

In this system, the two atoms or groups attached to each of the doubly bonded carbon are put in order of preference on the basis of sequence rules. The symbol 'E' is assigned to an isomer in which the atoms or groups of higher preference are on the opposite side (E from German word *Entgegen* = across or opposite).

The symbol 'Z' is assigned to an isomer in which the atoms or groups of higher preference are on the same side (Z from German word, Zusammen = together).

$$\begin{array}{c} 1 \\ 2 \\ \hline \\ E-\text{isomer} \end{array} \begin{array}{c} 0 \\ \hline \\ 1 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ \\ Z-\text{isomer} \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ \\ Z-\text{isomer} \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ Z-\text{isomer} \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \\ 2 \\ \hline \end{array} \begin{array}{c} 0 \\ \hline \end{array} \end{array}$$

 \Box 1 signifies higher preference and 2 signifies lower preference. Preference in most of the cases '*Z*' corresponds to *cis*-form and '*E*' to *trans*-form. However, there are many exceptions.

The following rules are followed for deciding the precedence order of the atoms or groups;

(i) Higher priority is assigned to the atoms of higher atomic number. For example, the order of preference in the following atoms, H, Cl, I, Br is : I (at. no. 53)> Br (at. no. 35)>Cl (at. no. 17)>H (at. no. 1).

(ii) If isotopes of the same element are attached, the isotope with higher mass number is given higher order of preference. For example, deuterium $\begin{pmatrix} 2 \\ 1 \end{pmatrix}$ is assigned higher priority in comparison to hydrogen $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$.

(iii) In the groups, the order of preference is also decided on the basis of atomic number of first atom of the group. For example, in the following set,

 $-Cl, -OH, -COOH, -NH - CH_3, -SO_3H$.

The order of the precedence is :

$$-Cl > -SO_{3}H > -O_{4}H > -NHCH_{3} > -COOH_{4}$$

(atno.16) (atno.8) (atno.7) (atno.6)

When the order of preference of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered. For example, in the set $-CH_2 - CH_3$, -COOH, the order cannot be decided on the basis of first atom as it is same in all the groups. However, in $-CH_2 - CH_3$, the second atom is carbon, in $-CH_3$, the second atom is hydrogen while in -COOH, the second atom is oxygen. Hence, the order of preference is :

(iv) A doubly or triply bonded atom is considered equivalent to two or three such atoms. For example,

The group > C = O is equal to > C - O and the group

0

$$-C \equiv N$$
 is equal to $- \begin{matrix} N \\ -C - N \\ N \end{matrix}$.

(4) Number of geometrical isomers in polyenes

(i) When a compound has *n* double bonds and ends of a polyene are different, the number of geometrical isomers = 2^n

$$C_6H_5 - CH = CH - CH = CH - CH = CH - CH = CH - Cl$$

The given compound has four double bonds and the two ends are different (One is C_6H_5 and other is *Cl*). Therefore, number of geometrical isomers $= 2^n = 2^4 = 16$.

(ii) When the ends of polyene are same.

Case I: When number of double bonds (=*n*) is even then the number of geometrical isomers $=2^{n-1}+2^{[(n/2)-1]}$

$$Cl - CH = CH - CH = CH - CH = CH - CH = CH - Cl$$

Number of geometrical isomers $= 2^{n-1} + 2^{(n/2)-1}$ = $2^3 + 2^1 = 8 + 2 = 10$.

Case II : When number of double bonds (=n) is odd.

Number of geometrical isomers
$$= 2^{n-1} + 2^{\left\lfloor \frac{n+1}{2} \right\rfloor^{-1}}$$

 $C_6H_6 - CH = CH - CH = CH - CH = CH - C_6H_5$
(n=3, odd)

Number of geometrical isomers $= 2^2 + 2^{2-1}$ = $2^2 + 2^1 = 4 + 2 = 6$.

(5) Geometrical Isomerism in nitrogen compounds

(i) Geometrical isomerism due to C = N -bond.

The important class of compounds exhibiting geometrical isomerism due to C = N-bond are oximes, nitrones, hydrazones and semicarbazones. But the most common compound is oxime.

Oximes : In aldoxime, when hydrogen and hydroxyl groups are on the same side, the isomer is known as syn. (analogous to *cis*) and when these groups are on the opposite side, the isomer is known as

anti (analogous to trans)

$$\| N - OH$$
Syn-benzaldoxi me

 $C_{6}H_{5} - C - H$

 $C_6H_5 - C - H$ || HO - NAnti-benzaldoxi me

In ketoximes the prefixes **syn** and **anti** indicate which group of ketoxime is syn or anti to hydroxyl group. For example:

$$CH_3 - C - C_2H_5$$

 \parallel this compound will be named as;
 $N - OH$

(a) Syn-ethyl methyl ketoxime $\Rightarrow HO$ and C_2H_5 are syn or

(b) Anti-methyl ethyl ketoxime $\Rightarrow HO$ and C_2H_5 are anti.

Similarly consider the following structure

$$C_2H_5 - C - CH_3$$

 $N - OH$

Syn-methy lethy l ketoxime or Anti-ethy l methy l ketoxime

(ii) Geometrical isomerism due to N = N bond.

$$\begin{array}{ccc} C_6H_5-N & & C_6H_5-N \\ \parallel & & C_6H_5-N \\ \text{Syn-azobenzene} & & \text{Anti-azobenzene} \end{array}$$

(6) **Geometrical isomerism show by cumulatrienes :** Cumulatrienes (Trienes with three adjacent double bonds) show only geometric isomerism. This is because their molecule is planar, as such the terminal $-CH_3$ groups and H- atoms lie in the same plane. Therefore, in this case their planar structure can exist in two diastereoisomeric forms, *cis*and *trans*- but no enantiomeric forms are possible.

$$\begin{array}{c} H_{3}C\\H\end{array} > C = C = C = C < CH_{3}\\H\end{array}$$

$$\begin{array}{c} C = C = C = C < H\\H\end{array}$$

$$\begin{array}{c} H_{3}C\\H\end{array} > C = C = C = C < H\\CH_{3}\\H\end{array}$$

$$\begin{array}{c} H_{3}C\\H\end{array}$$

$$\begin{array}{c} C = C = C = C < H\\CH_{3}\\H\end{array}$$

(7) **Geometrical isomerism in cycloalkanes :** Disubstituted cycloalkanes show geometrical isomerism.



□ Certain compounds show geometrical as well optical isomerism. Such type of isomerism is known as **geometrical enantiomerism**.

Optical isomerism

(1) Compounds having similar physical and chemical properties but they have the ability to rotate the plane of polarised light either to the right (Clockwise) or to the left (Anticlockwise) are termed as optically active or optical isomers and the property is called optical activity or optical isomerism.

The optical activity was first observed in organic substances like quartz, rock-crystals and crystals of potassium chlorate (*KClO*₃), potassium bromate (*KBrO*₃) and sodium periodate (*NalO*₄).

(2) **Measurement of optical activity :** The measurement of optical activity is done in terms of specific rotation which is defined as the rotation produced by a solution of length of 10 centimetres (One

decimetre) and unit concentration (1 g/mL) for the given wavelength of the light at the given temperature.

Specific rotation, $[\alpha]_{wavelength}^{\nu c} = \frac{\alpha_{obs}}{l \times C}$

Where α_{obs} is the rotation observed, *l* is the length of the solution in decimeters and *C* is the number of grams in 1*mL* of solution. The specific rotation of the sucrose at 20°*C* using sodium light (*D*-line, λ =5893Å) is +66.5°*C* and is denoted as: $[\alpha]_D^{20°C} = +66.5°C(C = 0.02 g/mL$ water)

+ sign indicates the rotation in clockwise direction.

(3) On the basis of the study of optical activity, the various organic compounds were divided into four types :

(i) The optical isomer which rotates the plane of the polarised light to the right (Clockwise) is known as dextrorotatory isomer (Latin: dextro = right) or *d*-form or indicated by +*ve* sign.

(ii) The optical isomer which rotates the plane of the polarised light to the left (Anticlockwise) is known as laevorotatory isomer (Latin; laevo = left) or *l*-form or indicated by -ve sign.

(iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive due to external compensation. This mixture is termed as racemic mixture or *dl*-form or (\pm) mixture.

(iv) Optical isomer with a plane of symmetry is called *meso* form. It is optically inactive due to internal compensation, *i.e.*, the rotation caused by upper half part of molecule is neutralised by lower half part of molecule.

(4) **Chirality**, (i) *Definition* : A molecule (or an object) is said to be chiral or dissymmetric, if it is does not possess any element of symmetry and not superimposable on its mirror image and this property of the molecule to show non-superimposability is called chirality.

On the other hand, a molecule (or an object) which is superimposable on its mirror image is called achiral (non-dissymmetric or symmetric).

To understand the term chiral and achiral let us consider the alphabet letters 'P' and 'A' whereas 'P' is chiral, 'A' is achiral as shown in fig.



(ii) *Elements of symmetry* : There are three elements of symmetry,

(a) *Plane of symmetry* : It may be defined as a plane which divides a molecule in two equal parts that are related to each other as an object and mirror image. e.g.,

$$COOH$$

$$H - C - OH$$

$$H - C - OH$$

$$H - C - OH$$

$$COOH$$

(b) Centre of symmetry : It may be defined as a point in the molecule through which if a line is drawn in one direction and extended to equal distance in opposite direction, it meets another similarregroupmetry atom, eg.



Since *trans* form contains a centre of symmetry, it is optically inactive.

(c) Alternating axis of symmetry : A molecule is said to possess an alternating axis of symmetry if an oriention indistinguishable from the original is obtained when molecule is rotated Q degree around an axis passing through the molecule and the rotated molecule is reflected in a mirror that is perpendicular to the axis of rotation in step (I).



(iii) Symmetric, Asymmetric and Dissymmetric molecules

(a) *Symmetric molecules* : If any symmetry is present in the molecule then molecule will be symmetric molecule.

(b) *Dissymmetric molecules* : Molecule will be a dissymmetric molecule if it has no plane of symmetry,

no centre of symmetry and no alternating axis of symmetry.

(c) Asymmetric molecules : Dissymmetric molecule having at least one asymmetric carbon is known as asymmetric molecule. All asymmetric molecules are also dissymmetric molecules but the reverse is not necessarily true.



(iv) *Chiral or asymmetric carbon atom* : A carbon bonded to four different groups is called a chiral carbon or a chirality centre. The chirality centre is indicated by asterisk. *e.g.*,

$$\begin{array}{ccc} a & CH_3 \\ d - C^* - b & HO - C^* - H \\ c & COOH \\ Lactic acid \end{array}$$

□ Carbons that can be chirality centres are sp^3 - hybridised carbons; sp^2 and sp -hybridised carbons cannot be chiral carbons because they cannot have four group attached to them.

 $\hfill\square$ Isotopes of an atom behave as different group in stereoisomerism.



 $\hfill\square$ Carbon of the following groups will not be a chiral carbon

$$-CH_3, -CH_2OH, -CHX_2, -CHO, -C-Z$$

□ Maleic acid (HOOC - CH = CH - COOH) show geometrical isomerism while malic acid

 $(HOOC - CH_2 - CHOH - COOH)$ show optical isomerism.

(5) Calculation of number of optical isomers

(i) If molecule is not divisible into two identical halves and molecule has n asymmetric carbon atoms then

Number of optically active forms $= 2^n = a$

Number of enantiomeric pair	= a / 2
Number of racemic mixture	= a / 2

Number of *meso* form = 0

(ii) If molecule is divisible into two identical halves, then the number of configurational isomers depends on the number of asymmetric carbon atoms.

Case I : When compound has even number of carbon atoms, i.e., $n = 2, 4, 8, 10, 12, \dots$:

(i) Number of optically by active forms $= a = 2^{n-1}$

(ii) Number of enantiomeric pairs = a/2

(iii) Number of racemic mixture = a/2

(iv) Number of meso forms $= m = 2^{(n/2)-1}$

(v) Total number of configurational isomers = a + m

Case II : When compound has odd number of carbon atoms, *i.e.*, $n = 3, 5, 7, 9, 11, \dots$:

(i) Number of optically active forms = $a = 2^{n-1} - 2^{(n-1)/2}$

(ii) Number of enantiomeric pairs = a/2

(iii) Number of racemic mixutre = a/2

(iv) Number of *meso* forms $= m = 2^{(n-1)/2}$

(v) Total number of configurational isomers = a + m

(6) Optical activity of compounds containing one asymmetric carbon

Examples :

$$CH_3 - CHOH - COOH$$
; $CH_3 - CHOH - CHO$
Lactic acid
 $CH_2OH - CHOH - CHO$; $C_6H_5 - CHCI - CH_3$
Giveeraldev de

Any molecule having one asymmetric carbon atom exists in two configurational isomers which are nonsuperimposible mirror images.

(I) and (II) have the same molecular formula, the same structure but different configurations, hence (I) and (II) are known as configurational isomers. (I) and (II) are nonsuperimposable mirror images, hence (I) and (II) are optical isomers. Configurational isomers which are nonsuperimposable mirror images are known as **enantiomers**. Thus (I) and (II) are

enantiomers. Pair of (I) and (II) is known as enantiomeric pair.

(i) **Properties of Enantiomers :** All chemical and physical properties of enantiomers are same except two physical properties.

Mode of rotation : One enantiomer rotates light to the right and the other by an **equal magnitude** to the left direction.

(ii) **Racemic Mixture** : An equimolar mixture of two enantiomers is called a racemic mixture (or racemate, \pm form, (*dl*) form or racemic modification). Such a mixture is optically inactive because the two enantiomers rotate the plane polarised light equally in opposite directions and cancel each other's rotation. This phenomenon is called **external compensation**.

 \Rightarrow Racemic mixture can be separated into (+) and (-) forms. The separation is known as **resolution**.

 \Rightarrow The conversion of (+) or (-) form of the compound into a racemic mixture is called **racemisation**. It can be caused by heat, light or by chemical reagents.

 \Rightarrow Racemic mixture is designated as being (±) or (dl).

(7) Optical activity of compounds containing two asymmetric carbon

Case I : When molecule is not divisible into two identical halves.

The number of optical isomers possible in this case is four $(a = 2^2 = 4)$. Further there will be two pairs of enantiomers and two racemic modifications. In practice also it is found to be so.

Configurational isomers which are not mirror images are known as **diastereomers**.

Properties of Diastereomers : Diastereomers have different physical properties, *e.g.*, melting and boiling points, refractive indices, solubilities in different solvents, crystalline structures and specific rotations. Because of differences in solubility they often can be separated from each other by fractional crystallisation; because of slight differences in molecular shape and polarity, they often can be separated by chromatography.

Diastereomers have different chemical properties towards both **chiral** and **achiral** reagents. Neither any two diastereomers nor their transition states are mirror images of each other and so will not necessarily have the same energies. However, since the diastereomers have the same functional groups, their chemical properties are not very dissimilar.

Case II : When molecule is divisible into two identical halves.

Number of optical isomers $= a = 2^{2-1} = 2$

Number of meso forms $= m = 2^0 = 1$

Total number of configurational isomers = 3

(8) **Optical activity in compounds containing no assymmetric carbon :** Although the largest number of known optically active compounds are optically active due to the presence of chiral carbon atom, some compounds are also known which do not possess any chiral carbon atom, but on the whole their molecules are chiral (such molecules were earlierly called **dissymmetric**); hence they are optically active. Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spirans) and properly substituted biphenyls.

(i) *Allenes* : Allenes are the organic compounds of the following general formulae.

$$>C=C=C=C$$

Allenes exhibit optical isomerism provided the two groups attached to each terminal carbon atom are different, *i.e.*,



(ii) *Alkylidene cycloalkanes and spiro compounds*: When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spirans.



(iii) **Biphenyls**: Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two nonsuperimposable mirror images of each other. Such types of stereoisomerism which is due to restricted rotation about single bond, is known as atropisomerism

and the stereoisomers are known and **atropisomers**. Examples



The above discussion leads to the conclusion that the essential condition for optical isomerism is the molecular disymmetry or molecular chirality and not the mere presence of a chiral centre. However, it may be noted that the molecules having only one chiral centre are always chiral and exhibit optical isomerism.

(9) **Fischer projection formulae :** The arrangement of the atoms or groups in space that characterises a stereoisomer is called its configuration.

Emil Fischer (1891) provided an easy method to represent the three dimensional formulae of various organic molecules on paper. *Fischer projection is, thus, a planar representation of the three dimensional structure.*

By convention, the following points are followed in writing the Fischer formula.

(i) The carbon chain of the compound is arranged vertically, with the most oxidised carbon at the top.

(ii) The asymmetric carbon atom is in the paper plane and is represented at the interaction of crossed lines.



(iii) Vertical lines are used to represent bonds going away from the observer, *i.e.*, groups attached to the vertical lines are understood to be present behind the plane of the paper.

(iv) Horizontal lines represent bonds coming towards the observer, *i.e.*, groups attached to the horizontal lines are understood to be present above the plane of the paper.

(10) **Name of optical isomers :** Following three nomenclatures are used for optically active compounds,

(i) **D,L.** System of nomenclature : This nomenclature is mainly used in sugar chemistry or optically active polyhydroxy carbonyl compounds. This

nomenclature was given by Emil Fischer to designate the configurations of various sugars relative to the enantiomeric (+) and (-) glucose as reference.

All sugars whose Fischer projection formula shows the *OH* group on the chiral carbon atom adjacent to the terminal CH_2OH group on the right hand side belong to the *D*-series. Similarly if *OH* is on the left hand side, then the sugars belong to the *L*-series.

H - C - OH	HO - C - H
CH ₂ OH D-series	CH_2OH L-series
Examples :	
СНО	СНО
$H - \overset{ }{C} - OH$	HO - C - H
CH_2OH	CH_2OH
D(d)gly ceraldehy de	L(l)gly ceraldehy de
Or D(1) alu aanal dahu da	or () ohu aanaldahu da
D(+)giy ceraidely de	L(-)giy ceraidely de

 \Rightarrow It must be noted that there is no relation between the sign of rotation (+, - or *d*, *l*) and the configuration (*D* and *L*) of an enantiomer.

 \Rightarrow Any compound that can be prepared from, or converted into D(+) glyceraldehyde will belong to Dseries and similarly any compound that can be prepared from, or converted into L(-) glyceraldehyde will belong to the *L*-series.

 \Rightarrow This nomenclature is also used in α -amino acids.

(ii) *Erythro and Threo system of nomenclature* : This nomenclature is used only in those compounds which have

(a) Only two chiral carbons and

(b) The following structure, R' - Cab - Cbc - R''

i.e., out of six substituents on two asymmetric carbons, at least two should be same.

When two like groups in Fischer projection formula are drawn on the same side of the vertical line, the isomer is called *erythro* form; if these are placed on the opposite sides, the isomer is said to be *threo* form.

R'	CH ₃	CH ₃
	I	
a - C - b	H - C - Cl	H - C - Cl
	1	
c - C - b	H - C - Br	Br - C - H
	1	
<i>R</i> ″	C_6H_5	C_6H_5
Erythro form	Erythro form	Threo form

(c) R,S Nomenclature (Absolute configuration)

The order of arrangement of four groups around a chiral carbon (stereocentre) atom is called the absolute configuration around that atom. System which indicates the absolute configuration was given by three chemists **R.S. Cahn, C.K. Ingold** and **V. Prelog**. This system is known as (R) and (S) system or the **Cahn-Ingold Prelog** system. The letter (R) comes from the latin **rectus** (means right) while (S) comes from the latin **sinister** (means left). Any chiral carbon atom has either a (R) configuration or a (S) configuration. Therefore, one enantiomer is (R) and other is (S). A racemic mixture may be designated (R) (S), meaning a mixture of the two. (R) (S) nomenclature is assigned as follows :

Step I : By a set of sequence rules given below the atoms or groups connected to the chiral carbon are assigned a priority sequence.

Sequence Rules for Order of Priority

Rule 1 : If all four atoms directly attached to the chiral carbon are different, priority depends on their atomic number. The atom having highest atomic number gets the highest priority, *i.e.*, (1). The atom with the lowest atomic number is given the lowest priority, *i.e.*, (2), the group with next higher atomic number is given the next higher priority (3) and so on. Thus,

$$CI \qquad (3)$$

$$| \qquad |$$

$$F - C - I = (4) - C - (1)$$

$$| \qquad |$$

$$Br \qquad (2)$$

$$F CI Br I$$
Increasing atomic number
$$(4) (3) (2) (1)$$
Increasing priority



Rule 2 : If two or more than two isotopes of the same element is present, the isotope of higher atomic mass receives the higher priority.

$_1H^{-1}$	$^{1}H^{2}$	Η°
Incre	easin	B
3	2	(1)

Rule 3 : If two or more of the atoms directly bonded to the chiral carbon are identical, the atomic number of the next atoms are used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at the first point of difference along the chain. The atom that has attached to it an atom of higher priority has the higher priority.

In this example the atoms connected directly to the chiral carbon are iodine and three carbons. Iodine has the highest priority. Connected, to the three carbons are 2*H* and *Br*, 2*H* and *C* and 2*H* and *C*. Bromine has the highest atomic number among *C*,*H* and *Br* and thus CH_2Br has highest priority among these three groups (*i.e.*, priority no. 2).The remaining two carbons are still identical (*C* and 2*H*) connected to the second carbons of these groups are 2*H* and *I* and 2*H* and *C*. Iodine has highest priority among these atoms, so that $-CH_2 - CH_2 - I$ is next in the priority list and $CH_2 - CH_2 - CH_3$ has the last priority.

$$I - CH_{2} - CH_{2} - CH_{2} - CH_{2} - Br = (3)$$

Rule 4 : If a double or a triple bond is linked to chiral centre the involved atoms are duplicated or triplicated respectively.

$$- \underset{|}{C} = O = - \underset{|}{C} - O; - C = N = - \underset{|}{C} - N; - C - OH = - \underset{|}{C} - OH$$

By this rule, we obtained the following priority sequence $\dot{R}\dot{H} = CR_2$, -CN, CH_2OH , CHO, CO, COOH

In	cro	20	in	
111	CIE	as	111	١g

Step 2 : The molecule is then visualised so that the group of lowest priority (4) is directed away from the observes (At this position the lowest priority is at the bottom of the plane). The remaining three groups are in a plane facing the observer. If the eye travels clockwise as we look from the group of highest priority to the groups of second and third priority (*i.e.*, $1 \rightarrow 2 \rightarrow 3$ with respect to 4) the configuration is designated as *R*. If arrangement of groups is in anticlocwise direction, the configuration is designated as *S*.

For example:



Let us apply the whole sequence to bromochlorofluoro methane.

$$Br - \begin{matrix} F & (3) \\ - C - H = & (1) - C - (4) \\ - C & (2) \end{matrix}$$

In this Fischer projection the least priority number is not at the bottom of the plane.

In such cases the Fischer projection formula of the compound is converted into another equivalent projection formula in such a manner that atom or group having the lowest priority is placed vertically downward. This may be done by two **interchanges** between four priority numbers. The first interchange involves the two priority numbers, one is the least priority number and other is the priority number which is present at the bottom of the plane. In the above case first interchange will takes place between 2 and 4.



First interchange of two groups at the chiral centre inverts the configuration and this gives enantiomer of the original compound. Thus (*A*) and (*B*) are enantiomer. The second interchange involves the remaining two groups.



Glyceraldehyde (For example) has one asymmetric carbon, hence it has two configurational isomers (I) and (II).

$$\begin{array}{ccc} CHO & CHO \\ H - C - OH & HO - C - H \\ CH_2OH & CH_2OH \\ (R)gly ceraklehy de & (S)gly ceraklehy de \\ (I) & (II) \end{array}$$

One can draw a number other configurations for glyceraldehyde but each of them will be a repetition of either (I) or (II). In this connection it is important to note that if two projection formulae differ by an odd number of interchanges (1, 3, 5, 7,) of positions of groups on the chiral carbon, they are different. But if the two differ by an even number of interchanges (2, 4, 6,) they are identical.

For example :

$$\begin{array}{c}
CHO \\
H - \begin{array}{c}
CHO \\
- \\
C - OH \\
- \\
H \\
CH_2OH \\
(I)
\end{array} \xrightarrow{H, CH_2OH} CH_2OH \xrightarrow{CHO} CHO \\
- \\
CH_2OH \\
(II)
\end{array} \xrightarrow{between OH, CHO} CHO \\
H \\
(II)
\end{array}$$



Thus (*I*), (*III*) and (*V*) are identical. Similarly (*II*) and (*IV*) are identical.

(11) **Resolution of racemic modifications :** The separation of racemic mixture into its enantiomers is known as resolution.

 $\square Group X reacts with group O to give new group W.$

(12) Asymmetric synthesis and Walden inversion

(i) Asymmetric synthesis : The synthesis of an optically active compound (asymmetric) from a symmetrical molecule (having no asymmetric carbon) without resolution to form (+) or (-) isomer directly is termed asymmetric synthesis. For example the O reduction of pyruvic acid ($CH_3 - C - COOH$) in presence of nickel catalyst gives (±) lactic acid (racemic mixture). On the other hand, pyruvic acid is reduced to (-) lactic acid only by yeast.



(ii) **Walden inversion:** The conversion of (+) form into (-) form and vice-versa is called **Walden inversion**. When an atom or group directly linked to an asymmetric carbon atom is replaced; the configuration of the new compound may be opposite to (inverse) that of the original, *i.e.*,

 CH_3 CH_3 COOH PCl_5 $\xrightarrow{AgOH} HO - C - H$ H - C - OH $\rightarrow Cl - C - H$ CH,COOH CH,COOH CH,COOH (+) Malic acid (-) Malic acid (-) Chloro succinic acid СООН COOH PCl_5 AgOH $\rightarrow H - C - Cl$ $\rightarrow H - C - OH$ CH₂COOH CH₂COOH (+) Malic acid (+) Chloro succinic acid

General Organic Chemistry 1041

Conformational isomerism

(1) **Definition :** The different arrangement of atoms in a molecule which can be obtained due to rotation about carbon-carbon single bond are called conformational isomers (conformers) or rotational isomers (rotamers). This type of isomerism is found in alkanes and cycloalkanes and their substituted derivatives.

It may be noted that rotation around a C-C sigma bond is not completely free. It is in fact hindered by an energy barrier of 1 to 20 $kJ \ mol^{-1}$ in different bonds. There is a possibility of weak repulsive interactions between the bonds or electron pairs of the bonds on adjacent carbon atoms. Such type of repulsive interaction is known as **torsional strain**.

(2) **Difference between conformation and configuration :** The term conformation should not be confused with the *configuration which relates to those spatial arrangements of the atoms of a molecule that can be changed only by the breaking and making of bonds whereas the spatial arrangements in conformation are changed simply by rotation about a single bond.*

(3) **Representation of conformations :** Conformers can be represented in two simple ways. These are : (i) Saw horse representation and (ii) Newman projection

(i) Saw horse representation : In this projection, the molecule is viewed along the axis of the model from an oblique angle. The central carbon-carbon bond (C-C) is draw as a straight line slightly tilted to right for the sake of clarity. The front carbon is shown as the lower left hand carbon and the rear carbon is shown as the upper right hand carbon. The three bonds around each carbon atom (C-H) in ethane or C-C in higher alkanes) are shown by three lines.



(ii) **Newman projection** : This is a simple method to represent the conformations. In this method, the molecule is viewed from the front along the carboncarbon bond axis. The two carbon atoms forming the σ bond are represented by two circles; one behind the other so that only the front carbon is seen. The front

carbon atom is shown by a point whereas the carbon further from the eye is represented by the circle. Therefore, the C-H bonds of the front carbon are depicted from the centre of the circle while C-H bonds of the back carbon are drawn from the circumference of the circle at an angle of 120° to each other.

(4) Conformation in alkanes

(i) **Conformations of ethane** : When one of the carbon atom is kept fixed and other is rotated about C-C bond an infinite numbers of isomers are possible. Out of all the conformations for ethane, only two extreme conformations are important and these are:

(a) Staggered conformation

(b) Eclipsed conformation



Staggered conformation of ethane is more stable than eclipsed.

(ii) **Conformations of propane** : The next higher member in alkane series, propane $(CH_3 - CH_2 - CH_3)$ also has two extreme conformations, the energy barrier in propane is14*kJmol*⁻¹, which is slightly higher than that in ethan H_3 CH_3



(iii) **Conformations of butane** : As the alkane molecule becomes larger, the conformation situation becomes more complex. In butane $(CH_3 - CH_2 - CH_2 - CH_3)$, for example, the rotation about the single bond between two inner atoms (C_2 and C_3) is considered. In this case, all the staggered as well as eclipsed conformations will not have same stability and energy because of different types of interaction between C-C (of methyl) and C-H bonds.

The lowest energy conformation will be the one, in which the two methyl groups are as far apart as possible *i.e.*, 180° away form each other. This conformation will be maximum staggered, most stable and is called **anti or trans conformation** (marked I). Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms through an angle of 60° as shown ahead.



As is clear from the above Newman projection the Gauche or Skew conformations (III and V) are also staggered. However, in these conformations, the methyl groups are so close that they repel each other. This repulsion causes gauche conformations, to have about 3.8 kJ mol⁻¹ more energy than anti conformation. This conformations II and VI are eclipsed conformations. These are unstable because of repulsions. These are 16 $kJ mol^{-1}$ less stable than anti conformation. Conformation IV is also eclipsed and it is least stable having energy 19 kJ mol^{-1} more than anti conformation. This is because of repulsion between methyl-methyl groups which are very closed together. It is called **fully eclipsed conformation**.

The **order of stability** of these conformations is, Anti > Skew or Gauche > Eclipsed > Fully eclipsed.

(5) Conformations in cycloalkanes

(i) **Stability of cycloalkanes** : Compounds with three and four membered rings are not as stable as compounds with five or six membered rings.

The German chemist Baeyer was the first to suggest that the instability of these small rings compounds was due to angle strain. This theory is known as **Baeyer-strain theory**.

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is convert into a cyclic compound, a definite distortion of this normal



angle takes place leading to the development of a strain in the molecule.

Baeyer assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).

$$d = \frac{1}{2} \left[109.5 - \frac{2(n-2)}{n} \times 90 \right] \quad \text{or} \quad d = \frac{1}{2} [109.5 - \alpha]$$

Where n = number of carbon-carbon bonds in cycloalkane ring; α = inner bond angle in the cycloalkane ring.

Angle strain
$$\propto d \propto \frac{1}{\text{inner angle}}$$
; Stability $\propto \frac{1}{d} \propto \text{inner angle}(\alpha)$

Now let us take the case of three to eight membered cyclic compounds.



The positive and negative values of (d) indicate whether the inner angle is less than or more than the normal tetrahedral value.

Beayer thus predicted that a five membered ring compound would be the most stable. He also predicted that six membered ring compounds would be less stable and as the cyclic compounds become larger than five membered ring, then they would become less and less stable.

Contrary to what Baeyer predicted, however cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of sides increase. Thus Baeyer strain theory is applicable only to **cyclopropane**, **cyclobutane and cyclopantane**.

The mistake that Baeyer made was to assume that all cyclic compounds are planar. But only cyclopropane is planar and other cycloalkanes are not planar. Cyclic compounds **twist** and **bend** in order to achieve structure that minimises the three different kinds of strain and that can destabilise a cyclic compound.

(a) **Angle strain** is the strain that results when the bond angle is different from desired tetrahedral bond angle of 109.5° .

(b) **Torsional strain** is caused by repulsion of the bonding electrons of one substituent with bonding electrons of a nearby substituent.

(c) **Steric strain** is caused by atoms or groups of atoms approaching each other too closely.

(ii) **Conformation of cyclohexane** : Despite Baeyer's prediction that five-membered cyclic compounds would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation**. In a chair conformation of cyclohexane all bond angles are 109.38° which is very close to the 109.5° and all the adjacent carbon-hydrogen bonds are staggered.



 $\Rightarrow~$ Each carbon in chair conformation has an axial bond and an equatorial bond.

 \Rightarrow Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.

 \Rightarrow If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus

C-1, C-3 and C-5 axial bonds are above the plane

C-2, C-4 and C-6 axial bonds are below the plane



 \Rightarrow Thus C-1 axial and C-2 axial are *trans* to each other. Similarly C-1 and C-5 axials are *cis* to each other.

 \Rightarrow If axial bond on carbon-1 will be above the plane then equatorial bond on this carbon will be below the plane.



(a) Thus C-1 equatorial and C-2 equatorial bonds are *trans*.

(b) C-1 axial and C-2 equatorial will be *cis*.

 \Rightarrow As a result of rotation about carbon-carbon single bonds cyclohexane rapidly interconverts between two stable chair conformations. This interconversion is known as ring -flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.



 \Rightarrow Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the boat conformation is less stable than the chair conformation by 11 *kcal/mole*. Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.

The boat conformations is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 \mathring{A} apart but the vander Waal's radii is 2.4 \mathring{A} . The flagpole hydrogens are also known as *trans* nuclear hydrogens.

☐ The relative stabilities of the four conformations of cyclohexane decrease in the order:

Chair > twist boat > boat > half chair.



∠ Wohler synthesised the first organic compound urea in the laboratory.

✓ The number of optical isomers of a compound depends on its structure and number of asymmetric carbon atoms present in its molecule.

Stereoisomers that are not mirror images of each other are called diastereomers.

✗ Order of priority for both asymmetric carbon atoms using sequence rules is

-OH > -COOH > -CH(OH)COOH > -H

∠ The nitration and sulphonation of alkanes involve free radicals.

🙇 Carbenes undergo insertion reactions.

 \swarrow Alkanes usually undergo free radical substitution when hydrogen is replaced by a halogen. It is catalysed by benzoyl peroxide (C_6H_5COO)₂.

The polymerisation of alkenes is free radical addition reaction.

∠ Allyl free radical ($CH_2 = CH - CH_2$) is more stable than *n*-propyl free radical ($CH_3CH_2CH_2$).

∠ The stability of free radicals is explained on the basis of hyperconjugation or conjugation.

✓ Propene is more reactive than ethene towards electrophilic addition reaction due to the formation of more stable 2° carbocation.

E The reactivity of alkyl halides in SN^1 is $3^\circ > 2^\circ > 1^\circ > methyl$ while SN^2 is methyl $> 1^\circ > 2^\circ > 3^\circ$.

\mathscr{L} Polar solvents favour SN^1 while non polar solvents favour SN^2 reactions.

 \mathcal{L} Dipole moment of $CHCl_3$ is less than that of CH_2Cl_2 . This is because in CH_2Cl_2 all bond moments reinforce each other while in $CHCl_3$ the bond moment of one of the Cl opposes the net moment of the other two.

 \mathcal{L} Low concentration of nucleophiles favour SN^1 while high concentration favour SN^2 .

 \swarrow In SN^1 the attack of the nucleophile may be from either side and so recimization takes place. However, in SN^2 the attack of the nucleophile takes place from back side. So it leads to inversion of configuration.

& Hunsdieker reaction proceeds via free radical

mechanism.





1.	In methane molecule, the carbon are arranged as	the hydrogen atoms around [DPMT 1980; MNR 1981; MP PET 1997
	(a) Square planar	(b) Tetrahedral
	(c) Triangular	(d) Octahedral
2.	In carbon tetrachlorid	le, four valence of carbon
	are directed to four cor	rners of [CPMT 1973, 77]
	(a) Rectangle	(b) Square
	(c) Tetrahedron	(d) None of these
3.	In alkene (ethene) nui	mber of sp^2 hybrid carbon
	atoms are	
	(a) 1	(b) 2
	(c) 3	(d) O
4.	Each carbon atom in	benzene is in the state of
	nybrialzation	T 1072 82 80. MD DMT 1002.
	[CPM	KCET (Med.) 1999; DCE 2001
	(a) sp^{3}	(b) sp^2
	(c) <i>sp</i>	(d) $s^3 p$
5۰	Which of the following	g hybridisation has highest
	percentage of s-charact	ter [BHU 1986]
	(a) sp^{3}	(b) sp^2
	(c) <i>sp</i>	(d) None of these
6.	The hybridisation prese	ent in C_2H_2 is[EAMCET 1993]
	(a) <i>sp</i>	(b) sp^2
	(c) sp^{3}	(d) dsp^2
7.	What hybrid orbitals	will form the following
,.	compound $H_3C - CH = 0$	$CH - CH_2 - CH_3$ [AFMC 1991]
	(a) sp and sp^3	(b) sp^2 and sp^3
	(c) sp and sp^2	(d) Only sp^3
8.	The compound in whic	ch carbon uses only its sp^3
	hybrid orbitals for bon	d formation is[IIT-JEE 1989]
	(a) HCOOH	(b) $(NH_2)_2 CO$
	(c) $(CH_3)_3 COH$	(d) $(CH_3)_3 CHO$
	S	

9. A straight chain hydrocarbon has the molecular formula C_8H_{10} . The hybridisation for the carbon atoms from one end of the chain to the other are

respectively sp^3 , sp^2 , sp^2 , sp^3 , sp^2 , sp^2 , sp and sp. The structural formula of the hydrocarbon would 17. be [CBSE PMT 1992] (a) $CH_3 - C \equiv C - CH_2 - CH = CH - CH = CH_2$ (b) $CH_3 - CH_2 - CH = CH - CH_2 - C \equiv C - CH = CH_2$ (c) $CH_3 - CH = CH - CH_2 - C \equiv C - CH = CH_2$ (d) $CH_3 - CH = CH - CH_2 - CH = CH - C \equiv CH$ Which of the following has a bond formed by 10. overlap of $sp - sp^3$ hybrid orbitals[MNR 1993; UPSEAT 2001, 02] (iv) $H - C \equiv C - H$ (a) $CH_3 - C \equiv C - H$ (b) $CH_3 - CH = CH - CH_3$ (c) $CH_2 = CH - CH = CH_2$ (d) $HC \equiv CH$ The bond between carbon atom (1) and carbon 11. atom (2) in compound $N \equiv C - CH = CH_2$ involves the hybridised carbon as [IIT-JEE 1987; DCE 2000] (a) sp^2 and sp^2 (b) sp^3 and sp(c) sp and sp^2 (d) sp and sp Number of π bonds in 12. $CH_2 = CH - CH = CH - C \equiv CH$ is [Kurukshetra CEE 1991; KCET 2000] (a) 2 (b) 3 (d) 5 (c) 4 Number of π electrons present in naphthalene is 13. [AFMC 1991] (a) 4 (b) 6 (c) 10 (d) 14 Number of π electrons in cyclobutadienyl anion 14. $(C_4 H_4)^{-2}$ is [IIT-JEE 1991] (a) 2 (b) 4 (c) 6 (d) 8 Homolytic fission of C - C bond in ethane gives an 15. intermediate in which carbon is [IIT-JEE 1992] (a) sp^3 hybridised (b) sp^2 hybridised (d) sp^2d hybridised (c) *sp* hybridised In the reaction 16. $\underset{H}{\overset{Br}{\longrightarrow}} C = C \underset{H}{\overset{Catalyst}{\longrightarrow}} BrCH_2 CH_2 Br$ The hybridisation states of carbon atoms 1, 2, 3, 4 are [MP PET 1994] (a) 1 and 2 sp^2 ; 3 and 4 sp^3 (b) 1 and 2 sp^2 ; 3 and 4 sp

(c) 1, 2, 3 and 4 sp

(d) 1, 2 sp^3 ; 3, 4 sp^2

In which of the compounds given below is there more than one kind of hybridisation (sp, sp^2, sp^3) for carbon

(i)
$$CH_3CH_2CH_2CH_3$$

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

$$CH_2 = CH - CH = CH_2$$

(*iv*)

[CBSE PMT 1995]

(a) (*ii*) and (*iv*)

(iii)

(d) (ii)

18. Examine the following common chemical structures to which simple functional groups are often attached



Which of these systems have essentially planar geometry

		[CBSE PMT 1995]
	(a) (<i>i</i>) and (<i>v</i>)	(b) (<i>ii</i>) and (<i>iii</i>)
	(c) (<i>ii</i>), (<i>iii</i>) and (<i>iv</i>)	(d) (<i>iv</i>)
19.	The structure of di-chlor	romethane is[MP PMT 1995]
	(a) Tetrahedral	(b) Trigonal
	(c) Linear	(d) Hexagonal
20.	The numbers of sigma (σ) bonds in 1-butene is
		[MP PMT 1995]
	(a) 8	(b) 10
	(c) 11	(d) 12
21.	Which of the following	g statements is false for
	isopentane	
		[MP PET 1996]
	(a) It has three CH_3 groups of CH_3	oups
	(b) It has one CH_2 group	р
	(c) It has one <i>CH</i> group	
	(d) It has a carbon w	which is not bonded to
hydr	ogen	
22.	The number of σ bonds	in o-xylene is[MP PET 1996]
	(a) 6	(b) 9
	(c) 12	(d) 18
23.	In benzene the total nun	nber of σ bonds is[MP PMT 1997]
	(a) 3	(b) 6

(d) 12 (c) 9

(c) (*ii*) and (*iii*)
24.	The number of sp^3 hy	bridized carbon atoms in
	cyclohexene are	[MP PMT 1997]
	(a) 2	(b) 3
	(c) 4	(d) 6
25.	The number of π bonds	in 3-hexyne-1-ene is
		[MP PMT 1999]
	(a) 1	(b) 2
	(c) 3	(d) 4
26.	Example of sp^2 hybridiz	ation is [CPMT 1997]
	(a) CH_3^+	(b) <i>CH</i> ₃
	(c) $C_2 H_5^+$	(d) $C_2 H_5$
27.	Select the molecule which	ch has only one π – bond
		[Pb. PMT 1998]
	(a) $CH = CH$	(b) $CH_2 = CHCHO$
	(c) $CH_3CH = CH_2$	(d) $CH_3CH = CHCOOH$
28.	Carbon atoms in the con	npound $(CN)_4 C_2$ are
		[Roorkee 1999]
	(a) <i>sp</i> hybridized	
	(b) sp^2 hybridized	
	(c) sp and sp^2 hybridize	ed
	(d) sp , sp^2 and sp^3 hybrid	ridized
29.	Acetylene molecules con	tain [DCE 1999]
	(a) 5σ bond	
	(b) 4σ bond and 1π bor	nd
	(c) 3σ and 2π	
	(d) 3σ and 3π	
30.	Number of unhybrid	ised orbitals in vinyl
	acetylene are	
	(a) 2	[KPMI 1999]
	(c) 4	(d) 6
31.	Maximum bond energy of	of $C-H$ bonds is found in
	the compound	[RPMT 1999]
	(a) Ethane	(b) Ethene
	(c) Ethyne	(d) Equal in all the three
32.	Ethylene possess	[RPET 1999]
	(a) Two sigma and two	pi bonds
	(b) Two pi bonds	ai bond
	(d) Four sigma and one	ni bond
33.	The hybridization invo	olved in the six carbon
55.	atoms of benzene is	[BHU 1999]
	(a) $3sp^3$, $3sp^2$	(b) $3sp^3$, $3sp$
	(c) All 6 <i>sp</i>	(d) All $6sp^2$
34.	1, 3-butadiene has	[JIPMER 2000]

	(a) sp and sp^2 hybridised C-atoms				
	(b) sp , sp^2 and sp^3 hybridized C-atoms				
	(c) Only sp^2 hybridised <i>C</i> -atoms				
	(d) Only <i>sp</i> hybridised <i>C</i>	'-atoms			
35.	Which of the following $C - H$ bond has the lowestbond dissociation energy[CBSE PMT 2000]				
	(a) Primary (1°) $C-H$ b	oond			
	(b) Secondary (2°) $C-H$	<i>I</i> bond			
	(c) Tertiary (3°) $C-H$	bond			
	(d) All of these				
36.	Number of σ and π box	nds present in 1- butene-3-			
	yne respectively are [RP]	MT 1999; MP PET 2000; DCE 2000]			
	(a) $7\sigma, 5\pi$	(d) $5\sigma, 2\pi$			
25	(c) $\delta \sigma, \delta \pi$ Which is an acidic hydro	(u) $0\sigma_{2\pi}$			
3/•	(a) $CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}$	(b) $CH_2C \equiv CCH_2$			
	(c) $CH_{2}C \equiv CH$	(d) $CH_2 = CH - CH = CH_2$			
38.	A carbon-carbon triple	bond in ethype $(-C \equiv C^{-})$			
900	consists of	,,,,,,,,,			
		[AMU 2000]			
	(a) All σ bonds				
	(b) Two σ bonds and or	the π -bond			
	(c) One σ bond and two	π bonds			
39.	Toluene has	PMT 2000: Kerala CET 2005]			
55.	(a) 6σ and 3π bond	(b) 9 σ and 3 π bond			
	(c) 9 σ and 6 π bond	(d) 15 σ and 3 π bond			
40.	In compound X, all the	e bond angles are exactly			
	109°28', X is	[DPMT 2000]			
	(a) Chloroform	(b) Carbon tetrachloride			
41	(c) Chloromethane Which of the following	(d) lodoform			
41.	trigonal hybridization				
	tigonal nyoriaization	[MH CET 2000]			
	(a) sp^3	(b) <i>sp</i>			
	(a) sp^3 (c) sp^2	[MH CET 2000] (b) sp (d) dsp^2			
42.	(a) sp^3 (c) sp^2 The types of hybridiz	(b) sp (d) dsp^2 zation present in 1, 2-			
42.	(a) sp^3 (c) sp^2 The types of hybridized butadiene are	(b) sp (d) dsp^2 zation present in 1, 2-			
42.	(a) sp^3 (c) sp^2 The types of hybridized butadiene are	[MH CET 2000] (b) sp (d) dsp^2 zation present in 1, 2- [MH CET 2000]			
42.	(a) sp^3 (c) sp^2 The types of hybridize butadiene are (a) sp, sp^2 and sp^3	[MH CET 2000] (b) sp (d) dsp^2 zation present in 1, 2- [MH CET 2000] (b) sp^2 and sp^3			
42.	(a) sp^3 (c) sp^2 The types of hybridize butadiene are (a) sp, sp^2 and sp^3 (c) sp^2 and sp	[MH CET 2000] (b) sp (d) dsp^2 zation present in 1, 2- [MH CET 2000] (b) sp^2 and sp^3 (d) sp and sp^3			
42. 43 .	(a) sp^3 (c) sp^2 The types of hybridized butadiene are (a) sp, sp^2 and sp^3 (c) sp^2 and sp The <i>C</i> - <i>H</i> bond distance in (a) <i>C H</i>	[MH CET 2000] (b) sp (d) dsp^2 zation present in 1, 2- [MH CET 2000] (b) sp^2 and sp^3 (d) sp and sp^3 s longest in [BHU 2001] (b) C H			
42. 43.	(a) sp^3 (c) sp^2 The types of hybridize butadiene are (a) sp, sp^2 and sp^3 (c) sp^2 and sp The <i>C</i> - <i>H</i> bond distance i (a) C_2H_2 (c) C_1H_2	[MH CET 2000] (b) sp (d) dsp^2 zation present in 1, 2- [MH CET 2000] (b) sp^2 and sp^3 (d) sp and sp^3 s longest in [BHU 2001] (b) C_2H_4 (d) C_1H_4			

44. Conjugated double bond is present in

[RPMT 1999; JIPMER 2001]

	(a) 1, 2-butadiene	(b) 1, 3-butadiene (d) β -butylene		(c) Graphite is in plana tetrahedral form	ar form while diamond is in
45 .	In which of the fo	ollowing species is the		(d) Graphite is covalen	t and diamond is ionic
	underlined carbon havin	ng <i>sp</i> ³ hybridisation[AIEEE 20	oo2j∙		2 carbon atoms m
	(a) $CH_3 \underline{C}OOH$	(b) $CH_3 \underline{C}H_2OH$		$CH_2 = C = CH_2$	[BHU 2003]
	(c) $CH_3 \underline{C}OCH_3$	(d) $CH_2 = \underline{C}H - CH_3$		(a) <i>sp</i> , <i>sp</i>	(b) sp^2, sp^2
46.	The $H - C - H$ bond ang	le in <i>CH</i> 4 is [MP PET 2002]		(c) sp^2 , sp	(d) sp^{3}, sp^{2}
	(a) 109°28'	(b) 107 ° 28'	58.	Hydrogen bonding is m (a) C_2H_5OH	aximum in [UPSEAT 2003] (b) $CH_3 - O - CH_3$
	(c) 90°	(d) 180°		(c) $(CH_3)_2 C = O$	(d) CH_3CHO
47.	The hybridisation of ca of $HC \equiv C - CH = CH_2$ is	The probability of $C - C$ single bond [RPMT 2002]	59.	How many methyl gr	oup are present in 2, 5-
	(a) $sp^3 - sp^3$	(b) $sp - sp^2$		(a) 2	(b) 3
	(c) $sp^3 - sp$	(d) $sp^2 - sp^3$		(c) 4	(d) 5
48.	The shape of ethylene m	nolecule is [AFMC 2002]	60.	Which one of the foll	lowing does not have sp^2
-	(a) Square planar	(b) Furan		hybridised carbon	[AIEEE 2004]
	(c) Trigonal planar	(d) Tetrahedral		(a) Acetonitrile	(b) Acetic acid
49.	Acetylene molecule has	carbon in [Kerala (Engg.) 200 2	2]	(c) Acetone	(d) Acetamide
	(a) <i>sp</i> - hybridisation	(b) sp^2 - hybridisation	61.	Allyl cyanide contain σ	- and π -bonds[MP PET 2004]
	(c) sp^3 - hybridisation	(d) sp^3d - hybridisation		(a) 9σ , 3π	(b) 9σ , 9π
50.	In the formation of n	nethane molecule, carbon	6.0	(c) 3σ , 4π	(d) 5σ , 7π
50.	makes use of		62.	Strongest actuals (a) $HC = CH$	[MP PMT 2004]
		[DPMT 2001; MP PMT 2002]		(a) $HC = CH$	(d) $C_{2}n_{6}$
	(a) <i>sp</i> -hybridised orbit	als (b) sp^2 -hybridised orbita	als	C = C hand is found	
	(c) sp^3 -hybridised orbi	tals (d) Unhybridised orbital	63. ls	-C = C - bond is round (a) Ethene	(b) Butene
51.	In graphite C-atom is in	state [CPMT 2002]		(c) Ethyne	(d) Glycerine
	(a) sp^{3}	(b) <i>sp</i>		C	H ₃
	(c) sp^2	(d) None of these		Ĺ	
52.	How many π-bonds ar molecule	e present in naphthalene	64.	Number of σ bonds in) [СРМТ 1994]
		[RPMT 2002]		(a) 6	(b) 15
	(a) 3	(b) 4	6-	(c) 10	(d) 12
52	(C) 5 Hybridisation state of C	(a) o	65.	Number of bonds in being (a) 6σ and 3π	$\begin{array}{c} \text{nzene} \qquad \text{[DPMT 2005]} \\ \text{(b) } 12\sigma \text{ and } 3\pi \end{array}$
53.	(a) sn	(b) sn^2		(c) 3π and 12π	(d) 6σ and 6π
	(a) sp	(d) sp^{3}	66.	Which is most acidic of	the following [J & K 2005]
- 4	(C) sp	(a) sp a - hands present in part 4		(a) Methane	(b) Acetylene
54.	The number of σ and γ		-	(c) 1-butene	(d) Neo-pentane
	(a) 10. 3	(b) 3, 10	67.	The enolic form of acet	one contains [Pb. PMT 2002]
	(c) 4, 9	(d) 9, 4		(a) 88 bounds, 2π -bounds (b) 9σ -bounds 1π -bound	and 2 lone pairs
55.	Which one of the follow	ing is more acidic[DPMT 2002]	(c) 9σ -bonds, 2π -bond	ds and 1 lone pairs
	(a) Butane	(b) 1-butene		(d) 10 σ -bonds, 1 π -bonds	nds and 1 lone pairs
-	(c) 1-butyne	(d) 2-butyne	_		-
56.	Graphite is soft while di	amond is hard because[BHU 2	2003]	Dipole moment, reso	nance and reaction
	(a) Graphine is in power (b) Diamond has $an^2 b$	upridization but graphita		interme	diates
	han m ³ hahridiaati	nyoriuizationi out graphite			
	nas <i>sp</i> ² nybridizatio	11	1.	Which has zero dipole i	moment[NCERT 1990; BHU 2001]

				General Organic	Chemistry 1047
	(a) <i>cis</i> -2-butene	(b) <i>trans</i> -2-butene	12.	Carboxylic acids are	easily ionised. The main
	(c) 1-butene	(d) 2-methyl-1-propene		reason of this statemen	t [UPSEAT 1999]
2.	Dipole moment is show	vn by [DCE 1999]		(a) Absence of α -hydrog	gen
	(a) 1, 4-dichloro benze	ene		(b) Resonance stabilisa	tion of carboxylate ion
	(b) Cis-1, 2-dichloro et	hane		(c) Reactivity of α -hydr	rogen
	(c) Trans-1, 2-dichloro	, 2-pentene		(d) Hydrogen bond	
	(d) Trans-1, 2-dichloro	ether	13.	C - C' bond length in b	enzene lies between single
3.	Which compound show	vs dipole moment[RPMT 2002]		and double bond. The re	eason is [RPET 1999]
	(a) 1,4-di-chloro benze	ene		(a) Resonance	(b) Isomerism
	(b) 1, 2-di-chloro benz	ene		(c) Metamerism	(d) Inductive effect
	(c) Trans-1, 2-di-chlor	o ethene	14.	Credit for the ring struc	cture of benzene goes to
	(d) Trans-2-butene				[RPET 1999]
4.	Which of the following	is a polar compound		(a) Wholer	(b) Faraday
		[MH CET 2003]		(c) Kekule	(d) Baeyer
	(a) $C_2 H_6$	(b) CCl_4	15.	Polarisation of electr	ons in acroline may be
	(c) HCl	(d) CH_4		written as	
5٠	The dipole moment is	the highest for [AIIMS 2004]			[DCE 2000]
	(a) <i>Trans</i> -2-butene	(b) 1, 3-Dimethylbenzene		(a) $CH_2^{o-} = CH - CH^{o+} =$	0
	(c) Acetophenone	(d) Ethanol		(b) $CH_2^{\delta-} = CH - CH = O^{\delta}$	5+
6.	Resonance structure of	f molecule does not have [IIT-JEE 1984]		(c) $CH_2^{\delta-} = CH^{\delta+} - CH =$	0
	(a) Identical arrangem	ent of atoms		(d) $CH_2^{\delta+} = CH - CH = O^{\delta}$	δ-
	(b) Nearly the same er	nergy content	16	In the mixture of co	$\mathbf{n}_{\mathcal{C}} = H_{\mathcal{S}\mathcal{O}}$ and $H_{\mathcal{N}\mathcal{O}}$ the
	(c) The same number	of paired electrons	10.	nitrating species is	
	(d) Identical bonding				
7.	All bonds in benzene a	re equal due to		(a) $N_2 O_4$	(b) NO_2
		[Roorkee 1990; KCET 1998]		(c) <i>NO</i> ₂	(d) NO_2^-
	(a) Tautomerism	(b) Inductive effect	17.	Which of the following	are not aromatic[DCE 2001]
•	(c) Resonance	(d) Isomerism		(a) Benzene	
8.	Aromatic properties of	benzene are proved by		(b) Cyclo-octatetrareny	l dianion
		[MP PMI 1994]		(c) Tropyllium cation	
	(a) Aromatic sextet th	eory (b) Resonance theory		(d) Cyclopentadienyl ca	ation
	(c) Molecular orbital t	neory (d) All of these	18.	Arrangement of	
9.	which of the follow	wing will show aromatic		$(CH_3)_3 - C - (CH_2)_3 - CH$	$-CH_3 - CH_2 - CH_3$ when
	bellaviour			attached to benzyl or	an unsaturated group in
	~ ~	[KCET 1996]		increasing order of indu	uctive effect is
	$(a) \left[\right]$	(b)		(a) $(CH_3)_3 - C - < (CH_3)_2$	$-CH - < CH_3 - CH_2 -$
				(b) $CH_3 - CH_2 - < (CH_3)_2$	$-CH - < (CH_3)_3 - C -$
	\frown			(c) $(CH_3)_2 - CH - < (CH_3)_2$	$D_3 - C - < CH_3 - CH_2 - CH$
	(c)	(d)		(d) $(CH) = C = \langle CH =$	$CH = \langle (CH) \rangle = CH =$
				$(u) (cH_2)_3 - c - < cH_3 - c$	$\operatorname{cm}_2 = \langle \operatorname{cm}_3 \rangle_2 = \operatorname{cm}_2$
10.	Which one of the fo	ollowing orders is correct	19.	which of the followin	g is observed in ethylene
	regarding the inductiv	e effect of the substituents[CBs	SE PM	Г 1998]	[MH CET 2002]
	(a) $-NR_2 < -OR > -F$	(b) $-NR_2 > -OR > -F$		(a) Flectromeric effect	(b) Inductive effect
	(c) $-NR_2 < -OR < -F$	(d) $-NR_2 > -OR < -F$		(a) Homolytic fission	(d) None of these

- Benzene is unreactive because [KCET 1998] 11.
 - (a) It has double bonds
 - (b) It has carbon-carbon single bond
 - (c) Carbon are sp^2 hybridised
 - (d) π electrons are delocalised

- (c) Homolytic fission (d) None of these
- **20.** Cyclopentadienyl anion is [Orissa JEE 2003]
 - (a) Aromatic (b) Non-aromatic
 - (c) Non-planar (d) Aliphatic
- Orbital interaction between the sigma bonds of a 21. substitutent group and a neighbouring *pi* orbital is known as

(a) Hyperconjugation

- (b) Inductive effect
- (c) Steric effect
- (d) Dipole-dipole interactions
- (e) Electric quadruple interactions
- 22. Which of the following is the most stable compound

[BHU 2004]

[Kerala PMT 2004]

(a)
$$Ph_3C$$
 (b) Ph_2CH

(c) Ph_3CH_2 (d) $PhCH_2$

23. Which of the following will be most easily attacked by an electrophile [MP PET 2004]



24. Reactivity towards nucleophilic addition reaction of (I) *HCHO*, (II) *CH*₃*CHO*, (III) *CH*₃*COCH*₃ is

[Orissa JEE 2004]

 (a) II > III > I
 (b) III > II > I

 (c) I > II > III
 (d) I > II < III</td>

- 25. Which of the following resonating structures of 1methoxy-1, 3-butadiene is least stable[IIT Screening 2005]
 - (a) $\overset{\textcircled{}_{}}{CH}_2 CH = CH CH = \overset{\textcircled{}_{}}{O} CH_3$ (b) $CH_2 = CH_2 - \overset{\textcircled{}_{}}{CH} - CH = \overset{\textcircled{}_{}}{O} - CH_3$ (c) $\overset{\textcircled{}_{}}{CH}_2 - \overset{\textcircled{}_{}}{CH} - CH = CH - O - CH_3$
 - (d) $CH_2 = CH CH CH O CH_3$
- **26.** Which amongst the following is the most stable carbocation

[CBSE PMT 2005] *CH* 3

(a)
$$CH_3 - \frac{C}{C}$$

 CH_3
(b) $CH_3 - \frac{C}{C}$
 CH_3

(c) CH_3 (d) CH_3CH_3

27. Which is the decreasing order of stability
[IIT-JEE (Screening) 1993]

(i)
$$CH_3 - CH - CH_3$$

(ii) $CH_3 - \overset{+}{C}H - O - CH_3$
(iii) $CH_3 - \overset{+}{C}H - O - CH_3$
(a) $(i) < (ii) < (iii)$ (b) $(i) > (ii) > (iii)$
(c) $(iii) > (ii) > (i)$ (d) $(ii) > (iii) > (i)$

28. The order of decreasing stabilitv of the carbanions (1) $(CH_3)_3 \overline{\ddot{C}}$ (2) $(CH_3)_2 \overset{\overline{i}}{C} H$ (3) $CH_3 \overline{\ddot{C}} H_2$ (4) $C_6 H_5 \overline{\ddot{C}} H_2$ is (a) 1 > 2 > 3 > 4(b) 4 > 3 > 2 > 1(c) 4 > 1 > 2 > 3(d) 1 > 2 > 4 > 329. Choose the chain terminating step (1) $H_2 \rightarrow H^{\bullet} + H^{\bullet}$ (2) $Br_2 \rightarrow Br^{\bullet} + Br^{\bullet}$ (3) $Br^{\bullet} + HBr \rightarrow H^{\bullet} + Br_2$ (4) $H^{\bullet} + Br_2 \rightarrow HBr + Br^{\bullet}$ (5) $Br^{\bullet} + Br^{\bullet} \rightarrow Br_{2}$ [RPET 2000] (a) 1 (b) 3 (c) 4 (d) 5

30. The compound, which gives the most stable carbonium on dehydrogenation [UPSEAT 2001]
(a) CH₃ - CH - CH₂OH

(b)
$$CH_3 - CH_3$$

 CH_3
(c) $CH_3 - CH_2 - CH_2 - CH_2OH_2$
(c) $CH_3 - CH_2 - CH_2 - CH_2OH_2$
(d) $CH_3 - CH - CH_2 - CH_3$

$$H_3 = CH^2 + CH^2$$

 $CH_3 = CH^2$

Which of the following requires radical intermediate

[Orissa JEE 2004]

(a)
$$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - CH - CH_3$$

Br
(b) $CH_3 - CHO + HCN \rightarrow CH_3 - CH < \frac{CN}{OH}$

(c)
$$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - CH_2 - CH_2 - Br$$

(d) $CH_3CHO + NH_2OH \xrightarrow{H^+} CH_3 - CH = N - OH$

32. Which of the following species is paramagnetic in nature

	[NCERT 1984]
(a) Free radical	(b) Carbonium ion
(c) Carbanion	(d) All the above

- 33. In which of the following species the central *C*-atom is negatively charged [NCERT 1985]
 (a) Carbanion (b) Carbonium ion
 - (c) Carbocation (d) Free radical
- 34. Which of the following free radicals is most stable [NCERT 1982]

			Ľr
(a)	Primary	(b) Methyl	
(c)	Secondary	(d) Tertiary	,

35. Which of the following contains three pairs of electrons

General Organic Chemistry 1049 [BHU 1985] (c) *p*-dinitrobenzene (d) Nitrobenzene (a) Carbocation (b) Carbanion 46. An aromatic compounds among other things (c) Free radical (d) None of these should have a π -electron cloud containing **36.** Which of the following carbanion is most stable electrons where n can't be [NCERT 1983] [J & K 2005] (a) Methyl (b) Primary (a) 1/2 (b) 3 (c) Secondary (d) Tertiary (c) 2 (d) 1 Among the given cations, the most stable 37. Which of the following is an electrophile[J & K 2005] 47. carbonium ion is (a) H_2O (b) SO_3 [IIT-JEE 1981] (c) NH_3 (d) ROR (a) sec-butyl (b) *ter*-butyl (d) None of these (c) *n*-butyl 48. The presence of the chlorine atom on benzene ring makes the second substituent enter at a In the compound given below 38. position [J & K 2005] Ð NH H_3 (b) meta (a) ortho Ν (c) para (d) ortholpara 49. Which is the most stable carbocation [J & K 2005] СООН (a) iso-propyl (b) Triphenylmethyl (X)cation The correct order of the acidity of the positions (c) Ethyl cation (d) π -propyl cation [IIT-JEE Screening 2004] (X), (Y) and (Z) is (a) (Z) > (X) > (Y)(b) (X) > (Y) > (Z)(c) (X) > (Z) > (Y)(d) (Y) > (X) > (Z)Organic reactions and their mechanism **39.** *C*-*C* bond length in benzene is [MP PMT 1987; MP PMT 2001; AIIMS 2001] 1. To which of the following four types does this reaction belong $B^- + R - A \rightarrow B - R + A^-$ [Manipal MEE 1995] (a) 1.39 Å (a) Unimolecular electrophilic substitution (b) 1.54 Å (b) Bimolecular electrophilic substitution (c) 1.34 Å (c) Unimolecular nucleophilic substitution (d) Different in different bonds (d) Bimolecular nucleophilic substitution 40. Heterolysis of carbon-chlorine bond produces An alkyl halide may be converted into an alcohol 2. [MNR 1986; MP PET/PMT 1998] by (a) Two free radicals [Pb. PMT 2000] (b) Two carbonium ions (a) Elimination (b) Addition (c) Two carbanions (c) Substitution (d) Dehydrohalogenation (d) One cation and one anion CH_{2} $CH_2 - Cl$ 3. the bond that undergoes In CH_3CH_2OH , 41. heterolytic cleavage most readily is [IIT-JEE 1988] (a) C - C (b) C - O (c) C - H (d) O - HThe above reaction proceeds through [AMU 2000] 42. Which of the following intermediate have the (a) Nucleophilic substitution complete octet around the carbon atom[Orissa JEE 2003] (b) Electrophilic substitution (b) Carbanion ion (a) Carbonium ion (c) Free radical substitution (c) Free radical (d) Carbene (d) More than one of the above processes A solution of D (+) - 2-chloro-2-phenylethane in 43. SN^{-1} 4. Geometry of reaction intermediate in toluene racemises slowly in the presence of small reaction is amount of *SbCl*₅, due to the formation of[**IIT-JEE 1999**] [MH CET 2001] (a) Carbanion (b) Carbene (a) Tetrahedral (b) Planar (c) Free radical (d) Carbocation (c) Triangular bipyramidal (d) None of these The reagent in Friedel Craft's reaction is [DPMT 2005] 44. CH_{2} CH_{2} (a) Pyridine (b) RCOCl 5٠ $H_3C - C - Br + KOH(Aq.) \rightarrow H_3C - C - OH + KBr$ (c) RCOOH (d) *HCl* CH 3 CH_3 **45**. Which gives monosubstituted product [DPMT 2005]

(a) *o*-dinitrobenzene (b) *m*-dinitrobenzene

above reaction is

[RPMT 2003]

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	(a) SN^{-1}	(b) SN^2 (d) Both (a) and (b)	15.	Following reaction, $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$ is an example
_	(c) L_1			of
6.	(a) Mota directing	[Kerala (Med.) 2003]		(a) Elimination reaction (b) Free radical
	(a) Meta-ullecting	T		substitution
	(c) Para-directing	5	16	(c) Nucleophilic substitution(d)Electrophilic substitution
	(d) Not reactive	and does not undergo any	10.	(a) BC (b) $CH OH$
	substitution	and doed not andergo any		
	(e) Non-selective			(c) NH_3 (d) $AlCl_4$
7.	The most common compounds is	n type of reaction in aromatic [Orissa JEE 2003]	17.	The electrophile in the nitration of benzene is [Orissa JEE 2004]
	(a) Elimination re	action		(a) NO_2^+ (b) NO_2
	(b) Addition reacti	on		(c) NO^+ (d) NO_2^-
	(c) Electrophilic s	ubstitution reaction	18.	The following compound will undergo
	(d) Rearrangemen	t reaction		electrophilic substitution more readily than
8.	The function of Ale	Cl_3 in Friedel-Craft's reaction is		benzene [UPSEAT 2004]
		[KCET 2003]		(a) Nitrobenzene (b) Benzolc actu
	(a) To absorb HCl	(b) To absorb water	19.	Which represents nucleophilic aromatic
	(c) To produce nue	cleophile (d)To produce electrop	phile	substitution reaction
9.	Which of the follo Craft's reactions	owing can't be used in Friedal [AFMC 2004]		[Orissa JEE 2004] (a) Reaction of benzene with Cl_2 in sunlight
	(a) $FeCl_3$	(b) $FeBr_2$		(b) Benzyl bromide hydrolysis
	(c) $AlCl_3$	(d) NaCl		(c) Reaction of NaOH with dinitrofluorobenzene
10.	The nitration of a	compound is due to the[Pb. PMT 2	004]	(d) Sulphonation of benzene
	(a) <i>NO</i> ₂	(b) <i>NO</i> ₃	20.	Which is an electrophile[DCE 2000]
	(c) <i>NO</i>	(d) NO_{2}^{+}		(a) $AlCl_3$ (b) CN
	Dobudrohologonat	$(a) = \frac{1}{2}$		(c) NH_3 (d) CH_3OH
11.		[MH CET 2004]	21.	Strongest nucleophile is[BHU 2003](a) RNH 2(b) ROH
	(a) Nucleophilic su	Ibstitution reaction		(c) $C_6H_5O^-$ (d) CH_3O^-
	(b) Elimination re	action	22.	The major product obtained when Br_2/Fe is
	reaction			treated with M_{HN}^{O}
12.	Addition of <i>HCl</i>	to vinyl chloride gives 1, 1-		H_3C CH_3 is
	(a) Mesomeric effe	ect of Cl		[IIT-JEE Screening 2004]
	(b) Inductive effect	t of <i>Cl</i>		,0 ,0
	(c) Restricted rota	tion around double bond		
	(d) None of these			H_3C CH_3 H_3C CH_3
13.	Formation of et example of	nylene from acetylene is an		(a) $(\bigcirc \bigcirc \bigcirc$
	(a) Elimination re	action (b) Substitution reaction		Br Br
	(c) Addition reacti reaction	on (d) Condensation		
14.	Conversion of Ch	T_4 to CH_3Cl is an example of		H_3C \downarrow CH_3 H_3C \downarrow CH_3 CH_3
	which of the follow (a) Electrophilic s	ving reaction [Pb. CET 2001] ubstitution		(c) O O (d) O Br
	(b) Free radical ad	dition	23.	Which one of the following is least reactive in a
	(c) Nucleophilic su	Ibstitution		nucleophilic substitution reaction [CBSE PMT 2004]
	-			(a) $CU CU CI$ (b) $CU CU CI CI$

	(c) $(CH_3)_3 C - Cl$	(d) $CH_2 = CHCl$
24.	Among the following the	strongest nucleophile is [AIIMS 2005]
	(a) C_2H_5SH	(b) <i>CH</i> ₃ <i>COO</i> ⁻
	(c) CH_3NH_2	(d) NCCH $\frac{1}{2}$
25.	The reaction	[AIEEE 2005]
	$\begin{array}{c} O \\ R - C \swarrow \\ + Nu \rightarrow R - C \end{array}$	
	X	Nu
	when X is	
	(a) <i>Cl</i>	(b) <i>NH</i> ₂
	(c) OC_2H_5	(d) OCOR
26.	Elimination of bromin	ne from 2-bromobutane
	results in the formation (a) Equimolar mixture of (b) Predominantly 2-but (c) Predominantly 1-but (d) Predominantly 2-but	of [AIEEE 2004, 05] f 1 and 2-butene ene ene vne
27.	Examine the following	statements pertaining to
	an SN ² reaction	-
	(1) The rate of reaction concentration of the	n is independent of the nucleophile
	(2) The nucleophile atta	acks the C^- atom on the

- side of the molecule opposite to the group being displaced
- (3) The reaction proceeds with simultaneous bond formation and bond rupture/cleavage

Amongst the following which of the above were true

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

- (d) 2, 3 What is the decreasing order of reactivity 28. the following compounds towards amongst aromatic electrophilic substitution [IIT-JEE 1995] I. Chlorobenzene II. Benzene IV. Toluene III. Anilinium chloride (a) I > II > III > IV(b) IV > II > I > III(c) II > I > III > IV(d) III > I > II > IVWhich of the following applies in the reaction, 29.
- $CH_{3}CHBrCH_{2}CH_{3} \xrightarrow{alc.KOH} \rightarrow$
 - (i) $CH_3CH = CHCH_3$ (major product)
 - (ii) $CH_2 = CHCH_2CH_3$ (minor product)

[Orissa JEE 2005] (a) Markovnikov's rule (b) Saytzeff's rule

- (c) Kharasch effect (d) Hofmann's rule
- Bromination of alkanes involves 30. [J & K 2005] (a) Carbanions (b) Carbocations (c) Carbenes (d) Free radicals
- Which of following cannot 31. the undergo nucleophilic substitution under ordinary conditions [J & K 2005] (b) *tert*-butylchloride (a) Chlorobenzene (c) Isopropyl chloride (d) None of these
- Which of the following alkyl groups has the 32. maximum + *I* effect [KCET 2002]

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(a)	CH ₃ -	(b) $(CH_3)_2 CH -$
(c)	$(CH_{3})_{3}C -$	(d) CH_3CH_2 –

Structural and stereo isomerism

Only two isomers of monochloro product is 1. possible of

[IIT-JEE 1986]

- (a) *n*-butane (b) 2,4-dimethyl pentane (c) Benzene (d) 1-methyl propane
- Which is the example of branch isomerization 2.

[NCERT 1976]

(a)
$$C - C - C - C - C$$
 and $C - C - C - C$
(b) $C - C - C - C$ and $C - C - C$
(c) $C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$
(c) $C - C - C - C$ and $C - C - C$

The isomer of diethyl ether is [CPMT 1975] 3. (b) $(CH_3)_3 C - OH$ (a) $(CH_3)_2 CHOH$

(c)
$$C_3 H_7 OH$$
 (d) $(C_2 H_5)_2 CHOH$

- Isomers have essentially identical 4. [CBSE PMT 1988; MP PMT 1983, 86]
 - (a) Structural formula (b) Chemical properties
 - (c) Molecular formula (d) Physical properties
 - Which one of the following shows optical activity
 - [NCERT 1984, 90]

$$\begin{array}{cccccc}
H & H \\
| & H \\
(a) HO - C - COOH \\
| & H \\
H \\
(b) CH_3 - C - COOH \\
| & Cl \\
CH_3 \\
(c) CH_3 - C - COOH \\
| & (d) CH_3 - C - COOH \\
| & | \\
OH \\
Cl
 \end{array}$$

- In ethane and cyclohexane which one of the 6. following pairs of conformations are more stable (a) Eclipsed and chair conformations
 - (b) Staggered and chair conformations
 - (c) Staggered and boat conformations
 - (d) Eclipsed and boat conformations
- Which of the following may exist in 7. enantiomorphs

[NCERT 1982]

- - 5٠

	[CBSE PMT 1988]
CH ₃	
(a) $CH_3 - CH - COOH$	
(b) $CH_2 = CHCH_2CH_2CH_3$	
NH ₂	
(c) $CH_3 - CH - CH_3$	
NH ₂	
(d) $CH_3 - CH_2 - CH - CH_3$	
Which of the following compour	nds may not exist

- as enantiomers
 - (a) $CH_3CH(OH)CO_2H$
 - (b) $CH_3CH_2CH(CH_3)CH_2OH$
 - (c) $C_6H_5CH_2CH_3$

8.

12.

- (d) $C_6H_5CHClCH_3$
- Number of isomers of molecular formula $C_2H_2Br_2$ 9. are

[CPMT 1987]

		[СРМТ	1987]
(a) 1	(b) 2		
(c) 3	(d) 0		
	 	•	

- Lactic acid shows which type of isomerism 10. [CPMT 1987; MP PMT 1987; BHU 2003] (a) Geometrical isomerism (b) Tautomerism (c) Optical isomerism (d) Metamerism
- Which one of the following is an optically active 11. compound

[CBSE PMT 1988; DPMT 1983] (a) *n*-propanol (b) 2-chlorobutane (c) *n*-butanol (d) 4-hydroxyheptane Compounds with same molecular formula but different structural formulae are called[BHU 1979; AFMC 1989]

- (a) Isomers (b) Isotopes (c) Isobars (d) Isoelectronic
- Which one of the following compounds shows 13. optical isomerism [MP PET 1990] (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) $ClCH_2 CH_2 CH_3$

Which one of the following objects is 'achiral' 14. (a) Letter P (b) Letter F (c) Ball (d) A pair of hand

- Total number of isomers of a disubstituted 15. benzene compound is
 - (a) 1 (b) 2 (d) 4 (c) 3
 - Separating of d and l enantiomorphs from a
- 16. racemic mixture is called[CBSE PMT 1988; DPMT 1983; KCET 2002]
 - (a) Resolution (b) Dehydration (c) Rotation (d) Dehydrohalogenation
- Number of optical isomers of lactic acid are 17.

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

18. Which one of the following contains asymmetric carbon atom [IIT-JEE 1989; Roorkee 2000]

19. *n*-butane and isobutane are examples of

- (a) Chain isomers (b) Geometrical isomers
- (c) Position isomers (d) Tautomers
- Which of the following has chiral structure 20. CH_3

(a)
$$CH_3 - CH - CH_2COOH$$

(b)
$$CH_3 - CH = CH - CH_3$$

 CH_3

(c)
$$CH_3 - CH - CH_2OH$$

- (d) $CH_3 CHOH CH_2CH_3$
- Which of the following pairs is an example of 21. position isomerism

(a)
$$CH_3 - CH_2 - CH_2 - CH_3$$
 and $CH_3 - CH - CH_3$
 $|$
 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
 $CH_3 - C - CH_3$ and $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
 $|_{CH_3}$

22. Geometrical isomerism is shown by [IIT-JEE 1983; CPMT 1990, 94; CBSE PMT 1992; MP PET 1997; AMU (Engg.) 1999]

(a) 2-butene	(b) 2-butyne
(c) 2-butanol	(d) Butanal

An organic compound exhibits optical isomerism 23. when

[CPMT 1971, 78, 81; MP PET 1999]

(a) Four groups linked to carbon atom are different

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	(b) Three groups li	nked to carbon atom are			[CBSE PMT 1989]
diffe	erent			(a) $HC \equiv CH$	(b) $ClCH = CHCl$
1.00	(c) Two groups lin	ked to carbon atom are		(c) $CH_3.CHCl.COOH$	(d) $ClCH_2 - CH_2Cl$
11116	erent		34.	The number of geomet	rical isomers in case of a
	(d) All the groups line	ked to carbon atom are same		compound with the str	ucture
24.	isomerism	nowing exhibits geometrical		$CH_3 - CH = CH - CH = 0$	$CH - C_2H_5$ 1S
	INCERT 1970): DPMT 1984: CBSE PMT 1990]			[NCERT 1980]
	H _N /H	$C_{2}H > H$		(a) 4	(b) 3
	(a) $H_{2}C = C < CH_{2}$	(b) $\frac{C}{H} > C = C < \frac{C}{H}$		(c) 2	(d) 5
			35.	The property by virtue	e of which a compound can
	CH_{3}	H		(a) Photolysis	(b) Phosphorescence
	(c) $CH_3 > C = C < H$	(d) $H - C - C = C \leq H$		(a) Inotorysis	(d) Polarization
	2	H H	26	(c) Optical activity Meso-tartaric acid is c	(u) Foralization
5٠	Maximum number of	isomers of alkene C_4H_8 are	30.	presence of	pricarly macrive due to the
	[IIT-JEE 1982; M	P PMT 1985; MADT Bihar 1995;		Processo of	[AIIMS 1982; MP PMT 1987]
	(a) a	Kerala (Engg.) 2002]		(a) Molecular symmetr	ry
	(a) 2			(b) Molecular asymme	try
26	Rotation of plane pol:	(u) o		(c) External compensa	tion
	Rotation of plane por	[CPMT 1985; DCE 2001]		(d) Two asymmetric C	-atoms
	(a) Manometer	(b) Polarimeter	37.	Which of the follow	wing compounds exhibits
	(c) Viscometer	(d) Refractometer		optical isomerism[BHU	1983; AFMC 1990; CPMT 1993
1 7۰	An alkane forms iso	mers if the number of least			MP PMT 1999, 2000]
	carbon atom is	[CPMT 1976; BHU 1985, 89]		(a) CH_3CH_2COOH	(b) <i>CH</i> ₃ <i>CHOHCOOH</i>
	(a) 1	(b) 2		(c) $CH_3CH_2CH_2OH$	(d) $CH_3CHOHCH_3$
	(c) 3	(d) 4	38.	The maximum number	r of stereoisomers possible
28.	Which is not found in	alkenes[AIIMS 1982; RPMT 1999]	for 2-hydroxy-2-methy	l butanoic acid is[Roorkee 19
	(a) Chain isomerism	(b) Geometrical		(a) 1	(b) 2
son	ierism	(d) Desition isomenism		(c) 3	(d) 4
20	How many isomers ((U) Position isomerism	39.	Which one of the foll	owing pairs represents the
.9.	alcohola	$C_5 M_{11} O M$ will be primary		stereoisomerism	[AIIMS 1992]
	alcohois	[CBSE PMT 1002]		(a) Geometrical isome	rism, position isomerism
	(a) 2	(b) 3		(b) Geometrical iso	omerism, conformational
	(c) 4	(d) 5	ISOI	(c) Ontical icomorism	accompany is a second second
30.	The compound $C_4 H_{10}$	O can show		(d) Optical isomerism	metamerism
-	1 4 10	[IIT-IEE 1981: MP PET 2000]	40	Diethyl ether is not as	sociated with which one of
	(a) Metamerism	(b) Functional	40.	these isomers	[AFMC 1993]
son	nerism			(a) Butanoic acid	(b) Methyl propionate
	(c) Positional isomer	sm (d) All types		(c) Steroisomerism	(d) None of these
31.	The number of pos	sible alcoholic isomers for	41.	Diethyl ether and meth	yl <i>n</i> -propyl ether are
	$C_4 H_{10} O$ are			[MP PET 199	4; AFMC 1999; MP PMT 2002]
		[DPMT 1984; MNR 1986]		(a) Position isomers	(b) Functional isomers
	(a) 4	(b) 2		(c) Metamers	(d) Chain isomers
	(c) 3	(d) 5	42.	<i>n</i> -propyl alcohol an	d isopropyl alcohol are
;2.	How many isomers ar	The possible for $C_4 H_8 O$		examples of	[37]
		[MNR 1992; UPSEAT 2001, 02]		(a) Position icomoview	[MP PMT 1994]
	(a) 3	(b) 4		(a) FUSILION ISOMETISM	(d) Geometrical
	(c) 5	(d) 6	ison	herism	(u) Geometrical
33.	Which of the follo isomerism	wing can exhibit <i>cis-trans</i>	43·	It is possible to di isomers by	stinguish between optical

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	[Manipal MEE 1995; AFMC 1995]		(c) 4	(d) 6
	(a) Infrared spectroscopy	52.	Optically active ison	ners but not mirror images
	(b) Mass spectrometry		are called	
	(c) Melting point determination			[MP PET 1999]
	(d) Polarimetry		(a) Enantiomers	(b) Mesomers
4.	The isomerism exhibited by alkyl cyanide and		(c) Tautomers	(d) Diastereoisomers
	alkyl isocyanide is [AFMC 1995, 97]	53.	$C_7 H_9 N$ has how r	many isomeric forms that
	(a) Functional (b) Positional		contain a benzene rin	g[CPMT 1997, 99; JIPMER 2002
	(c) Tautomerism (d) Metamerism		(a) 4	(b) 5
5.	The following compound can exhibits		(c) 6	(d) 7
	CH-> <h h<="" td=""><td>54.</td><td>The total number of is</td><td>somers formed by $C_5 H_{10}$ is</td></h>	54.	The total number of is	somers formed by $C_5 H_{10}$ is
	$CH_{3} > C = C < C_{C} H$ [IIT-JEE 1995; DCE 2000]			[Bihar MEE 1996]
	CH ₃ CH ₃ COOH		(a) 2	(b) 3
	(a) Tautomerism		(c) 4	(d) 5
	(b) Optical isomerism		(e) None of these	
	(c) Geometrical isomerism	55.	Which of the follo	wing contains asymmetric
	(d) Geometrical and optical isomerisms		centre	
6.	Name the compound, that is not isomer with			[CPMT 1996]
	diethyl ether		(a) 2-butene	(b) 2, 2-dimethylpropane
	[IIT-JEE 1981; CPMT 1989; MADT Bihar 1995]		(c) 2-hexyne	(d) Lactic acid
	(a) <i>n</i> -propylmethyl ether	56.	Which of the follo	wing cannot be given to
	(b) Butane-1-ol		exemplify chiral struc	Cture [JIPMER 1997]
	(c) 2-methylpropane-2-ol		(a) A snoe	(b) A screw
	(d) Butanone		(c) A screw driver	(d) All of these
7.	Which statement is true for cyclohexane[MP PET 199	96] ⁵⁷	active	ig is expected to be optically
	(a) It has two possible isomers		delive	[IIPMER 1997]
	(b) It has three conformations		(a) $(CH_{a}), C$	(b) $C_2H_2CH(CH_2)C_2H_2$
	(c) Boat conformation is most stable		(c) (C, H) CHCH	(d) CU CU - CUCU
	(d) Chair and boat conformations differ in energy	_	(c) $(C_2 H_5)_2 CHCH_3$	(u) $CH_3CH = CHCH_3$
	by 44 kJ/mol	58.	Which compound d	oes not show geometrical
8.	Two compounds have the structural formulae		ISOINELISII	[PDMT 1007]
	$CH_3 - O - CH_2CH_3$ and $CH_3 - CH_2 - CH_2OH$. The		(a) 2-hutene	(b) 2-pentene
	above is an example of		(a) 2 -butche	(b) 2-pentene tene (d) 2-methyl propene
om	(a) Metamerism (b) Functional	50	The isomers which ca	an be converted into another
50111	(c) Positional isomerism (d) Chain isomerism	59.	forms by rotation of	the molecules around single
0	Which of the following pairs are not isomeric		bond are	5
9.	compounds			[AIIMS 1997]
	(a) Ethyl ethanoate and methyl propanoate		(a) Geometrical isom	ers (b) Conformers
	(b) Butanone and butanal		(c) Enantiomers	(d) Diastereomers
	(c) Ethoxy propage and propoxy ethane	60.	The number of ena	ntiomers of the compound
	(d) Methoxy methane and ethanol		CH ₃ CHBrCHBrCOOH	is [AIIMS 1997]
0.	Functional isomerism is exhibited by the		(a) 0	(b) 1
-	following pair of compounds		(c) 3	(d) 4
	(a) Acetone, propionaldehyde	61.	$C_6H_5C \equiv N$ and C_6H_5	$_{5}N \equiv C$ exhibit which type of
	(b) Diethyl ether, methyl propyl ether		isomerism	[CPMT 1997]
	(c) Butane, isobutane		(a) Position	(b) Functional
	(d) 1-butene, 2-butene		(c) Dextro isomerism	(d) Metamerism
j1.	The total number of possible isomeric trimethyl	62.	Which of the followin	g compounds is not chiral
	benzene is			[CBSE PMT 1998; DPMT 2002]
	[MP PET 1997]		(a) $DCH_2CH_2CH_2Cl$	(b) CH_3CH_2CHDCl

63.	cis and trans 2-butene are [BHU 1998; DPMT 2002]		(b) <i>n</i> -propyl alcohol and isopropyl alcohol
	(a) Conformational isomers (b) Optical isomers		(c) 2-methyl-1 propanol and 2-Methyl-2 propanol
	(c) Position isomers (d) Geometrical isomers		(d) 2-methyl butane and neopentane
64.	Which one of the following is the chiral molecule	77.	Which of the following compounds will exhibit
	[BHU 1998; 2005]		geometrical isomerism [IIT-JEE Screening 2000]
	(a) CH_3Cl (b) CH_2Cl_2		(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
	(c) CHBr ₃ (d) CHClBrI		(c) 2-phenyl-1-butene (d) 1, 1-Diphenyl-1-
65.	Cyanide and isocyanide are isomers of type[AFMC 19	97]	propene
	(a) Positional (b) Functional	78.	On bromination, propionic acid yields two
	(c) Tautomer (d) Structural		isomeric 2-bromopropionic acids. This pair is an
66.	Glucose and fructose are [AMU (Engg.) 1999]		Important example of [BHU 2000]
	(a) Optical isomers (b) Functional isomers		(a) Chain isomers (b) Optical isomers
	(c) Position isomers (d) Chain isomers		(c) Cis-trans isomers (d) Position isomers
67.	Which of the following compounds which is an	7 9 .	Geometrical isomerism is not possible in [CPMT 200
-	optically active compound [UPSEAT 1999]		(a) Propene (b) 3-hexane
	(a) 1-butanol (b) 2-butanol		(c) Butenedioic acid (d) Cyclic compound
	(c) 3-butanol (d) 4-heptanol	80.	Only two isomeric monochloro derivatives are
68.	<i>d</i> -tartaric acid and <i>l</i> -tartaric acid are[MH CET 1999]		possible for
	(a) Enantiomers (b) Tautomers		[Pb. PMT 2000]
	(c) Diastereoisomers (d) Structural isomers		(a) 2-methyl propane (b) <i>n</i> -pentane
69.	Minimum resistance in bond rotation will be observed in the compound [RPMT 1999]		(c) Benzene (d) 2, 4-dimethyl pentane
	(a) Hexachloroethane (b) Ethylene	81.	Lactic acid in which a methyl group, a hydroxyl
	(c) Acetylene (d) Ethane		group, a carboxylic acid group and a hydrogen
70.	Which pair show cis-trans isomerism [RPET 1999]		atom are attached to a central carbon atom,
	(a) Maleic-fumaric acid (b) Lactic-tartaric acid		shown optical isomerism due to the molecular
	(c) Malonic-succinic acid (d)Crotonic-acrylic acid	d	geometry at the [Pb. PMT 2000]
71.	1, 2-Dichloroethene shows [RPET 1999]		(a) Central carbon atom
	(a) Geometrical isomerism (b) Optical isomerism		(b) Carbon atom of the methyl group
	(c) Ring-chain isomerism (d) Resonance		(c) Carbon atom of the carboxylic acid group
72.	Which compound is optically active [DCE 1999]		(d) Oxygen of the hydroxyl groups
	(a) 4-chloro, 1 hydroxy butane	82.	The number of possible alkynes with molecular
	(b) 3° -butyl alcohol		formula C_5H_8 is [MP PMT 2000]
	(c) Secondary butyl amine		(a) 2 (b) 3
	(d) <i>n</i> -butyl alcohol		(c) 4 (d) 5
73.	Choose the pair of chain isomer [RPMT 2000]	83.	Which of the following will not lose asymmetry
	(a) CH_3CHBr_2 and CH_2BrCH_2Br		on reduction with $LiAlH_4$ [Roorkee 2000]
	(b) 1-propanol and 2-propanol		СНО
	(c) Neo-pentane and isopentane		(a) $HOH_{2}C \rightarrow CH_{2}CH_{2}$
	(d) Diethyl ether and methyl- <i>n</i> -propyl ether		$CH = CH_{\circ}$
74.	Optical isomerism arises due to the presence of		
-	[RPMT 2000]		CH ₃
	(a) An asymmetric carbon atom		(b) $H_2C = HCO$ CHO
	(b) Centre of symmetry		CH_2CH_3
	(c) Axis of symmetry		CH_3
	(d) Plane of symmetry		(c) $HOH_{2}C + COOH$
75.	Least hindered rotation about carbon-carbon bond		$C \equiv CH$
	is observed in [RPMT 2000]		CHO
	(a) Ethane (b) Ethylene		
	(c) Ethyne (d) Hexachloroethane		(a) $H_3C \longrightarrow C \equiv N$
76.	Which pair represents chain isomer [RPMT 2000]		$CH_2 NH_2$
	(a) CH_3CHCl_2 and $ClCH_2CH_2Cl_2$	84.	Reason for geometrical isomerism by 2-butene is
	(a) CH_3CHCl_2 and $ClCH_2CH_2Cl$	-	0

[CBSE PMT 2000]

- (a) Chiral carbon
- (b) Free rotation about single bond
- (c) Free rotation about double bond
- (d) Restricted rotation about double bond
- Stereoisomers which are not the mirror images of 85. one another are called [RPMT 2000]
 - (a) Enantiomers (b) Mesomers
 - (c) Tautomers (d) Diasteroisomers
- 86. The isomerism shown by *n*-butyl alcohol and isobutyl alcohol is [RPMT 2000] (a) Metamerism (b) Chain
 - (c) Position (d) Stereo
- 87. Which is optically active [MH CET 2001]
 - (a) CH_2Cl_2
 - (b) CHCl₃
 - (c) Meso form of tartaric acid
 - (d) Glyceraldehyde
- Which of the following will show geometrical 88. isomerism

		[CPMT 2001; BHU 2005]
(a) <i>Cl</i>	$H_3CH = CHCH_3$	(b) $(CH_3)_2 C = C(CH_3)_2$

(c)
$$(CH_3)_2 C = C(CH_3)_2$$
 (d) $CH_3 - CH = C(CH_3)_2$

- What is the maximum number of open chain 89. structures possible for $C_4 H_8$ [MP PET 2001]
 - (a) 2 (b) 3 (d) 1 (c) 4
- 90. Glucose has optical isomers [DCE 2001]
 - (a) 8 (b) 12
 - (c) 16 (d) Cannot be predicted

91. An organic compound ${}^{1}CH_{3} - {}^{2}CH_{2} - {}^{3}CH_{2} - {}^{4}CH_{2} - {}^{5}CH_{2} - {}^{6}CH_{2} - {}^{7}CH_{3}$

To make it chiral compound the attack should be on which carbon atom [DCE 2001]

- (a) 1 (b) 3 (c) 4 (d) 7
- Which of the following statements is not true 92. about enantiomers [DCE 2001]
 - (a) They have same physical properties
 - (b) They have different biological properties
 - (c) They have same chemical properties towards chiral compounds
 - (d) None of these
- 93. Meso-tartaric acid is [BHU 2001]
 - (a) Optically inactive
 - (b) Optically active because of molecular symmetry
 - (c) Optically inactive due to external compensation
 - (d) Optically active because of asymmetric carbon atom

- The number of possible isomers of the compound 94. with molecular formula $C_7 H_8 O$ is [BHU 2001]
 - (b) 5 (a) 3
 - (c) 7 (d) 9
- The number of isomers for the compound with 95. molecular formula *C*₂*BrClFI* is **[IIT-JEE (Screening) 2001]**
 - (b) 4 (a) 3
 - (c) 5 (d) 6
- Hydrogenation of the adjoining compound in the 96. presence of poisoned palladium catalyst gives

[IIT-JEE (Screening) 2001]

Me H Ме Н

- (a) An optically active compound
- (b) An optically inactive compound
- (c) A racemic mixture
- (d) A diastereomeric mixture
- 97. The number of possible structural isomers for a compound with the molecular formula $C_7 H_{16}$ is[DCE 2001]
 - (a) 8 (b) 9
 - (c) 10 (d) 12
- 98. Which of the following molecule contains asymmetric carbon atom [JIPMER 2002] (a) CH₃CHClCOOH (b) CH_3CH_2COOH
 - (c) ClCH₂CH₂COOH (d) $Cl_2CHCOOH$
- A similarity between optical and geometrical 99. isomerism is that [AIEEE 2002] (a) Each forms equal number of isomers for a
 - given compound
 - (b) If in a compound one is present then so is the other
 - (c) Both are included in stereoisomerism
 - (d) They have no similarity
- **100.** If the light waves pass through a nicol prism then all the oscillations occur only in one plane, such beam of light is called as [Kerala (Med.) 2002]
 - (a) Non-polarised light (b) Plane polarised light
 - (c) Polarised light (d) Optical light
- **101.** Racemic mixture is formed by mixing two[AIEEE 2002]
 - (a) Isomeric compounds (b) Chiral compounds
 - (c) Meso compounds (d) Optical isomers
- 102. Which of the following does not show geometrical isomerism [AIEEE 2002]
 - (a) 1, 2 dichloro-1-pentene
 - (b) 1, 3-dichloro-2-pentene
 - (c) 1, 1-dichloro-1-pentene
 - (d) 1, 4-dichloro-2-pentene

- Н Mo

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(a) 2

[CPMT 1999; UPSEAT 1999, 2000, 02]

(b) 4

	H ₃ C CH ₃	H ₃ C H		
103.	C = C and	C = C		()
	H H	H CH_3	114	() V
	exhibit which isomerism	MP PET 2002]	114.	v a
	(a) Position isomerism	(b) Geometrical		
	isomerism			(
	(c) Optical isomerism	(d) Functional		(
104.	Which compound is chir	a] [RPMT 2002]	115	` C
1.	(a) butane		11.5.	(
	(b) 1-chloro-2-methyl bu	ıtane		6
	(c) 2-methyl butane		116.	Ĭ
	(d) 2-methyl propane			_
105.	Methyl acetate and prop	ionic acid are [RPMT 2002]		с
	(a) Functional isomer	(b) Structural isomer		
106	(c) Stereoisomer Which compound shows	(d) Geometrical isomer	5 1	(
100.	(a) 1-butene	(b) 2-propene	2]	(
	(c) 2-butene	(d) Benzene	117.	I
107.	Isomers of propionic aci	d are [MP PMT 2002]		с
	(a) $HCOOC_2H_5$ and CH_3	SCOOCH ₃		(
	(b) $HCOOC_2H_5$ and C_3H_5	$I_7 COOCH_3$		(
	(c) CH_3COOCH_3 and C_3	H ₇ OH	118.	V
	(d) C_2H_7OH and CH_2CO	CH ₂		e
108.	The functional isomer of	f ethyl alcohol is[MP PMT 2002]	1	
100.	(a) CH_2OCH_2	(b) CH_2COCH_2		
	(c) <i>CH</i> ₂ <i>COOH</i>	(d) $CH_{2}CH_{2}CHO$		(
100	Disymmetric object is or	which is [Kerala (Engg.) 200	51	
109.	(a) Superimposable on i	ts mirror image	<u>-</u>]	
	(b) Non-superimposible	on its mirror image		
	(c) Optically inactive			(
	(d) Achiral			
110.	Geometrical isomers dif	fer in [CBSE PMT 2002]		
	(a) Position of atoms			
	(b) Length of carbon	of atoms		(
	(d) Position of function:	al group		
111.	Which of the followin	g hydride is capable of		
	showing conformations	[JIPMER 2002]		,
	(a) $NH_2 - NH_2$	(b) $B_2 H_6$		(
	(c) <i>CH</i> ₄	(d) None of these		
112.	Which of the following i	s an chiral compound		
	-	[AIIMS 2002]	119.	,
	(a) Hexane	(b) Methane		ŀ
	(c) <i>n</i> -butane	(d) 2,3,4-trimethyl		H
	nexane			

113. What is the possible number of optical isomers for a compound containing 2-dissimilar asymmetric carbon atom

(c) 6	(d) 8
Which of the following active	compounds is optically
[Pb. PMT 2001; AI	MU 2002; Kerala (Med.) 2003]
(a) $(CH_3)_2 CHCH_2 OH$	(b) CH_3CH_2OH
(c) CCl_2F_2	(d) $CH_3CHOHC_2H_5$
Optically active compoun	d is [UPSEAT 2002]
(a) 3-chloropentane	(b) 2-chlorobutane
(c) 2-chloropropane	(d) None of these
If a carbon atom is attach	ed to -H,-OH,-COOH and
$-OCOC_2H_5$ number of	chiral C – atoms in
compound is	
	[RPMT 2003]
(a) 1	(b) 2
(c) 3	(d) 4
Isomerism due to rotati carbon-carbon is	on round single bond of [UPSEAT 2003]
(a) Conformation	(b) Enantiomerism
(c) Diasterio isomerism	(d) Position isomerism

118. Which of the following pairs of compounds are enantiomers

[CBSE PMT 2003]



How many structures of *F* is possible

[IIT-JEE (Screening) 2003]

(a) 2	(b) 5
(c) 6	(d) 3

1058 General Organic Chemistry 120. An enantiomerically pure acid is treated with (c) A and B are enantiomers racemic mixture of an alcohol having one chiral (d) None of these carbon. The ester formed will be[IIT-JEE (Screening) 20928. Ethyl acetoacetate shows, which type of isomerism (a) Optically active mixture (b) Pure enantiomer [Pb. CET 2003] (c) Meso compound (d) Racemic mixture (a) Chain (b) Optical 121. Which one of the following will not show (c) Metamerism (d) Tautomerism geometrical isomerism [MP PMT 2003] 129. Which of the following will have a mesoisomer also $H_{3}C$ C = C $H_{3}C$ Br(a) $\begin{array}{c} H_{3}C \\ C = C \\ H \end{array} \begin{array}{c} Cl \\ Br \\ H_{3}C \\ H_{3}C \end{array}$ [AIEEE 2004] (a) 2, 3-Dichloropentane (b) 2, 3-Dichlorobutane (c) H C = C (d) C = C(c) 2-Chlorobutane (d) 2-Hydroxypropanoic acid 130. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values ? (Assume **122.** Isomerism shown by ideal behaviour) [AIEEE 2004] $CH_{3} - (CH_{2})_{3} - O - CH_{3}$ (a) Boiling points $CH_3 - CH_2 - O - CH_2 - CH_2 - CH_3$ (b) Vapour pressure at the same temperature $CH_3 - CH - O - CH_2 - CH_3$ is [RPMT 2003] (c) Heat of vaporization (d) Gaseous densities at the same temperature CH_3 and pressure (a) Position isomerism (b) Chain isomerism **131.** The geometrical isomerism is shown by[**AIIMS 2004**] (c) Metamerism (d) Optical isomerism CH_{2} CH_{2} **123.** A compound whose molecules are superimposable (a) (b) on their mirror images even through they contain an asymmetric carbon atom is called[Kerala (Med.) 2003] (a) A meso compound (b) An erythro isomer ≠ CH Cl ∥CH Cl (c) A threo isomer (d) a glycol (d) (c)**124.** Of the following, the compound possessing optical isomerism [Kerala (Med.) 2003] 132. Which of the following compounds will exhibit (a) CH_3CH_2OH (b) $CH_2CHClBr$ cis-trans isomerism [Kerala PMT 2004] (c) CCl_2BrF (d) CCl_2F_2 (a) 2-butene (b) 2-butyne 125. Which of the following statement is wrong[EAMCET 2003] (c) 2-butanol (d) Butanone (a) Diethyl ketone and methyl propyl ketone are (e) Butanol position isomers 133. Which of the following compounds exhibit (b) 2-chloro pentane and 1-chloro pentane are stereoisomerism position isomers [MP PMT 2004] (c) *n*-butane and 2-methyl propane are chain (a) 2-methyl-butane I (b) 3-methyl-butanoic isomers acid (d) Acetone and propinaldehyde are functional (c) 3-methyl-butyne I (d) 2-methyl butanoic isomers acid 126. Dimethyl ether and ethyl alcohol are 134. The chirality of the compound [CBSE PMT 2005] [MH CET 2004; Pb. CET 2002] (a) Metamers (b) Homologues (c) Functional isomers (d) Position isomers The correct statement about the compounds A 127. and B is

[DCE 2002; UPSEAT 2004; IIT-JEE 1997; DPMT 2005]

$$H \longrightarrow OH H \longrightarrow OH (B)$$

(a) A and B are identical

(b) A and B are diastereomers

135. Which of the following is most likely to show optical isomerism [UPSEAT 2004]

(b) S

(d) E

(a) R

(c) Z

(a) $HC \equiv C - \frac{H}{C} - C \equiv CH$ (b) $HC \equiv C - \frac{H}{C} - CH_{3}$

(c)
$$HC \equiv C - C - H$$
 (d) $HC \equiv C - C = CH_2$

- **136.** Nitroethane can exhibit one of the following kind of isomerism [DCE 2004]
 - (a) Metamerism (b) Optical activity
- (d) Position isomerism (c) Tautomerism **137.** $CH_3CH(OH).COOH$ shows [BVP 2004]
 - (a) Geometrical isomerism (b) Optical isomerism (c) Both (d) None
- 138. Which will have enantiomer [BVP 2004] (a) $CH_3CH_2CH - CH_3$ (b) $CH_2CH_2CH_2CH_2CH_2CI$ Cl
 - (c) $CH_3CH_2CH_2CHCl_2$ (d) None
- 139. The total number of acylic isomers including the stereoisomers with the molecular formula C_4H_7Cl

[Pb.	СЕТ	2004]
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- (b) 12 (a) 11 (d) 10 (c) 9
- 140. The number of possible enantiomeric pairs that can be produced during mono-chlorination of 2methylbutane is

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

141. Which one of the following pairs represents stereoisomerism

[CBSE PMT 2005]

[Pb. CET 2004]

(a) Chain isomerism and rotational isomerism

(b) Structural isomerism geometric and isomerism

- (c) Linkage isomerism and geometric isomerism
- (d) Optical isomerism and geometric isomerism
- **142.** When isomers have the same structural formula but differ in relative arrangement of atoms or groups are called

[CPMT 2000; KCET (Med.) 2000] (b) Stereoisomers

- (a) Mesomers (c) Optical isomers (d) Geometrical
- mesomers
- 143. $CH_3CH_2CH = CH_2$ and $CH_3 CH = CH CH_3$ show

(a) Chain isomerism (b) Position isomerism (c) Functional isomerism (d) Metamerism

144. The number of possible isomers of butene are [Kerala (Engg.) 2002]

(a) 3	(b) 2
(c) 4	(d) 5
(e) 6	

145. Which of the following show geometrical isomerism

	[BCECE 2005]
(a) C_2H_5Br	(b) $(CH_2)(COOH)_2$
(c) $(CH)_2(COOH)_2$	(d) $C_2 H_6$

- **146.** Among the following the most stable compound is [AIIMS 2005]
 - (a) cis 1, 2 cyclohexan ediol
 - (b) trans 1, 2 cyclohexan ediol
 - (c) cis 1, 3 cyclohexan ediol
 - (d) trans 1.3 cyclohexan ediol
- 147. Chirality of carbon compound is because of its [Kerala (Med.) 2002]
 - (a) Tetrahedral nature of carbon
 - (b) Monovalent nature of carbon
 - (c) Divalent nature of carbon
 - (d) Trivalent nature of carbon
- 148. Which kind of isomerism is possible for 1-chloro-2-nitroethene [J & K 2005]
 - (a) Functional group isomerism
 - (b) Position isomerism
 - (c) E/Z isomerism
 - (d) Optical isomerism
- 149. Which will give chiral molecule [DPMT 2005]

(a)
$$CH_3COCl$$
 LiAlH_4

. .

(b)
$$C_2H_5CHO \xrightarrow{CH_3MgBr}_{H^+/H_2O}$$

(c)
$$(CH_3)_2 CHC_2 H_5 \xrightarrow{Cu}$$

(d)
$$\underset{CH_2}{\overset{H}{\longrightarrow}} C = C \underbrace{\overset{CH_3}{\longleftarrow}}_{CH_2} \xrightarrow{CI_2}$$

150. Which of the following will be chiral

[J & K 2005]

- (a) CH_3CHCl_2 (b) CH₃CHBrCl
- (c) CD_2Cl_2 (d) CH_2ClBr
- **151.** Which of the following fischer projection formula is same as *D*-Glyceraldehyde [Kerala CET 2005] $CH_{\circ}OH$

(a)
$$OH \xrightarrow{CH_2OH} CHO$$

 H
(b) $H \xrightarrow{CH_2OH} OH$
 CHO
(c) $OH \xrightarrow{CHO} CH_2OH$
 H
(d) $H \xrightarrow{CHO} CH_2OH$
 HO
(e) $OH \xrightarrow{H} CH_2OH$



1. In the given conformation C_2 is rotated about $C_2 - C_3$ bond anticlockwise by an angle of 120° then the conformation obtained is [AIIMS 2004]



- (a) Fully eclipsed conformation
- (b) Partially eclipsed conformation
- (c) Gauche conformation
- (d) Staggered conformation
- 2. The molecular formula of diphenyl methane,

 $\begin{array}{c|c} & & & \\ &$

3. SN^{1} reaction is faster in [Orissa JEE 2004] (a) $CH_{3}CH_{2}Cl$ (b) $CH_{3} > CH - Cl$

(c)
$$CH_3 - CH_3$$

 $-C-Cl$
 $CH_3 - CH - Cl$
 $CH_3 - CH - Cl$
 CH_2
 CH_3

- 4. How many enantiomer pairs are obtained by monochlorination of 2, 3-dimethylbutane[Kerala PMT 2004]
 (a) Nil
 (b) Four
 - (c) Two (d) Three
 - (e) One
- 5. Among the following compounds which can be dehydrated very easily is [AIEEE 2004]

(a)
$$CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - CH_$$

(b)
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

(c) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH_3$
(d) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH_3$

6. Which of the following statements is not characteristic of free radical chain reaction[**JIPMER 1997**]

- (a) It gives major product derived from most stable free radical
- (b) It is usually sensitive to change in solvent polarity
 - (c) It proceeds in three main steps like initiation, propagation and termination
 - (d) It may be initiated by U.V. light

7. Most stable carbanion is

(

(c)

[BHU 2003]

(a) CH_3^- (b) $CH_3CH_2^-$ (c) CH_2^- (d) $CH_2^ O_{NO_2}^ CH_3^-$

8. Among the following the dissociation constant is highest for

(a)
$$C_6H_5OH$$
 (b) $C_6H_5CH_2OH$
(c) $CH_3C \equiv CH$ (d) $CH_3NH_3^+Cl^-$

9. Which one of the following compounds is most acidic

[CBSE PMT 2005]

NO

a)
$$Cl - CH_2 - CH_2 - OH$$
 (b) \bigcirc

- 10. Which one is electrophilic addition[AMU (Engg.) 1999] (a) $CH_3 - CH_3 + Cl_2 \rightarrow C_2H_5Cl + HCl$
 - (b) $CH_3CH = O + HCN \rightarrow (CH_3)_2 C(OH)CN$
 - (c) $(CH_3)_2 C = O + HCN \rightarrow CH_3 CH(OH)CN$

(d) $CH_2 = CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$

- A compound has 3 chiral carbon atoms. The number of possible optical isomers it can have[DCE 2004]
 - (a) 3 (b) 2 (c) 8 (d) 4
- How many chiral isomers can be drawn from 2bromo, 3-chloro butane [DCE 2003]

(a) 2	(b) 3
(c) 4	(d) 5

13. Number of isomers of $C_4 H_{10}$ is

[CBSE PMT 1996; AFMC 1997; RPMT 2002; MP PMT 1997]

- (a) 2 (b) 3
- (c) 4 (d) Isomerism not exist

- 14. The number of possible isomers for compound
 $C_2H_3Cl_2Br$ is[MP PMT 1999]
 - (a) 2 (b) 3
 - (c) 4 (d) 5
- 15. The optically active tartaric acid is named as D-(+)- tartaric acid because it has a positive[IIT-JEE 1999]
 - (a) Optical rotation and is derived from D-glucose
 - (b) *pH* in organic solvent
 - (c) Optical rotation and is derived from D(+) glyceraldehyde
 - (d) Optical rotation only when substituted by deuterium
- 16. Among the following compounds (I-III) the correct order of reaction with electrophilic reageoutis
 NO2 [CBSE PMT 1997]



(a) II > III > I	(b) III < I < II
(c) I > II > III	(d) $I = II > III$

- 17. Carbocation which is most stable [BHU 2003]
 - (a) $CH_3CH_2^+$ (b) CH_3^+
 - (c) $C_6H_5CH_2^+$ (d) $CH_3CH_2CH_2^+$
- 18. Tautomerism is exhibited by

[CBSE PMT 1997; KCET 2002]

(a) $(CH_3)_3 CNO$ (b) $(CH_3)_2 NH$

- (c) $R_3 CNO_2$ (d) $RCH_2 NO_2$
- **19.** Which of the following will have geometrical isomers

[MP PET 1996; MP PMT 1997; AFMC 1997]

- (a) 2-methylpropene (b) 2-butene
- (c) 1-butene (d) Propene
- **20.** Examine the following three pairs of possible isomers



Now state whether the pairs represent identical compounds or different isomers

- (a) All three pairs represent different compounds
- (b) (*ia*) and (*ib*) are identical; (*iia*) and (*iib*) are identical; and (*iiia*) and (*iiib*) are identical
- (c) (*ia*) and (*ib*) are isomers; (*iia*) and (*iib*) are identical; and (*iiia*) and (*iiib*) are isomers
- (d) (*ia*) and (*ib*) are identical; (*iia*) and (*iib*) are identical, and (*iiia*) and (*iiib*) are isomers
- 21. Tautomerism is exhibited by [IIT-JEE 1998]



22. The following reaction is described as[**CBSE PMT 1997**] $CH_3(CH_2)_5$ ($CH_2)_5CH_3$



23. Which one of the following represents eclipsed form of ethane







	(a) 1 and 4	(b) 3 and 4
	(c) 2 and 4	(d) 1 and 3
_		C 11 · · · · · · · · · · · · · · · · · ·

Which of the following is the most stable cation 25. [CBSE PMT 1988; MNR 1988; AIIMS 1985]

(a)
$$CH_{3}CH_{2}CHCH_{3}$$
 (b) $CH_{3}-CCH_{3}$
|
 CH_{3}

(c) $CH_3CH_2CH_2\overset{T}{C}H_2$ (d) CH_{3}^{+}

26. In a reaction of C_6H_5Y , the major product (> 60%) is *m*-isomer, so the group Y is[AIIMS 1997; UPSEA3400Which of the following orders regarding relative (a) -COOH(b) MI

(a)
$$-COOH$$
 (b) $-NH_2$
(c) $-OH$ (d) $-Cl$

Dehydrohalogenation in presence of OH^- is 27. correctly represented by [Orissa JEE 2004]



28. Number of structural isomers of $C_4 H_{10} O$ are [CPMT 1983, 84, 89, 91; MADT Bihar 1984; MNR 1984; MP PET 1997; Pb. PMT 1999; MH CET 2003] < > -

(a) 3	(b) 6
(c) 7	(d) 10

Among the following the aromatic compound is 29.



- 30. Which of the following compounds are not arranged in order of decreasing reactivity towards electrophilic substitution [DCE 2003] (a) Fluoro benzene > chloro benzene > bromo benzene
 - (b) Phenol > *n*-propyl benzene > benzoic acid
 - (c) Chloro toluene > para-nitro toluene > 2chloro-4-nitro toluene
 - (d) Benzoic acid > phenol > *n*-propyl benzene
- Most stable carbonium ion is 31. [Pb. CET 2004] (a) $\overset{+}{C}_{2}H$ (b) $(CH_2)_2 \stackrel{T}{C}$

(c)
$$(C_6H_5)_3C$$
 (d) $C_6H_5CH_2$

Which one of the following species is most stable 32.

- (a) $p O_2 N C_6 H_4 \overset{+}{C} H_2$
- (b) $p CH_3O C_6H_4 C_6H_2$
- (c) $p Cl C_6 H_4 \overset{+}{C} H_2$

(d) $C_6 H_5 - C H_2$

Which of the following gives most stable 33. carbocation by dehydration [RPMT 2002] (a) $(CH_3)_2CH - OH$

(b)
$$(CH_3)_3 C - OH$$

(c)
$$CH_3 - CH_2 - OH$$

(d) $CH_3 - CH_2 - O - CH_2 - CH_3$

stability of free radicals is correct [UPSEAT 2004] (a) $3^{\circ} < 2^{\circ} < 1^{\circ}$ (b) $3^{\circ} > 2^{\circ} > 1^{\circ}$ (c) $1^{\circ} < 2^{\circ} > 3^{\circ}$ (d) $3^{\circ} > 2^{\circ} < 1^{\circ}$ The +*I* effect of alkyl groups is in the order[**DCE 2002**] 35. (a) $2^{\circ} > 3^{\circ} > 1^{\circ}$ (b) $1^{\circ} > 2^{\circ} > 3^{\circ}$ (c) $3^{\circ} > 2^{\circ} > 1^{\circ}$ (d) None of these 36. Which one has asymmetric *C*-atom [Roorkee 1995] (a) $CH_3 - CH_2 - CH_2$ Br

(b)
$$CH_3 - CH - -CH - CH_3$$

 $| | |$
 $Br CH_3$
(c) $CH_3 - CH_2 - CH - CH_3$
 $| Br$
 CH_3
(d) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2$

Br

Which of the following compounds will show 37. metamerism

3

[KCET 1996]
(a)
$$CH_3COOC_2H_5$$
 (b) $C_2H_5 - S - C_2H_5$
(c) $CH_3 - O - CH_3$ (d) $CH_3 - O - C_2H_5$

38. How many carbon atoms in the molecule $HCOO - (CHOH)_2 - COOH$ are asymmetric

[MP PET 2001]

(c) 3 (d) None of these Which of the following act as nucleophiles [Roorkee 1999] 39. (b) *RO*⁻ (a) CH_3NH_2

(c)
$$AlCl_3$$
 (d) CH_3MgBr

40. Which of the following has the highest nucleophilicity

[IIT-JEE Screening 2000]

(a) F⁻ (b) *OH*⁻ $(d) M U^{-}$ (c) CH^{-}

(c)
$$CH_3$$
 (d) NH_2

41.

Keto-enol tautomerism is found in

[IIT-JEE 1988; MADT Bihar 1995]

[IIT-JEE 1995]

- **42.** Which of the following compounds will show
geometrical isomerism[IIT-JEE 1998]
 - (a) 2-butene (b) Propene
 - (c) 1-phenylpropene (d) 2-methyl-2-butene
- **43.** Which behaves both as a nucleophile and electrophile

[IIT-JEE Screening 1991; Pb. CET 1985]

(a)
$$CH_3NH_2$$
 (b) CH_3Ch

- (c) CH_3CN (d) CH_3OH
- 44. The number of optical isomers of an organic compound having *n* asymmetric carbon atoms will be [MP PET 1994]
 - (a) 2^{n+1} (b) n^2

(c) 2^n (d) 2^{n-1}

45. Total number of isomers of C_6H_{14} are

[IIT-JEE 1987; DPMT 1983; CPMT 1991; MNR 1990; MP PET 1995; UPSEAT 2001]

(a) 4	(b) 5
(c) 6	(d) 7

46. With a change in hybridisation of the carbon bearing the charge, the stability of a carbanion increase in the order

[DCE 2003]

(a)
$$sp < sp^2 < sp^3$$

(b) $sp < sp^3 < sp^2$
(c) $sp^3 < sp^2 < sp$
(d) $sp^2 < sp < sp^3$

- 47. The C C bond length of the following molecules
is in the order[IIT-JEE 1991]
 - (a) $C_2H_6 > C_2H_4 > C_6H_6 > C_2H_2$
 - (b) $C_2H_2 < C_2H_4 < C_6H_6 < C_2H_6$

(c)
$$C_2H_6 > C_2H_2 > C_6H_6 > C_2H_4$$

(d)
$$C_2H_4 > C_2H_6 > C_2H_2 > C_6H_6$$

48. In the reaction $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ a chiral centre is produced. This product would be [CBSE PMT 1995]

(a) Laevorotatory (b) Meso compound

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(c) Dextrorotatory

ry (d) Racemic mixture

49. Cyclic hydrocarbon molecule '*A*' has all the carbon and hydrogen in a single plane. All the carbon-carbon bonds are of same length less than 1.54Å, but more than 1.34Å. The C-C bond angle will be [BVP 2003]

(a) $109^{\circ}28'$ (b) 100°

(c) 180° (d) 120°

50. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl [CBSE PMT 200]

(a) 2	(b) 5
(c) 7	(d) 9



Read the assertion and reason carefully to mark the correct option out of the options given below:

- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
- (c) If assertion is true but reason is false.
- (d) If the assertion and reason both are false.
- (e) If assertion is false but reason is true.
- Assertion : Aniline is better nucleophile than anilium ion.
 Reason : Anilium ion have +ve charge.[AIIMS 1996]
 Assertion : Neopentane forms one mono substituted compound.
 Reason : Neopentane is isomer of pentane.

[AIIMS 2001]

- **3.** Assertion : *Trans*-2-butene on reaction with Br_2 gives *meso*-2, 3-dibromobutane.
 - Reason : The reaction involves syn-addition of bromine. [AIIMS 2003]

4. Assertion : Cis-1, 3-dihydroxy cyclohexane exists in boat conformation.

Reason : In the chair form, there will not be hydrogen bonding between the two hydroxyl groups.

[AIIMS 2003]

- 5. Assertion : Hydroxyketones are not directly used in Grignard reaction.
 - Reason : Grignard reagents react with hydroxyl group.

[AIIMS 2003]

 Assertion : Benzyl bromide when kept in acetone water it produces benzyl alcohol.

	Reason :	The reaction follows SN^2 mechanism.
		[AIIMS 2003]
7.	Assertion	: Carbon possesses property of
	Descen .	Carbon stome form double as well as
	Reason :	cal boll atoms for in double as well as
Q	Accertion	· Olefing have the general formula
0.	ASSELLIOII	
		$C_n H_{2n+1}$.
	Reason :	There is one double bond between
		two carbon atoms in their molecules.
9.	Assertion	: Saturated hydrocarbons are
		chemically less reactive.
	Reason :	All isomeric paraffins have same
		parent name.
10.	Assertion	: A mixture of glucose and <i>m</i> -
		dinitrobenzene can be separated by
		shaking it with ether.
	Reason :	Glucose is soluble in water.
11.	Assertion	: Tertiary carbonium ions are
		generally formed more easily than
		primary carbonium ions.
	Reason :	Hyperconjugative as well as inductive
		effect due to additional alkyl groups
		stabilize tertiary carbonium ions.
12.	Assertion	: Heterolytic fission involves the
		breaking of a covalent bond in such a
		way that both the electrons of the
		shared pair are carried away by one
		of the atoms.
	Reason :	Heterolytic fission occurs readily in
		polar covalent bonds.
13.	Assertion	: The order of reactivity of
	_	carbonium ions is $2^{\circ} > 3^{\circ} > 1^{\circ}$.
	Reason :	Carbon atom in carbonium ions is in
		<i>sp</i> ³ state of hybridisation.
14.	Assertion	: Free radicals are short lived and
		highly reactive.
	Reason :	Free radicals are highly unstable.
15.	Assertion	: Each carbon in ethylene molecule is
		sp^2 hybridised.
	Reason :	The $H - C - H$ bond angle in ethylene
		molecule is 120°.
16.	Assertion	: Cyclohexanone exhibits keto-enol
		tautomerism.
	Reason :	In cyclohexanone, one form contains
		the keto group $(C = O)$ while other
		contains enolic group $(-C = C - OH)$.
17.	Assertion	: Staggered form is less stable than
•	-	the eclipsed form.
	Reason :	The conformation in which the bond
		pairs of two central atoms are very
		far from one another is called
		staggered form.

18.	Assertion	:	Trans	isomers	are	more	stable	than
		ci	s isom	ier.				

- Reason : The *cis* isomer is the one in which two similar groups are on the same side of double bond.
- **19.** Assertion : Propadiene is optically active.

Reason : Propadiene has a plane of symmetry.

20. Assertion : Lactic acid is optically active.

Reason : A symmetry in the inner structure of the organic compound causes optical activity.

21. Assertion : Same number of electron pairs are present in resonance structures.

Reason : Resonance structures differ in the location of electrons around the constituent atoms.

- **22.** Assertion : Carbon-oxygen bonds are of equal length in carbonate ion.
 - Reason : Bond length decreases with the multiplicity of bond between two atoms.

Structural and stereo isomerism



1	b	2	c	3	b	4	b	5	c
6	а	7	b	8	C	9	d	10	a
11	С	12	с	13	c	14	d	15	b
16	а	17	d	18	а	19	а	20	с
21	d	22	d	23	d	24	С	25	c
26	ac	27	с	28	c	29	С	30	d
31	C	32	С	33	d	34	С	35	с
36	а	37	С	38	С	39	d	40	b
41	C	42	а	43	C	44	b	45	b
46	а	47	b	48	С	49	а	50	C
51	C	52	С	53	C	54	а	55	d
56	C	57	С	58	а	59	d	60	а
61	а	62	d	63	C	64	b	65	b
66	b	67	b						

Bonding and hybridisation in organic compounds

Dipole moment, resonance and reaction intermediates

1	b	2	b	3	b	4	C	5	с
6	d	7	C	8	d	9	b	10	C
11	d	12	b	13	а	14	C	15	d
16	b	17	d	18	b	19	а	20	а
21	а	22	a	23	b	24	c	25	C
26	b	27	b	28	b	29	d	30	b
31	С	32	C	33	а	34	d	35	а
36	а	37	b	38	b	39	a	40	d
41	d	42	b	43	d	44	b	45	b
46	a	47	b	48	d	49	b		

Organic reactions and their mechanism

1	d	2	C	3	C	4	b	5	а
6	C	7	C	8	d	9	d	10	d
11	b	12	d	13	C	14	d	15	C
16	a	17	a	18	d	19	b,c	20	a
21	d	22	а	23	d	24	а	25	а
26	b	27	d	28	b	29	b	30	d
31	d	32	C						

1	а	2	а	3	b	4	с	5	b
6	b	7	d	8	C	9	C	10	C
11	b	12	а	13	а	14	C	15	C
16	а	17	b	18	d	19	а	20	d
21	b	22	а	23	а	24	а	25	d
26	b	27	d	28	C	29	C	30	d
31	а	32	d	33	b	34	а	35	C
36	а	37	b	38	b	39	C	40	d
41	C	42	а	43	d	44	а	45	b
46	d	47	d	48	b	49	C	50	a
51	b	52	d	53	b	54	d	55	d
56	d	57	b	58	d	59	b	60	d
61	b	62	а	63	d	64	d	65	b
66	b	67	b	68	а	69	d	70	а
71	а	72	C	73	C	74	а	75	а
76	d	77	a	78	b	79	а	80	а
81	а	82	b	83	b	84	d	85	d
86	b	87	d	88	a	89	b	90	C
91	b	92	a	93	a	94	d	95	d
96	b	97	b	98	а	99	C	100	b
101	b	102	C	103	b	104	b	105	a
106	C	107	a	108	a	109	b	110	C
111	а	112	d	113	b	114	d	115	b
116	а	117	a	118	b	119	а	120	d
121	b	122	C	123	a	124	b	125	a
126	C	127	C	128	d	129	b	130	d
131	d	132	a	133	d	134	а	135	b
136	C	137	b	138	а	139	b	140	d
141	d	142	b	143	b	144	а	145	C
146	d	147	а	148	c	149	b	150	b
151	C								

Critical Thinking Questions

1	с	2	d	3	с	4	е	5	а
6	b	7	С	8	d	9	b	10	d
11	С	12	С	13	а	14	b	15	с
16	С	17	С	18	d	19	b	20	d
21	acd	22	С	23	b	24	С	25	b
26	a	27	a	28	c	29	a	30	d
31	C	32	b	33	b	34	b	35	с
36	bc	37	b	38	b	39	abd	40	с
41	cd	42	ac	43	С	44	C	45	b
46	С	47	b	48	d	49	d	50	а

Assertion & Reason									
1	а	2	b	3	с	4	d	5	а
6	а	7	b	8	е	9	b	10	b
11	а	12	b	13	d	14	b	15	b
16	а	17	е	18	b	19	е	20	b
21	е	22	b						



Bonding and hybridisation in organic compounds

- 3. (b) $CH_2 = CH_2$ both the carbon atoms are sp^2 hybridised.
- 5. (c) Type
 s-character

 sp^3 25%

 sp^2 33.33%

 sp 50%

 $6. (a) \quad CH = CH$

7.

(b)
$$sp^2$$
 and sp^3
 $CH_{3p^3} - CH_{sp^2} = CH_{sp^2} - CH_{2p^3} - CH_{3p^3}$

8. (c) $CH_{3}^{sp^{3}} - OH_{3}^{sp^{3}} - OH_{3}^{sp^{3}} - OH_{3}^{sp^{3}}$

All the carbon atoms are sp^3 hybridized.

9. (d)
$$CH_{3} - CH = CH_{sp^{2}} - CH_{2} - CH_{sp^{2}} = CH - CH_{sp} = CH_{sp}$$

10. (a) $CH_{3} - C_{sp} = C_{sp} - H$
11. (c) sp and sp^{2}

$$N \equiv \frac{sp}{1} - \frac{sp^2}{2} = \frac{CH}{3}$$

13. (c)
$$\pi$$
 electrons = 10.
 π bonds = 5
hence electrons are double

14. (d) Cyclobutadienyl anion $(C_4H_4)^{2-}$

$$\begin{bmatrix} HC & CH \\ HC & CH \end{bmatrix}^{2-} \pi \text{ electrons} = 8.$$

15. (b) $CH_3 - CH_3 \xrightarrow{\text{Homolytic}} CH_3^{\bullet} + CH_3^{\bullet}$ Methylfreeradicals free radical is formed which is sp^2 hybridized.

$$H \xrightarrow{0} H$$

- **16.** (a) $Br CH_{sp^2} = CH_{sp^2} Br \xrightarrow{H_2}_{Cataly \, st} Br CH_2 CH_2 Br$
- **17.** (d) (i) $CH_3^{sp^3} CH_2^{sp^3} CH_2^{sp^3} CH_2^{sp^3}$

(ii)
$$CH_{3}^{sp^{3}} - CH_{3}^{sp^{2}} = CH_{3}^{sp^{2}} - CH_{3}^{sp^{3}}$$

Both sp^2 and sp^3 hybridized carbon.

(iii)
$$CH_2^{sp^2} = CH - CH_2^{sp^2} = CH_2^{sp^2}$$

Only sp^2 hybridized carbon.

(iv)
$$H - \underset{sp}{C} \equiv \underset{sp}{C} - H$$

Only *sp* hybridized carbon.

18. (a) (i) Benzene and its derivatives are always planar because all the carbon in benzene are sp^2 hybridized.

(v)
$$CH_2 = 6 \int_{H}^{H} H$$

Both the carbon are sp^2 hybridized. Therefore planar.

21. (d)
$$CH_3 - CH - CH_2 - CH_3$$

It has $3 CH_3$ groups, one CH_2 group and one CH group.

It has 18σ bonds and 3π bonds.

$$\mathbf{23.} \quad (\mathbf{d}) \quad \begin{array}{c} H \\ H \\ H \\ H \\ H \end{array}$$

24.

$$C-C = \sigma \text{ bonds } = 6$$

$$C-H = \sigma \text{ bonds } = 6$$

$$sp^{3} \qquad \underbrace{12}_{sp^{2}} \qquad sp^{3} \qquad sp^{3}$$

$$sp^{2} \qquad sp^{3} \qquad sp^{3}$$

Cyclo hexene

Two carbon atoms are sp^2 -hybridized while remaining 4 are sp^3 hybridized.

25. (c)
$$\overset{1}{CH}_2 = \overset{2}{CH} - \overset{3}{C} \equiv \overset{4}{C} - \overset{5}{CH}_2 - \overset{6}{CH}_3$$

3-hexy ne-1-ene

Three π bonds.

26. (a, c) Carbonium ions an sp^2 hybridized species.

$$H \rightarrow + C - H \qquad CH_{3} \rightarrow + CH_{3} \rightarrow + CH_{3} \rightarrow + C - H$$

$$H \rightarrow C - H \qquad H \rightarrow C_{2\pi-bonds} - H \qquad (C_{2}H_{5}^{+})$$
27. (c) (a) $H - C \equiv C - H$ (b) $CH_{2} = CH - C = O$

$$H$$

 $2\pi-bonds$

(c)
$$CH_3CH = CH_2$$

 $1\pi \text{ bond}$
(d)
 $CH_3 - CH = CH - C - OH$
 $2\pi - \text{bonds}$
(d)
 $N \equiv C = CH - C - OH$
 $N \equiv C = C = N$
 $N \equiv C = Sp^2$
 $N \equiv C = Sp^2$
 $Sp = N$

29. (c) $H \stackrel{\sigma}{-} C \stackrel{\sigma}{=} C \stackrel{\sigma}{-} H \quad 3\sigma$ and 2π bonds are present.

30. (d) Vinyl acetylene there are 6 unhybridised orbitals.

$$CH_2 = CH - C \equiv CH$$

$$sp^2 sp^2 sp sp$$

$$1 2 2$$
(no. of unhybridised orbitals)

31. (c) Bond energy is maximum for triple bond.

- **32.** (c) $CH_2 = CH_2$ $5\sigma, 1\pi$
- **33.** (d) In benzene all 6 carbons are sp^2 hybridised.

34. (c)
$$CH_{sp^2} = CH_{sp^2} - CH_{sp^2} = CH_{sp^2}$$

- **36.** (a) $CH_2 = CH C \equiv CH$ $_{7\sigma,3\pi}$
- 37. (c) Propyne has one acidic hydrogen.

39.

15 σ and 3 π .

- **40.** (b) In CCl_4 all bond angles are same *i.e.* of $109^{\circ}28'$ the carbon is sp^3 hybridised.
- **41.** (c) Geometry in sp^2 -hybridisation is trigonal.

42. (a)
$$CH_{sp^2} = C = CH_{sp^2} - CH_{3}$$

43. (c) Single bond has longest distance of bonds so C_2H_6 ethane is correct answer.

47. (b)
$$HC \equiv C - CH_{2} = CH_{2}$$

48. (c) In ethylene molecule carbons are sp^2 hybridised so its structure is trigonal planar

$$49. (a) $CH_{sp} \equiv CH_{sp}$$$

52. (c) 5 π bonds are present in naphenalene.

54. (a)
$$H - C = C - C - C = C$$

 $H - C = C - C - C = C$

57. (c)
$$\begin{matrix} 1 \\ CH_2 \\ sp^2 \end{matrix} = \begin{matrix} 2 \\ C \\ sp \end{matrix} = CH_2$$

59. (d)
$$H = \begin{pmatrix} H & H & H & CH_2CH_3 & H & CH_3 & H \\ | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & | & - & H \\ | & - & & - & C & - & C & - & C & - & C & - & C & - & H \\ | & H & H & CH_3 & H & H & H & H & H & H & H & H & - & 2, 5 & d; methyl4 - ethylheptane (5 Methylgroup) \end{pmatrix}$$

60. (a)
$$CH_3^{sp^3} - CO_{Acetonie}^{sp^2} - CH_3^{sp^3}$$

 $CH_3^{sp^3} - CO_{Acetonie}^{sp^3} - CH_3^{sp^2} + C$

61. (a)
$$\overset{\downarrow 2\sigma}{CH}_{2} = \overset{\sigma}{=} \overset{\downarrow \sigma}{CH}_{\sigma} - \overset{\downarrow 2\sigma}{CH}_{2} - \overset{\pi}{\sigma} C \frac{\pi}{\underline{\sigma}} N$$

Ally k y anide

Total 9σ bond and 3π bond.

62. (d) Because hydrogen is attached with high electronegative element.

63. (c)
$$CH \equiv CH$$

Ethyne
64. (b) has 15σ bonds.
65. (b) $H-C$
 $H-C$
 $C-H$
 $H-C$
 $C-H$
 H
 12π and 3π bonds

66. (b) The *s*-character of C-H bond of acetylene is higher in comparison to C-H bond of ethene and ethane. The electrons of the C-H bond in acetylene are strongly held by carbon nuclei. This facilitates the removal of hydrogen as proton.

67. (b) $CH_3 - C = CH_2$ $9\sigma 1\pi \& 2L.p$

(b)

1.

Dipole moment, resonance and reaction intermediates

 CH_3

CH = CH H_3C

- $\mu = 0$ symmetrical structure.
- (b) Due to presence of two chlorine atom on the same side of carbon atom produces dipole moment in molecule.
- 4. (c) We know that there is more difference in the electronegativities of hydrogen and chlorine. Therefore *HCl* is a polar compound.

5. (c) (i)
$$-C-C = C-C-$$

 $I = C-C-$
 $(u=0)$
(ii) CH_3
 $+ I$
(iii) CH_3
 $+ I$
(iv) C_2H_5OH

The dipole moment is the highest for Acetophenone.

6. (d) Resonance structure of molecule does not have identical bonding.

7. (c)
$$\longleftrightarrow$$

All the bonds (C - C) are equal in benzene. The C - C bond length is 1.39 Å which is in between C - C bond (1.54 Å) and C = C (1.34 Å).

9. (b) \bigcirc (1) Molecule is planar.

(2) 6π electrons are present.

- 11. (d) Benzene is unreactive instead of having 3π bonds because of resonance π -electrons are delocalized.
- 12. (b) Carboxylic acids are easily ionized because there is resonance in carboxylate ion due to π -electron shifting so H^+ get ionised very easily.

$$\rightarrow C \underbrace{\bigcirc O}_{-H} = C \underbrace{\bigcirc O^{-}}_{O} + H^{+}$$

13. (a) Due to delocalisation of π electrons benzene has resonance.

19. (a)
$$> C^+ = C <$$

- **21.** (a) It is hyperconjugation process.
- **22.** (a) Triphenyl methyl cation has three benzene resonating ring so it is most stable compound.
- 23. (b) Due to mesomeric effect (+) of OH group the electron density on benzene ring increase. So the electrophile easily attacked on these electron rich center.
- 24. (c) Carbonyl carbon become more reactive toward nucleophilic addition by increasing the +I effect of alkyl group so the reactivity order is as

$$HCHO > CH_{3}CHO > CH_{3}COCH_{3}$$

$$H \to C = O \quad CH_{3} \to C = O \quad CH_{3} \to C = O$$

$$H \to C = O \quad CH_{3} \to C = O \quad CH_{3} \to C = O$$

25. (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). CH_3

26. (b)
$$CH_3 - C^+$$
 Due to (+1) effect of three methyl CH_3

group 3° carbocation is more stable.

27. (b)
$$CH_3 - CH_3 - COCH_3 -$$

28. (b)
$$C_6H_5 - CH_2^{\overline{\cdot \cdot}} > CH_3CH_2^{\overline{\cdot \cdot}}$$

Benzyl carbanion
 $(CH_3)_2 CH^{\overline{\cdot \cdot}} > (CH_3)_3 C^{\overline{\cdot \cdot}}$
Isopropyl carbanion
 $Carbanion$

- **30.** (b) 3° alcohol on dehydrogenation gives most stable carbonium ion.
- **32.** (c) Without intermediate reaction take place as under

 $CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - CH - CH_3$

(According to markownikoff rule)

But the halogen bonded with terminal carbon so it take place in presence of peroxide by free radical mechanism.

$$R - O - OR \rightarrow 2RO$$
; $HBr + RO \rightarrow ROH + Br$
peroxide

$$CH_3 - CH = CH_2 + Br^{\cdot} \rightarrow CH_3 - CH - CH_2 - Bt$$

 $CH_{3}-CH-CH_{2}Br+HBr\rightarrow$

			CH 3 -	$-CH_2 - CH_2Br + Br$
33.	(a)	Species	Valence	Magnetic
			electro	ns behaviour
	1.	Free radical	7	Paramagnetic
	2.	Carbonium	6	Diamagnetic
		ion		
	3.	Carbanion	8	Diamagnetic
	4.	Carbene	6	Diamagnetic
	5.	Nitrene	6	Diamagnetic
		CH ₃	CH_{2}	
				0
34.	(d) ($CH_3 - C^o > CH_3 - C$	-CH > CH	$_{3} - CH_{2}$
		20 GI	0	- 0
		$\sim CH_3$	2.	10

Greater the no. of alkyl groups attached to the carbon atom carrying the odd electrons, greater is the delocalization of odd electron and hence more stable is the free radical.

35. (a)
$$\overrightarrow{R} = \overrightarrow{C} \times \overrightarrow{R}$$

Greater the no. of alkyl groups, greater would be the dispersal of the charge and hence more stable will be the carbonium ion.

39. (a) C-C bond length in benzene is 1.39Å which is in between C-C (1.54Å) and C = C(1.34 Å)because of resonance.

40. (d)
$$C - Cl \xrightarrow{\text{Heterolytic}}_{\text{bond fission}} C^+ + Cl^-_{\text{Anion}}$$

41. (d)
$$CH_3CH_2OH \xrightarrow{\text{Heterolytic cleavage}} CH_3CH_2^+ + OH^-$$

43. (d)
$$CH_3 - \stackrel{|}{C} - Cl \xrightarrow{SbCl_5} Cl - \stackrel{|}{C} - CH_3 + CH_3 - \stackrel{|}{C} - Cl$$

(d) form (l) form

44. (b) The reaction of an alkyl halide or aryl halide with benzene in the presence of a Lewis acid, generally $AlCl_3$ is known as Friedel Craft's reaction.

45. (b)
$$\bigvee_{NO_2}$$
 gives only monosubstitution
 NO_2 product as $-NO_2$ group is meta
directing and only one *m* -position
is possible in *m* -dinitrobenzene.

- **46.** (a) According to Huckel ruel, all aromatic compounds must have $(4n + 2)\pi$ electrons where *n* is an integer, *i.e.*, n = 0, 1, 2, 3, ... and possesses unusual stability due to the complete delocalisation of π -electrons.
- **47.** (b) H O H, : NH_3 , R O R nucleophiles SO_3 has electron deficient centre (a reagent which can accept an electron pair in a reaction, is called an electrophile)
- **48.** (d) Chlorine atom is *orth-para* directing group.
- **49.** (b) Stability of carbonium ions.

tertiary alkyl > secondary alkyl > primary alkyl > methyl.

More the number of alkyl groups, the greater the dispersal of positive charge and therefore, more the stability of carbonium ion is observed.



triphenylmethyl cation

Dispersal of positive charge increases with the increase in the number of benzene ring.

Organic reactions and their mechanism

- 1. (d) It is SN^2 type of reaction.
- 3. (c) $Cl_2 \xrightarrow{\text{Light}} 2Cl^{\bullet}$

$$CH_3 \xrightarrow{CH_2Cl} +H^+ \quad (Free radical substitution)$$

- 5. (a) It is nucleophilic substitution reaction which is in first order.
- **9.** (d) All cations are expected to act as Lewis acid since they are electron deficient in nature. However cation such as Na^+ , K^+ etc. (Inert gas configuration) have a very little tendency to accept electrons. Therefore they do not acts as lewis acids in friedel Craft's reaction.
- 10. (d) The process of nitration takes place as below

$$HONO_2 + 2H_2SO_4 \approx H_3O^+ + 2HSO_4^- + NO_2^+$$

(nitronium ion)

The electrophile responsible for nitration is NO_2^+ ion.

 (b) Dehydrohalogenation of an alkyl halide on presence of alcoholic potash is an example of elimination reaction.

$$R - CH_2CH_2 - Cl + KOH \xrightarrow{\Delta}_{alc.}$$

$$RCH = CH_2 + KCl + H_2O$$

12. (d)
$$\begin{array}{c} CH_2 \\ \parallel \\ CH + HCl \end{array} \rightarrow \begin{array}{c} CH_3 \\ \downarrow \\ Cl \end{array} \xrightarrow{(1, 1 \text{ dichloroethane})} H < Cl \\ (1, 1 \text{ dichloroethane}) \end{array}$$

~

It is addition reaction.

Which is according to Markownikoff rule.

13. (c)
$$CH \equiv CH + H_2 \rightarrow CH_2 = CH_2$$

That is called addition reaction.

- 14. (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.
- **15.** (c) Due to *OH*⁻ attack it is nucleophilic substitution.
- **16.** (a) Electron deficient species (in complete octet) acts as an electrophile *i.e. BCl*₃.
- **17.** (a) NO_2^{\oplus} is produced when conc. HNO_3 reacts with conc. H_2SO_4 .

$$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + NO_2^{\oplus} + H_2O_2^{\oplus}$$

18. (d) Phenol will undergo electrophilic substitution more readily than benzene.



- **20.** (a) $AlCl_3$ is lewis acid *i.e.*, electron deficient compound. So it is electrophile.
- **21.** (d) $CH_3 O^-$ is the strongest nucleophile which is capable of acting as donar of electon pair.
- **22.** (a) The phenyl ring having H N < group is activated while another one is deactivated due to -C-, so electrophilic aromatic bromination

will occur at para position with respect to H - N < group inactivated ring.

(d) The non reactivity of the chlorine atom in 23. vinyl chloride may be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridization the C - *Cl* bond will be a σ -bond and the two lone pairs of electron would occupy the other two sp^2 orbitals. This would leave a *p*-orbital containing a lone pair and this orbital could not conjugate with the π bond of the ethylenic link. Thus two M.O.S. will be required to accommodate these four π electrons. Further more since chlorine is more electronegative than carbon, the electron will tend to be found in the chlorine atom has now lost full control of the one pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each atom acquires a small negative charge. Hence, owing 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.

$$CH_2 - CH - 0$$
 $CH_2 - CH - 0$

24. (a) Nucleophiles are those substances which can donate a pair of electrons. These can be neutral or negative. The nucleophilic power depends on the tendency of species to donate electrons. This is more, when an electron pushing group (+*I* group) is present. Among the alkyl groups, those having higher number of *C*-atoms will push more, hence ethyl > methyl.

$$C_2H_5 \xrightarrow{\bullet} S - H, CH_3 \xrightarrow{\bullet} C - O^-, CH_3 \xrightarrow{\bullet} NH_2,$$

$$(+I)$$
 $(+I)$ $(+I)$
 $CH_5 + CH_2$
 $(-I)$

- **25.** (a) Conjugated acid of Cl^- is a stronger acid i.e., HCl.
- **26.** (b) Saytzeffs product.
- **29.** (b) If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to the saytzeff rule, the main product is the most highly substituted alkene.

$$HO^{-} \bigvee_{H \to H} OH$$

$$H \to OH$$

- **30.** (d) Halogenation of alkanes takes place in presence of light (sunlight or UV) or at elevated temperature via free radical.
- **31.** (d) All the given species undergo nucleophilic substitution reaction. This reactivity can be explained in terms of the nature of C-X bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms.

$$-\overset{\delta}{C}-\overset{\delta}{X}$$

32. (c) Increasing + I effect $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$

Structural and stereo isomerism

5. (b)
$$CH_3 - COOH_1 - COOH_1$$

7.

In this structure chiral carbon atom is present since it is optical active.

6. (b) In ethane staggard form and in cyclohexane chair form is more stable.



Chiral centre is present. Hence, it exists as optical isomers or enantiomorphs.

- **8.** (c) In $C_6H_5CH_2CH_3$ chiral centre is absent.
- **9.** (c) $C_2H_2Br_2$ has three isomers.

(1)
$$H - C = C - H$$

 Br
 Br
 Br
 Br
(2) $CH = CH$
 Br
 Br
 Br
(1) $H - C = C - H$
 Br
 Br
(2) $CH = CH$
 Br
 Br
(1) $H - C = CH$
 $H - CH$
 Br
 $H - CH$
 $H - CH$
 Br
 $H - CH$
 $H - CH$
 $H - CH$
 Br
 $H - CH$
 $H - CH$
 $H - CH$
 $H - CH$
 Br
 $H - CH$
 $H - C$

11. (b)
$$CH_3 - C^* - CH_2 - CH_3$$

 Cl_2
2-Chlorobuta ne

because they contain chiral carbon atom.

12. (a)
H
13. (a)
$$CH_3 - C^* - CH_2 - CH_3$$

Cl

In other compounds chiral carbon is absent.

14. (c) Ball is achiral where other objects are chiral because objects and their mirror images are non-super imposable



Only one chiral centre. Hence two optical isomers are possible.



No. of optical isomer = 2^n (where n = no. of chiral carbon) = $2^1 = 2$.

19. (a)
$$CH_3 - CH_2 - CH_2 - CH_3$$
 and $CH_3 - CH - CH_3$
 $I = CH_3$
 $Iso-butane$

20. (d) $CH_3 - C^* - CH_2 - CH_3$ Chiral structure is that

in which one carbon atom is attached to 4 different atoms or groups.

21. (b)
$$CH_3 - CH_2 - CH = CH_2 & CH_3 - CH = CH - CH_3$$

1-butane
 CH_3

22. (a) HC = CH and HC = CH HC = CH $CH_3 CH_3 CH_3 CH_3 CH_3$ (Cis)2-butene 2-butene

Η

23. (a) Four groups linked to carbon atom are different



25. (d) Five isomers of C_4H_8



26. (b) Polarimeter is an instrument used for measuring the optical rotation. It consists of two Nicol prisms, one called the polarizer (near the light source) and the other called the analyser (near the eye). In between the polarizer and analyser, a glass tube containing the solution of an optically active compound is placed.



Ray diagram of

27. (d)
$$CH_3 - CH_2 - CH_2 - CH_3$$
 and $CH_3 - CH - CH_3$
 n -butane
 CH_3
Iso-butane

28. (c) Metamerism is a special types of isomerism shown by secondary amines, ethers and ketones.

29. (c)
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH_2 - OH_2 - OH_2 - OH_2 - CH_2 - OH_2 - OH_2 - CH_3 - CH_2 - CH_2 - OH_2 - CH_3 - CH_2 - CH_2 - OH_2 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_2 - OH_2 - OH_2 - OH_2 - OH_2 - OH_3 - CH_3 - CH_2 - OH_2 - OH_2 - OH_2 - OH_2 - OH_3 - CH_3 - CH_2 - OH_2 - OH_2 - OH_3 - CH_3 - CH_3 - CH_2 - OH_2 - OH_2 - OH_2 - OH_3 - CH_3 - CH_3 - CH_3 - CH_2 - OH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_2 - OH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_3 - CH_2 - OH_3 - CH_3 -$$

30. (d) Position isomers : $CH_3 - CH_2 - CH_2 - CH_2 - OH$ and Butan -1-ol $CH_3 - CH_2$

$$H_3 - CH_2 - CH - CH_3$$

 OH
Butan -2-ol

Functional isomers:

$$CH_3CH_2CH_2 - CH_2 - OH$$
 and $C_2H_5 - O - C_2H_5$
Butanol Diethylether
Metamers: $C_2H_5 - O - C_2H_5$ and $CH_2 - O - C_2H_5$

Metalliers:
$$C_2H_5 - O - C_2H_5$$
 and $CH_3 - O - C_3H_7$
Diethylether Methylpropylether

31. (a) 1.
$$CH_3 - CH_2 - CH_2 - CH_2 - OH_3$$

Butan -1-ol
2. $CH_3 - CH_2 - CH - CH_3$
 OH_3
Butan -2-ol
3. $CH_3 - CH - CH_2 - OH_2$
 CH_3
2 methyl propan -1-ol
 CH_3
4. $CH_3 - C - CH_3$
 OH_2
2-Methyl propan -2-ol

32. (d) $C_4 H_{10} O$ have six isomers are possible

1.
$$CH_{3}CH_{2}CH_{2}CH_{2} - OH_{Butan - 1 - ol}$$

2. $CH_{3} - CH_{2} - CH - CH_{3}$
 $OH_{Butan - 2 - ol}$
3. $CH_{3} - CH - CH_{2} - OH_{2} - OH_{1}$
 CH_{3}
2-Methyl propan - 1 - ol
 CH_{3}
4. $CH_{3} - C - CH_{3}$
 $OH_{2} - Methyl - Propan - 2 - ol$

5.
$$CH_3 - O - C_3H_7$$

Methylpropylether
6. $C_2H_5 - O - C_2H_5$
Diethylether

33. (b)
$$CH = CH$$
 Cl $CH = CH$
 Cl Cl Cl $CH = CH$
(trans)
34. (a) ${}^{1}CH_{3} - CH = CH - CH = CH - C_{2}H_{5}$

1.

$$H_{3}C$$

$$CH = CH$$

$$CH = CH - C_{2}H_{5}$$

$$CH = CH - C_{2}H_{5}$$

2.
$$CH = CH$$

 H_3C (mans)

3.

$$CH_{3} - CH = HC$$

$$CH = CH$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$CH_{3} - CH = HC$$

$$CH = HC$$

$$CH = HC$$

$$C_{2}H_{5}$$

$$C_{2}H_{5$$

36. (a) Molecular symmetry COOH

3

$$H - C - OH$$

$$H - C - OH$$

$$H - C - OH$$

$$COOH$$
Plane of Symmetry

Mesotartaric acid is optically inactive due to internal compensation *i.e.* the effect one half of the molecule is neutralized by other.

37. (b)
$$CH_3 - C^* - COOH$$
 * chiral centre is present.
 OH
38. (b) $COOH - C^* - CH_2 - CH_3$

OH

One chiral centre. Therefore two forms are possible.

39. (c) Optical isomerism and geometrical isomerism.

40. (d) (a)
$$CH_3CH_2CH_2COOH(C_4H_8O_2)$$

(b) $CH_3CH_2 - COOCH_3(C_4H_8O_2)$
Diethyl ether $C_2H_5 - O - C_2H_5$ is position

isomer and not stereoisomer.
41. (c)
$$C_2H_5 - O - C_2H_5$$
 and $CH_3 - O - C_3H_7$
are metamers.

42. (a)
$$CH_3 - CH_2 - CH_2 - OH$$
 and $CH_3 - CH - CH_3$
 $n-propylalcohol$
 OH
Iso-propylalcohol

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are position isomers of each other.

- (a) $R N \stackrel{-}{=} C$ and $R - C \equiv N$ are functional 44. isomers.
- (b) Optical isomerism because chiral centre is 45.

Н

present
$$(CH_3)_2 - C = CH - C^* - COOH$$
.

46. (d) Butanone $CH_3 - C - CH_2 - CH_3 (C_4H_8O)$ is not O

an isomer of $C_2H_5 - O - C_2H_5(C_4H_{10}O)$

(d) Chair and boat form differ in energy by 44 47. kJ/mol.



48. (b) $CH_3 - O - CH_2 - CH_3$ and $CH_3CH_2CH_2 - OH$

ethylmethyl ether and propylalcohol are functional isomers.

49. (c) $CH_3 - CH_2 - CH_2^-O - C_2H_5$ Ethoxy propane

$$CH_3 - CH_2 - CH_2 - O - C_2H_5$$

Propoxy ethane

Both are same compounds.

- **50.** (a) $CH_3 CO CH_3$ and $CH_3 CH_2 CHO$ are functional isomers.
- (b) Three isomers are possible 51.



(d) Diastereoisomers - Optical isomers which are 52. not mirror images of each other.

e.g.

$$\begin{array}{ccc}
COOH & COOH \\
H - C - OH & and & H - C - OH \\
H - C - OH & HO - C - H \\
COOH & COOH \\
Diastereoisomer \\
\end{array}$$

53. (b) $C_7 H_9 N$ has 5 isomers



54. (d) (1)
$$CH_3 - CH_2 - CH_2 - CH = CH_2$$

Pent-1-ene
(2) $CH_3 - CH_2 - CH = CH - CH_3$
Pent-2-ene
(3) $CH_3 - CH_2 - C = CH_2$
 CH_3
2-Methyl-1-butene
(4) $CH_3 - CH = C$
 CH_3
2-Methyl-2-butene

(5)
$$H_2C$$

 H_2C
 H_2C
Cyclopentane

H asymmetric centre

55. (d)
$$CH_3 - C^* - COOH$$
 2-hydroxy propanoic acid
OH

58. (d)
$$CH_3 - C = CH_2$$

2-methyl propene does not show geometrical isomerism.

59. (b) Conformers - Conformation arises because of free rotation around C-C bond axis.

60. (d)
$$CH_3 - C_4 - C_7 - C_7 - COOH$$

| Br Br

62.

Number of enantiomers = 2^n (*n* = asymmetric Carbon atom) = 2^2 = 4.

61. (b) $C_6H_5C \equiv N$ and $C_6H_5N \equiv C$ are functional isomers.

$$\begin{array}{c}
H\\
CH_{3} - C^{*} - CH_{2}D\\
Cl
\end{array}$$

64. (d)

69.

63. (d) Cis and trans 2-butene are geometrical isomers.

$$CH_{3} = CH \text{ and } CH = CH$$
$$CH_{3} = CH_{3} = CH_{3}$$
$$H$$
$$CH_{3} = CH_{3} = CH_{3}$$
$$H$$
$$CH_{3} = CH_{3}$$
$$H$$
$$CH_{3} = CH_{3}$$

A carbon atom which is attached to four different atoms or groups is called a chiral or asymmetric carbon atom. such a carbon atom is often marked by an asterisk.

- **65.** (b) $R C \equiv N$ and $R N \equiv C$ are functional isomers.
- **66.** (b) Glucose and fructose have similar molecular formula with difference of functional group, so they are functional isomers.

67. (b) 2-butanol
$$(CH_3 - CH - CH_2 - CH_3)$$
 is optically
 OH

active because it has asymmetric carbon atom. (d) Ethane has all single (σ) bonds so there is

minimum resistance in bond rotation.



$$H = CHC^{H} =$$

72. (c)
$$CH_3 - C - CH_2 - CH_3$$

Secondary butyl amine is optically active.

73. (c) Neopentane and isopentane are chain isomers. CH_3

$$CH_3 - \overset{i}{C} - \overset{i}{C} H_3$$
 and $CH_3 - CH_2 - \overset{i}{C} H_3 - CH_3$

- 75. (a) Due to single bond there is no hindrance
- **77.** (a) Only 1-phenyl-2-butene will exhibit *cis-trans* isomerism.

- **79.** (a) Geometrical isomerism is not possible in propene.
- **80.** (a) Two isomeric forms are possible for 2-methyl propane.

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

 $CH_3 - CH_3 = CH_3$
 CH_3
 n -butane 2-methyl propane

 (d) Restricted rotation is essential condition for geometrical isomerism.

88. (a)
$$\begin{array}{c} H \\ C = C \\ H_3C_{\text{cis isomer}} \\ CH_3 \end{array}$$
 $\begin{array}{c} H_3C \\ H_3C_{\text{cis isomer}} \\ H_3C_{\text{cis isomer}} \\ H_3C_{\text{Trans isomer} \\ H_3$

89. (b) Three isomeric structures are possible for C_4H_8

$$H_2C = CH - CH_2 - CH_3$$
$$CH_3 - CH = CH - CH_3$$
$$CH_3 - C = CH_2$$
$$CH_3 - C = CH_2$$

- **92.** (a) Enantiomers have same chemical properties but different physical properties.
- **93.** (a) Meso isomer have two achiral carbon with opposite spin so it becomes optically inactive







- **96.** (b) Due to formation of the plane of symmetry by the syn addition of hydrogen in the triple bond, the compound formed is optically inactive.
- **101.** (b) Racemic mixture is combination of *d* and *l* isomers.
- **102.** (c) $Cl_2C = CH CH_2 CH_2 CH_2$. It can't show geometrical isomerism due to unsymmetrical alkene.
- 103. (b) Geometrical isomerism.

104. (b)
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

- **105.** (a) Functional isomerism
- **109.** (b) Non superimposible on its mirror image.

112. (d)
$$CH_3 - CH_2 - CH - CH - CH - CH_3$$
, it is a chiral compound.

114. (d)
$$CH_3 - C - H$$

In this structure chiral carbon is present that is why it is optically active.

- **115.** (b) 2-chloro butane will be optically active.
- 118. (b) Structures are mirror images of each other which are non super impossible so they are enantiomers.
- **120.** (d) Both have one chiral carbon atom hence racemic mixture will be obtain
- **121.** (b) Structure have 3-different atoms and group so it is unable to show geometrical isomerism
- **122.** (c) Metamerism is shown by the different arrangement of alkyl group about functional group.
- **126.** (c) $CH_3 O CH_3$ and C_2H_5OH are functional isomers.
- **127.** (c) Both are enantiomer.
- **128.** (d) $CH_3COOC_2H_5$ shows tautomeric isomerism.

$$O \qquad OH \\ CH_3 - C - O - CH_2 - CH_3 \rightleftharpoons CH_2 = C - OC_2H_5$$

$$CH_3 \qquad CH_3 \qquad CH_3$$
129. (b)
$$H - C - Cl \qquad H - C - Cl \qquad CH_3 \qquad CH_3$$

$$2 \text{ chlorobuta ne} \qquad 2, 3 \text{ dichlorobut ane} \qquad CH_3 \qquad H - C - Cl \qquad OH \qquad H - C - Cl \qquad H_3C - C - COOH \qquad H - C - Cl \qquad H_3C - C - COOH \qquad H - C - H \qquad H \qquad 2 \text{ hydroxy propanoic acid} \qquad CH_3 \qquad$$

130. (d) Gaseous density of both ethanol and dimethyl ether would be same under identical condition of temperature and pressure while the rest of these three properties vapour pressure, boiling point and heat of vaporization will differ as ethanol has hydrogen bonding where as ether does not.

132. (a)
$$\begin{array}{c} CH_{3} \\ H \end{array} > C = C < \begin{array}{c} CH_{3} \\ H \end{array} \qquad \begin{array}{c} CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ H \\ CH_{3} \\ H \end{array} > C = C < \begin{array}{c} H \\ CH_{3} \\ CH_{3} \\ H \\ CH_{3} \\ CH_{3}$$

Cis-trans isomerism shown by compound which have double or triple bond by which

they restrict their rotation, since 2 butyne have no hydrogen on triple bonded carbon. $CH_3 - C \equiv C - CH_3$ [It does not show cis-trans]

133. (d) Because it contain asymmetric carbon atom.

$$CH_3 - CH_2 - CH - COOH$$

 CH_3
 H_1
(b) $HC = C - C - CH$ shows optical isomeries

135. (b) $HC = C - C - CH_3$ shows optical isomerism Cl

because of molecule is unsymmetrical. That is called chiral.

136. (c) Nitroalkanes exhibit tautomerism. In it, $\alpha - H$ – atom is labile and form nitrolic acid.

$$H_{3}C - CH_{2} - N \triangleleft_{O}^{O} \leftrightarrow H_{3}C - CH = N \triangleleft_{O}^{OH}$$
$$CH_{3}$$

137. (b) H - C - COOH shows optical isomerism due to OH

presence of asymmetric carbon atom.

138. (a) 2-chloro butane has a chiral carbon atom, hence only it will show optical activity and will possess two enantiomers (one chiral carbon atom).

139. (b) C_4H_7Cl is a monochloro derivative of C_4H_8 which itself exists in three isomeric forms.

(i) $CH_3 - CH_2 - CH = CH_2$: Its possible monochloro derivatives are :

 $CH_3 - CH_2 - CH = CH - Cl$

2 isomers : cis and trans forms

$$CH_3 - CH - CH = CH_2$$

٠

optically active (exists in two forms) $ClCH_2 - CH_2 - CH = CH_2$ (one form)

 $H_3C - CH_2 - \stackrel{|}{C} = CH_2$ (one form) (ii) $CH_3 - CH = CH - CH_3$: Its possible monochloro derivatives are : $CH_3 - CH = \stackrel{|}{C} - CH_3$ ClExists in two geometrical forms

 $CH_3 - CH = CH - CH_2Cl$

Exists in two geometrical forms

(iii)
$$CH_3 - C = CH_2$$
 : Its possible monochloro
 CH_3
derivatives are
 $CH_3 - C = CH - Cl$
 CH_3
Only one form
 $ClCH_2 - C = CH_2$
 CH_3
Only one form

Thus, the total acylic isomers forms of C_4H_7Cl are 12.

140. (d)
$$\stackrel{1}{CH}_{3} - \stackrel{2}{\stackrel{C}{CH}}_{-} - \stackrel{3}{CH}_{2} - \stackrel{4}{CH}_{3}$$

Its monochloro derivatives are as follows :

(i)
$$ClCH_2 - CH_2 - CH_2 - CH_3$$

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

It will exist as enantiomeric pair (d and l-forms)

(ii)
$$CH_3 - C - CH_2 - CH_3$$

 CH_3
no asymmetric C atom
 Cl
(iii) $CH_3 - CH - CH - CH_3$

CH₃

It will exist as enantiomeric pair (*d*- and *l*-forms)

(iv)
$$CH_3 - CH - CH_2 - CH_2 - Cl_2$$

 H_3

No asymmetric carbon atom

Hence, only two enantiomeric pairs will be obtained by the monochlorination of 2-methylbutane.

141. (d) When isomers have the structural formula but differ in the relative arrangement of atoms or groups in space with in the molecule, these are known as sterioisomers and the phenomenon as sterio isomerism. Stereoisomerism is of three types (i) Geometrical isomerism (ii) Optical isomerism (iii) Conformational isomerism.

144. (a)
$$CH_3 = CH - CH_2 - CH_3$$
; $CH_3 - CH = CH - CH_3$;

$$CH_3 - C = CH_2$$
$$CH_3 - C = CH_2$$



and

- 146. (d) *Trans* configuration is more stable than *cis* configuration because in *cis*-configuration the *H* groups are thrown closely enough together to cause crowding or repulsion. Again between 1,2-and 1,3-configurations, in 1-3, the *OH* groups are placed further apart to minimise the repulsion. Hence, more stable is 1,3-configuration.
- **147.** (a) Chirality of carbon compound is because of its tetrahedral nature of carbon.

148. (c) $O_2NHC = CHCl$ 1-chloro-2-nitroethene For highly substituted alkenes *E* and system of nomenclature is used which

For highly substituted alkenes E and Z system of nomenclature is used, which is based on a priority system developed by Cahn, Ingold and Prelog.

149. (b)
$$C_2H_5CHO \xrightarrow{CH_3M_gBr}_{H^+/H_2O} C_2H_5 \xrightarrow{-} C^* - OH$$

 C^* -chiral carbon as all the four valencies are attached with different substituents or groups.

$$CH_3$$

150. (b) $Br - C^* - Cl$ * asymmetric or chiral carbon H

All the four valencies of carbon are satisfied with different atoms/substituents.

151. (c) The configuration in which, OH group are on right side, H-atom are on left side, CHO group are on upper side & CH_2OH are on lower side found in fischer projection known as D-configuration.

$$H \xrightarrow{CHO} OH$$

$$CH_2OH$$

$$D$$
-glyceralddyde

$$H \xrightarrow{(2)} CHO \\ (4) \xrightarrow{(3)} CH_2OH \\ (3) \xrightarrow{(1)} CH_2OH \\ (3) \xrightarrow{(1)} CH_2OH \\ (4) \xrightarrow{(1)} H \xrightarrow{(1)} CH_2OH \\ (4) \xrightarrow{(1)} H \xrightarrow{(1)} OH \\ (4) \xrightarrow{$$

Critical Thinking Questions



 (d) Only four structural isomers are possible for diphenyl methane.



3. (c) *SN*¹ mechanism proceeds through carbocation intermediate.

$$CH_3$$

 $CH_3 - C-Cl$ provides stable carbocation CH_3 intermediate because it has

4. (e)
$$CH_3 - CH - CH - CH_3 + Cl_2 \rightarrow CH_3 CH_3$$

 $CH_3 CH_3$
 $2, 3-dimethyl butane$

$$CH_3 - CH - CH - CH_2Cl$$

 \downarrow
 $CH_3 CH_3$
2, 3-dimethyl chloro butane

Due to the presence of chiral carbon it shows the optical activity and its mirror image are non superimposable so it shows one enantiomer pair.

$$CH_{3} - CH - CH - CH_{2}Cl \qquad CICH_{2} - CH - CH - CH_{3}$$

$$CH_{3} CH_{3} \qquad CH_{3} CH_{3} \qquad CH_{3}$$

$$CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$$

$$CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$$

5. (a)
$$CH_3 - CH_2 - \overset{|}{C} - CH_2 - CH_3 \xrightarrow{H^+} OH$$

$$CH_{3} - CH_{2} - \bigcup_{\oplus}^{l} - CH_{2} - CH_{3}$$

The more stable carbocation is generated thus more easily it will be dehydrated.

- **6.** (b) This option is not characteristics of free radical chain reaction.
 - (c) Due to NO_2 group in benzene ring, CH_2 is most stable carbanion. NO_2

7.

8. (d) Dissociation of proton from $CH_3 - NH_3Cl^-$ is very difficult due to -I effect of Cl^- and N^+ while in C_6H_5OH due to resonance stabilization of phenoxide ion proton eliminate easily similarly due to *H*-bonding in

145. (c)

 $C_6H_5CH_2OH$ it can be eliminate and $CH_3C \equiv CH$ show acidic character by triple bond by which proton can be dissociate.

9.

Electron withdrawing group increases acidic character due to -I and -R effect of NO_2 hence orthonitrophenol is most acidic.

10. (d) Halogenation on alkene occurs by electrophilic addition.

 (c) The number of possible optical isomers = 2ⁿ (where 'n' is the number of chiral catoms) = 2³ = 8

12. (c) 2-bromo, 3-chloro-butane has 2 chiral carbon atoms, hence has $2^2 = 4$ optical isomers.

$$CH_{3} - C-C - C-CH_{3}$$

13. (a)
$$CH_3 - CH_2 - CH_2 - CH_3$$
, $CH_3 - CH_3 - CH_3$
n-Butane CH_3

14. (b) $C_2H_3Cl_2Br$ three isomers are possible

$$CH_3 - C - Cl$$
 1-bromo-1, 1-dichloroethane
Br

$$Br - CH_2 - CH_1$$
 1-bromo-2,2-di-chloroethane
Br

$$Cl - CH_2 - CH$$
 1-bromo-1, 2-dichloroethane

15. (c) D(+)-tartaric acid has positive optical rotation and is derived from D (+) glyceraldehyde.



Methoxy group is electron releasing it increases electron density of benzene nucleus while $-NO_2$ decreases electron density of benzene.

17. (c) Due to resistance benzyl carbonium ion is most stable.





Both 1, 2-dichloro

benzene

Hence, identical compounds.



Both, 1, 3-dimethyl

3

benzene

Hence, identical compounds.



(iiia) and (iiib) are position isomers.



22. (c)
$$\begin{array}{c} CH_3(CH_2)_5 \\ CH_3(CH_2)_5 \\ CH_3 \\ H \end{array} \xrightarrow{C-Br} Optical inversion HO - C \\ H \\ CH_3 \\ H \\ CH_3 \end{array}$$

In this reaction inversion of configuration takes place this is called optical inversion. It is an example of SN^2 reaction (Bimolecular Nucleophillic Substitution).

- **23.** (b) This option shows eclipsed form of ethane.
- **24.** (c) 2^{nd} and 4^{th} forms of ethane are staggered.
- **25.** (b) $(CH_3)_3 C^+ 3^\circ$ carbonium ion is most stable.

$$26. (a) \bigcirc \xrightarrow{Y} \xrightarrow{Y} \xrightarrow{Y} \bigcup X^+ \longrightarrow \bigcup X$$

Y = -COOH because it is meta directing group while $-NH_2$. -OH and -Cl are O and Pdirecting groups.

27. (a)
$$\begin{array}{c} Br \\ H \\ CH_{3} \\ CH_{3} \\ H \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ H \\ CH_{3} \\ CH_{3$$

m-isomer (>60%)

28. (c) $C_4H_{10}O$ have 7 isomers out of which 4 are alcohols and 3 are ethers.

1.
$$CH_3 - CH_2 - CH_2 - CH_2 - OH$$
,
 n -butyl alcohol
2. $CH_3 - CH_2 - CH - CH_3$
 OH
Sec - butyl alcohol
3. $CH_3 - CH - CH_2 - OH$
 CH_3
Isobutyl alcohol
 CH_3

4.
$$CH_3 - C - CH_3$$

 OH
Ter-buty-alcohol

5.
$$CH_3 - CH_2 - O - CH_2 - CH_3$$

Diethylether

6.
$$CH_3 - O - CH_2 - CH_2 - CH_3$$

Methylpropylether

7.
$$CH_3 - O - CH < CH_3 \\ CH_3 \\ Methy lisopropyl ether$$

29. (a) According to Huckel rule for aromaticity the molecule must be planar, cyclic system having delocalised (4n + 2)π electron where n is an integer equal to 0, 1, 2, 3, thus the aromatic comp. have delocalised electron cloud of

2, 6, 10 or 14π electron cyclopropeny ation have the 2π electron (n = 0) so it is a romance.

30. (d) -COOH group is a deactivating group, hence benzoic acid is less reactive towards electrophilic substitution than phenol.

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31. (c) In the triphenyl methyl carbonium ion the π electrons of all the three benzene rings are delocalised with the vacant *p*-orbital of central carbon atom. So, it is resonance stabilised. It is the most stable of all the carbonium ions given

The ion $CH_3 - CH_3$ $CH_3 - C^+$ is stabilised by CH_3

hyperconjugation, a second order resonance.



Nitro-group is electron withdrawing therefore decreases stability.



Methoxy group is electron releasing.

Therefore increases stability by donating electron.



Chlorine is also electron withdrawing but its effect is less than $-NO_2$ group.

Hence, correct order of stability.



33. (b) 3° alcohols Me - C - Me is most stable

carbocation

(b)

32.

34. (b) Due to the increasing no. of hyperconjugative structures free radical stabilise following as $3^{\circ} > 2^{\circ} > 1^{\circ}$.

OH OH

38. (b)
$$HCOO - CH - CH - COOH$$

Two carbon atoms in the molecule are asymmetric.

39. (a,b,d)
$$CH_3NH_2, R-O-, CH_3-Mg-Br:$$
 are

nucleophiles due to presence of lone pairs.

40. (c) CH_3^- has the highest nucleophilicity.

41. (c,d)
$$C_6H_5 - C - CH_3$$
 and $C_6H_5 - C = CH_2$
(Ketoform)
 $C_6H_5 - C - CH_2 - C - CH_3$ and
 $C_6H_5 - C - CH_2 - C - CH_3$ and
 $C_6H_5 - C - CH = C - CH_3$
 $O O H$

42. (a,c) 2-butene



$$H_2 - C = C - C_c H_s$$
 and c_{H_s}

$$CH_3 - C = C - C_6H_5$$
 and $CH_3 - C = C - C_6H_5$
 $H H H H$
(cis) (Trans)

Η

- **43.** (c) CH_3CN behaves both as nucleophile and electrophile.
- **44.** (c) 2^n , n = no. of asymmetric carbon atoms.

45. (b) 1.
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

2.
$$CH_{3} - CH - CH_{2} - CH_{2} - CH_{3}$$

 CH_{3}
 $2 - methyl pentane$
3. $CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{3}$
 CH_{3}
 $3 - methyl pentane$
4. $CH_{3} - CH - CH_{3} - CH_{3}$
 $CH_{3} CH_{3}$
 $2,3 - Dimethyl butane$
5. $CH_{3} - C - CH_{2} - CH_{3}$
 CH_{3}
 $2,2 - dimethyl butane$

46. (c) Stability of carbanions increase with increase in *s*-character of hybrid orbitals of carbon bearing charge, hence correct order is : $sp^3 < sp^2 < sp$.

47. (b)
$$C_2H_2 < C_2H_4 < C_6H_6 < C_2H_6$$

 $1.20 \text{ } 1.34 \text{ } 1.34 \text{ } 1.39 \text{ } 1.39 \text{ } 1.54 \text{ } 1$

48. (d)
$$CH_3CHO + HCN \rightarrow CH_3 - CH - CN$$

(Both d and l forms are obtained) Hence, product will be a racemic mixture.

- 49. (d) Molecule 'A' is benzene because in benzene bond length is between single and double bond.
- **50.** (a) Two isomers $CH_3 CH CH_3$ and Cl

$$CH_3 - CH_2 - CH_2Cl$$
 are possible for C_3H_7Cl .

Assertion & Reason

1. (a) It is fact that aniline is better nucleophile than anilium ion. Anilium ion contain +ve charge, which reduces the tendency to donate lone pair of electron $C_6H_5NH_3^+$.

Therefore, both assertion and reason are true.

- 2. (b) Neopentane is isomer of pentane and neopentane forms only one substitution product. Both assertion and reason are true but reason is not a correct explaination of assertion. Neopentane forms mono substituted product due to presence of four identical methyl groups present on carbon atom.
- 3. (c) The assertion that *trans-2* butene reacts with Br_2 to product meso-2, 3-dibromobutane is
correct but it does not involve syn-addition of Br_2 .

- (d) Here both assertion and reason are incorrect because *cis*-1, 3-dihydroxy cyclohexane exist in chair conformation and in chair conformation hydrogen bonding is present.
- (a) Hydroxy ketones are not directly used in Grignard reagent. Grignard reagents are very reactive. Therefore, they react with hydroxyl group. Here both are correct.
- 6. (a) The assertion that on keeping benzyl bromide in acetone water it produces benzyl alcohol is correct. Because $C_6H_5CH_2Br$ hydrolysed to produce $C_6H_5CH_2OH$. This conversion is of

 SN^2 mechanism.

- 7. (b) Catenation property of carbon is primarily due to its small size. Electronic configuration and unique strength of carbon-carbon bonds.
- 8. (e) Olefins are unsaturated hydrocarbons containing two hydrogen atoms less than the corresponding paraffin *i.e.* there is one double bond between two carbon atoms in their molecules and they have the general formula $C_n H_{2n}$.
- (b) Less reactivity of saturated hydrocarbons are due to presence of single bonds between carbon atoms.
- 10. (b) Glucose is insoluble in ether.
- 11. (a) An alkyl group attached to the positively charged carbon of a carbonium ion tends to release electrons towards that carbon; thus the positive charges gets dispersed as the alkyl group becomes some what positively charged itself. More the number of alkyl groups, the greater is the dispersal of positive charge and therefore more easily it will be formed.
- 12. (b) Heterolytic fission occurs when the two atoms differ considerably in their electronegativities and shared pair of electrons is carried by more electronegative atom.
- 13. (d) The order of reactivity of carbonium ions is $1^\circ > 2^\circ > 3^\circ \; .$

Carbon atom in carbonium ion is in sp^2 state of hybridisation. The three hybridized orbitals lie in the same plane and are involved in the formation of three σ bonds with three atoms or groups while the unhybridised *p*-orbital remains vacant.

14. (b) Since free radicals contain odd electrons, so they are short lived and they readily try to pair up the odd electrons to form neutral molecules, that is why they are highly reactive.

- 15. (b) Each carbon atom in ethylene is attached to two hydrogen atoms by single covalent bonds and to another carbon atoms by a double bond. Since each carbon is attached to three other atoms, it uses sp^2 hybrid orbitals and an unhybridised p_Z orbital to form its bond. Each C-H bond is a σ bond resulting from the overlap of 1s orbital of hydrogen atom and sp^2 orbital of a carbon atom. One C-Cbond results from the linear overlap of sp^2 orbitals one from each carbon atom. One π bond results from the lateral overlap of two unhybridised p_Z orbitals, one from each carbon atom.
- 16. (a) In cyclohexanone keto enol tautomerism is as follows



- 17. (e) The staggered form is more stable than the eclipsed form because the potential energy of staggered form in which the bond pairs of two carbons are far away from each other is minimum. Also the *H*-atoms are as far apart as possible and non bonded interaction between them is maximum. In occupied form, the *H*-atom are very close and so the increased overlap between them non-bonded orbitals is repulsive. That is why staggered form is more stable than eclipsed form.
- 18. (b) Trans isomer is more stable than cis isomer because in cis isomer, the bulky groups are on

the same side of the double bond. The steric repulsion of the groups makes the cis isomer less stable than the trans isomer in which the bulky groups are far apart. (They are on the opposite side of the double bond).

- **19.** (e) 1, 2-propadiene is not optically active because the terminal sp^2 -hybridised carbons have the same atoms *i.e. H*-atoms. As a result, it has a plane of symmetry passing through the three carbon atoms and hence the molecule is optically inactive.
- 20. (b) Lactic acid is a chiral molecule because it has a chiral carbon atom or asymmetric carbon atom and is therefore optically active.
- **21.** (e) Resonance structures contain the same number of unpaired electrons.
- **22.** (b) CO_3^{2-} shows resonance and thus all the three bonds are of identical bond length.

$$\begin{array}{c} O = C - O^- \leftrightarrow O^- - C = O \leftrightarrow O^- - C - O \\ | & | \\ O_- & O_- & O \end{array}$$

General Organic Chemistry

ET Self Evaluation Test -23

1.	The most stable conformation of <i>n</i> -butane is						
		[CBSE PMT 1997]					
	(a) Skew boat	(b) Eclipsed					
_	(c) Gauche	(d) Staggered	_				
2.	Which of the following undergoes nucleophilic						
	substitution by SN ⁺ mechanism [CBSE PMT 2005]						
	(a) Benzyl chloride	(b) Ethyl chloride					
	(c) Chlorobenzene	(d) Isopropyl chloride	1				
3.	Which type of isomerism is shown by propanal						
	and propanone	[CPMT 2004]					
	(a) Functional group	(b) Metamerism					
	(c) Tautomerism	(d) Chain isomerism					
4.	Which of the following exhibits optical isomerism						
	[BHU 1980; NCERT 1983; AIIMS 1992;						
	M	(h) Buten el 2					
	(a) Butanol-1	(b) Butanol-2					
	(c) Butene-1	(d) Butene-2					
5.	In carbonium ion the carbon bearing the positive charge in the [Pb. PMT 1999; MH CET 2002]						
	(a) <i>sp</i> ² -hybridized state state	(b) sp^3d -hybridized					
	(c) <i>sp</i> -hybridized state	(d) sp^3 -hybridized state	1				
6.	Which of the following is not an electrophile						
	[CBSE PMT 2001]						
	(a) Cl^+	(b) Na^+					
	(a) U^+	(d) PE					
		(d) <i>BF</i> ₃					
7.	Heterolytic bond dissociation energy of alkylhalides follows the sequence[AMU 2000]						
	(a) $R-F > R-Cl > R-Br$	r > R - I					
	(b) $R - I > R - Br > R - Cl$	> R - F					
	(c) $R-I > R-F > R-Br > R$	> R - Cl					
	(d) $R - Cl > R - Br > R - I > R - F$						
8.	The shape of carbonium	is [AMU (Engg.) 1999]	1				
	(a) Planar	(b) Pyramidal	T				
	(c) Linear	(d) None of these					
9.	Which of the follov tautomerism	ving compounds shows	1				
		[MP PET 2001]					
	(a) <i>HCHO</i>	(b) CH_3CHO					
	(c) CH_3COCH_3	(d) HCOOH					
10.	In which bond angle is the highest [CBSE PMT 1991]						
	(a) sp^3	(b) sp^2					
	(c) sn	(d) $an^3 d$					
	(c) sp	(u) sp u	1				

11.	How r	many	primary	amines	are	possible	for	the
	formula $C_4 H_{11} N$					[MNR 1995]		
	(a) 1			(b)	2			

- (c) 3 (d) 4
- 12. On monochlorination of 2-methyl butane, the total number of chiral compounds is[IIT-JEE Screening 2004]
 (a) 2
 (b) 4
 - (c) 6 (d) 8
- 13. An isomer of ethanol is
 [DPMT 1982, 88; CPMT 1973, 75, 78, 84; IIT-JEE 1986; BHU 1984, 85; EAMCET 1993; MP PET 1995; RPET 1999; BHU 2000; AFMC 2002]
 - (a) Methanol (b) Dimethyl ether
 - (c) Diethyl ether (d) Ethylene glycol
- Due to the presence of an unpaired electron, free radicals are
 (a) Chemically reactive
 (b) Chemically inactive
 (c) Anions
 (d) Cations
- **15.** Tertiary alkyl halides are practically inert to substitution by S_{N^2} mechanism because of [AIEEE 2005]
 - (a) Insolubility (b) Instability
 - (c) Inductive effect (d) Steric hindrance
- **16.** The decreasing order of nucleophilicity among the nucleophiles

(i)
$$CH_3 C - O^-$$
 (ii) $CH_3 O^-$
 O

 $H_3C -$

$$O$$

 $-S - O^{-}$

0

[AIEEE 2005]

is [AIEEE 2005 (a) (i), (ii), (iv) (b) (iv), (iii), (i), (i) (c) (ii), (iii), (i), (iv) (d) (iii), (ii), (i), (iv)

 CN^{-}

(iv)

- Which of the following is optically active [BHU 2005]
 (a) Butane
 (b) 4-methylheptane
 (c) 3-methylheptane
 (d) 2-methylheptane
- **8.** Correct configuration of the following is

$$\begin{array}{c} CH_{3} \\ H \longrightarrow OH \\ CH_{3} \longrightarrow OH \\ H \end{array}$$
[AIIMS 2005]

19. Which types of isomerism is shown by 2, 3-dichlorobutane

- [AIEEE 2005] (a) Distereo (b) Optical
- (c) Geometric (d) Structural

Who synthesised the first organic compound urea 20. in the laboratory [RPMT 2000]





Anti or completely staggard

Staggard form is most stable because of minimum repulsion between bulky methyl groups.

- (a) Due to more stable carbocation. 2.
- (a) When two compounds have similar molecular 3. formula but differ in the functional group then the isomerism is called functional group

isomerism *i.e.* CH_3CH_2CHO and CH_3 .

4. (b)
$$CH_3 - C^* - CH_2 - CH_3$$

Because it has chiral carbon atom.

- (a) The central carbon atom in carbonium ion is 5٠ sp^2 hybridised and it has three sp^2 hybrid single bonding orbitals for to three substituents.
- (b) Na^+ is not an electrophile. 6.
- (b) R I > R Br > R Cl > R F7.
- 8. (a) Carbonium ion is planar species
- (c) Ketones show tautomerism. They form keto 9. and enol form

$$CH_{3} - \overset{||}{C} - CH_{3} \xleftarrow{\text{Tautomerism}} CH_{3} - \overset{OH}{C} = CH_{2}$$

10. (c) Type

- Bond angle sp^3 109.5° sp^2 120° sp^3d $90\,^o$ and $120\,^o$ sp 180°
- (d) $CH_3 CH_2 CH_2 CH_2 NH_2$ 11. (1-aminobutan e)

$$CH_{3} - CH_{2} - CH_{3}$$

$$NH_{2}$$
(2-aminobutan e)
$$CH_{3}$$

$$CH_{3} - C - CH_{3}$$

$$NH_{2}$$
(2-Methy-1-2-aminopropa ne)
$$CH_{3} - CH_{3} - CH_{2} - NH_{2}$$

$$CH_{3}$$
(2-Methy-1-aminopropa ne)
$$CH_{3}$$
(2-Methy-1-aminopropa ne)

(SET -23)

(b) The possible monochlorinated products of 2-12. methyl butane are



Therefore, a total of four chiral compounds are obtained.

- (b) Dimethyl ether is an isomer of ethanol. 13.
- (a) Free radicals are very reactive due to the 14. presence of free e⁻.
- (d) Due to steric hinderance 15.
- 16. (c) (ii) > (iii) > (i) > (iv)

18.

$$CH_3$$

(c) $CH_3CH_2^*CHCH_2CH_2CH_3$ has a chiral carbon 17. atom and hence is optically active.

(a)
$$CH_3$$

 H O
 CH_3 O
 H

(b) Wohler (d) Berzilius

(a) Kolbe (c) Fraizer Following the procedure outlined under 'Golden Rule' the absolute configuration is 1*s*, 2*s*.

19. (b)
$$H \xrightarrow[CH_3]{CH_3} Cl, H \xrightarrow[CH_3]{CH_3} Cl, H$$

 $H \xrightarrow[CH_3]{CH_3} Cl, Cl \xrightarrow[CH_3]{CH_3} Cl, H$

$$\begin{array}{c} Cl & \xrightarrow{CH_3} H \\ H & \xrightarrow{CH_2} Cl \end{array}$$

20. (b) Wohler synthesised the first organic compound urea in the laboratory.