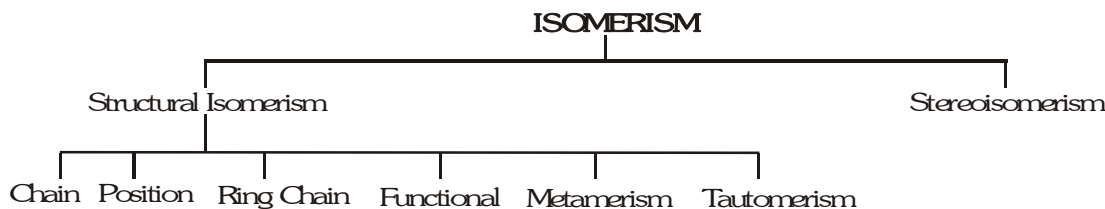# ISOMERISM

The name was given by Berzilius. Two or more than two organic compounds having the same molecular formula and molecular weight but different physical and chemical properties are called isomers and the phenomenon is called isomerism.
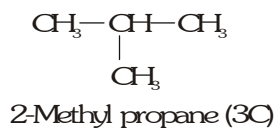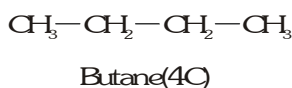
ISOMERISM

- Structural Isomerism
  - Chain Position Ring Chain Functional Metamerism Tautomerism
- Stereoisomerism

❑ **Structural Isomerism :**

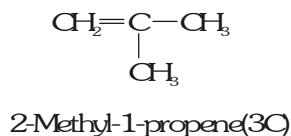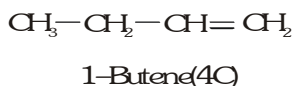| S.No.	Isomers	Characteristics	Conditions
1	Chain Isomers	They have different size of main chain or side chain	They have same nature of locant
2	Positional Isomers	They have different position of locant	They should have same size of main chain and side chain and same nature of locant
3	Functional Isomers	Different nature of locant	Chain and positional isomerism is not considered
4	Metamerism	Different nature of alkyl group along a polyvalent functional group	They should have same nature of functional group chain & positional isomer is ignored
5	Tautomerism	Different position of hydrogen atoms	The two functional isomers remains in dynamics equilibrium with each other

1. Chain Isomerism (CI) :

The compounds which have same molecular formula, same functional group, same position of functional group or multiple bond or substituent but different arrangement of carbon chain (different parent name of compound) shows chain isomerism.
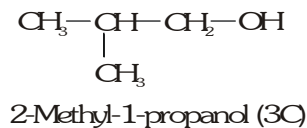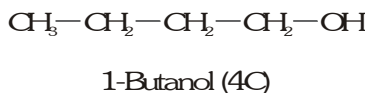
Example : $CH_3-CH_2-CH_2-CH_3$

Butane(4C)

$CH_3-CH-CH_3$
$\quad\quad\quad |$
$\quad\quad\quad CH_3$

2-Methyl propane (3C)

Example : $CH_3-CH_2-CH=CH_2$

1–Butene(4C)

$CH_2=C-CH_3$
$\quad\quad\quad |$
$\quad\quad\quad CH_3$

2-Methyl-1-propene(3C)

Example : $CH_3-CH_2-CH_2-CH_2-OH$

1-Butanol (4C)

$CH_3-CH-CH_2-OH$
$\quad\quad\quad |$
$\quad\quad\quad CH_3$

2-Methyl-1-propanol (3C)

Example :

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

Pentanoic acid

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

3-Methyl butanoic acid

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

2,2-Dimethyl propanoic acid

2. Position Isomerism (PI) :

The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, shows position isomerism.

Example : $CH_2=CH-CH_2-CH_3$

But–1–ene

$CH_3-CH=CH-CH_3$

But–2–ene

Example : $CH_3-CH_2-CH_2-CH_2-OH$

1–Butanol

$$CH_3-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

2–Butanol

Example : $CH_3-CH_2-CH_2-CH_2-Cl$

1–Chlorobutane

$$CH_3-CH_2-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3$$

2–Chlorobutane

❑ **Example of CI and PI :**

(i) C_4H_{10} **have two isomers :** Both butane and isobutane are chain isomers.

Example : $CH_3-CH_2-CH_2-CH_3$

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

Butane

Isobutane

(ii) C_5H_{12} **have three isomers :** All of three structures are chain isomers because only carbon chain (parent) is different.

Example :

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

$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$,

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

Pentane

2–Methyl butane

2,2–Dimethylpropane

(iii) C_6H_{14} **has 5 isomers :**

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

(b) $CH_3-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

2–Methyl pentane

(c) $CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$

3–Methyl pentane

(d) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

2,3–Dimethyl butane

(e)

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

H₃C—C—CH₂—CH₃

2,2–Dimethyl butane

◆ a–b, b–d, a–c, c–d ⟶ Chain Isomers

◆ b–c, d–e ⟶ Position Isomers

(iv) C_7H_{16} has 9 isomers

1. ⟶ $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ — Heptane

2. ⟶ $CH_3-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ — 2–Methylhexane

3. ⟶ $CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$ — 3–Methylhexane

4. ⟶ $CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ — 2,2–Dimethyl pentane

5. ⟶ $CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$ — 3,3–Dimethylpentane

6. ⟶ $CH_3-CH-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$ with $\overset{CH_3}{|}$ — 2,3–Dimethylpentane

7. ⟶ $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$ — 2,4–Dimethylpentane

8. ⟶ $CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2-CH_3}{|}}{CH}}-CH_2-CH_3$ — 3–Ethylpentane

9. ⟶ $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ — 2,2,3–Trimethylbutane

(v) $C_3H_6Cl_2$ has 4 isomers : Position of chlorine atom is different in all the structure, so these are position Isomers.

1. $H_3C-CH_2-\overset{\overset{Cl}{|}}{CH}-Cl$

    1,1–Dichloropropane

2. $H_2C-CH_2-CH_2-Cl$ with $\overset{Cl}{|}$

    1,3–Dichloropropane

3. $H_3C-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$

    2,2–Dichloropropane

4. $H_2C-\overset{\overset{Cl}{|}}{CH}-CH_3$ with $\underset{Cl}{|}$

    1,2–Dichloropropane
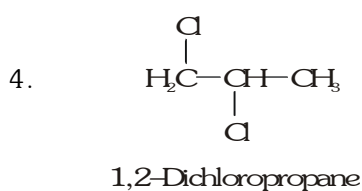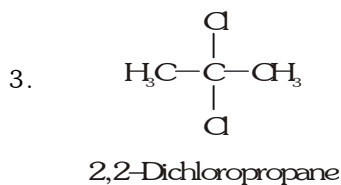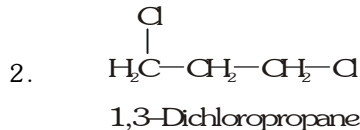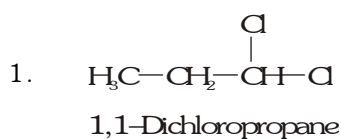
(vi) $C_5H_{11}Cl$ has 8 isomers

(vii) C_8H_{10} has **4 aromatic isomers**

CH_3 / CH_3 (o,m,p) CH_2-CH_3
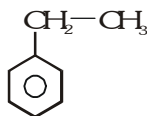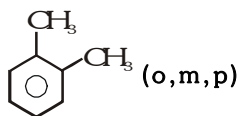
(viii) $C_6H_4X_2 \longrightarrow$ 3 Aromatic isomers
$C_6H_4XY \longrightarrow$ 3 Aromatic isomers
$C_6H_3X_3 \longrightarrow$ 3 Aromatic isomers
$C_6H_3XYZ \longrightarrow$ 10 Aromatic isomers

Ex. Structures $CH_3-CH_2-CH=CH_2$ and $CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$ are :-
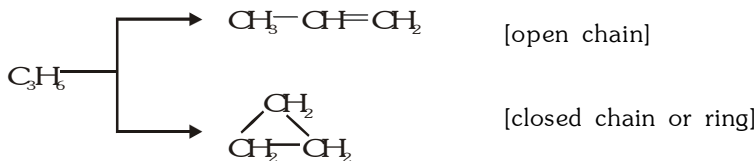
Sol. Chain Isomers

Molecular formula	No. of Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9

Molecular formula	No. of Isomers
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75

3. **Ring chain isomerism (RCI) :**

Same molecular formula but different mode of linking (open chain or closed chain) of carbon atoms.

$C_3H_6 \longrightarrow CH_3-CH=CH_2$ [open chain]

$\longrightarrow$ (ring structure)   [closed chain or ring]

They have same molecular formula so they are Ring chain isomers.

Ex. Relate a,b and c:-

(a) $H_3C-C\equiv CH$
(b) $CH_2=C=CH_2$
(c) (cyclopropene ring)
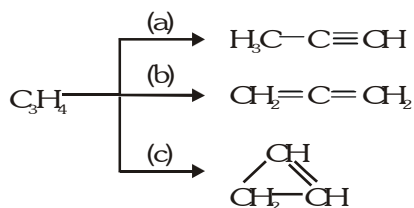
Sol.   a–b $\longrightarrow$ Functional Isomers
a–c , b–c $\longrightarrow$ Ring-chain Isomers, Functional Isomers

Special points :

◆ Alkenes with cycloalkane and alkynes (Alkadienes) with cycloalkenes show Ring-chain Isomerism.
◆ Ring-chain Isomers are also Functional Isomers.

Ex. Relate structures a,b,c and d.   (a) $CH_3-CH_2-C\equiv CH$ (b) $CH_2=C=CH-CH_3$

(c)   (d)
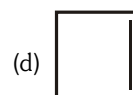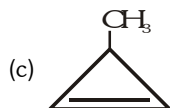
Sol. a, b $\longrightarrow$ Functional Isomers
a, c. $\longrightarrow$ Ring-chain Isomers and Functional Isomers
b, c $\longrightarrow$ Ring-chain Isomers and Functional Isomers
a, d. $\longrightarrow$ Ring-chain Isomers and Functional Isomers
c, d. $\longrightarrow$ Chain Isomers
b, d. $\longrightarrow$ Ring-chain Isomers and Functional Isomers

Ex. $\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}$ and $\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}-CH_3$ are ?

$\quad\quad\quad\quad\quad\underset{1CN}{|}\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\underset{1CN}{|}$
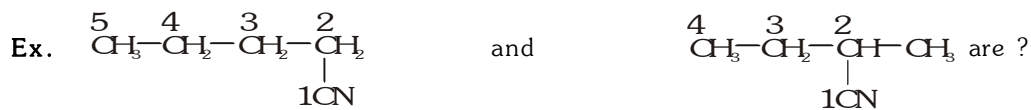
$\quad\quad\quad$ Pentanenitrile $\quad\quad\quad\quad\quad\quad\quad\quad$ 2–Methyl butanenitrile

Sol. Molecular formula same, Functional group same, position of Functional group same but different parent carbon atom chain so both are Chain isomers

Ex. How many minimum carbons required for Chain isomerism and Position isomerism in alkanes ?

Sol. 4, 6

Ex. How many minimum carbons required for Chain isomerism and Position isomerism in alkenes ?

Sol. 4, 4

Ex. How many minimum carbons required for Chain isomerism and Position isomerism in alkynes ?

Sol. 5, 4

4. Functional Isomerism :-

Same molecular formula but different functional groups.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

(i) Alcohol and ether $\longrightarrow$ CH_3-CH_2-OH and CH_3-O-CH_3

(ii) Aldehydes and ketones $\longrightarrow$ $CH_3-CH_2-\overset{\quad}{\underset{||}{C}}-H$ and $CH_3-\overset{\quad}{\underset{||}{C}}-CH_3$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O \quad\quad\quad\quad\quad\quad\quad\quad O$

(iii) Acids and ester $\longrightarrow$ $CH_3-\overset{\quad}{\underset{||}{C}}-OH$ and $H-\overset{\quad}{\underset{||}{C}}-O-CH_3$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O \quad\quad\quad\quad\quad\quad\quad\quad O$

(iv) Cyanide and isocyanide $\longrightarrow$ $CH_3-CH_2-CH_2-CN$ and $CH_3-CH_2-CH_2-NC$

(v) Nitro and Nitrite $\longrightarrow$ $CH_3-CH_2-N\overset{O}{\underset{O}{\diagdown}}$ and $CH_3-CH_2-O-N=O$

(vi) Keto and enol $\longrightarrow$ $CH_3-\overset{\overset{O}{||}}{C}-CH_3$ and $CH_2=\underset{\underset{OH}{|}}{C}-CH_3$

(vii) Amide and Oxime $\longrightarrow$ $CH_3-\overset{\quad}{\underset{\underset{O}{||}}{C}}-NH_2$ and $CH_3-CH=NOH$

(viii) 1 , 2 , 3 amines

$\quad\quad$ (i) $CH_3-CH_2-CH_2-NH_2$ (ii) $CH_3-NH-CH_2-CH_3$ (iii) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_3$

(ix) Alcoholic and phenolic compounds : (⬡)—CH₂OH and (⬡) with OH and CH₃
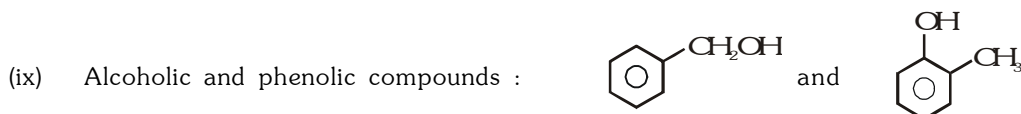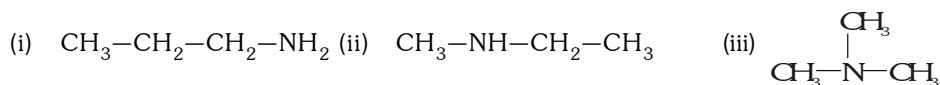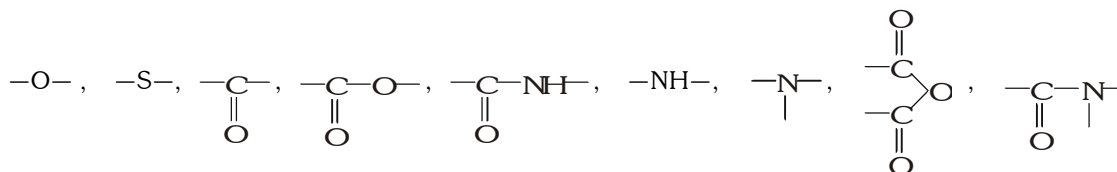
(x) Alkyl halides do not show Functional isomerism.

5. **Metamerism** :

Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group.

Polyvalent Functional group [More than one valency] are :

$$-O-, \quad -S-, \quad -\overset{\overset{\displaystyle ||}{O}}{\underset{}{C}}-, \quad -\overset{\overset{\displaystyle ||}{O}}{\underset{}{C}}-O-, \quad -\overset{\overset{\displaystyle ||}{O}}{\underset{}{C}}-NH-, \quad -NH-, \quad -\overset{|}{\underset{|}{N}}-, \quad \overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O}{||}}{\overset{C}{\underset{C}{}}}}O, \quad -\overset{\overset{\displaystyle ||}{O}}{\underset{|}{C}}-\overset{|}{\underset{|}{N}}-$$

Example : $CH_3-O-CH_2-CH_2-CH_3$; $CH_3-CH_2-O-CH_2-CH_3$

Both are metamers.

Example : $CH_3-CH_2-NH-CH_2-CH_3$ $CH_3-NH-CH_2-CH_2-CH_3$

N–Ethyl ethanamine   N–Methyl propanamine

They are only metamers not CI

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

2–Hexanone   3–Hexanone

Both are metamers and Position isomer

Example : $CH_3-\overset{\overset{\displaystyle ||}{O}}{\underset{}{C}}-CH_2-CH_2-CH_2-CH_3$ $CH_3-CH_2-\overset{\overset{\displaystyle ||}{O}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH-CH_3$

2–Hexanone   2–Methyl–3–pentanone

Both are Metamers, Chain and Position isomers

Ex. Structures $\overset{\overset{\displaystyle O}{||}}{\underset{}{CH_3-C-O-C_6H_5}}$ and $\overset{\overset{\displaystyle O}{||}}{\underset{}{C_6H_5-C-O-CH_3}}$ are

Sol. Both are metamers.

6. **Tautomerism or Desmotropism** :

Tautomerism was introduced by "Laar". It's also called desmotropism.

◆   Desmotroism means bond turning. [Desmos = Bond ; Tropos = Turn]

◆   Tautomers have same molecular formula but different structural formula due to wandering nature of active hydrogen between two atoms.

◆   The tautomerism is also called **kryptomerism or allotropism or desmotropism or dynamic isomerism.**

$\left.\begin{array}{c}\overset{\displaystyle CH_2-C-H}{\underset{\displaystyle H \quad\;\; O}{|\quad\;\; ||}} \\ \alpha-\text{Hydrogen or active H}\end{array}\right]$ $\alpha-$H attached to carbonyl compound is active H

Example : $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle ||}{O}}{\underset{}{C}}-H$ $\rightleftharpoons$ $H-\overset{\overset{\displaystyle H}{|}}{\underset{}{C}}=\underset{\underset{\displaystyle O-H}{}}{C}-H$

Example :

$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{||}}{C}}-CH_2 \quad \rightleftharpoons \quad CH_3-\underset{\underset{\displaystyle O-H}{|}}{C}=CH_2$$
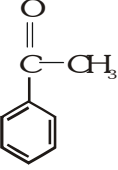
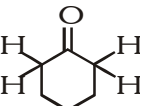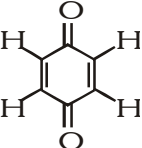keto   ene + ol = enol
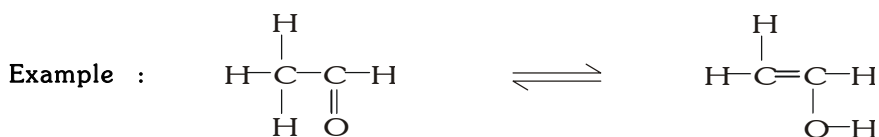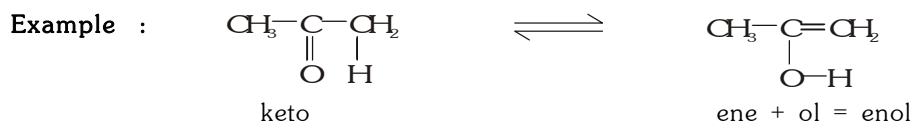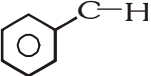
Note :

(i)   Tautomers are also F. I. and exist in dynamic equilibrium $\rightleftharpoons$ is used to show tautomerism]

(ii)   By shifting of H–atom π bond also change its position.

(iii) Tautomers always exist in dynamic equilibrium.

(iv) Number of electrons and lone pairs in both tautomers always remain the same.

(v)   It is a chemical phenomenon which takes place only in liquids and gaseous phase only. It never takes place in solid state.

(vi) The process can be catalyzed by the acid as well a bases.

❑   **Condition for Tautomerism :**

(a)   **For carbonyl compounds :-** Carbonyl compounds having atleast one α–H show tautomerism

(i) $CH_3-\underset{\underset{\displaystyle O}{||}}{C}-H$ 3 α H,   show tautomerism.

(ii) $CH_3-\underset{\underset{\displaystyle O}{||}}{C}-CH_3$ 6 α H,   show tautomerism

(iii) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle O}{||}}{C}-H$ 1 α H,   show tautomerism

(iv) $H-\underset{\underset{\displaystyle O}{||}}{C}-H$ No α H,   No tautomerism

(v)   (benzaldehyde structure)   No α H,   No Tautomerism

(vi) (acetophenone structure)   3 α H,   shows tautomerism (Aceto phenone)

(vii) $Ph-\underset{\underset{\displaystyle O}{||}}{C}-Ph$ No α H,   No tautomerism (Benzophenone)

(viii) $Ph-\underset{\underset{\displaystyle O}{||}}{C}-CH_2-\underset{\underset{\displaystyle O}{||}}{C}-Ph$ 2 α H,   shows tautomerism

(ix) (cyclohexanone structure with H's)   4 α H,   shows tautomerism

(x)   (cyclohexadienedione structure) α–H, attached sp^2 carbon does not take part in tautomerism

Ex. Which of the following show keto enol tautomerism.

(A)   (B)   (C)   (D)
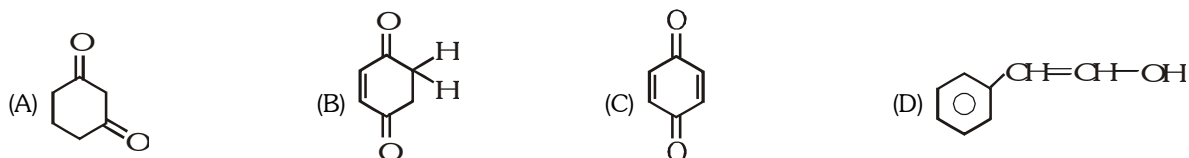
Sol. (A), (B) and (D)

(b) **For nitro compounds :** Nitro compounds having atleast one α – H show tautomerism
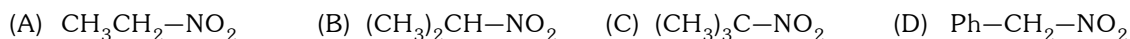

Nitro form   Aci nitro form
(acidic form so soluble in base)
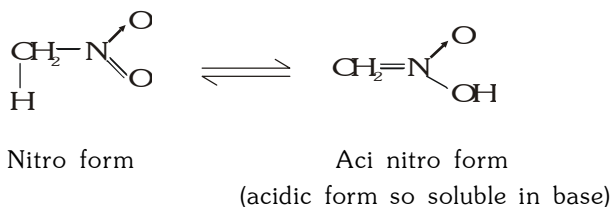
Note : Nitro compounds with at least one α–H are soluble in NaOH.
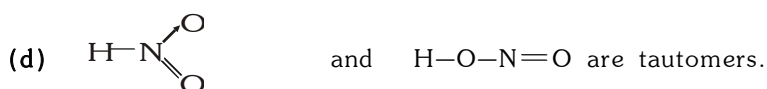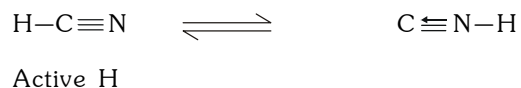
Ex. Which of the following show tautomerism.

(A) $CH_3CH_2-NO_2$ (B) $(CH_3)_2CH-NO_2$ (C) $(CH_3)_3C-NO_2$ (D) $Ph-CH_2-NO_2$
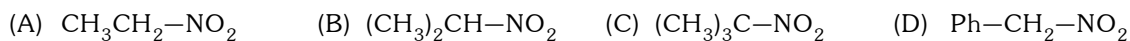
Sol. (A), (B) and (D)

Ex. Which of the following do not soluble in NaOH.

(A) $CH_3CH_2-NO_2$ (B) $(CH_3)_2CH-NO_2$ (C) $(CH_3)_3C-NO_2$ (D) $Ph-CH_2-NO_2$

Sol. Only (C)

(c) $H-C\equiv N$ and $H-N\equiv C$ are tautomers [also Functional isomers] while $R-C\equiv N$ and $R-N\equiv C$ are only Functional isomers.

$$H-C\equiv N \rightleftharpoons C\equiv N-H$$

Active H

(d)   and $H-O-N=O$ are tautomers.

Enol Content :

1.

"keto" ($\approx 99\%$)   "enol" ($\approx 1\%$)

2.   Less stable or unstable

$\approx 99\%$ $\approx 1\%$

3.

"keto" ($\approx 1\%$)   "enol" (stable by resonance and aromatic nature) ($\approx 99\%$)

4.
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-OC_2H_5$$
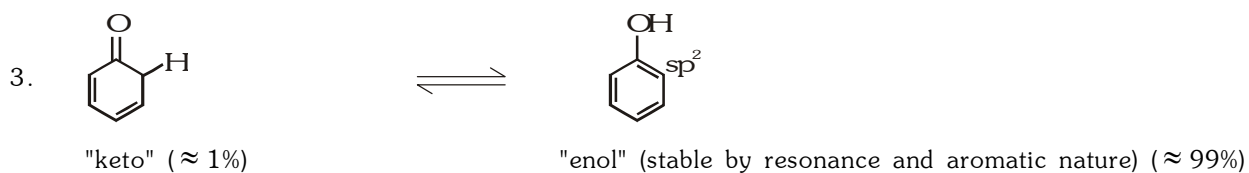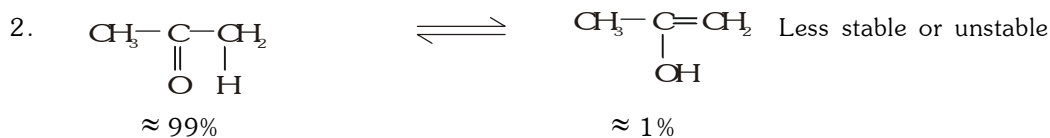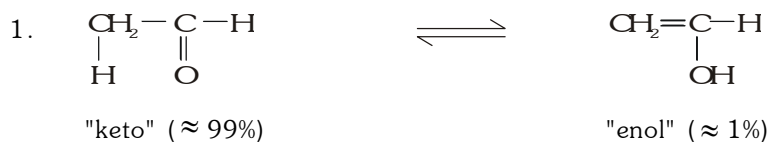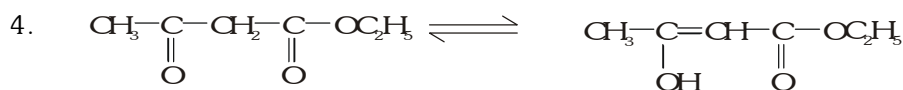
Aceto acetic ester (AAE)

AAE
- aqueous solution → keto : enol = 93 : 7
- liquid state → keto : enol = 25 : 75
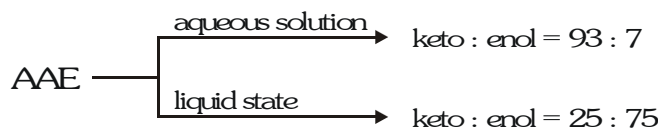
In aqueous solution

$$CH_3-\underset{\underset{\overset{:}{H-O-H}}{\|}}{C}-CH_2-\underset{\underset{\overset{:}{H-O-H}}{\|}}{C}-O-C_2H_5$$

◆ Keto from is stablised by intermolecular H–Bonding.

In liquid state

$$CH_3-\underset{\underset{O-H\cdots O}{|}}{C}=CH-\underset{\|}{C}-OC_2H_5$$
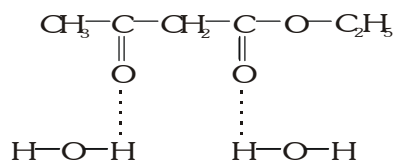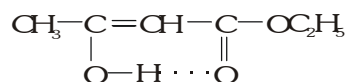
◆ Enol form is stabilised by intramolecular H–Bonding.

(i) Enol content $\propto$ number of >C=O group.

(ii) If number of >C=O groups are equal then proportional to number of α–H.

(iii) Group −OH attached to sp^2 carbon or double bond is less stable or unstable.

(iv) More active H, more take part in tautomerism.

(v) Stability of enol form depnds on (i) Resonance and (ii) H – Bond.

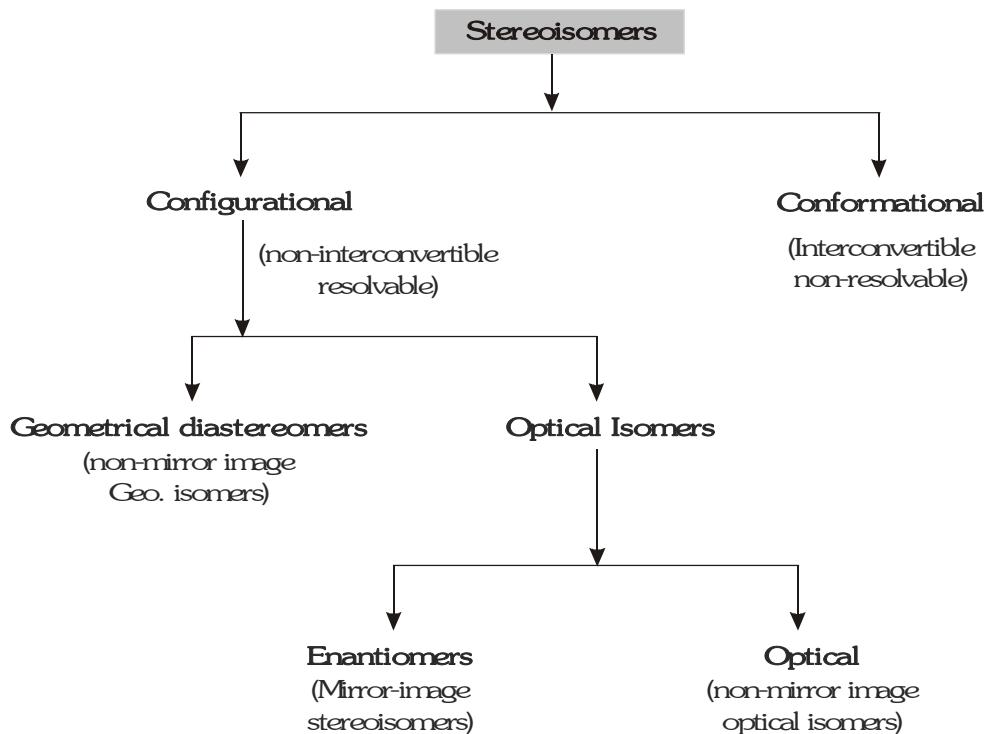**Ex.** Arrange the following in correct order of enol content.

(A) $CH_3-\underset{\underset{O}{\|}}{C}-H$

(B) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

(C) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-H$

(D) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$
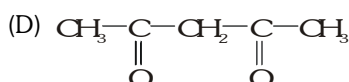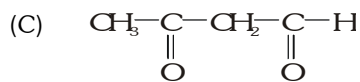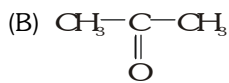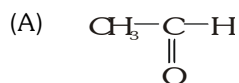
Sol. (A) < (B) < (C) < (D)

Ex. Which have maximum stable enol form

(A) ⇌

(C) ⇌

(B) ⇌

(D) ⇌
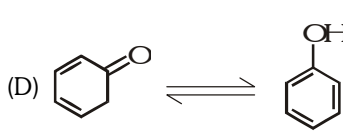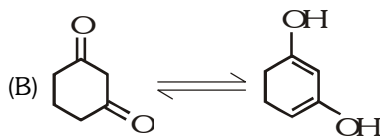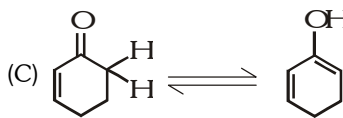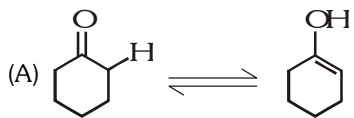
Sol. (D) Stable by Resonance and is Aromatic

STEREO ISOMERISM

Stereoisomers

Configurational
(non-interconvertible resolvable)

Conformational
(Interconvertible non-resolvable)

Geometrical diastereomers
(non-mirror image Geo. isomers)

Optical Isomers

Enantiomers
(Mirror-image stereoisomers)

Optical
(non-mirror image optical isomers)

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

(A) **CONFIGURATIONAL ISOMERISM :** Stereo isomers which have following characteristics.

◆ Stereo isomer which cannot interconvert in each other at room temperature due to restricted rotation known as Geometrical isomerism.

◆ Stereo isomer which cannot super impose on each other due to chirality know as optical isomerism.

❑ **Geometrical isomerism (G. I) :** Alkenes (>C=C<), oximes (>C= N−) and azo compounds [−N=N−], show Geometrical Isomers due to restricted rotation about double bond while cycloalkanes show Geometrical Isomers due to restricted rotation about single bond.

◆ **Geometrical Isomers in Alkenes :**

Reason : Restricted rotation about double bond : It is due to overlapping of p−orbital.

Restricted Rotation   Free Rotation

$$CH_3-\underset{\underset{sp^2}{\uparrow}}{CH}=\underset{\underset{sp^2}{\uparrow}}{CH}-CH_3$$

Example :

$$\underset{H}{\overset{CH_3}{>}}C=C\underset{H}{\overset{CH_3}{<}} \quad \rightleftharpoons \quad \underset{H}{\overset{CH_3}{>}}C=C\underset{CH_3}{\overset{H}{<}}$$

cis–2–butene   trans–2–butene
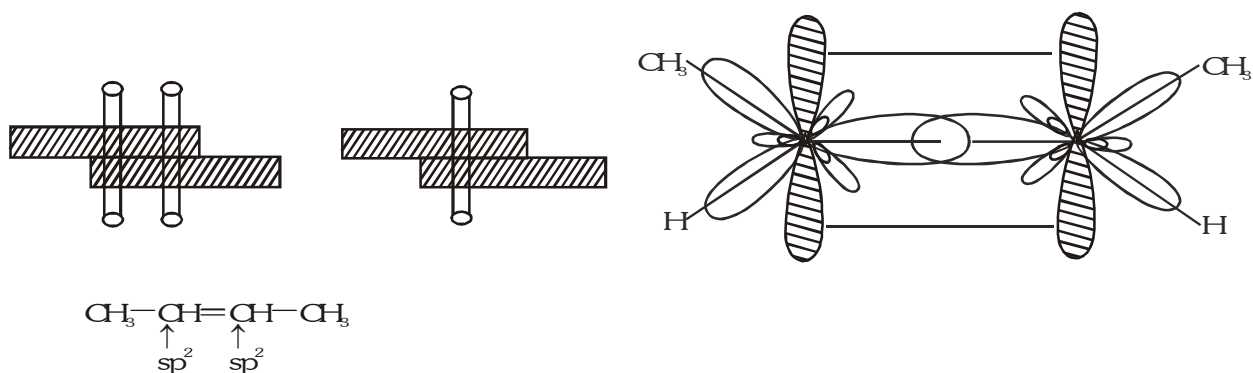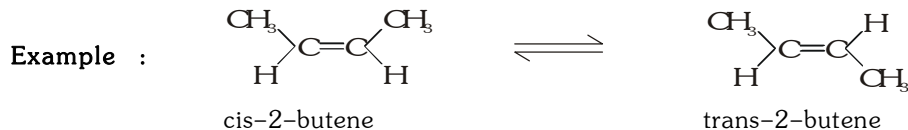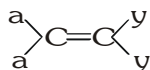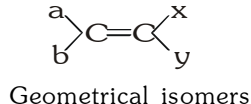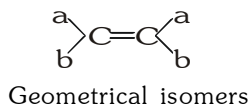
Note : cis $\rightleftharpoons$ trans is possible only when π bond break.

❑ **Condition for Geometrical isomerism :**

Only those alkenes show G. I. in which "Each sp^2 carbon have different atoms or groups"

$$\underset{b}{\overset{a}{>}}C=C\underset{b}{\overset{a}{<}} \qquad\qquad \underset{b}{\overset{a}{>}}C=C\underset{y}{\overset{x}{<}}$$

Geometrical isomers   Geometrical isomers

$$\underset{a}{\overset{a}{>}}C=C\underset{y}{\overset{y}{<}} \qquad\qquad \underset{q}{\overset{p}{\underset{C}{\overset{C}{\|}}}}\overset{p}{q}$$

Not Geometrical isomers   Not Geometrical isomers

Ex. Which of the following show Geometrical isomerism –
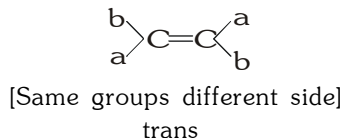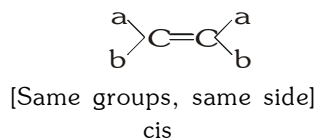(A) 1,1–diphenyl–1–butene   (B) 1,1–diphenyl–2–butene
(C) 2,3–dimethyl–2–butene   (D) 3-phenyl–1–butene

Sol. (B)

(B) NOMENCLATURE SYSTEMS OF GEOMETRICAL ISOMERS :

(a) Cis–Trans System : If same groups at same side then cis and if same groups at different side then trans.
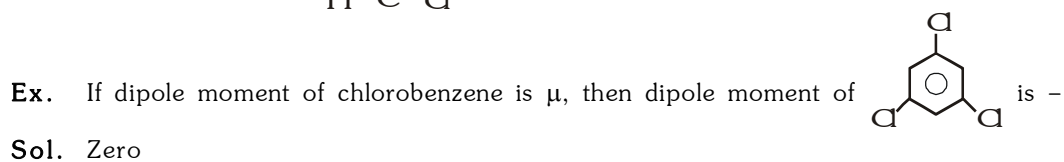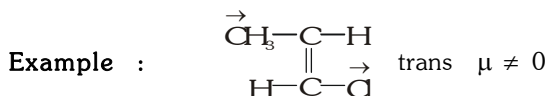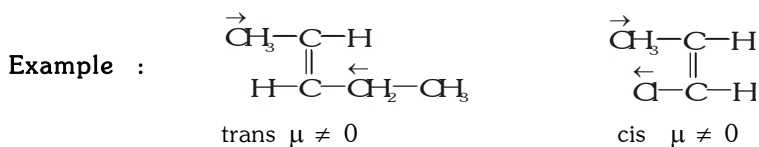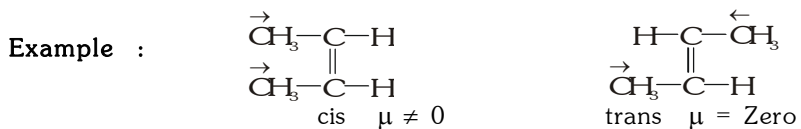
$$\underset{b}{\overset{a}{>}}C=C\underset{b}{\overset{a}{<}} \qquad\qquad \underset{a}{\overset{b}{>}}C=C\underset{b}{\overset{a}{<}}$$

[Same groups, same side]   [Same groups different side]
cis   trans

Example :

$$\underset{x}{\overset{a}{>}}C=C\underset{y}{\overset{a}{<}} \qquad\qquad \underset{x}{\overset{z}{>}}C=C\underset{y}{\overset{z}{<}}$$

cis   cis

Example :

$$\underset{H}{\overset{CH_3}{>}}C=C\underset{CH_2-CH_3}{\overset{H}{<}} \qquad\qquad \underset{Br}{\overset{a}{\underset{C}{\overset{C}{\|}}}}\overset{a}{Br}$$
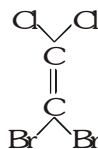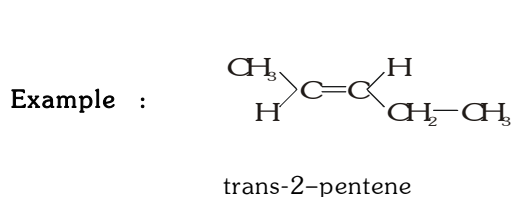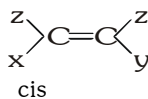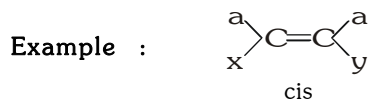
trans-2–pentene   It does not show Geometrical isomers So no cis–trans

Physical Properties of Cis–Trans Isomers :

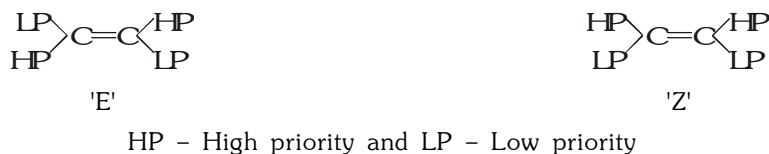| S.No.	Physical properties	Comparison	Remarks
1	Dipole moment	cis > trans	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out
2	Boiling point	cis > trans	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction
3	Solubility (in H_2O)	cis > trans	More polar molecules are more soluble in H_2O
4	Melting point	trans > cis	More symmetric isomers have higher melting points due to better packing in crastalline lattice & trans isomers are more symmetric than cis.
5	Stability	trans > cis	The molecule having more vander wall strain are less stable. In cis isomer the bulky group are closer they have larger vander waal strain.

Dipole moment [μ] :

Example :

$$\overset{\rightarrow}{CH_3}-C-H$$
$$\overset{\rightarrow}{CH_3}-C-H$$
cis   μ ≠ 0

$$H-C-\overset{\leftarrow}{CH_3}$$
$$\overset{\rightarrow}{CH_3}-C-H$$
trans   μ = Zero

Example :

$$\overset{\rightarrow}{CH_3}-C-H$$
$$H-C-\overset{\leftarrow}{CH_2}-CH_3$$
trans μ ≠ 0

$$\overset{\rightarrow}{CH_3}-C-H$$
$$\overset{\leftarrow}{Cl}-C-H$$
cis   μ ≠ 0

Example :

$$\overset{\rightarrow}{CH_3}-C-H$$
$$H-C-\overset{\rightarrow}{Cl}$$ trans   μ ≠ 0

Ex. If dipole moment of chlorobenzene is μ, then dipole moment of ⟨structure⟩ is –

Sol. Zero

(b)   E – Z System :

E (Entgegen) : When high priority groups are opposite side.

Z (Zussaman) : When high priority groups are same side.

$$\overset{LP}{\underset{HP}{}}C=C\overset{HP}{\underset{LP}{}}$$
'E'

$$\overset{HP}{\underset{LP}{}}C=C\overset{HP}{\underset{LP}{}}$$
'Z'

HP – High priority and LP – Low priority

Priority Rules :

Rule I : Priority is proportional to atomic number of atom which is directly attached to sp² carbon.

$$\overset{Br}{\underset{[HP]\;\boxed{I}}{}}C=C\overset{F}{\underset{\boxed{Cl}\;[HP]}{}}$$
'Z'

$$\overset{[HP]\;\boxed{Cl}}{\underset{Cl-C}{}}C=C\overset{CH_3}{\underset{\boxed{N}H_2[HP]}{}}$$
Cl Cl 'E'

Rule II : If rule-I is failed then consider next atom

$$\overset{[HP]\;\boxed{F}}{\underset{[LP]\;CH_3H_2C}{}}C=C\boxed{C}$$
CH₃ CH₃ –CH₃ [C, C, C] [HP]
C–CH₃ [C, C, H] [LP]
H
'Z'

decreasing order of atomic number

Rule III :– If multiple bond is present then consider them as :-

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

$$C\equiv C \longrightarrow -\underset{C}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-$$

$$C=O \longrightarrow C\overset{O}{\underset{O}{\diagdown}}$$

$$C\equiv N \longrightarrow C\overset{N}{\underset{N}{\langle}}N$$

$$N\equiv C \quad \overset{H}{\underset{H}{N}} \quad C=C \overset{C-H}{\underset{C-OH}{}}$$
[HP]
O ‖ [O, O, H]
O ‖ [O, O, O] [HP]
'Z'
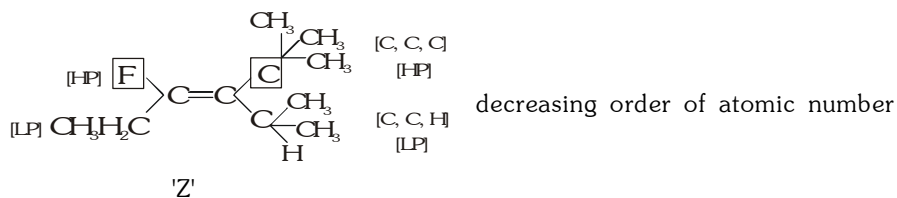
Priority order for some groups is :
$Br > Cl > OH > NH_2 > COOH > CHO > CH_2OH > CN > C_6H_5 > C \equiv CH > C(CH_3)_3 > CH = CH_2 > CH(CH_3)_2$

Rule IV : If isotopes are present then consider atomic weight.

'Z'

Example :

;

'Z'   'E'

Example :
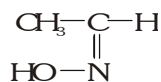

;

'E'   'E'
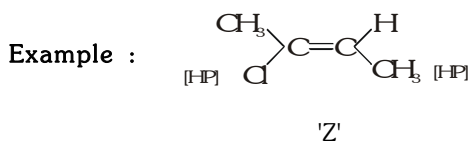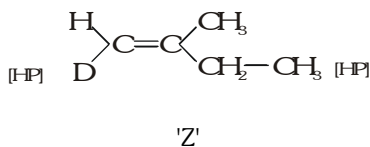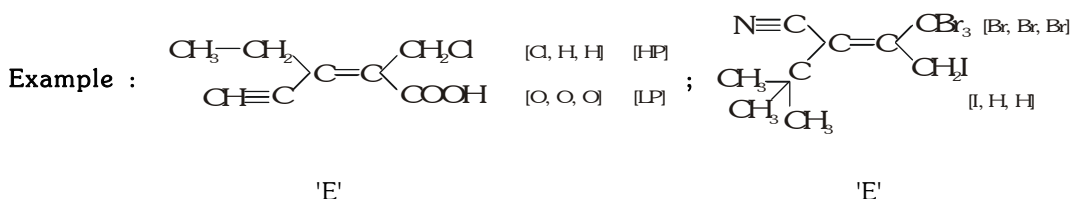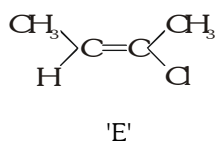
❑ **GEOMETRICAL ISOMERS IN OXIMES [>C = N–OH] :**

◆ Oximes show G. I. due to restricted rotation about double bond.

◆ Only those oximes show Geometrical isomerism in which sp^2 carbon have two different groups.

$[CH_3-CH=O + H_2N-OH] \longrightarrow CH_3-CH=N-OH$ (oxime)
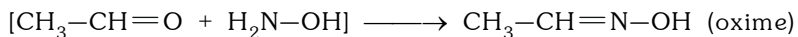
Example : Acetaldoximes has two Geometrical isomers –
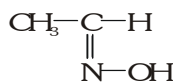
syn   anti

When H and OH are on the same side   When H and OH are on the opposite side

Example : $Ph-CH=N-OH$

Benzaldoxime

Ex. Which of the following show Geometrical isomerism –

(A) $CH_3-CH_2-CH=N-OH$ (B) $H_2C=N-OH$

(C)

(D)
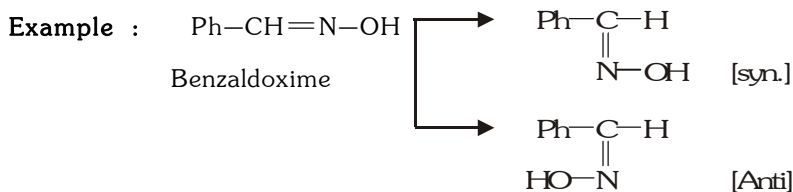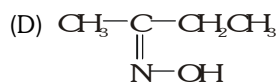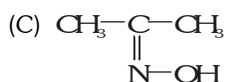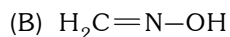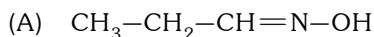
Sol. (A), (D)

❑ **GEOMETRICAL ISOMERS IN AZO COMPOUNDS :** $(-\ddot{N}=\ddot{N}-)$
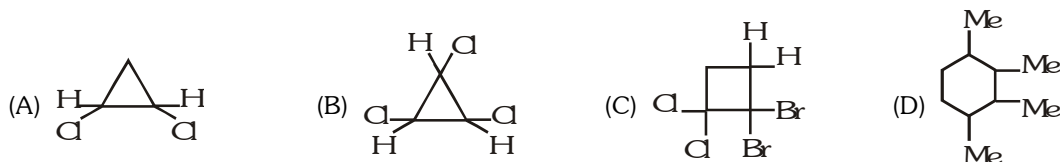

(syn)   (Anti)

Ph—N=N—Ph (Azo benzene)
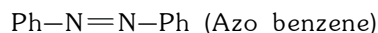
❑ **GEOMETRICAL ISOMERS IN CYCLOALKANES :**

Cycloalkanes show Geometrical isomers due to restricted rotation about single bond. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.
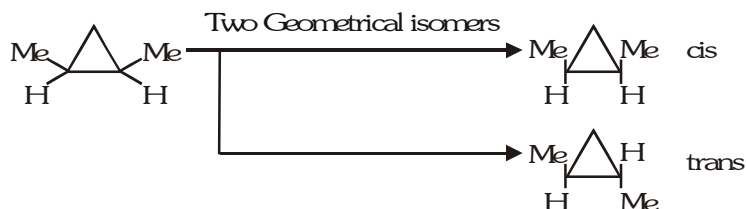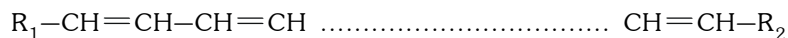

Ex. Which of the following show Geometrical isomerism –

Sol, (A), (B) and (D)

❑ **NUMBER OF GEOMETRICAL ISOMERS IN POLYENES :**

$$R_1-CH=CH-CH=CH \text{ .... } CH=CH-R_2$$

(a) If $R_1 \ne R_2$ then number of Geometrical isomers = 2^n [n = number of double bonds.]

Example : $CH_3-CH=CH-CH=CH-CH=CH-CH_2CH_3$
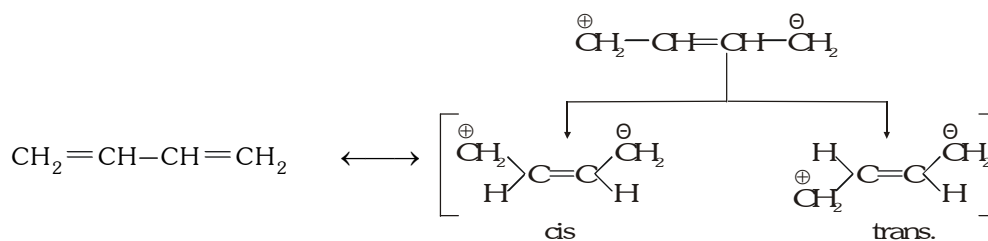
As n = 3 → number of Geometrical isomers = 2^3 = 8

(b) If $R_1 = R_2$ then number of Geometrical isomers = $2^{n-1} + 2^{p-1}$

where $p = \dfrac{n}{2}$ (when n is even)   and $p = \dfrac{n+1}{2}$ (n is odd)

Example : $CH_3-CH=CH-CH=CH-CH=CH-CH_3$ [n = 3]

Number of Geometrical isomers = $2^{n-1} + 2^{p-1}$ [p = $\dfrac{3+1}{2}$]

= $2^2 + 2^1$ = 4 + 2 = 6

Special Point : $CH_2=CH-CH=CH_2$　　　[1,3–butadiene] show Geometrical isomerism due to resonance.

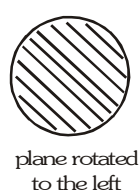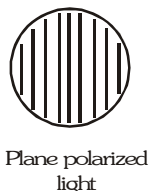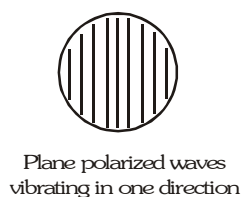$$CH_2=CH-CH=CH_2 \longleftrightarrow$$

cis　　　　　　　　trans.

❑　**OPTICAL ISOMERISM :**

Certain substances possess the property to rotate the plane of polarized light. Such substances are called optically active substances and this phenomenon is called optical activity.

◆　**Optical activity :**

Light is propagated by a vibratory motion of the 'ether' particles present in the atmosphere. Thus in ordinary light vibrations occur in all planes at right angles to the line of propagation. In plane polarized light the vibrations take place only in one plane, vibrations in other planes being cut off. Plane polarized light can be obtained by passing ordinary light through a Nicol prism.

ordinary light
waves vibrating in
all directions

Nicol prism

Plane polarized waves
vibrating in one direction

plane rotated
to the right

Plane polarized
light

plane rotated
to the left

Certain organic compounds, when their solutions are placed in the path of a plane polarized light, have the remarkable property of rotating its plane through a certain angle which may be either to the left (or) to the right. This property of a substance of rotating the plane of polarized light is called optical activity and the substance possessing it is said to be optically active.

The observed rotation of the plane of polarized light [determined with the help of polarimeter] produced by a solution depends on :

(a)　the amount of the substance in tube ;

(b)　on the length of the solution examined ;

(c)　the temperature of the experiment and

(d)　the wavelength of the light used.

The instrument used to measure angle of rotation is called polarimeter. The measurement of optical rotation is expressed in terms of specific rotation $[\alpha]_D^t$; this is given by the following relation :

$$[\alpha]_D^t = \frac{\alpha_{obs}}{\ell \times C} \qquad [\text{where } \alpha = \text{observed angle of rotation}]$$

$[\alpha]_D^t$ = specific rotation determined at t C, using D-line of sodium light.

ℓ = length of solution in decimeters

C = concentration of the active compound in grams per millilitre.

For example, the specific rotation of amyl alcohol [2-methyl-1butanol] at 25 C for D-line of sodium light is given by

$$[\alpha]_D^{25°} = -5.756°$$

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (–) indicates that the rotation is towards the left, while positive (+) sign means that the direction of rotation is toward right.

The rotation may be different in different solvents and this needs to be mentioned while reporting the specific rotation. Thus,
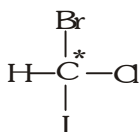
$$[\alpha]_D^{25°} = +24.7 \quad \text{(in chloroform)}$$

◆ **Asymmetric carbon (or) Chiral Carbon :**

If all the four bonds of carbon are satisfied by four different atoms/groups, it is chiral. Chiral carbon is designated by an asterisk (*).

◆ **Optical isomerism in bromo chloro iodo methane :**

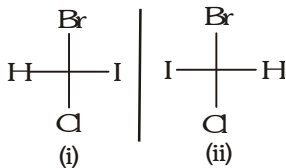The structural formula of bromo chloroiodomethane is

The molecule has one chiral carbon as designated by star. So molecule is chiral. It is non-super imposable on its mirror image.

According to Van't Hoff rule.

Total number of optical isomers should be = 2^n.

where n is number of chiral centre.

The fischer projections of the two isomers are

These are optically active, which are non-super imposable mirror image of each other and can rotate plane of polarized light.

Stereoisomers which are mirror-image of each other are called enantiomers (or) enantimorphs. Thus (i) and (ii) are enantiomers. All the physical and chemical properties of enantimoers are same except two :

(i)   They rotate PPL to the same extent but in opposite direction. One which rotates PPL in clockwise direction is called dextro-rotatory [dextro is latin word meaning thereby right] and is designated by d (or) (+). One which rotates PPL in anti-clockwise direction is called laevo rotatory [means towards left] and designated by l (or) (–).

(ii)   They react with optically active compounds with different rates.

♦ Properties of enantiomers :

S.No.	Properties	Remarks
1	Molecular formula	Same
2	Structural formula	Same
3	Stereochemical formula (str. Formula with orientation)	Different
4	Physical properties (m.p., b.p. density, solubility), refractive index etc.	Same
5	Chemical propeties	
	(a) with optically inactive compound	Same
	(b) with optically active compound	Different

❑ **Optical isomerism in compounds having more than one chiral carbons** :

If an organic molecule cotains more than one chiral carbons then the molecule may be chiral (or) achiral depending whether it has element of symmetry or not.

Elements of symmetry : If a molecule have either.

(a)   a plane of symmetry, and/or

(b)   centre of symmetry, and /or

(c)   n-fold alternating axis of symmetry.

If an object is super imposable on its mirror image ; it can not rotate PPL and hence optically inactive. If an object can be cut exactly into two equal halves so that half of its become mirror image of other half, it has plane of symmetry.

$$COOH$$
$$|$$
$$H-C-OH \quad (I)$$
$$|$$
-------------------- Mirror plane
$$|$$
$$H-C-OH \quad (II)$$
$$|$$
$$COOH$$
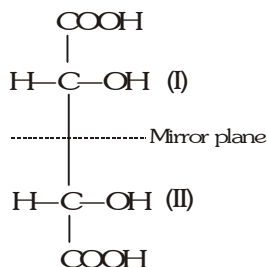
(I) and (II) are mirror images, hence plane of symmetry is present in the molecule.

$$COOH$$
$$|$$
$$H-C-OH \quad (I)$$
$$|$$
-------------------- Mirror plane
$$|$$
$$HO-C-H \quad (II)$$
$$|$$
$$COOH$$
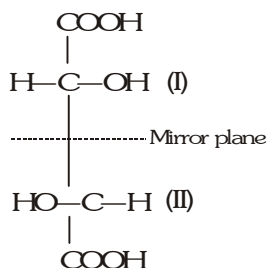
(I) and (II) are not mirror images, hence plane of symmetry is absent in the molecule.

♦ **Centre of symmetry** : It is a point inside a molecule from which on travelling equal distance in opposite directions one takes equal time.

A centre of symmetry is usually present only in an even numbered ring. For example, the mole of trans-2,4-dimethyl-cyclobutane-trans-1, 3 dicarboxylic acid has a centre of symmetry.
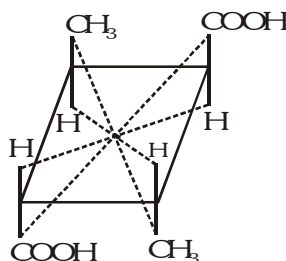
Thus, if an organic molecule contains more than one chiral carbon but also have any elements of symmetry, it is super imposable on its mirror-image, cannot rotate PPL and optically inactive. If the molecule have more than one chiral centres but not have any element of symmetry, it must be chiral.

◆ **Stereoisomerism in Tartaric Acid** :

Compounds which contain two asymmetric carbon atoms and are the type Cabc-Cabc exist in only three isomeric forms. Two of these are non-superimposable mirror images of each other and are optically active and the third, a diastereomer of the first two, contains a plane of symmetry, is super imposable on its mirror image and is not optically active e.g.,
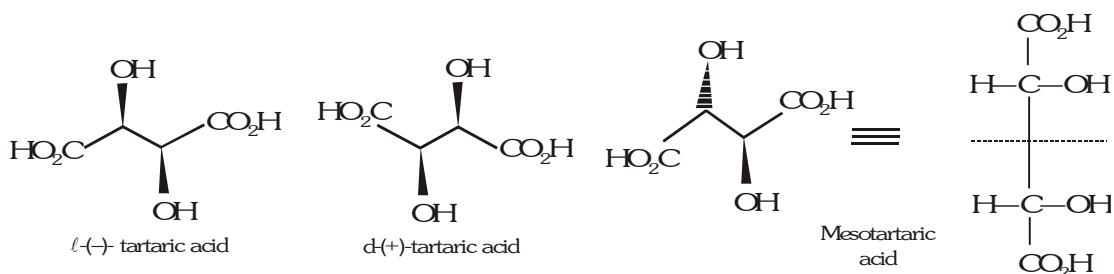
The inactive diastereomer is usually described as a meso form. As with other examples of diastereomers, the properties of meso forms are different from those of the isomeric mirror-image pairs ; for example, mesotartaric acid melts at a lower temperature [140 C] than the d and ℓ isomer [170 C] and is less dense, less soluble in water, and a weaker acid.

Compounds with two asymmetric carbon atoms in which at least one substituent is not common to both carbons occur in four optically isomeric forms, e.g., the four isomers of structure.

2,3-dibromopentane
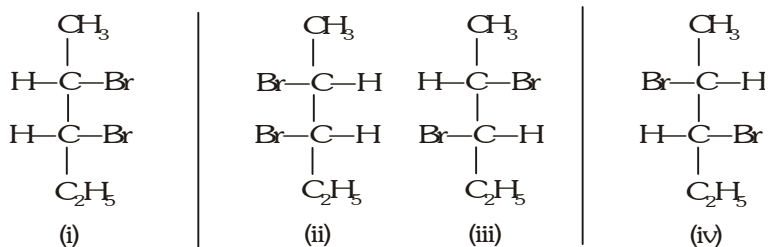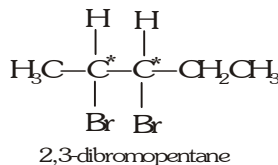
In general, a compound possessing n distinct asymmetric carbon atoms exists in 2^n optically active forms.

It should be noted that, whereas (i) and (ii) and (iii) and (iv) are mirror-image pairs and therefore have identical properties in a symmetric environment, neither of the (i) and (ii) bears a mirror-image relationship to either of those (iii) and (iv). These and other stereoisomers which are not enantiomers are described as diastereomers (or diastereo isomers) and unlike enantiomers, they differ in physical and chemical properties.

❑ **Calculation of number of optical isomers** :

The number of optical isomers of an organic compound depends on its structure and number of asymmetric carbon atoms. Thus, the number of optical isomer may be determined from the knowledge of the structure of the compound as follows :

(a) When the molecule is unsymmetrical

No. of optically active isomers, $a = 2^n$

Number of meso forms (m) = 0

Number of racemic mixtures, $r = a/2$

∴ Total no. of optically active isomers = $(a + m) = 2^n$

(b) When the molecule is symmetrical and has even no. of asymmetric carbon atoms.

No. of optically active isomers, $a = 2^{(n-1)}$

No. of meso forms, $m = 2^{\frac{n}{2}-1}$

No. of racemic mixtures, $r = a/2$

∴ Total no. of optically active isomers = $a + m$

(c) When the molecule is symmetrical and has an odd no. of asymmetrical carbon atoms.

no. of optically active isomers, $a = 2^{(n-1)} - 2^{(n/2-\frac{1}{2})}$

No. of meso forms, $m = 2^{(n/2-\frac{1}{2})}$

∴ Total no. of optically active isomer = $(a + m) = 2^{(n-1)}$

❑ **Optically active compounds having no asymmetric carbon** :

1. **Allenes** : An sp-hybridized carbon atom possess one electron in each of two mutually perpendicular p orbitals. When it is joined to two sp^2-hybridized carbon atoms, as in allene, two mutually perpendicualr π-bonds are formed and consequently the π-bonds to the sp^2-carbons are in perpendicular planes. Allenes of the type abC=C=Cab (a ≠ b) are therefore not superimposable on their mirror images and despite the absence of any asymmetric atoms, exist as enantiomers and several optically active compounds have been obtained. (Ex. a = phenyl, b=1-naphthyl)
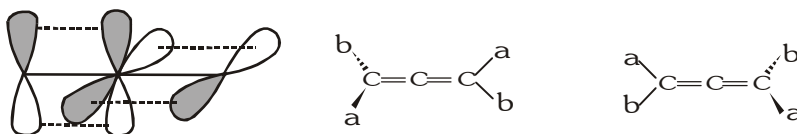

2. Any molecule containing an atom that has four bonds pointing to the corners of a tetrahedron will be optically active if the groups are different.
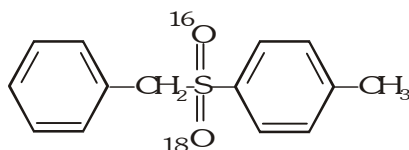
3. **Alkylidene cyclo alkanes** : The replacement of one double bond in an allene by a ring does not alter the basic geometry of the system and appropriately substituted compounds exist in optically active forms.
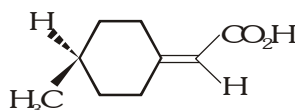
Related compounds in which sp^2-carbon is replaced by nitrogen have also been obtained as optical isomers.
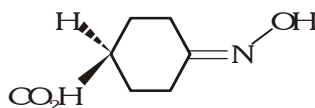
❑ **Difference between Racemic mixture and Meso compound** :

A racemic mixture contains equimolar amounts of enantiomers. It is optically inactive due to external compensation.
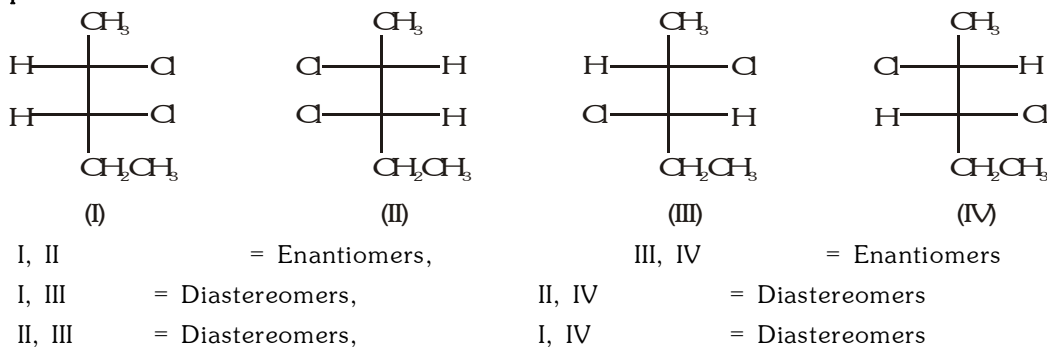
◆ **External compensation** :

If equimolar amounts of d and ℓ-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced (or) compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to external compensation. Such mixtures of (+) and (−) isomer (Racemic mixtures) can be separated into the active components.

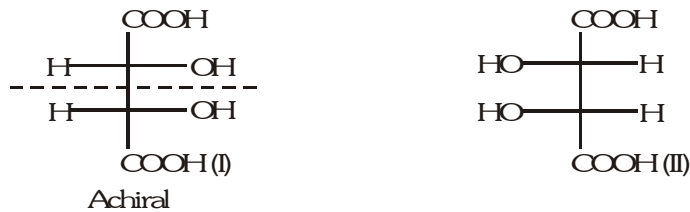A meso compound is optically inactive due to internal compensation

◆ **Internal compensation** :

In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to internal compensation. It occurs whenever a compound containing two (or) more asymmetric carbon atoms has a plane (or) point of symmetry. Since the optical inactivity of such a compound arises within the molecule, the question of separating into active components does not arise.

Example :

I, II = Enantiomers, III, IV = Enantiomers

I, III = Diastereomers, II, IV = Diastereomers

II, III = Diastereomers, I, IV = Diastereomers

Example :

I and II are identical
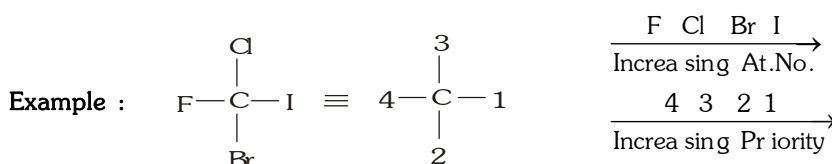
❑ **Absolute Configuration (R, S configuration)** :

The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed **absolute configuration**.

System which indicates the absolute configurastion 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 system. The letter (R) comes from the latin rectus (means right) while (S) comes from the latin sinister (means left).
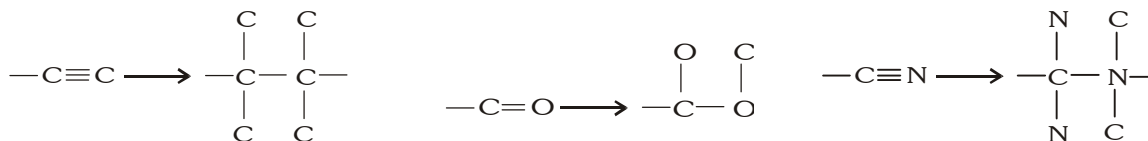
It is better system because in manycases configuration to a compound cannot be assigned by D, L method.

(R) (S) nomenclature is assigned as follows :

1. Each group attached to stereocentre is assigned a priority on the basis of atomic number. The group with the directly attached atom with highest atomic number out of the four groups gets top priority while the group with the atom of least atomic number gets the least priority.

Example :

$$F-\underset{\underset{Br}{|}}{\overset{\overset{Cl}{|}}{C}}-I \equiv 4-\underset{\underset{2}{|}}{\overset{\overset{3}{|}}{C}}-1$$

$$\xrightarrow[\text{Increasing At.No.}]{\text{F Cl Br I}}$$

$$\xrightarrow[\text{Increasing Priority}]{\text{4 3 2 1}}$$

2. If out of the four attached atoms in consideration, two are isotopic (like H and D), then priority goes to higher atomic mass i.e. D.

3. If out of the four attached atoms in consideration, two or more are same, then priority is decided on the basis of the atom attached next to it in its group. e.g. out of CH_3 and COOH, COOH gets priority.

4. While deciding the priority, if the atom in consideration is attached is further to an atom through a double bond then it is treated as if it is attached to two such atoms. For example :

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

$$-C=O \longrightarrow -\underset{\underset{C}{|}}{\overset{\overset{O}{|}}{C}}-O$$

$$-C\equiv N \longrightarrow -\underset{\underset{N}{|}}{\overset{\overset{N}{|}}{C}}-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{N}}-$$

5. After assigning priorties, the least priority group is written at remotest valency (going away), while the top priority group is written at the top directed valency (towards viewer).
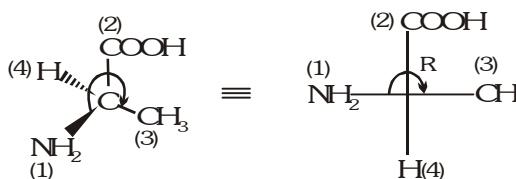
◆ If lowest priority group is not on the dash position then,
Step 1 : Bring the lowest priority group to dash by even simultaneous exchanges.
Step 2 : Draw an arrow from first priority group to second priority group till third priority group.
Step 3 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.
Step 4 : Draw the Fisher projection formula having equivalent configuration to the wedge-dash formula.
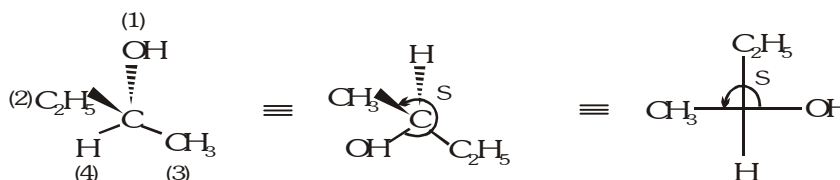
◆ Now the order from top priority to the one of second priority and then to the one of third priority is determined. If this gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration.

◆ **Important :** Note that the designation of a compound as R or S has nothing to do with the sign of rotation. the Cahn-Ingold rule can be applied to any three dimensional representation of a chiral compound to determine whether it is R or S only. For example in above case (i.e. lactic acid), R configuration is laevo rotatory is designated as R-(−)-lactic acid. Now the other configuration of it will have opposite sign of rotation i.e. S-(+)-lactic acid.

Special Point :

◆ Chiral nitrogen containing tetra alkyl ammonium ion show optical isomerism.

(I)   (II)
I and II enatiomers
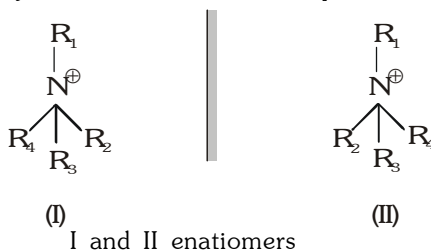
◆ Chiral nitrogen containig tertiary amine do not show optical isomerism
Reason :- Rapid umbrella inversion.
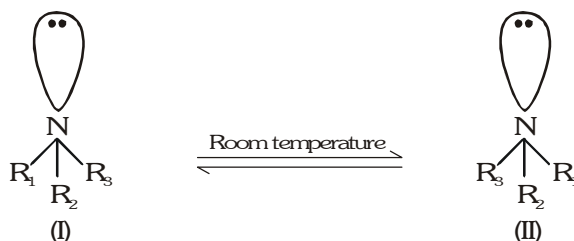
(I)   (II)

Energy required for this interconversion is available at room temperature so I and II are identical

◆ Chiral C containing carbanion do not show optical isomerism.
Reason :- Rapid umbrella inversion.
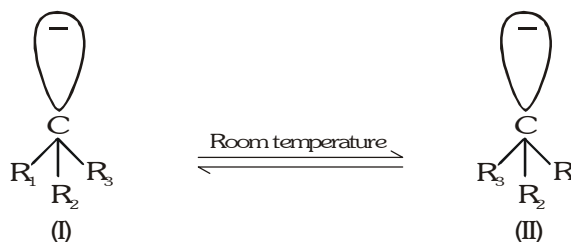
(I)   (II)

Energy required for this interconversion is available at room temperature.So, I and II are identical.

◆ Substituted Allenes do not have chiral carbons but molecule is chiral, so show optical isomerism.

$CH_2=C=CH_2 \longrightarrow$
Allene
No chiral C but molecule is chiral
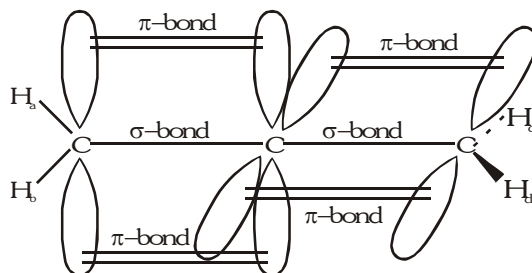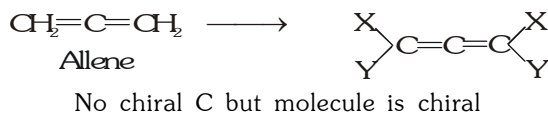
Only those substituted allenes will be optically active in which "each sp^2 C have different atoms or group".

Ex. Which of the following is optically active –

(A) $CH_3-CH=C=CH-CH_3$

(B) $CH_2=C=CH_2$

(C)

(D)
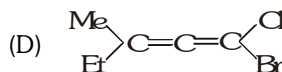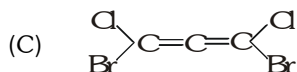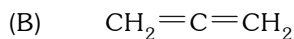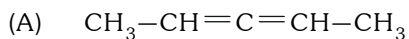
Sol. (A), (C) and (D)

◆ Ortho substituted biphenyl compounds do not have any chiral carbon but due to chiral molecule, they are optically active.

Horizontal   Vertical
plane   plane

Optically active
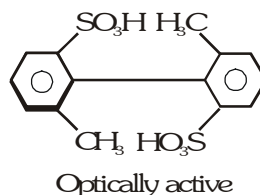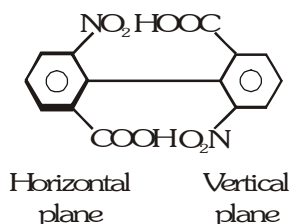
❑ **CONFORMATIONAL ISOMERISM :**

The different arrangement of atoms in space that result from the free rotation arround C—C bond axis are called conformations. The phenomenon is called conformational isomerism
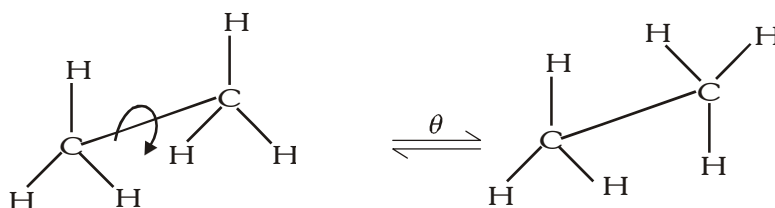
Here θ(60) is dihedral angle, angle between two planes.

Ex. Which of the following show conformational isomerism.

(1)   (2)   (3)

(4)   (5)   (6)
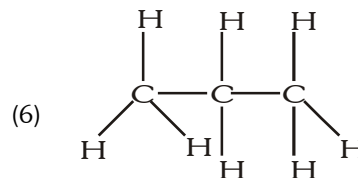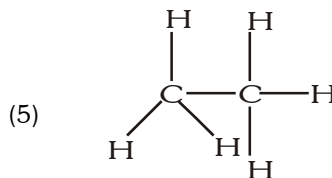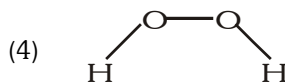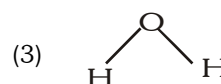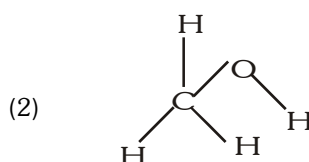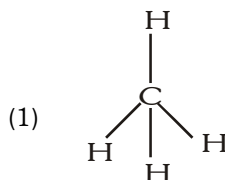
Sol. 2, 4, 5, 6 [Hint : Condition to show conformational isomerism ⇒There should be at least three continuous sigma bonds.]

❑ **Conformers of ethane [CH_3-CH_3] :**

(I)   (II)
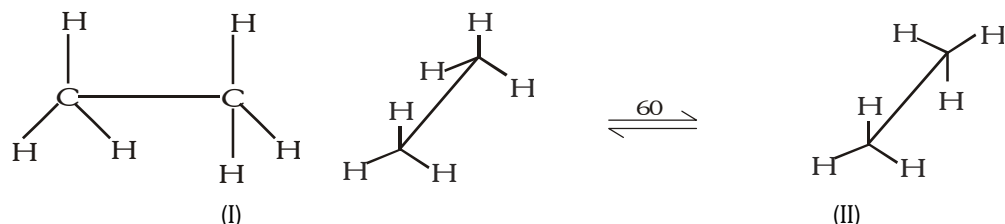
(Saw horse projection)

(Newman projection)

I = III (Eclipsed form) in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.

II = IV (Staggered form) in this form distance between 2C–H bonds is maximum so minimum repulsion so maximum stable.
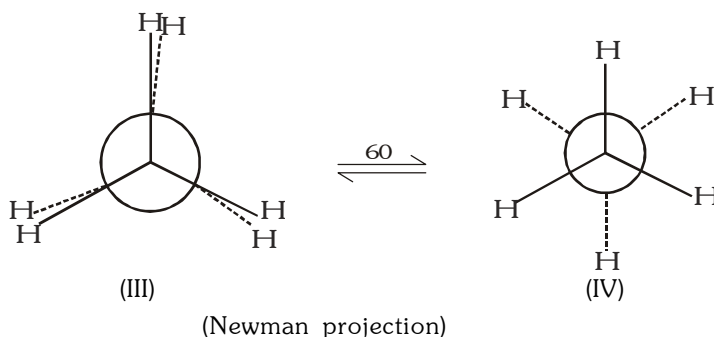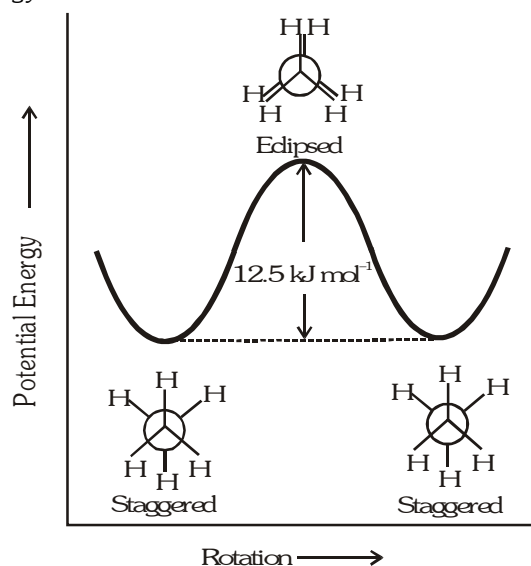
There are infinite conformers between eclipsed and staggered forms which are called as skew forms

Stability order : Staggered > Skew > Eclipsed.

◆ **Dihedral Angle :** Dihedral angle in eclipsed form of ethane is 0 .

Dihedral angle in staggered form of ethane is 60 .

The variation of energy with rotation about the C–C bond in ethane has been shown in figure below :

Changes in energy during rotation about C–C bond in ethane

The difference in the energy of various conformers constitutes an energy barrier to rotation. The energy required to rotate the ethane molecule about carbon-carbon single bond is called **torsional energy**. But this energy barrier is not large enough to prevent the rotation. Even at ordinary temperature the molecules possess sufficient thermal and kinetic energy to overcome the energy barrier through molecular collisions. Thus, conformations keep on changing form one form to another very rapidly and cannot be isolated as separate conformers.

◆ **Torsional energy :** The energy required to rotate the ethane molecule about 'C–C' bond is called torsional energy.

Conformation of Butane $[CH_3-CH_2-CH_2-CH_3]$

(I)   (II)   (III)   (IV)
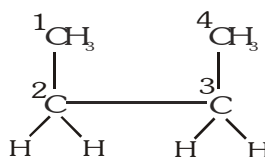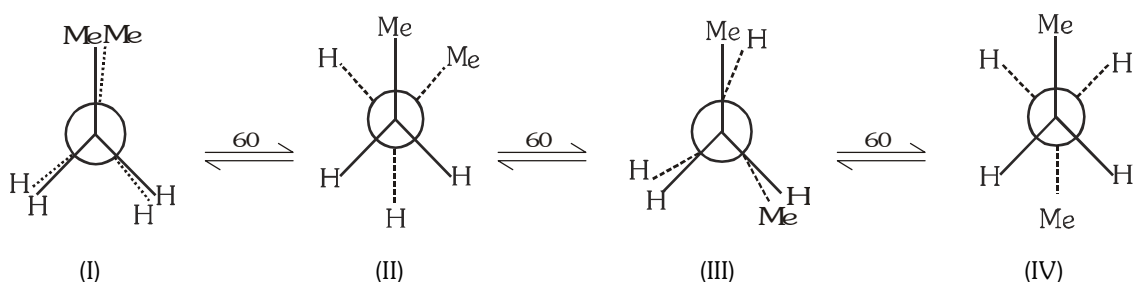
I (Fully eclipsed form) : In this form distance between 2 methyl groups is minimum so maximum repulsion or minimum stable.

IV (Anti or antistaggered) : In this form distance between 2 methyl groups is maximum so minimum repulsion or maximum stable.

Stability order : IV > II > III > I

◆ **Dihedral angle :** Angle between two planes.

 ◆ Angle of rotation to get minimum stable to maximum stable form in butane is 180 .

 ◆ Angle of rotation to get maximum stable to maximum stable form in butane is 360 .

 ◆ The energy profile diagram for the conformation of butane is given below along with the difference of energy between various conformation of butane.

Energy changes that arises from rotation about the C_2–C_3 bond of butane.
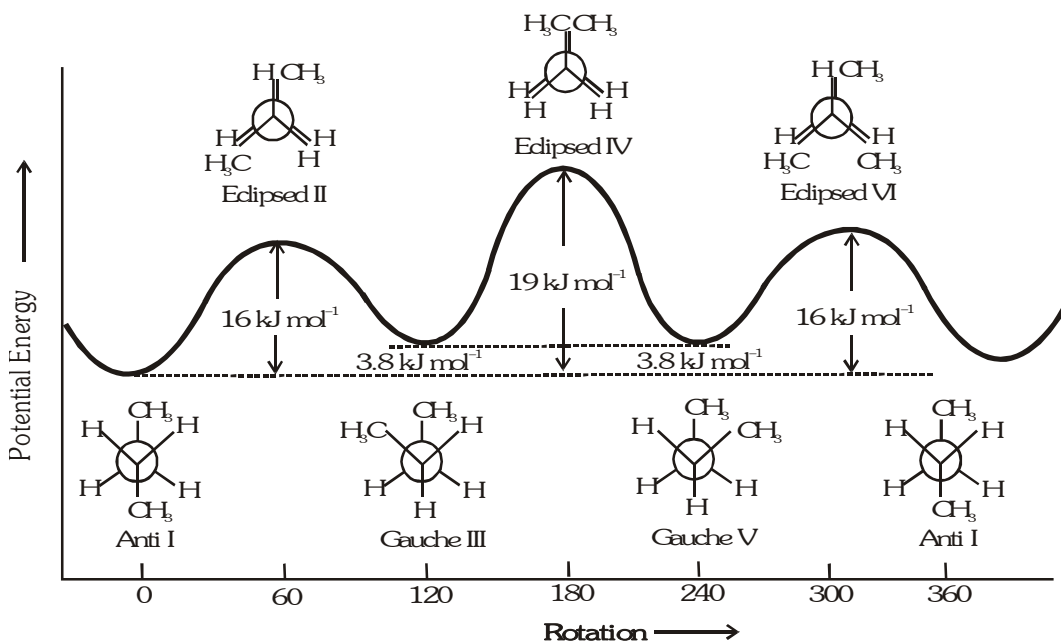
❑ **Conformational analysis of cyclohexane :**

(A) Chair form :

Experimental evidences show that cyclohexane is non-planar. If we look to the models of the different conformations that are free of angle strain first there is chair conformation. If we sight along each of the carbon-carbon bonds in turn we see in every case perfectly staggered bonds.

Chair conformation   Chair conformation(all staggered bonds)
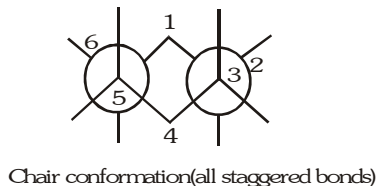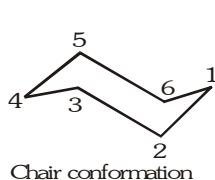
The conformation is thus free of all the strains, it lies at energy minimum and is therefore a conformational isomer. The chair form is the most stable conformation of cyclohexane.

Axial and equatorial bonds in chair form of cyclohexane :

Axial C–H bonds   Equatorial C–H bonds   Axial & equatorial bonds together

The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens, called axial hydrogens, hence their bonds parallel to a vertical axis that passes through the rings centre. These axial bonds are directed up & down on adjacent carbons. The second set of six hydrogens called equatorial hydrogens are located approximately along the equator of the molecule.
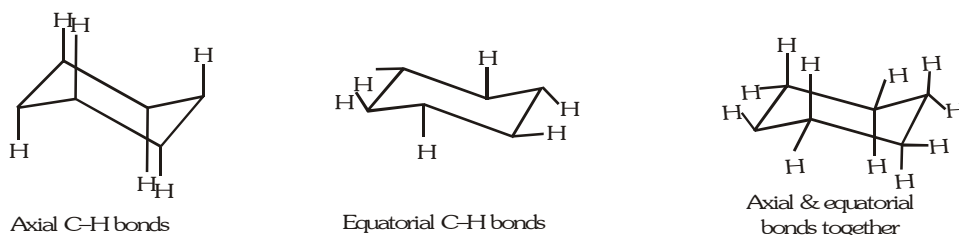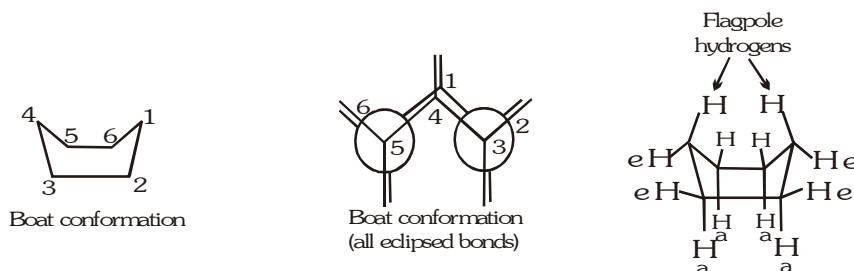
(B) Boat form :

Another conformation which is known as boat conformation has exactly eclipsed conformations.

Boat conformation   Boat conformation (all eclipsed bonds)

In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to torsional strain among axial hydrogens and due to van der waals strain caused by crowding between the "flagpole" hydrogens.

❑ **Conformational inversion (Ring flipping) in cyclohexane :**

Like alkanes cyclohexane too is conformationally mobile. Through a process known as ring inversion, Chair-chair interconversion, or more simple ring flipping one chair conformation is converted to another chair.
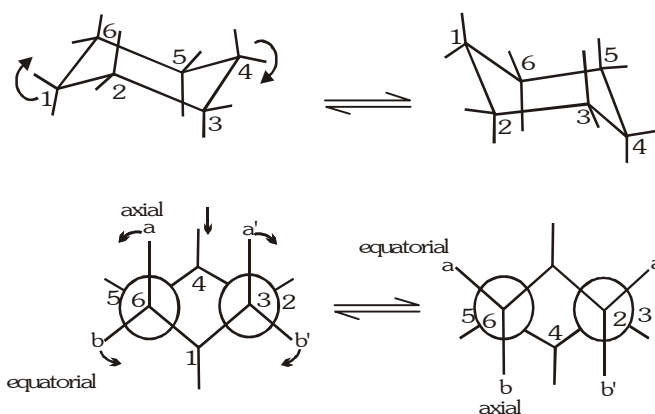
By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cyclohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about 10^{-5} sec at 25 C.

❑ **Conformational analysis of monosubstituted cyclohexanes :**

In ring inversion in methylcyclohexane the two chair conformations are not equivalent. In one chair the methyl group is axial ; in the other it is equatorial. At room temperature 95% of the methylcyclohexane exist in equatorial methyl group whereas only 5% of the molecule have an axial methyl group.

(5%)   (95%)
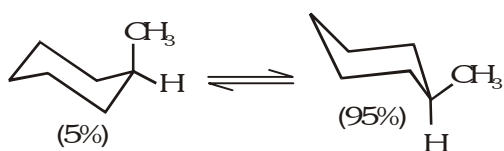
1,3-diaxial repulsion :

A methyl group is less crowded when it is equatorial than when it is axial. The distance between the axial methyl groups at C-1 and two hydrogens at C-3 and C-5 is less than the sum of their vander waal radii which causes vander waal strain in the axial conformation this type of crowding is called 1,3-diaxial repulsions. When the methyl group is equatorial, it experience no significant crowding.
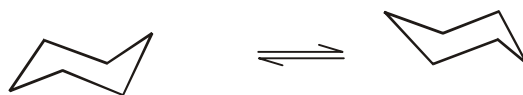
Vander waals strain between
hydrogen of axial CH_3 and axial
hydrogens at C-3 and C-5

Ex.1 Evaporation of an aqueous solution of ammonium cyanate gives urea. This reaction follows the class of-

(A) Polymerization   (B) Isomerization   (C) Association   (D) Dissociation

Sol. $NH_4CNO \xrightarrow{\text{heat}} H_2N-CO-NH_2$ Ans.**(B)**

Ex.2 The possible number of alkynes with the formula C_5H_8 is -

(A) 2   (B) 3   (C) 4   (D) 5

Sol. $CH_3CH_2CH_2C \equiv CH$ $(CH_3)_2CH-C \equiv CH$ $CH_3CH_2C \equiv CCH_3$ Ans.**(B)**
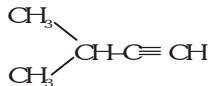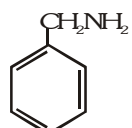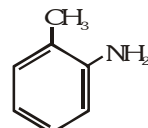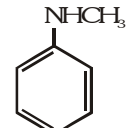
Ex.3 How many isomers of $C_5H_{11}OH$ will be primary alcohols -

(A) 2   (B) 3   (C) 4   (D) 5

Sol. $CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CHCH_2CH_2OH$ with CH_3 branch   Ans.**(C)**

(i)   (ii)

$HOCH_2-CHCH_2CH_3$ with CH_3 branch $CH_3-C(CH_3)_2-CH_2OH$

(iii)   (iv)

Ex.4 Number of isomeric forms of C_7H_9N having benzene ring will be -

(A) 7   (B) 6   (C) 5   (D) 4

Sol. (benzene ring with CH_2NH_2)   (benzene ring with CH_3 and NH_2)   (benzene ring with $NHCH_3$)   Ans.**(C)**

(i)   o-, m-, p-   (v)
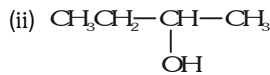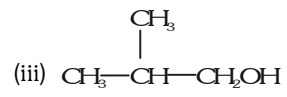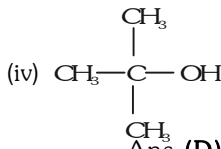
                                       (ii)(iii)(iv)

Ex.5 Which of the following is an isomer of diethyl ether-

(A) $(CH_3)_3COH$ (B) CH_3CHO (C) C_3H_7OH (D) $(C_2H_5)_2CHOH$

Sol. Diethyl ether has 4 carbon atoms, among different alternative alcohols only $(CH_3)_3COH$ has 4 carbon atoms.

Ans.**(A)**

Ex.6 Total number of isomeric alcohols with formula $C_4H_{10}O$ are -

(A) 1   (B) 2   (C) 3   (D) 4

Sol. (i) $CH_3CH_2CH_2CH_2OH$ (ii) $CH_3CH_2-CH(OH)-CH_3$ (iii) $CH_3-CH(CH_3)-CH_2OH$ (iv) $CH_3-C(CH_3)_2-OH$

                                                                                        Ans.**(D)**

Ex.7 The molecular formula of a saturated compound is $C_2H_4Cl_2$. The formula permits the existence of two
(A) functional isomers   (B) Position isomers   (C) Optical isomers   (D) cis-trans isomers

Sol. (i)
$$\underset{\overset{|}{H}\;\;\;\overset{|}{Cl}}{H-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-Cl}$$
     1,1-dichloro ethane   (ii)
$$\underset{\overset{|}{Cl}\;\;\;\overset{|}{Cl}}{H-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-H}$$
   1,2-dichloro ethane   Ans.**(B)**

Both are position isomers
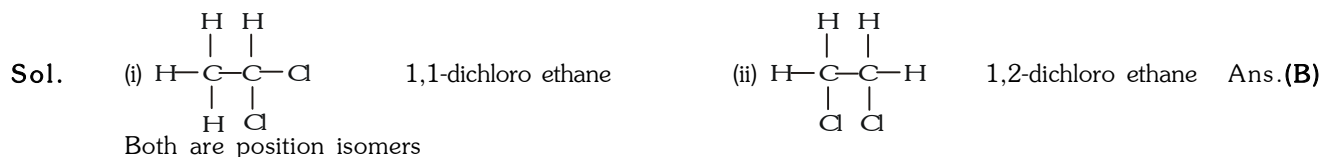
Ex.8 The type of isomerism found in urea molecule is -
(A) Chain   (B) Position   (C) Tautomerism   (D) None of these

Sol.
$$\underset{\underset{\text{urea}}{O}}{NH_2-\overset{\overset{\displaystyle ||}{}}{C}-NH_2} \rightleftharpoons \underset{\underset{\text{Isourea}}{OH}}{NH_2-\overset{}{C}=NH}$$
                                                         Ans.**(C)**

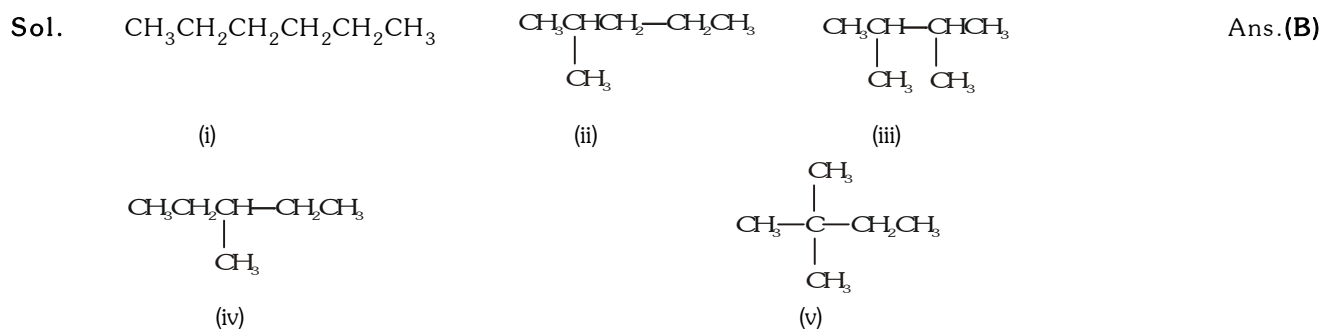**Ex.9** An alkane can show structural isomerism if it has .... number of minimum carbon atoms -
(A) 1   (B) 2   (C) 3   (D) 4

Sol. $CH_4, CH_3- CH_3$, $CH_3-CH_2-CH_3$ exist only in one structural form, while $CH_3CH_2CH_2CH_3$ can exist in more than one structural form.   Ans.**(D)**

Ex.10 How many chain isomers can be obtained form the alkane C_6H_{14} is :-
(A) 4   (B) 5   (C) 6   (D) 7

Sol. $CH_3CH_2CH_2CH_2CH_2CH_3$
$$\underset{\overset{|}{CH_3}}{CH_3CHCH_2-CH_2CH_3}$$

$$\underset{\overset{|}{CH_3}\;\;\overset{|}{CH_3}}{CH_3CH-CHCH_3}$$
               Ans.**(B)**

        (i)   (ii)   (iii)

$$\underset{\overset{|}{CH_3}}{CH_3CH_2CH-CH_2CH_3}$$

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

        (iv)   (v)

Ex.11 Keto - enol tautomerism is observed in -

(A) $\underset{}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-H}$ (B) $\underset{}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$

(C) $\underset{}{C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-C_6H_5}$ (D) $C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-\underset{\overset{|}{CH_3}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-C_6H_5$

Sol. Only compound (B) contains α hydrogen atom for showing keto enol tautomerism.   Ans.**(B)**

Ex.12 The number of geometrical isomers in case of a compound with the structure :
$CH_3-CH=CH-CH=CH-C_2H_5$ is -
(A) 4   (B) 3   (C) 2   (D) 5

Sol. Given alkene is unsymmetrical one and has two double bonds, the number of geometrical isomers is given by 2^n. (n = 2) therefore number of geometrical isomers will be $2^2 = 4$ Ans.**(A)**

**Ex. 13** Which one of the following will show geometrical isomerism -

(A)

(B)

(C)
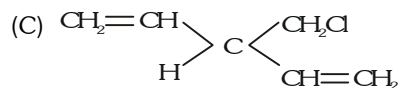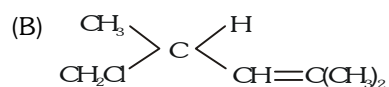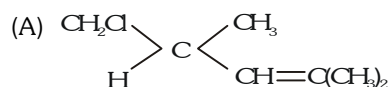
(D) $CH_3CH_2CH=CHCH_2CH_3$ Ans.**(D)**

Ex. 14 In the reaction

$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

a chiral centre is produced. Thus product would be -

(A) Meso compound   (B) Racemic mixture (C) Laevorotatory   (D) Dextrorotatory

Sol.   Synthesis of a chiral compound from a chiral compound in the absence of optically active agent always produces a racemic modification :
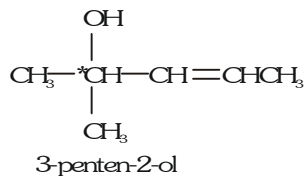

Ans.**(B)**

ℓ – lactonitrile   acetaldehyde   d – lactonitrile
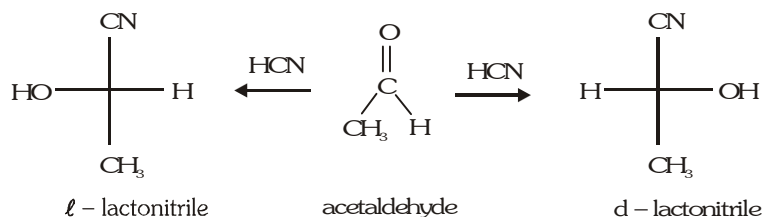
Ex.15   The molecule 3-penten–2–ol can exhibit -

(a) Optical isomerism   (b) Geometrical isomerism   (c) Metamerism (d) Tautomerism

The correct answer is -

(A) a and b   (B) a and c   (C) b and c   (D) a and d

Sol.

Ans.**(A)**

3-penten-2-ol

As given compound contains a assymmetric carbon atom and a double bond (with sufficient conditions for geometrical isomerism). Therefore it can shown both optical and geometrical isomerism.