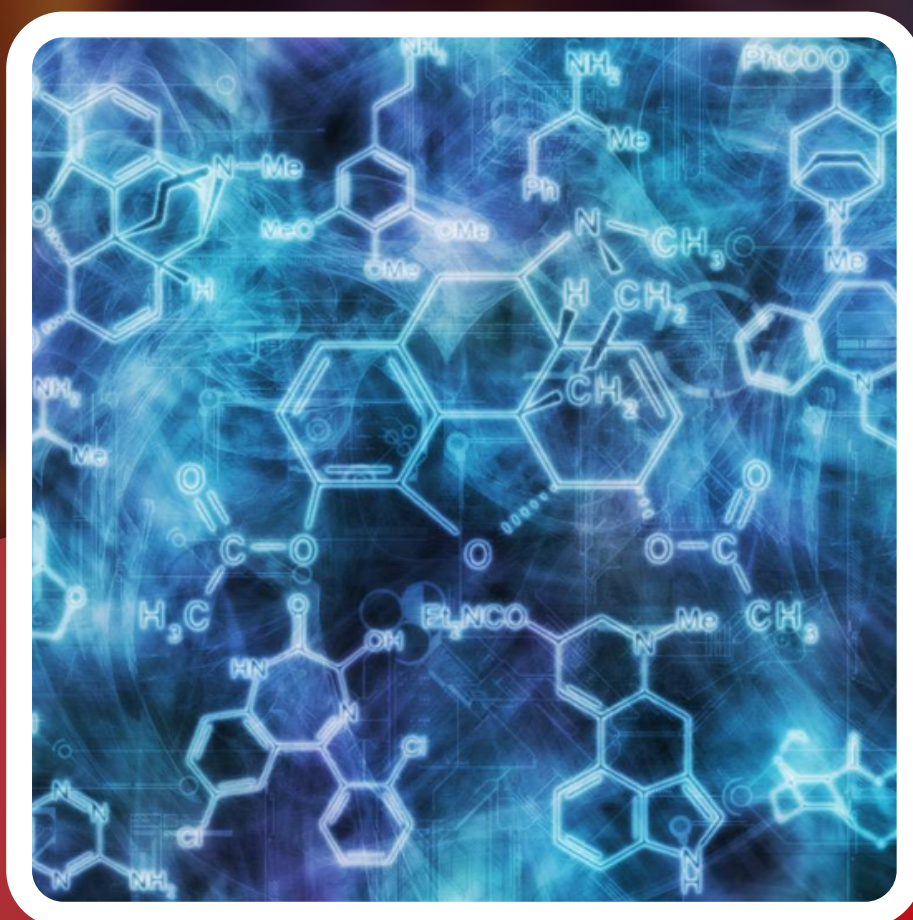


# ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



**STUDY MATERIAL**

Isomerism

ENGLISH MEDIUM

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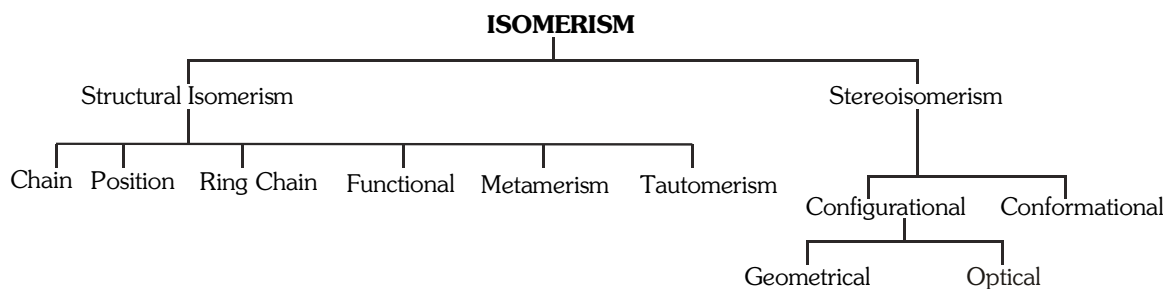
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## ISOMERISM

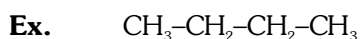
Two or more than two compounds having the same molecular formula but different physical/chemical or both properties are called isomers and the phenomenon is called isomerism.



### 2.1 Structural Isomerism

#### 2.1.1 Chain Isomerism (C.I.)

The compounds which have same molecular formula, same functional group but different arrangement of carbon chain (Parental or side chain) show chain isomerism.



Butane (4C)

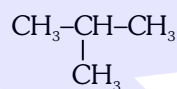


1-Butanol (4C)

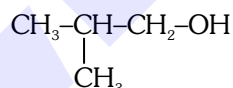
**Ex.**



Methylcyclobutane



2-Methyl propane (3C)



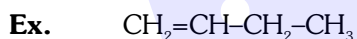
2-Methyl-1-propanol (3C)



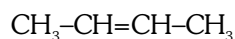
Cyclopentane

#### 2.1.2 Position Isomerism (P.I.)

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, show position isomerism.



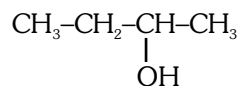
But-1-ene



But-2-ene

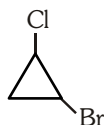


1-Butanol



2-Butanol

**Ex.**



1-Bromo-2-chlorocyclopropane



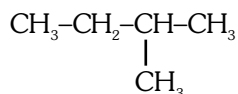
1-Bromo-1-chlorocyclopropane

**Example of CI and PI :**

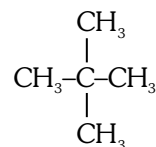
(i)  $C_5H_{12}$  has three structural isomers :



Pentane



2-Methyl butane

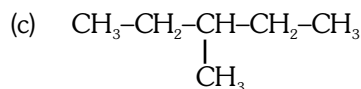


2,2-Dimethylpropane

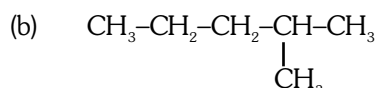
(ii)  $C_6H_{14}$  has 5 structural isomers



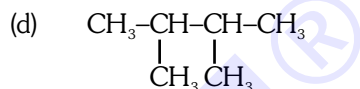
Hexane



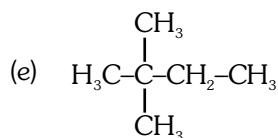
3-Methyl pentane



2-Methyl pentane



2,3-Dimethyl butane

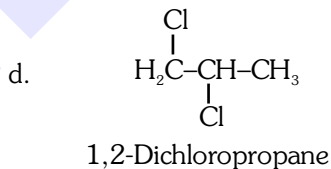
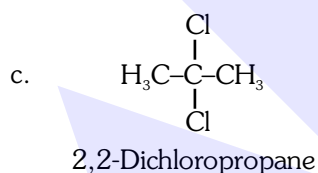
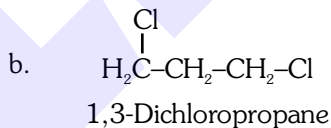
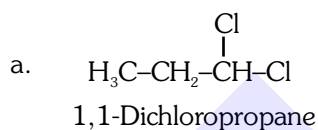


2,2-Dimethyl butane

• (a-b), (a-c), (a-d), (a-e) → Chain Isomers  
(b-d), (b-e), (c-d), (c-e)

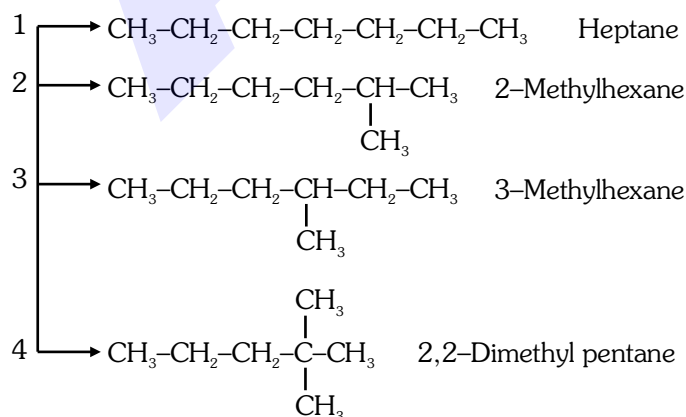
• b-c, d-e → Position Isomers

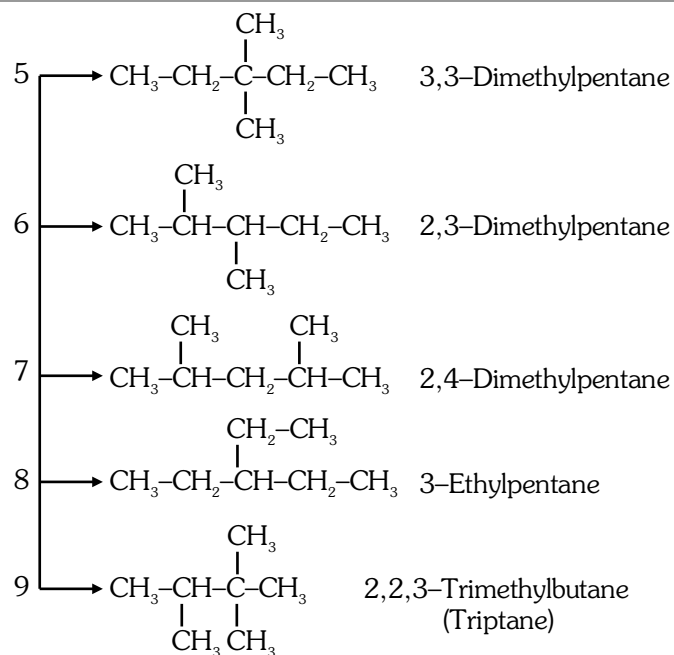
(iii)  $C_3H_6Cl_2$  has 4 isomers : Position of chlorine atom is different in all the structure, so these are position Isomers.



**Ex.** How many structural isomers of  $C_7H_{16}$  are possible ?

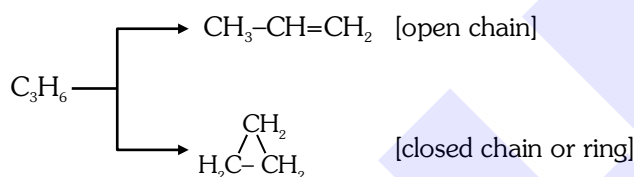
**Ans. (9)**





### 2.1.3 Ring chain isomerism (RCI)

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



### GOLDEN KEY POINTS

- Alkenes with cycloalkane and alkynes and alkadienes with cycloalkenes show Ring-chain Isomerism.
- Ring-chain Isomers are also Functional Isomers but priority must be given to Ring-chain Isomers.

### 2.1.4 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       | → | $\text{CH}_3-\text{CH}_2-\text{OH}$   | and | $\text{CH}_3-\text{O}-\text{CH}_3$  |
| (ii) Aldehydes and Ketones  | → | $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{C}-\text{H} \\    \\ \text{O} \end{array}$                  | and | $\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_3 \\    \\ \text{O} \end{array}$       |
| (iii) Acids and Ester       | → | $\begin{array}{c} \text{CH}_3-\text{C}-\text{OH} \\    \\ \text{O} \end{array}$                             | and | $\begin{array}{c} \text{H}-\text{C}-\text{O}-\text{CH}_3 \\    \\ \text{O} \end{array}$ |
| (iv) Cyanide and Isocyanide | → | $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CN}$   | and | $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NC}$   |
| (v) Nitro and Nitrite       | → | $\begin{array}{c} \text{O} \\ // \\ \text{CH}_3-\text{CH}_2-\text{N} \\ \backslash \\ \text{O} \end{array}$ | and | $\text{CH}_3-\text{CH}_2-\text{O}-\text{N}=\text{O}$                                    |





## BEGINNER'S BOX-1

1. Structures  $\text{CH}_3\text{—CH}_2\text{—CH=CH}_2$  and  $\text{CH}_3\text{—C=CH}_2$  are :-  
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- (1) Chain isomers (2) Position isomers  
 (3) Both chain & position isomers (4) Not isomers
2. How many minimum carbons required for Chain isomerism and Position isomerism in alkanes ?  
 (1) 4, 5 (2) 3, 5 (3) 4, 6 (4) 4, 4
3. The minimum number of carbon atoms in ketone to show position isomerism :-  
 (1) 3 (2) 4 (3) 5 (4) 6
4. Number of structural isomers of  $\text{C}_6\text{H}_{14}$  is -  
 (1) 3 (2) 4 (3) 5 (4) 6
5.  $\text{CH}_3\text{—CH=CH—CH}_3$  and  $\text{CH}_2\text{—CH}_2$  are :-  
 $\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ | \quad | \\ \text{CH}_2\text{—CH}_2 \end{array}$   
 (1) Ring-chain Isomers (2) Chain Isomers (3) Functional Isomers (4) Position Isomers
6.  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—C(=O)OH}$  and  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—C(=O)H}$  are  
 $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{—CH}_2\text{—CH}_2\text{—C—OH} \end{array}$  and  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{—CH}_2\text{—CH—C—H} \\ | \\ \text{OH} \end{array}$   
 (1) Position isomers (2) Functional isomers (3) Identical (4) Chain isomers
7.  $\text{CH}_3\text{—S—CH}_2\text{—CH}_3$  and  $\text{CH}_3\text{—CH}_2\text{—S—CH}_3$  are -  
 (1) Ring-chain Isomers (2) Chain Isomers (3) Functional Isomers (4) Identical
8.  $\text{CH}_3\text{—C(=O)—O—C(=O)—C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{—C(=O)—O—C(=O)—CH}_3$  are -  
 (1) Metamers (2) Chain Isomers (3) Identical (4) Position Isomers

SR0007

SR0010

## 2.2 Stereo Isomerism

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.

- (a) Stereo isomer which cannot interconvert at room temperature due to restricted rotation known as Geometrical isomerism.
- (b) Stereo isomers which have different behaviour towards plane polarised light are known as optical isomers.

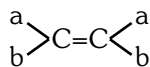
**(B) Conformational Isomerism**

## 2.2.1 Geometrical isomerism (G. I) :

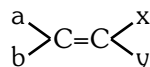
- (i) Alkenes ( $>\text{C}=\text{C}<$ ), oximes ( $>\text{C}=\text{N—OH}$ ) and azo compounds [ $\text{—N}=\text{N—}$ ] etc., show G. I. due to restricted rotation about double bond and (ii) cycloalkanes show G. I. due to restricted rotation about single bond in ring.

**G. I. IN ALKENES :**
**Reason :** Restricted rotation about double bond :

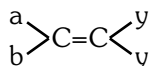
**Condition for Geometrical isomerism :**

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


Geometrical isomerism possible



Geometrical isomerism possible



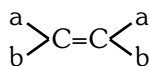
Geometrical isomerism not possible



Geometrical isomerism not possible

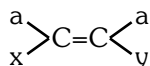
**Nomenclature Systems of Geometrical isomers**
**(a) Cis-Trans System**

If same groups are at same side then cis and if same groups are at different side then trans.

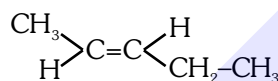


[Same groups, same side]

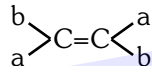
cis

**Ex.**


cis

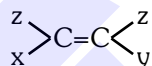
**Ex.**


trans-2-pentene



[Same groups different side]

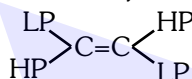
trans



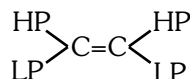
cis


 It does not show Geometrical isomers  
So no cis-trans

**(b) E - Z System :**
**E (Entgegen) :** When high priority groups are at opposite side.

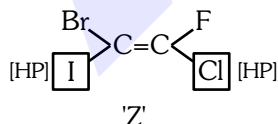
**Z (Zusammen) :** When high priority groups are at same side.


'E'

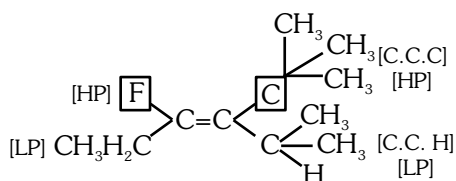


'Z'

HP – High priority and LP – Low priority

**Priority Rules [CIP Sequence Rule] :**
**Rule I :** Priority is proportional to atomic number of atom which is directly attached to  $sp^2$  carbon.


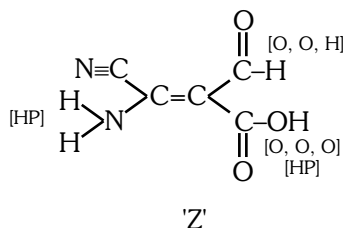
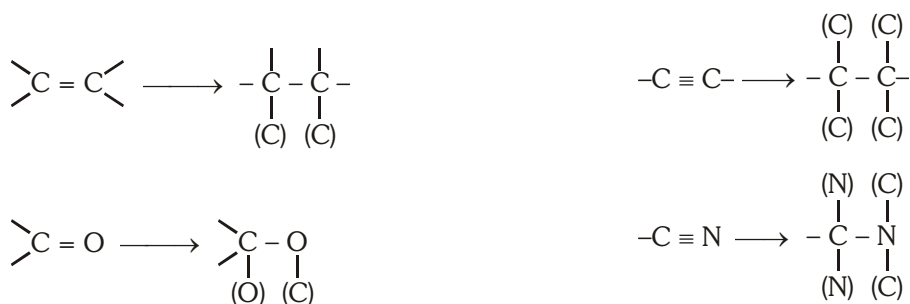
'Z'

**Rule II :** If rule-I is failed then consider the atomic number of next atom and so on.


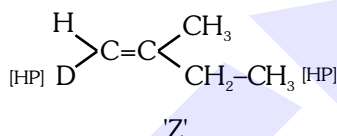
'Z'



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

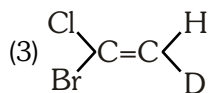
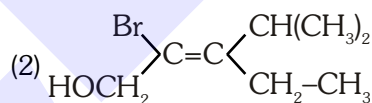
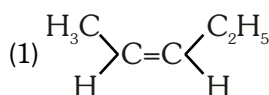


**Rule IV :** If isotopes are present then consider atomic weight.



### BEGINNER'S BOX-2

1. Which of the following has Z-configuration :

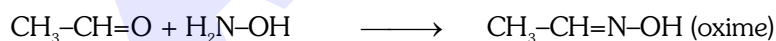


(4) All the above

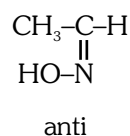
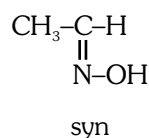
SR0013

### GEOMETRICAL ISOMERS IN OXIMES [ $>\text{C} = \text{N}-\text{OH}$ ] :

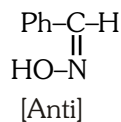
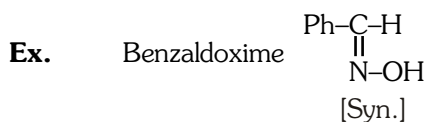
- Oximes show G. I. due to restricted rotation about double bond.
- Only those oximes show Geometrical isomerism in which  $\text{sp}^2$  carbon have two different groups.

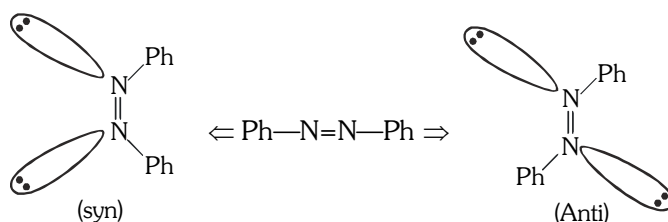


**Ex.** Acetaldoximes has two Geometrical isomers –

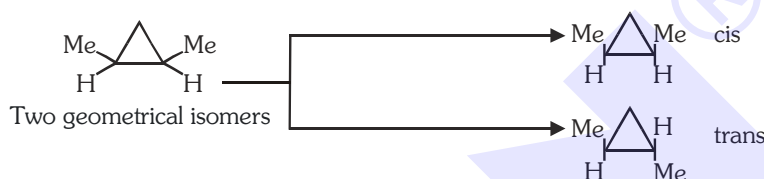


When H and OH are on the same side. When H and OH are on the opposite side



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


**GEOMETRICAL ISOMERS IN CYCLOALKANES :** Cycloalkanes show Geometrical isomerism due to restricted rotation about single bond. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.


**NUMBER OF GEOMETRICAL ISOMERS IN POLYENES :**


(a) If  $\text{R}_1 \neq \text{R}_2$  then number of Geometrical isomers =  $2^n$

[n = number of double bonds which show G.I.]

**Ex.**  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{CH}_3$

As  $n = 3$ , number of Geometrical isomers =  $2^3 = 8$

(b) If  $\text{R}_1 = \text{R}_2$  then number of Geometrical isomers =  $2^{n-1} + 2^{p-1}$

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

**Ex.**  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$  [n = 3]

Number of Geometrical isomers =  $2^2 + 2^1$

=  $4 + 2 = 6$

**BEGINNER'S BOX-3**

1. Which of the following shows Geometrical isomerism –

(a)  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{N}-\text{OH}$

(b)  $\text{H}_2\text{C}=\text{N}-\text{OH}$

(c)  $\text{CH}_3-\text{C}-\text{CH}_3$   
 $\parallel$   
 $\text{N}-\text{OH}$

(d)  $\text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3$   
 $\parallel$   
 $\text{N}-\text{OH}$

(1) a, c

(2) c, d

(3) a, d

(4) b, c

2. Which of the following show Geometrical isomerism –

(1) 1,1-Diphenyl-1-butene

(2) 1,1-Diphenyl-2-butene

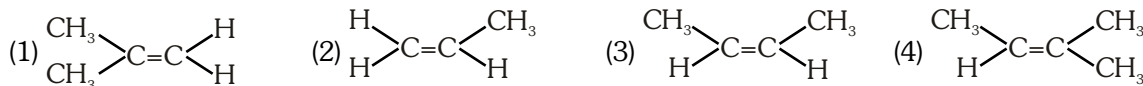
(3) 2,3-Dimethyl-2-butene

(4) 3-Phenyl-1-butene

3. The isomerism shown by Benzaldoxime  $\left[ \text{C}_6\text{H}_5\text{CH}=\text{N}-\text{OH} \right]$  is :-  
 (1) Optical (2) Geometrical (3) Metamerism (4) All of these

SR0012

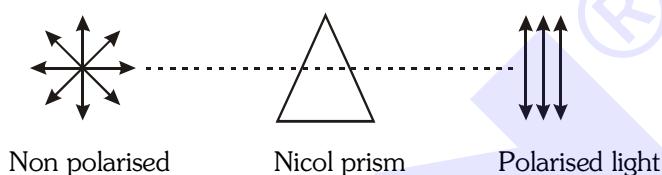
4. Which can show 'Geometrical isomerism' :-



SR0016

## 2.2.2 OPTICAL ISOMERISM :

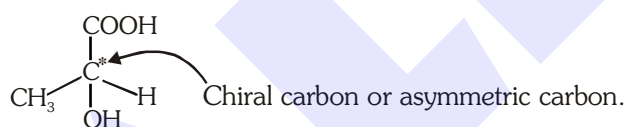
**Optical isomers :** Two or more than two compound have same molecular formula, same structural formula but different behaviour towards PPL (plane polarised light).



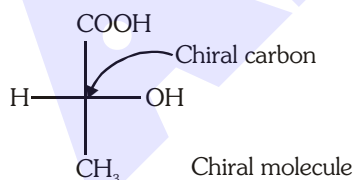
**Optical activity :** Tendency to rotate plane of PPL in a particular direction. If a compound rotates plane of PPL in clockwise direction then it will be dexterorotatory or  $d$  or  $(+)$  and if a compound rotates plane of PPL in anticlockwise direction then it will be levorotatory or  $\ell$  or  $(-)$ .



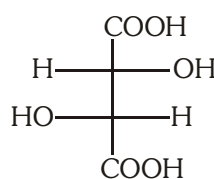
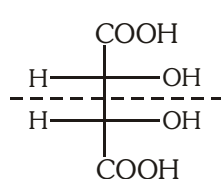
**Chiral carbon :** Carbon which is bonded to four different atoms or groups.



**Chiral molecule :** (i) A molecule having only one chiral centre then it will be always Chiral.



(ii) A molecule having atleast two chiral carbons and no symmetry then it will be chiral molecule.



**Essential and sufficient condition for optical activity is :**

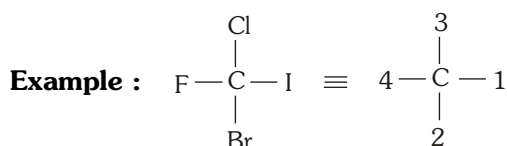
"Molecule should be **chiral**"  
 or  
 "Molecule should be **unsymmetrical**"  
 or  
 "**Nonsuperimposable** mirror images"

**Absolute Configuration (R, S configuration) :**

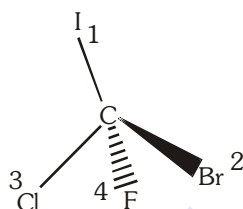
The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed as **absolute configuration**.

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

- Each group attached to stereocentre is assigned a priority on the basis of CIP sequence rule.

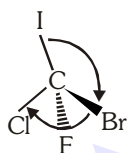


- After assigning priorities, the least priority group is written at remotest valency (going away).



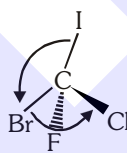
Note that priority order is :  $\text{I} > \text{Br} > \text{Cl} > \text{F}$

- ◆ Now view groups attached with chiral carbon in priority sequence  $1 \rightarrow 2 \rightarrow 3$ . If it gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration. For example.



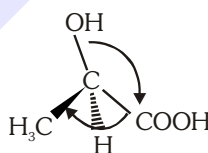
**R-configuration**

(clockwise from top priority)



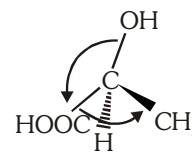
**S-configuration**

(Anti clockwise from top priority)



**R-configuration**

(clockwise from top priority)



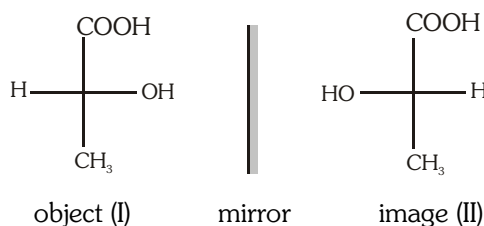
**S-configuration**

(Anti clockwise from top priority)

**Enantiomers :**

Stereoisomers which are mirror images to each other and not superimpose to each other.

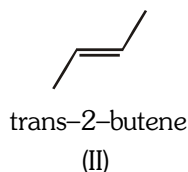
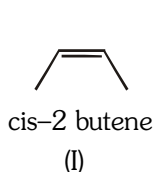
Nonsuperimposable mirror images are called as enantiomers.



I and II are nonsuperimposable mirror images, so I and II are enantiomers.

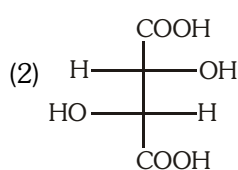
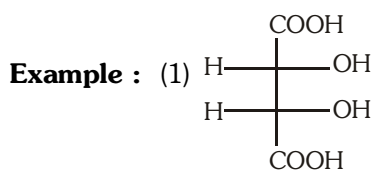
- (i) Enantiomers have chiral structures.  
 (ii) Enantiomers are optically active substances. They rotate the plane polarized light in opposite directions but to the equal extent.

**Diastereomers** : Stereoisomers which are not mirror images of each others.



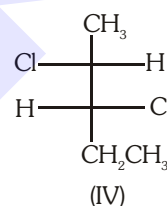
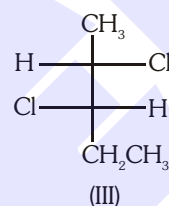
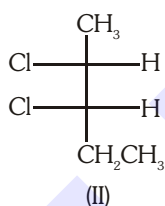
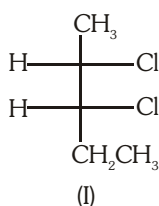
I and II are not mirror images, so I and II are diastereomers.

### EXAMPLES OF OPTICAL ISOMERISM



(1) and (2) are diastereomers.

**Example :**



I, II = Enantiomers,

I, III = Diastereomers,

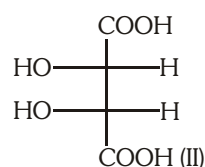
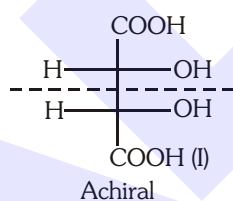
II, III = Diastereomers,

III, IV = Enantiomers

II, IV = Diastereomers

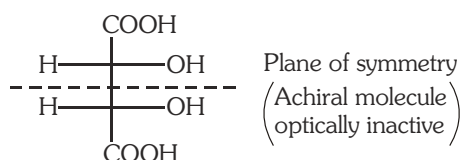
I, IV = Diastereomers

**Example :**

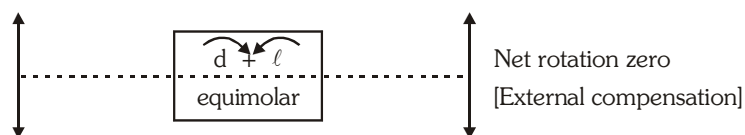


I and II are identical

**Meso compounds** : Compounds having atleast two chiral carbons and plane of symmetry/cos/symmetry is called meso compounds. It is optically inactive due to internal compensation.



**Racemic mixture** : Equimolar mixture of d and l enantiomers is called as racemic mixture. (dℓ or ±).



"Racemic mixture is optically inactive due to external compensation.

**BEGINNER'S BOX-4**

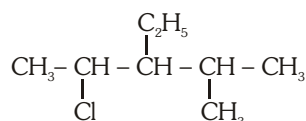
1. Which of the following molecule is chiral :-

- (1) Isobutane                      (2) Neopentane                      (3) Sec. butylchloride                      (4) All

2. Which of the following molecule has chiral carbon :-



3. How many chiral carbon atoms are present in following molecule :-

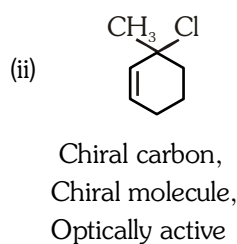
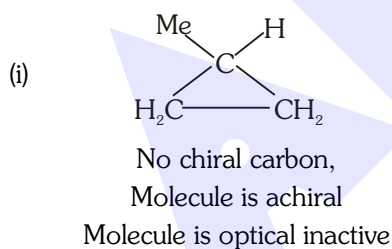


- (1) 1                      (2) 2                      (3) 3                      (4) 4

**Number of stereoisomers :**

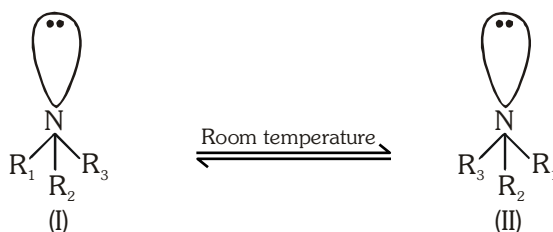
S.N.	Nature of compounds	No. of optically active isomers (a)	No. of meso compounds (m)	Total no. of Stereoisomer (a + m)
1	Compounds having dissimilar ends	$2^n$ (n = No. of chiral centre)	0	$(2^n + 0)$
2	Compounds having similar ends with even chiral centres	$2^{n-1}$	$2^{\frac{n}{2}-1}$	$(2^{n-1} + 2^{\frac{n}{2}-1})$
3	Compounds having similar ends with odd chiral centres	$2^{n-1} - 2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$	$2^{n-1}$

**Optical Isomerism in cyclic compounds :**



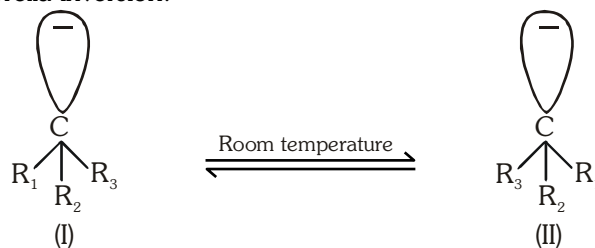
**Special Point :**

1. Chiral nitrogen containing/tertiary/open chain amine shows optical isomerism  
Reason :- Rapid umbrella inversion.



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

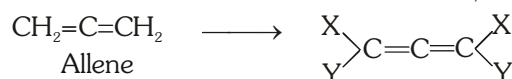
2. Chiral C containing carbanion shows optical isomerism.  
Reason :- Rapid umbrella inversion.



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

**Note :-** Only 2<sup>nd</sup> period elements show flipping.

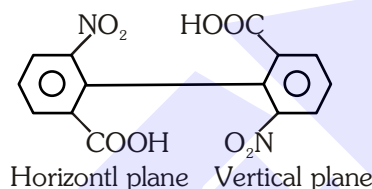
3. Substituted Allenes do not have chiral carbons but molecule is chiral, so show optical isomerism.



(No chiral C but molecule is chiral)

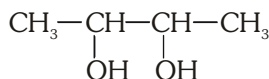
Only those substituted allenes will be optically active in which "each sp<sup>2</sup> C have different atoms or group".

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



### BEGINNER'S BOX-5

1. Calculate total number of optical isomers in following compound :-



- (1) 4                      (2) 3                      (3) 2                      (4) 1

2. The simplest alkanol exhibiting optical activity is

- (1) n-butyl alcohol      (2) Isobutyl alcohol      (3) s-butyl alcohol      (4) t-butyl alcohol

SR0018

3. Which is optically active molecule :-

- (1)  $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{OH}$       (2)  $\text{CH}_3-\text{CH}(\text{OH})-\text{C}_2\text{H}_5$       (3)  $\text{C}_6\text{H}_5-\text{CH}(\text{H})-\text{OH}$       (4)  $\text{C}_6\text{H}_5-\text{CH}(\text{CH}_3)-\text{CH}_3$

SR0020

4. The following two compounds are  $\begin{array}{c} \text{Cl} \\ | \\ \text{H}-\text{C}-\text{F} \\ | \\ \text{Br} \end{array}$  and  $\begin{array}{c} \text{Br} \\ | \\ \text{F}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$

- (1) Enantiomers      (2) Diastereomers      (3) Identical      (4) Epimers

SR0024

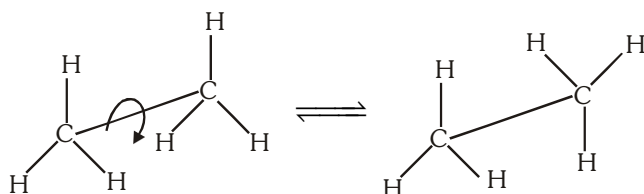
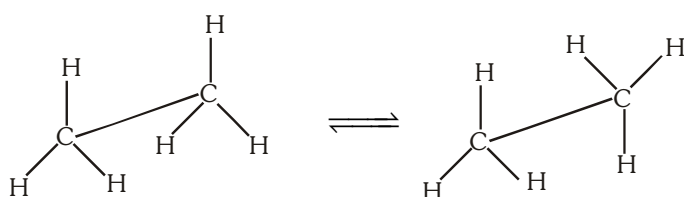
5. Which of the following has 'S' configuration :-

- (1)  $\begin{array}{c} \text{Et} \\ | \\ \text{H}-\text{C}-\text{F} \\ | \\ \text{Me} \end{array}$       (2)  $\begin{array}{c} \text{F} \\ | \\ \text{H}_3\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{CH}_2\text{CH}_3 \end{array}$       (3)  $\begin{array}{c} \text{H} \\ | \\ \text{H}_3\text{C}-\text{C}-\text{F} \\ | \quad | \\ \text{CH}_2\text{CH}_3 \end{array}$       (4)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{F}-\text{C}-\text{H} \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$

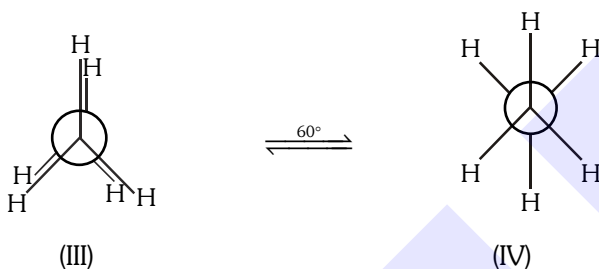


**(B) Conformational Isomerism**

The different arrangement of atoms in space that result from the free rotation around single bond, are called conformations. The phenomenon is called conformational isomerism


**Conformations of ethane [ $\text{CH}_3\text{—CH}_3$ ] :**


(Saw horse projection)

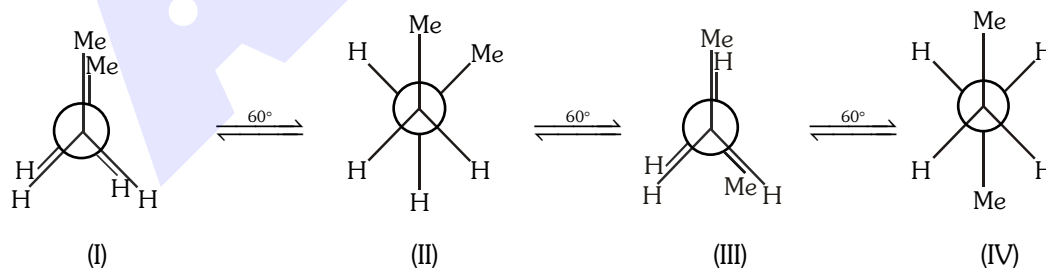
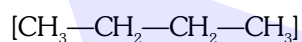


(Newman projection)

Stability order : Staggered > Eclipsed

**Dihedral Angle :** Dihedral angle in eclipsed form of ethane is  $0^\circ$ .

Dihedral angle in staggered form of ethane is  $60^\circ$ .

**Conformation of Butane**


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

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

**Stability order :** IV > II > III > I

## BEGINNER'S BOX-6

1. Rotational angle require to get maximum stable conformer from minimum stable conformer in n-butane is :  
 (1)  $360^\circ$  (2)  $180^\circ$  (3)  $120^\circ$  (4)  $240^\circ$
2. Most stable conformation of butane is :-  
 (1) Partial eclipsed (2) Full eclipsed (3) Staggered (4) Gauche
3. Which of the following is not a pair of isomers :  
 (1) Propyne and Cyclopropene (2) Propyne and Propadiene  
 (3) Propene and Cyclopropene (4) 1-Propanol and Methoxy ethane
4. What is dihedral angle in staggered form of ethane :-  
 (1)  $30^\circ$  (2)  $45^\circ$  (3)  $75^\circ$  (4)  $60^\circ$

SR0034

## ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	
	Ans.	1	3	3	3	1	2	4	3	

BEGINNER'S BOX-2	Que.	1	
	Ans.	4	

BEGINNER'S BOX-3	Que.	1	2	3	4	
	Ans.	3	2	2	3	

BEGINNER'S BOX-4	Que.	1	2	3	
	Ans.	3	4	2	

BEGINNER'S BOX-5	Que.	1	2	3	4	5	
	Ans.	2	3	2	1	3	

BEGINNER'S BOX-6	Que.	1	2	3	4	
	Ans.	2	3	3	4	