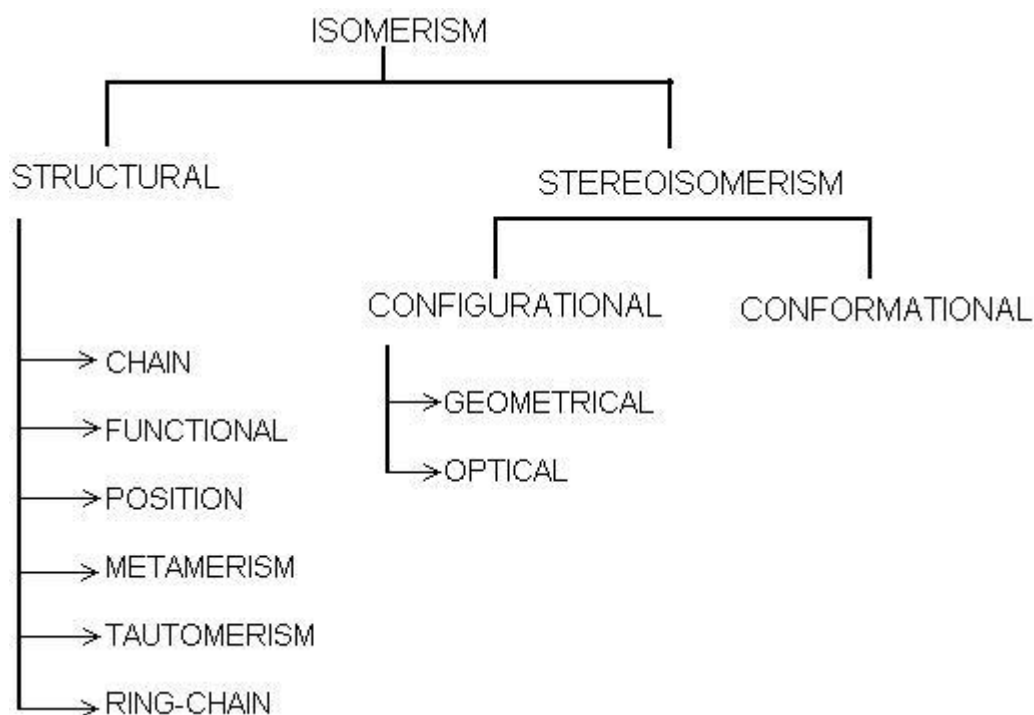


## ISOMERISM

- The phenomenon of existence of two or more compounds with same molecular formula but different properties ( physical, chemical or both) is known as isomerism and the compound exhibiting this phenomenon are called isomers
- The term was used by Berzelius
- Isomerism are of two types



### STRUCTURAL ISOMERISM:

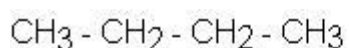
- It is due to the difference in arrangement of atoms or groups within the molecule, without any reference to space.
- Structural isomers are compound having same molecular formula but different structural formula.
- These are of following types

#### (a) CHAIN ISOMERISM

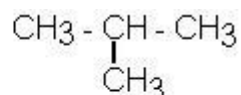
When the isomers have similar molecular formula but differ in nature of carbon chain are called chain isomers and phenomenon is known as chain isomerism.

Example:

$C_4H_{10}$  (Butane) exists in two forms

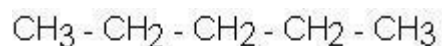


butane ( n-butane)

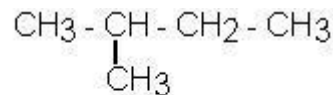


2-methylpropane  
(isobutane)

Pentane ( $\text{C}_5\text{H}_{12}$ ) exists in three form



pentane ( n-pentane)

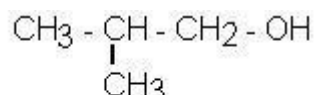


2-methylbutane  
(isobutane)

$\text{C}_4\text{H}_{10}\text{O}$

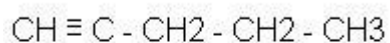


Butan-1-ol

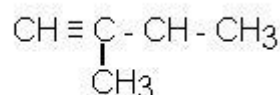


2-methylpropan-1-ol

$\text{C}_5\text{H}_8$



pent-1-yne



3-methylbut-1-yne

### (b) FUNCTIONAL ISOMERISM

Compounds having same molecular formula but different functional group are known as functional isomers and the phenomenon is functional isomerism.

Examples

- Alcohol and ether (  $\text{C}_n\text{H}_{2n+2}\text{O}$  )

$\text{C}_3\text{H}_8\text{O}$

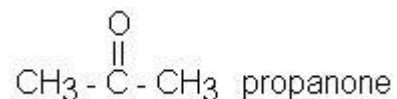
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$  : n-propyl alcohol

$\text{C}_2\text{H}_5 - \text{O} - \text{CH}_3$  : ethyl methyl ether

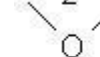
- Aldehydes, ketones, ethers etc. (  $\text{C}_n\text{H}_{2n}\text{O}$  )

$\text{C}_3\text{H}_6\text{O}$

$\text{CH}_3 - \text{CH}_2 - \text{CHO}$  : propanal

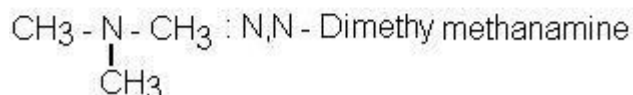
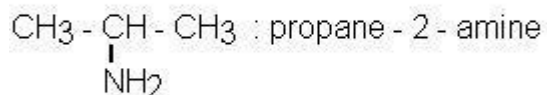
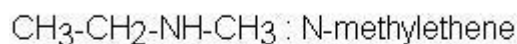
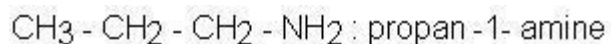


$\text{CH}_2 - \text{CH} - \text{CH}_3$  : 1,2-epoxy propane

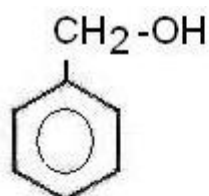


$\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$  : prop-2-en-1-ol  
(allyl alcohol)

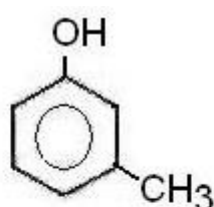
- Amines ( Primary, secondary, tertiary)



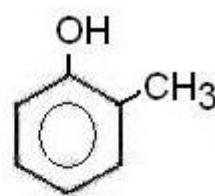
- Alcohol, phenol and ethers



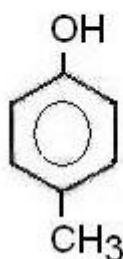
Benzyl alcohol



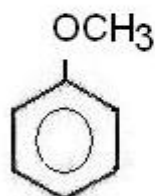
m- cresol



o - cresol



p- cresol



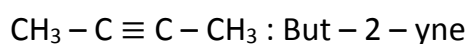
anisole

### (c) POSITION ISOMERISM

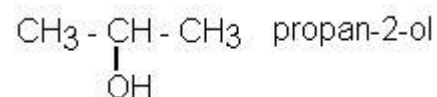
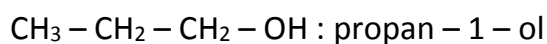
It is due to the difference in the positions occupied by the particular atom or group ( substituent) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.

Example:

- $C_4H_6$

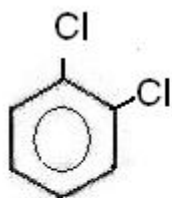


- $C_3H_8O$

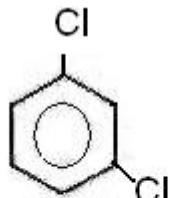


- $C_4H_8$   
 $CH_3 - CH_2 - CH = CH_2$  : But-1-ene  
 $CH_3 - CH = CH - CH_3$  : But - 2 - ene

- $C_6H_4Cl_2$



o-dichlorobenzene



m-dichlorobenzene



p-dichlorobenzene

Aldehydes, carboxylic acid and their derivatives do not exhibit position isomerism

#### (d) Metamerism

Metamers are the isomers which have same molecular formula but differ in nature of alkyl group, groups attached to the either side of the same functional group. This isomerism is shown by ethers, ketones, esters, secondary amines.

Examples

- $C_4H_{10}O$   
 $C_2H_5 - O - C_2H_5$  : Diethyl ether  
 $C_3H_7 - O - CH_3$  : Methyl propyl ether

- $C_5H_{10}O$   
 $C_2H_5 - \overset{O}{\parallel}C - C_2H_5$  : Diethyl ketone



- $C_4H_{10}S$   
 $C_2H_5 - S - C_2H_5$  : Diethyl thio ether  
 $C_3H_7 - S - CH_3$  : Methyl propyl ketone

- $C_4H_{11}N$   
 $C_2H_5 - NH - C_2H_5$  : Diethyl amine  
 $C_3H_7 - NH - CH_3$  : Methyl propyl amine

#### (e) TAUTOMERISM

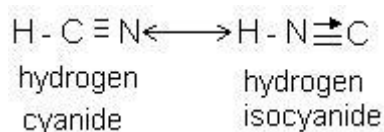
( Greek word : tauto = same ; meros = parts)

It was used by Laar in 1885

Tautomerism may be defined as the phenomenon in which a single compounds exists in two readily inter convertible structures that differ markedly in the relative position of at least one atomic nucleus generally hydrogen. The two different structures are known as tautomers of each other. There are two types of tautomerism

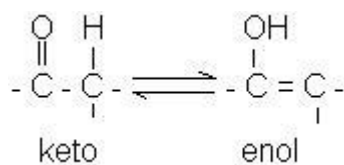
(i) Dyad system

If two hydrogen atom oscillates between two polyvalent atoms, linked together, then system is called dyad system.



(ii) Triad system

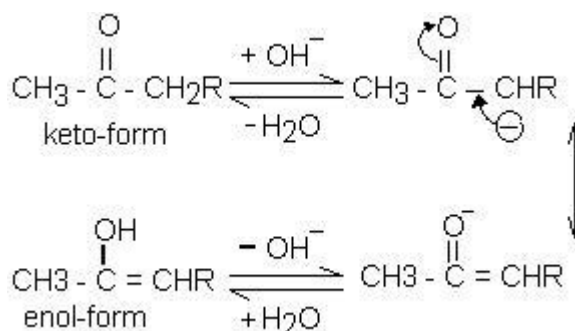
- If the hydrogen atom travels from first to third in a chain, the system is triad
- The most important type of triad system is keto-enol tautomerism keto-enol system



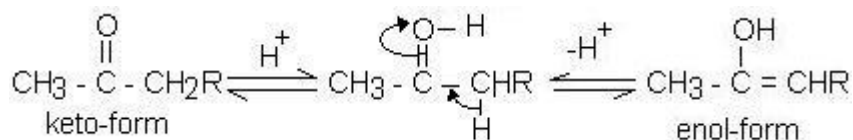
The keto form is more stable

### Mechanism of tautomerism

(i) Base catalysed tautomerism

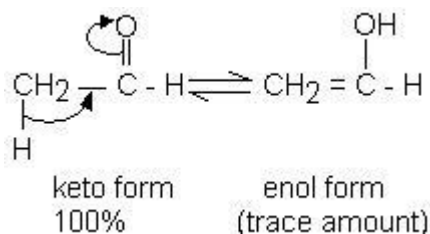


(ii) Acid catalysed tautomerism

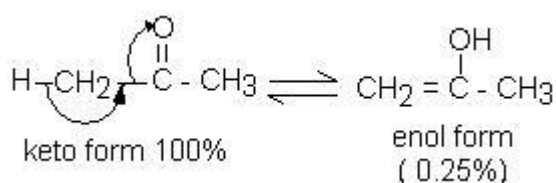


## Examples of keto-enol system

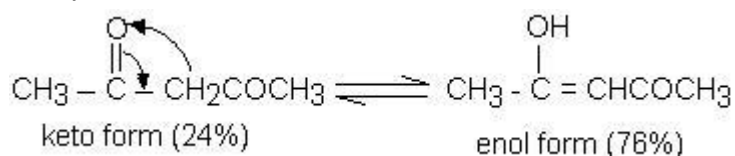
- Acetaldehyde



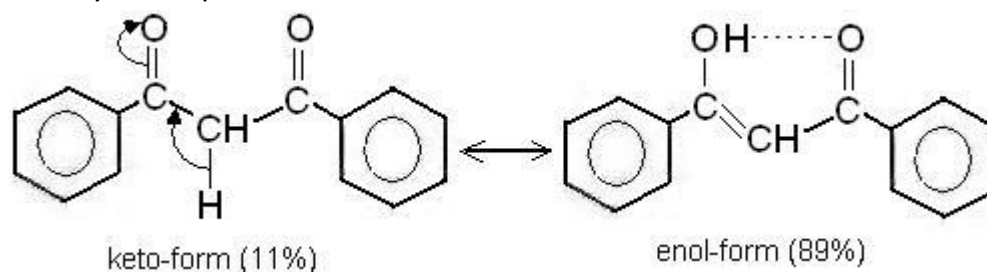
- Acetone



- Acetyl acetone



- Benzoyl acetophenone



## Enolisation

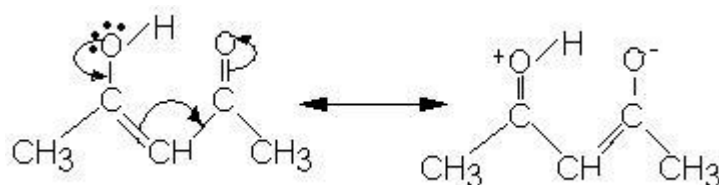
- The conversion of keto form into enol form is known as enolisation.
- The percentage of enol form has been found to increase in the order:  
Simple aldehydes and ketone <  $\beta$  keto ester <  $\beta$  diketones having phenyl group < phenols
- Enolisation is in order  
 $\text{CH}_3\text{COCH}_3 < \text{CH}_3\text{COCOC}_2\text{H}_5 < \text{C}_6\text{H}_5\text{COCH}_2\text{COC}_2\text{H}_5 < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{COCH}_3 < \text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3 < \text{phenoxide ion} < \text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$

## Composition of tautomeric mixture

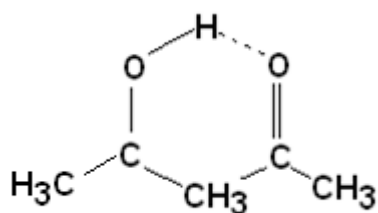
The relative amount of keto and enol form of tautomeric mixture depends upon their relative stabilities. In simple monocarbonyl compounds like acetaldehyde, acetone etc, the amount of enolic form is negligibly small because of comparatively lower stability.

However if enolic form is stabilized by intermolecular bonding, the amount of enolic form becomes higher. In 1,3-dicarbonyl compounds also called  $\beta$ -dicarbonyl compounds can be attributed to the following reasons.

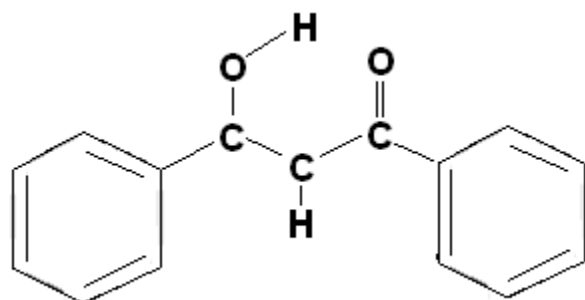
- i) Stability gained through resonance stabilization of conjugated double bond  
eg. Acetylacetone



- ii) H-Bonding in enol form results in the formation of cyclic structure. Eg. Acetyl

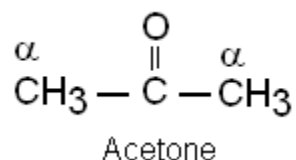
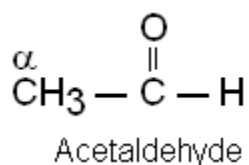


- iii) Stabilisation of enolic form increases if double bond of enol form is in conjugation with electron cloud of benzene ring. Eg. Benzoylacetophenone.



## Essential conditions for tautomerism.

In order to exhibit keto-anol tautomerism, an aldehyde or ketone or ester must possess at least, one  $\alpha$ -hydrogen atom. Which can show 1,3 - migration. Example



Difference between tautomerism and resonance

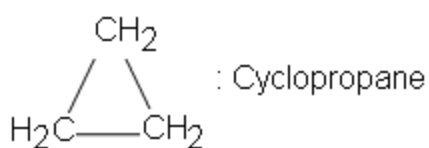
- i) Tautomers are definite compounds and can be separated and characterized by suitable methods, but resonating structure cannot be separated as they are imaginary structures of same compounds
- ii) Two tautomers have different functional groups, but the various resonating structures have the same functional group.
- iii) Tautomerism has no effect on bond length, while resonance is accompanied by an increase in bond length of double bond and decrease of a single bond length.
- iv) Tautomerism has no contribution in stabilizing the molecule but resonance give rise to extra stability to molecule.
- v) Tautomerism may occur in planar or non-planar molecules while resonance occurs only in planar molecules.

(f) RING-CHAIN ISOMERISM

In this type of isomerism compounds are having same molecular formula but differ in modes of linking of carbon atoms, i.e. it may either be open chain or closed chain structures.

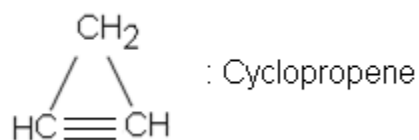
Eg. 1  $\text{C}_3\text{H}_6$

$\text{CH}_3 - \text{CH} = \text{CH}_2$  : Propene



Eg2  $\text{C}_3\text{H}_4$

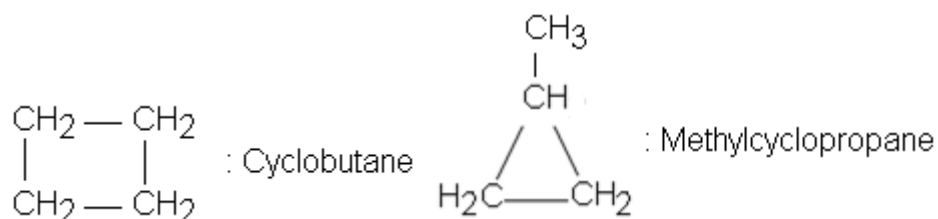
$\text{CH}_3 - \text{C} \equiv \text{CH}$  : Propyne



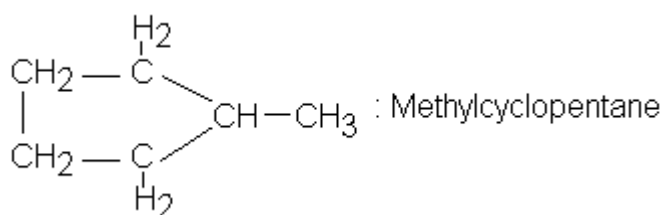
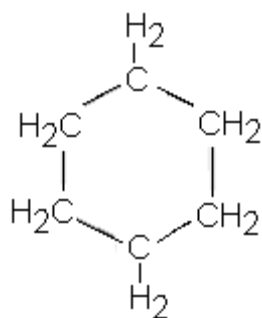
Eg 3  $\text{C}_4\text{H}_8$

$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$  : But -1 - ene





Eg 4

 $C_6H_{12}$  $CH_3 - CH_2 - CH_2 - CH_2 - CH = CH_2$  : hex-1-ene

DOUBLE BOND EQUIVALENT ( D.B.E )

Number of structural isomers can be predicted using double bond equivalents.

Double bond equivalent gives the number of double bonds (  $\pi$  - bonds ) or rings in compounds

$$D.B.E = \sum \frac{n(V-2)}{2} + 1$$

N = number of different kinds of atoms present in molecules

V = valency of each atom.

Eg 1  $C_4H_6$ 

$$D.B.E = \frac{4(4-2) + 6(1-2)}{2} + 1$$

$$D.B.E = 2$$

Thus the compound may contain

- i) Two double bond or a triple bond
- ii) One ring and one double bond
- iii) Two rings

For the compounds of general formula  $C_aH_bN_cO_d$ 

$$D.B.E = a + 1 - \frac{(b-c)}{2}$$

# ISOMERISM

Univalent atoms such as halogen atom may be replaced by one hydrogen atom and bivalent atom such as oxygen may be ignored example

Eg, Benzene (  $C_6H_6$  )

$$D.B.E = 6 + 1 - \frac{6}{2} = 4$$

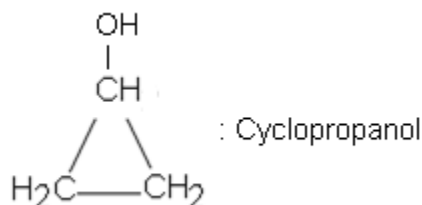
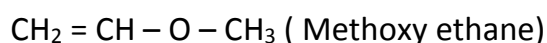
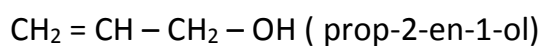
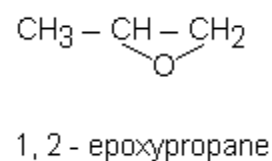
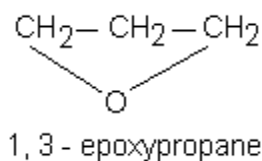
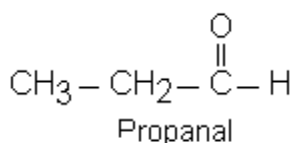
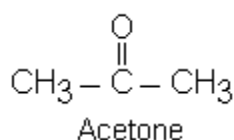
4 D.B.E. in benzene corresponds to 3 double bond and one ring

$C_3H_6O$

$$D.B.E = 3 + 1 - \frac{6}{2} = 1$$

i.e. Molecule may contain double bond (  $C=C$  ) or (  $C=O$  ) or a ring

It's possible isomers are



## STEREOISOMERISM

Compounds have same molecular and structural formulae but different spatial arrangement of atoms or groups

There are two types of stereoisomerism:

- a) Conformational isomerism.
  - b) Configurational isomerism.
- a) CONFORMATIONAL ISOMERISM

The different arrangements of atoms in space that result from the free rotation of groups about C – C bond axis are called conformation or conformational isomers or rotational isomers and the phenomenon as conformational isomerism

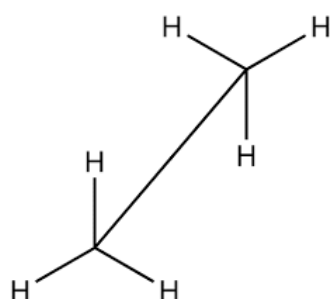
This type of isomerism is found in alkanes, cycloalkanes and their derivatives.

#### Representation of conformers

##### (i) Sawhorse formula

In this representation, molecule is viewed slightly from above and from right side of one carbon atom

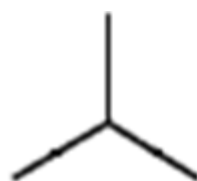
Carbon – carbon bond is drawn diagonally and slightly elongated and remaining six bonds attached to each carbon atom are represented as straight line



##### (ii) Newman projection formula

In this representation, the molecule is viewed along the carbon – carbon single bond

The front carbon atom is represented by a point and groups attached to it are represented by equally spaced radii. Whereas rear carbon atom is represented by circle and groups attached to it are represented by three equally spaced radial extensions



Front carbon



Rear carbon

#### Conformations of ethane ( $\text{CH}_3 - \text{CH}_3$ )

Two extreme conformation are important, staggered and eclipsed. There can be number of arrangements between staggered and eclipsed forms and these arrangements are called skew forms.

##### (i) Eclipsed conformation

In this conformation rotation about C – C single bond is such that hydrogen atoms of front carbon atom completely cover or eclipse the hydrogen atom of rear carbon atom.

In this conformation, hydrogen atoms of two carbon atoms are at minimum distance which makes conformation unstable

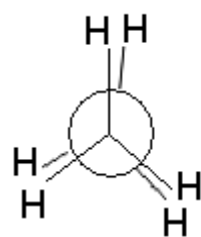
(ii) Staggered conformation

In this confirmation rotation about C – C bond is by an angle of  $60^\circ$  so that hydrogen atoms of two carbon atoms are at maximum distance from each other making it stable.

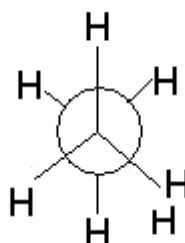
In staggered conformation, all the six hydrogen atoms are visible

(iii) Skew conformation

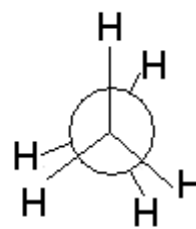
In this conformations, hydrogen atoms are closer than in staggered but way than in eclipsed conformation



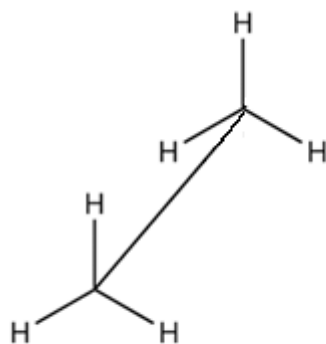
Eclipsed



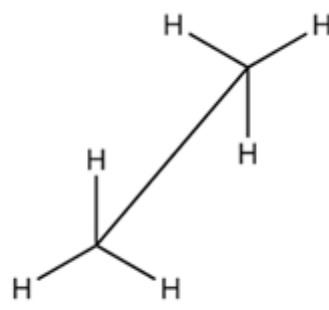
Staggered



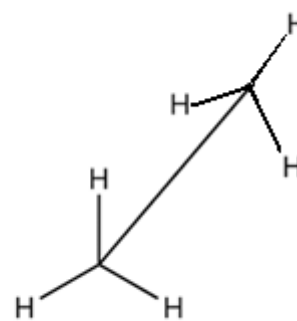
skew



Eclipsed



Staggered



Skew

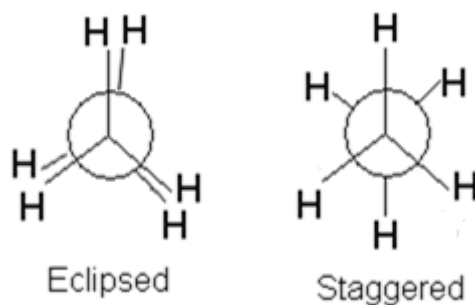
The relative stabilities of the various conformation of ethane are in the following order

Staggered > Skew > eclipsed

Ethane is mostly in staggered form.

### Conformations of propane

Since it has two C – C single bonds, rotation about any of C-C bond give rise to two extreme conformation like that of ethane



Propane molecules exist mostly in the more stable staggered conformation.

### Conformation of Butane

n-Butane may be considered as derivative of ethane whose one hydrogen of each carbon atom is replaced by a methyl group

#### 1) Eclipsed conformations of n-butane

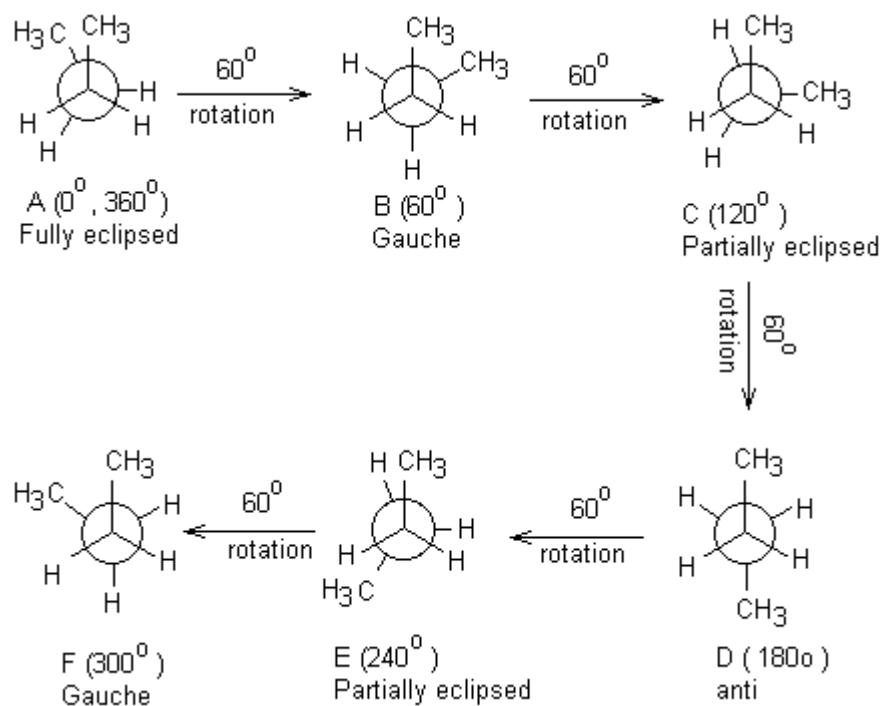
There are three eclipsed conformations of n-butane. In the fully eclipsed form, a methyl group is eclipsed by another methyl group, while in partially eclipsed form, a methyl group is eclipsed by hydrogen.

Fully eclipsed feel more repulsive force than partially eclipsed. Thus fully eclipsed is less stable than partially eclipsed

#### 2) Staggered conformations of n-Butane

Three staggered conformations are possible; anti and two gauche.

In anti-conformation, the methyl groups are  $180^\circ$  apart and hence confirmations is most stable. In gauche conformations, the two methyl group are only  $60^\circ$  apart and hence less stable than anti-form



The order of stability of n-Butane conformations is

Anti > gauche = gauche > partially eclipsed = partially eclipsed > fully eclipsed

#### Factors affecting stability of conformations

(i) Torsional strain

Torsional strain arise due to repulsive interaction between bonds on adjacent atoms

As the repulsive interaction between electronic cloud increases, torsional strain increases and thus stability decreases.

(ii) Steric strain

Steric strain arises due to crowding around central atom more the bulky groups present around the central more will be steric strain and thus less will be stability.

For example, gauche conformation of n-Butane is less stable than anti-conformation

(iii) Dipole – dipole interactions

Molecule in which polar bonds are attached in central atom, stability of greatly affected by dipole-dipole interactions.

Stronger the dipole – dipole interaction lesser will be the stability

(iv) Angle strain

Any deviation from the bond angle suggested by the state of hybridization bring angle strain in the molecule. It mainly influences stability of cycloalkane.

## Baeyer's strain theory

In year 1885, Baeyer proposed a theory of angle strain for cycloalkanes and the main postulates of this theory are

- (i) Baeyer assumed the planer structure for all cycloalkanes. Thus the deviation from the tetrahedral bond angle varies with the size of the ring.
- (ii) Deviation from regular tetrahedral angle introduces strain in the ring which brings unstability. Larger the deviation, greater will be the strain and thus lesser will be its stability.

Amount of deviation (d) = (  $109^{\circ}28'$  – Bond angle of the ring)

In cyclopropane =  $109^{\circ}28' - 60^{\circ} = 49.5^{\circ}$

In cyclobutane =  $109^{\circ}28' - 90^{\circ} = 19^{\circ}28'$

In cyclopentane =  $109^{\circ}28' - 108^{\circ} = 1^{\circ}28'$

Thus relative order of their stability is

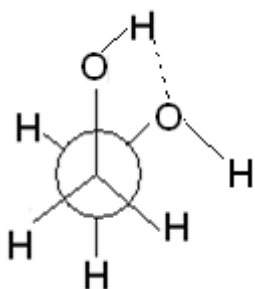
Cyclopentane > cyclobutane > cyclopropane

In cyclohexane =  $109^{\circ}28' - 120^{\circ} = 10.5^{\circ}$

Cyclohexane is free from angle strain and hence is quite stable and unreactive.

Therefore, cyclohexane adopts a non-planar structure.

- (v) Intramolecular hydrogen bonding also influences the relative stability of conformations of a molecule

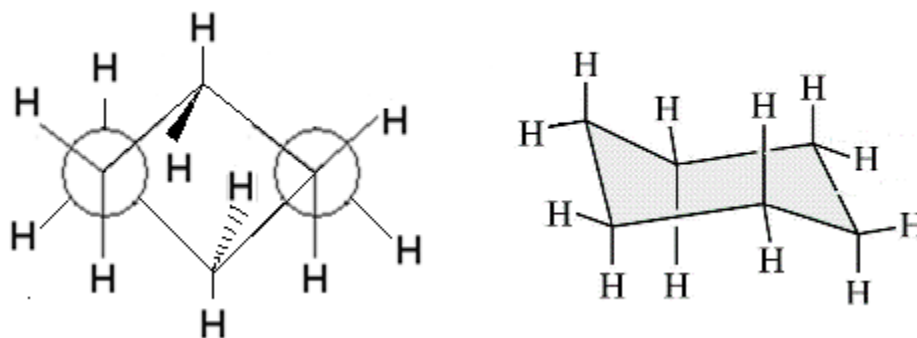


For example in ethylene glycol gauche conformations are more stable than anti form due to intramolecular hydrogen bonding.

### Conformations of cyclohexane

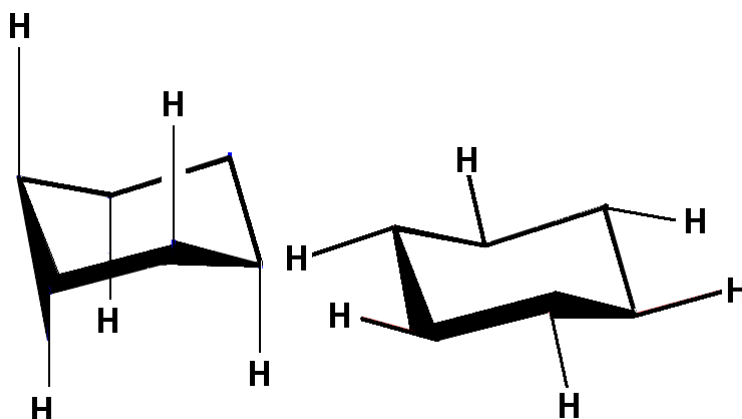
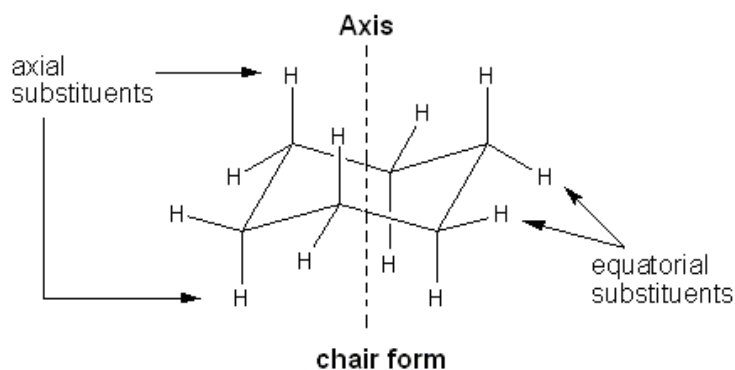
## 1. Chair conformations

It is most stable conformation of cyclohexane as it is free angle and torsional strain as all groups are staggered and bond angles are tetrahedral.



Axial and equatorial bond in cyclohexane

Hydrogen atoms perpendicular to the ring are called axial hydrogen atoms and hydrogen atom lying in the plane of ring are called equatorial hydrogen atom.

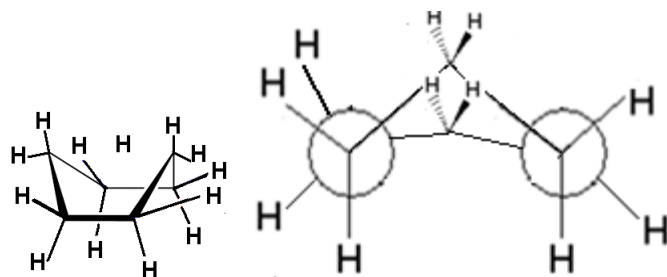


## 2. Boat conformation

If left end of the chair conformation is flipped, keeping rest of the molecule fixed, we get boat conformation of cyclohexane

It is highly unstable conformation

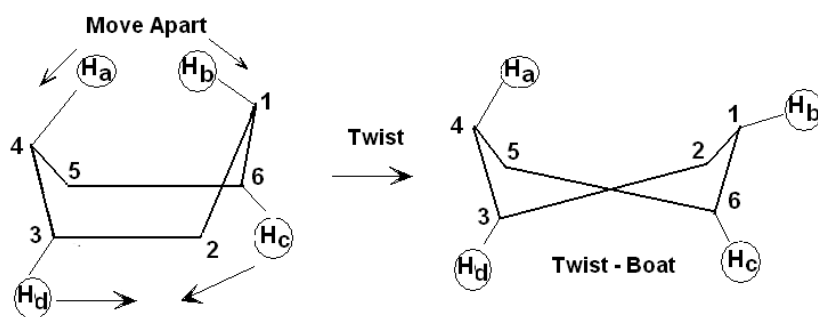




### 3. Twist boat confirmation

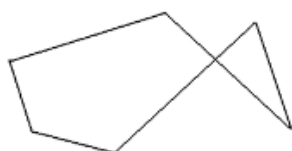
If in the boat conformation of cyclohexane bond along  $C_2 - C_3$  and  $C_5 - C_6$  is twisted in such a way that flagpole hydrogens move away.

Torsional strain in this conformation is less, making it more stable than boat conformation



### 4. Half chair conformation

It transition state conformation chair and twist boat conformation



Order of relative stabilities of various conformations of cyclohexane is :  
chair > twist boat > boat > half chair

## CONFIGURATIONAL ISOMERISM

These are the stereoisomers which differ in spatial arrangement of atoms and thus show different properties.

The isomers cannot be obtained by free rotation around C-C single bond

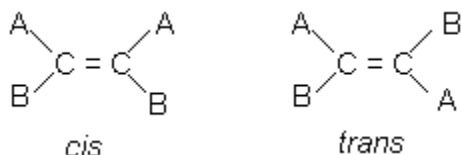
### 1. Geometrical isomerism

Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around rigid framework of double bonds

Geometrical isomerism is generally seen in alkenes ( $>C=C<$ ) and oximes ( $>C=NOH$ )

### Geometrical isomerism in alkene

Isomer in which similar groups or atoms lie on the same side of double bond are called cis-isomer whereas isomers in which similar groups lie on the opposite side of double bond are called trans-isomer.



Necessary conditions for geometrical isomerism

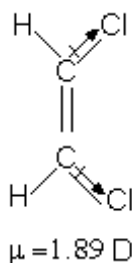
- i) The molecule must have a C - C double bond.
- ii) Two atoms or groups attached to doubly bonded carbon atom must be different.

### Distinction between *cis* and *trans* isomer

#### 1. Dipole moment :

Cis -isomer

In cis isomer, dipole moment of polar groups have additive effect thus have higher dipole moment than corresponding trans isomer



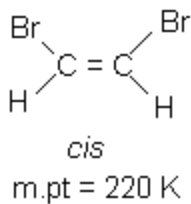
Trans-isomer

In trans isomer, dipole moment of polar groups have opposing effect, thus tends to cancel each other

#### 2. Melting point

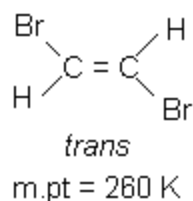
Cis isomer

Cis-isomer has lower melting point because the structure is not symmetrical



Trans isomer

Due to symmetry, trans isomer fits better in crystal lattice, thus has higher lattice energy and hence higher melting point.



## 3. Solubility

Cis isomer

Cis isomer have higher solubility because these are weakly held in lattice

Trans isomer

Trans – isomers have lower solubility because these are tightly held in the lattice

## 4. Density

Cis isomers

Cis – isomers have lower density

Trans isomers

Trans isomer due to higher lattice energy has higher density

## 5. Boiling point

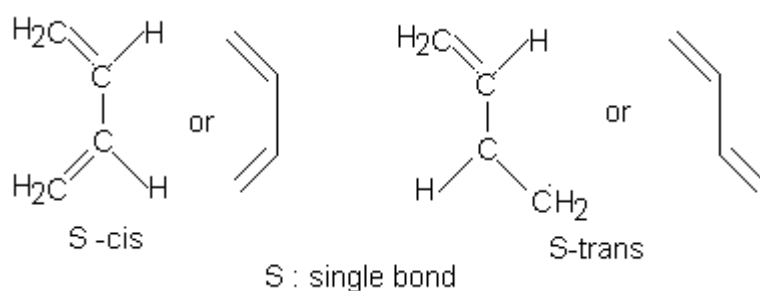
Cis isomer

Cis-isomer have higher boiling point due to dipole-dipole interaction

Trans isomer

Trans isomers have comparatively low boiling point

Cis – trans isomer around single bond



Geometrical isomerism in oximes and azo compounds

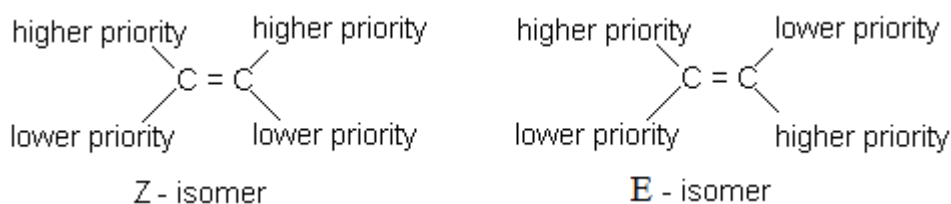
In syn-isomers H atom of doubly bonded carbon and –OH group of doubly bonded nitrogen lie on the same side of double bond

In anti-isomers H atom of doubly bonded carbon and –OH group of doubly bonded nitrogen lie on opposite side of double bond

E – Z NOTATION OF GEOMETRICAL ISOMERISM

This new system of nomenclature of geometrical isomerism was developed by Ingold and Prelog

In this system we assign a priority to the groups attached to double bonded carbon atom. If groups of similar priority lie on the similar side of double bond, the isomer is designated as Z (Zusammen, means together). If groups of similar priority lie on the opposite side of double bond, the isomer is designated as E (Entgegen, means opposite)

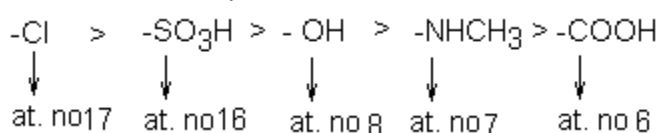


Sequence rules: The following rules are followed for deciding the precedence order of the atoms or groups:

- (i) Higher atomic number atoms get higher priority.
- (ii) Among the isotopes of same element, isotope of higher mass is given higher priority.
- (iii) In the groups, the order of precedence is also decided on the basis of atomic number of first atom of the group.

For example

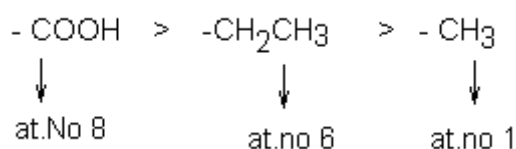
The order of precedence



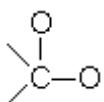
When the order of precedence of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered.

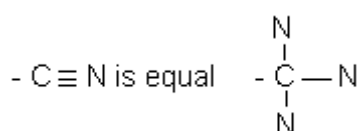
For example

The order of precedence



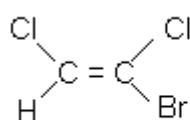
- (iv) A double or triple bonded atom is considered equivalent to two or three such atoms

For example, the group  $>\text{C}=\text{O}$  is equal to  and the group

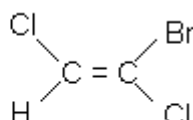


- (v) If one of the position is occupied by lone pair, it is given higher priority over the bonded group.

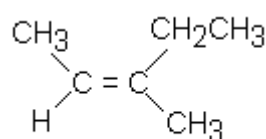
Examples of E-Z isomerism



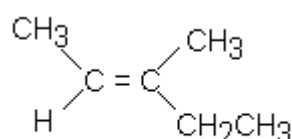
E - isomer



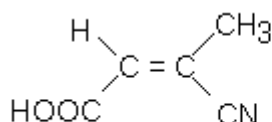
Z-isomer



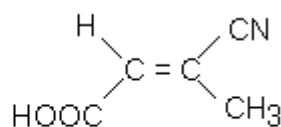
Z-isomer



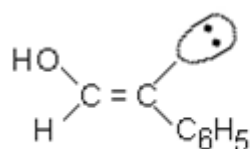
E - isomer



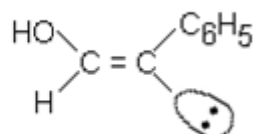
Z-isomer



E - isomer



Z-isomer



E - isomer

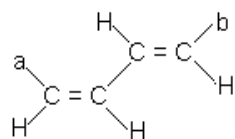
### Number of geometrical isomers

If a compound has more than one double bond, the number of geometrical isomers is  $2^n$ , where n is number of double bond

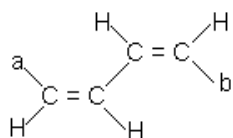
This formula applies only to the molecules in which ends are different. For example,

$\text{CH}_a = \text{CH} - \text{CH} = \text{CH}_b$  occurs in four geometrical isomers

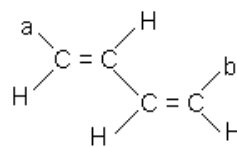
# ISOMERISM



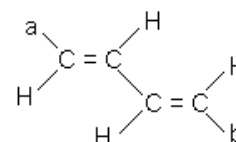
cis-trans



cis - cis



trans - cis



trans - trans

When the ends of polyene are same

- i) When  $n$  is even number of geometrical isomers =  $2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$
- ii) When  $n$  is odd number of geometrical isomers =  $2^{(n-1)} + 2^{\left(\frac{n-1}{2}\right)}$

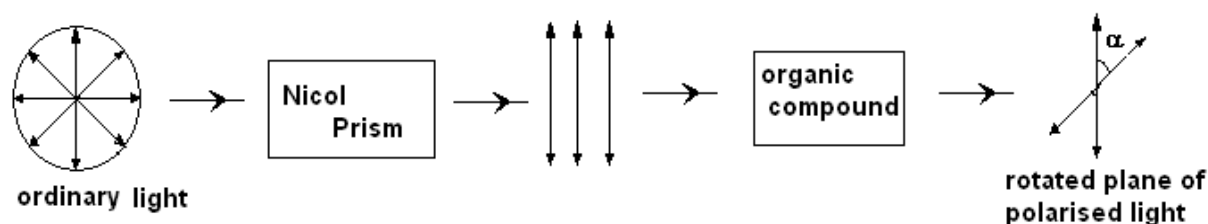
## OPTICAL ISOMERISM

Compounds having similar physical and chemical properties but differing only in the behavior towards polarized light are called optical isomers and this phenomenon is known as optical isomerism

Plane polarized light and optical activity

The beam of light which vibrates only in one plane is called plane polarized light. It can be obtained by passing ordinary light through a Nicol prism which cuts vibrations in all planes except in one.

Sometimes on passing a plane polarized light through solution of certain substances, a change in plane polarized light occurs. Such substances which rotate the plane of plane polarized light are called optically active substances



On the basis of study of optical activity, the various organic compounds were divided into three types.

- i) The optical isomer which rotates the plane polarized light to the right (clockwise) is known as dextro-rotatory isomer or d-form or indicated by +ve sign
- ii) The optical isomer which rotates the plane polarized light to the left (anticlockwise) is known as laevo-rotatory isomer or l-form or indicated by -ve sign

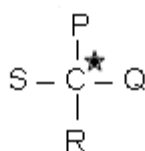
- iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive. This mixture is termed as racemic mixture or fl- form or ( $\pm$ ) mixture

### Enantiomers

An optically active substances may exist in two or more isomeric forms which have same chemical and physical properties but differ in terms of direction of rotation of plane polarized light. Such optical isomers which rotate the plane of polarized light with equal angle but in opposite directions are known as enantiomers and phenomenon is known as enantiomerism.

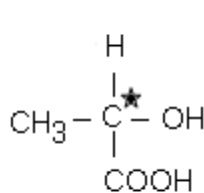
In order to exhibit optical activity an object must be chiral. A carbon atom whose tetra valency is satisfied by four altogether different substituents is called chiral carbon atom or asymmetric carbon atom. A molecule possessing chiral carbon atom and non-superimposable to its own mirror image is said to be chiral and the property is called chirality.

Molecule which is superimposable on its own mirror image is said to achiral

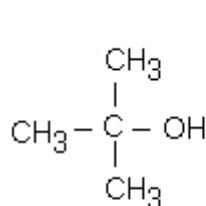
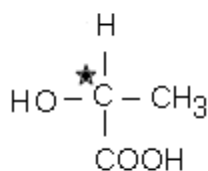


$\text{C}^*$  - Chiral carbon atom

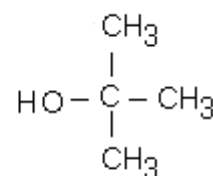
MIRROR



Lactic acid ( chiral molecule)

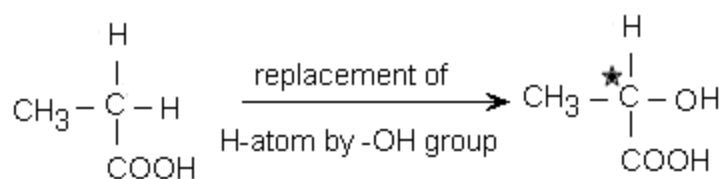


Achiral molecule



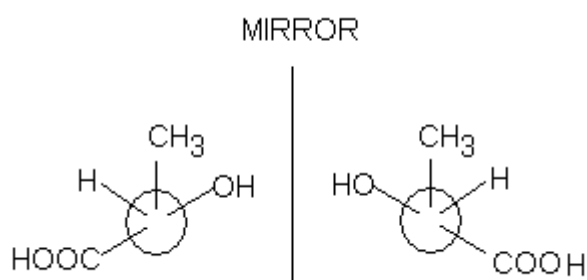
### Prochiral carbon

A carbon atom is said to be prochiral if replacement of one of its group or atom by other substituent makes it chiral centre. For example propanoic acid is prochiral molecule.

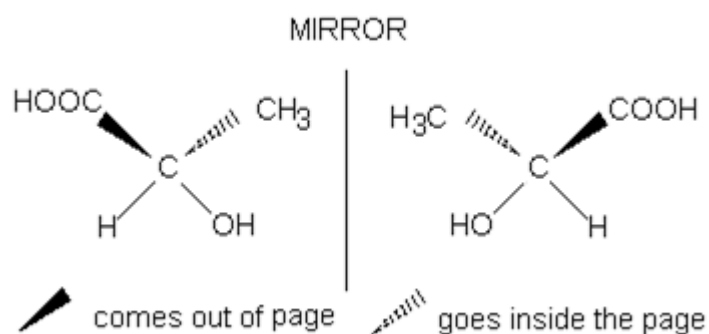


## Representation of enantiomers

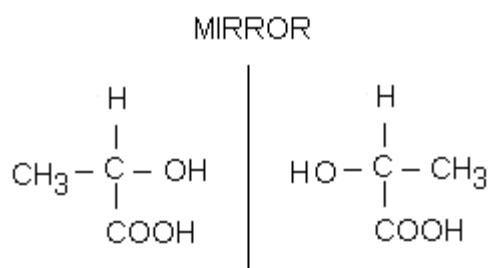
## i) Newman projection formulae



## ii) Wedge and dash formulae



## iii) Fischer projection

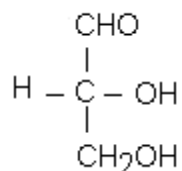


## Specification of configuration

## i) Relative configuration ( D, L – Nomenclature)

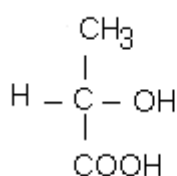


Earlier than 1951, the absolute configuration of a compound was not known. Therefore glyceraldehydes was chosen as standard compound and all compounds were studied which respect is

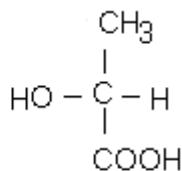


Now the configuration with –OH group at right side was given D-configuration where as the configuration with –OH group at left side was given L-configuration.

Example

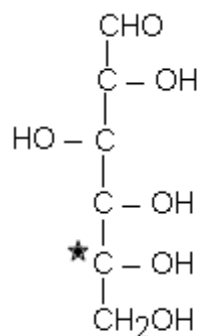


D - Lactic acid

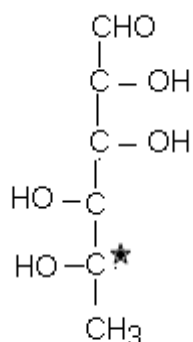


L - Lactic acid

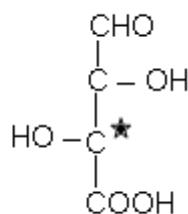
In polyhydroxy compounds ( sugars ) having more than one chiral centre, the configuration of stereocentre farthest from carbonyl group is compared with glyceraldehydes. Example



D- glucose

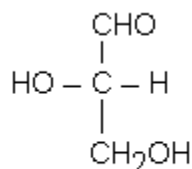


L -Rhamnose

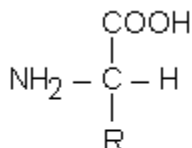


L -tartaric acid

In case of  $\alpha$ - amino acids, the configuration is assigned by comparing –NH<sub>2</sub> group of  $\alpha$ - amino acid with –OH group of glyceraldehydes.



L (-) - Glyceraldehyde

L (-) -  $\alpha$ - amino acid

The sign (+) or (-) added after D- and L- letters indicates the direction of optical rotation

### (iii) Absolute configuration ( R, S – nomenclature)

Limitations of D and L notations were overcome by R and S notations developed by R.S. Cahn and C.K. Ingold and V. Prelog

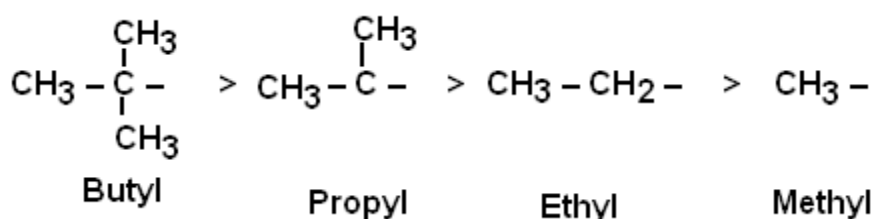
The centre is then viewed with the substituent with lowest priority pointing away from the viewer.

If the path for remaining three substituents going from highest priority to lowest priority is clockwise, the configuration is R ( R stands for Rectus i.e. right) and if the path is anticlockwise the configuration is assigned as S ( S stands for sinister i.e. left)

Sequence rules for assigning the priority order :

Rule 1: The atom with highest atomic number has highest priority. For example  $\text{I} > \text{Br} > \text{Cl} > \text{F} > \text{C} > \text{H}$

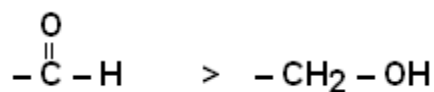
Rule 2 : If the atom attached to the asymmetric carbon atom are the same. We determine the priority by considering the next atom from the asymmetric carbon atom. For example



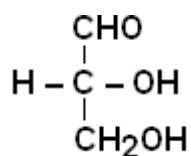
Ethyl has a higher priority than methyl because the ethyl group has ( C, H, H) attached to first carbon, whereas the methyl carbon has only hydrogen ( H, H, H)

Rule 3: If the atoms attached to two groups are of the same atomic number then the priority is given to the group which has more substituents  $\text{CHCl}_2 > \text{CH}_2\text{Cl}$

Rule 4 : If the groups attached to the asymmetric carbon atom has double bond or triple bond then the priority is given to the group which has the maximum bonds.



Example Glyceraldehyde



Priority order : OH > CHO > CH<sub>2</sub>OH > H

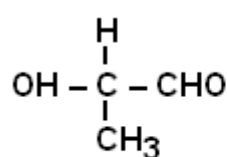
The priority sequence for most common groups

-I, -Br, -Cl, -SH, -F, -OCOR, -OR, -OH, -NO<sub>2</sub>, -COCl, -COOR, -COH, -CONH<sub>2</sub>, -COR, -CHO, -CN, CH<sub>2</sub>OH, -C<sub>6</sub>H<sub>5</sub>, -CR<sub>3</sub>, -CHR<sub>2</sub>, -CH<sub>2</sub>R

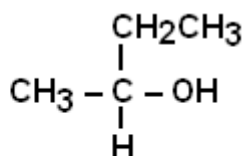
### Golden rule

There is an easy way of assigning R and S configuration to optical isomers represented by Fischer projection formula. First assign priorities to the group, atom attached to chiral centre.

If the lowest priority group occupies vertical position in the original Fisher projection then the configuration obtained above gives the actual configuration in the molecule

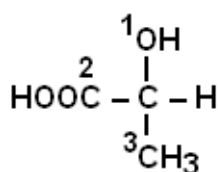


R - configuration

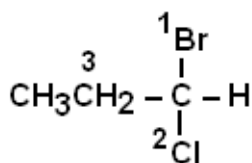


S - configuration

If the lowest priority group occupies horizontal position in the Fischer projection formula, then change the configuration obtained above from (R) to (S) or (S) to (R)



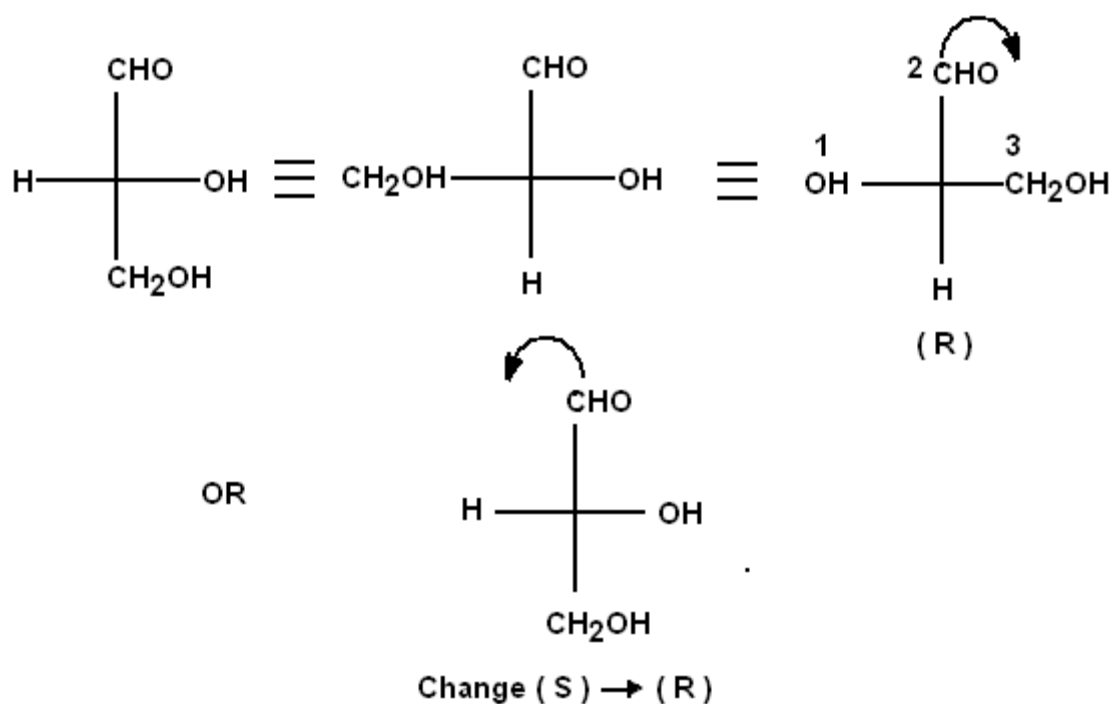
change S → R  
(R) -configuration



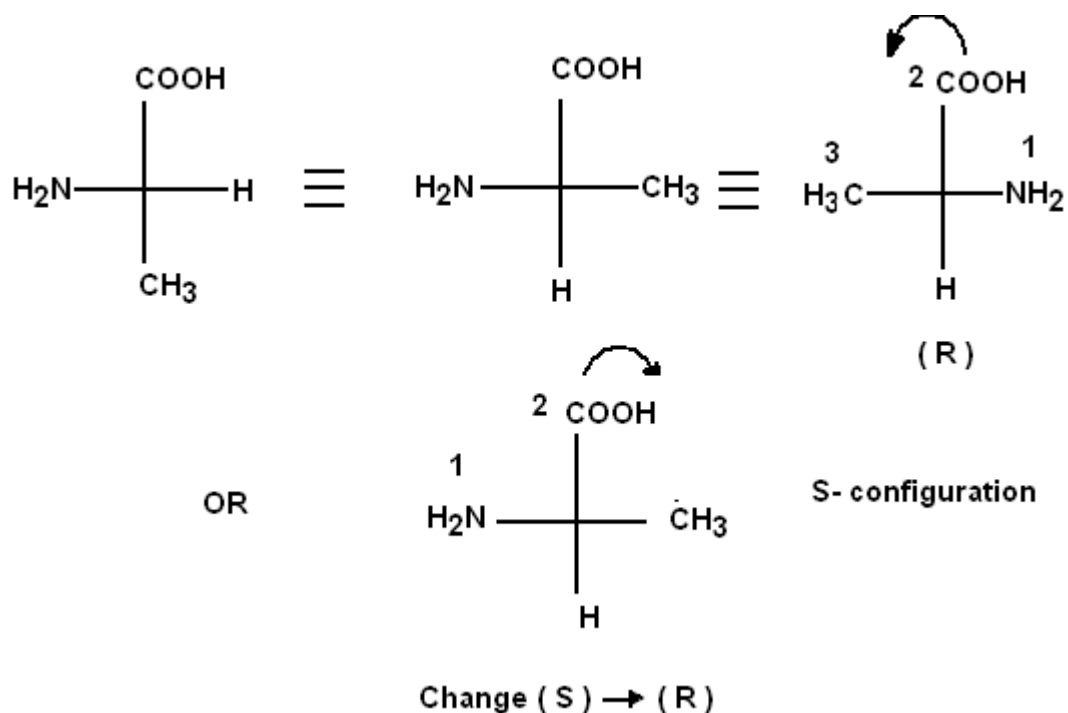
change R → S  
(S) - configuration

# ISOMERISM

## Examples



## Example II



## MESO COMPOUNDS:

A compound with two or more asymmetric carbon atoms but also having a plane of symmetry (a mirror plane) is called meso compounds. The figure shows two meso compounds. These molecules have plane of symmetry dividing them midway

## ISOMERISM

between the two asymmetric carbon in each. Notice that one half of the molecule is the mirror image of the other. Both molecules are optically inactive; even though each has two asymmetric centres. Neither will rotate the plane polarized light.

