

UNIT – I  
Stereo Isomerism – I  
18K5CH08

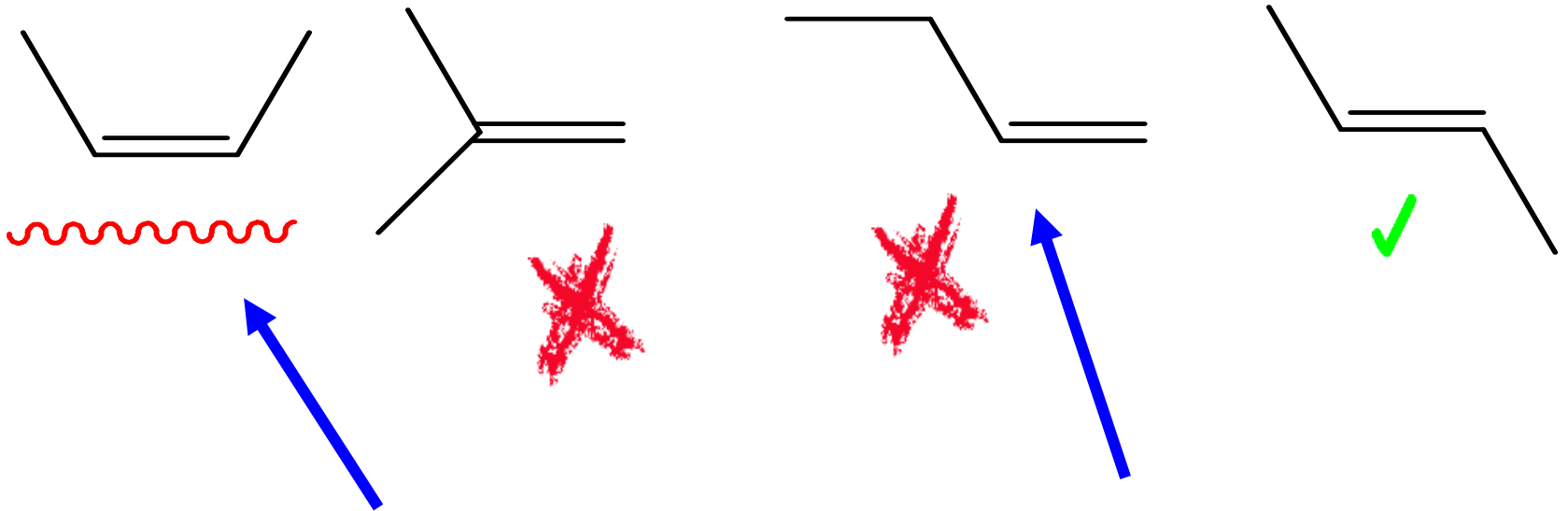
Isomerism:

Different compounds have same molecular formula

ex:  $C_2H_5OH$ ,  $CH_3OCH_3$

# STREOISOMERISM

- **Stereoisomers:** Same molecular formulae, same connectivity; same constitutional isomer. Different spatial orientation of the bonds.



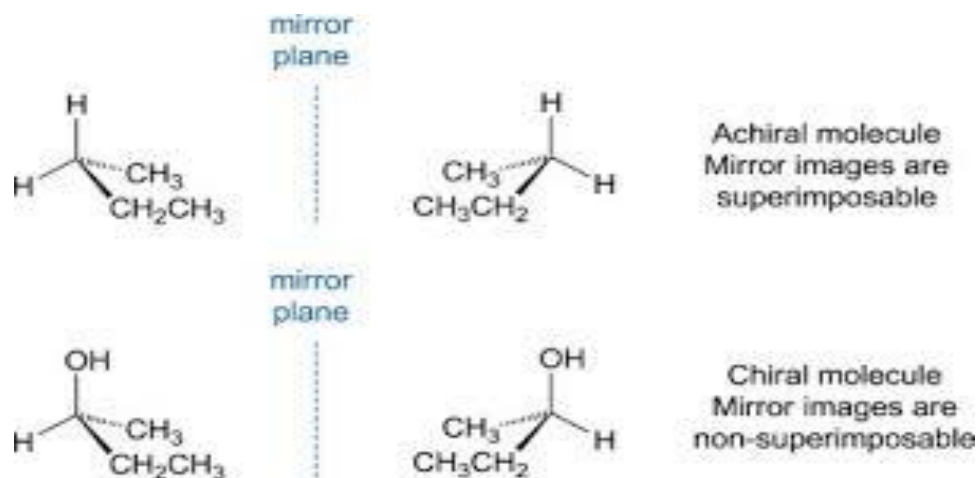
# Two kinds of **Stereoisomers**

- **Enantiomers**: stereoisomers which are mirror objects of each other. Enantiomers are different objects, not superimposable.
- **Diastereomers**: stereoisomers which are not mirror objects of each other.

If a molecule has one or more tetrahedral carbons having four different substituents then enantiomers will occur. If there are two or more such carbons then diastereomers may also occur.

- **OPTICAL ISOMERS:** Some compounds rotate the plane of the polarised light in different directions
- **OPTICAL ACTIVITY:** Rotating the plane of the plane polarised light
- **DEXTROROTATORY-**towards right(clockwise)
- **LAEVOROTATORY-**towards left(anti clockwise)

- Conditions for optical activity-molecule must be chiral
- Asymmetric centre-molecule which gives rise to optical activity
- Chiral/Asymmetric carbon-four different atoms or groups attached to central carbon atom.
- Achiral carbon-superimposable on its mirror image.



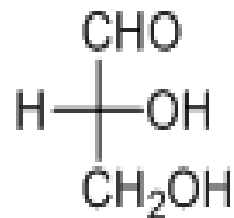
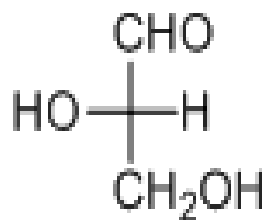
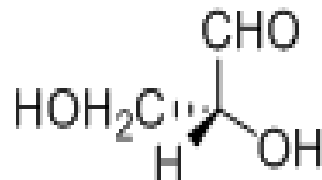
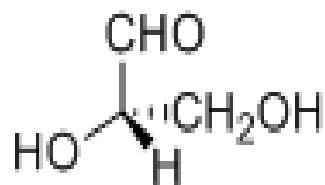
D notation- right of the asymmetric carbon.

L notation-left to the asymmetric carbon.

Ex.

L-glyceraldehyde

D-glyceraldehyde



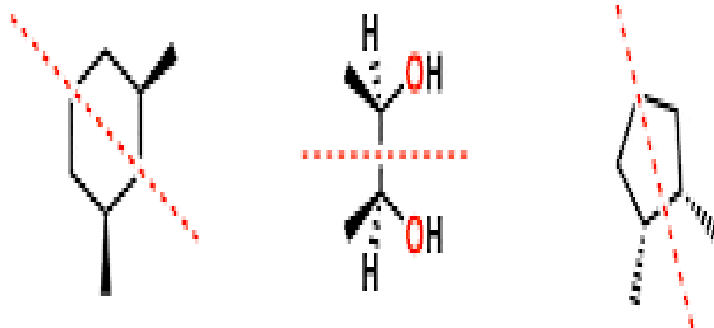
# ELEMENTS OF SYMMETRY

- 1.Plane of symmetry
- 2.Centre of symmetry
- 3.Alternating axis of symmetry

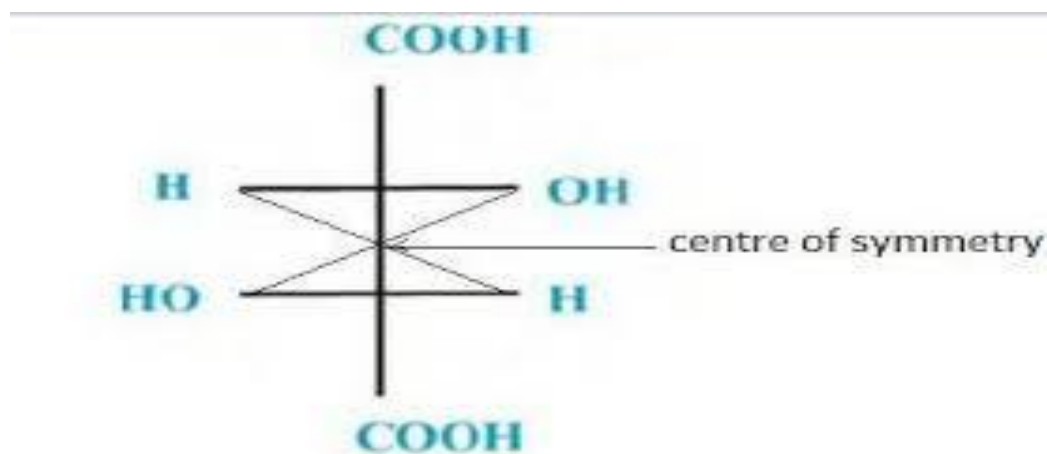


- Plane of symmetry-a plane divides an object into two identical halves.

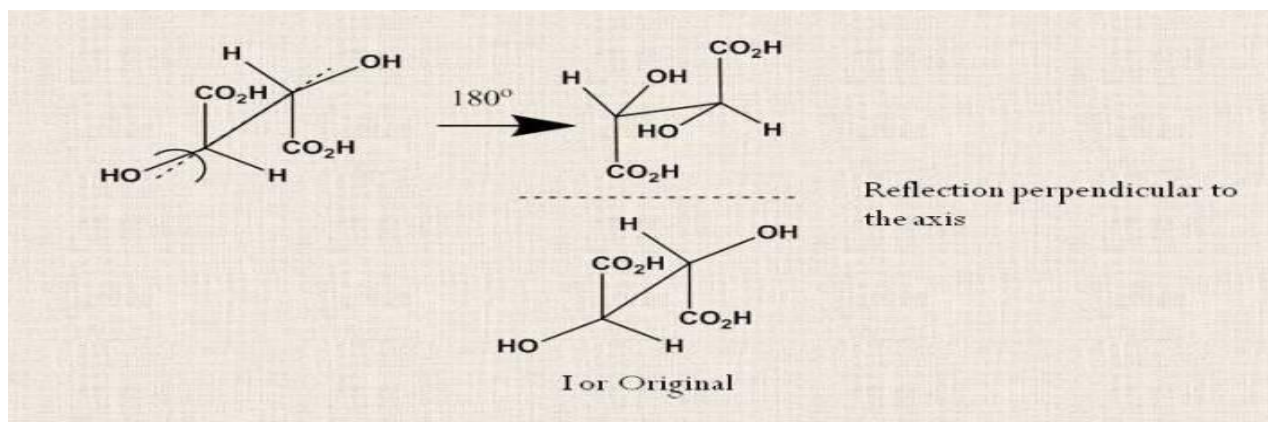
Planes of symmetry can cut through both atoms and bonds:



- Centre of symmetry-point from which lines,when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.



- Alternating axis of symmetry-when rotated through an angle of  $360/n$  about this axis and then followed by reflection in a perpendicular to the axis, the molecule is the same as it was in the starting position.



# RACEMIZATION

- Definition: Process of converting an optically active compound into the racemic modification
- Racemic modifications are also called as racemic mixture or racemates.

# METHODS TO BRING ABOUT RACEMISATION

- i) Action of heat
- ii) Treatment with chemical reagents
- iii) Substitution and rearrangements
- iv) Auto-racemisation

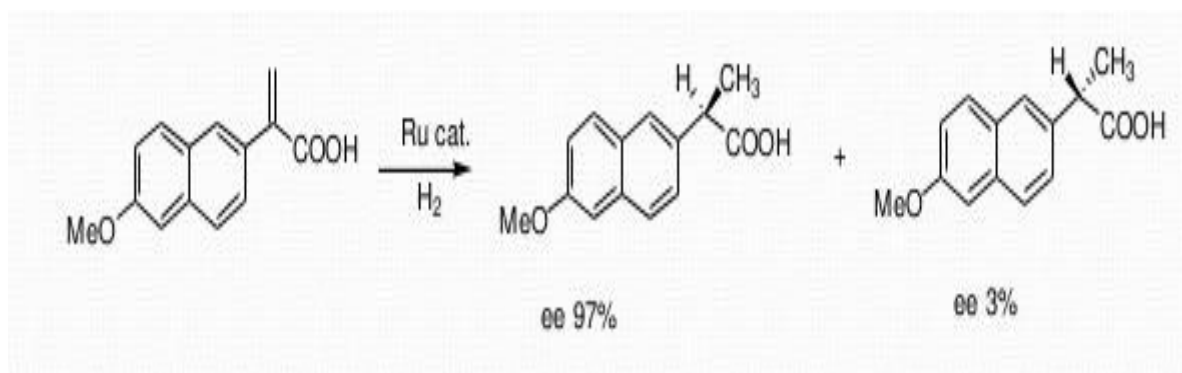
# RESOLUTION

- DEFINITION: Separation of a racemic mixture into its enantiomers(dextro and laevo compounds)
- Optically active compounds ends up in a racemic mixture only.
- Process of separation is termed as resolution.

# METHODS OF RESOLUTION

- i) Mechanical separation
- ii) Bio chemical separation
- iii) By means of salt formation
- Diastereo Isomers-pairs may be optical isomers, with different configurations but not mirror images
- Enantiomers-optical isomers which are mirror images

- **ASYMMETRIC SYNTHESIS**-Production of an optically active compound from a symmetric molecule without the necessity of resolution



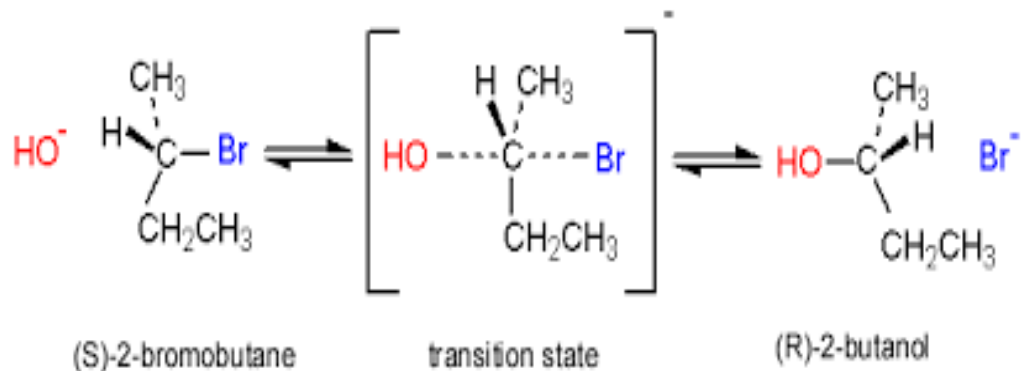


- PARTIAL ASYMMETRIC SYNTHESIS-Method involves the use of optically active compounds.
- ABSOLUTE ASYMMETRIC SYNTHESIS – Preparation of an optically active compound without intermediate use of optically active reagents

- WALDEN INVERSION

Transformation of an optically active compound into a compound opposite configuration

central atom undergoes a type of flipping



- VANT'S HOFF'S RULE OF SUPERPOSITION

Two or more asymmetric carbon in an active compound make independent contributions to the total molecular rotation.

This concept is called as vicinal action.

- **FRENDENBERGS RULE OF SHIFT**

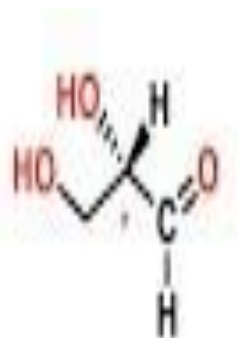
Otherwise called as displacement rule.

When two compounds having dissymmetric constitution are chemically changed in the same way and the change produces a considerable shift in optical rotation in the same direction then two compounds may have the same configuration.

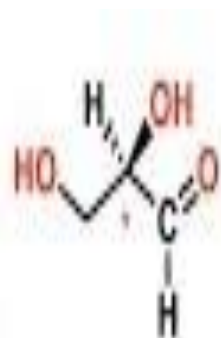
# RS Nomenclature

- Configuration
- Definition: Arrangement of atoms that characterises a particular stereo isomer is called as configuration.

- Ex:



(S)-(-)-glyceraldehyde



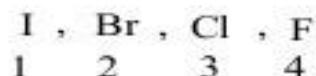
(R)-(+)-glyceraldehyde

# Cahn – Ingold Prelog Rules

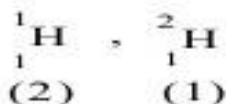
- According to this system it specifies the configurations of each chiral centre in a molecule. Here we use a set of rules called sequence rules. These rules are used to determine the order priority

- Sequence rule.

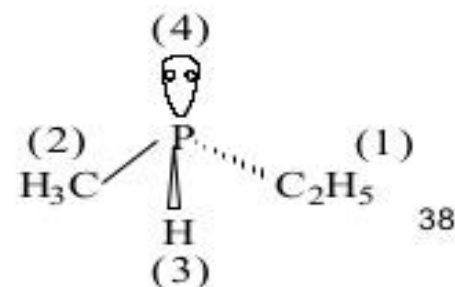
- 1) Atoms of higher atomic number get highest priority than the atoms of lower atomic number



- 2) Isotopes of higher atomic weight gets highest priority than the isotope of lower atomic weight.

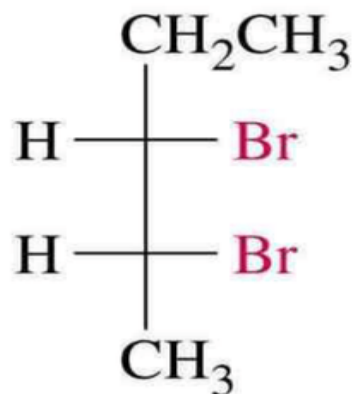


- 3) Lone pair electrons get lowest priority.



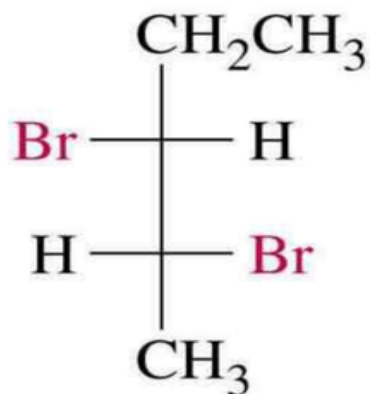
# Erythro and Threo

- Terms used for diastereomers with two adjacent chiral Carbons, without symmetric ends.
- For symmetric molecules, use meso or *d,l*.

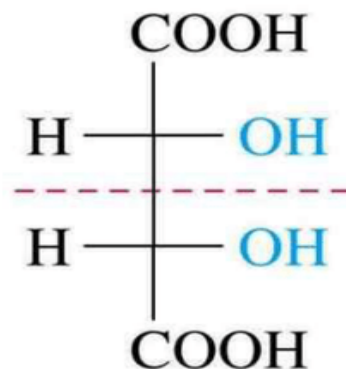


erythro

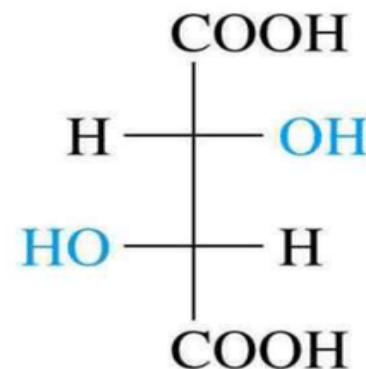
2,3-dibromopentane



threo



meso



(*d,l*)

tartaric acid

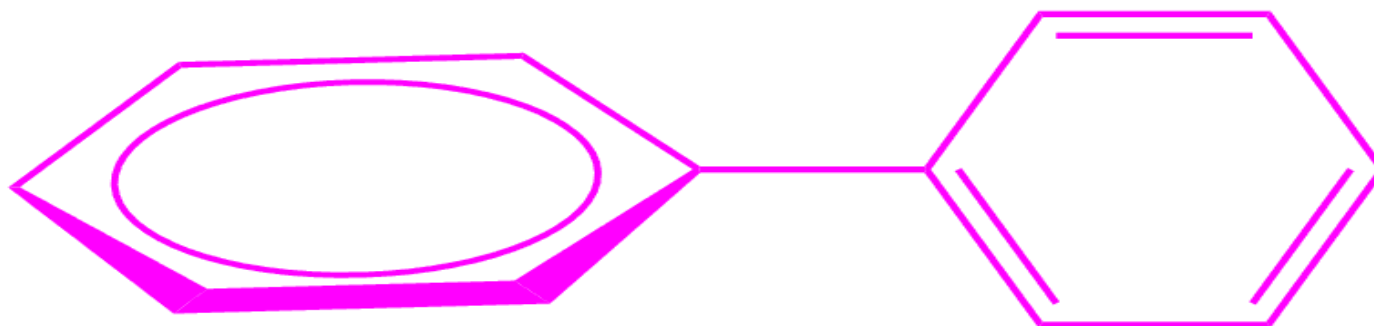
# Unit II

## Stereoisomerism II



# Optical Activity of Biphenyls

- Dipole moment measurements and X-ray diffraction have been shown that the two benzene ring in biphenyl are co-axial, that is, the two rings lie in different planes.



1,1'-biphenyl

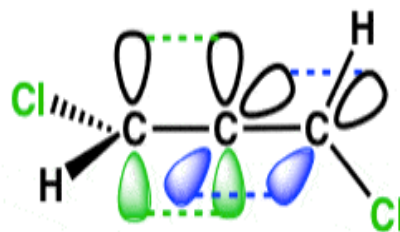
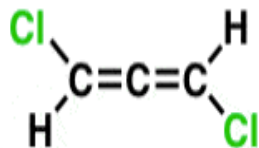
# Conditions for Biphenyl compounds to exhibit optical activity

- It was found that two conditions were necessary for biphenyl compounds to exhibit **optical activity**,
- - (I) neither ring must have a vertical **plane of symmetry**
  - (II) the substitutions in the ortho positions must have a large .

# Optical Activity of Allenes

- Allenes are cumulated Dienes
- The Central Carbon in Allene is SP Hybridized
- Chiral Allenes have an Axis of Chirality

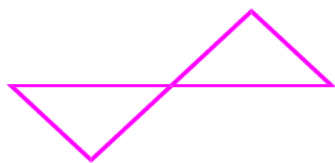
*Disubstituted allene*



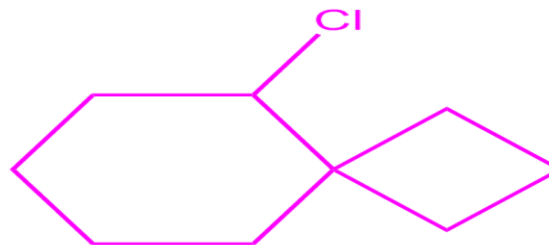
*orbital drawing*

# Optical Activity of Spiranes

- If both double bonds in allene are replaced by ring systems, the resulting molecules are called spirans. For example, spiro-2,2-pentane, 1-chloro spiro-5,3-nonane.



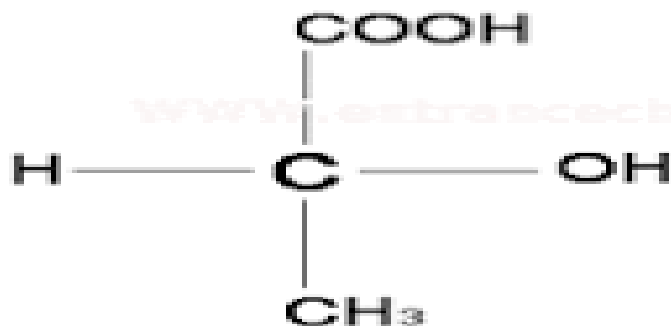
spiro2,2pentane



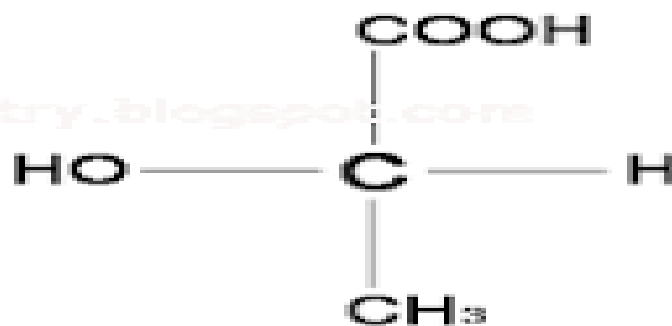
1-chlorospiro-5,3 nonane

# Optical Isomerism of Lactic acid

Optical Isomerism – Compounds having same molecular formula and same structural formula but differ in behavior of plane polarized light are called optical isomers and this phenomenon is called optical isomerism.



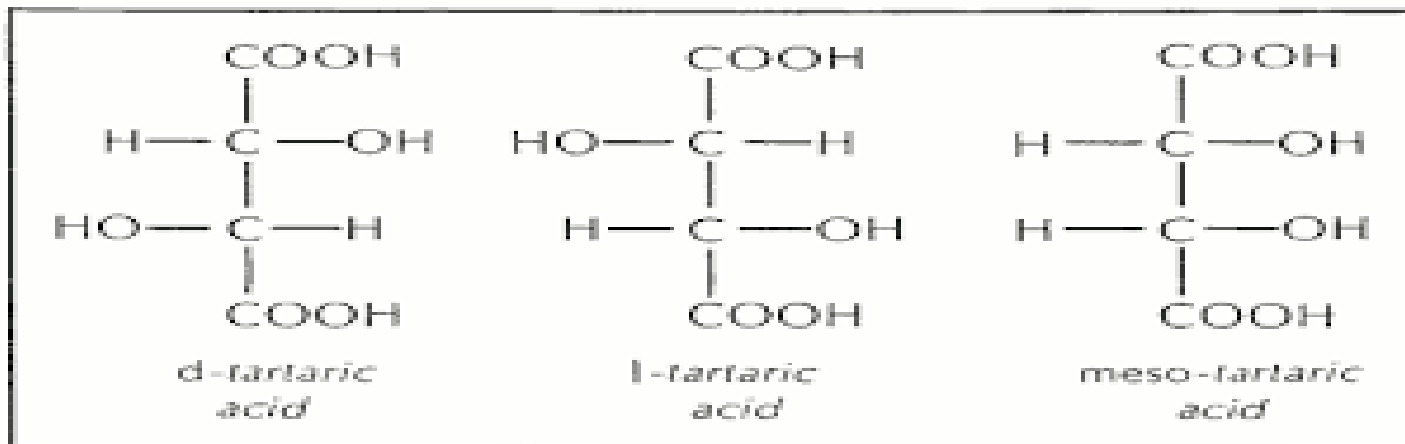
**d- lactic acid**



**l- lactic acid**

# Optical Isomerism of Tartaric Acid

- Tartaric acid contains two chiral carbon atoms
- Four forms of tartaric acid are known, of which two are optically active and two are optically inactive. The two optically active forms are mirror images of each other but not superimposable, that is, they are Enantiomers



# Four forms of Tartaric acid

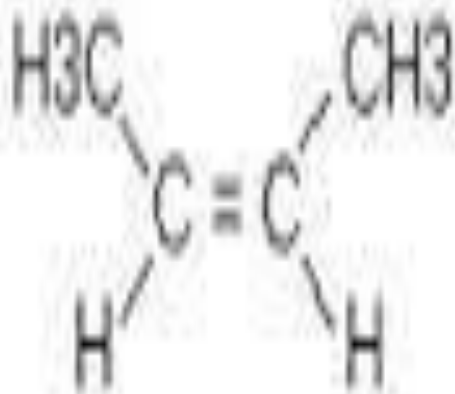
- (+)-TartaricAcid: Rotate the PPL to the right(clockwise) and is dextrorotatory
- (-)-TartaricAcid:Rotate the PPL to the left (anti-clockwise) and is levorotatory.
- *mesoTartaricAcid:It possesses a plane of symmetry and is opticallyinactive. This optically inactive form is said to be internally compensated; means optical rotation of one chiral carbon is cancelled by that of the other.*
- ( $\pm$ )-TartaricAcid:Does not rotate PPL and isoptically inactive because it is aracemic mixture of (+)and(-)forms

# Geometrical Isomerism

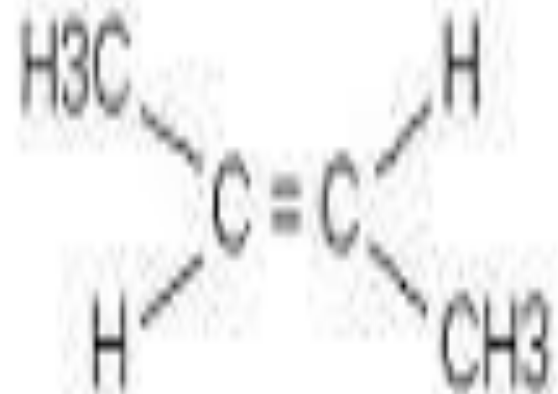
- This type of isomerism is found in heteroleptic complexes due to different possible geometrical arrangements of the ligands. When two identical groups occupy adjacent positions, the isomer is called cis and when arranged opposite to one another, the isomer is called trans.



# Examples of Geometrical Isomerism

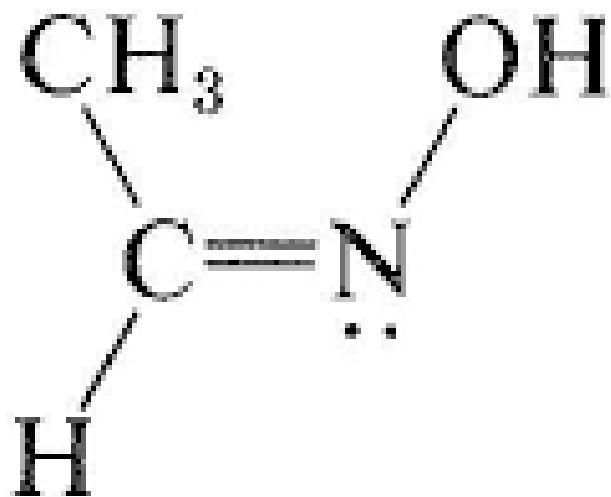


Cis - 2 - butene  
(Cis - Isomer)



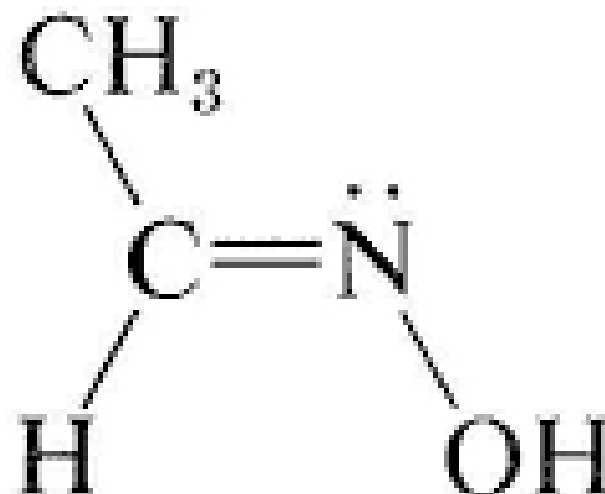
Trans - 2 - Butene  
(trans - Isomer)

# SYN & ANTI Notation



**11**

Z (syn)



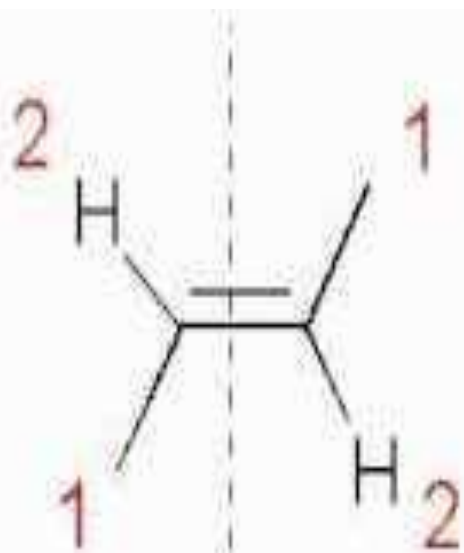
**12**

E (anti)

# E- Z Notation

- Definition: A system for naming the stereoisomers of a molecule. The configuration at each double bond is determined by the priority of the side groups and whether the highest priority groups are on the same or opposite side. A Z indicates that the highest-priority side groups are on the same side and an E indicates that the highest-priority side groups are on opposite sides. Priority is given to the bonded atom with the higher atomic number

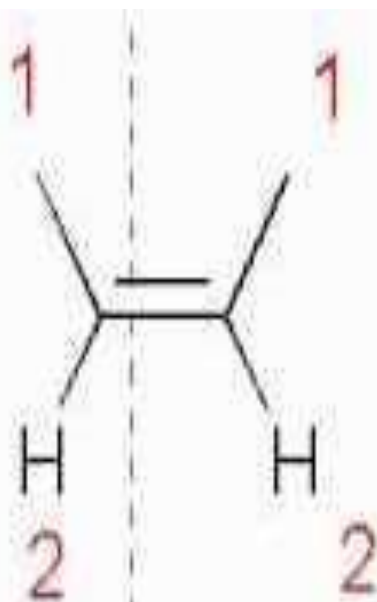
# E-Z Notation Example



Opposite sides

*E*

German entgegen

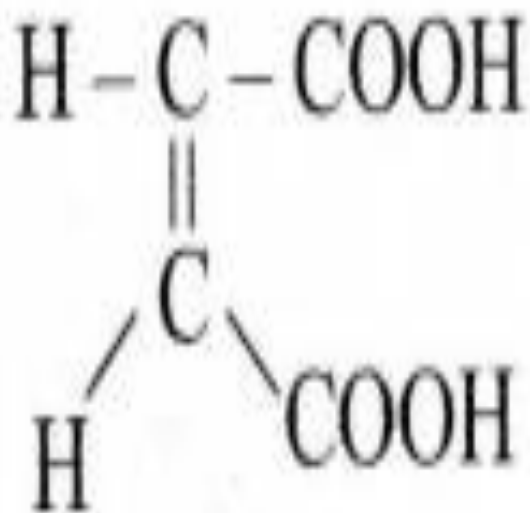


Same side

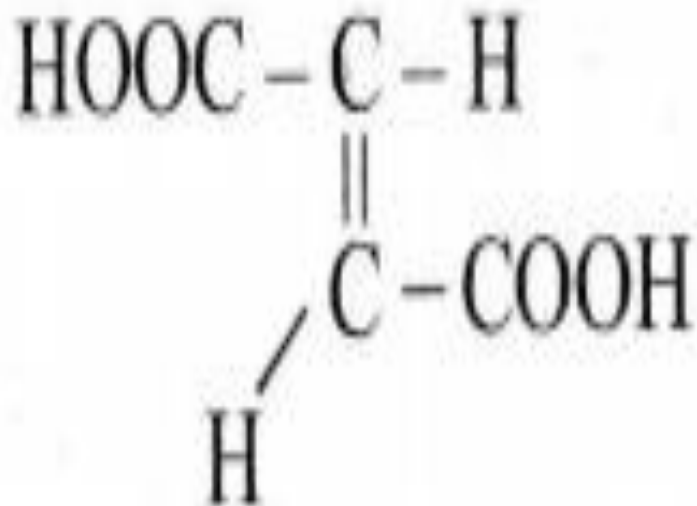
*Z*

German zusammen

# Geometrical Isomerism of maleic and fumaric acid



(*cis*-form)  
(Maleic acid)



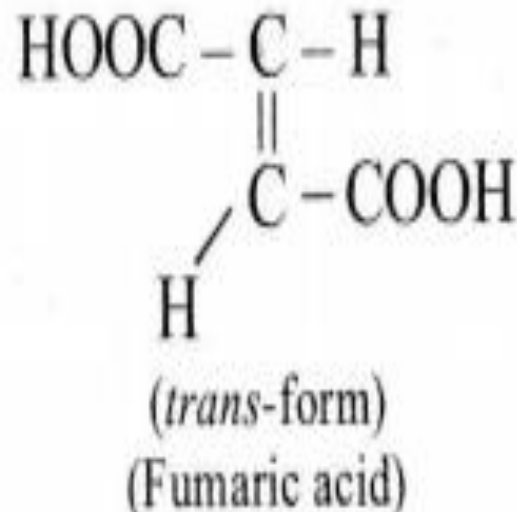
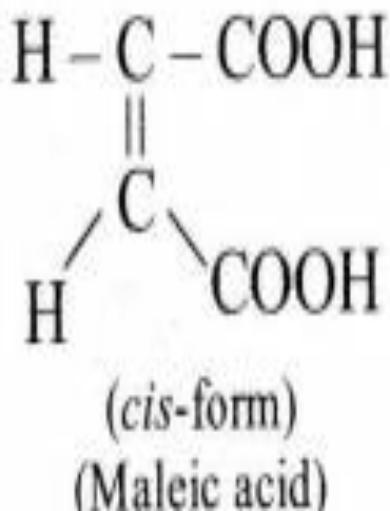
(*trans*-form)  
(Fumaric acid)

# Properties of Geometrical Isomerism

- The melting point and the stability of the CIS are lower than those of trans isomer.
- The density, refractive index, solubility, dipole moment, heat of combustion and the dissociation constant of the CIS are greater than those of trans isomer

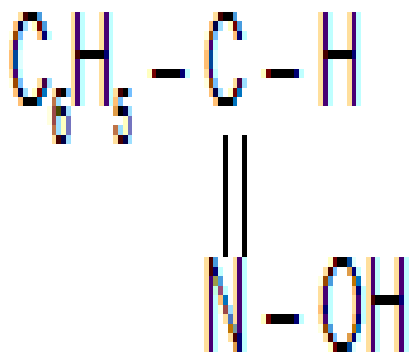
# Inter conversion

- The CIS isomer which is labile can be converted into the stable trans isomer.  
Example: Maleic acid may be converted into fumaric acid by heating it above its melting point.

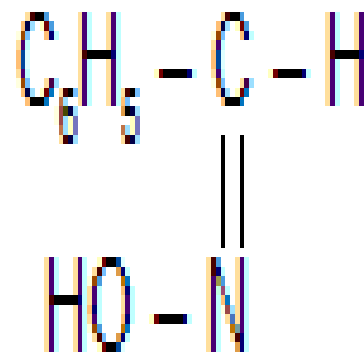


# Geometrical Isomerism in Unsymmetrical ketoximes

- Aromatic aldoximes and aromatic ketoximes also show geometrical isomerism. In aldoximes, when H and OH groups are on the same side, the isomer is known as *syn* (analogous to *cis*) and when these groups are on the opposite sides, the isomer is known as *anti* (analogous to *trans*).



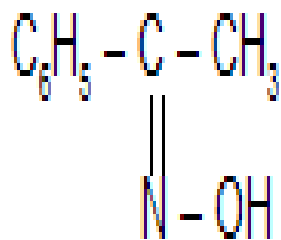
*syn*-Benzaldoxime



*Anti*-Benzaldoxime

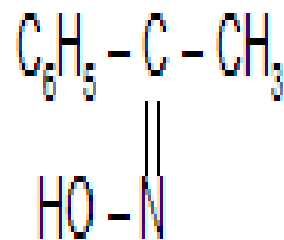


- In ketoximes the prefixes *syn* and *anti* indicate which group of ketoxime is *syn* (on the same side) or *anti* (on the opposite sides) to the OH group. For example,



*syn*-Methylphenyl ketoxime

(*anti*-Phenylmethyl ketoxime)



*syn*-Phenylmethyl ketoxime

(*anti*-Methylphenyl ketoxime)

# Methods of Distinguishing Geometrical Isomers

- Formation of cyclic anhydride
- Degree of dissociation
- Dipole moment
- Stability, heat of combustion and melting point