Name of Unit	Geometrical Isomerism
Subject /Course Name	Pharmaceutical Organic Chemistry-III
Subject/Course ID	BP401T
Class: B.Pharm. Semester	IV
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Learning Outcome of Module 02

LO	Learning Outcome	Course Outcome Code
LO1	To gain knowledge about Geometrical Isomerism.	BP401.2
LO2	To understand about Nomenclature of Geometrical Isomerism.	BP401.1
LO3	To Understand about configuration and methods of determination of configuration of geometrical isomerism.	BP401.2
LO4	To get the knowledge about Conformational Isomerism in alkanes.	BP401.2
LO5	To get the knowledge about Stereoisomerism in Biphenyl Compounds.	BP401.4
LO6	To understand about Stereospecific and Stereoselective Reactions.	BP401.2

Content Table

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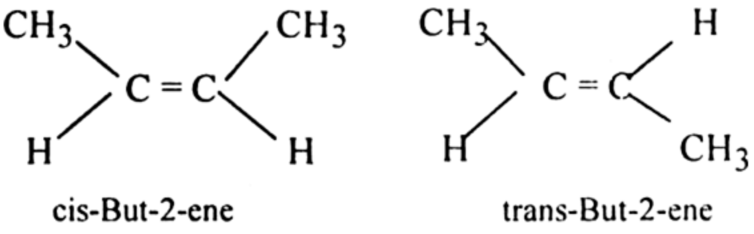
GEOMETRICAL ISOMERISM

Geometrical Isomerism:- Geometrical isomerism is a type of **stereoisomerism** having the same molecular formula and same structure but differ in the relative arrangement of atoms.

For example,



Types of Geometric Isomerism:-

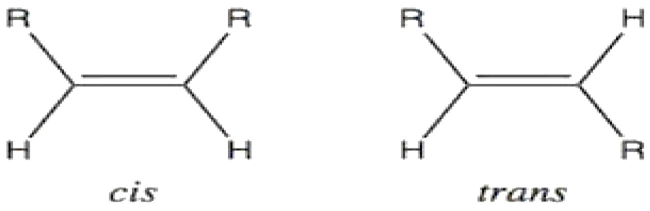
The two most common types of geometric isomers are those arising

1. From a double bond and

2. From a ring structure.

These type of geometric isomers are also called **cis/trans isomers.**

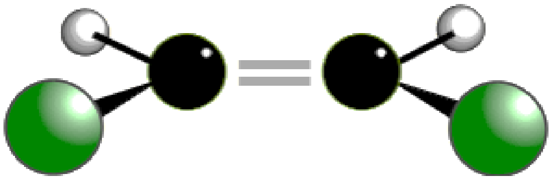
- When two identical groups occupy adjacent positions, the isomer is called **cis isomer**.
- When arranged opposite to one another, the isomer is called a **trans isomer.**



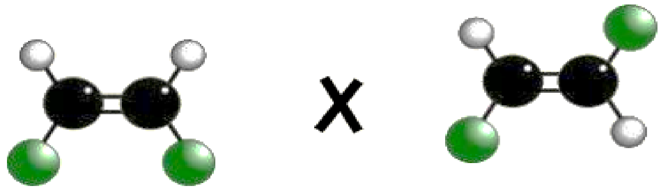
Two forms are not interconvertible due to **restricted rotation** of double bond.

Restricted Rotation:- The bond across which atoms cannot rotate without breaking the bonds is called restricted rotation.

Restricted Rotation Of C=C Bonds:- C=C bonds have restricted rotation so the groups on either end of the bond are 'frozen' in one position; it isn't easy to flip between the two.



This produces two possibilities. The two structures cannot interchange easily so the atoms in the two molecules occupy different positions in space.

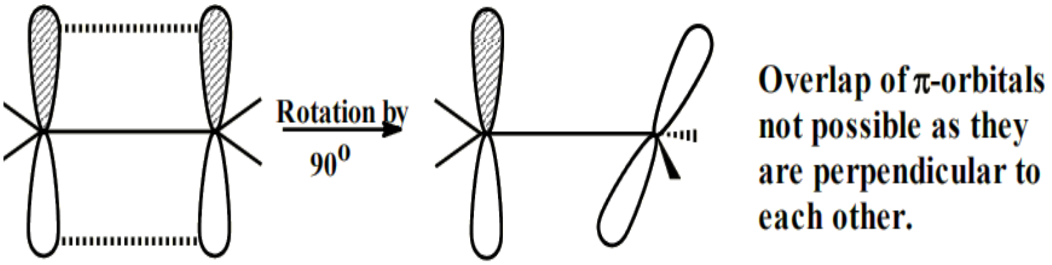


Geometric isomerism is not confined only to the compounds having carbon-carbon double bonds. In fact the following compounds exhibit this type of isomerism:

i) Compounds having a double bond, i. e., olefins (C=C), imines (C=N) and azo compounds (N=N).
ii) Cyclic compounds.
iii) Compounds exhibiting geometric isomerism due to restricted rotation about carbon-carbon. single bond.

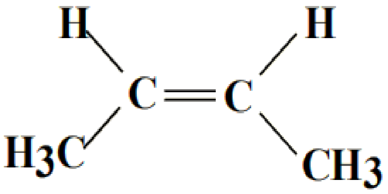
Cause of Geometric Isomerism:

Hindered Rotation Carbon atoms involved in double bond formation and all the atoms attached to these doubly bonded carbon atoms must lie in the same plane because p-bond can be formed only by parallel overlap of the two porbitals. There will be decrease in the overlap of porbitals if an attempt is made to destroy this coplanarity. In other words, neither of the doubly bonded carbon atom can be rotated about the double bond without destroying the p-orbital.

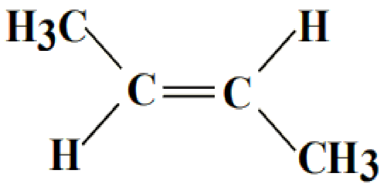


Rotation about a C = C bond.

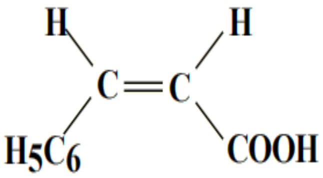
This process of rotation which is really a transfer of electrons from the p-molecular is prevented and hence compounds such as orbital to the p-atomic orbital are associated with high energy (271.7 kJ mol-1). Thus at ordinary temperatures, rotation about a double bond CH3CH =CHCH3 exist as isolable and stable geometrical isomers.



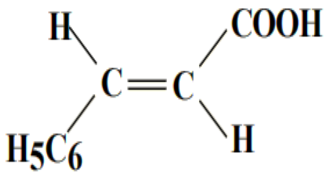
Cis-But-2-ene



Trans-But-2-ene



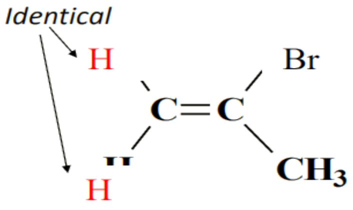
Cis-Cinnamic acid



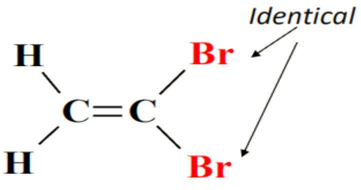
Trans-Cinnamic acid

Necessary and Sufficient Condition for Geometric Isomerism

Alkenes cannot have cis-trans isomers if a carbon atom in the double bond is attached to identical groups.



2-bromopropene
(not cis or trans)

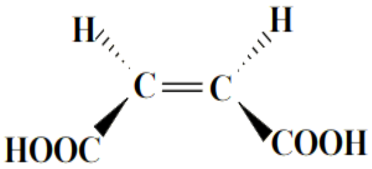


1,1-dibromoethene
(not cis or trans)

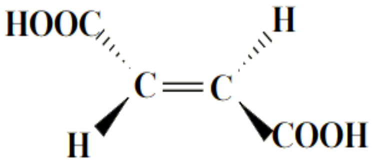
Determination of the Configuration of the Geometric Isomers:- There is no general method for determining the configuration of geometrical isomers. There are no. of methods and one uses one or more of them depending on the nature of the compound.

I. Physical methods:-

(a) Melting points :- The melting point of trans isomers is generally higher than that of cis isomers because in trans isomer, bulky groups lie on the opposite side of the double bond. Therefore, the molecule is symmetrical and hence packed well in the crystal lattice. On the other hand in the cis isomer, the bulky groups are present on the same side of the double bond. Hence, the cis isomer is unsymmetrical and its molecules are not packed well in crystal lattice. So, the intermolecular forces of attraction in the trans isomer are stronger than in the cis isomer, because of which the melting point of trans isomer is more than that of cis isomer.

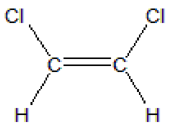


m.p. 403K

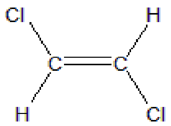


m.p. 575K

(b) Boiling point:- Boiling point of cis isomers are higher than trans isomers because cis isomers are polar and hence they have strong intermolecular forces between the molecules. Because of this high polarity and high intermolecular force, a lot of energy will be required to break the bonds. Hence, cis isomers have higher boiling point.



cis-1,2-dichloroethene
BP = 60.3 °C

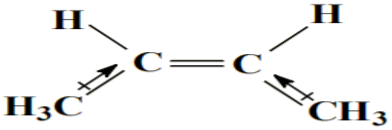


trans-1,2-dichloroethene
BP = 47.5 °C

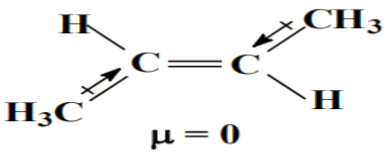
(c) Solubility:- In general, solubility of a cis isomer is higher than that of the corresponding trans isomer. This is due to the reason that the molecules of a cis isomer are less tightly held in the crystal lattice.

Solubility (gm/100ml) → Maleic acid (*cis* form) = 79g/100ml
Solubility (gm/100ml) → Fumaric acid (*trans* isomer) = 0.7g/100ml

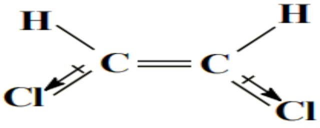
(d) Dipole Moment:- In general, cis isomers have the greater dipole moment than trans isomer which have zero or nearly zero diploe moment. In cis- isomer orientation of dipoles at same angle but in trans-isomer in opposite direction and thus they cancel out.



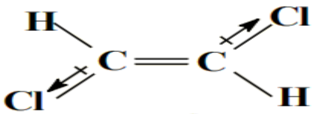
μ = 0.4 D



μ = 0



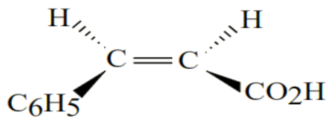
μ = 1.85 D



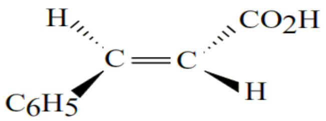
μ = 0

(e) Spectroscopic Data:- **IR:-** Trans isomer is readily identified by the appearance of a characteristic band near 970-960 cm-1 . No such band is observed in the spectrum of the cis isomer.

NMR:- The protons in the two isomers have different coupling constants e.g. trans – vinyl protons have a larger value of the coupling constant than the cisisomer, e.g. cis- and trans-cinnamic acids.



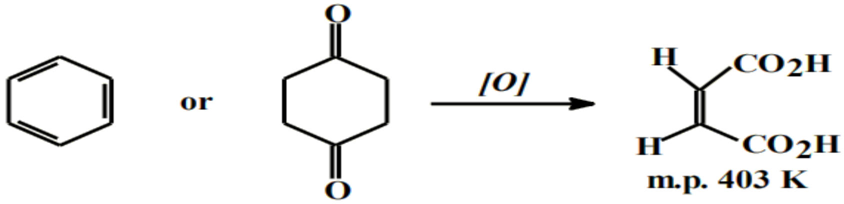
***cis*-Cinnamic acid**
($J_{H,H} = 12Hz$)



***trans*-Cinnamic acid**
($J_{H,H} = 16Hz$)

II Chemical Methods:-

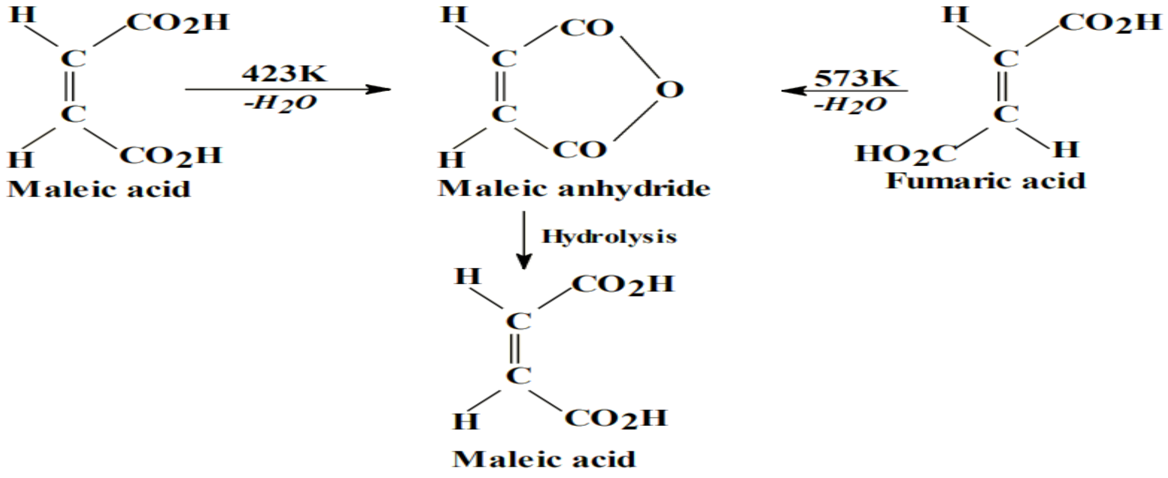
a) Methods of formation from cyclic compounds:- Oxidation of benzene or quinone gives maleic acid (m. p. 403K). From the structure of benzene or quinone, it becomes clear that the two carboxyl groups must be on the same side (cis).



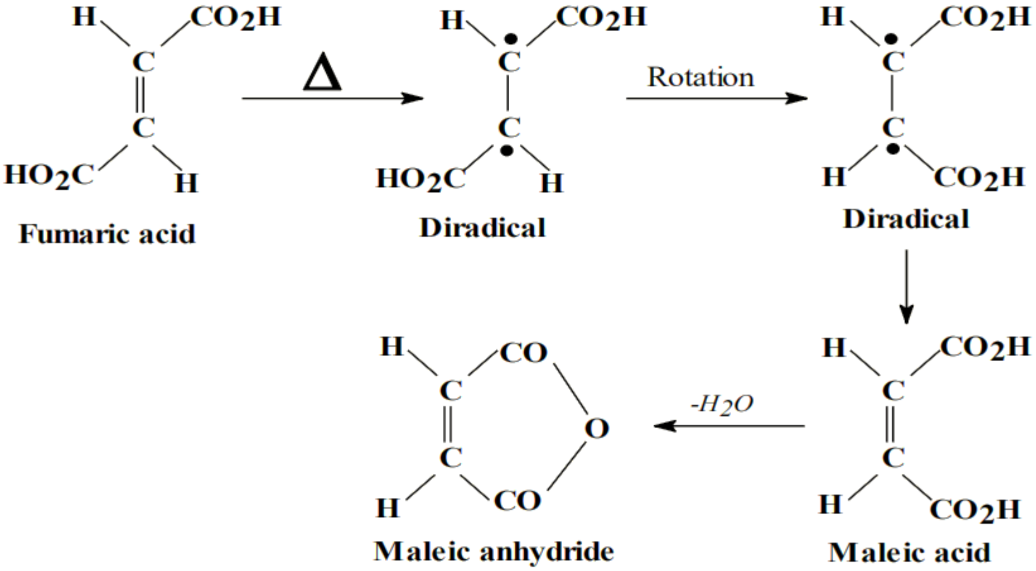
Therefore, maleic acid i.e. the isomer having m. p. 403K, must be cis and the other isomer fumaric acid (m. p. 575K) must be trans.

b) Method of formation of cyclic compounds:-

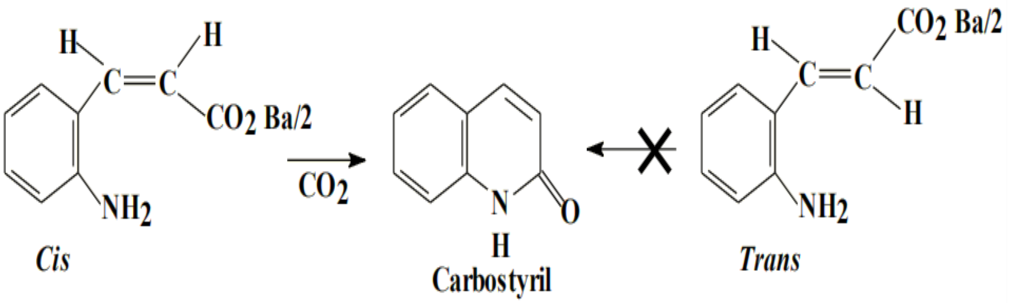
1. Cis isomer will undergo ring closure much more readily than the trans isomer.



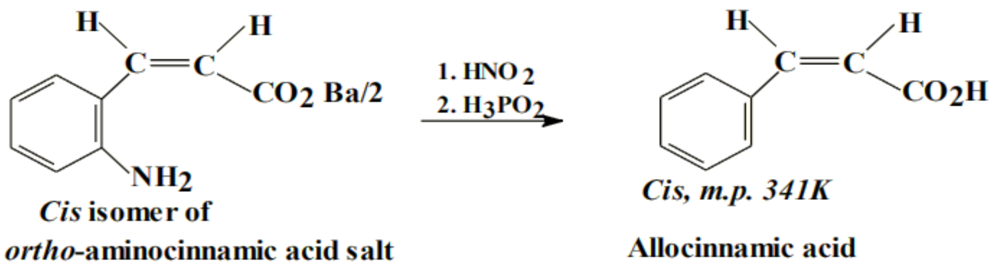
It is, therefore, reasonable to conclude that maleic acid is the cis isomer and fumaric acid is the trans–isomer. The latter forms the anhydride via the formation of maleic acid at high temperature which involves rupture of p-bond and rotation of the acid groups followed by reformation of the π- bond and loss of water.

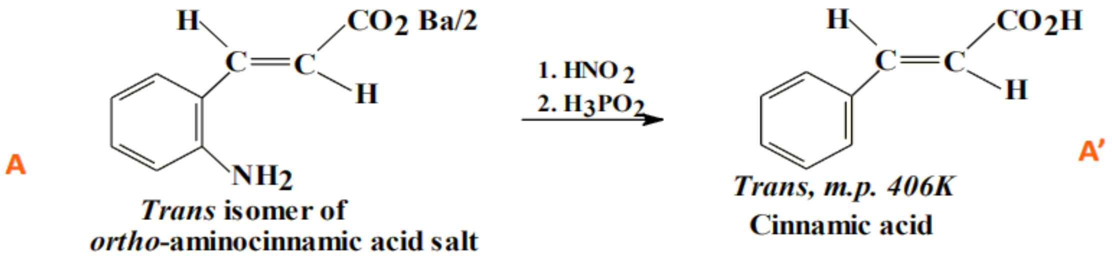


2. Ortho-amino cinnamic acids: The Ba-salt of an isomer of ortho-amino cinnamic acid on treatment with CO2 at room temperature gives carbostyril. This shows that the carboxyl group and the substituted phenyl group must be cis in this isomer. On the other hand, the Ba-salt of the other isomer of ortho-amino cinnamic acid does not give carbostyril under the same condition and, therefore, it must have the trans configuration.



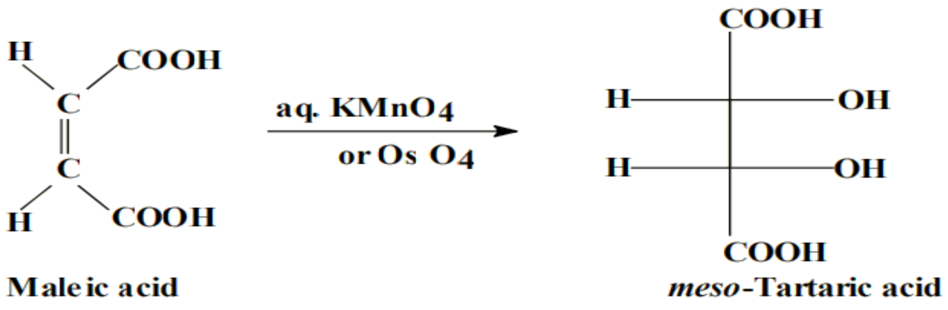
c) Method of chemical correlation:- Suppose configuration of a geometric isomer, say A is known. Let A be converted under mild conditions to a geometric isomer A', of another compound. Since under mild conditions interconversion of the geometric isomers will not take place, therefore, the configuration of A' will be the same as that of A.

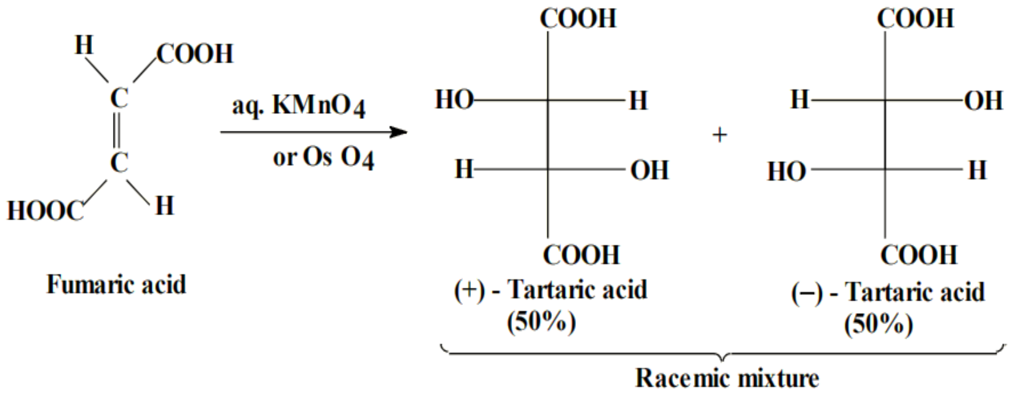




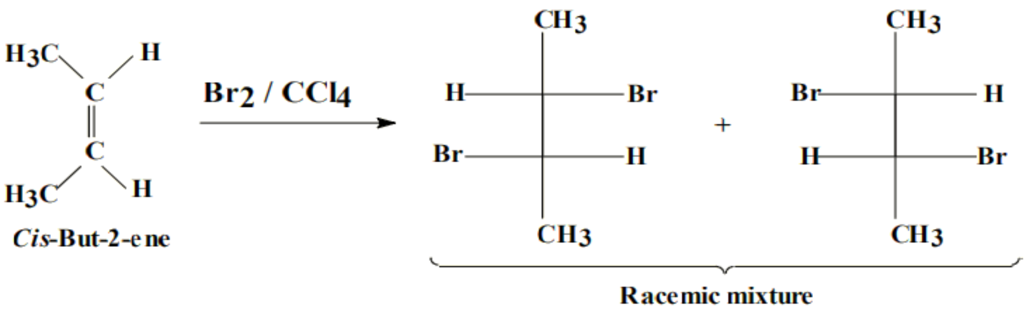
d) Method of stereo selective addition reactions:-

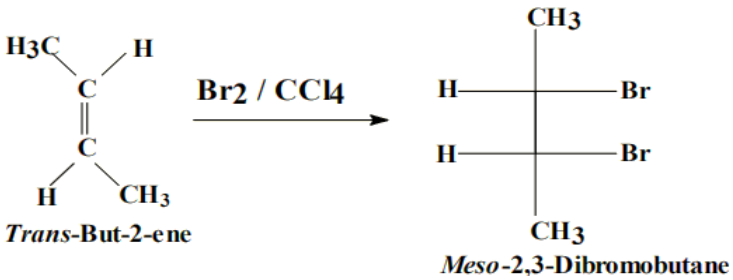
(i) Hydroxylation of double bond is stereospecifically cis.





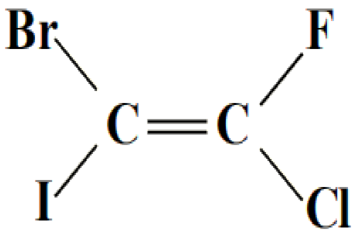
ii) Addition of bromine to double bond:- In contrast to hydroxylation, addition of bromine to alkenes is stereospecifically trans. Therefore, addition of bromine to trans-isomer will give rise to meso and to cis-isomer gives racemic mixture.





E and Z System of Nomenclature:-

Consider a molecule in which the two carbon atoms of a double bond are attached with four different halogens.



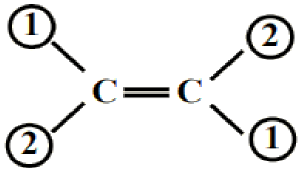
When we say that Br and CI are trans to each other we can also say with equal degree of confidence that I and CI are cis to each other. It is thus difficult to name such a substance either the cis or the trans isomer. To eliminate this confusion, a more general and easy system for designating configuration about a double bond has been adopted. This method, which is called the **E and Z system**, is based on a priority system originally developed by Cahn, Ingold and Prelog for use with optically active substance.

According to this method, if the groups with higher priorities are present on the opposite sides of the double bond, that isomer is denoted by E. Where E = Entgegen (the German word for 'opposite') or E = Enemy.

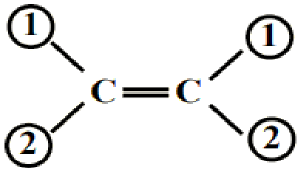
If the higher priorities are present on same side of the double bond, that isomer is denoted by Z. Where Z = Zusammen (the German word for 'together').

The priorities are assigned by following **Cahn-Ingold-Prelog sequence rules:** -

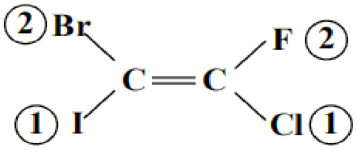
Rule 1: Rank the atoms directly attached to the olefinic carbon according to their atomic number. High priority is given to the atom with higher atomic number.



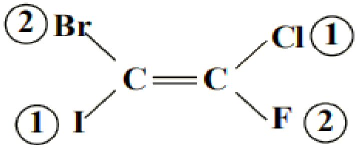
E



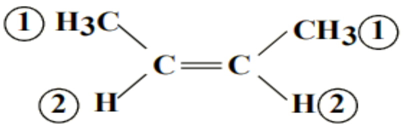
Z



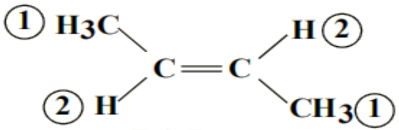
Z-1-Bromo-2-chloro-2-fluoro-1-iodoethene



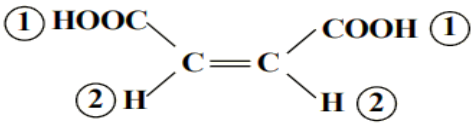
E-1-Bromo-2-chloro-2-fluoro-1-iodoethene



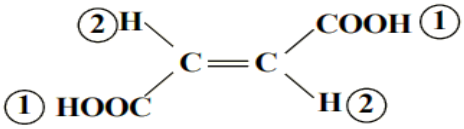
Z-2-Butene



E-2-Butene

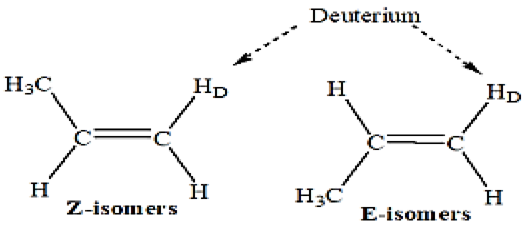


Z-But-2-ene-1,4-dioic acid
(Maleic acid)

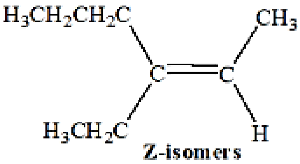


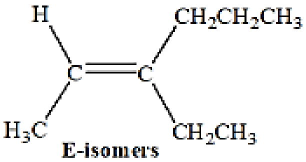
E-But-2-ene-1,4-dioic acid
(Fumaric acid)

Rule 2: If isotopes of same element are present, the higher priority is given to the isotope with higher atomic mass. E.g. the Deuterium isotope (H2 or D) has more priority than protium (H1 or H). The C13 isotope has more priority than C12.



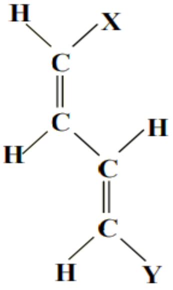
Rule 3: If the relative priority of two groups cannot be decided by Rule 1, it shall be determined by applying to the next atom or sequence of atoms in the group 'X'. e.g. for typing groupings in organic molecules where X is more than one atom .... X = -CH2CH2CH3 > -CH2CH3 > -CH3 > -H i.e. the longer the hydrocarbon carbon chain the higher its priority,

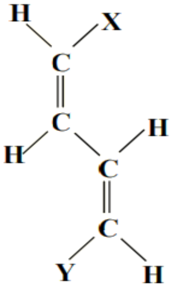

Z-isomers

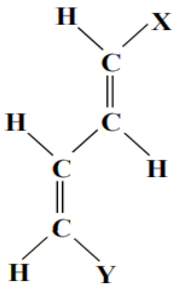

E-isomers

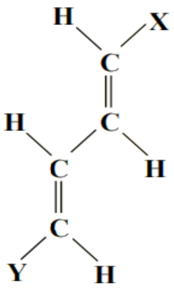
Number of Geometrical isomer of compounds containing two or more Double Bonds with Non-equivalent termini :-

Dienes in which the two termini are different (i.e. XHC=CH–CH=CHY), has four geometrical isomers .


Z,E, or *cis-trans*


Z,Z, or *cis-cis*


E,Z or *trans-cis*

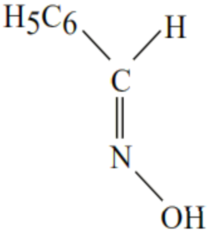

E,E or *trans-trans*

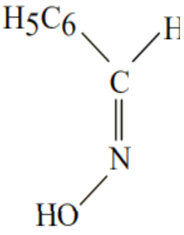
It means the number of geometrical isomers is 2 n where n is the number of double bonds.

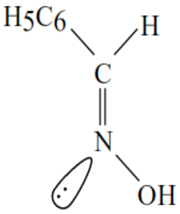
Geometric Isomerism of Oximes:-

The carbon and nitrogen atoms of oximes are sp2- hybridized, as in alkenes.

Thus, all groups in oximes lie in the same plane and hence they should also exhibit geometric isomerism if groups R and R 1 are different. Accordingly Beckmann (1889) observed that benzaldoxime existed in two isomeric forms and Hantzsh and Werner (1890) suggested that these oximes exist as the following two geometric isomers (I and II).


I


II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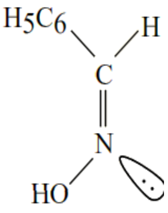
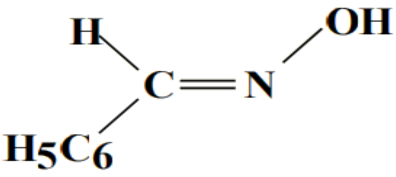
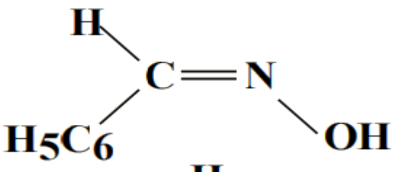

II

Nomenclature of Oximes :-

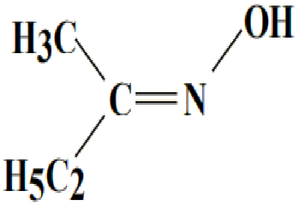
The prefixes syn and anti are used in different context for aldoximes and ketoximes**.**

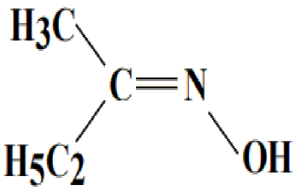
Aldoximes


I
syn-Benzaldoxime

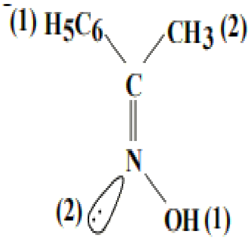

II
anti-Benzaldoxime

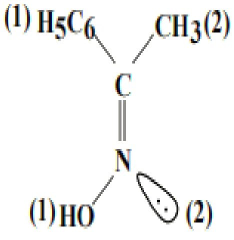
Ketoximes

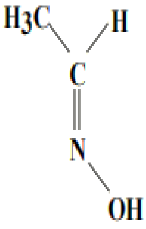

anti-Ethylmethylketoxime

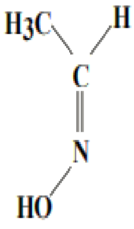

syn-Ethylmethylketoxime

As in the case of cis-trans isomerism, this nomenclature is ambiguous and often creates confusion. To avoid this, the system of E-Z nomenclature has been adopted. For fixing priority the lone pair of electrons on nitrogen is taken as group of lowest priority. Some examples are given below


E-Methylphenylketoxime


Z-Methylphenylketoxime

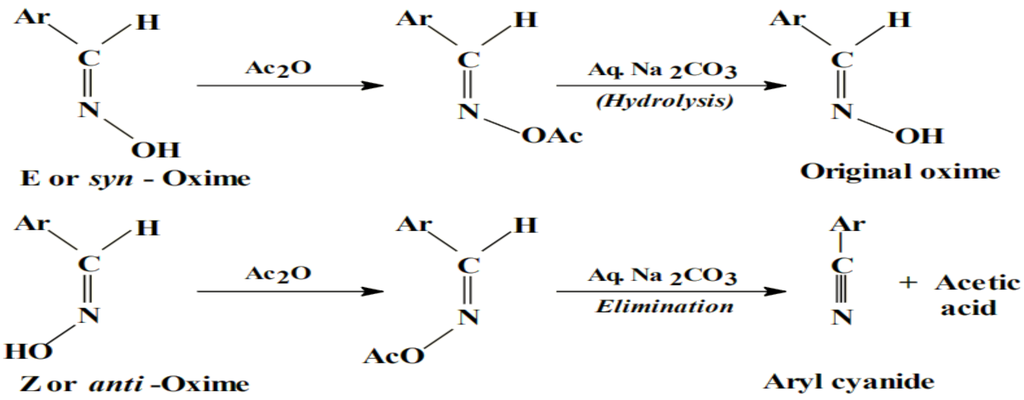

E-Acetaldoxime


Z-Acetaldoxime

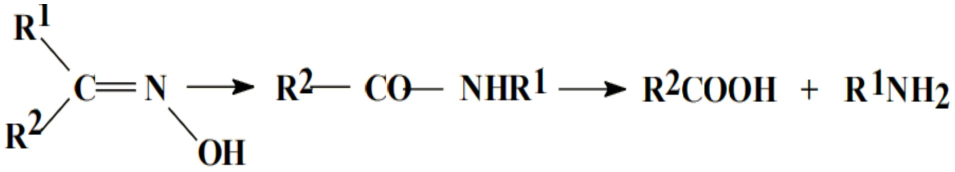
Determination of Configuration of Oximes:-

1. **Aldoximes-**: The acetyl derivative of one isomer regenerated the original oxime whereas that of the other isomer eliminated acetic acid by E2 mechanism to form aryl cyanide.

mechanism to form aryl cyanide.



2. Ketoximes:- The configuration of the geometric isomers of the unsymmetrical ketoximes are determined by Beckmann rearrangement which consists in treating ketoxime with acidic reagents such as PCI5 , H3PO4 , P2O5 , etc. when the oxime isomerizes to a substituted amide by migration of the group (R1 or R 2) which is anti to the hydroxyl group.

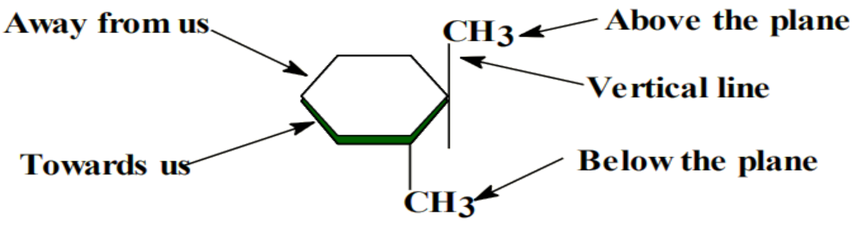


$$R^1R^2C{=}N{-}OH \longrightarrow R^2{-}CO{-}NHR^1 \longrightarrow R^2COOH + R^1NH_2$$

Determination of structure of amine formed in the above sequence of reactions plays a key role in deciding which group has migrated during Beckmann rearrangement.

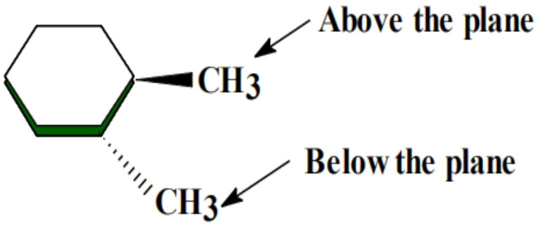
Geometric Isomerism in Alicyclic Compounds:-

Cyclic compounds such as the disubstituted derivatives of cyclopropane, cyclobutane, cyclopentane and cyclohexane can also show **cis-trans isomerism**, because the basic condition for such isomerism- that there should be sufficient hindrance to rotation about a linkage between atoms- is also satisfied in these systems. Atoms joined in a ring are not free to rotate around the sigma bond.



1,2-Dimethylcyclohexane

Sometimes, a broken wedge is used to indicate a group below the plane of the ring, and a solid line represent a group above the plane.



cis-1,4-dimethylcyclohexane

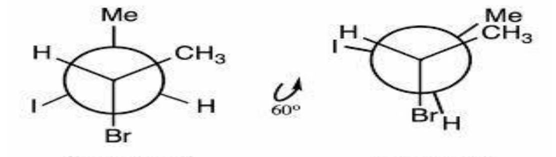
trans-1,4-dimethylcyclohexane

Conformational Isomerism In Alkanes:- In the organic chemistry, it is found that you can rotate a single bond of a molecule to change the arrangement of atoms, without changing the chemical formula of the compound.

Isomers of a compound can be created by different forms of rotation about one single bond. So the different arrangements of atoms due to such rotations of bonds are known as conformations.This phenomenon is called Conformational Isomerism.

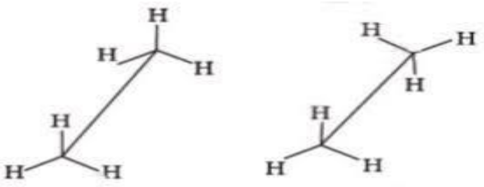
Representation of Conformation of Alkanes:-

1. Newman Projections:- This is one of the ways to represent conformations of alkanes. It visually represents the bonding of atoms from front to back. A Dot represents the first carbon atom (the one that is nearer). The further carbon atom is a circle. Lines show the hydrogen atoms bonded to each carbon atoms. This representation clearly indicates the dihedral angles.



Staggered Eclipsed

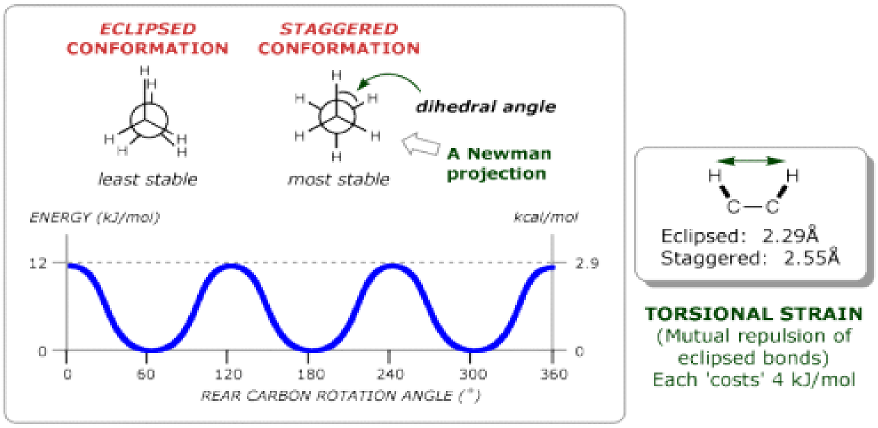
2. Sawhorse Projections: This represents the conformations of alkanes in form of a straight line. The first carbon is at the lower end of the line on the left side. And the second carbon is at the upper end of the diagram. Here, the lines attached to carbon atoms show hydrogen atoms.



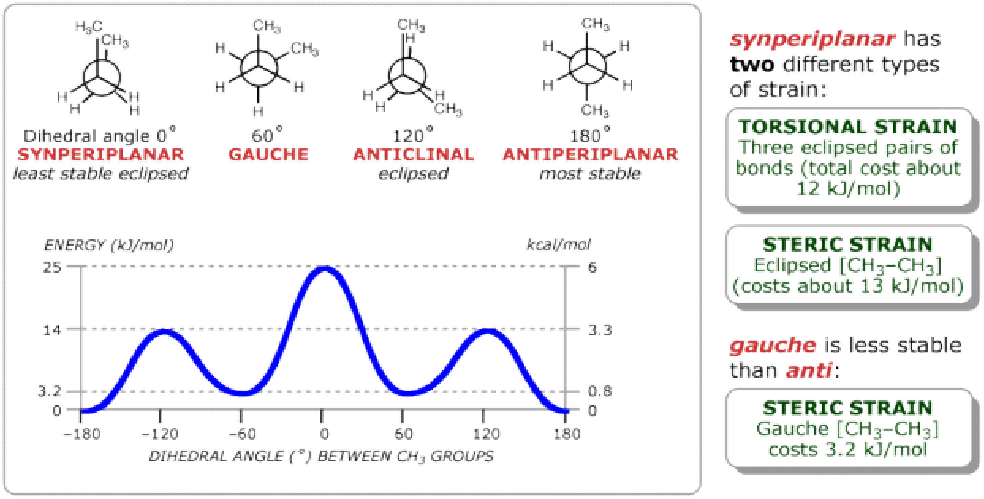
Eclipsed Staggered

Conformation in Ethane:- There is a 12 kJ/mol (2.9 kcal/mol) barrier to rotation in ethane. The most stable (low energy) conformation is the one in which all six C–H bonds are as far away from each other as possible (staggered when viewed end-on in a Newman projection). The least stable (high energy) conformation is the one in which the six carbon–hydrogen bonds are as close as possible (eclipsed in a Newman projection). All other conformations lie between these two limits. The barrier to rotation is the result of three equal C–H bond-eclipsing interactions, so we can assign a value of about 4.0 kJ/mol (1.0 kcal/mol) to each of these interactions. The corresponding energy in propane is 14 kJ/mol (3.4 kcal/mol).

The 12 kJ/mol of extra energy in the eclipsed conformation of ethane is called torsional strain. The barrier to rotation that results from this strain can be represented in a graph of potential energy versus degree of rotation in which the angle between C–H bonds on C-1 and C-2 (the dihedral angle) completes one revolution. Energy minima occur at staggered conformations, and energy maxima occur at eclipsed conformations. The torsional strain is thought to be due to the slight repulsion between electron clouds in the eclipsed bonds.



Conformations In n-Butane:- The conformational possibilities increase as alkanes become larger. A plot of potential energy against rotation about the C(2)–C(3) bond in butane is shown below. The lowest-energy arrangement, called the antiperiplanar (or anti) conformation, is the one in which the two large methyl groups are as far apart as possible. As rotation around the C(2)–C(3) bond occurs, another eclipsed conformation (anticlinal) is reached in which there are two Me–H interactions and one H–H interaction. If we assign the energy value (4 kJ/mol) for H–H eclipsing interactions that was previously derived from ethane, we can predict that each Me–H interaction in the anticlinal conformation costs about 5 kJ/mol.



synperiplanar has **two** different types of strain:

TORSIONAL STRAIN
Three eclipsed pairs of bonds (total cost about 12 kJ/mol)

STERIC STRAIN
Eclipsed [CH_3–CH_3] (costs about 13 kJ/mol)

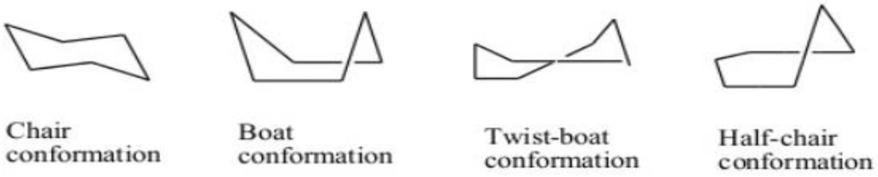
gauche is less stable than *anti*:

STERIC STRAIN
Gauche [CH_3–CH_3] costs 3.2 kJ/mol

As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are 60° apart (a gauche relationship). This lies 3.2 kJ/mol higher in energy than the anti-conformation even though it has no eclipsing interactions. This energy difference is due to the fact that the hydrogen atoms of the methyl groups are near each other in the gauche conformation, resulting in steric strain, which is the repulsive interaction that occurs when atoms would otherwise tend to occupy the same space.

As the dihedral angle between the methyl groups approaches 0°, an energy maximum is reached. The methyl groups are forced even closer together than in the gauche conformation, and both torsional strain and steric strain are present. A total strain energy of 25 kJ/mol has been estimated for this conformation, allowing us to calculate a value of 17 kJ/mol for the Me–Me eclipsing interaction. Completing the 360° rotation after the syn periplanar point produces the mirror images of what we've already seen; another gauche conformation, another eclipsed conformation and finally a return to the anti-conformation.

Conformation in Cyclohexane:- Cyclohexane has two non-planar puckered conformation and both are completely free from strain. These are called Chair Form and Boat Form because of their shape. There are so many examples of common cyclohexane conformations such as the **chair form, boat form, twist boat form, and half chair conformations**. The naming of the molecules is based on their own shape.



Chair conformation – most stable

In Half chair form has some **angle strain** and some **torsional strain**.

In the boat form has no significant angle strain and has the torsional strain. In this form hydrogen atoms are attached with the **Van Der Waals forces.** This interaction is known as **flagpole interactions**.

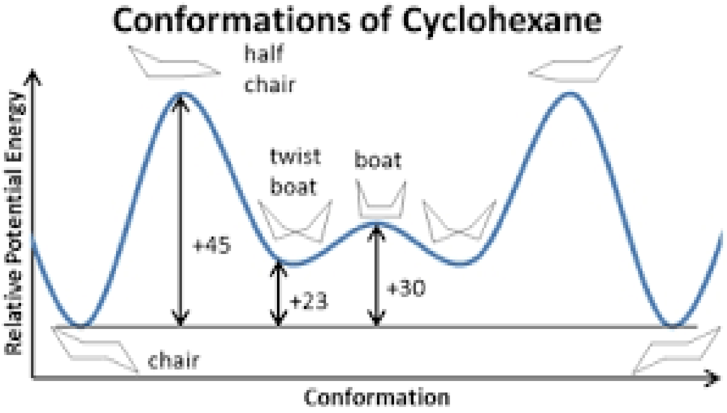
In twist boat is twisted in nature and it has a consolation **flagpole interaction**. Also, it has less angle strain and less torsional strain.

In chair form has **no angle strain** and here in the chair form all C - C bonds are staggered.

The conformations arise due to rotation around carbon-carbon bonds, but the chair form and the boat form are the two extreme cases.

Energy Levels of the Cyclohexane Conformers are:

1. Half Chair Form (Potential Energy=45 kcal/mol)
2. Boat Form (Potential Energy =30 kcal/mol)
3. Twist Boat (Potential Energy =23 kcal/mol)
4. Chair Form (Potential Energy =0 kcal/mol)

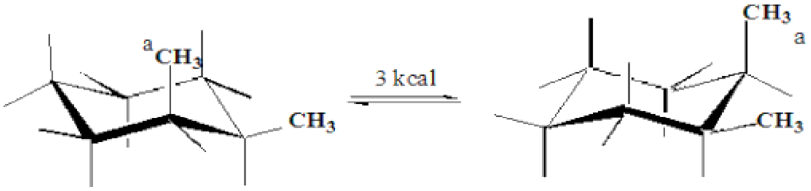


Stability of Cyclohexane Conformers is:

Half Chair < Boat Form < Twist Boat Form< Chair Form.

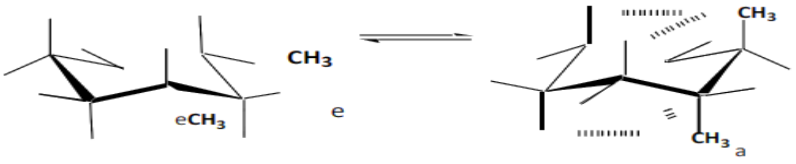
Conformations of Disubstituted Cyclohexane:- When the cyclohexane ring contains substituents, the chair forms that result from the conformational flipping can be of different energy. The more stable conformational isomer, also called a conformer, is the one usually with the least crowding of substituents. Equatorial substituents are the least crowded and the more stable structures are the ones that contain more equatorial substituents.

Example, Cis-1,2-Dimethylcyclohexane can inter convert to another conformation, but the new conformation is identical with the starting structure because one methyl is axial while the other is equatorial in each structure. Thus there is no energy difference.



cis-1,2-dimethylcyclohexane

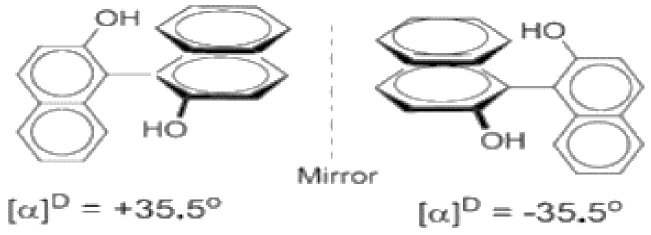
In trans-1,2-dimethycyclohexane one conformation exist with both methyl equatorial while the other conformer has both methyl axial. The structure with two equatorial methyl is much more stable and represents the major isomer in the equilibrium. The reason for instability in the di axial isomer is that the methyl become crowded by the hydrogens in other axial positions, as shown by the dotted lines in the di axial isomer. The crowding is termed a 1,3-diaxial interaction.



95 % trans-1,2-dimethylcyclohexane 5 %

Stereoisomerism in biphenyl compounds (Atropisomerism):- Biphenyls are compounds whereby a phenyl ring is connected to another through a central σ bond. In unsubstituted biphenyl, there is sufficient amount of freedom of rotation around the central single bond to allow for free interconversion between the various conformers or rotamers so that the various rotamers cannot exist independently.

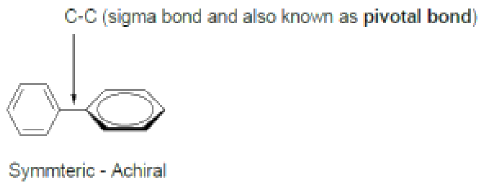
But biphenyls with large substituents at the ortho positions on either side of the central σ bond experience restricted rotation along this bond due to steric hindrance. If the substituents are different, a chiral molecule existing as a pair of enantiomers called atropisomers. Polynuclear aromatic systems such as binol also exist asenantiomers.



Atrop isomerism are stereoisomers as a result of restricted rotation about a single bond.

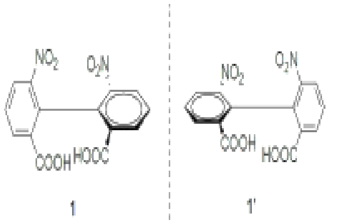
Atropisomers are stereoisomers resulting from hindered rotation about single bonds where the steric strain barrier to rotation is high enough to allow for the isolation of the conformers. Bulky substituents or strained rings may enhance the barrier to rotation between two distinct conformations to such an extent as to allow observation of atropisomers.

Atrop isomerism is also called **axial chirality** and the chirality is not simply a center or a plane but an axis.

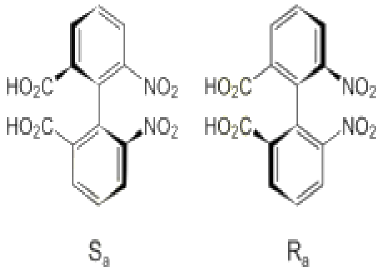


Structure of biphenyl

Biphenyl substituted on ortho position, which contains a chiral axis along the biphenyl linkage. The biphenyl rings are perpendicular to each other in order to minimize steric clashes between the four ortho substituents meaning that rotation about the biphenyl bond through pivotal bond is restricted.



Enantiomers of the 6,6'-dinitrobiphenyl-2,2'-dicarboxylic acid



Requirements for Atropisomerism:

1. A rotationally stable axis
2. Presence of different substituents on both sides of the axis
3. The configurational stability of axially chiral bi aryl compounds is mainly determined by three following factors:

(i) The combined steric demand of the substituent in the combined steric demand of the substituents in the proximity of the axis.

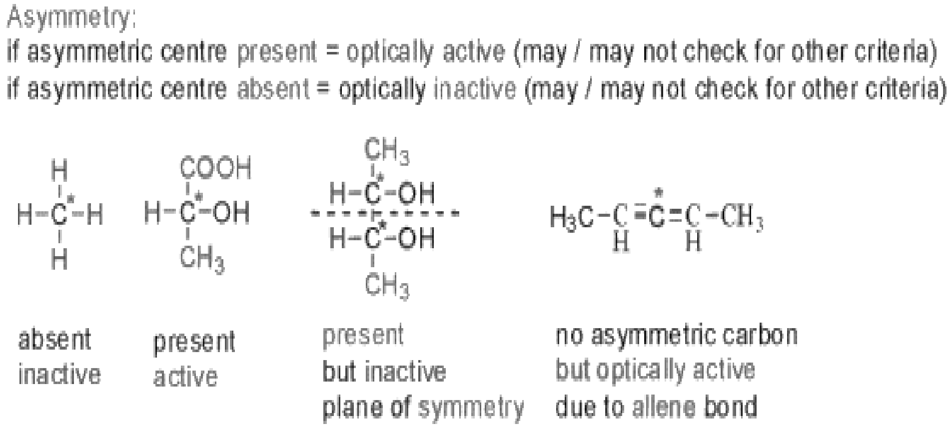
(ii) The existence, length and rigidity of bridges.

(iii) Atropisomerisation mechanism different from a merely physical rotation about the axis, e.g. photo chemically or chemically induced processes.

Conditions For Optical Activity:-

Following conditions must possess compound

1. To exhibit optical activity molecule must possess asymmetric carbon: Asymmetric carbon compounds are optically active. But, presence of asymmetric is not only the requirement.



Asymmetry:

if asymmetric centre present = optically active (may / may not check for other criteria)

if asymmetric centre absent = optically inactive (may / may not check for other criteria)

2) To exhibit optical activity molecule must not have the symmetry elements,

(a) plane of symmetry

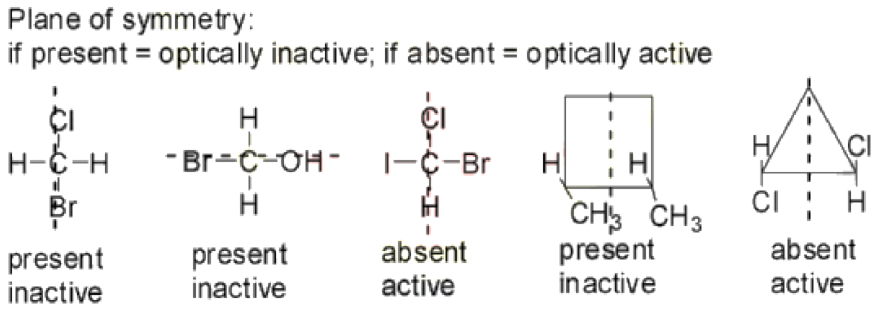
(b) center of symmetry

(c) n-fold alternating access of symmetry.

If these three are absent then only the compounds exhibit optical activity

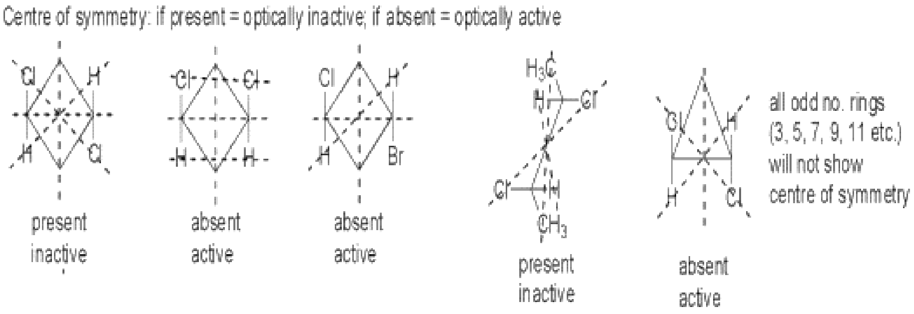
A. Plane of symmetry:

A plane which bisects the molecules into two mirror images are called plane of symmetry. If the plane of symmetry is present then the molecule is optically inactive, if absent then optically active.


Plane of symmetry:
if present = optically inactive; if absent = optically active

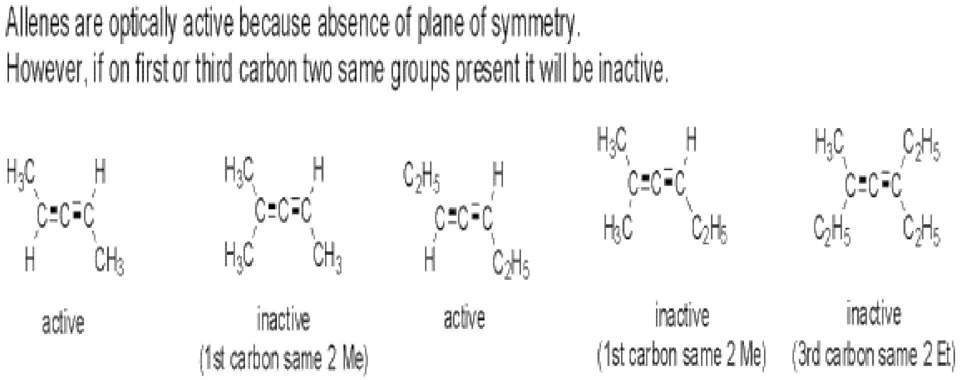
B. Centre of symmetry:

If all the lines two identical groups pass through a single point or a central point is called centre of symmetry.


Centre of symmetry: if present = optically inactive; if absent = optically active

C. n-Fold alternating Access of Symmetry:

If a rotation by 360º/n degrees (n = 1, 2, 3, …) followed by reflection in plane perpendicular to the access taken results in identical molecule the compound said to be possess n-fold alternating access of symmetry. If plane of symmetry or center of symmetry is present then n-fold alternative access of symmetry is present. If plane of symmetry or centers of symmetry are absent then n-fold alternating access of symmetry will be absent. If the n-fold alternating access of symmetry present then the molecule is optically inactive, if absent then optically active.

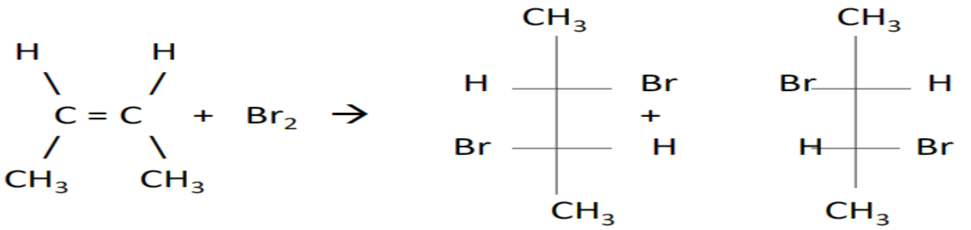


Allenes are optically active because absence of plane of symmetry.
However, if on first or third carbon two same groups present it will be inactive.

Stereospecific reaction:-

A reaction in which a particular stereisomers react to give one specific stereoisomer of the product is called a **stereospecific reaction**. Such a reaction is said to display stereospecificity. A stereospecific reaction gives different stereoisomers of the starting material.

For example: Addition of bromine to cis-2-butene gives racemic 2-3-dibromobutane while the trans isomer give meso 2-3-dibromobutane. This reaction is stereospecific because different stereoisomer gives different stereoisomer.



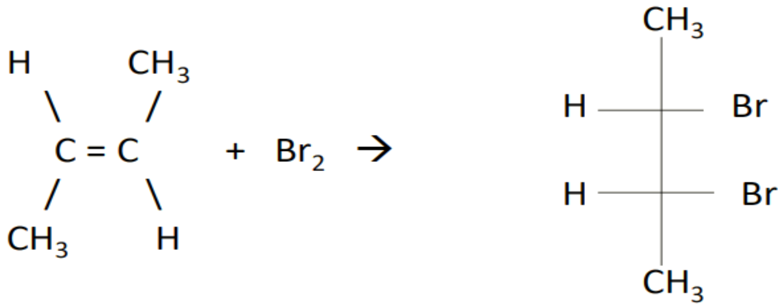
cis-2-butene

(*S,S*)- & (*R,R*)-2,3-dibromobutane
racemic modification only products

A reaction in which stereochemically different molecules react differently is called a stereospecific reaction. In this case the cis- and transstereoisomers give different product.

Stereoselective reaction:- A reaction in which one stereoisomer is formed predominantly or exesively out of several stereoisomers possiblilities is called a stereoselective reaction. Such a reaction is said to display stereoselectivity. In this one stereoisomer is formed more rapidly thus resulting in a selective reaction .

The stereoelectronic requirement of the mechanism of a stereoselective reaction offers alternatively parts so that the reaction proceeds either via the most favourable path or via the path which gives the most stable stereoisomers as the major product

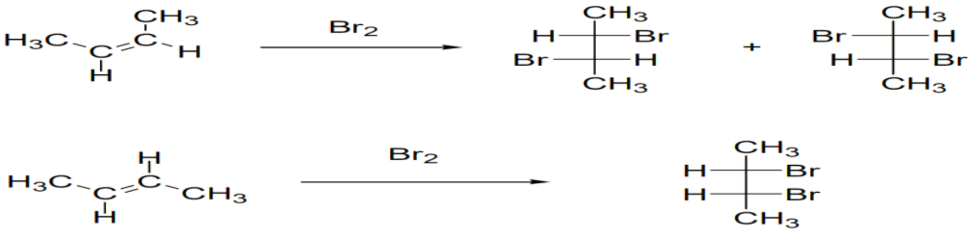


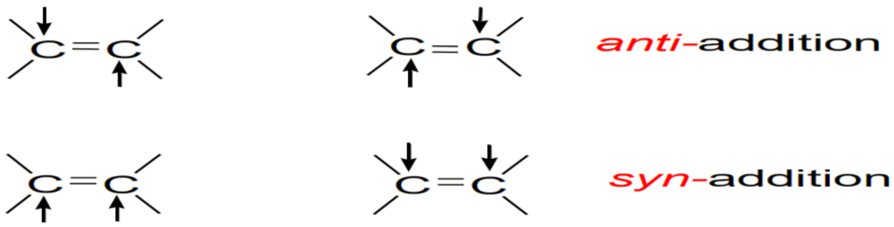
trans-2-butene *meso*-2,3-dibromobutane

only product

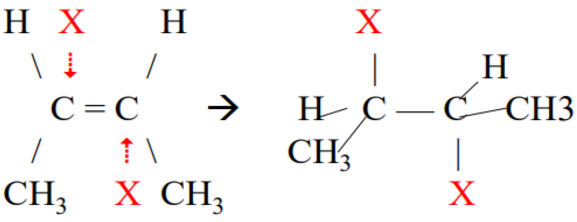
A reaction that yields predominately one stereoisomer (or one pair of enantiomers) of several diastereomers is called a stereoselective reaction. In this case the meso product is produced and not the other two diastereomers.

The fact that the addition of halogens to alkenes is both stereoselective and stereospecific gives us additional information about the stereochemistry of the addition and the mechanism for the reaction.



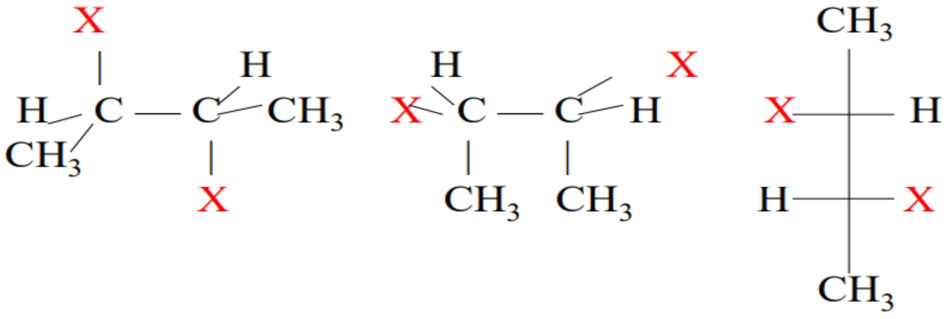


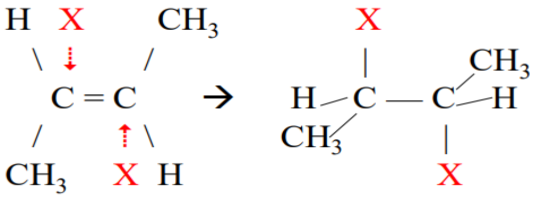
Is the addition of Br2 syn or anti?



anti-addition of X_2 to the *cis*-isomer

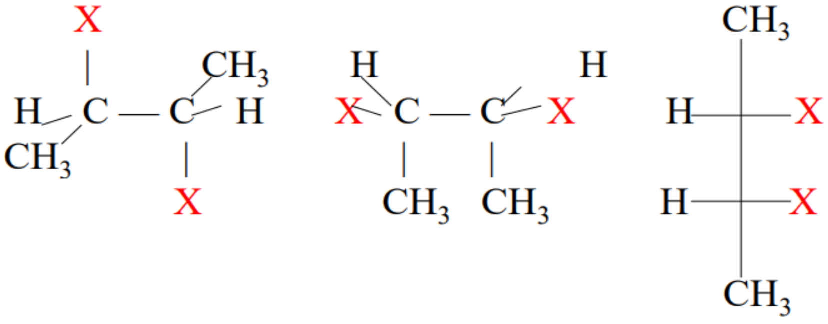
Note: must rotate about C-C to get to the Fischer projection!

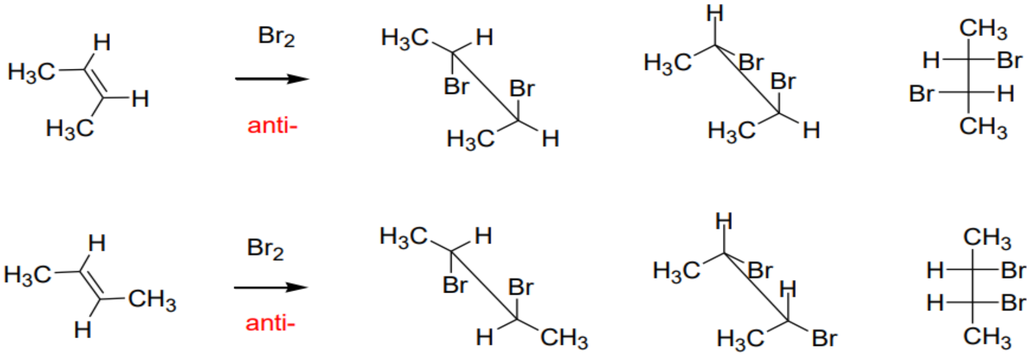




anti-addition of X_2 to the *trans*-isomer

Note: must rotate about C-C to get to the Fischer projection!





rotate about C2-C3 to get to Fischer projection!

Comparison between stereoselective and stereospecific reaction:-

1. Each stereoisomeric reactant produces a different stereoisomeric product or a different set of stereoisomeric products.	1. A single reactant gives two or more steroisomeric products, and one product is more prominent than the other product or products.
2. All stereospecific reactions are essentially stereoselective.	2. All stereoselective reactions are not essentially stereospecific.

Questions Carrying 2 Marks

1. Define Conformations.
2. Draw conformations of n- butane.
3. Draw chair and boat Forms of cyclohexane.
4. Which type of compounds follow E and Z system of nomenclature.
5. Define Cis and Trans isomers.
6. Define Geometrical Isomerism.
7. Name the methods for determination of configuration of Geometrical Isomers.
8. Will trichloroethane exhibit geometrical isomerism? Give reasons for your answer.
9. Write basic conditions for geometrical isomerism.
10. Give reasons for exhibit of geometrical isomerism.
11. Define stereoselective and stereospecific reactions.

Questions Carrying 5 and 10 Marks

1. Write short note on: E and Z method of configuration determination of geometrical Isomers.
2. Draw the various conformations of cyclohexane and compare their stability.
3. State and Explain the necessary and sufficient conditions for a compound to show geometrical isomers.
4. Give any two methods by which geometrical isomers can be distinguished.
5. Difference between the terms configuration and conformations.
6. What do you understand by chair and boat conformations? Why is chair conformation of cyclohexane mora stable than boat conformations?
7. What is conformational Analysis? Draw the various conformations of n-butane and represent them on a potential energy diagram.
8. Write a note on conformation of ethane.
9. Why the equatorial conformation of methyl cyclohexane is more stable than the corresponding axial conformations?
10. Difference between the absolute and relative configuration.
11. .Explain stereoselective and stereospecific reactions with suitable examples.