ORGANIC
CHEMISTRY - III

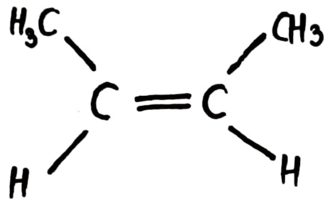
UNIT 2 NOTES

GEOMETRICAL ISOMERISM

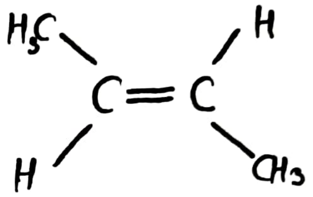
Nomenclature of geometrical isomers (Cis Trans, EZ, Syn Anti systems)
Methods of determination of configuration of geometrical isomers.
Conformational isomerism in Ethane, n-Butane and Cyclohexane. Stereo isomerism in biphenyl compounds (Atropisomerism) and conditions for optical activity.
Stereospecific and stereoselective reactions

GEOMETRICAL ISOMERISM

The compounds having the same molecular formula and connectivity of atoms but differ in the spatial arrangement of groups around a rigid structure, such as double bond or ring system are known as Geometrical Isomers & the phenomenon is known as Geometrical Isomerism.



Cis-2-butene



trans-2-butene

CONDITIONS FOR GEOMETRICAL ISOMERISM

- The rotation should be restricted around double bonds or cyclic compounds.
- For a molecule to exhibit geometrical isomerism, each carbon of the C=C double bond must have two different groups attached.

NOMENCLATURE OF GEOMETRICAL ISOMERISM

Following nomenclature system are used for naming of Geometrical Isomerism :

① cis & trans nomenclature
② E & Z nomenclature
③ Syn & Anti nomenclature

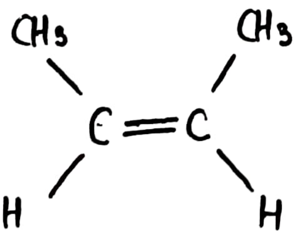
① cis & trans Nomenclature

cis- trans nomenclature is used to describe the spatial arrangement of atoms or groups around a double bond or within a cyclic system.

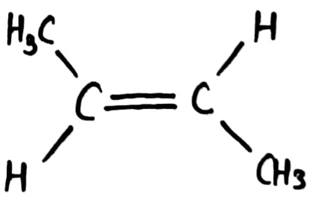
ⓐ cis- trans in Alkenes

- cis - Isomer : The same or similar groups are on the same side of the double bond.

- trans- Isomer : The same or similar groups are on opposite side of the double bond.



cis - 2 - butene



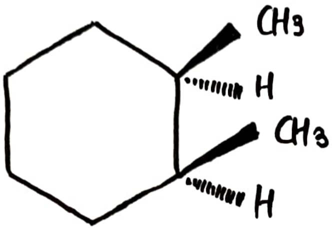
trans - 2 - butene

- In cis - ~~But~~-2- butene both methyl groups are on same side.
- In trans - 2- butene , the methyl groups are on opposite side.

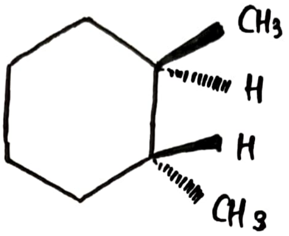
ⓑ cis- trans in Cyclic compounds

Due to rigidity of ring, cis- trans isomerism also applies to substituted cycloalkanes.

- cis- Isomer : The substituents are on the same faces of the ring.
- trans Isomer : The substituents are on opposite faces of the ring.



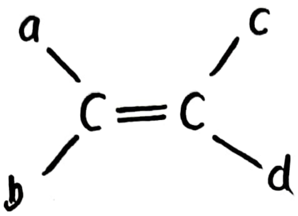
cis- 1,2 dimethylcyclohexane



trans- 1,2 dimethylcyclohexane

② E & Z NOMENCLATURE

- The E-Z system is a precise method for naming geometrical isomers of alkenes when 4 different groups are attached to the double bonded carbons
- This system follow Cahn-Ingold-Prelog (CIP) priority rules to determine the relative position of substituents.

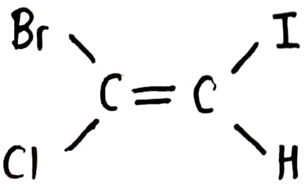


Steps to Assign E-Z Configuration

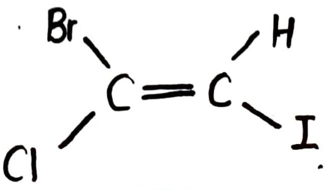
- Identify the C=C double bond
- Now assign priorities to each group on the double-bonded carbons by using CIP rules
- The group with higher atomic no. gets higher priority.
- If there is a tie, compare the next set of atoms in the chain.
- Now :

- Z-Isomer ("Zusammen" = Together) : The higher priority groups are on the same side of the double bond.

- E-Isomer ("Entgegen" = Opposite) : The higher priority groups are on the opposite sides of the double bond.



Z-form

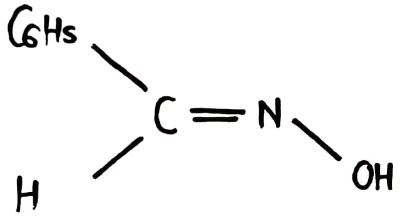


E-form

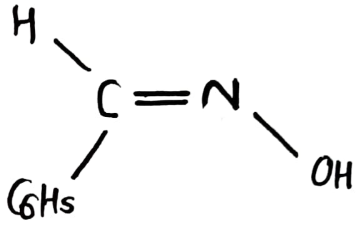
③ SYN- ANTI SYSTEM OF NOMENCLATURE.

- Syn- Anti system of nomenclature is used for compounds which have $C=N$ or $N=N$ double bonds.
- The nomenclature is mainly used in the case of :

- Oximes ($C=NOH$ compounds)
- & Aldoximes ($R-CH=NOH$) , R can be alkyl or aryl group .



Syn- benzaldehyde



Anti- benzaldehyde

- In the above example , the isomer is named as syn, when H atom and OH group are on same side and anti when they are on opposite sides.

METHOD OF DETERMINATION OF CONFIGURATION OF GEOMETRICAL ISOMERISM

The configuration of Geometrical Isomerism can be determined by using various :

① Physical Methods

② Chemical Methods

① PHYSICAL METHODS

ⓐ Melting & Boiling Points

- Cis- Isomers : Often have lower melting points & higher boiling points due to polarity. e.g. Cis-2-butene : BP ~ 4°C.
- Trans- Isomers : They are usually less polar, have higher melting points and lower boiling points. e.g. trans-2-butene ~ 1°C.

ⓑ Dipole Moment Measurment

- Cis Isomer : They usually have a net dipole moment, making them more polar.
  e.g. : cis 1,2-dichloroethane : Dipole Moment ≈ 1.9 D
- Trans Isomer : Dipoles often cancel out, hence they are usually non-polar or less polar
  e.g. : trans-1,2-dichloroethane : Dipole Moment ≈ 0D

© Solubility

- Cis isomer are typically more soluble than their matching trans isomers .
- Maleic acid = 79 g/ 100 ml (cis form)
- Fumaric Acid = 0.7g / 100ml (trans form)

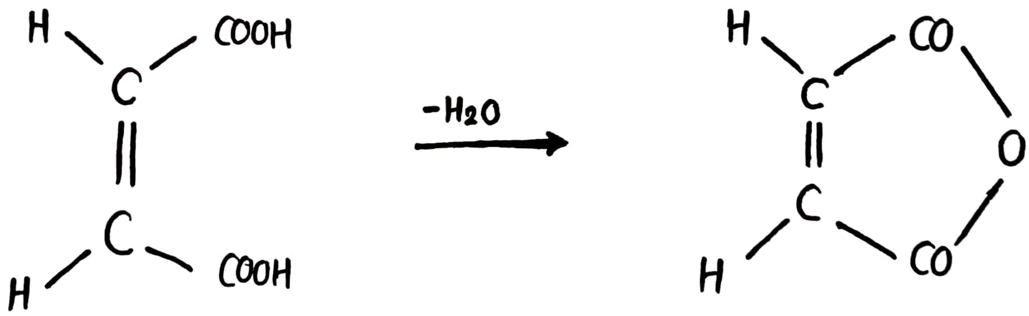
② CHEMICAL METHODS

ⓐ Selective Reactions with reagents

- cis & trans isomers react differently with certain reagents.
- cis- alkenes generally react faster in halogenation due to their closer groups

ⓑ Cyclization or Ring formation Reactions

- cis- isomers easily undergone cyclization reaction compare to trans - isomers because the two reactive groups are on same side & can easily come close together.

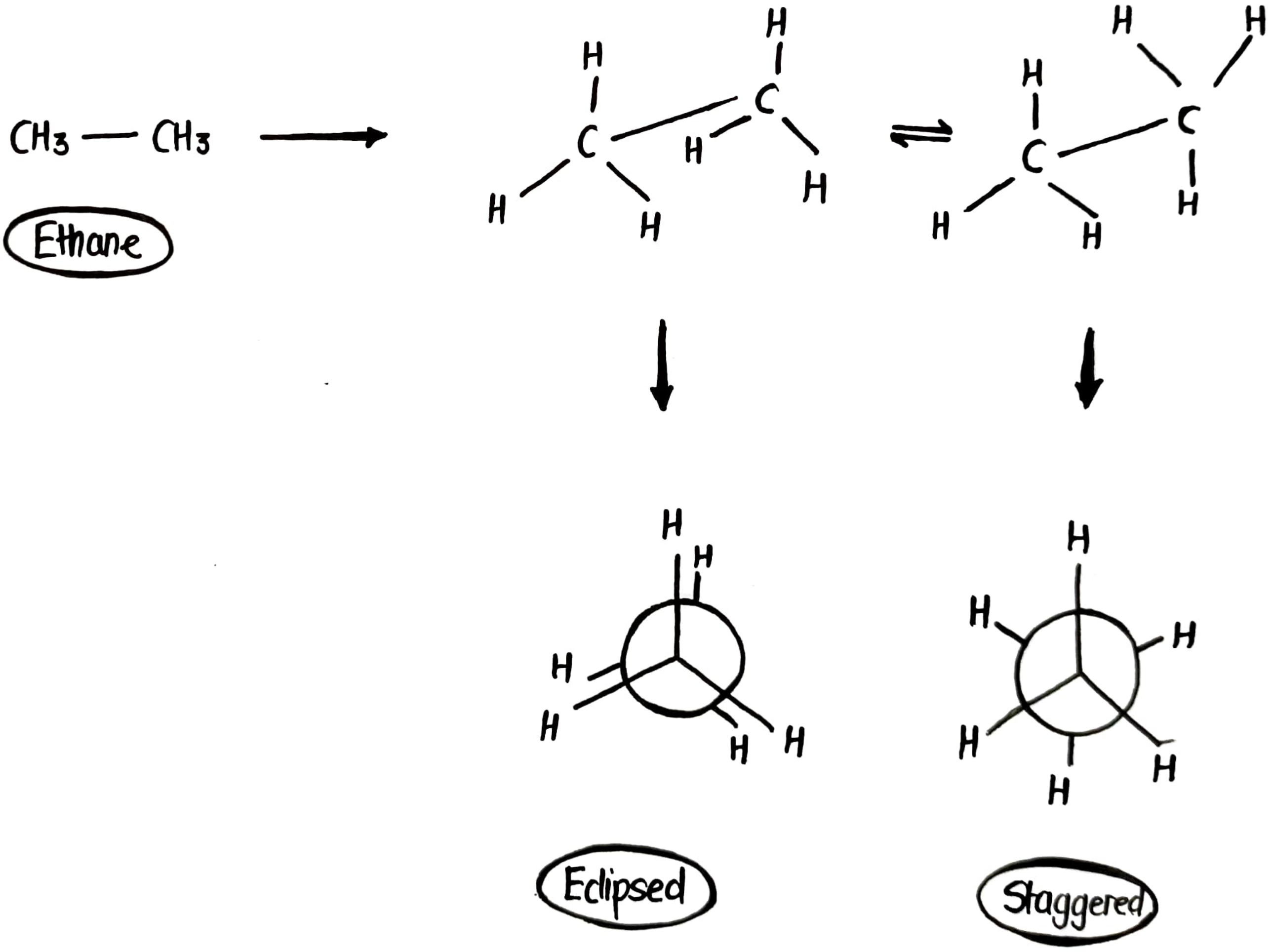


Maleic Acid

Maleic Anhydride

CONFORMATIONAL ISOMERISM

- Conformational Isomerism (also known as Rotational Isomerism) is a type of Stereoisomerism in which molecules with the same molecular formula and connectivity differ only by rotation around a single bond.
- Conformational Isomers are Interconvertible without breaking any bond.
- The most common example is Ethane which has staggered and eclipsed conformations.



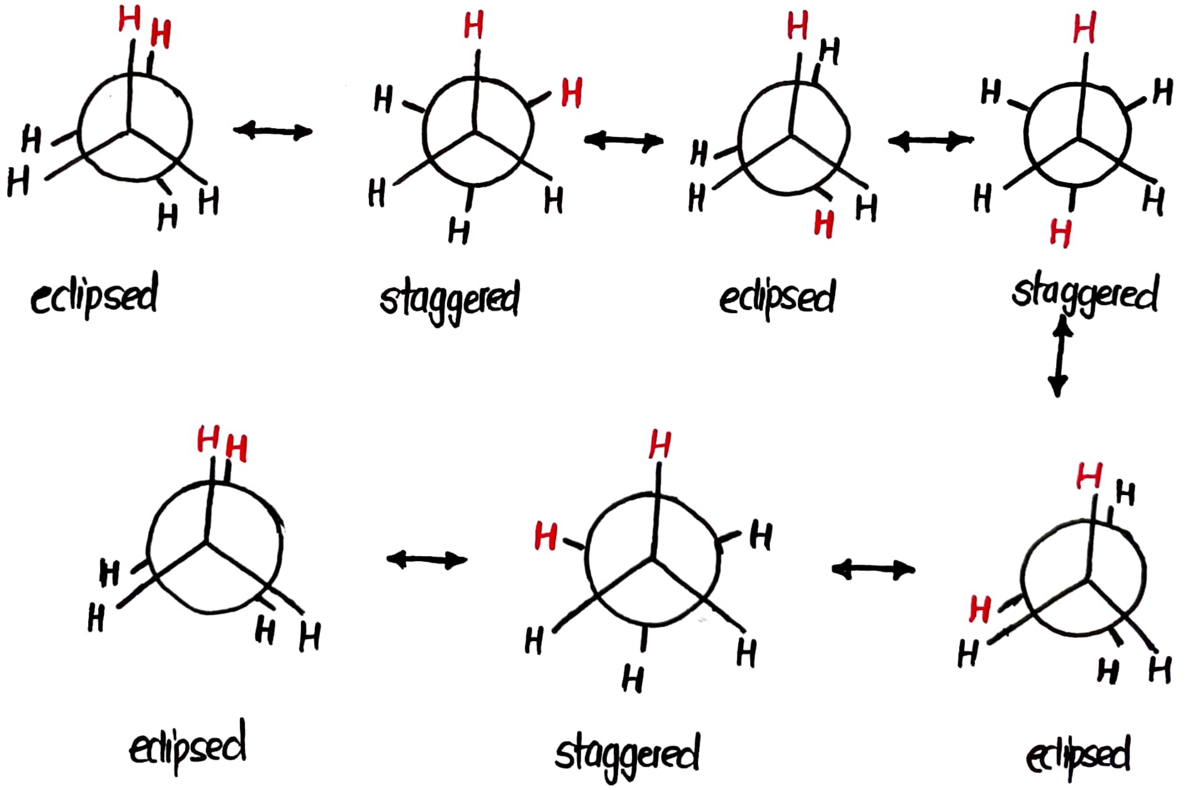
① CONFORMATIONAL ISOMERISM IN ETHANE

Conformational Isomerism in Ethane refers to the different spatial arrangements of the atoms in Ethane molecule (C_2H_6) that result from rotation around the carbon - carbon ~~double bond~~ single bond.

KEY POINTS

- In Ethane, the two carbon atoms are connected by σ bond, which allows free rotation.
- As one methyl group (CH_3) rotates relative to the other, various conformations are formed.
- They are of mainly two types :

① Staggered Conformation
② Eclipsed Conformation

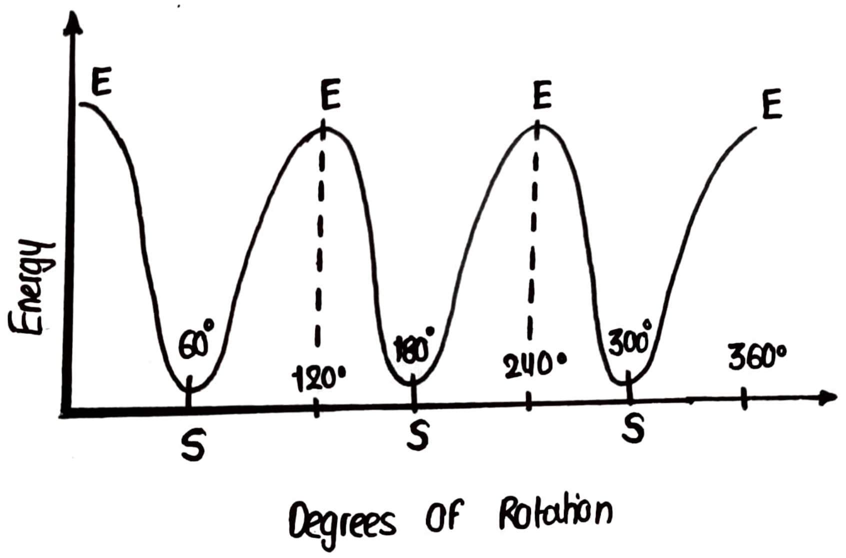


ⓐ Staggered Conformation

- Staggered conformation in ethane is when the hydrogen atoms on the two carbon atoms are as far apart as possible
- It is the most stable form.

ⓑ Eclipsed Conformation

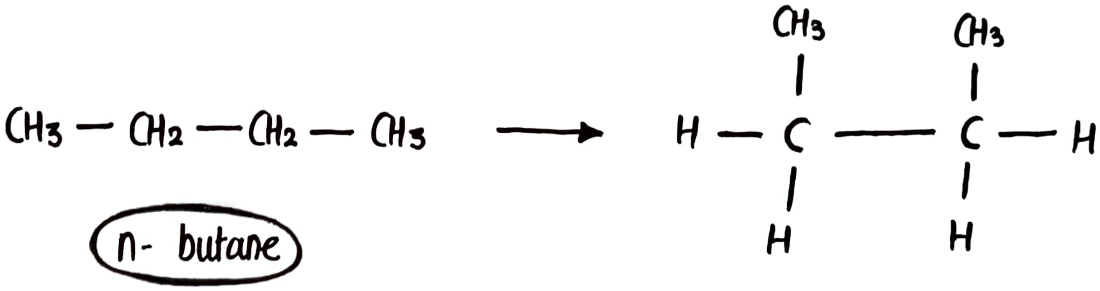
- Eclipsed conformation is when the hydrogen atoms on the two carbon atoms are directly in line with each other.
- It is less stable due to repulsion.



- Eclipsed Conformations has higher energy
- Staggered Conformations has lower energy

② CONFORMATIONAL ISOMERISM IN n- BUTANE

- Conformational Isomerism in n- butane refers to the different spatial arrangements of its atoms that result from the rotation around the central carbon- carbon single bond ($C_2 - C_3$).
- n- butane has the structure : $CH_3 - CH_2 - CH_2 - CH_3$
- Rotation around $C_2 - C_3$ bond creates various conformations



$CH_3 - CH_2 - CH_2 - CH_3 \longrightarrow H - \underset{H}{\overset{CH_3}{C}} - \underset{H}{\overset{CH_3}{C}} - H$

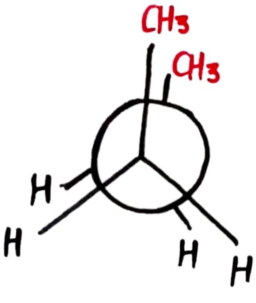
n- butane

The main conformations are :

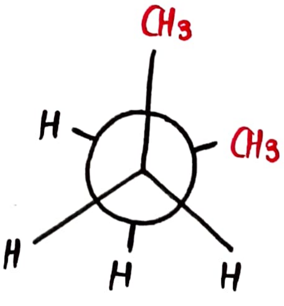
ⓐ Anti conformation

ⓑ Gauche confirmation

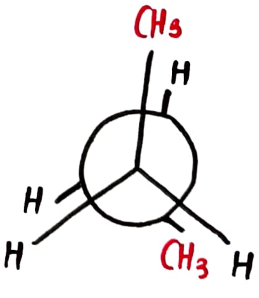
ⓒ Eclipsed Confiromation



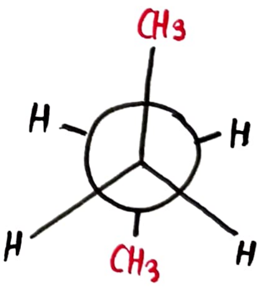
Fully Eclipsed
(eclipsed)
θ = 0°



Gauche
(staggered)
θ = 60°



Partially Eclipsed
(eclipsed)
θ = 120°



Anti
(staggered)
θ = 180°

ⓐ Anti- Conformation

- The two methyl (-CH_3) groups are positioned opposite to each other.
- This is the most stable conformation.

ⓑ Gauche Conformation

- The two methyl groups are 60° apart.
- This conformation is less stable than anti- conformation.

ⓒ Eclipsed Conformation

- In this methyl groups align directly behind each other (0° or 120°)
- It is of two types :

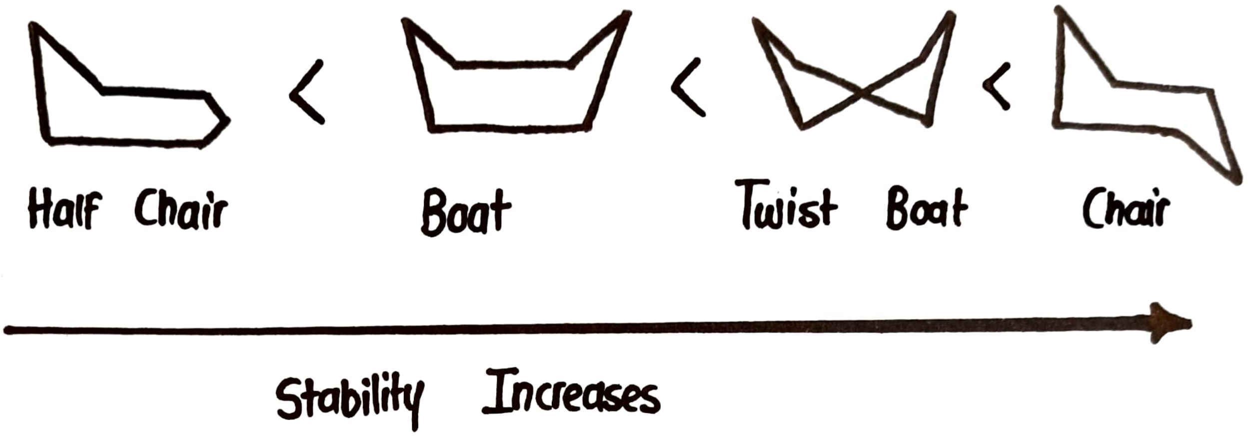
① Partially Eclipsed : 120°
② Fully Eclipsed : 0° (least stable)

ENERGY PROFILE

Lowest : Anti - Conformation
Highest : Fully Eclipsed Conformation

③ CONFORMATIONAL ISOMERISM IN CYCLOHEXANE

Conformational Isomerism in cyclohexane refers to different shapes that cyclohexane can adopt due to rotation of its single bonds. These conformations helps the molecule to avoid strain & stay stable.



① Chair Conformation

- It looks like reclining chair.
- There is no angle strain in this form.
- It is most stable & common form.

② Boat Conformation

- It looks like a boat
- It is less stable form & having higher energy.

③ Twist Boat Conformation

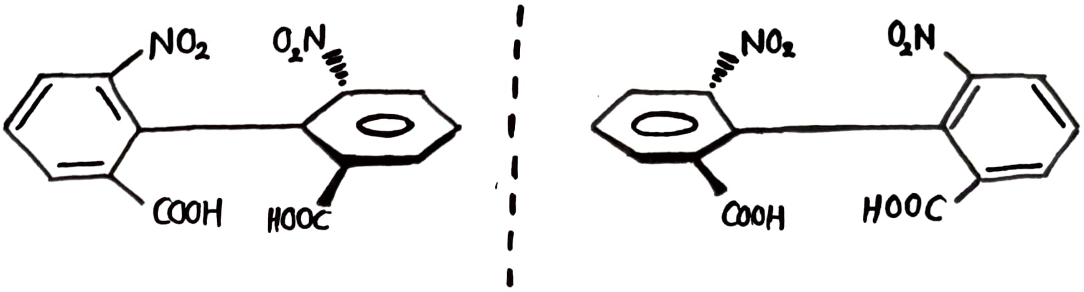
- It is a twisted version of boat form.
- It is slightly more stable than boat form.

④ Half Chair Conformation

- It is the least stable conformation of cyclohexane.
- It quickly converts into either a chair or boat form.

STEREOISOMERISM IN BIPHENYL COMPOUNDS

Stereoisomerism in Biphenyl compounds occurs when two benzene rings are connected by a single bond & certain conditions prevent them from rotating freely around that bond.



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

KEY POINTS

① Restricted Rotation

- The C-C bond in biphenyl cannot rotate freely due to the presence of large groups (like $-NO_2$, $-CH_3$, $-Br$) at the ortho positions of both rings.

② Atropoisomerism

- When rotation is restricted, the biphenyl can exist as non-superimposable mirror images (enantiomers), even though there are no chiral centres.
- This is a type of Atropoisomerism, a form of stereoisomers.

CONDITIONS FOR STEREOISOMERISM

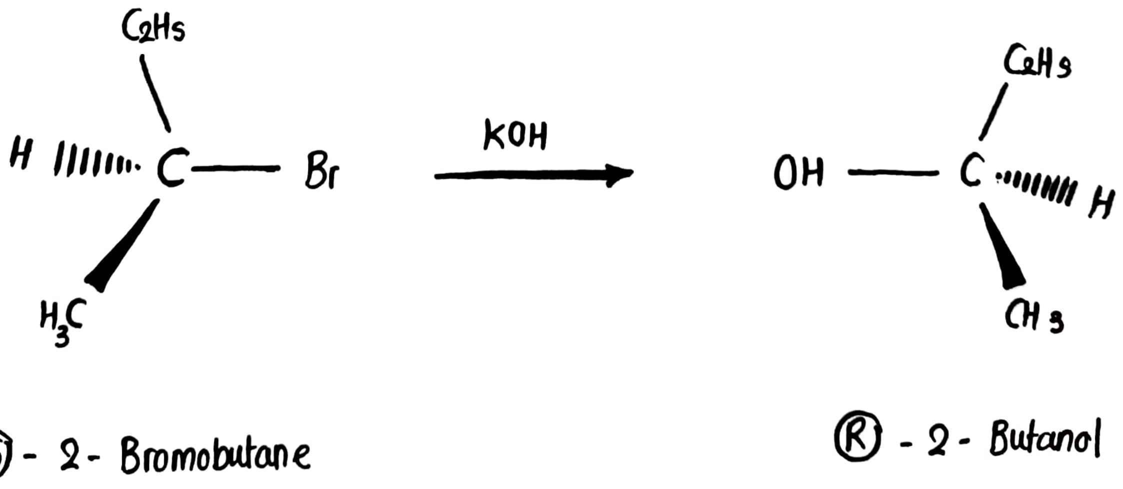
- Bulky substituents at ortho positions on both rings.
- Restricted rotation around C–C bond.
- Non-planer arrangement of rings.

STEREOSPECIFIC REACTIONS

- A Stereospecific Reactions is a chemical reaction where the stereochemistry of starting material (reactant) directly determines the stereochemistry of the product.
- Different stereoisomers of the starting product will give different stereoisomers of end product.
- No other stereoisomers are formed as byproducts from a single stereoisomeric reactant
- The reaction is 100% selective for a particular stereoisomer.

Example

SN2 Reactions :
- These reactions always proceed with inversion of configuration at the carbon centre undergoing nucleophilic attack.
- If you start with (R) enantiomer, you will get (S) enantiomer & vice versa.

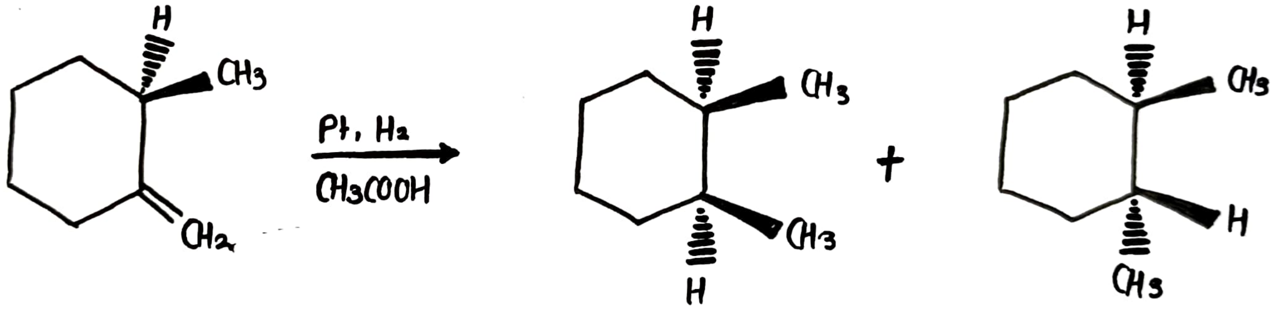


STEREOSELECTIVE REACTIONS

- A Stereoselective reaction is a reaction in which more than 1 stereoisomeric product is possible, but the reaction favous the formation of one over the others.
- In other words, the reaction can give multiple stereoisomers, but one is formed more than the other.

Example

In the hydrogenation of an ~~alke~~ cycloalkane, both cis & trans product might be possible. but the reaction can be selective for Cis over trans form.



Cis (68%)   Trans (32%)