

Chapter-4
Cycloalkanes, cycloalkenes & Dienes

B. Sc I Year (Semester-I)

Presented by

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Vice Principal &

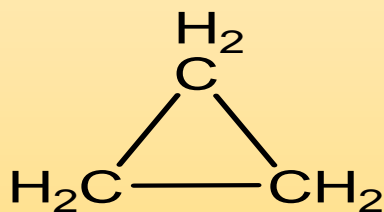
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A] Cycloalkane

- Cyclic compounds containing saturated hydrocarbons are called as cycloalkanes.
- They are also called as alicyclic compounds.
- The general molecular formula of cycloalkane is $(\text{CH}_2)_n$
- where $n = 3, 4, 5 \dots$

■ Ex.



IUPAC Nomenclature of Cycloalkanes

Compound



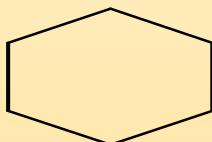
Cyclopropane



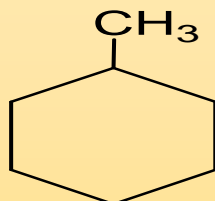
Cyclobutane



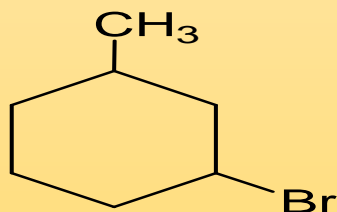
Cyclopentane



Cyclohexane



methyl cyclohexane

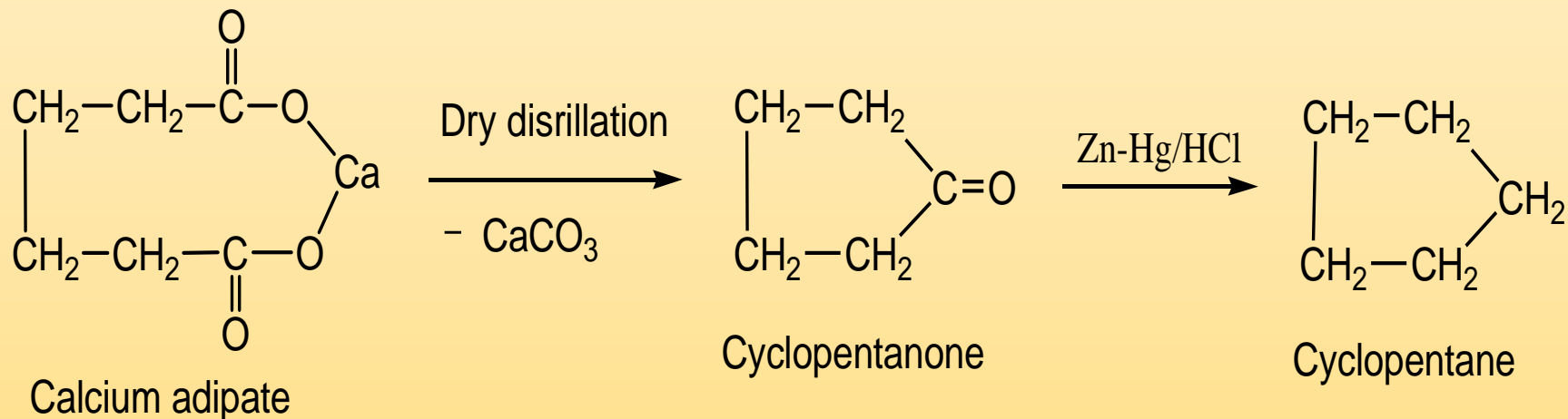


1-bromo-3-methyl cyclohexane

Preparation methods of Cycloalkanes

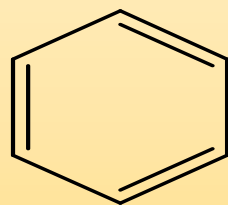
a) From Adipic acid :

- Calcium salt of adipic acid (calcium adipate) on dry distillation gives cyclopentanone. Which on clemenson reduction gives cyclopentane.



b) From Aromatic hydrocarbons :

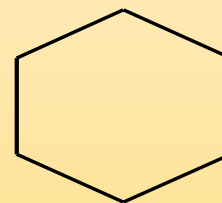
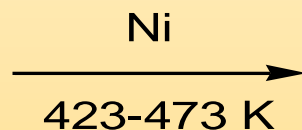
- Benzene on reduction with H_2/Ni catalyst at 423-473 K temperature to give cyclohexane.



Benzene

+

3H_2

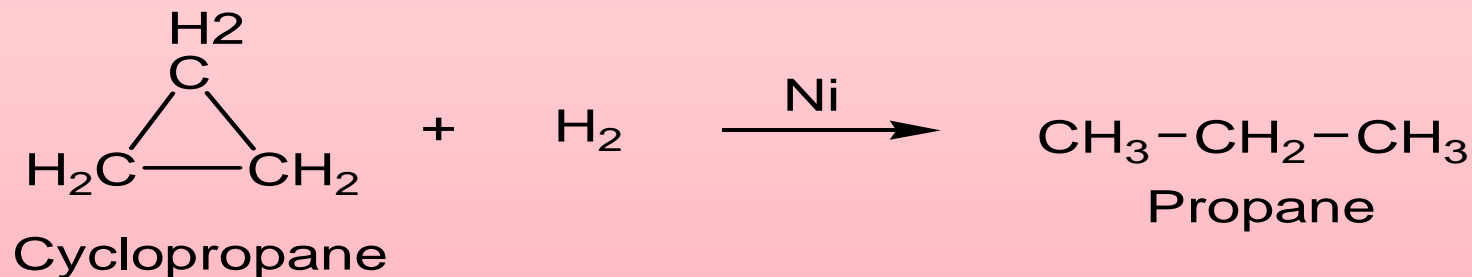


Cyclohexane

Chemical reactions of Cycloalkanes

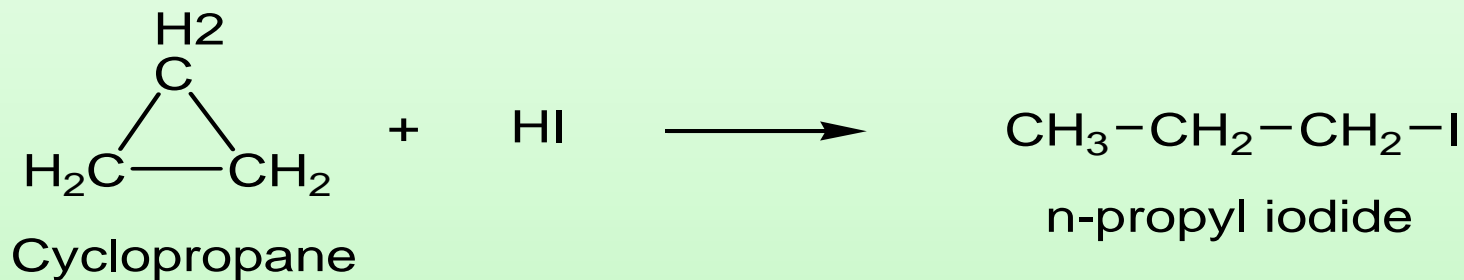
a) Reaction with Hydrogen

- When cyclopropane heated with H_2 in the presence of nickel gives propane.



b) Reaction with HI

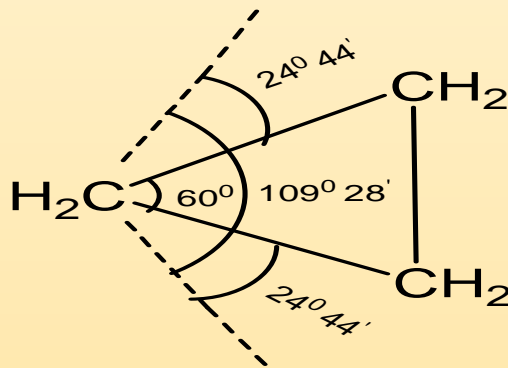
- When cyclopropane react with HI gives n-propyl iodide.



Baeyer Strain Theory

- In 1885 Adolf Baeyer proposed a theory to explain the relative stability of first few cycloalkanes which is based on mechanical concept of bonding.
- The main points of this theory are as given below.
- i) Baeyer proposed a theory on deviation of bond angle from normal tetrahedral value would result in internal strain in the molecule called as angle strain.
- ii) He assumed all cycloalkanes were planar and calculated the angle strain.
- iii) Any deviation, positive or negative from normal tetrahedral bond angle i.e. $109^{\circ} 28'$ during the formation of ring creates a strain in the molecule which makes the molecule unstable.

- Angle strain = $\frac{1}{2} (109^{\circ} 28' - \text{Bond angle in cycloalkane})$
- Angle strain in cyclopropane = $\frac{1}{2} (109^{\circ} 28' - 60^{\circ})$
- = $\frac{1}{2} (49^{\circ} 28')$
- = $24^{\circ} 44'$
- Angle strain in cyclopropane shown as follows.



- Angle strain of other cycloalkanes calculated for various ring sizes are given below.

Compound	Bond angle	Angle strain
Cyclopropane	60°	$24^{\circ} 44'$
Cyclobutane	90°	$9^{\circ} 44'$
Cyclopentane	108°	$0^{\circ} 44'$
Cyclohexane	120°	$- 5^{\circ} 16'$

- vi) The angle strain is maximum in case of cyclopropane. Thus according to Bayer strain theory cyclopropane should be higher strained molecule and consequently most unstable. Hence cyclopropane ring undergo ring opening reaction very easily.
- vii) The angle strain in cyclobutane is less than cyclopropane, this shows greater stability of cyclobutane than cyclopropane.
- viii) The angle strain is minimum in case of cyclopentane, it should be more stable than cyclopropane and cyclobutane. Hence cyclopentane do not undergo ring opening reaction.
- ix) The angle strain in case of cyclohexane is higher than that of cyclopentane. This strain increases continuously with increase in no. of carbon atoms.
- x) According to Baeyer strain theory cyclohexane and higher cycloalkanes are very unstable, hence more reactive.

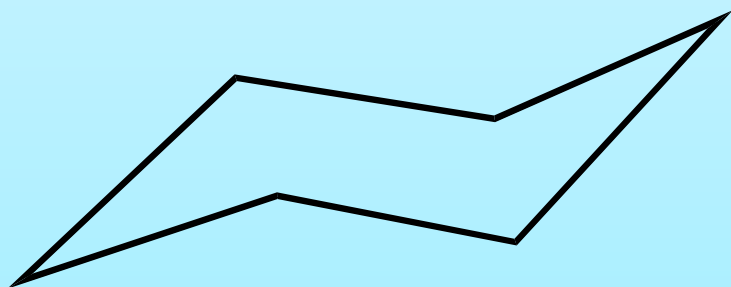
- But in fact cyclohexane and higher cycloalkanes are found to be quite stable. They do not undergo ring opening reactions. Therefore, Baeyer strain theory is restricted for cyclopropane, cyclobutane and cyclopentane.

Limitations :

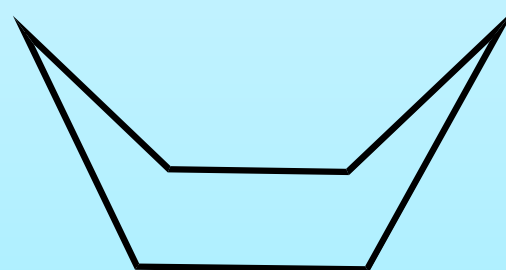
- i) Baeyer strain theory apply for cyclopropane, cyclobutane and cyclopentane only.
- ii) According to Baeyer strain theory cyclopentane is more stable than cyclohexane but in fact cyclohexane is more than cyclopentane.

Sachse Mohr Theory

- Stability of cyclohexane and higher cycloalkanes are explained by Sachse Mohr in 1890.
- According to this theory, large rings molecules and bigger ring molecules present in different planes and molecule having strainless.
- Cyclohexane can exist in two non planer puckered structures. Both are free from strain. These are called as chair and boat form of cyclohexane as follows.

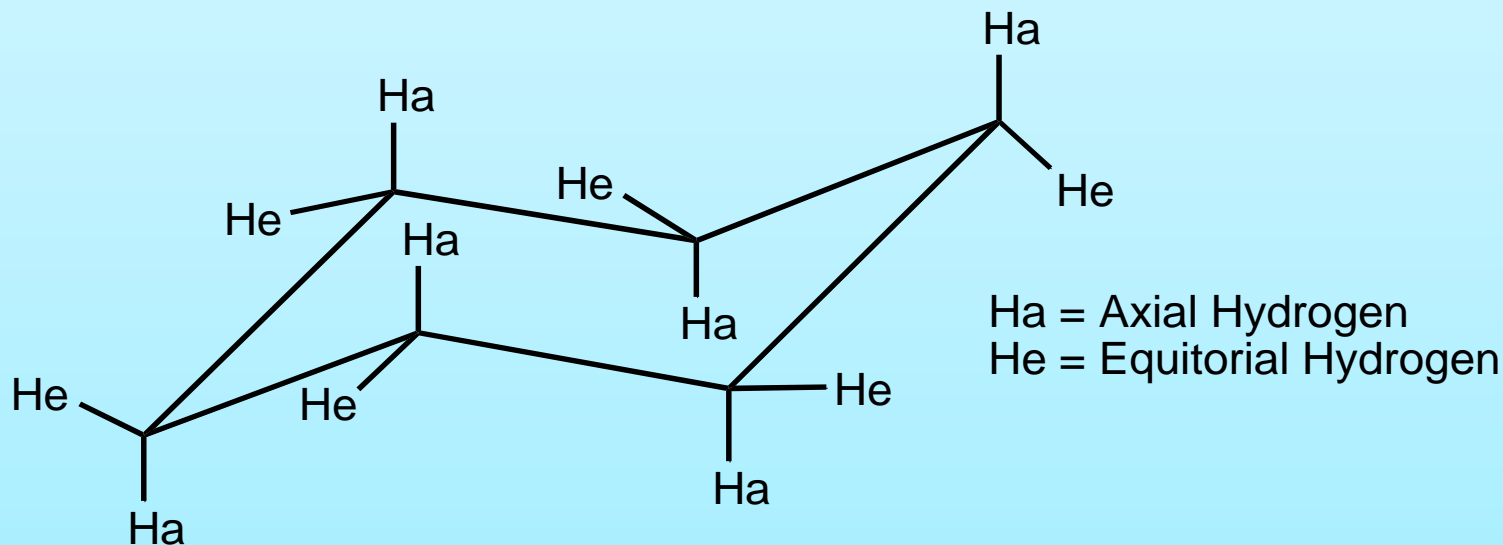


Chair form of Cyclohexane



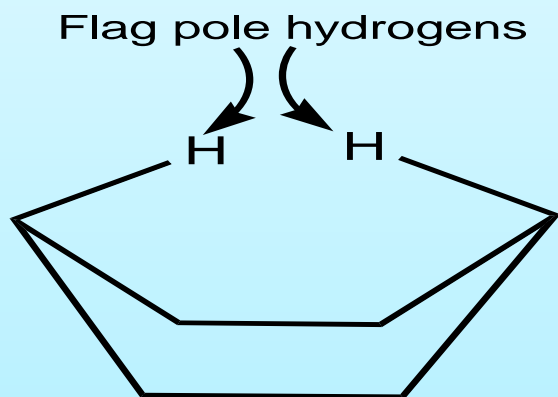
Boat form of Cyclohexane

- The chair form of cyclohexane is more stable than boat form. Cyclohexane reveals that the hydrogen atoms can be divided into two categories. Six bonds of hydrogen atom pointed straight up or down almost perpendicular to the plane of the molecule. These are called as axial hydrogens. Other six hydrogen atoms lie slightly above or slightly below to the plane of the cyclohexane ring. These are called as equatorial hydrogens.



Chair form of Cyclohexane

- Boat form of cyclohexane is less stable due to flag pole hydrogens as follows.



Boat form of Cyclohexane

B] Cycloalkene

- Alicyclic hydrocarbons having one carbon-carbon double bond are called as cycloalkenes.
- The general molecular formula of cycloalkene is $C_nH_{2(n-1)}$
- Where, n - no. of carbon atoms



Cyclopropene

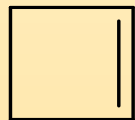
- **Nomenclature :**
- The IUPAC nomenclature of cycloalkenes as follows :

Compound

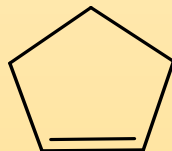
IUPAC Names



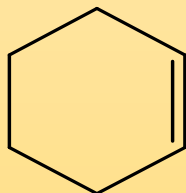
Cyclopropene



Cyclobutene



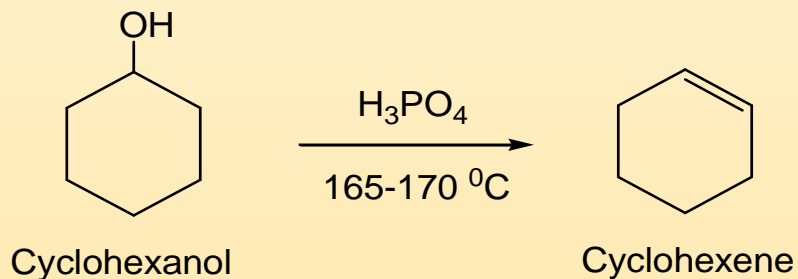
Cyclopentene



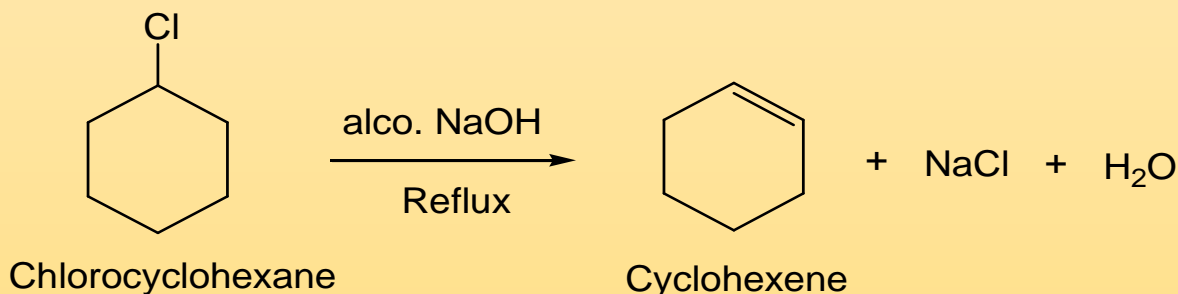
Cyclohexene

- **Preparation methods :**

- **a) Dehydration of cyclohexanol :** Cyclohexanol on heating with 85% phosphoric acid at 165-170 °C forms cyclohexene.

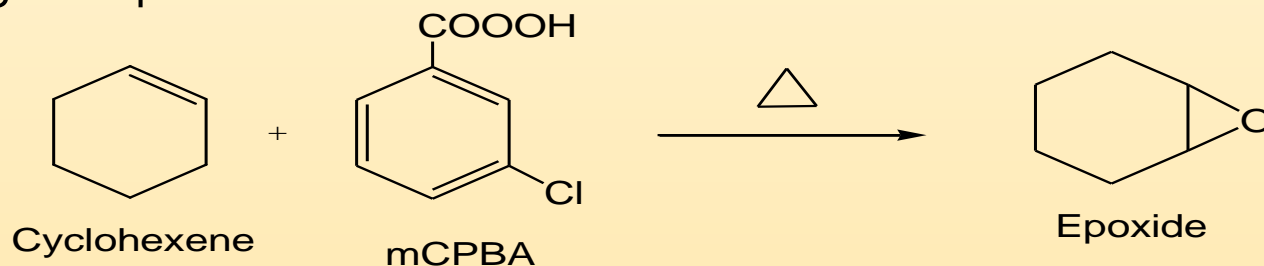


- **b) Dehydrohalogenation of halocyclohexane :** Chlorocyclohexane on refluxed with alcoh. NaOH undergo elimination reaction to give cyclohexene.

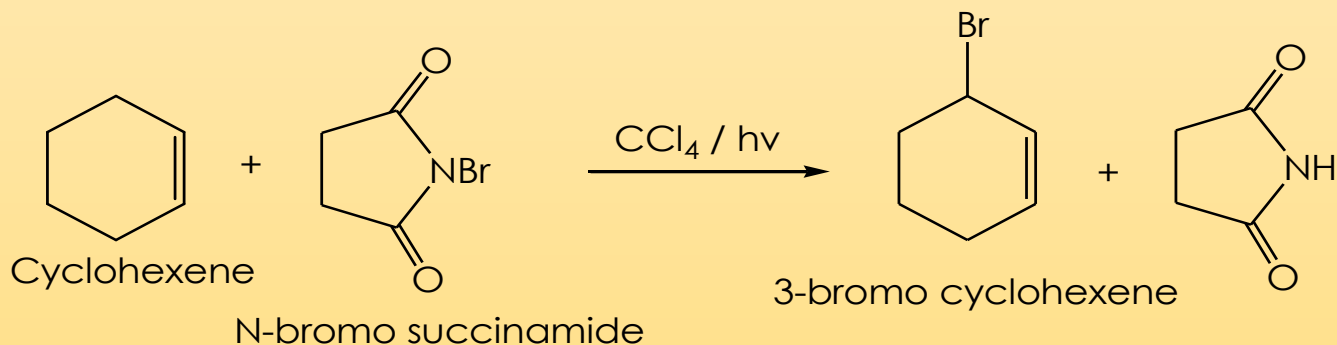


- **Chemical reactions:**

- **a) Epoxidation of cyclohexene:** Cyclohexene react with m-chloro perbenzoic acid gives epoxide.



- **b) Allylic halogenations :** Cyclohexene react with N-bromo succinamide in the presence of CCl_4 solvent gives 3-bromo cyclohexene.



C] Dienes :

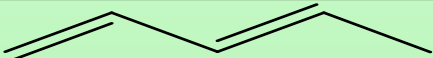
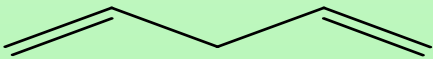
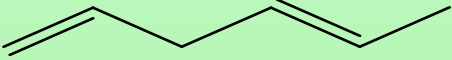
Unsaturated hydrocarbons containing two carbon-carbon double bonds are called as dienes. They are also called as alkadienes.

The general molecular formula of diene is C_nH_{2n-2}

Where, n - no. of carbon atoms

Ex. $CH_2=CH-CH=CH_2$
1,3-butadiene

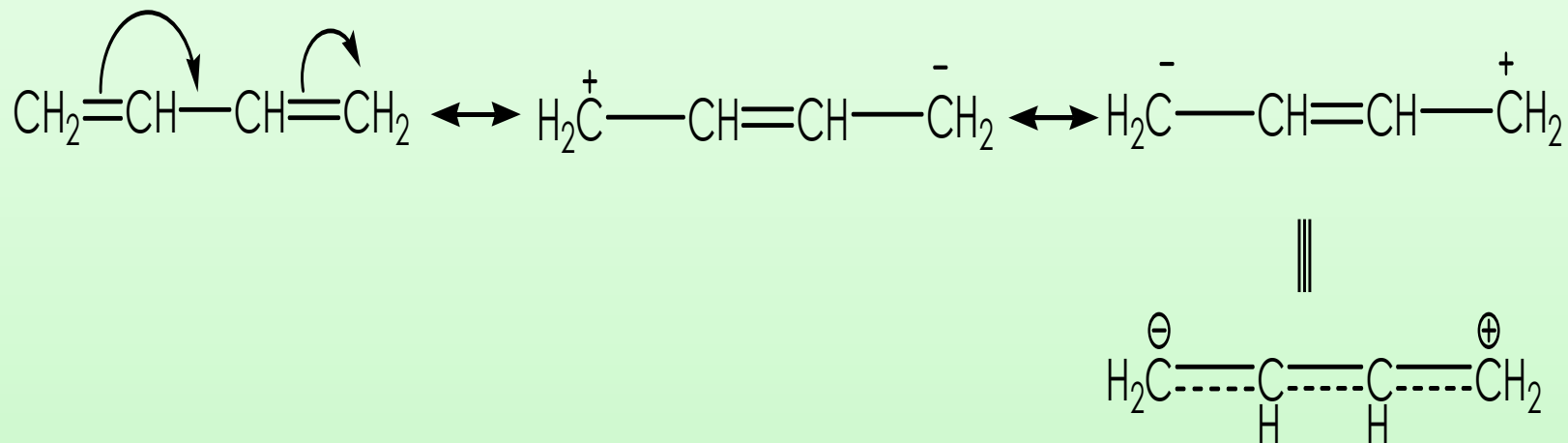
IUPAC Nomenclature of dienes :

S.No.	Examples	IUPAC Names
1	$CH_2=C=CH_2$	1,2-propadiene
2	$CH_2=CH-CH=CH_2$	1,3-butadiene
3	$CH_2=C=CH-CH_3$	1,2-butadiene
4		1,3-pentadiene
5		1,4-pentadiene
6		1,4-hexadiene

Classification of dienes:

- Dienes are classified as follows
- **a) Isolated dienes:** The dienes in which two double bonds are separated by more than one single bond. Such type of diene is called as Isolated diene.
- Ex. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$
- 1,4-pentadiene
- **b) Conjugated dienes:** The dienes in which two double bonds are separated by one single bond. Such type of diene is called as conjugated or alternative diene.
- Ex. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
- 1,3-butadiene
- **c) Cumulated diene :** The dienes in which two double bonds are attached to same carbon atom. Such type of diene is called as cumulated diene or Allene.
- Ex. $\text{CH}_2=\text{C}=\text{CH}_2$
- 1,2-propadiene

Resonating structures of 1,3-Butadiene :

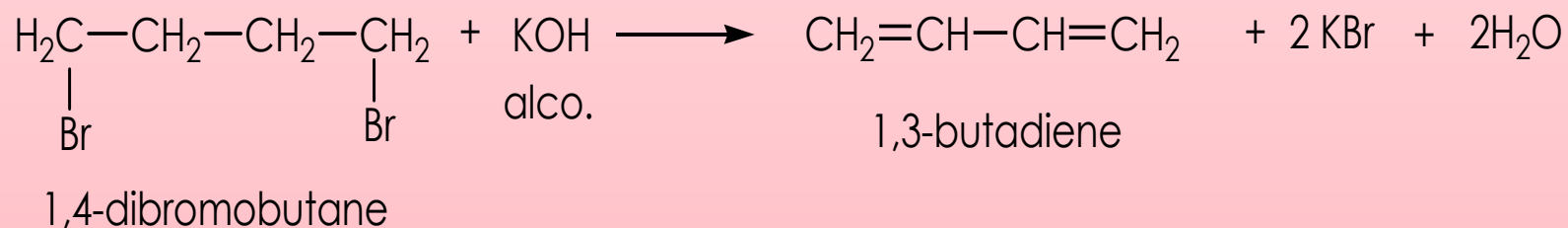


- The above resonating structure shows that C-C bond in 1,3-butadiene neither pure single bond (bond length 1.54 Å) nor pure double bond (bond length 1.34 Å) but they are placed in between single and double bond i.e. 1.40 Å

Preparation methods of 1,3-Butadiene :

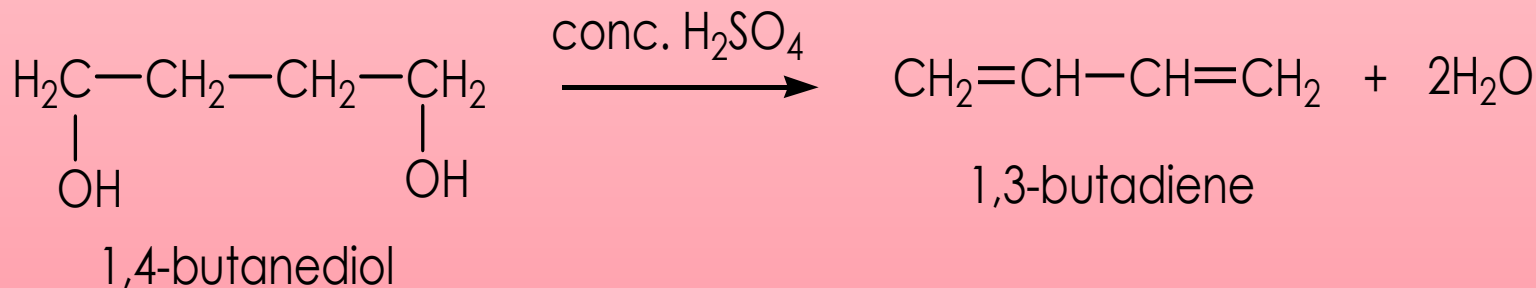
a) From 1,4-dibromobutane :

Dehydrohalogenation of 1,4-dibromobutane with alcoholic KOH gives 1,3-butadiene.



b) From 1,4-butanediol :

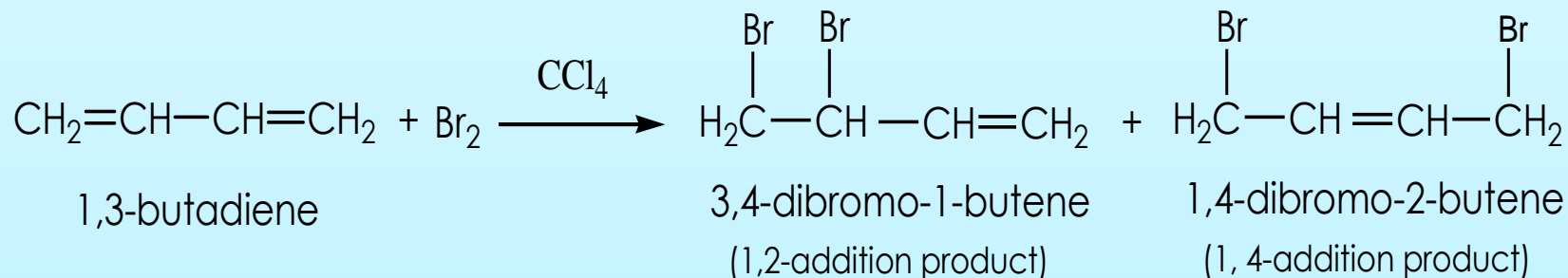
Acid catalysed dehydration of 1,4-butanediol gives 1,3-butadiene.



Chemical reactions of 1,3-Butadiene :

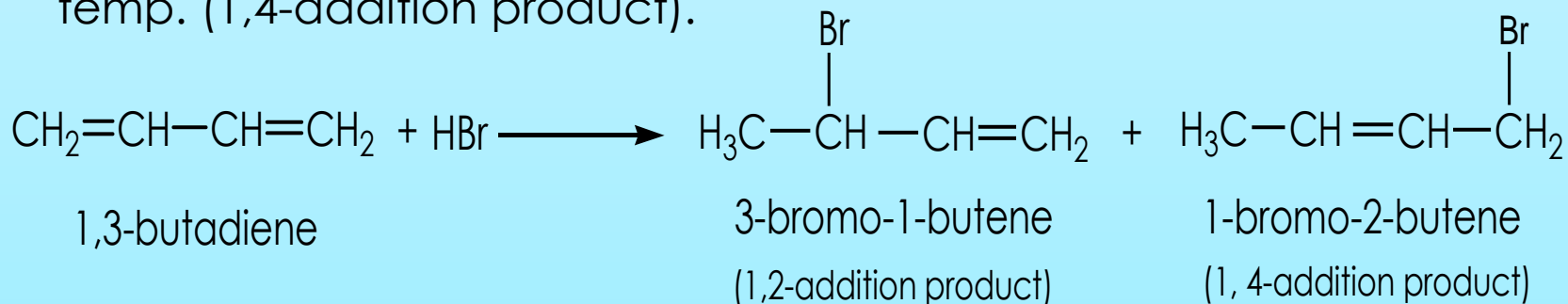
➤ **a) Addition of Br₂ on 1,3-Butadiene :**

- Addition of Br₂ on 1,3-butadiene in the presence of CCl₄ solvent gives mixture of 3,4-dibromo-1-butene (1,2-addition product) and 1,4-dibromo-2-butene (1,4-addition product).



➤ **b) Addition of HBr on 1,3-butadiene :**

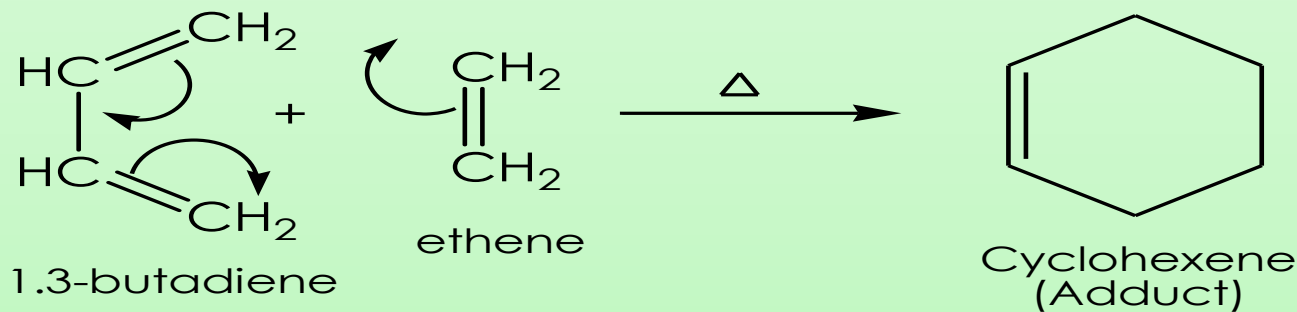
- Addition of HBr on 1,3-butadiene gives mixture of 3-bromo-1-butene at low temp. (1,2-addition product) & 1-bromo-2-butene at high temp. (1,4-addition product).



➤ **c) Addition of ethene to 1,3-Butadiene (Diels Alder Reaction)**
:

➤ Cycloaddition of (4+2)pi electrons to form six membered cyclic adduct. This reaction is called as Diel's alder reaction.

➤ **Ex. i)** Ethene react with 1,3-butadiene gives cyclohexene. In this reaction, ethene acts as dienophile & 1,3-butadiene acts as diene.





Thank You ...