

UNIT - V

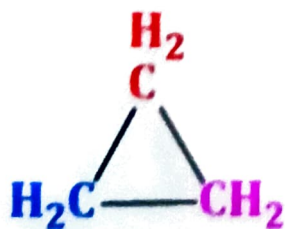
CYCLO ALKANES

Points to be covered in this topic

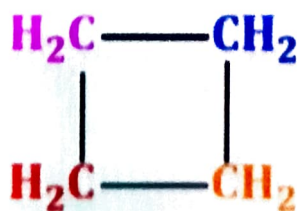
- 1. INTRODUCTION
- 2. NOMENCLATURE
- 3. METHOD OF PREPARATION
- 4. CHEMICAL PROPERTIES

□ CYCLO ALAKNES

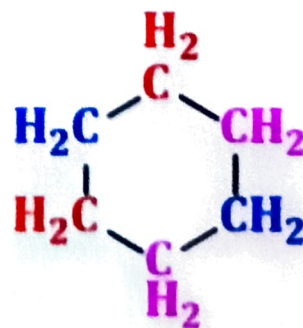
- Cycloalkanes or cycloparaffins or polymethylenes are **saturated, closed chain hydrocarbons** in which the **carbon atoms** connected by **single covalent bonds** lead to the **formation of rings**, hence they are called as **carbocyclic or homocyclic compounds**
- These are known as **alicyclic compounds**, the **suffix cyclic** indicates the **presence of a ring** and the **prefix ali** indicates their similarity to **aliphatic compounds**.
- The general formula for this series is C_nH_{2n} , here **n** is said to be the **number of carbon atoms** present in the organic compound



Cyclopropane



Cyclobutane

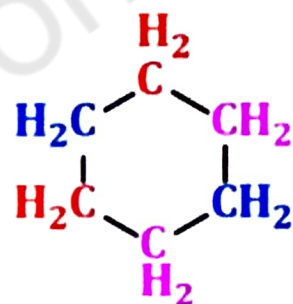
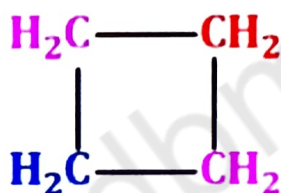
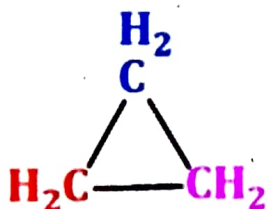


Cyclohexane

❑ NOMENCLATURE

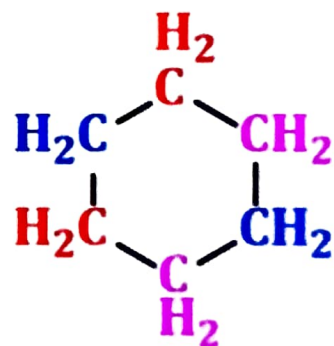
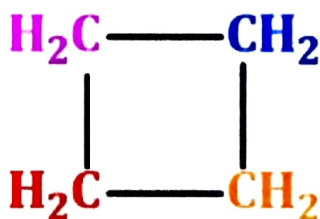
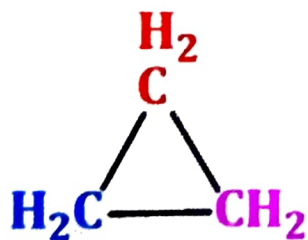
❖ COMMON NAME

- The name of cycloalkanes is obtained by **prefixing the number of carbon atoms in the ring before the word methylene**.
- The **prefix tri, tetra penta** etc. are used to **present three, four or five carbon atoms in the ring**.



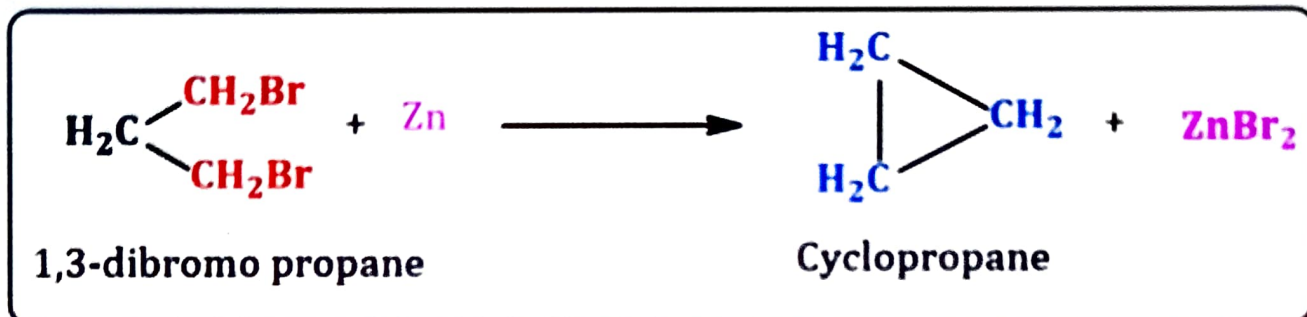
❖ IUPAC NAME

- In this system **saturated alicyclic compounds** are named by **prefixing the word cyclo** to the name of corresponding **open chain alkanes** having the **same number of carbon atoms as the ring**

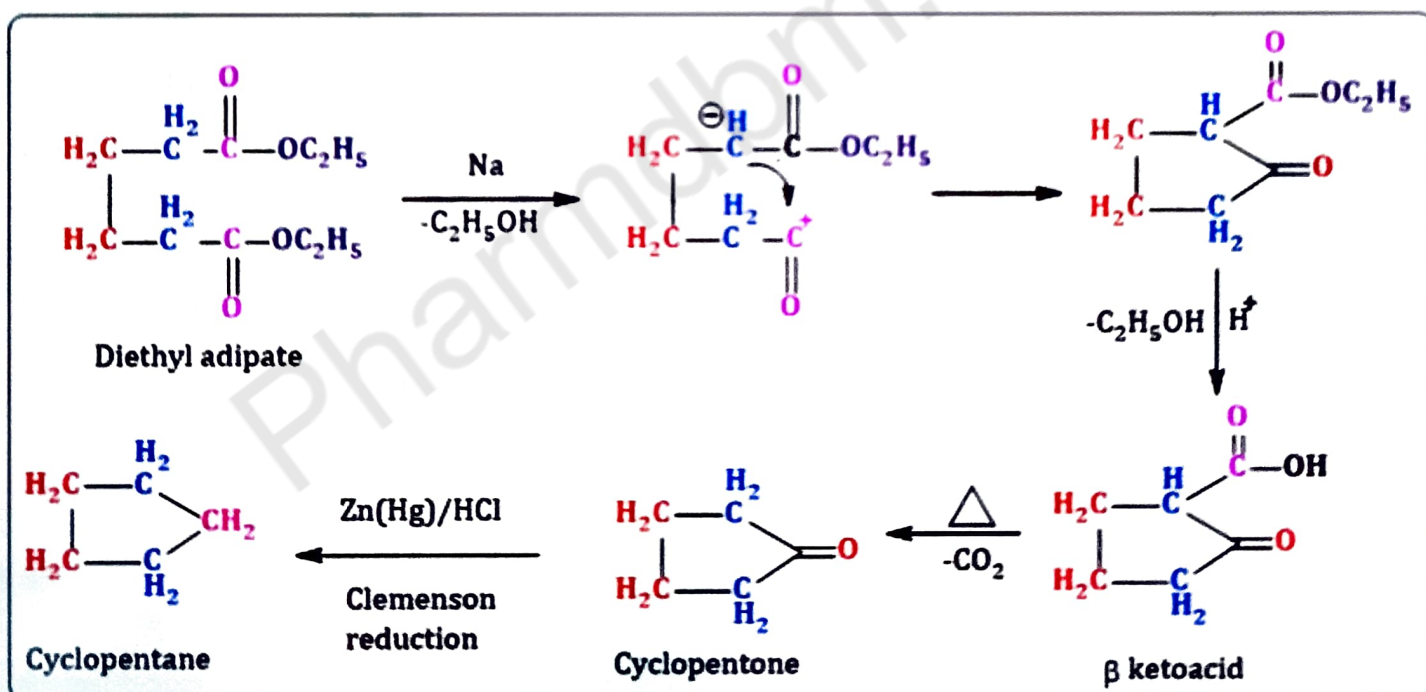


□ METHOD OF PREPARATION

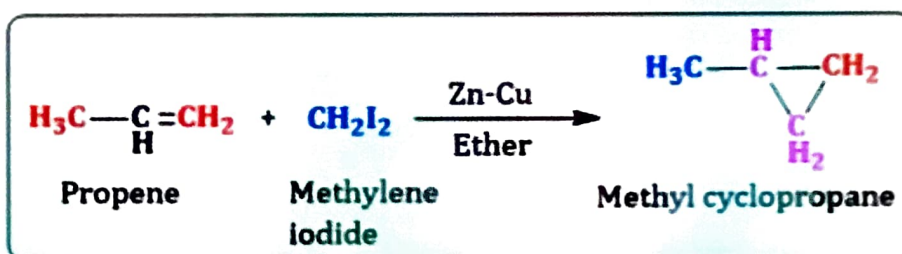
1. From dihalide or dihalogen derivative's of alkanes: The **dihalogen derivatives of the alkanes** are treated with **sodium metal or zinc** to yield **cycloalkanes**.



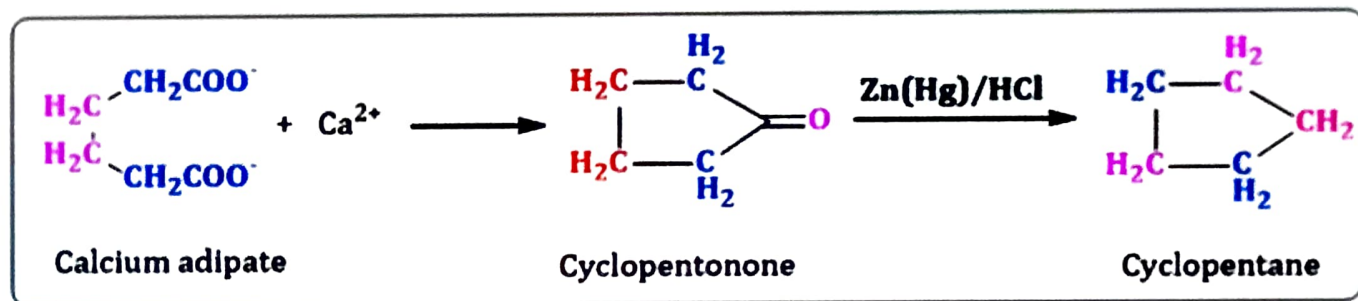
2. Diekmann reaction: This reaction involve reaction between the **esters of dicarboxylic acid** with **sodium ethoxide** to give **β -keto ester** which upon hydrolysis yield **cyclic ketones**, this on reduction with **Zn(Hg) / HCl** gives the respective **cycloalkanes**



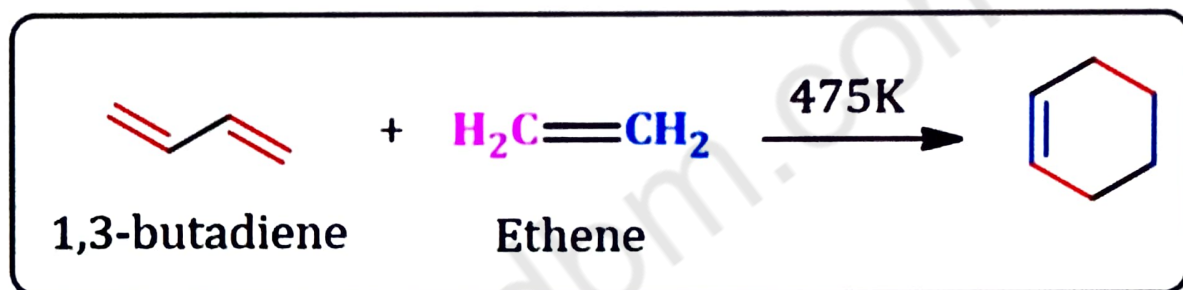
3. Simmons smith reaction: **Alkenes** on treating with **methylene iodide** in the presence of **zinc copper couple** and give **cyclohexane**



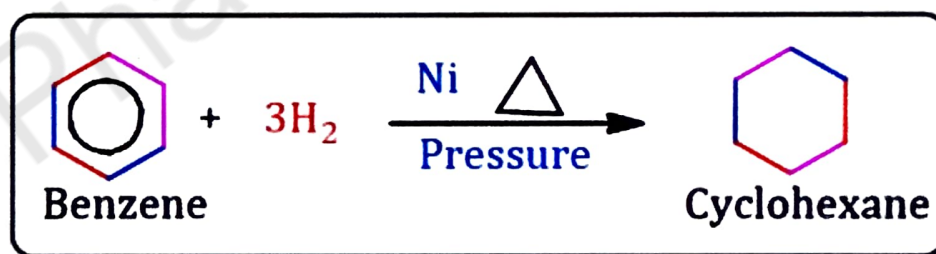
4. From calcium or barium salt of dicarboxylic acid: When the barium or calcium salt of dicarboxylic acid is distilled, a cyclic ketone is obtained, further reduction with Zn(Hg)/ HCl yield corresponding cycloalkanes



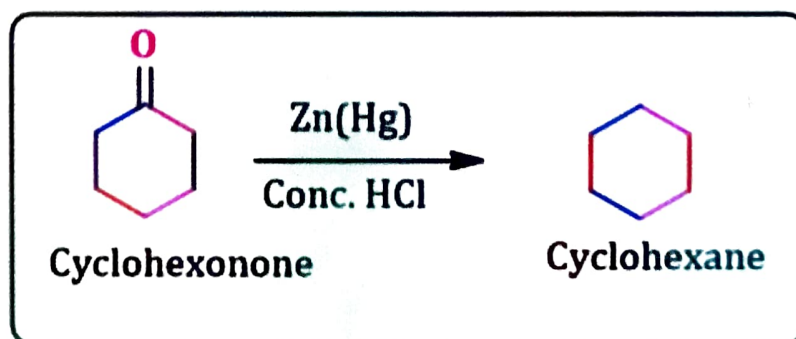
5. Diels-Alder reaction: This reaction involve reaction the **addition an alkenes** which act as **dienophiles** and **a conjugated diene** to form **six membered system**



6. From benzene: **Six membered alicyclic compound** are prepared from **benzene**



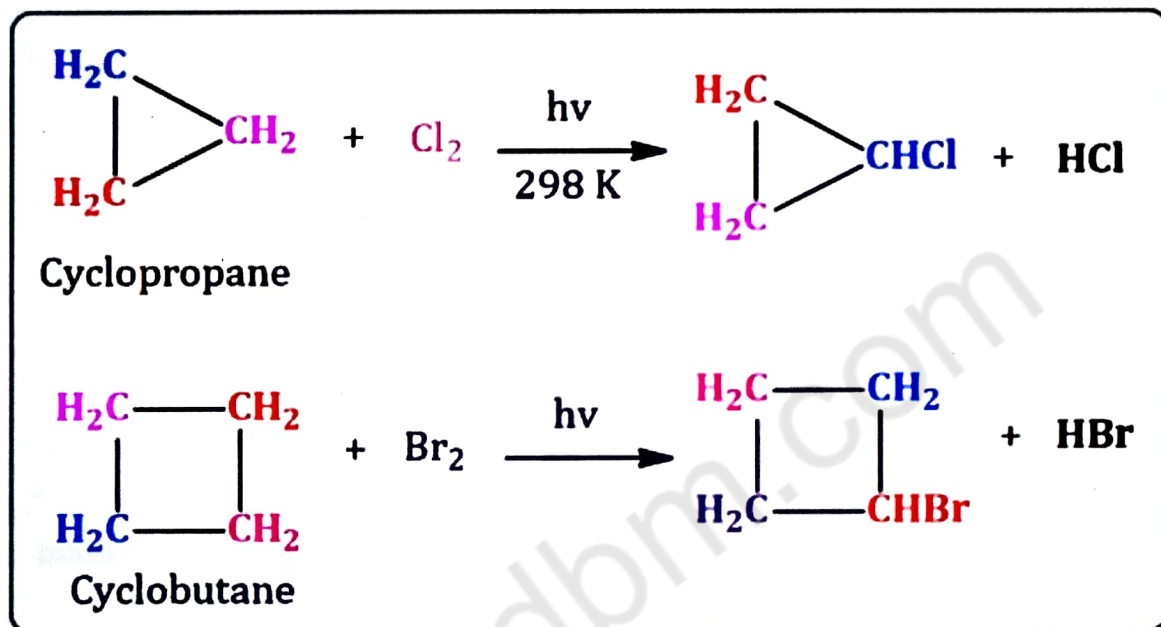
7. Clemensen's reduction: **Cyclic ketones** reduced in presence of **Zn amalgam and conc. HCl** gets converted to **cycloalkanes**



❑ CHEMICAL REACTION

❖ FREE RADICAL SUBSTITUTION REACTION

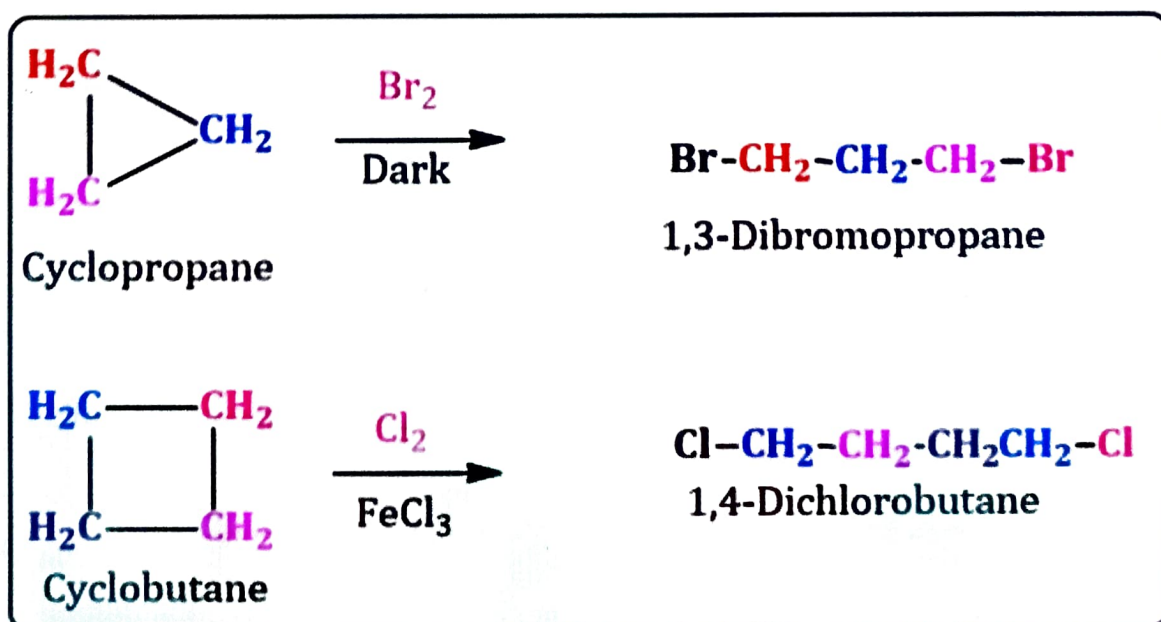
- Cycloalkanes undergoes **free radical substitution reaction** when they are treated with **halogens** at **298 K** in the dark or at room temperature in the presence of light



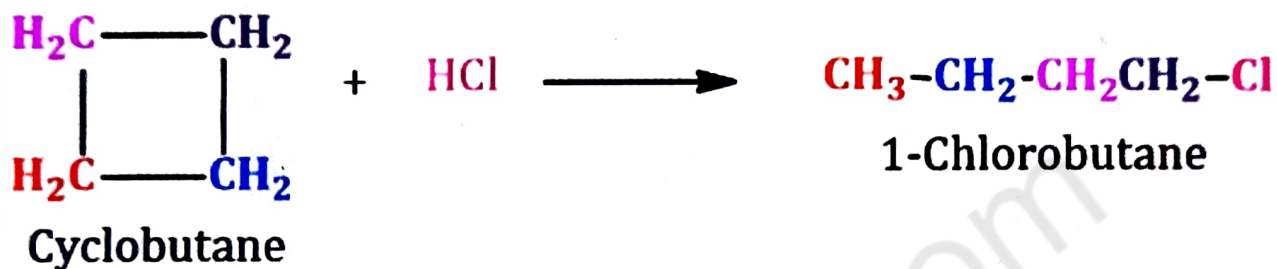
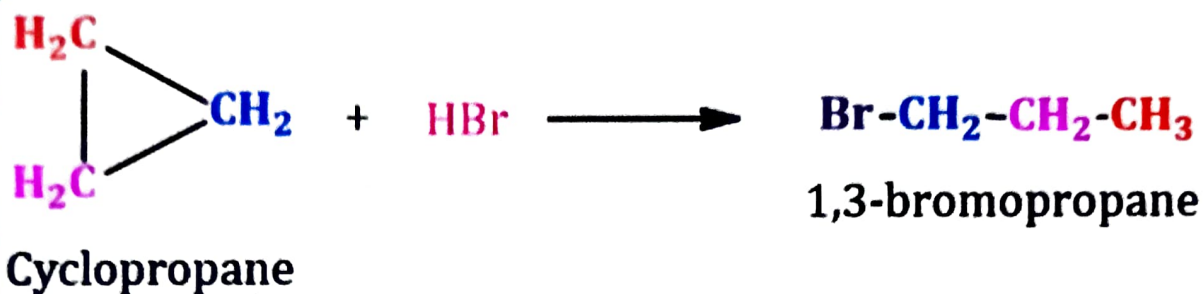
❖ ADDITION REACTION

➤ ADDITION OF HALOGENS

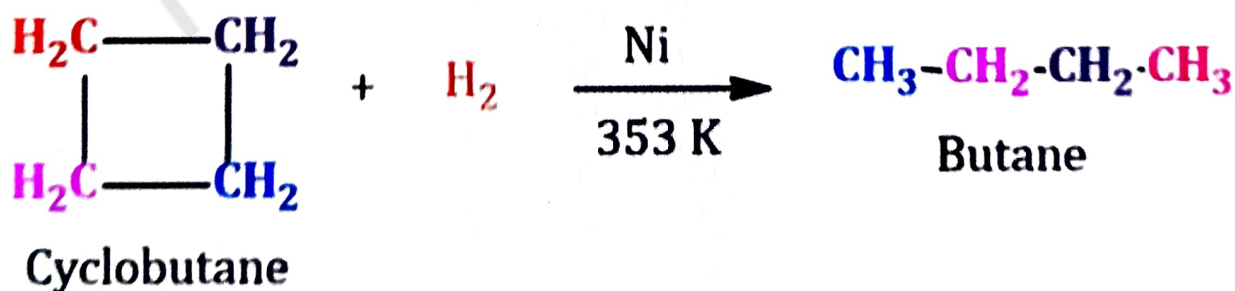
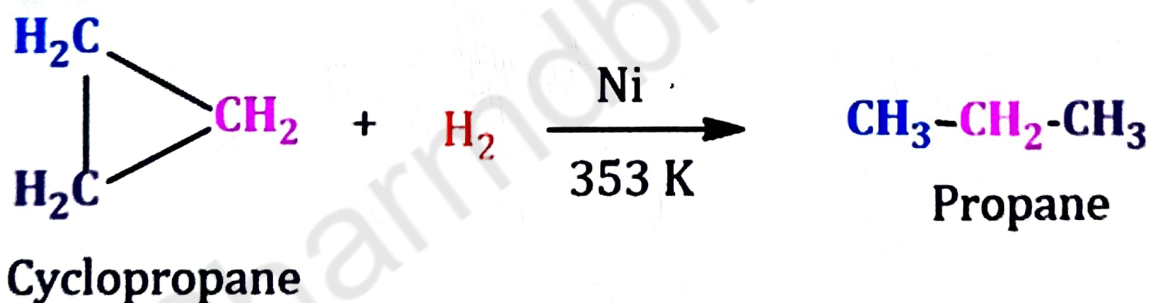
- Cycloalkanes undergo addition reaction and yield **open chain products**



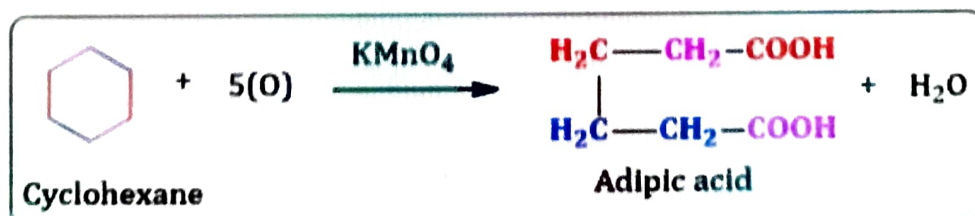
➤ ADDITION OF HALOGEN ACID



➤ ADDITION OF HYDROGEN



➤ OXIDATION



UNIT - V

CYCLO ALKANES

Points to be covered in this topic

1. BAYER STRAIN THEORY
2. LIMITATION OF BAYER STRAIN THEORY
3. COULSON AND MOFFITT'S MODIFICATION
4. SACHSE MOHR'S THEORY

□ BAYER STRAIN THEORY

- The theory says that the **normal angle** between any pair of bonds of carbon at $109^{\circ} 28'$ which lies between the value of angles in a regular pentagon (108°) and a regular hexagon (120°).
 - Bayer postulated that any **deviation of bond angles** from the normal tetrahedral value would impose a **condition of internal strain** on the ring it is called as **Bayer strain theory**
1. In cycloalkanes each **carbon atom is sp^3 hybrid** and bonded to other four carbon atoms. The **angle between any pair** of adjacent bonds should be **tetrahedral (109.5°)**.
 2. Due to **cyclic nature**, cycloalkanes are **planar in nature**. As a result the bond angles **between adjacent carbon atoms** in the ring are **not longer equal to the normal tetrahedral angle** i.e. 109.5° .
 3. **Any distortion or deviation** from the **normal tetrahedral angle** causes **a strain in the ring** and produce instability to resultant molecule. This strain is known as **angle strain**.

$$\text{Angle strain} = \frac{1}{2} [109.5^{\circ} - \text{Bond angle in the planer ring}]$$

4. The **greater the deviation from the normal angle**, greater will be **angle strain** and hence **greater the reactivity of cycloalkane**.

5. The **more the stability of ring system**, the **more easily it is formed**

Compound	Bond angle	Angle strain
Cyclopropane	60°	Angle strain = $\frac{1}{2}[109.5' - 60] = 24.44'$
Cyclobutane	90°	Angle strain = $\frac{1}{2}[109.5' - 90] = 9.44'$
Cyclopentane	108°	Angle strain = $\frac{1}{2}[109.5' - 108] = 0.44'$
Cyclohexane	120°	Angle strain = $\frac{1}{2}[109.5' - 120] = -5.16'$

❖ STABILITY OF CYCLOALKANES

$$\text{Angle strain} \propto \frac{1}{\text{Stability}}$$

Stability order: **Cyclopentane** > **Cyclohexane** > **Cyclobutane** > **Cyclopropane**

❑ LIMITATION OF BAEYER STRAIN THEORY

- Baeyer's Strain Theory explains the **relative stabilities of ring size up to 5 and 6** in a better way. It can't explain the **exact stability of the higher ring system**.
- In **alkenes angle strain is large** therefore it **should be formed with difficulty**, but in **alkenes the double bond is formed easily** by dehydration of alcohol, so Bayer strain theory could **not explain the formation of carbon - carbon double bond**.
- According to the baeyer, **larger ring systems are not planar** but **puckered to minimize angle strain**
- According to the Baeyer, **larger ring systems are not possible** but they **exist and highly stable**
- According to Baeyer, **cyclopentane** should be **much stable** than **cyclohexane** but **practically it is reversed**

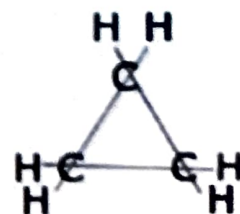
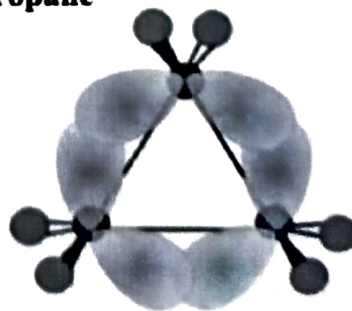
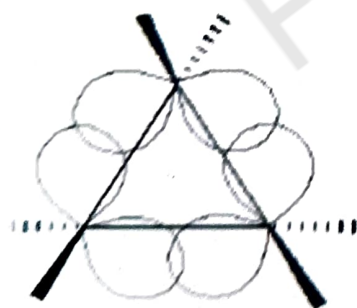
❑ MOLECULAR ORBITAL THEORY OF CYCLOALKANES

- For **bond formation** effective **atomic orbital overlap** is required.
- For **carbon atom, in a molecule** if it is **sp^3 hybridized** then the bond angle is 109.5° and **orbital overlap is maximum**.
- This is the reason for **highly stable compounds**.
- In **cyclopropane**, the **bond angle is 60°** instead of **109.5°**
- The carbon atom **don't use sp^3 hybridized orbital** to form **the bond**
- Hence, the **bond is weaker** as compare to usual carbon-carbon bond.

❑ COULSON AND MOFFITT'S MODIFICATION

- Coulson-Moffitt modify Baeyer strain theory to show **the actual position of carbon-carbon bonds in cyclopropane**, which somewhat **relieves the strain on C-C bonds**
- So, to satisfy **regular tetrahedral geometry** ($109^\circ.28'$) and **equilateral triangle angle** (60°) they introduce a **new type of bond** called **banana bond/bent bond** which is intermediate **between sigma bond and pi-bond** in case of overlapping.
- A **bent bond**, also known as a **banana bond**, is a type of covalent **chemical bond with geometry somewhat indicative of a banana**

Bent bonds in cyclopropane

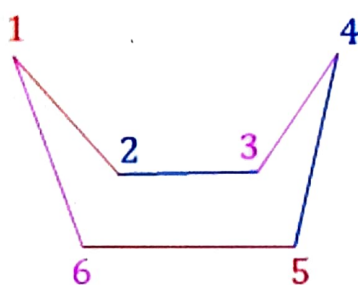


Atomic orbital overlap in cyclopropane

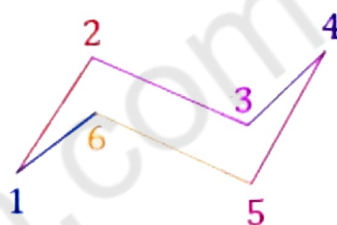
- Due to formation of bent bond, the **cyclopropane C-C bond weaker than normal C-C sigma bond**, so due to this **weaker bond cyclopropane is unstable** and it can **gives ring opening reaction easily**

❑ Sachse Mohr's theory (Theory of strainless rings)

- Sachse Mohr's theory proposed that **higher member ring** can become **free from strain** if all the **ring carbons** are not forced **into one plane**.
- They exhibit in **two non-planar puckered conformations** both of which are completely **free from strain**.
- These are called the **Chair Form and Boat Form**.
- These are **strainless** as the **carbon atom lie in different planes** and the **normal angle $109^{\circ}28'$** is retained.



Boat form



Chair form

- In the **Boat form**, **carbons 1, 2, 4 and 5** lie in the same plane and **carbons 3 and 6** above the plane.
- In the **chair form**, **carbons 1, 2, 4 and 5** lie in the same plane, but **carbon 6** is above the plane and **carbon 3** is below it.

❑ STABILITY OF CHAIR AND BOAT FORMS OF CYCLOHEXANE

- The **chair form of cyclohexane** is **more stable** than its **boat form**.
- This is because the **boat form has unfavorable non-bonded interactions** between the **hydrogen atoms**.
- **Chair form of Cyclohexane** reveals that the **hydrogen atoms** can be divided into **two categories**.
- **Six of the bonds to hydrogen** atoms point **straight up or down almost perpendicular** to the plane of the molecule. These are called **axial hydrogens**.
- The other **six hydrogens** lie **slightly above or slightly below** the plane of the cyclohexane ring, and are called **equatorial Hydrogens**.