

# Alicyclic Compounds

## Introduction to Alicyclic compounds

### What are Alicyclic Compounds?

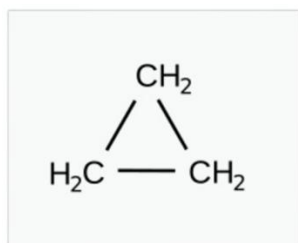
- Alicyclic compounds are organic compounds that are both aliphatic (non-aromatic) and cyclic (contain one or more rings).
- The term "alicyclic" is a combination of "aliphatic" and "cyclic". These compounds show properties that are intermediate between alkanes/alkenes and aromatic compounds.

### Structure and Nature:

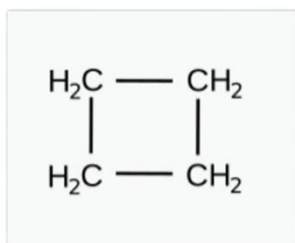
- Alicyclic compounds contain one or more carbon rings, which may or may not have substituents.
- Unlike aromatic compounds, alicyclic rings do not have delocalized pi electrons (as seen in benzene). Hence, they follow the typical rules of saturated or unsaturated hydrocarbons.
- They can be:
  - Saturated (cycloalkanes):** contain only single bonds.
  - Unsaturated (cycloalkenes, cycloalkynes):** contain double or triple bonds in the ring.
  - Substituted alicyclic compounds:** contain one or more substituents attached to the ring.

### Examples:

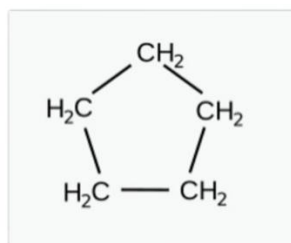
- Cyclopropane ( $C_3H_6$ ):** a three-membered saturated ring.
- Cyclobutane ( $C_4H_8$ ):** a four-membered ring.
- Cyclohexane ( $C_6H_{12}$ ):** a six-membered ring.
- Methylcyclopentane ( $C_6H_{12}$ ):** a five-membered ring with a methyl group.



Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane



Cycloheptane



Cyclooctane

## Preparation of Cycloalkanes

### 1. From Dihaloalkanes via Intramolecular Wurtz Reaction

- **Reaction Type:** Intramolecular Coupling
- **Reagents and Conditions:**
  - **Starting Material:**  $\alpha,\omega$ -Dihaloalkane (e.g., 1,3-dibromopropane, 1,4-dibromobutane)
  - **Reagent:** Sodium (Na) metal
  - **Solvent:** Dry ether
  - **Reaction Type:** Reduction and Coupling
- **Mechanism:**
  - Sodium reduces the halogen atoms forming a carbanion intermediate.
  - Two ends of the molecule couple to form a ring via intramolecular bond formation.
- **Example:**



This method is most suitable for three- to six-membered rings, as larger rings may suffer from low yields due to ring strain or side reactions.

### 2. Cyclization of Dicarboxylic Acids (Decarboxylation Method)

- **Reagents and Conditions:**
  - **Starting Material:** Dicarboxylic acids (like adipic acid)
  - **Catalyst:** Heat and barium oxide (BaO) or soda lime
- **Mechanism:**
  - Thermal decomposition leads to loss of carbon dioxide from both ends.
  - The residual hydrocarbon structure folds into a ring, forming a cycloalkane.
- **Example:**



- This method is particularly effective for preparing five- and six-membered cycloalkanes, which are thermodynamically stable.

### 3. Dieckmann Condensation (Intramolecular Claisen Condensation)

- **Reagents and Conditions:**
  - **Starting Material:** Diesters
  - **Base:** Sodium ethoxide (NaOEt)

- **Followed by:** Acidic hydrolysis and decarboxylation
- **Mechanism:**
  - Base abstracts an  $\alpha$ -proton to generate an enolate ion.
  - Enolate attacks the ester group intramolecularly to form a  $\beta$ -keto ester.
  - Acidic hydrolysis and decarboxylation yield a cycloalkanone or can be further reduced to cycloalkane.
- **Example:**



## 4. Reduction of Aromatic Compounds

- This method involves hydrogenation of aromatic rings to obtain saturated cycloalkanes.
- **Reagents and Conditions:**
  - **Starting Material:** Benzene or substituted aromatics
  - **Reagents:**  $\text{H}_2$  gas
  - **Catalyst:** Nickel (Ni), Platinum (Pt), or Palladium (Pd)
  - **Pressure:** High hydrogen pressure
- **Example:**



- This is an industrially significant method for producing cyclohexane, a precursor to nylon (via adipic acid and caprolactam).

## 5. Diels-Alder Reaction

- The Diels-Alder reaction is a [4+2] cycloaddition reaction between a conjugated diene and a dienophile.
- **Reagents and Conditions:**
  - **Diene:** Conjugated diene (e.g., 1,3-butadiene)
  - **Dienophile:** Alkene with electron-withdrawing groups (e.g., maleic anhydride)
  - **Conditions:** Moderate heat, inert solvent
- **Mechanism:**
  - Concerted reaction forms a six-membered ring with stereospecificity.
- **Example:**



- Though the initial product is a cycloalkene, further hydrogenation yields cycloalkane.

## 6. Simmons–Smith Reaction (Carbenoid Reaction)

- This method is useful for synthesizing three-membered cycloalkanes (cyclopropanes).
- **Reagents and Conditions:**
  - **Starting Material:** Alkene
  - **Reagent:** Diiodomethane ( $\text{CH}_2\text{I}_2$ ) and Zinc-Copper couple ( $\text{Zn}(\text{Cu})$ )
  - **Solvent:** Ether
- **Mechanism:**
  - Zinc carbenoid species ( $\text{ICH}_2\text{ZnI}$ ) forms.
  - Transfers a  $\text{CH}_2$  group across the double bond in a concerted fashion, forming cyclopropane.
- **Example:**



- This method gives high stereospecificity and retains the configuration of the alkene.

## Baeyer Strain Theory

### Historical Context:

- Proposed by Adolf von Baeyer in 1885.
- One of the earliest theories to explain the stability of cycloalkanes.
- He assumed that carbon atoms prefer a tetrahedral angle ( $109.5^\circ$ ), and any deviation from this leads to angle strain, reducing stability.

### Key Concepts:

- In saturated hydrocarbons, the carbon atoms are  **$\text{sp}^3$  hybridized**, and they ideally form bond angles of  **$109.5^\circ$** .
- Baeyer suggested that **deviation from this ideal angle** creates **angle strain**, which makes the molecule less stable.
- He applied this concept to **planar rings** only (which is a limitation of the theory).

### Calculating Angle Strain (Angle of Deviation):

$$\text{Angle Strain} = 109.5^\circ - \text{Internal Angle of the Ring}$$

- The internal angle of a regular polygon is calculated by:

$$\text{Internal Angle} = \frac{(n - 2) \times 180^\circ}{n}$$

- Where **n** = number of ring members



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