

# Unit-5

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## Pharmaceutical Organic-II

**Unit V****8 Hours****Unit: 5****Cyclo alkanes\***

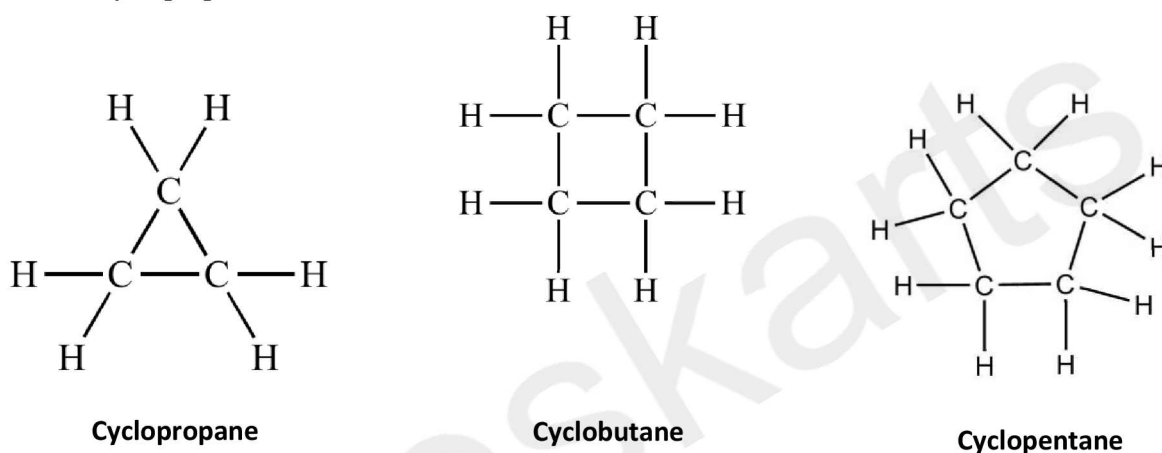
Stabilities – Baeyer's strain theory, limitation of Baeyer's strain theory, Coulson and Moffitt's modification, Sachse Mohr's theory (Theory of strainless rings), reactions of cyclopropane and cyclobutane only



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### Cycloalkanes:

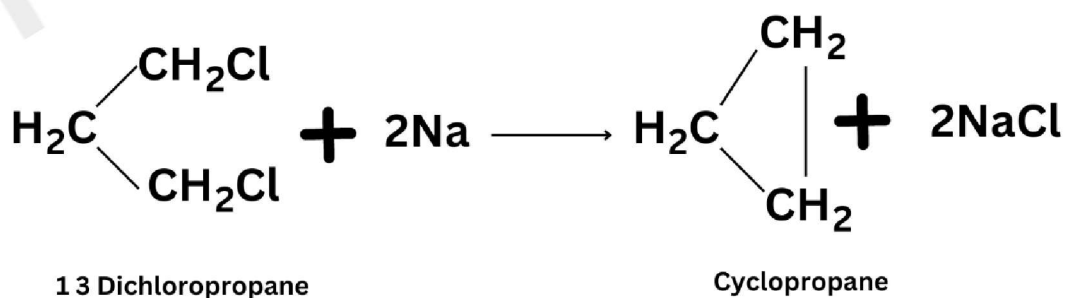
- Cycloalkanes are saturated hydrocarbon in which the carbon atoms are paired by single covalent bonds to form a ring.
- Cycloalkanes are alkanes which have same of their carbon atom arranged in a ring.
- The rings of different size begins with 3 carbon.
- They are also known alicyclic compound because their properties are very similar to aliphatic hydrocarbon such as alkane.
- Cycloalkane has two less hydrogen than aliphatic alkane with same no of carbon atoms.
- The general molecular formula for cycloalkane is  $C_nH_{2n}$ .
- Where n is the no of C atom in the molecule.
- The first number of cycloalkane series has molecular formula  $C_6H_6$  and is known as cyclopropane.



### Method of preparation of Cycloalkanes:

#### 1. From Dihalides:

- Terminal dihalides when treated with sodium (Na) or Zinc (Zn) form cycloalkanes.

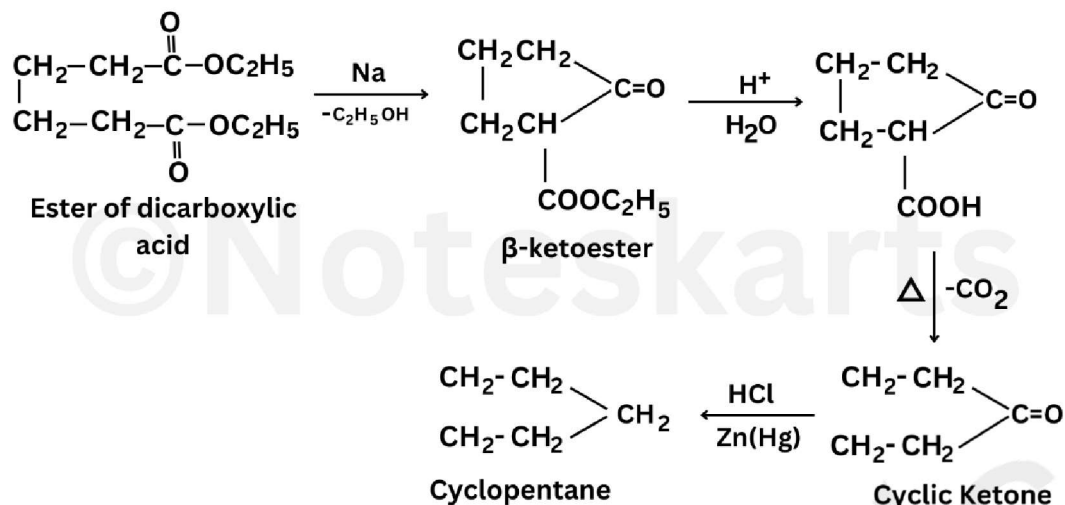


#### 2. Dieckmann reaction (From ester of dicarboxylic acid):

- Ester of dicarboxylic acid when treated with sodium,  $\beta$ -ketoester is formed. Which further on hydrolysis give cyclic ketones, which on clemmensen reduction give cycloalkanes.

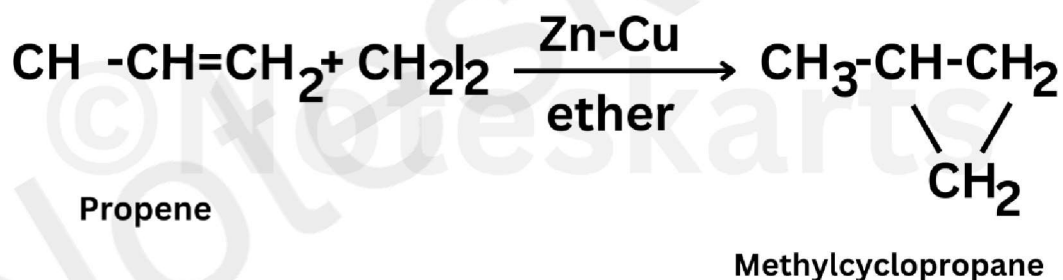


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### Simmons-smith reaction (from alkenes):

- When alkene are treated with methylene iodide ( $\text{CH}_2\text{I}_2$ ) in the presence of a zinc-copper (Zn-Cu) couple, cyclopropane derivatives are formed.



### Physical Properties of Cycloalkanes:

- The first four classes of cycloalkanes are said to be in gaseous state in the room temperature
- These saturated hydrocarbons are said to have their boiling points ranging between 10 – 20 K.
- These compounds are also reported exhibiting higher melting points and densities
- These are also called as saturated hydrocarbons since saturated compounds form ring structure.

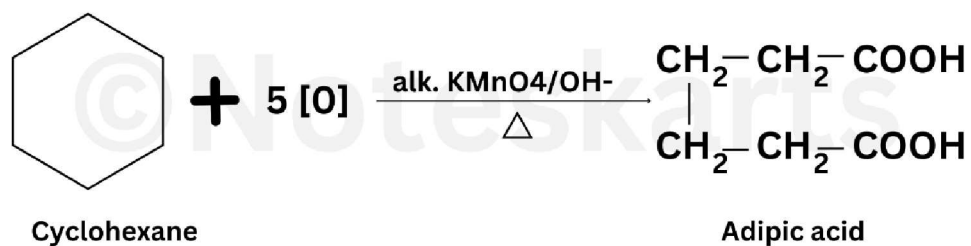
### Chemical Reactions:

#### 1. Oxidation:

- Cycloalkanes undergoes oxidation in the presence of alkaline potassium permanganate ( $\text{KMnO}_4$ ) to form dicarboxylic acid.

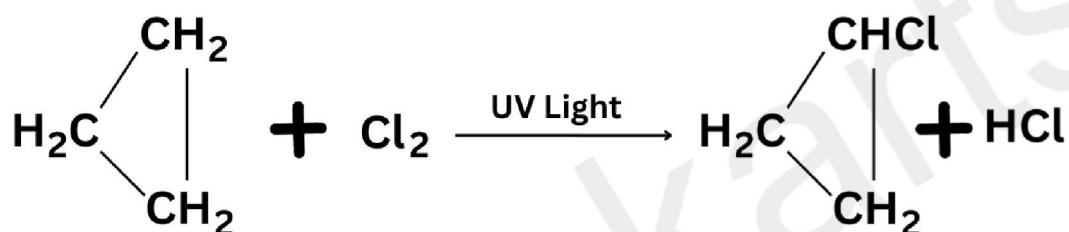


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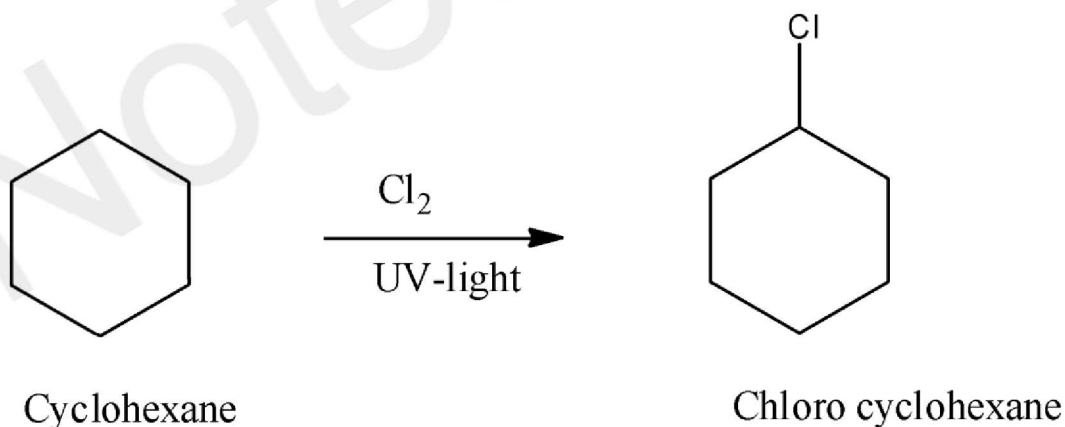


### 2. Substitution reaction:

- In this reaction one hydrogen atom replaced but ring does not affected.
- **Substitute with Cl<sub>2</sub> or Br<sub>2</sub>**
- When cycloalkanes react with chlorine or bromine in the presence of UV light, it gives substitute products.



- When cyclopropane react with chlorine in the presence of UV light it gives chlorocyclopropane.



- When cyclohexane react with chlorine in the presence of UV light, it gives Chlorocyclohexane.

### Baeyer's strain theory:

- Adolf Baeyer proposed in 1885 and he get noble prize for this theory in 1905.
- The explain the relative stability of starting few cycloalkanes.



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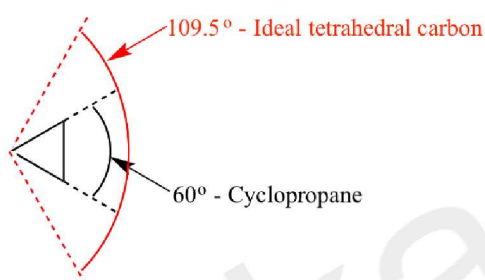
- This theory is based on the fact that the normal angle between pair of a carbon atom is  $109^{\circ}28'$ .
- Now he assumed that all cycloalkanes are planar.
- Stability of cycloalkanes depends upon angle strain.

$$\text{Angle Strain} \uparrow = \text{Stability} \downarrow$$

- In cycloalkanes the more angle strain more unstable

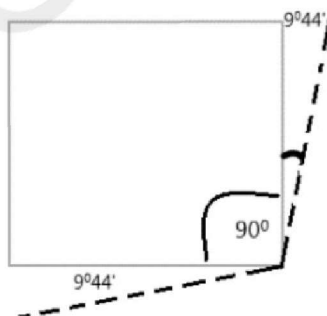
### Angle Strain (bond angle strain):

- Strain due to deviation from one or more ideal bond angles.
- Cyclopropane has angle strain because its C-C-C bond angles are constrained to be  $60^{\circ}$ , which is less than  $109.5^{\circ}$ , the ideal bond angle for tetrahedral carbon.



### Cyclobutane:

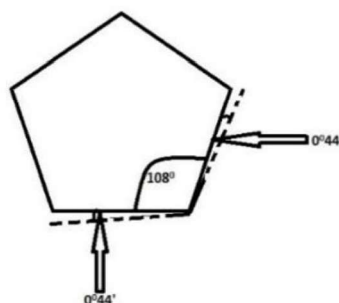
- The four carbon atoms occupy the corners of a square. So it has C—C—C bond angles of  $90^{\circ}$  & angle strain on each bond is  $\frac{1}{2}(109^{\circ}28' - 90^{\circ}) = 9^{\circ}44'$ .



### Cyclo-Pentane:

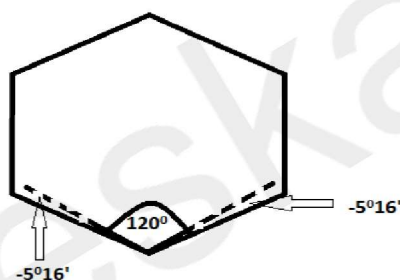
- The five carbon atoms lie at the corners of a regular pentagon. Thus cyclopentane has C—C—C bond angles of  $108^{\circ}$ . The angle strain which each bond fills is  $\frac{1}{2}(109^{\circ}28' - 108^{\circ}) = 00^{\circ}44'$ .





### Cyclo-hexane:

- In cyclohexane the six carbon atoms occupy the corners of a regular hexagon. Thus cyclohexane has C—C—C bond angles of  $120^\circ$ .
- The angle strain will be  $\frac{1}{2}(109^\circ 28' - 120^\circ) = -5^\circ 16'$ . Similarly, in the case of cyclo-heptane the deviation from the normal tetrahedral angle is  $-9^\circ 03'$ . In the case of cyclooctane it is  $-12^\circ 46'$ .



### Limitation:

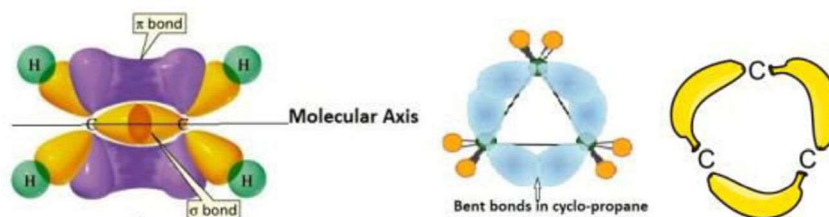
- This theory only applies on the lower cycloalkanes, Baeyer Cyclopentane should be much stable than cyclohexane but practically it is reversed (cyclohexane is more stable than cyclopentane).
- So Higher cyclohexanes are not follow this rule (cyclohexane, cycloheptane are more stable)
- They do not give ring opening reaction easily like cyclopropane.

### Coulson and Moffitt's modification (Bent bond/Banana bond):

- 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 ( $60^\circ$ ).
- 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.

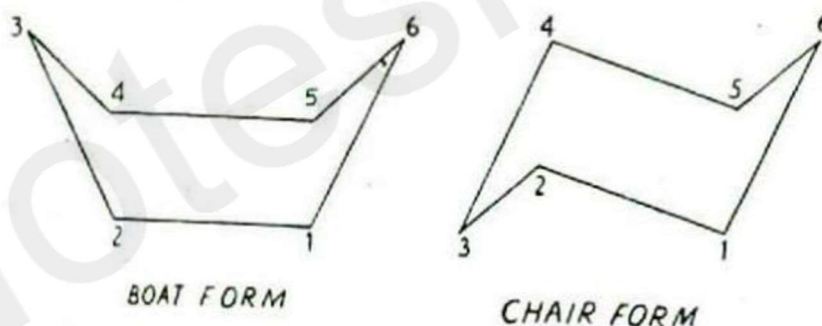


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### Sachse mohr's concept of strainless rings:

- The stability of cycloalkanes beyond cyclopentane, Sachse and Mohr (1918) pointed out that such rings can become absolutely free of strain if all the ring carbons are not forced into one plane as was supposed by Baeyer.
- If the ring assumes a such 3D condition the normal tetrahedral angles of  $109^{\circ}28'$  are retained and as a result, the strain within the ring is relieved.
- Thus, cyclohexane can exist in two non-planar stainless forms, namely, the Boat form and the 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.



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