ORGANIC CHEMISTRY-II

UNIT 5 NOTES

CYCLOALKANES

- BAEYER'S STRAIN THEORY
- COULSON AND MOFFITT'S MODIFICATION
- SACHSE MOHR'S THEORY
- REACTION OF CYCLOBUTANE AND CYCLOPENTANE

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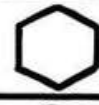
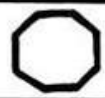
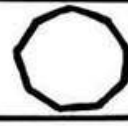
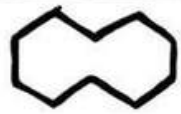
CYCLOALKANES

- Cycloalkanes are saturated, closed chain hydrocarbons that means all the carbon-carbon bonds in cycloalkanes are single covalent bonds.
- They are also called Cycloparaffins.
- General Formula = C_nH_{2n}.
- First member of cycloalkanes family is Cyclopropane.
- The IUPAC name of some of the cycloalkanes are as follows :

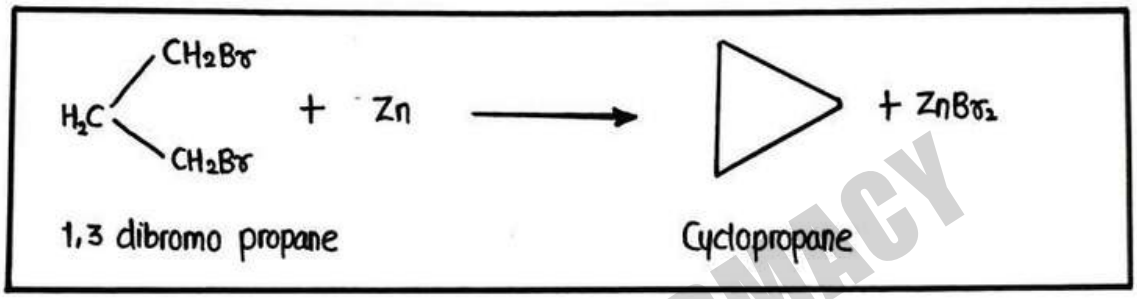
CYCLOALKANE	MOLECULAR FORMULA	STRUCTURE
Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	
Cyclodecane	$C_{10}H_{20}$	

METHOD OF PREPARATION

Cycloalkanes are prepared by following methods :

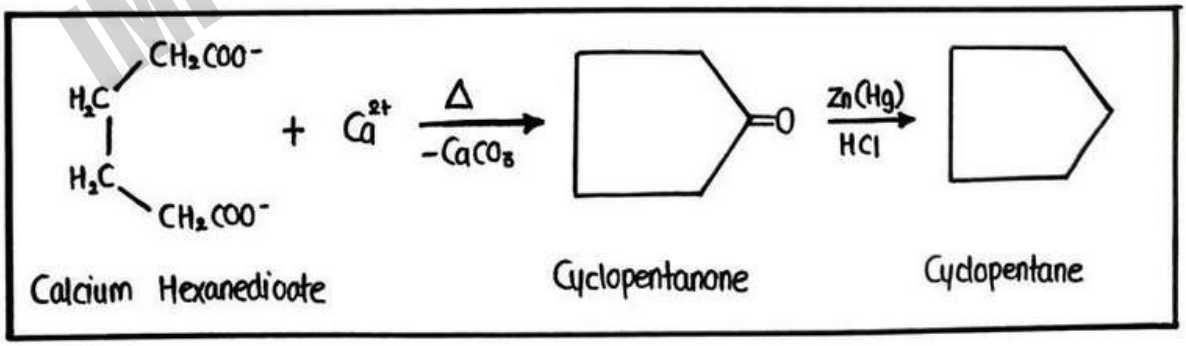
① From Dihalogen Compounds

Treatment of dihalogen derivatives of Alkanes with sodium metal or zinc leads to the formation of Cycloalkanes.



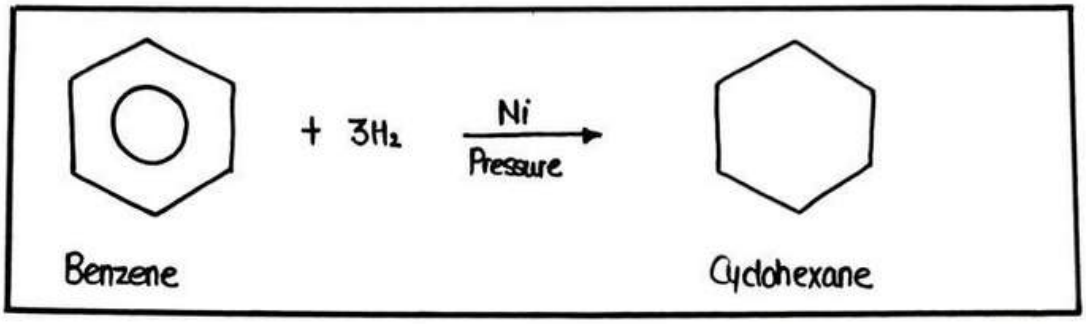
② From Calcium salt of Dicarboxylic Acids

On distillation of calcium salt of dicarboxylic acid, Cyclic ketone is obtained which on further redction with Zn(Hg)/HCl yeilds Cycloalkanes.



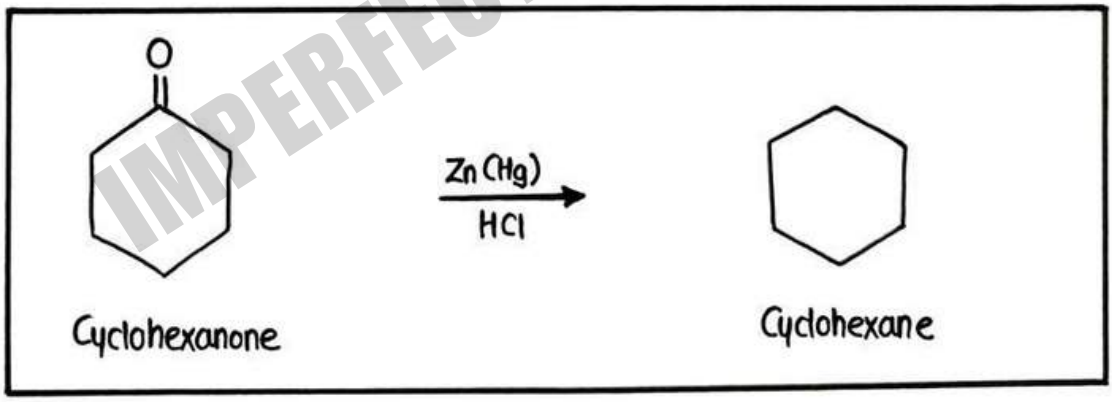
③ From Benzene

Catalytic reduction of Benzene under pressure in the presence of nickel (catalyst) yeilds Cyclohexane.



④ Clemensen's Reduction

Cyclic ketones reduced in the presence of Zn amalgam and concentrated HCl to give Cycloalkanes.

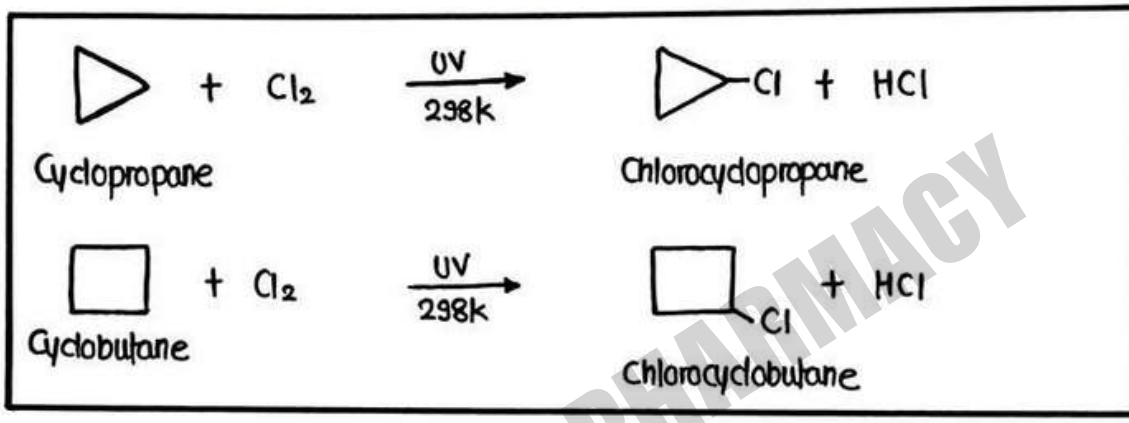


CHEMICAL REACTIONS

Cycloalkanes mainly undergoes following chemical reactions :

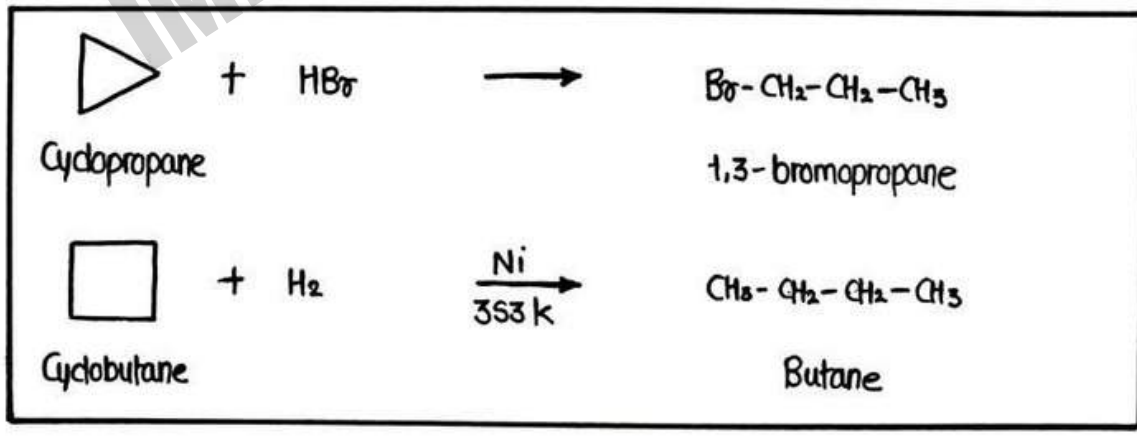
① Substitution Reaction

Cycloalkanes undergoes substitution reaction when they treated with halogens at 298 k in the presence of UV light.



② Addition Reactions

Cycloalkanes undergoes addition reaction to given open chain compounds :



Physical Properties Of Cycloalkanes

- The first two members of Cycloalkanes family (i.e., Cyclopropane & Cyclobutane) are colourless gases while higher members are liquids.
- They are lighter than water & non-polar in nature.
- They are insoluble in water but soluble in ethanol & ether.
- Their Melting & Boiling Point increases with increase in Molecular Weight.
- They are relatively inert in nature.

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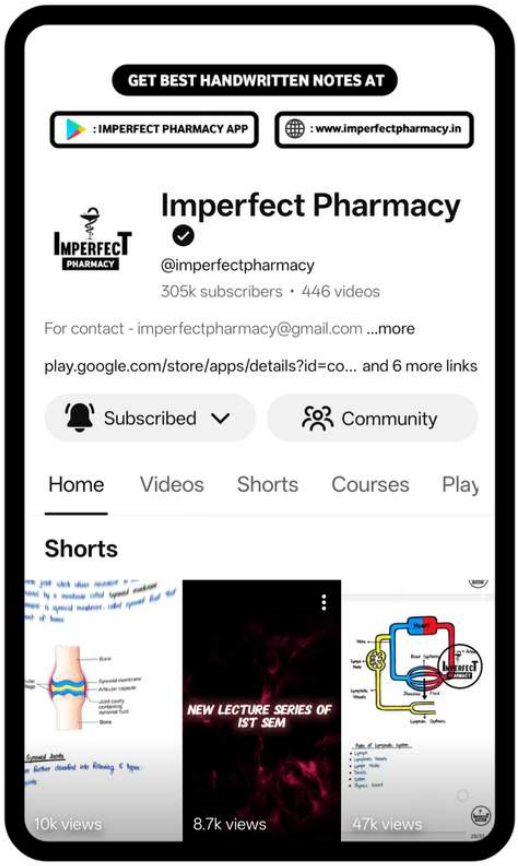

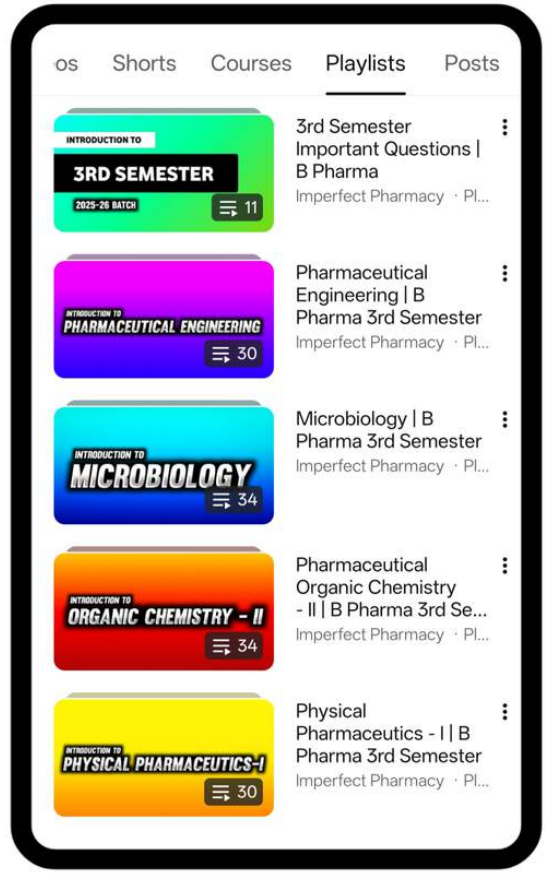

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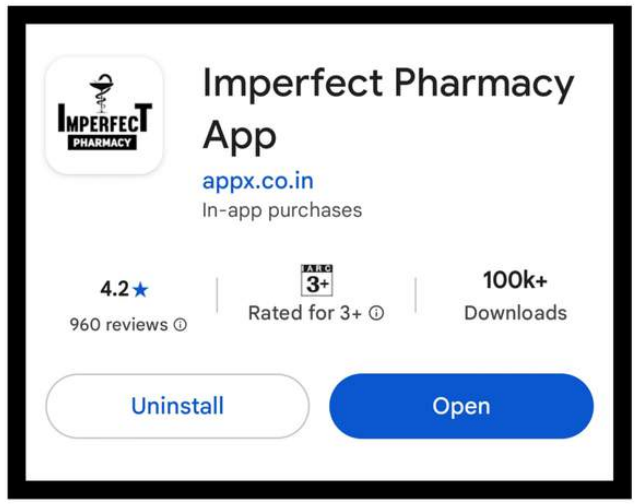


BAYER'S STRAIN THEORY

- Adolf Von Bayer in 1885 proposed a theory to explain the relative stability of Cycloalkanes.
- He proposed the theory of Angle Strain on the fact that since all the carbons of cycloalkanes are sp^3 hybridized, hence the bond angle b/w carbon atoms will have to be 109°28' in Cycloalkanes.
- But when Baeyer measures the angle of cycloalkanes he found different bond angle in different Cycloalkanes.
- On this basis, he proposed the theory of Angle Strain.
- The theory explains reactivity and stability of Cycloalkanes.
- According to him the distortion or deviation from normal tetrahedral angle (109°28') causes a strain in the ring that leads to the instability of Cycloalkanes.

ANGLE STRAIN

- The deviation in ideal bond angle from the real bond angle is called Angle Strain.
- Higher the angle strain, lesser will be the stability & higher the reactivity of Cycloalkanes.

$$\text{ANGLE STRAIN} = \frac{1}{2}(109°28' - \text{Bond Angle})$$

Bond Angle

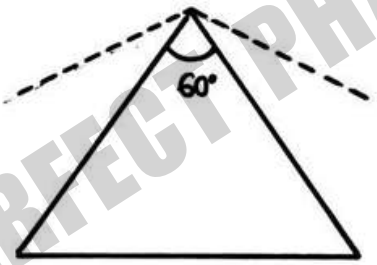
The actual bond angle can be calculated by following method :

$$\text{Bond Angle} = \frac{180(n-2)}{n}$$

n = no. of internal angles

Angle Strain In Cyclopropane

- Since all the carbon atoms of cyclopropane are sp^3 hybridized hence bond angle should be 109°28'
- But since the ring of cyclopropane is a triangle, hence all the angle are of 60° instead of 109° 28' that leads to angle strain in cyclopropane.



$$\text{Angle Strain} = \frac{1}{2}(109°28' - 60°) = \frac{49°28'}{2} = 24°44'$$

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

- The angle strain is maximum in Cyclopropane compare to other cycloalkanes hence it is very unstable & highly reactive hence easily undergoes Ring Opening reactions.

ANGLE STRAIN IN VARIOUS CYCLOALKANES

- Angle strain according to baeyer's theory in first five members of Cycloalkanes are given as follows :

CYCLOALKANES	ACTUAL BOND ANGLE	ANGLE STRAIN
Cyclopropane	60°	24°44'
Cyclobutane	90°	9° 44'
Cyclopentane	108°	0°44'
Cyclohexane	120°	−5°16'
Cycloheptane	128°·34'	−9°33'

- According to this table it is clear that Cyclopropane has maximum distortion hence it is most unstable cycloalkane that is true.
- But according to the above table Cyclopentane will be more stable than Cyclohexane that is not true at all.

LIMITATIONS :

- Baeyer's strain theory is applicable only for upto first 3 members of Cycloalkanes family.
- He assumed that all the Cycloalkanes are planer in nature.
- He did not explain angle strain in larger Cycloalkanes
- According to Baeyer, Cyclopentane should be more stable than cyclohexane but actually it is reversed.

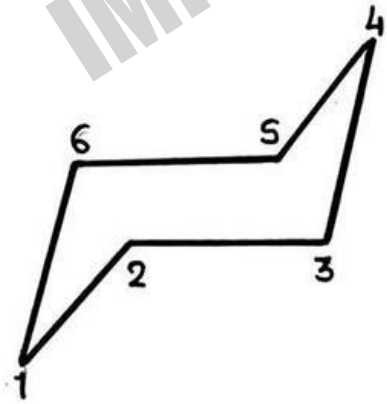
CYCLOPENTANE > CYCLOHEXANE > CYCLOBUTANE > CYCLOPROPANE

SACHSE MOHR'S THEORY

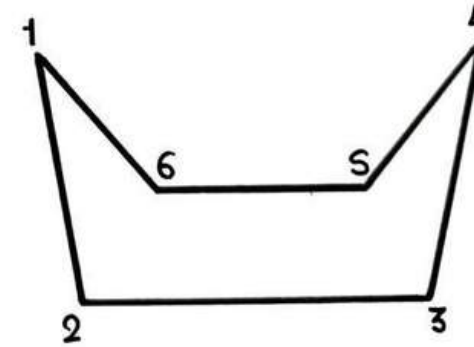
- It is also known as Theory of Strainless Rings.
- Baeyer's theory failed to explain the stability of higher cycloalkanes (i.e., Cyclohexane, Cycloheptane) because he assumed that all the cycloalkanes are planer in nature.
- Sachse and Mohr in 1918 proposed a theory to explain the stability of higher Cycloalkanes.
- According to Sachse Mohr's theory the higher cycloalkanes are free from any kind of strain and very stable if they are not forced into a plane.
- He assumed that ring are folded or in puckered condition & that's why they retained their normal tetrahedral angle (109°28') and as a result they become free from any kind of strain.

CHAIR & BOAT FORM OF CYCLOHEXANE

According to Sachse Mohr's theory Cyclohexane exist in two non-planer form i.e., Chair Form & Boat Form.



CHAIR FORM



BOAT FORM

- In the Boat Form, Carbon no. 2, 3, 5 and 6 lie in the same plane and carbons 1 & 4 above the plane.
- In the Chair Form, Carbon no. 2, 3, 5, 6 lie in the same plane and carbon 4 is above the plane & carbon 1 below it.
- Between Both Chair form of Cyclohexane is more stable than its boat form because Boat form has unfavourable non-bonded interaction b/w hydrogen atoms.
- The Chair & Boat form of cyclohexane rapidly interconverted into each other & that's why they can not be isolated individually.

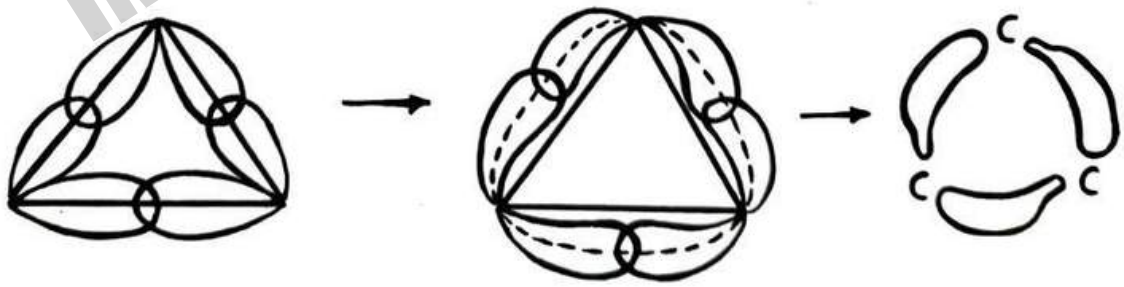
Coulson & Moffit's Modification

- It is also known as Banana Bond Theory or Bent Bond Theory.
- Coulson & Moffit modifies Baeyer's strain theory and proposed the Bent Bond Theory to explain the stability of cycloalkanes.
- They proposed a new type of Bent or Banana bond blw carbon atoms of Cyclopropane ring based on the basis of quantam mechanical condition.
- The theory of Banana Bond is based upon overlapping of Atomic Orbitals.

- Sigma Bond : Axial / Head-On Overlapping
- Pie Bond : Sidewise / Parallel Overlapping
- Bent Bond : Intermediate of σ & π bond

Bent Bond

- A Bent bond also known as Banana Bond is a type of covalent bond that somehow looks like a banana.
- It is weaker than C-C sigma bond but stronger than C=C π bond.



- Due to the formation of Bent Bond, the cyclopropane C-C bond are weaker than normal C-C sigma bond, so due to this weaker bond, Cyclopropane is unstable and easily gives ring opening reactions.

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