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COLLEGE OF PHARMACY
(An Autonomous College)
BELA (Ropar) Punjab



Name of Unit	Benzene and its Derivatives
Unit no.	5
Subject /Course Name	Pharmaceutical Organic Chemistry-II
Subject/Course ID	BP301T
Class:B.Pharm.Semester	3 rd
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Learning Outcome of Module-5

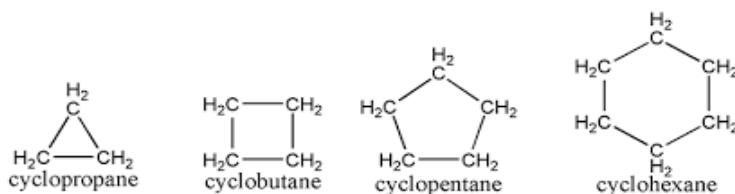
LO	Particular	Course Outcome Code
LO1.	Students are able to understand about Cycloalkanes.	BP301.3
LO2.	To gain knowledge about reactions of Cycloalkanes.	BP301.3
LO3.	To understand about the Stability of Cycloalkanes.	BP301.4
LO4.	To understand about Baeyer's strain theory and Sachse Mohr's Theory.	BP301.4

Module Content Table

No.	Topic
1.	Introduction of Cycloalkanes.
2.	Isomerism of Cycloalkanes.
3.	Nomenclature of Cycloalkanes.
4.	Methods Of Preparation Of Cycloalkanes
5.	Chemical reactions of Cycloalkanes.
6.	Stability of Cycloalkanes.
7.	Baeyer-Strain Theory
8.	Sachse-Mohr Theory
9.	Coulson and Moffitt's modification

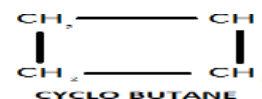
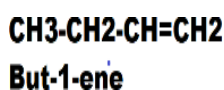
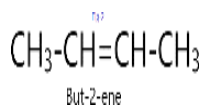
INTRODUCTION OF CYCLOALKANES: -

Cyclo-alkanes are also called **Cycloparaffins**. They are **Alicyclic Compounds** i.e. they are both **aliphatic and cyclic compounds**, and their properties are almost similar to alkanes. Cyclo-alkanes are **saturated hydrocarbons**, that means all the carbons present do not contain any pi bond, all their valency are satisfied with sigma bonds. Cyclo-alkanes have **General Formula C_nH_{2n}** with 1st member Cyclo-propane (Formula: C_3H_6).



Isomerism: -

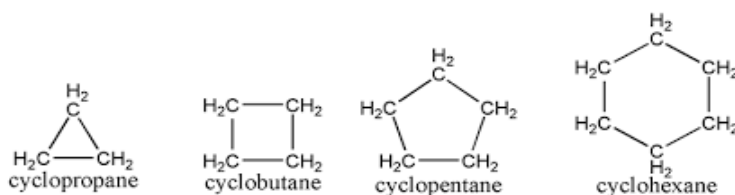
Cycloalkanes have same molecular formula to that of corresponding Alkenes. So they are functional isomers with alkenes of same carbon number. Example,



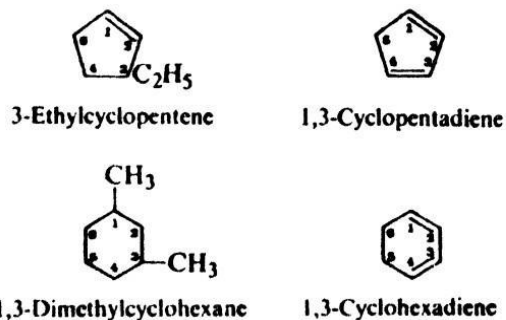
All the above three structures have same molecular formula C_4H_8 . But first two figures are functional isomer with the third figure.

Nomenclature: It can be read in 3 sections

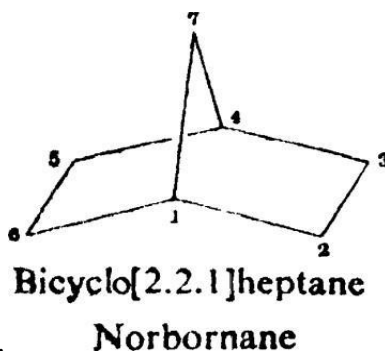
1. Naming of simple cycloalkanes: - It is done by attaching the prefix **cyclo** to the name of the corresponding normal alkane having the same number of carbon atoms as in the ring. For example



2. Naming of substituted cycloalkanes: - Naming of substituents in cycloalkanes as shown in 1st figure below are similar to that of straight chain compounds. But in 2nd compound which is a fused cycloalkane its typical

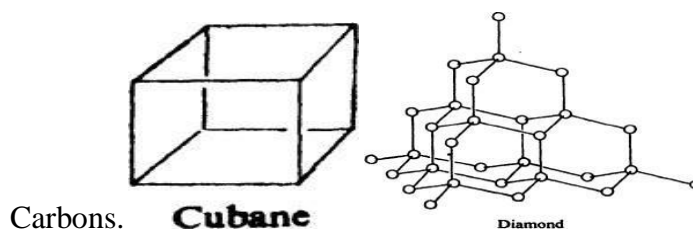


Let break the name Bicyclo[2.2.1]heptane. Bi cyclo implies the compound has two rings i.e. if we break two carbon bonds, the compound will be an alkane of 7 carbon and can be a heptane. Now the most important part naming of '2.2.1'. It is so named because the number of carbons except bridgeheads and shared carbons is two (C-2 and C-3), two (C-5 and C-6), and the bridge



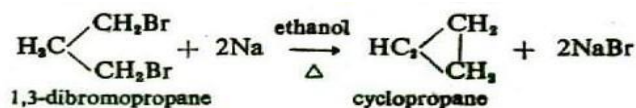
head made of one carbon i.e. C-7.

3.Example of typical Cycloalkanes: - Some typical fused cyclo-alkanes are given below. In Cubane each carbon attached to three other carbon, in diamond each carbon attached to 4 other



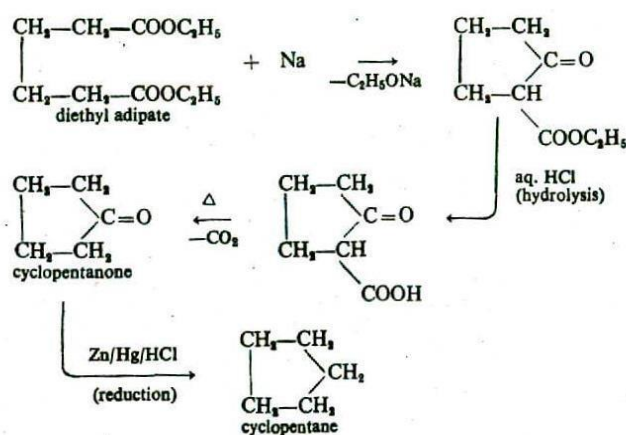
Methods of Preparation: -

1.From Di-halogen Compounds: - Suitable 1,3 or 1,4 like di- halogen alkanes on treatment with sodium or zinc give corresponding cycloalkanes. For example,

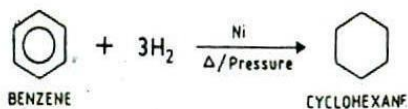


2. From Calcium or Barium salts of Dicarboxylic acids: - When the calcium or barium salt of adipic, pimelic, or suberic acid is heated, a cyclic ketone is formed. Cyclic ketones may be readily converted into the corresponding cycloalkanes by means of **the Clemmensen Reduction**.

3. From Esters of Dicarboxylic acids (Dieckmann Reaction): - The diester of adipic, pimelic, or suberic acid when treated with sodium undergoes intramolecular acetoacetic ester condensation and a keto- ester is formed. The keto- ester on hydrolysis give corresponding cyclic ketones. Cyclic ketones on reduction yield the corresponding cyclo- ketones.

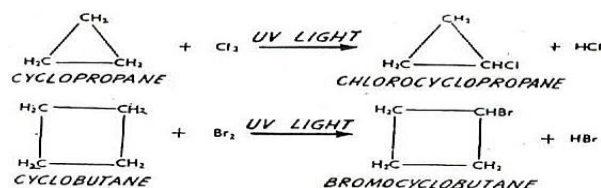


4. From Aromatic Compounds: - Benzene may be catalytically hydrogenated at elevated temperature and pressure to yield cyclohexane.

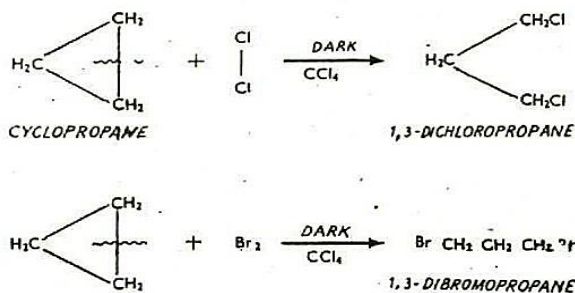


Chemical Reactions: -Cyclo-alkanes react mostly like their corresponding to their straight chain alkanes.

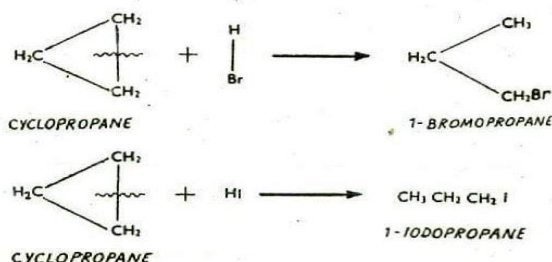
1. Halogenation in presence of UV-light: - Produce mono substituted halogen without breaking the ring.



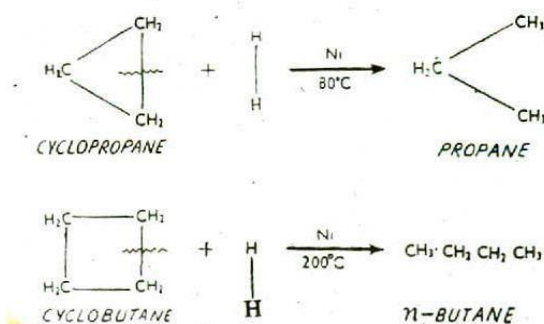
2. Addition of Cl₂/ Br₂ in presence of CCl₄ in dark: -Cyclopropane reacts with Cl₂/ Br₂ at room temperature and in the absence of diffused sunlight to produce 1,3-dichlorocyclopropane and 1,3-dibromocyclopropane respectively. One of the carbon-carbon bonds of cyclopropane is broken and the two halogen atoms appear at the ends of the propane chain.



3. Reaction with concentrated HBr and HI: - Produce 1-bromopropane and 1-iodopropane respectively with ring breaking.



4. Addition of Hydrogen / Catalytic Reduction: - Cyclo-propane and cyclo-butane react with hydrogen in the presence of a nickel catalyst to produce n-propane and n-butane respectively. Cyclopentane and higher members of the family do not give this reaction.



Stability of Cyclo-Alkanes: -

A stable organic compound means it is very less reactive. By the term stability we get an idea about chemical reactivity of a compound. To describe **stability of cycloalkanes** some very **famous theoretical concepts** are there viz.

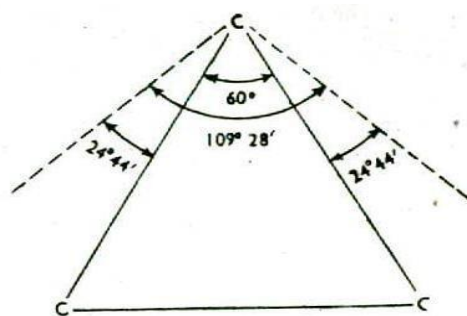
- Baeyer Strain Theory
- Sachse Mohr Concept
- Coulson and Moffitt's modification

Baeyer Strain Theory

Adolf von Baeyer, a German chemist and a Nobel prize winner from university of **Munich, Germany in 1885** proposed a theory to explain the relative stability of the first few cycloalkane. The theory based on following facts.

- Cyclo-alkanes are saturated compounds. So all the carbons should have normal tetrahedral angle of 109.5°
- Any deviation of bond angles from the normal tetrahedral value would, impose a condition of internal strain on the ring called **Angle Strain**.
- More the value of angle strain less stable the compound is.
- He assumes that all the cyclo-alkanes are flat and coplanar that means they are two dimensional and present in one plane.

Cyclopropane: -

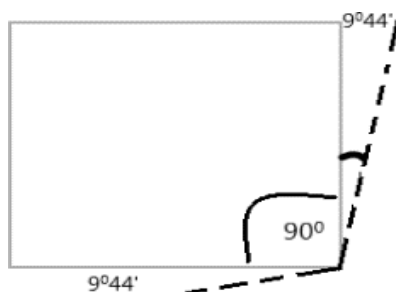


In cyclopropane, the three carbon atoms occupy the corners of an **Equilateral Triangle**. Thus cyclopropane has C—C—C bond angles of 60° . This implies that the normal tetrahedral angle of 109.5° between any two bonds is compressed to 60° , and that each of the

two bonds involved is pulled in by

$$1/2(109^{\circ}28' - 60^{\circ}) = 24^{\circ}44'.$$

The value $24^{\circ}44'$ then represents the **Angle Strain** or the deviation through which each bond bends from the normal tetrahedral direction.



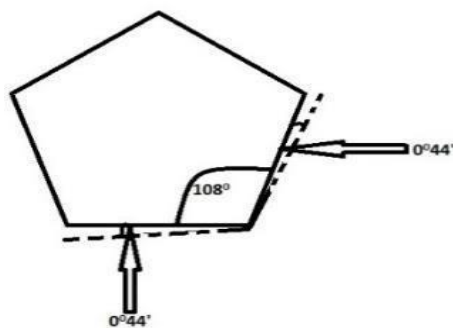
Cyclo-Butane: -

Here the four carbon atoms occupy the corners of a **square**. So it has C—C—C bond angles of 90° .

Angle Strain on each bond is

$$1/2(109^{\circ}28' - 90^{\circ}) = 9^{\circ}44'.$$

Cyclo-Pentane: -

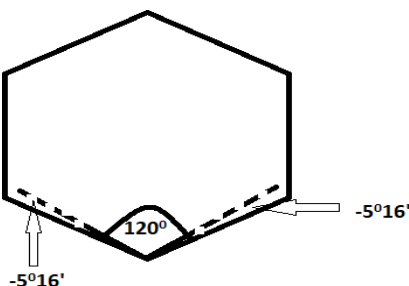


Here the five carbon atoms lie at the corners of a **Regular Pentagon**. Thus cyclopentane has C—C—C bond angles of 108° .

The **Angle Strain** which each bond fills is

$$1/2(109^{\circ}28' - 108^{\circ}) = 0^{\circ}44'.$$

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° .

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 $-9^\circ 33'$.

In the case of **Cyclooctane** it is $-12^\circ 46'$.

Derivation: -

Sr. No	Name	Angle strain
1	Cyclo-propane	$+24^\circ 44'$
2	Cyclo-butane	$+9^\circ 44'$
3	Cyclo-pentane	$+0^\circ 44'$
4	Cyclo-hexane	$-5^\circ 16'$
5	Cyclo-heptane	$-9^\circ 33'$
6	Cyclo-octane	$-12^\circ 46'$

1. The + sign indicates that the C—C bonds have to be **compressed to satisfy the geometry of the ring**. The - sign indicates that the C—C bonds have to be **widened to satisfy the geometry of the ring**. Whether the angle strain is positive or negative, its magnitude determines the extent of strain in the ring.

2. The deviation from the **normal tetrahedral angle is maximum** in the case of **cyclopropane**. So, it is **most unstable** and open up on the slightest provocation and thus releasing the strain within.
3. The deviation from the **normal tetrahedral angle is minimum** in the case of **cyclopentane**. This implies that **cyclopentane is under least strain and should be most stable**.
4. According to the Baeyer Strain Theory, **cyclohexane and the higher cycloalkanes should become increasingly unstable and hence more reactive**.

Drawbacks of Baeyer-Strain Theory: -

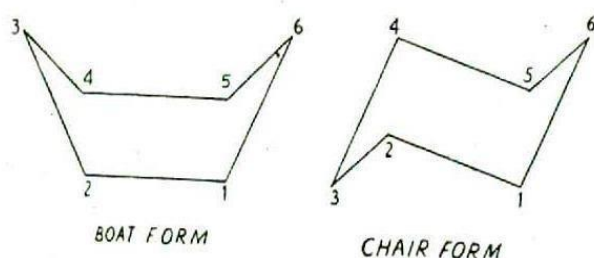
1. The **limitation of Baeyer strain theory** is that he assumed that **all cycloalkanes are planar**.
2. Baeyer was **unable to explain the effect of angle strain in Larger Ring System**.
3. According to Baeyer **Cyclopentane should be much stable than cyclohexane but practically it is reverse**.
4. **Larger ring systems are not possible** according to Baeyer as they **have negative strain** but they exist and much stable. Larger ring systems are not planar but puckered to eliminate angle strain.

Sachse Mohr's Concept of Strain less Rings: -

In order to account for 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 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 strainless 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.



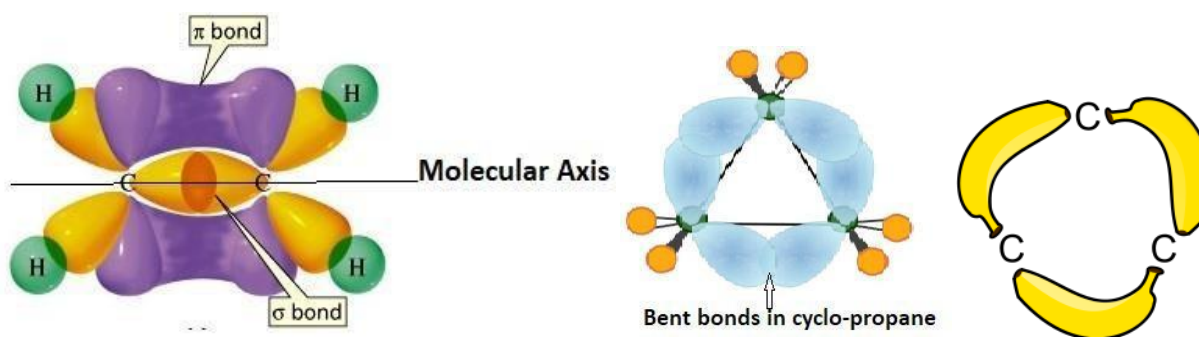
Actually, only one form of cyclohexane is known and not two forms as shown above. The failure to isolate the two forms is **due to rapid interconversions** between them. Such non-planar strain less rings in which the ring carbon atoms can have normal tetrahedral angles are also possible for larger ring compounds.

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°) 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.

What is this Bent bond: - Sigma bonds have head-on or end-to-end overlapping. The hybrid orbitals including the intersection bonding region are present equally on both side of the molecular axis. But in case of pi-bonds the lateral or sidewise overlapping of p-orbitals occur and here the bonding intersection area is totally out of the molecular axis.



In Bent-bond (usually they are sigma bonds) the hybrid orbitals and intersection bonding area are not present equally on the both side of molecular axis. The bonds are bent towards the direction of angle strain. So they are some what more unstable than sigma bonds and less unstable than pi bonds.

IMPORTANT QUESTION

Questions carrying 2 marks

1. Explain why cyclobutane is more stable than cyclopropane
2. Write any two reactions of cyclobutane.
3. Write any two reactions of cyclopropane.
4. Write any two methods of preparation reactions of cyclopropane.
5. Define angle strain.

Questions carrying 5 or 10 marks

1. Compare the stability of cyclobutane with cyclohexane using Baeyer's strain theory.
2. Write a brief note on Baeyer's strain theory and its limitations.
3. Comment upon "the stability of cycloalkanes with the help of various theories."
4. Explain opening of cyclopropane ring using Coulson-Moffitt's modification.
5. Discuss Sachse – Mohr's theory to explain the concept of strain less ring.
6. What are limitations of Baeyer's strain theory? Explain how these limitations are overcome by Sachse-Mohr's theory.
7. Explain why cyclopentane and cyclohexane are more stable than lower cycloalkane?