SRI V.S. SIVALINGAM CHETTIAR GOVERNMENT DEGREE COLLEGE, SULLURUPET-524121 TIRUPATHI, DISTRICT

DEPARTMENT OF CHEMISTRY

GUEST LECTURE PROGRAM BY SRI. N. GANESH ON CYCLOALKANE

Sri N.Ganesh Lecturer in chemistry Government Degree College , Kuppam visited to our college to deliver a lecturer on Cycloalkane.

Sri N Ganesh visited our college on 02-09-2022 . He was introduced to the students by Sri Ch Subrahmany Sastry Lecturer in Chemistry. He is Lecturer in Government Degree College, Kuppam previously he work in this college from 2014 as a Lecturer. By that time he work was in charge For PG (M.Sc Chemistry) and also in charge to IGNOU (Indira Gandhi National Open University) .

Sri N Ganesh has explain ed about the general Introduction of Cycloalkane . He also briefed the preparation methods and properties of Cycloalkane students satisfied by his lecture. After completion of topic students interacted clarified doubts .

Principal Honoured a Memento and this lecturer is conclude write Oaths of thanks by one of the students .


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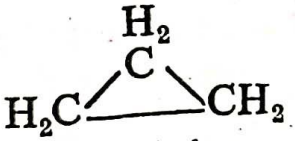
N GANESH GDC KUPPAM
02.09.2022
Newline

Cycloalkanes

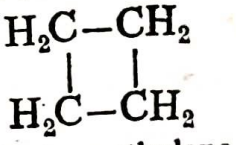
9·1. Introduction. *Alicyclic (aliphatic cyclic) compounds are those carbocyclic* compounds which resemble with the aliphatic compounds in their properties.* Thus we can say that our knowledge of aliphatic compounds can be applied to the chemistry of alicyclic compounds.

Occurrence. Alicyclic compounds occur widely in essential oils. The five and six membered cycloparaffins are obtained from naphtha (a fraction of petroleum), hence these are also known as **naphthenes.**

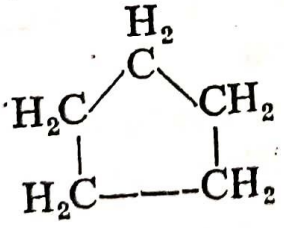
9·2. Nomenclature. Since the saturated alicyclic hydrocarbons possess a number of methylene groups joined together to form a cyclic structure, they are also known as **polymethylenes;** the number of methylene group is indicated by a Greek or the Latin prefix *i.e., tri- tetra-, penta-,* etc. For example,



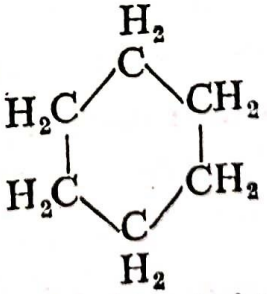
Common name: Trimethylene
IUPAC name: (Cyclopropane)



Tetramethylene
(Cyclobutane)



Pentamethylene
(Cyclopentane)



Hexamethylene
(Cyclohexane)

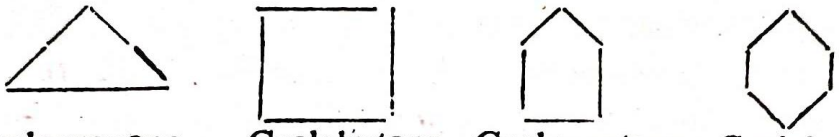
Common name
IUPAC name

According to IUPAC system, these are named as **cycloalkanes** or **cycloparaffins;** *i.e.* their names are derived by adding the

*Carbocyclic or homocyclic compounds may be defined as those cyclic compounds in which rings are formed by carbon atoms only. They are further divided into two types, *viz.* alicyclic and aromatic.

prefix *cyclo* to the name of the corresponding open chain hydrocarbon *e.g.*, trimethylene is named as cyclopropane, tetramethylene as cyclobutane and so on.

9·3. Symbols of Cycloalkanes. For convenience and simplicity, cycloalkanes are usually represented by simple geometric figures corresponding to the number of carbon atoms constituting the ring. Thus cyclopropane is represented by a *triangle*, cyclobutane by a *square*, cyclopentane by a *pentagon* and cyclohexane by a *hexagon*.



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

9·4. General Methods of Preparation. Following general methods are commonly used for the preparation of cycloalkanes.

1 Freund's method (*From α, ω-dihalides*). This method is extension of Wurtz reaction and may be regarded as *intenal Wurtz reaction.* It consists in treating α, ω[1]-dichloro or dibromoalkane with sodium or zinc.

$$(CH_2)_n\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + Zn \rightarrow (CH_2)_n\begin{matrix}CH_2\\|\\CH_2\end{matrix} + ZnBr_2$$

α, ω-Dibromoalkane — Cycloalkane (n=1, 2, 2 3, or 4)

The method has been used for the preparation of cyclopropane (n=1), cyclobutane (n=2), cyclopentane (n=3) and cyclohexane (n=4), however the best yield is obtained in case of cyclopropane. The method cannot be applied for the formation of compounds containing more than six carbon atoms because the yields are poor due to Wurtz reaction.

2. Wislicenus method. *By heating calcium or barium sait of a* 1, 6- *or* 1, 7-*dicarboxyic acid* (*Blanc rule*[2]) *and reduing the ketone so obtained.*

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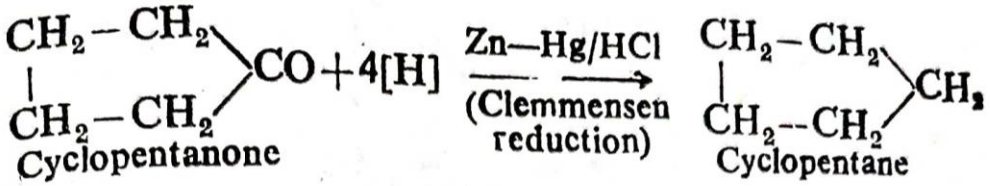
1. The greek letter omega (ω) is generally used to designate a substituent at the end of a cha.n.

2. The effect of heat.ng on various dicarboxylic acids can be summarised in the form of **Blanc rule** according to which *dicarboxylic acids having two carboxylic groups on the same carbon atom* (1, 3-*dicarboxylic acids*) *when heated form monocarboxylic acids*; 1, 4- *and* 1, 5-*dicarboxylie acids on heating or on distillatiou with acetic anhydride form cyclic anhydrides, while* 1, 6- *and* 1, 7-*dicarboxylic acids on distillation with acetic anhydride form cyclic ketones.

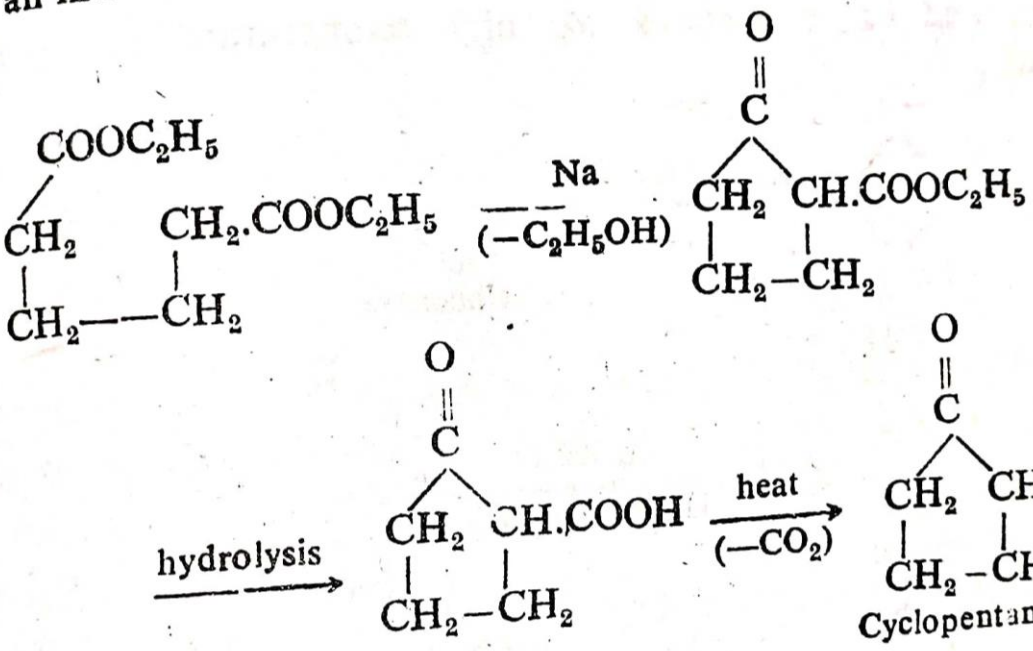
Calcium adipate



Cyclopentanone — Cyclopentane

This method is suitable for the synthesis of 5- and 6-membered ring ketones; 6-membered ring is obtained from calcium pimelate.

3. **Dieckmann's method.** (*By heating esters of dicarboxylic acids with sodium or sodium ethoxide*). This reaction is considered as an intramolecular Claisen condensation[1].



Cyclopentanone

As in method No. 2, cyclopentanone may be converted into cyclopentane by Clemmensen reduction (reduction of carbonyl group $>C=O$ to methylene group $>CH_2$ by amalgamated zinc and hydrochloric acid).

4. **From active methylene compounds.** Acetoacetic ester and malonic ester condense with suitable dihalides to form cyclic compounds. For example,

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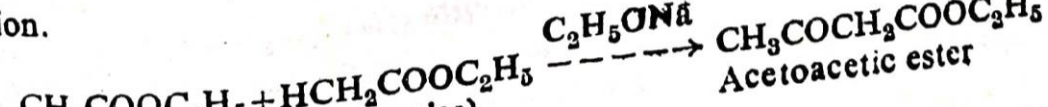
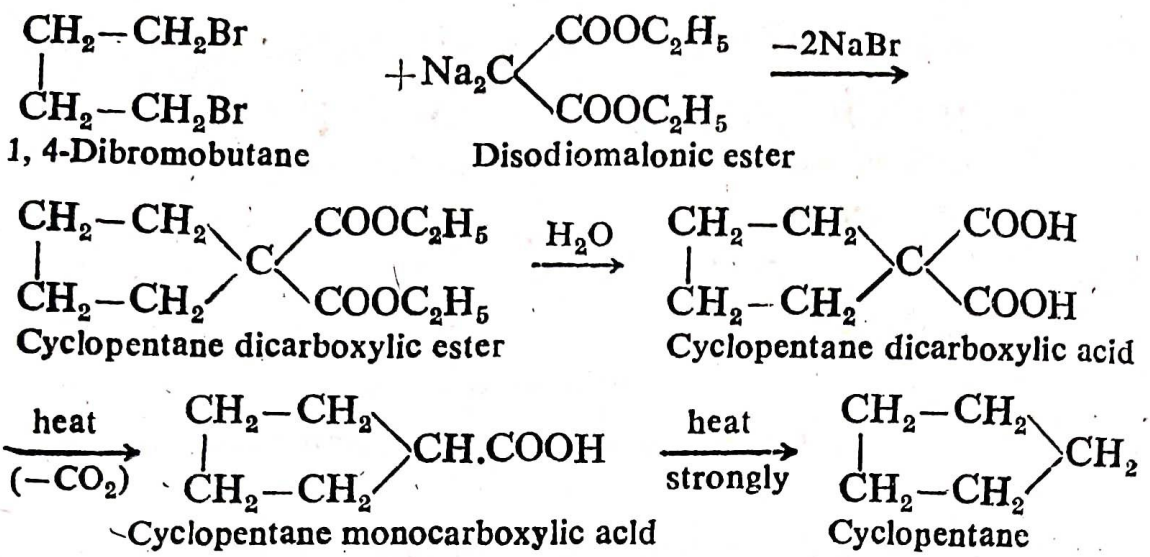
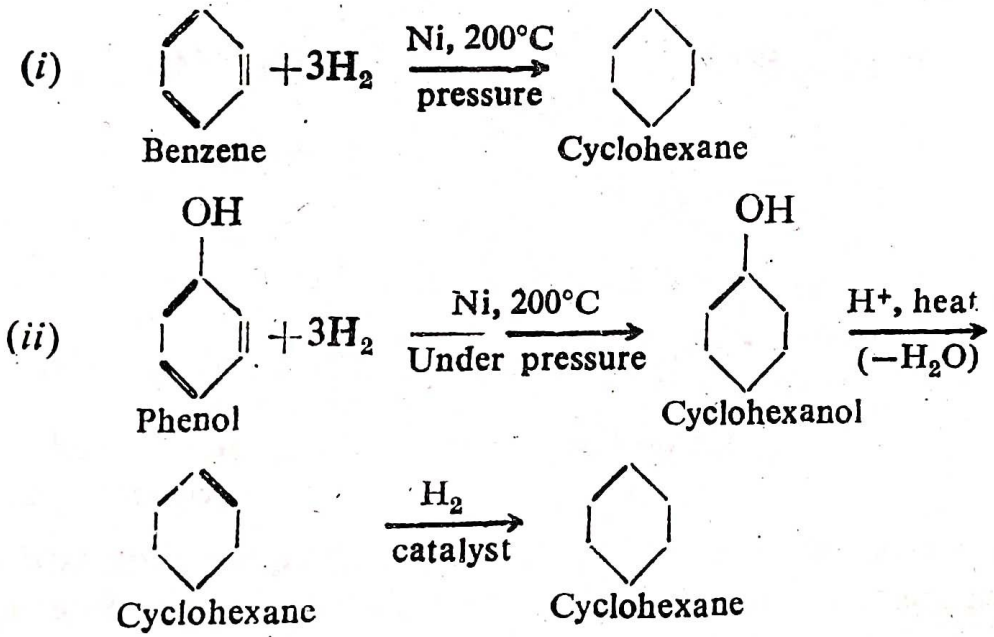
1, Condensation of two molecules of ester (*e.g.* ethyl acetate) in presence of sodium ethoxide to form β-keto esters is known as Claisen condensation.



Ethyl acetate (2 molecules) — Acetoacetic ester

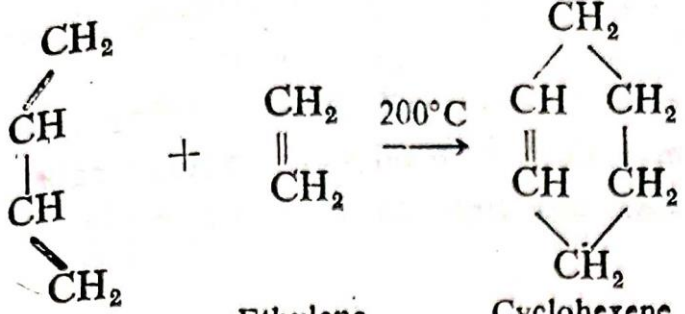


5. From aromatic hydrocarbons. Cyclohexane and its derivatives may best be prepared by the catalytic hydrogenation of benzene and its derivatives at high temperature and under pressure.



6. Cycloaddition reactions. *An addition reaction between two unsaturated molecules resulting in the formation of a cyclic product is known as cycloaddition reaction.* In these reactions, π electrons of the two molecules form two σ bonds. These reactions are designated by writing the number of π electrons of each component in a square bracket. Thus they are of following two types.

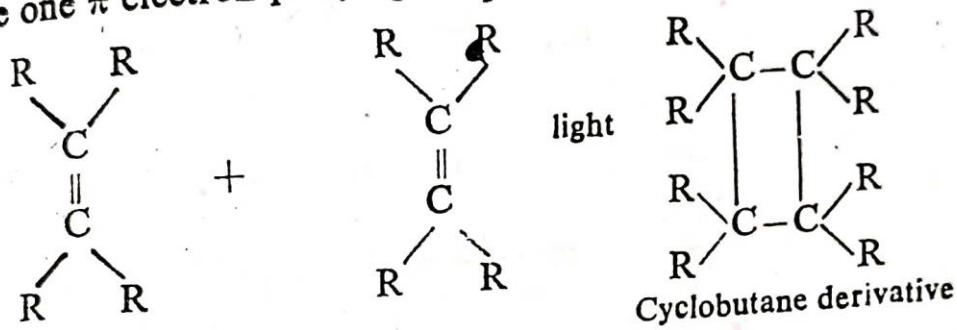
(*a*) **[4+2] Cycloaddition (Diel's-Alder reaction).** *This reaction involves the addition of an alkene molecule (with 2π electrons) called a* **dienophile** *to a conjugated* **diene** *(4π electrons) resulting in the formation of a cyclohexane derivative, e.g.*



1, 3–Butadiene (a diene) | Ethylene (a dienophile) | Cyclohexene (cyclic adduct)

The reaction takes place readily even at room temperature if the dienophile has an electron withdrawing group like –CHO, >CO, –CN, –COOH, Cl, etc.

(*b*) **[2+2] Cycloadditions.** When both of the components have one π electron pair, *e.g.*



Cyclobutane derivative

9·5. General Physical Properties. 1. The first two members *i.e.* cyclopropane and cyclobutane are colourless, pleasant smelling gases while higher members upto cycloheptane are liquids, and still higher ones are solids.

2. They are insoluble in water but soluble in ethanol and ether.

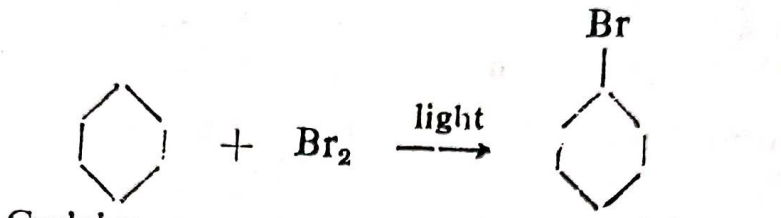
3. Their b.p., m.p. and density show a gradual increase with the increase in molecular weight. The boiling points are higher than those of isomeric alkenes and alkanes.

4. **Spectroscopic properties.** Cycloalkanes do not show any absorption in *UV and visible region.* Like alkanes they show characteristic C–H stretching absorption in the *IR region* at 3050–2850 cm^{-1}. The *NMR spectra* of simple cycloalkanes show one sharp absorption band due to the equivalence of all protons.

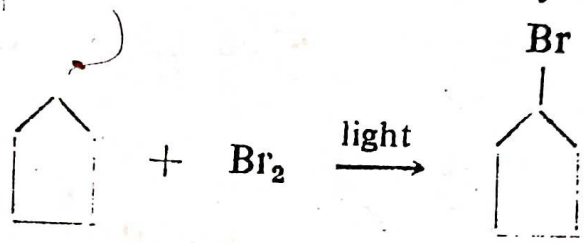
9·6 General Chemical Properties. Cycloparaffins resemble with the paraffins in several chemical properties, but at the same time the lower members (cyclopropane and cyclobutane) form addition compounds with the ring fission. Thus cycloalkanes

behave both like alkanes as well as alkenes. Some of the important chemical properties are given below.

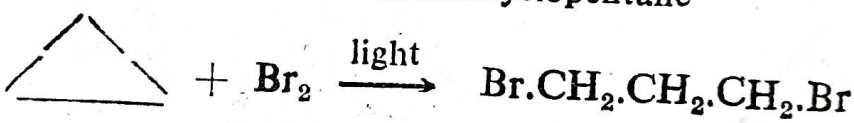
1. **Substitution reactions :** All cycloparaffins, except cyclopropane which forms addition products, undergo substitution by halogen in the diffused day light to form the respective halogen derivative, *e.g.*



Cyclohexane Bromocyclohexane



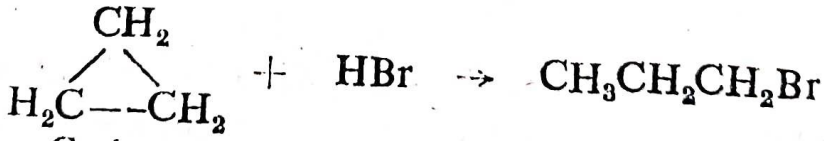
Cyclopentane Bromocyclopentane



Cyclopropane 1, 3-Dibromopropane

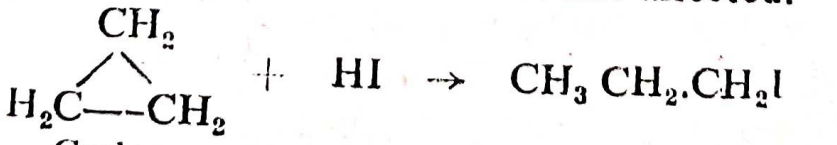
2. **Addition reactions :** Lower cycloparaffins add hydrogen bromide, hydrogen iodide and hydrogen in the presence of nickel as a catalyst to form the respective addition products.

(*a*) *Addition of hydrogen bromide.* Hydrogen bromide attacks only cyclopropane to form *n*-propyl bromide, whereas the other members are not affected at all.

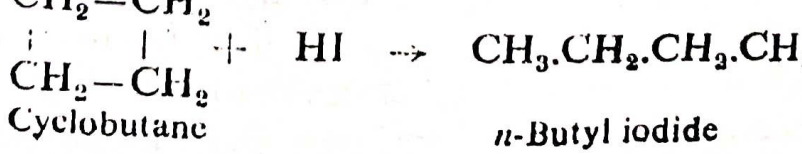


Cyclopropane *n*-Propyl bromide

(*b*) *Addition of hydrogen iodide.* Hydrogen iodide adds on cyclopropane at room temperature, and on cyclobutane at higher temperature, the other higher members are not affected.

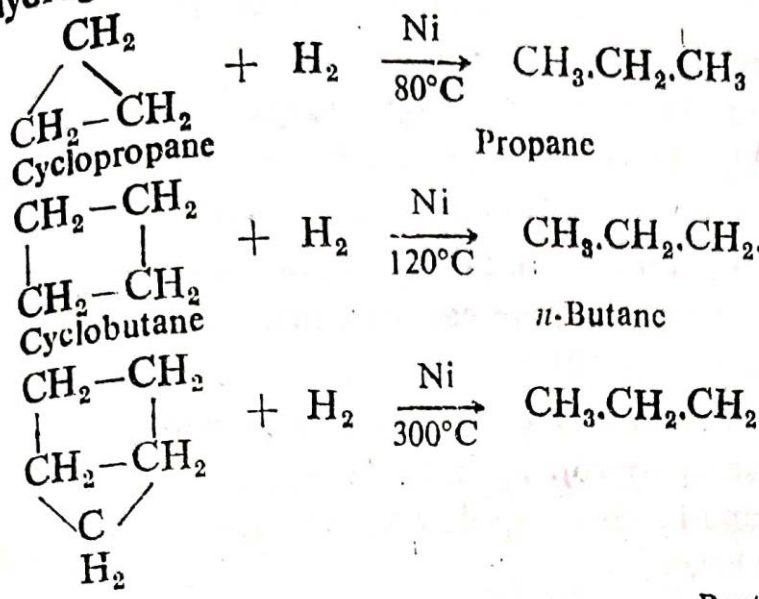


Cyclopropane *n*-Propyl bromide



Cyclobutane *n*-Butyl iodide

(c) *Addition of hydrogen.* Cycloalkanes upto cyclopentane add hydrogen is presence of nickel at the specific temperature, *e.g.*



The higher cycloalkanes are not affected by hydrogen in presence of nickel.

3. **Relative stability.** The above properties indicate that the lower cycloparaffins, *viz.* cyclopropane and cyclobutane are less stable and the rings are easily opened by the various reagents. Moreover, these reactions also indicate that the stability of the ring increases as the ring becomes larger, *i.e.* the stability of the various cycloparaffins upto six-membered can be represented as below.

cyclopropane < cyclobutane < cyclopentane < cyclohexane

The opening of the ring (or unstability) in case of three and four-membered compounds was explained by Adolf Von Baeyer (1885) in the form of his theory commonly known as **Baeyer strain theory.**

9·7. Baeyer Strain Theory. The Baeyer strain theory is based on the following assumptions.

(*i*) Since carbon atom is tetrahedral in nature with all the four valencies directed towards four corners of a regular tetrahedron, the angle between any two bonds should be 109° 28′. Thus *any deviation from this value would result in an internal strain in the molecule.*

(*ii*) All carbon atoms of a cycloalkane ring are planar indicating that *cyclopropane ring is an equilateral triangle, cyclobutane ring is a square* and other *cycloalkane rings are regular polygons.*