



Shree H.N.Shukla College of Science Rajkot

B.Sc. (Sem- 6) (CBCS)

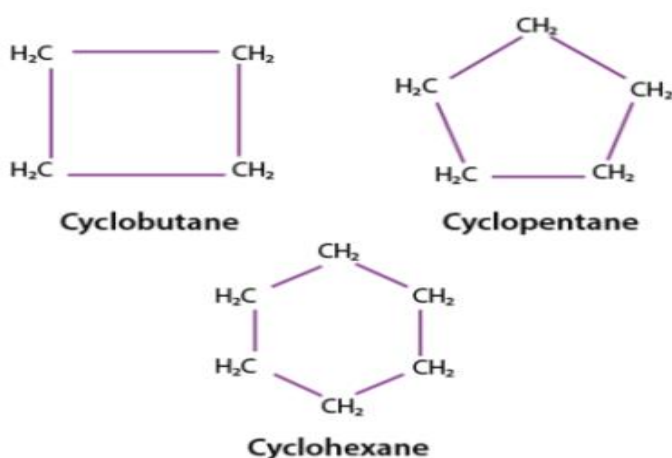
CHEMISTRY: [602]

Unit-3 Chapter-5: Cycloalkane

What are Cycloalkane?

Cycloalkanes are the class of hydrocarbons having a ring-like structure. This ring is formed due to their saturated nature, and they have three compounds of alkane present in the structure which helps them in forming a ring. They have the general formula C_nH_{2n} , Where n is said to be the number of carbon atoms present in the organic compound.

Examples of some cycloalkanes



Classification of Cycloalkanes

Hydrocarbons having more than one ring are common, and are referred to as bicyclic (two rings), tricyclic (three rings) and in general, polycyclic compounds. The molecular formulas of such compounds have H/C ratios that decrease with the number of rings. In general, for a hydrocarbon composed of n carbon atoms associated with r rings the formula is: $C_n H_{(2n + 2-2r)}$. The structural relationship of rings in a polycyclic compound can vary. They may be separate and independent, or they may share one or two common atoms. Some examples of these possible arrangements are shown in the following table.

Examples of Isomeric C_8H_{14} Bicycloalkanes

Isolated Rings	Spiro Rings	Fused Rings	Bridged Rings
No common atoms	One common atom	One common bond	Two common atoms



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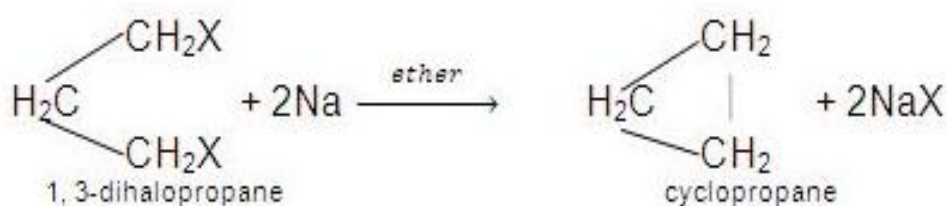
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Short Question/Blank	
1. What is general formula of Cycloalkane?	C_nH_{2n}
2. How many Number of C- atom common in Spiro compounds?	One
3. In Cyclo alkane repetating unit is _____	$-CH_2$ group
4. Angle strain also known as _____	Pitzer strain

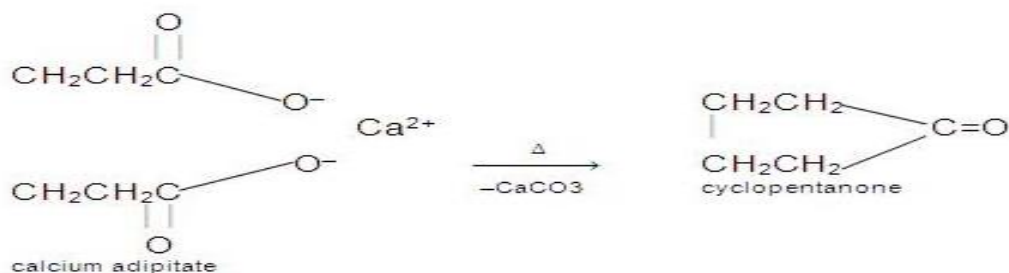
Preparation of Cycloalkanes

Following methods are commonly used for the preparation of cycloalkanes.

(a) **From dihalogen compounds** : α - ω elimination from dihalides having halogen atoms on two ends of carbon chain (α - ω dihalides) with Na or Zn dust gives rise to the formation of cycloalkanes. The method can be regarded as intramolecular Wurtz reaction and is called Freund reaction. This can be used to prepare cycloalkanes from three to six carbon atoms.



(b) **By Clemmensen reduction**: The reduction of cyclic ketones by Zn-Hg/HCl gives cycloalkanes.





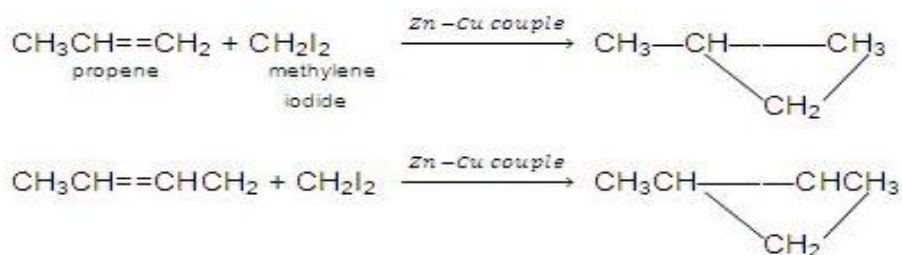
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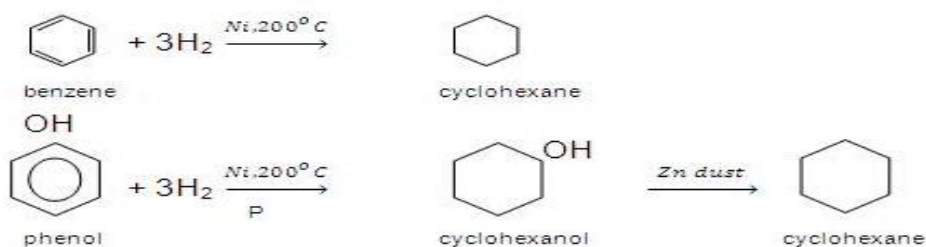
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(c) **From alkenes:** Alkenes on treating with CH_2I_2 in presence of Zn-Cu couple or by diazomethane (CH_2N_2) in presence of U.V. light gives derivatives of cycloalkanes.



(d) **From aromatic compounds:** Six membered cyclo compounds can be easily obtained by the catalytic reduction of benzene and its derivatives.



➤ Physical Properties of Cycloalkanes

The various physical properties of Cycloalkanes are given below-

- ✓ 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



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- ✓ Since the electronegativity between the carbon-hydrogen bonds is found to be too less for these compounds, they are said to be not having any polarity between the bonds.
- ✓ These class of saturated hydrocarbons is said to be insoluble in water, and the cycloalkanes in liquid form are said to be the good form of solvents for other organic compounds.
- ✓ The molecule of cycloalkane gets destroyed when burned
- ✓ Cyclopropane is said to be the most reactive compound when compared to other cycloalkanes.



Chemical Properties of Cycloalkanes

Cyclopropane and Cyclobutane are comparatively less stable due to more strain in ring (Follow Baeyer's strain theory) and thus tend to breakup and open the ring to act like a double bond species to give addition reactions. The cycloalkanes from cyclopentane and onwards show remarkable similarities with alkanes due to their stability. The stability of higher cycloalkanes is due to less strained ring as well as each carbon atom being sp^3 hybridized like alkanes. It is therefore higher cycloalkanes are not attacked by acids, alkalis and common oxidizing under normal conditions. Following are some important reaction of cycloalkanes.

- (a) **Free radical substitution** : Cycloalkanes are halogenated in presence of sun light or UV light like alkane.

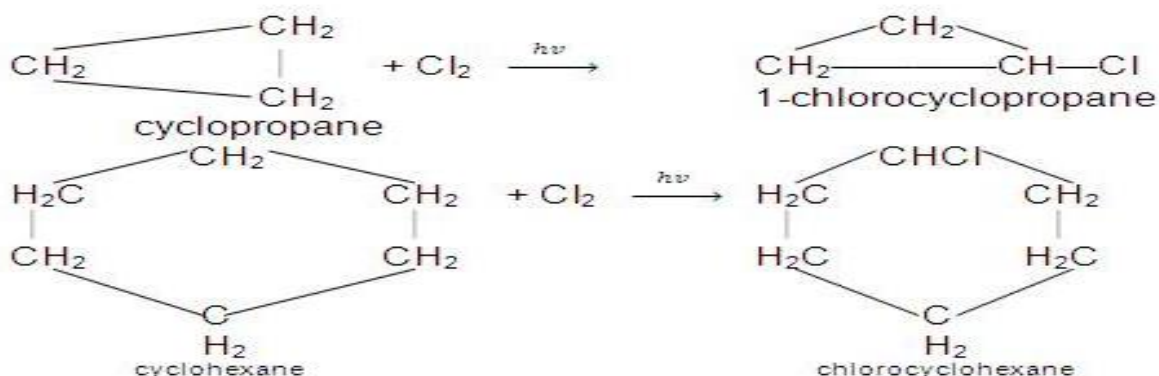


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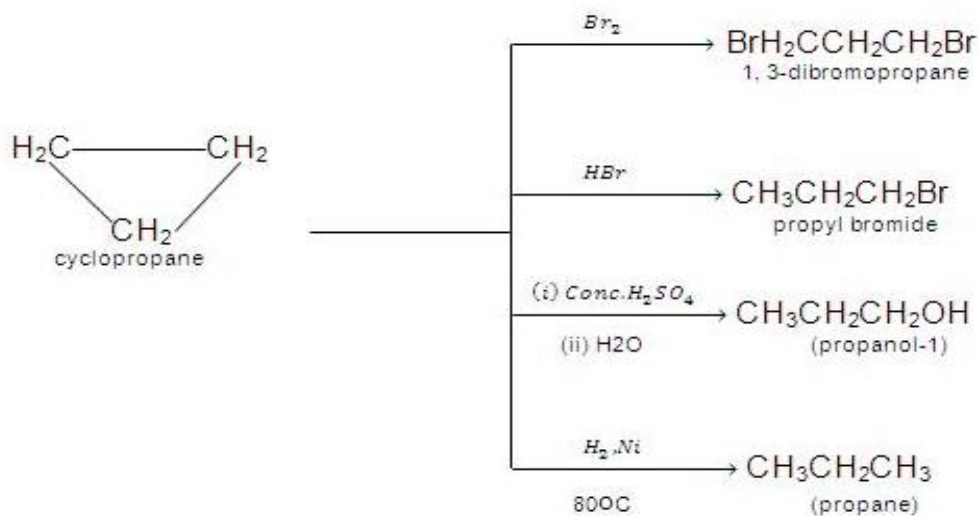
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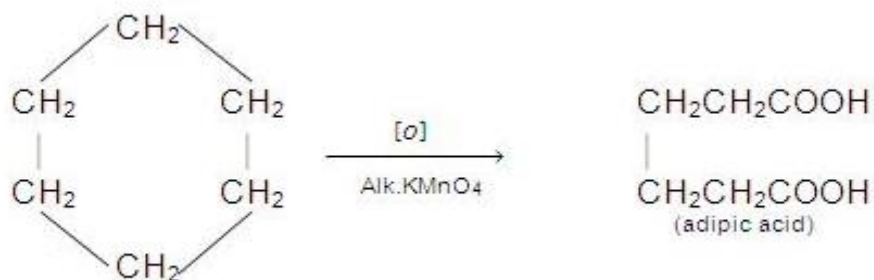
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- (b) **Addition reactions:** Cyclopropane being the most strained ring and more reactive undergoes addition reactions like alkenes.



- (c) **Oxidation:** Cycloalkanes are oxidized by alkaline potassium permanganate to dicarboxylic acids involving ring fusion.





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Short Question/Blank	
1. Which cycloalkane more reactive?	Cyclopropane
2. Which method best formation of cycloalkane?	Simmons-smith reaction
3. The reagent used in simmon smith reaction?	$\text{CH}_2\text{I}_2\text{-Zn/Cu}$
4. Oxidation of Cycloalkane to obtained _____	Dicarboxylic acid

➤ Baeyer Strain Theory

Van't Hoff and Lebel proposed tetrahedral geometry of carbon.

- The bond angle is of $109^\circ 28'$ (or 109.5°) for carbon atom in tetrahedral geometry (methane molecule).
- Baeyer observed different bond angles for different cycloalkanes and also observed some different properties and stability.
- On this basis, he proposed angle strain theory.
- The theory explains **reactivity and stability of cycloalkanes**.
- Baeyer proposed that the **optimum overlap of atomic orbitals** is achieved for bond angle of **109.5°** . In short, it is **ideal bond angle** for alkane compounds.
- Effective and optimum overlap of atomic orbitals produces **maximum bond strength and stable molecule**.
- If bond angles deviate from the ideal then ring produce **strain**.
- Higher the strain **higher the instability**.
- Higher strain produce **increased reactivity** and increases **heat of combustion**.
- Baeyer proposed “**any deviation of bond angle from ideal bond angle value (109.5°) will produce a strain in molecule. Higher the deviation lesser the instability**”.



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➤ What is Conformation?

In alkanes, the distribution of electrons in sigma molecular orbital is symmetrical around the internuclear axis of the C-C bond. Thus, it permits the possibility of free rotation about the C-C single bond. Due to this rotation, different spatial arrangements of carbon atoms in space are observed which can change into one another. Such spatial arrangement of carbon, hydrogen atoms which can be converted into one another by rotation around a C-C single bond is called confirmation or conformer or rotamer. Alkanes can thus have an infinite number of conformations by rotation around C-C single bonds. However, this rotation is not completely free due to repulsive interactions between the electron clouds of C-H bonds. This repulsive interaction is termed as torsional strain.

➤ Conformational Isomers

Let us understand the fundamentals of conformation with the example of ethane. If we observe the ball and stick model of ethane and rotate one carbon atom keeping another carbon atom stationary about C-C axis. We will observe that the rotations will result in an infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These different arrangements are better known as conformational isomers or conformers.

Predominantly, these can be broadly classified into two different cases:

1. Eclipse conformation

Conformation in which hydrogen atoms attached to two carbons areas nearest to each other as possible is known as eclipsed



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2. Staggered conformation

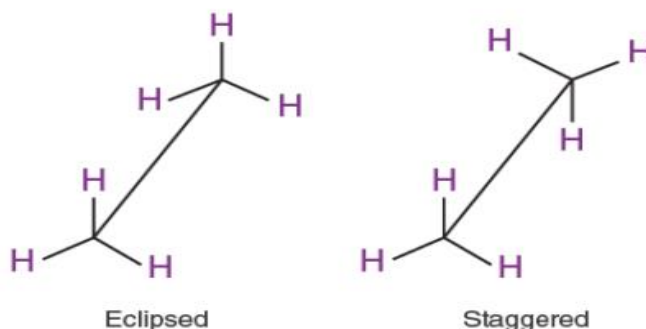
Conformation in which hydrogen atoms attached to two carbons are as far as possible with respect to each other is known as staggered. The staggered conformation is thus relatively more stable in comparison to eclipse conformation as there are minimum repulsive forces, minimum energy due to many separations between the electron clouds of C-H bonds.

Conformations of Ethane

Representation of Eclipsed and staggered Conformation

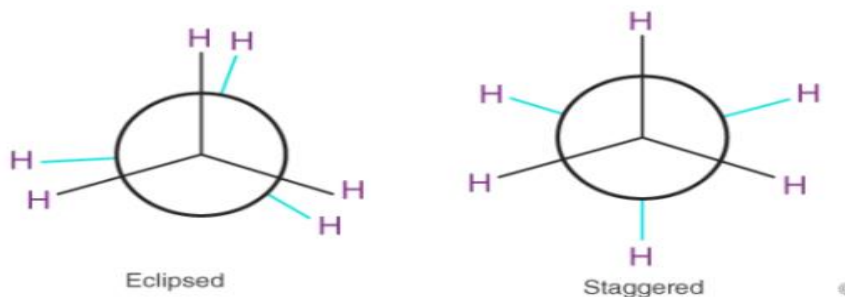
Sawhorse projections:

In this kind of projection, the bond between carbon atoms is shown as a long straight line. The lower end of the line designates the front carbon atom whereas the upper end designates the rear carbon atom. Since each carbon atom in ethane is attached to three hydrogen atoms; each carbon atom has three lines attached designating C-H bonds inclined at an angle of 120° to each other.



Newman projections:

In this projection, out of the two carbon atoms present in ethane one which is nearer is shown as a dot whereas the rear carbon atom is represented as a circle. The three hydrogen atoms attached to each carbon atom are represented with the help of three lines either bulging out of the circle or diverging of the dotted lines. These lines are inclined to each other at an angle of 120° to each other.





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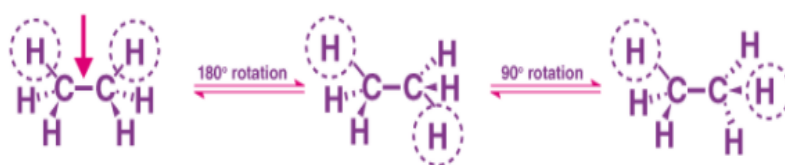
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Conformation of ethane

Ethane is an organic Chemical Compound. It is a colorless and odor gas at a standard temperature. Ethane molecule consists of seven sigma bonds. There will be a change in the shape of the molecule when there is a rotation of about six carbon-hydrogen bonds. But many possible differences occur when there is a rotation about the carbon-carbon bond.



Conformations of Ethane

Now suppose we rotate CH_3 group clockwise at an angle of 60 degrees, there would be a possible that hydrogen present at the front carbon is close to the hydrogen present at the back carbon. That is Eclipsed Conformation.



Eclipse Conformation is one of the highest Conformation. Another clockwise rotation at an angle of 60 degrees would lead to second eclipsed conformation. The solid line in the above figure represents the 6 carbon-hydrogen bond that is extended at an angle of 120 degrees from 2 carbons.

Uses Of Ethane: It is widely used in the production of Ethane. It is mainly done through steam cracking. It acts as a ripening agent for food. It is a primary ingredient in mustard gas.



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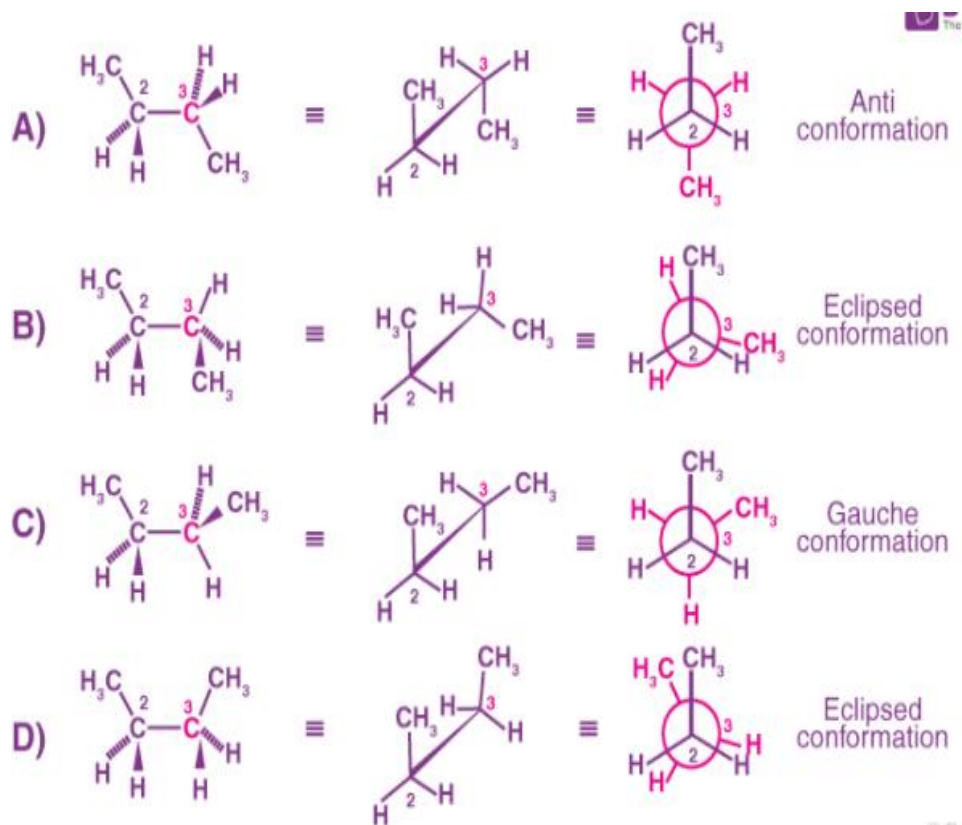
➤ Conformations of Butane

Butane is an organic compound which consists of an alkane with 4 carbon atoms. It may refer to a mixture of 3 isomers. At atmospheric pressure, Butane is a gas. They are liquefied gas that is highly flammable.

Compared to ethane, hydrogen butane consists of the complex set of conformations that is related to the constitution. The below figure represents the 4 conformations of butane.

The above diagram explains the rotation about C₂-C₃ bond due to the change in potential energy.

Uses of Butane: Pure of butane can be used as a refrigerant. It is used in Butane Torch. It is widely used in gasoline blending. Butane Cartridges are used to powered cordless hair irons.





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2. Which conformer is more stable of ethane?	Staggered
3. More stable conformer of butane?	Staggered
4. How dihedral angle in gauche form of n-butane?	60°
5. According to Baeyer strain theory Which cycloalkane more stable?	Cyclopentane
6. n-butane gas mainly constitute of _____	LPG gas