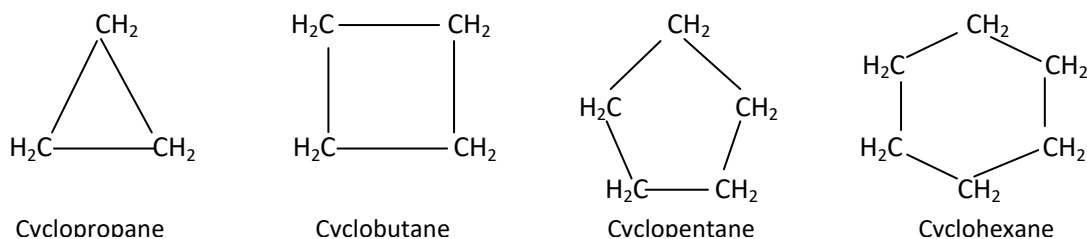# CYCLOALKANES

Cycloalkanes:

Cycloalkanes are saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form a ring. They obey the general formula C_nH_{2n}. They are also called alicyclic compounds.

Nomenclature of Cycloalkanes:

In IUPAC system of naming, the prefix cyclo- is added to the corresponding alkane. Thus cycloalkane with three carbon atoms is called cyclopropane and cycloalkane with four carbon atoms is called Cyclobutane and so on.
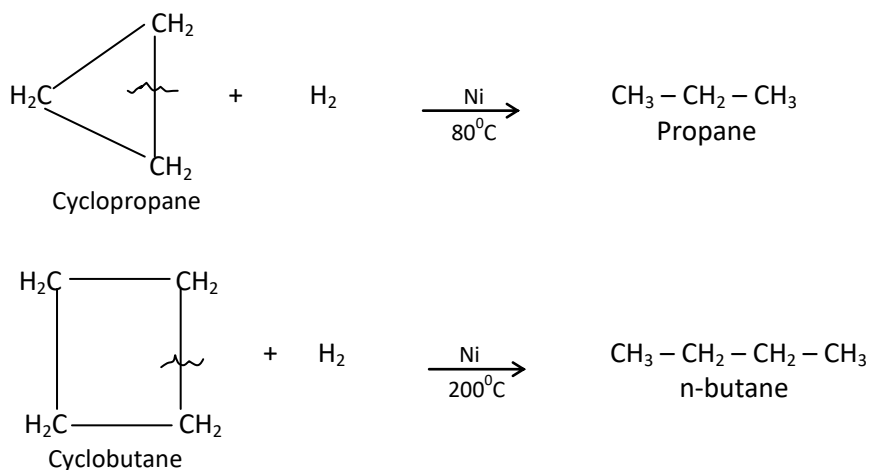

Cyclopropane   Cyclobutane   Cyclopentane   Cyclohexane

Symbolic representation of cycloalkanes:

Cyclopropane   Cyclobutane   Cyclopentane   Cyclohexane
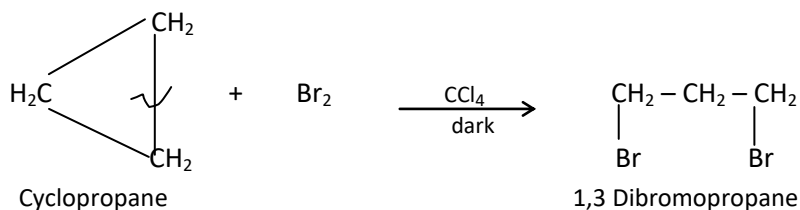
REACTIONS OF CYCLOALKANES

1. **Hydrogenation:** (ring opening) Cycloalkanes undergo hydrogenation in the presence of catalysts like Ni or Pt to form the corresponding saturated hydrocarbons. The ease of hydrogenation decreases as the size of the ring increases. Higher Cycloalkanes having six or more carbon atoms are usually stable to hydrogenation. It may be observed from the conditions of the reactions given below.

2. **Halogenation:**

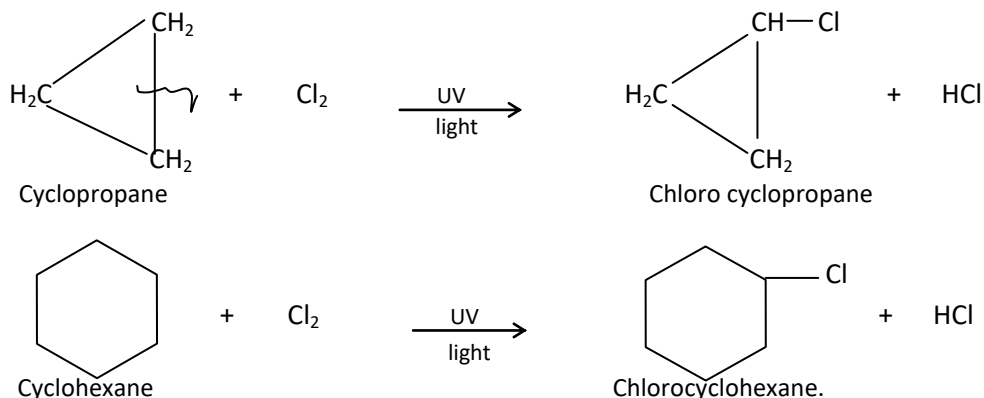   a. **Addition reaction of halogen:** (Leading to ring opening)

   Cyclopropane reacts with chlorine and bromine in dark to form addition products. CCl_2 is used as the solvent.

Cyclopropane   1,3 Dibromopropane

Cyclobutane and higher members do not give this reaction.

b. **Substitution reaction with halogen:**

Cycloalkanes react with chlorine and bromine in the presence of UV light to give substitution products.

Cyclopropane + Cl_2 $\xrightarrow{\text{UV light}}$ Chloro cyclopropane + HCl

Cyclohexane + Cl_2 $\xrightarrow{\text{UV light}}$ Chlorocyclohexane. + HCl

STABILITY OF CYCLOALKANES

1. BAEYER'S STRAIN THEORY

In 1885 Adolf von Baeyer, a German chemist proposed a theory to explain the relative stability of cycloalkanes. It is based on the classical theory of Le Bel and Van't Hoff, postulated in 1874, which states that the four valencies of carbon are directed towards the four corners of a regular tetrahedron. Hence the bond angle between any two bonds is $109^0 \, 28'$ (tetrahedral angle).

The main postulates of Baeyer's strain theory are:

1. The cycloalkanes are planar molecules.
2. Any deviation of bond angle from the normal tetrahedral value ($109^0 \, 28'$) causes a strain on the ring this is called as 'angle strain'.
3. Greater the angle strain, greater is the instability of the ring.
4. Higher the stability of the ring, greater would be its ease of formation.

Using Baeyer's theory the angle strain can be calculated.

e.g. In cyclopropane, the three carbon atoms are at the corners of an equilateral triangle. Therefore the C-C-C bond angle is 60^0. This implies that the normal tetrahedral angle of $109^028'$ between any two bonds involved is reduced to 60^0. Hence the angle strain in cyclopropane is calculated as:

$$\tfrac{1}{2}(109^028' - 60^0) = 24^0 \, 44'$$

Thus the angle strain in cyclopropane is $24^0 \, 44'$.

Angle Strain in Cyclopropane
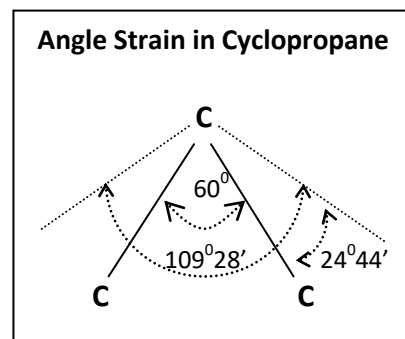
Compound	Structure	Bond angle	Angle strain
Cyclopropane	△	60^0	$\tfrac{1}{2}(109^028' - 60^0) =$ **+24⁰44'**
Cyclobutane	▢	90^0	$\tfrac{1}{2}(109^028' - 90^0) =$ **+9⁰44'**
Cyclopentane	⬠	108^0	$\tfrac{1}{2}(109^028' - 108^0) =$ **+0⁰ 44'**
Cyclohexane	⬡	120^0	$\tfrac{1}{2}(109^028' - 120^0) =$ **-5⁰16'**

Similarly the angle strain of other cycloalkanes can be calculated. The values are given in the above table.

The positive sign indicates that the C-C bonds are bent inwards and the negative sign indicates that the C-C bonds are bulged outwards from the normal tetrahedral angle. Whether the angle strain is positive or negative, its magnitude only determines the extent of strain in the ring.

Thus according to Baeyer's strain theory, cyclopropane which has the maximum angle strain should be highly strained molecule and consequently most unstable. This is found to be true as cyclohexane undergoes ring opening reactions comparatively easily.

The angle strain is minimum in the case of cyclopentane; therefore, it is a less strained molecule and consequently should be a most stable molecule. It is found to be true as cyclopentane undergoes ring opening in drastic conditions.

The angle strain increases with the increase in the number of carbon atoms further from cyclohexane onwards. Hence according to Baeyer's strain theory, cyclohexane and other higher members should be unstable and therefore more reactive.

Limitations of Baeyer's strain theory:

1. According to Baeyer strain theory cyclopentane is stabler than cyclohexane. In fact cyclohexane is more stable than cyclopentane.
2. Baeyer's theory is suitable only for cyclopropane, cyclobutane and cyclopropane.
3. The theory proposes planar structures to all cycloalkanes.

2. SACHSE-MOHR THEORY:

In order to account for the stability of cyclohexane and higher members, Sachse and Mohr (1918) proposed that such rings can become free from strain if all the ring carbons are not forced into one plane, as was assumed by Baeyer. If the ring assumed a 'folded' or 'puckered' condition, the normal tetrahedral angles of $109^{0}28'$ are retained and as a result, the strain within the ring is relieved.

For example, cyclohexane can exist in two non-planar puckered conformations both of which are completely free from strain. These are called **Chair form** and the **Boat form** because of their shape. Such non-planar strain-free rings in which the ring carbons can have normal tetrahedral angles are also possible for higher cycloalkanes.

Cyclohexane

Boat form   **Chair form**

H_a - Axial hydrogen
H_e - Equatorial hydrogen
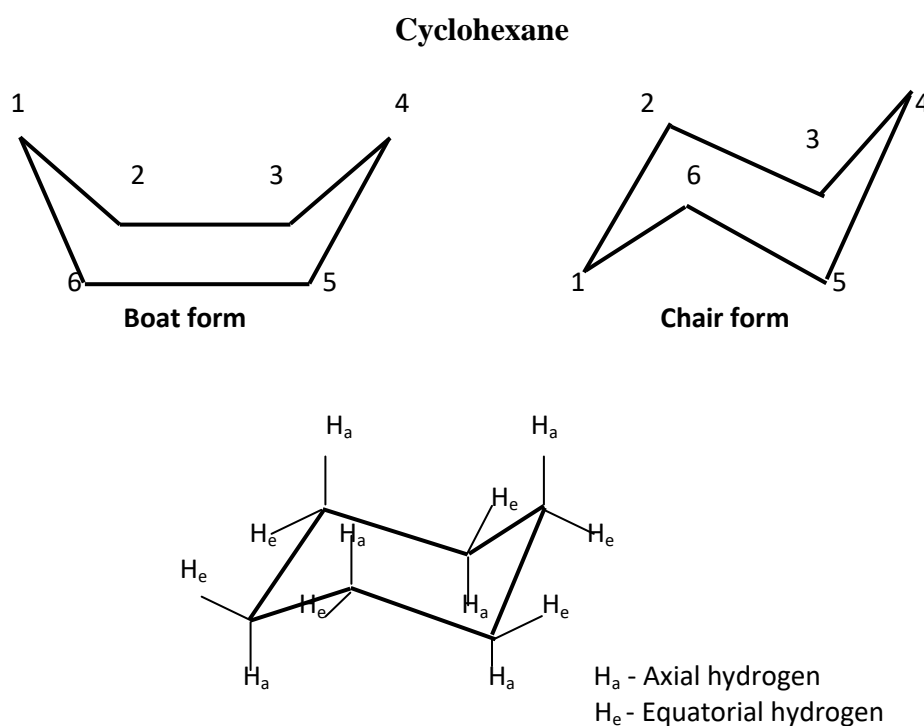
The chair form of Cyclohexane is more stable than the boat form. Under ordinary conditions, cyclohexane molecules will mostly exist in the chair form.

Examination of the chair form of Cyclohexane reveals that the hydrogen atoms can be divided into two categories. Six of the bonds to hydrogen atoms point straight up or down almost perpendicular to the plane of the molecule. These are called **axial hydrogens**. The other six hydrogens lie slightly above or slightly below the plane of the cyclohexane ring, and are called **equatorial Hydrogens**.

**Stability of chair and boat forms of cyclohexane:**
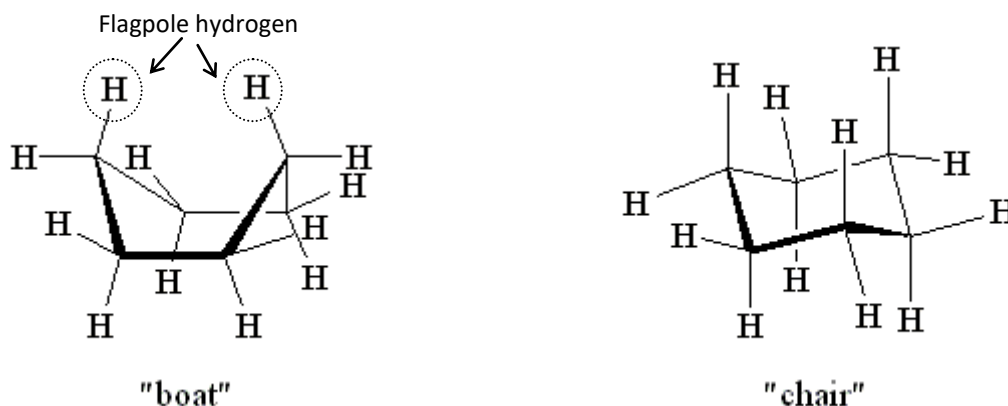
The chair form of cyclohexane is more stable than its boat form. This is because the boat form has unfavourable non-bonded interactions between the hydrogen atoms, which increase the potential energy of it. In the boat form of cyclohexane the 1, 4 axial hydrogen atoms or flagpole hydrogen atoms are in close proximity $(1.83A^0)$. This leads to steric-hidrance between the flagpole hydrogens, which correspond to repulsion energy of 3 kcal mol^{-1}.

Stability of methyl cyclohexane (monosubstitution):

Conformations of chair form of methylcyclohexane
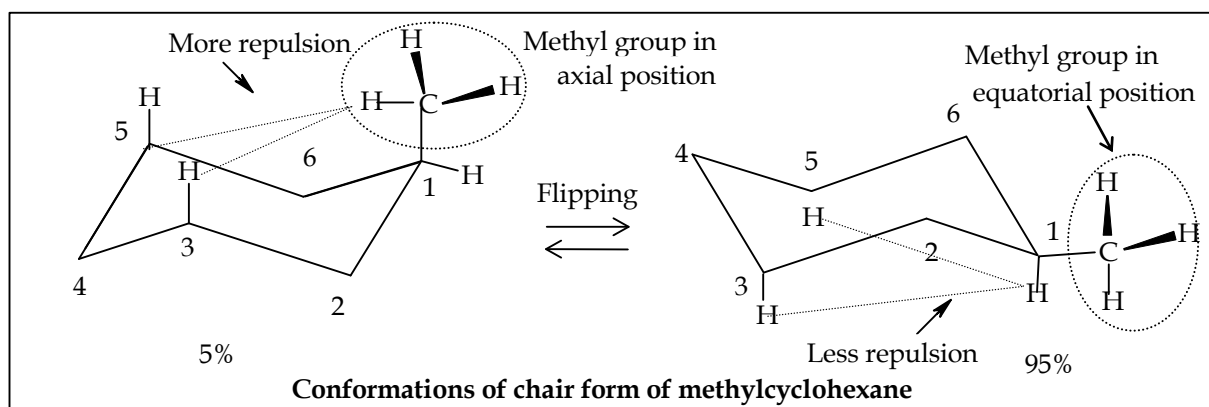
When a hydrogen atom of a cyclohexane is replaced by a bulkier group, like $-CH_3$ group, crowding occurs. The most severe crowding is among atoms by the three *axial bonds* on the same side of the molecule. The methyl group in the axial position and the axial hydrogens repel each other. These interactions are called '**axial-axial or 1,3-diaxial interaction**'. This causes a steric strain in the molecule. Thus, monosubstituted cyclohexane will assume chair confirmation in which the substituent occupies an *equatorial position*, which reduces the repulsion. Thus, the energy of the conformation with equatorial methyl group is lower. At room temperature, about 95% of methyl cyclohaxane molecules are in the conformation in which the methyl group is equatorial.

When the two chair forms interconvert so that the axial bonds become equatorial and vice-versa is known as **ring-flip**.

Stability of dimethyl cyclohexane (disubstitution):

More stable   Less stable   Less stable   More stable
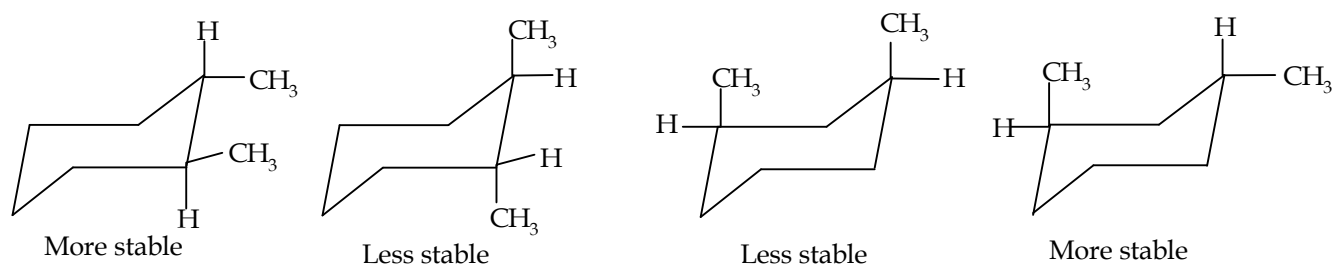
In disubstituted cycloalkanes, like Dimethylcyclohexane the chair form containing both the substituents in equatorial position will be preferred conformation. In general the conformation with bulkier substituent in an equatorial position will be the preferred confirmation.