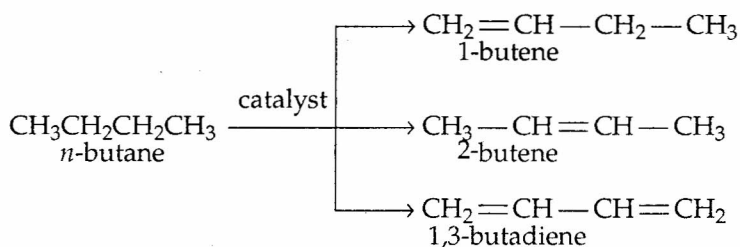


10. Dehydrogenation of alkanes. Alkanes can be selectively dehydrogenated in the presence of suitable catalysts which bring about dehydrogenation at temperatures lower than those at which pyrolysis occurs. The catalysts used for dehydrogenation of alkanes are oxides of chromium, molybdenum and vanadium. The dehydrogenation of *n*-butane to butenes takes place at 550–600°C in the presence of chromium oxide as a catalyst.



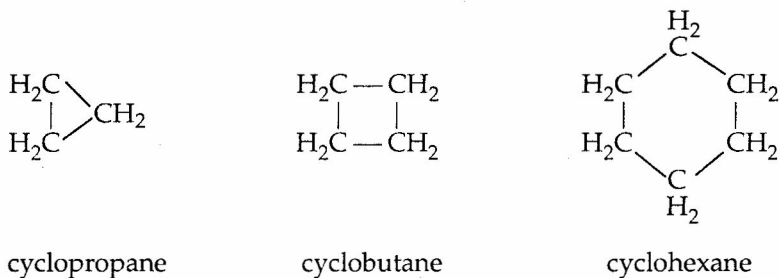
This reaction is of great commercial importance because the product, butenes and butadiene, are useful material for petrochemical industry, and gasoline manufacture.

CYCLOALKANES

Cyclic hydrocarbons having C—C and C—H bonds like those of alkanes but general formula like that of alkenes C_nH_{2n} are known as cycloalkanes. A cycloalkane may be theoretically assumed to be formed from an alkane by removing two hydrogen atoms from two carbon atoms of the chain and linking these carbons to one another. Some of the properties of cycloalkanes are like the properties of alkanes, while some of the cycloalkanes specially the small ring cycloalkanes have special properties due to the strained cyclic ring which resemble those of alkenes.

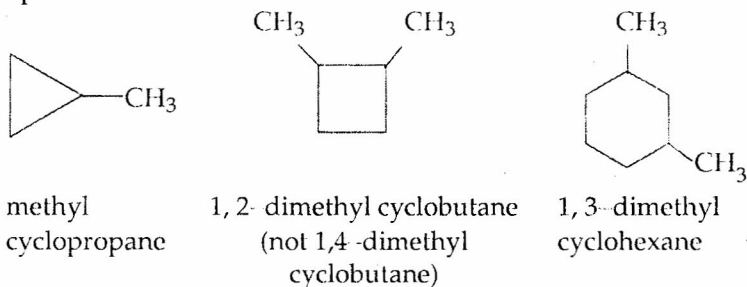
Nomenclature

Cycloalkanes are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring. For example:

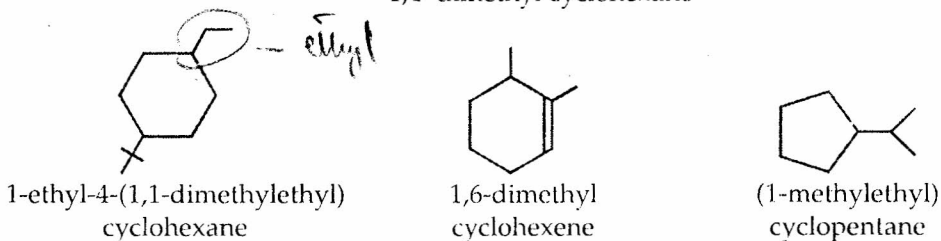
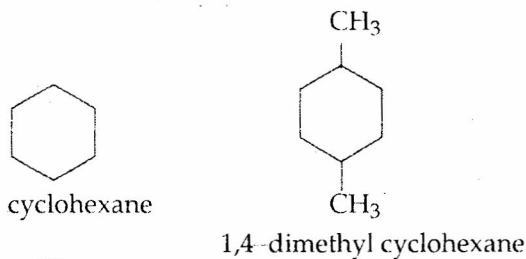
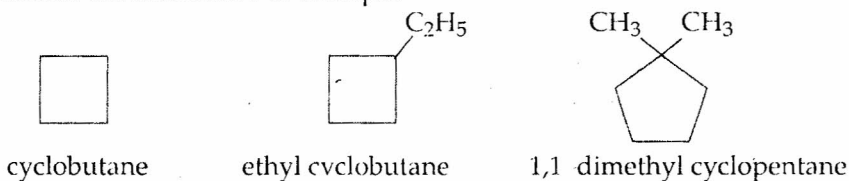


Substituents on the ring are named and their positions are indicated by numbers. Position number 1 is assigned to a particular carbon of the ring and the other carbon atoms of the ring are numbered by going either clockwise or counter clockwise around the ring in

such a way as to give the lowest combination of numbers to the substituents. For example:



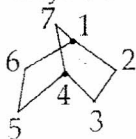
For convenience cycloalkane rings are often represented by simple, geometrical figures, *i.e.*, a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon for cyclohexane and so on. It is understood that two hydrogens are attached to each carbon atom present at each corner of the figure, therefore, hydrogens are not shown in the structure. A group other than hydrogen is invariably indicated in the structure. For example:



Bicycloalkanes and spiranes

A bicycloalkane contains two rings that share two carbon atoms in common. The shared carbon atoms are called **bridgehead** carbons and the carbon chain connecting them are called **bridges**. The general formula of a bicycloalkane is $C_{2n+2}H_{4n+6}$ like an alkane.

Common and IUPAC names of bicyclo alkanes are given below.

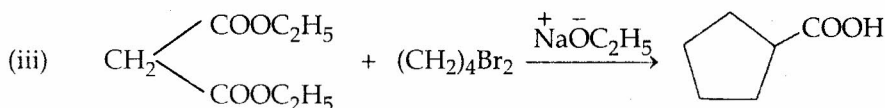
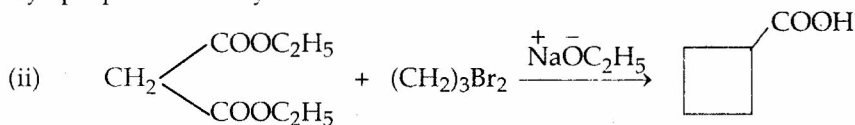
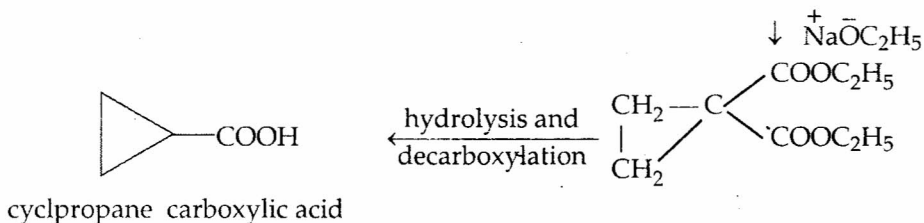
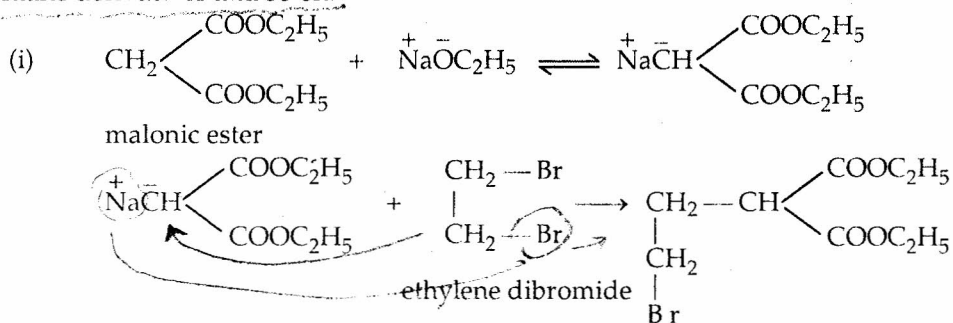


(norbornane) Bicyclo [2.2.1] heptane

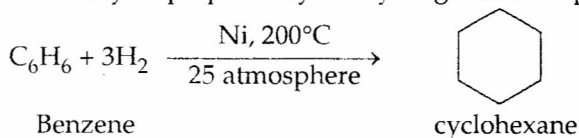


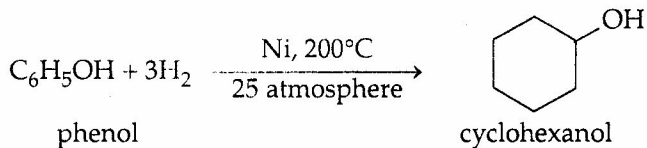
4. Perkin Ring Closure (malonic ester synthesis) Malonic ester has been used to prepare different types of organic compounds using different reagents and conditions. The scheme given below is known as the **Perkin ring closure reaction** and is a useful synthetic reaction for preparation of cyclic compounds. In this reaction both active

hydrogens of malonic ester are removed by NaOC_2H_5 and the anion formed is alkylated with a dibromide, which undergoes internal alkylation in the second step to give a cyclic compound, which on hydrolysis and decarboxylation gives cycloalkane derivatives. Higher cycloalkanes may be obtained by taking higher dibromides such as 1, 3-dibromopropane for cyclobutane derivatives, and 1, 4-dibromobutane for cyclopentane derivatives and so on.



5. Catalytic hydrogenation of benzene and its derivatives. Cyclohexane and its derivatives may be prepared by the catalytic hydrogenation of aromatic compounds. For example cyclohexane may be obtained by the catalytic hydrogenation of benzene and cyclohexanol may be prepared by the hydrogenation of phenol.





Physical Properties

Cyclopropane is a gas while cyclobutane is a low boiling liquid (b.p. 12°C). Cyclopentane boils at 49°C and the boiling points of higher cycloalkanes rise rather rapidly so that cyclodecane boils at 210°C .

As compared to alkanes and alkenes cycloalkanes possess higher boiling points and higher densities. Thus cyclohexane, *n*-hexane and 1-hexene have boiling points respectively 81°C , 68.8°C and 63.9°C , and specific gravity of 0.7787, 0.6504 and 0.6736 respectively. Like other hydrocarbons, cycloalkanes are insoluble in water and soluble in alcohol and ether.

Structure of Small Ring Cycloalkanes

The cycloalkanes form a homologous series, of which cyclopropane is the smallest member. The higher members are cyclobutane, cyclopentane, cyclohexane and so on. Rings which contain 3 or 4 carbons are called *small rings*, those containing 5 to 7 carbons are referred to as *common rings*, while those containing 8 to 11 carbons are *medium rings*. Rings containing 12 or more carbons are termed as *large rings*.

The common and large rings are similar to alkanes in almost all of their physical and chemical properties, whereas both the small and medium rings behave rather differently.

The unusual behaviour of small rings stems from the fact that the sp^3 carbon tends to have bond angles near the tetrahedral value, i.e., 109.5° , while the geometric requirements of the small rings reduce these angles to much smaller values.

Two *p* orbitals on the same carbon have an angle of 90° between them. If these orbitals are hybridized by adding *s* character to them, the angle between them increases steadily, reaching a value of 180° when the amount of *s* character reaches 50% ($\text{sp}^3 = 109.5^\circ$, $\text{sp}^2 = 120^\circ$, $\text{sp} = 180^\circ$). There is no hybrid combination of *s* and *p* orbitals possible which will yield an inter orbital angle of less than 90° . This means that in cyclopropane the carbons do not have their bonding orbitals pointing directly at one another, and the carbon-carbon bonds are best described as bent. Such bonds are not as strong as ordinary bonds, and such a molecule has higher energy than usual. High energy molecules of this type are said to be *strained molecules*.

If we assume that the C—C—C inter orbital angles in cyclobutane, (90°), are formed by overlap of pure *p* orbitals then the resulting bond would be very weak. The addition of some *s* character makes them strong, but, non collinear. Thus cyclopropane and cyclobutane have bent bonds and are highly strained.

Baeyer's Strain Theory

According to Baeyer's Strain Theory, a molecule which is more strained is less stable. The stability of cycloalkanes can be predicted by measuring the heat of combustion per CH_2 group. The heats of combustion per CH_2 group for some cycloalkanes are given below (Table 3.3).

Table 3.3

Cycloalkane	Heat of Combustion per CH ₂ group / kJ mol ⁻¹	Deviation of valence angle from tetrahedral angle
Cyclopropane	700	24° 44'
Cyclobutane	688	9° 44'
Cyclopentane	666	0° 44'
Cyclohexane	658	5° 16'

The heat of combustion per CH₂ group decreases upto cyclopentane, showing that the stability of the ring is increasing. This is in accordance with the deviation of valence angle from the tetrahedral. For cyclohexane onwards the heat of combustion per CH₂ group becomes practically constant showing minimum angular strain, although the angular deviation as calculated by assuming planar rings, is increasing. The reason for no angular strain in cyclohexane and higher rings is that the rings are puckered and the angle between C—C bonds is tetrahedral. Thus only the small ring cycloalkanes have angular strain. Bent structure of cyclopropane and cyclobutane are shown in Fig. 3.1.

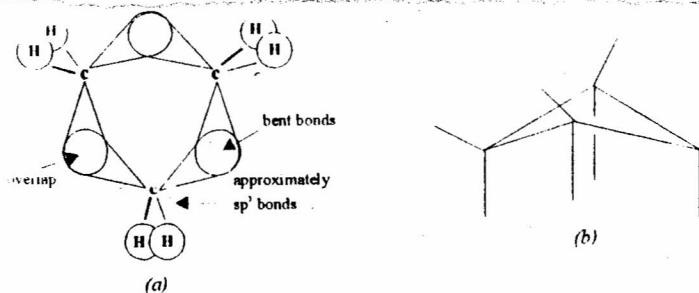


Fig. 3.1. (a) bent structure of cyclopropane
(b) puckered structure of cyclobutane

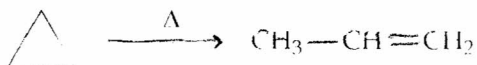
Reactions of Cycloalkanes

The reactions of cycloalkanes are of two types. Reactions in which cycloalkanes resemble alkenes and those in which they resemble alkanes.

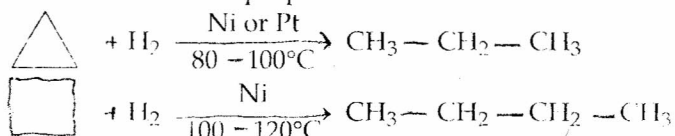
Small ring cycloalkanes undergo chemical reactions which lead to the rupture of the strained system to release their strain.

Examples that show behaviour of small ring cycloalkanes which resemble that of alkenes.

1. Isomerization. Cyclopropane is like propene as it isomerizes to propene on heating.

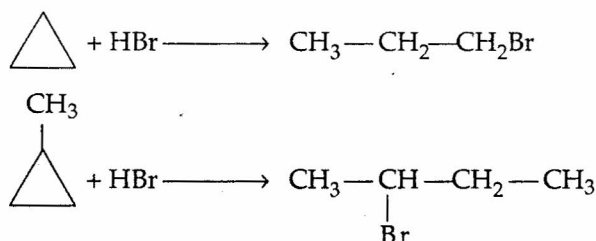


2. Catalytic hydrogenation. Cyclopropane gives propane on hydrogenation with Ni/Pt a catalyst at 80–100°C, whereas cyclobutane gives butane at 100–200°C, showing that cyclopropane is under more strain than cyclobutane. This reaction of cyclopropane and cyclobutane is similar to that of propene and butene.

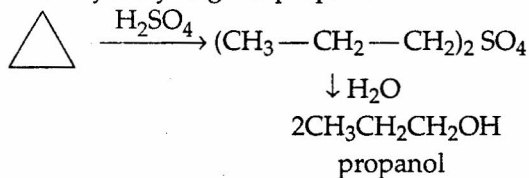


3. Addition of hydrogen halide. Hydrogen bromide, adds to cyclopropane to give *n* propyl bromide and to methyl cyclopropane to give 2-bromobutane in

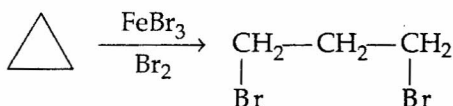
accordance with Markovnikov's rule. This reaction also shows similarity with reaction of alkenes.



4. Hydration. Cyclopropane reacts with dilute H_2SO_4 like alkenes to give propyl sulphate. The later on hydrolysis gives propanol.

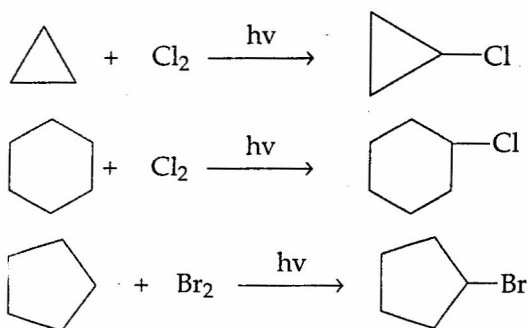


5. Addition of bromine. Bromine adds to cyclopropane in the presence of FeBr_3 with rupture of ring to give 1,3-dibromopropane.

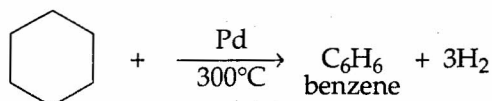


In the following reactions small ring cycloalkanes and higher cycloalkanes resemble in behaviour to alkanes.

1. Halogenation. Cycloalkanes react with chlorine and bromine, in the presence of sunlight, to give substitution reaction.



2. Aromatization of cyclohexane ring. Cyclohexane may be converted to benzene at 300°C in the presence of palladium.



The reverse reaction is also possible which is called catalytic hydrogenation and has been discussed in the preparations of cyclohexane.