

SATURATED HYDROCARBONS ALKANES AND CYCLOALKANES

Organic compounds which contain only carbon and hydrogen atoms in their molecules are called **Hydrocarbons**.

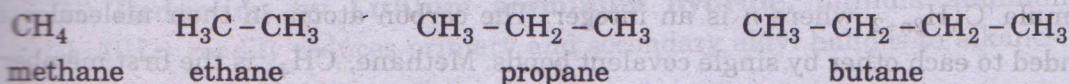
4.1 Classification of Hydrocarbons

Hydrocarbons can be divided on the basis of their structure into two main categories:

1. Open-chain hydrocarbons or acyclic hydrocarbons
2. Closed-chain hydrocarbons or cyclic hydrocarbons

The **Open-chain hydrocarbons** are generally called **aliphatic hydrocarbons**. They are further classified into two classes: (i) Saturated hydrocarbons (alkanes) (ii) Unsaturated hydrocarbons (alkenes and alkynes).

(i) **Saturated hydrocarbons or Alkanes** are those compounds of carbon and hydrogen in which the valencies of carbon are fully satisfied. The carbon atoms are joined to each other only by single bonds and each carbon is bonded to four other atoms. They have the general formula C_nH_{2n+2} . They are also known as "**paraffins**" (Latin parum = little, affins = affinity or reactivity). For example;



(ii) **The unsaturated hydrocarbons** are those compounds of carbon and hydrogen which contain carbon-carbon multiple bonds, and to which other atoms can be added to form saturated compounds. They include alkenes, having a carbon-carbon double bond, and alkynes, having a carbon-carbon triple bond. The general formula for alkene is C_nH_{2n} and for alkyne is C_nH_{2n-2} .

The examples of alkenes are ethene, $H_2C = CH_2$, propene, $CH_3 - CH = CH_2$. The double bond is also known as "**Olifinic bond**" or **ethylenic bond**". The alkenes are also called olifins (Latin, oleum = oil; ficare = to make) because the lower members form oily products on treatment with chlorine or bromine.

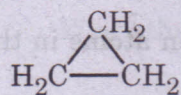
The general formula for alkynes is C_nH_{2n-2} . Examples are ethyne, $HC \equiv CH$, propyne, $CH_3 - C \equiv CH$. The triple bond is also known as the "**acetylenic bond**".

2. **Cyclic hydrocarbons** are the compounds of carbon and hydrogen which contain rings of carbon atoms. These are of two types:

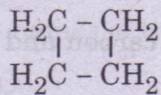
- (i) Alicyclic hydrocarbons
- (ii) Aromatic hydrocarbons

(i) **Alicyclic hydrocarbons:** Hydrocarbons in which the carbon atoms are arranged in a ring and do not have benzene ring are called alicyclic hydrocarbons. With a few exceptions, they are similar to aliphatic hydrocarbons in properties. The prefix ali- is added because of their similarity to aliphatic compounds. They include

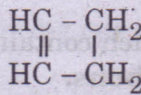
(i) Cycloalkanes (resembling alkanes) (ii) Cycloalkenes (resembling alkenes) and (iii) Cycloalkynes (resembling alkynes). Some examples of alicyclic hydrocarbons are given below:



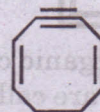
Cyclopropane



Cyclobutane

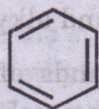


Cyclobutene

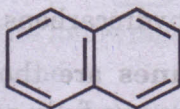


1,5 cyclooctadiene-3-yne

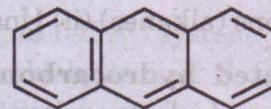
(ii) Aromatic hydrocarbons: Hydrocarbons which contain at least one benzene ring in their molecules are called aromatic hydrocarbons. A benzene ring is made of six carbon atoms with three alternate (Conjugated) double bonds. They include benzene and those compounds of carbon and hydrogen that resemble benzene in their chemical behaviour.



Benzene



Naphthalene



Anthracene

4.2 ALKANES

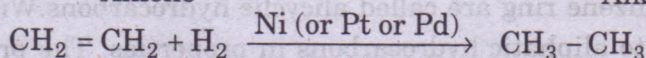
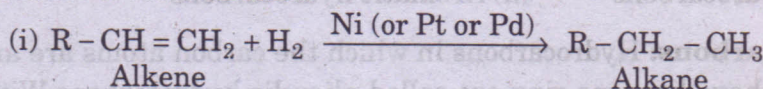
Alkanes are open-chain (acyclic) saturated hydrocarbons with the general formula C_nH_{2n+2} where n is an integer. The carbon atoms in their molecules are bonded to each other by single covalent bonds. Methane, CH_4 , is the first member of the alkane family and is the principal constituent of "sui gas".

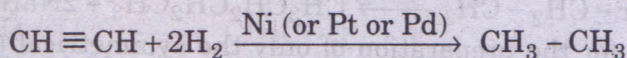
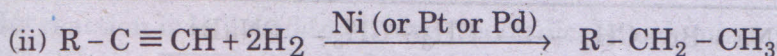
Natural Sources of Alkanes

The two principal sources of alkanes are natural gas and petroleum. Both of these substances are frequently found together in underground deposits. Natural gas contains about 80% methane, along with the small amounts of ethane, propane and butane. Petroleum contains a wide range of alkanes, from the low molecular mass gases to the high molecular mass solids. Methane is also found in marshes and hence also known as marsh gas. Methane, ethane, propane and butane are isolated from natural gas and the light oil fraction of petroleum distillation.

4.3 Methods of Preparation of Alkanes

1. Hydrogenation of alkenes or alkynes: (Conversion of C - C multiple bond into a C - C single bond). Alkenes or alkynes react with hydrogen in the presence of a finely divided nickel catalyst at $200 - 300^\circ\text{C}$ or Pt or Pd catalyst at room temperature to form alkanes.

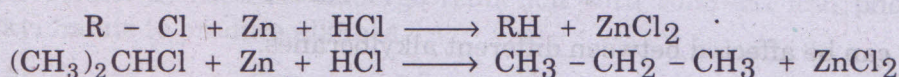




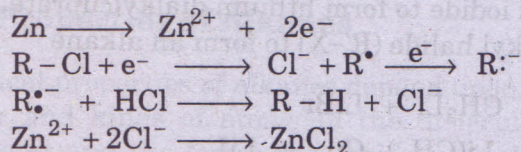
Production of vegetable ghee by the catalytic hydrogenation of vegetable oil is an important application of this method on industrial scale.

2. From Alkyl Halides

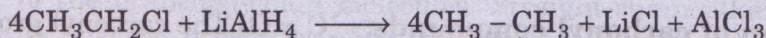
(i) **Reduction of alkyl halides by dissolving metals in acid.** Alkyl halides may be reduced to the corresponding alkanes by dissolving metals e.g., zinc in aqueous acid such as hydrochloric or acetic acid.



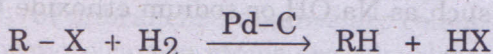
It is believed that the reduction is due to electron transfer from the metal to the substrate, followed by the transfer of proton from the acid, as shown below:



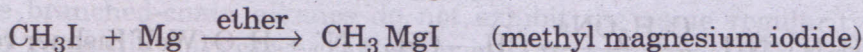
(ii) **Reduction by Lithium aluminium hydride.** Lithium aluminium hydride ($LiAlH_4$) readily reduces primary and secondary alkyl halides to alkanes. (Tertiary alkyl halides mainly give alkenes).



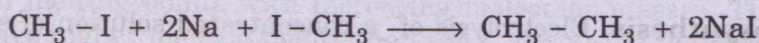
(iii) **Catalytic hydrogenolysis** (hydrogenation accompanied by bond cleavage). Alkyl halides may be reduced catalytically by using palladium-charcoal as a catalyst.



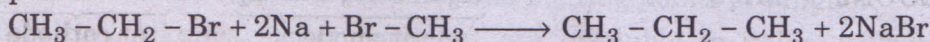
(iv) **Through Hydrolysis of Grignard Reagents:** Alkyl magnesium halides (Grignard reagents) are obtained by treating alkyl halides with magnesium in dry ether, which on treatment with water gives alkanes.

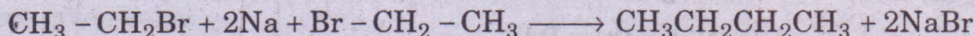
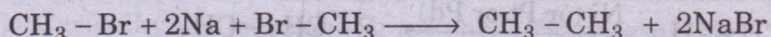


(v) **Coupling of alkyl halides (Wurtz Reaction):** Higher alkanes are produced by heating an alkyl halide with sodium metal in dry ether solution. The net result is the coupling of two alkyl groups to yield a symmetrical alkane ($R - R$) with even number of carbon atoms.



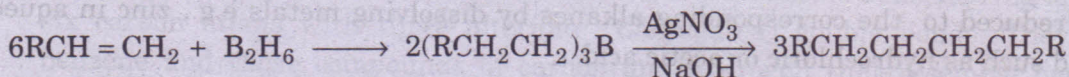
The reaction between two different alkyl halides and sodium gives a mixture of different alkanes that are difficult to separate because of little difference in their boiling points.





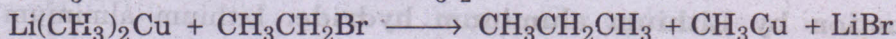
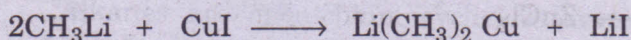
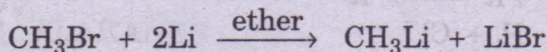
This method is suitable for the preparation of only the symmetrical alkanes. This reaction is also not suitable for tertiary alkyl halides due to side reaction involving elimination.

3. Coupling of alkyl boranes. Coupling of alkylboranes by means of silver nitrate in the presence of NaOH yields long-chain alkanes. Trialkyl boranes can be prepared by the reaction of alkenes with diborane (B_2H_6).



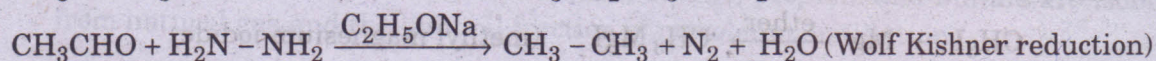
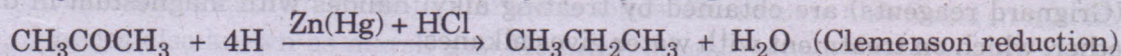
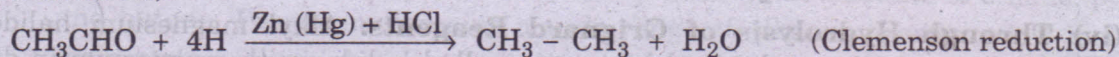
Coupling can be affected between different alkylboranes.

4. Coupling of alkyl halides (Corey-House Synthesis): In this method, the alkyl halide (R-X) is first treated with Li metal to form an alkyllithium (RLi), which is further treated with cuprous iodide to form lithium dialkylcuprate, R_2CuLi , which is then treated with another alkyl halide (R'-X) to form an alkane.

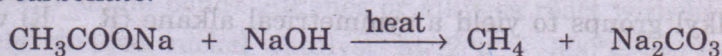


This method is particularly suitable for the preparation of unsymmetrical alkanes ($\text{R-R}'$).

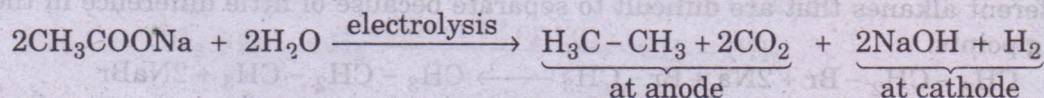
5. Reduction of carbonyl compounds: ($\text{>C} = \text{O}$) The carbonyl group of aldehydes or ketones is reduced to methyl ($-\text{CH}_3$) or methylene ($-\text{CH}_2-$) group respectively either by zinc - mercury amalgam in hydrochloric acid (**Clemmensen reducton**) or by hydrazine and a strong base such as Na OH or sodium ethoxide (**Wolff-Kishner reduction**).



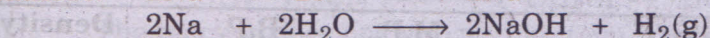
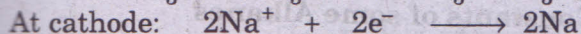
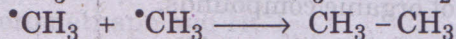
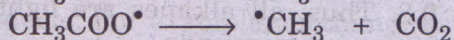
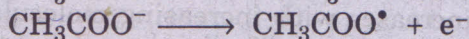
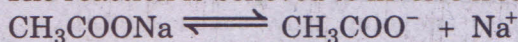
6. Decarboxylation. When the sodium salt of a carboxylic acid and sodalime ($\text{NaOH} + \text{CaO}$) is heated together, an alkane is formed with the elimination of CO_2 as carbonate.



7. Kolbe's Electrosynthesis. Electrolysis of a concentrated solution of sodium or potassium salt of a carboxylic acid yields a higher alkane.

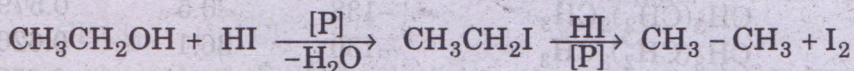


The reaction is believed to involve free-radical mechanism.



This method can also be applied to a mixture of alkali salts of two different carboxylic acid, and a mixture of alkanes would be obtained. Therefore, Kolbe's electrolysis method is useful for the synthesis of symmetrical alkanes only.

9. From Alcohols. (i) Alcohols undergo reduction with conc. HI and phosphorus through alkyl halide to produce alkanes.



4.4 Physical Properties of Alkanes

The physical properties of alkanes depend upon the structure of the molecule, and the number and kinds of atoms in the molecule. The alkane molecules are generally non-polar and the forces that hold the molecules together are the weak van der Waals attractive forces which influence their physical properties. Generally, these forces are larger in straight-chain molecules than in the branched-chain molecules, because the straight-chain molecules have more surface area available to act as compared to the branched-chain molecules. Straight-chain alkanes show a smooth gradation of physical properties while branched-chain alkanes do not show the smooth gradation of physical properties.

The first four members of alkanes are colourless gases, the next thirteen members, C_5 to C_{17} of unbranched alkanes are colourless liquids and the unbranched alkanes with 18 or more carbon atoms are colourless solids.

Boiling points. The boiling points of straight-chain alkanes show a regular increase with increasing molecular mass. The increment is approximately $20\text{-}30^\circ\text{C}$ per $-\text{CH}_2$ groups of two homologues.

The branched-chain alkanes do not exhibit the same regularity in boiling points and generally have lower boiling points as compared to the straight-chain alkanes of the same molecular formula; the greater the branching, the lower the boiling point.

Melting points. The melting points of n-alkanes, like their boiling points, also increase with increasing molecular mass but the increase in melting points is not regular. However, with the even- and odd-numbered alkanes, there is a smooth increase in melting points with increasing molecular masses. The branched-chain alkanes have higher melting points than the n-alkanes of the same molecular mass. X-ray diffraction studies have shown that alkane chains with an even number of carbon atoms packed more closely in the crystalline state. As a result, attractive forces between individual chains are greater and melting points are higher.

Solubility. Alkanes, being nonpolar, are insoluble in polar solvents like

water but soluble in nonpolar solvents like benzene, CCl_4 , CHCl_3 . As a general rule "like dissolves like".

Density. The density of alkanes increases with increasing molecular mass till it reaches a maximum value of about 0.8. Thus, all alkanes are lighter than water and are the least dense of all groups of organic compounds.

Table 4.1 Physical Constants of some Alkanes

Name	Formula	M.P. (°C)	B.P. (°C)	Density At 20°C
Straight-chain alkanes				
Methane	CH_4	-183	-161.5	0.424
Ethane	C_2H_6	-172	-88.6	0.546
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	-188	-42.0	0.501
n-Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	-138	-0.5	0.579
n-Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	-130	36.1	0.626
n-Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	-95	69.0	0.659
n-Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	-91	98.4	0.684
n-Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	-57	125.7	0.703
n-Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	-54	150.8	0.718
n-Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	-30	174.1	0.730
Branched-chain alkanes				
Isobutane	$(\text{CH}_3)_2\text{CHCH}_3$	-159	-12.0	
Neopentane	$(\text{CH}_3)_3\text{CCH}_3$	-17	10.0	
Isopentane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	-160	28	0.620
Isohexane	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}_3$	-154	60	0.653
3-Methylpentane	$\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_3$	-118	63	0.665
2,3-dimethylbutane	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$	-129	58	0.662
2,2-dimethylbutane	$(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$	-99	50	0.649

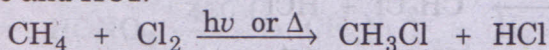
4.5 Chemical Properties

Alkanes are unreactive toward common reagents such as acids, alkalis, oxidizing agents at room temperature. This is due to the fact that the alkane molecules do not have any atom with unshared pairs of electrons, the C - C bonds are completely nonpolar and the C - H bonds are only slightly polarized (i.e. almost nonpolar) because carbon and hydrogen have nearly the same electronegativity. Therefore, polar reagents find no reaction sites on alkane molecules. Moreover, the C - H and C - C bonds are strong bonds. This explains why alkanes do not react with acids, alkalis, oxidizing and reducing agents etc., at room temperature. However, alkanes undergo substitution reactions and thermal catalytic reactions at high temperatures or on absorption of light energy. Some important reactions of alkanes are discussed below.

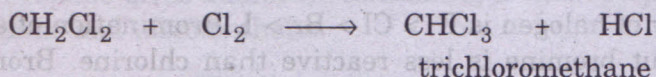
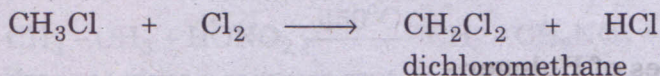
1. Halogenation. A reaction in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms is called a **substitution**

reaction, and if the substituent is halogen, reaction is called **halogenation**.

Alkanes react with halogens (except iodine) in the presence of ultraviolet light, or diffused sunlight, or at a temperature of 250 – 400°C, to form a mixture of products. For example, methane reacts with chlorine in the presence of light to give chloromethane and HCl.



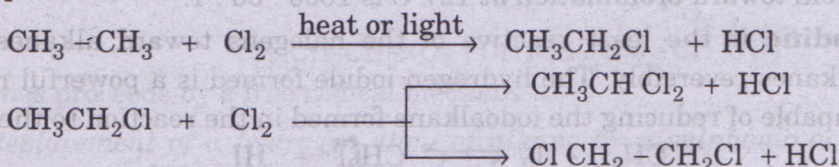
The reaction does not stop at this stage. The remaining three hydrogen atoms of chloromethane can be successively replaced by chlorine atoms.



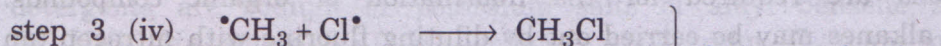
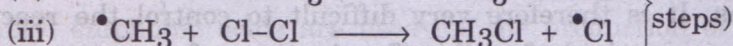
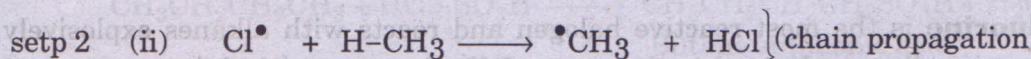
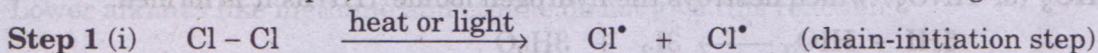
In actual practice, all the four substitution products (CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4) are obtained. The extent to which each product is formed depends upon the initial chlorine to methane ratio.

Fluorine reacts explosively, bromine reacts under similar conditions, but less vigorously than chlorine and iodine does not react.

Ethane and higher alkanes react with chlorine in a similar way and all possible substitution products are obtained.



Mechanism. Halogenation of alkanes proceeds by a free-radical chain mechanism. For example, chlorination of methane involves the following three steps.



1. Chain-Initiation Step. In this step, chlorine free radicals are generated by the homolysis of chlorine molecule by light or heat.

2. Chain-Propagation steps, (ii) Chlorine free radical abstracts a hydrogen atom from methane generating another free radical $\bullet\text{CH}_3$ which reacts with another chlorine molecule to regenerate chlorine free radical and these two steps of propagation are repeated several times until CH_4 and Cl_2 molecules are consumed.

3. Chain-Termination Steps. The free radicals are destroyed by the coupling of

any two radicals and therefore the reaction terminates or stops.

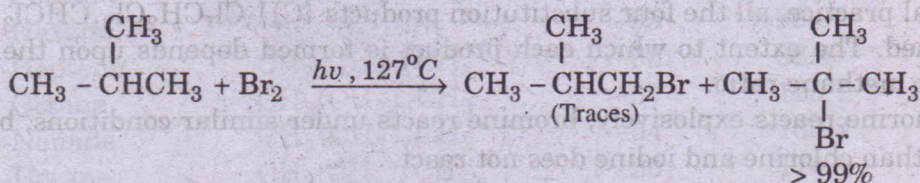
A chlorine free radical can also react with methyl chloride to form chloromethyl free radical, $\cdot\text{CH}_2\text{Cl}$ which on reacting with chlorine molecule forms dichloromethane



Similarly, trichloromethane and tetrachloromethane are obtained by further chain reaction.

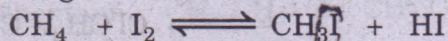
Comparison of Reactivities of Halogens

The order of reactivity of halogen is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Bromination of alkanes is similar to halogenation but bromine is less reactive than chlorine. Bromine is more selective in the site of attack and mainly attacks the tertiary hydrogen atoms.



The ratio of the relative reactivity of a tertiary, secondary and primary hydrogen atom toward bromination at 127°C is 1600 : 80 : 1.

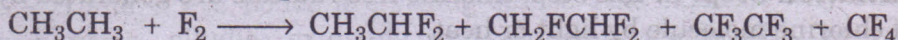
Iodine is the least reactive of the halogens toward alkanes. Iodine reacts with alkanes reversibly. The hydrogen iodide formed is a powerful reducing agent and is capable of reducing the iodoalkane formed in the reaction to the alkane.



However, alkanes can be iodinated in the presence of an oxidizing agent such as HIO_3 (or HNO_3) which destroys the hydrogen iodide (HI) as it is formed.

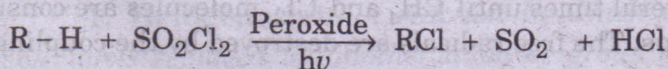


Fluorine is the most reactive halogen and reacts with alkanes explosively under most conditions. It is therefore very difficult to control the reaction and special conditions are required for the fluorination of organic compounds. Fluorination of alkanes may be carried out by diluting fluorine with nitrogen (an inert gas) and carrying out the reaction in an apparatus specially designed to remove the heat produced in the reaction because the reaction is highly exothermic. The product is usually a complex mixture.



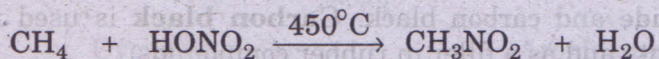
Monofluoroethane and symmetrical difluoroethane are not formed.

Direct chlorination of alkanes may be effected by means of sulphuryl chloride (SO_2Cl_2) in the presence of light and traces of an organic peroxide.

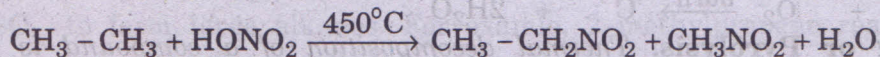


Sulphoryl chloride is more reactive, and therefore less selective, than chlorine.

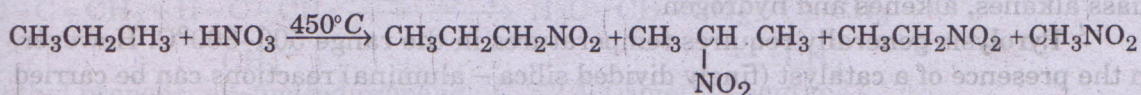
2. Nitration. The substitution of a hydrogen atom of alkane (or compound) by a nitro group ($-NO_2$) is called **nitration**. When a mixture of an alkane and nitric acid vapours is heated at $400 - 500^\circ C$ in a metal tube, it gives nitroalkanes.



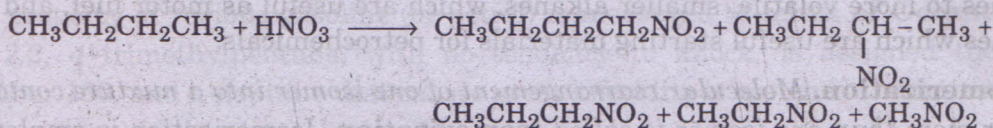
Since the reaction takes place at high temperatures the C - C bonds of alkanes break during the reaction. Thus ethane gives:



Propane gives a mixture containing 1 - nitropropane, 2 - nitropropane, nitroethane and nitromethane.

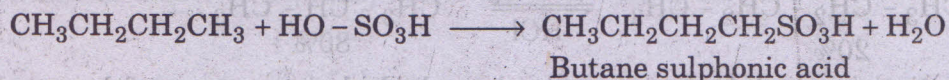


Higher alkanes yield even more complex mixtures. The nitration of alkane can be predicted by a simple rule, "all those nitro alkanes are produced that would result from the replacement of any hydrogen atom or any alkyl group of the starting alkane. Thus n-butane gives following nitration products.



The nitration of alkanes proceeds by a free radical mechanism.

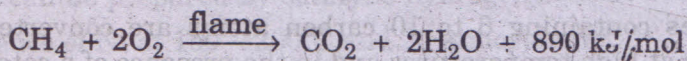
3. Sulphonation. Replacement of a hydrogen atom of alkane by a sulphonic acid group ($-SO_3H$) is known as **sulphonation**. Sulphonation of alkanes is carried out with fuming sulphuric acid. The reaction occurs at moderate temperature ($50-60^\circ C$). Lower alkanes like methane and ethane do not give this reaction.



Alkyl sulphonic acids are used for the production of detergents. Synthetic detergents are sodium or potassium salts of alkyl benzene sulphonic acids, $RC_6H_5SO_3^-Na^+$ where $R = C_9H_{19}$ or larger alkyl group. They are most widely used for laundry work.

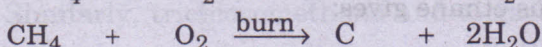
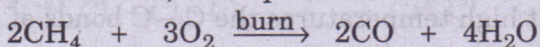
Synthetic detergents have an advantage over soaps, because their Ca, Mg and iron salts as well as their Na and potassium salts, are water soluble. Hard water contains Ca^{2+} , Mg^{2+} and Fe^{3+} ions and these cause precipitation of soap, and hence involve considerable wastage of soap.

4. Combustion. Alkanes when ignited in the presence of air or oxygen, they burn to form carbon dioxide and water. The reaction is highly exothermic and the heat generated is used as a source of heat and power.



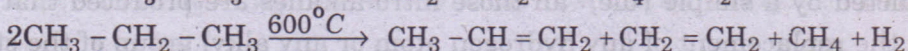
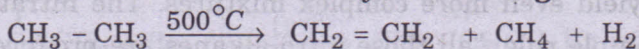
The heat of **Combustion** increases regularly as the series ascends, The increment, per $-\text{CH}_2$ group, being about 660 kJ/mol. Thus its value for ethane is 1559 kJ/mol, for propane is 2225 kJ/mol and for n-butane is 2877 kJ/mol.

Incomplete combustion of alkanes (i.e. burning them in insufficient supply of oxygen), gives carbon monoxide and carbon black. **Carbon black** is used in the manufacture of ink, black paints and as a filler in rubber compounds.



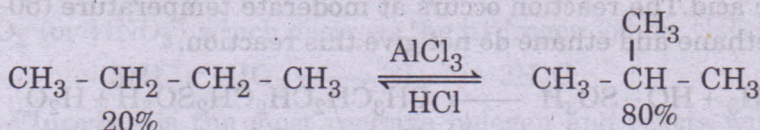
5. Cracking or Pyrolysis. *Thermal decomposition of a compound is called Pyrolysis.* When alkanes are heated to a high temperature in the absence of air, C - C bond cracks resulting in the formation of a mixture of smaller, lower molecular mass alkanes, alkenes and hydrogen.

Pyrolysis generally requires temperatures in the range 500-800°C. However, in the presence of a catalyst (finely divided silica - alumina) reactions can be carried at low temperatures. This is called Catalytic **cracking**.



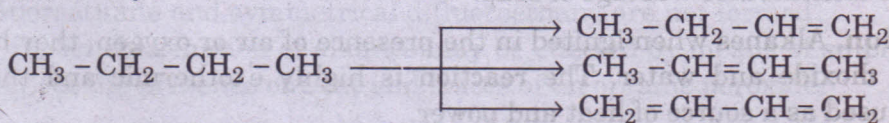
Pyrolysis serves two important purposes: (i) it converts less volatile, higher alkanes to more volatile, smaller alkanes, which are useful as motor fuel, and (ii) to alkenes which are useful starting materials for petrochemicals.

6. Isomerization. *Molecular rearrangement of one isomer into a mixture containing one or more than one isomer is called isomerization.* Isomerization is employed in reforming straight-chain alkanes into branched-chain hydrocarbons, which renders them as better fuels. Alkanes are readily isomerized by strong Lewis acids such as AlCl_3 , H_2SO_4 . For example, n-butane isomerizes to isobutane.

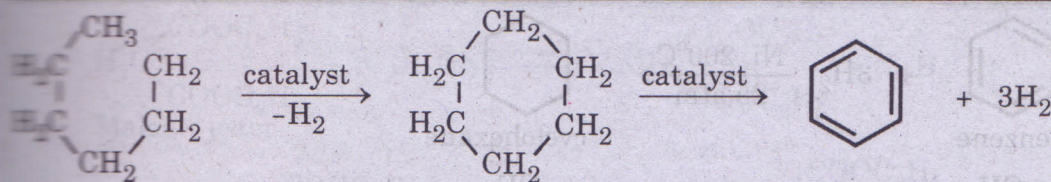


Isomerization is used to increase the branched chain content of lower alkanes produced by cracking, as branched chain alkanes are more valuable than n-alkanes in motor spirit.

7. Dehydrogenation of alkanes. Alkanes can be dehydrogenated in the presence of a suitable catalyst such as Cr_2O_3 , V_2O_5 at high temperatures. Dehydrogenation may result in the formation of alkenes, alicyclic or aromatic compounds. The dehydrogenation of n-butane to butenes occurs at 550-660°C in the presence of Cr_2O_3 as a catalyst.



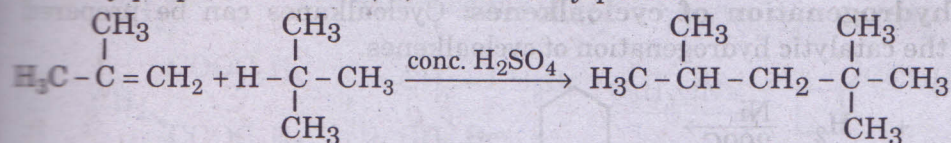
Aromatization of alkanes containing 6 to 10 carbon atoms are converted into benzene and its homologues at high temperatures and in the presence of a catalyst.



Cyclization

Aromatization

3. Alkylation. Introduction of alkyl group into alkene is termed as alkylation. Alkenes (obtained by cracking) react with alkanes in the presence of Lewis acid like AlCl_3 , H_2SO_4 to form large alkanes. For example, 2-methylpropene reacts with 2-methylpropane to form 2, 2, 4-trimethylpentane.



2-methyl propene 2-methyl propane 2,2,4-trimethyl pentane

Normal alkanes detonate and cause knocking of the engine and are bad fuels. The branched-chain alkanes give a relatively smooth performance when burnt in the internal combustion engines of motor cars, and are excellent fuels. Cracking, isomerization, dehydrogenation and alkylation improve the quality of motor fuels. The knock property of various gasoline (or petrol) is measured in terms of **Octane Number**. 2,2, 4-trimethylpentane, with no tendency to knock, is assigned the octane number 100, and n-heptane that causes great knocking is assigned the octane number 0.

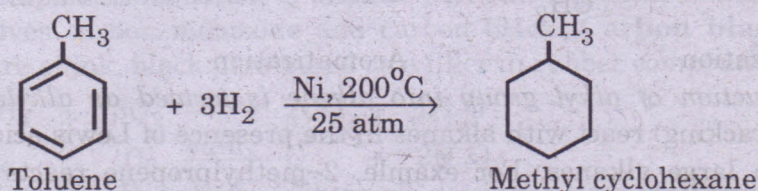
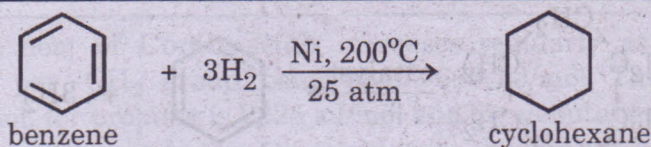
The octane number of a particular gasoline is that percent of 2, 2, 4-trimethylpentane in a mixture of 2, 2, 4-trimethylpentane and n-heptane which gives equivalent knock performance. For example, the knock performance of a given sample of gasoline is found to be the same as that of a mixture of 42% of 2,2,4-trimethylpentane and 58% of heptane, the octane number of the gasoline, therefore is 42.

4.6 CYCLOALKANES

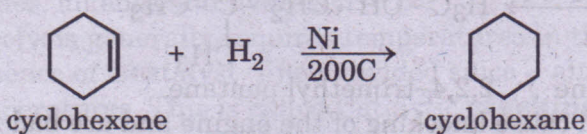
Cycloalkanes are saturated hydrocarbons in which the carbon atoms are joined by single covalent bond to form a ring. They are also called **alicyclic compounds**. The prefix ali- is added because of their similarity to aliphatic compounds. They have the general formula C_nH_{2n} and hence are isomeric with alkenes.

Methods of preparation of cycloalkanes

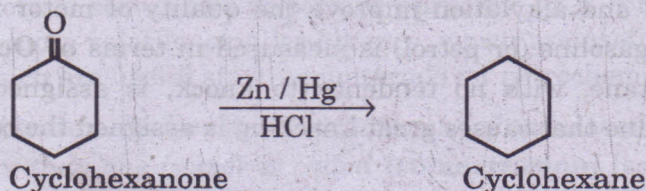
1. Catalytic Hydrogenation of Aromatic compounds. Cycloalkanes or its derivatives can be prepared by catalytic hydrogenation of benzene or its derivatives in the presence of Ni at $150 - 200^\circ\text{C}$ and 25 atmospheres.



(ii) **Catalytic hydrogenation of cycloalkenes:** Cycloalkanes can be prepared conveniently by the catalytic hydrogenation of cycloalkenes.

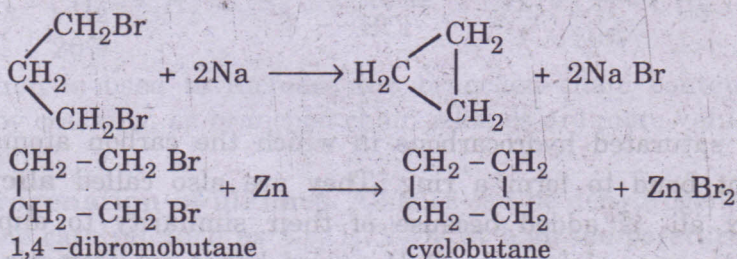


2. Reduction of cyclic ketones. Cycloalkanes can be prepared by the Clemmensen reduction of the corresponding cyclic ketones.



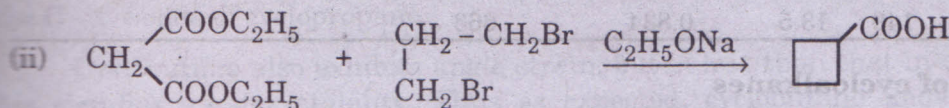
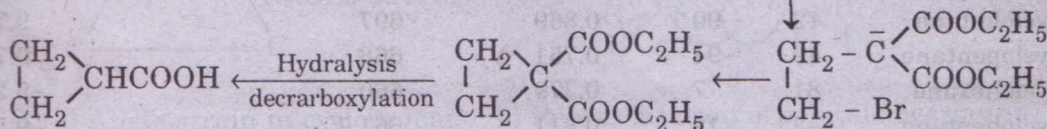
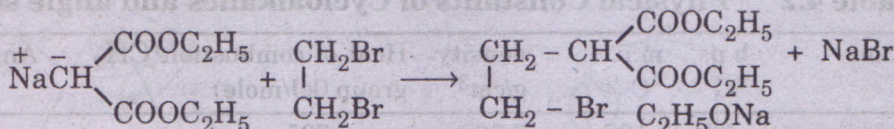
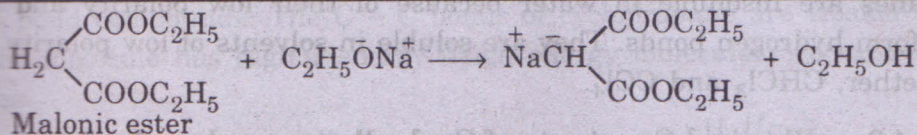
From Open - chain compounds

3. Dehalogenation of dihalides (Freund synthesis). Terminal dihalides when treated with Na or Zn form cycloalkanes. This reaction is a modified Wurtz reaction and is useful for the preparation of three to six-membered rings.

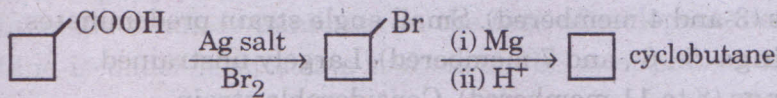


4. Perkin ring closure reaction or Perkin condensation.

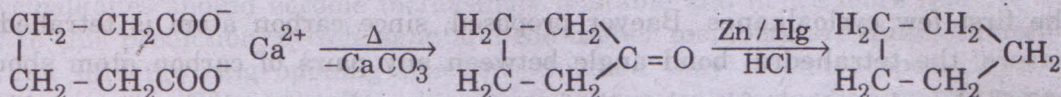
Perkin ring closure reaction is a useful synthetic reaction for the preparation of cyclic compounds. In this reaction both active hydrogens of malonic ester are removed by sodium ethoxide and the anion formed is alkylated with an ethylene dibromide which undergoes internal alkylation in the second step to give a cyclic compound which on hydrolysis and decarboxylation yields cycloalkane derivatives.



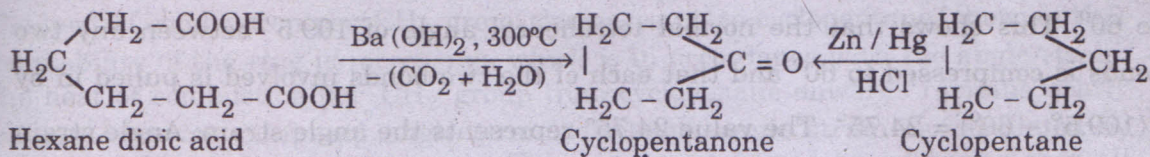
The cycloalkane carboxylic acid can be converted to cycloalkane by the following route.



5. From Salts of dicarboxylic acids. When the calcium or barium salts of dicarboxylic acids are heated, cyclic ketones are formed. The cyclic ketones can be readily converted into the corresponding cycloalkanes by Clemmensen reduction.



6. Pyrolysis of dicarboxylic acids. Dicarboxylic acids containing 4 or 5 carbon atoms in between the two carboxylic groups on heating at 300°C in presence of Ba(OH)₂, lose CO₂ and H₂O to form cycloketones which can be reduced to the corresponding cycloalkane by Clemmensen reduction or Wolff-Kishner reduction.



Physical properties.

1. Cyclopropane and cyclobutane are gases at room temperature; the remaining cycloalkanes are liquids.
2. Melting and boiling points of cycloalkanes show a gradual increase with the increase in molecular mass. However, cycloalkanes have higher melting and boiling points and higher densities as compared to the corresponding normal alkanes due to their greater symmetry and pack more tightly into a crystal lattice.

3. Cycloalkanes are insoluble in water because of their low polarity and their inability to form hydrogen bonds. They are soluble in solvents of low polarity such as benzene, ether, CHCl_3 and CCl_4 .

Table 4.2 Physical Constants of Cycloalkanes and angle strain

Cycloalkane	b.p. °C	m.p. °C	density g/cm ³	Heat of combustion/CH ₂ group (kJ/mole)	Angle strain
Cyclopropane	-33	-127	0.680	705	24.75°
Cyclobutane	12	-90	0.869	697	9.75°
Cyclopentane	49	-94	0.751	668	0.75°
Cyclohexane	81	7	0.779	660	-5.25°
Cycloheptane	-33	-12	0.811	661.7	-9.5°
Cyclooctane	149	13.5	0.834	663	

Classification of cycloalkanes

Cycloalkanes are divided into four groups (classes), depending on the ring size. They are as follows:

1. **Small rings** (3- and 4-membered). Small angle strain predominates.
2. **Common rings** (5-, 6-, and 7-membered). Largely unstrained.
3. **Medium rings** (8 to 11-membered). Considerable strain.
4. **Large rings** (12-membered and larger). Little or no strain.

Baeyer's Strain Theory; structure and stability of cycloalkanes.

In 1885, Adolf Baeyer proposed a theory to explain the relative stability of the first few cycloalkanes. Baeyer proposed, since carbon atom is tetrahedral in nature, the tetrahedral bond angle between any pairs of carbon atom should be 109.5° . Any deviation of bond angle from the normal tetrahedral value would result in internal strain of the ring, called **angle strain**, which determined the stability of the ring.

In cyclopropane, each of the three carbon-carbon bonds are formed by overlap of two sp^3 orbitals. Cyclopropane is an equilateral triangle, the internal angles must be 60° . This shows 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 $\frac{1}{2}(109.5^\circ - 60^\circ) = 24.75^\circ$. The value 24.75° represents the angle strain. Angle strain exists in a cyclopropane ring because the sp^3 orbitals of carbon cannot overlap as effectively as they do in alkanes (where perfect end-on overlap is possible). The bonds of cyclopropane are banana-shaped and are often described as bent bonds. Orbital overlap is less effective, since carbon atoms adopt a hybridization state that is not purely sp^3 , it contains more p -character. Molecular orbital calculations show that such bonds are not completely σ in character. These bonds are intermediate in character between σ and π , that is why cyclopropane behaves in some respects like

single - bond compounds. The C - C bonds of cyclopropane are weaker and as a result the molecule has higher energy. High energy molecules are called strained molecules.

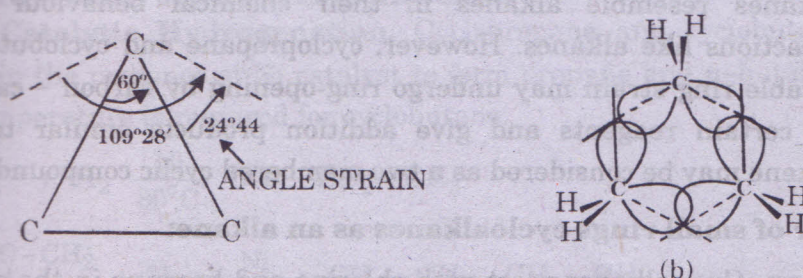


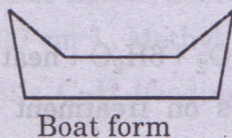
Fig. (a) Angle strain in cyclopropane (b) Representation of orbitals overlap in the C - C bonds of cyclopropane.

Cyclobutane also exhibits angle strain, but is less than that in cyclopropane. This signifies greater stability. Thus as expected, cyclobutane undergoes ring - opening reactions but only under more drastic conditions. Cyclobutane ring is not planar but is slightly "folded".

The angle strain is minimum in the case of cyclopentane. This implies that cyclopentane is under least strain and should be most stable. It does not undergo ring - opening reactions.

The angle strain in the case of cyclohexane is higher than that in the case of cyclopentane. This strain increases continuously with increase in the number of carbon atoms in the ring. According to Baeyer's strain theory, cyclohexane and the higher cycloalkanes should become increasingly unstable and hence more reactive. Contrary to this prediction, cyclohexane and the higher members are quite stable. They do not undergo ring opening reactions. Instead they resemble open chain alkanes in reactivity. Thus, the Baeyer's strain theory satisfactorily accounts for the exceptional reactivity of cyclopropane, cyclobutane and cyclopentane, but it is not valid for cyclohexane and higher members.

A molecule which is more strained is less stable. The stability of cycloalkanes can be predicted by determining the heat of combustion per CH_2 group. A higher value of heat of combustion per CH_2 group indicates a relatively unstable molecule. The heat of combustion per CH_2 group decreases up to cyclopentane, showing that the stability of the ring is increasing, which is in accordance with the angle strain. The heat of combustion per CH_2 group from cyclohexane onwards remains nearly constant showing minimum angle strain, although, angle strain as calculated by assuming planar ring, is increasing. This can be explained by assuming that all rings are not planar and rings with six or more carbon atoms are puckered, the normal bond angle being retained and thereby producing strainless rings. For example, cyclohexane can exist in two non-planar puckered conformations called the **Chair form** and **Boat form**.

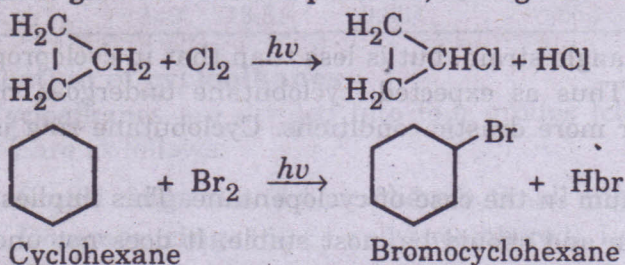


4.8 Chemical properties (reactions) of cycloalkanes

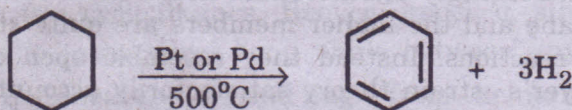
Cycloalkanes resemble alkanes in their chemical behaviour and give substitution reactions like alkanes. However, cyclopropane and cyclobutane, being under considerable ring strain may undergo ring-opening by carbon – carbon bond cleavage with certain reagents and give addition products similar to those of alkenes. An alkene may be considered as a two membered cyclic compound.

(A) Behaviour of small rings cycloalkanes as an alkane:

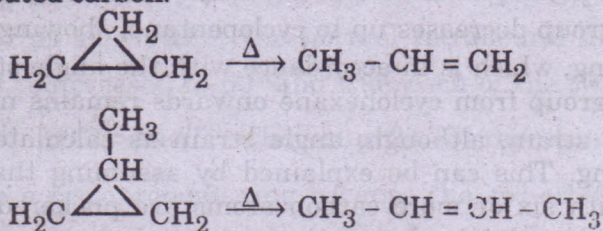
1. Halogenation. Cycloalkanes react with chlorine and bromine in the presence of UV light to give substitution products, through a free radical mechanism.



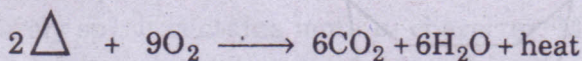
2. Aromatization. Cyclohexane and its derivatives may be converted into aromatic compounds at 500°C in the presence of Pt or Pd catalyst by catalytic reforming.



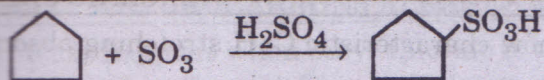
3. Isomerization. Cycloalkanes like alkanes may undergo isomerization. Cyclopropane and cyclobutane are isomerized to alkene when heated strongly. Alkyl substituted cyclopropanes isomerize in such a way that the ring fission occurs at the substituted carbon.



4. Combustion. Cycloalkanes like alkanes on combustion give CO₂ and H₂O with the evolution of heat.

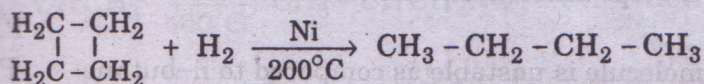
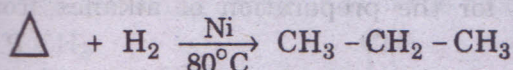


5. Sulphonation. Cycloalkanes on treatment with fuming sulphuric acid form sulphonic acid derivatives.



B. Reactions of small rings like alkenes:

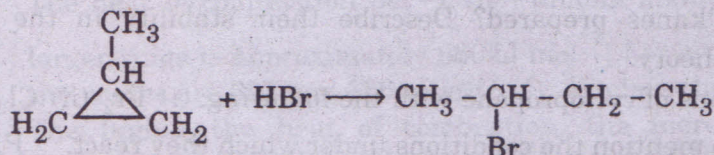
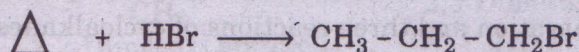
6, Catalytic Hydrogenation. Cyclopropane and cyclobutane react with hydrogen in the presence of Ni catalyst to form propane and n-butane respectively. Higher temperature is required for cyclobutane.



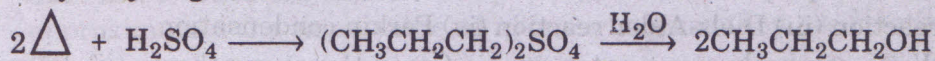
7. Addition of Cl₂ and Br₂. Cyclopropane reacts with Cl₂ and Br₂ in the presence of FeCl₃ and FeBr₃ to give 1,3-dichloropropane and 1,3-dibromopropane respectively.



8. Addition of hydrogen halide. Cyclopropane reacts with hydrogen halide to form an alkyl halide. Methylcyclopropane with HBr gives 2-bromobutane in accordance with Markovnikov's rule.



9. Hydration. Cyclopropane reacts with conc. H₂SO₄ to give alkyl sulphate which on hydrolysis gives alcohol.



Common, medium and large sized cycloalkanes, however behave like n-alkanes towards the above mentioned reagents.

Spectroscopic identification of alkanes and Cycloalkanes.

The alkanes and cycloalkanes contain carbon-carbon single bonds, the only electronic transitions possible are $\sigma - \sigma^*$ type. These transitions are of such a high energy that they absorb UV light at very short wavelength so that they are beyond the range of usual spectrophotometers.

The infrared spectra of alkanes exhibit absorptions corresponding to the C-H stretching frequencies at 2850-3000 cm⁻¹. Methyl (CH₃-) and methylene (-CH₂-) groups normally have characteristic C-H bending vibrations at 1435-1470 cm⁻¹, and 1440-1480 cm⁻¹ respectively.

Like alkanes, cycloalkanes show characteristic C-H stretching absorption at 2850-3050 cm^{-1} .

Questions

1. Write three different methods for the preparation of alkanes from alkyl halides. P.U. 2000
 2. Explain all possible steps and conditions in the chlorination of methane. P.U. 2000
 3. Why cyclobutane molecule is unstable as compared to n-butane. P.U.2000
 4. How will you convert ethyl bromide into:
 - (i) Ethan
 - (ii) Methane
 - (iii) Propane
 5. Give two methods each to prepare: (i) n-butane (ii) cyclobutane. P.U.2003
 6. Discuss the mechanism of chlorination of methane.
- Ans.** (b) Free radical substitution.
7. How alkanes are prepared by the following methods:
 - (i) Corey-House synthesis
 - (ii) Kolbe's electrosynthesis
 - (iii) Coupling of alkyl boranes
 - (vi) Reduction of carbonyl compounds.
 8. Give three methods of preparation and three reactions of cycloalkanes.
 9. Describe Baeyer's Strain Theory.
 10. How are cycloalkanes prepared? Describe their stability in the light of Baeyer's strain theory.
 11. Write the reactions of cyclopropane with the following: (i) Br_2 (ii) Cl_2 (iii) HI (iv) H_2SO_4 . Also mention the conditions under which they react. P.U. 1990
 12. Discuss briefly structural aspects of cycloalkanes. P.U.1987,89
 13. Give the preparation of cycloalkanes by (i) Freund synthesis (ii) Simon-Smith reaction (iii) Diels-Alder reaction (iv) Perkin condensation.
 14. Write comprehensive notes on: (i) Corey-House synthesis (ii) Isomerization (iii) Octane number (iv) Pyrolysis (v) Angle strain.

SHORT QUESTIONS

1. Why are alkanes inert?

Ans. A reactive site in a molecule usually has one or more unshared pairs of electrons, a polar bond, an electron-deficient atom or an atom with an expandable octet. Alkanes have none of these and therefore, they are inert.

2. Why do the C-C rather than the C-H bonds break when alkanes are pyrolyzed?

Ans. The C-C bond has a lower mean bond energy ($\Delta H = +375\text{kJmol}^{-1}$) than does the C-H bond ($\Delta H = 415\text{kJ mol}^{-1}$). Therefore, C-C rather than the C-H bonds break when alkanes are pyrolyzed.