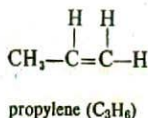
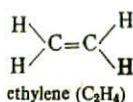


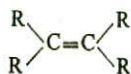
# Alkenes

Alkenes are hydrocarbons that contain a carbon-carbon double bond (C=C) in their molecules. They have the general formula  $C_nH_{2n}$  ( $n$ =number of C atoms) in comparison to  $C_nH_{2n+2}$  of alkanes. Alkenes contain two hydrogen atoms less than alkanes and are thus designated as **Unsaturated Hydrocarbons**. As a class alkenes are commonly known as **Olefins** (*L. Oleum*=oil; *ficare*=to make) because the lower members form 'oily' products on treatment with chlorine or bromine.

Since there can be no alkene with one carbon, the first member of the series (putting  $n=2$  in  $C_nH_{2n}$ ) has the molecular formula  $C_2H_4$  and is commonly known as *ethylene*. The second member of the family has the molecular formula  $C_3H_6$  ( $n=3$ ) and is commonly called *propylene*. Ethylene and propylene may be represented by the following structures.



In general, alkenes can be represented by the type formula



where R = alkyl group or H

The double bond present in alkenes largely determines their chemical behaviour. This bond which is made of two covalent bonds between the adjacent carbon atoms,



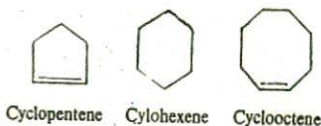
constitutes the *functional group* or *function* of alkenes. It is commonly referred to as the **Olefinic bond** or **Ethylenic bond**.

Alkenes may be classified as **Acyclic** or **Cyclic** depending upon whether they have open chain or cyclic structure. A few examples of each class are given below.

### ACYCLIC ALKENES

Ethylene	$CH_2=CH_2$
Propylene	$CH_3CH=CH_2$
2-butylene	$CH_3CH=CHCH_3$

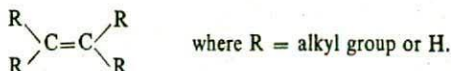
### CYCLIC ALKENES



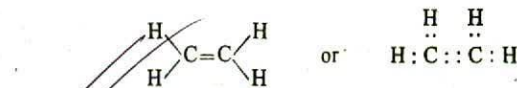
Alkenes being much more reactive than alkanes, seldom occur free in nature. They are, however, produced in large amounts during the cracking of petroleum.

## STRUCTURE

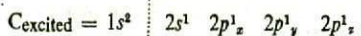
We have described alkenes as unsaturated hydrocarbons containing a carbon-carbon double bond. They could be assigned the general structural formula :



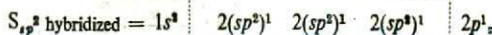
Thus the simplest member ethylene could be represented as



**Orbital Structure.** We have discussed the orbital structure of ethylene in detail earlier in Chapter 5. The electronic configuration of carbon atom in the excited state is as follows.



In each of the two carbon atoms of ethylene one  $2s$  and two  $2p$  orbitals are mixed to form three  $sp^2$  hybrid orbitals. The third  $2p_z$  orbital is left 'pure' or unhybridized.



The three  $sp^2$  orbitals, each containing an unpaired electron, lie in the same plane with their axes directed towards the corners of an equilateral triangle *i.e.*, subtending an angle of  $120^\circ$  with each other. The unhybridized  $p_z$  orbital is oriented along an axis perpendicular to the plane of  $sp^2$  orbitals, with one lobe above and one below the plane of  $sp^2$  orbitals.

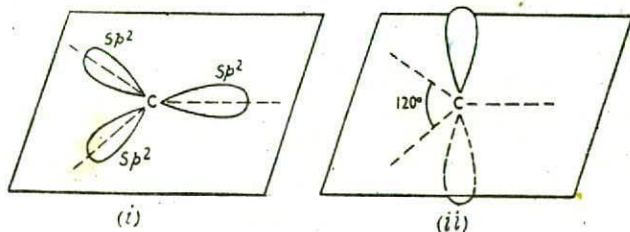


Fig. 11.1. The three  $sp^2$  orbitals lie in the same plane (i); while the pure  $p_z$  orbital is shown at right angles to this plane, one lobe above and one below it (ii).

Let us now examine the bonding in ethylene molecule. Two  $sp^2$  orbitals of each carbon form  $\sigma$  bonds with two hydrogen atoms. The third  $sp^2$  orbital of one carbon atom overlaps with the one of the second carbon to form carbon-carbon  $\sigma$  bond. The pure  $p_z$  orbitals present on each of the two carbon atoms overlap laterally and establish a  $\pi$  bond. In doing so the upper lobes of the  $p_z$  orbitals of the two carbons form a loaf above, while their lower lobes form a

leaf below. Thus these two leaves, one above and one below the plane of carbons, together make one  $\pi$  bond.

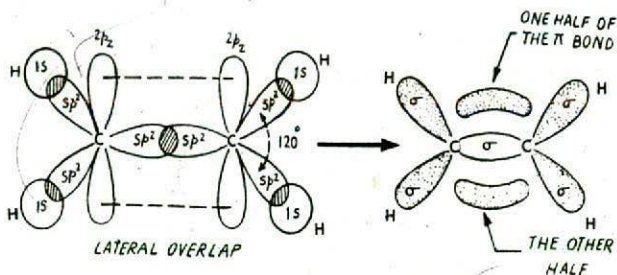


Fig. 11.2.  $\sigma$ - $\pi$  model of ethylene.

Electron diffraction and spectroscopic studies have also shown that ethylene is a flat or planar molecule. All bond angles ( $\text{H}-\text{C}-\text{H}$ ) and ( $\text{H}-\text{C}-\text{C}$ ) are  $120^\circ$ . The  $\text{C}-\text{H}$  bond length is  $1.09 \text{ \AA}$ . The  $\text{C}-\text{C}$  bond length in ethylene is  $1.34 \text{ \AA}$  as compared to the  $\text{C}-\text{C}$  bond length of  $1.54 \text{ \AA}$  in ethane. This shortening is to be expected on the basis of additional orbital overlap associated with the two bonds.

**The Double Bond.** As described above, a carbon-carbon double bond is made up of one  $\sigma$  bond and one  $\pi$  bond. For convenience it is generally represented by two equivalent lines (=). But it may be clearly understood that while one of these lines indicates a  $\sigma$  bond, the other line indicates a  $\pi$  bond.

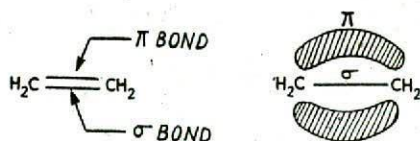


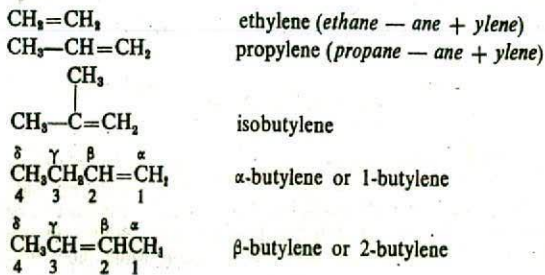
Fig. 11.3. Representation of ethylenic double bond.

It may be noted that the  $\pi$  bond is weaker than the  $\sigma$  bond because electrons in the  $\pi$  bond are more diffused in space *i.e.*, they are more exposed to the environments than the electrons in a  $\sigma$  bond. Furthermore, a  $\pi$  bond is formed by the lateral overlap of  $p$  orbitals which provides less extensive overlap. Since the  $\pi$  bond in alkenes is a weaker bond, it is the site of chemical reactivity in the molecule.

## NOMENCLATURE

There are two ways of naming alkenes.

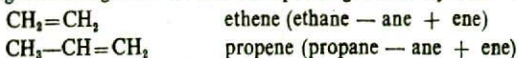
(1) **Common System.** The lower alkenes are often referred to by their common names. The common name of an alkene is obtained by changing the ending *-ane* of the corresponding alkane to *-ylene*. The numbers 1, 2, 3, or Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc are used to indicate the position of the double bond. Thus,





The use of common system of nomenclature should be avoided for alkenes having more than four carbons because then the system loses its practicability.

(2) **IUPAC System.** According to the IUPAC system, the name of an alkene is derived by replacing the ending *-ane* of the corresponding alkane by *-ene*. Thus,



The IUPAC names of higher alkenes are obtained by the application of the following rules.

(1) The longest continuous chain containing both carbon atoms of the double bond is chosen as the parent hydrocarbon chain.

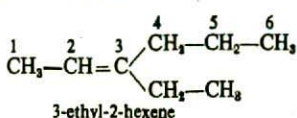
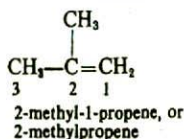
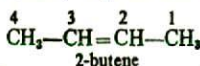
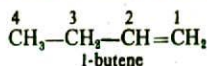
(2) The name of the parent hydrocarbon is obtained by replacing the suffix *-ane* of the corresponding alkane by *-ene*.

(3) The carbon atoms of the parent chain are numbered from the end that gives the lowest possible numbers to the carbon atoms of the double bond. The smaller of the numbers of the carbons involved in the double bond indicates its position. This number is placed immediately before the primes of the parent alkene with a hyphen (-) in between.

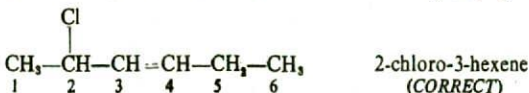
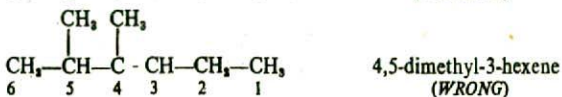
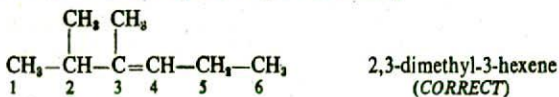
(4) Each substituent (say Cl or Br or alkyl group) present on the chain is indicated by its name and the number of the carbon to which it is attached. The position number is written before the name of the substituent with a hyphen (-) in between.

(5) If while numbering the chain, the double bond receives the same number when counted from either side, then the system is numbered to give the substituent group the lowest number.

The above rules are illustrated by the examples given below.



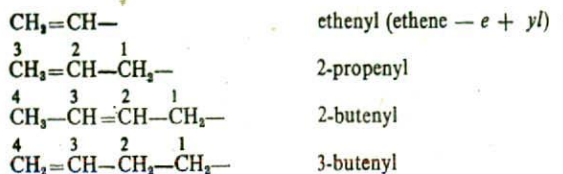
(When double bond is equidistant from two ends)



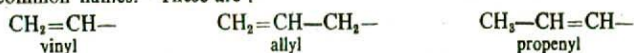
The IUPAC system of nomenclature of higher alkenes has now replaced the 'common system'. However, for the first two members of the series the common names ethylene and propylene are used in preference to the IUPAC names, ethene and propene.

**Alkenyl groups.** The monovalent unsaturated groups resulting by the removal of one hydrogen atom from alkenes are called *alkenyl groups*. The IUPAC names of these groups are derived by replacing the terminal *-e* of the name of the corresponding alkene by *-yl*. The carbon atoms of the alkenyl chain are numbered so that the carbon with free valency gets number 1. Thus,





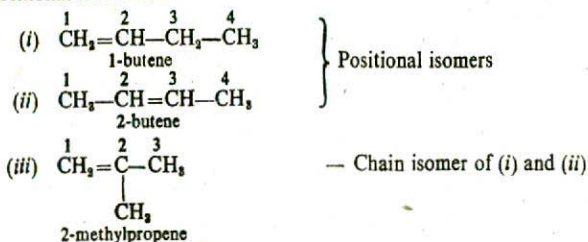
However, the unsaturated groups that are quite important are frequently called by their trivial or common names. These are :



Therefore chloroethene,  $\text{CH}_2=\text{CH}-\text{Cl}$  is more commonly called vinyl chloride and 3-bromo-1-propene is known as allyl bromide.

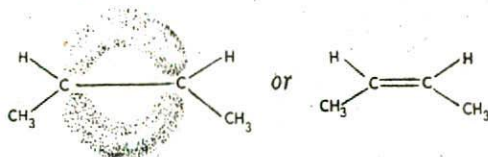
### ISOMERISM

The presence of double bond in alkenes increases the opportunity of isomerism. In addition to chain isomerism, they offer positional isomerism due to different positions of the double bond on the carbon chain. For example, the three butenes ( $\text{C}_4\text{H}_8$ ) possibly exhibit both chain and positional isomerism.

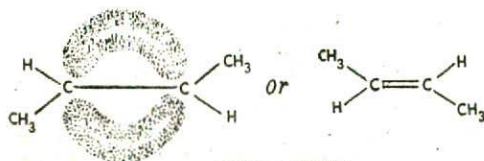


**Geometrical Isomerism.** We have seen that a C—C double bond in alkenes is made of one  $\sigma$  bond and one  $\pi$  bond. The presence of a  $\pi$  bond 'locks' the molecule in one position. The two carbon atoms of the C—C double bond and the four atoms that are attached to them all lie in one plane and their positions in space are fixed.

If the two groups attached to each carbon atom of the double bond are different, then two compounds are possible. They will differ only in the spatial arrangement of the substituents about the C—C double bond. The two compounds are referred to as **Geometrical isomers** and are differentiated from each other by the terms *Cis* and *Trans*. The **Cis isomer** is one in which two identical substituents or groups are on the same side of the double bond. The **Trans isomer**



*CIS-2-BUTENE*



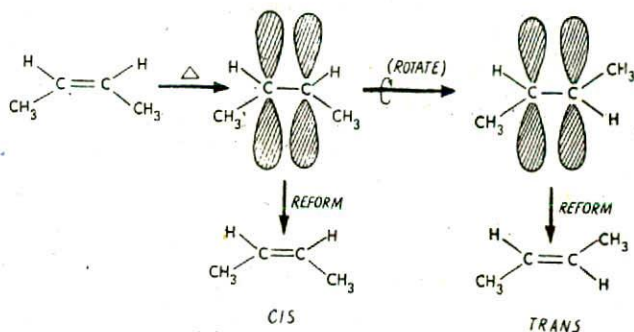
*TRANS-2-BUTENE*

is that in which two identical substituents are on opposite sides of the double bond. Thus two

geometrical isomers are possible for 2-butene. The molecule in which two methyl groups are on the same side of the C—C double bond, is the *cis* isomer. And the molecule in which two methyl groups are on opposite sides of the double bond, is the *trans* isomer.

The two geometrical isomers which are also called configurational isomers differ in their physical and chemical properties and can thus be distinguished from each other.

**Cis-trans interconversion.** The conversion of the *cis* geometric isomer into the *trans* compound or vice versa is made possible if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 kcal/mole) to break the  $\pi$  bond and now the rotation about the  $\sigma$  bond becomes possible. Upon cooling, the reclosing of the  $\pi$  bond takes place in two ways giving mixture of isomers. For example, if *cis*-2-butene is heated, it will give rise to a mixture of *trans*-2-butene and *cis*-2-butene.



The geometrical isomers since they have different physical properties such as melting points, boiling points, densities etc., they can be separated by conventional techniques—fractional distillation, gas chromatography etc.

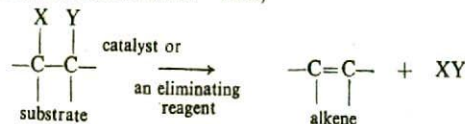
For greater details of the phenomenon of geometrical isomerism, the reader may refer to chapter on isomerism.

**Isomerism with Alicyclic compounds.** Alkenes and cycloalkanes having the same number of carbon atoms, are also isomeric. For example,



## METHODS OF PREPARATION

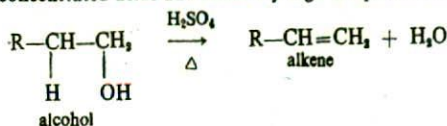
Most of the methods of preparation of alkenes depend upon the principle that the removal of two atoms or groups (say X and Y) located on adjacent carbon atoms results in the creation of a carbon-carbon double bond. Thus,



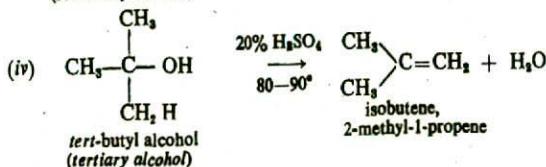
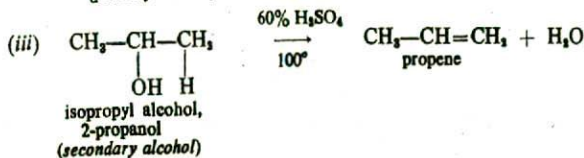
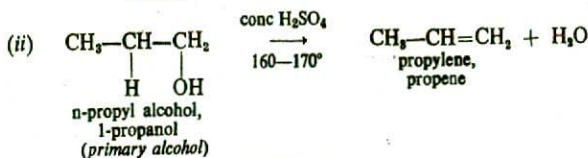
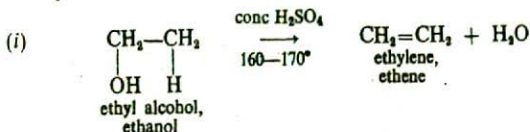
where X and Y may be same or different atoms or groups. The compound XY is usually a small inorganic molecule such as water (H—OH) or a hydrogen halide (H—Br; H—Cl). The process illustrated above is called **Elimination Reaction** because the molecule XY is eliminated from the original substrate. The general methods of preparation of alkenes are described below.

(1) **By Dehydration of Alcohols.** Dehydration means the removal of a molecule of water from a reactant molecule. When an alcohol is heated in the presence of sulphuric acid, a molecule of water is eliminated and an alkene is formed. The ease of dehydration of an alcohol

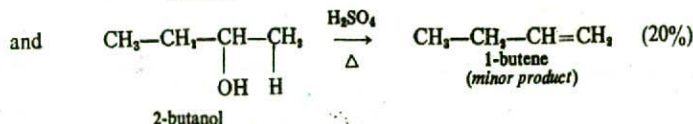
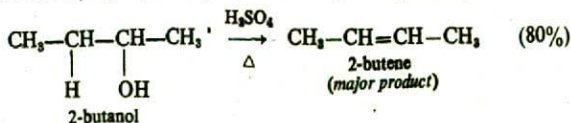
depends markedly on its structure. Tertiary alcohols dehydrate under mild conditions (moderate temperature, dilute acid). Secondary alcohols are intermediate in reactivity. Primary alcohols generally require concentrated acids and relatively high temperatures.



Examples :



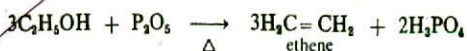
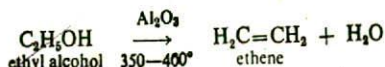
With unsymmetrical secondary (or tertiary) alcohols, elimination can proceed in two ways and a mixture of alkenes is obtained. Thus the dehydration of 2-butanol leads to the formation of 2-butene (major product) and 1-butene (minor product).



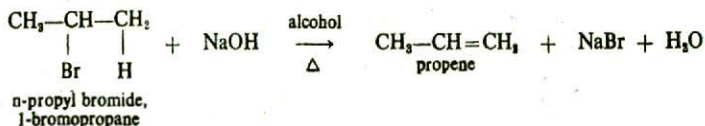
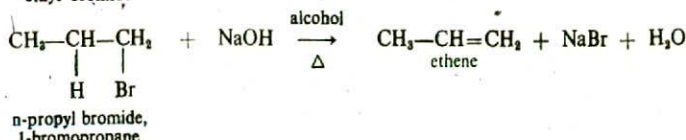
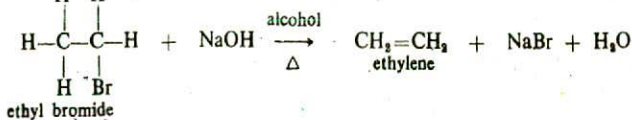
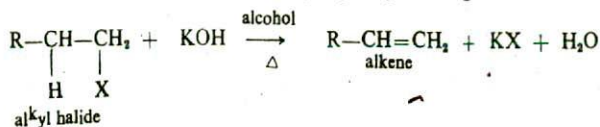
This is in accordance with the **Saytzeff Rule** which states that *when alternatives exist, hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms.* Stated differently, the major product will be the alkene with larger number of alkyl groups attached to the double bond.

Dehydration of an alcohol may also be brought about by passing the alcohol vapours over heated alumina at 350–400°. Other dehydrating agents which may be employed are phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>).

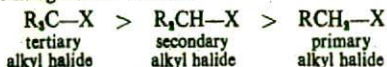




(2) **By dehydrohalogenation of Alkyl halides.** Dehydrohalogenation involves the removal of the elements of hydrogen halide ( $\text{H-X}$ ) from adjacent carbon atoms. When an alkyl halide is heated with an alcoholic solution of sodium or potassium hydroxide, a molecule of hydrogen halide is eliminated and an alkene is formed. Alkyl bromides are more reactive than chlorides, and alkyl iodides are still more reactive in undergoing dehydrohalogenation.

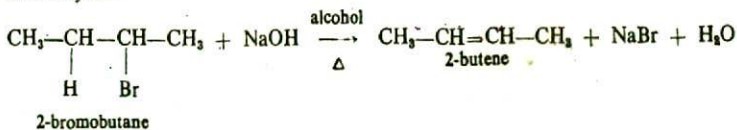


Tertiary alkyl halides react most readily, then secondary, and finally primary. The ease of dehydrohalogenation is thus:

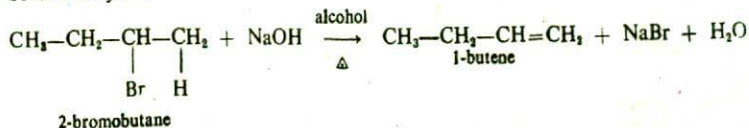


As was the case with the dehydration of alcohols, the dehydrohalogenation of unsymmetrical secondary or tertiary alkyl halides can take place in more than one way and a mixture of alkenes results. For example, the dehydrohalogenation of 2-bromobutane gives 1-butene and 2-butene. The *Saytzeff Rule* is again followed and 2-butene is formed as the major product.

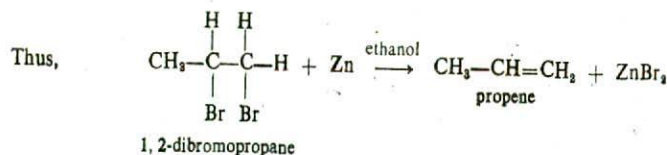
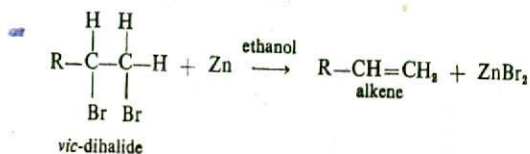
One Way :-



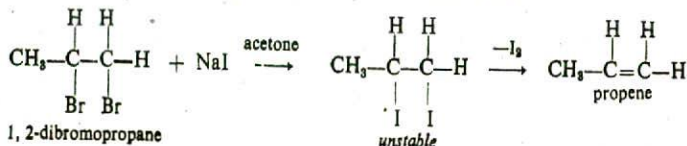
Second Way :-



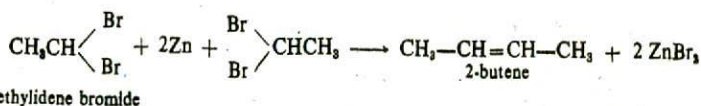
(3) **By Dehalogenation of Vicinal dihalides.** Dehalogenation involves the removal of a halogen molecule ( $X-X$ ) from a reactant molecule. A compound having two halogen atoms on adjacent carbon atoms is called a vicinal dihalide (or *vic*-dihalide). The treatment of *vic*-dihalides with zinc dust using ethyl alcohol as solvent, results in dehalogenation, and an alkene is formed.



Another convenient method of this reaction is to reflux (boil) the dihalide with an acetone solution of sodium iodide. This will convert dichlorides or dibromides into diiodides. Diiodides being unstable will spontaneously decompose to give the alkene and iodine.

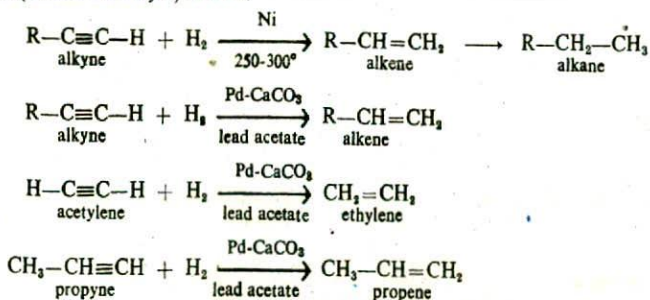


When the two halogen atoms are attached to the same carbon atom (*gem*-dihalide), zinc eliminates four halogen atoms from two molecules of dihalide to form alkane.



This reaction is of limited application since the *gem*-dihalides themselves are ordinarily prepared from alkenes by the addition of halogens. However, this reaction is useful in separating an alkene from non-olefinic substrates and also in the purification of alkenes.

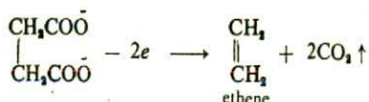
(4) **By Partial hydrogenation of Alkenes.** Alkenes can be hydrogenated using *Raney nickel* or finely divided platinum or palladium to give alkenes. Under these conditions alkenes are further reduced to alkanes. However, it is possible to stop the reduction at the alkene stage if a mild catalyst such as palladium on calcium carbonate partially deactivated by lead acetate (*Lindlar's catalyst*) is used.



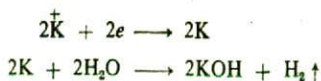




at anode :



at cathode :



This method is, in fact, an extension of Kolbes method for the preparation of alkanes and is seldom used in actual practice as the product obtained is not pure.

### PHYSICAL PROPERTIES

The physical properties of alkenes are similar to those of the corresponding alkanes.

(1) Unbranched alkenes containing 2 to 4 carbon atoms (ethylene, propylene, butenes) are gases at room temperature ; those containing 5 to 18 carbon atoms are liquids ; while those containing more than 18 carbons are solids.

(2) They are insoluble in water but are soluble in organic solvents such as ethers, alcohols, and carbon tetrachloride.

(3) They are lighter than water ; the series has a limiting density of rather less than 0.7.

(4) The melting points and boiling points rise with increasing molecular weight. Furthermore, branched chain alkenes have lower boiling points than straight-chain alkenes.

(5) In general, alkenes have higher melting points than the alkanes with the same carbon skeleton. This is attributed to the stronger attractive forces in alkenes than in alkanes. Due to the mobility of the electrons in the  $\pi$  bond, the double bond is more polarizable than single bond. This permits the ready formation of induced dipoles in alkenes molecules which are responsible for stronger intermolecular forces of attraction.

**Table.** Physical Constants of the Alkenes

Name	Formula	bp° C	mp °C	Density (g/m as liquid)
ethylene	$\text{CH}_2=\text{CH}_2$	-103.8	-169.4	0.566
propylene	$\text{CH}_3\text{CH}=\text{CH}_2$	-47.7	-185.2	0.609
1-butene	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	-6.5	-130.0	0.625
2-butene	$\text{CH}_3\text{CH}=\text{CHCH}_3$	1.4	-127.0	0.630
2-methylpropene	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}=\text{CH}_2 \end{array}$	-6.9	-140.7	0.594
1-pentene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	30.1	-138.0	0.641
1-hexene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	64.1	-141.0	0.673
1-heptene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	93.6	-119.0	0.697

## REACTIONS OF ALKENES

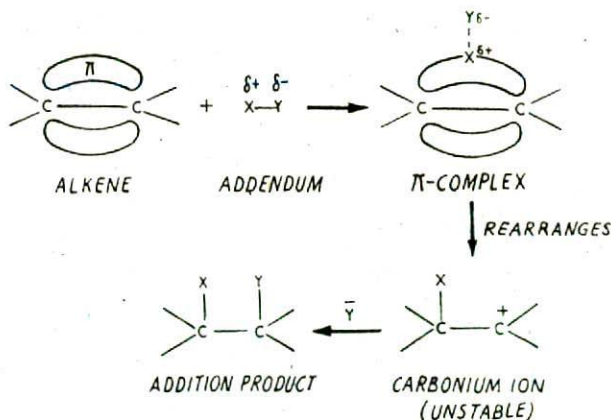
We have already observed that the functional group in alkenes is C—C double bond which is made up of one  $\sigma$  bond and one  $\pi$  bond. It is noteworthy that :

(1) The  $\pi$  bond since it is formed by the lateral overlap of  $p$  orbitals which allows less extensive overlap, is weaker than a  $\sigma$  bond. The energy of a  $\sigma$  bond is 83 kcal/mole, while that of  $\pi$  bond is 63 kcal/mole.

(2) The electrons in the weaker  $\pi$  bond are more diffused in space and are more exposed to any reactant.

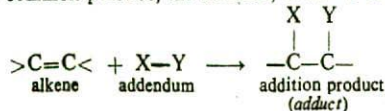
From the above it follows that the weaker  $\pi$  bond would tend to convert itself to two  $\sigma$  bonds, giving stable addition products. Also, the  $\pi$  bond in alkene acts as a source of electrons. Hence electrophiles which are positively charged species and can accept electrons, would be attracted by the  $\pi$  cloud while nucleophiles with completed shell structure will be repelled. Therefore, the characteristic reactions of alkenes are the **Electrophilic addition reactions**.

The detailed mechanism of the addition of X—Y to an alkene is given below. If Y is more electronegative than X, the addendum could be represented as  $\overset{\delta+}{X}-\overset{\delta-}{Y}$ . Thus,

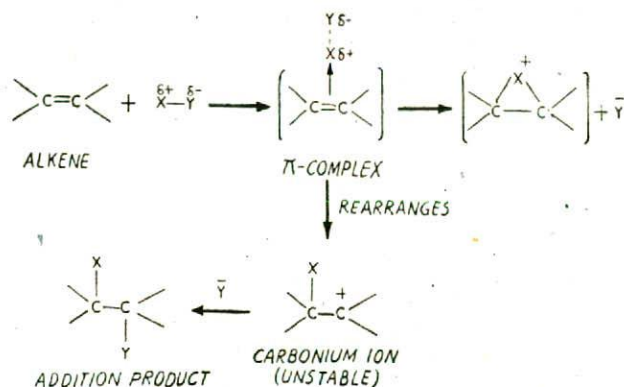


In the first step of the addition reaction, the peripheral electrons of the  $\pi$  bond attract the electrophilic end of the addendum (X) to form a loose  $\pi$  complex. The positive end of the addendum buried in the  $\pi$  electron cloud gives positive charge to the  $\pi$  complex, leaving the nucleophile  $\text{:Y}^-$ . The  $\pi$  complex then rearranges to a carbonium ion which reacts with the nucleophile remainder to form the addition product.

According to common practice, the addition, of X—Y to an alkene is written as



and the mechanism of addition is then represented as



**Cis and Trans additions to alkenes.** We know that an alkene molecule is planar with the  $\pi$  cloud above and below the plane. Thus the addition of  $\text{X}-\text{Y}$  to alkenes proceeds in two distinct pathways. In one, both parts of the reagent add to the  $\pi$  bond from the same side of the double bond *i.e.*, either above or below the plane. This is called *cis addition*. In the other way, one part of the reagent adds from one side of the double bond and the other from the

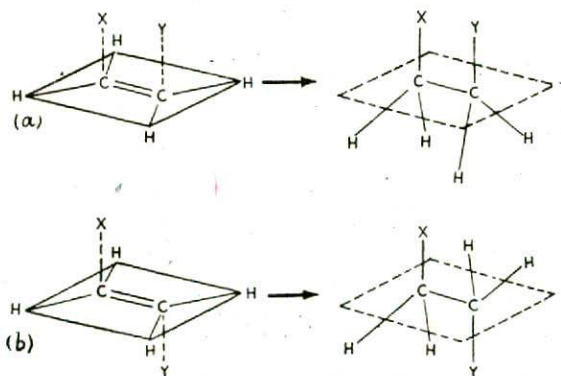


Fig. 11.4. (a) *cis* and (b) *trans* addition to alkenes.

opposite side when it is known as *trans addition*. The addition of a symmetrical reagent like  $\text{Br}-\text{Br}$  also gives *cis* and *trans* products in the same fashion.

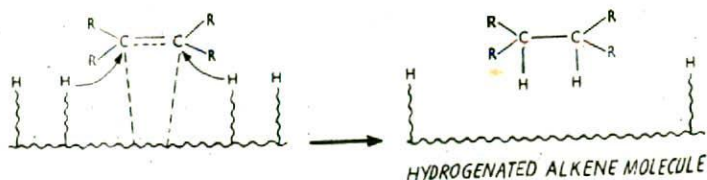
The general reactions of alkenes are given below.

(1) **Addition of Hydrogen ; Catalytic hydrogenation.** Alkenes add hydrogen in the presence of a metal catalyst forming the corresponding alkane. This process known as *catalytic*



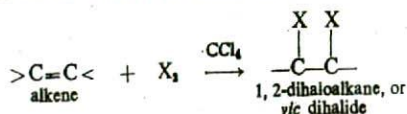


**Step 3 :** The hydrogen atoms from metal surface are transferred to the 'bound' alkene molecule.



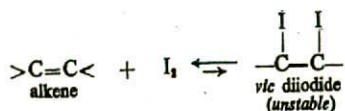
It may be noted that both the adding hydrogen atoms approach the double bond from the same side, that is from below the plane of the alkene molecule. Therefore, the catalytic hydrogenation of an alkene is, in fact, a *cis* addition and results only in the formation of *cis* isomer if isomeric products are possible.

(2) **Addition of Halogens (Halogenation).** When an alkene is treated with chlorine or bromine in carbon tetrachloride in dark, the halogen adds rapidly across the carbon-carbon double bond of the alkene to form 1, 2-dihaloalkane or *vicinal* dihalide.

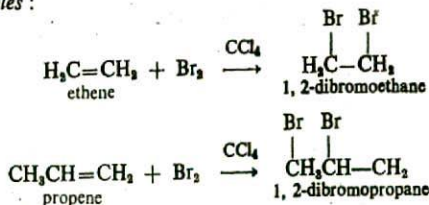


where X = Cl, Br.

Fluorine cannot be used for the preparation of *vicinal* difluorides because it causes extensive fragmentation of the alkene molecule. Iodine reacts slowly with alkenes to form *vicinal* diiodides which are unstable and eliminate iodine very readily to regenerate the original alkene.



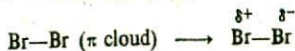
**Examples :**



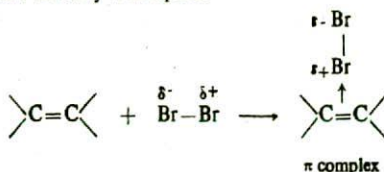
Bromine solution in carbon tetrachloride has orange colour. When it is added dropwise to an alkene, bromine is used up to form colourless *vicinal* dibromide and the orange colour disappears immediately. This is a diagnostic test for the presence of a carbon-carbon double bond in unknown compounds.

**MECHANISM.** The addition of halogens, say  $Br_2$ , to alkenes forming 1, 2-dihaloalkanes takes place by the following steps.

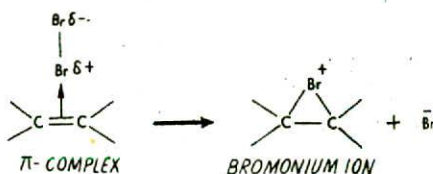
(1) When a bromine molecule comes in the proximity of an alkene, the negative  $\pi$  electron cloud of the alkene causes polarization of the bromine molecule — that is displacement of the pair of electrons joining the bromine atoms towards one of the atoms.



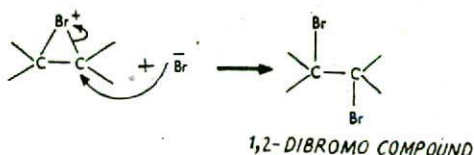
(2) The positive end of the polarized bromine molecule is then attracted near to the  $\pi$  cloud to form a low stability  $\pi$  complex.



(3) The positively charged bromine atom is then attracted by both carbons of the double bond and the Br—Br bond breaks down. The negatively charged bromine leaves as Br<sup>-</sup> and bromonium ion is formed.



(4) Nucleophilic attack of bromide ion (Br<sup>-</sup>) yields dibromo compound.



That the addition of halogen to an alkene leads to the formation of *trans* dihalide is pictorially illustrated below.

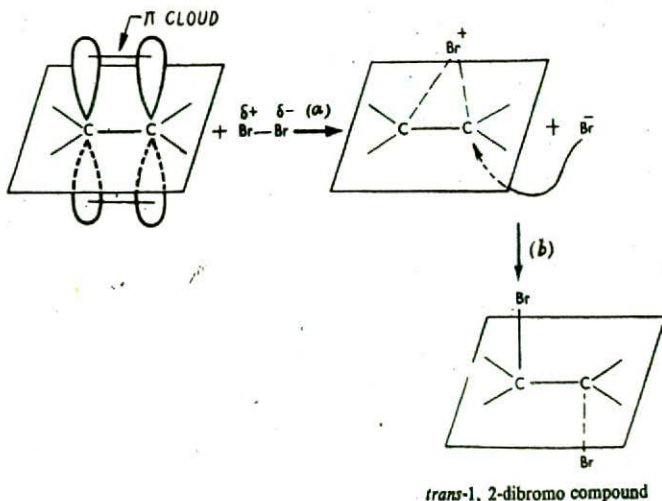
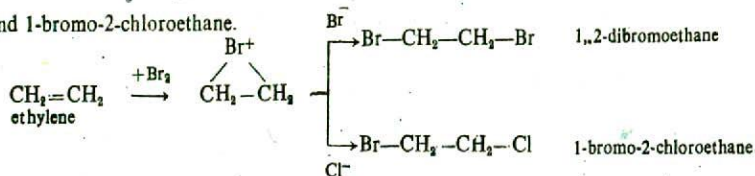


Fig. 11.5. Two-step mechanism of *trans* bromination.

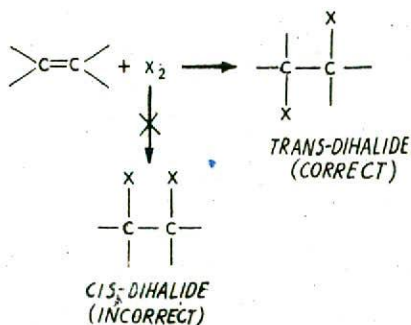
It may be noticed that  $\text{Br}^-$  attacks the bromonium ion from the opposite (more open) side of the plane of the alkene molecule to form the *trans* dibromide as depicted in Fig. 11.5 (b).

The two-step mechanism of *trans* addition of bromine as shown in Fig. 11.5 is supported by the fact that if bromination of alkene is done in the presence of chloride ion ( $\text{Cl}^-$ ), a dihalide containing one bromine atom and one chlorine atom is produced along with the dibromide. Thus the bromination of ethylene in the presence of  $\text{Cl}^-$  ( $\text{Na}^+\text{Cl}^-$ ) gives both 1, 2-dibromoethane and 1-bromo-2-chloroethane.

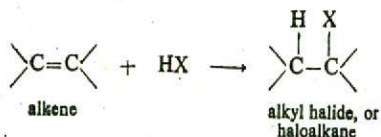


This indicates clearly that the bromonium ion obtained in the first step (a) is attacked by the nucleophilic ion  $\text{Br}^-$  (like  $\text{Cl}^-$ ) in the second step (b) to form 1, 2-dibromoalkane.

As proved above, the addition of halogens to alkenes is a *trans* addition process in contrast to catalytic hydrogenation which is a *cis* addition. Thus addition of a molecule of halogen ( $\text{X}_2$ ) to carbon-carbon double bond could be simply represented as



(3) **Addition of Hydrogen halide (Hydrohalogenation).** Alkenes react with hydrogen halides (HX) by addition across the carbon-carbon double bond to form alkyl halides or haloalkanes.

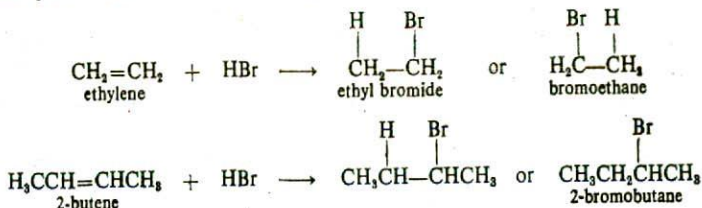




reaction as above which involves the addition of a hydrogen atom and a halogen atom to the carbons of a carbon-carbon double bond, is known as *hydrohalogenation*.

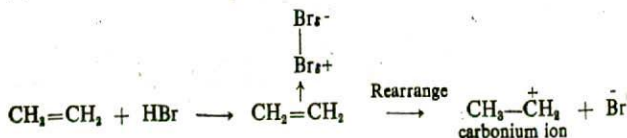
**Addition to Symmetrical alkenes.** The addition of a hydrogen halide to a symmetrical alkene gives only one product because it does not matter as to on which carbon of the double bond the halogen atom is placed.

*Examples.* Hydrobromination of ethylene and 2-butene.



**MECHANISM.** Hydrohalogenation of a symmetrical alkene, for example ethylene, follows a carbonium ion mechanism by steps given below.

(1) The hydrogen halide forms a  $\pi$  complex which rearranges to give a carbonium ion.

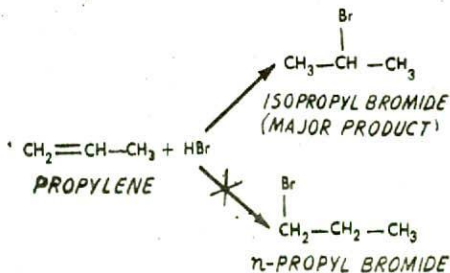


(2) Alkyl halide (or haloalkane) is then obtained by the nucleophilic attack of  $\text{Br}^-$  on the carbonium ion.

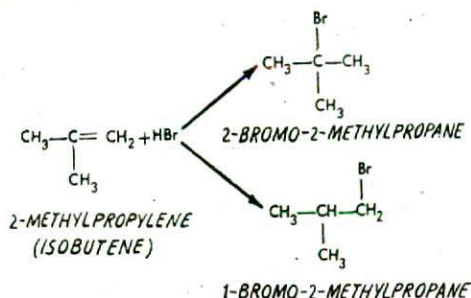


As shown in step (1), only one type of carbonium ion ( $1^\circ$  carbonium ion) is possible from a symmetrical alkene; and hence a single product would be formed in step (2).

**Addition to Unsymmetrical alkenes.** When a hydrogen halide reacts with an unsymmetrical alkene, there are two possible addition products according as the halogen atom is placed on one or the other carbon of the double bond. Thus propylene with HBr can form n-propyl bromide and isopropyl bromide. But it has been established experimentally that isopropyl bromide is obtained predominantly.



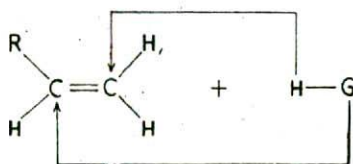
Similarly when 2-methylpropylene (isobutene) reacts with HBr, of the two possible products it actually forms 2-bromo-2-methylpropane and not 1-bromo-2-methylpropane.



The Russian chemist Markovnikov studied a number of addition reactions such as above in 1869 and he suggested a rule to predict the course of reaction for addition of hydrogen halides and other unsymmetrical reagents (HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HOCl, etc) to unsymmetrical alkenes. The empirical rule named after him as **Markovnikov Rule** may be stated as below.

(In the ionic addition of an unsymmetrical reagent (H—G), the hydrogen or positive end of the reagent becomes attached to the carbon atom of the double bond bearing the larger member of hydrogen atoms.)

Thus for the addition of unsymmetrical reagent to an unsymmetrical alkene, Markovnikov Rule be illustrated as

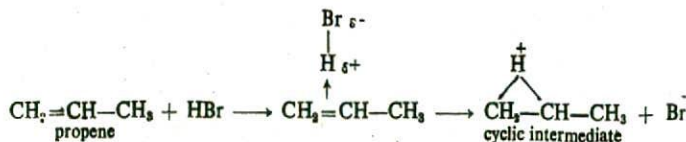


when HG=unsymmetrical reagent : R=alkyl.

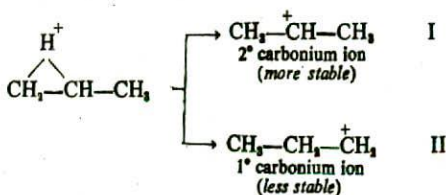
The addition reactions of an alkene which follow Markovnikov Rule are referred to as **Markovnikov additions**.

**EXPLANATION.** The *mechanism* of addition of halogen halides to unsymmetrical alkenes involves the formation of carbonium ions as was described in the case of symmetrical alkenes (ethylene). It may be illustrated by taking example of addition of HBr to propylene. The various steps are :

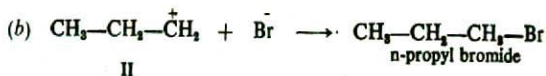
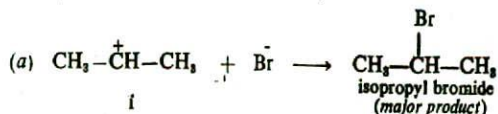
- (1) Formation of  $\pi$  complex, giving a cyclic intermediate and Br.



(ii) The cyclic intermediate is capable of forming two carbonium ions, one primary ( $1^\circ$ ) and one secondary ( $2^\circ$ ).



(iii) The carbonium ions I and II then react with the nucleophile  $\text{Br}^-$  from step (i) to give two possible alkyl bromides.



We may recall that stabilities of carbonium ions are in the order  $3^\circ > 2^\circ > 1^\circ$ . Thus the carbonium ion I dominates in step (ii) because it is more stable than II; and also because of its greater ease of formation compared to I. Then in step (iii), I reacts with  $\text{Br}^-$  to form isopropyl bromide as the major product.

The energy changes occurring during the course of the addition of  $\text{HBr}$  to propylene, to form carbonium ions are shown in Fig. 11-6. Since the isopropyl cation (I) has the lower energy content, it is more stable than n-propyl cation (II). Also, the energy of activation ( $E_{a,r}$ ) of I is smaller than that of II and hence it is relatively easily formed.

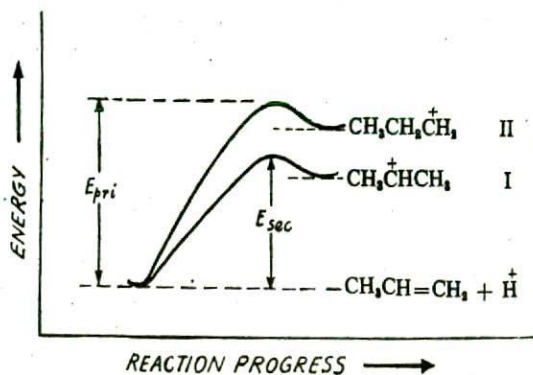


Fig. 11-6. Energy diagram of the formation of  $1^\circ$  and  $2^\circ$  carbonium ions obtained from propylene.

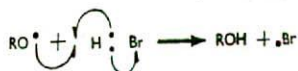
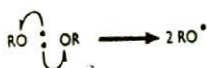
In the addition of  $\text{HBr}$  to 2-methylpropylene one of the carbonium ions produced in step (ii) of the mechanism is  $3^\circ$  and the other  $1^\circ$ . The  $3^\circ$  carbonium ion is much more stable



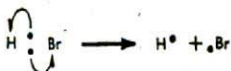


(i) Chain initiating step :

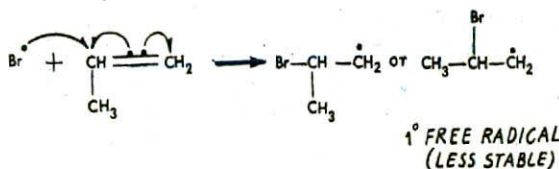
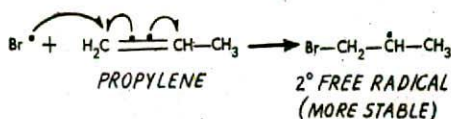
(a) peroxide dissociates to give two free alkoxy radicals which attack HBr to form bromine free radical (Br·).



(b) HBr on photochemical dissociation (UV light) gives the free radicals H· and Br·

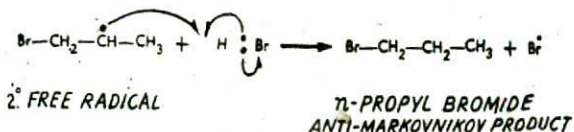


(ii) Bromine free radical then attacks the alkene molecule giving two possible bromo-alkyl free radicals.



The order of stability of free radicals is  $3^\circ > 2^\circ > 1^\circ$ . Therefore,  $2^\circ$  free radical in this step is formed predominantly.

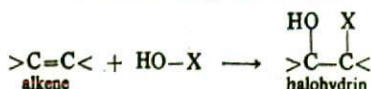
(iii) The more stable radical from step (ii) reacts with HBr forming anti-Markovnikov product, and another bromine free radical which propagates the chain reaction.



**An Important Note.** HCl and HI do not give anti-Markovnikov products in the presence of peroxides. This is because :

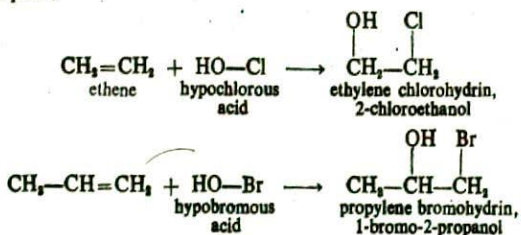
- The H-Cl bond (103 kcal/mole) is stronger than H-Br bond (87 kcal/mole). It is not broken by the alkoxy free radicals obtained from peroxides.
- The H-I bond (71 kcal/mole) is weaker than H-Br (87 kcal/mole). It is broken by the alkoxy free radicals obtained from peroxides. But the iodine atoms so formed readily combine with each other to give iodine molecules, rather than attack the double bond alkenes.

(4) **Addition of Hypohalous acids.** The addition of chlorine or bromine to alkenes, when carried in the presence of water, has the net result of adding a hypohalous acid (HO—X) molecule across the double bond. The compounds produced are known as *halohydrins* in which a hydroxyl group and a halogen atom are attached to adjacent carbons.

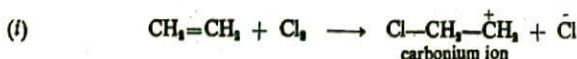


when HO—X = HO—Cl, HO—Br. It may be noted that here OH group behaves as the negative part of the adding species (HO—X<sup>+</sup>). If HO—X is assumed to add to alkenes ionically, the addition follows Markovnikov Rule.

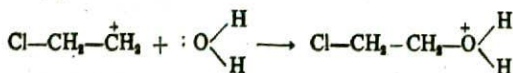
*Examples :*



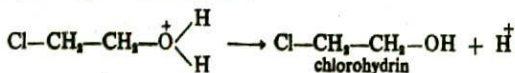
**MECHANISM.** Addition of halogens to alkenes in water undergoes the following carbonium ion mechanism. It is illustrated by the reaction of ethylene with chlorine.



(ii) The carbonium ion reacts with a molecule of water (and not with Cl<sup>-</sup>) which is as reactive as Cl<sup>-</sup> and is present in excess.

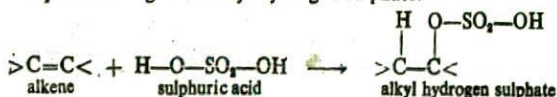


(iii) Loss of proton gives chlorohydrin.

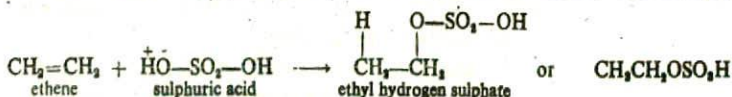


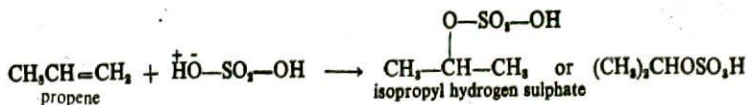
The net result of the three steps in the addition of a molecule of HO—Cl to ethylene is to form chlorohydrin. The fact that OH has been added in preference to Cl<sup>-</sup> in steps (ii) and (iii) shows that OH behaves as a more negative group than Cl, or that HOCl  $\equiv$  HO—Cl<sup>+</sup>

(5) **Addition of Sulphuric acid; Hydration of alkenes.** Alkenes react with sulphuric acid at room temperature to give an alkyl hydrogen sulphate.

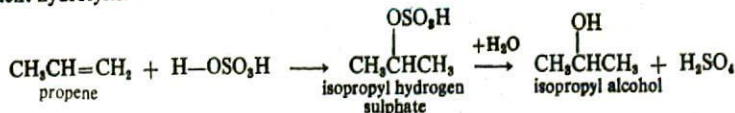


The mechanism of the addition is exactly similar to that of ionic addition of hydrogen halides, and Markovnikov Rule applies for additions to unsymmetrical alkenes. For example,



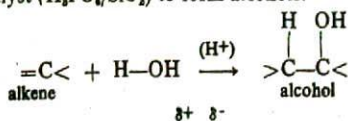


The resulting alkyl hydrogen sulphates upon hydrolysis with warm water give the respective alcohols. Thus an alkene can be converted into alcohol by addition of sulphuric acid and subsequent hydrolysis.



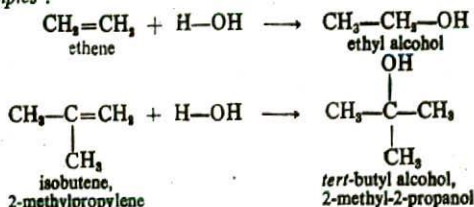
This is an important method for the industrial preparation of alcohols from petroleum products.

(6) **Addition of Water; Hydration.** Water adds to the more reactive alkenes in the presence of an acid catalyst ( $\text{H}_3\text{PO}_4/\text{SiO}_2$ ) to form alcohols.

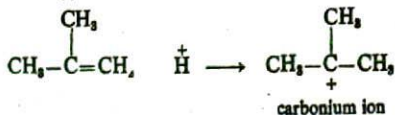


Since a water molecule is polar ( $\text{H}-\text{OH}$ ), the addition of water or hydration follows Markovnikov Rule.

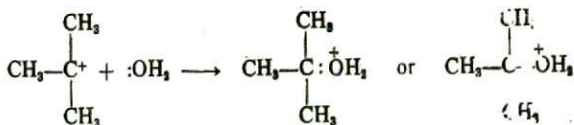
Examples :



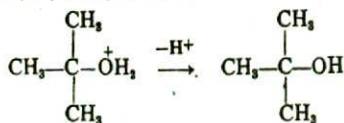
**MECHANISM.** (i) Protonation of alkene to form carbonium ion.



(ii) Addition of  $\text{H}_2\text{O}$  by donating a spare electron pair of oxygen to the deficient carbonium carbon.

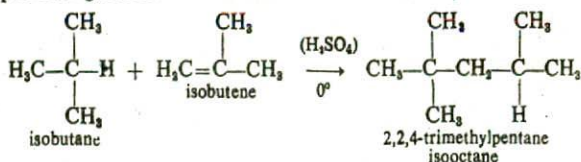


(iii) Loss of proton ( $\text{H}^+$ ) giving the alcohol.



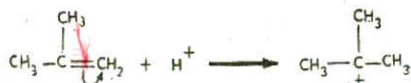
Hydration of alkenes is a useful method for the synthesis of secondary and tertiary alcohols.

(7) **Alkylation.** Addition of alkanes to alkenes is carried out in the presence of acidic catalysis ( $\text{H}_2\text{SO}_4$ , HF). This reaction called 'alkylation of alkenes' has been used for large scale production of 2,2,4-trimethylpentane which is commonly known as isooctane, a principal ingredient of premium gasoline.

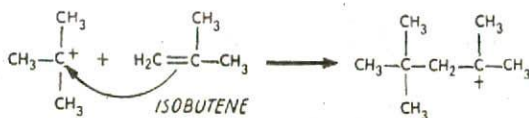


**MECHANISM.** This alkylation proceeds by the following pathway.

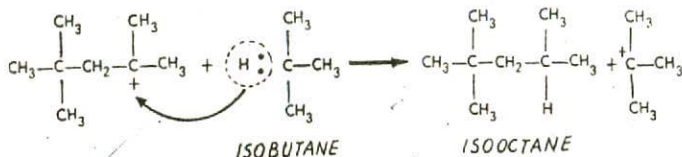
(i) Protonation of isobutene and formation of more stable carbonium ion



(ii) Electrophilic addition of carbonium ion to another molecule of isobutene

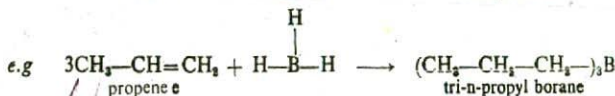
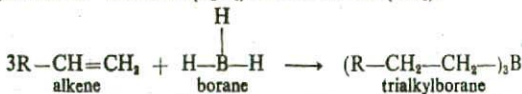


(iii) Formation of isooctane by transfer of hydride  $\text{H}^-$



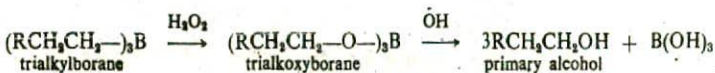
tert-butyl cation released in this step is reused in step (ii)

(8) **Hydroboration.** Boron hydrides add readily to alkenes across the double bond to form trialkylboranes. Diborane ( $\text{B}_2\text{H}_6$ ) adds as borane ( $\text{BH}_3$ ).



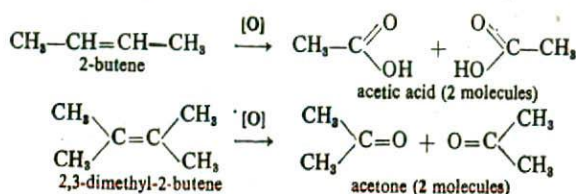
This reaction is called *hydroboration of alkenes*.

Trialkylboranes are used for the synthesis of primary alcohols by reaction with alkaline aqueous solution of  $\text{H}_2\text{O}_2$ .



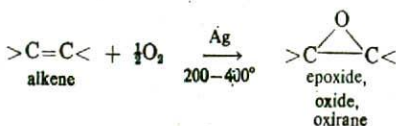




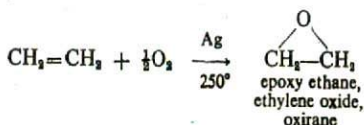


The oxidative degradation of alkenes is useful as (a) synthetic means of preparing ketones and carboxylic acids from available alkenes; (b) a reaction for determining the structure of alkenes by identifying the degradation products obtained from them. The carbon bearing the oxygen atom in each of these products, is the carbon which was doubly bonded in the original alkene.

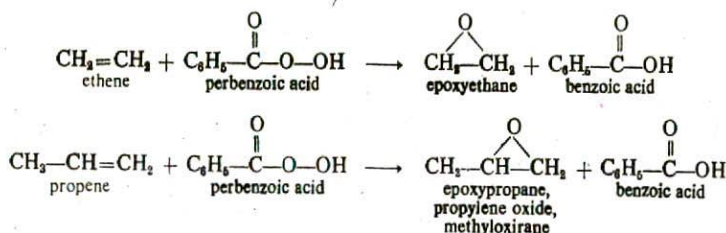
(c) **Epoxidation.** Lower alkenes add on oxygen atom across the carbon-carbon double bond when reacted with oxygen ( $\text{O}_2$ ) in the presence of silver catalyst, to form epoxides.



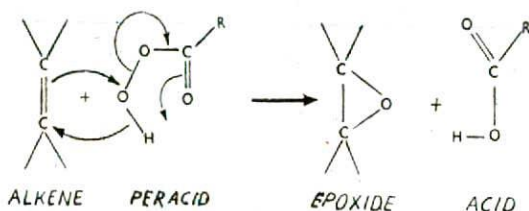
This oxidation reaction of alkenes giving epoxides is known as *epoxidation*. Thus,



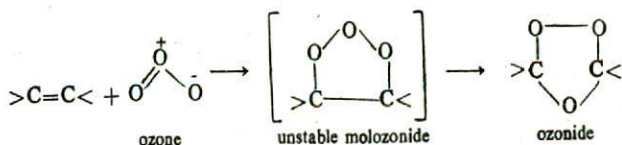
A better and more important method of epoxidation is by the treatment of alkenes by peracids which are the organic derivatives of hydrogen peroxide ( $\text{HO}-\text{OH}$ ). Peracetic acid, perbenzoic acid, and trifluoroperacetic acid are frequently used.



**MECHANISM.** The accepted mechanism of epoxidation with the help of peracids involves all the bond making and breaking simultaneously,

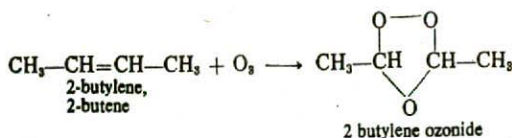
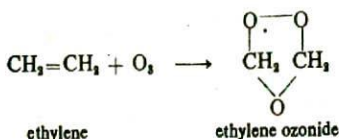


(d) **Ozonization ; Ozonolysis.** When ozone is passed through a solution of an alkene in an inert solvent ( $\text{CHCl}_3$  or  $\text{CCl}_4$ ) at low temperatures, it reacts by addition across the carbon-carbon double bond of the alkene. First an unstable intermediate, *molozone* is formed which spontaneously isomerises to give the *ozonide*.



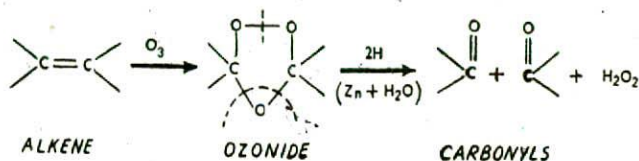
This reaction is known as *Ozonization* of alkenes. It may be noted that ozonization breaks both  $\pi$  and  $\sigma$  bonds of the alkene double bond.

Examples :

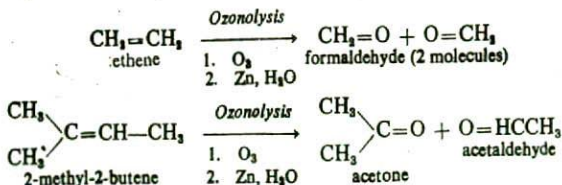


Ozonides like other compounds containing the peroxide group,  $-\text{O}-\text{O}-$ , explode violently and unpredictably. They are therefore, seldom isolated and are used for further reaction while in solution.

Ozonides when treated with a reducing agent like zinc and water or hydrogen in the presence of palladium, are cleaved at the seat of the double bond to give two carbonylic fragments. The products are aldehydes, ketones, or an aldehyde and a ketone (carbonyls), depending on the nature of the alkene.

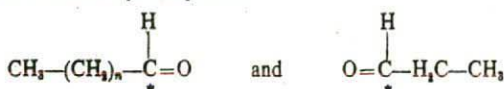


The two-step process of preparing the ozonide and then decomposing it to get the carbonyl compounds is called **Ozonolysis**. For example,



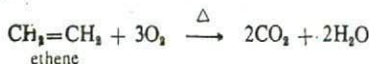
Ozonolysis is probably the best method for locating the position of double bonds in unknown alkenes. The oxygenated carbons in the carbonyl compounds obtained by ozonolysis are

the ones that were joined by a double bond in the original alkene. Suppose a given alkene on ozonolysis gives the carbonyl compounds

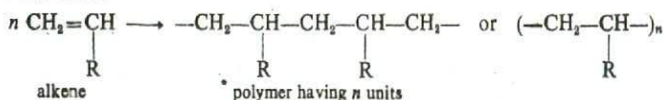


Joining the oxygenated carbons (marked by asterisk) by a double bond, we get the structure of the unknown alkene in which the double bond is located between  $(n+2)$  carbons on one side and three carbons on the other.

(e) **Combustion.** When burnt in air or treated with concentrated nitric acid, alkenes are oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



(10) **Polymerization of alkenes.** Many simple alkenes give a peculiar reaction when two or more alkene molecules join together to form a new compound which is made up of several identical units. This reaction is called *Polymerization* and the product is referred to as a **Polymer** (Gr. *poly*=many; *meros*=part). The individual molecular unit comprising the polymer is termed a **Monomer**.

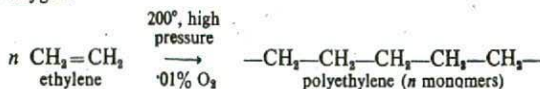


The type of polymerization shown by alkenes which proceeds by addition of molecules each to each across the double bonds, without any loss of atoms, is particularly called **Addition Polymerization**. In addition polymerization, the polymer has the same empirical formula but a higher formula weight than the monomer.

Ethylene, propylene, isobutene and many other substituted alkenes undergo polymerization readily to form polymers known as *plastics*. These synthetic plastics can be easily moulded into required shapes and possess other properties which enable them to be used for the manufacture of a wide range of articles of common use. Dyes and pigments are added to give attractive colours to the plastic goods.

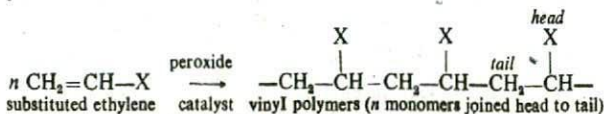
Addition polymerization can be brought about by free radicals, cations, anions or organometallic reagents or Ziegler catalysts.

(a) **Free Radical Polymerization.** Polyethylene (or polyethene) is manufactured by heating ethylene at about  $200^\circ$  under a pressure of 1500 to 2000 atmospheres, in presence of a very small amount of oxygen.



Polyethylene prepared in this way has a low density with formula weight ranging from 50,000 to 3,00,000. It can be readily coloured, moulded, blown and rolled into thin films at a fairly low temperature. Therefore, it is widely used for making wire insulations, bottles, tubing, toys and packing material.

Substituted ethylenes,  $\text{CH}_2=\text{CHX}$  ( $\text{X} = -\text{Cl}, -\text{O}-\text{CO}-\text{CH}_3, -\text{CN}, -\text{C}_6\text{H}_5$  etc.), also undergo free radical polymerization like ethylene, and furnish a wide variety of polymers of industrial importance.





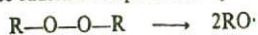
The polymers thus produced are called *vinyl polymers* since the monomers from which they are made have the vinyl group in them.

Table. Some Vinyl Polymers ( $\text{CH}_2=\text{CH}-\text{X}$ )

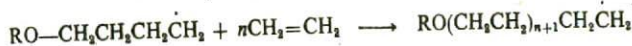
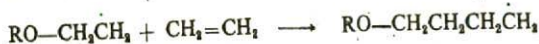
X	Polymer	Use
-Cl	Polyvinyl chloride (PVC)	Rubber substitute, rain coats
-O-CO-CH <sub>3</sub>	Polyvinyl acetate (PVA)	Sheets, films, fibers, adhesives, chewing gum
-CN	Polyvinyl cyanide ( <i>Orlon</i> )	Fabrics, clothing
-C <sub>6</sub> H <sub>5</sub>	Polystyrene	Foam plastic fabrication, electrical insulators

The polymerization of ethylene and substituted ethylenes follows free radical mechanism. The free radical often produced from peroxide,  $\text{R}-\text{O}-\text{O}-\text{R}$ , combines with a monomer in the first step to generate a new free radical. In the second step this free radical combines with another molecule of monomer, and the process continues till a large free radical is obtained. In the third step the two large radicals from the previous step combine to give the polymer. This may be illustrated by taking example of ethylene itself.

(i) *Initiation*. Free radicals are produced by the initiator, peroxide.



(ii) *Propagation*. Continued addition of ethylene molecule to the free radical from the previous step produces a large free radical.

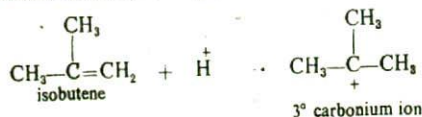


(iii) *Termination*. The large free radicals finally combine to give polyethylene.



(b) *Cationic Polymerization*. Alkenes polymerize in the presence of acids e.g.,  $\text{H}_2\text{SO}_4$ , HF or Lewis acids such as  $\text{BF}_3$  or  $\text{AlCl}_3$ , via a carbonium ion mechanism. One important example of this reaction is afforded by the controlled dimerization of isobutene (obtained from petroleum cracking) at elevated temperatures and in the presence of 60%  $\text{H}_2\text{SO}_4$ , to form isooctene. The formation of isooctene takes place by the following steps.

(1) Protonation of isobutene to give more stable 3° carbonium ion.

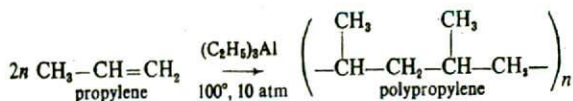


(2) Dimerization by electrophilic addition



(d) **Ziegler-Natta Polymerization.** Ziegler and Natta (1953) developed this elegant method of preparing high grade polymers. They discovered that a special catalyst which consists of a complex of triethylaluminium,  $(C_2H_5)_3Al$ , and titanium tetrachloride,  $TiCl_4$ , brings about the polymerization of alkenes in inert solvents at ordinary temperatures and pressures. Thus polyethylene produced by this method has higher density, higher softening point, and is stronger than obtained by free radical mechanism.

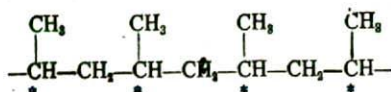
Polypropylene is manufactured by Ziegler-Natta method in which propylene is passed under 10 atmosphere pressure into an inert solvent (hexane) containing the special catalyst, at  $100^\circ C$ .



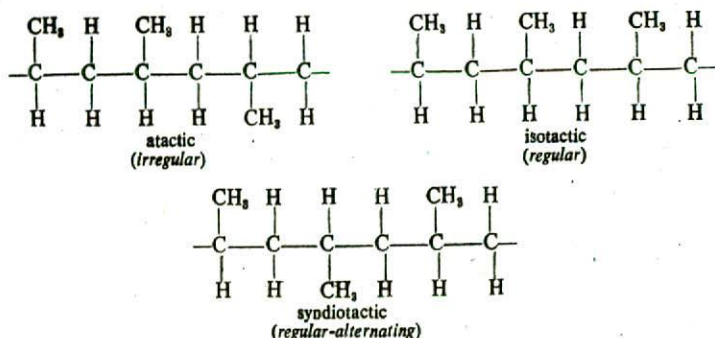
Polypropylene so produced has the advantage of being stronger and lighter and having a higher softening point than polyethylene. It is particularly used for making wrapping films and ropes.

In general, Ziegler-Natta polymerization takes place under milder condition of temperature and pressure than those required for free radical polymerization. That is why it produces polymers which are much more uniform and have regular polymer chain with no branching.

In polymers obtained from unsymmetrical alkenes it will be noticed that every other carbon atom is asymmetric (marked by asterisks).



Free radical mechanism results in polymers in which there is random configuration of side-chains (here  $\text{CH}_3$  groups) at the asymmetric carbons (**atactic polymers**). If Ziegler-Natta catalyst is used, in the polymer thus produced all the asymmetric carbons have the same configuration (**isotactic polymers**), or there is a regular alternation of configuration (**syndiotactic polymers**)



The stereoregular polymers (isotactic and syndiotactic) are highly crystalline, denser, high melting and mechanically stiff than their randomly polymerized (atactic) counterparts.

**MECHANISM.** The mechanism of Ziegler-Natta Polymerization is not clearly understood. It appears to occur with the monomers being added to the growing chain (carbanion).

Possibly the carbanions are held by the titanium atoms in the catalyst surface by coordination, and hence this mode of polymerization has also been named as Coordination Polymerization.

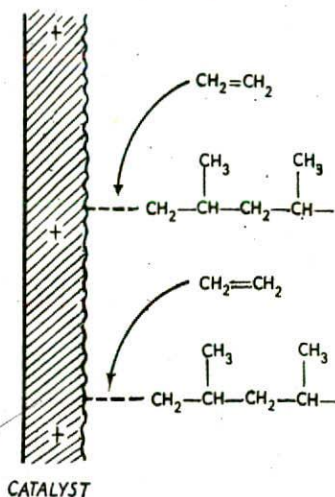
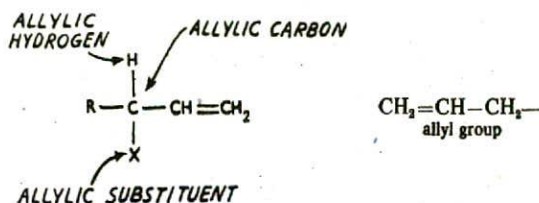
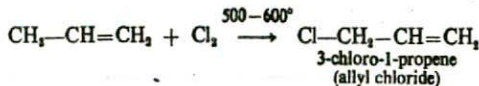


Fig. 11-7. Mechanism of Zeigler-Natta polymerization.

(11) **Halogen substitution reaction; Allylic halogenation.** All alkenes except ethylene contain alkyl groups and the carbon of the alkyl group next to the double bond is called an allylic carbon after the name of the allyl group. The substituents on an allylic carbon are referred to as allylic substituents.

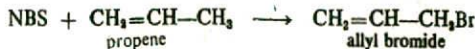


When alkenes are treated with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ) at high temperatures, one of their allylic hydrogens is substituted by halogen atom and the reaction is named as allylic halogenation. Thus,



Allylic halogenation takes place by a free radical mechanism. At high temperatures employed for allylic halogenation, the halogen addition to the double bond being reversible does not take place.

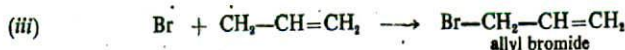
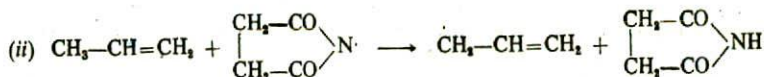
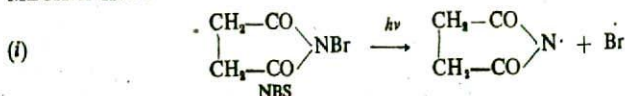
On a laboratory scale, allylic bromination can be carried out conveniently by using N-bromosuccinimide (NBS) in an inert solvent (Wohl-Ziegler reaction). Thus when propene is mixed with NBS in carbon tetrachloride ( $\text{CCl}_4$ ) and warmed, allyl bromide is formed.





The reaction is known to be a free radical process since it is catalysed by light or peroxides. Under these conditions, NBS is a source of bromine free radicals which bring about allylic bromination as follows.

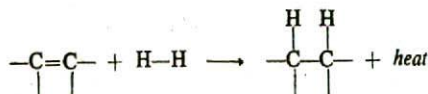
## MECHANISM :



Similarly N-chlorosuccinimide can also be used for allylic chlorination.

## RELATIVE STABILITY OF ALKENES FROM HEATS OF HYDROGENATION

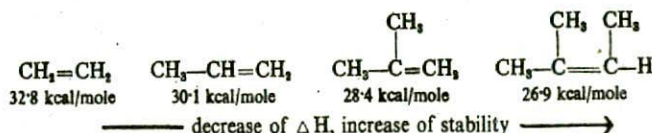
The hydrogenation of alkenes is an exothermic reaction.



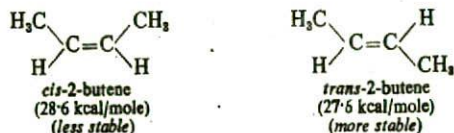
As shown above, in the hydrogenation of a double bond, one  $\pi$  bond and one H—H bond is cleaved and two C—H bonds are formed. About 60 kcal/mole are needed to break a  $\pi$  bond and 104 kcal/mole to break the H—H bond. The formation of two C—H bonds gives off  $2 \times 97$  kcal/mole. Thus the heat of hydrogenation on the average for a compound containing a double bond is  $\Delta H = 2 \times 97 - (104 + 60) = 30$  kcal/mole. The actual value of  $\Delta H$  depends on the structure and the number of alkyl groups attached to the double bond carbons as also on the orientation of such groups (*cis* or *trans*).

Heat of hydrogenation is measurable experimentally and can be used directly for the measurements of the energy content of an alkene. If an alkene has a higher heat of hydrogenation, this means it has more energy content and is less stable. The following examples illustrate the energy relationships between the heat of hydrogenation,  $\Delta H$  and the relative stability of alkenes in comparison with the corresponding alkanes.

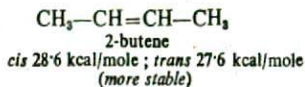
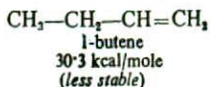
(1)  $\Delta H$  decreases with the branching of double bond carbons and, therefore, stability increases. Thus,



(2) *Trans* isomer is more stable than *cis* isomer as it has lower  $\Delta H$ . Thus,



(3)  $\Delta H$  of an alkene with a double bond in the middle of the chain is lower than that of the alkene with double bond between the end carbons of the chain. Thus,



## INFRARED SPECTRA OF ALKENES

The infrared (IR) spectra of alkenes are sufficiently different from those of alkanes. Therefore, it is often possible to ascertain the position of a double bond in an organic molecule by inspecting its IR spectrum. Alkenes show moderate to weak absorption bands in the region  $1620-1600 \text{ cm}^{-1}$  due to stretching vibration of the double bond. The position of absorption bands of the double bond depends upon the structure of the alkene and varies with the degree of branching at the double bond carbons. The  $=\text{C}-\text{H}$  stretching vibrations appear near  $3000 \text{ cm}^{-1}$  while  $=\text{C}-\text{H}$  bending vibrations are normally located near  $1400 \text{ cm}^{-1}$  and  $1000 \text{ cm}^{-1}$ . The IR spectrum of cyclohexene is given in Fig. 11.8 to bring out the salient features of IR spectra of alkenes.

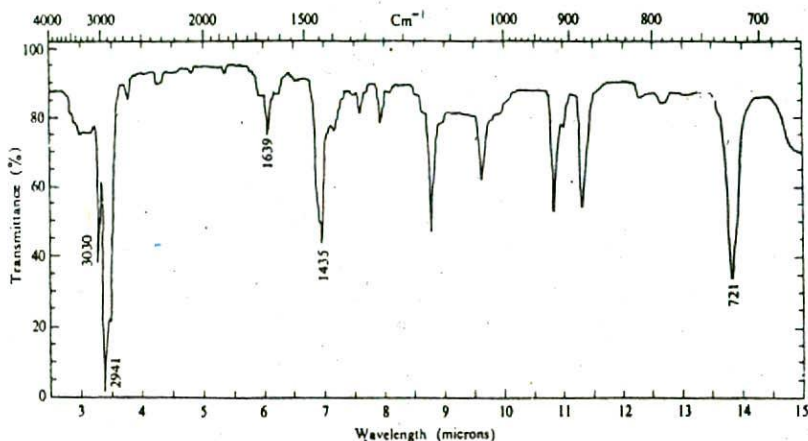


Fig. 11.8. Infrared spectrum of cyclohexene.

## ETHYLENE, Ethene, $\text{CH}_2=\text{CH}_2$

It is the most important alkene and a highly reactive one.

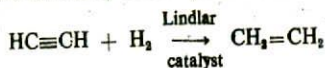
**Preparation.** Ethylene can be obtained by any of the general methods described before. However, it is conveniently prepared in the laboratory from ethyl alcohol by heating it to  $170^\circ$  with excess of concentrated sulphuric acid, preferably in the presence of anhydrous aluminium sulphide which lowers the working temperature to  $140^\circ$ .

**MANUFACTURE.** (1) *From Natural gas.* Ethylene is obtained in USA by high temperature conversion of the ethane derived from natural gas.



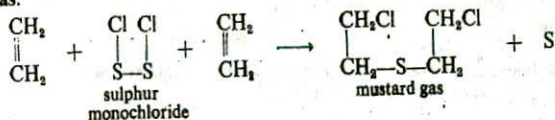
(2) *From Naphtha.* In Western Europe, ethylene is obtained from the naphtha fraction of petroleum. The fraction contains alkanes with four to ten carbon atoms and is passed through pipes heated at  $700-900^\circ$ . The ethylene produced by cracking is purified by fractional distillation.

(3) *From Acetylene by partial reduction.* At places where acetylene is produced commercially from calcium carbide, it is used for the manufacture of ethylene. A mixture of acetylene and hydrogen is passed over finely divided palladium or iron at 200°, or over Lindlar catalyst.



**Properties (Physical).** Ethylene is a colourless gas with a rather sweet odour. Liquid ethylene boils under atmospheric pressure at -150° and the solid hydrocarbon melts at -169°. It is slightly soluble in water but dissolves more readily in organic solvents such as ethanol and ether. When inhaled, ethylene produces general anaesthesia.

**(Chemical).** Ethylene gives all the general reactions of alkenes. One special reaction which remains uncovered, is the addition of sulphur monochloride to ethylene to produce Mustard gas.



Mustard gas was used as a poison gas in the World War I in 1914.

**Uses.** Ethylene is used : (1) for producing 'oxyethylene' flame for cutting and welding of metals ; (2) for ripening green fruits by exposing them to the gaseous hydrocarbon ; (3) as a general anaesthetic ; (4) as a starting material for ethylene glycol (*anti-freeze*), ethanol, diethyl ether etc., and (5) polyethylene for making plastic goods.

### PROPYLENE, Propene, $\text{CH}_3-\text{CH}=\text{CH}_2$

It is obtained from propane and from naphtha fraction obtained by the distillation of petroleum much in the same way as ethylene.

Propylene is a colourless gas ; liquid hydrocarbon boils at -48°. The chemistry of this alkene is similar to that of ethylene. It polymerizes to polypropylene which is an important *plastic material*. It differs from ethylene in respect of addition of halogen acids (HX). Since two products are possible, it reacts with halogens under appropriate conditions to give alkyl chloride and alkyl bromide.

Propylene prepared from petroleum is used for the commercial preparation of isopropyl alcohol, acetone and alkyl chloride.

## DIENES

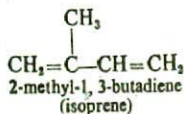
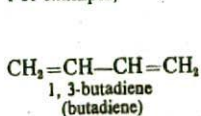
These are open-chain alkenes which contain two double bonds on the carbon chain and are, therefore, called **dienes** or **diolefines**. Their IUPAC name is **alkadiene**. The systematic name of an individual member is derived from the name of the corresponding alkane by replacing the terminal 'ne' by 'diene'. The position of the double bonds is indicated by the numbers for alkenes. Their nomenclature will be illustrated in the following treatment.

Dienes are of three types depending on the position of the two double bonds on the carbon chain.

(1) **Conjugated dienes** are those in which the double bonds are separated by one single bond. Since double and single bonds alternate on the carbon chain, they are also referred to as *alternating dienes*.



For example,



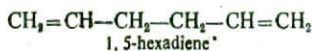
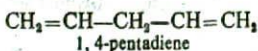


Conjugated dienes have a unique chemistry and their properties are sufficiently different from simple alkenes.

(2) **Non-conjugated dienes or Isolated dienes** are those in which the double bonds are separated by more than one single bond.



For example,

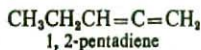
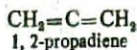


In this type of dienes the two double bonds do not interact, being virtually isolated by the intervening  $\text{CH}_2$  group/groups. They simply show normal double bond properties like simple alkenes twice over.

(3) **Cumulated dienes or allenes** are those in which the bonds appear on successive carbon atoms and one carbon is a part of the two double bonds.



For example,



The properties of cumulated dienes are different from both simple alkenes and conjugated dienes. Here the  $\pi$  systems are not conjugated because they are at right angles to one another.

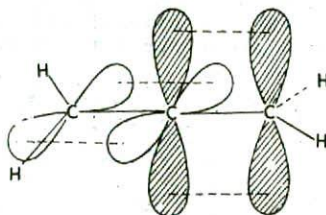
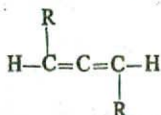


Fig. 11-9.  $\pi$ -systems of cumulated dienes lie in different planes.

Therefore, the substituted cumulated dienes or allenes have no asymmetric carbon atoms but they have asymmetric molecules, i.e., they have no plane of symmetry. The allenes represented by the general formula



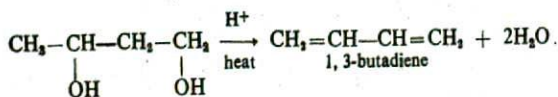
are *optically active* because the terminal substituents R, are in different planes.

Of the three types of dienes discussed above, conjugated dienes are the most important. Therefore, we will restrict our discussion to 1, 3-butadiene which is a typical conjugated diene

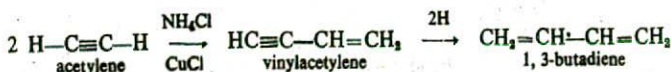




(2) Acid-catalysed dehydration of butane-1,3-diol.

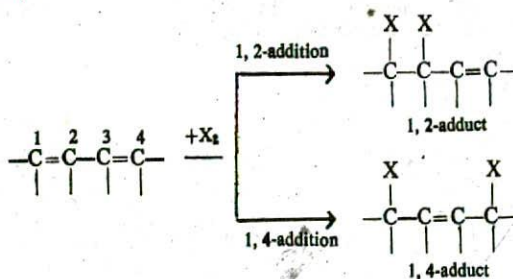


(3) Dimerization of acetylene in the presence of  $\text{NH}_4\text{Cl}$ ,  $\text{CuCl}$  (Niewland catalyst) to form vinylacetylene which upon hydrogenation yields 1, 3-butadiene.

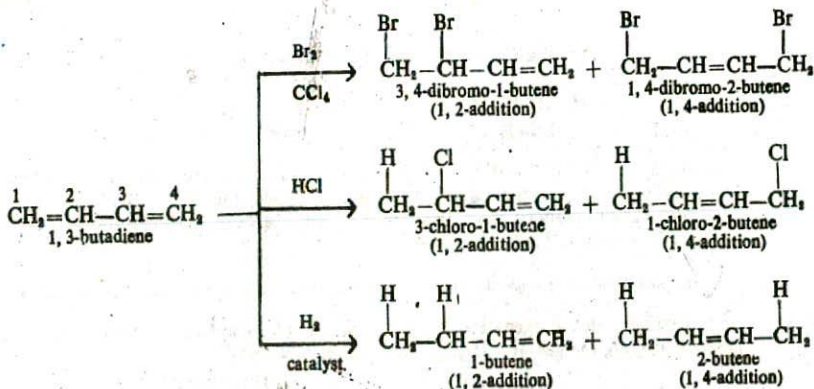


**Properties.** 1, 3-Butadiene is a colourless gas, bp  $-4.4^\circ$ .

(j) **Addition Reactions.** 1, 3-Butadiene undergoes addition reactions with reagents such as halogens ( $\text{Br}_2$ ,  $\text{Cl}_2$ ),  $\text{HBr}$  and  $\text{H}_2$ . Although it contains two double bonds but only one molecule of the addendum is added either to 1, 2-carbons (1, 2-addition) or to 1, 4-carbons (1, 4-addition).

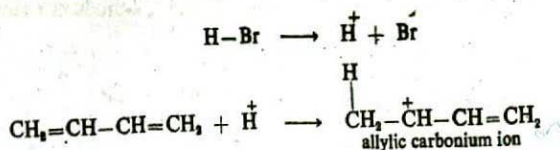


Thus, invariably a mixture of 1, 2-adduct and 1, 4-adduct is obtained. At low temperature 1, 2-addition takes place in preference, while at high temperature 1, 4-addition dominates. For example,  $\text{Br}_2$ ,  $\text{HCl}$  and  $\text{H}_2$  add to 1, 3-butadiene to form mixtures of 1, 2- and 1, 4-adducts as shown below.

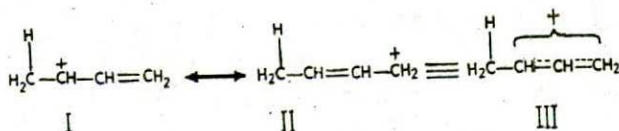


**MECHANISM.** Let us take the addition of  $\text{HBr}$  to 1, 3-butadiene for illustrating the mechanism of the above reactions. This involves the formation of a carbonium ion stabilized by resonance.

(i) Formation of allylic carbonium ion.

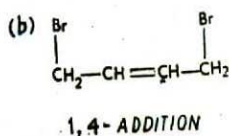
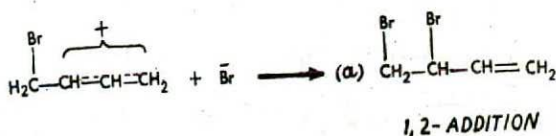


The allylic carbonium ion is a hybrid of two resonance structures (I and II) which are equivalent to structure III.



The allylic ion is thus said to be resonance stabilized.

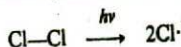
(ii) Formation of 1, 2- and 1, 4-adducts, the nucleophile  $\text{Br}^{-}$  adding either to  $\text{C}_2$  or  $\text{C}_4$  of the allylic carbonium ion.



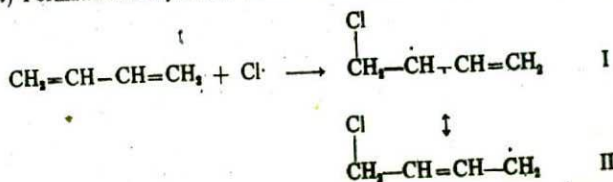
The energy of activation of the carbonium ion III is higher for 1,4-addition than for 1,2-addition. Therefore 1, 4-addition is favoured at high temperature and 1, 2-addition at low temperature.

**Free Radical Addition.** Dienes also undergo addition through free radicals. Thus 1, 3-butadiene adds  $\text{Cl}_2$  in the presence of light or peroxides to give 1, 2- and 1, 4-addition products. This involves the intermediate formation of allylic free radicals.

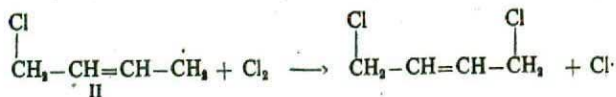
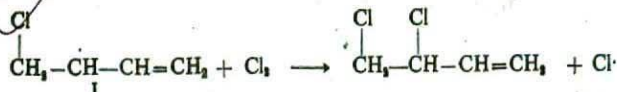
(i) Formation of free radicals (*Chain initiation*).



(ii) Formation of allylic free radical which is resonance stabilized (*Chain propagation*).

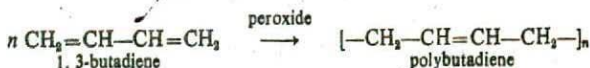


(iii) Each of the forms I and II reacts with  $\text{Cl}_2$  to give 1, 2- and 1, 4-products respectively.



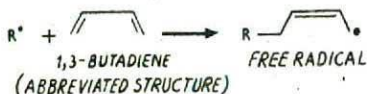
The  $\text{Cl}\cdot$  from step (iii) is used in step (ii).

(2) **Polymerization.** 1, 3-butadiene in the presence of peroxides, polymerizes to a rubbery product called polybutadiene whose structure suggests that 1, 4-addition takes place predominantly.

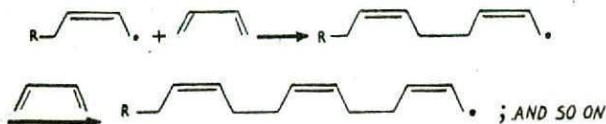


**MECHANISM.** The reaction follows free radical mechanism.

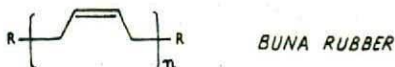
(1) **INITIATION STEP-**



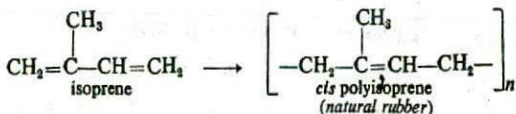
(2) **PROPAGATION STEP-**



(3) **TERMINATION STEP (UNION OF LARGE FREE RADICALS)-**



Natural rubber is the polymer of 2-methyl-1, 3-butadiene (*isoprene*).

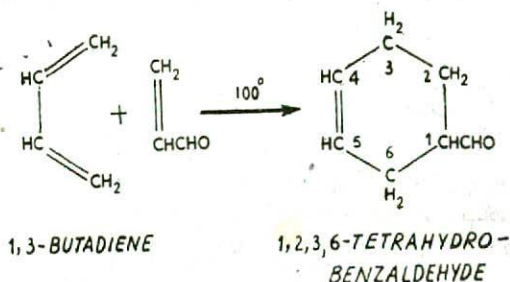


Neoprene, a superior substitute of Natural rubber, is obtained by polymerization of 2-chloro-1, 3-butadiene (*chloroprene*).

(3) **Diels-Alder Reaction.** The Diels-Alder reaction consists in the 1, 4-addition of the double bond of a suitable vinyl derivative (called the *dienophile*) to the two ends of a

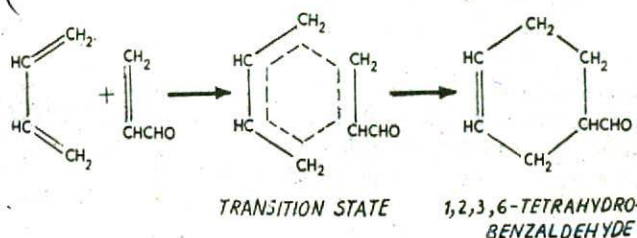


conjugated diene system. Thus 1,3-butadiene combines with acrolein at  $100^\circ$  to form tetrahydrobenzaldehyde.



This reaction is highly stereospecific and occurs exclusively in the *cis* fashion.

MECHANISM. The exact mechanism of Diels-Alder reaction is still uncertain. It has been suggested that a six-membered transition state compound is formed. That is,



### QUESTIONS

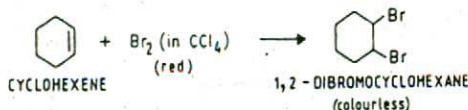
- Outline the methods of preparation of alkenes. Indicate their properties and uses.
- Write structural formulas for the products when 1-pentene reacts with each of the following reagents :
 

(a) HBr	(b) HOBr
(c) $\text{Br}_2/\text{CCl}_4$	(d) $\text{H}_2\text{O}/\text{H}^+$ , heat
(e) $\text{Br}_2/\text{R}_2\text{O}_2$	(f) $\text{O}_3$ , then $\text{Zn}/\text{H}_2\text{O}$
- How will you synthesise :
  - Propene from propane
  - 2-Bromopropane from propane
  - 2-Bromobutane from 1-bromobutane
  - 1,2-Dibromobutane from 1-bromobutane
  - Isopropyl alcohol from propene
  - tert*-Butyl alcohol from 2-methylpropane
  - 2-Methyl-propanol from *tert*-butyl alcohol
  - 1-Bromo-3-chloro-2-propanol from 1-propanol
  - Biphenyl from cyclohexene
  - 1,3-Cyclohexadiene from cyclohexene

**Hint.** (g) (i) conc  $\text{H}_2\text{SO}_4$ /heat, (ii)  $\text{B}_2\text{H}_6$  and (iii)  $\text{H}_2\text{O}_2/\text{OH}^-$ ; (h) (i) conc  $\text{H}_2\text{SO}_4$ /heat, (ii) NBS or  $\text{Br}_2/600^\circ\text{C}$ , and (iii) HOCl; (i) (i) HBr, and (ii) Na, ether (Wurtz reaction); (j) (i)  $\text{Br}_2/\text{CCl}_4$ , and (ii) alc KOH; (k) (i) NBS or  $\text{Br}_2/600^\circ\text{C}$ , and (ii) alc. KOH.

4. How will you distinguish between cyclohexene and cyclohexane ?

**Answer.** Cyclohexene decolourises red colour of  $\text{Br}_2/\text{CCl}_4$ . Cyclohexane does not react.

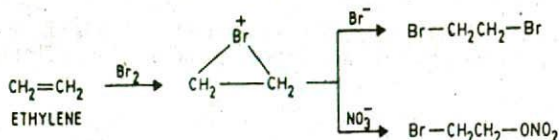


5. Write the mechanism of addition of bromine to ethylene. (Andhra BSc, 1994)

6. Write the mechanism for the reaction of ethylene with  $\text{Br}_2$  in the presence of  $\text{NaCl}$ . (Jadavpur BSc, 1993)

7. When  $\text{NaNO}_2$  is added to the reaction mixture, both  $\text{BrCH}_2\text{CH}_2\text{Br}$  and  $\text{BrCH}_2\text{CH}_2\text{ONO}_2$  are obtained as products in the addition of  $\text{Br}_2$  to ethylene. Suggest an explanation for this in terms of the proposed mechanism.

**Answer.** Only one of the two Br atoms from  $\text{Br}_2$  is used in forming the bromonium ion intermediate. After it is formed either nucleophile  $\text{Br}^-$  or  $\text{NO}_2^-$ , may attack :



8. Write a mechanism for the reaction of  $\text{HBr}$  with propene. (Saugar BSc, 1993 ; Marathwada BSc, 1994)

9. Write a mechanism for the peroxide initiated addition of  $\text{HBr}$  to propene. (Nehru BSc Hons., 1994)

10. Suggest a possible reason why the peroxide effect is obtained for  $\text{HBr}$  and not for  $\text{HCl}$ .

11. Write a mechanism for the bromination of propylene with *N*-bromosuccinimide. (Punjab BSc, 1994)

12. Write a note on : Markovnikov rule. (Bundelkhand BSc, 1994)

13. Write a note on : Peroxide effect. (Bombay BSc, 1994)

14. Write a note on : Ozonolysis.

15. Compound (A)  $\text{C}_6\text{H}_{12}$ , gave the following results :

(i)  $(\text{A}) + \text{Br}_2/\text{CCl}_4 \longrightarrow$  Colourless solution

(ii)  $(\text{A}) + \text{Dil cold KMnO}_4 \longrightarrow$  Brown precipitate

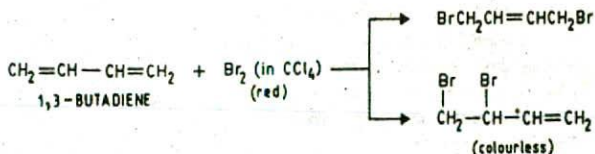
(iii)  $(\text{A}) + \text{O}_3$  followed by treatment with  $\text{Zn}/\text{H}_2\text{O}$  gave  $\text{CH}_3\text{CH}_2\text{CHO}$  as the only product. What are the two possible structures of (A) ?

**Answer.** The two possible structures of (A) are : *cis*-3-Hexene or *trans*-3-Hexene.

16. Discuss the molecular orbital structure of 1,3-butadiene or allene. (Aligarh BSc Hons, 1994)

17. How will you distinguish between 1,3-butadiene and *n*-hexane.

**Answer.** 1,3-Butadiene decolourises red colour of  $\text{Br}_2/\text{CCl}_4$ . *n*-Hexane does not react.



18. Write a mechanism for the reaction of bromine with 1,3-butadiene. (Madurai BSc, 1994)

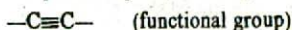
19. Write a note on : Diels-Alder reaction. (Baroda BSc, 1993 ; Anna BSc, 1994)

## Alkynes

Alkynes are unsaturated hydrocarbons which contain a carbon-carbon triple bond ( $C\equiv C$ ). The general formula of this class of compounds is  $C_nH_{2n-2}$  in comparison to  $C_nH_{2n}$  for alkenes. Therefore, they contain two hydrogen atoms less than the corresponding alkene. The simplest member of this homologous series (putting  $n=2$ ) has the molecular formula  $C_2H_2$ . Hence this series of hydrocarbons are often referred to as Acetylenes and could be represented as



where  $R = \text{alkyl or H}$ . The triple bond present in alkynes :

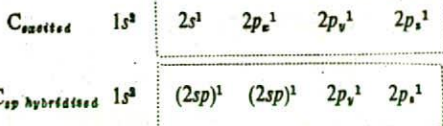


determines their chemical reactivity and constitutes the functional group. This is also named as *acetylenic bond*.

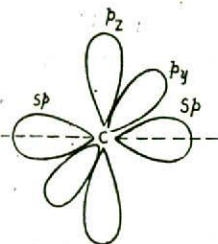
Alkynes like alkenes are reactive compounds and hence they never occur in the free state in nature. They are present to a sizeable extent in the gases obtained by cracking of petroleum.

### STRUCTURE

Alkynes use  $sp$  hybridized orbitals of carbon for their formation. The  $sp$  orbitals result through hybridization of the  $2s$  orbital and one  $2p$  (say  $2p_z$ ) orbital of the excited carbon. These



$sp$  orbitals lie along a straight line that passes through the carbon nucleus and the angle between them is thus  $180^\circ$



$p$  orbitals of an excited carbon.

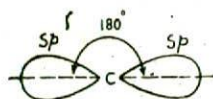


Fig. 12.2.  $sp$  hybridized orbitals of carbon.

One of the  $sp$  orbitals of each of the two carbons of the triple bond overlap in a head-on fashion to form a carbon-carbon  $\sigma$  bond. The remaining  $sp$  orbital on each carbon overlaps with  $s$  orbital of a hydrogen or with one  $sp^3$  orbital of an alkyl group, depending on the structure of the alkyne, to form a sigma bond (I).

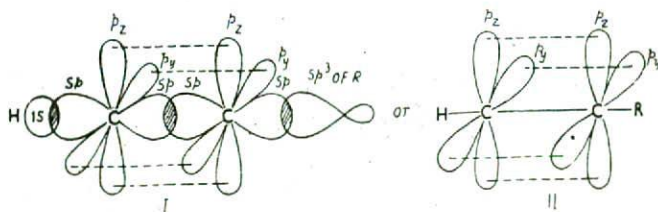


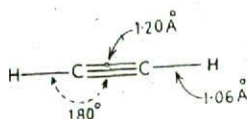
Fig. 12-3. Formation of triple bond in alkynes.

Each carbon of the triple bond is now left with two unhybridized  $p$  orbitals i.e.,  $p_y$  and  $p_z$  (II) which are perpendicular to each other and also to the axis of the two  $sp$  orbitals. The  $p_y$  orbital of one carbon atom overlaps side-wise with a similar  $p_y$  orbital of the other carbon to form a  $\pi$  bond. Likewise the  $p_z$  orbitals of the two carbons overlap to give the second  $\pi$  bond.

If the  $\pi$  cloud of one  $\pi$  bond is thought as lying above and below the line of joining the carbon nuclei, then the  $\pi$  cloud of the other bond lies in front and back of the line. However, actually the two  $\pi$  clouds merge to form a cylindrical sheath.

Thus, the alkyne triple bond is made up of one strong  $\sigma$  bond and two weak  $\pi$  bonds. A carbon-carbon triple bond (199.0 kcal/mole) is stronger than a carbon-carbon double bond (115.8 kcal/mole) or carbon-carbon single bond (82.0 kcal/mole). Obviously it would be incorrect to represent a triple bond by three equivalent lines but for simplicity we do so.

Electron diffraction, X-ray diffraction and spectroscopic analysis reveal that acetylene has a linear molecule.

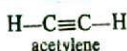


It may be noted that C—H distance is shorter than C≡C distance because of the greater  $\sigma$  character of the former.

## NOMENCLATURE

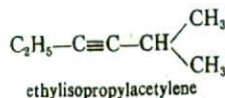
There are three ways of naming this class of compounds.

(1) **The Common System.** The common names for the simple members are



Except acetylene, these names are now obsolete.

(2) **The Acetylene System** Here, the higher members are regarded as alkyl derivatives of acetylene. Thus,





(3) **The IUPAC System.** The IUPAC names for alkynes are constructed by dropping the ending *-ane* of the parent alkene and adding the suffix *-yne*. If necessary the carbon chain containing the triple bond is numbered from the end nearest this bond. The position of the triple bond is indicated by prefixing the number of the carbon preceding it to the name of the alkyne.

Thus,

Structure	IUPAC Name
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	ethylene (acetylene)
$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$	propyne
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	2-butyne
$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$	1-butyne
$\begin{array}{cccc} 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH} & -\text{C}\equiv\text{C} & -\text{H} \\ &   & & \\ & \text{CH}_3 & & \end{array}$	3-methyl-1-butyne

**Alkynyl Groups.** The monovalent groups derived from the alkynes are named by deleting the final 'e' of the parent hydrocarbon and adding the suffix *-yl*. Thus,

$\text{HC}\equiv\text{C}-$	ethynyl (ethyne $-e + yl$ )
$\text{H}_3\text{C}-\text{C}\equiv\text{C}-$	propynyl
$\text{HC}\equiv\text{C}-\text{CH}_2-$	2-propynyl or propargyl

Alkynes are further classified as *terminal* or *nonterminal* according as the triple bond is at the end of the chain or in between the chain. For example,

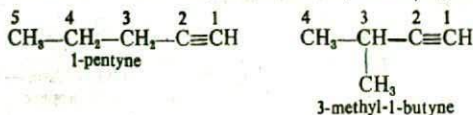
$\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$	$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$
2-butyne (nonterminal alkyne)	propyne (terminal alkyne)

Alkynes with two and three triple bonds, are called alkadiynes and alkatriynes respectively.

## ISOMERISM

Their molecules being linear, alkynes do not exhibit *cis-trans* isomerism. They, however, display the following types of isomerism.

- (1) **Chain Isomerism.** Like other classes of compounds alkynes show chain isomerism.



- (2) **Position Isomerism.** The terminal and nonterminal alkynes with the same molecular formula are position isomers of each other.



- (3) **Functional Isomerism.** Alkynes show functional isomerism with alkadienes. For example,



## METHODS OF PREPARATION

The first member acetylene is prepared on a large scale by the hydrolysis of calcium carbide ( $\text{CaC}_2$ ) and by the partial combustion of methane which will be discussed later. The methods of synthesis of other alkynes are of two types :

(a) those in which a triple bond ( $C\equiv C$ ) is created by removal of sufficient atoms as  $HX$  or  $X_2$  from adjacent carbons.

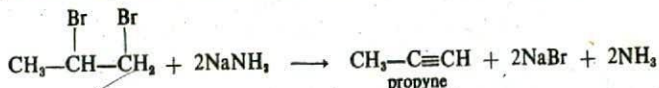
(b) those in which a compound already containing a triple bond is taken as the starting material and the length of its carbon chain is built up.

Methods (1), (2) and (3) given below are of the first type, while the method (4) belongs to the second type.

(1) **Dehydrohalogenation of 1, 2-dihalides.** 1,2-dihalides (vicinal dihalides) when treated with alcoholic  $KOH$  eliminate two molecules of hydrogen halide from adjacent carbons to yield an alkyne.



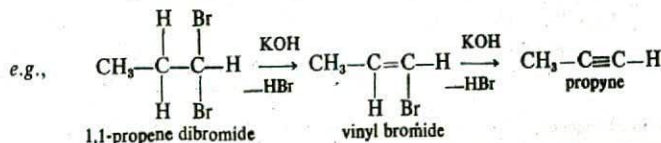
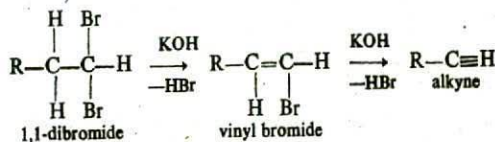
The use of  $KOH$  gives rise to side reactions and causes the migration of the  $C=C$  bond to the centre of the molecule. This limits the utility of this method. However, when sodium amide ( $NaNH_2$ ) is used for dehydrohalogenation, the difficulty is overcome and this reagent causes the migration of the triple bond towards the end of the carbon chain to give pure 1-alkyne. Thus,



Since 1,2-dihalides themselves are obtained by the addition of halogens to alkenes, the above method can be used for preparing alkynes from alkenes.

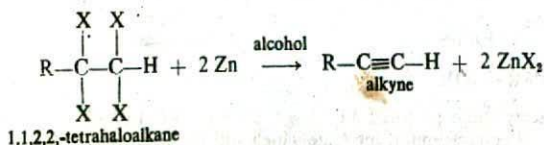
(2) **Dehydrohalogenation of 1,1-dihalides.** 1,1-dihalides upon treatment with alcoholic  $KOH$  or with sodamide, bring about the double dehydrohalogenation yielding 1-alkynes.

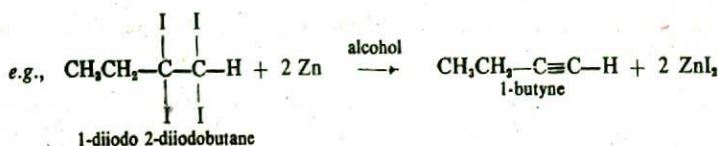
Thus,



1,1-dihalides can be prepared by the action of phosphorus pentahalides ( $PCl_5$  or  $PBr_5$ ) on aldehydes and ketones. Therefore, the above method can be used for getting alkynes from aldehydes and ketones.

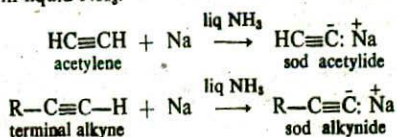
(3) **Dehalogenation of tetrahalides.** Tetrahalides in which the halogen atoms are attached to adjacent carbon atoms (two on each carbon) when heated with zinc dust in alcohol yields alkynes.



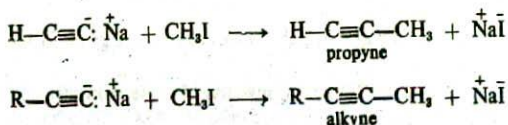


This method is of limited application because the required tetrahalides are themselves prepared from alkynes. However, it can be employed for the purification of alkynes by converting them into tetrahalides followed by subsequent dehalogenation.

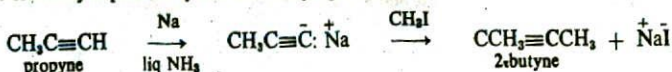
(4) **Alkylation of acetylene and terminal alkynes.** Acetylene,  $\text{HC}\equiv\text{CH}$ , terminal alkynes,  $\text{RC}\equiv\text{CH}$ , can be converted into metal acetylides and metal alkynides respectively by treating them with sodium in liquid  $\text{NH}_3$ .



These sodium derivatives upon reaction with alkyl halides give substituted alkynes.

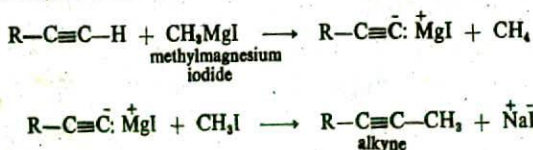


The propyne obtained above still contains a hydrogen on a triply bonded carbon atom which can be similarly replaced by another alkyl group



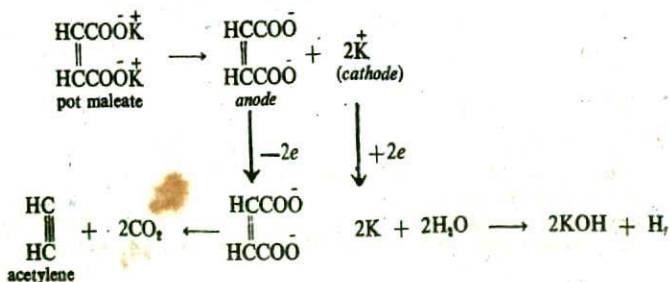
Evidently this method is very useful in converting a lower alkyne to higher alkyne.

Alkylation of alkynes can also be accomplished by treating with an appropriate Grignard reagent followed by the action of an alkyl halide.



This is an excellent procedure for introducing alkyne functions into other molecules.

(5) **Electrolysis of salts of unsaturated dicarboxylic acids.** Potassium salts of maleic acid and fumaric acid in concentrated solutions upon electrolysis form alkynes.





## PHYSICAL PROPERTIES

The physical properties of alkynes are similar to those of the alkanes and alkenes with the same carbon skeleton.

(1) The first three members ( $C_1 \rightarrow C_3$ ) are gases, next eight ( $C_4 \rightarrow C_{11}$ ) are liquids, and the higher alkynes ( $C_{12} \rightarrow$ ) are solids. They are all colourless and odourless except acetylene which has characteristic garlic odour. This garlic odour is due to contaminants like phosphine and arsine which are often associated with it.

(2) Alkynes are compounds of low polarity and hence they are slightly soluble in water but are more soluble in solvents of low polarity like ligroin, benzene and carbon tetrachloride. They are, however, slightly more soluble in water than the corresponding alkanes and alkenes. This is perhaps due to greater electron density at the triple bond which permits some degree of association with dipolar water molecules.

(3) The boiling points, melting points, and specific gravities of alkynes are slightly higher than the corresponding alkanes and alkenes. This is presumably due to greater polarity of alkynes than the alkanes and alkenes. Further, these properties show a regular increase with rising molecular weight. As in the case of alkanes and alkenes, branched chain alkynes have lower melting points than their respective n-chain isomers.

The physical constants of some straight chain alkynes are given in the Table below.

Table. Physical Constants of some Alkynes

Alkyne	Formula	bp °C	mp °C	sp gr g/ml at 20°
Acetylene	$HC \equiv CH$	-84.0	-80.8	
Propyne	$HC \equiv CCH_3$	-23.2	-102.7	
1-Butyne	$HC \equiv CCH_2CH_3$	8.1	-125.7	0.65
2-Butyne	$H_3CC \equiv CCH_3$	27.0	-32.3	0.691
1-Pentyne	$HC \equiv CCH_2CH_2CH_3$	40.2	-105.7	0.694
2-Pentyne	$H_3CC \equiv CCH_2CH_3$	56.1	-109.3	0.711
1-Hexyne	$HC \equiv CCH_2CH_2CH_2CH_3$	71.3	-131.9	0.715
2-Hexyne	$H_3CC \equiv CCH_2CH_2CH_3$	84.5	-89.5	0.732
3-Hexyne	$H_3CCH_2C \equiv CCH_2CH_3$	81.4	-103.5	0.723
1-Heptyne	$HC \equiv CCH_2CH_2CH_2CH_2CH_3$	99.7	-80.9	0.733

## CHEMICAL PROPERTIES

The chemical behaviour of alkynes is much similar to that of alkenes. This should be so because an alkyne involves a  $\pi$  electron system similar to that of the double bond in an alkene. Thus like alkenes, alkynes also undergo electrophilic addition reactions. However, the greater unsaturation of alkynes may prompt the thought that they should react with electrophilic reagents more easily than do alkenes. But this is not so. Rather the triple bond is less



reactive to electrophiles than is the double bond. As we pass from ethane to ethylene and then to acetylene the C—H bonding of carbon has progressively more *s* and less *p* character.

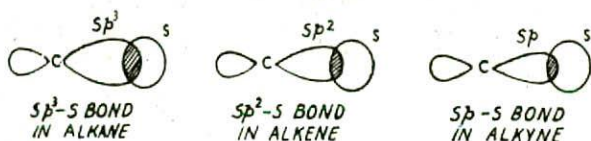
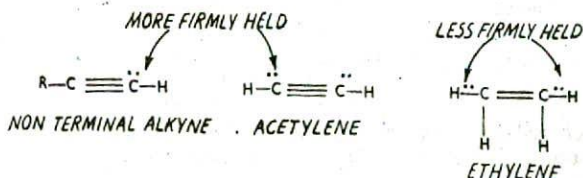


Fig. 12-4. Illustration that *s* character of C—H bond increases progressively from alkane to alkene to alkyne.

The bonding electron pair is, therefore, closer to the carbon atom. In other words  $\pi$  electrons of the  $C\equiv C$  bond are more firmly held by the carbon nuclei than the  $\pi$  electrons of the  $C=C$  bond, and therefore less accessible to an electrophile.

Also, the alkynes are characterised by their acidic behaviour in contrast to alkenes. The hydrogen atoms linked to the triple bond are easily ionizable than the hydrogen atoms of the double bond. This is again due to the fact that the bonding electrons of C—H in alkynes are nearer to carbon nuclei and thus more firmly held than in alkenes.



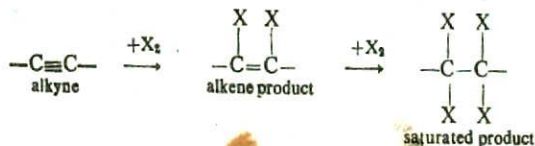
The acidic H atoms of acetylene or nonterminal alkynes are, therefore, readily replaced by a number of metal atoms.

The different reactions of alkynes are described below under the following heads.

- (i) Addition Reactions ;
- (ii) Substitution Reactions ;
- (iii) Oxidation Reactions ,
- (iv) Polymerization
- (v) Isomerization.

#### A. ADDITION REACTIONS

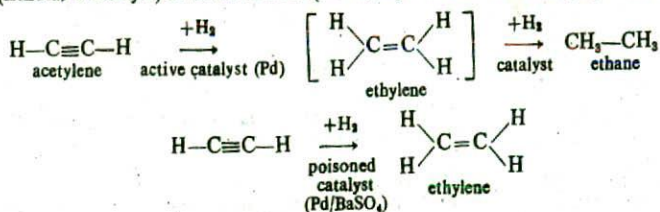
We have seen that a triple bond is made of two  $\pi$  bonds ( $\pi_x$  and  $\pi_y$ ) forming a sheath around the  $\sigma$  bond. In an addition reaction, first the electrons of one of these  $\pi$  orbitals are uncoupled and the electrons of the other constitute the  $\sigma$  part of an ordinary double bond. Then the remaining  $\pi$  bond reacts with another molecule of the reagent to give a saturated compound. Thus an alkyne can add two molecules of a reagent while an alkene can add one molecule only.



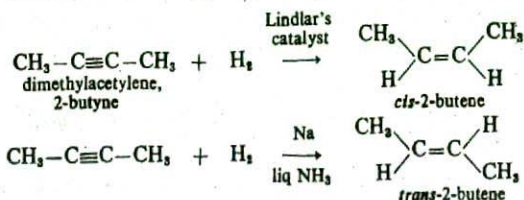
Whether actually one molecule of reagent is added to alkyne or two molecules, depends on the conditions of the reaction.

(1) **Addition of Hydrogen (Catalytic Hydrogenation).** In the presence of catalysts like finely divided platinum, palladium or Raney nickel, alkynes add up two molecules of hydrogen first forming the corresponding alkenes and finally the alkanes.

The reduction can, however, be stopped at the alkene stage by using Pd poisoned with  $\text{BaSO}_4$  (Lindlar's catalyst) or nickel boride (P-2 catalyst or Brown's catalyst). Thus,



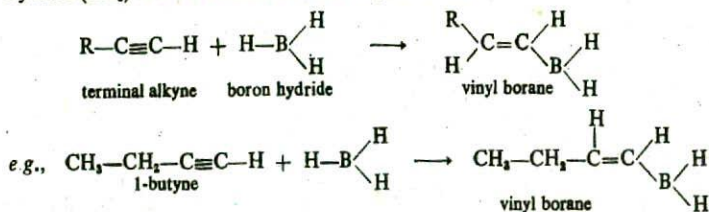
The catalytic hydrogenation of disubstituted acetylenes ( $\text{RC}\equiv\text{CR}$ ) with Lindlar's catalyst gives the *cis* alkene exclusively. On the other hand when the reduction is carried chemically with Na or Li in liquid ammonia, predominantly *trans* alkene is obtained.



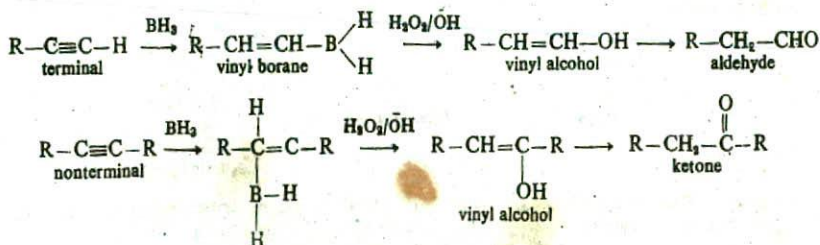
The *trans* addition of alkenes as above is possible because the intermediate dianion form assumes a configuration in which the anions lie farthest apart.

Such reactions which produce predominantly one stereoisomer are in general called *Stereoselective Reactions*.

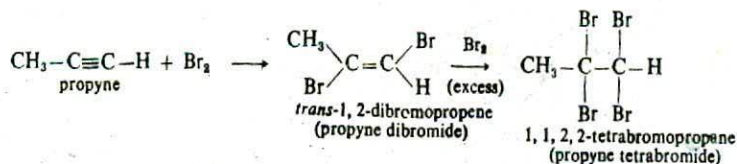
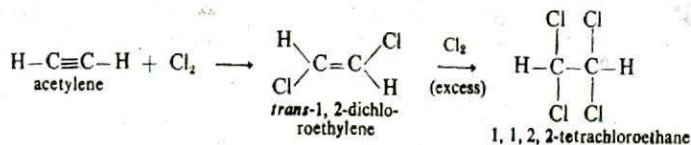
(2) **Addition of Boron hydride (Hydroboration).** Alkynes like alkenes add on boron hydride ( $\text{BH}_3$ ) in a *cis* manner to form vinyl boranes.



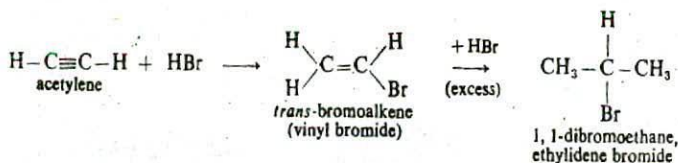
The vinyl boranes of terminal and nonterminal alkynes can be oxidised with alkaline hydrogen peroxide to form aldehydes and ketones respectively.



(3) **Addition of Halogens** Alkynes add on two molecules of halogens forming first a dihaloalkene and then a tetrahaloalkane.

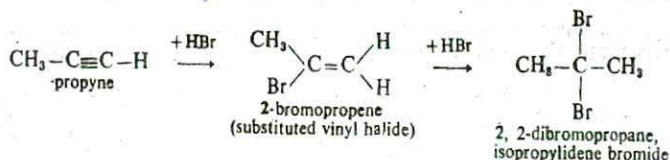


(4) **Addition of Hydrogen halides (Hydrohalogenation).** The addition of hydrogen halides to alkynes can also be made to go in two stages, either stopping at the haloalkene stage or going on to give a dihaloalkane.



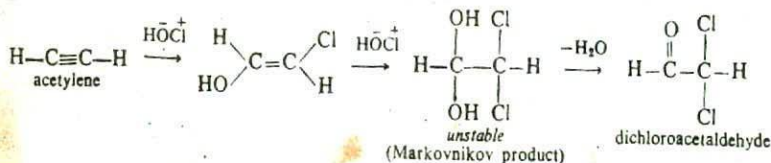
Thus when one molecule of the halide has been added to a symmetrical alkyne, the product is an unsymmetrical derivative of alkene. The addition of the second molecule of hydrogen halide, therefore, takes place in accordance with Markovnikov Rule. Hence both the halogens become attached to the same carbon atom.

The addition of hydrogen halides to unsymmetrical alkynes follows Markovnikov Rule in the first as well as in the second step. Again, both the halogens go to the same carbon.

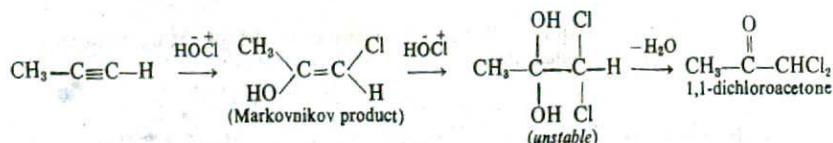


Vinyl halides are less nucleophilic than acetylenes. Therefore the addition of the second molecule of hydrogen halide requires more drastic conditions (higher temperatures).

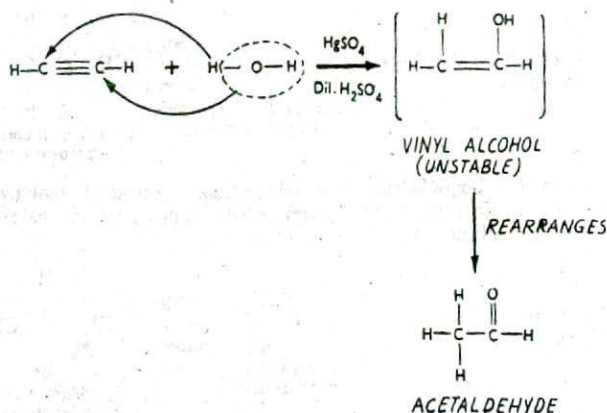
(5) **Addition of Hypohalous acids.** Addition of two molecules of hypohalous acids (HOX) to alkynes takes place in two steps. Thus acetylene reacts with hypochlorous acid to form dichloroacetaldehyde.



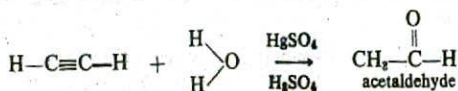
In the case of unsymmetrical alkynes the final product is a 1, 1-dihaloketone. Thus,



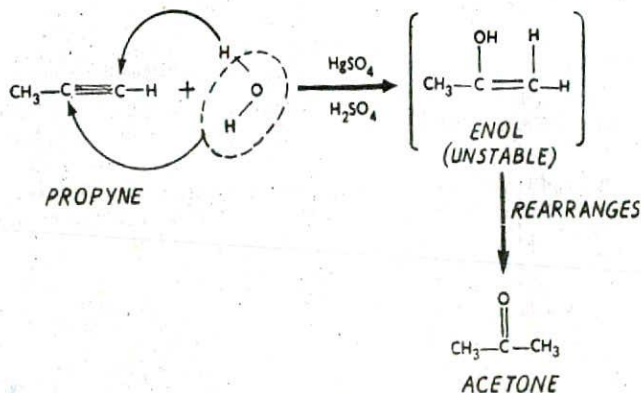
(6) **Addition of Water (Hydration).** Alkynes undergo hydration under milder conditions than do alkenes. Thus acetylene in the presence of  $\text{HgSO}_4$  dissolved in dil.  $\text{H}_2\text{SO}_4$  at  $75^\circ$  adds a molecule of water to form unstable vinyl alcohol which at once rearranges giving acetaldehyde.



Hence for most practical purposes it can be considered that the hydration of acetylene gives acetaldehyde directly.

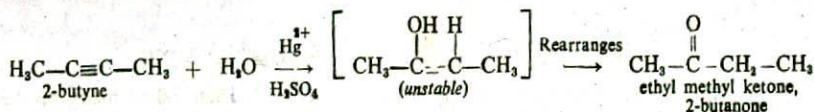


Similarly, addition of water to monosubstituted alkynes ( $\text{R}-\text{C}\equiv\text{C}-\text{H}$ ), gives a methyl ketone as predicted by Markovnikov Rule.

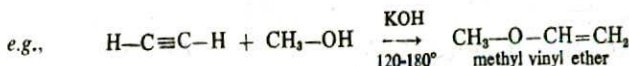
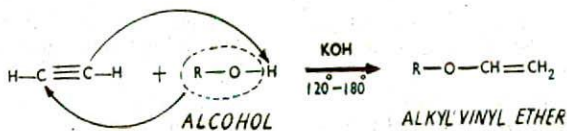


The hydration of a disubstituted alkyne ( $\text{RC}\equiv\text{CR}$ ), also gives a ketone.

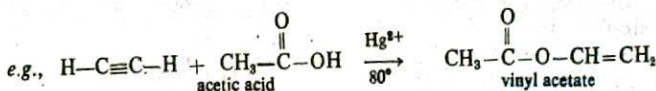
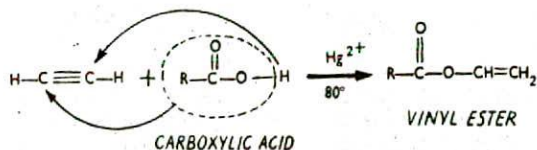




(7) **Addition of Alcohols and Carboxylic acids (Vinylation).** Alcohols add on to alkynes in the presence of alkali (KOH) at high temperatures and pressures, giving vinyl ethers. Thus,

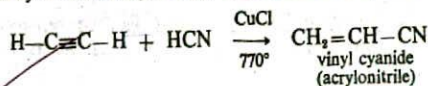


Similarly, alkynes add carboxylic acids in presence of mercuric salts to form vinyl esters.



The process whereby acetylene adds to compounds containing an active H atom to form vinyl compounds is called *Vinylations*.

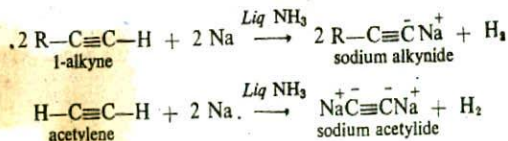
(8) **Addition of Hydrogen Cyanide.** Alkynes add hydrogen cyanide across the carbon-carbon triple bond under the influence of copper salt catalysts, giving alkenyl cyanides. Thus acetylene yields vinyl cyanide or acrylonitrile from which the synthetic fiber 'orlon' is made.



## B. SUBSTITUTION REACTIONS

(1) **Formation of Metal Salts.** We have already discussed that hydrogens in acetylene and terminal alkynes containing  $\equiv\text{C}-\text{H}$  group are acidic in character.

(i) **Sodium alkynides.** Thus acetylene and terminal or 1-alkynes react with Na in liquid ammonia as solvent to form ionic compounds sodium acetylides and sodium alkynides respectively.



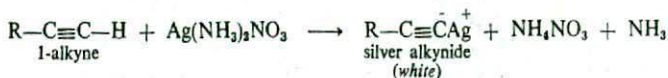
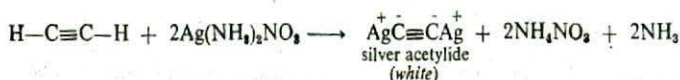
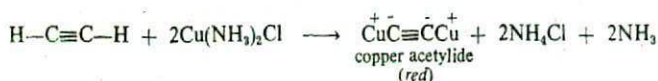
We can also prepare sodium salts by the reaction of alkynes with a strong base like sodamide ( $\text{NaNH}_2$ ).



Alkynes form similar salts with potassium and lithium. These alkali metal alkynes are stable when dry but are readily hydrolysed by water, regenerating the original alkynes,

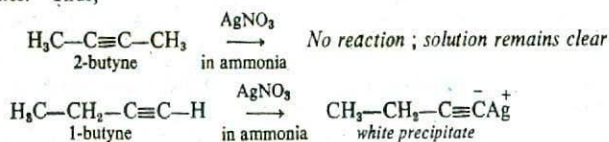


(ii) *Heavy Metal alkynides.* Acetylene and 1-alkynes also react with ammoniacal solutions of cuprous chloride and silver nitrate to form the corresponding copper (*red*) and silver (*white*) alkynides.



The heavy metal alkynides have different properties than alkali metal alkynides. These are stable to water but while wet are decomposed by dilute acids to regenerate the parent alkynes. These are extremely sensitive to shock and explode violently in the dry state.

Since 2-alkynes do not form alkynides, this reaction is conveniently used to distinguish them from 1-alkynes. Thus,



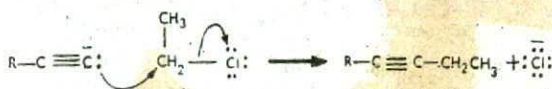
In general, the formation of heavy metal salts could be employed as a diagnostic test for  $-\text{C}\equiv\text{CH}$  group.

(2) **Alkylation of Alkynes.** Acetylenic hydrogens can be replaced by alkyl groups by treating acetylene and 1-alkynes with primary and secondary chlorides in presence of Na and liquid ammonia. Thus,

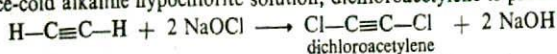


This process does not work with tertiary alkyl chlorides which eliminate HCl and form the corresponding alkenes.

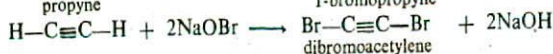
**MECHANISM.** This reaction involves a displacement of the nucleophile Cl by a stronger nucleophile, the carbanion. The electrons of the carbanion form a new bond to the carbon of the alkyl chloride while the electrons of C-Cl bond get associated with the Cl<sup>-</sup>.



(3) **Substitution by Halogens.** The acidic hydrogen of alkynes can be replaced by halogens under conditions which promote the formation of positive halogen. Thus, when acetylene is passed into ice-cold alkaline hypochlorite solution, dichloroacetylene is produced.



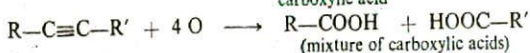
Similarly 1-alkynes and acetylene react with NaOBr to form the corresponding mono and dibromo derivatives.



### C. OXIDATION REACTIONS

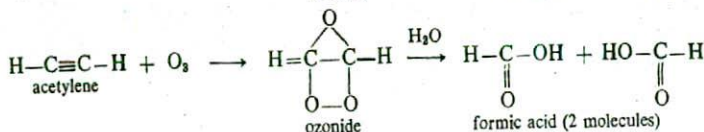
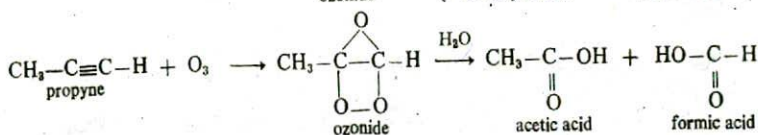
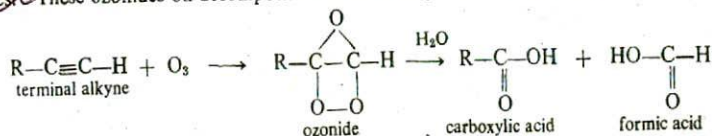
The oxidising agents that are effective against C=C bond are usually effective against the C≡C bond also. However, the triple bond is less responsive owing to the π electrons being more firmly held by the carbon nuclei.

(1) **Degradation with Potassium Permanganate.** The oxidation of alkynes with alkaline potassium permanganate cleaves the molecule at the site of the triple bond to yield carboxylic acids and carbon dioxide.



This degradation reaction of alkynes is useful in determining the structure of alkynes.

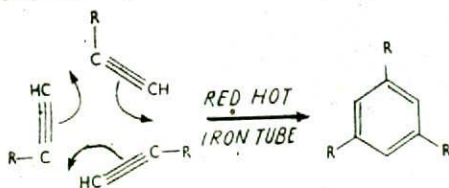
(2) **Ozonolysis.** In contrast to alkenes, alkynes react slowly with ozone to produce ozonides. These ozonides on decomposition with water yield carboxylic acids.



Ozonolysis of alkynes is also used for determining the structure of alkynes.

### D. POLYMERIZATION REACTIONS

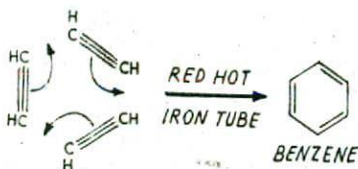
(1) **Polymerization to Benzene hydrocarbons.** Alkynes when passed through a red hot quartz or iron tube polymerize to yield benzene hydrocarbons.



SYM-TRIALKYL BENZENE

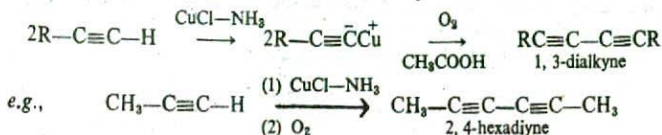


Thus propyne gives mesitylene while acetylene furnishes benzene itself.



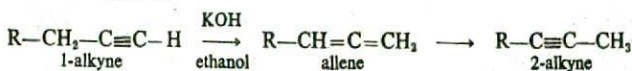
This reaction provides a method for passing from aliphatic to aromatic compounds.

(2) **Oxidative Coupling.** Terminal alkynes upon treatment with ammoniacal cuprous chloride form the corresponding copper acetylides. The copper acetylides when heated in acetic acid in the presence of air, undergo oxidative coupling (**Glaser coupling**). Thus two molecules of the alkyne join together to form a 1, 3-dialkyne.

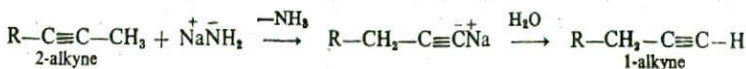


## E. ISOMERIZATION ; ACETYLENE-ALKENE REARRANGEMENT

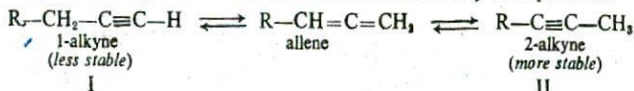
1-Alkynes can be readily isomerized to the more stable 2-alkynes on treatment with potassium hydroxide in ethanol.



On the other hand, a 2-alkyne can also isomerize to 1-alkyne by the action of  $NaNH_2$  in an inert solvent. The free hydrocarbon is recovered by hydrolysis with water.



The above rearrangements which take place through the formation of allene are called acetylene-allene rearrangements. These are reversible and may be depicted as



The rearrangement occurs in either direction under conditions described above—from I to II in presence of ethanolic KOH and from II to I in presence of  $NaNH_2$ .

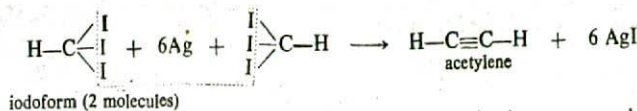
## ACETYLENE, *Ethyne*, $H-C\equiv C-H$

Acetylene, the simplest member of the alkyne series, is the only alkyne which is of significant industrial importance. Many of the industrial uses of acetylene, however, are now losing importance as methods of making the same compounds from ethylene (much cheaper raw material) are being developed. For example, acetaldehyde which was earlier produced by the catalytic hydration of acetylene is now obtained by a similar process from ethylene. The production of vinyl chloride by the addition of  $HCl$  to acetylene is being superseded by the chlorination of ethylene.

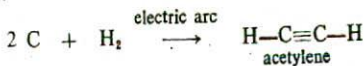
**Preparation.** Acetylene can be produced by the general methods of preparation of alkynes described before. It can also be obtained by the following special methods.

(1) By heating iodoform ( $CHI_3$ ) with silver powder



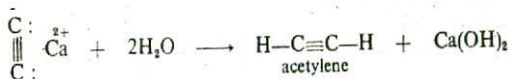


(2) By striking an electric arc between carbon electrodes in an atmosphere of hydrogen (Berthelot's Synthesis).



This method is of significance inasmuch as it affords a synthesis of acetylene from elements (Total Synthesis). The gas thus produced is contaminated with methane and ethylene which are formed at the same time.

LABORATORY PREPARATION. Acetylene is conveniently prepared in the laboratory by the action of water on calcium carbide.



calcium carbide

The apparatus is arranged as in Fig. 12-5. Water is added dropwise by pressing the teat of dropper on to the pieces of calcium carbide in the test tube. The gas produced is collected in a test tube inverted over the delivery tube.

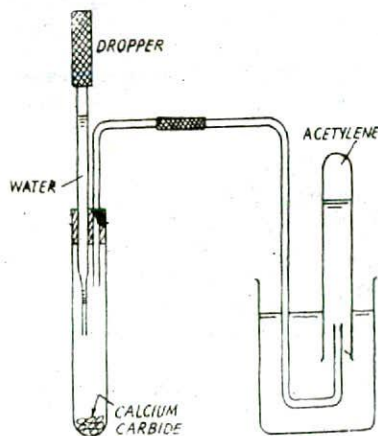
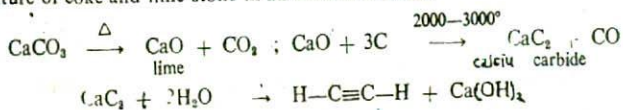


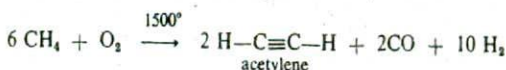
Fig. 1-25. Small scale preparation of Acetylene.

Acetylene prepared as above method is often contaminated with impurities like  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{NH}_3$  etc. The gas is purified by bubbling it through acidified copper sulphate solution.

MANUFACTURE. (1) From Calcium Carbide. Acetylene is prepared on a large scale also by the action of water on calcium carbide ( $\text{CaC}_2$ ). Calcium carbide in turn is obtained by heating a mixture of coke and lime stone in an electric furnace.



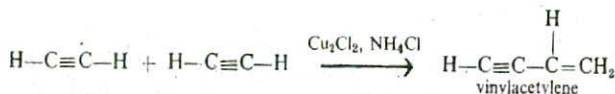
(2) *From Methane.* Acetylene is now being increasingly made industrially by the partial combustion of methane derived from natural gas.



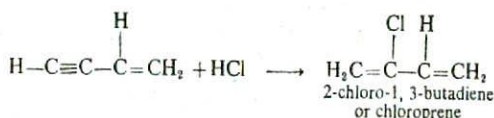
**Properties (Physical).** Acetylene is a colourless gas with ethereal odour when pure. As prepared from calcium carbide, it has garlic odour owing to the presence of traces of phosphine and hydrogen sulphide gas. It can be liquefied at  $1^\circ\text{C}$  under a pressure of 48 atmospheres. Liquid acetylene boils at  $-82^\circ\text{C}$ . It is slightly soluble in water, somewhat more soluble in alcohol but very soluble in acetone. Thus, when needed for industrial purposes acetylene is transported dissolved in acetone under high pressure, because ordinary liquid acetylene explodes violently by shock or heat. Acetylene is somewhat poisonous and produces general anaesthesia when inhaled.

**(Chemical).** Acetylene gives the general reactions of alkynes as enlisted before. Some special reactions are mentioned here.

(1) **Dimerization.** Acetylene can add to itself to form a dimer when treated with cuprous chloride in aqueous ammonium chloride solution.

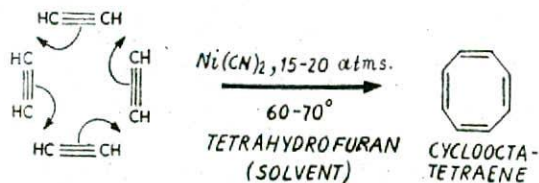


Vinylacetylene thus produced adds on hydrogen chloride to give 2-chloro-1, 3-butadiene or chloroprene.

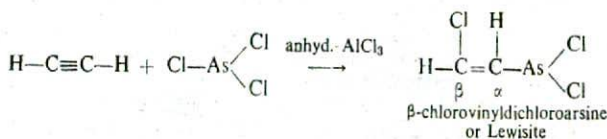


Chloroprene is an important industrial material for the production of plastic called **Neoprene**.

(2) **Tetramerization.** In presence of nickel cyanide and high pressure, acetylene tetramerizes to produce cyclooctatetraene.



(3) **Formation of Lewisite.** Acetylene adds to a molecule of arsenic trichloride to form  $\beta$ -chlorovinylidichloroarsine which was used as a poison gas under the name **Lewisite** in World War II.



(4) **Ethynylation.** Acetylene reacts with formaldehyde in presence of copper acetylide to form 2-butyne-1, 4-diol along with small quantities of propargyl alcohol.



## QUESTIONS

- Outline the methods of preparation, properties, and uses of alkynes. (North Eastern Hill BSc, 1994)
- Give two methods for the preparation of acetylene. What is its industrial importance? (Andhra BSc, 1994)
- Write structural formulas for the products when 1-butyne reacts with each of the following reagents:
 

(a) $2\text{H}_2/\text{Ni}$	(b) $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HgSO}_4$
(c) $2\text{HCl}$	(d) $\text{CH}_3\text{OH}/\text{KOH}/\text{heat}$
(e) $\text{Na}/\text{liq NH}_3$	(f) ammoniacal $\text{AgNO}_3$

 (Aligarh BSc Hons, 1993)
- How will you distinguish between:
  - Acetylene and ethylene
  - Propyne and propane
  - 1-Heptyne and 2-heptyne

**Hint.** (a) Acetylene forms precipitate with ammoniacal  $\text{AgNO}_3$ . Ethylene does not react; (b) Propyne gives precipitate with ammoniacal  $\text{AgNO}_3$ . Propane does not react; (c) 1-Heptyne forms precipitate with ammoniacal  $\text{AgNO}_3$ . 2-Heptyne does not react.

- Explain: Acetylene is more acidic than ethane. (Delhi BSc Hons, 1994)
- Explain: Acetylene and 1-alkynes are acidic in nature. (Madras BSc, 1994)
- How will you synthesise the following compounds from acetylene:
  - Acetaldehyde
  - Benzene
  - Vinylacetylene
  - Lewisite
  - Vinyl methyl ether
  - Chloroprene
  - Acetone
  - 2-Butanone
  - 1-Butyne
  - 2-Butyne
  - Vinyl bromide

**Hint.** (f) (i)  $\text{Cu}_2\text{Cl}_2/\text{NH}_4\text{Cl}$ , (ii)  $\text{HCl}$ ; (g) (i)  $\text{Na}/\text{liq NH}_3$ , (ii)  $\text{CH}_3\text{I}$ , and (iii)  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HgSO}_4$ ; (h) (i)  $\text{Na}/\text{liq NH}_3$ , (ii)  $\text{CH}_3\text{CH}_2\text{Br}$ , and (iii)  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HgSO}_4$ ; (j) (i)  $\text{Na}/\text{liq NH}_3$ , (ii)  $\text{CH}_3\text{I}$ , and (iii)  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/\text{HgSO}_4$ ; and (k) (i)  $2\text{HBr}$  and (ii) alcoholic  $\text{KOH}$ .

- An unknown compound (A) has the molecular formula  $\text{C}_5\text{H}_8$ . Suggest a possible structure from the following data:
  - One mole of (A) takes up two moles of hydrogen.
  - (A) forms a precipitate with ammoniacal  $\text{AgNO}_3$ .
  - Treatment of (A) with  $\text{H}_2\text{O}$  in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  catalyst yields 2-pentanone ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ ) as the main product.

**Answer.** (A) is 1-Pentyne.

- An unknown compound (B) has the molecular formula  $\text{C}_5\text{H}_8$ . Suggest a possible structure from the following data:
  - One mole of (B) takes up two moles of chlorine.
  - Compound (B) decolourises a solution of  $\text{Br}_2$  in carbon tetrachloride.
  - Compound (B) forms no precipitate with ammoniacal silver nitrate solution.
  - Treatment of (B) with  $\text{H}_2\text{O}$  in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  catalyst yields an equimolecular mixture of 2-pentanone ( $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$ ) and 3-pentanone ( $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ ).

**Answer.** (B) is 2-Pentyne.



## Petroleum and Petrochemicals

Petroleum is a complex mixture of hydrocarbons, mostly alkanes and cycloalkanes. It occurs deep below earth's crust entrapped under rocky strata. It is taken out by drilling wells. The natural oil thus derived is a viscous black liquid. In its crude form, the oil is called **Petroleum** (Latin, *petra* = rock; *oleum* = oil) or **Crude oil**. There occurs invariably a gas in contact with petroleum deposits in dome-shaped rocky pockets. This gas which flows out naturally from oil wells is referred to as **Natural gas**. Natural gas is primarily a mixture of methane and ethane, along with small amounts of propane.

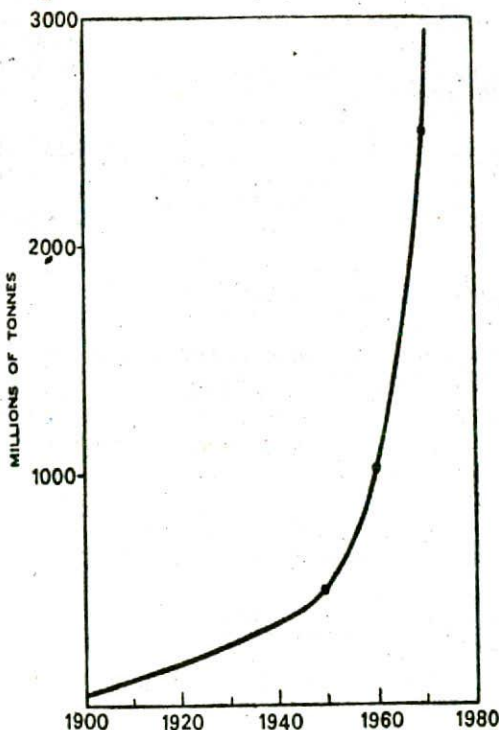


Fig. 13-1. World's consumption of Crude oil.

Petroleum and natural gas are generally considered to be formed by the decomposition of plants and microscopic animals. When buried under earth, these are converted to petroleum

and natural gas under geological conditions of high temperature and pressure in absence of oxygen. Since the energy for plant growth comes from the sun, petroleum and natural gas can be regarded stored form of solar energy. It seems probable that petroleum and natural gas are being formed at the present times. However, the rate at which these natural resources are being used up is very much greater than the rate at which they are formed.

Petroleum constitutes the principal energy source for our modern industrial society. It is the major source for most of the chemicals used to form the synthetic fibres, plastics, films, drugs, food additions and pesticides. Industry, agriculture, communication and means of transportation in the present-day world depend largely upon this 'black gold'. In fact, it is the most valuable material for nations in peace and war. A statesman has observed. "The nation that has petroleum dominates world politics."

**World's Reserves of Crude Oil** With the fast industrialisation and advancing all round progress of all nations, the world's consumption of crude oil is ever on the increase. In 1978, total world production crude oil was 19.7 billion barrels (bbl). Between 1976 and 1979, the proven reserves of crude oil decreased by 17 billion bbl. According to agreed estimates, the world's supply of crude oil will run out between 2020 and 2075. It is a hard fact that in the next 20 to 30 years we will not be left with enough oil to meet our requirements of energy. The solution to the energy crisis will lie in developing alternate sources of energy right now.

Although other sources of energy will certainly replace petroleum and coal (fossil fuels), there would still be need of an adequate source of carbon compounds. As the petroleum reserves are depleted, probably vegetable and animal waste products will form alternate source of carbon compounds that are presently derived from petroleum.

**Indian Situation.** Before independence, oil was a myth in India. After 1947, the need of search for indigeneous 'black gold' was felt. Shri Jawahar Lal Nehru, the first Prime Minister of India set up an organisation named as Oil and Natural Gas Commission (ONGC) for exploration and exploitation of crude oil and natural gas resources of the country. It is largely due to the sustained efforts of ONGC that India has attained a significant place on the world map of oil-producing countries. Oil was struck at Cambay in 1968 and at Ankleshwar in 1960. Subsequently other oil fields in North Gujarat came into production:

The indigenous production of crude oil has gone up from as low as 0.25 million tons in 1948 to 16.19 million tons in 1982.

Table. Production of Crude oil and Natural gas in India.

Period	Crude oil in million tons	Natural gas in million cubic metres
1977-78	10.76	2839
1978-79	11.63	2811
1979-80	11.77	2767
1980-81	10.51	2358
1981-82	16.19	3851
1982-83 (estimated)	20.98	—

### Growth of Petrochemical Industry in India

Indian petrochemical industry is comparatively of recent origin. But its growth has been spectacular during the last decade. With the availability of the raw materials: natural gas, refinery gas and naphtha, Govt. of India has set up a number of complexes in Bombay, Gujarat and Assam to manufacture petrochemicals: Organic chemicals, Synthetic fibres, Plastics, Synthetic Rubber, Detergents, Insecticides, etc.

### NATURAL GAS

In many parts of the world large quantities of what is called *natural gas* is found in association with petroleum. The gas flows to the surface of the earth through natural outlets (say springs) from gas deposits. It is also found dissolved in natural petroleum and is given out when the oil comes to the surface. Some wells produce nothing else but gas.

The gas emerging from gas fields is a mixture of mostly methane with small amounts of ethane, propane and butane, nitrogen and carbon dioxide. The composition of a typical sample of natural gas is:

CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , C <sub>4</sub> H <sub>10</sub>	CO <sub>2</sub>	N <sub>2</sub>
95.0%	3.6%	0.48%	1.92%

The proportion of ingredients of the gas varies with the source. C<sub>2</sub>—C<sub>4</sub> gases are present to the extent of 20% in the petroleum field gases.

In early days, natural gas was considered a hazard in the petroleum industry as it formed explosive mixtures with air, and was taken away from the source and burnt. The production and utilisation of the gas dates to the beginning of the 20th century in USA. It was not before 1950 that USSR and other countries did so. In India the gas industry is in infancy and it is largely derived from the cracking units of petroleum refineries and from the gas fields at Cambay (Gujarat). As compared to 172 million cu mt of gas produced in 1961, India produced .9855 million cu mt in 1980. In petroleum countries like USA and USSR the gas is stored in large steel reservoirs and distributed through a system of pipe lines as fuel for domestic stoves or for boilers. Liquefied natural gas is now being transported from North Africa to France and Great Britain by tankers. In Britain the 'coal gas' supply for domestic use has been almost replaced by the 'oil gas' supply.

A liquid mixture of propane and butane can be obtained from natural gas or refinery gases at room temperature under a pressure of 3.5 atmospheres. This is stored and distributed in 40-100 litre capacity steel cylinders which can be directly connected to domestic gas stoves. The fuel gases themselves are odourless but to warn against leakage a very small amount of foul smelling substance is added. In India, the 'bottled gas' is being made available for domestic consumption in large towns under the trade names 'Indane' and 'Bursane'. The use of liquid gas in this way obviates the need for gas pipes, which would be both costly and cumbersome.

In USA and USSR natural gas serves as starting material for making useful 'petrochemicals'.

### COMPOSITION OF PETROLEUM

Petroleum is essentially a mixture of the alkane hydrocarbons which are present in it right from methane up to the higher members containing as many as thirty five carbon atoms. It also contains varying amounts of aromatic hydrocarbons and cycloalkanes. The actual composition of the oil, however, varies with the place of origin. Besides the various types of hydrocarbons, there are present in petroleum organic compounds containing nitrogen and sulphur. Most of the natural oils are found to be optically active.



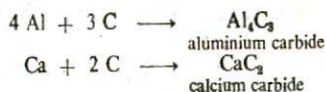
Since petroleum has entirely different composition from that of the vegetable and animal oils, to differentiate it from them it is commonly called *mineral oil*. This name points to its origin in mines.

### ORIGIN OF PETROLEUM IN NATURE

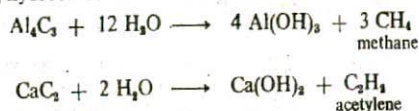
Many theories have been put forward to explain the formation of petroleum in nature. Of these, the more important are :

(1) **Carbide Theory.** This theory was originally suggested by Mendeleeff and supported by Moissan, Sabatier and Senderens. It regards petroleum as of inorganic origin being formed by the action of steam or water on metallic carbides in the inner portion of earth's crust. The Carbide theory describes the formation of petroleum by the following steps.

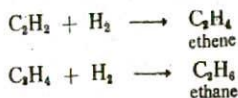
(i) **Formation of Carbides.** The molten metals in the hot interior of the earth came in contact with coal and carbides were formed. Thus,



(ii) **Action of Steam with Carbides.** Carbides reacted with steam under high pressure and at high temperature forming hydrocarbons.

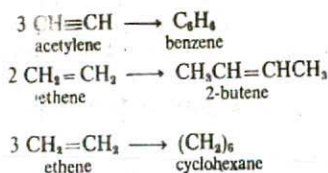


(iii) **Reduction of Unsaturated hydrocarbons.** The unsaturated hydrocarbons formed by step (ii) are reduced with hydrogen in the presence of metallic catalyst at high temperature.



The hydrogen needed for reduction is obtained by the action of hot metals with steam.

(iv) **Polymerization.** Unsaturated hydrocarbons polymerized in the presence of hot metals forming aromatic hydrocarbons, cycloalkanes, and higher open chain hydrocarbons.



2-Butene will again be hydrogenated forming butane.

There is no doubt that the Carbide theory explains the formation of petroleum in a rational way but there are serious objections against it and at present this theory commands little consideration. The two main facts which go against it are :

(a) *Natural petroleum contains sulphur and nitrogen compounds, chlorophyll, haemin, etc.* The Carbide theory fails to explain their presence in petroleum as they are all essentially of organic origin



(b) *Petroleum contains optically active compounds.* According to the Carbide theory, the natural mode of formation of petroleum is a strict laboratory one and we know that we cannot get optically active substances by ordinary synthetic methods in the laboratory.

(2) **Engler's Theory.** Engler (1900) discovered that by the destructive distillation of fish blubber, a product exactly similar to natural petroleum could be obtained. It contained sulphur and nitrogen compounds commonly found in petroleum, and was also optically active. This affords a direct experimental evidence of the production of petroleum from sea animals by some natural process akin to destructive distillation. This can happen if, say, there is a volcano by the sea side. The volcanic gases contain sulphur dioxide which dissolves in sea water. Thus fish and other sea animals coming towards this region would die there of suffocation. In due course of time a huge accumulation of dead animals formed in this way would be covered

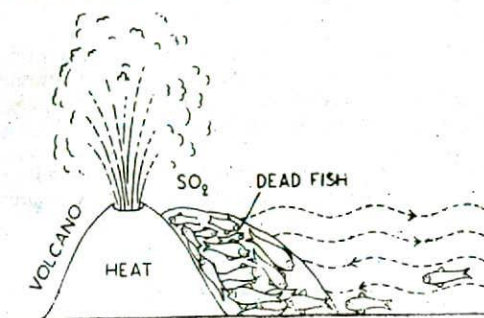


Fig. 13-2. Formation of petroleum from sea animals. by earth's crust. Under the influence of heat from the volcano, decomposition sets in which ultimately results in a petroleum deposit.

Another fact that lends weight to Engler's theory is that mineral oil is always found in company with salt and brine which must have been obtained from sea water.

(3) **Modern Views.** It has been described above that petroleum is very probably of animal origin. The presence of compounds which are derived from haemin, the pigment of the red blood corpuscles, and the discovery of fossils in petroleum areas are enough proof to support this theory.

Many oils contain compounds derived from chlorophyll, the green of the plants, thus pointing to the vegetable origin of petroleum. May be that some upheaval brought a forest well under the earth's crust where by the action of heat and water, the plants were converted to petroleum. This view is supported by the fact that coal is found in the neighbourhood of oil deposits. The high resin content of Burma oil is also accounted for by the vegetable origin of the oil.

In face of the above evidence, it appears very likely that while some oils are of animal origin, there are others of vegetable origin.

Astronomers have recently established that the atmosphere of the large planets Jupiter and Saturn consists chiefly of methane. This has led to the idea that at one time our earth's crust also contained huge quantities of methane. Since methane is converted to higher hydrocarbons by the action of ultraviolet rays and radioactive rays, it has been conjectured that radioactive substances in the earth's crust may have transformed methane into petroleum. The fact that helium, which is a disintegration product of radio elements, is often present in natural gas issuing in petroleum areas lends support to this view.

## PROSPECTING FOR OIL

Prior to the systematic search of oil-bearing deposits, an explorer had to depend upon certain visible signs on the surface of the earth. Sometimes the petroleum gas seeped through the ground and burnt on the surface resulting in 'natural fire', as we have at Jwalamukhi, Punjab. The rainbow smears of oil in water from springs were often suggestive and gave a clear indication of the prospects for finding hidden oil deposits. Such clues to the existence of oil are available in Jammu and Kashmir state, and in several other regions in India.

For locating the prospective areas which are likely to be petroleum bearing, various scientific methods are now employed. The more important ones are stated below.

(1) **Gravimetric Method.** It depends on the fact that the pull of gravity in a given area on earth's surface varies with the density of the rocks beneath. The sedimentary rocks below the oil reserves are less dense compared to igneous rocks elsewhere, and show a relatively lower gravitational attraction. Thus gravity-meters show a fall in the value of gravity near the petroleum fields. By a 'gravity survey' of a region, a geologist can adequately guess the location of oil fields.

(2) **Magnetic Method.** Oil fields are often found in the vicinity of the salt domes within the crust of the earth. These salt domes are diamagnetic and, therefore, weaken the intensity of the magnetic field of the earth. By determining the magnetic gradient with the help of magnetometers at various places in the area, the situation of petroleum rich rocks can be found.

(3) **Seismic Method.** This is by far the most reliable and effective method for locating oil fields. In this method, a heavy charge of dynamite buried under the earth's surface is exploded.

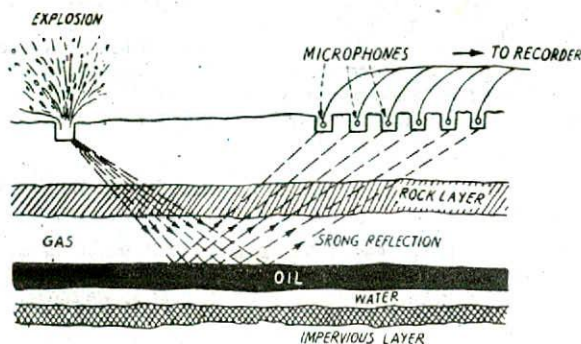


Fig. 133. Seismic method of locating oil reserves.

It creates a sort of miniature earthquake and sends shock waves through the ground. These waves are reflected from the petroleum surface and the dense underlying strata, and are thus returned to the ground surface. Here the shock waves or vibrations are received by the geophones (special type of microphones) connected to an automatic recording device called *seismometer*. The time noted between the dynamite blast and the reception of vibrations on the surface reveals the nature of the rock beneath as also the existence and depth of the oil reserve.

In spite of all the evidences collected by the above methods, the explorer cannot be sure about the presence of oil below. The only real proof is to bore down into the rock and find out. Nearly twenty per cent of these trial borings strike oil.

## DRILLING FOR OIL

The oil having been located, it has to be pumped to the surface. Therefore, we have first to bore down into the rock to obtain an 'oil well'. An efficient rotary drill bites into the rock with a circular motion kept in order by an engine on the surface. The cutting part of the drill called *bit* is kept cool by a current of lubricating mud which flushes out the rock pieces and helps to prevent a blow out of oil. The pipes are fed into the bored hole with the help of 'derrick' constructed at the surface. With such a device oil wells as deep as five miles have been drilled.

After the drill strikes oil, the underground pressure of the gas above the oil is normally sufficient to force the oil to the surface. The flow of oil from such wells called 'gushers' may continue unabated for years.



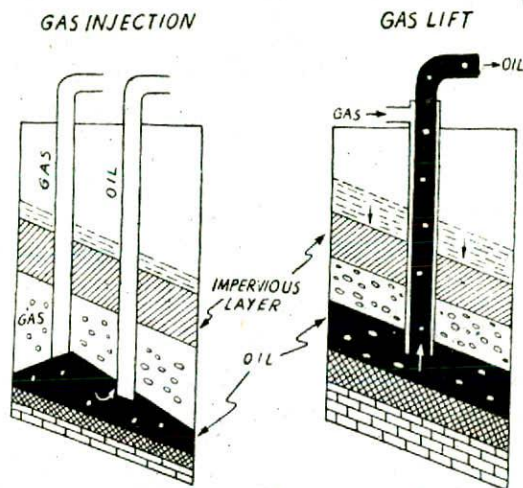


Fig. 134. Getting petroleum from an oil well.

As the gas pressure subsides, or when there is no gas, air pressure is applied to lift the oil from the well. When an oil well is completely run out, nuclear explosions have been recently employed to rejuvenate the dried well. Such explosions hit the unexplored rocks in the vicinity thereby causing a system of fissures so as to restore the productivity of the well.

The oil obtained from the mine is conveyed by a system of pipe lines to a distant place and distilled. The distillation is not carried out on the spot so that the inflammable *natural gas* or other dissolved gases may not catch fire and thus damage the whole mine.

### PETROLEUM REFINING

Petroleum as it comes from the ground is a rather viscous and highly coloured liquid. It often possesses unpleasant odour which is largely due to the presence of sulphur compounds in it. Technically it is called **Crude Oil**.

Crude oil consists chiefly of mixtures of alkanes boiling between a wide range, say  $0^{\circ}$  and  $400^{\circ}$ , and as such it is unsuitable for most technical purposes. If, however, the oil is subjected to fractional distillation, it can be separated into a number of fractions each of which has a technical name and finds use in industry. The process of dividing petroleum into fractions with different boiling ranges and free from undesirable impurities, is termed **Refining**.

The distillation of petroleum is carried in a tubular furnace with a tall steel fractionating column (bulb). The crude oil is pumped continuously through heated pipes and flashed into the fractionating column. The vapours of the oil as they rise up the fractionating column become cooler and condense at the shelves at various heights. The highest boiling fraction condenses at the bottom and the lowest boiling fraction at the top. The uncondensed gases escape along with the gasoline vapours at the head of the column. Outlets are provided in the side of the column at suitable heights to withdraw a number of fractions, the actual number of fractions and their boiling point ranges depending on the source of the petroleum

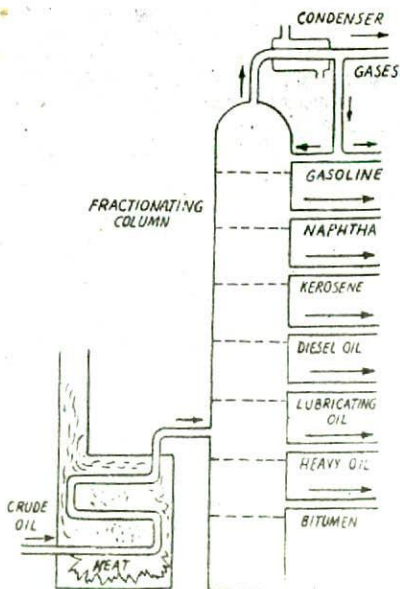


Fig. 135. Flowsheet of petroleum distillation.

and the trade demand. In the following table are given the details of the fractions commonly separated in modern practice. The main fractions are written in bold type and the 'sub-fractions' obtained from them by refractionation are given in small type. According to the most recent processes, the lubricating oil is now obtained from the residual oil by vacuum distillation.

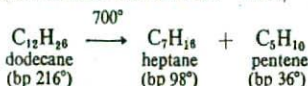
Fraction	Boiling Range	No. of Carbons	Uses
1. <b>Refinery gases or casing-head gases.</b>	Up to room temperature	C <sub>1</sub> to C <sub>4</sub>	As portable fuel gases after liquefaction and filling in cylinders.
2. <b>Gasoline, petrol or motor spirit.</b> (Colourless liquid)	30°—150°C	C <sub>5</sub> to C <sub>9</sub>	Motor fuel, aviation spirit, dry cleaning and solvent.
3. <b>Naphtha.</b> (Colourless liquid)		C <sub>7</sub> to C <sub>10</sub>	Solvent, drycleaning agent, and a source of aromatics.
4. <b>Kerosene, or paraffin oil.</b> (Colourless liquid)	150°—240°C	C <sub>10</sub> to C <sub>12</sub>	Fuel for stoves, for lamps as illuminant, fuel for jet aircrafts engines.
5. <b>Diesel oil, or gas oil.</b> (Brown liquid)	240°—350°C	C <sub>13</sub> to C <sub>18</sub>	Fuel for high speed diesel engines in trains, lorries and buses.
6. <b>Lubricating oil.</b> (Thick dark liquid)	Above 270°C	C <sub>18</sub> to C <sub>18</sub>	Lubrication.
7. <b>Paraffin wax.</b>	Above 400°C	C <sub>18</sub> to C <sub>30</sub>	Ointments, candles, toilets, vaseline, wax paper.
8. <b>Heavy fuel oil and Bitumen.</b>	From residue	C <sub>30</sub> →	Paints, road surfacing.

The above method of refining of petroleum is called the *Straight run process* and the various fractions thus obtained are termed '*Straight run oils*'.

In order to secure a higher yield of petrol or gasoline, the higher boiling straight run '*Gas oil*' or '*Residual oil*' is cracked and simultaneously fractionally distilled. The catalytic cracking is more modern and efficient. The process is used in preference to the simple *Thermal Cracking*. The stock is charged into the '*Reactor*' containing the catalyst at elevated temperature. The vapours of the cracked stock then pass to the fractionating unit and the products are: (i) cracked gasoline and; (ii) cracked fuel oil.

### WHAT IS CRACKING ?

When liquid alkanes are heated under pressure, they are decomposed to give hydrocarbons of lower molecular weights which are more volatile. The products contain both alkanes and alkenes. Thus,



This process of getting lower boiling hydrocarbons from higher boiling hydrocarbons by the application of heat is called **Cracking**.

The term cracking (*crack* = to break) is very descriptive of what happens when the molecules of hydrocarbons are heated to a high temperature. The kinetic energy of molecules in-

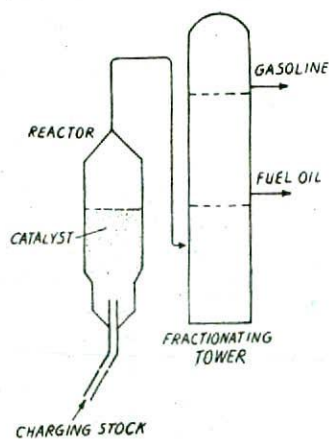
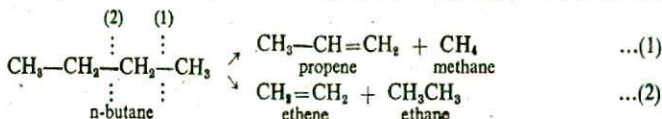


Fig. 13.6. Catalytic cracking process



creases and as a result they move faster, strike harder and are subject to more intense internal vibrations. These results of increased kinetic energy overcome some of the chemical bonds holding the atoms together, and the molecule may literally be said to have 'cracked' into simpler parts. This rupture of the molecule is accompanied by a redistribution of valence bonds and readjustment of some of the hydrogen atoms, resulting in the formation of lower hydrocarbons. The mechanism of the process of cracking may be illustrated by the decomposition of n-butane at 600°.



It is obvious that the carbon chain cracks at positions (1) and (2) and the redistribution of valence bonds and hydrogen atoms in each case produces one alkane and one alkene.

Actually the 'cracking reactions' are never clear cut and the splitting of the molecules may take place at many points, yielding a number of small fragments, including alkanes, hydrogen and carbon.

**Applications of Cracking.** The process of cracking has become very important on account of its useful applications.

(1) *Preparation of Oil Gas.* Kerosene oil is cracked by pouring dropwise into a red hot iron retort. It is thus converted into gaseous hydrocarbons (methane, ethane, ethene, hydrogen, etc.), along with a large amount of volatile, tarry matter. The cracked products are bubbled through water in the hydraulic syphon where the tar vapours are condensed and removed. The gas thus obtained, commonly named as **Oil gas**, is then stored in an iron gas holder over water and conveyed to the laboratory through a pipe-line. The burning oil gas is a very convenient and suitable agency of heating in the laboratory.

(2) *Preparation of Petrol gas.* Petrol can be converted into permanent gaseous hydrocarbons by cracking. This is done by passing the petrol vapour through electrically heated coils or by heating it in a closed retort. The preparation of petrol gas is convenient as compared to that of oil gas, and the initial cost of the plant is low.

(3) *'Cracked Gasoline' from 'Residual Oil' or 'Gas Oil'.* As mentioned earlier, the less useful fractions of petroleum, viz., the Residual oil (Heavy oil) or the Gas oil are cracked

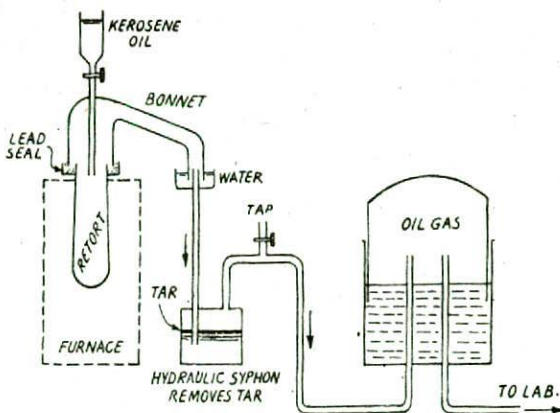


Fig. 137. Manufacture of oil gas for laboratory use.

with or without a catalyst at elevated temperature. The higher boiling hydrocarbons are thus split out into lower ones which constitute 'cracked gasoline'. The increased demand of motor fuel has been greatly met by this method.

## SYNTHETIC PETROL

With the extraordinary development of the automobile and *aeroplane* industry the world's demand for petrol has increased enormously. In spite of the great number of oil fields which have been discovered, our supply of petrol is inadequate. The increasing demand for petrol has been largely shouldered by the introduction of cracking methods and actually more petrol is now obtained by cracking than in the original petroleum distillation process. But that is no satisfaction as the world's oil supply cannot last indefinitely.

In a country like India with practically no oil fields so far, we are immediately confronted with the problem of 'synthetic petrol'. To recoup from the aftermath of past slavery and then to rise again to occupy a respectable position in the comity of nations, India must have enough of the motor fuel. Petrol has soon got to be produced somehow and it is left to the Chemist to accomplish the task. The situation, however, is not so pessimistic as it seems to be. We can certainly count on our vast coal fields for a supply of the synthetic product. Already, the work on production of the fuel oil from this source has progressed enough in countries like UK and Germany. The chief methods of preparing 'Synthetic Petrol' are given below.

(1) **Bergius Process.** In this method, finely powdered coal and suitable catalyst is made into a paste with *Heavy oil* produce in the process. The coal paste is then preheated and pumped to the *converter*. Here the paste is heated to  $450^{\circ}$  and hydrogen bubbled through it at 250 atmospheres pressure. The coal, which is really a mixture of high molecular complex organic compound deficient in hydrogen and elementary carbon, combines with hydrogen to form higher saturated compounds. These as a result of cracking and simultaneous hydrogenation yield mixtures of alkanes. Thus the vapours leaving the *converter* upon condensation yield 'Synthetic Petroleum' or *Crude oil*. This crude oil upon fractional distillation produces: (i) *Petrol*; (ii) *Middle oil*; and (iii) *Heavy oil*. The middle oil fraction is again hydrogenated in the vapour phase in contact with a solid catalyst to give more *petrol*. Actually the second process yields four times the petrol obtained by the primary hydrogenation of coal.

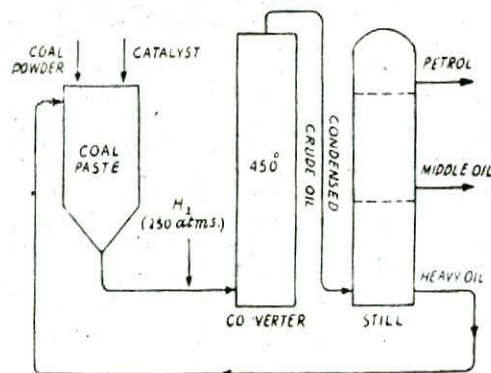


Fig. 13-8. Manufacture of Synthetic Petrol from coal.

The Heavy oil obtained in the process is recirculated for making fresh coal paste. One ton of soft coal treated as above yields 140 gallons of petrol. The Bergius process is at present the most promising of all methods so far invented for the production of synthetic motor fuel.

(2) **Fischer-Tropsch Process (Reduction of Carbon monoxide).** This method was given in 1923 by two German chemists, Franz Fischer and Hans Tropsch. Carbon monoxide needed in the process is made by passing steam over red hot 'coke'. The water gas thus obtained is mixed with hydrogen and passed at a pressure of 5–10 atmospheres into a chamber containing a 'cobalt catalyst' at  $200^{\circ}$ . The product is a mixture consisting mainly of liquid hydrocarbons.



The 'artificial petroleum' so obtained is separated by fractional distillation as described under the Bergius Process. The various fractions separated are petrol, kerosene oil, lubricating oil, diesel oil and paraffin wax. Germany employed this method for producing 'artificial petroleum', the annual output exceeding 1,000,000 tons. The Fischer-Tropsch Process has also a bright future in India.



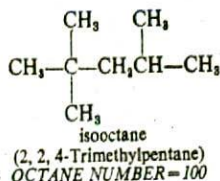
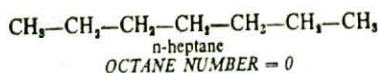
The Fischer-Tropsch Process is now also worked in the United States. Here, the carbon monoxide-hydrogen mixture is obtained by the oxidation of Natural gas by oxygen.



### WHAT IS MEANT BY OCTANE NUMBER ?

The structure of a hydrocarbon determines its efficiency in an automobile engine. The straight chain alkanes are very poor fuels and cause the engine to 'knock', while the use of branched-chain hydrocarbons and alkanes eliminates the knocking considerably.

The knocking quality of an automobile fuel is measured in term of the so-called 'Octane Number'. The hydrocarbon 'isooctane' (2, 2, 4-trimethylpentane), which was found to be free from knocks in highest compression motors was arbitrarily given an 'octane number' of 100, whereas n-heptane, which knocked badly, was rated at 0.



The Octane Number of a gasoline is defined as the percentage of isooctane present in a mixture of isooctane and n-heptane, when the mixture has the same knocking performance in the experimental engine as the gasoline under examination.

Thus a motor fuel is said to have an octane number of 80 when it is as good as a mixture of 20 per cent n-heptane and 80 per cent isooctane. The higher the octane number, the better the gasoline. Commercial gasolines have octane numbers 81, 74, and 65 for the premium, regular, and third grade gasolines.

The modern cracking methods of producing gasoline not only increase its yield but also give better quality of fuel having higher octane number. This is so because during cracking of petroleum, alkanes are formed which also undergo isomerization, polymerization etc., to give branched-chain hydrocarbons. Other methods of raising the octane number of a poor fuel are 'alkylation', 'reforming', 'hydroforming' etc., the discussion of which is beyond the scope of this book. The addition of tetraethyllead also improves the anti-knocking character of gasoline.

### FLASH POINT

Kerosene oil is used in lamps for illuminating purposes. The burning oil should not be sufficiently volatile at ordinary temperatures, otherwise its vapours would form explosive mixtures with air and thus making its use in lamps a source of danger. Just a lighted match-stick or a smouldering cigarette end if thrown into the oil godown might put the whole stock on fire. To ensure safety, the government of every country requires that only those oils should be used which do not give enough vapours at a certain minimum temperature. This temperature which is commonly known as Flash Point or the Ignition Temperature may be defined as :

*The minimum temperature at which an oil gives off enough vapours to form a momentary flash of light when a naked flame is brought near its surface.*

The ignition temperature of an oil depends on the proportion of volatile hydrocarbons present in it. An oil used in cold climates must necessarily be 'low boiling' and the one used in tropical climates must be 'high boiling'. Thus the flash point fixed in cold countries is low, while in hot countries it is high.

**Determination of Flash point.** The flash point of an oil is usually determined by means of *Abel's Apparatus* a modified form of which is shown in Fig. 13-9. A beaker is fitted with a cork having a big hole in its centre. A thermometer and two platinum electrodes are fitted through the cork so that their tips are about 5–10 mm apart just above the oil surface. The bulb of the thermometer should be kept dipped in the oil. The beaker containing the whole arrangement is then fixed in a water bath as shown in the diagram. The central cork is covered with a watch glass or a thin glass plate. The temperature of the bath is now gradually raised and sparks are sent across the electrodes by connecting them with an induction coil and accumulator. Just when the temperature of the oil reaches the flash point, the watch glass or the plate is lifted by an explosion. The temperature shown by the inner thermometer at this point is recorded.

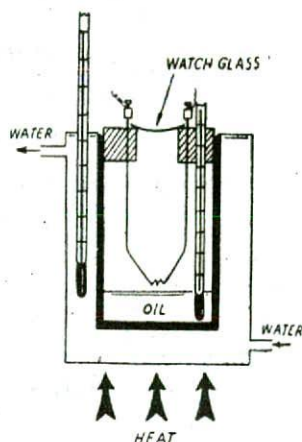


Fig. 13-9. Abel's apparatus.

## PETROCHEMICALS

The term 'Petrochemicals' is applied to those numerous organic chemicals that are derived from petroleum sources. Petrochemicals are produced either from *natural gas* or any of the fractions obtained during the refining of crude oil. Today petroleum has assumed a supreme position as a potent source of a very large number of organic compounds required for industry. It is estimated that more than half a million organic compounds could be synthesised from hydrocarbons derived from natural gas and petroleum fractions, namely *gasoline* and *naphtha*. Refining gases also form a valuable source of lower hydrocarbons (methane, ethane, ethylene, etc.)

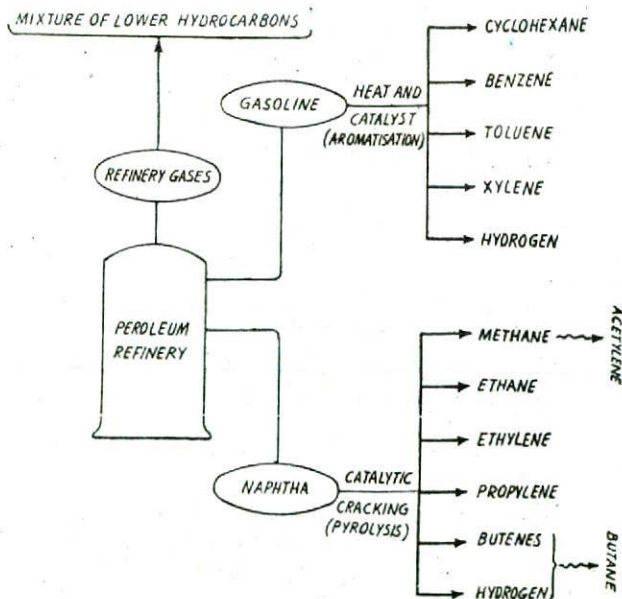


Fig. 13-11. Hydrocarbons obtained from Petroleum refinery.



Gasoline upon catalytic aromatisation yields benzene, toluene, xylene, hydrogen along with cyclohexane. Naphtha when subjected to catalytic cracking gives methane, ethane, ethylene, propylene, butene and hydrogen. Butene on catalytic hydrogenation forms butane and also further pyrolysis of methane produces acetylene.

All the hydrocarbons listed above that are derived from petroleum are now valuable starting materials for the preparation of a variety of useful organic compounds. The liquid aromatic hydrocarbons (obtained from gasoline) particularly form excellent raw materials for the synthesis of detergents, fibers, herbicides and pesticides etc. Hydrogen gas, found in natural and refining gases, is obtained as a byproduct in catalytic cracking of petroleum fractions. It is used as a hydrogenating agent in industry and for the production of fertilisers.

### Synthesis of Pure Chemicals

Pure organic chemicals are now prepared in large quantities by synthesis from the different aliphatic and aromatic hydrocarbons derived from petroleum. Since it is impossible to record here all the chemicals synthesised from each hydrocarbon, only a few important ones will be mentioned below.

(a) **From methane.** Methane, a component of refining gases, natural gas and cracked gases, is economically converted into  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  (by chlorination), methyl alcohol, formaldehyde and formic acid (by oxidation), and acetylene, carbon black (by pyrolysis). With steam, methane gives very useful *synthesis gas* ( $\text{CO} + \text{H}_2$ ) required for use in hydrogenation and fixation of nitrogen.

(b) **From ethane.** Ethane produces ethyl chloride — a useful starting material to obtain tetraethyllead, ethylene, ethylene oxide and ethyl alcohol.

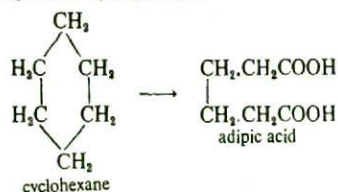
(c) **From propane and butanes.** Higher alkanes such as propane, n- and iso-butanes have been utilised to produce acetone, acetic acid, propylene, butadiene, 1- and 2-nitrobutanes and many alkylated polymers.

(d) **From ethylene.** Ethylene is by far the most important starting material in petrochemical industry because of its ease to get polymerized. It is manufactured into ethyl alcohol, ethylene oxide, dichloroethane, vinyl chloride, polyethylene and other products. Acetaldehyde has been the latest commercial product of ethylene.

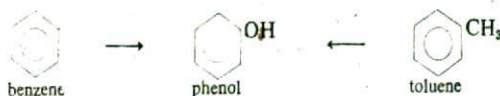
(e) **From propylene and butanes.** Propylene, isopropyl alcohol and isopropylbenzene are the main chemicals obtained from propylene. Propylene also accounts for the manufacture of phenol, acetone and glycerol. Butadiene (required for rubber and rayon manufacture) and butanol are synthesised from butenes.

(f) **From acetylene.** Acetylene, obtained by pyrolysis of methane, is a potential source of a large number of chemicals such as vinyl chloride, vinyl acetate, vinylacetylene, acetaldehyde and acrylonitrile.

(g) **From cyclohexane.** Cyclohexane derived from gasoline fraction is extensively employed to prepare adipic acid by oxidation.



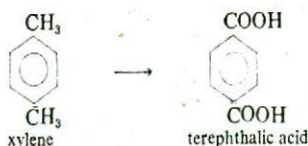
(h) **From benzene and toluene.** Simple aromatic hydrocarbons got from petroleum are very useful starting materials for a large number of aromatic compounds. Phenol and cyclohexanol are by far the most important of all these from commercial angle.



Styrene, a very significant chemical used in rubber industry, is also obtained from benzene.



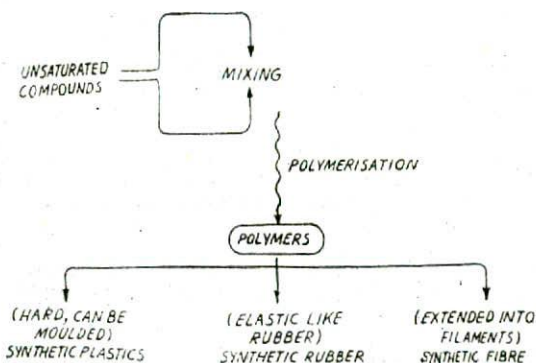
(i) **From xylenes.** Ortho and para xylenes yield a number of useful chemicals such as ethylbenzene, styrene, cumene (isopropylbenzene), dodecylbenzene etc. Phthalic acid and phthalic anhydride are also very important chemicals obtained from xylene.



The chemicals synthesised from petroleum sources are utilised for the industrial production of useful materials required in daily life.

### Polymers as Petrochemicals

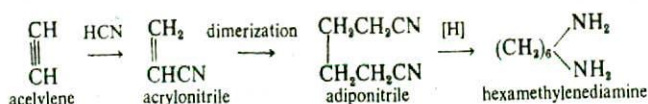
Polymers of varying size and character are obtained by the combination of unsaturated compounds derived from petroleum. These are classified as follows.



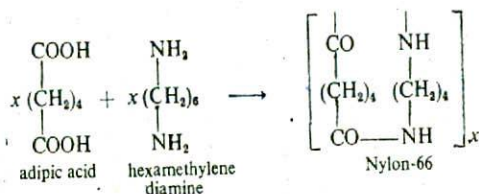
(a) **Synthetic Plastics.** Plastics are high molecular mass substances now manufactured from petroleum sources. They are prepared from synthetic polymers obtained by polymerization and polycondensation of lower alkenes, formaldehyde etc. Polyethylene, polypropylene and formaldehyde plastics are extensively used to prepare various articles by colouring, moulding and stamping.

(b) **Synthetic fibers.** The manufacture of synthetic fibers, again a petroleum product, has revolutionised the textile industry. Light, elastic, mothproof and water proof cloth prepared from such fibers does not require frequent ironing, and dries quickly. Nylon and polyesters are two important synthetic fibers.

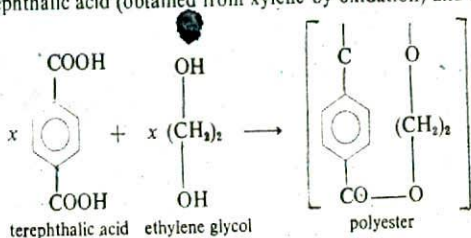
**Nylon-66.** Adipic acid and hexamethylene diamine, required for the manufacture of nylon-66, are petroleum products. While adipic acid is obtained from cyclohexanol, hexamethylene diamine is prepared from acetylene as follows.



Condensation of adipic acid,  $(\text{CH}_2)_4(\text{COOH})_2$ , with hexamethylenediamine produces Nylon-66.

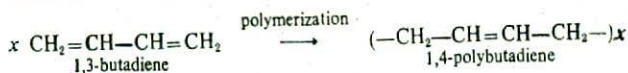


**Polyester Fibers.** These are obtained by the polymerization of two important petrochemicals namely terephthalic acid (obtained from xylene by oxidation) and ethylene glycol.

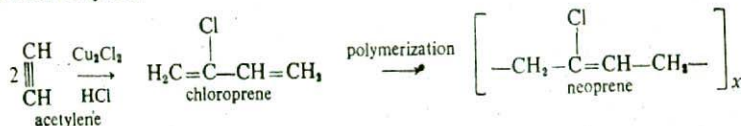


Polyester thus obtained is converted into fibers and marketed as the trade marks **terylene** and **dacron**.

**Synthetic Rubbers.** Butadiene or its derivatives obtained from petroleum sources, polymerize to form rubber. Like elastic polymers **Styrene-Butadiene Rubber (SBR)** is the emulsion polymer of styrene and butadiene. **Butadiene Rubber (BR)** is 1,4-polybutadiene prepared by polymerization of butadiene.



**Neoprene Rubber** is obtained by polymerization of 2-chloro-1, 3-butadiene (chloroprene) available from acetylene.

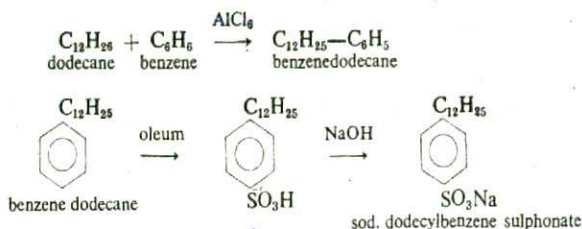


### Synthetic Detergents

A detergent is a modern cleansing agent and is yet another significant petrochemical. Most commonly used detergents are sodium alkylbenzenesulphonates  $\text{R---C}_6\text{H}_4\text{---SO}_3\text{Na}$ , when R is a group containing 10 to 15 carbon atoms. Propene and propylene obtained from



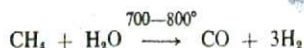
petroleum are polymerized over solid phosphoric acid as catalyst to give dodecane,  $C_{12}H_{26}$ . Benzene and dodecane combine in presence of  $AlCl_3$  to form benzenedodecane. This upon sulphonation yields dodecylbenzene sulphonic acid which when neutralised with  $NaOH$  gives the soluble detergent, sodium dodecylbenzene sulphonate.



### Synthetic Gas ; Fertilisers.

Synthetic gas is the generic name for hydrogen, and for mixtures of hydrogen, carbon monoxide and carbon dioxide in various proportions. It is also a petrochemical obtained from methane. It is used for the synthesis of primary chemicals, ammonia and methyl alcohol.

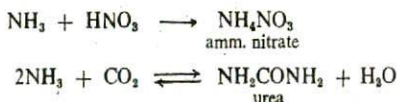
At present 90 per cent of the world's production of hydrogen is based on either fuel oil or refinery gas or natural gas. Thus,



By far the largest use of synthesis gas is the production of ammonia and thence manufacture of nitrogenous fertilisers.



Ammonia when reacted with nitric acid form *ammonium nitrate* and with carbon dioxide it gives *urea*.



Both ammonium nitrate and urea are useful fertilisers.

### Petrochemical Industry in India

Table. Production of Petrochemicals in India (in '000 tonnes)

Products	1970-71	1978-79	1979-80	1980-81	1981-82
<i>Organic Chemicals :</i>					
1. Benzene	53.2	96.8	94.8	79.7	82.7
2. Butadiene	18.2	19.9	21.8	18.1	22.7
3. Butyl Acetate	2.7	4.1	3.8	3.9	4.1
4. Butyl Alcohol	4.2	9.0	8.3	8.8	9.3
5. Diethylene Glycol	0.53	0.61	0.44	0.25	0.34
6. Dichloro Ethane	0.64	0.39	0.34	0.31	0.24
7. Ethylene	59.7	115.8	126.5	139.8	147.8
8. Ethylene Oxide	1.5	13.4	12.1	11.9	11.5
9. Monoethylene Glycol	4.5	8.6	11.8	12.0	15.5
10. 2-Ethyl Hexanol	7.9	9.3	8.6	6.6	6.9
11. Methyl Isobutyl Ketone	1.2	0.54	0.58	0.46	0.44
12. Isopropanol	1.6	2.3	2.0	2.5	1.8
13. Maleic Anhydride	7.9	21.2	23.2	23.1	21.2

Table. Production of Petrochemicals in India (in '000 tonnes)

Products	1970-71	1978-79	1979-80	1980-81	1981-82
<i>Organic Chemicals :</i>					
14. Polyethylene Glycol	0.56	1.2	1.0	1.2	0.64
15. Propylene	5.7	5.6	6.6	7.3	6.8
16. Styrene	—	25.5	22.8	19.5	16.0
17. Toluene	8.3	24.5	23.9	19.0	25.7
18. D.M.T.	—	27.0	27.9	23.1	27.3
19. Ortho-Xylene	—	19.1	18.5	18.1	15.9
20. Para-Xylene	—	14.9	14.6	13.2	12.2
21. Mixed Xylene	—	2.3	3.5	2.8	5.2
22. Vinyl Chloride	—	23.9	19.2	16.7	11.8
23. Caprolactam	—	14.3	13.5	13.1	9.9
24. Carbon Black	—	5.9	5.2	5.9	7.7
25. Linear Alkyl Benzene	—	4.6	13.1	17.1	30.4
26. Acrylonitrile	—	1.8	3.7	9.3	14.0
<i>Synthetic Fibres :</i>					
1. Acrylic fibre	—	0.18	3.5	10.3	13.6
2. Nylon Staple fibre	—	—	—	—	—
3. Nylon Filament yarn	9.3	18.5	17.7	20.8	23.4
4. Nylon Indl. yarn	0.44	8.6	11.2	11.8	14.3
5. Polyester Staple fibre	5.4	25.3	23.6	22.4	29.7
6. Polyester Filament yarn	0.60	7.2	9.0	10.7	15.4
<i>Plastic Raw Materials :</i>					
1. Polyethylene L.D.	24.4	56.0	71.2	87.1	94.3
2. Polyethylene H.D.	21.2	28.1	25.4	24.3	31.7
3. Polystyrene	8.9	14.5	12.0	10.2	7.6
4. P.V.C. Resins	41.4	62.6	50.0	42.0	37.0
5. Polypropylene	—	8.5	13.4	16.7	20.6
6. Moulding Powder	6.2	7.8	8.6	8.1	8.4
<i>Synthetic Rubbers :</i>					
1. Styrene Butadiene Rubber	29.7	23.3	21.6	19.0	17.4
2. Polybutadiene Rubber	—	5.3	8.7	6.5	11.5

A beginning was made by M/s Union Carbide in 1967 near Bombay, producing 20,000 tonnes of ethylene per annum (*pa*). This was consumed to manufacture polyethylene, propylene, benzene, butyl alcohol, etc. A large petrochemical complex, the Indian Petrochemical Corporation Ltd., (IPCL) was set up in Gujarat in 1969. In 1979-80, it produced 27,939 tonnes of DMT, 18,544 tonnes of orthoxylene and 14,589 tonnes of paraxylene. Gujarat Olefins Project commissioned in 1979 produces ethylene (130,000 tpa), propylene (78,300 tpa), butadiene (22,000 tpa), benzene (23,600 tpa) and various organic chemicals listed in Table 1. A new complex at Vadodara in Gujarat has begun production of polyester filament yarn (35,000 tpa). Another petrochemical complex at Bongaigaon (Assam) registered in 1974 is expected to be commissioned this year. It will manufacture 30,000 tpa of polyester fibre and 6,000 tpa of orthoxylene.

### QUESTIONS

- Discuss the possible origin of Petroleum. What is its chemical composition?
- What is implied by the term 'Refining of Petroleum'? What are the various fractions obtained by the fractional distillation of petroleum? Give one use of each.
- Define or explain the following terms :
 

(a) Cracking	(b) Reforming
(c) Knocking	(b) Antiknock compound
(e) Octane number	(f) Aviation gasoline
(g) Synthetic petrol	(h) Fischer-Tropsch process

4. What do you mean by 'Synthetic Petrol'? How can it be obtained from coke by Fischer-Tropsch process?
5. What is Octane Number? A petrol sample produces the same knocking in an internal combustion engine as a mixture of 80% of Isooctane and 20% of *n*-Heptane. What is the Octane Number of the given sample of petrol?

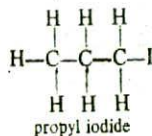
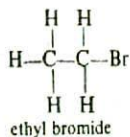
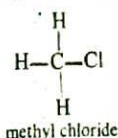
Answer: 80

6. What is petroleum? Describe various theories for its origin in nature. Describe refining of petroleum. Name four different important petrochemicals with their uses. (Magadh BSc Hons, 1993)
7. Write a note on: Refining of petroleum. (Dibrugarh BSc, 1993; Udaipur BSc, 1994)
8. Write a note on: Cracking of petroleum. (Punjab BSc, 1993; Saugar BSc, 1994)
9. Write a note on: Octane number. (Meerut BSc, 1993; Anna BSc, 1994)
10. What is Octane number? How can the octane number of a liquid petroleum-based fuel be increased? (Delhi BSc Hons, 1993; Madras BSc, 1994)
11. From what sources, other than mineral oil, is petroleum obtainable? Describe these methods briefly. What is cracking. How is it different from reforming? (Nehru BSc Hons, 1994)
12. Write a note on: Synthetic petrol (or Synthetic fuel) (Bharathidasan BSc Hons, 1993)
13. Write a note on: Petrochemicals. (Shivaji BSc, 1994)



## Alkyl Halides

Alkyl halides are the derivatives of alkanes in which a hydrogen atom is replaced by a halogen atom (F, Cl, Br or I). They are called alkyl halides because their molecules are made of an alkyl group attached to a halogen atom.

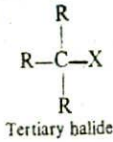
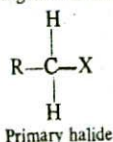


They are represented by the type formula



where R = alkyl group and X = a halogen atom. The reactive halogen atom in them is the functional group.

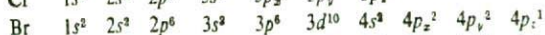
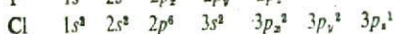
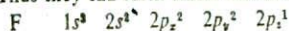
In general we could say that the compounds containing a halogen atom bonded to a saturated carbon are referred to as alkyl halides. These can be divided into three classes according as the halogen is attached to a primary, secondary or tertiary carbon.



Alkyl halides do not occur free in nature and yet they are amongst the most useful of the aliphatic compounds. They are frequently used for introducing alkyl groups into other molecules and thus form the basis for the synthesis of innumerable organic compounds. Alkyl halides are excellent solvents for many organic materials and are much used in industry.

## STRUCTURE

The highly electronegative halogens are only one electron short of a rare gas configuration. Thus they can form stable molecules through the formation of a single covalent bond.



The properties of alkyl halides essentially depend upon the nature and strength of the carbon-halogen bond (C—X). This carbon-halogen bond is formed by the overlapping of a  $sp^3$  hybridized orbital of an alkyl carbon with a half-filled  $p$ -orbital of the halogen. Thus in methyl chloride, the C—Cl bond is formed by the overlapping of a  $sp^3$  hybridized orbital of the methyl carbon with a  $3p_z$  orbital of chlorine as shown in Fig. 14-1.

Let us now compare the bond strength of the various carbon-halogen bonds. It has been shown experimentally that the bond strength falls off as we go from  $\text{CH}_3\text{—F}$  to  $\text{CH}_3\text{—I}$ . This may be visualized on the principle that: *the strongest bonds are formed by the overlaps of orbitals of the same principle quantum number.* Evidently, the C—F bond would be strongest

since here the overlap involves orbitals of the same principle quantum number (second). But on the other hand in  $\text{CH}_3\text{-Cl}$ ,  $\text{CH}_3\text{-Br}$  and  $\text{CH}_3\text{-I}$ , the relatively small  $2sp^3$  orbital of the

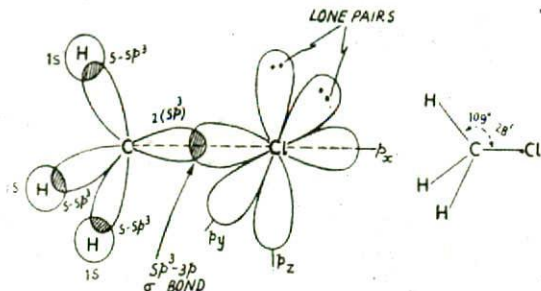


Fig. 14-1. Orbital structure of methyl chloride. Since the carbon in  $\text{CH}_3\text{-Cl}$  is  $sp^3$  hybridized, both  $\angle\text{HCH}$  and  $\angle\text{HCCl}$  are approximately tetrahedral angles. Likewise, the  $\text{C-F}$  bond in methyl fluoride,  $\text{C-Br}$  bond in methyl bromide and  $\text{C-I}$  bond in methyl iodide are formed by similar overlaps of a  $sp^3$  hybridized orbital of the methyl group with  $2p_x$ ,  $4p_z$  and  $5p_z$  orbitals of fluorine, bromine and iodine respectively.

methyl group has to overlap with larger  $3p_x$ ,  $4p_z$  and  $5p_z$  orbitals of chlorine, bromine and iodine respectively. Consequently the bond strengths would fall off as we pass from  $\text{CH}_3\text{-F}$  to  $\text{CH}_3\text{-I}$  since  $2sp^3$  orbital cannot penetrate into the larger  $p$  orbitals sufficiently to form a strong bond. This is illustrated in Fig. 14-2.

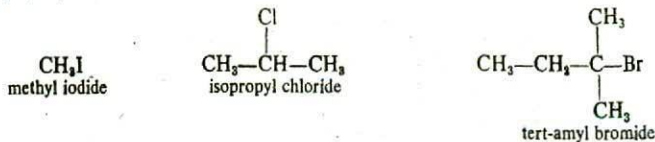
Bond	Bond energy kcal/mole	Bond length ( $\text{\AA}$ )
 	105.4	1.42
 	78.5	1.77
 	65.9	1.91
 	57.4	2.12

Fig. 14-2. Formation of carbon-halogen bonds;  $sp^3$  orbital of carbon-penetrating to different extents into the halogen  $p$  orbital depending upon its size which increases from F to I. Further, as the size of the overlapping orbital increases, the length of the bond formed through their overlaps would also progressively increase. This is in agreement with the increasing bond length of the carbon-halogen bond from  $\text{CH}_3\text{F}$  to  $\text{CH}_3\text{I}$ .

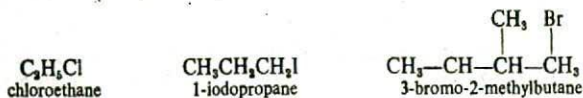
## NOMENCLATURE

More simple alkyl halides are called by the common names while the higher complex members are named by the IUPAC system.

(1) **The Common Names.** These compounds are named as alkyl derivatives of hydrogen halides: HF hydrogen fluoride, HCl hydrogen chloride, HBr hydrogen bromide, and HI hydrogen iodide. Thus the common names of alkyl halides (RX) are two-word names — the name of the alkyl group followed by the separate word fluoride, chloride, bromide or iodide as the case may be. Branched-chain alkyl halides may be distinguished as primary (pri), secondary (sec), or tertiary (tert) where necessary.

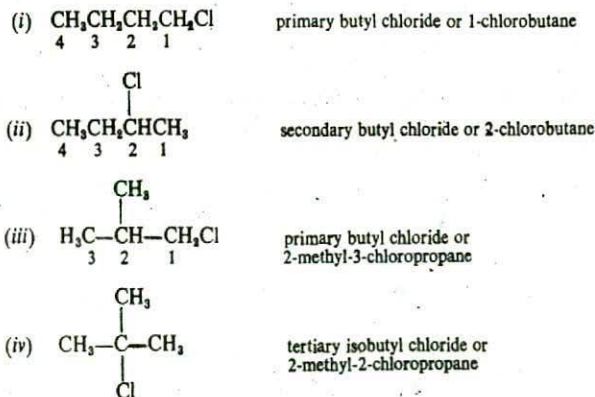


(2) **The IUPAC Names.** According to the IUPAC SYSTEM, alkyl halides are named as monohalogen substituted alkanes. Thus their systematic name is a one-word name obtained by prefixing fluoro, chloro, bromo or iodo directly to the name of the parent hydrocarbon. In complex derivatives, the numeral indicating the position of the halogen atom is prefixed by the conventions of the IUPAC System.



## ISOMERISM

Alkyl halides show chain isomerism and position isomerism which is due to the different positions of the halogen atoms on the carbon chain. Thus butane can give rise to as many as four isomeric monohalogen derivatives.



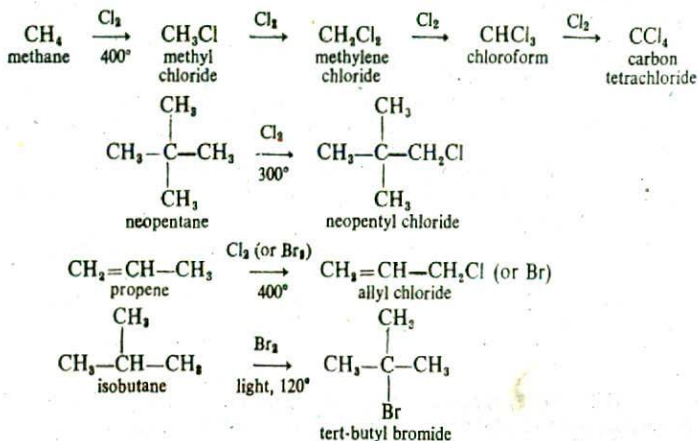
While compound (i) and (ii) illustrate position isomerism, compounds (i) and (iii) present a case of chain isomerism.

## METHODS OF PREPARATION

Alkyl halides can be prepared by the following general methods.

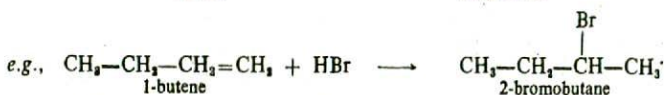
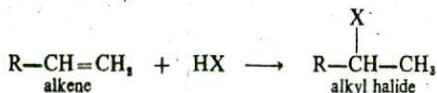
(1) **Direct Halogenation of alkanes.** The lower alkyl chlorides and some bromides are prepared by the *gas phase halogenation* of alkanes in the presence of heat, light or a catalyst. Thus,



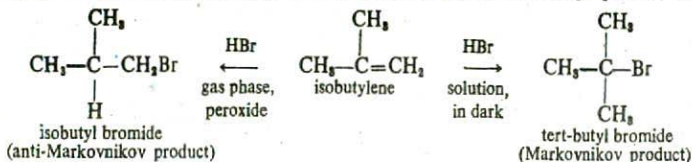


Under the influence of heat or light, halogenation takes place *via* free radical mechanism. Although this method usually gives a mixture of halogen products, it is industrially useful because of its cheapness and also due to the fact that the mixture of the products can be conveniently separated into its individual components by fractional distillation.

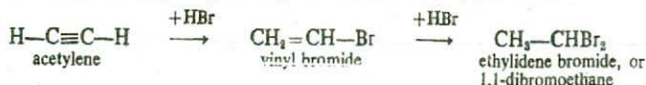
(2) **Addition of Hydrogen halides to alkenes and alkynes.** Alkyl halides may be prepared by the addition of hydrogen halides HX (X=Cl, Br, I) to alkenes and alkynes (in the dark, at low temperature, in solution).



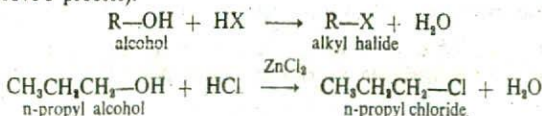
The addition of halogen halides follows Markovnikov Rule. However, in the presence of peroxide (high temperature, gas phase), anti-Markovnikov product can be prepared. Thus,



Addition of HX to alkynes gives vinyl halides and then 1, 1-dihalides.

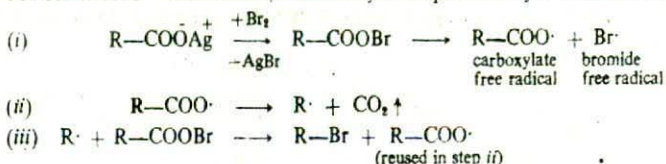


(3) **Action of Hydrogen halides on alcohols.** Alkyl bromides and iodides are prepared by the action of the respective hydrogen halide (HBr or HI) on an appropriate alcohol. Alkyl chlorides are produced by the action of concentrated HCl in the presence of anhydrous zinc chloride as catalyst (Grove's process).





MECHANISM. Hunsdiecker decarboxylation proceeds by a free-radical mechanism.



### PHYSICAL PROPERTIES

(1) The lower alkyl halides are gases at room temperature:  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{CH}_2\text{F}$ ,  $\text{CH}_3\text{CH}_2\text{Cl}$ . All other alkyl halides up to about  $\text{C}_{15}$  are liquids.

(2) Alkyl halides are colourless when pure and have a pleasant sweetish odour. Those beyond  $\text{C}_{18}$  are generally odourless solids.

(3) Although they are slightly polar, alkyl halides are insoluble in water because of their inability to form hydrogen bonds. They are readily soluble in organic solvents.

(4) The alkyl iodides and bromides are heavier than water, while the alkyl chlorides and fluorides are lighter than water and float over it. The specific gravities go on falling with increasing molecular weight.

(5) Alkyl halides are generally quite toxic substances and need be handled with care.

(6) The boiling points of alkyl halides are much higher than those of alkanes with the same carbon skeleton. In general, the boiling points rise with increase of molecular weight, and decrease with branching of alkyl group. For the various types of alkyl halides, the boiling points are in the order  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ .

Table. Physical Properties of some Alkyl halides

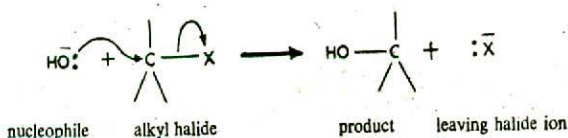
Name	Formula	mp °C	bp °C	sp gr (liq)
Methyl fluoride	$\text{CH}_3\text{F}$	-79	-14.2	0.877
Methyl chloride	$\text{CH}_3\text{Cl}$	-97	-23.7	0.920
Methyl bromide	$\text{CH}_3\text{Br}$	-93	4.60	1.732
Methyl iodide	$\text{CH}_3\text{I}$	-64	42.3	2.279
Ethyl chloride	$\text{CH}_3\text{CH}_2\text{Cl}$	-139	13.1	0.910
Ethyl bromide	$\text{CH}_3\text{CH}_2\text{Br}$	-119	38.4	1.430
n-Propyl chloride	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	-123	46.4	0.890
Isopropyl chloride	$\text{CH}_3\text{CHClCH}_3$	-117	36.5	0.860
n-Butyl bromide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	-112	101.6	1.275
Isobutyl bromide	$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$	-120	91.3	1.250
sec-Butyl bromide	$\text{CH}_3\text{CH}_2\text{CHBrCH}_3$	-	91.0	0.871
tert-Butyl bromide	$(\text{CH}_3)_3\text{CBr}$	-20	73.3	1.222

### CHEMICAL PROPERTIES

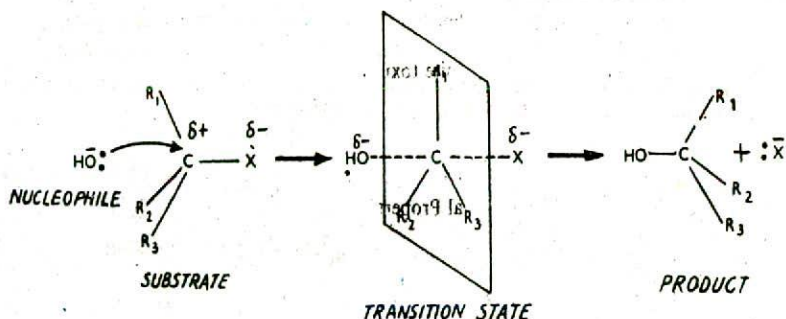
In alkyl halides ( $\text{R}-\text{X}$ ), the carbon of the alkyl group is directly bonded to halogen and the  $\text{C}-\text{X}$  group constitutes the functional group. Halogens being of greater electronegativity than carbon, the  $\text{C}-\text{X}$  bond is slightly polarised ( $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{X}}$ ). Thus reagents as are more basic (negative)



than the halogen atom can attack the positively charged carbon with the ejection of a halide ion. Such bases are nucleophiles capable of donating electron pair, and thus nucleophilic substitution reactions are characteristic of alkyl halides. For example, in the following reaction the stronger nucleophile  $\text{HO}^-$  displaces the weaker nucleophile  $\text{X}^-$  from the carbon nucleus of the alkyl halide.



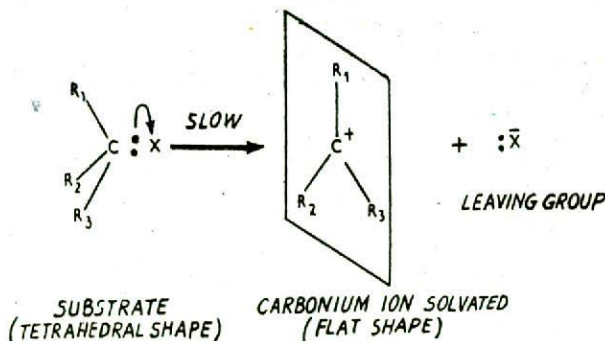
We have already studied in the chapter on Reaction Mechanisms that the above nucleophilic reactions are of two types  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$ .  $\text{S}_{\text{N}}2$  reactions are those in which the attack of the nucleophile and the ejection of the halide ion ( $\text{X}^-$ ) take place simultaneously. The reactants on their way to products pass through a transition state where the  $\text{C}-\text{OH}$  bond is 'half formed' and  $\text{C}-\text{X}$  bond is 'half broken'.



It may be noted that in  $\text{S}_{\text{N}}2$  reactions, the attack of the nucleophile takes place from the side opposite to that of the leaving group  $\text{X}^-$ . Therefore such a reaction proceeds with inversion of configuration.

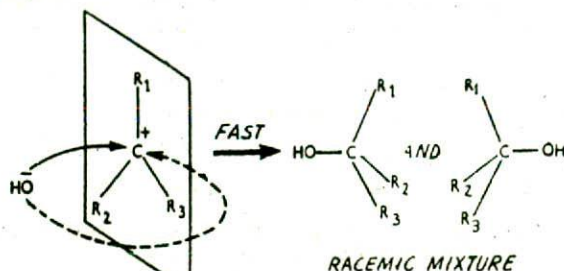
On the other hand  $\text{S}_{\text{N}}1$  reaction takes place in two steps. In the first step the alkyl halide forms a carbonium ion by removal of the leaving group by solvation.

First Step :

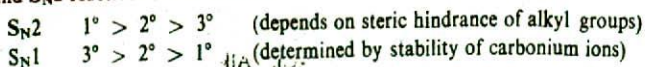


In the second step the nucleophile attacks the electron-deficient carbon from either side of the planar carbonium ion. The products are, therefore, racemic mixtures.

Second Step :



The order of reactivity of the primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) alkyl halides towards  $S_N1$  and  $S_N2$  reactions are as follows.



Thus primary alkyl halides normally undergo substitution by  $S_N2$  mechanism, tertiary by  $S_N1$  mechanism, and secondary by both  $S_N2$  and  $S_N1$  mechanisms.

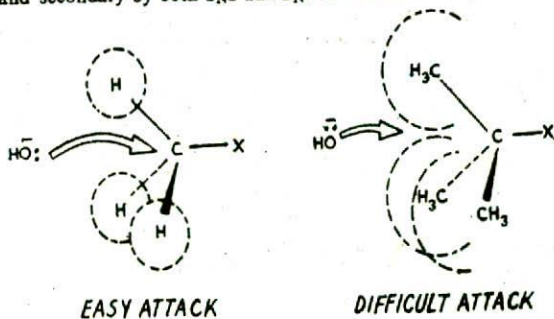


Fig. 14.3 How steric hindrance of  $\text{CH}_3$  groups makes the attack of nucleophile ( $-\text{OH}$ ) difficult; the dotted circles indicate the effective size of the group.

The nature of the leaving group also affects the rate of  $S_N1$  or  $S_N2$  reaction. The order of displacement of X in RX by stronger nucleophile is in the order :

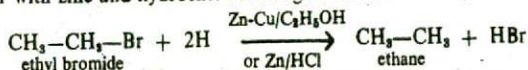


The general reactions of alkyl halides will be discussed under the following headings.

- (A) Reduction ; (B) Nucleophilic substitution reactions ;  
(C) Elimination reactions ; (D) Reactions with Metals.

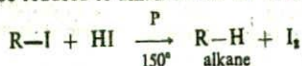
It will be noted that alkyl halides are the most valuable and versatile synthetic reagents since almost all classes of organic compounds can be prepared from them.

(A) **Reduction of Alkyl halides.** Alkyl halides on reduction with Zn-Cu couple and alcohol or with zinc and hydrochloric acid give alkanes. Thus,

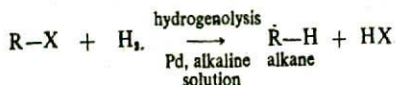


Lithium aluminium hydride can also bring about the reduction of alkyl halide to alkane.

Alkyl iodides may be reduced to alkanes with HI and red phosphorus at  $150^\circ$ .

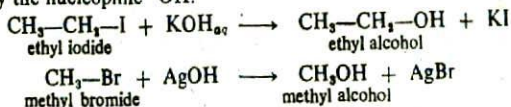


Catalytic hydrogenolysis offers a better procedure for reducing alkyl halides to the respective alkanes.

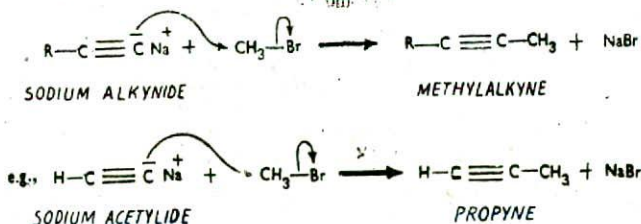


(B) **Nucleophilic Substitution reactions.** As already discussed, these are the reactions in which the substituting agent is a nucleophile. Some such reactions will be concisely described as follows.

(1) **Substitution by hydroxyl group.** When treated with aqueous potash or silver oxide suspended in boiling water, alkyl halides are hydrolysed to form *alcohols*. Here the halogen is substituted by the nucleophile  $-\text{OH}$ .

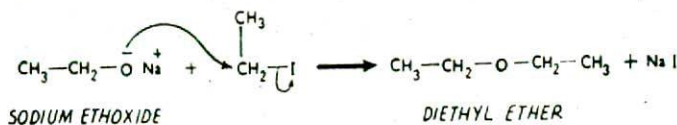


(2) **Substitution by alkynyl group ( $\text{R-C}\equiv\text{C}$ ).** Alkyl halides react with sodium acetylides to form *higher alkynes*. Thus,

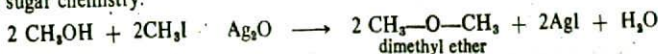


This reaction occurs by  $\text{S}_{\text{N}}2$  mechanism with primary alkyl halides and by  $\text{S}_{\text{N}}1$  mechanism with tertiary alkyl halides.

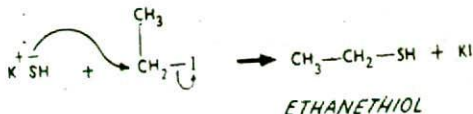
(3) **Substitution by alkoxy group.** Alkyl halides on treatment with metal alkoxides ( $\text{R-ONa}$ ) produce *ethers*. This method of preparation of ethers is often referred to as **Williamson Synthesis**. Thus,



A modification of this method involves the reaction of an alkyl halide and alcohol in presence of dry silver oxide. This method is known as **Purdie method of alkylation** and is quite useful in sugar chemistry.

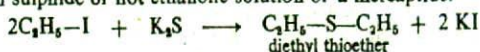


(4) **Substitution by thiol group (SH).** Alkyl halides react with ethanolic potassium hydrogen sulphide to form *thiols*. Thus,





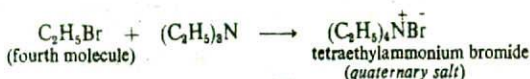
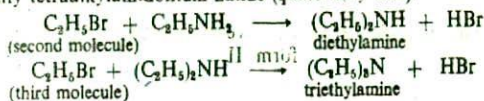
(5) **Substitution by thioether group (—S—).** Thioethers are produced when alkyl halides react with potassium sulphide or hot ethanolic solution of a mercaptide.



(6) **Substitution by amino group (—NH<sub>2</sub>).** Alkyl halides when treated with ethanolic ammonia under pressure give *primary amines*.

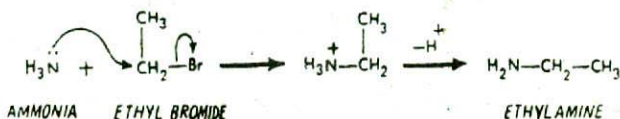


If excess of alkyl halide is used, the reaction continues to form secondary amine, tertiary amine and finally tetraalkylammonium halide (*quaternary salt*).

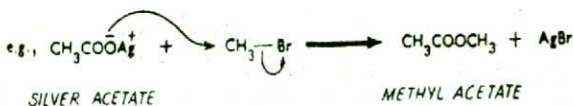
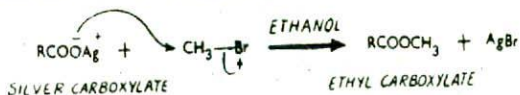


Primary alkyl halides give a good yield of amines. Secondary (except isopropyl halide) and tertiary halides preferentially undergo elimination to form alkenes.

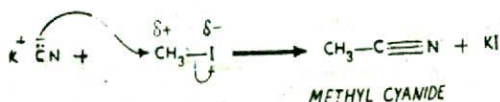
**MECHANISM.** This reaction probably follows S<sub>N</sub>2 mechanism.



(7) **Substitution by an ester group, (RCOO—).** When heated with ethanolic solution of silver salt of carboxylic acids, alkyl halides yield *esters*.

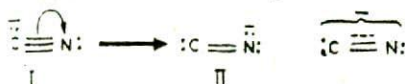


(8) **Substitution by a Cyano or Isocyano group.** With ethanolic potassium cyanide, an alkyl halide gives the corresponding alkyl cyanide (or nitrile) as the chief product along with a small amount of alkyl isocyanide. This involves the nucleophilic attack of the cyanide ion on the alkyl halide

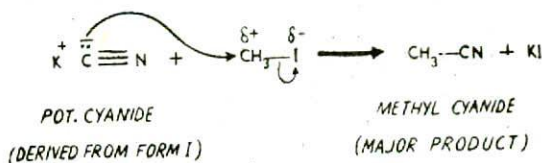


The reaction proceeds either by S<sub>N</sub>1 or S<sub>N</sub>2 mechanism

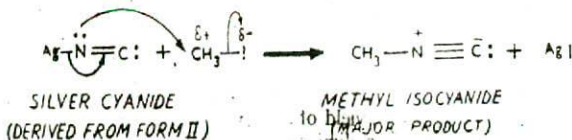
Cyanide is an ambident ion and has two nucleophilic sites as shown below.



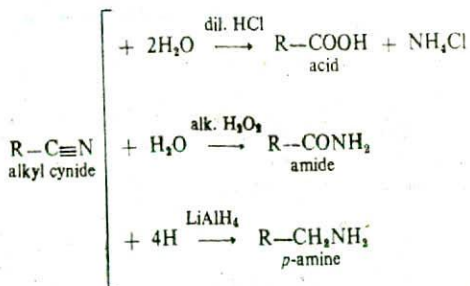
Therefore, cyanides can attack the positive carbon of the alkyl group either through carbon (form I) or nitrogen (form II) to form alkyl cyanides or alkyl isocyanides respectively. Thus with alkali metal cyanides (KCN) it is the form I that reacts with alkyl halides to give alkyl cyanides as the major product.



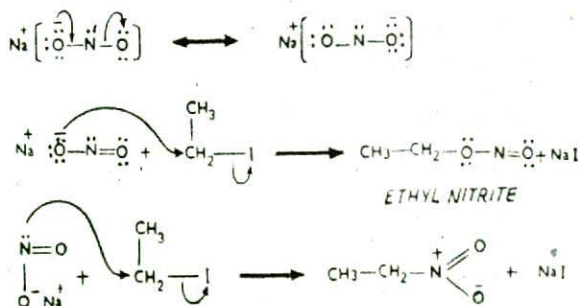
Unlike alkali metal cyanides which are ionic, silver cyanide is predominantly covalent and hence reacts with the alkyl halides through form II to produce alkyl isocyanides as the major product.



Alkyl cyanides are very useful synthetic reagents since they can be conveniently converted into acids, amides and amines.



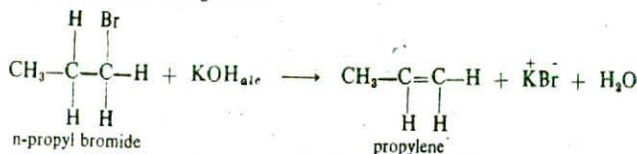
(9) **Substitution by a nitrite or a nitro group.** The nitrite ion, like the cyanide ion, is an ambident ion and its nucleophilic attack on an alkyl halide can yield either an *alkyl nitrite* or a *nitroalkane* according as the attack on alkyl halides takes place through oxygen or nitrogen.



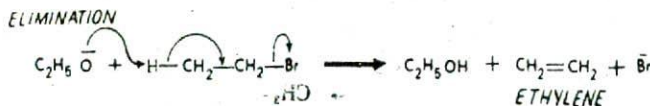
Thus with  $\text{NaNO}_2$  or  $\text{KNO}_2$  alkyl nitrites are obtained while with  $\text{AgNO}_2$  nitroalkanes are produced.

(10) **Substitution reaction with malonic and acetoacetic ester.** Sodium salts of malonic and acetoacetic esters react with alkyl halides to form *alkyl-substituted malonic* and *acetoacetic esters* respectively. These in turn can be converted into a variety of organic compounds.

(C) **Elimination Reactions.** Alkyl halides on treatment with ethanolic KOH are converted into alkenes. This elimination reaction in which HBr is removed from the alkyl halide molecule is termed *dehydrohalogenation*.



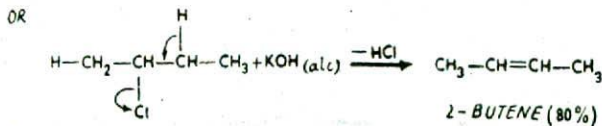
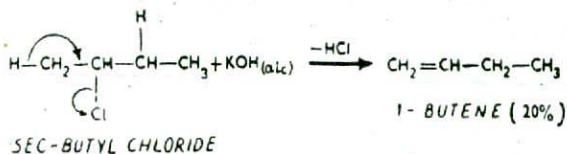
Actually, potassium hydroxide (which contains some  $\text{C}_2\text{H}_5\text{OK}$ ) favours both elimination and substitution reactions. There is always a competition between elimination and substitution reactions. For example, ethyl bromide on treatment with alcoholic KOH can give either ethylene or diethyl ether.



The ratio of the elimination to substitution product depends upon the structure of the alkyl halide taken as also the experimental conditions. Thus with ethanolic KOH, ethyl bromide produces only 10% of ethylene while the major product is diethyl ether. Isopropyl bromide on the other hand, gives 80% of propylene while tert-butyl bromide yields 100% of isobutylene. Thus tertiary alkyl halides are most suitable for the preparation of alkenes.

Primary and secondary alkyl halides undergo dehydrohalogenation by E2 (elimination, bimolecular) while tertiary alkyl halides do so by E1 (elimination, unimolecular) mechanism.

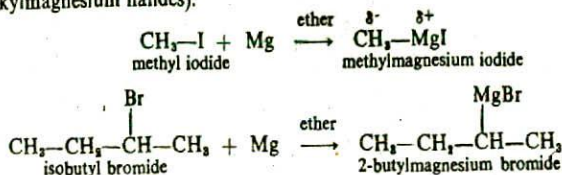
If structure of the alkyl halide is such that it permits the formation of more than one alkene, then according to *Saytzeff Rule* the most substituted alkene predominates. Thus sec-butyl chloride produces 80% of 2-butene and 20% of 1-butene.



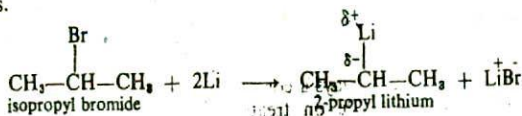


(D) **Reactions with Metals (Metallation).** Alkyl halides react with a number of metals to form organometallic compounds.

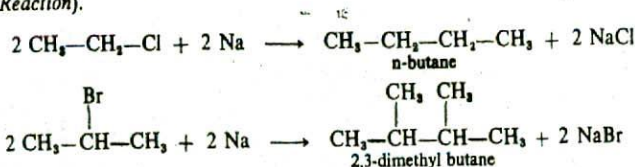
(i) *With Magnesium.* They react with magnesium in ether solution to form Grignard reagents (alkylmagnesium halides).



(ii) *With Lithium,* alkyl halides give lithium alkyls which are more reactive than Grignard reagents.



(iii) *With Sodium,* alkyl halides do not give isolable metal organic compounds. Rather, a coupling reaction takes place to produce symmetrical alkanes with double the number of carbon atoms (*Wurtz Reaction*).



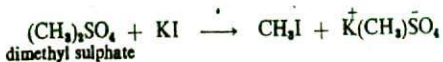
### METHYL IODIDE, *Iodomethane*, $\text{CH}_3\text{I}$

It is prepared both in the laboratory and industrially :

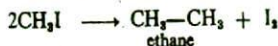
(1) by warming a mixture of methyl alcohol, red phosphorus and iodine.



(2) By the action of dimethyl sulphate on potassium iodide solution in presence of calcium carbonate.



**Properties and Uses.** Methyl iodide is a sweet smelling liquid, bp  $42.5^\circ$ ; sp gr 2.27. When freshly prepared it is colourless but becomes brown on standing which is due to its decomposition to iodine.

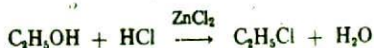


Since it is a liquid, it is easier to handle than methyl chloride (a gas) and is used a great deal as a methylating agent in the laboratory organic syntheses.

### ETHYL CHLORIDE, *Chloroethane*, $\text{C}_2\text{H}_5\text{Cl}$

It can be prepared :

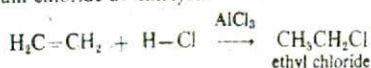
(1) By passing dry HCl gas into ethyl alcohol in the presence of zinc chloride (*Grove's method*).



(2) By the chlorination of ethane at about 400°C (Industrial).



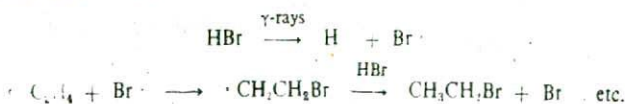
(3) By the addition of hydrogen chloride to ethylene (from cracked petroleum) in the presence of aluminium chloride as catalyst.



**Properties and Uses** Ethyl chloride is a pleasant smelling liquid, bp 12.5° and sp g. 0.921 at 20°. It is used: (i) as a refrigerant and local anaesthetic; (ii) in the preparation of ethyl cellulose, tetraethyllead and sulphonal; and as ethylating agent.

### ETHYL BROMIDE, *Bromoethane*, $C_2H_5Br$

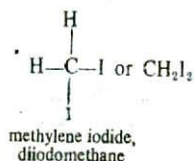
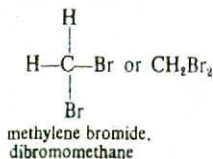
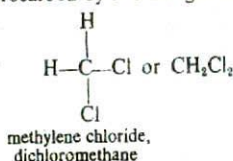
It is manufactured by irradiating a mixture of ethylene and hydrogen bromide with  $\gamma$ -radiation obtained from a cobalt-60 source.



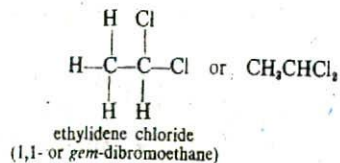
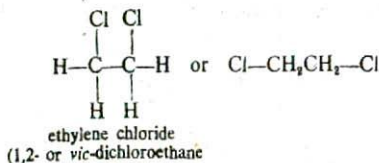
Ethyl bromide boils at 39.5°C and is used for preparing barbiturate drugs

## DIHALOGEN DERIVATIVES

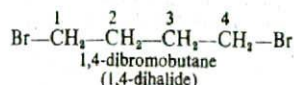
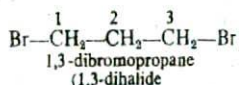
Dihalogen derivatives are compounds obtained by replacing two hydrogen atoms of a hydrocarbon by two halogen atoms. Thus methane forms:



In higher members, the two halogens may be linked to the same or different carbon atoms.



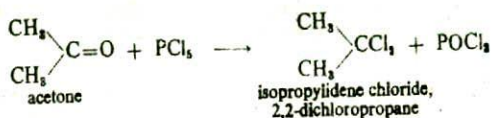
The dihalides having two halogens on the same carbon are called 1,1-dihalides (or *gem*-dihalides) and those having the halogens on different carbons are called 1,2-dihalides (or *vic*-dihalides). Similarly we have 1,3-, 1,4-, 1,5-dihalides etc., depending on the location of halogens on the carbon chain. Thus,



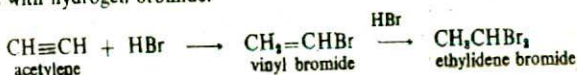
## METHODS OF PREPARATION

1,1-Dihalides may be prepared:

(1) By the action of phosphorus pentahalides on aldehydes or ketones. For example, acetone gives isopropylidene chloride on treatment with  $PCl_5$ .



(2) By the addition of halogen halides to alkynes. Thus ethylidene bromide is formed when acetylene reacts with hydrogen bromide.

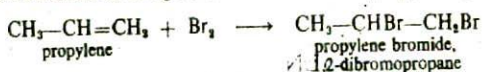


(3) By further halogenation of monohalogen derivatives and reduction of tri- and tetra-halogen derivatives. For example,

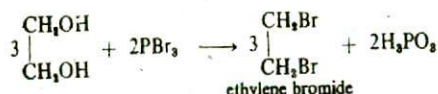
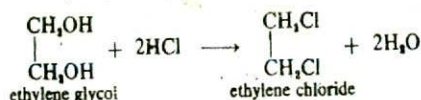


1,2-Dihalides may be prepared :

(1) By the addition of halogens to alkenes. Thus propylene gives propylene bromide.



(2) By the action of hydrogen halides or phosphorus halides on glycols.



## PHYSICAL PROPERTIES

(1) They are sweet smelling colourless liquids, having comparatively high boiling points. Highest members are solids.

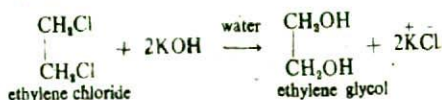
(2) They are in general heavier than water. Methylene iodide is the densest organic liquid known, its density being 3.325.

(3) They are insoluble in water and soluble in organic solvents.

## CHEMICAL PROPERTIES

Chemically the dihalides are similar to monohalogen derivatives, giving all the reactions of the halogen atom in duplicate. They, however, differ from the latter in certain reactions in which both the halogens are involved together. Besides the usual reactions of alkyl halides, they give the following typical reactions.

(1) **Hydrolysis with aqueous alkalis.** 1,2-Dihalides upon heating with aqueous KOH give the respective glycols. Thus,







**CHLOROFORM, Trichloromethane, CHCl<sub>3</sub>**

The name chloroform was given to trichloromethane by Dumas who established that its molecule contained chlorine in union with 'formyl', an old name for CH≡ group.

**Preparation.** (1) By heating ethanol or acetone with bleaching powder, Ca(ClO)Cl. The bleaching powder provides chlorine and the reaction takes place in three stages. Thus the formation of chloroform from ethanol occurs as follows.

(i) Oxidation of ethanol to acetaldehyde.



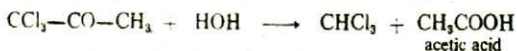
(ii) Chlorination of acetaldehyde to chloral.



(iii) Hydrolysis of chloral by lime present in bleaching powder to form calcium formate and chloroform.

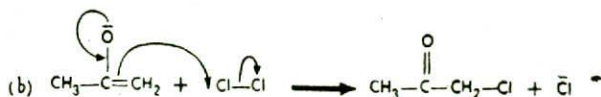
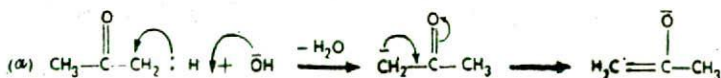


With acetone as the starting material, the conversion into chloroform takes place by similar steps.

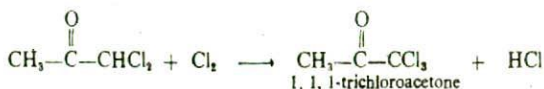
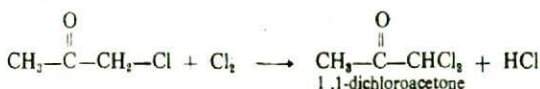


**MECHANISM.** The formation of chloroform from acetone involves the following steps.

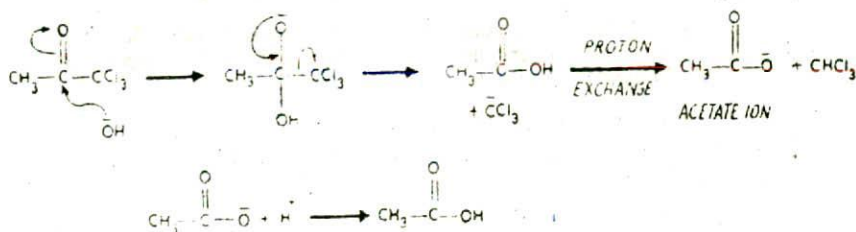
(i) Base induced chlorination of acetone to form trichloroacetone.



Further chlorination by similar steps gives dichloroacetone and then trichloroacetone.



(ii) Trichloroacetone from step (i) undergoes nucleophilic attack by OH<sup>-</sup> ion on carbonyl carbon to produce chloroform and acetic acid according to the following sequence of reactions.



Similarly, base induced chlorination of acetaldehyde (produced by oxidation of ethanol by chlorine) to chloroacetaldehyde followed by alkaline hydrolysis yields chloroform and formic acid.

(2) Chloroform is also prepared on a large scale by the reduction of carbon tetrachloride with water and iron.

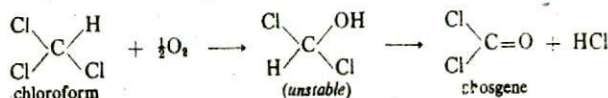


(3) Pure chloroform is obtained by treatment of chloral with aqueous alkali.



**Properties.** (Physical). Chloroform is colourless liquid having a peculiar sickly smell and a sweetish burning taste, bp 61°, sp gr 1.485. It is practically insoluble in water but soluble in most organic solvents. It acts as a solvent for many organic substances such as oils, fats and waxes. Chloroform vapour when inhaled causes temporary unconsciousness and hence its use as anaesthetic.

(Chemical). (1) **Oxidation.** (a) In the presence of light, chloroform is oxidised slowly by the oxygen of air to form carbonyl chloride or *phosgene*.

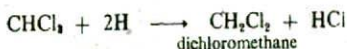


Since phosgene is highly poisonous, chloroform intended for medical purposes is stored in dark blue or brown bottles filled up to the stopper, kept away from the light. It is usual also to add about one per cent ethanol to discourage the formation of phosgene.

(b) Fehling solution oxidises chloroform when a red deposit of copper (I) oxide is produced.

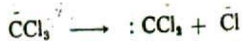
(c) It is not inflammable but when a Bunsen burner is played on to the liquid chloroform it vaporises and burns with a green-edged flame.

(2) **Reduction.** Nascent hydrogen generated by the action of zinc on ethanolic hydrogen chloride, reduces chloroform to dichloromethane.

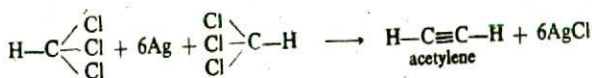




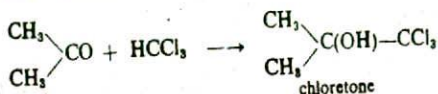




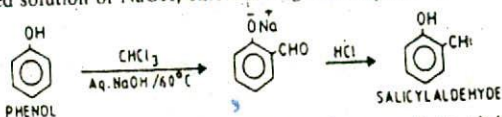
(6) **Dehalogenation.** When warmed with silver powder, chloroform gives acetylene.



(7) **Condensation with Acetone.** Chloroform undergoes condensation with acetone in the presence of alkali to form *chloroform* which is used as a hypnotic.



(8) **Action with Phenol and Sodium hydroxide (Reimer Tiemann Reaction).** When heated with concentrated solution of NaOH, chloroform gives salicylaldehyde.



Uses. (1) Chloroform is to some extent used as anaesthetic; it has fallen into disrepute as slight overdoses are dangerously toxic; (2) It is used as a solvent for fats and iodine; (3) As a reagent for testing primary amines; and (4) It is added to decomposable organic materials to prevent putrefaction.

### IODOFORM, Triiodomethane, CHI<sub>3</sub>

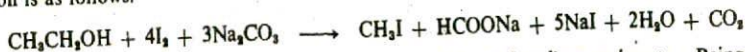
From its structural similarity to chloroform, it was named Iodoform by Dumas. Its methods of preparation and properties are analogous to those of chloroform.

**Preparation.** (1) By the action of iodine and alkali upon ethanol or acetone.



The mechanism of the reaction is the same as described under chloroform.

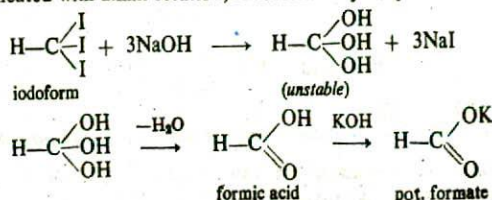
Sodium carbonate can also be used in place of KOH. With sodium carbonate, the overall reaction is as follows.



(2) *By the electrolysis of a solution of ethanol, an iodide and sodium carbonate.* Being a cheaper method it is used for the industrial preparation of iodoform. The solution is maintained at 60–70°. During electrolysis iodine is set free at the anode and sodium hydroxide at the cathode which is subsequently converted into sodium carbonate by passing a current of carbon dioxide. These substances then react with ethanol or acetone to form iodoform.

**Properties.** Iodoform is a yellow crystalline solid, mp 119°. It has a characteristic unpleasant smell. It is insoluble in water but dissolves readily in ethanol, chloroform and ether. Chloroform has marked antiseptic action.

In chemical properties, iodoform resembles chloroform. It is, however, less stable than the latter. When heated with alkali solution, iodoform is hydrolysed to a formate.

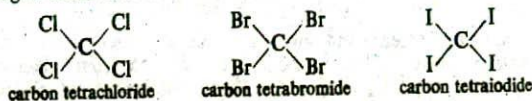


Iodoform also undergoes the carbylamine reaction. When warmed with a mixture of aniline and ethanolic KOH solution, it reacts in a manner analogous to the corresponding reaction of chloroform.

Iodoform at one time was extensively used as antiseptic for dressing wounds, but now it has been almost entirely superseded by more efficient compounds.

### TETRAHALOGEN DERIVATIVES

The tetrahalogen derivatives of methane are the compounds which contain carbon linked to four halogen atoms and are named as **Carbon tetrahalides**.



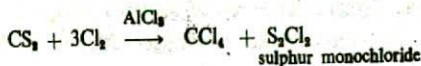
Of these, carbon tetrachloride is important industrially.

#### CARBON TETRACHLORIDE, *Tetrachloromethane*, $\text{CCl}_4$

**Preparation.** It is prepared on industrial scale: (1) By chlorination of methane,



(2) By the action of chlorine on carbon disulphide ( $\text{CS}_2$ ) in the presence of aluminium chloride as a catalyst.

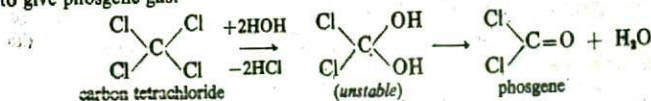


The products of this reaction, both of which are liquids, are separated by fractional distillation.

**Properties.** (*Physical*). Carbon tetrachloride is a colourless liquid, bp 77°C. It is insoluble in water but soluble in all organic solvents. It is an excellent solvent for fatty substances. For this reason it finds use as cleaning agent for removing stains from cloth. It is not flammable and hence was used as a fire extinguisher (Pyrene). When a spray of the liquid is directed at the fire, its dense vapours prevent the oxygen of air from reaching the burning articles. However, carbon tetrachloride is toxic and also forms phosgene ( $\text{COCl}_2$ ). For this reason, it is no longer used in fire extinguishers. Carbon tetrachloride has been used in the treatment of hookworm and tapeworm.

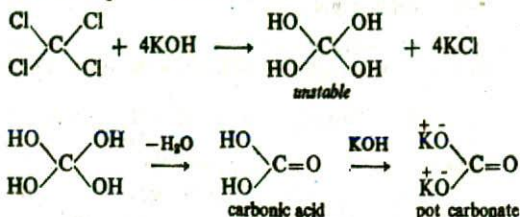
(*Chemical*). Carbon tetrachloride is relatively inert substance. It gives the following reactions.

(1) *Action with Steam.* Its vapours when mixed with steam react at high temperature to give phosgene gas.





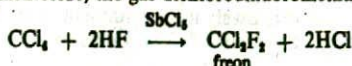
(2) *Action with Alkalis.* When boiled with ethanolic KOH solution, carbon tetrachloride is hydrolysed to form potassium carbonate.



(3) *Reduction.* Carbon tetrachloride can be reduced by moist iron filings to chloroform. This is an industrial method for the preparation of chloroform.



(4) *Action with HF.* When hydrogen fluoride is passed into carbon tetrachloride in presence of antimony pentachloride, the gas dichlorodifluoromethane is obtained.

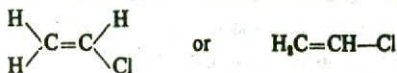


This gas (freon) is widely used as operating fluid for refrigerators and in air-conditioning equipment.

## UNSATURATED HALOGEN DERIVATIVES

They are the derivatives of alkenes and alkynes in which one or more hydrogen atoms have been replaced by halogen atoms. The mono-halides derived from alkenes are called *Alkenyl halides* e.g., vinyl chloride,  $\text{CH}_2=\text{CH}-\text{Cl}$ . Those obtained from alkynes are called *Alkynyl halides* e.g., propargyl chloride,  $\text{CH}\equiv\text{C}-\text{CH}_2\text{Cl}$ .

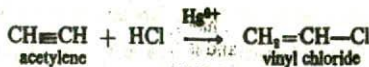
**VINYL CHLORIDE, Chloroethene,**



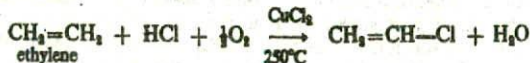
It is the most important of the unsaturated halogen derivatives.

**Preparation.** Vinyl chloride can be prepared industrially:

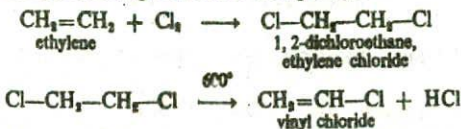
(1) By the controlled addition of hydrogen chloride in the presence of mercury salts as catalyst.



(2) By passing a mixture of ethylene, hydrogen chloride and oxygen at 250°C over copper (II) chloride.



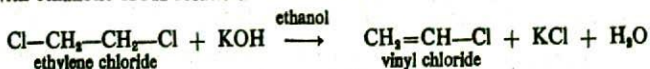
(3) By addition of chlorine to ethylene in the liquid or vapour phase to form 1, 2-dichloroethane and then heating it at 600°C over pumice.



By operating the processes (2) and (3), the HCl reduced in process (3) can be utilised in (2).

## Alkyl Halides

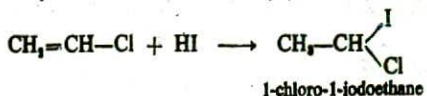
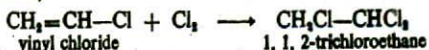
(3) In the laboratory, vinyl chloride can conveniently be prepared by heating ethylene chloride with ethanolic KOH solution.



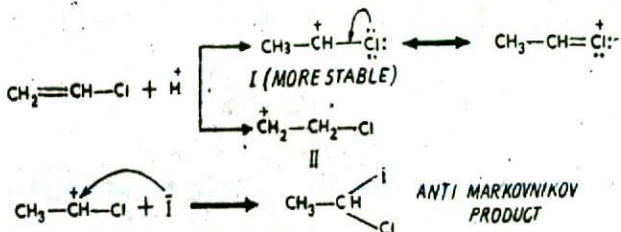
**Properties.** Vinyl chloride is a colourless gas under ordinary conditions. Liquid substance boils at  $-13.9^\circ$ .

The reactions of vinyl chloride are those of the two functional groups present in its molecule viz., (i) carbon-carbon double bond; (ii) the chlorine atom attached to the doubly bonded carbon.

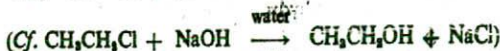
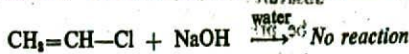
(1) *Reactions of Carbon-Carbon Double bond.* Vinyl chloride gives the usual electrophilic reactions of alkenes. Thus,



The addition of HI takes place in accordance with Markovnikov Rule. This can be attributed to the greater stability of the intermediate carbonium ion I rather than II.



(2) *Reactions of Chlorine atom.* The reactions of vinyl chloride at the chlorine atom are strikingly different from those of alkyl chlorides. It does not react with nucleophilic reagents giving substitution products. For example, it is not hydrolysed by sodium hydroxide.



The reason for the non-reactivity of the halogen atom is that the C-Cl bond in vinyl chloride is stronger than one in alkyl chloride, and is therefore less readily broken. This is so because a *p* orbital on chlorine interacts with the *p* orbital on the adjacent carbon atom. The new delocalized orbital permits the movement of the unshared electrons of the *p* orbital of the halogen atom and those of the  $\pi$  orbital of the double bond. Or that, the C-Cl bond becomes slightly stronger than in alkyl chloride. Also, the delocalization of electrons makes the chlorine atom slightly less negative and the adjacent carbon slightly more negative. This makes the

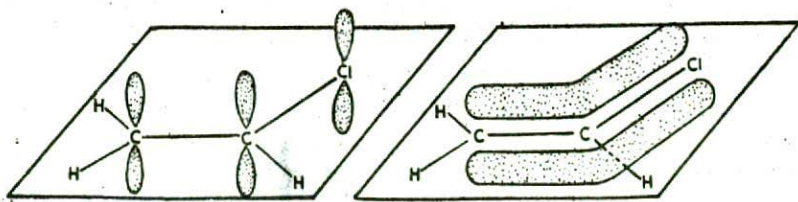
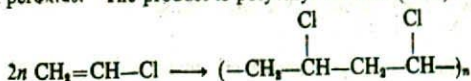


Fig. 14.4. Delocalized  $\pi$  orbital in Vinyl chloride.

carbon holding the chlorine less prone to nucleophilic attack. Hence the nonreactivity of Cl of vinyl chloride in respect of nucleophilic substitution reactions.

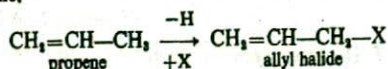
(3) **Polymerization to PVC.** Vinyl chloride polymerizes when heated in an inert solvent in presence of dibenzoyl peroxide. The product is polyvinyl chloride (PVC).



PVC is a very tough polymer and a plasticiser (esters of phthalic acid) is added to soften it. PVC is easy to colour. It is resistant to fire and chemicals, and is a good electrical insulator. It is used for making hundreds of products such as insulator for cables, artificial leather (e.g., car upholstery, shoe soles), raincoats, table cloth, curtains, gramophone records and floor coverings.

### ALLYL HALIDES, 3-Halopropenes, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$

Allyl halides form another type of alkenyl halides. These may be regarded as monohalogen derivatives of propene.



Unlike vinyl halides, these are more reactive and are therefore more frequently employed in organic syntheses. The orbital representation of an allyl halide is as follows.

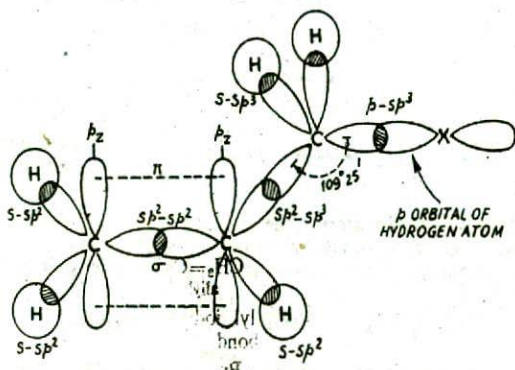
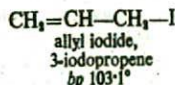
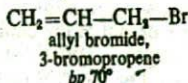
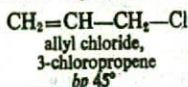


Fig. 14-5. Orbital picture of an Allyl halide; only one (bonding) orbital of the halogen atom has been depicted.

The three allyl halides with their boiling points are:

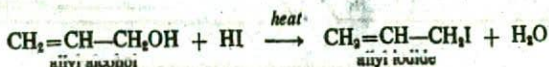


Of these three unsaturated halides, allyl iodide is more important because of its ease of formation and greater reactivity towards nucleophilic displacement reactions.

### ALLYL IODIDE, 3-Iodo-1-propene, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{I}$

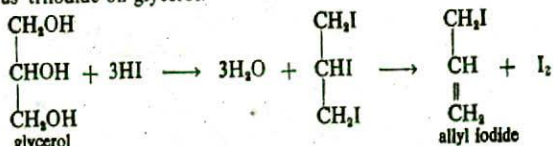
Allyl iodide is a typical allyl halide.

**Preparation.** (1) It can be prepared by the addition of concentrated hydriodic acid (HI) on allyl alcohol.



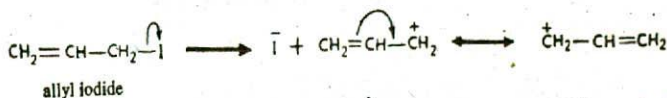


(2) Allyl iodide is generally prepared by the action of small amount of hydrogen iodide or phosphorus triiodide on glycerol.

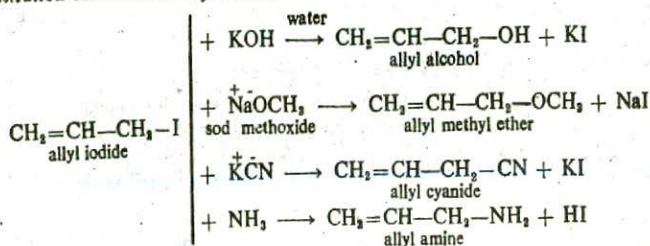


**Properties.** Allyl iodide is a colourless liquid with a garlic odour, bp 103.1°.

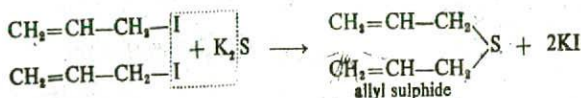
It gives the reactions of both an alkene and an alkyl halide. In contrast to vinyl halides, which are characteristically inert, the allyl halides are very reactive. This extraordinary reactivity of allyl iodide may be explained by the fact that its ionization gives a carbonium ion which is resonance stabilized.



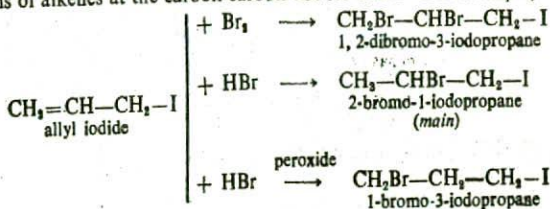
(1) *Substitution Reactions of Iodine atom.* Following are some of the typical nucleophilic substitution reactions of allyl iodide.



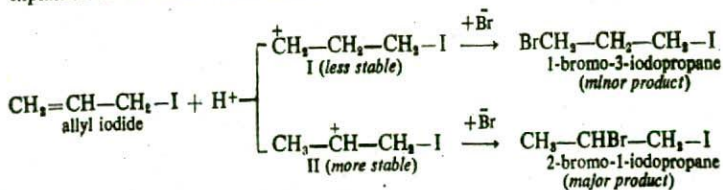
Similarly allyl iodide reacts with potassium sulphide to form allyl sulphide or thioether.



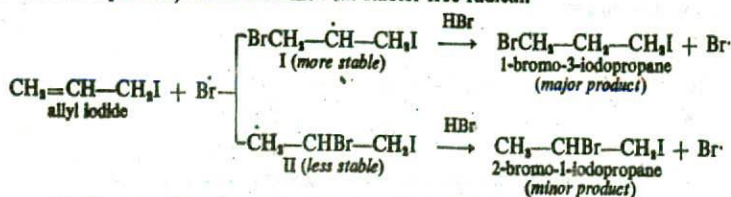
(2) *Electrophilic Addition reactions.* Allyl iodide undergoes the characteristic addition reactions of alkenes at the carbon-carbon double bond. For example,



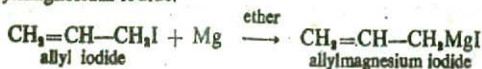
The formation of 2-bromo-1-iodopropane as the main product upon addition of HBr is explained on the basis of intermediate stable carbonium ion.



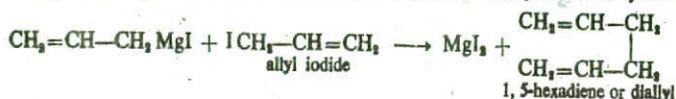
On the other hand, in the presence of peroxide the chief product is 1-bromo-3-iodopropane (anti-Markovnikov product) which is formed *via* stabler free radical.



(3) *Formation of Grignard Reagent.* Allyl iodide reacts with magnesium in anhydrous ether to form allylmagnesium iodide.



The above Grignard reagent then reacts with another molecule of allyl iodide to yield diallyl.



Allyl iodide is chiefly used in organic syntheses for introducing allyl group into organic compounds.

### INFRARED SPECTRA OF HALOGEN DERIVATIVES

The various carbon-halogen bonds (C—X) show infrared absorption bands in the regions: C—F in 1000—1110  $\text{cm}^{-1}$ , C—Cl in 650—780  $\text{cm}^{-1}$ , C—Br in 650—750  $\text{cm}^{-1}$ , and C—I in 500—600  $\text{cm}^{-1}$ . Apart from absorption peaks in these regions, IR spectra also have absorption peaks of various C—H and C—C bonds as shown below in case of a typical infrared spectrum of

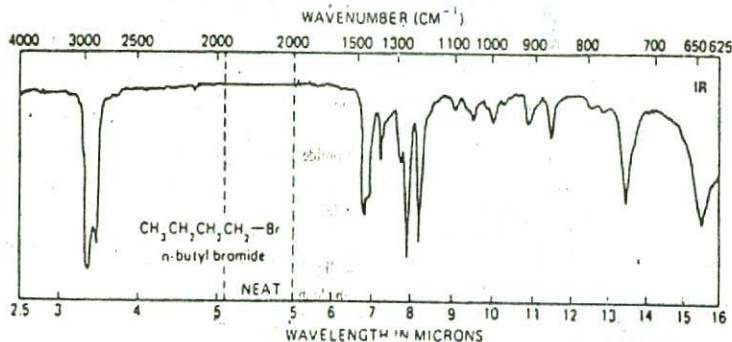


Fig. 14-6. Infrared Spectrum of *n*-Butyl bromide

### QUESTIONS

- What are alkyl halides? How are they prepared? Outline their synthetic uses.
- How will you prepare the following compounds:
  - Ethyl chloride
  - Ethyl iodide
  - Chloroform
  - Iodoform

3. What happens when : (a) Ethyl bromide is treated with KOH ; (b) Chloroform is treated with KOH ; (c) Ethyl iodide is treated with zinc. (Jammu BSc, 1993)

4. How will you distinguish between :

- (a) *n*-Hexyl bromide and *n*-hexane  
 (b) 2-Bromoheptane and 2-heptanol  
 (c) Allyl bromide and 1-bromopropane

Hint. *n*-Hexyl bromide produces a white precipitate with alcoholic  $\text{AgNO}_3$  solution. *n*-Hexane does not react ; (b) 2-Heptanol reacts with sodium metal to produce hydrogen gas (see as bubbles). No gas bubbles will be apparent in the case of 2-bromoheptane ; and (c) Allyl bromide is unsaturated. It will decolourise the red colour to  $\text{Br}_2$  in carbon tetrachloride.

5. How will you synthesise the following compounds from ethyl iodide :

- (a) Ethylene (b) Ethyl cyanide  
 (c) Butane (d) Propionic acid

(Jiwaji BSc, 1993)

Hint. (a) (i)  $\text{NaCN}$ , and (ii)  $\text{H}_2/\text{O}^+$ .

6. How will you synthesise the following compounds from the indicated materials ?

- (a) Propane from *n*-propyl bromide  
 (b) Isopropyl bromide from *n*-propyl bromide  
 (c) 2-Bromobutane from 1-butyne  
 (d) 2-Bromobutane from 1-butanol  
 (e) Diethyl ether from ethyl iodide  
 (f) 1-Methoxypropane from 1-chloropropane  
 (g) *n*-Propylamine from isopropyl alcohol  
 (h) Vinyl chloride from ethylene  
 (i) Allyl chloride from propane

Hint. (a) (i)  $\text{Mg/ether}$ , and (ii)  $\text{H}_2/\text{O}$  ; (b) (i) alcoholic KOH, and (ii) HBr ; (c) (i) HBr, and (ii)  $\text{H}_2/\text{Pt}$  ; (d) (i)  $\text{SOCl}_2$ , (ii) alcoholic KOH, and (iii) HBr ; (e) (i) aqueous KOH, (ii)  $\text{Na/ether}$ , and (iii)  $\text{CH}_3\text{CH}_2\text{I}$  ; (f)  $\text{CH}_3\text{ONa}$  ; (g) (i) conc  $\text{H}_2\text{SO}_4/\text{heat}$  (ii) HBr in the presence of peroxide, and (iii)  $\text{NaNH}_2$  ; (h) (i)  $\text{Cl}_2$  in  $\text{CCl}_4$ , and (ii) alcoholic KOH ; and (i) (i)  $\text{Cl}_2/\text{UV}$ , (ii) alcoholic KOH, and (iii)  $\text{Cl}_2/600^\circ\text{C}$ .

7. Write a note on : Saytzeff rule. (Utkal BSc, 1994)

8. Explain : Allyl chloride is less reactive than ethyl chloride. (Calicut BSc, 1993)

9. Explain : Allyl chloride is more reactive than vinyl chloride. (Gulbarga BSc, 1994)

10. Explain : Nucleophilic substitution at the saturated carbon.

11. Discuss the mechanism of  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions of alkyl halides. (Andhra BSc, 1994 ; Nagpur BSc, 1994)

12. Write a note on  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions. (Karnataka BSc, 1994)

13. Write the mechanism for the reaction of methyl bromide with aqueous KOH to form methyl alcohol. (Madras BSc, 1994)

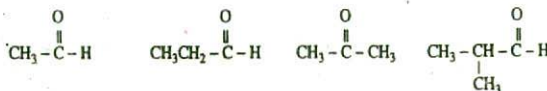
14. Write the mechanism for the reaction of *tert*-butyl bromide with aqueous NaOH to form *tert*-butyl alcohol. (Sambalpur BSc, 1993)

15. Discuss the mechanism of E2 and E1 reactions of alkyl halides. (Punjab BSc, 1994)

16. A primary alkyl bromide (A),  $\text{C}_4\text{H}_9\text{Br}$ , reacted with alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give an isomer of (A), (C). When (A) was reacted with sodium metal it gave compound (D),  $\text{C}_8\text{H}_{18}$ , which was different from the compound produced when *n*-butyl bromide was reacted with sodium. Draw the structure of (A) and write equations for all the reactions.

Answer. (A) is 1-Bromo-2-methylpropane ; (B) is 2-Methylpropene ; (C) is 2-Bromo-2-methylpropane and (D) is 2,5-Dimethylhexane.

17. A white precipitate was formed when alcoholic silver nitrate solution was added to compound (A), with the formula  $\text{C}_6\text{H}_{13}\text{Cl}$ . When (A) was treated with hot alcoholic KOH, a mixture of two alkenes, (B) and (C), with the formula  $\text{C}_6\text{H}_{12}$  was formed. Compounds (B) and (C) could not be separated easily, so the mixture of the two was subjected to ozonolysis. Four compounds :



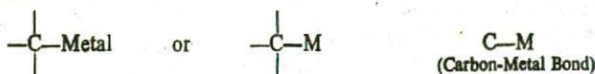
were obtained. Write the structures of (A), (B), and (C):

Answer. (A) is 3-Chloro-2-methylpentane ; (B) is 4-Methyl-2-pentene ; and (C) is 2-Methyl-2-pentene.



## Organometallic Compounds

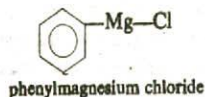
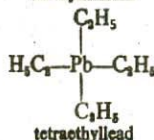
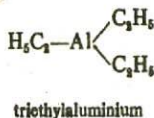
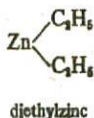
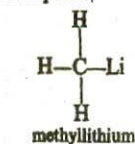
An organometallic compound is defined as a compound which contains a direct carbon-metal bond.



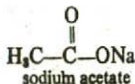
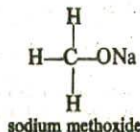
where  $M = \text{K, Na, Li, Ca, Mg, Al, Zn, Cd, Sn, Pb, Hg}$  etc.

Organometallic compounds are named by simply adding the name of the metal (M) to that of the organic group which may be alkyl, alkenyl or aryl.

Examples :



It may be noted that the above definition of organometallic compounds excludes substances such as sodium methoxide and sodium acetate in which the metal is not directly bonded to carbon.



Here the metal is linked to carbon through oxygen and these compounds are not organometallic compounds.

**Ionic Character.** Organometallic compounds could be represented as I or II.



0% ionic  
(covalent)



100% ionic



partial ionic character  
(between 0% and 100%)

The structure I is covalent, while II is ionic. In other words, I is zero per cent ionic and II is hundred per cent ionic. The true situation is somewhere in between which is represented by

III. The extent of the ionic character of C—M bond depends on the electropositive nature of the metal. In general, more electropositive the metal the more ionic the carbon-metal bond.

Table. Per cent Ionic character of some Carbon-Metal bonds

C—M	% Ionic	C—M	% Ionic	C—M	% Ionic
C—K	51	C—Mg	35	C—Sn	12
C—Na	47	C—Al	22	C—Pb	12
C—Li	43	C—Zn	18	C—Hg	9
C—Ca	43	C—Cd	15		

The reactivity of organometallic compounds increases with the ionic character of the C—M bond. Thus highly ionic compounds such as organosodium (RNa) and organopotassium (RK) compounds are among the most reactive organometallics. They are spontaneously inflammable in air, react violently with water, are nonvolatile and do not dissolve readily in nonpolar solvents. On the other hand more covalent compounds like tetraethyllead and dimethylmercury,  $(C_2H_5)_2Hg$ , are far less reactive, relatively stable in air, volatile and soluble in nonpolar solvents like hydrocarbons and ether. The organometallic compounds of intermediate ionic character such as those of lithium and magnesium are of greater interest to the Organic Chemist. These are relatively easy to prepare and handle, and are useful synthetic reagents.

#### ORBITAL STRUCTURE OF CARBON-METAL BONDS

The orbital structure of organometallic compounds furnishes useful information regarding the relative reactivities of these compounds. The reactivity of such a compound is largely determined by the strength of carbon-metal bond. The stronger the bond the less reactive the compound would be. Let us proceed to study the relative strength of the carbon-metal bonds in organometallic compounds derived from Li, Mg and Pb in light of their orbital structure.

The carbon-metal bond in methyl lithium ( $H_3C-Li$ ) results from overlap of an  $s$  orbital of lithium and an  $sp^3$  hybrid orbital of carbon of the methyl group. Because of the diffused character of  $s$  orbital, the extent of overlap is poor which results in a very polar weak carbon-metal bond. On the other hand, a Mg atom has the electronic structure  $1s^2, 2s^2, 2p^6, 3(sp)^1, 3(sp)^1$ . The two  $sp$  orbitals which are oriented at  $180^\circ$ , are available for bond formation with  $sp^3$  orbitals of an alkyl group or a valency orbital of a halogen atom (X). Here the  $sp$  orbital of Mg being less diffused than pure  $s$  orbital of Li, the degree of overlap to form C—Mg bond will be comparatively more effective and thus this bond will be stronger (less polar).

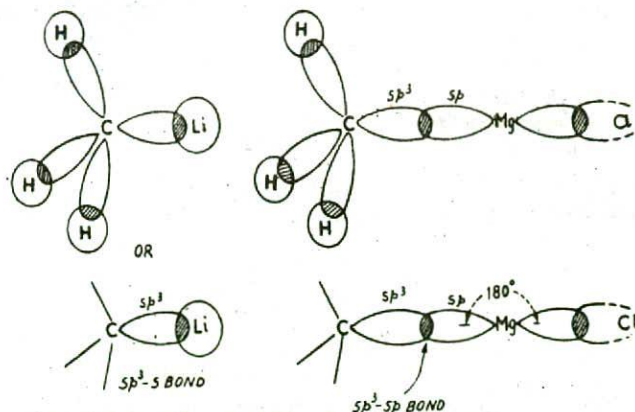


Fig. 15-1 Orbital models of  $CH_3-Li$  and  $CH_3-Mg-Cl$ , depicting greater orbital overlap in the formation of C—Mg bond compared to C—Li bond which is relatively weak.

Like carbon, Pb belongs to group IV of the periodic table and would, therefore, form  $sp^3$  hybrid orbitals. Therefore, an  $sp^3$  orbital of Pb overlaps with  $sp^3$  orbital of carbon to form a C—Pb bond, since  $sp^3$  orbitals have least  $s$  character and are least diffused, the overlap would be more effective resulting in stronger carbon-metal bond in case of organometal compounds of Pb. Such a bond would be least polar (or more covalent) and least reactive. Thus tetraethyllead is a stable and volatile compound compared to methyllead or methylmagnesium halides.

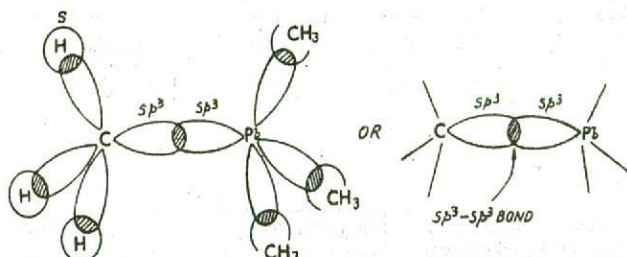


Fig. 15.2. Orbital model of tetraethyllead involving the formation  $sp^3-sp^3$  bond between Carbon and Lead. This produces a relatively strong and covalent C—Pb bond.

## GRIGNARD REAGENTS

Of all the organometallic compounds known, organomagnesium halides ( $RMgX$ ) or Grignard Reagents are the most important. They are so named after Victor Grignard who discovered them and developed their use as synthetic reagents. They occupy pride of place in organic synthesis by virtue of their versatility and wide application. Almost all classes of organic compounds can be prepared from them. Grignard earned one-half of a Nobel Prize in 1912 for his remarkable contribution to synthetic organic chemistry.

The general formula for Grignard reagents can be written as

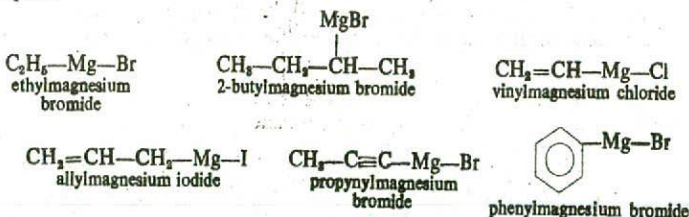


where  $R$  = alkyl, alkenyl, alkynyl or aryl group.

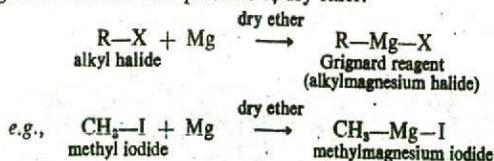
$X$  = Cl, Br or I

Organomagnesium fluorides are not known.

Examples :



**Preparation.** Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.



For a given alkyl group (say  $R$ ), the ease of formation of the Grignard reagent is in the order  $RI > RBr > RCl$



In actual practice a Grignard reagent is produced by dropping a solution of the alkyl halide in dry ether into the reaction flask containing magnesium ribbon suspended in dry ether. The ether solution of the Grignard reagent thus obtained is used immediately in the flask in which it is prepared.

In the preparation of Grignard reagents care must be taken that all the apparatus and reactants are absolutely dry. The moisture or any other impurities present will react with the Grignard reagent produced. Thus even traces of moisture or impurities prevent the formation of Grignard reagent.

The magnesium needed for the Grignard reaction is in the form of short lengths (5 mm) of ribbon which is dried by placing in a desiccator for a long time. Ether is washed with water to remove any ethanol and then allowed to stand over fused  $\text{CaCl}_2$  overnight. It is then distilled over sodium to get absolutely anhydrous ether free from ethanol. Alkyl halide is purified by distillation followed by allowing it to stand over anhydrous  $\text{CaCl}_2$  or  $\text{MgSO}_4$  for a few hours.

**Procedure.** The apparatus used for the preparation of Grignard reagent is assembled as shown in Fig. 15-3.

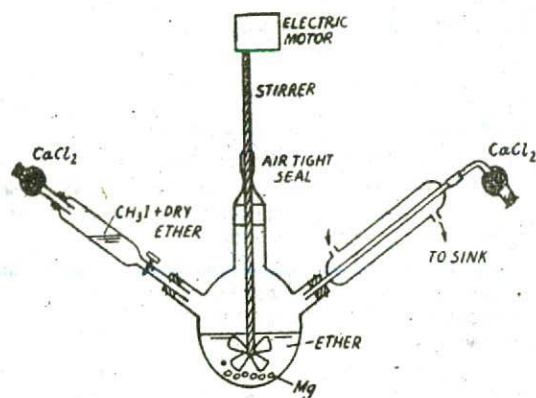


Fig. 15-3. Preparation of Methylmagnesium iodide.

Magnesium ribbon cut into small pieces is suspended in dry ether placed in the three-necked round-bottom flask. In the dropping funnel is placed approximately 1:1 mixture of methyl iodide and anhydrous ether. Add 2-3 ml of the solution from the dropping funnel into the reaction flask and wait till the reaction commences. When the reaction starts, the ether becomes cloudy and also begins to boil gently. Further, there are visible signs of attack on magnesium. If the reaction does not start, drop one or two crystals of iodine into the flask. Then the reaction would start. Once the reaction has commenced, the addition of solution ( $\text{CH}_3\text{I}$  in ether) from the dropping funnel is maintained at such a rate that the ether in the flask refluxes gently. When the reaction is complete, a clear solution of the Grignard reagent in ether is obtained. This is then treated *in situ* with various substances to get the desired synthetic products.

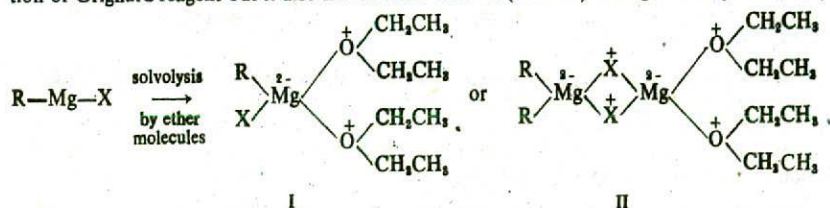
**MECHANISM OF FORMATION.** The formation of Grignard reagents by the above procedure probably occurs *via* free radical mechanism as given below.



This mechanism also elegantly explains the initiating effect of iodine which may be ascribed to the formation of magnesium iodide from magnesium and iodine.



**Role of Ether.** The role of ether here is not only to provide a medium for the function of Grignard reagent but it also makes them dissolve (in ether) through solvolysis.



If the function of ether is to dissolve the Grignard reagent by coordination of the type shown above, then it should be possible to prepare a Grignard reagent even in benzene in presence of a base like triethylamine. It has actually been found to be so. Only one mole of the base per mole of the alkyl halide is required.

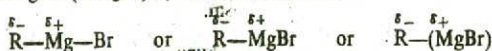
Grignard reagent in ether can exist either in structure I or II. It has been pointed out recently that there is established an equilibrium between alkylmagnesium halide (Grignard reagent) and the corresponding dialkyl magnesium in ether solution as



In light of the above fact, structure II seems to be more probable. Further, since the reactions of  $\text{R}_2\text{Mg}$  in presence of  $\text{MgX}_2$  are the same as those of  $\text{RMgX}$ , it seems reasonable to represent Grignard reagent solvated in ether by the formulation I.

**Properties (Physical).** Grignard reagents are nonvolatile, colourless solids. They are seldom isolated in the free state on account of their explosive nature. However, unlike alkylzincs they do not ignite spontaneously when in ether solution. Therefore, for synthetic purposes they are always prepared and used in ether solution.

**(Chemical).** As pointed out earlier, the molecule of a Grignard reagent has sufficient polar character. The carbon-magnesium bond in  $\text{RMgX}$  is 35% ionic. Thus it is logical to represent a Grignard reagent ( $\text{RMgBr}$ ) by the formulation :



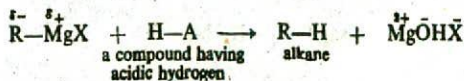
Further, it is expected that the alkyl-group carrying negative charge being electron-rich can function as a carbanion or a nucleophile. Such electron-rich species, therefore, would attack polarized molecules at points of low-electron density. Thus the characteristic reactions of Grignard reagents are nucleophilic substitution and addition reactions.

As we will see presently, Grignard reagents enter into reactions with a variety of substances yielding almost all classes of organic compounds. The main **Synthetic Reactions** of Grignard reagents may be discussed under the following heads.

- (a) Reactions with active hydrogens ;
- (b) Nucleophilic substitution reactions ;
- (c) Nucleophilic addition reactions ; and
- (d) Insertion reactions.

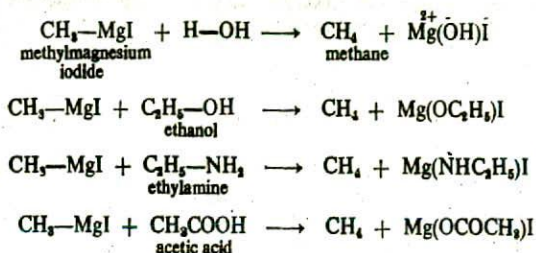
## A. REACTIONS WITH ACTIVE HYDROGEN

By active hydrogen we mean a hydrogen that is more acidic than in alkanes. Thus compounds like water, alcohols, carboxylic acids and amines which contain active hydrogens react with Grignard reagents to produce *hydrocarbons*.





when  $A = OH, OR, RNH, NH_2, RCOO$  etc. For example,

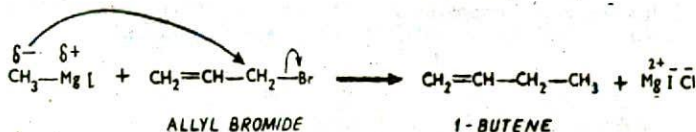


This reaction not only provides a method for the synthesis of alkanes but also forms a basis for the **Zerevitinoff determination** of active hydrogens. This is done by measuring the amount of methane ( $\text{CH}_4$ ) produced, one molecule of which indicates the presence of one active (H) atom in the original compound. Thus this reaction can be used to distinguish primary, secondary and tertiary amines ( $\text{RNH}_2, \text{R}_2\text{NH}, \text{R}_3\text{N}$ ) by measuring the volume of the gas produced per mole of the amine.

## B. NUCLEOPHILIC SUBSTITUTION REACTIONS

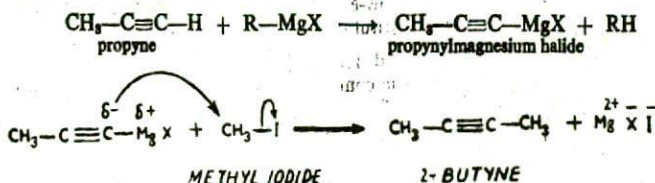
The weak negative charge on R in  $\text{R-MgX}$  makes Grignard reagents weak nucleophiles. Thus they would not react with simple alkyl halides like ethyl bromide. However, Grignard reagents undergo  $\text{S}_\text{N}2$  displacements with reactive halides. The following are some of the typical nucleophilic substitution reactions given by Grignard reagents.

(1) **Reaction with reactive Halides.** Grignard reagents react with reactive halides like benzyl chloride and allyl bromide to form *alkanes* and *alkenes* respectively.

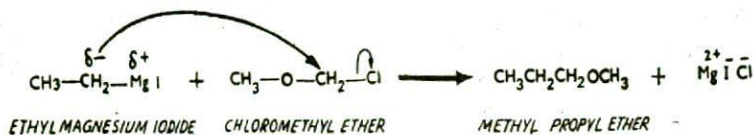


These reactions probably proceed by  $\text{S}_\text{N}2$  mechanism.

(2) **Reaction with Alkynes.** The terminal alkynes react with Grignard reagents to produce alkynylmagnesium halides which on subsequent treatment with alkyl halides undergo  $\text{S}_\text{N}2$  displacements to form *higher alkynes*.

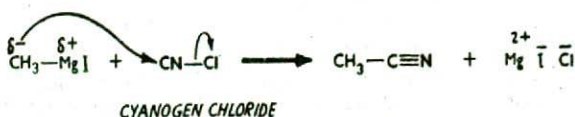
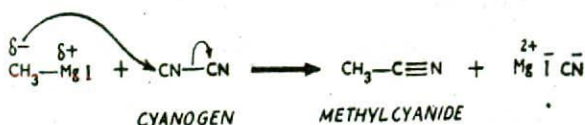


(3) **Reaction with lower Halogenated Ethers.** Grignard reagents react with lower halogenated ethers to produce *higher ethers*.

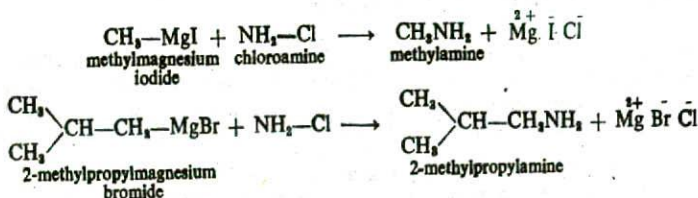




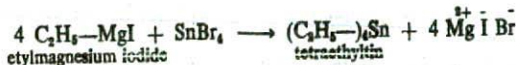
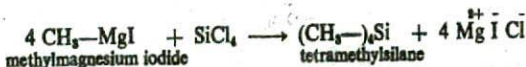
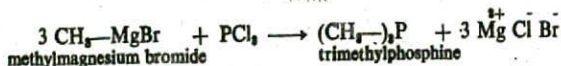
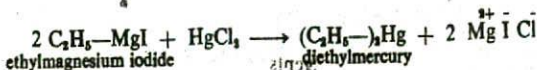
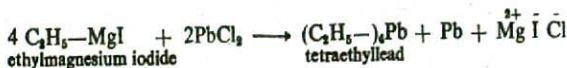
(4) **Reaction with Cyanogen and Cyanogen chloride.** Alkyl cyanides are produced when Grignard reagents react with cyanogen and cyanogen chloride.



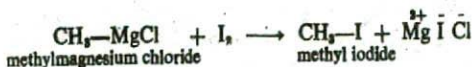
(5) **Reaction with Chloroamines.** Grignard reagents react with chloroamines to give primary amines. This reaction provides the best method for preparing primary amines containing a tertiary alkyl group.



(6) **Reaction with Inorganic halides.** Organometallic and organo-nonmetallic compounds result when Grignard reagents react with inorganic halides. For example,

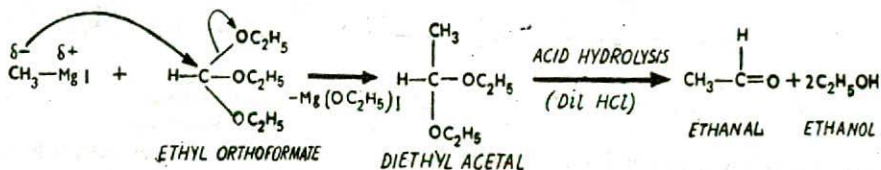


(7) **Reaction with Iodine.** When an alkylmagnesium chloride or bromide is treated with iodine, alkyl iodides are formed.

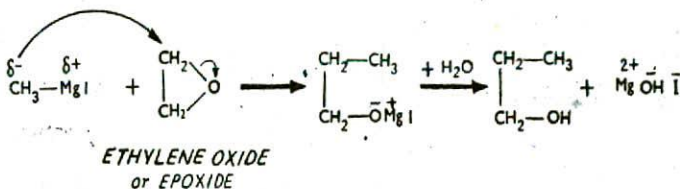


This is a good method for preparing an alkyl iodide from the corresponding alkyl chloride or bromide.

(8) **Reaction with Ethyl Orthoformate.** Grignard reagents react with ethyl orthoformate to produce *acetals* which upon subsequent acid hydrolysis give *aldehydes*.

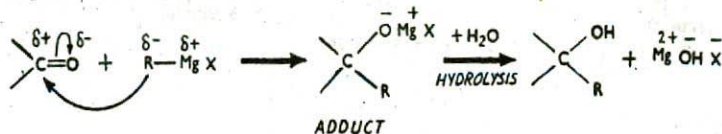


(9) **Reaction with Epoxides.** Grignard reagents react with epoxides to form *primary alcohols*.



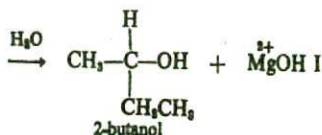
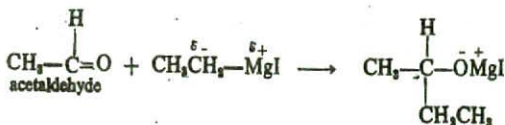
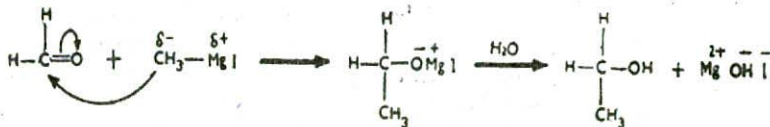
### C. NUCLEOPHILIC ADDITION REACTIONS

The reactions of Grignard reagents with carbonyl compounds (aldehydes and ketones) are examples of nucleophilic addition reactions and occur by the following mechanism.

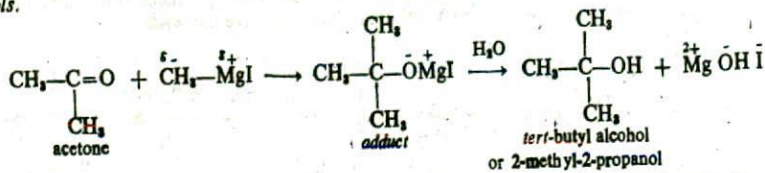


Other compounds which contain certain multiple bonded groups like  $\text{C}\equiv\text{N}$ ,  $>\text{C}=\text{S}$ , etc. also react with Grignard reagents to produce addition products. Some typical nucleophilic addition reactions are given below.

(1) **Reaction with Aldehydes.** Grignard reagents react with aldehydes to produce alcohols. The reaction with formaldehydes gives *primary alcohols*, while with other aldehydes *secondary alcohols* are produced.



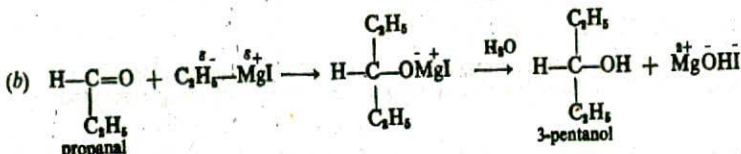
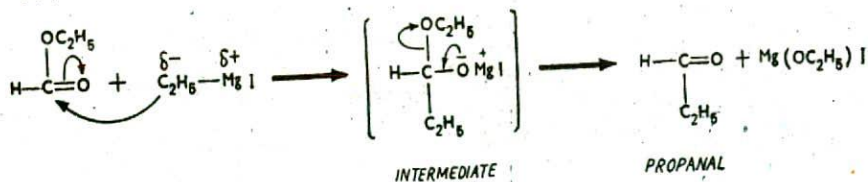
(2) **Reaction with Ketones.** Ketones react with Grignard reagents to form *tertiary alcohols*.



(3) **Reaction with Esters.** Grignard reagents (2 moles) react with formic ester (1 mole) to produce secondary alcohols, while other esters yield tertiary alcohols.

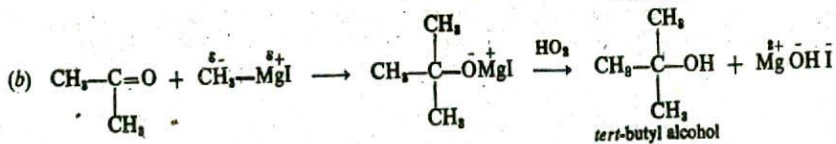
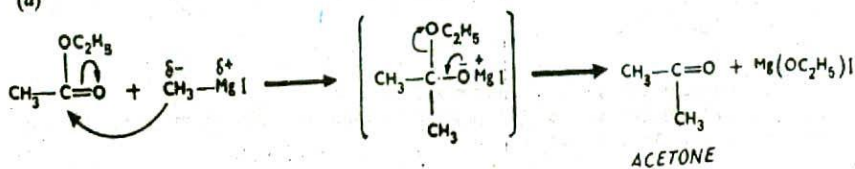
(i) **With Formic ester (2 moles) in two steps :-**

(a)



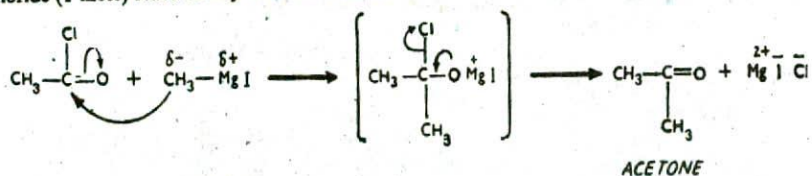
(ii) **With Ethyl acetate (2 moles) in two steps :-**

(a)



The reaction may be stopped either at the aldehyde or ketone stage by using one equivalent of the Grignard reagent per mole of the ester. Nevertheless, aldehyde or ketone prepared by this method would always be contaminated with secondary and tertiary alcohols respectively.

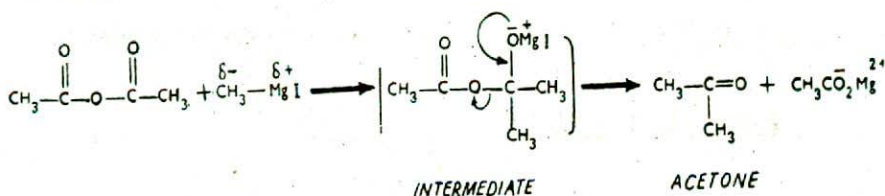
(4) **Reaction with Acid chlorides and Anhydrides.** Grignard reagent (1 mole) and an acid chloride (1 mole) react readily to form ketones.



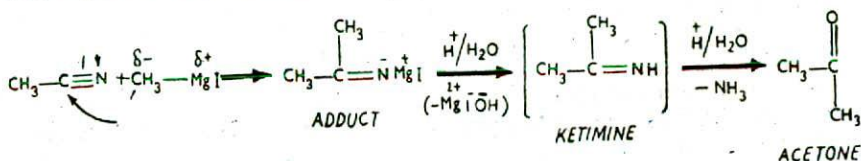


The acetone produced will further react with another mole of Grignard reagent to form *tert*-butyl alcohol as already described in reaction (2). That is why this reaction is not a good method to produce ketones.

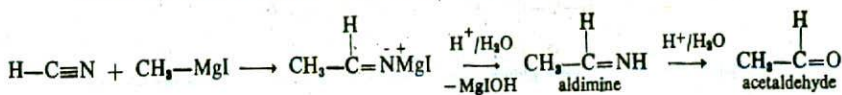
Acid anhydrides also form ketones in good yield provided the reaction is carried at  $-70^{\circ}\text{C}$ .



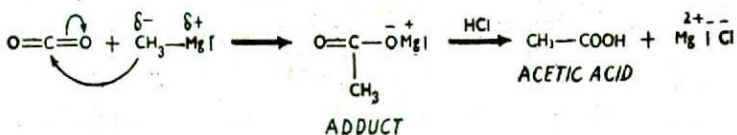
(5) **Reaction with Cyanides or Nitriles.** Grignard reagents add on to cyanides to form addition products which on treatment with dilute mineral acid give *ketones*.



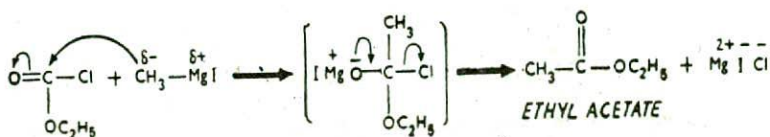
Similarly, Grignard reagents react with  $\text{H-C}\equiv\text{N}$  to produce *aldehydes*.



(6) **Reaction with Carbon dioxide.** Carboxylic acids can be obtained in good yield by pouring the solution of Grignard reagent on finely powdered solid carbon dioxide (*dry ice*) and then decomposing the complex with dilute mineral acid.



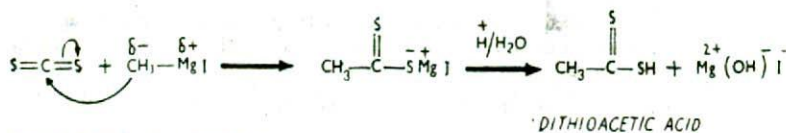
(7) **Reaction with Ethyl chloroformate.** Higher esters are obtained by the action of Grignard reagent (1 mole) and ethyl chloroformate (1 mole).



ETHYL CHLOROFORMATE

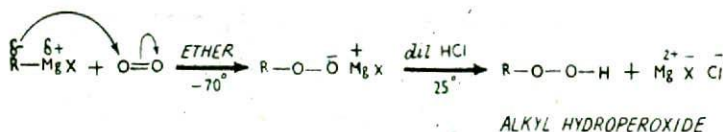
To avoid the further reaction of the ester thus produced with the Grignard reagent, ethyl chloroformate is kept in excess.

(8) **Reaction with Carbon disulphide.** Grignard reagents react with carbon disulphide to form dithionic acids.

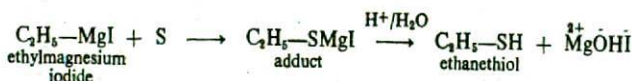


#### D. INSERTION REACTIONS

(1) **Reaction with Oxygen.** Grignard reagents react with oxygen at low temperatures to form *alkyl hydroperoxides*.

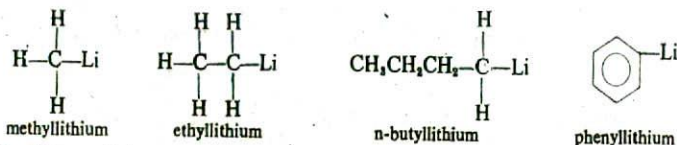


(2) **Reaction with Sulphur.** Sulphur reacts with a Grignard reagent giving the corresponding *thioalcohol*.



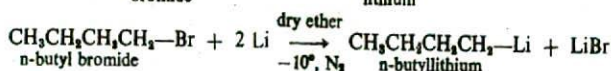
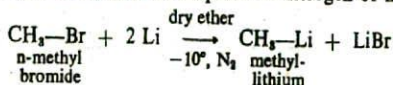
#### ORGANOLITHIUM COMPOUNDS

In these compounds carbon atom of the hydrocarbon group is directly bonded to lithium. For example,

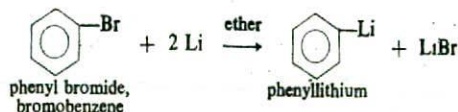


Alkylolithiums behave much in the same way as Grignard reagents, but with enhanced reactivity. Therefore, they are now being increasingly used in organic synthesis.

**Preparation.** Organolithium compounds are obtained by the reaction of alkyl halides with metallic lithium in ether in an inert atmosphere of nitrogen or helium.



Phenyllithium can be prepared by the reaction of lithium on bromo- or iodobenzene in ethereal solution.

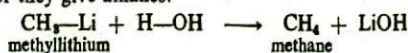


**Properties.** The increased reactivity of organolithium compounds over Grignard reagents may be attributed to the greater ionic character of C—Li bond in comparison to C—Mg bond.

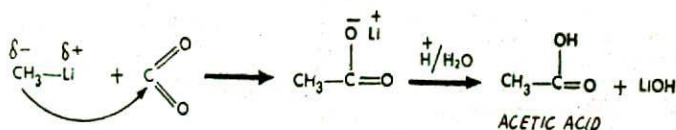


Organolithium compounds are particularly sensitive towards air and moisture. These react with cyclic ethers, alkyl halides, active halogen compounds and carbonyl compounds much in the same fashion as do Grignard reagents.

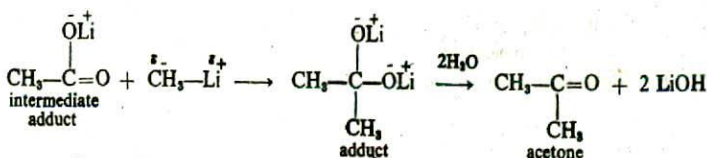
(a) With water they give alkanes.



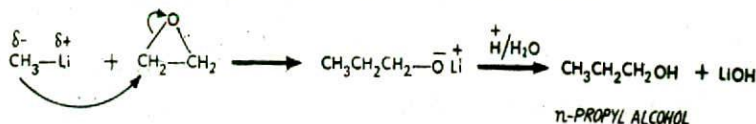
(b) With carbon dioxide they produce carboxylic acids.



However, if excess of  $\text{CH}_3\text{Li}$  is present, the acid obtained is contaminated with ketone.

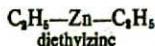
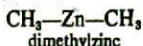


(c) With epoxyethane (ethylene oxide) they produce primary alcohols.

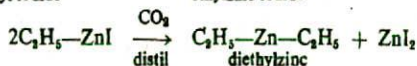
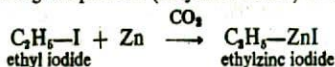


## ORGANOZINC COMPOUNDS

Organozinc compounds are less reactive than Grignard reagents and are sometimes used in organic synthesis in preference to the former. The two derivatives of zinc discovered by Frankland (1849) are :

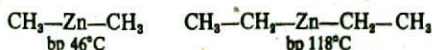


**Preparation.** Dialkylzincs are prepared by heating alkyl iodides with zinc in an atmosphere of  $\text{CO}_2$ , and then distilling the product (alkylzinc iodide) in an inert atmosphere of  $\text{CO}_2$ .



Dimethylzinc can also be prepared similarly

**Properties.** Dialkylzincs are colourless, unpleasant smelling liquids which have comparatively low boiling points.



They are spontaneously inflammable in air and produce painful burns when brought into contact with skin.

Their slow chemical reactivity in comparison to Grignard reagents is due to their lower ionic character of carbon metal bond.



They give reactions similar to those of Grignard reagents but being difficult to handle are sparingly used in organic synthesis.



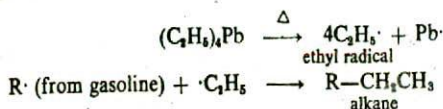


(2) On a commercial scale it is mostly made by the reaction of ethyl chloride with sodium-lead alloy ( $\text{Na}_4\text{Pb}$ ).



**Properties.** Tetraethyllead is a colourless liquid with a strong smell, bp  $202^\circ$ . Like other lead compounds it is a highly toxic substance, its vapours being absorbed through skin and lungs. It is soluble in organic liquids like gasoline but is insoluble in water. Being largely covalent in character, tetraethyllead has low reactivity. Thus unlike other organometallic compounds it is not decomposed by water.

**Use as Antiknock.** Tetraethyllead (1 to 3 ml per gallon) serves as an 'antiknock' for gasoline (petrol) used in automobile engines. The rate of combustion reaction of gasoline hydrocarbons increases sharply under high compression which causes knocking of the engine. Viewed chemically, over-rapid combustion of motor fuel under high pressure produces free hydrocarbon radicals and knocking is due to the chain reactions set up by these radicals. The antiknocking property of TEL is probably explained by the fact that it produces ethyl free radicals which act as 'radical traps' for the radicals ( $\text{R}\cdot$ ) produced from gasoline and chain reactions are thus terminated.

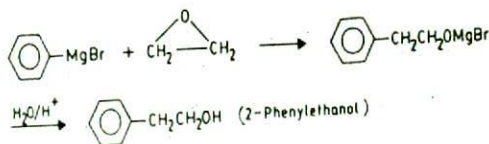


The combustion of 'leaded gasoline' produces lead oxide which deposits in the exhaust pipe of the engine. To avoid this, a small amount of ethyl bromide is also added to gasoline to convert lead oxide into volatile lead bromide and it escapes alongwith the exhaust gases. However, lead compounds are toxic so that the automobile exhaust gases pose a big health hazard in large cities.

### QUESTIONS

- What are Grignard reagents? Give their preparation and synthetic uses.  
(Kakatiya BSc, 1992; Delhi BSc, 1993; Madras BSc, 1993; Manipur BSc, 1994)
  - What is the role of diethyl ether in the preparation of Grignard reagents?  
(Banaras BSc Hons, 1994)
  - Describe the preparation and uses of organolithium compounds.  
(Poona BSc, 1994)
  - Write a note on: Organozinc compounds.  
(Karnataka BSc, 1994)
  - How is ethylmagnesium iodide prepared? Give equations to illustrate the use of the above compound in the synthesis of (a) a carboxylic acid; (b) a tertiary alcohol; and (c) ethane.  
(Kerala BSc II, 1994)
  - How is methylmagnesium bromide prepared? Starting with ethylmagnesium bromide how will you prepare the following compounds:  
(a) Ethyl alcohol  
(b) Ethylmethylcarbinol  
(c) 1-Propanol  
(d) Propionic acid  
(Nehru BSc Hons, 1993)
- Hint. (b) Ethylmethylcarbinol is 2-Butanol.
- What happens when phenylmagnesium bromide is treated with ethylene oxide followed by acid-hydrolysis.  
(Delhi BSc, 1994)

Answer. 2-Phenylethanol is formed.



- How does ethylmagnesium iodide react with (i) an ester, (ii) a ketone, and (iii)  $\text{CO}_2$   
(Nagpur BSc, 1993)

9. Complete the following :



(Baroda BSc, 1993)

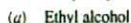
10. How are the following synthesised from Grignard reagents : (i) a primary alcohol, (ii) a secondary alcohol, and (iii) a tertiary alcohol. (Saugar BSc, 1994)

11. Starting from RMgI, how will you obtain :

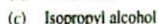


(Berhampur BSc, 1993)

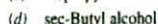
12. How will you synthesise the following compounds from methyl magnesium iodide ?



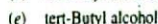
(Karnataka BSc, 1994)



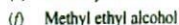
(Calicut BSc, 1993; Gulbarga BSc, 1993)



(Bharathidasan BSc, 1993)



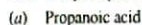
(Kakatiya BSc III, 1994)



(Punjab BSc, 1994)

**Hint.** (a) (i) CHO, and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; (b) (i)  $\text{CO}_2$  and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; (c) (i)  $\text{CH}_3\text{CHO}$ , and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; (d) (i)  $\text{CH}_3\text{CH}_2\text{CHO}$ , and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; (e) (i)  $\text{CH}_3\text{COCH}_3$ , and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; and (f) (i)  $\text{CH}_3\text{CH}_2\text{CHO}$ , (ii)  $\text{H}_2\text{O}/\text{H}^+$ , and (iii)  $\text{LiAlH}_4$

13. How will you synthesise the following compounds from ethylmagnesium iodide ?



(Baroda BSc, 1993)



(North Bengal BSc Hons, 1994)

**Hint.** (a) (i)  $\text{CO}_2$ , and (ii)  $\text{H}_2\text{O}/\text{H}^+$ ; and (b)  $\text{CH}_3\text{COCH}_3$ , and (ii)  $\text{H}_2\text{O}/\text{H}^+$ .

14. Compound (A),  $\text{C}_3\text{H}_7\text{Br}$ , reacts with aqueous KOH to form (B),  $\text{C}_3\text{H}_7\text{O}$ , which can be oxidised to (C),  $\text{C}_3\text{H}_6\text{O}$ . The Grignard reagent from (A) reacts with (C) to form (D),  $\text{C}_6\text{H}_{14}\text{O}$ . Deduce the structural formulas of (A), (B), (C) and (D).

**Answer.** (A) is Isopropyl iodide; (B) is Isopropyl alcohol; (C) is Acetone; and (D) is 2,3-Dimethyl-2-butanol.

15. A carbonyl compound (A),  $\text{C}_8\text{H}_{16}\text{O}$ , reacts with ethylmagnesium iodide to form a compound which on acid-hydrolysis yields an alcohol (B). compound (B) undergoes dehydration with conc  $\text{H}_2\text{SO}_4$  to give (C) which on ozonolysis forms 3-pentanone as the only product. Deduce the structural formulas of (A), (B) and (C).

**Answer.** (A) is 4-Ethyl-3-hexanone; (B) is 3,4-Diethyl-3-hexanol; and (C) is 3,4-Diethyl-3-hexene