

## 15. Hydrocarbons

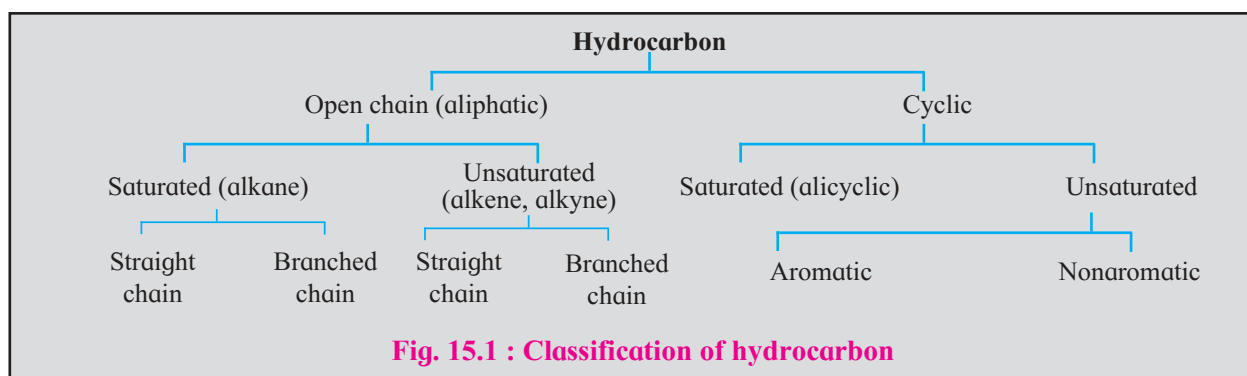


### Can you recall?

1. What are hydrocarbons?
2. Write structural formulae of the following compounds : propane, ethyne, cyclobutane, ethene, benzene.

The compounds which contains carbon and hydrogen as the only elements are called hydrocarbons.

Hydrocarbons can be **open chain** or **cyclic**. In accordance with presence or absence of carbon-carbon multiple bond ( $C=C$  and/or  $C \equiv C$ ) the hydrocarbons are called **unsaturated** or **saturated**. Cyclic unsaturated hydrocarbon can be either **aromatic** or **nonaromatic** (Fig. 15.1).



### Do you know ?

Why are alkanes called paraffins?

Alkanes contain only carbon-carbon and carbon-hydrogen single covalent bonds. They are chemically less reactive and do not have much affinity for other chemicals. Hence they are called paraffins.

### 15.1 Alkanes

Alkanes are aliphatic saturated hydrocarbons containing carbon-carbon and carbon-hydrogen single covalent bonds. You have learnt in Chapter 14 that alkanes have general formula  $C_nH_{2n+2}$  where 'n' stands for the number of carbon atoms in the alkane molecule.

#### 15.1.1 Isomerism in alkanes

Alkanes with more than three carbon atoms generally exhibit, structural isomerism and in particular, the chain isomerism (refer to section 14.5.1)



### Internet my friend

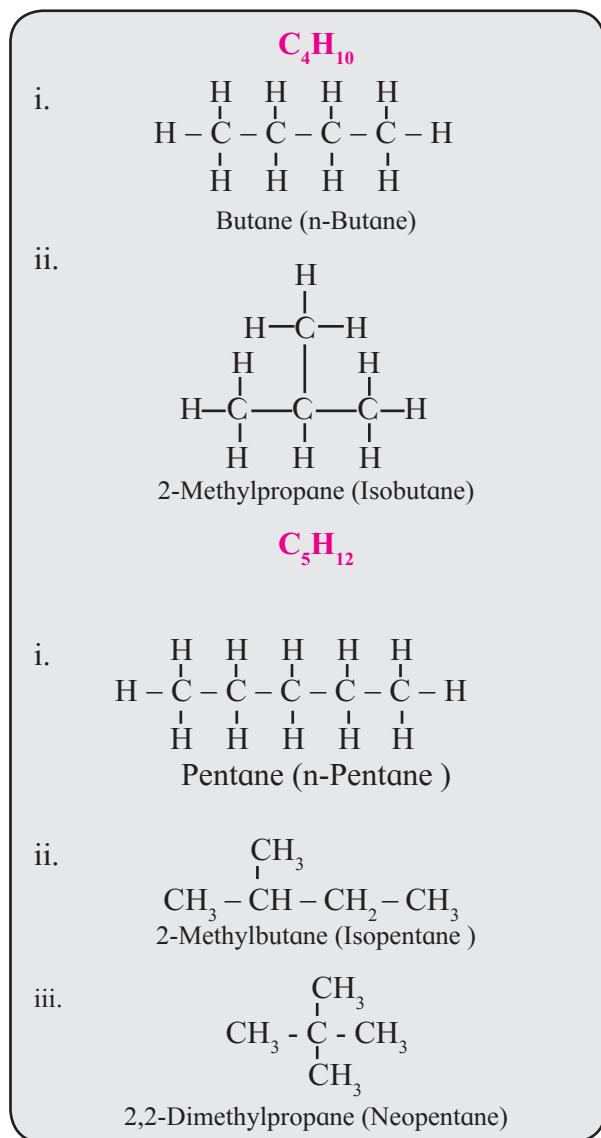
Collect information about Hydrocarbon

Figure 15.2 shows IUPAC and common names of structural isomers of  $C_4H_{10}$  and  $C_5H_{12}$ .

The number of possible structural isomers increase rapidly with the number of carbon atoms. (See the Table 15.1).

**Table 15.1 : Alkanes and isomer number**

Number of Carbon	Alkane	Number of isomers
1	Methane	No structural isomer
2	Ethane	No structural isomer
3	Propane	No structural isomer
4	Butane	Two
5	Pentane	Three
6	Hexane	Five



**Fig. 15.2 : Structural isomers of butane and pentane**

**15.1.2 Conformation in alkanes :** Alkanes have only single bonded atoms. You have learnt that a single covalent bond is formed by coaxial overlap of orbital and is called sigma ( $\sigma$ ) bond (Refer to Chapter 5). As a direct consequence of coaxial overlap of orbitals, a sigma bond is cylindrically symmetrical and the extent of orbital overlap is unaffected by rotation about the single bond and therefore C-C bonds undergo rotation. The atoms bonded to one carbon of a C-C single bond change their relative position with reference to the atoms on the other carbon of that bond on rotation of that C-C single bond.

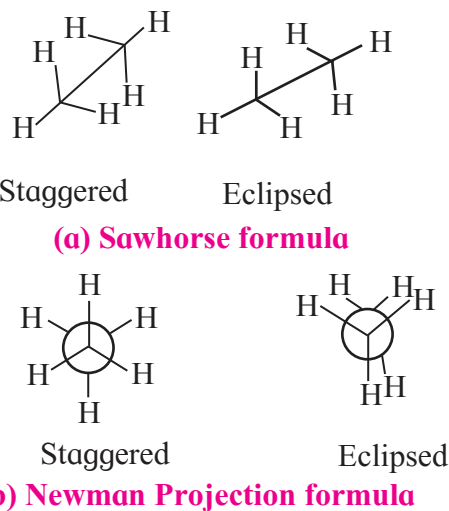


**Use your brain power**

1. Write the structures of all the chain isomers of the saturated hydrocarbon containing six carbon atoms.
2. Write IUPAC names of all the above structures

The resulting arrangements of the atoms in space about the C - C single bond are called conformations. Innumerable **conformations** result on complete rotation of a C - C single bond through 360°.

In chapter 14 you have learnt about **isomerism**. The phenomenon of existence of conformation is a type of **stereoisomerism**. In conformational isomerism the conformations (or **conformational isomers**) interconvert by rotation about a C - C single bond. Out of infinite **conformations of ethane** molecule two are extreme and called **staggered and eclipsed** conformation. They are represented by **Sawhorse formula** and **Newman projection formula** as shown in Fig. 15.3. Conformational isomerism in other alkanes is more complex.



**Fig. 15.3 : Representation of staggered and eclipsed conformation of ethanes**

### 15.1.3 Industrial preparation of alkanes

**a. Industrial source :** Crude petroleum and natural gas are the source of alkanes. Dead plants buried under earth billions of year ago got converted into crude oil under the high temperature and pressure conditions. The crude oil collected in dome shaped cavities under the earth surface, which we call oil wells. Alkanes are obtained by fractional distillation of crude oil in oil refineries.

**b. Methods of preparation of alkanes :**

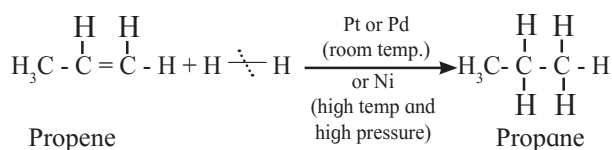
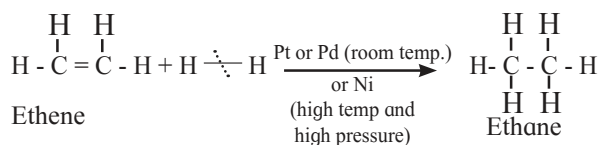


#### Can you recall?

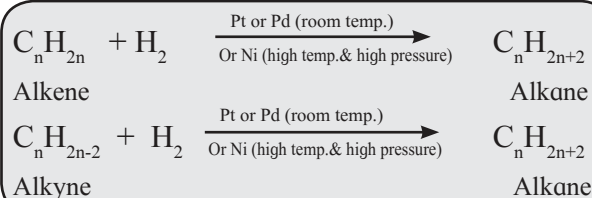
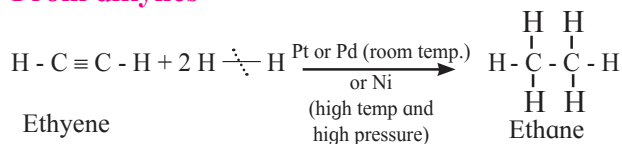
- What is a catalyst ?
- What is addition reaction ?

**1. From unsaturated hydrocarbons :** Catalytic hydrogenation of alkenes or alkynes with dihydrogen gas gives corresponding alkane. Finely divided powder of platinum (Pt) or palladium (Pd) catalyse the hydrogenation of alkenes and alkynes at room temperature. Relatively high temperature and pressure are required with finely divided nickel as the catalyst.

#### From alkenes

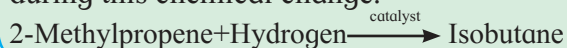


#### From alkynes



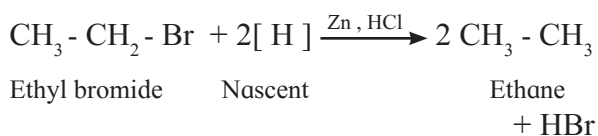
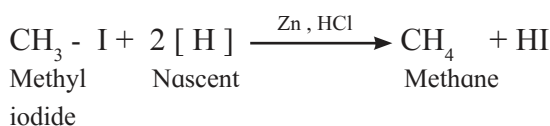
#### Try this

Transform the following word equation into balanced chemical equation and write at least 3 changes that occur at molecular level during this chemical change.

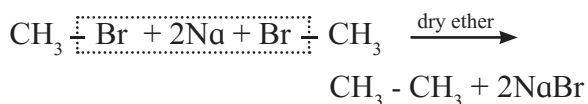


### 2. From alkyl halides

**a. By reduction of alkyl halides :** Alkyl halides on reduction with zinc and dilute hydrochloric acid form alkanes. The reduction of alkyl halides is due to nascent hydrogen obtained from the reducing agent Zn and dilute HCl.

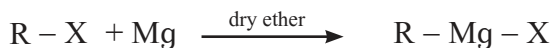


**b. By using reactive metal :** In 19<sup>th</sup> century alkyl halide were transformed to alkane having double the number of carbons by Wurtz coupling reaction using the reactive metal sodium.

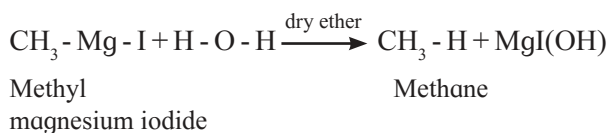
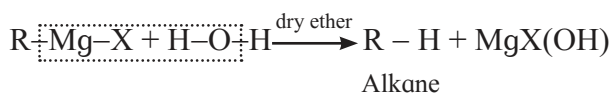


Later better methods using metals such as Mg, Li were developed. Grignard reaction is one of the new methods widely employed for preparation of alkanes.

**Alkyl magnesium halides ( Grignard reagent)** are obtained by treating alkyl halides with dry metal magnesium in the presence of dry ether. These on treatment with water give alkanes.



Alkyl halide Alkyl magnesium halide





### Do you know ?

Preparation of Grignard reagent is an exothermic reaction. Hence no heating is required. In this reaction :

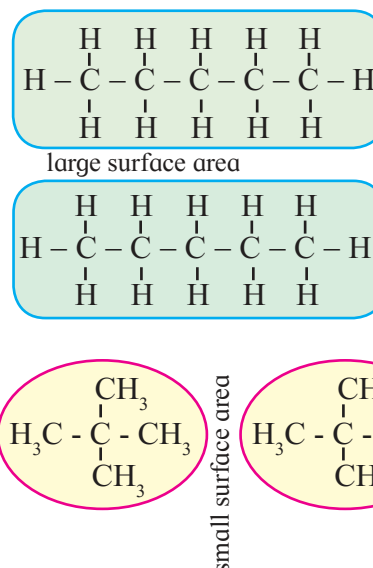
- Magnesium metal gradually disappears.
- Magnesium atoms gets bonded to the same carbon that previously held halogen.
- Alkyl group remains as it is or intact during the preparation grignard reagent.

#### 15.1.4 Physical properties of alkanes

**i. Polarity :** The electronegativity of carbon and hydrogen is nearly the same. C-H and C-C bonds are non-polar covalent bonds and alkanes are, thus, nonpolar. The forces which hold non-polar molecules together are the van der Waals forces. Those are usually weak. Larger the surface area of molecules, stronger are such intermolecular van der Waals forces.

The intermolecular forces are relatively stronger in straight chain alkanes than in branched alkanes (See Fig. 15.4).

Therefore straight chain alkanes have higher melting and boiling points.



**Fig. 15.4 : Relative surface area of straight chain and branched alkanes**

Branched alkanes have lower melting and boiling points. Intermolecular forces are overcome partly during melting process and completely during boiling process. Table 15.2 shows the melting and boiling points of some alkanes. Alkanes are colourless and odourless. At room temperature, the first four alkanes are gases, next alkanes having 5 to 17 carbons are liquids and carbons 18 onwards are solids.



### Use your brain power

Why are alkanes insoluble in water and readily soluble in organic solvents like chloroform or ether ?

**Table 15.2 : Melting and Boiling points in alkanes**

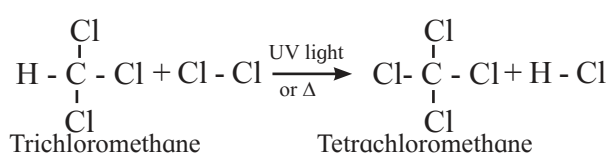
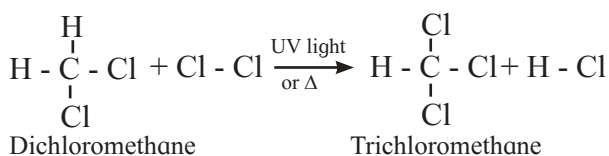
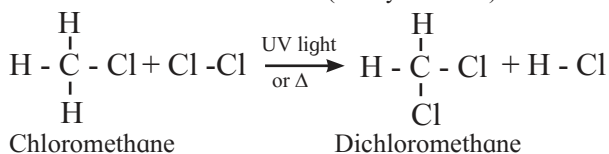
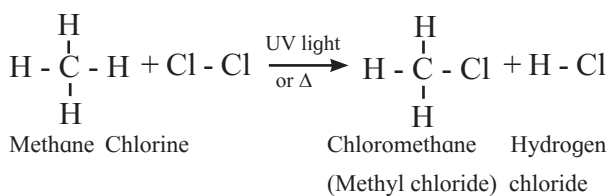
Molecular formula	Name	Molecular mass/u	b.p. (K)	m.p. (K)
CH <sub>4</sub>	Methane	16	111.0	90.5
C <sub>2</sub> H <sub>6</sub>	Ethane	30	184.4	101.0
C <sub>3</sub> H <sub>8</sub>	Propane	44	230.9	85.3
C <sub>4</sub> H <sub>10</sub>	Butane	58	272.4	134.6
C <sub>4</sub> H <sub>10</sub>	2-Methylpropane	58	261.0	114.7
C <sub>5</sub> H <sub>12</sub>	Pentane	72	309.1	143.3
C <sub>5</sub> H <sub>12</sub>	2-Methylbutane	72	300.9	113.1
C <sub>5</sub> H <sub>12</sub>	2,2-Dimethylpropane	72	282.5	256.4
C <sub>6</sub> H <sub>14</sub>	Hexane	86	341.9	178.5

### 15.1.5 Chemical properties of alkanes :

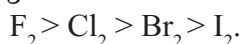
Alkanes are relatively unreactive towards acids, bases, oxidizing and reducing agents. They undergo the following reactions under specified conditions.

**1. Halogenation of alkanes :** The reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms are known as **substitution reactions**. Substitution of H atoms of alkanes by X (halogen, X= Cl, Br, I and F) atom is called **halogenation of alkanes**. Alkanes react with halogens in presence of UV light or diffused sunlight or at higher temperature ( 573 To 773 K) to give mixture of alkyl halides.

#### Chlorination of methane :



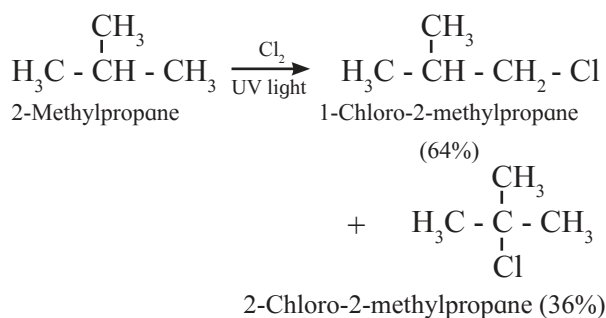
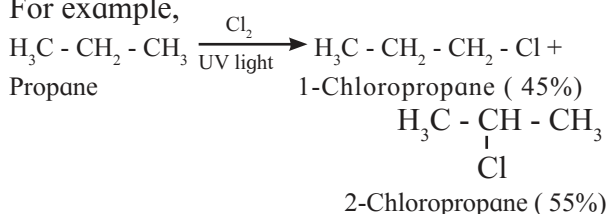
Tetrachloromethane is a major product when excess of chlorine is used. Chloromethane is obtained as major product when excess of methane is employed. The reactivity of halogens toward alkanes follows the order



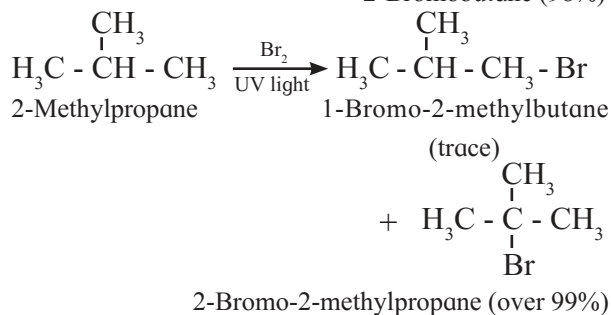
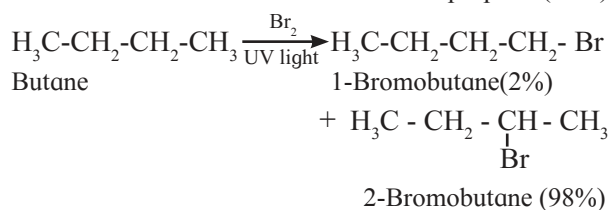
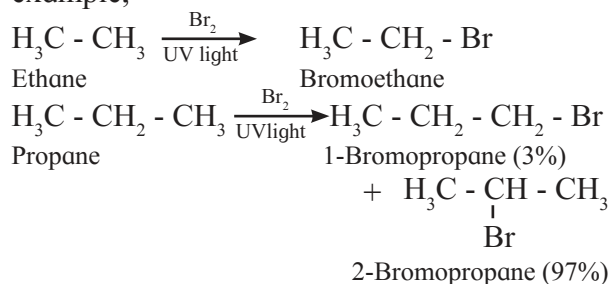
The ease of replacement of hydrogen atoms from the carbon is in the order of



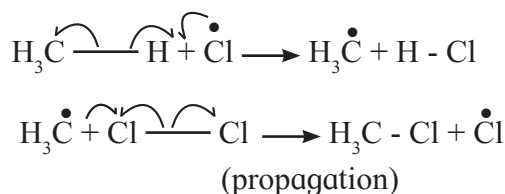
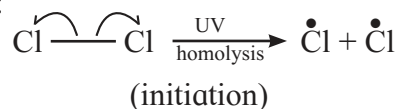
For example,



Bromination gives corresponding bromides, but in different proportions. For example,



In bromination, there is high degree of selectivity as to which hydrogen atoms are replaced. Halogenation of alkanes follows the free radical mechanism. Homolysis of halogen molecule ( $\text{X}_2$ ) generates halogen atoms i.e., halogen free radicals. The mechanism of the first step of chlorination of methane is shown below :

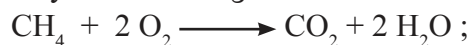




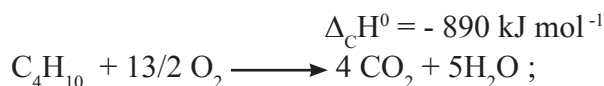
### Remember

1. Depending upon which hydrogen atom is replaced, a number of isomeric products can be formed from alkane. For example, n-Butane and isobutane yield two isomers each.
2. Halogenation of an alkane yields a mixture of all possible isomeric products, indicating all the hydrogen atoms are susceptible to substitution.

**2. Combustion :** Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of a large amount of heat. That is why alkanes are good fuels.



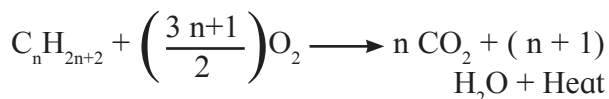
Methane



Butane

$$\Delta_c H^\circ = - 2875.84 \text{ kJ mol}^{-1}$$

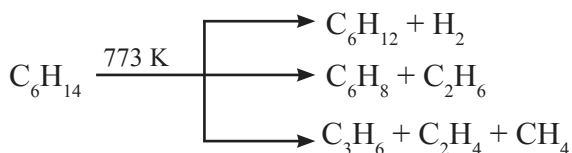
A representative combustion equation for alkane is



### Can you recall?

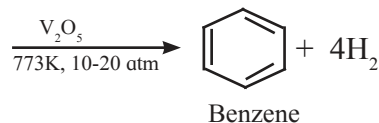
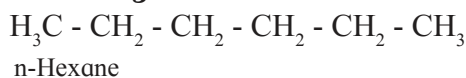
What is the product which is poisonous and causes air pollution formed by incomplete combustion of alkane ?

**3. Pyrolysis :** Alkanes on heating at higher temperature in absence of air decompose to lower alkanes, alkenes and hydrogen etc. This is known as **pyrolysis or cracking**.



**4. Reforming :** Straight chain alkanes containing 6 to 10 carbon atoms are converted to benzene and its homologues on heating under 10 to 20 atm pressure at about 773 K

in the presence of  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Mo}_2\text{O}_3$  etc. supported over alumina. The reaction involves simultaneous dehydrogenation and cyclization. This reaction is known as **aromatization or reforming**.



This process is used in refineries to produce high quality gasoline (the fuel used in automobiles).



### Use your brain power

Name the alkane from which methyl benzene is obtained by reforming?

Collect the information of CNG and LPG with reference to the constituents and the advantages of CNG over LPG.

### 15.1.6 Uses of alkanes :

1. First four alkanes are used as a fuel mainly for heating and cooking purpose. for example, LPG and CNG.
2. CNG, petrol, diesel are used as fuels for automobiles.
3. Lower liquid alkanes are used as solvent.
4. Alkanes with more than 35 C atoms (tar) are used for road surfacing.
5. Waxes are high molecular weight alkanes. They are used as lubricants. They are also used for the preparation of candles and carbon black that is used in manufacture of printing ink, shoe polish, etc.



### Can you recall?

- What are alkenes?
- Calculate the number of sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds in 2-Methylpropene ?
- Write structural formula of pent-2-ene.

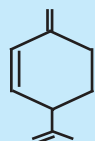
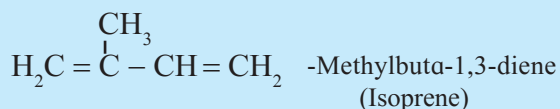


**15.2 Alkenes :** Alkenes are unsaturated hydrocarbons containing a least one carbon-carbon double bond. Alkenes with one carbon-carbon double bond, contain two hydrogen atoms less than corresponding alkanes. They have general formula  $C_nH_{2n}$ , where  $n = 2, 3, 4, \dots$  etc. You have also learnt about the IUPAC names of alkenes in Chapter 14.



### Do you know ?

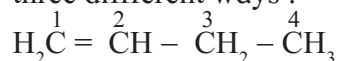
1. Alkenes are also known as olefins, because the first member ethylene or ethene reacts with chlorine to form oily substance.
2. The aliphatic unsaturated hydrocarbon containing two or three carbon-carbon double bonds are called alkadienes and alkatrienes, respectively. for example,



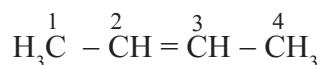
$\beta$ -Phellandrene (oil of eucalyptus)

**15.2.1 Isomerism in alkenes :** Alkenes with more than three carbon atoms show both **structural isomerism** and **geometrical isomerism**.

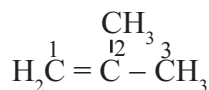
**i. Structural isomerism :** Alkenes with molecular formula  $C_4H_8$  is butene. The structural formulae for  $C_4H_8$  can be drawn in three different ways :



(I) But-1-ene (Chain of 4 carbon atoms)



(II) But-2-ene (Chain of 4 carbon atoms)

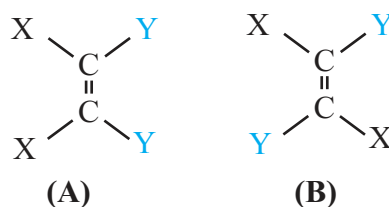


(III) 2-Methylprop-1-ene (Chain of 3 carbon atoms)

Structure I and III along with II and III are the examples of chain isomerism. They differ in carbon chain length. Structure I and II are the examples of position isomerism because they differ in the position of double bond in the same carbon chain.

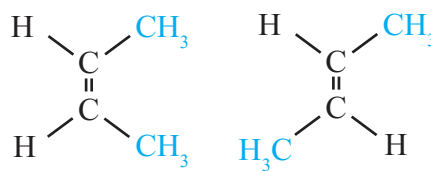
### ii. Geometrical isomerism

The isomerism which arises due to the difference in spatial arrangement of atoms or groups about doubly bonded carbon ( $C=C$ ) atoms is called *geometrical isomerism*. If the two atoms or groups bonded to each end of the  $C=C$  double bond are different, then molecule can be represented by two different special arrangements of the groups as follows :



In structure (A), two identical atoms or groups lie on the same side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the same side of the double bond is called *cis-isomer*.**

In structure (B), two identical atoms or groups lie on the opposite side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the opposite side of the double bond is called *trans-isomer*.** Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented as :





### Do you know ?

1. No terminal alkenes i.e. those with  $C=CH_2$  unit can exist as cis- and trans-isomers.
2. No 1,1-disubstituted alkenes i.e. those with  $C=CR_2$  unit can exist as cis- and trans-isomers.
3. Alkenes with general formulae  $RCH=CHR$ ,  $R_1R_2C=CR_1R_2$ ,  $R_1CH=CR_1R_2$ ,  $R_1CH=CR_2R_3$ ,  $R_1CH=CHR_2$  and  $R_1R_2C=CR_3R_4$  exhibit cis-trans isomerism.

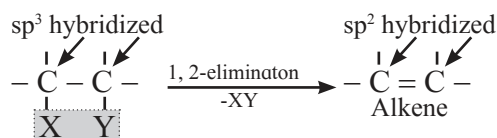
## 15.2 Preparation of alkenes

**a. Industrial sources :** The most important alkenes for chemical industry are ethene, propene and buta-1,3-diene. Alkenes containing upto four carbon atoms can be obtained in pure form from the petroleum products. Ethene is produced from natural gas and crude oil by cracking.

### b. Methods of preparation of alkenes

#### (I) Elimination reactions : (1,2 -elimination)

The reactions in which two atoms or groups are eliminated or removed from adjacent carbon atoms are called **1,2 - elimination reactions**.



### Remember

1. The carbon - carbon double bond can be generated from a carbon -carbon single bond by elimination reaction.
2. During elimination reaction  $sp^3$  carbon atom changes to  $sp^2$  carbon atom.

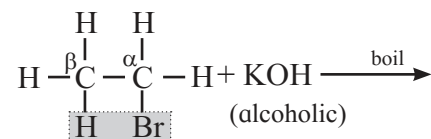
Some elimination reactions useful to prepare alkenes are described below.

#### i. Dehydrohalogenation of alkyl halides

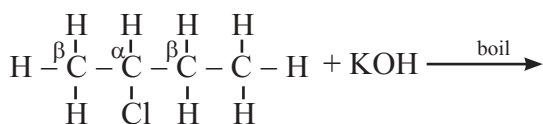
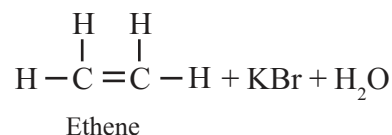
Dehydrohalogenation means removal of hydrogen (H) atom and halogen (X) atom from adjacent carbon atoms. The carbon carrying X is called  $\alpha$ -carbon atom.

The hydrogen atom from adjacent carbon called  $\beta$ -carbon atom, is removed and the reaction is known as  $\beta$ -elimination.

Dehydrohalogenation suffers from the disadvantage that -H can be eliminated from the carbon on either side of the  $\alpha$ -carbon bearing the -X. When an alkyl halide is boiled with a hot concentrated alcoholic solution of a strong base like KOH or NaOH, alkene is formed with removal of water molecule.

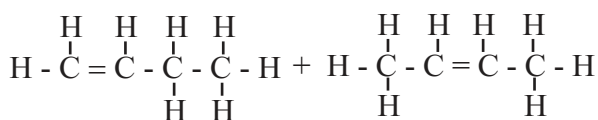


Bromoethane



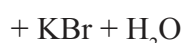
2-Chlorobutane

alcoholic



But-1-ene (20%)

But-2-ene (80%)

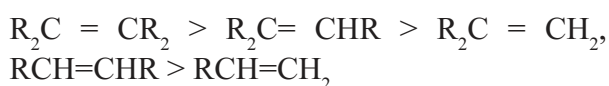


In dehydrohalogenation of 2-Chlorobutane, but-2-ene (disubstituted alkene) is the preferred product because it is formed faster than but-1-ene (monosubstituted alkene). This is in accordance with Saytzeff rule.

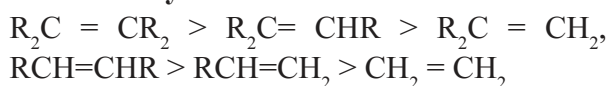
**Saytzeff rule :** In dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to doubly bonded carbon atoms.

The ease of dehydrohalogenation of alkyl halides accordingly is in the order  $3^\circ > 2^\circ > 1^\circ$

#### The ease of formation of alkenes :



#### The stability of alkenes :





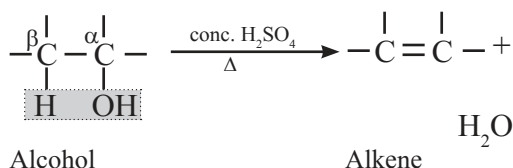


### Can you recall?

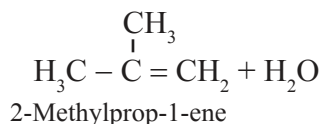
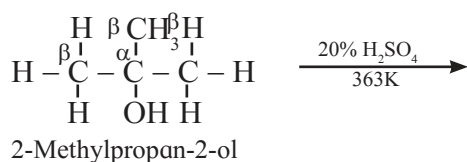
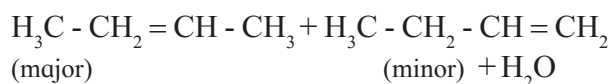
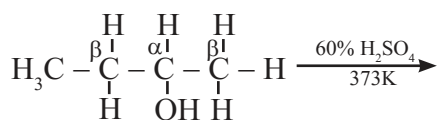
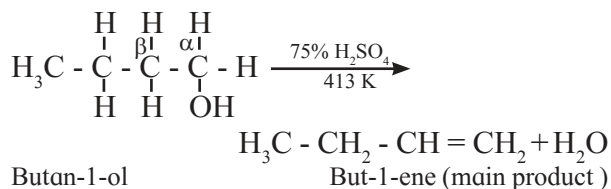
- What are alcohols ?
- What is a dehydration of reaction?
- What is a catalyst ?

**ii. Dehydration of alcohols :** Alcohols on heating with sulphuric acid form alkenes with elimination of water molecule. The reaction is known as catalyzed dehydration of alcohols. The exact conditions of dehydration depend upon the alcohol.

Dehydration of alcohol is an example of  $\beta$ -elimination since OH group from  $\alpha$ -carbon along with a H atom from  $\beta$ -carbon atom is removed.



The ease of dehydration of alcohols is in the order  $3^\circ > 2^\circ > 1^\circ$

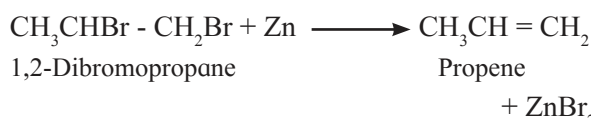
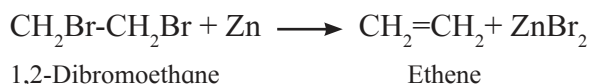
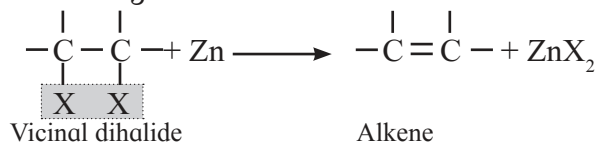


### Can you tell?

1. Explain by writing a reaction, the main product formed on heating 2-methylbutan-2-ol with concentrated sulphuric acid.
2. Will the main product in the above reaction show geometrical isomerism?

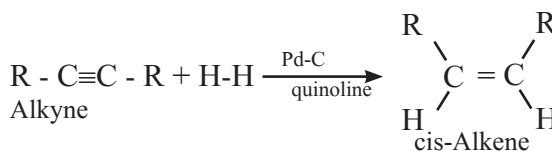
### iii. By dehalogenation of vicinal dihalides :

Removal of two halogen atoms from adjacent carbon atoms is called dehalogenation. The dihalides of alkane in which two halogen atoms are attached to adjacent carbon atoms are called vicinal dihalides. Vicinal dihalides on heating with zinc metal form an alkenes.

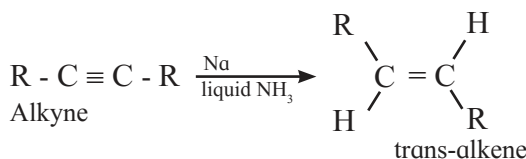


**(II) Addition reactions :** By partial reduction of alkynes (or controlled hydrogenation of alkynes) :

The  $\text{C} \equiv \text{C}$  triple bond of alkynes can be partially reduced to a  $\text{C} = \text{C}$  double bond with calculated quantity of dihydrogen in presence of Lindlar's catalyst (palladised charcoal deactivated partially with quinoline or sulfur compound). The *Cis* isomer is obtained by this method.



Trans alkene is obtained from alkyne on reduction with sodium in liquid ammonia.



**Table 15.3 : Melting point and boiling point of alkenes**

Formula	Name	Molecular mass (u)	b.p. (K)	m.p. (K)
$\text{CH}_2=\text{CH}_2$	Ethene	28	171	104
$\text{CH}_2=\text{CHCH}_3$	Propene	42	225	88
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	But-1-ene	56	267	--
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3$	Pent-1-ene	70	303	--
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$	Hex-1-ene	84	337	135
cis $\text{CH}_3\text{CH}=\text{CHCH}_3$	cis-But-2-ene	56	277	134
trans $\text{CH}_3\text{CH}=\text{CHCH}_3$	trans-But-2-ene	56	274	167
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	Isobutylene	56	266	132

**15.2.3 Physical properties of alkenes :** Alkenes are nonpolar or weakly polar compounds those are insoluble in water, and soluble in non-polar solvents like benzene, ether, chloroform. They are less dense than water. From Table 15.3, it is clear that the boiling point of alkane rises with increasing number of carbons. Branched alkenes have lower the boiling point than straight chain alkane. The boiling point of alkene is very nearly the same as that of alkane with the same carbon skeleton.

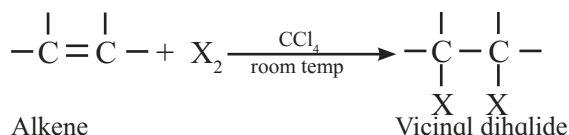
**15.2.4 Chemical properties of alkenes :**

Alkenes are more reactive than alkanes due to the presence of pi ( $\pi$ ) electrons. They undergo electrophilic addition reactions. The different reactions of alkenes are given below:

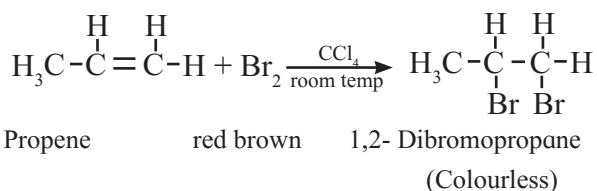
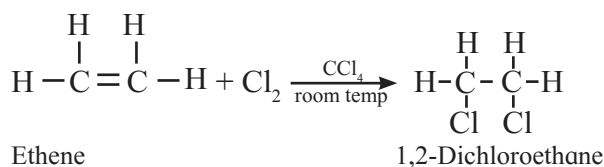
1. Addition of dihydrogen/hydrogenation ( see section 15.1.4).

2. Addition of halogens/halogenation.

Alkenes are converted into the corresponding vicinal dihalides by addition of halogens ( $\text{X}_2 = \text{Cl}_2$  or  $\text{Br}_2$ ).

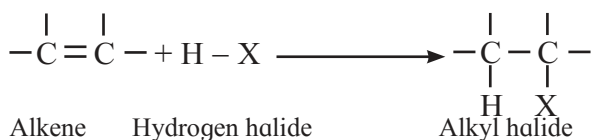


Iodine generally fails to react.



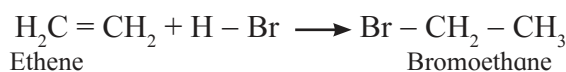
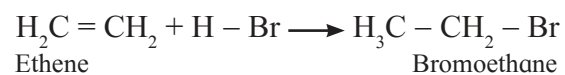
Addition of bromine is useful test for detection  $\text{C}=\text{C}$  in unknown compounds. Red brown colour of bromine rapidly disappears in carbontetrachloride solution if a  $\text{C}=\text{C}$  double bond is present in the compound.

**3. Addition of hydrogen halides/ hydrohalogenation :** Addition of hydrogen halides (HX) like hydrogen chloride, hydrogen bromide and hydrogen iodide converts alkene into the corresponding alkyl halides.

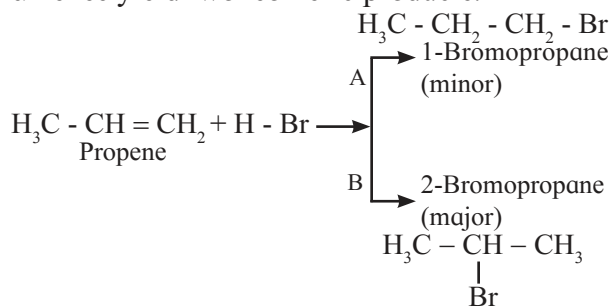


The order of reactivity of hydrogen halides is  $\text{HI} > \text{HBr} > \text{HCl}$

**Addition reaction of HBr to symmetrical alkenes :** The addition of HBr to symmetrical alkenes yield only one product.



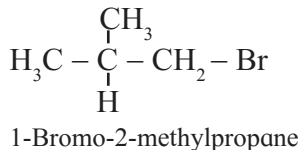
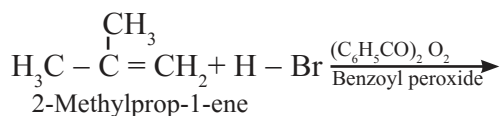
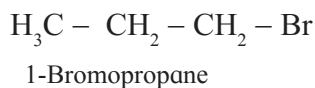
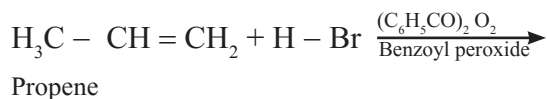
**Addition reaction of HBr to unsymmetrical alkenes :** Addition of HBr to unsymmetrical alkenes yield two isomeric products.



Experimentally it has been found that 2-Bromopropane is the major product. Russian chemist Markovnikov studied hydrohalogenation of a number of unsymmetrical alkenes and formulated a general rule (1869) as follows :

**Markovnikov's rule :** When an unsymmetrical reagent is added to unsymmetrical alkene, the negative part (X<sup>-</sup>) of the reagent gets attached to the carbon atom which carries less number of hydrogen atoms.

**Anti- Markovnikov addition Or peroxide effect or Kharasch - Mayo effect :** In 1933, M. S. Kharasch and F. R. Mayo discovered that the addition of HBr to unsymmetrical alkene in the presence of organic peroxide (R-O-O-R) takes place in the opposite orientation to that suggested by Markovnikov's rule.



**Internet my friend**

http://www.britanica.com>science>hydrocarbon

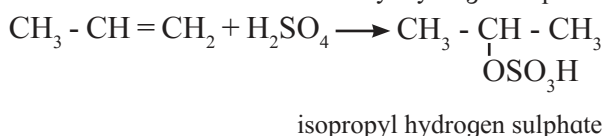
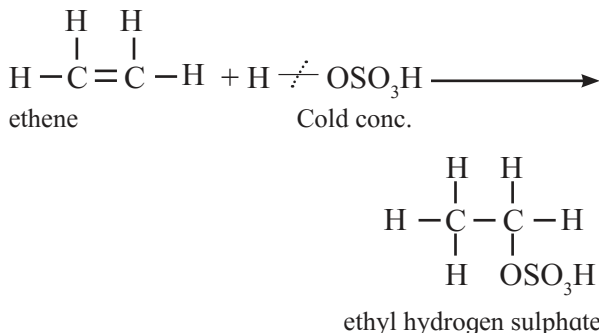
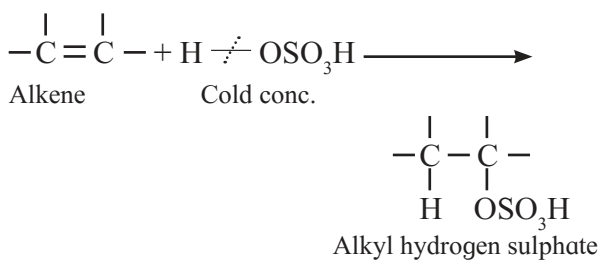


**Remember**

1. The orientation of addition of HBr to unsymmetrical alkene is determined by the presence or absence of peroxide.
2. The peroxide has no effect upon the addition of HCl and HI.

#### 4. Addition of sulphuric acid

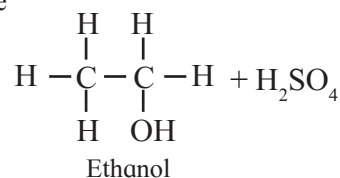
Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphate (ROSO<sub>3</sub>H). The addition takes place according to **Markovnikov's rule**.

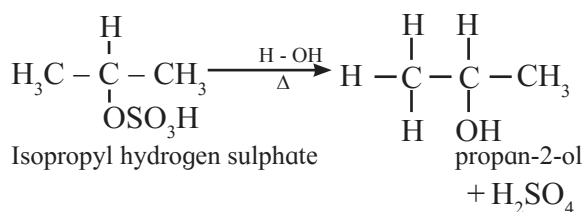


If alkyl hydrogen sulphate is diluted with water and heated, then an alcohol having the same alkyl group as the original alkyl hydrogen sulphate is obtained. This is an excellent method for the large scale manufacture of alcohols.

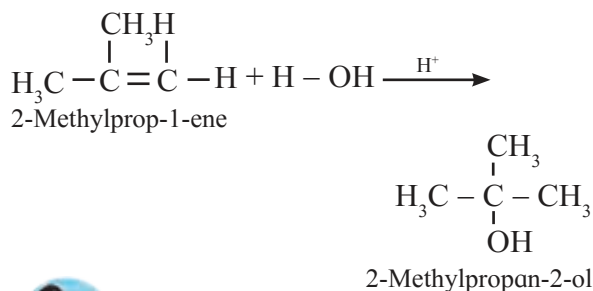


Ethyl hydrogen sulphate





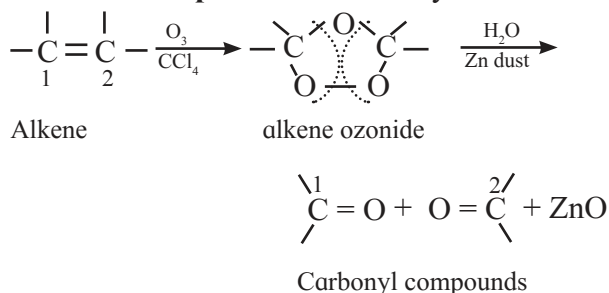
Reactive alkenes on adding water molecules in the presence of concentrated sulphuric acid, form alcohol. The addition of water takes place according to **Markovnikov's rule**. This reaction is known as hydration of alkenes.



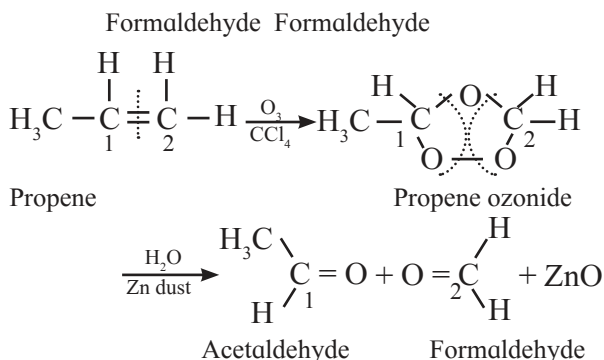
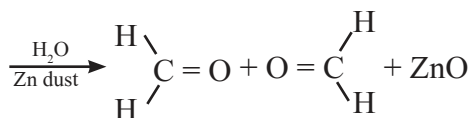
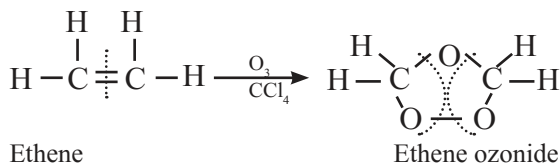
**Can you tell?**

Why Propan-1-ol and 2-Methylpropan-1-ol is not prepared by this method?

**5. Ozonolysis of alkenes :** The C = C double bond gets cleaved on reaction with ozone followed by reduction. This overall process of formation of ozonide by reaction of ozone with alkene in the **first step** and then decomposing it to the carbonyl compounds by reduction in the **second step** is called ozonolysis.



Ozone gas is passed into solution of the alkene in an inert solvent like carbon tetrachloride, unstable alkene ozonide is obtained. This is subsequently treated with water in the presence of a reducing agent zinc dust to form carbonyl compounds, namely, aldehydes and/or ketones.



**Remember**

1. In the cleavage products a carbonyl group (C=O) is formed at each of the original doubly bonded carbon atoms.
2. Knowing the number and arrangement of carbon atoms in these aldehydes and ketones produced, we can identify the structure of original alkene.
3. The role of zinc dust is to prevent the formation of hydrogen peroxide which oxidizes aldehydes to corresponding acids.
4. This reaction is used to locate the position and determine the number of double bonds in alkenes.



**Use your brain power**

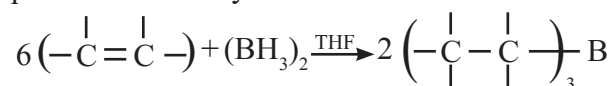
On ozonolysis an alkene forms the following carbonyl compounds. Draw the structure of unknown alkene from which these compounds are formed.



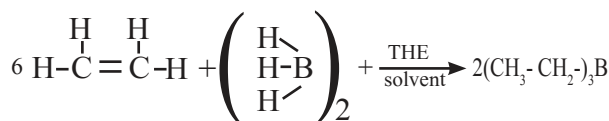
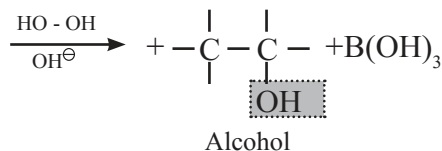
## 6. Hydroboration- oxidation of alkene

Alkenes with diborane in tetrahydrofuran (THF) solvent undergo hydroboration to form trialkylborane, which on oxidation with

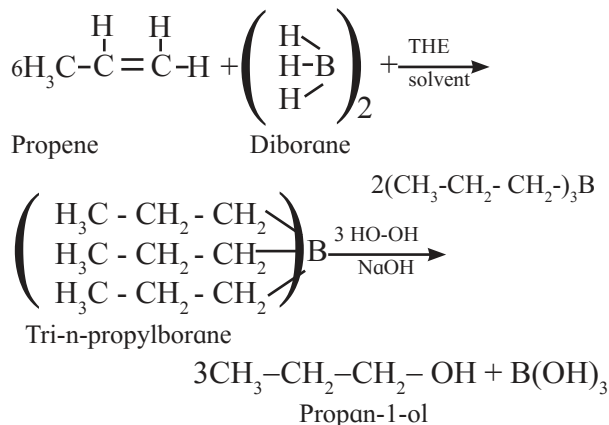
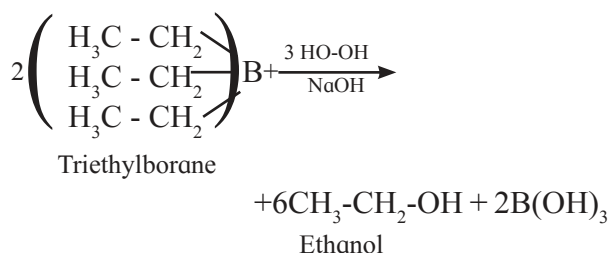
alkaline peroxide forms primary alcohol. The overall reaction gives **Anti-Markovnikov's** product from unsymmetrical alkenes



Alkene                      Diborane                      Trialkylborane

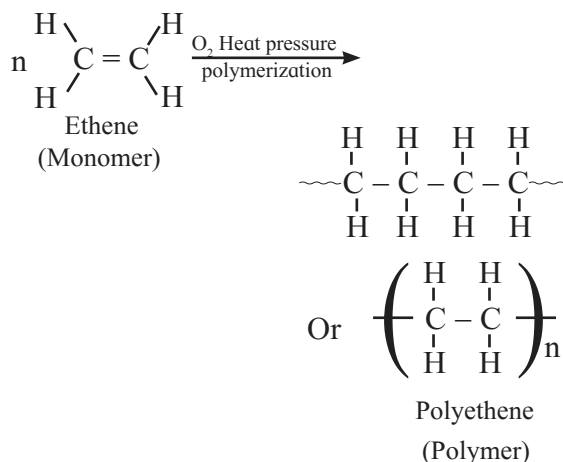


Ethene                      Diborane



**7. Polymerization :** The process in which large number of small molecules join together and form very large molecules with repeating units is called **polymerization**. The compound having very large molecules made of large number repeating small units is called **polymer** and the simple compound forming the repeating units in the polymer is called **monomer**.

For example, ethene at high temperature and under high pressure interacts with oxygen, and undergoes polymerization giving high molecular weight polymer called polyethene.



Here n represents the number of repeating units and is a large number.



### Use your brain power

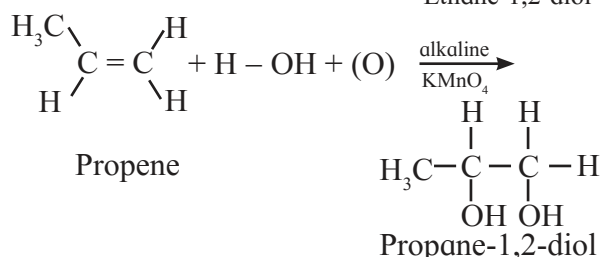
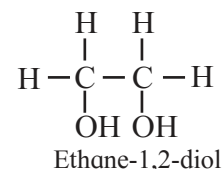
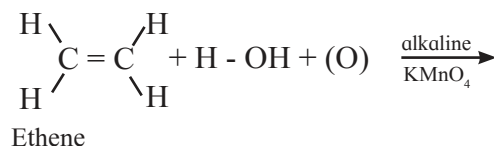
Write the structure of monomer from which each of the following polymers are obtained.

a. Teflon  $-(\text{CF}_2-\text{CF}_2)-$

b. Polypropene  $\left( \begin{array}{c} \text{CH}_3\text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array} \right)_n$

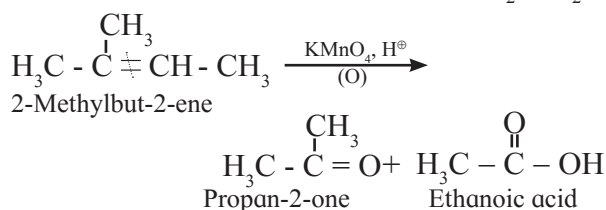
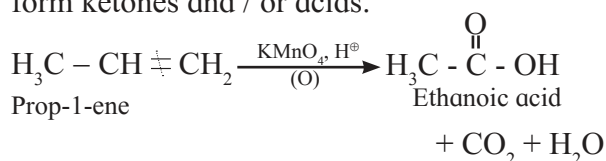
c. Polyvinyl chloride  $\left( \begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array} \right)_n$

**8. Hydroxylation :** Alkenes react with cold and dilute alkaline potassium permanganate to form glycols.



Hydroxylation of alkenes is the most important method for the synthesis of 1,2-diols (Glycols). During this reaction the purple colour of  $\text{KMnO}_4$  disappears. Hence such reaction serves as qualitative test for detecting the presence of double bond in the compound under test. This is known as **Baeyer's test**.

**9. Oxidation :** Alkenes on oxidation with acidic  $\text{KMnO}_4$  or acidic potassium dichromate form ketones and / or acids.



### 15.2.5 Uses of alkenes

1. Alkenes, are used as starting materials for preparation of alkyl halides, alcohols, aldehydes, ketones, acids etc.
2. Ethene and propene are used to manufacture polythene, polypropylene those find use in polyethene bags, toys, bottles, etc.
3. Ethene is used for artificial ripening of fruits, such as mangoes.

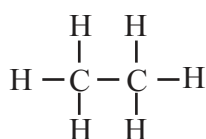


#### Can you tell?

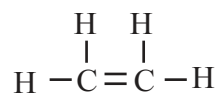
- What are aliphatic hydrocarbons?
- Compare the proportion of carbon and hydrogen atoms in ethane, ethene and ethyne. Which compound is most unsaturated with hydrogen?

**15.3 Alkynes :** Alkynes are aliphatic unsaturated hydrocarbons containing at least one  $\text{C} \equiv \text{C}$ . The number of hydrogen atoms is still less in alkynes as compared to alkenes. Their general formula is  $\text{C}_n\text{H}_{2n-2}$ . Table 15.4 shows names and formulae of lower alkynes.

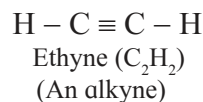
**15.3 Isomerism in alkynes :** Alkynes show position isomerism which is a type of structural isomerism. For example 1-butyne and 2-butyne. 1-Alkynes are also called terminal alkynes.



Ethane ( $\text{C}_2\text{H}_6$ )  
(An alkane)



Ethene ( $\text{C}_2\text{H}_4$ )  
(An alkene)



**Table 15.4 : Lower alkynes**

n	Molecular formula	Structural formula and Common name	IUPAC name
2	$\text{C}_2\text{H}_2$	$\text{H}-\text{C} \equiv \text{C}-\text{H}$ Acetylene	Ethyne
3	$\text{C}_3\text{H}_4$	$\text{CH}_3-\text{C} \equiv \text{CH}$ Methyl acetylene	Propyne
4	$\text{C}_4\text{H}_6$	$\text{CH}_3-\text{CH}_2-\text{C} \equiv \text{CH}$ Ethyl acetylene	But-1-yne
5	$\text{C}_4\text{H}_6$	$\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$ Dimethyl acetylene	But-2-yne



#### Do you know ?

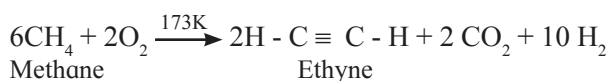
1. Simplest alkyne is ethyne which is known as acetylene.
2. The carbon-carbon triple bond is a functional group.
3. The aliphatic unsaturated hydrocarbons containing two or three carbon-carbon triple bonds are called alkadiynes and alkatriynes, respectively.
4. Cicutoxin from poisonous plants 'water hemlock'.



### 15.3.2 Preparation of alkynes

#### a. Industrial sources :

i. Ethyne is industrially prepared by controlled, high temperature partial oxidation of methane.



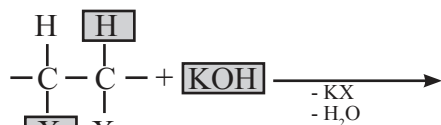
ii. From calcium carbide : Industrially the alkyne ethyne is prepared by reaction of calcium carbide with water.



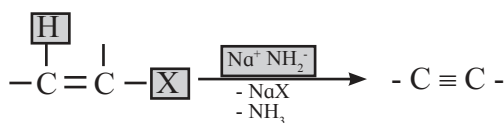


## b. Methods of preparation of alkynes

**1. By dehydrohalogenation of vicinal dihalides :** Removal of H and X from adjacent carbon atoms is called dehydrohalogenation. Vicinal dihalides react with alcoholic solution of potassium hydroxide to form alkenyl halide which on further treating with sodamide forms alkyne.

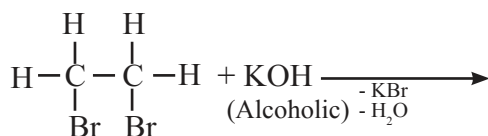


Vicinal dihalide (Alcoholic)

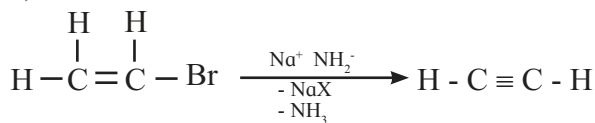


Alkenyl halide

alkyne

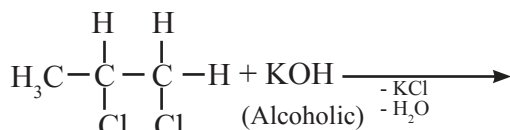


1,2-Dibromoethane

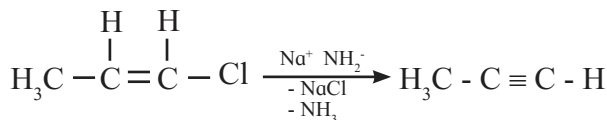


Bromoethene

Ethyne



1,2-Dichloropropane



1-Chloropropanene

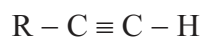
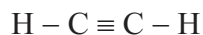
Propyne



### Can you tell?

Why sodamide is used in second step to remove HX from alkenyl halide in place of alcoholic KOH?

**2. From terminal alkynes :** Terminal alkynes are the compounds in which hydrogen atom is directly attached to triply bonded carbon atom.



Such hydrogen atom shows appreciable acidity and can be given away as proton on reaction with sufficiently strong base.

In this method a smaller terminal alkyne first reacts with a very strong base like lithium amide to form metal acetylide (Lithium amide is easier to handle than sodamide).

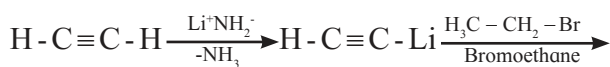
Higher alkynes are obtained by reacting metal acetylides (alkyn-1-yl lithium) with primary alkyl halides.



Terminal alkyne    Lithium amide    Alkyn-1-yl lithium

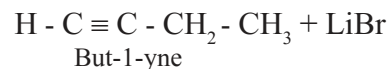


Alkyn-1-yl lithium    Primary alkyl halide    Higher alkyne

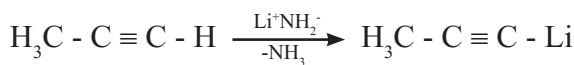


Ethyne

Ethynyllithium

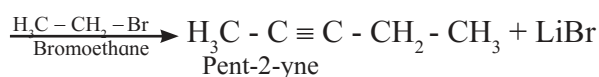


But-1-yne



Propyne

Prop-1-yn-1-yl lithium



Pent-2-yne



### Use your brain power

Convert : 1-Bromobutane to Hex-1-yne.

**15.3.3 Physical properties of alkynes :** The physical properties of alkynes are similar to those of alkanes and alkenes. They are less dense than water. They are insoluble in water and quite soluble in less polar organic solvents like ether, benzene, carbon tetrachloride. The melting points and boiling points of alkynes increase with an increase in molecular mass (Table 15.5).

**Table 15.5 : Melting point and Boiling point of alkynes**

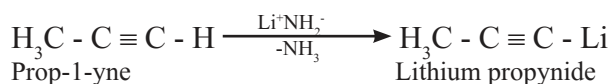
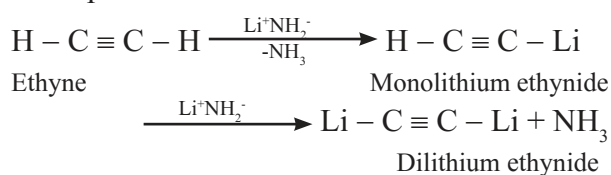
Formula	Name	Molecular mass/u	Physical State	b.p.(K)	m.p.(K)
CH <sub>2</sub> =CH <sub>2</sub>	Ethyne	26	Gas	198	191
CH <sub>3</sub> -C≡CH	Propyne	40	Gas	250	171.5
CH <sub>3</sub> -C≡C-CH <sub>3</sub>	But-1-yne	54	Gas	282	151
CH <sub>3</sub> -C≡C-CH <sub>2</sub> -CH <sub>3</sub>	Pent-1-yne	68	Liquid	313	175
CH <sub>3</sub> -C≡C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Hex-1-yne	82	Liquid	345	149

### 15.3.4 Chemical properties of alkynes :

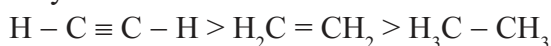
#### 1. Acidity of alkynes :

The hydrogen bonded to C ≡ C triple bond has acidic character. Lithium amide (LiNH<sub>2</sub>) is very strong base and it reacts with terminal alkynes to form lithium acetylides with the liberation of hydrogen indicating acidic nature of terminal alkynes. Why is it so ? In terminal alkynes, hydrogen atom is directly attached to sp hybridized carbon atom. In sp hybrid orbital, the percentage of s-character is 50%. An electron in s-orbital is very close to the nucleus and is held tightly. The sp hybrid carbon atom in terminal alkynes is more electronegative than the sp<sup>2</sup> carbon in ethene or the sp<sup>3</sup> carbon in ethane. Due to high electronegative character of carbon in terminal alkynes, hydrogen atom can be given away as proton (H<sup>+</sup>) to very strong base.

Examples



The relative acidity of alkanes, alkenes and alkynes follows the order



**Can you tell?**

Alkanes and alkenes do not react with lithium amide. Give reason.



**Use your brain power**

Arrange following hydrocarbons in the increasing order of acidic character.  
propane, propyne, propene.

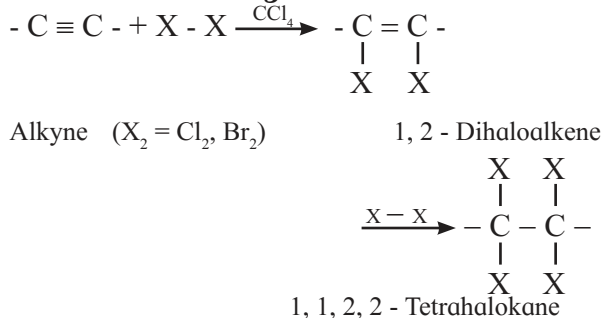


**Do you know ?**

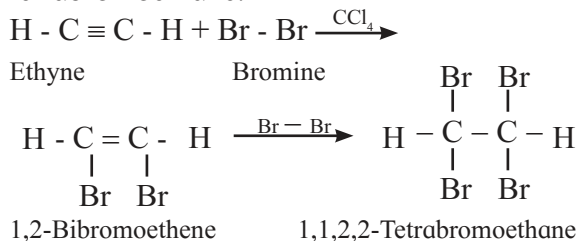
Acidic alkynes react with certain heavy metal ions like Ag<sup>+</sup> and Cu<sup>+</sup> and form insoluble acetylides. On addition of acidic alkyne to solution of AgNO<sub>3</sub> in alcohol form a precipitate which indicates that the hydrogen atom is attached to triply bonded carbon. This reaction is used to differentiate terminal alkynes and non-terminal alkynes.

#### 2. Addition of dihydrogen (See method of preparation of alkenes from unsaturated hydrocarbons)

#### 3. Addition of halogens

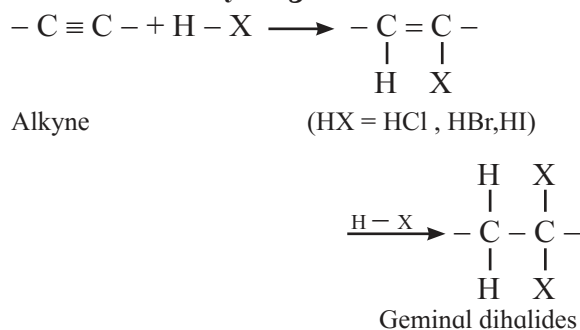


Ethyne reacts with bromine in inert solvent such as carbon tetrachloride to give tetrabromoethane.

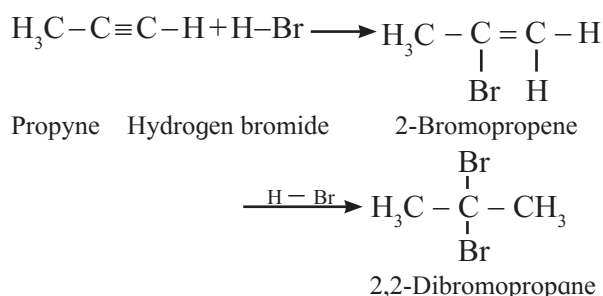
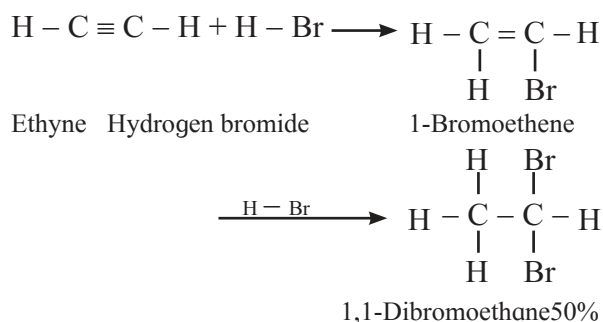


Red-brown colour of solution of bromine in carbon tetrachloride disappears. This test can be used to detect the presence of unsaturation in given compound.

#### 4. Addition of hydrogen halides

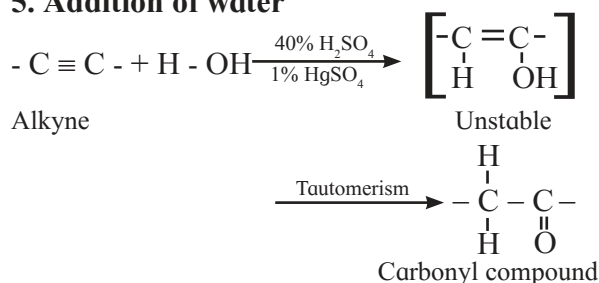


Hydrogen halides (HCl, HBr and HI) add to alkynes across carbon-carbon triple bond in two steps to form geminal dihalides (in which two halogen atoms are attached to the same carbon atom). The addition of HX in both the steps takes place according to **Markovnikov's rule**.

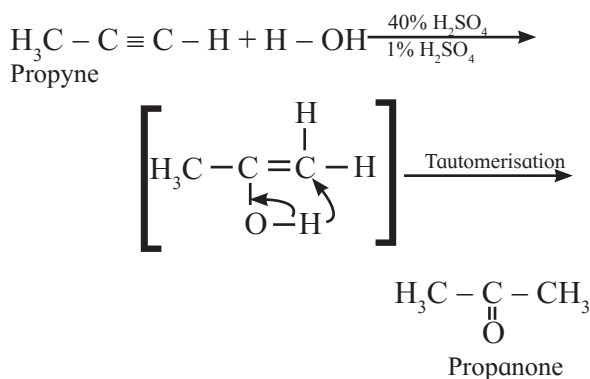
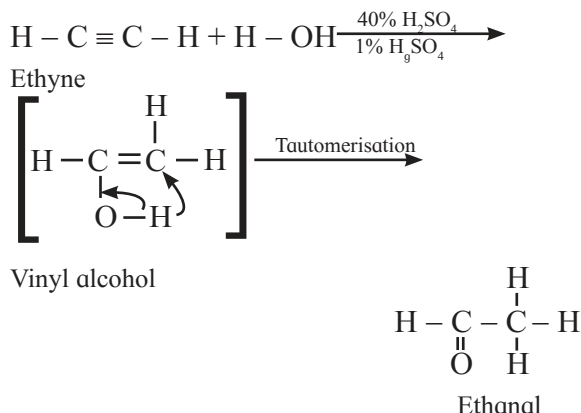


The order of reactivity of hydrogen halides is  $\text{HI} > \text{HBr} > \text{HCl}$

#### 5. Addition of water



Alkynes react with water in presence of 40% sulphuric acid and 1% mercuric sulphate to form aldehydes or ketones i.e. carbonyl compounds.



#### Use your brain power

Convert : 3-Methylbut-1-yne into 3-Methylbutan-2-one.

#### 15.3.5 Uses of acetylene :

1. Ethyne (acetylene) is used in preparation of Ethanal (acetaldehyde), Propanone (acetone), ethanoic acid (acetic acid).
2. It is used in the manufacture of polymers, synthetic rubber, synthetic fibre, plastic etc.
3. For artificial ripening of fruits.
4. In oxy-acetylene ( mixture of oxygen and acetylene) flame for welding and cutting of metals.

#### 15.4 Aromatic Hydrocarbons :



#### Can you recall?

- What are aromatic hydrocarbons?
- What are benzenoid and non-benzenoid aromatics ?

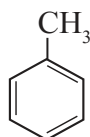
Many organic compounds obtained from natural sources like resins, balsams, oil of wintergreen, etc. possessing pleasant fragrance (aroma = smell) are named as aromatic compounds. Aromatic hydrocarbons (also called arenes) contain only carbon and hydrogen. Benzene is the simplest aromatic compound.

*Benzene and all compounds that have structures and chemical properties resembling benzene are classified as aromatic compounds.*

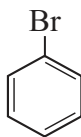
Examples are :



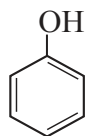
Benzene



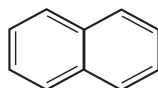
Methylbenzene



Bromobenzene



Phenol



Naphthalene

**15.4.1 Benzene :** The molecular formula of benzene is  $C_6H_6$ . Benzene is parent compound of most of the aromatic compounds.

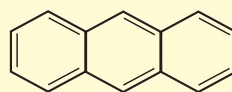
Coal-tar and petroleum are the two large-scale sources of benzene (and aromatic compounds like toluene, phenol, naphthalene.).



### Remember

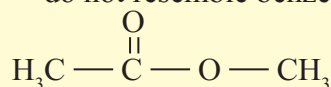
1. Aromatic compounds contain planar cyclic rings.
2. Not all compounds those resemble benzene have pleasant odour (smell).

Anthracene

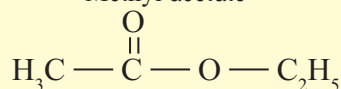


Anthracene is odourless.

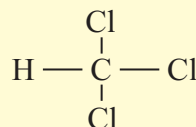
3. Many compounds having pleasant odour do not resemble benzene.



Methyl acetate



Ethyl acetate



Trichloromethane or chloroform

It is a colourless liquid having characteristic odour. Its boiling point is 353K.

It was synthesized by Berthelot (1870) from acetylene. Benzene was originally called **phene** and hence  $C_6H_5$  is called **phenyl group**.

**Table 15.6 : Difference between aromatic and aliphatic compounds**

Aromatic compounds	Aliphatic compounds
1. Aromatic compounds contain higher percentage of carbon.	1. Aliphatic compounds contain lower percentage of carbon.
2. They burn with sooty flame.	2. They burn with non-sooty flame.
3. They are cyclic compounds with alternate single and double bonds.	3. They are open chain compounds.
4. They are not attacked by normal oxidizing and reducing agents.	4. They are easily attacked by oxidizing and reducing agents.
5. They do not undergo addition reactions easily. They do not decolourise dilute alkaline aqueous $KMnO_4$ and $Br_2$ in $CCl_4$ , though double bonds appear in their structure.	5. Unsaturated aliphatic compounds undergo addition reactions easily. They decolourise dilute aqueous alkaline $KMnO_4$ and $Br_2$ in $CCl_4$ .
6. They prefer substitution reactions.	6. The saturated aliphatic compounds give substitution reactions.

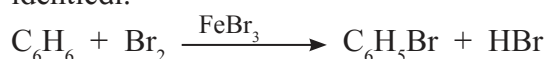
### 15.4.2 Structure of benzene :

1. Molecular formula of benzene,  $C_6H_6$ , indicates the high degree of unsaturation.
2. Open chain structure NOT possible : Open chain or cyclic structure having double and triple bonds can be written for  $C_6H_6$ . But benzene does not behave like alkenes or alkynes (see Table 15.7). This indicates that benzene can not have the open chain structure.

**Table 15.7 : Comparative reactivity of alkenes and benzene**

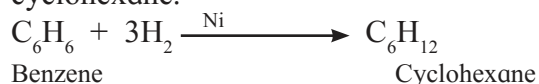
Reaction	Alkene	Benzene
With dil. alka. $KMnO_4$	Decolourisation of $KMnO_4$	No decolourisation
With $Br_2$ in $CCl_4$	Decolourisation of red brown colour of bromine	No decolourisation
With $H_2O$ in acidic medium	Addition of $H_2O$ molecule	No reaction

**3. Evidence of cyclic structure :** Benzene yields only one and no isomeric monosubstituted bromobenzene ( $C_6H_5Br$ ) when treated with equimolar bromine in  $FeBr_3$ . This indicates that all the six hydrogen atoms in benzene are identical.



This is possible only if benzene has cyclic structure of six carbons bound to one hydrogen atom each.

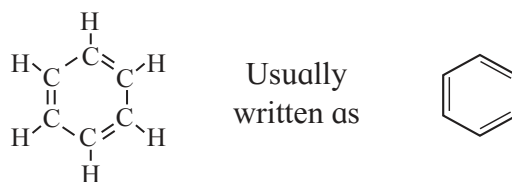
Benzene on catalytic hydrogenation gives cyclohexane.



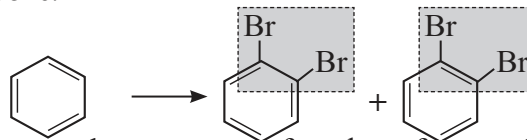
This confirms the cyclic structure of benzene and three  $C = C$  in it.

### 4. Kekulé structure of benzene :

August Kekulé in 1865 suggested the structure for benzene having a cyclic planar ring of six carbon atoms with alternate single and double bonds and hydrogen atom attached to each carbon atom.



The Kekulé structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms would be attached to the doubly bonded carbon atoms whereas in the other, they would be attached to single bonded carbons.



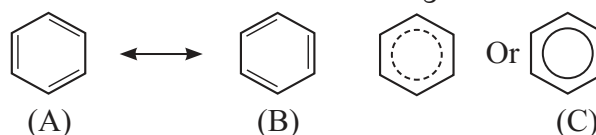
However, benzene was found to form only one ortho-disubstituted benzene. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



Even with this modification, Kekulé's structure of benzene failed to explain unusual stability and preference to substitution reactions rather than addition reactions, which was later explained by resonance.

### 5. Stability of benzene:

Benzene is a hybrid of various resonance structures. The two structures, A and B given by Kekulé are the main contributing structures. The resonance hybrid is represented by inserting a circle or a dotted circle inscribed in the hexagon as shown in (C). The circle represents six electrons delocalized over the six carbon atoms of benzene ring.

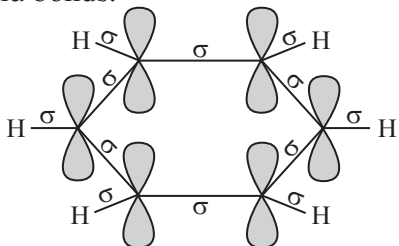


A double headed arrow between the resonance structures is used to represent the resonance phenomenon.

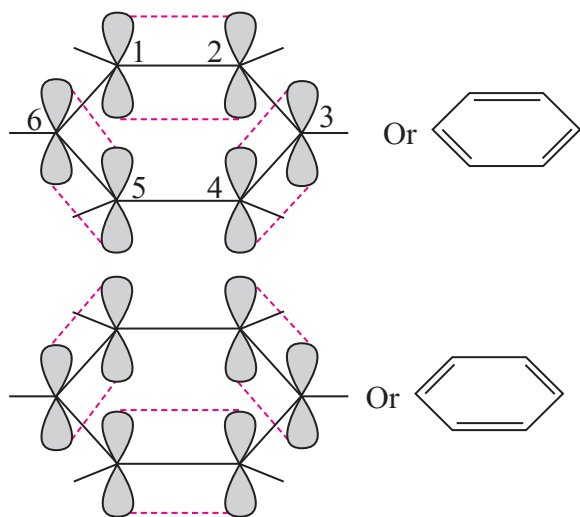
**Stability of benzene :** The actual molecule is more stable than any of its resonance structures. For benzene, the stability due to resonance

is so high that  $\pi$ -bonds of the molecule resist breaking. This explains lack of reactivity of benzene towards addition.

The orbital overlap gives us better picture of structure of benzene. All six carbon atoms in benzene are  $sp^2$  hybridised. Two  $sp^2$  hybrid orbitals of carbons overlap and form carbon-carbon sigma ( $\sigma$ ) bond and the remaining third  $sp^2$  hybrid orbital of each carbon overlaps with s orbital of a hydrogen atom to form six C-H sigma bonds.



The unhybrid p orbitals of carbon atoms overlap laterally forming  $\pi$  bonds. There are two possibilities of forming three  $\pi$  bonds by overlap of p orbitals of  $C_1-C_2$ ,  $C_3-C_4$ ,  $C_5-C_6$  or  $C_2-C_3$ ,  $C_4-C_5$ ,  $C_6-C_1$ , respectively, as shown in Fig. 15.5; both are equally probable. According to **resonance theory** (Chapter 5) these are two resonance structures of benzene.

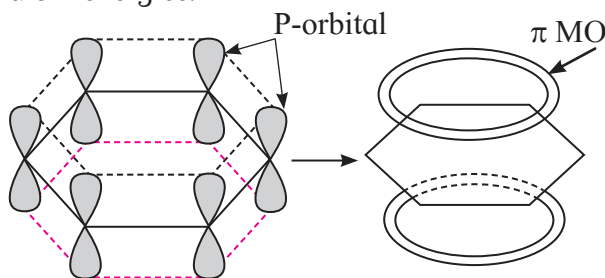


**Fig. 15.5 Overlap of p orbitals in benzene**

According to **molecular orbital (MO) theory** (Chapter 5) the six p orbitals of six carbons give rise to six molecular orbitals of benzene. Shape of the most stable MO is as shown in Fig. 15.6.

Three of these  $\pi$  molecular orbitals lie above and the other below those of free carbon

atom energies.

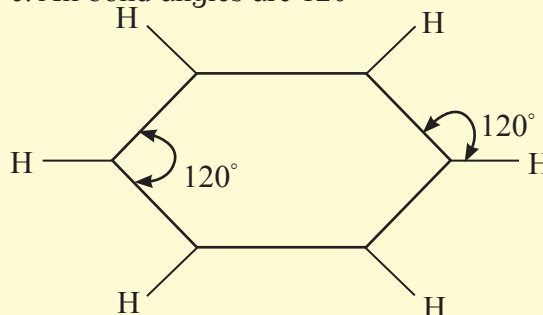


**Fig 15.6 : Representative  $\pi$  molecular orbital in benzene**



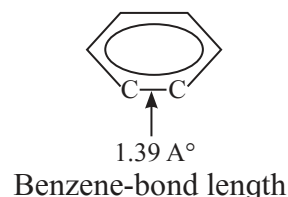
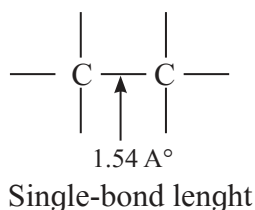
### Remember

- All carbon and hydrogen atoms lie in the same plane.
- Six sigma ( $\sigma$ ) bonds lie in the same plane.
- All bond angles are  $120^\circ$

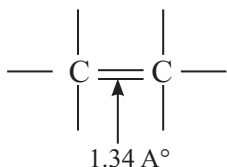


The six electrons of the p orbitals cover all the six carbon atoms and are said to be delocalized. Delocalization of  $\pi$  electrons results in stability of benzene molecule.

**6. Bond parameters of benzene :** X-ray diffraction data indicate that all C-C bond lengths in benzene are equal (139 pm) which is an intermediate between C-C (154 pm) and C=C bond (133 pm). Thus absence of pure double bond in benzene accounts for its reluctance to addition reactions under normal conditions, which explains unusual behaviour of benzene.







Double-bond length

### 15.4.3 Aromatic character (Huckel Rule) :

Benzene undergoes substitution reaction rather than addition reactions. This property is common to all aromatic compounds and is referred to as **aromaticity** or **aromatic character**. The aromatic character of benzene is correlated to its structure.

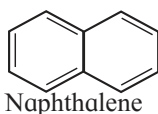
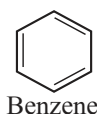
Aromaticity is due to extensive cyclic delocalization of p electrons in planar ring structures.

The following **three rules of aromaticity** are useful in predicting whether a particular compound is

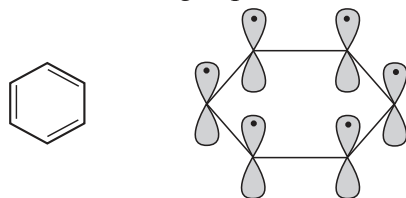
aromatic or non-aromatic.

1. Aromatic compounds are cyclic and planar (all atoms in ring are  $sp^2$  hybridized).
2. Each atom in aromatic ring has a p-orbital. The p-orbitals must be parallel so that continuous overlap is possible around the ring.
3. **Huckel Rule** : The cyclic  $\pi$  molecular orbital formed by overlap of p-orbitals must contain  $(4n + 2)$  p electrons, where  $n = \text{integer } 0, 1, 2, 3 \dots \text{etc.}$

Let us apply these rules to the following compounds



1. **Benzene** : It is cyclic and planar. It has three double bonds and six  $\pi$  electrons. It has a p orbital on each carbon of the hexagonal ring. Hence a continuous overlap above and below the ring is possible.



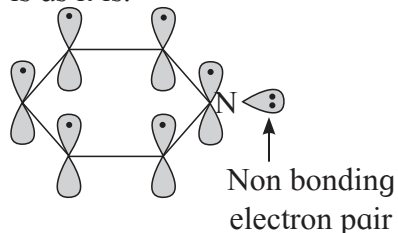
This compound is aromatic,  $4n + 2 = \text{Number of } \pi \text{ electrons.}$

$4n + 2 = 6, \quad \therefore 4n = 6 - 2 = 4$   
 $n = 4/4 = 1$ , Here 'n' comes out to be an integer.  
Hence benzene is aromatic.

2. **Naphthalene** : It is cyclic and planar. It has 5 double bonds and 10  $\pi$  electrons. It has p orbital on each carbon atom of the ring. Hence a continuous overlap around the ring is possible. This is in accordance with Huckel rule.

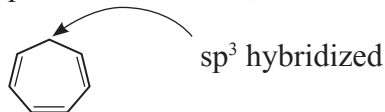
$4n + 2 = \text{Number of } \pi \text{ electrons}$   
 $4n + 2 = 10, \quad \therefore 4n = 10 - 2 = 8$   
 $n = 8/4 = 2$ , Here 'n' comes out to be an integer.  
Hence naphthalene is aromatic.

3. **Pyridine** : Pyridine has three double bonds and 6  $\pi$  electrons. The six p orbital containing six electrons form delocalized p molecular orbital. The unused  $sp^2$  hybrid orbital of nitrogen containing two non-bonding electrons is as it is.



$4n + 2 = \text{Number of p electrons}$   
 $4n + 2 = 6, \quad \therefore 4n = 6 - 2 = 4$   
 $n = 4/4 = 1$ , Here 'n' comes out to be an integer.  
Hence pyridine is aromatic.

4. **Cycloheptatriene** : It is cyclic and planar. It has three double bonds and 6  $\pi$  electrons. But one of the carbons is saturated ( $sp^3$  hybridized) and does not possess a p orbital. Hence a continuous overlap around the ring is not possible. Therefore, it is non-aromatic.



### 15.4.4 Preparation of aromatic compounds

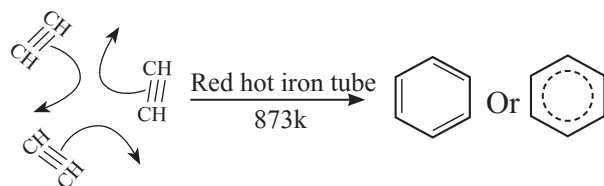
#### a. Industrial source of aromatic compounds

Coal tar and petroleum are major sources of aromatic compounds.

#### b. Methods of preparation of benzene

1. **From ethyne (By trimerization)** : Alkynes when passed through a red hot iron tube at 873 K, polymerize to form aromatic hydrocarbons.

Ethyne when passed through a red hot iron tube at 873 K undergoes trimerization to form benzene.



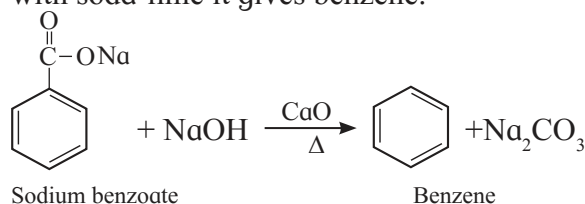
**Can you recall?**

What is decarboxylation ?

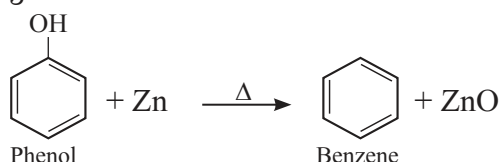
## 2. From sodium benzoate :

(By decarboxylation)

When anhydrous sodium benzoate is heated with soda-lime it gives benzene.



**3. From phenol ( By reduction) :** When vapours of phenol are passed over heated zinc dust, it gives benzene.



### 15.4.5 Physical properties of benzene

1. Benzene is colourless liquid.
2. Its boiling point is 353K and melting point is 278.5 K.
3. It is insoluble in water. It forms upper layer when mixed with water.
4. It is soluble in alcohol, ether, and chloroform.
5. Benzene vapours are highly toxic which on inhalation lead to unconsciousness.

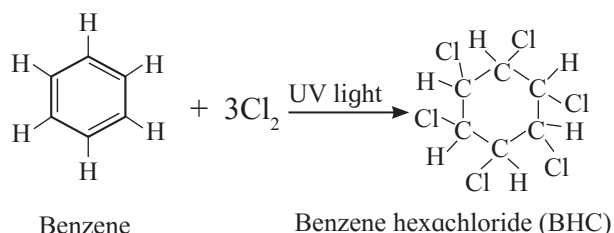
### 15.4.6 Chemical properties of benzene

Aromatic compounds are characterised by electrophilic substitution reactions. However, they undergo addition and oxidation reactions under special conditions. Some reactions of benzene are discussed below.

#### I. Addition reactions

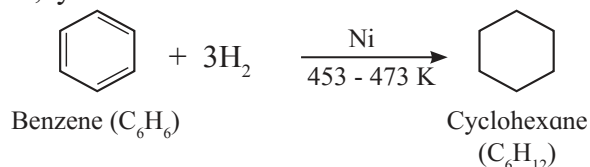
**i. Addition of chlorine :** Benzene when treated with chlorine in presence of bright sunlight or UV light, adds up three molecules of chlorine

to give benzene hexachloride .

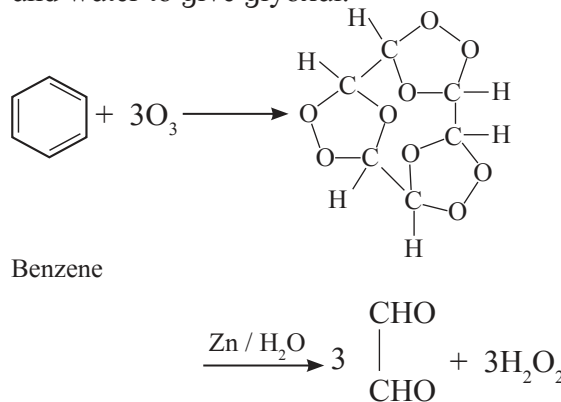


$\gamma$  - isomer of benzene hexachloride is called **gammexane** or **lindane** which is used as insecticide.

**ii. Addition of hydrogen :** When a mixture of benzene and hydrogen gas is passed over heated catalyst nickel at 453 K to 473 K, cyclohexane is formed.



**iii. Addition of ozone :** When benzene is treated with ozone in presence of an inert solvent carbon tetrachloride, benzene triozone is formed which is then decomposed by zinc dust and water to give glyoxal.

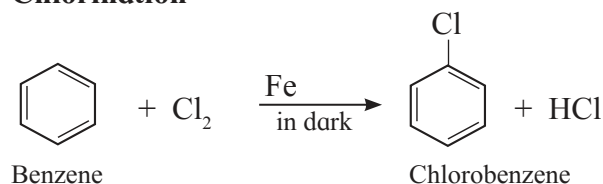


Ethanedial or glyoxal

**II. Substitution reactions :** Benzene shows electrophilic substitution reactions, in which one or more hydrogen atoms of benzene ring are replaced by **electrophilic groups** like -Cl, -Br, -NO<sub>2</sub>, -SO<sub>3</sub>H, -R (alkyl group) , -COR (Acyl group) etc. (see Chapter 14).

**i. Halogenation :** In this reaction, hydrogen atom of benzene ring is replaced by halogen atom .

## Chlorination



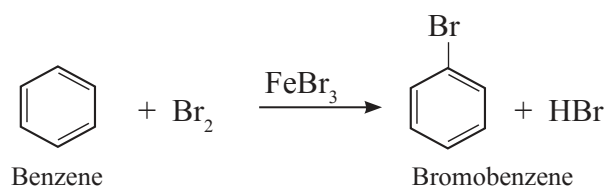
Chlorine reacts with benzene in dark in the presence of iron or ferric chloride or anhydrous aluminium chloride or red phosphorous as catalyst to give chlorobenzene.

Electrophile :  $\text{Cl}^\oplus$ , Chloronium ion

Formation of the electrophile :

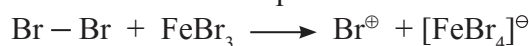


**Bromination** of benzene is similar to chlorination :



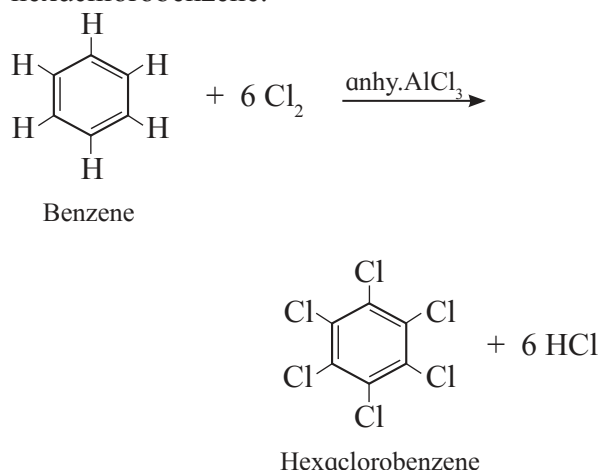
Electrophile :  $\text{Br}^\oplus$ ,

Formation of electrophile :

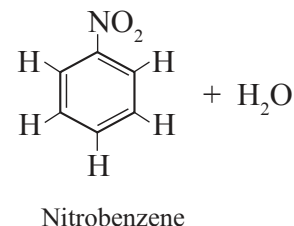
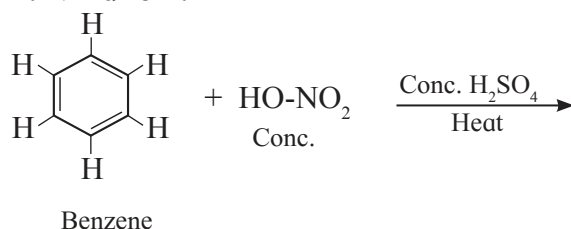


**Iodination** of benzene is **not possible** as it is reversible process.

With excess of chlorine, benzene gives hexachlorobenzene.

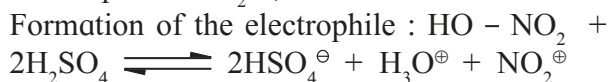


## ii. Nitration :

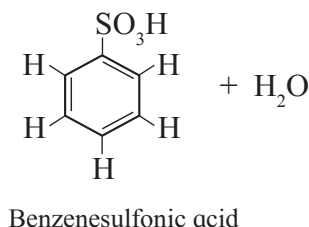
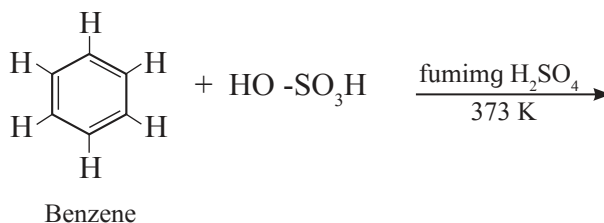


When benzene is heated with a mixture of concentrated nitric acid and concentrated sulfuric acid (nitrating mixture) at about 313 K to 333 K, it gives nitrobenzene.

Electrophile :  $\text{NO}_2^\oplus$ , nitronium ion.



## iii. Sulfonation :



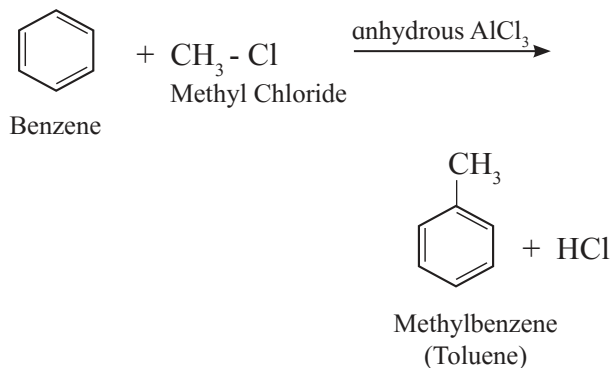
When benzene is heated with fuming sulfuric acid (oleum) at 373 K, it gives benzene sulfonic acid.

Electrophile :  $\text{SO}_3$ , free sulfur trioxide

Formation of the electrophile :



## iv. Friedel-Craft's alkylation reaction :

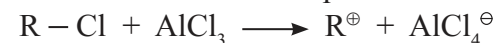


When benzene is treated with an alkyl halide like methyl chloride in the presence of anhydrous aluminium chloride, it gives toluene.

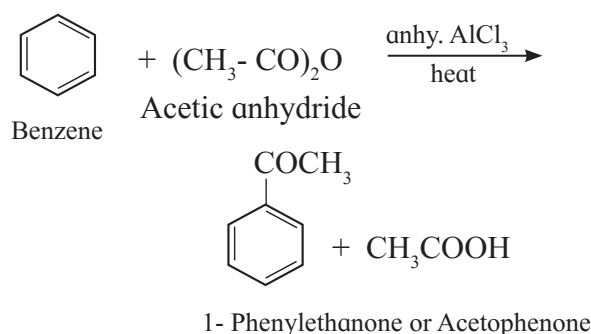
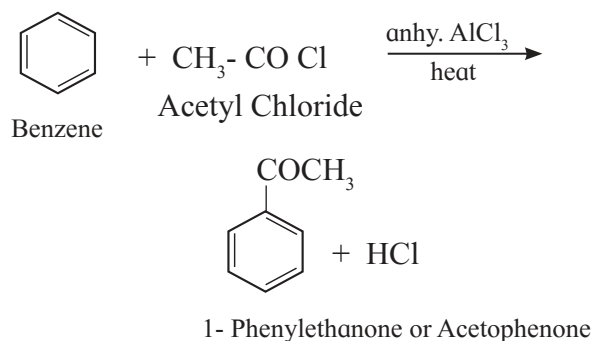
The reaction is used to extend the chain outside the benzene ring.

Electrophile :  $R^{\oplus}$

Formation of the electrophile :



#### v. Friedel-Craft's acylation reaction :



When benzene is heated with an acyl halide or acid anhydride in the presence of anhydrous aluminium chloride, it gives corresponding acyl benzene.

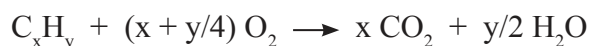
Electrophile :  $R-C^{\oplus}=O$  acylium ion

Formation of the electrophile :  $R-COCl + AlCl_3 \longrightarrow R-C^{\oplus}=O + AlCl_4^{\ominus}$

**6. Combustion :** When benzene is heated in air, it burns with sooty flame forming carbon dioxide and water.

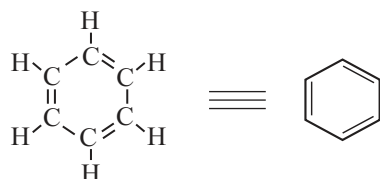


General combustion reaction for any hydrocarbon ( $C_xH_y$ ) can be represented as follows:



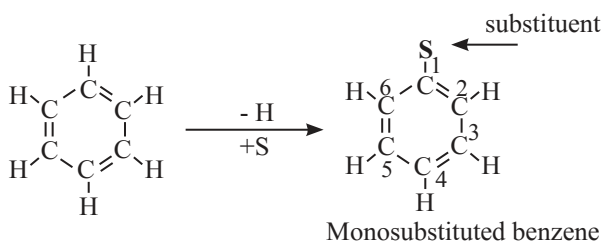
#### 15.4.7 Directive influence of a functional group in monosubstituted benzene

Structure of benzene :



In benzene, all hydrogen atoms are equivalent. Therefore, only one product is possible when it undergoes electrophilic substitution reactions.

#### Monosubstituted benzene :



#### Positions of carbon atoms in mono substituted benzene :

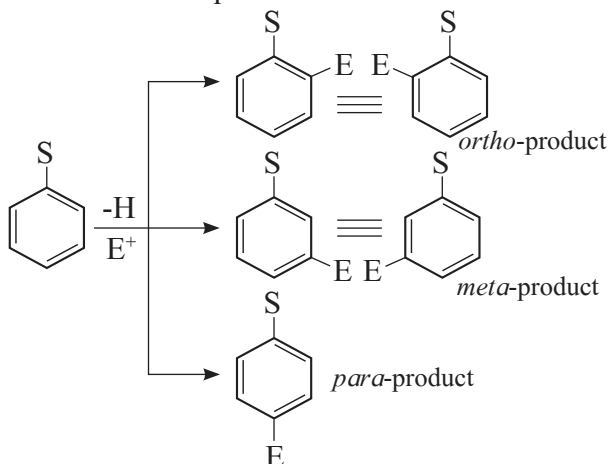
The positions 2 and 6 are equivalent and give ortho (o-) products.

The position 3 and 5 are equivalent and give meta (m-) products.

The position 4 is unique and gives para (p-) product.

Now in benzene, five positions are available for electrophilic substitution.

When monosubstituted benzene is subjected to further electrophilic substitution, the second substituent i.e. electrophile (see Chapter 14) or incoming group (E) can occupy any of these positions and give three disubstituted products. But these products are not formed in equal amounts.

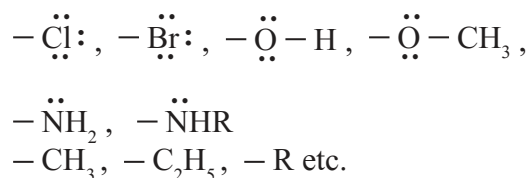


Two types of behaviour are observed.

**a. ortho- and para - products or b. meta-products are found as major products :**

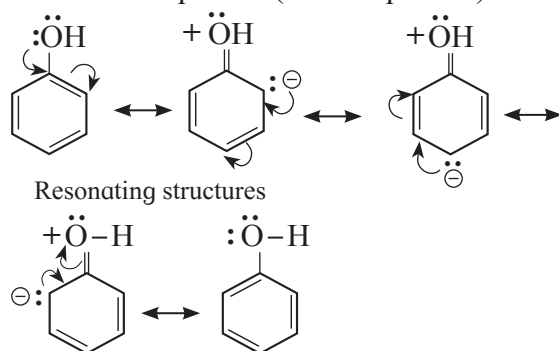
This behaviour mainly depends on the nature of the substituent (S) already present in the benzene ring and not on the nature of second substituent (E) i.e. incoming group.

### Ortho and para directing groups :



The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups.

**Ortho and para directive influence of -OH group :** The resonance theory clearly explains why certain substituents are ortho/para or meta directing. Let us study the various resonance structures of phenol (see Chapter 14).



It is clear from the above resonance structures that the ortho and para positions have a greater electron density than the meta positions. Therefore, -OH group activates the benzene ring for the attack of second substituent E at these electron -rich centres.



#### Remember

Due to -I effect of -OH group (see Chapter 14), the electron density on ortho positions of the benzene ring gets slightly reduced. Thus resonance effect and inductive effect of OH group act opposite to each other.

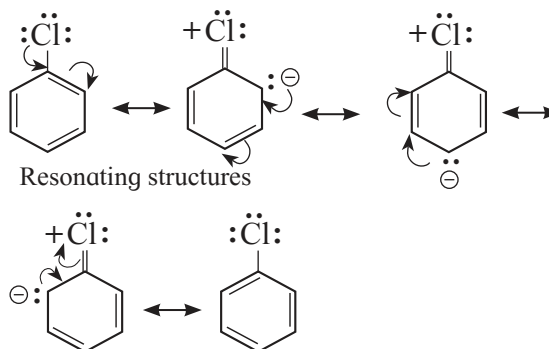
*All ortho and para directing groups possess nonbonding electron pair on the atom which is directly attached to aromatic ring.*

**Methyl group is an exception :** The only exception to above rule is methyl or alkyl groups. It is ortho and para directing, although it has no nonbonding electron pair on the key atom. This is explained on the basis of special

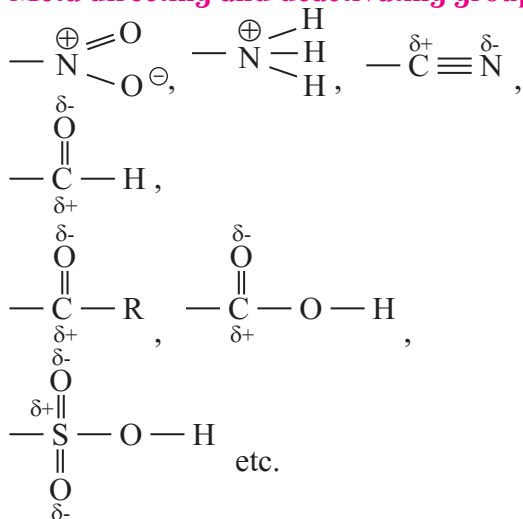
type of resonance called hyperconjugation or no bond resonance (see Chapter 14).

In case of **aryl halides**, halogens are moderately deactivating. Because of their strong -I effect, overall electron density on the benzene ring decreases. It makes the electrophilic substitution difficult. However, due to resonance the electron density on ortho and para positions is greater than meta positions. Halogens are ortho and para directing.

Let us study the various resonating structures of chlorobenzene.



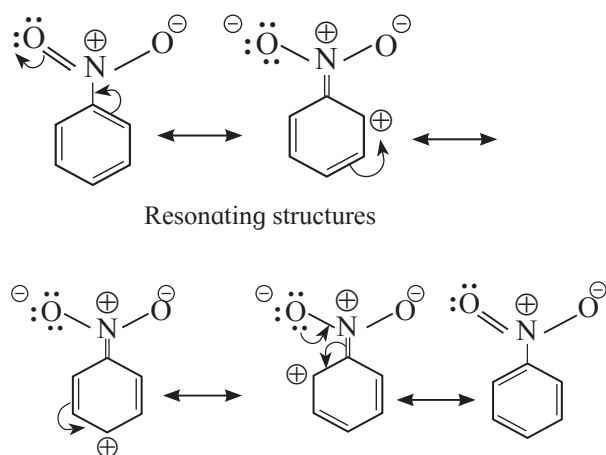
### Meta directing and deactivating groups



All meta directing groups have positive (or partial positive) charge on the atom which is directly attached to an aromatic ring.

The groups which direct the incoming group to meta positions are called **meta directing groups**.

**Metadirective influence of  $-\text{NO}_2$  group can be explained by resonance theory :** Meta directing group withdraws electrons from the aromatic ring by resonance, making the ring electron-deficient. Therefore, meta groups are ring deactivating groups. Due to  $-I$  effect,  $-\text{NO}_2$  group reduces electron density in benzene ring on ortho and para positions. So the attack of incoming group becomes difficult at ortho and para positions. Incoming group can attack on meta positions more easily. Let us study the various resonance structures of nitrobenzene.



It is clear from the above resonance structures that the ortho and para positions have comparatively less electron density than at meta positions. Hence, the incoming group/electrophile attacks on meta positions.

#### 15.4.6 Carcinogenicity and Toxicity :

Benzene is both toxic and carcinogenic (cancer causing). In fact, it might be considered "the mother of all carcinogens" as a large number of carcinogens have structures those include benzene rings. Several polycyclic aromatic compounds (containing more than two fused benzene rings) are produced by incomplete combustion of tobacco, coal and petroleum. In liver, benzene is oxidized to an epoxide. Benzopyrene is converted into an epoxy diol. These substances are carcinogenic and can react with DNA which can induce mutation leading to uncontrolled growth of cancer cells.



#### Internet my friend

1. [chemed.chem.purdue.edu](http://chemed.chem.purdue.edu)>lorganic>Organic Chemistry
2. [www.ncert.nic.in](http://www.ncert.nic.in)>ncerts>kech206(pdf)
3. <https://www.britannica.com>>science>benzene
4. <https://pubchem.ncbi.nlm.nih.gov>>Benzene





## Exercises

### 1. Choose correct options

- A. Which of the following compound has highest boiling point ?  
a. n-pentane  
b. iso-butane  
c. butane  
d. neopentane
- B. Acidic hydrogen is present in :  
a. acetylene  
b. ethane  
c. ethylene  
d. dimethyl acetylene
- C. Identify 'A' in the following reaction:  
$$\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{C}}} = \text{CH}_2 \xrightarrow{\text{A}}$$
  
$$\text{CH}_3 - \underset{\text{O}}{\underset{||}{\text{C}}} - \text{CH}_3 + \text{CO}_2 + \text{H}_2\text{O}$$
  
a.  $\text{KMnO}_4/\text{H}^+$   
b. alkaline  $\text{KMnO}_4$   
c. dil.  $\text{H}_2\text{SO}_4$ /1%  $\text{HgSO}_4$   
d.  $\text{NaOH}/\text{H}_2\text{O}_2$
- D. Major product of chlorination of ethyl benzene is :  
a. m-chlorethyl benzene  
b. p - chloroethyl benzene  
c. chlorobenzene  
d. o - chloroethylbenzene
- E. 1 - chloropropane on treatment with alc. KOH produces :  
a. propane  
b. propene  
c. propyne  
d. propyl alcohol

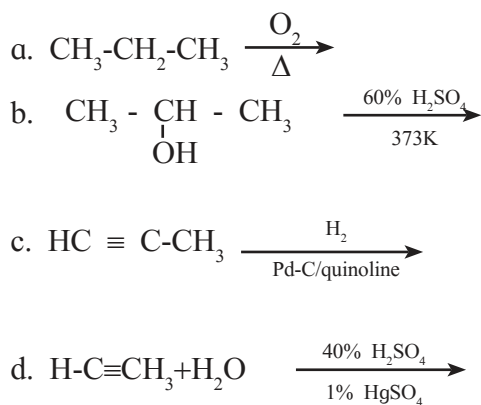
### 2. Name the following :

- A. The type of hydrocarbon that is used as lubricant.
- B. Alkene used in the manufacture of polythene bags.
- C. The hydrocarbon said to possess carcinogenic property.
- D. What are the main natural sources of alkane?

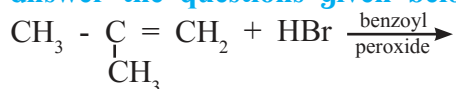
- E. Arrange the three isomers of alkane with molecular formula  $\text{C}_5\text{H}_{12}$  in increasing order of boiling points and write their IUPAC names.
- F. Write IUPAC names of the products obtained by the reaction of cold concentrated sulphuric acid followed by water with the following compounds.  
a. propene      b. but-1-ene
- G. Write the balanced chemical reaction for preparation of ethane from  
a. Ethyl bromide  
b. Ethyl magnesium iodide
- H. How many monochlorination products are possible for  
a. 2-methylpropane ?  
b. 2-methylbutane ?  
Draw their structures and write their IUPAC names.
- I. Write all the possible products for pyrolysis of butane.
- J. Which of the following will exhibit geometrical isomerism ?  
a.  $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_2}{\underset{||}{\text{C}}} - \text{CH}_3$   
b.  $(\text{CH}_3)_2\text{C} = \text{CH}_2$   
c.  $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{C}}} = \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{C}}} - \text{CH}_3$
- K. What is the action of following on ethyl iodide ?  
a. alc, KOH  
b. Zn, HCl
- L. An alkene 'A' on ozonolysis gives 2 moles of ethanal. Write the structure and IUPAC name of 'A'.
- M. Acetone and acetaldehyde are the ozonolysis products of an alkene. Write the structural formula of an alkene and give IUPAC name of it.
- N. Write the reaction to convert  
a. propene to n-propylalcohol.  
b. propene to isopropyl alcohol.

- O. What is the action of following on but-2-ene ?  
 a. dil alkaline  $\text{KMnO}_4$   
 b. acidic  $\text{KMnO}_4$
- P. Complete the following reaction sequence :  
 $\text{HC} \equiv \text{CH} \xrightarrow{\text{LiNH}_3} \text{A} \xrightarrow{\text{CH}_3\text{CH}_2\text{Cl}} \text{B} \xrightarrow{\text{HBr}} \text{C}$   
 Comment on the acidic nature of B.
- Q. Write the balanced chemical reactions to get benzene from  
 a. Sodium benzoate.  
 b. Phenol.
- R. Predict the possible products of the following reaction.  
 a. chlorination of nitrobenzene,  
 b. sulfonation of chlorobenzene,  
 c. bromination of phenol,  
 d. nitration of toluene.

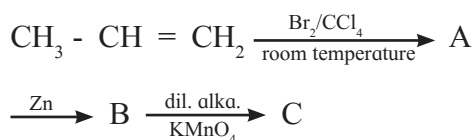
**3. Identify the main product of the reaction**



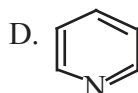
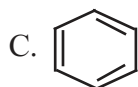
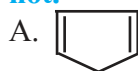
**4. Read the following reaction and answer the questions given below.**



- a. Write IUPAC name of the product.  
 b. State the rule that governs formation of this product.
- 5. Identify A, B, C in the following reaction sequence :**

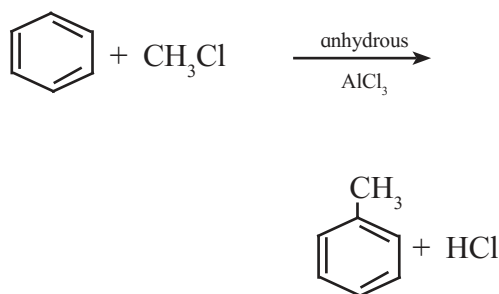


**6. Identify giving reason whether the following compounds are aromatic or not.**



**7. Name two reagents used for acylation of benzene.**

**8. Read the following reaction and answer the questions given below.**



- A. Write the name of the reaction.  
 B. Identify the electrophile in it.  
 C. How is this electrophile generated?



**Activity :**

**Prepare chart of hydrocarbons and note down the characteristics.**