

Hydrocarbons

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6.1 Introduction

Simple organic compounds in which only carbon and hydrogen atoms are present, are called Hydrocarbons. Hydrocarbons are very important compounds in our daily life. Hydrocarbons are obtained from natural sources such as plants and animals. The main sources of hydrocarbons in nature are petroleum, natural gas, coal etc. Hydrocarbon compounds also include petrol, diesel, LPG, CNG etc. Hydrocarbons can be used to manufacture different types of polymers, dyes, paints, drugs etc. Therefore, it is necessary to study them for better understanding and the importance of hydrocarbon in our daily life.

6.2 Hydrocarbons

Hydrocarbons are considered as the simplest compounds in organic chemistry, as only carbon and hydrogen atoms are present in them. Hydrocarbons are obtained from natural sources such as coal, natural gas and petroleum.

6.2.1 Classification of Hydrocarbons :

Different types of organic compounds can be obtained by replacing the hydrogen atom of hydrocarbon by appropriate functional group.

There are four main types of hydrocarbons based on the different types of bonds between carbon-carbon atoms in them. They are as follows : (i) Alkane compounds (ii) Alkene compounds (iii) Alkyne compounds and (iv) Arene compounds.

(i) Alkanes are saturated hydrocarbons. Alkanes contain single bond between carbon-carbon atoms and carbon-hydrogen atoms. Alkanes are acyclic and cyclic compounds.

(ii) Alkenes are unsaturated hydrocarbons. Alkenes contain at least one carbon-carbon double bond. Like alkanes, alkenes also contain acyclic and cyclic compounds.

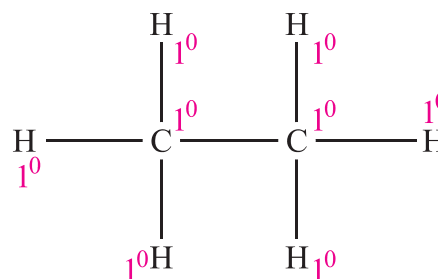
(iii) Alkynes are unsaturated hydrocarbons. Alkynes contain at least one carbon-carbon triple bond. Alkynes mainly contain acyclic compounds.

(iv) Arene compounds are special type of unsaturated hydrocarbons. Arenes contain characteristic carbon-carbon double-bond. Arene compounds are mainly cyclic compounds.

6.2.2 Classification of Carbon and Hydrogen atoms in hydrocarbons :

Each carbon and hydrogen of a hydrocarbon is classified based on the number of other carbon atoms attached to them.

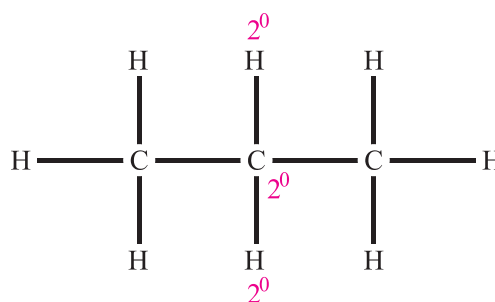
If a carbon atom is attached to only one carbon atom, it is called primary (1^0) carbon. Hydrogen attached with this primary carbon is called primary (1^0) hydrogen.



Ethane

In the above example, both the carbon atoms are primary (1^0) carbon, and also all the hydrogen atoms linked to them are primary hydrogen.

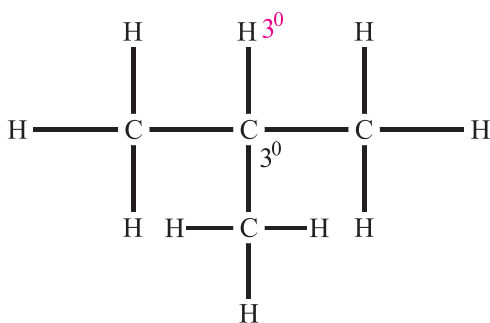
If one carbon atom is attached to two other carbon atoms then that carbon is known as secondary (2^0) carbon. The hydrogen atoms linked to this (2^0) secondary carbon are called secondary (2^0) hydrogen.



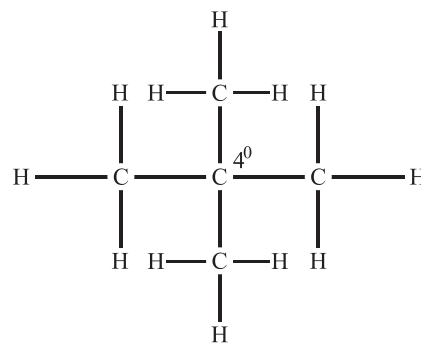
Propane

In the above example, the central carbon is attached with two other carbon atoms, hence, it is called secondary (2^0) carbon, and the two hydrogen atoms attached to it are also secondary (2^0) hydrogens.

If one carbon atom is attached to three other carbon atoms, then, that carbon is known as tertiary (3^0) carbon and the hydrogen attached to that carbon is called tertiary (3^0) hydrogen.



2 Methyl Propane



Dimethyl propane

In the above example the tertiary (3^0) carbon is attached with three other carbon atoms and the three hydrogens attached to it are tertiary (3^0) hydrogens.

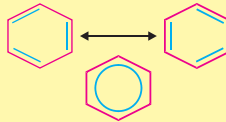
If a carbon atom is attached to four other carbon atoms it is called quarternary (4^0)

carbon. The four carbons complete its tetravalency, and hence, no hydrogen can be attached to it. As a result, quarternary (4^0) hydrogen is not possible.

The classification of hydrocarbons is given in Table 6.1.

Table 6.1 Classification of Hydrocarbons

Hydrocarbon	Type	Characteristic	General Formula	Bond	Shape	Example	Structure
Alkane	Acyclic	Saturated	$C_n H_{2n+2}$	C – C	Three Dimensional	Methane	CH_4
						Ethane	CH_3CH_3
						Propane	$CH_3CH_2CH_3$
	Cyclic	Saturated	$C_n H_{2n}$	C – C	Planar Three Dimensional	Cyclopropane	
Cyclobutane							
Alkene	Acyclic	Unsaturated	$C_n H_{2n}$	C = C	Planar	Ethene	$CH_2 = CH_2$
				C – C		Propene	$CH_2 = CH-CH_3$
	Cyclic	Unsaturated	$C_n H_{2n-2}$	C = C	Planar	Cyclopropene	
				C – C		Cyclobutene	

Alkyne	Acyclic	Unsaturated	$C_n H_{2n-2}$	$C \equiv C$ $C - C$	Linear	Ethyne Propyne	$CH \equiv CH$ $CH \equiv C-CH_3$
Arene	Cyclic	Characteristic Unsaturated	$C_n H_{2n-6}$	$C - C$ and $C = C$	Planar	Benzene	

6.3 Alkane Compounds

Alkane compounds are saturated hydrocarbons. The hydrocarbons which contains single bond between carbon-carbon are called alkanes. The general formula for alkanes is $C_n H_{2n+2}$, where n = number of carbon atoms.

In alkanes sp^3 hybrid orbitals of carbon and $1s$ orbitals of four hydrogen atoms form tetrahedral structure of hydrocarbon. In tetrahedral structure of alkane $C - C$ and $C - H$ possesses a σ -bond. The bond lengths of $C - C$ is 154 pm and $C - H$ bond length is 112 pm. All $H - C - H$ bond angles are of $109^{\circ}28'$. The shape of methane molecule is represented in Figure 6.1.

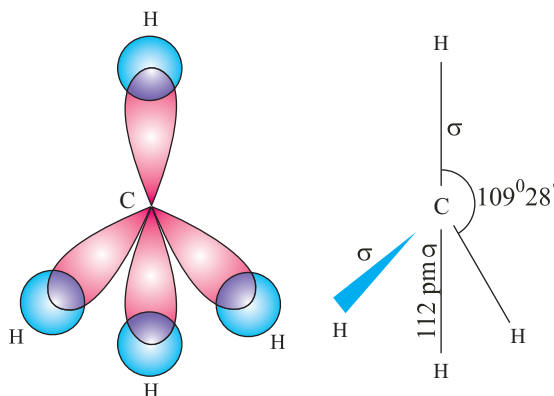
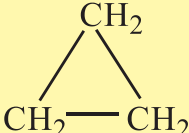
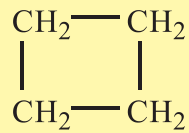
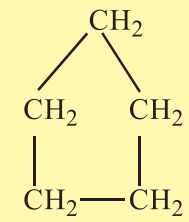
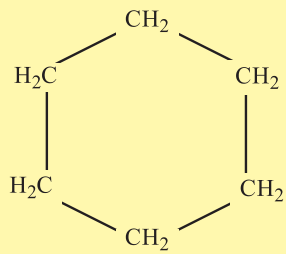


Figure 6.1 Shape of methane molecule

6.3.1 IUPAC Nomenclature of Alkanes and Cyclo-alkanes : The structural formula and IUPAC names of alkanes and cycloalkanes are given in Table 6.2.

Table 6.2 IUPAC Nomenclature

Structural formula	IUPAC name
CH_4	Methane
$CH_3 CH_3$	Ethane
$CH_3 CH_2 CH_3$	Propane
$CH_3 CH_2 CH_2 CH_3$	Butane
$CH_3 CH_2 CH_2 CH_2 CH_3$	Pentane
$CH_3 CH_2 CH_2 CH_2 CH_2 CH_3$	Hexane
$CH_3 CH_2 CH_2 CH_2 CH_2 CH_2 CH_3$ or $CH_3-(CH_2)_5-CH_3$	Heptane

$\text{CH}_3-(\text{CH}_2)_6-\text{CH}_3$	Octane
$\text{CH}_3-(\text{CH}_2)_7-\text{CH}_3$	Nonane
$\text{CH}_3-(\text{CH}_2)_8-\text{CH}_3$	Decane
	Cyclopropane
	Cyclobutane
	Cyclopentane
	Cyclohexane

6.3.2 Isomerism and Nomenclature in Alkanes :

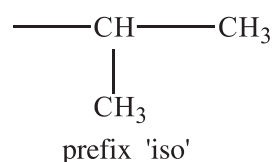
The compounds having same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism. Compounds which have same molecular formula, but their structural formulas are different, are called structural isomers.

The study of isomerism can be done very well in alkane chains. In the first three hydrocarbons methane, ethane and propane isomerism is not observed. Isomers are observed in the successive members having more than three carbon atoms.

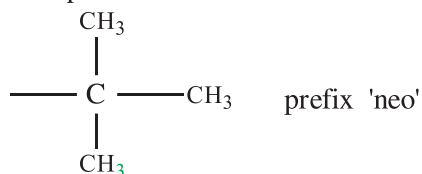
In common nomenclature method, all the isomers of alkane have same fundamental name,

e.g., both the isomers having C_4H_{10} molecular formula are known as butane, but the name of each isomer is separated by its prefix. The prefix is known according to the branch in the molecule.

- (1) Prefix 'n' is used for such alkanes in which all the carbon atoms are combined in same long chain. Here, n-means normal, e.g., $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (n-butane)
- (2) Prefix 'iso' is used in such alkanes in which an alkyl group like methyl group ($-\text{CH}_3$) is attached to carbon second from last carbon. e.g.



- (3) Prefix 'neo' is used in such alkanes in which two alkyl groups like methyl groups are combined with the carbon second from left of the long chain of carbon. Prefix 'neo' applicable to pentane and nonane like alkanes.



This type of nomenclature is convenient for simple hydrocarbons, but for more complex hydrocarbons IUPAC nomenclature is more convenient. You have studied IUPAC nomenclature of alkane compounds in Semester-1. In the following Table 6.3 some alkanes, structural formula of their isomers, IUPAC name, common name, boiling points and melting points are given :

Table 6.3 Structural formula of alkanes, IUPAC Name, Common Name, Melting Point and Boiling Point

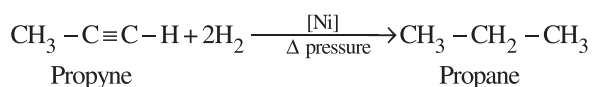
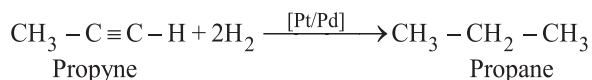
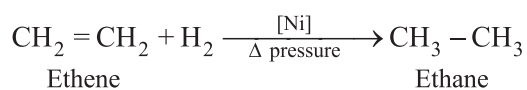
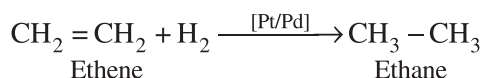
No.	Molecular formula	Structural formula	IUPAC Name	Common Name	Melting point (K)	Boiling point (K)
	CH ₄	CH ₄	Methane	Methane	90.5	111.0
	C ₂ H ₆	CH ₃ -CH ₃	Ethane	Ethane	101.0	184.0
	C ₃ H ₈	CH ₃ -CH ₂ -CH ₃	Propane	Propane	85.3	231.0
	C ₄ H ₁₀	CH ₃ -(CH ₂) ₂ -CH ₃	Butane	n-Butane	134.6	272.0
		$\begin{array}{c} \text{CH}_3 \text{--- CH --- CH}_3 \\ \\ \text{CH}_3 \end{array}$	2 Methyl propane	Iso-butane	114.7	261.0
	C ₅ H ₁₂	CH ₃ -(CH ₂) ₃ -CH ₃	Pentane	n-pentane	143.3	309.1
		$\begin{array}{c} \text{CH}_3 \text{--- CH --- CH}_2 \text{--- CH}_3 \\ \\ \text{CH}_3 \end{array}$	2 Methyl butane	Iso-pentane	113.1	301.0
		$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C --- C --- CH}_3 \\ \\ \text{CH}_3 \end{array}$	2, 2-Dimethyl propane	Neo-pentane	265.4	282.5
	C ₆ H ₁₄	CH ₃ -(CH ₂) ₄ -CH ₃	Hexane	n-Hexane	178.5	342.0
		$\begin{array}{c} \text{CH}_3 \text{--- CH --- CH}_2 \text{--- CH}_2 \text{--- CH}_3 \\ \\ \text{CH}_3 \end{array}$	2 Methyl pentane	Iso-hexane	113.0	301.0
		$\begin{array}{c} \text{CH}_3 \text{--- CH}_2 \text{--- CH --- CH}_2 \text{--- CH}_3 \\ \\ \text{CH}_3 \end{array}$	3 Methyl pentane	—	155.0	336.0
		$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C --- C --- CH}_2 \text{--- CH}_3 \\ \\ \text{CH}_3 \end{array}$	2,2 Dimethyl butane	Neo hexane	175.0	323.0
		$\begin{array}{c} \text{CH}_3 \text{--- CH --- CH --- CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	2,3 Dimethyl butane	—	144.0	331.0

7	C ₇ H ₁₆	CH ₃ -(CH ₂) ₅ -CH ₃	Heptane	n-Heptane	182.4	371.4
8	C ₈ H ₁₈	CH ₃ -(CH ₂) ₆ -CH ₃	Octane	n-octane	216.2	398.7
9	C ₉ H ₂₀	CH ₃ -(CH ₂) ₇ -CH ₃	Nonane	n-nonane	222.0	423.8
10	C ₁₀ H ₂₂	CH ₃ -(CH ₂) ₈ -CH ₃	Decane	n-decane	243.3	447.1

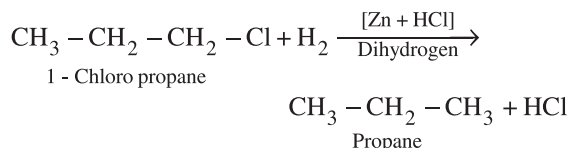
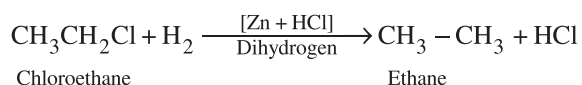
6.3.3 Preparation of alkane compounds :

(1) From unsaturated hydrocarbons :

Alkane compounds are obtained by addition reaction of unsaturated hydrocarbons like alkene and alkyne compounds with dihydrogen in presence of catalyst like Pt or Pd at normal temperature. This reaction is known as hydrogenation. If this reaction is carried out in presence of Ni catalyst, it requires high temperatures and pressure.

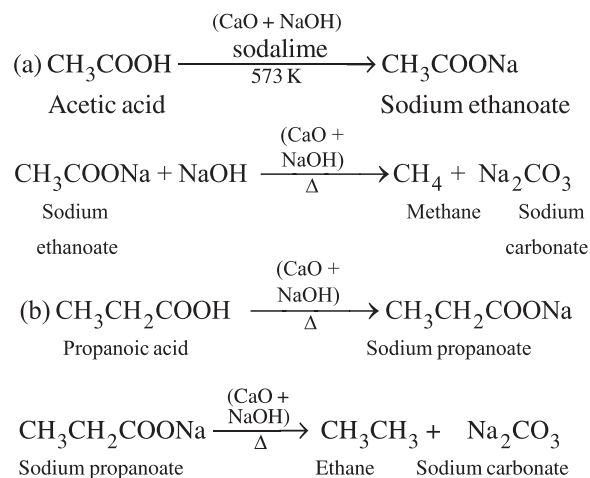


(2) **From alkyl halide :** Alkane is obtained by reduction reaction of alkyl halide in presence of Zn and HCl



(3) **From carboxylic acids :** Sodium salts of carboxylic acid are first obtained by reaction of carboxylic acid with sodalime (solid NaOH + CaO). When these sodium salts are allowed to react with sodalime at high temperature, they give alkanes containing one carbon less than the carbon atoms in original carboxylic acid.

This reaction is known as decarboxylation reaction because carbon dioxide is released from carboxylic acid during this process.

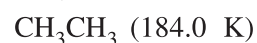
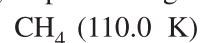


6.3.4 Properties of Alkane Compounds :

(1) **Physical Properties :** Alkanes have covalent nature of C – C and C – H bonds. Alkanes are non-polar molecules because of less difference in electronegativities of carbon and hydrogen atoms.

Due to non-polar character, alkane compounds create weak intermolecular attraction (van der Waals force) between two molecules. Because of the weak intermolecular attraction forces in alkane, C₁ to C₄ carbon containing alkane compounds are in gaseous form. C₅ to C₁₇ carbon containing alkane compounds are in liquid form and alkanes containing C₁₈ or more carbon atoms are in solid form at normal temperature (298 K). Due to non-polar nature, alkanes are insoluble in polar solvent like water. The intermolecular attraction forces increase with increase in carbon atom in the alkane series.

It is observed that alkanes having high molecular weights possess high boiling point. e.g.

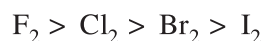


The boiling points of secondary (2^o) and tertiary (3^o) alkanes are less as compared to primary alkanes containing similar number of carbons.

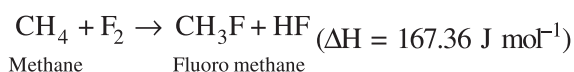
The boiling points of secondary methyl butane (301 K) and tertiary 2,2-dimethyl propane (282.5 K) are less than n-pentane (309 K). The reason for decrease in the boiling points from primary (1^0) to tertiary (3^0) can be given as under. As the branching increases, there occurs a decrease in the contact surface area. Due to the decrease in contact surface area intermolecular forces decrease. Thus, less amount of energy is required to convert liquid into vapour state.

(2) Chemical properties (Chemical reactions) : Alkane compounds are saturated compounds and so give only substitution reactions.

(i) Halogenation : At very high temperature or in presence of ultraviolet radiation of sunlight, alkane reacts with halogen to form alkyl halide. This phenomenon is called halogenation. The order of reactivity of halogens for halogenation reaction is as follows.

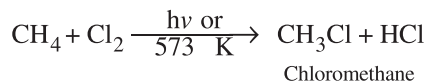


As fluorine molecule is highly active, according to free radical mechanism, this reaction does not need a catalyst.

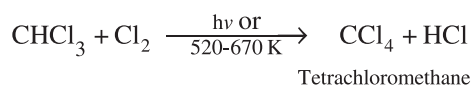
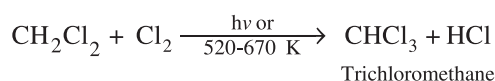
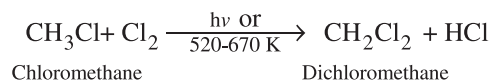


(a) Chlorination : In chlorination of alkane, in presence of sunlight or high temp (573 – 673 K) alkanes react with chlorine Cl_2 ,

e.g. in presence of uv radiation or at 573 K methane reacts with chlorine and chloro methane is obtained.

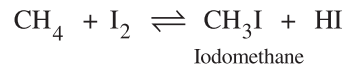


As the reaction proceeds continuously the substitution of remaining three hydrogen by chlorine takes place and, finally, tetrachloromethane is obtained.



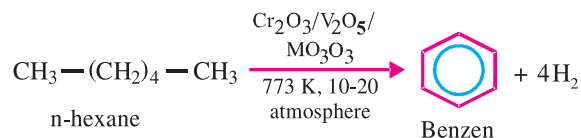
(b) Bromination : Bromine reacts with alkane which is similar to chlorination reaction but it is slow.

(c) Iodination : Alkane with iodine gives reversible reaction.

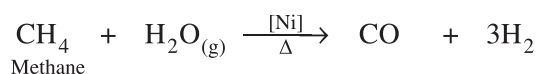


(ii) Cyclization : When normal alkane having 6 or more carbon atoms heated at 773 K temperature and 10-20 atmosphere pressure in the presence of catalyst to benzene and its derivatives are obtained. This reaction is known as cyclization or dehydrogenation.

e.g. n-hexane at 773 K temperature and 10-20 atmosphere pressure in the presence of V_2O_5 or Cr_2O_3 or Mo_2O_3 as catalyst, dehydrogenation takes place and benzene is formed.

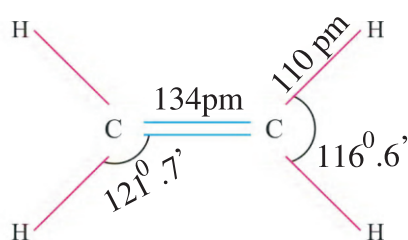
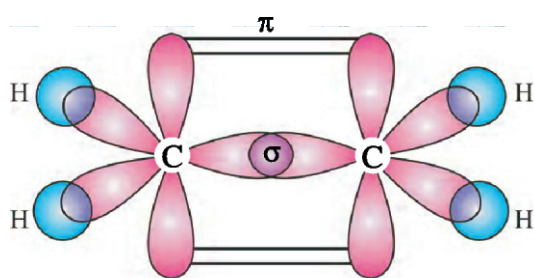


(iii) Reaction with water (vapour) : Reaction of alkane in presence of Ni catalyst with water vapour at higher temperature, dihydrogen gas is released. This process is used in industries to obtain dihydrogen gas. Likewise, reaction of methane with water vapour in presence of Ni catalyst at higher temperature, a mixture of CO and H_2 called water gas is obtained.



6.4 Alkene Compounds

Alkene compounds are unsaturated hydrocarbons i.e. hydrocarbons in which at least one double bond between two carbon atoms is present. The general formula of alkene is C_nH_{2n} . Ethene is the first member of this group. There is sp^2 hybridization between the two carbon atoms in ethene. Three hybrid orbitals are formed by sp^2 hybridization and form three σ -bond. The orbitals which do not take part in the hybridisation overlap to form one π bond. Ethene has total four C – H σ -bond. The bond length of each C – H bond is 110 pm and bond length of C = C is 134 pm while bond angle of H – C – H is $116^{\circ}6'$ and bond angle of C – C – H is $121^{\circ}7'$. The shape of ethene molecule is triangular planar, which is represented in Figure 6.2.



H – C – H bond angle $116^{\circ}6'$

H – C – C bond angle $121^{\circ}7'$

C = C bond length 134 pm

C – H bond length 110 pm

Fig. 6.2 Shape of Ethene

6.4.1 IUPAC Nomenclature and Isomerism in alkene :

(1) For the IUPAC nomenclature of alkene, the longest branch containing – C = C – is selected.

(2) The order to number carbon is decided by the longest branch containing – C = C – double bond which must have at least an order.

(3) The 'ane' suffix is removed from the main name of alkane and 'ene' suffix is attached to it, viz. 'ane' suffix removed from the butane and add 'ene' suffix attached to it will make **but + tene = butene**. If the number of same substituted group is 2, 3 or 4 then the suffix di, tri and tetra are put respectively before its name on the basis of above rules IUPAC nomenclature of alkene is given in Table 6.4.

Table 6.4

Structural formula	IUPAC Name
$\text{CH}_2=\text{CH}_2$	Ethene
$\text{CH}_3-\text{CH}=\text{CH}_2$	Propene
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	But-1-ene
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	But-2-ene
$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2,Methyl prop-1 ene
$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	3,Methyl but-1 ene
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Buta-1, 3-diene
$\begin{array}{c} (\text{CH}_3)_2-\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH} \\ \\ \text{H}_3\text{C}-\text{CH} \\ \\ \text{C}_2\text{H}_5 \end{array}$	2, 7-dimethyl- Nona-3,5-diene
	Deca-1,3,5,9-tetraene
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2 \quad \quad \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{H}_3\text{C}-\text{CH}-\text{CH}=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	4-Ethyl-2, 6-dimethyloct 4-ene
$\text{CH}_3-\text{CH}=\text{C}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$	3-(n-propyl) hex-2-ene

Isomerism in Alkene : Alkene compounds give two types of isomerism : (i) Structural isomerism (ii) Geometrical isomerism

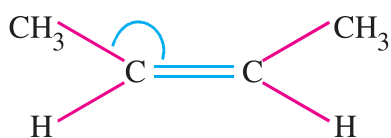
(i) **Structural isomerism :** The alkene compounds containing two or three carbon atoms do not show structural isomerism, but the alkene compounds containing four or more carbon atoms show structural isomerism.

For example, the alkene having molecular formula C_4H_8 shows structural isomerism and the isomers can be shown as under :

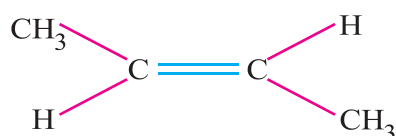
Molecular formula	Structural formula	IUPAC name
C_4H_8	(i) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$	But-1-ene
	(ii) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	But-2-ene
	(iii) $\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	2,Methyl prop-1 ene

(ii) **Geometrical isomerism** : Although some alkene compounds have same structural formula and molecular formula, their functional group and/or spatial arrangement of atoms is in different directions. Here, due to the presence of $-C=C-$ the molecular structure is planar. This type of isomerism is known as geometrical isomerism.

Usually, geometrical isomers are known as cis and trans isomers. For example,

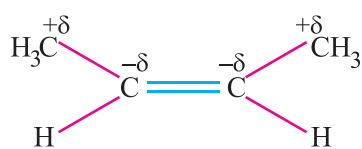


Cis But - 2 - ene



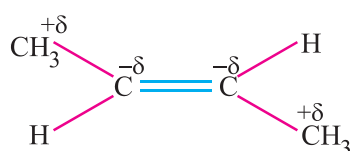
Trans But - 2 - ene

In cis isomer, two carbon atoms having double bonds are attached to the similar atom or group of atoms present on same side of $C=C$. While in trans isomer, similar groups are found in diagonal position of $C=C$. If double bond containing carbons have same functional groups on same side, it does not show geometrical isomerism. The polarity in cis and trans isomers is as under.



Cis But - 2 - ene

$$(\mu = 0.33 \text{ D})$$



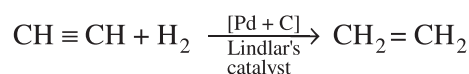
Trans But - 2 - ene

$$(\mu = 0.0 \text{ D})$$

From the above figure, it becomes clear that cis isomer is polar while trans isomer is non-polar, because in trans isomer both methyl groups are in opposite directions due to which resulting value of dipole moment is zero.

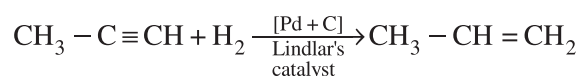
6.4.2 Preparation of alkene compounds :

(i) **From alkyne** : Alkene is obtained by the addition reaction of alkyne with H_2 gas in presence of mixture of palladium (Pd) and charcoal as catalyst. This catalyst mixture of palladium and charcoal is known as 'Lindlar's' catalyst. Thus, addition of hydrogen in group is called hydrogenation reaction.



Ethyne

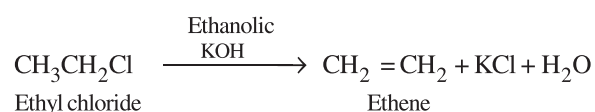
Ethene



Propyne

Propene

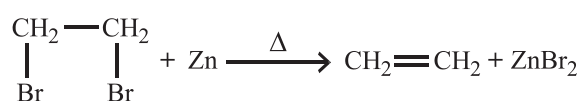
(ii) **From alkyl halide** : Alkene is obtained by reacting with potassium hydroxide dissolved in ethanol. (ethanolic KOH) with alkyl chloride at higher temperature. During this reaction, removal of halogen from α -carbon and hydrogen from β -carbon of alkyl halide takes place. Because of this, the reaction is known as β -elimination or dehydrohalogenation reaction.



Ethyl chloride

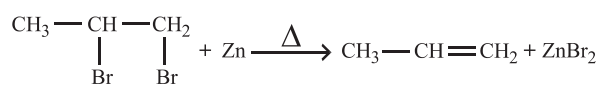
Ethene

(iii) **From vicinal dihalide (From dihalogen alkane)** : Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal gives a molecule of ZnX_2 ($X = \text{halogen}$) and forms an alkene. This reaction is known as dehalogenation.



1, 2 dibromo ethane

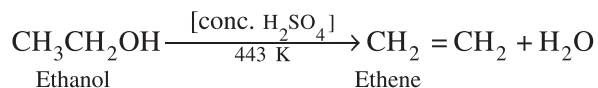
ethene



1, 2 dibromo propane

propene

(iv) **From alcohol** : Alkene is obtained by reacting alcohol with conc H_2SO_4 at 443 K temperature. During this process water molecule is released. This process is called dehydration. It is also known as acidic dehydration of alcohols.



6.4.3 Properties of alkene compounds :

(1) Physical properties of alkenes :

- Variation is observed in physical properties of alkene due to polar nature. Isomerism is also observed in alkene.
- Alkene containing two, three or four carbon atoms are in gaseous form, C_5 to C_{18} members are in liquid form and those with more number of carbons are obtained in solid form.

- Ethene is colourless gas with a fruity sweet smell.
- Except ethene all other alkenes are odourless and tasteless.
- Except ethene all alkene are insoluble in polar solvent like water, but it is soluble in non-polar organic solvents like petrol, benzene, ether and carbon tetrachloride.
- Alkenes have lower melting points and boiling points than alkanes, and these increase with the increase in the molecular mass.
- The boiling points of isomers having linear chain are higher than those of alkenes having branched chain.

IUPAC name structural formula, boiling points and melting points of some alkenes are given in the Table 6.5 :

Table 6.5

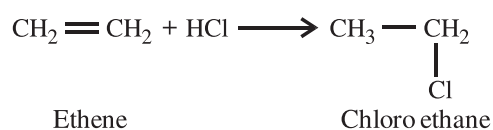
The IUPAC Name, structural formula, melting and boiling points of alkenes

IUPAC Name	Structural formula	Melting point K	Boiling point K
Ethene	$\text{CH}_2 = \text{CH}_2$	104	171
Propene	$\text{CH}_2 = \text{CH} - \text{CH}_3$	–	225
But-1-ene	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$	–	266.5
Pent-1-ene	$\text{CH}_2 = \text{CH}(\text{CH}_2)_2 - \text{CH}_3$	–	303
Hex-1-ene	$\text{CH}_2 = \text{CH}(\text{CH}_2)_3 - \text{CH}_3$	135	336.5
Hept-1-ene	$\text{CH}_2 = \text{CH}(\text{CH}_2)_4 - \text{CH}_3$	154	366.0
Oct-1-ene	$\text{CH}_2 = \text{CH}(\text{CH}_2)_5 - \text{CH}_3$	169	395.5
2-Methyl but-2-ene	$\text{CH}_3 - \text{CH} = \text{C}(\text{CH}_3)_2$	150	313.0
2, 3 -Dimethyl but-2-ene	$(\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2$	199	346

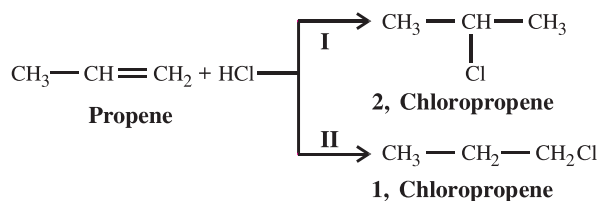
(ii) **Chemical properties of alkene (chemical reactions)** : – $\text{C} = \text{C}$ – present in alkene has weak π -bond which breaks easily and electrons of π -bond are released. In alkene with – $\text{C} = \text{C}$ –; π -bond of carbon breaks and the addition of atom or functional group (group of atoms) of reactants on carbon atom takes place. This addition reaction is known as electrophilic addition reaction.

(1) **Reaction with halogen acid** : Alkyl halide is obtained by the reaction of alkene with halogen acid. This is known as hydrohalogenation reaction.

Reaction of symmetrical alkene is as under



(a) Reaction of asymmetrical alkene ($\text{CH}_3\text{-CH=CH}_2$) with halogen acid and Markovnikov Rule :

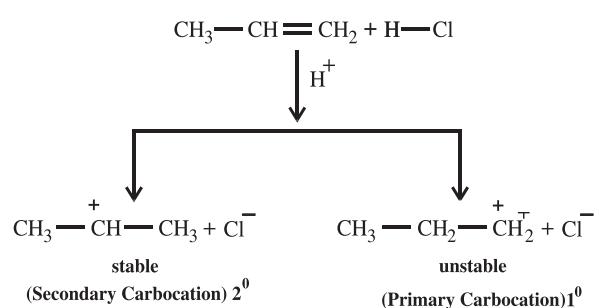


Here, by the reaction of propene with hydrochloric acid, two products I and II are obtained. It is necessary to know the Markovnikov rule to understand the stability of products obtained.

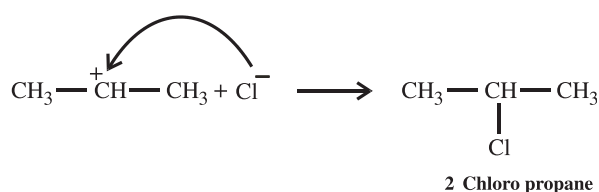
In 1869, Russian scientist Markovnikov proposed the rule as under :

"In the addition reaction of compounds having asymmetric ethylinic double bond the electronegative part of asymmetric reagent attaches with the ethylinic carbon having less number of hydrogens." This principle is better understood by the following reaction mechanism :

Reaction Mechanism : Initially, electrophilic H^+ ion of hydrochloric acid (HCl) is attached with carbon containing ethylinic double bond and forms carbocation as under.



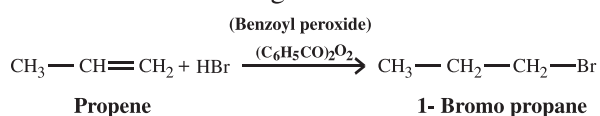
Primary carbocation is less stable than secondary carbocation. Due to this Cl^- ion of HCl attaches rapidly to the carbon of secondary carbocation. When carbon has positive charge in its molecule, it is called carbocation.



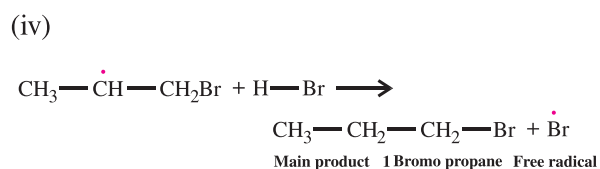
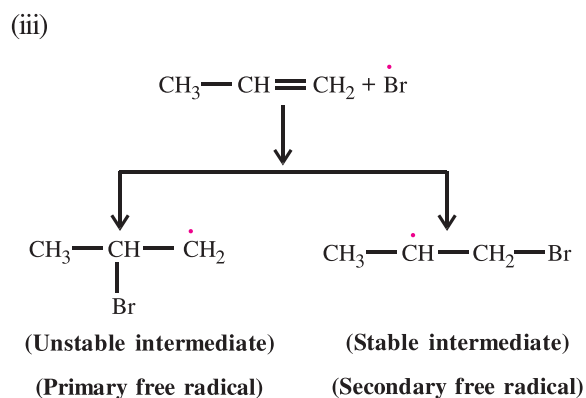
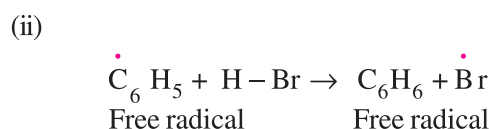
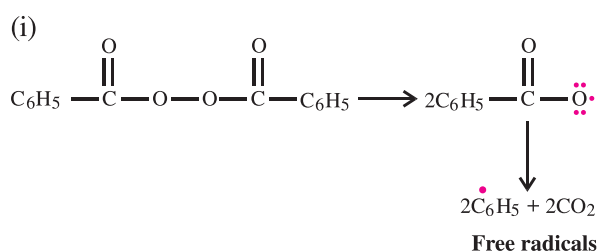
Thus, Cl^- ion attaches to the ethylinic carbon containing less hydrogen. The product obtained is stable, as a result, the product is 2-chloro propane.

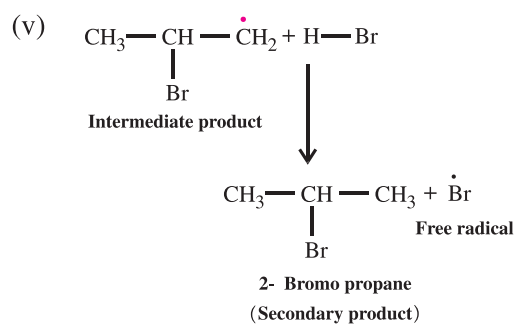
(b) Reaction of asymmetric alkene with halogen acid and peroxide effect : If the reaction occurs between asymmetric alkene with halogen acid like HBr in presence of hydrogen peroxide then the product obtained is against the Markovnikov's rule. HCl and HI do not show this type of reaction. Only HBr shows this reaction.

In 1933, M.S Kharsh and F. R. Mayo studied this reaction mechanism which is known as Kharsh effect, peroxide effect or anti-Markovnikov rule. e.g.

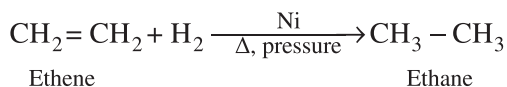
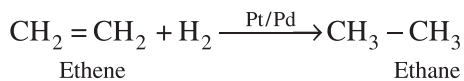


According to peroxide effect, free radical addition reaction mechanism is shown as under. Free radical is obtained by the homolytic covalent bond fission.

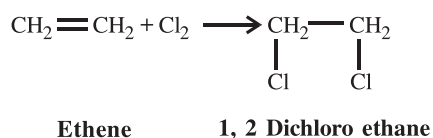




(2) Reaction with dihydrogen : At normal temperature alkane is obtained by addition reaction of alkene with dihydrogen in presence of catalyst like Pt or Pd. This reaction is called hydrogenation. If this reaction is carried out in presence of Ni catalyst, then higher temperature and pressure are required.



(3) Reaction with halogen : By the addition of halogen to alkene, π bond of ethylinic double bond breaks and the addition of halogen molecule takes place to form dihalogenated alkane.



6.5 Alkyne Compounds

Like alkenes, alkynes are also unsaturated hydrocarbons. The hydrocarbons, in which there is at least one triple bond between two carbon atoms, are called alkyne compounds. General formula of alkynes is $\text{C}_n\text{H}_{2n-2}$.

Acetylene (ethyne) is the first member of the alkyne series in which two carbon atoms are attached by one triple bond and possess sp hybridisation. Thus, ethyne molecule has bond angle of 180° and is a linear molecule. Bond length between C–H bond is 106 pm and between $\text{C} \equiv \text{C}$ bond, bond length is 120 pm as represented in Fig. 6.3.

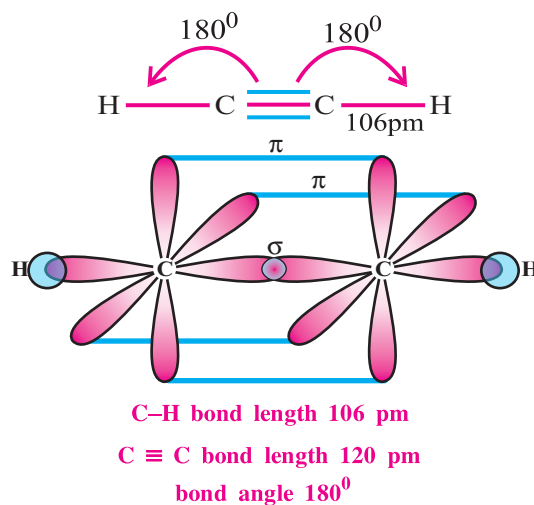


Fig. 6.3 Shape of ethyne molecule

6.5.1 IUPAC Nomenclature of alkyne Compounds and Isomerism : In IUPAC nomenclature of alkynes, 'ane' suffix of alkanes is removed from the name and 'yne' suffix is attached to it. (Except suffix all the other rules are the same as those for alkanes and alkenes), e.g. Ethane \rightarrow Ethyne.

In the following Table 6.6, IUPAC nomenclatures of various alkyne compounds are given :

Table 6.6

Structural formula	IUPAC Name
$\text{CH} \equiv \text{CH}$	Ethyne
$\text{H}_3\text{C}-\text{C} \equiv \text{CH}$	Propyne
$\text{H}_3\text{C}-\text{CH}_2-\text{C} \equiv \text{CH}$	But-1-yne
$\text{H}_3\text{C}-\text{C} \equiv \text{C}-\text{CH}_3$	But-2-yne
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{C} \equiv \text{CH} \\ \\ \text{CH}_3 \end{array}$	3-Methyl but-1-yne
$\begin{array}{c} \text{CH}_3-\text{C} \equiv \text{C}-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	4-methyl pent-2-yne
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \equiv \text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	3,3 Dimethyl but-1-yne

Isomerism of Alkyne compounds : The carbon containing compounds having same molecular formula but different structural formulae are called structural isomers. This phenomenon is known as structural isomerism. Alkyne

compounds containing two or three carbon atoms having same structural formula do not give structural isomers. Structural isomers of alkynes containing four carbon atoms are given in Table 6.7.

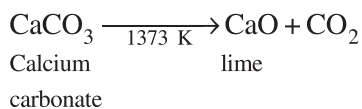
Table 6.7

The Molecular formula, structural formula and IUPAC Name of Alkyne

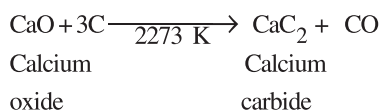
Molecular formula	Isomer (Structural formula)	IUPAC Name
C ₄ H ₆	(i) CH ₃ -CH ₂ -C≡CH	But-1-yne
	(ii) CH ₃ -C≡C-CH ₃	But-2-yne
C ₅ H ₈	(i) CH≡C-CH ₂ -CH ₂ -CH ₃	Pent-1-yne
	(ii) CH ₃ -C≡C-CH ₂ -CH ₃	Pent-2-yne
	(iii) CH ₃ -CH(CH ₃)-C≡CH	3 Methyl but-1-yne

6.5.2 Preparation of Alkyne Compounds :

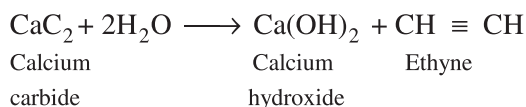
(i) **From calcium carbide :** Ethyne is prepared by the industrial process in which carbide reacts with water. Initially, calcium carbonate is heated at higher temperature from which calcium oxide (lime) is obtained by decomposition.



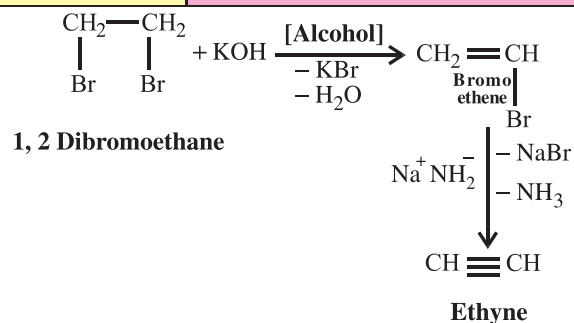
Now heating calcium oxide with coke, calcium carbide and carbon monoxide are obtained.



By reaction of calcium carbide with water ethyne is obtained as follows.



(ii) **From vicinal dihalides :** Alkenyl halide is obtained by reaction of vicinal dihalide with alcoholic potassium hydroxide reaction and this alkynyl halide on reaction with sodamide (NaNH₂) gives alkyne. This reaction is called dehydro-halogenation.



6.5.3 Properties of Alkyne Compounds :

(1) Physical properties :

- (i) The first three members of alkyne series are in gaseous form, then after upto C₈ are in liquid form and alkyne containing more than 8 carbons are obtained in solid form.
- (ii) All alkyne compounds are colourless. The smell of ethyne is specific. Except ethyne all alkynes are odorless.
- (iii) Alkynes are weak polar compounds.
- (iv) Alkynes are lighter than water, and are insoluble in polar solvents like water. They are soluble in non-polar organic solvents like ether, carbon, tetrachloride, benzene.
- (v) With the increase in molecular mass of alkynes, melting point, boiling point, and density also increase.

In the following Table 6.8 the melting points and boiling points of some alkyne compounds are given.

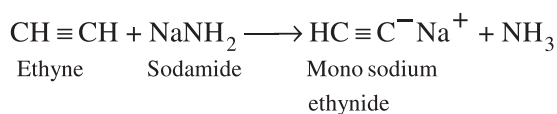
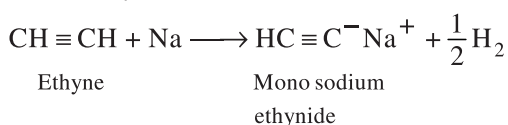
Table 6.8

The IUPAC Name, Structural formula melting point and boiling point of alkyne Compounds

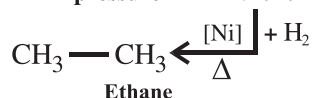
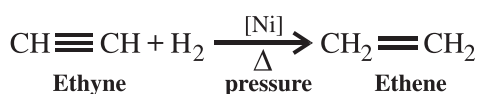
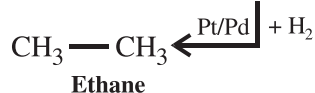
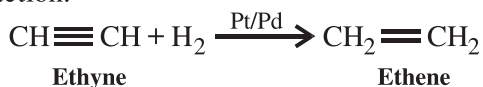
Alkyne	Structural formula	Melting point (K)	Boiling point (K)
Ethyne	HC≡CH	192.2	189
Propyne	HC≡C-CH ₃	170.3	249.8
But-1-yne	HC≡C-CH ₂ -CH ₃	147.3	281.1
But-2-yne	H ₃ C-C≡C-CH ₃	240.7	300.0
Pent-1-yne	HC≡CCH ₂ CH ₂ CH ₃	167.3	313.2
Pent-2-yne	H ₃ CC≡C-CH ₂ -CH ₃	163.7	329.1
Hex-1-yne	HC≡CCH ₂ CH ₂ CH ₂ CH ₃	141.1	344.3
Hex-2-yne	H ₃ CC≡CCH ₂ CH ₂ CH ₃	183.5	357.5
Hex-3-yne	H ₃ CCH ₂ C≡C-CH ₂ -CH ₃	169.5	354.4
Hept-1-yne	HC≡CCH ₂ CH ₂ CH ₂ CH ₂ CH ₃	192.1	372.7

(2) Chemical Properties (Chemical Reactions) of Alkynes :

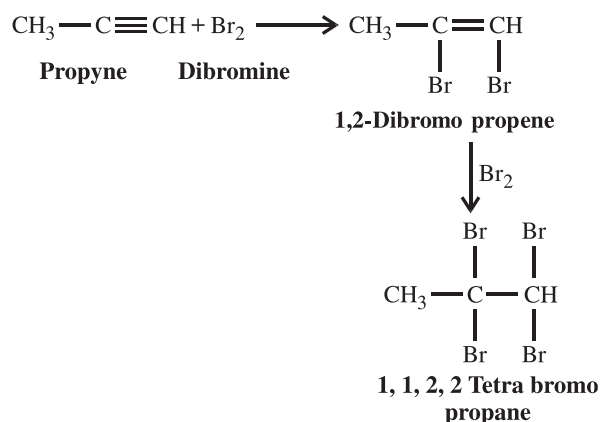
(i) **Acidic properties of Alkynes :** Only ethyne possesses acidic properties. Ethyne is a weak acid, it reacts with strong base like sodium or sodamide to give mono sodium ethynide (sodium acetylide)



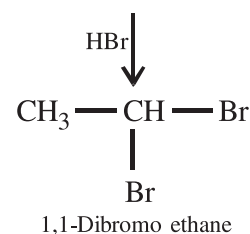
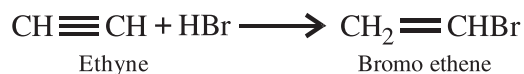
(ii) **Addition Reaction (Electrophilic addition reaction with dihydrogen) :** Alkyne on heating with dihydrogen reacts in presence of catalysts like Pt, Pd or Ni and gives alkene by addition reaction, which further on reacting with more hydrogen gives alkane by addition reaction. This reaction is known as hydrogenation reaction.



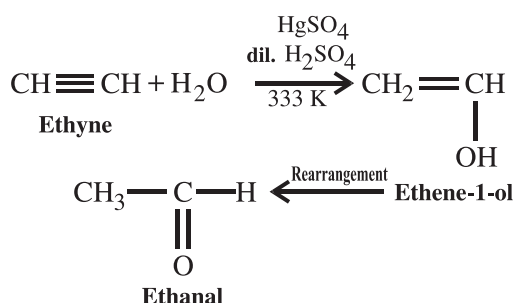
With dihalogen : When alkyne reacts with dihalogen the π -bond breaks and alkenyl dihalide is formed. Further reacting with more dihalogen, this gives tetrahalo alkane by addition reaction. This reaction is known as halogenation reaction.



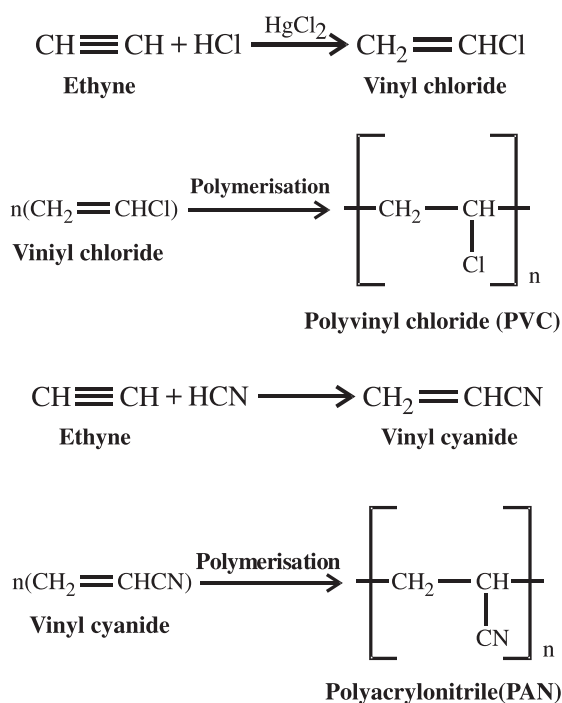
With hydrogenhalide : By addition reaction of alkyne with hydrogen halides like HCl, HBr, HI, it gives alkene halide. On reacting with more hydrogen halide, this gives dihalide of alkane. This reaction is known as hydrohalogenation.



With water : Alkyne does not react with water at normal temperature, but in presence of mercuric sulphate and dilute sulphuric acid at 333 K temperature it gives carbonyl compounds.



Polymerisation : The reaction of ethyne with HCl and HCN gives vinyl chloride and vinyl cyanide (acrylonitrile) respectively. A large number molecules of vinyl chloride join with each other by chemical bond forming large molecule of polyvinyl chloride polymer. This reaction is known as polymerisation. In the same way polyacrylonitrile is obtained from vinyl cyanide.



6.6 Aromatic Hydrocarbons

Aromatic hydrocarbons are also known as arene compounds.

Most of these compounds possess characteristic fragrance (aroma) due to which they are known as aromatic compounds, for example, the components of organic compounds

present in bitter almond, clove, bishop's seed etc, have specific smell (aroma) in the essential oils available from them and so they are called aromatic compounds. Organic compounds containing carbon and hydrogen showing aromatic characteristics are called Aromatic Hydrocarbons. The first member of aromatic hydrocarbons is benzene, other members of aromatic hydrocarbon forming homologous series have general formula $\text{C}_n\text{H}_{2n-6m}$ where m = number of rings in cyclic structure. Cyclic hydrocarbons containing benzene ring are known as benzenoids and when cyclic hydrocarbons do not contain benzene ring they are known as non-benzenoids. Some examples of aromatic hydrocarbons are given below in Figure 6.4.

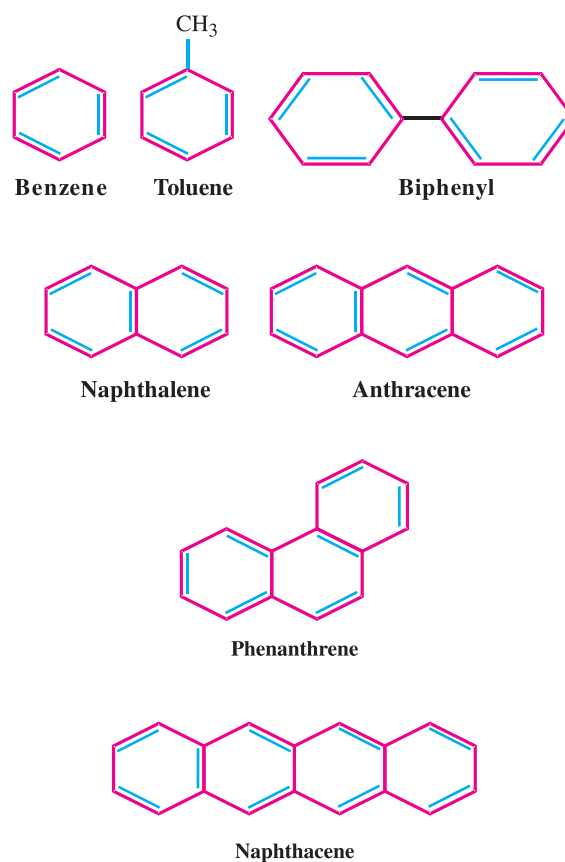
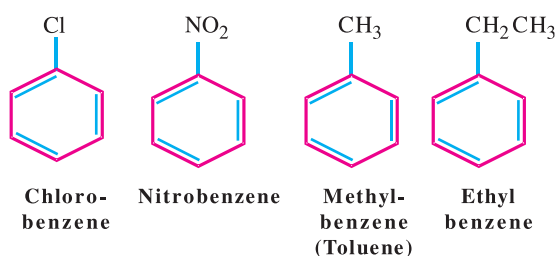


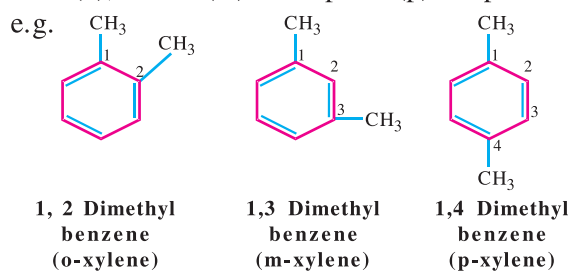
Fig 6.4 Aromatic Hydrocarbon Compounds

6.6.1 Nomenclature and Isomerism :

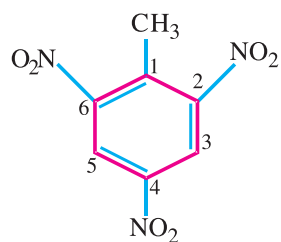
Benzene contains 6 carbon and 6 hydrogen atoms which are identical and thus does not have isomers. When any carbon of benzene substitutes its hydrogen it gives monosubstituted benzene it also does not have any isomer. In the IUPAC nomenclature of monosubstituted benzene, the displaced group is indicated, and then word benzene is expressed. e.g.



When two hydrogens of two carbon atoms in benzene are substituted, then the obtained disubstituted benzenes have three isomers.e.g. ortho, meta and para. If the substituted groups on carbon in benzene are on 1-2 position, 1-3 position and 1-4 position, then their nomenclatures are indicated by the prefixes ortho(o), meta (m) and para (p) respectively.



For the nomenclature of benzene, with the substitution of more than two positions, the reactivity of substituted groups on carbon are taken into consideration and numbering of carbon in benzene is done as 1,2,3... The remaining groups are indicated by considering the alphabetical order.



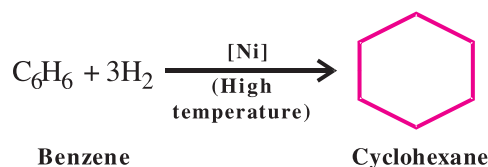
2, 4, 6 Trinitromethylbenzene
2, 4, 6 Trinitro toluene (TNT)

6.6.2 Structure of Benzene : The scientist Michael Faraday for the first-time obtained benzene from illuminating gases, in 1825. In 1845, the scientist August Hofmann obtained benzene from coaltar. Destructive distillation of coal gives coal gas, coaltar and coke. Coaltar has large amount of aromatic hydrocarbons, Destructive distillation of coaltar gives toluene, xylene, naphthalene etc. whereas the alkanes can be obtained as a result of fractional distillation of petroleum. When heated in presence of catalyst at higher pressure benzene, xylene, toluene can be obtained.

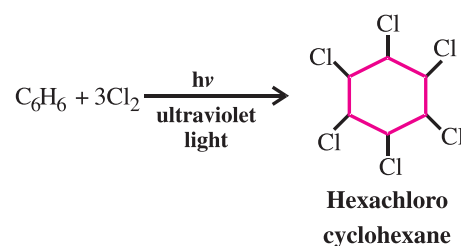
Structure of benzene based on chemical properties : From the qualitative and quantitative analysis of benzene, ratio of carbon and hydrogen atoms is found to be 1:1. Thus, the empirical formula is found to be CH and empirical formula weight = 13. Molecular mass of benzene is 78 gmol^{-1} , hence, the molecular formula of benzene is confirmed as C_6H_6 .

Structure of benzene is proved by the following chemical reactions :

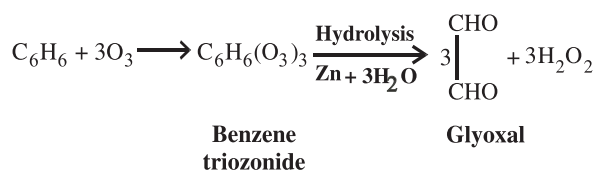
- (i) On reacting one mole of benzene with three moles of dihydrogen at high temperature and pressure in presence of Ni catalyst, cyclohexane is obtained.



- (ii) In reaction with one mole of benzene with three moles of chlorine in presence of ultraviolet light, hexachloro cyclohexane is obtained.

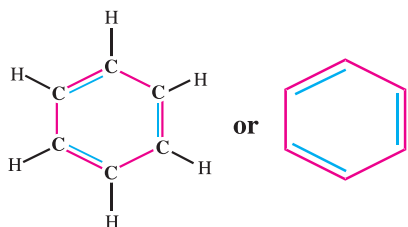


- (iii) On reacting one mole of benzene with three moles of ozone, unstable benzene triozone is obtained. On hydrolysis in presence of zinc it gives three moles of glyoxal.



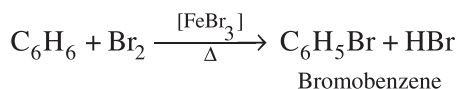
From the above reactions (i), (ii) and (iii), it can be proved that benzene contains hexagonal cyclic structure and in the ring three single bond between C – C and three double bond between C = C are present alternately.

In 1865, scientist August Kekule suggested the following structure of benzene :



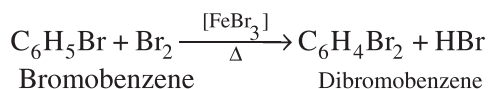
According to Kekule's proposed benzene structure, the following reactions show that it has two structures :

- (i) On reacting one mole of benzene with one mole of bromine in presence of FeBr_3 catalyst, one isomer bromobenzene is obtained by substitution reaction. As the rate of the reaction is slow, higher temperature is necessary.



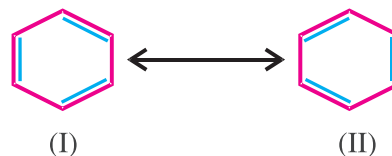
From the above reaction, it can be proved that 6 carbons and 6 hydrogens of benzene are equivalent in position and in reactivity.

- (ii) On second substitution of benzene with bromine in presence of FeBr_3 catalyst, a mixture of o, p-isomers of dibromobenzene in different proportions are obtained.



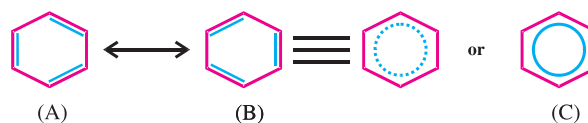
From the above reaction it can be said that during second substitution 6 carbon atoms of benzene are not equivalent. From this result, Kekule gave following structures of benzene in which three double bonds are arranged alternately and these bonds continuously and very rapidly

interconvert so that they resonate between structure (I) and (II).

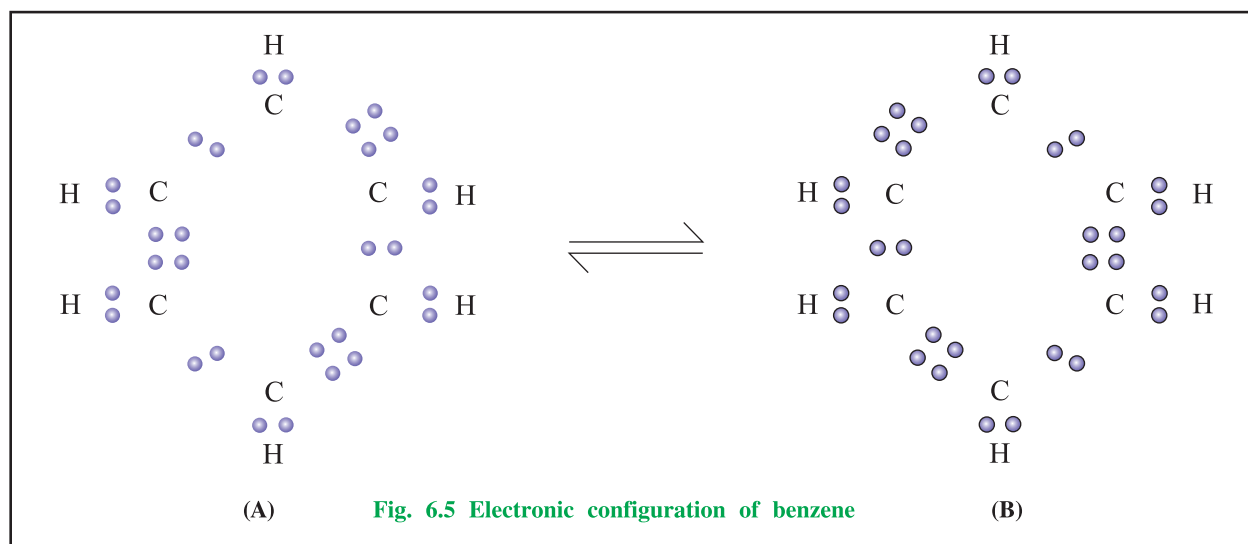


The structures proposed by Kekule do not resemble with the chemical properties. In fact three double bonds are present in benzene, but it gives substitution reaction like saturated alkane. In normal conditions, like alkenes benzene does not react with bromine water and cold KMnO_4 to give addition reaction. Further, polymerisation does not occur in benzene. Hence, it can be said that although benzene contains three double bonds, it possesses stability.

Stability and Resonance structure of benzene : On the basis of the chemical properties and stability of benzene, Kekule gave two resonating structures A and B for benzene. So that the intermediate position, structure C is represented. Position of alternate double bond is different.



Structure of Benzene based on the physical properties : After 70 years Lewis in 1937 represented Kekule structure of benzene which was based on the information obtained about covalent bonding of organic compound and the electronic configuration of their atom. This can be shown in Fig 6.5.



Benzene has 6 carbon atoms containing sp^2 hybridisation. Any of its σ -bond between C – C and C – H remain in one single plane. Bond angle between C – C – C and C – C – H is 120° . Further more every p_z orbital on each carbon will remain perpendicular to the plane of molecule which is represented in Fig. 6.6 (i). Those p_z orbitals which do not take part in hybridization remain perpendicular from the main axis and form π -bond by sharing electrons. As a result structure of benzene is obtained in which alternate double bond is present. This supports the two structures (A) and (B) of benzene proposed by Kekule.

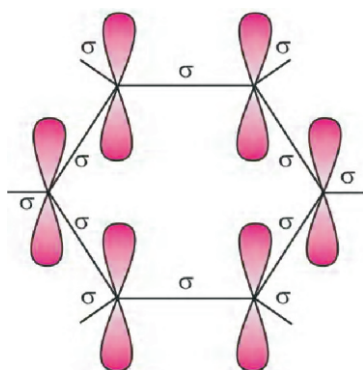


Fig. 6.6 (i)

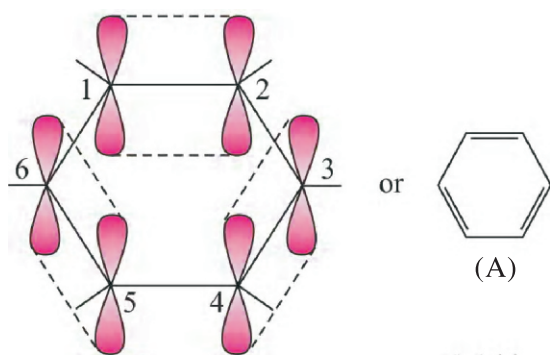


Fig. 6.6 (ii-a)

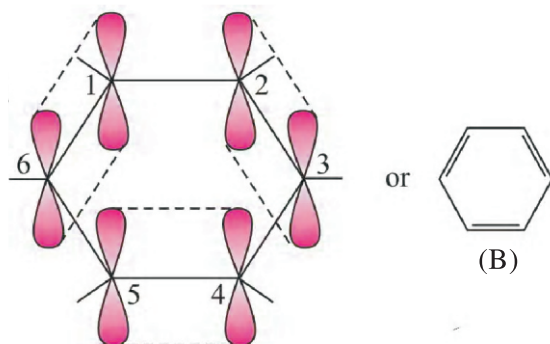


Fig. 6.6 (ii-b)

By the X-ray analysis of benzene, it was found that each C – C bond length is 139 pm. The bond length of – C – C – single bond in alkane is 154 pm and bond length of – C = C – double bond in alkene is 134 pm. Bond length 139 pm in benzene shows its intermediate value. This phenomenon represents the resonance between structures A and B of benzene that means inter- conversion phenomenon is continuous and very rapid. Based upon the resonance, it can be said that the structure of benzene should be between A and B.

Resonating structures of benzene can be further proved by their resonating energy. Cyclohexene, containing one double bond has hydrogenation enthalpy $119.66 \text{ kJ mol}^{-1}$. Therefore, benzene having three double bond should have hydrogenation enthalpy of $119.66 \times 3 = 358.98 \text{ kJ mol}^{-1}$. But the experimental hydrogenation enthalpy of benzene is $208.36 \text{ kJ mol}^{-1}$. Thus, benzene has $358.98 - 208.36 = 150.62 \text{ kJ mol}^{-1}$ enthalpy less than expected. This $150.63 \text{ kJ mol}^{-1}$ value is known as resonance energy of benzene. This resonance energy indicates its stability and also less chemical reactivity. This is known as aromaticity or aromatic character.

Aromatic character of benzene is based on the following facts : (i) Resonance bond energy $150.63 \text{ kJ mol}^{-1}$ of benzene (ii) sp^2 hybridisation of carbon in benzene (iii) Continuous transformation of the three π -bonds among 6 carbons in benzene.

Kekule's represented structure (C) of benzene is known as aromatic or resonance structure. Its ring shape of molecular orbitals and charge clouds (electron clouds) are represented in Figure. 6.6

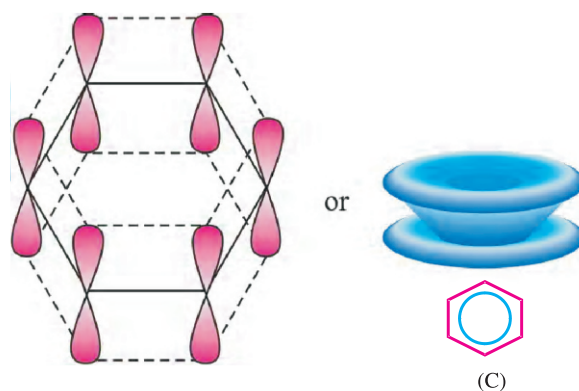


Fig. 6.7 Ring shape of molecular orbital of benzene

Aromatic Structure :

- (i) The aromatic structure of benzene is represented on the basis of the molecular orbital theory.
- (ii) This structure is accepted on the basis of information obtained from X-ray spectrum.
- (iii) Each carbon atom of benzene possesses sp^2 hybridisation.
- (iv) In benzene 6 carbon atoms, 6 hydrogen atoms, 6 (C-C) Carbon-Carbon, σ -bond and 6 (C-H) Carbon-Hydrogen σ -bond lie in a same plane.
- (v) In benzene, 6 carbon atoms have perpendicular p_z orbitals. Each p_z contains one π electron. So there are 6π electron which takes part in the formation of 3π -bonds.
- (vi) The six p_z orbitals overlap with each other and form a huge π -electron cloud above or below the molecular plane, in which 6π electrons revolve over the carbon atom.
- (vii) The nature of all the 6 carbon atoms in benzene is the same.
- (viii) Bond lengths between all C – C bond in benzene are equal.
- (ix) Electron clouds of 6π electrons in benzene support the less potential energy or the presence of resonance energy in it.

6.6.3 Huckel's rule and Aromatization :

In 1931, the scientist Huckel indicated that if the number of π -electrons in planar cyclic compound equals to $(4n + 2)$, then these compounds possess aromatic properties, (aromaticity) where n = number of cyclic structures. According to Huckel's rule, some aromatic cyclic compounds are as under:

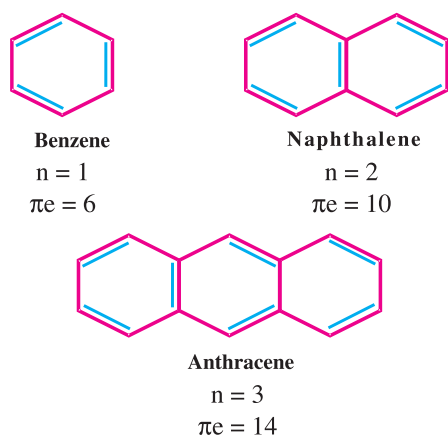


Fig 6.8 Aromatic cyclic compounds

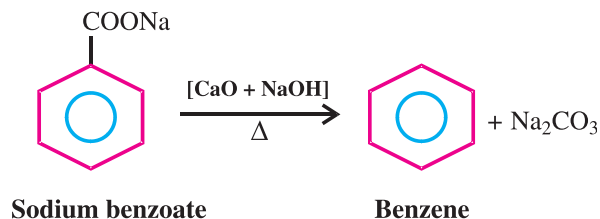
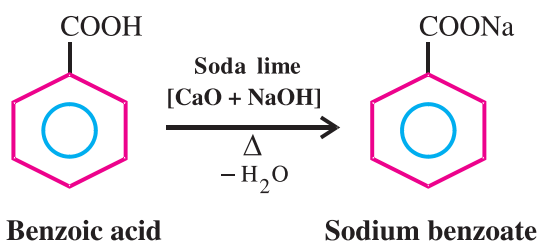
In benzene, naphthalene and anthracene, when we put $n = 1, 2, 3$ then the number of π -electrons we get in benzene is (6) naphthalene (10) and anthracene (14) respectively. This follows Huckel's rule. Hence, on the basis of Huckel's rule, it can be said that cyclic compounds like benzene, naphthalene and anthracene are aromatic compounds.

Characteristics in Aromatic Benzene :

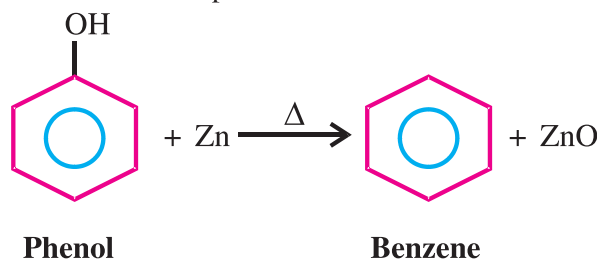
- (i) At normal temperature, just like alkanes, benzene resists oxidation with $KMnO_4$ and addition reaction with H_2, Cl_2, Br_2 .
- (ii) Like alkane, benzene also gives electrophilic substitution reactions like nitration, sulphonation, chlorination, bromination, alkylation, acylation etc. under suitable but vigorous conditions.
- (iii) Just like alkenes, benzene also gives reaction with dihydrogen (H_2), dichlorine (Cl_2) and ozone (O_3) in suitable but vigorous reaction conditions.
- (iv) Benzene has much more stability than alkene compounds.
- (v) Like alkene, benzene does not undergo polymerisation.
- (vi) There is only one isomer of monosubstituted benzene but there are three isomers of disubstituted benzene.
- (vii) Aromatic or resonating structure is the modern structure of benzene.
- (viii) The C – C bond length in benzene is less than C – C bond length of alkane and more than that of C = C double bond in alkene.
- (ix) The electron cloud of 6π electrons moves around in ring shape on both the sides of its plane.
- (x) Benzene obeys Huckel's rule.

6.6.4 Preparation of Benzene :

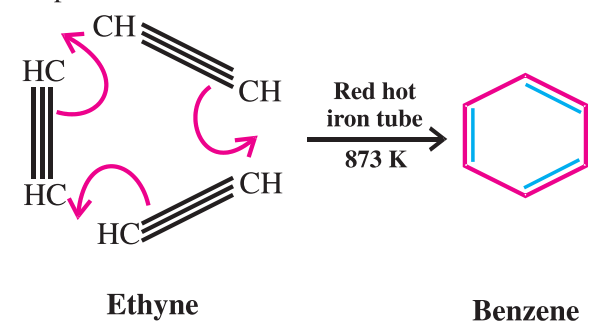
(1) From the decarboxylation of aromatic acid : The reaction of benzoic acid with sodalime forms sodium salt of benzoic acid (sodiumbenzoate) which reacts with sodalime at higher temperature to produce benzene.



(2) **By the reduction of phenol** : By passing phenol vapours through zinc dust reduction takes place and benzene is obtained.



(3) **By cyclic polymerisation** : Ethyne on passing through red hot iron tube, at 873 K temperature benzene is obtained.



6.6.5 Properties of Benzene :

(1) Physical properties :

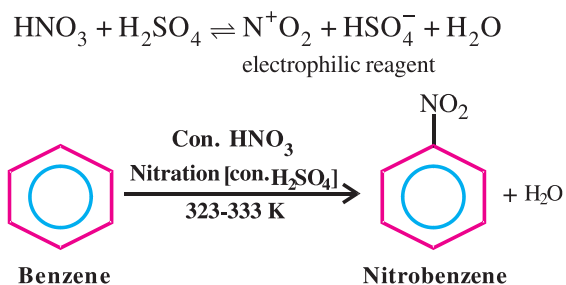
- (i) Benzene has kerosene like odour and is colourless liquid.
- (ii) Benzene is non-polar aromatic hydrocarbon.
- (iii) Benzene is insoluble in polar solvent like water.
- (iv) Benzene is soluble in non-polar organic solvent like carbontetrachloride.
- (v) Benzene is a good organic solvent.
- (vi) Benzene burns with a sooty flame because it is an aromatic compound.
- (vii) Boiling point of benzene is 353 K.

(2) Chemical Properties of Benzene

(Chemical Reactions) : Electrophilic substitution reaction is characteristic of arene compounds. Benzene is aromatic, hence, electrophilic substitution reaction occurs with it. In strong conditions benzene also gives addition and oxidation reactions.

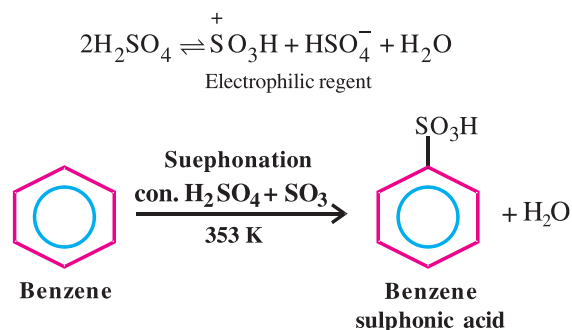
6.6.6 Electrophilic substitution reactions : The Lewis acid or positively charged ions obtained from the reagents involved in substitution reaction. in presence of catalyst are known as electrophilic ions like NO_2^+ , SO_3H^+ , Cl^+ , Br^+ , CH_3^+ , CH_3CO^+ etc. Substitution reactions by these ions are known as nitration, sulphonation, chlorination, bromination, Friedel Crafts alkylation, Friedel-Crafts acylation respectively.

(1) **Nitration of Benzene** : When benzene is heated with the mixture of con. HNO_3 and con. H_2SO_4 at 323-333 K temperature, one hydrogen of benzene is replaced to give nitrobenzene.



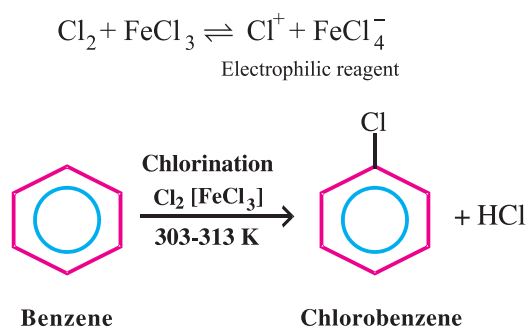
Here, N^+O_2 ion attacks as an electrophilic reagent on the carbon of benzene and H^+ is released from that carbon. Hence, nitration is known as electrophilic substitution reaction.

(2) **Sulphonation of Benzene** : A mixture of benzene and fuming H_2SO_4 or oleum ($\text{H}_2\text{SO}_4 + \text{SO}_3$) when heated at 353 K temperature one hydrogen of benzene is replaced to give benzene sulphonic acid.



Here, the carbon on which SO_3H^+ electrophilic reagent is substituted, liberates proton (H^+) from it. Thus sulphonation is known as an electrophilic substitution reaction.

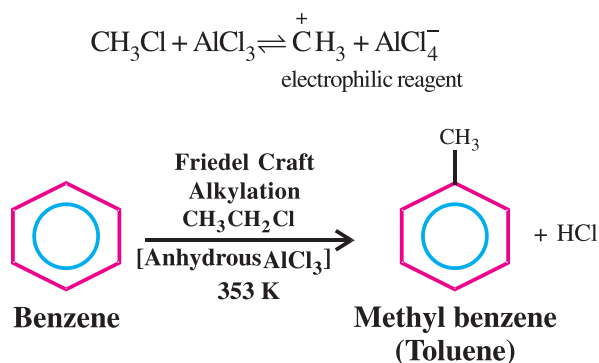
(3) Chlorination of Benzene (Halogenation) : In the reaction between benzene and chlorine, in presence of anhydrous FeCl_3 catalyst at 303-313 K temperature, one hydrogen is replaced to form chlorobenzene.



Here, the carbon at which electrophilic ion Cl^+ enters, proton H^+ is liberated from that carbon. Thus, chlorination is known as electrophilic substitution reaction.

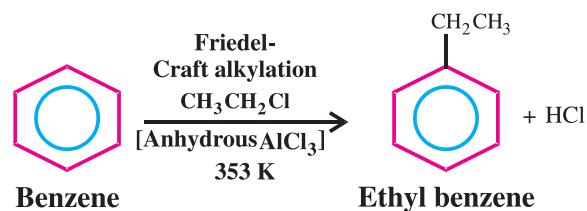
(4) Friedel - Crafts Alkylation of Benzene : Scientists Friedel and Crafts invented this reaction in 1877, therefore, it is known as Friedel-Crafts Alkylation reaction

Reaction between benzene and alkyl halide in presence of anhydrous AlCl_3 helps to get alkyl benzene. Likewise on heating benzene with, methyl chloride at 353 K temperature and one hydrogen is substituted to give methyl benzene (toluene)

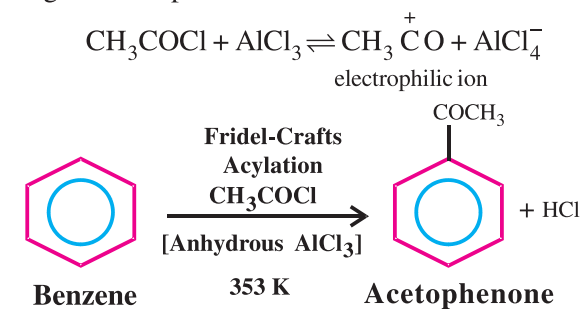


Here, the carbon at which electrophilic ion $^+\text{CH}_3$ enters, liberates proton H^+ from that carbon. Thus alkylation is known as electrophilic substitution reaction.

In place of methyl chloride, if ethyl chloride is taken, ethyl benzene is formed as shown below.

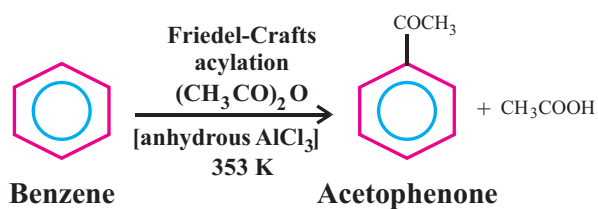


(5) Friedel-Craft's Acylation of Benzene: When benzene is heated with acetyl chloride in presence of anhydrous AlCl_3 at 353 K temperature, one of its hydrogen is replaced to give acetophenone.



Here, the carbon at which electrophilic ion $\text{CH}_3\text{C}^+\text{O}$ enters, liberates H^+ proton from that carbon. Thus, acylation is also known as electrophilic substitution reaction.

In this reaction, in place of acetyl chloride, if acetic anhydride is taken, then the reaction is as follows :



6.6.7 Inductive group and its Directing effect in monosubstituted Benzene :

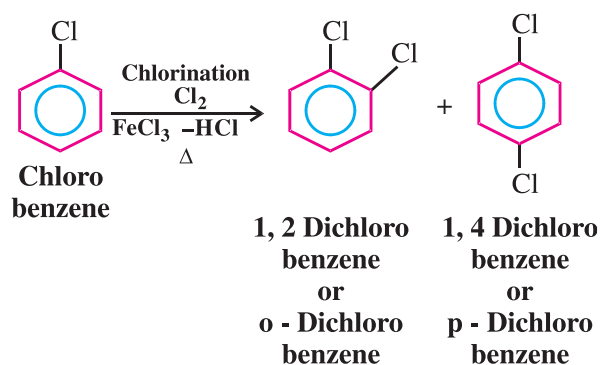
Six carbon atoms of benzene possess equal reactivity. Thus, as seen earlier monosubstituted isomers are not obtained. But when any functional group enters in benzene by first substitution, the obtained reactivity of remaining five carbon atoms are not similar in substituted benzene derivative. When second substitution is carried out on a monosubstituted benzene, the position of second entering functional group depends on monosubstituted derivative and characteristics of first functional group. Thus, the effect of first functional group

already present in monosubstituted benzene decides the place of second entering functional group. It will attach to carbon to which, the group already present in monosubstituted benzene directs the second entering group to become an inductive group. Effect of first functional group is known as directing effect. This directing effect is of two types :

(1) Ortho-Para directing effect : If first functional group present in monosubstituted benzene is $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{NHCOR}$, $-\text{OH}$, $-\text{OR}$, $-\text{OCOR}$, $-\text{R}$, and $-\text{X}$, (where R = alkyl group : X = F, Cl, Br, I) etc, due to its effect attached to ortho and/or para position it can be represented as 1-2 (ortho) and 1-4 (para) respectively. Usually, functional group containing ortho and para directive effect are to pass on electron towards the phenyl ring and hence they are known as electron donating or positive groups.

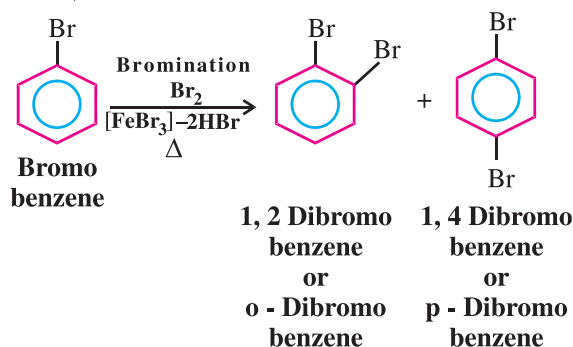
In monosubstituted derivative, second substitution occurs at ortho and para position, and therefore, disubstituted derivative will be a mixture of ortho and para isomers.

Likewise, in first substitution reaction of chlorobenzene with excess chlorine, the first entered Cl^- group is ortho-para directive. So the second substituting functional group enters at ortho and para position. As a result, mixture of two isomers 1, 2 dichloro benzene and 1, 4 dichloro benzene are obtained.

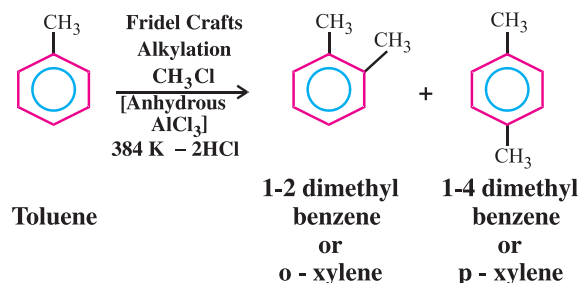


Some other examples of this directive effect are as under :

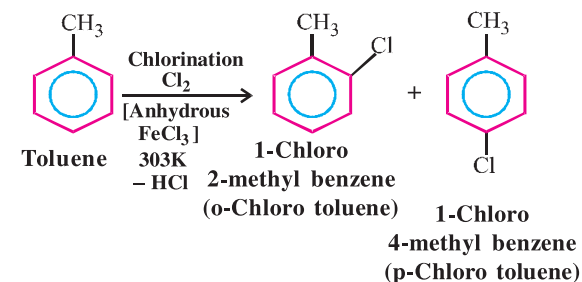
(1) Bromination of bromobenzene, by second substitution, mixture of 1, 2 dibromobenzene and 1, 4 dibromobenzene are obtained.



(2) On performing Friedel-Crafts' alkylation in toluene, due to the effect of ortho-para directing methyl group, the second substitution, produces mixture of ortho and para xylene.



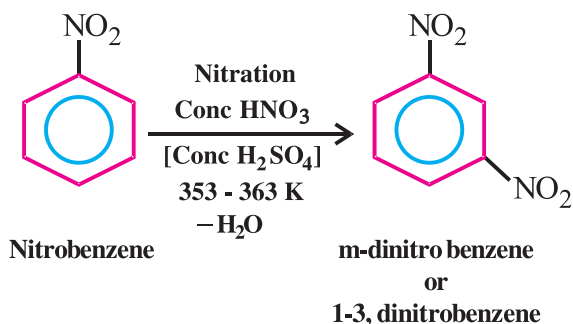
(3) On chlorination of toluene due to the presence of ortho-para directing group in toluene by second substitution, mixture of ortho chloro-toluene and para chloro toluene is obtained. Due to the difference in their boiling-points ortho and para isomers are separated by distillation.



(2) Meta-directing Effect : If the first functional group present in monosubstituted benzene is $-\text{NO}_2$, $-\text{CHO}$, $-\text{COOH}$, $-\text{CN}$, $-\text{CCl}_3$, $-\text{COR}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$ etc., due to the effect of any one of these, the second entering functional group will attach to the meta position. Usually, such types of functional groups are attractive electrons from the phenyl ring towards themselves, hence, they are known as electron attracting or negative groups. In monosubstituted benzene derivatives, second substitution occurs

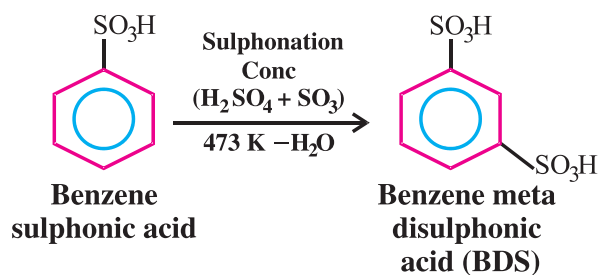
at meta position, then only one isomer is obtained, for such disubstituted benzene.

E.g. In nitrobenzene nitration takes place at 353-363 K temperature, then second substitution reaction occurs, nitrobenzene obtained from the first substitution due to the presence of meta directing functional group, the second entering-NO₂ functional group enters to the meta position on second substitution. As a result only one isomer metadinitrobenzene is obtained.

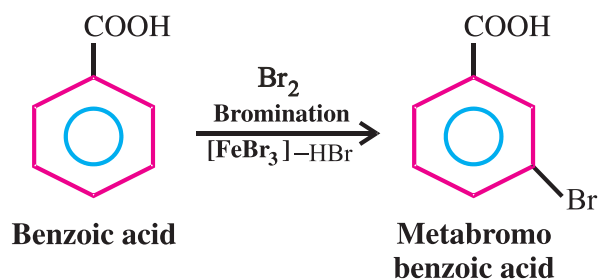


Some examples of meta-directing effects are given below :

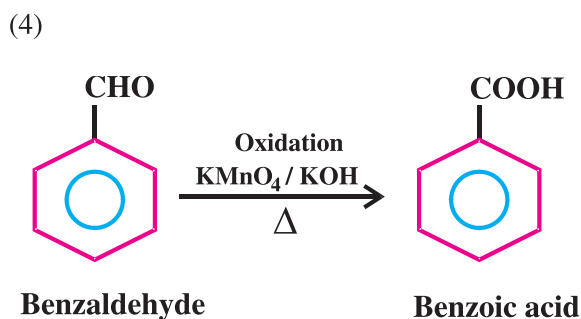
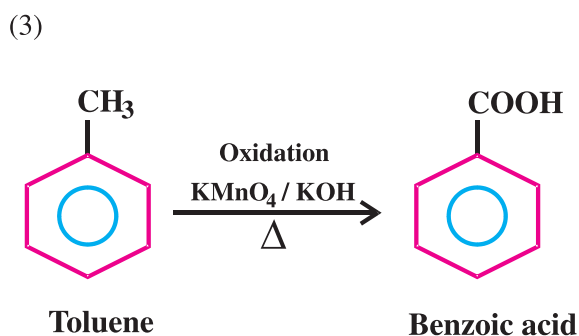
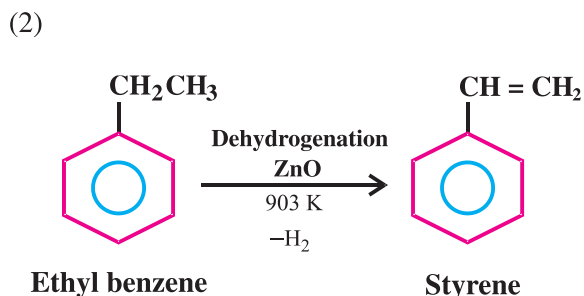
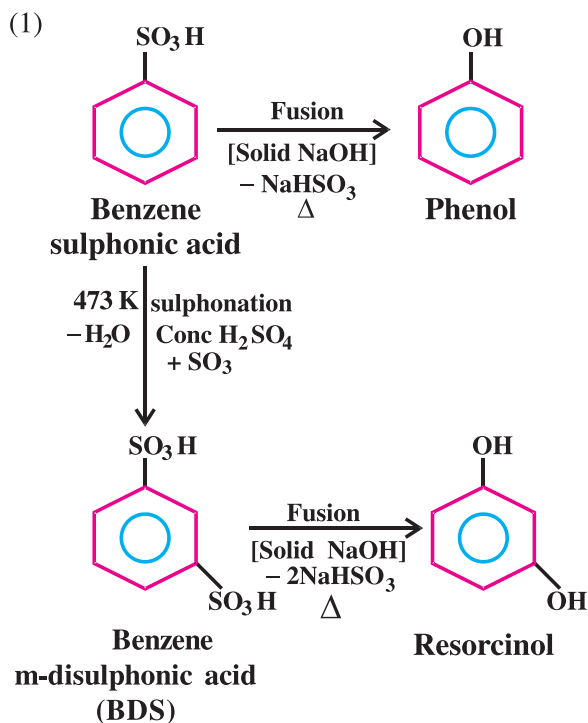
(1) Sulphonation of benzene sulphonic acid at 473 K temperature, due to the effect of meta directing -SO₃H group, the newly entering -SO₃H group attaches to the meta position and benzene m-disulphonic acid is obtained.



(2) Bromination of benzoic acid in presence of FeBr₃ as a catalyst due to the effect of meta directing -COOH group, the newly entering -Br group attaches at m-position and meta bromobenzoic acid is obtained.



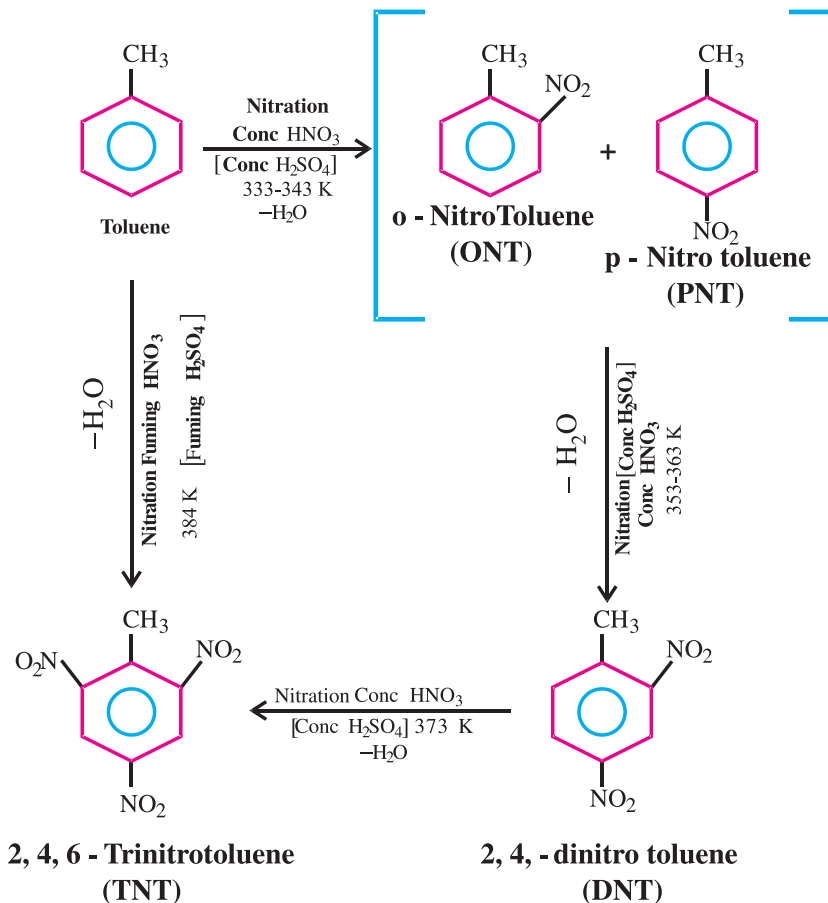
6.6.8 Reactions of functional group :



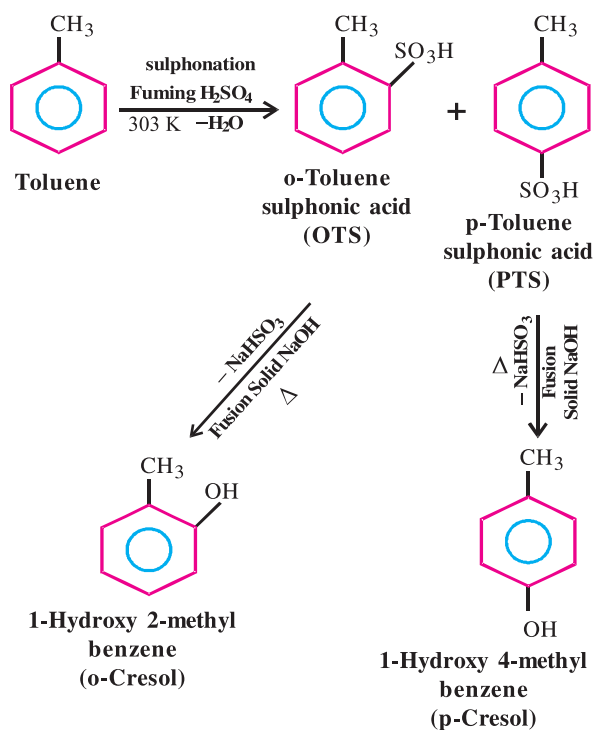
Chemical Reactions of Toluene :

Reactions in the phenyl ring :

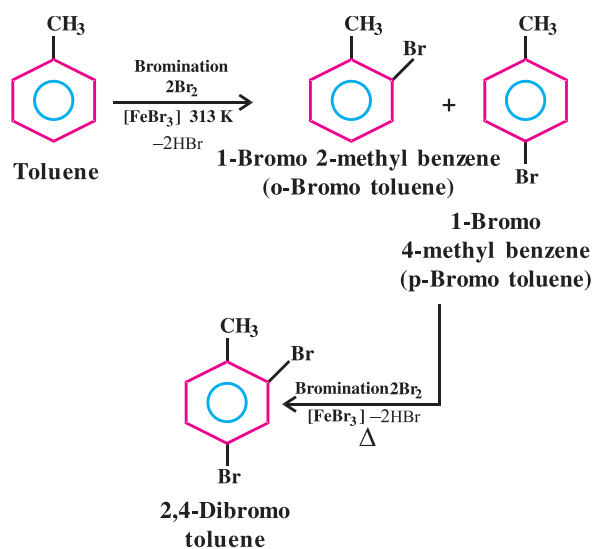
(1) Nitration :



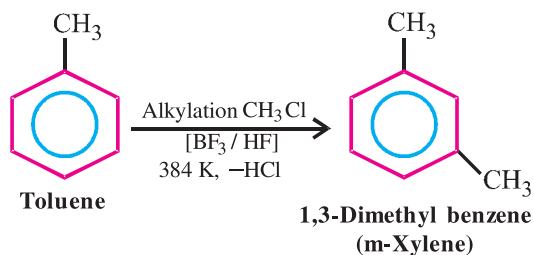
(2) Sulphonation :



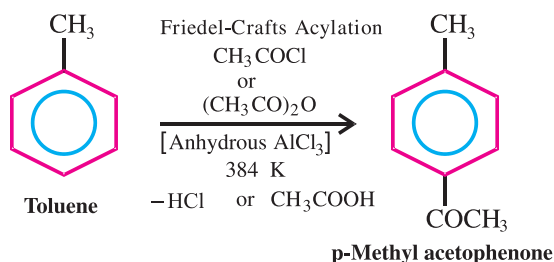
(3) Bromination :



(4) Alkylation :

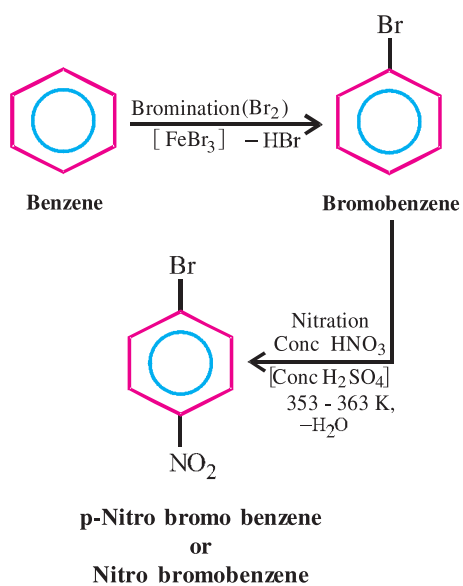


(5) Acylation (Friedel-Crafts) :

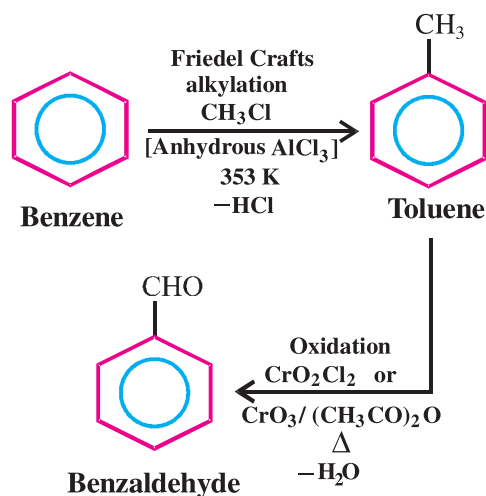


6.6.9 Organic Conversions :

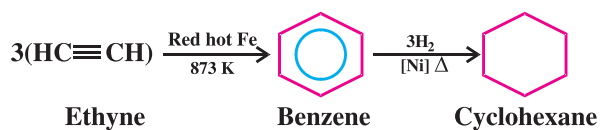
(1) p-Nitrobromobenzene from benzene :



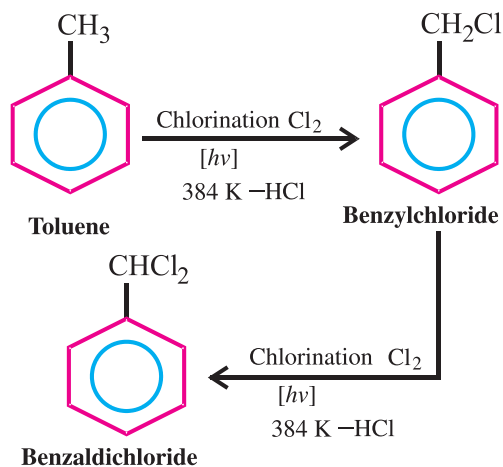
(2) Benzene to Benzaldehyde :



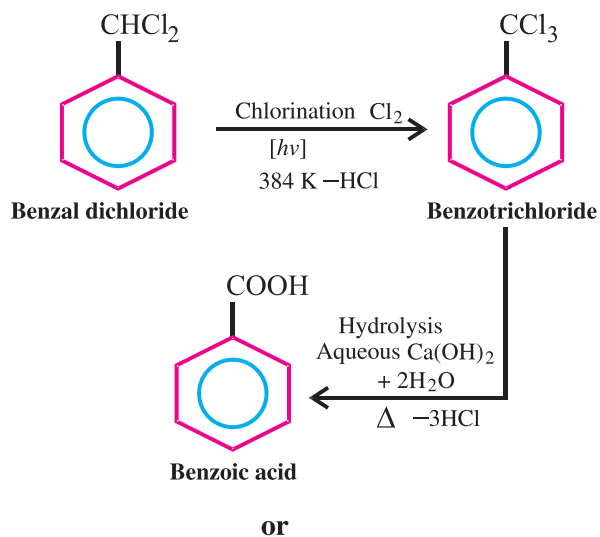
(3) Ethyne to cyclohexane :



(4) Toluene to Benzaldichloride :



(5) Benzoic acid from Benzal dichloride



SUMMARY

Hydrocarbons are compounds of carbon and hydrogen. Mostly hydrocarbons are obtained from coal and petroleum, which is a big source for obtaining energy. Petrochemicals are used as the raw material in the large scale production of important industrial products. Hydrocarbons are classified on the basis of the structure, as straight chain, saturated alkanes, unsaturated alkenes, unsaturated alkynes, cyclic aliphatic and cyclic aromatic compounds.

Alkanes can be prepared from unsaturated hydrocarbons, alkyl halide, and carboxylic acid. According to the different number of carbon atoms in alkane, physical state changes due to weak intermolecular forces.

When the number of carbon atom increases in alkane, the molecular weight increases, as a result we can see an increase in the boiling points.

In alkane, alkene and alkyne compounds nomenclature is based according to IUPAC system. In hydrocarbon compounds when molecular weights are same, but physical and chemical properties are different, they show isomerism phenomenon.

Alkene compounds are prepared from alkyne, alkylhalide, vicinal dihalide and alcohol. The melting points and boiling points of alkenes are higher compared to alkynes. In 1869 Russian scientist Markovnikov gave a rule which is known as Markovnikov's rule. In 1933 anti-Markovnikov's rule was given by M.S. Kharsh and F.R. Mayo which is also known as peroxide effect. Alkyne compounds are prepared from calcium carbide and vicinal dihalides. In alkyne compounds, melting points, boiling points and densities increase with the increase in molecular masses, polymerisation of alkyne compound gives polymers like PVC and PAN.

Important reactions of alkanes like free radical formation, substitution, combustion, oxidation and cyclisation, while in alkene and alkyne mainly electrophilic addition reactions are taking place. Benzene is the first member of aromatic hydrocarbon compounds. Benzene and benzenoids possess aromatic characteristics. Kekule represented the resonating structure of benzene. Benzene is aromatic and its proof is obtained by Huckel's rule. The concept of planar cyclic compounds are clarified by Huckel's law. In 1937 scientist Lewis gave the electronic configuration of benzene. By this sp^2 hybridization of carbon in benzene can be understood.

Ortho, meta and para isomer compounds can be easily understood by inductive group in benzene and its directive effects.

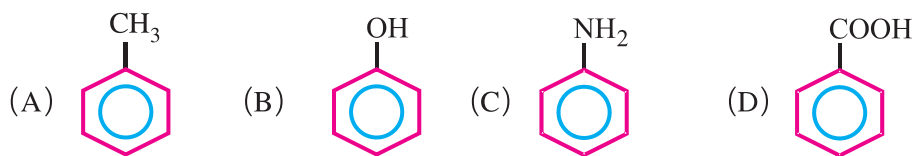
Aromatic hydrocarbons give mainly electrophilic substitution reactions and sometimes addition reactions although it is saturated.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) Which is the saturated hydrocarbon from the compounds mentioned below :
(A) Phenyl group (B) Alkane (C) Alkene (D) Alkyne
- (2) Which substance has (2^0) secondary carbon ?
(A) Propane (B) n-Butane (C) 2 Methyl propane (D) Methane
- (3) What is obtained by reduction reaction of alkyl halide ?
(A) Alcohol (B) Alkene (C) Alkane (D) Cl_2
- (4) Which gas is released in decarboxylation reaction ?
(A) CO_2 (B) CO (C) O_2 (D) N_2
- (5) Sodalime is a mixture of which substances ?
(A) NaOH, CaCO_3 (B) NaOH, CaO
(C) KOH, Ca(OH)_2 (D) KOH, CaO
- (6) The general formula of alkene is
(A) $\text{C}_n\text{H}_{2n+2}\text{O}$ (B) C_nH_{2n} (C) $\text{C}_n\text{H}_{2n+1}$ (D) $\text{C}_n\text{H}_{2n+2}$
- (7) Which mixture is used as Lindlar's catalyst ?
(A) Pd + Pt (B) Ni + P (C) Pt + halogen (D) Pt + charcoal
- (8) The catalyst used for obtaining carbonyl compound from alkyne with H_2O
(A) Pt (B) HgSO_4 (C) HgCl_2 (D) HCN
- (9) What is the bond length of C = C in benzene ?
(A) 139 pm (B) 133 pm (C) 154 pm (D) 111 pm
- (10) The value of resonance energy in benzene
(A) 119.66 kJ (B) 208.36 kJ (C) 150.63 kJ (D) 358.99 kJ
- (11) Which is the electrophilic ion in nitration reaction of benzene ?
(A) SO_3H^+ (B) NO_2^- (C) NO_2^+ (D) HNO_3

(12) From the following which is the formula of toluene ?



(13) What is the number of σ -bonds and π -bonds in benzene ?

- (A) Six σ and 3π (B) Six σ and 1π
 (C) Eight σ and 3π (D) Twelve σ and 3π

(14) Which catalyst is used in bromination of toluene ?

- (A) FeBr_3 (B) FeSO_4 (C) FeCl_3 (D) AlBr_3

(15) The general formula of arene compounds is

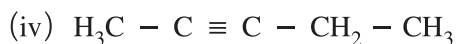
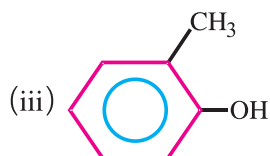
- (A) $\text{C}_n\text{H}_{2n-6}$ (B) $\text{C}_n\text{H}_{2n-3m}$ (C) $\text{C}_n\text{H}_{2n+6m}$ (D) $\text{C}_n\text{H}_{2n-6m}$

2. Answer the following questions in brief :

(1) Give IUPAC name and structural formula of the following :

Neopentane, Isobutane, Formaldehyde, n-Butane, Benzyl chloride, TNT

(2) Give IUPAC names of the compounds having following structural formulae :



(3) Why quaternary hydrogen is not possible in alkane ?

(4) Moving from primary to tertiary alkane the boiling point decreases. Why ?

(5) What is called dehydrohalogenation reaction ?

(6) Give only equation for the preparation of PVC.

(7) Give the structural formulae and the names of the aromatic compounds containing three rings.

-
- (8) What is the resonance energy ?
 - (9) What is called electrophilic ion ? Give example.
 - (10) Give only equation of Friedel-Crafts alkylation reaction in benzene ?
 - (11) Which functional groups are responsible for meta directing effect ?
 - (12) Give the structure of benzene suggested by Kekule ?
 - (13) Give the electronic configuration of benzene given by Lewis ?
 - (14) Mention Huckel's rule of aromatization.

3. Write answers to the following questions :

- (1) Give the following organic conversions :
 - (i) Ethyne from 1, 2 dibromoethane
 - (ii) Ethanoic acid from chloroethane
 - (iii) 1 – Bromo propane from propyne
 - (iv) 4 Nitro 1- Bromobenzene (p – Nitrobromobenzene) from benzene
 - (v) 4 Nitro 4- methylbenzene (p – Nitrotoluene) from benzene
 - (vi) 1, 3 Dimethyl benzene (m-Xylene) from benzene
 - (vii) Phenol from benzene
- (2) Who discovered benzene and when ?
- (3) Explain the classification of aliphatic hydrocarbons giving the suitable examples.
- (4) Give the preparation reaction of alkane from alkyl halide.
- (5) Mention the difference between physical state and boiling point of alkane due to increase in number of carbon atoms.
- (6) Give formation of benzene by reduction of phenol
- (7) Explain the reaction mechanism of asymmetric alkene with HCl according to Markovnikov rule.
- (8) Prove the acidic properties of alkynes.
- (9) Explain the addition reactions in alkynes.
- (10) Discuss the physical properties of alkynes.

4. Answer the following questions in detail :

- (1) Write a note on preparation of alkyne compounds.
 - (2) What is aromaticity ? Give its details.
 - (3) Explain the structure of benzene based on its chemical reactions.
 - (4) Discuss the mechanism of nitration, halogenation and sulphonation of benzene.
 - (5) Write a note on directing effect of second substitution in benzene.
 - (6) Explain the ortho-para and meta directive effect in toluene giving two examples of each.
 - (7) Explain the modern structure of benzene based on its physical properties.
 - (8) Explain the structure of aromatic benzene according to molecular orbital theory.
 - (9) Nitration of bromobenzene gives 2-Bromo, 1-Nitrobenzene and 4-Bromo, 1-Nitrobenzene but bromination of nitrobenzene gives 3-Bromo, 1-Nitrobenzene. Why ?
 - (10) Why polymerisation of benzene is not possible even when it possesses double bonds ?
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