

# Chapter

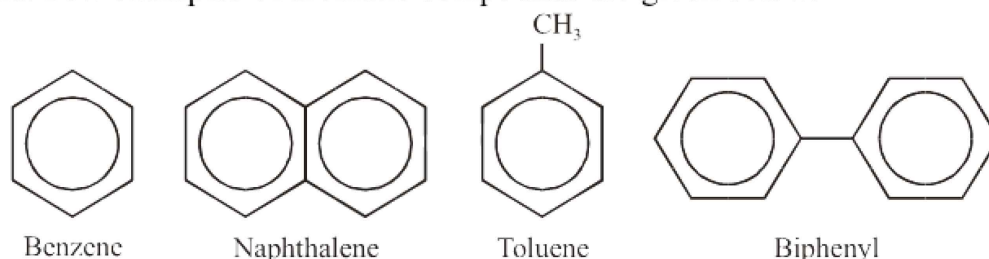
# 9

## AROMATIC HYDROCARBOS

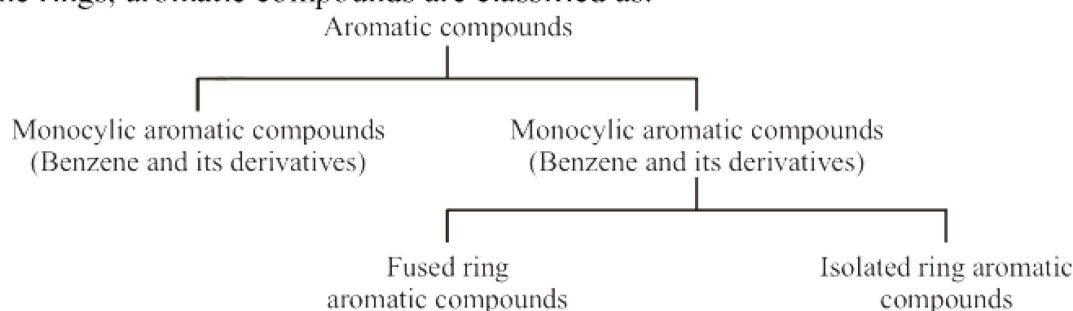
### INTRODUCTION

The term “aromatic” was derived from the Greek word “**aroma**” meaning “fragrant”.

These compounds have a **low hydrogen to carbon ratio** in their molecular formula and have a characteristic odour. However, it was soon realized that many aromatic compounds are odourless whereas many others are fragrant though they are not aromatic. Further, when aromatic compounds of higher molecular mass were subjected to various methods of degradation, they often produced benzene or derivatives of benzene. All aromatic compounds have a six carbon unit in their molecules like benzene, toluene, naphthalene, biphenyl, etc. Benzene is the simplest and the parent member of this class of compound. Few examples of aromatic compounds are given below.



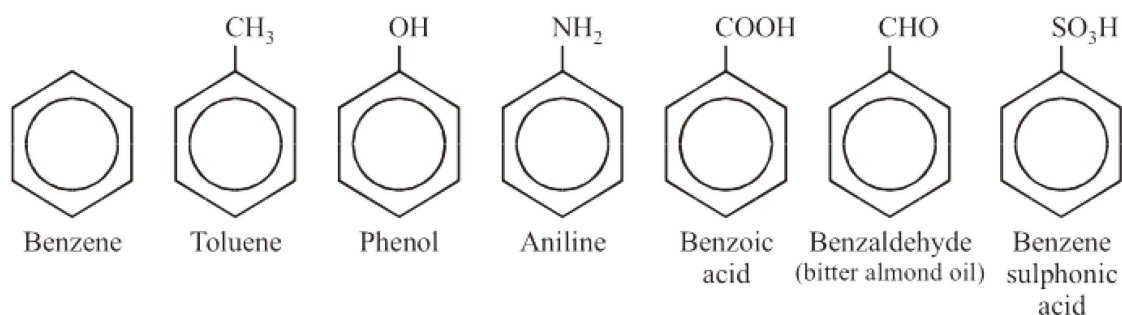
Benzene has regular planar hexagonal structure. On the basis of number of benzene rings, aromatic compounds are classified as:



#### (1) **Monocyclic Aromatic Compounds:**

*“The aromatic compounds which have only one benzene ring in their molecule are called monocyclic aromatic compounds.”*

They consist of benzene and their derivatives. For examples:



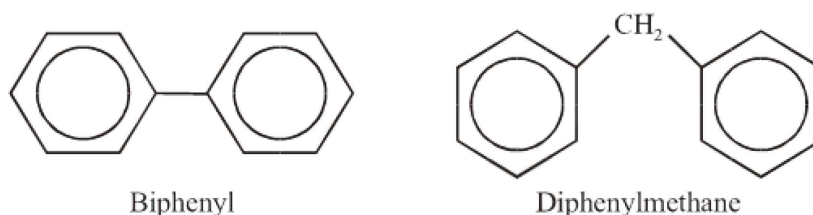
**(2) Polycyclic Aromatic Compounds:**

*“Aromatic compounds containing two or more benzene rings in their molecules are called polycyclic aromatic compounds.”*

They may be divided further into two classes:

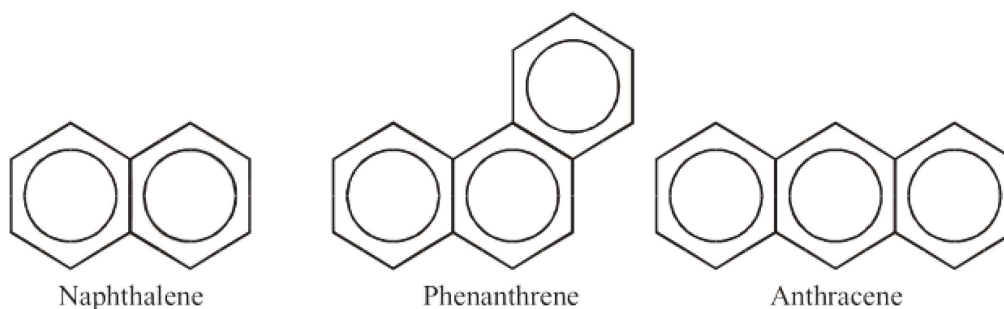
**(i) Isolated Rings Aromatic Compounds:**

They polycyclic compounds containing isolated benzene rings in them are called isolate polycyclic compounds. e.g.,



**(ii) Fused Polycyclic Compounds:**

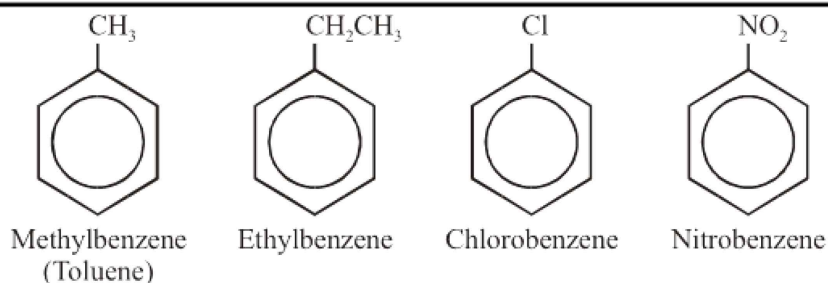
The compounds in which the benzene rings are fused together at ortho positions so that the adjacent rings have a common carbon to carbon bonds. e.g., naphthalene, phenanthrene and anthracene.



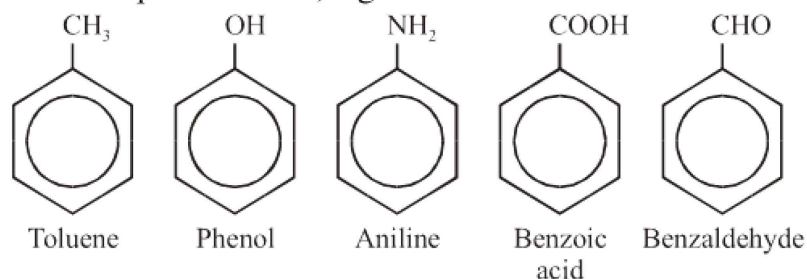
## NOMENCLATURE

Following rules are used for naming the aromatic compound. The names given in brackets are traditional or non-systematic.

- (1) Mono-substituted benzene derivatives are named by using prefix “Benzene” after the name of the constituents.

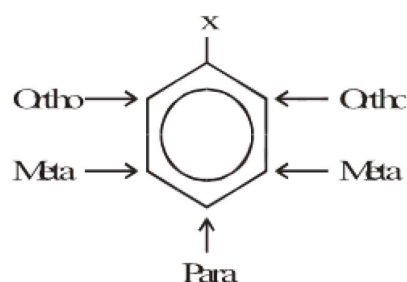


- (2) Some monosubstituted benzene derivatives have been accepted as systematic names, or called special names, e.g.

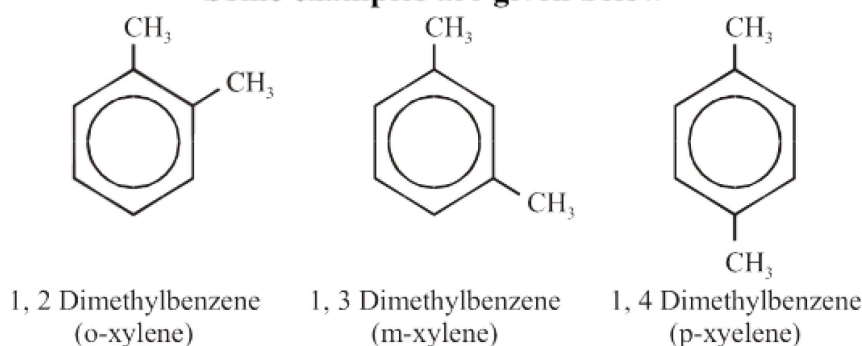


**Note:** When one hydrogen of benzene is removed, phenyl radical  $C_6H_5$  – is formed. It is also called aryl group and its symbol is Ph –.

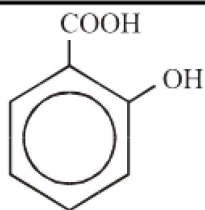
- (3) Disubstituted benzene are named, using one of prefixes, ortho (1, 2) meta (1, 3) or para (1, 4).



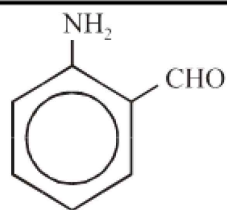
Some examples are given below



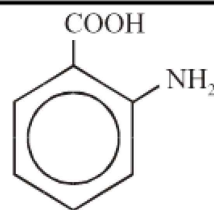
- (4) If two or more different substituents are present at benzene, they are named according to the priority list – higher in polarity will be given number 1. Other substituents are numbered by counting from position 1 in the manner which gives then the lowest number. The order of priority of substituents are given from left to right.  
 $-COOH$ ,  $-CN$ ,  $-CHO$ ,  $-COCH_3$ ,  $-OH$ ,  $-NH_2$ ,  $-OR$ ,  $-R$



2-Hydroxybenzoic acid  
(Salicylic acid)

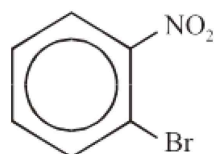


2-Aminobenzaldehyde

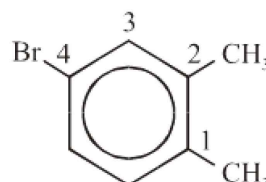


2-Aminobenzoic acid

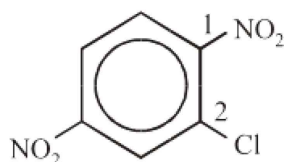
- (5) If two or more different substituents are present on benzene ring and have no priority order, then lowest possible numbers are used. The substituents are listed alphabetically when writing the name.



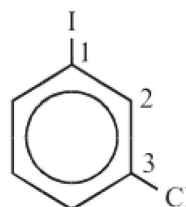
1-bromo 2-nitrobenzene  
(o, bromonitro benzene)



4-bromo-1,2-dimethylbenzene

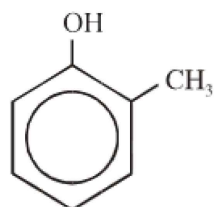


2-chloro 1, 4  
dinitro benzene

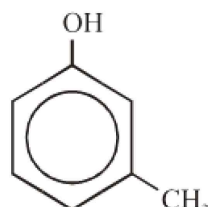


3-chloro 1-iodobenzene  
(m-chloroiodo benzene)

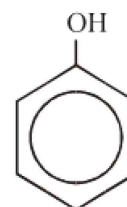
- (6) If there is a substituent on the benzene ring which gives a special name to the molecule, then special name is used as parent name to the molecule.



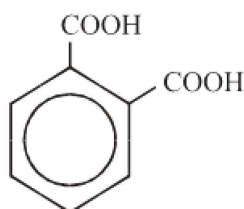
(o-Cresol)



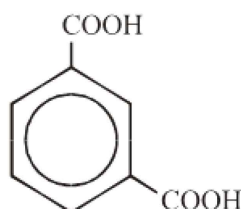
(m-Cresol)



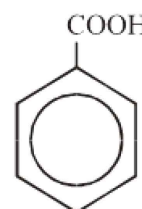
(p-Cresol)



Phthalic acid

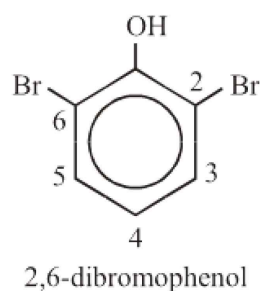
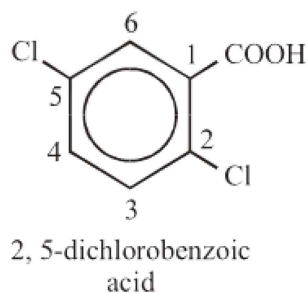
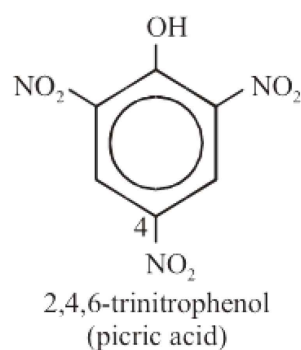
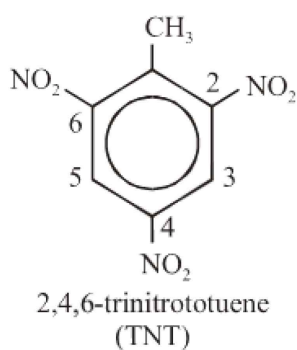
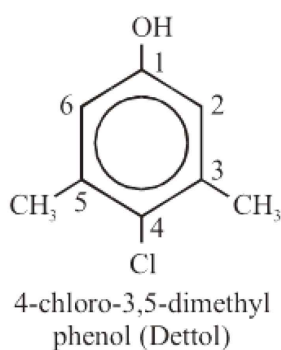
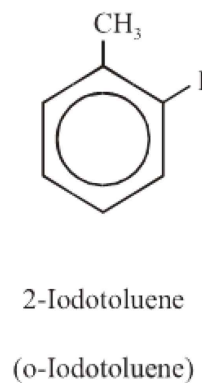
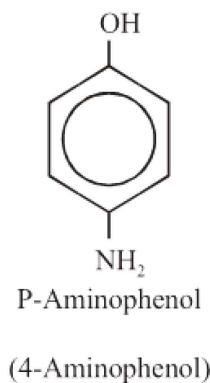
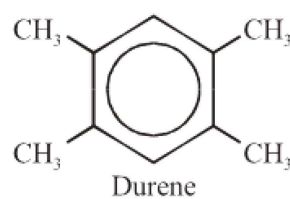
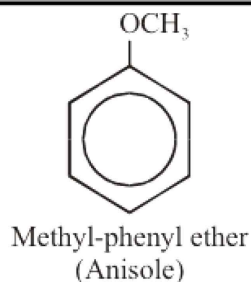
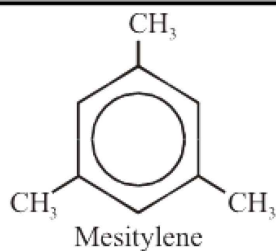


Iso-Phthalic acid



Tere-Phthalic acid





## BENZENE

Benzene was discovered by Michael Faraday's in 1825 in the gas produced by destructive distillation of vegetable oil. In 1845 Hoffman obtained benzene from coal tar which is still a commercial source of benzene. Large quantity of benzene and alkyl benzenes prepared in USA by cracking of petroleum.

## STRUCTURE OF BENZENE

- (i) The empirical formula of benzene is CH. This formula is determined by the elemental analysis.
- (ii) Its molecular mass determined by the vapour density method is 78.108. This is six times the empirical formula mass ( $\text{CH} = 12 + 1 = 13$ ). Therefore, the molecular formula is  $\text{C}_6\text{H}_6$ .
- (iii) The molecular formula of benzene indicates that it is highly unsaturated compound.

### Nature of unsaturation in benzene (benzene is not an open chain compound):

The open chain formula of  $\text{C}_6\text{H}_6$  can be written in the following ways:

- (i)  $\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C} \equiv \text{CH}$  (1,5 hexadiyne)
- (ii)  $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - \text{CH} = \text{CH}_2$  (Hex 1,5-dien-3-yne)
- (iii)  $\text{CH}_2 = \text{C} = \text{CH} - \text{CH} = \text{C} = \text{CH}_2$  (1,2,4,5, hexatetraene)

Above structures can add 4 molecules of  $\text{H}_2$  as well as 4 molecules of  $\text{Cl}_2$  or  $\text{Br}_2$  in it. But actually benzene can add only three molecules of  $\text{H}_2$  or  $\text{Cl}_2$  separately. These reactions indicate that benzene has three double bonds.

On the other hand above structures are of alkenes or alkynes, alkenes or alkynes oxidize with  $\text{KMnO}_4$  solution but benzene does not decolorize  $\text{KMnO}_4$  solution. This indicates that benzene is a saturated hydrocarbon. Benzene also gives substitution reaction with conc.  $\text{HNO}_3$  or conc.  $\text{H}_2\text{SO}_4$ . This indicates that it is a saturated compound but addition reactions indicate that it is unsaturated.

Result of the above discussion is that benzene is not an open chain compound.

- (2) Considering a straight chain structure for benzene and further assuming that each carbon carries one H-atom, it should be capable of forming three monosubstitution products but it gives only one monosubstitution product.



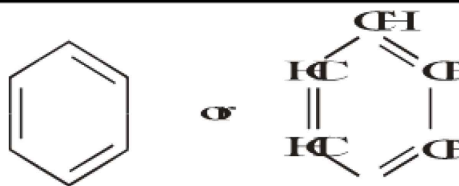
Monosubstituent product

- (3) The molecular formula of benzene is  $\text{C}_6\text{H}_6$ . This formula does not correspond to any aliphatic hydrocarbon like alkane  $\text{C}_n\text{H}_{2n+2}$ , alkene  $\text{C}_n\text{H}_{2n}$  or alkyne  $\text{C}_n\text{H}_{2n-2}$ .

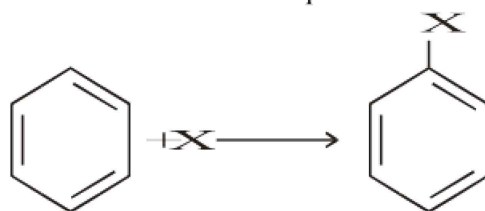
All above points indicate that benzene does not belong to open chain hydrocarbon.

## KEKULE STRUCTURE OF BENZENE

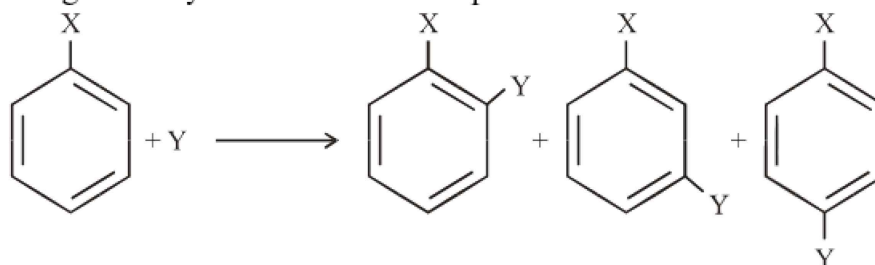
The structure of benzene continued to be a serious problem for chemists for about 40 years. A German chemist, Kekulé, at last solved the problem in 1865. Kekulé proposed a cyclic regular hexagonal structure for benzene, which contains three double bonds alternating with three single bonds. He supported his theory by the following arguments.



- (i) Benzene gives only one monosubstituted product.

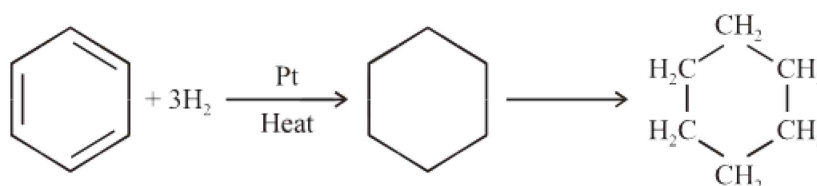


- (ii) Benzene gives only three disubstituted products.

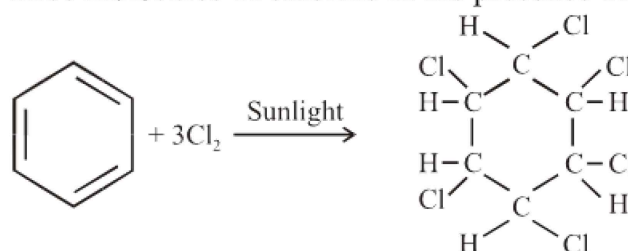


These points confirm the regular hexagonal structure for benzene in which all the carbon atoms are occupying identical positions in the molecule. Therefore, benzene forms only one toluene, one phenol and one nitrobenzene.

- (iii) Benzene adds three hydrogen molecules in the presence of a catalyst. It indicates that it has three double bonds.



- (iv) Benzene adds three molecules of chlorine in the presence of sunlight.

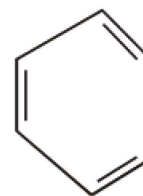


These reactions confirm the presence of three double bonds alternating with three single bonds.

### Objection in Kekulé structure:

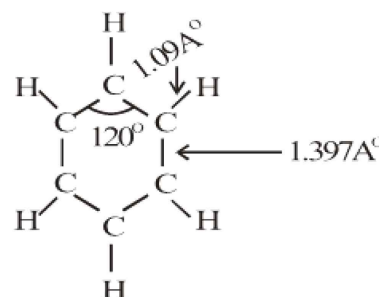
- (1) Kekulé's formula of benzene has three double bonds in it. It has a high degree of unsaturation in it while substitution reaction of benzene indicates that it is a saturated compound.

- (2) Kekule model suggest that bond distance between carbon-carbon atoms are unequal. Double bond has less bond length than the single bond. X-rays analysis shows that all bond distances between C – C are equal.
- (3) The theoretical value of heat of formation of gaseous benzene is greater than the actual value of heat of formation of benzene. This indicates that actual structure of benzene is more stable than proposed kekule structure.



### X-rays Studies of Benzene Structure:

The X-ray studies of benzene have confirmed the hexagonal structure for it. These studies have also revealed that all the carbon and hydrogen atoms are in the same plane. All the angles are of  $120^\circ$ . All C – C and C – H bond lengths are  $1.397\text{\AA}$  and  $1.09\text{\AA}$ , respectively.

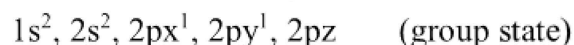


## MODERN STRUCTURE OF BENZENE

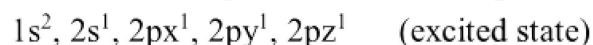
(Atomic orbital treatment of benzene)

According to hybridization theory, all six carbon atoms in benzene are  $sp^2$  hybridized.

The electronic configuration of carbon is:

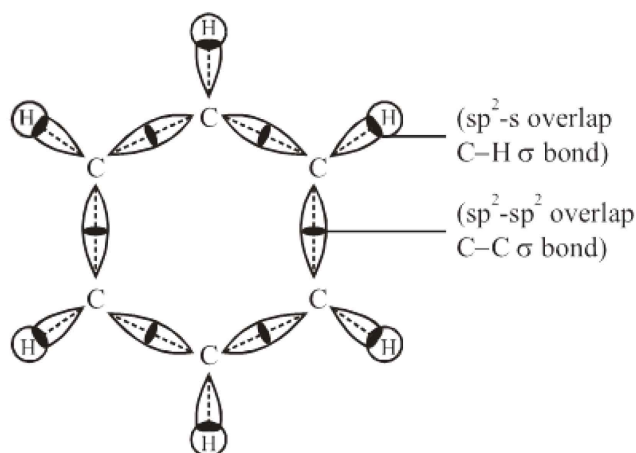


One electron is promoted from s to p orbital:



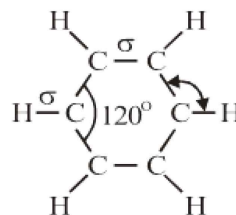
One s and two p orbitals of carbon atom intermix and form three  $sp^2$  hybrid orbitals.

The  $sp^2$ -hybrid orbitals overlap with each other and with s-orbitals of the six hydrogen atoms, forming C – C and C – H bonds as shown in the figure.



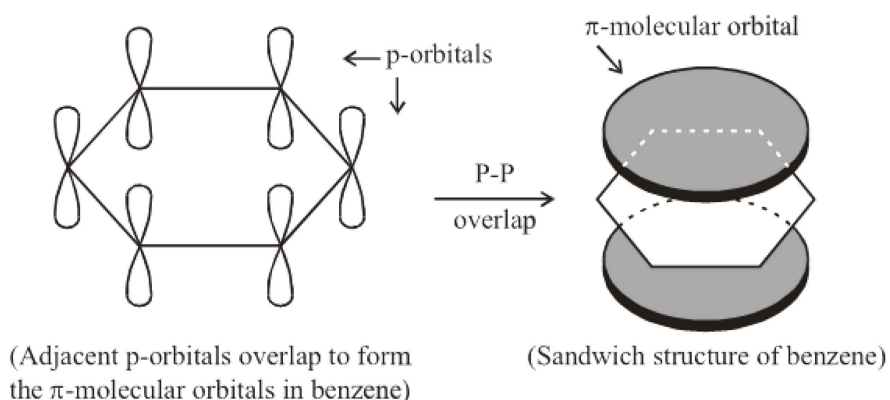
(Formation of sigma bonds in benzene)

Since the bonds result from the overlap of **planar  $sp^2$ -orbitals**, all carbon and hydrogen atoms in benzene lie in the same plane. All sigma ( $\sigma$ ) bonds in benzene lie in one plane and all bond angles are  $120^\circ$  as shown below.



(sigma bonds of C – C and C – H in benzene)

Each carbon atom in benzene has an unhybridized p-orbital containing one electron. These p-orbitals are perpendicular to the plane of sigma bonds. The parallel overlap of these p-orbitals produces a  $\pi$ -molecular orbital containing six electrons. One half of this  $\pi$ -molecular orbital lies above and the other half lies below the plane of sigma bonds. The six electrons of the p-orbitals cover all the six carbon atoms and are said to be delocalised.



As a result of **delocalization**, a stronger  $\pi$ -bond is formed. A continuous sheath of electrons is present above and below the carbon plane and this structure is called sandwich structure. The  $\pi$ -bonds of benzene are different from  $\pi$ -bonds of alkenes.  $\pi$ -bonds of alkenes are localized between two carbon atoms while  $\pi$ -bonds of benzene are delocalized. That is why, the chemical behaviour of benzene is different from alkenes. Benzene is less reactive than alkenes due to delocalization of  $\pi$ -electrons in benzene.

### STABILITY OF BENZENE

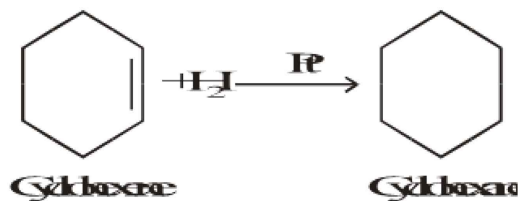
Benzene is a stable molecule. Stability of benzene is due to the extensive delocalization of  $\pi$ -electrons cloud. Extent of stability of benzene (1, 3, 5 cyclohexatriene) can be measured from heat of hydrogenation.

*“The heat of hydrogenation is the amount of heat evolved when one mole of hydrogen is added to a molecule.”*



Stability of benzene can be understood by the heat of hydrogenation of cyclohexene, 1, 3-cyclohexadiene and 1, 3, 5-cyclohexatriene.

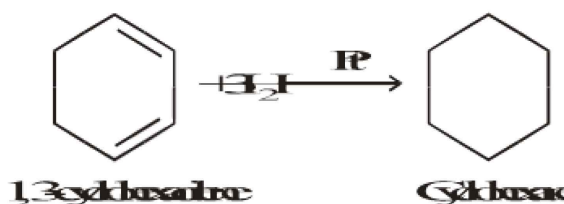
Cyclohexene, a six membered ring containing one double bond, can be easily hydrogenated to give cyclohexane. When the  $\Delta H$  for this reaction is measured, it is found to be  $-119.5 \text{ kJ/mole}$  very much like that of any similarly substituted alkene.



$$\Delta H = -119.5 \text{ kJ/mol}$$

We would expect, that hydrogenation of 1, 3-cyclohexadiene would liberate roughly twice as much heat, and thus have  $\Delta H$  equal to about  $-239 \text{ kJ/mole}$ . When this experiment is done, the result is  $\Delta H = -231.5 \text{ kJ/mole}$ . This result is quite close to what we calculated, and the difference ( $7.5 \text{ kJ}$ ) can be explained by taking into account the fact that compounds containing conjugated double bonds are usually somewhat more stable than those containing isolated double bonds.

(The compound with alternate multiple bond is called conjugate system)



$$\text{Calculated } \Delta H = (-119.5 \times 2) = -239 \text{ kJ/mol}$$

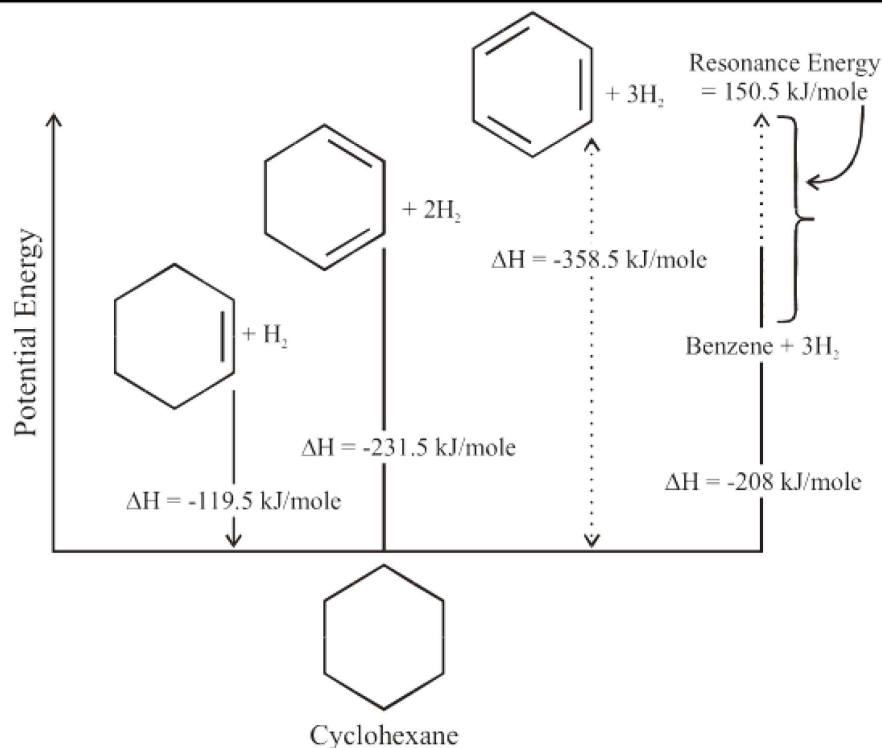
$$\text{Observed } \Delta H = -231.5 \text{ kJ/mol}$$



$$\text{Calculated } \Delta H_{\text{hydrogenation}} = (-119.5 \times 3) = -358.5 \text{ kJ mol}^{-1}$$

$$\text{Observed } \Delta H_{\text{hydrogenation}} = -208 \text{ kJ mole}^{-1}$$

$$\text{Difference} = -358.5 - (-208) = -150.5 \text{ kJ mol}^{-1}$$



(A comparison of heat of hydrogenation of cyclohexene, 1, 3-cyclohexadiene and 1, 3, 5, cyclohexatriene).

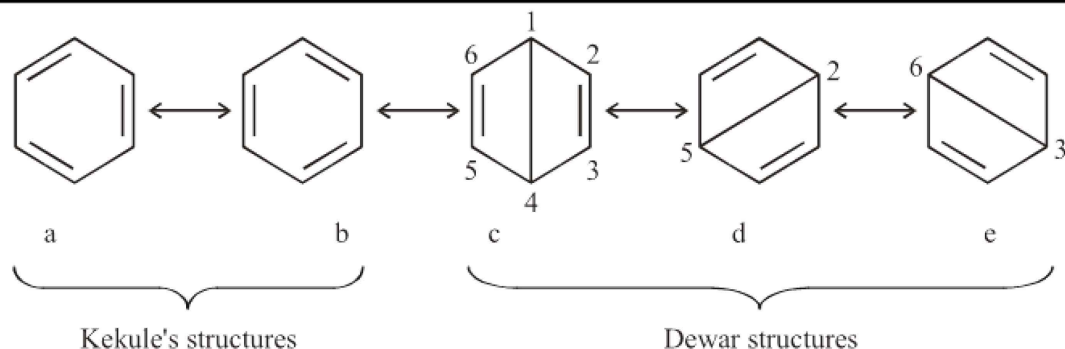
“The difference in energy between hypothetical structure (1, 3, 5, cyclohexatriene) and actual structure (benzene) is called resonance energy.”

Resonance energy gives a measure of stability of the compound. Greater is the resonance energy, greater will be the stability of compound. In polycyclic aromatic hydrocarbon, more extensive delocalization is present and they are more stable than benzene. The resonance energy of benzene is  $150.5 \text{ kJ mol}^{-1}$  but resonance energy of naphthalene is  $250 \text{ kJ mol}^{-1}$  due to greater delocalization of  $\pi$ -cloud at 10 carbon atoms rather than at six carbon atoms.

### RESONANCE STRUCTURE OF BENZENE

“The possibility of different pairing schemes of valence electrons of atoms in a molecule is called resonance” and the different structures thus arranged are called “Resonance structures”.

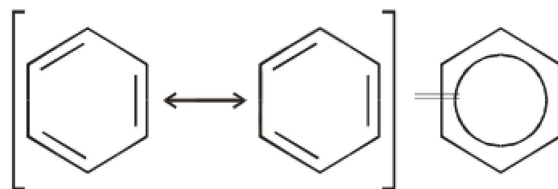
The resonance is represented by a double headed arrow ( $\leftrightarrow$ ) e.g., the following different pairing schemes of the fourth valence (p-electrons) of carbon atoms are possible in benzene.



(a), (b) were proposed by Kekule and c, d, e, were proposed by Dewar. The stability of a molecule increases with increase in the number of its resonance structures. Thus molecules of benzene is chemically quite stable.

In Dewar structure, the carbon atom at opposite positions 1-4, 2-5 and 3-6 are at larger distances than those in the adjacent positions 1-2, 2-3, 3-4, 4-5, 5-6 and 6-1. Therefore the bondings between  $C_1 - C_4$ ,  $C_2 - C_5$  and  $C_3 - C_6$  are not favourable energetically. Hence the Dewar structures for benzene have minor contribution towards the actual structure of benzene.

Infact, the structure of benzene is a resonance hybrid of all the five structures (a), (b), (c), (d) and (e) in which the Kekule's structure (a) and (b) have the larger contribution. Therefore, benzene molecule can be represented by either of the two Kekule's structure.



The three alternate single and double bonds in the above structures are called conjugate bonds or resonating bonds.

Since the structure of benzene is a resonance hybrid, therefore all the C – C bond lengths equal but different from those in alkanes, alkenes and alkynes.

In alkanes the C – C bond length is  $1.54\text{\AA}$ .

In alkenes the  $C = C$  bond length is  $1.34\text{\AA}$ .

In alkynes the  $C \equiv C$  bond length is  $1.20\text{\AA}$ .

In benzene the C – C bond length is  $1.397\text{\AA}$ .

The C – C bond length in benzene is intermediate between those in alkanes and alkenes.

## PREPARATION OF BENZENE

Some methods for the preparation of benzene are given below:

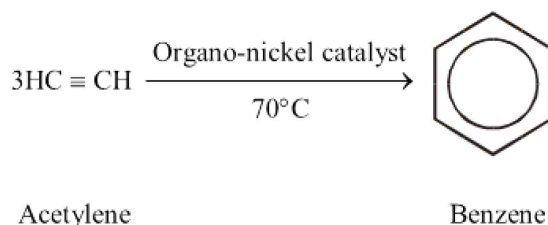
**(1) Dehydrogenation of Cyclohexane:**

Benzene can be prepared by the dehydrogenation of cyclohexane, when heated at  $250^{\circ}\text{C}$  in the presence of catalyst platinum or pladinum.



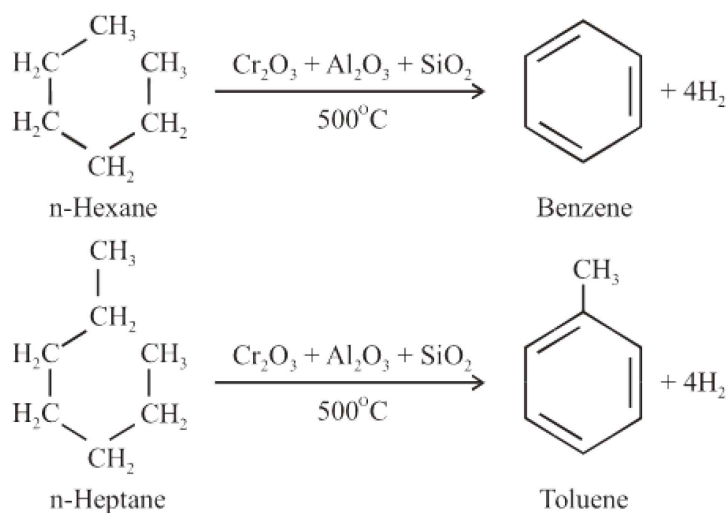
**(2) From Acetylene:**

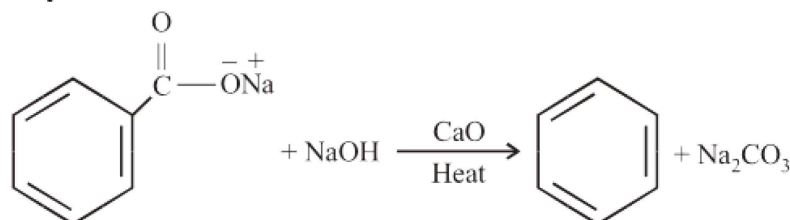
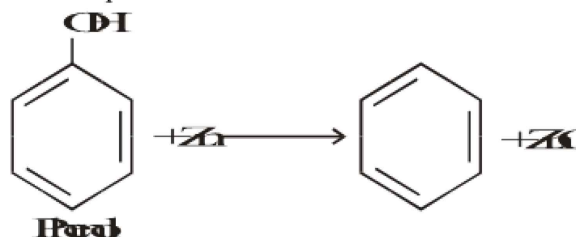
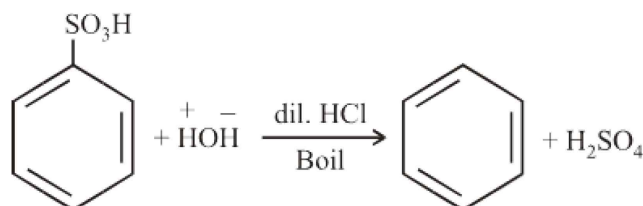
Benzene is formed by passing acetylene under pressure over an organo-nickel catalyst at  $70^{\circ}\text{C}$ .



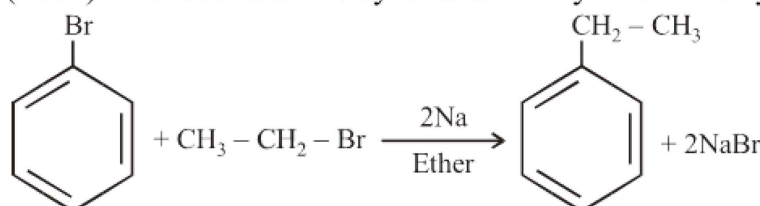
**(3) From Alkanes:**

Benzene and toluene can also be prepared by passing the vaporous of n-haxane or n-heptane over a mixture of catalysts  $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2$  at  $500^{\circ}\text{C}$ .

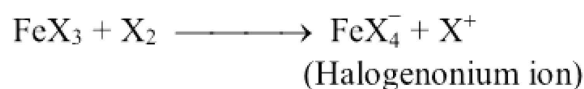


**(4) Laboratory Preparation:****(i) Decarboxylation:** Sodium benzoate is heated with soda lime to form benzene.**(ii)** Distillation of phenol with zinc dust.**(iii)** Hydrolysis of benzene sulphonic acid with superheated steam or by boiling with dil. HCl.**(5) Wurtz-Fitting Reaction:**

Fitting (1864) extended Wurtz's synthesis to alkyl aromatic hydrocarbins.

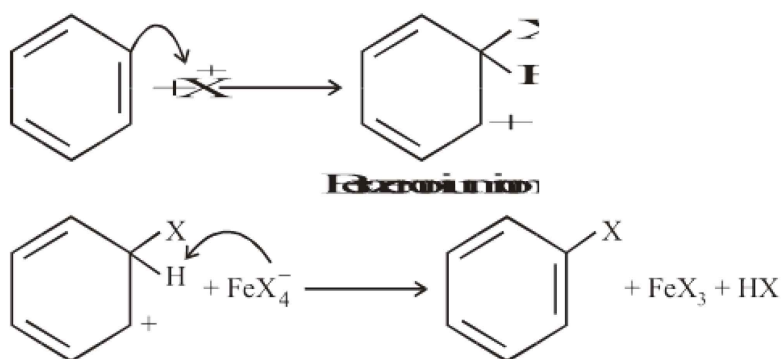

**GENERAL MECHANISM OF REACTIVITY OF  
BENZENE TOWARDS ELECTROPHILES**

The highly stable, delocalized electrons of benzene are not readily available for the nucleophilic attack like the electrons of alkenes. Therefore, the electrons of benzene ring do not assist the attack of weak electrophile. Therefore, more powerful electrophile is needed to penetrate and break the continuous sheath of electron cloud of benzene. For example; in the halogenation of benzene, iron is converted to  $\text{FeX}_3$  which reacts with halogen to form a powerful electrophile ( $\text{X}^+$ ).



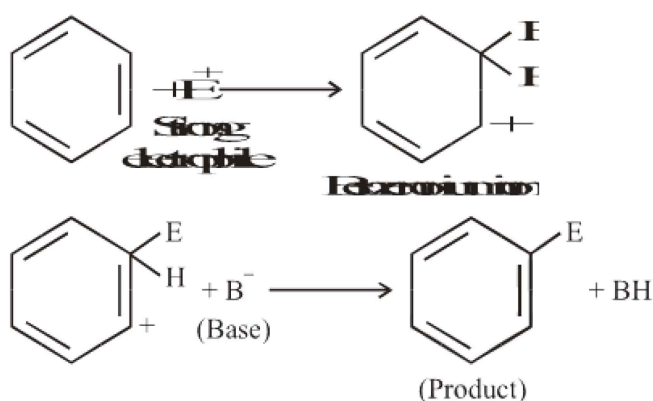


The halogenonium ion attacks the benzene ring as a powerful electrophile.



The addition product is not favoured because the stability of benzene is lost. The only possibility is the formation of substitution product in which the stability of benzene is retained.

General Mechanism of electrophilic substitution reaction of benzene is:



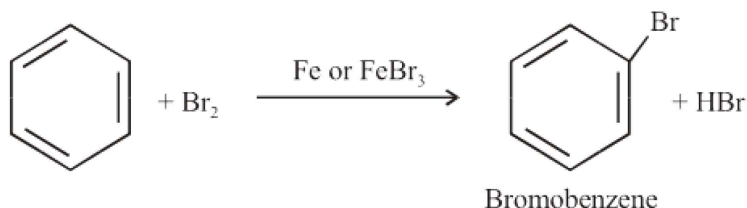
### SOME EXAMPLES OF ELECTROPHILIC SUBSTITUTION REACTIONS

In all given reactions  $H^+$  electrophile is replaced by another strong electrophiles. All electrophilic substitution reactions indicates that benzene is a saturated hydrocarbon.

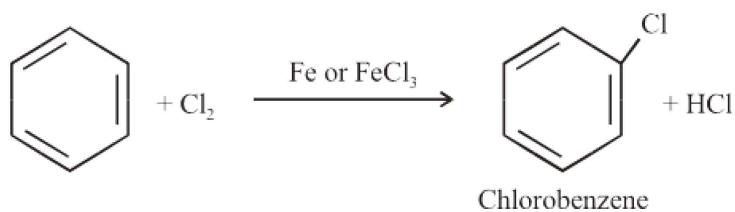
#### (1) Halogenation:

*"If  $H^+$  of benzene ring is substituted by halogen atom, it is called halogenation."*

Benzene reacts with halogen in the presence of a catalyst. Chlorination and bromination are normal reactions but fluorination is too vigorous to control. Iodination gives poor yield.

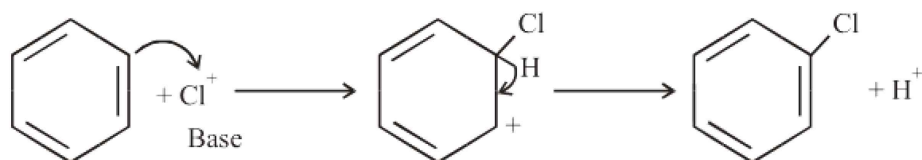
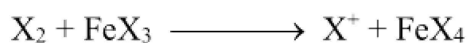


Similarly,

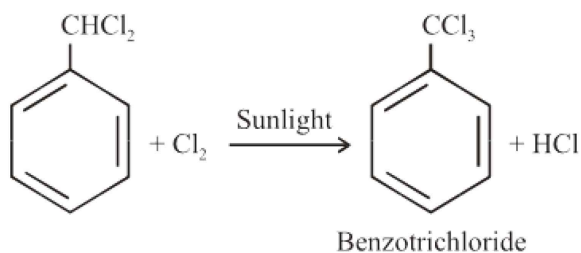
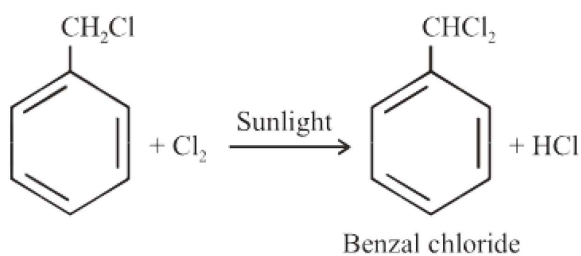
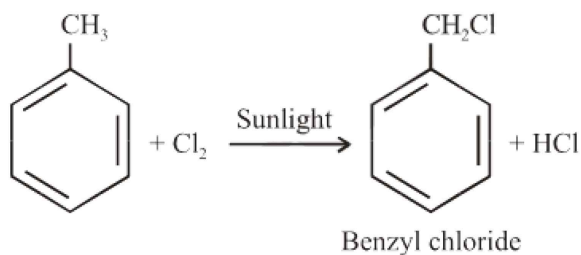


**Mechanism:**

The actual halogenating agent is  $X^+$  that is formed by the following mechanism:



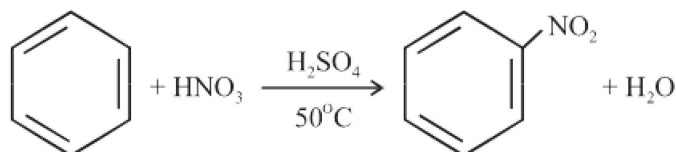
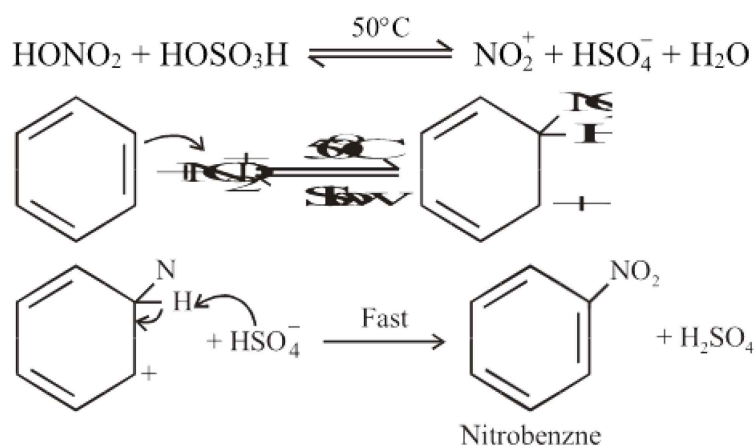
When alkyl benzene are treated with chlorine or bromine in the presence of sunlight, only the alkyl groups are substituted. It is a free radical mechanism.



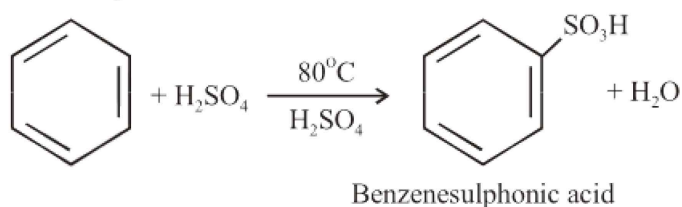
**(2) Nitration:**

"Substitution of an electrophile  $H^+$  of ring with  $NO_2^+$  is called nitration. or introduction of  $-NO_2$  nitro group in benzene is called nitration."

The nitration of benzene takes place when it is heated with a mixture of conc.  $HNO_3$  and conc.  $H_2SO_4$  (1 : 1) at  $50^\circ C$ . Sulphuric acid reacts with nitric acid and generate nitronium ion.

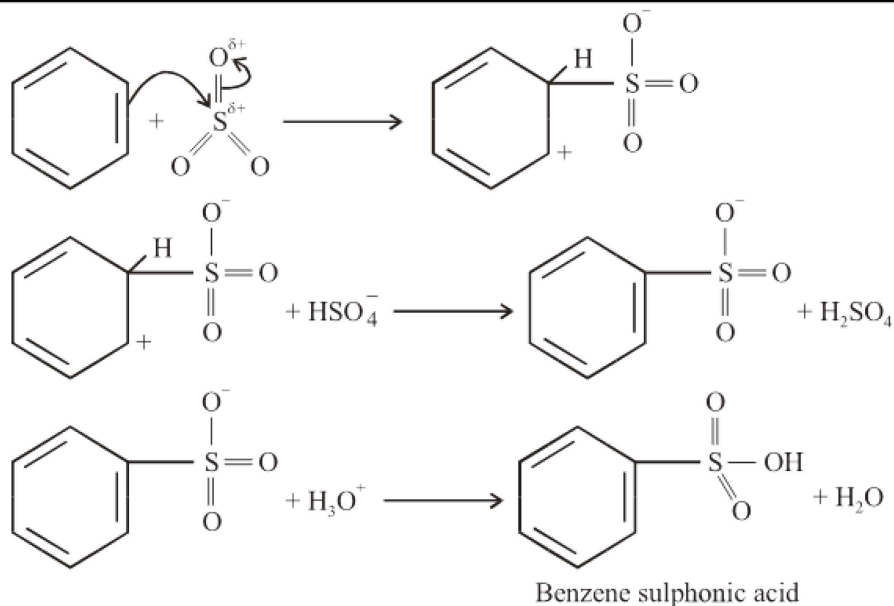
**Mechanism:****(3) Sulphonation:**

"The introduction of sulphonic acid group ( $-SO_3H$ ) in benzene ring is called sulphonation." When benzene is heated with fuming  $H_2SO_4$  or conc.  $H_2SO_4$  it yields benzene sulphonic acid.

**Mechanism:**

When sulphuric acid alone is used, the actual electrophile in this reaction is  $SO_3$ .





#### (4) Friedal Crafts Reactions:

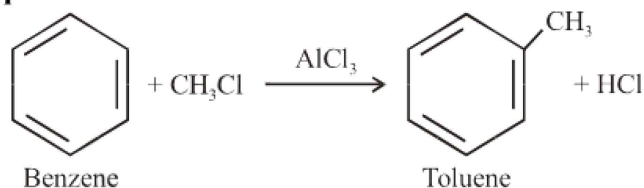
*"The alkylation and acylation of benzene is called Friedal Crafts reactions."*

##### (a) Friedal Craft Alkylation:

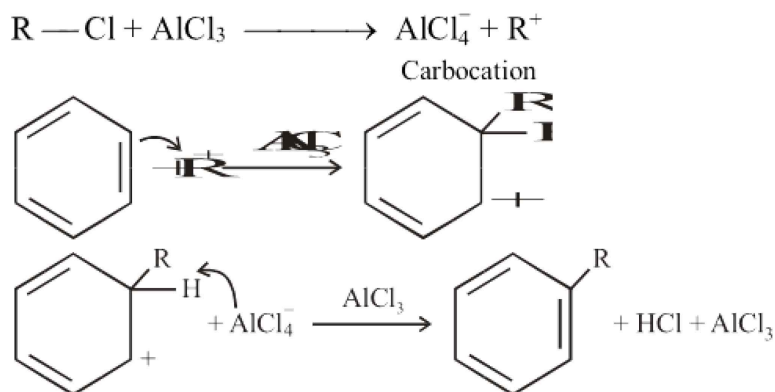
The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst  $\text{AlCl}_3$  is called Friedel Crafts alkylation or Alkylation.



For example:

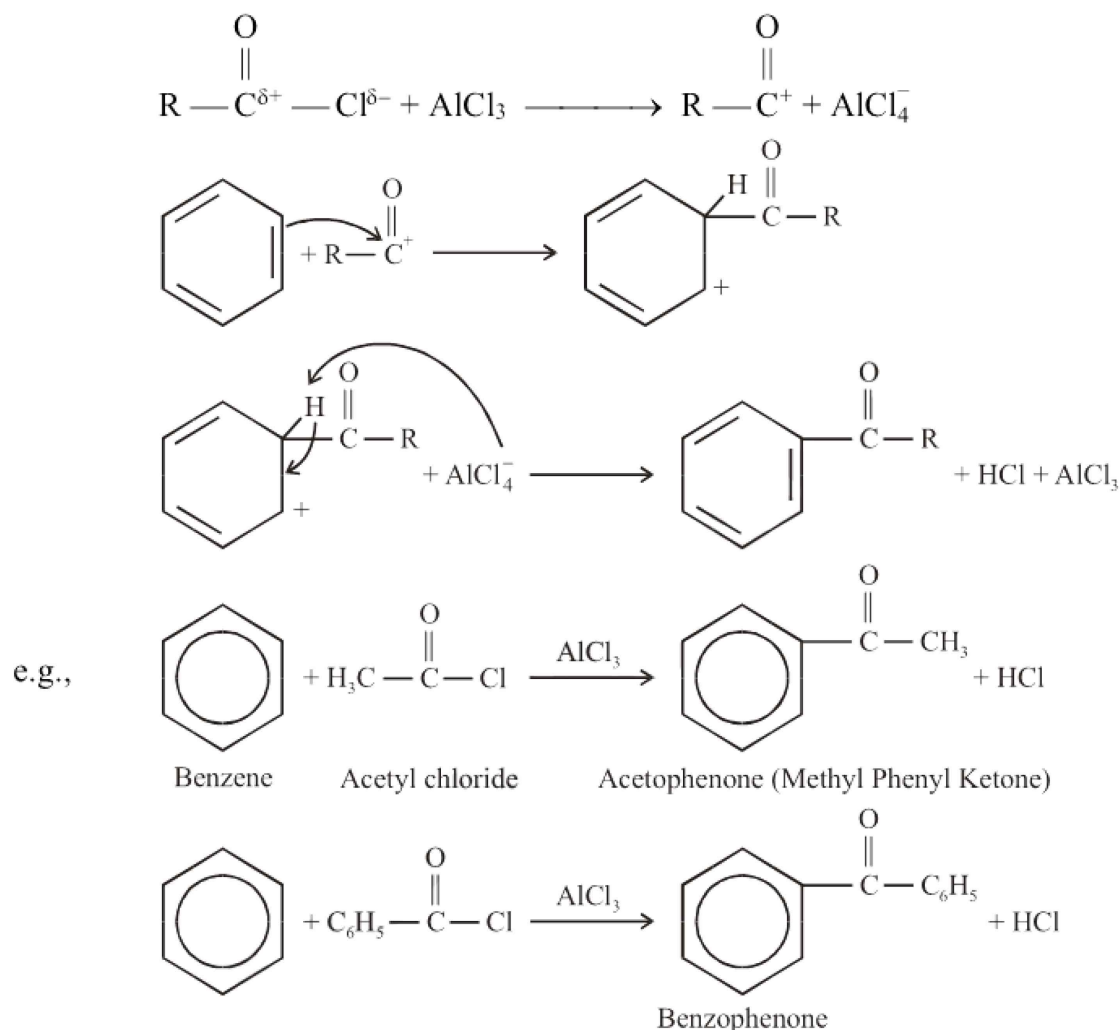


**Mechanism:**



**(b) Friedel Craft Acylation:**

The introduction of an acyl group  $R - \overset{\overset{O}{\parallel}}{C} -$  in the benzene ring in the presence of an acyl halide and a catalyst  $AlCl_3$  is called Friedel Crafts Acylation or Acylation.

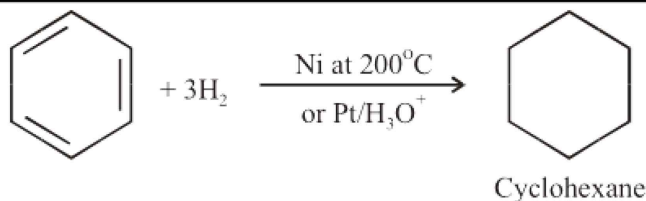

**THE REACTIONS IN WHICH  
RING IS AFFECTED**
**(1) Addition Reaction:**

Addition reactions of benzene indicates that benzene has three double bonds in it. Addition reactions also indicates that benzene is an unsaturated hydrocarbon.

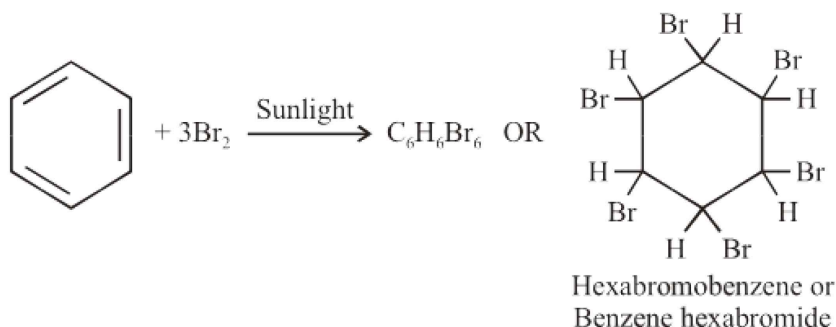
**(a) Addition of Hydrogen (Reduction):**

Benzene is reduced to cyclohexane on heating at high temperature, with hydrogen in the presence of Pt in an acidic solvent (acetic acid) or Ni at 200°C as a catalyst.



**(b) Halogenation:**

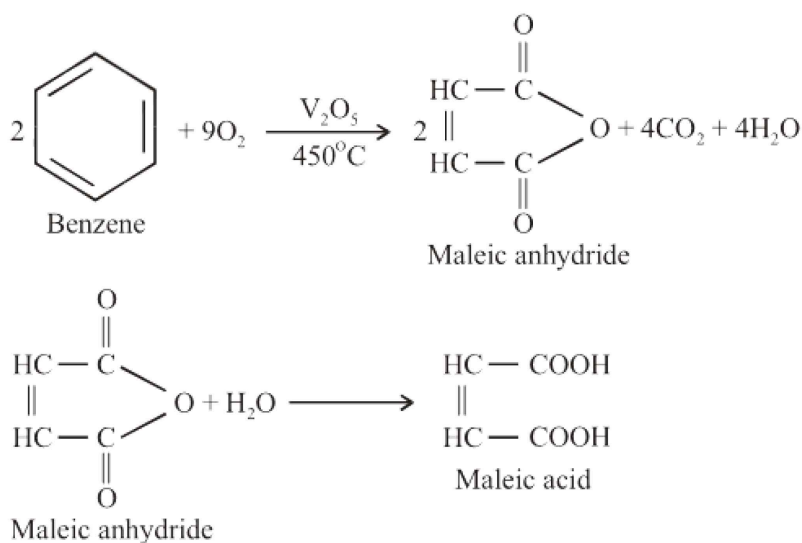
Benzene reacts with chlorine and bromine in the presence of sunlight to give addition products, hexachlorobenzene or hexabromobenzene. Fluorination is too vigorous while iodination is slow.

**(2) Oxidation:****(i) Combustion:**

When benzene is burnt in free supply of air, it is completely oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

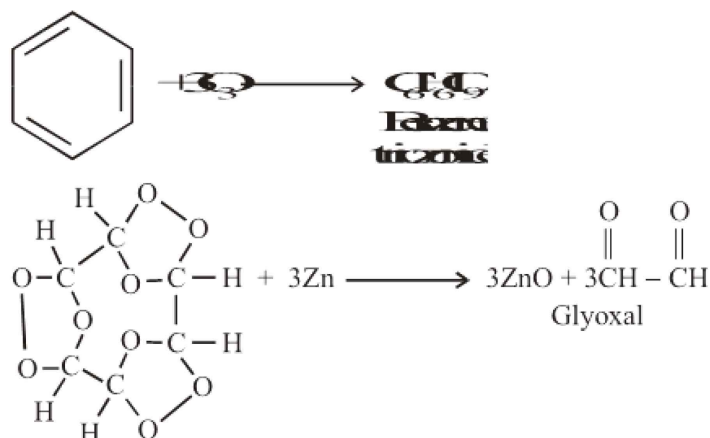
**(ii) Catalytic Oxidation:**

Benzene is not oxidized by  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  at room temperature. The ring is destroyed when benzene is strongly heated with air in the presence of  $\text{V}_2\text{O}_5$  as a catalyst.

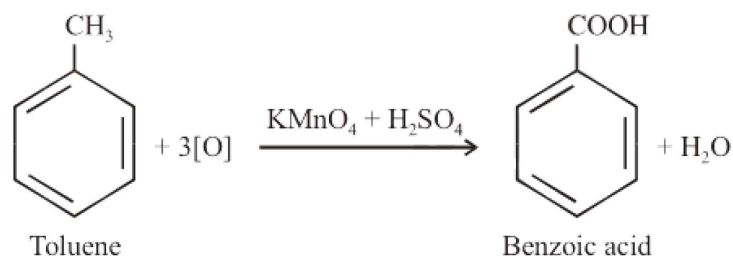
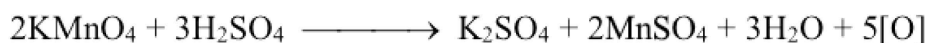


**(iii) Ozonolysis:**

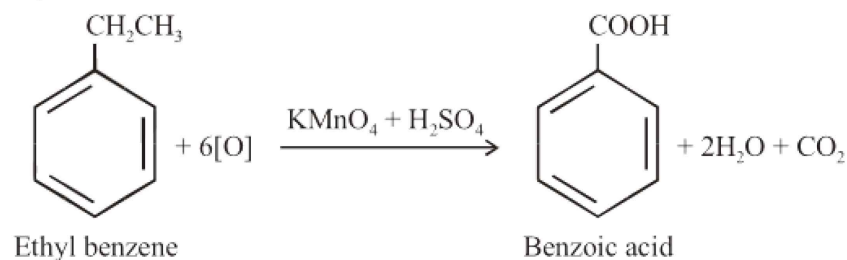
Benzene reacts with ozone and gives glyoxal through benzene triozone.

**(iv) Oxidation of Side Chain of Benzene:**

Alkyl benzene are readily oxidized by acidified  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ . In these reactions, the alkyl groups are oxidized keeping the benzene ring intact.

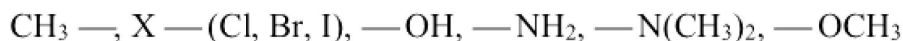


Whatever the length of an alkyl group may be, it gives only one carboxyl group. Moreover, the colour of  $\text{KMnO}_4$  is discharged. Therefore, this reaction is used as a test for alkyl benzene.


**ORIENTATION IN ELECTROPHILIC  
SUBSTITUTION REACTIONS**

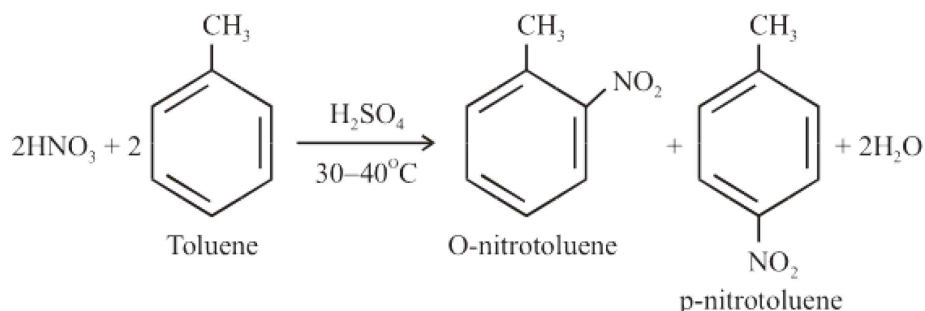
When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent. However, the introduction of a second group into the ring may give three isomeric disubstituted products, ortho, meta and para.



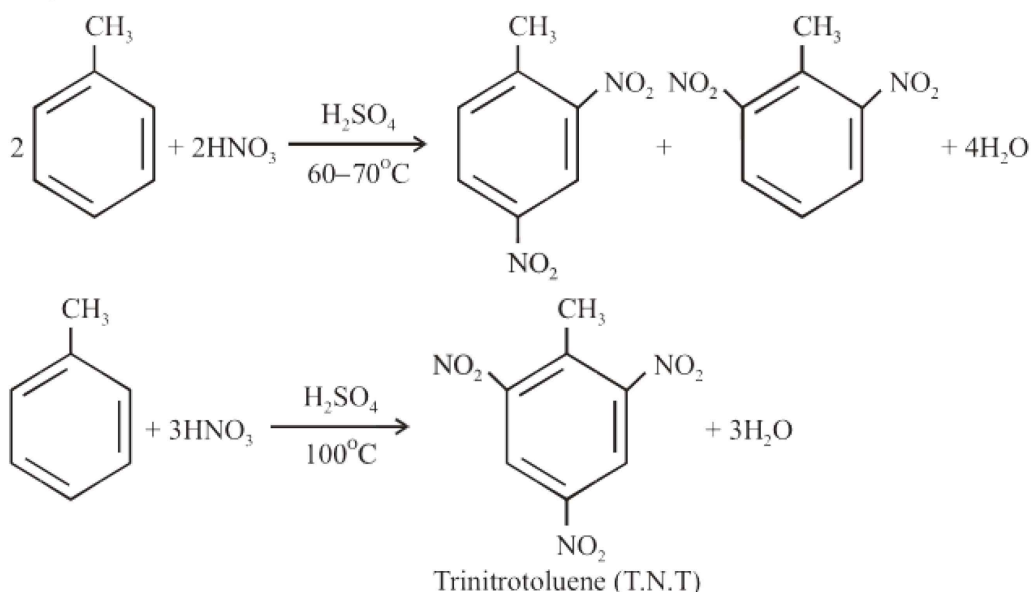


All these groups increases electron density at ortho and para position and facilitate the attack of electrophile at ortho and para position.

For example, nitration of the toluene gives two products, o, nitro toluene and p-nitro toluene.



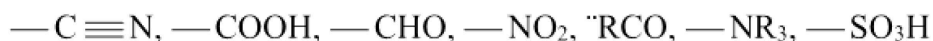
The electron releasing effect of methyl group is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.



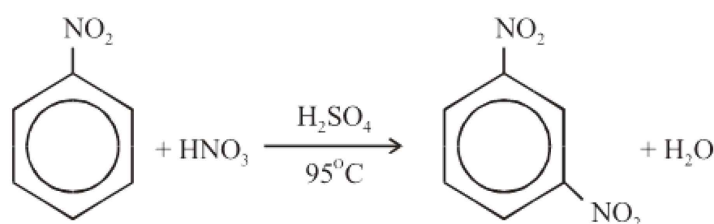
### Meta Directors:

These groups **withdraw the electron** of the benzene ring towards themselves, thereby reducing their availability to the electrophiles. This results in the **decreased chemical reactivity of benzene**. Moreover, due to the electron withdrawing effect of such substituents, the ortho and para positions are rendered more electron deficient than the meta position. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups.

Following groups are meta directors:



All these groups deactivate the ring and decreases electron density at ortho and para position. They facilitate the attack of incoming electrophiles only at the meta position. For example, nitration of the nitrobenzene takes place at meta position.



**Note:** Usually ortho and para directors activate the ring and meta directors deactivate the ring. However halogens are exceptional. They direct incoming electrophile at ortho and para and deactivate the ring. Halogen, have electron withdrawing nature and decreases electron density from ring.

### COMPARISON OF REACTIVITY OF ALKANES, ALKENES AND BENZENE

**Alkane** are un-reactive class of hydrocarbons. Alkanes are least reactive. All bonds are sigma bonds. Sigma bonds are strong and they required greater amount of energy to break down. All these compounds are non-polar in nature and do not reacts with acids, alkalis, oxidizing agents or the reducing agents. However, alkanes undergoes substitution reactions and involve free radical mechanism.

**Alkenes** are very reactive class of hydrocarbons. They contain double bond between C – C atoms. The reactivity of alkenes is due to the presence of exposed  $\pi$ -electron cloud. Alkenes reacts easily with electrophiles and itself behave as nucleophiles. Alkenes usually undergoes addition reaction. Alkenes are relatively unstable class of compound so they undergo polymerization. Alkenes are readily oxidized by the oxygen gas and ozone.

**Benzene** is highly unsaturated compound and it very stable as compared to alkenes. The stability in benzene is due to the extensive delocalization of  $\pi$ -electrons.  $\pi$ -electrons are present above and below the carbon plane in the form of sheath. Large amount of energy is required to break this delocalization of electrons. Benzene does not undergo polymerization reactions. Benzene usually undergoes electrophilic substitution reactions and reacts with strong electrophiles. Addition reactions of benzene are very few. Benzene shows addition reactions with  $\text{H}_2$  in the presence of catalyst,  $\text{Cl}_2$  in the presence of sunlight and ozone. The decreasing order of reactivity of alkane, alkene and benzene is:





## EXERCISE

**Q.1 Fill in the blanks:**

- (i) The term aromatic was derived from Greek word ——— meaning ———.
- (ii) Aromatic hydrocarbons include benzene and all those compounds which are ——— related to benzene.
- (iii) ——— is recognized as the simplest member of the class of aromatic hydrocarbons.
- (iv) Benzene has ——— structure.
- (v) These removal hydrogen atom from aromatic hydrocarbons gives a radical. The radicals is called ———.
- (vi) Benzene was discovered by Michael Faraday in ———.
- (vii) The unhybridized  $2p_z$  orbitals in benzene partially overlap to form a ——— of electron cloud.
- (viii) The introduction of halogen group in benzene ring is called ———.
- (ix) The molecular formula of  $C_6H_6$  indicates that it is highly ——— compound.
- (x) On oxidation in the presence of  $V_2O_5$  benzene gives ———.

## ANSWERS

(i)	aroma, fragrant	(ii)	structurally	(iii)	benzene
(iv)	cyclic hexagonal	(v)	aryl (phenyl)	(vi)	1825
(vii)	sheath	(viii)	halogenation	(ix)	unsaturated
(x)	maleic anhydride				

**Q.2 Indicate True or False:**

- (i) Benzene is more reactive than alkene and less reactive than alkane.
- (ii) Benzene has a pentagonal structure.
- (iii) The C–C bond length in benzene molecule is  $1.397 \text{ \AA}$ .
- (iv) The state of hybridization of carbon in benzene molecule is  $sp^3$ .
- (v) There are six sigma bonds in benzene molecule.

- (vi) Halogenonium ion produced in electrophilic substitution reactions is a powerful electrophile.
- (vii) In electrophilic substitution reactions, addition products are favourable.
- (viii) Sulphonation is carried out when benzene is heated with conc.  $\text{HNO}_3$ .
- (ix) In ozonolysis benzene directly gives glyoxal.
- (x) Benzene has five resonance contributing structures.

## ANSWERS

(i)	False	(ii)	False	(iii)	True	(iv)	False	(v)	False
(vi)	True	(vii)	False	(viii)	False	(ix)	False	(x)	True

### Q.3 Multiple choice questions. Encircle the correct answer:

(i) The benzene molecule contains:

- (a) Three double bonds
- (b) Two double bonds
- (c) One double bond
- (d) Delocalized  $\pi$ -electron charge

(ii) Aromatic hydrocarbons are the derivatives of:

- (a) Normal series of paraffins
- (b) Alkene
- (c) Benzene
- (d) Cyclohexane

(iii) Which of the following acid can be used as a catalyst in Friedel-Crafts reactions:

- (a)  $\text{AlCl}_3$
- (b)  $\text{HNO}_3$
- (c)  $\text{BeCl}_2$
- (d)  $\text{NaCl}$

(iv) Benzene cannot undergo:

- (a) Substitution reactions
- (b) Addition reactions
- (c) Oxidation reactions
- (d) Elimination reactions

(v) Amongst the following the compound that can be most readily sulphonated is:

- (a) Toluene
- (b) Benzene
- (c) Nitrobenzene
- (d) Chlorobenzene

(vi) During nitration of benzene, the active nitrating agent is:

- (a)  $\text{NO}_3$
- (b)  $\text{NO}_2^+$
- (c)  $\text{NO}_2$
- (d)  $\text{HNO}_3$

- (vii) Which compound is the most reactive one:
- (a) Benzene (b) Ethene  
(c) Ethane (d) Ethyne
- (viii) The electrophile in aromatic sulphonation is:
- (a)  $\text{H}_2\text{SO}_4$  (b)  $\text{HSO}_4^-$   
(c)  $\text{SO}_3$  (d)  $\text{SO}_3^+$
- (ix) Aromatic compounds burn with sooty flame because:
- (a) They have high percentage of hydrogen  
(b) They have a ring structure  
(c) They have high percentage of carbon  
(d) They resist reaction with air
- (x) The conversion of n-hexane into benzene by heating in the presence of Pt is called:
- (a) Isomerization (b) Aromatization  
(c) Dealkylation (d) Rearrangement

## ANSWERS

(i)	(d)	(ii)	(c)	(iii)	(a)	(iv)	(d)	(v)	(a)
(vi)	(b)	(vii)	(b)	(viii)	(c)	(ix)	(c)	(x)	(b)

**Q.4** What are aromatic hydrocarbons? How are they classified?

**Ans.** **Aromatic Hydrocarbons:** Among hydrocarbons, the compounds having at least one benzene ring is called aromatic compounds. e.g., toluene.

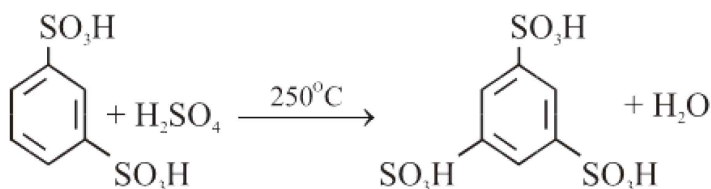
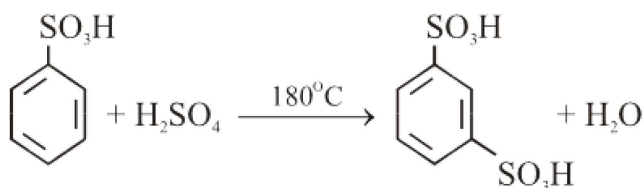
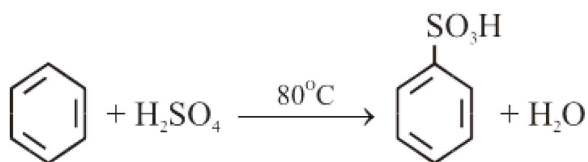
Classification see in text book.

**Q.5** What happens when:

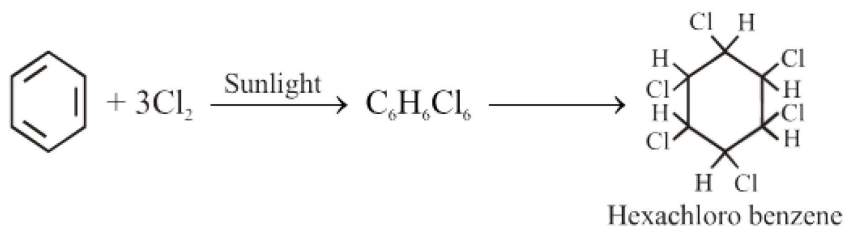
- (a) Benzene is heated with conc.  $\text{H}_2\text{SO}_4$  at  $250^\circ\text{C}$ .  
 (b) Chlorine is passed through benzene in sunlight.  
 (c) A mixture of benzene vapours and air are passed over heated vanadium pentoxide.  
 (d) Benzene is burnt in free supply of air.

**Ans.**

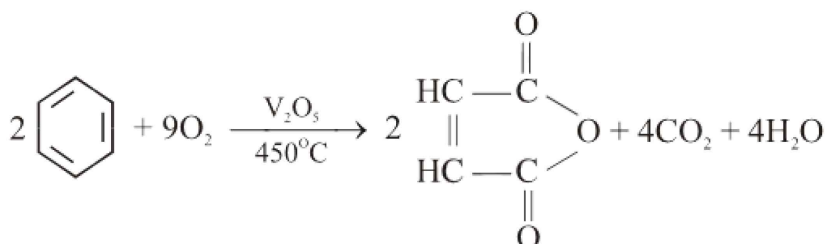
(a)



(b)



(c)

(d)  $2\text{C}_6\text{H}_6 + 15\text{O}_2 \longrightarrow 12\text{CO}_2 + 6\text{H}_2\text{O}$ **Q.6** What is meant by the terms:

- (i) Aromatic                      (ii) Oxidation                      (iii) Sulphonation  
 (iv) Nitration                      (v) Halogenation

**Ans.**

For definitions, consult text book.

**Q.7** (a) Draw structural formulas for the following compounds:

- (i) m-chlorobenzoic acid                      (ii) p-hydroxybenzoic acid  
 (iii) o-bromonitrobenzene                      (iv) o-ethyltoluene  
 (v) p-nitroaniline                      (vi) 2, 4, 6 trinitrotoluene  
 (vii) m-nitrophenol                      (viii) p-dibenzylbenzene  
 (ix) 2-amino-5-bromo-3 nitrobenzenesulphonic acid

(b) Give names and the possible isomeric structures of the following:

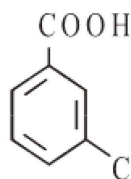
(i) Xylenes

(ii) Trimethylbenzene

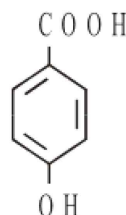
(iii) Bromonitrotoluene

**Ans.** (a)

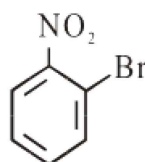
(i) m-Chlorobenzoic acid



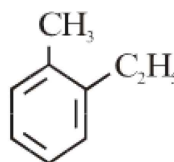
(ii) p-Hydroxybenzoic acid



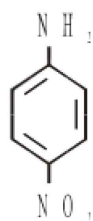
(iii) o-Bromonitrobenzene



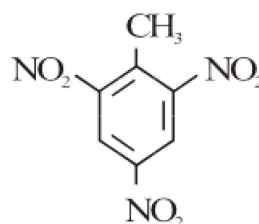
(iv) o-Ethyltoluene



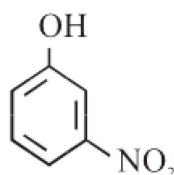
(v) p-Nitroaniline



(vi) 2, 4, 6-Trinitrotoluene



(vii) m-Nitrophenol

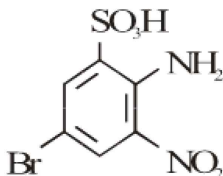




(viii) p-dibenzylbenzene

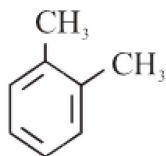


(ix) 2-amino-5-bromo-3-nitro benzenesulphonic acid

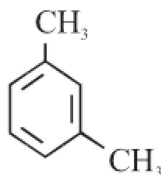


(b)

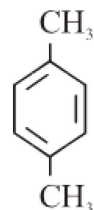
(i) Xylene:



o-xylene

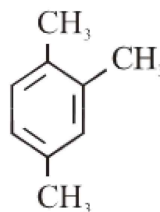
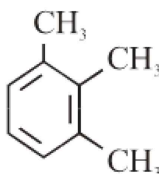
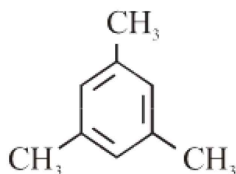


m-xylene

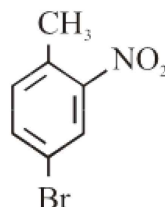
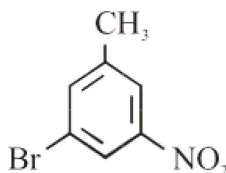
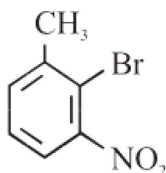


p-xylene

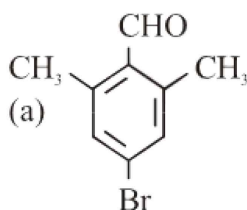
(ii) Trimethylbenzene:



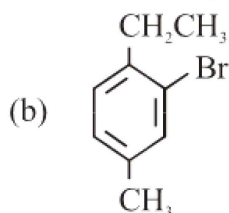
(iii) Bromonitrotoluene:



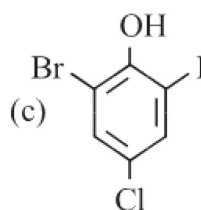
Q.8 Write IUPAC names of the following molecules.



(a)



(b)



(c)

**Ans.**

(a) 4-bromo-2,6-dimethyl benzaldehyde

(b) 3-bromo-4-ethyl toluene

(c) 6-bromo-4-chloro-2-iodophenol

**Q.9** Give the general mechanism of the electrophilic aromatic substitution reactions.

**Ans.** Descriptive question. Consult text book.

**Q.10** (a) Describe the structure of benzene on the basis of following:

(i) Atomic orbital treatment (ii) Resonance method

(b) Prove that benzene has a cyclic structure.

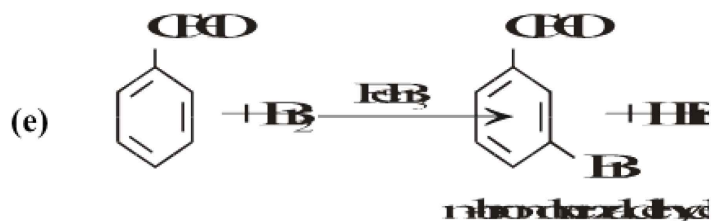
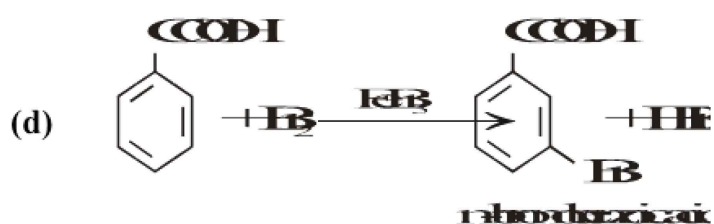
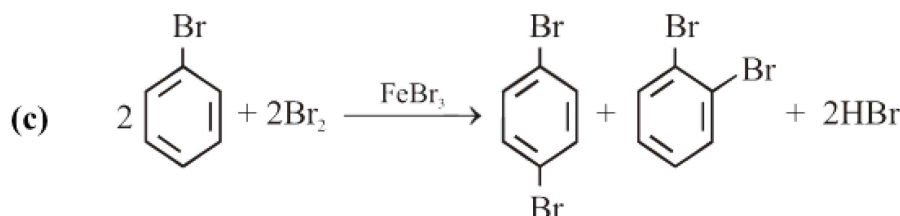
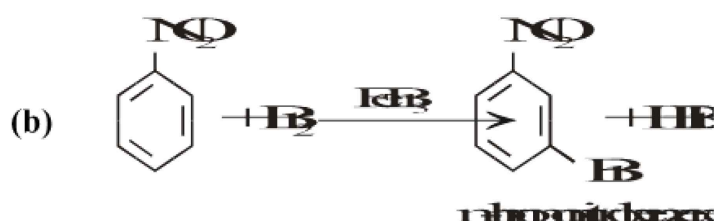
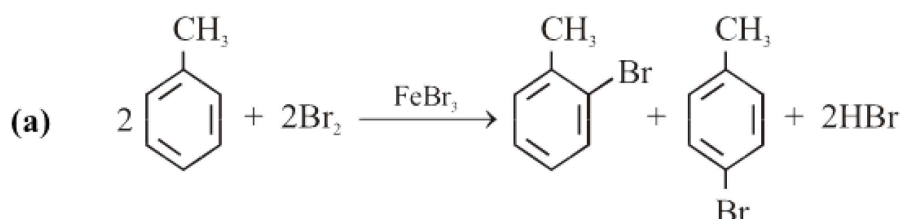
**Ans.** Descriptive questions. Consult text book for details.

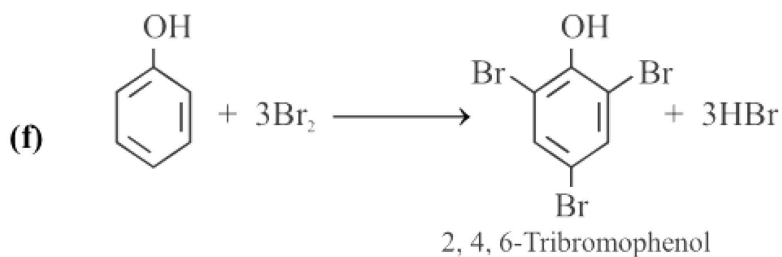
**Q.11** Predict the major products of bromination of the following compounds:

(a) Toluene (b) Nitrobenzene (c) Bromobenzene

(d) Benzoic acid (e) Benzaldehyde (f) Phenol

**Ans.**





**Q.12** How will you prepare the following compounds from benzene in two steps:

(a) m-chloronitrobenzene

(b) p-chloronitrobenzene

**Ans.**

(a) Benzene  $\longrightarrow$  m-chloronitrobenzene

Steps Involved:

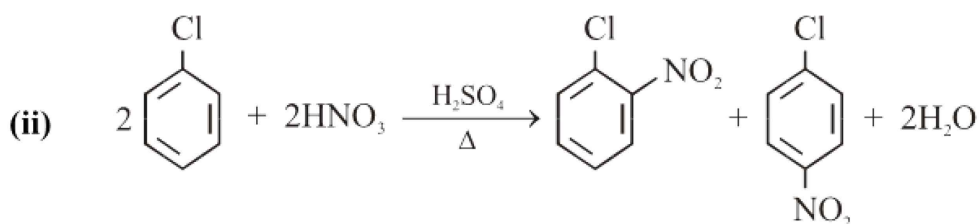
(i) Nitration:



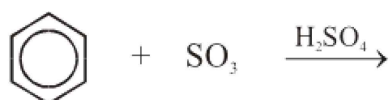
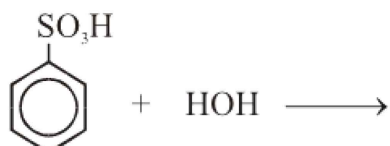
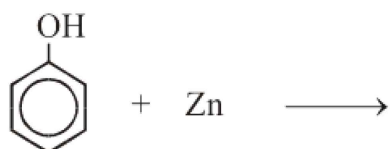
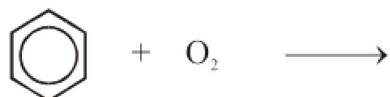
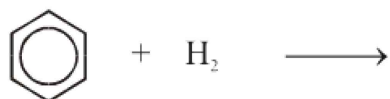
(ii) Chlorination:



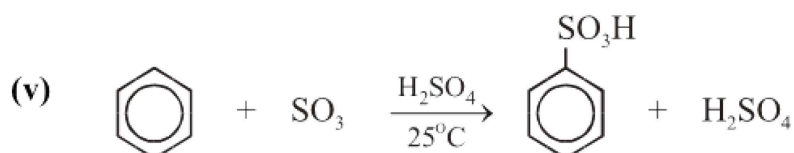
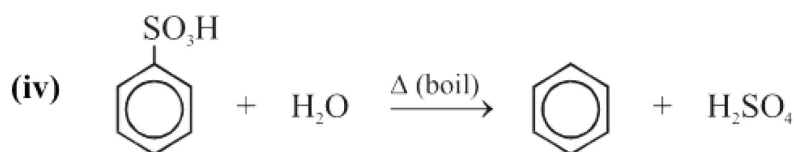
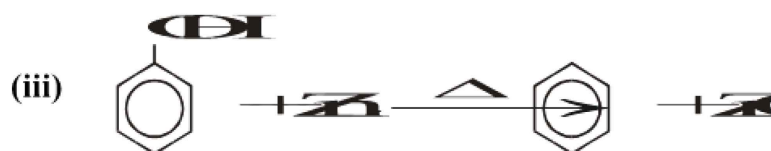
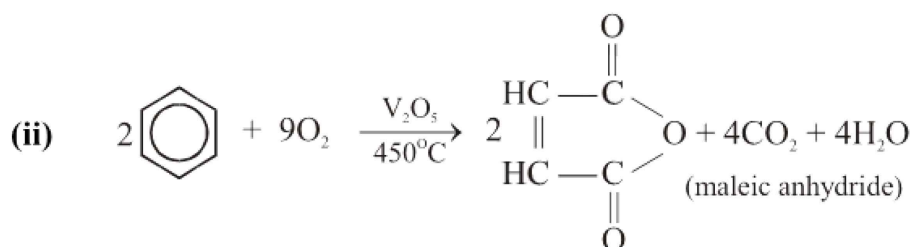
(b) Benzene  $\longrightarrow$  p-chloronitrobenzene



**Q.13** Complete the following reactions. Also mention the conditions needed to carry out these reactions.



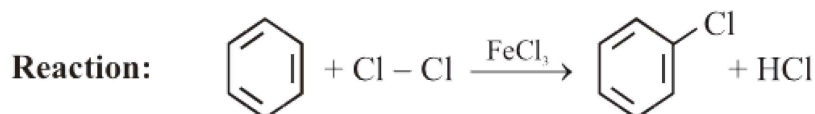
**Ans.**



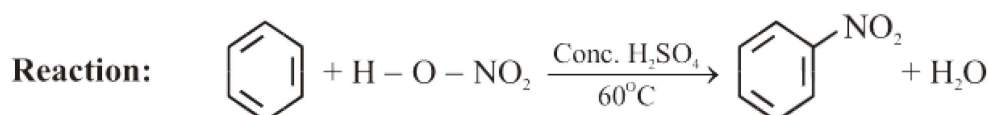
**Q.14** Detail out three reactions in which benzene behaves as if it is a saturated hydrocarbon and three reactions in which it behaves as if it is unsaturated.

**Ans.** **Benzene as Saturated Hydrocarbon:** In following reactions benzene behaves as a saturated hydrocarbon.

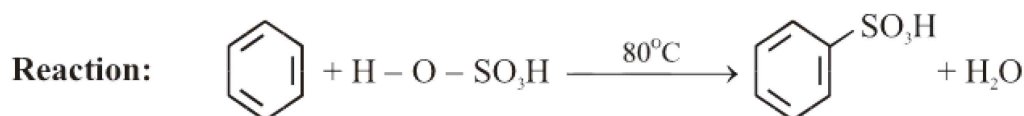
- (i) **Halogenation:** Benzene reacts with  $\text{Cl}_2$  in the presence of  $\text{FeCl}_3$  to give chlorobenzene. A hydrogen atom of benzene is replaced by a halogen atom so, gives a substitution products.



- (ii) **Nitration:** Benzene reacts with concentrated nitric acid in the presence of conc.  $\text{H}_2\text{SO}_4$  to give a substitution product nitrobenzene.

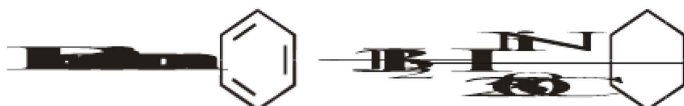


- (iii) **Sulphonation:** Benzene reacts with conc.  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}$  to give a

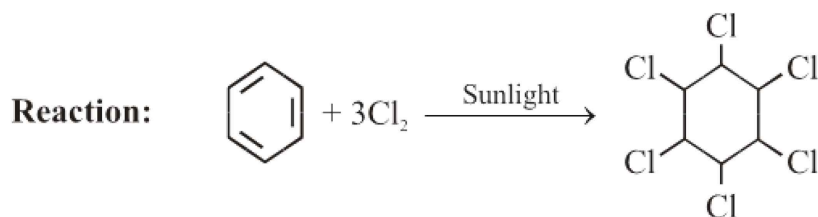


**Benzene as Unsaturated Hydrocarbon:**

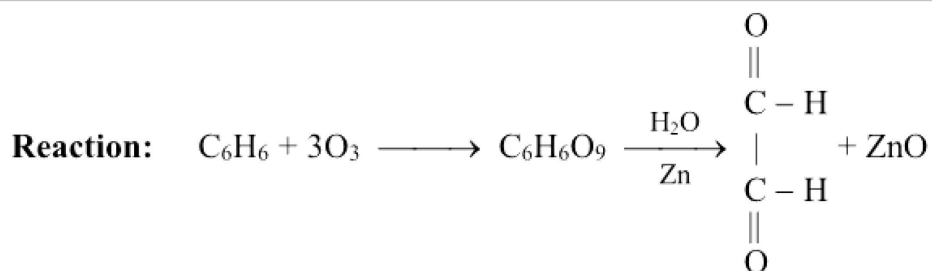
- (i) **Hydrogenation:** Benzene adds three molecules of hydrogen in the presence of Ni at  $250^\circ\text{C}$  gives addition product cyclohexane.



- (ii) **Chlorination:** Benzene adds three molecules of  $\text{Cl}_2$  in the presence of sunlight and gives addition product hexachlorobenzene.



- (iii) **Ozonolysis:** Benzene adds three molecules of ozone and give benzene triozone which is an addition product.



**Q.15 What are Friedel-Crafts reactions? Give mechanism with example of the following reactions:**

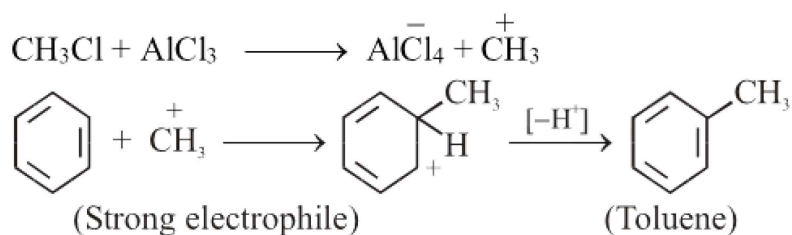
- (i) Friedel-Crafts alkylation reactions
- (ii) Friedel-Crafts acylation reactions

**Ans.**

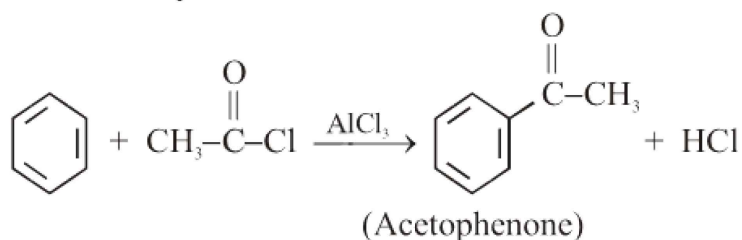
### Friedel-Crafts Alkylation:



**Mechanism:**



### Friedel-Craft's Acylation:



**Mechanism:**

