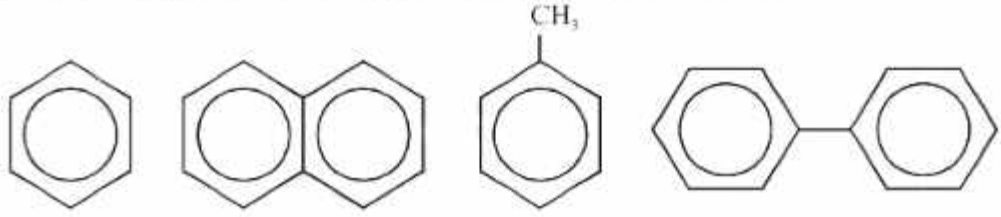
Chapter
9

AROMATIC HYDROCARBOS

INTRODUCTION

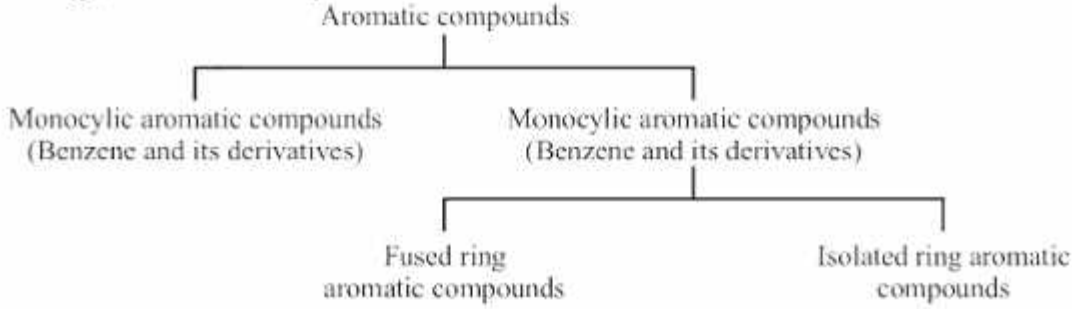
The term "aromatic" was derived from the Greek word **"aroma"** meaning "fragrant".

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 Naphthalene Toluene Biphenyl

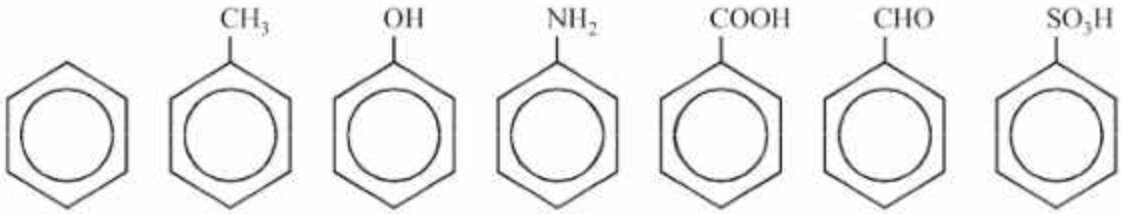
Benzene has regular planar hexagonal structure. On the basis of number of benzene rings, aromatic compounds are classified as:



(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:



Benzene | Toluene | Phenol | Aniline | Benzoic acid | Benzaldehyde (bitter almond oil) | Benzene sulphonic acid

(2) Polycyclic Aromatic Compounds:

"Aromatic compounds containing two a more benzene rings in their molecules are called polycyclic aromatic compounds."

They may be divided further into two classes:

(i) Isolated Rings Aromatic Compounds:

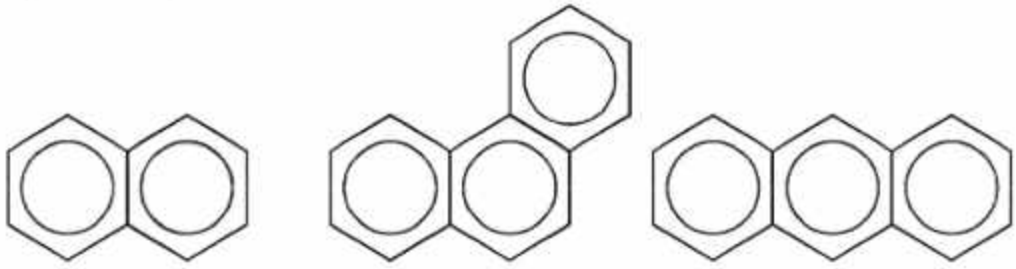
They polycyclic compounds containing isolated benzene rings in them are called isolate polycyclic compounds. e.g.,



Biphenyl | Diphenylmethane

(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.

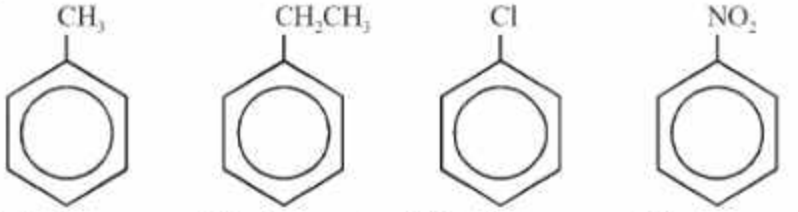


Naphthalene | Phenanthrene | Anthracene

NOMENCLATURE

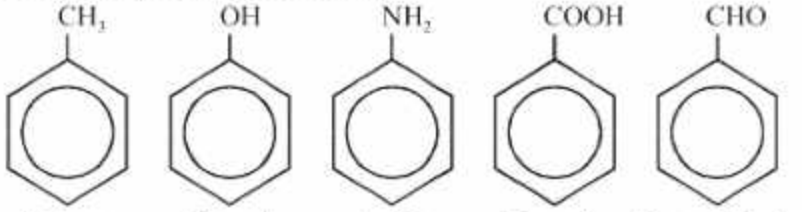
Following rules are used for naming the aromatic compound. The names given in brackets are traditional of non-systematic.

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



Methylbenzene (Toluene) | Ethylbenzene | Chlorobenzene | Nitrobenzene

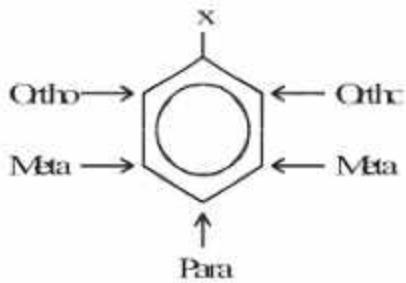
(2) Some monosubstituted benzene derivatives have been accepted as systematic names, or called special names, e.g.



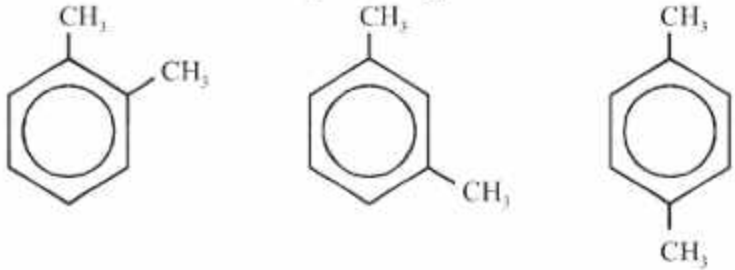
Toluene | Phenol | Aniline | Benzoic acid | Benzaldehyde

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) Dissubstituted benzene are named, using one of prefixs, ortho (1, 2) meta (1, 3) or para (1, 4).



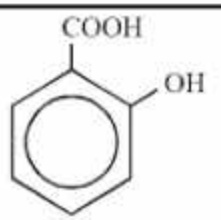
Some examples are given below



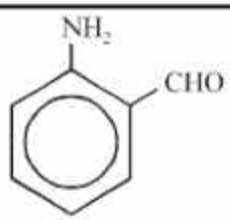
1, 2 Dimethylbenzene (o-xylene) | 1, 3 Dimethylbenzene (m-xylene) | 1, 4 Dimethylbenzene (p-xyelene)

(4) If two or more different substituents are present at benzene, they tare 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 given then the lowest number. The order of priority of substituents are given from left to right.

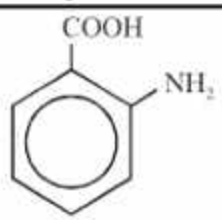
$-COOH$, $-CN$, $-CHO$, $-COCH_3$, $-OH$, $-NH_2$, $-OR$, $-R$



2-Hydroxybenzoic acid
(Salicyclic acid)

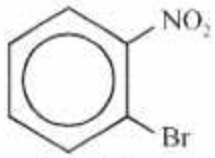


2-Aminobenzaldehyde

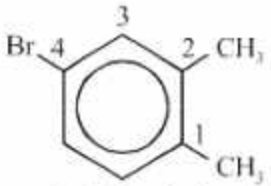


2-Aminobenzoic acid

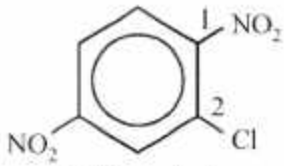
(5) If two or more different substituents are present on benzene ring and have no priority order, then lowest possible numbers are used. The substituents are listed alphabetically when writing the name.



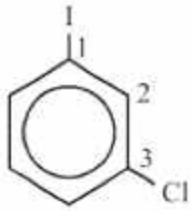
1-bromo 2-nitrobenzene
(0, bromonitro benzene)



4-bromo-1,2-dimethylbenzene

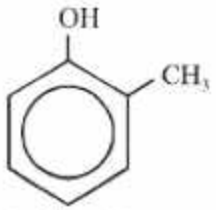


2-chloro 1, 4
dinitro benzene

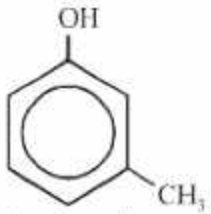


3-chloro 1-iodobenzene
(m-chloroiodo benzene)

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



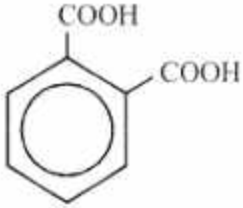
(o-Cresol)



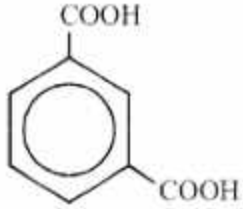
(m-Cresol)



(p-Cresol)



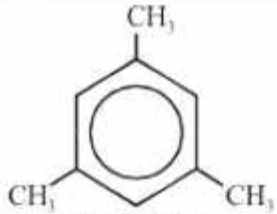
Phthalic acid



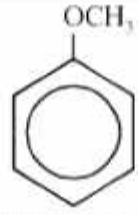
Iso-Phthalic acid



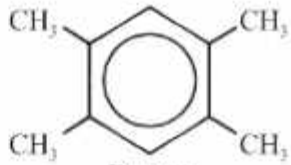
Tere-Phthalic acid



Mesitylene



Methyl-phenyl ether
(Anisole)



Durene

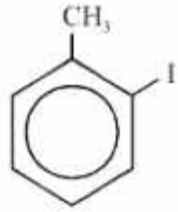


P-Aminophenol

(4-Aminophenol)

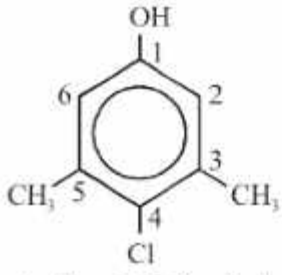


4-Chlorobenzene
sublphonic acid
(p-Chlorobenzene
sublphonic acid)

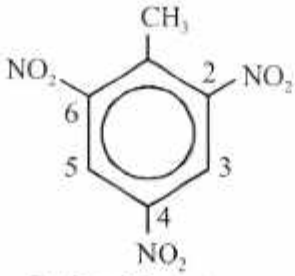


2-Iodotoluene

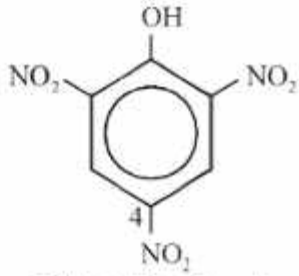
(o-Iodotoluene)



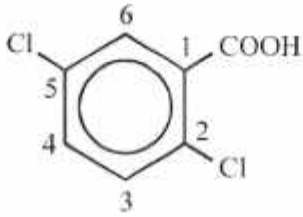
4-chloro-3,5-dimethyl
phenol (Dettol)



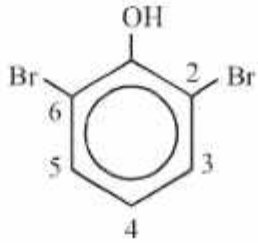
2,4,6-trinitrototuene
(TNT)



2,4,6-trinitrophenol
(picric acid)



2, 5-dichlorobenzoic
acid



2,6-dibromophenol

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 a prepared is 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 (CH = 12 − 1 = 13). Therefore, the molecular formula is C_6H_6.

(iii) The molecular formula of benzene indicates that it is highly usaturated compound.

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

The open chain formula of C_6H_6 can be written in the following ways:

(i) $HC \equiv C - CH_2 - CH_2 - C \equiv CH$ (1,5 hexadiyne)

(ii) $CH_2 = CH - C \equiv C - CH = CH_2$ (Hex 1,5-dien-3-yne)

(iii) $CH_2 = C = CH - CH = C = CH_2$ (1,2,4,5, hexatetraene)

Above structures can add 4 molecules of H_2 as well as 4 molecules of Cl_2 or Br_2 in it. But actually benzene can add only three molecules of H_2 or Cl_2 separately. These reactions indicates that benzene has three double bonds.

On the other hand above structures are of alkenes or alkynes, alkenes or alkynes oxidize with $KMrO_4$ solution but benzene does not decolorize $KMnO_4$ solution. This indicates that benzene is a saturated hydrocarbon. Benzene also gives substitution reaction with conc. HNO_3 or conc. H_2SO_4. This indicates that it is 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.



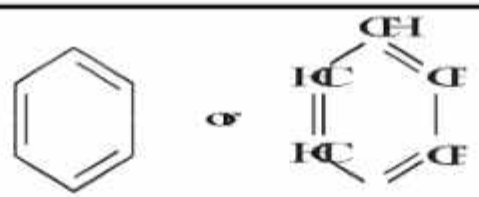
Monosubstituent product

(3) The molecular formula of benzene is C_6H_6. This formula does not corresponds to any aliphatic hydrocarbon like alkane C_nH_{2n+2}, alkene C_nH_{2n} or alkyne C_nH_{2n-2}.

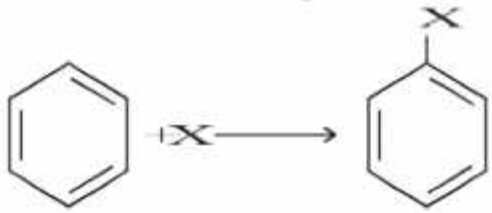
All above points indicate the benzene does not belong to open chain hydrocarbon.

KEKULE STRUCTURE OF BENZENE

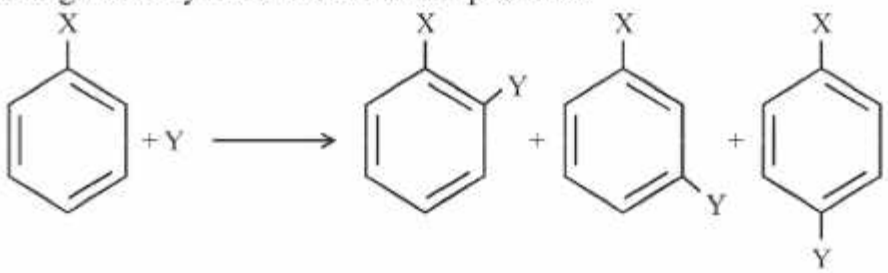
The structure of benzene continued to be a serious problem for chemists for about 40 years. A German chemist, Kekule, at last solved the problem in 1865. Kekule proposed a cyclic regular hexagonal structure for benzene, which contains three double alternating with three single bonds. He supported his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



(i) Benzene gives only one monosubstituted product.

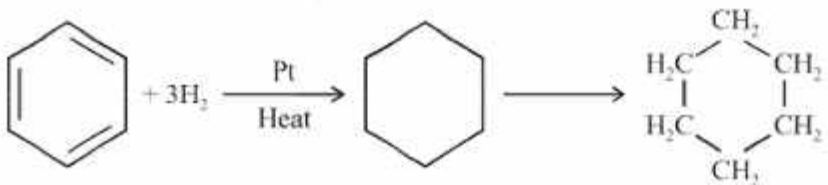


(ii) Benzene gives only three disubstituted products.

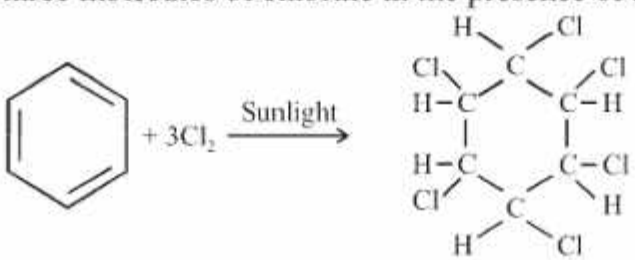


These points confirm the regular hexagonal structure for benzene in which all the carbon atoms are occupying identical positions in the molecule. Therefore, benzene form only one toluene, one phenol and one nitrobenzene.

(iii) Benzene adds three hydrogen molecules in the presence of a catalyst. It indicate 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 kekule structure:

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

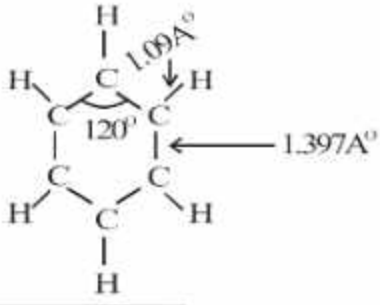
(2) Kekule model suggest that bond distance between carbon-carbon atoms are unequal. Double bond has less bond length than the single bond. X-rays analysis shows that all bond distances between C – C are equal.



(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°. All C – C and C – H bond lengths are 1.397A° and 1.09A°, 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:

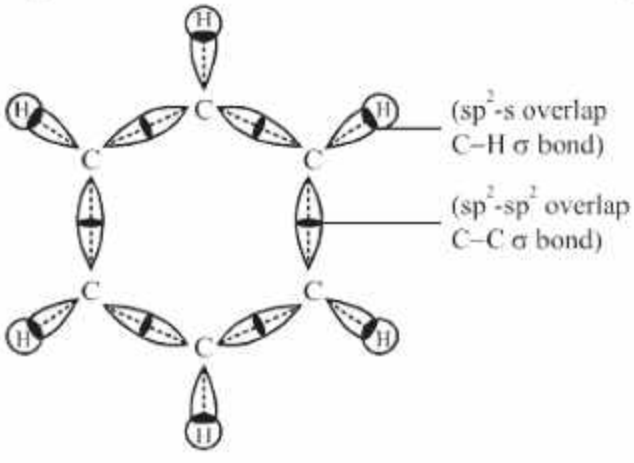
$1s^2, 2s^2, 2px^1, 2py^1, 2pz$ (group state)

One electron is promoted from s to p orbital:

$1s^2, 2s^1, 2px^1, 2py^1, 2pz^1$ (excited state)

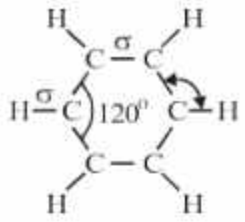
One s and two p orbitals of carbon atom intermix and form three sp^2 hybrid orbitals.

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.



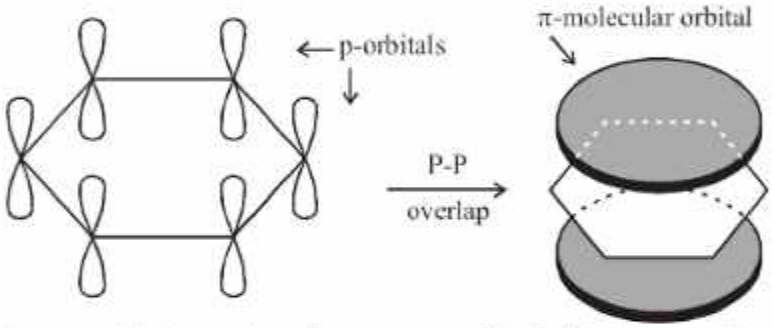
(Formation of sigma bonds in benzene)

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 (σ) bonds in benzene lie in one plane and all bond angles are **120°** as shown below.



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

Each carbon atom in benzene have 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 π-molecular orbital contianing six electrons. One half of this π-molecular orbitals lies above and the other half life 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.



(Adjacent p-orbitals overlap to form the π-molecular orbitals in benzene)

(Sandwich structure of benzene)

As a result of **delocalization**, a stronger π-bond is formed. A continuous sheath of electrons in present above and below the carbon plane and structure is called sandwich structure. The π-bonds of benzene are different from π-bonds of alkenes. π-bonds of alkenes are localized between two carbon atoms while π-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 π-electrons in benzene.

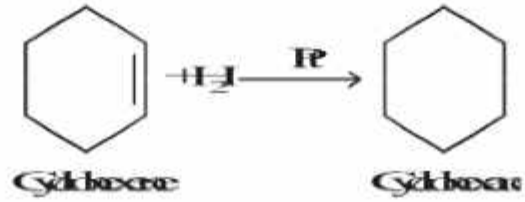
STABILITY OF BENZENE

Benzene is a stable molecule. Stability of benzene is due to the extensive delocalization of π-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 understand by the heat of hydrogenation of cyclohexene, 1, 3-cydohexadiene and 1, 3, 5-cyclohexatrien.

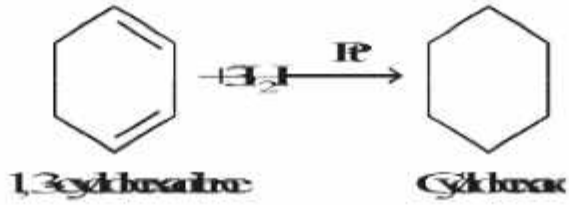
Cyclohexene, a six membered ring containing one double bond, can be easily hydrogenated to give cycloexane. When the ΔH for this reaction is measured, it is found to be –119.5 kJ/mole very much like that of any similarly substituted alkene.



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

We would expect, that hydrogenation of 1, 3-cyclohexadiene would liberate roughly twice as much heat, and thus have ΔH equal to about –239 kJ/mole. When this experiment is done, the result is ΔH = –231.5 kJ/mole. This result is quite close to what we calculated, and the difference (7.5 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)



Calculated ΔH = (–119.5 × 2) = –239 kJ/mol

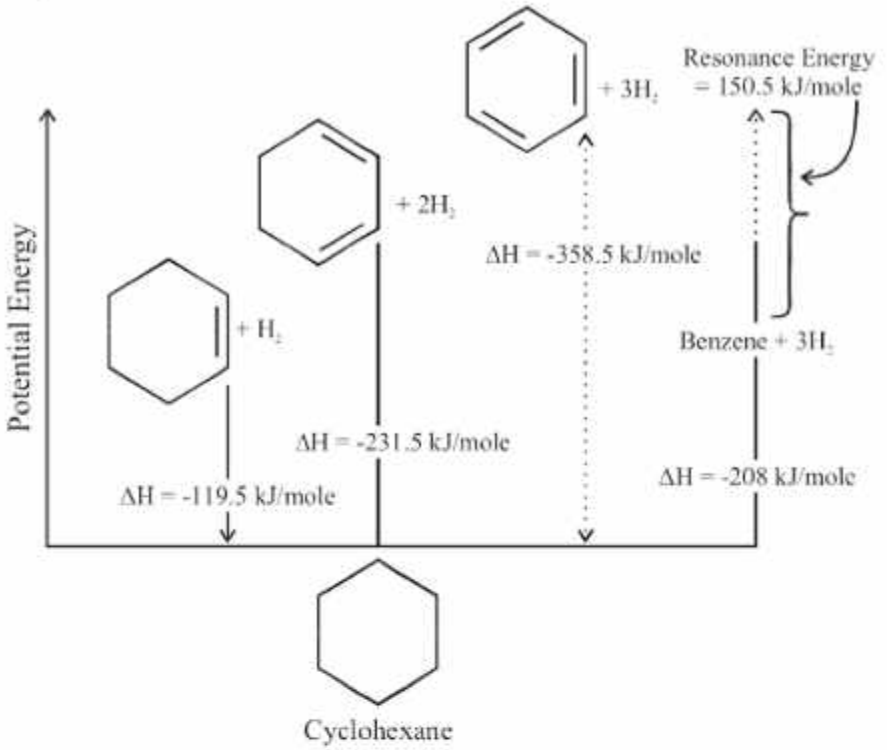
Observed ΔH = –231.5 kJ/mol



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

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

Difference = –358.5 – (–208) = –150.5 kJ mol^{-1}



(A comparision of heat of hydrogenation of cyclohexe, 1, 3-chclohexadiene and 1, 3, 5, cyclohexatriene).

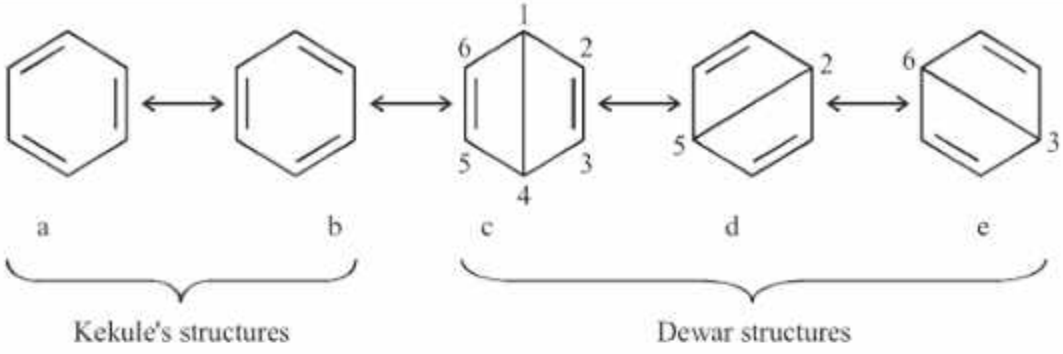
"The difference in energy between hypothetical structure (1, 3, 5, cyclohexatriene) and actual structure (benzene) is called resonance energy."

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 kJ mol^{-1} but resonance energy of naphthalene is 250 kJ mol^{-1} due to greater delocalization of π-cloud at 10 carbon atoms rather than at six carbon atoms.

RESONANCE STRUCTURE OF BENZENE

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

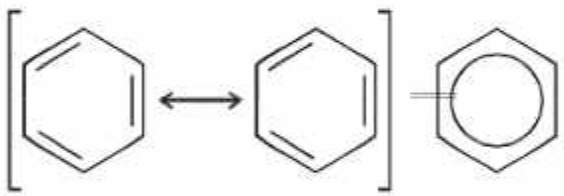
The resonance is represented by a double headed arrow (↔) e.g., the following different pairing schemes of the fourth valence (p-electrons) of carbon atoms are possible in benzene.



(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 1.54A°.

In alkenes the C ═ C bond length is 1.34A°.

In alkynes the C ≡ C bond length is 1.20A°.

In benzene the C – C bond length is 1.397A°.

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:

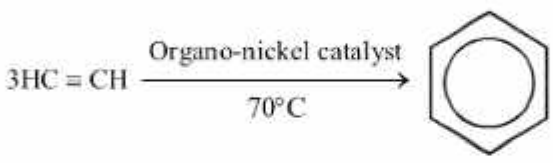
(1) Dehydrogenation of Cyclohexane:

Benzene can be prepared by the dehydrogenation of cyclohexane, when heated at 250°C in the presence of catalyst platinum or pladinum.



(2) From Acetylene:

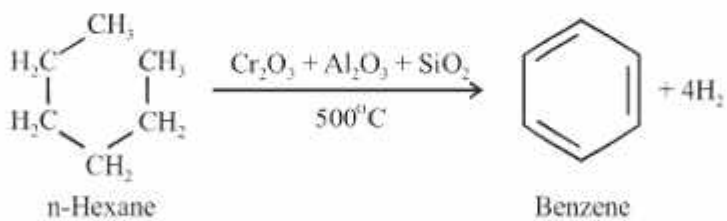
Benzene is formed by passing acetylene under pressure over an organo-nickel catalyst at 70°C.



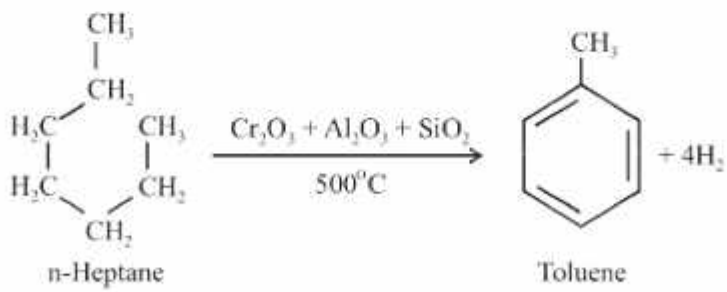
Acetylene Benzene

(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 $Cr_2O_3 + Al_2O_3 + SiO_2$ at 500°C.



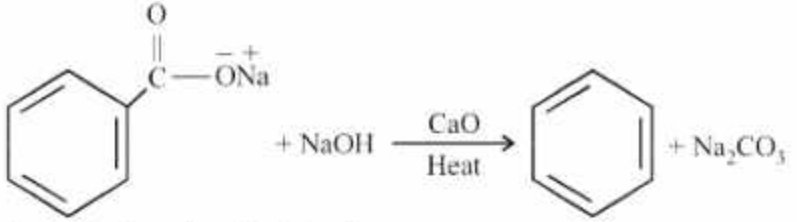
n-Hexane Benzene



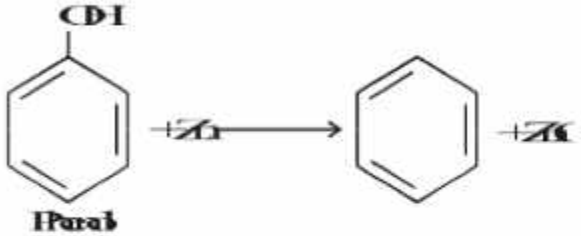
n-Heptane Toluene

(4) Laboratory Preparation:

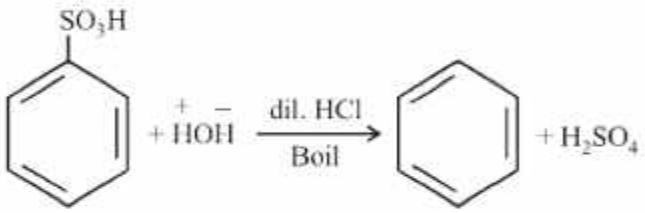
(i) Decarboxylation: Sodium benzoate is heated with soda lime to form benzene.



(ii) Distillation of phenol with zinc dust.

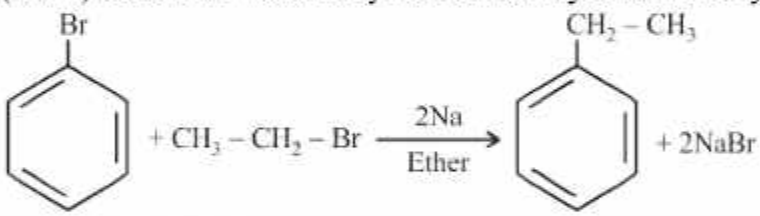


(iii) Hydrolysis of benzene sulphonic acid with superheated steam or by boiling with dil. HCl.



(5) Wurtz-Fitting Reaction:

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



GENERAL MECHANISM OF REACTIVITY OF BENZENE TOWARDS ELECTROPHILES

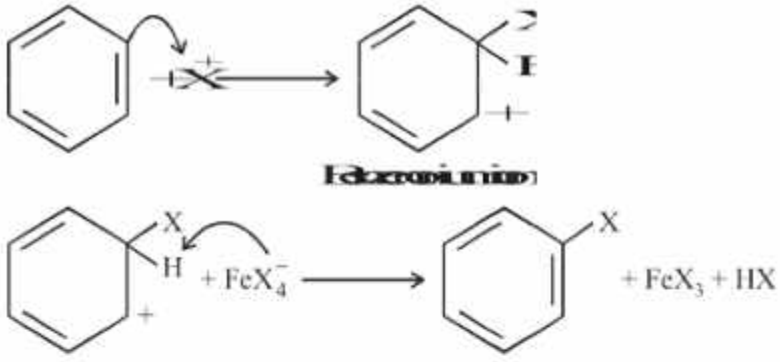
The highly stable, delocalized electrons of benzene are not readily available for the nucleophilic attack like the electrons of alkenes. Therefore, the electrons of benzene ring do not assist the attack of weak electrophile. Therefore, more powerful electrophile is needed to penetrate and break the continuous sheath of electron cloud of benzene. For example; in the halogenation of benzene, iron is converted to FeX_3 which reacts with halogen to form a powerful electrophile (X^+).

$$2Fe + 3X_2 \longrightarrow 2FeX_3$$

$$FeX_3 + X_2 \longrightarrow FeX_4^- + X^+$$

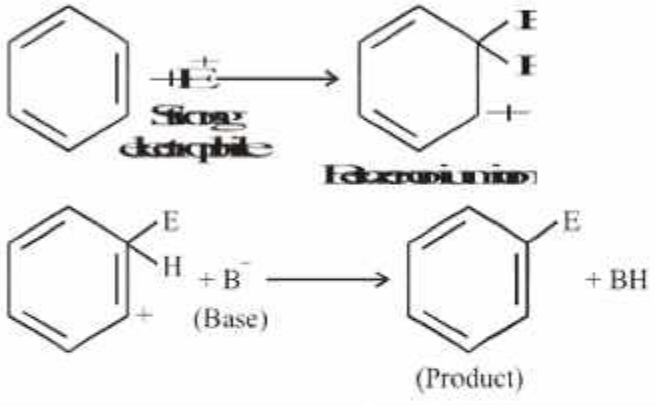
(Halogenonium ion)

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:



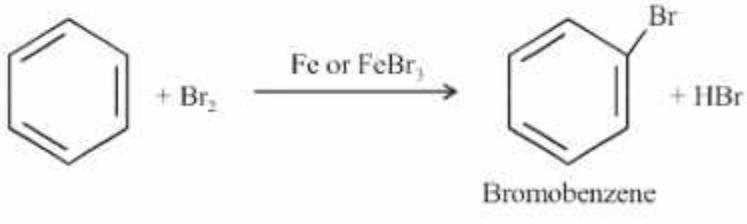
SOME EXAMPLES OF ELECTROPHILIC SUBSTITUTION REACTIONS

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

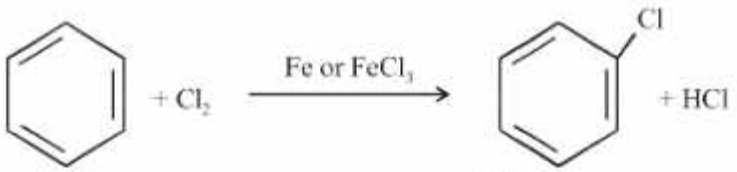
(1) Halogenation:

"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 flourination is too vigorous to control. Iodination gives poor yield.



Similarly,



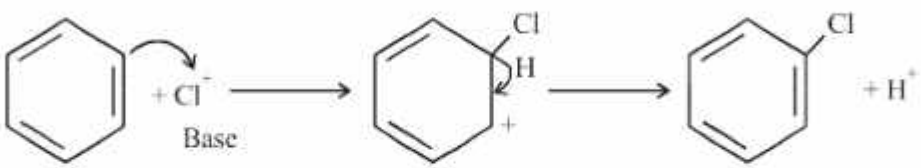
Chlorobenzene

Mechanism:

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

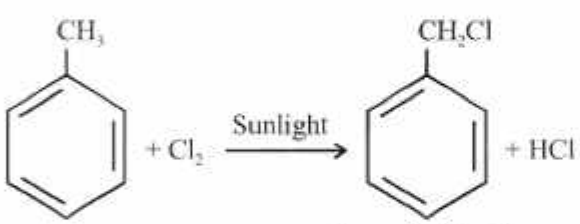
$$X_2 + FeX_3 \longrightarrow X^- + FeX_4$$

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

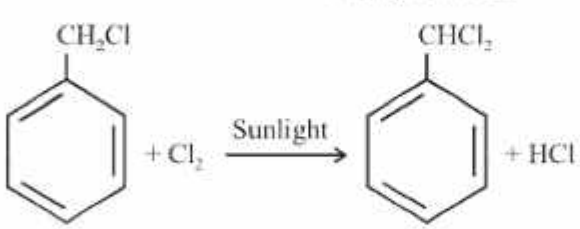


$$FeCl_4^- + H^+ \longrightarrow HCl + FeCl_3$$

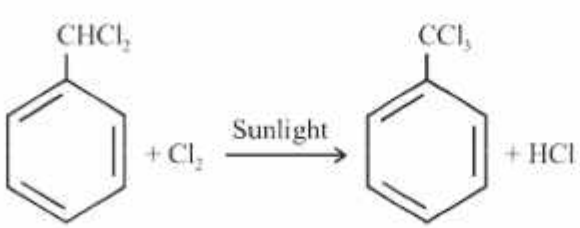
When alkyl benzene are treated with chlorine or bormine in the presence of sunlight, only the alkyl groups are substituted. It is a free radical mechanism.



Benzyl chloride



Benzal chloride

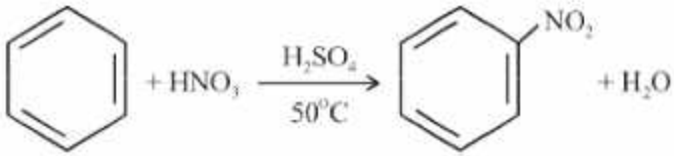


Benzotrichloride

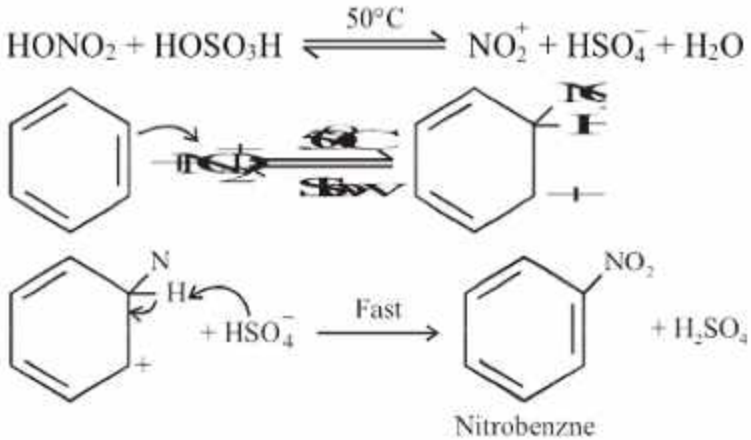
(2) Nitration:

"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°C. Sulphuric acid reacts with nitric acid and generate nitronium ion.

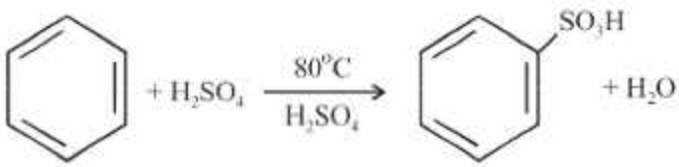


Mechanism:



(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.



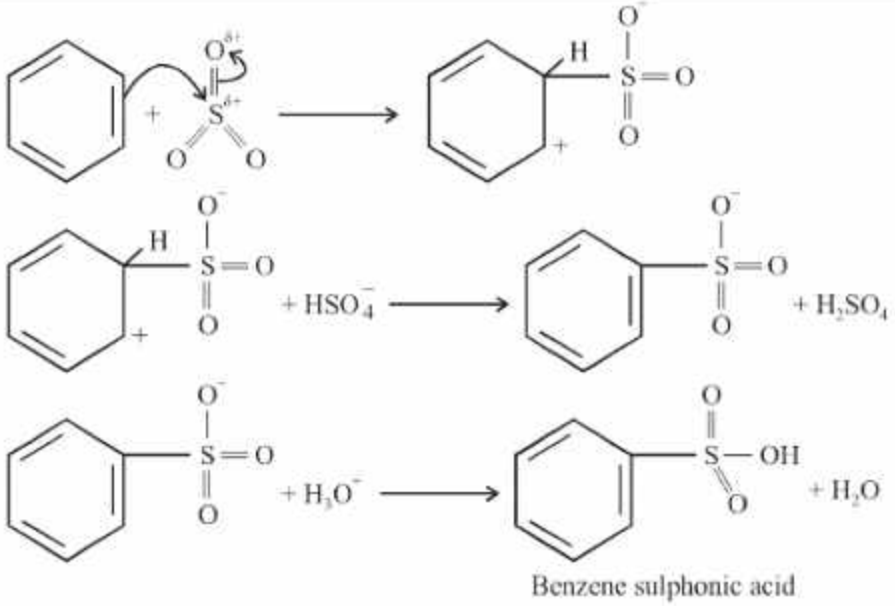
Benzenesulphonic acid



Mechanism:

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

$$H_2SO_4 + H_2SO_4 \longrightarrow H_3O^+ + SO_3 + HSO_4^-$$



Benzene sulphonic acid

(4) Friedal Crafts Reactions:

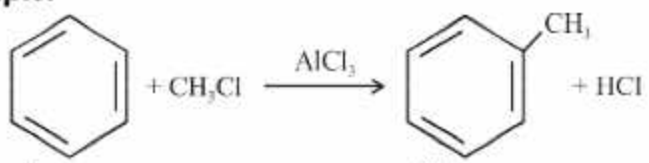
"The alkylation and acylation of benzene is called Friedal Crafts reactions."

(a) Friedal Craft Alkylation:

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst $AlCl_3$ is called Friedel Crafts alkylation or Alkylation.



For example:

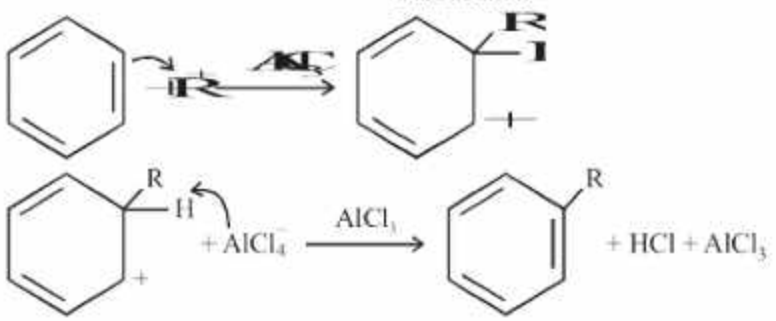


Benzene Toluene

Mechanism:

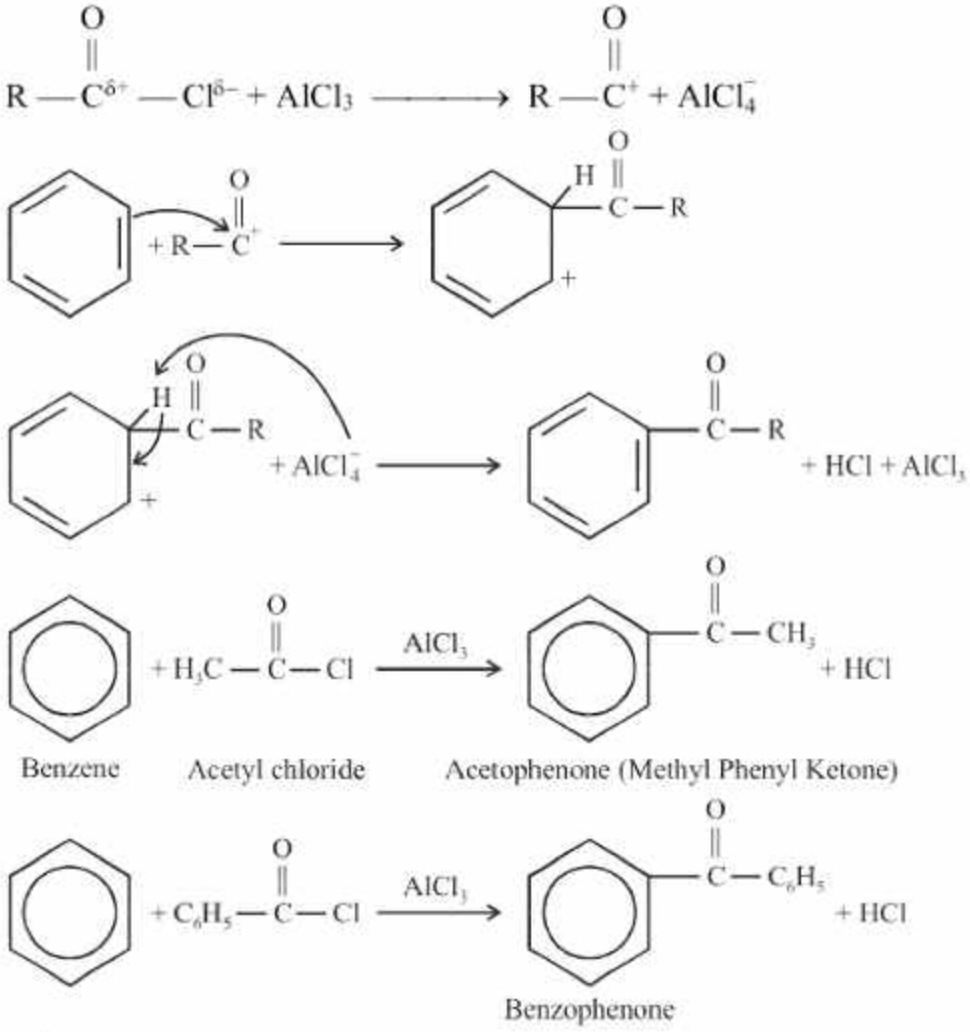
$$R—Cl + AlCl_3 \longrightarrow AlCl_4^- + R^+$$

Carbocation



(b) Friedel Craft Acylation:

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



e.g.,

Benzene Acetyl chloride Acetophenone (Methyl Phenyl Ketone)

Benzophenone

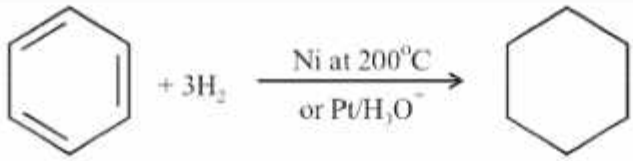
THE REACTIONS IN WHICH RING IS AFFECTED

(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):

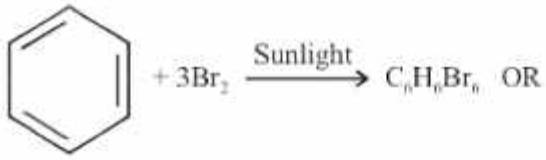
Benzene is reduced to cyclohexane on heating at high temperature, with hydrogen in the presence of Pt in an acidic solvent (acetic acid) or Ni at 200°C as a catalyst.

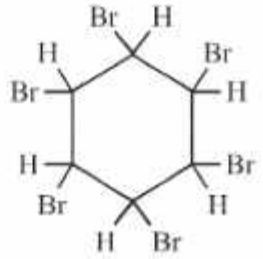


Cyclohexane

(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.





Hexabromobenzene or
Benzene hexabromide

(2) Oxidation:

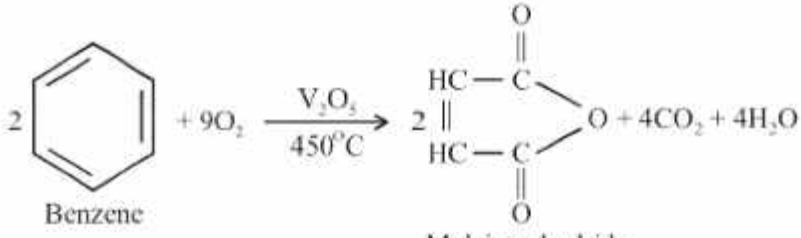
(i) Combustion:

When benzene is burnt in free supply of air, it is completely oxidized to CO_2 and H_2O.

$$C_6H_6 + 15/2O_2 \longrightarrow 6CO_2 + 3H_2O$$

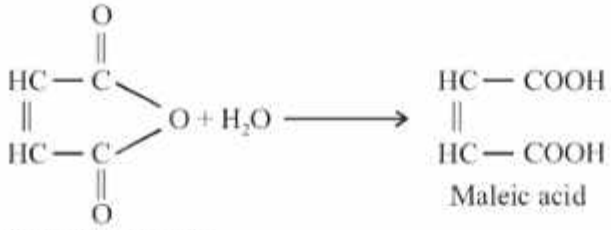
(ii) Catalytic Oxidation:

Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$ at room temperature. The ring is destroyed when benzene is strongly heated with air in the presence of V_2O_5 as a catalyst.



Benzene

Maleic anhydride

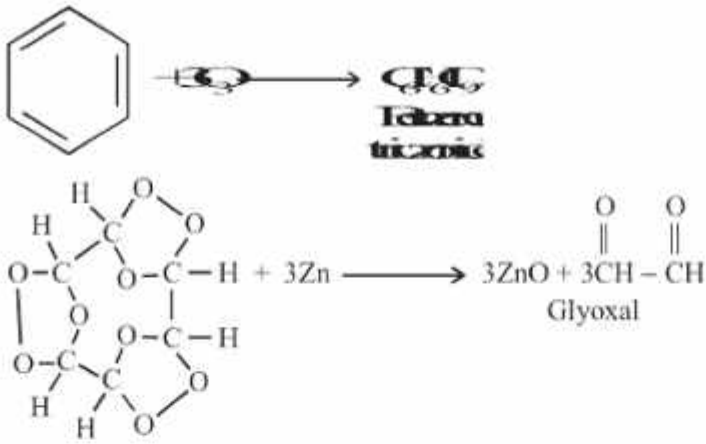


Maleic anhydride

Maleic acid

(iii) Ozonolysis:

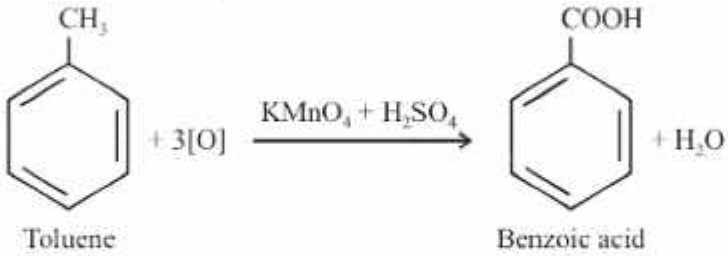
Benzene reacts with ozone and gives glyoxal through benzene triozonide.



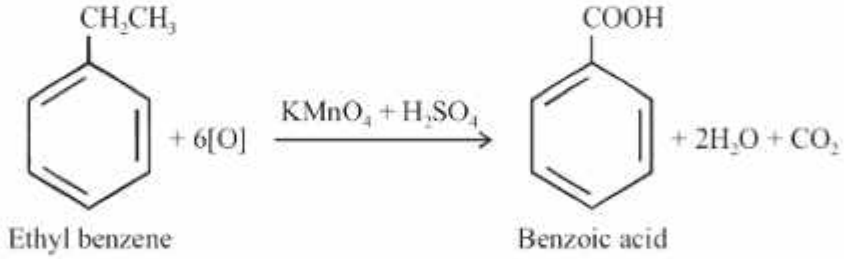
(iv) Oxidation of Side Chain of Benzene:

Alkyl benzene are readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$. In these reactions, the alkyl groups are oxidized keeping the benzene ring intact.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

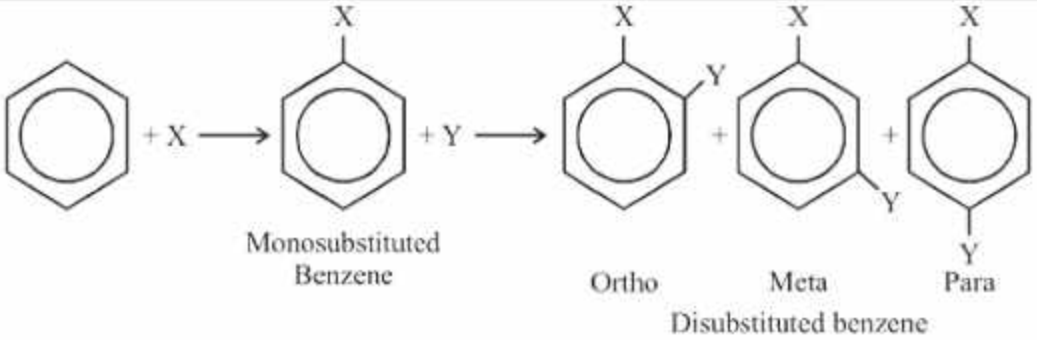


Whatever the length of an alkyl group may be, it gives only one carboxyl group. Moreover, the colour of $KMnO_4$ is discharged. Therefore, this reaction is used as a test for alkyl benzene.



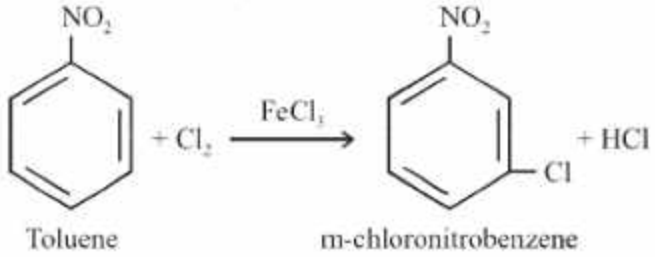
ORIENTATION IN ELECTROPHILIC SUBSTITUTION REACTIONS

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.

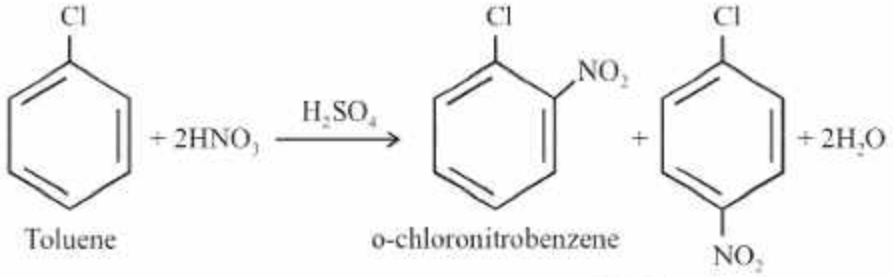


On chance basis, 40% ortho, 40% meta and 20% para disubstituted products are expected.

But the actual disubstitution of benzene does not follow this principle of chance, e.g., m-nitrochlorobenzene is the main product of the following halogenation reaction.



On the other hand, a mixture of o-nitrochlorbenzene and p-nitrochlorbenzene is obtained from the nitration of chlorobenzene.



A substituent which is already present on the ring affect the orientation and second substituent in two ways:

(1) A substituent already present affects the reactivity of the aromatic ring. Some substituents activate the ring and reactivity increases. Some substituent deactivate the ring and reactivity decreases.

(2) Substituents effect the orientation of the reaction. Some substituents are ortho and para directors and some are meta directors.

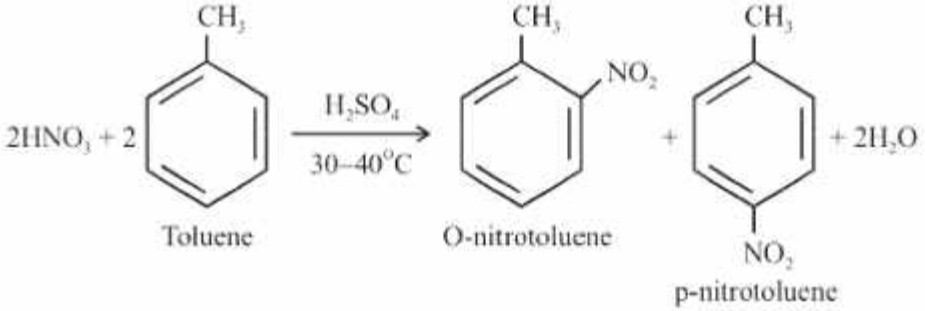
(a) Ortho-pera Directors:

Ortho-para directors donate electrons to the ring and they **activate the ring**. The electron clouds of π-bonds increases at the ortho and para position. An incoming electrophile attacks only at the ortho and para position because these positions are more reactive than meta position. Following groups if attached already to the aromatic ring makes it ortho-para directors.

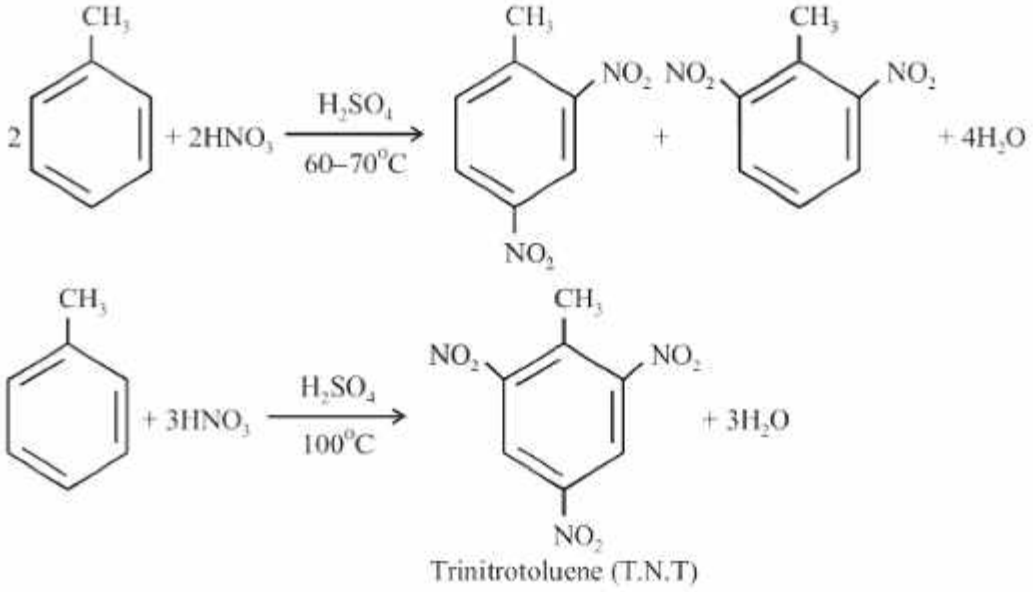
CH_3 —, X —(Cl, Br, I), —OH, —NH_2, —$N(CH_3)_2$, —OCH_3

All these groups increases electron density at ortho and para position and facilitiate 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.



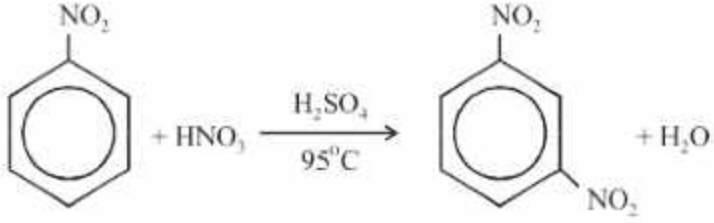
Meta Directors:

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 metal directors:

—C≡N, —COOH, —CHO, —NO_2, ¨RCO, —NR_3, —SO_3H

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 π-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 π-electrons. π-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 H_2 in the presence of catalyst, Cl_2 in the presence of sunlight and ozone. The decreasing order of reactivity of alkane, alkene and benzene is:

Alkene > Benzene > Alkane

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, fragant	**(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 Å.

(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. 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 π-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) $AlCl_3$ **(b)** HNO_3

(c) $BeCl_2$ **(d)** 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) NO_3 **(b)** NO_2^+

(c) NO_2 **(d)** 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) H_2SO_4 **(b)** HSO_4^-

(c) SO_3 **(d)** 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. H_2SO_4 at 250° C.

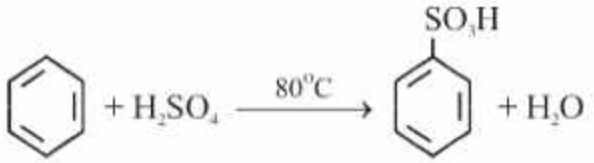
(b) Chlorine is passed through benzene in sunlight.

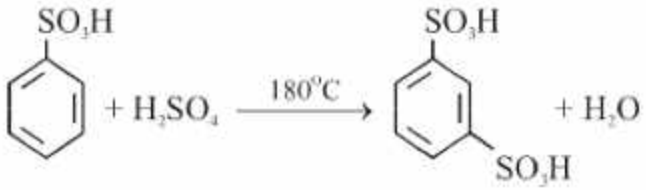
(c) A mixture of benzene vapours and air are passed over heated vandaium pentoxide.

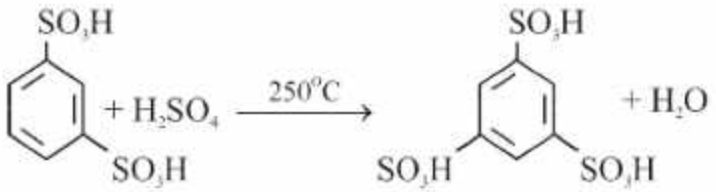
(d) Benzene is burnt in free supply of air.

Ans.

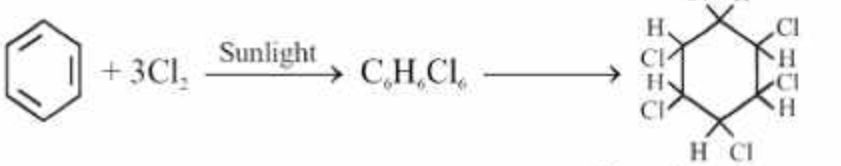
(a)





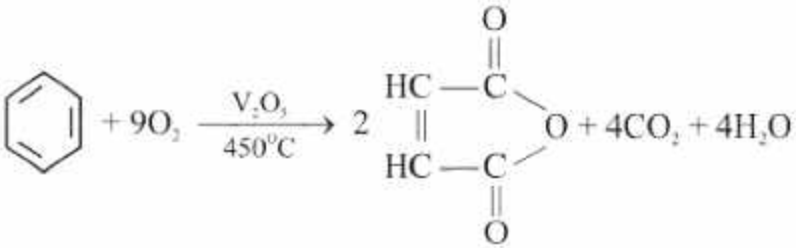


(b)



Hexachloro benzene

(c)



(d) $2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$

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**

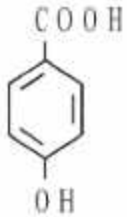
(iii) Bromonitrotoluene

Ans. (a)

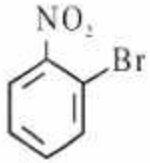
(i) m-Chlorobenzoic acid



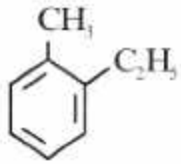
(ii) p-Hydroxybenzoic acid



(iii) o-Bromonitrobenzene



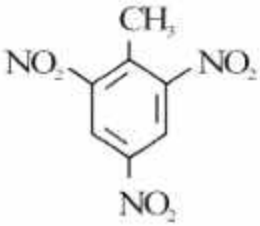
(iv) o-Ethyltoluene



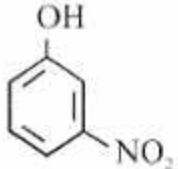
(v) p-Nitroaniline



(vi) 2, 4, 6-Trinitrotoluene



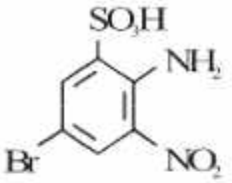
(vii) m-Nitrophenol



(viii) p-dibenzylbenzene

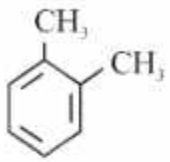


(ix) 2-amino-5 bromo-3-nitro benzenesulphonic acid

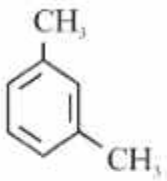


(b)

(i) Xylene:



o-xylene

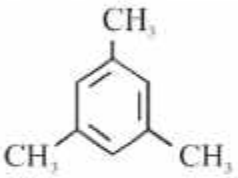


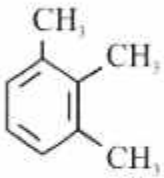
m-xylene

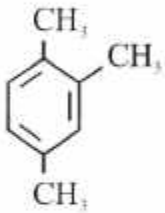


p-xylene

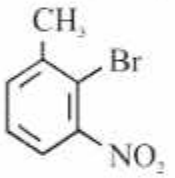
(ii) Trimethylbenzene:

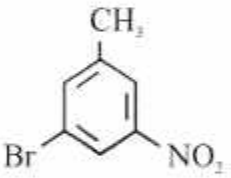


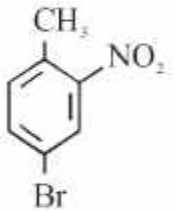




(iii) Bromonitrotoluene:

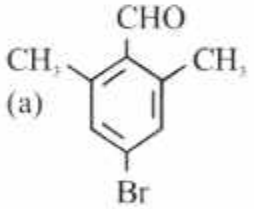




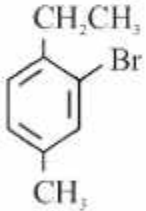


Q.8 Write IUPAC names of the following molecules.

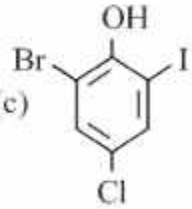
(a)



(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.

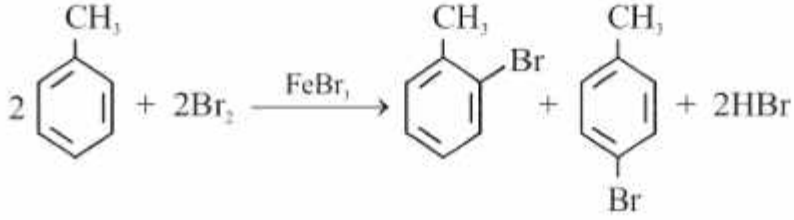
Q.11 Predict the major products of bromination of the following compounds:

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

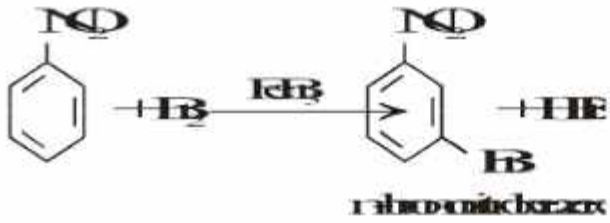
(d) Benzoic acid (e) Benzaldehyde (f) Phenol

Ans.

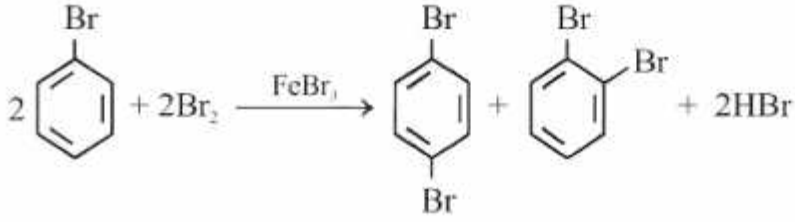
(a)



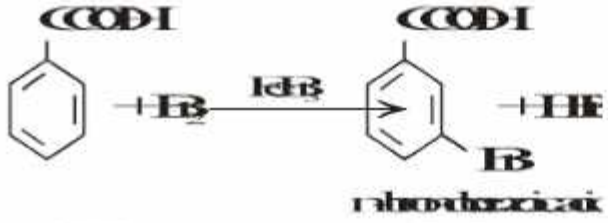
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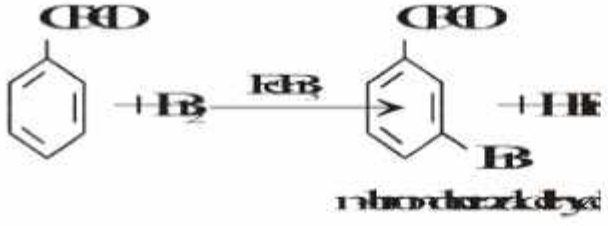
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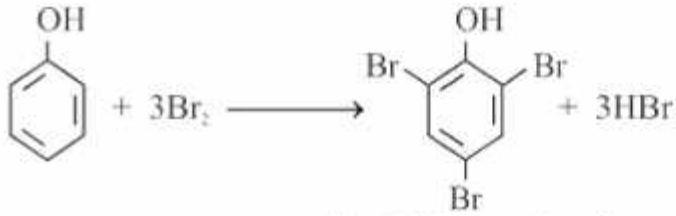


(d)



(e)



(f) 

2, 4, 6-Tribromophenol

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

(a) m-chloronitrobenzene **(b) p-chloronitrobenzene**

Ans.

(a) Benzene ⟶ m-chloronitrobenzene

Steps Involved:

(i) Nitration:

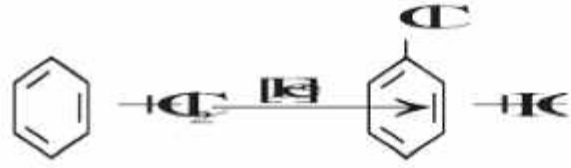


(ii) Chlorination:

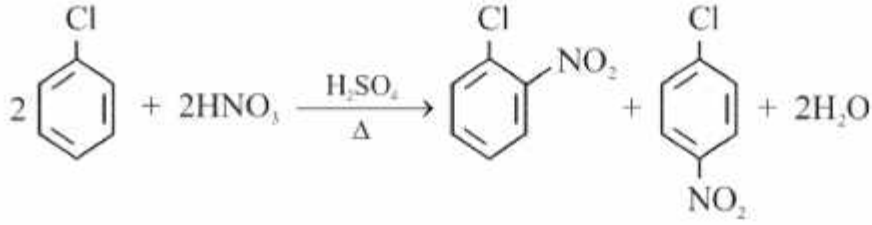


(b) Benzene ⟶ p-chloronitrobenzene

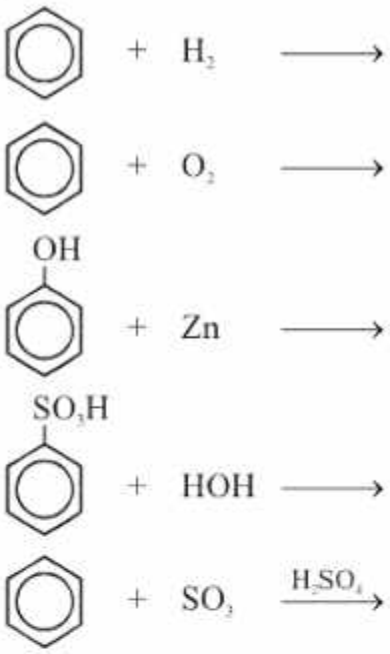
(i)



(ii)



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

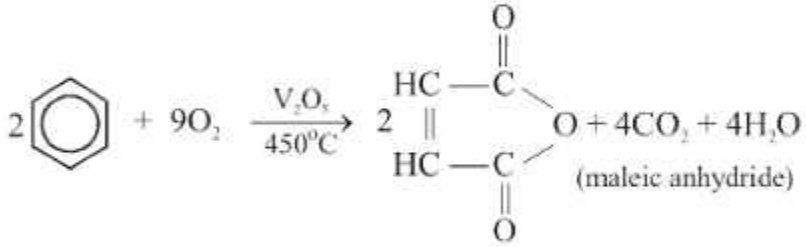


Ans.

(i)



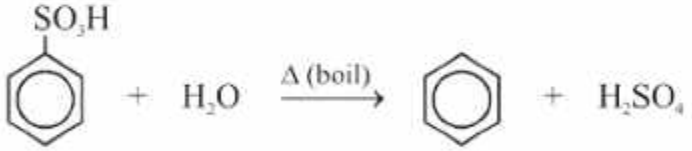
(ii)



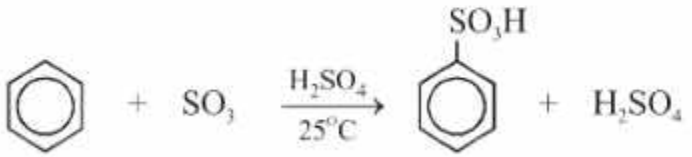
(iii)



(iv)



(v)



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.

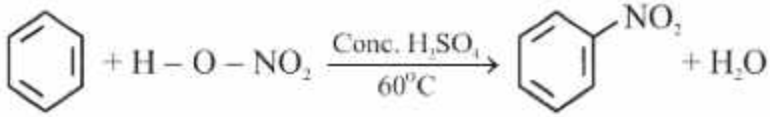
(i) **Halogenation:** Benzene reacts with Cl_2 in the presence of $FeCl_3$ to give chlorobenzene. A hydrogen atom of benzene is replaced by a halogen atom so, gives a substitution products.

Reaction:



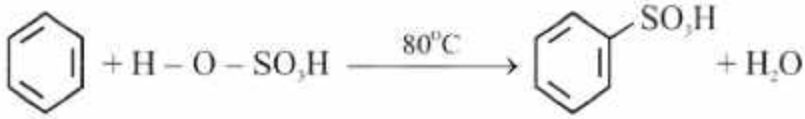
(ii) **Nitration:** Benzene reacts with concentrated nitric acid in the presence of conc. H_2SO_4 to give a substitution product nitrobenzene.

Reaction:



(iii) **Sulphonation:** Benzene reacts with conc. H_2SO_4 at 80°C to give a

Reaction:



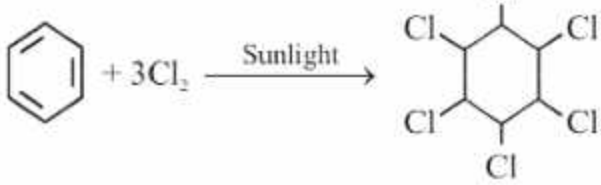
Benzene as Unsaturated Hydrocarbon:

(i) **Hydrogenation:** Benzene adds three molecules of hydrogen in the presence of Ni at 250°C gives addition product cyclohexane.

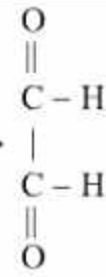


(ii) **Chlorination:** Benzene adds three molecules of Cl_2 in the presence of sunlight and gives addition product hexachlorobenzene.

Reaction:



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

Reaction: $C_6H_6 + 3O_3 \longrightarrow C_6H_6O_9 \xrightarrow[Zn]{H_2O}$  $+ ZnO$

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

(i) Friedel-Crafts alkylation reactions

(ii) Friedel-Crafts acylation reactions

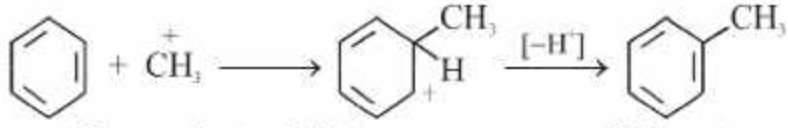
Ans.

Friedel-Crafts Alkylation:



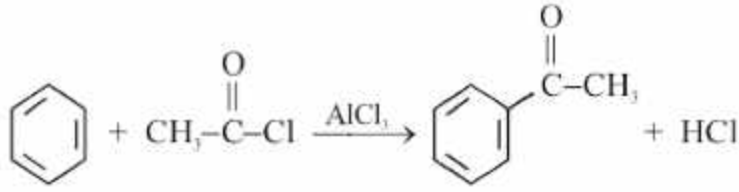
Mechanism:

$$CH_3Cl + AlCl_3 \longrightarrow \overset{-}{AlCl_4} + \overset{+}{C}H_3$$



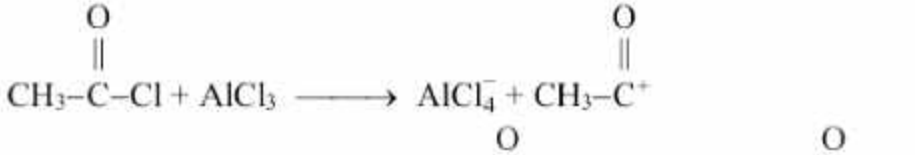
(Strong electrophile) (Toluene)

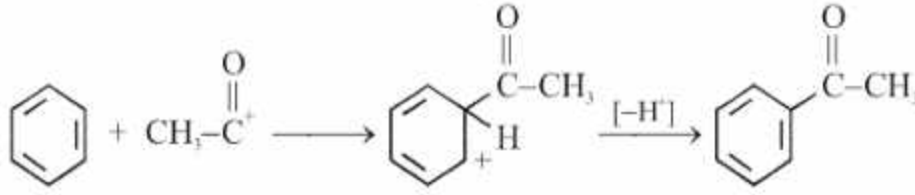
Friedel-Craft's Acylation:



(Acetophenone)

Mechanism:





DO YOU KNOW?

(1) Benzene was discovered by Michael Faraday in 1825.

(2) Benzene was found in coal tar in 1845 by Hoffmann.

(3) Vinyl benzene is called styrene.

(4) Isopropyl benzene is called cumene.

(5) Methyl phenyl ether is called anisole.

(6) O-methyl phenol is called O-crsol.

(7) p-xylene on oxidation form tere-phthalic acid.

(8) Mixture of HNO_3 and H_2SO_4 used for nitration of benzene is called nitrating mixture.

(9) Benzene has regular cyclic hexagonal structure.

(10) Benzene on oxidation in the presence of V_2O_5 forms maleic anhydride.

(11) Benzene on ozonolysis forms glyoxal and finally oxalic acid.

(12) The substitution of hydrogen atom of benzene by the alkyl radical (R) is called alkylation.

(13) When the hydrogen atom of benzene is substituted by the acyl group $\left(R-\overset{\overset{O}{\|}}{C}-\right)$ in the presence of $AlCl_3$ it is called "acylation".

(14) Naphthalene is also called "moth balls".

(15) The C–C bond distance in benzene is 1.397 A°.

CHAPTER 9

AROMATIC HYDROCARBONS

MULTIPLE CHOICE QUESTIONS

1. Which of the following acid can be used as a catalyst in Friedel Craft's reaction:

(a) $AlCl_3$ **(b)** HNO_3

(c) $BeCl_2$ **(d)** NaCl

2. During nitration of benzene, the active nitrating agent is:

(a) NO_3 **(b)** NO_2^+

(c) NO_2^- **(d)** HNO_3

3. The electrophile in aromatic sulphonation is:

(a) H_2SO_4 **(b)** HSO_4^-

(c) SO_3^+ **(d)** SO_3

4. Hydrogen to carbon ratio in aromatic hydrocarbons is:

(a) Low **(b)** High

(c) Equal **(d)** None

5. The second substitution in benzene ring would give rise isomeric products:

(a) One **(b)** Two

(c) Three **(d)** Four

6. Molecular mass of benzene is determined by:

(a) Vapour density method **(b)** X-ray diffraction

(c) Elemental analysis **(d)** Degradation method

7. C – H bond lengths in benzene are:

(a) 0.99 Å **(b)** 1.09 Å

(c) 1.12 Å **(d)** 1.397 Å

8. Each carbon in benzene ring is ———— hybridized:

(a) sp **(b)** sp^2

(c) sp^3 **(d)** None of these

9. On hydrogenation benzene liberates energy:

(a) 358.5 kJ/mole **(b)** 119 kJ-mol^{-1}

(c) 208 kJ-mol^{-1} **(d)** 150.5 kJ-mol^{-1}

10. The benzene ring is oxidized to maleic anhydride when strongly heated with:

(a) Ni/200°C **(b)** V_2O_5/450°C

(c) $AlCl_3$/150°C **(d)** Sunlight

11. Main source of aromatic compound is:

(a) Petroleum **(b)** Coal-tar

(c) Living organism **(d)** Dead marine animals

12. When acetylene is heated at 300°C in Cu-tube, the product obtained is:

(a) Benzene **(b)** Thiophene

(c) Divinyl acetylene **(d)** Xylene

13. Which one of the following species is ortho and para director:

(a) CHO **(b)** $-SO_3H$

(c) $-NO_2$ **(d)** Cl

14. The carbon-carbon bond distance in benzene:

(a) 1.54°A **(b)** 1.34°A

(c) 1.2°A **(d)** 1.39°A

15. In toluene synthesis by Friedel Craft, the reactants in addition to anhydrous $AlCl_3$ are:

(a) $C_6H_6 + CH_4$ **(b)** C_6H_5Cl

(c) $C_6H_6 + CH_3Cl$ **(d)** $C_6H_5Cl + CH_4$

16. Benzophenone is also known as:

(a) Biphenyl **(b)** Dimethyl Ketone

(c) Diphenyl Ketone **(d)** Methylphenyl Ketone

17. The no. of possible isomers of xylene are:

(a) 2 **(b)** 3

(c) 4 **(d)** 5

18. The molecular formula of naphthalene is:

(a) $C_{10}H_8$ **(b)** $C_{10}H_{10}$

(c) $C_{10}H_{12}$ **(d)** $C_{12}H_{12}$

19. Chlorine react with benzene in the presence of sunlight to give:

(a) Chlorobenzene **(b)** Benzoyl chloride

(c) Ortho-para dichlorobenzene **(d)** Hexachlorobenzene

20. Effect of substituent on benzene ring is due to:

(a) Resonance **(b)** Inductive effect

(c) Both (a) and (b) **(d)** Unpredictable

21. In which of the following cases, the benzene rings are isolated:

(a) Naphthalene **(b)** Phenanthrene

(c) Anthracene **(d)** Triphenylmethane

22. Benzene is stable than ethene because it has:

(a) More π-bonds **(b)** Localized π-electrons

(c) Delocalized π-electrons **(d)** More σ-bonds

23. Which of the following is ortho and para directing group:

(a) $-OH$ **(b)** $-OCH_3$

(c) $-CHO$ **(d)** $-NH_2$

24. Among the following compounds which can be readily sulphonated:

(a) Phenol **(b)** Benzene

(c) Nitrobenzene **(d)** Chlorobenzene

25. Structure of benzene is resonance hybrid of all ———— structures:

(a) 3 **(b)** 4

(c) 5 **(d)** 6

26. Aromatic hydrocarbons are derivatives of:

(a) Paraffins **(b)** Alkene

(c) Benzene **(d)** Cyclohexane

27. Which of the following explains the structure of benzene:

(a) Atomic orbital treatment of benzene

(b) Resonance method

(c) Both (a) and (b)

(d) None

28. The conversion of n-hexane into benzene by heating in the presence of ($Al_2O_3 + SiO_2 + Cr_2O_3$) is called:

(a) Isomerization **(b)** Aromatization

(c) Dealkylation **(d)** Rearrangement

29. Which of the following is called benzyl radical:

(a) C_6H_5- **(b)** $C_6H_5-\overset{|}{\underset{|}{CH}}$

(c) $C_6H_5-CH_2-$ **(d)** $C_6H_5-\overset{|}{\underset{|}{C}}-$

30. Toluene can be converted to benzoic acid in the presence of:

(a) dil. NaOH **(b)** dil. HNO_3

(c) Conc. HNO_3 **(d)** Acidified $KMnO_4$

31. Cyclic structure of benzene was proposed by:

(a) Dewar **(b)** Faraday

(c) Down **(d)** Kekule

32. Benzene does not undergo:

(a) Addition **(b)** Substitution

(c) Polymerization **(d)** Aromatization

answers

1.	(a)	**2.**	(b)	**3.**	(d)	**4.**	(a)	**5.**	(c)
6.	(a)	**7.**	(b)	**8.**	(b)	**9.**	(c)	**10.**	(b)
11.	(b)	**12.**	(a)	**13.**	(d)	**14.**	(d)	**15.**	(c)
16.	(c)	**17.**	(b)	**18.**	(a)	**19.**	(d)	**20.**	(c)
21.	(d)	**22.**	(c)	**23.**	(a)	**24.**	(a)	**25.**	(c)
26.	(c)	**27.**	(c)	**28.**	(b)	**29.**	(c)	**30.**	(d)
31.	(d)	**32.**	(c)						

SOLVED 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 Å.

(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. 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 π-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) $AlCl_3$ **(b)** HNO_3

(c) $BeCl_2$ **(d)** 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) NO_3 **(b)** NO_2^+

(c) NO_2 **(d)** 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) H_2SO_4 **(b)** HSO_4

(c) SO_3 **(d)** 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 ring of benzene is called aromatic compounds. e.g., toluene.

Classification see in text book.

Q.5 What happens when:

(a) Benzene is heated with conc. H_2SO_4 at 250°C.

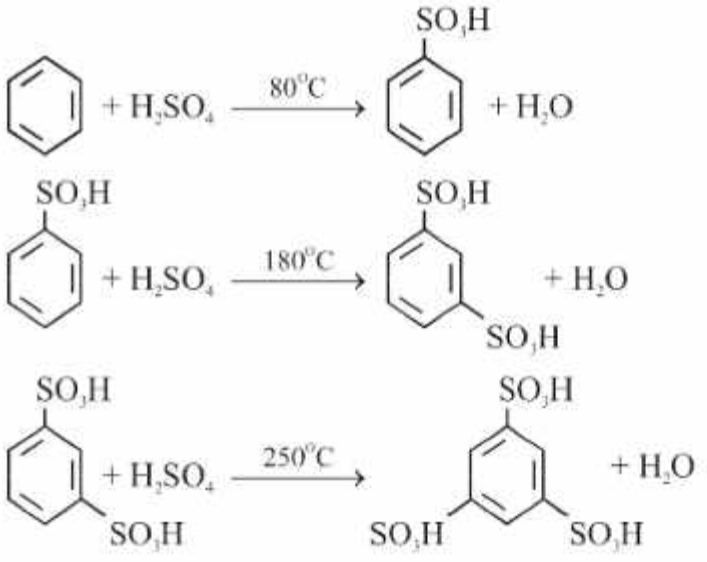
(b) Chlorine is passed through benzene in sunlight.

(c) A mixture of benzene vapours and air are passed over heated vandaium pentoxide.

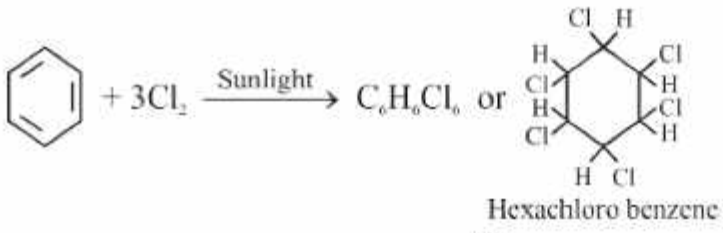
(d) Benzene is burnt in free supply of air.

Ans.

(a)

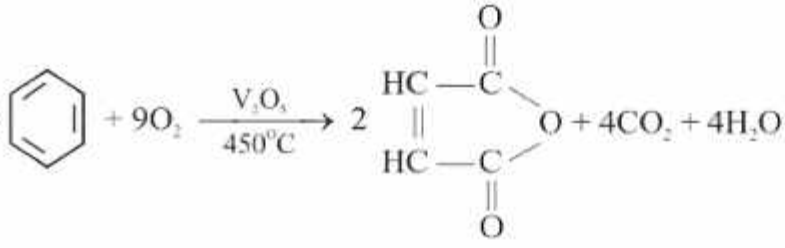


(b)



Hexachloro benzene

(c)



(d) $2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$

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**

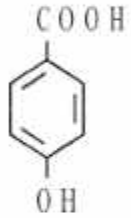
(iii) Bromonitrotoluene

Ans. **(a)**

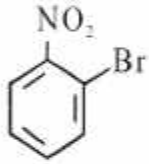
(i) m-chlorobenzoic acid



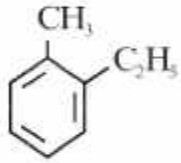
(ii) p-hydroxybenzoic acid



(iii) o-bromonitrobenzene



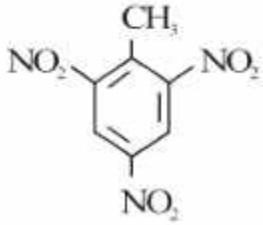
(iv) o-ethyltoluene



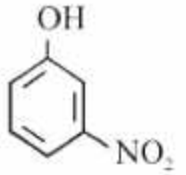
(v) p-nitroaniline



(vi) 2, 4, 6-trinitrotoluene



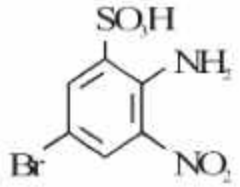
(vii) m-nitrophenol



(viii) p-dibenzylbenzene

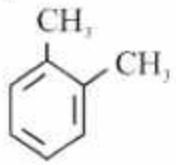


(ix) 2-amino-5 bromo-3-nitro benzenesulphonic acid

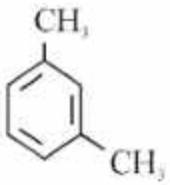


(b)

(i) Xylenes:



o-xylene

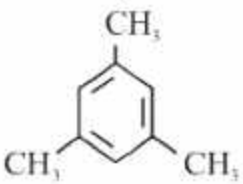


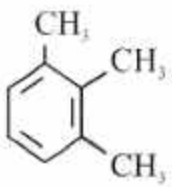
m-xylene

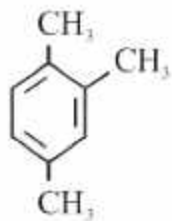


p-xylene

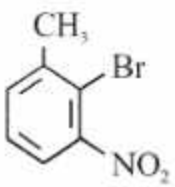
(ii) Trimethylbenzene:

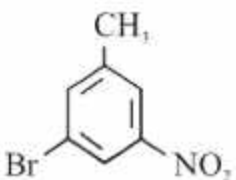


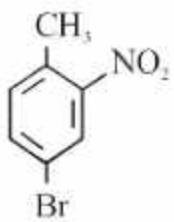




(iii) Bromonitrotoluene:

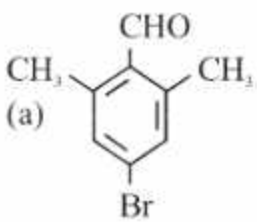




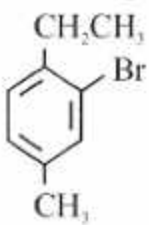


Q.8 Write IUPAC names of the following molecules.

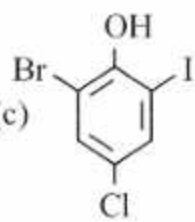
(a)



(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.

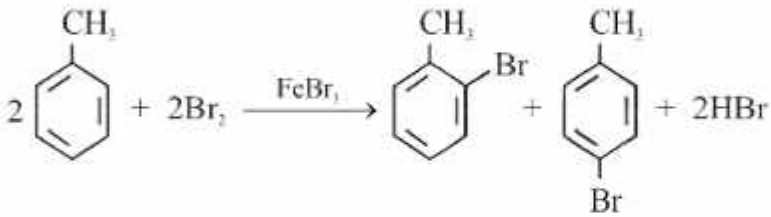
Q.11 Predict the major products of bromination of the following compounds:

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

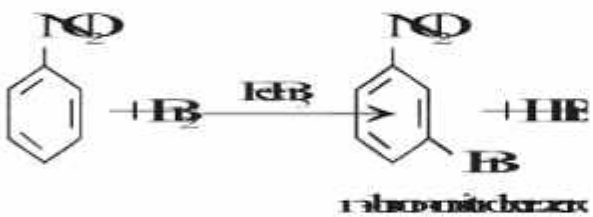
(d) Benzoic acid (e) Benzaldehyde (f) Phenol

Ans.

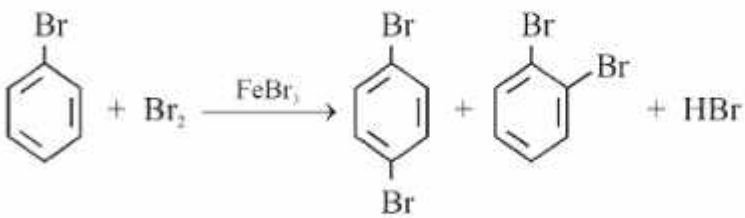
(a)



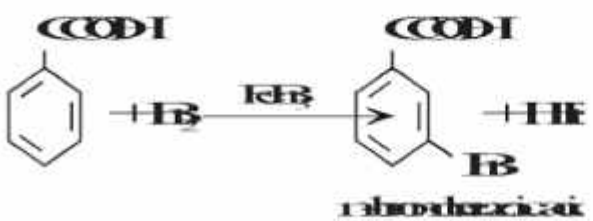
(b)



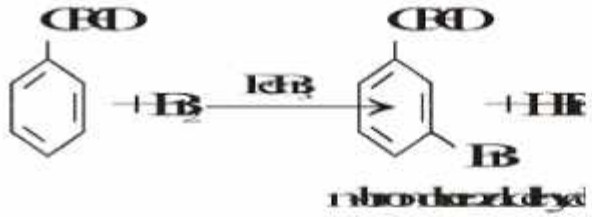
(c)



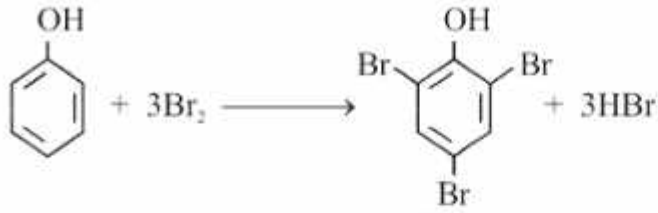
(d)



(e)



(f)



2, 4, 6-tribromophenol

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

(a) m-chloronitrobenzene **(b) p-chloronitrobenzene**

Ans.

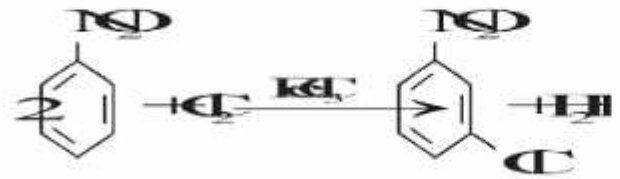
(a) Benzene ⟶ m-chloronitrobenzene

Steps Involved:

(i) Nitration:

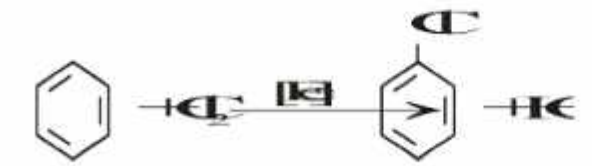


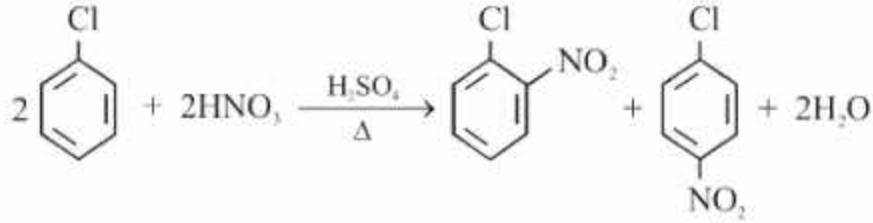
(ii) Chlorination:



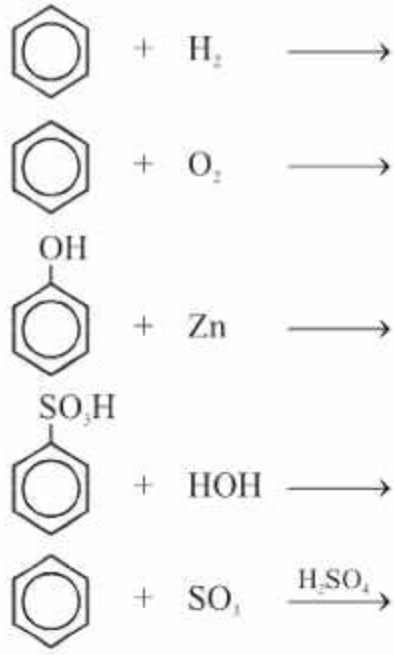
(b) Benzene ⟶ p-chloronitrobenzene

(i)



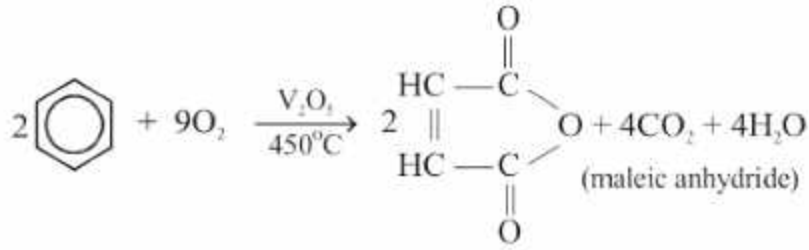
(ii) 

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

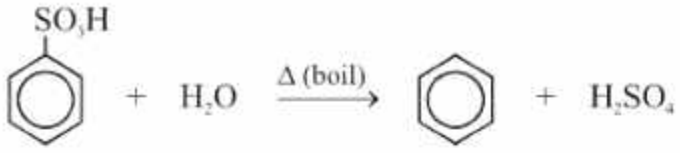


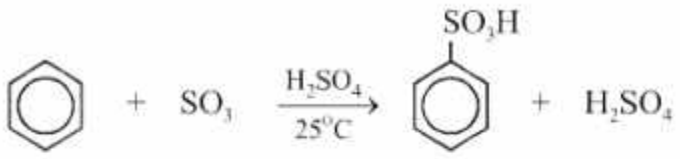
Ans.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

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.

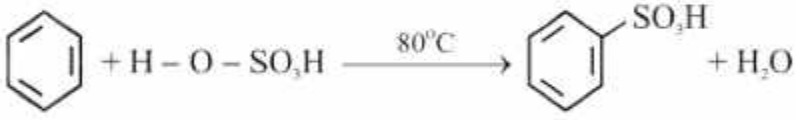
(i) **Halogenation:** Benzene reacts with Cl_2 in the presence of $FeCl_3$ to give chlorobenzene. A hydrogen atom of benzene is replaced by a halogen atom so, gives a substitution products.

Reaction: 

(ii) **Nitration:** Benzene reacts with concentrated nitric acid in the presence of conc. H_2SO_4 to give a substitution product nitrobenzene.

Reaction: 

(iii) **Sulphonation:** Benzene reacts with conc. H_2SO_4 at 80°C to give a

Reaction: 

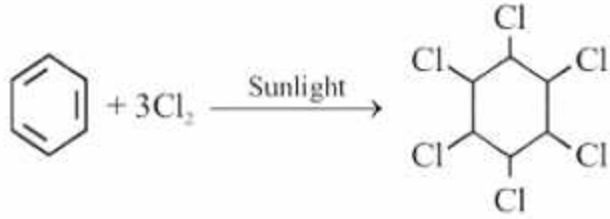
Benzene as Unsaturated Hydrocarbon:

(i) **Hydrogenation:** Benzene adds three molecules of hydrogen in the presence of Ni at 250°C gives addition product cyclohexane.



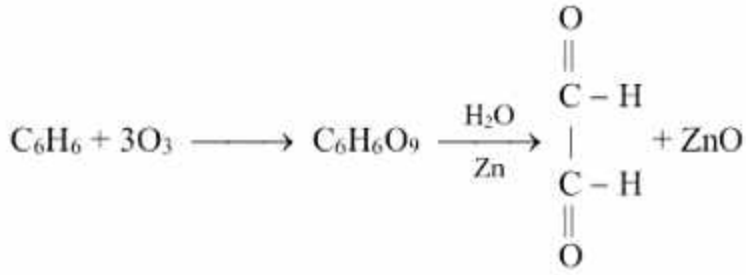
(ii) **Chlorination:** Benzene adds three molecules of Cl_2 in the presence of sunlight and gives addition product hexachlorobenzene.

Reaction:



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

Reaction:



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

(i) Friedel-Crafts alkylation reactions

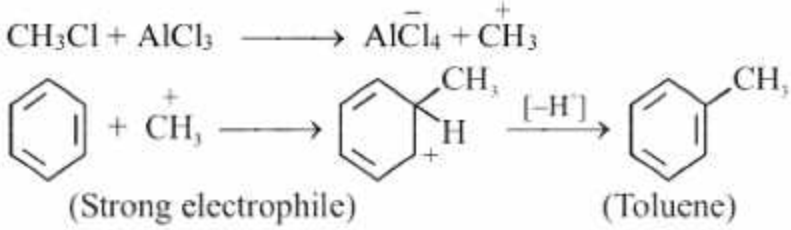
(ii) Friedel-Crafts acylation reactions

Ans.

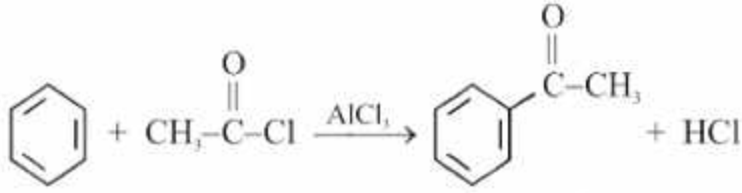
Friedel-Crafts Alkylation:



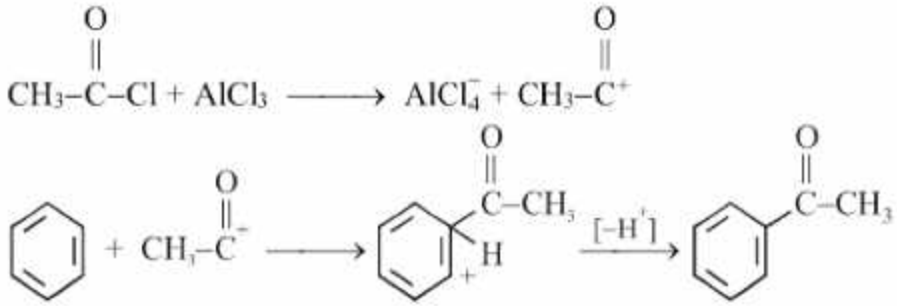
Mechanism:



Friedel-Craft's Acylation:



Mechanism:



DO YOU KNOW?

1. Benzene was discovered by Michael Faraday in 1825.
2. Benzene was found in coal tar in 1845 by Hoffmann.
3. Vinyl benzene is called styrene.
4. Isopropyl benzene is called cumene.
5. Methyl phenyl ether is called anisole.
6. O-methyl phenol is called O-cresol.
7. p-xylene on oxidation form tere-phthalic acid.
8. Mixture of HNO_3 and H_2SO_4 used for nitration of benzene is called nitrating mixture.
9. Benzene has regular cyclic hexagonal structure.
10. Benzene on oxidation in the presence of V_2O_5 forms maleic anhydride.
11. Benzene on ozonolysis forms glyoxal and finally oxalic acid.
12. The substitution of hydrogen atom of benzene by the alkyl radical (R) is called alkylation.
13. When the hydrogen atom of benzene is substituted by the acyl group $\left(R-\overset{\overset{O}{\|}}{C}-\right)$ in the presence of $AlCl_3$ it is called "acylation".
14. Naphthalene is also called "moth balls".
15. The C–C bond distance in benzene is 1.397 A°.

SHORT QUESTIONS

Q.1 Aromatic compounds burn with sooty flame, why?

Ans. Aromatic compounds have high percentage of carbon as compared to hydrogen. Aromatic compounds containing six carbon atoms have six hydrogen in it but the aliphatic compounds with six carbon atoms have fourteen hydrogen atoms aromatic compounds due to greater percentage of carbon, do not burn properly and give soot or smoke of carbon.

Q.2 What is meant by aromatic compounds?

Ans. The term aromatic was derived from the Greek word "aroma" meaning "fragrant" usually the compounds containing six membered benzene ring are called aromatic compound e.g., phenol, toluene, benzene, naphthalene, etc.

Q.3 Benzene usually undergoes electrophilic substitution reaction and not addition reactions, why?

Ans. In benzene ring, delocalized Pi-electrons are present in the form of sheath. This sheath of electrons above and below the carbon plane can be donated to the substance, which is electron deficient. During electrophilic substitution reactions, the aromaticity of ring remains as such. In addition reaction of bezene it changes to a non-aromatic compounds.





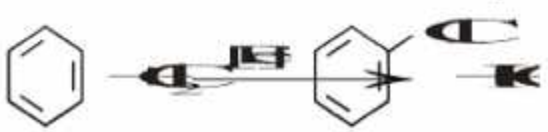
(Electrophilic substitution)

Q.4 Benzene is less reactive than alkanes, why?

Ans. In benzene ring, delocalized Pi-electrons are present in the form of sheath above and below the carbon plane. In case of ethene, localized Pi-electron cloud is present. Delocalized cloud of electrons is more stable as compared to localized cloud. Some energy is required to break the delocalization of electronic cloud called resonance energy. Due to this resonance stability benzene is less reactive than alkene.

Q.5 Give two reactions of benzene in which it behaves as saturated hydrocarbon.

Ans. (i) Benzene reacts with chlorine in the presence of Fe to form chlorobenzene.

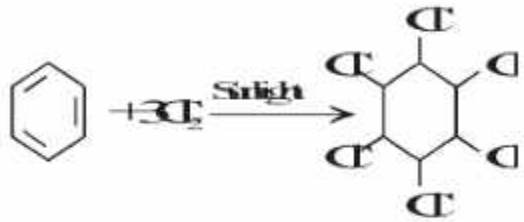


(ii) Benzene reacts with nitric acid in the presence of sulphuric acid to form nitrobenzene.

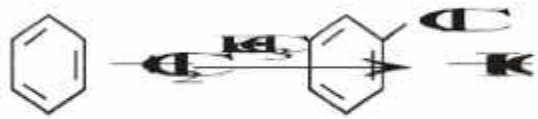


Q.6 What product will be formed when benzene reacts with chlorine (i) in the presence of sunlight (ii) in the presence of Fe catalyst?

Ans. Benzene in the presence of sunlight undergoes addition reaction and form hexachloride.



In the presence of Fe benzene undergoes electrophilic substitution.



Q.7 Why benzene is given a cyclic structure?

Ans. Benzene given a cyclic structure due to following reasons:

(i) It has one mono substitution product.

(ii) It has three di-substitution products.

(iii) It can add three molecules of chlorine and three molecules of hydrogen. It means it has three double bonds.

Above observation indicates that it has cyclic structure.

Q.8 Bond length of C-C in benzene is intermediate between single and double bonds, explain it.

Ans. X-rays analysis has shown that C-C bond length in benzene lies in between double and single bond. C-C double bond of benzene have intermediate properties of single and double bond.

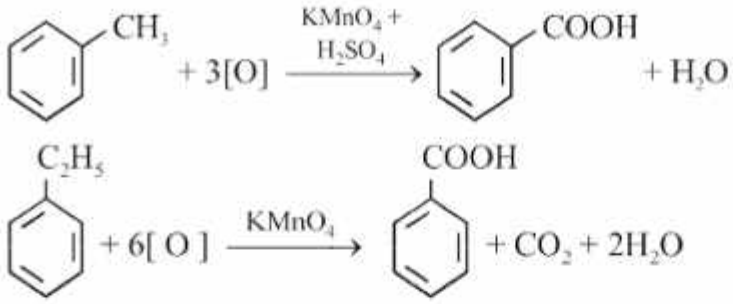
(i) In alkane C-C bond length is 1.54 Å.

(ii) In alkene C=C bond length is 1.34 Å.

(iii) In benzene C-C bond length is 1.397 Å.

Q.9 What products are formed by the oxidation of toluene and ethylbenzene in the presence of strong oxidizing agent?

Ans. In the presence of acidified $KMnO_4$ side chain of benzene oxidized to –COOH group irrespective to the number of carbon atoms in side chain.



Q.10 Halogens are more electronegative than carbon but halobenzenes have electron-donating effect, why?

Ans. According to electronegativity of halogens they should have electron withdrawing effect and meta directors. In actual practice, they have electron donating effect and ortho-para-directors due to resonance factor. Lone pairs present at halogen atom increases the electron density of benzene ring and activate the ring.