

Benzene

1. Aromatic Compounds : Main Source

Bituminous coal when subjected to destructive distillation in the absence of air [1000°–1200°C] the chief constituent obtained is coal tar.

Fractional distillation of coal tar : Different fractions are :

Fraction	Temperature	Main constituents
(a) Light oil	80 – 170°C	Benzene, toluene, xylene etc.
(b) Middle oil (carbolic oil)	170° – 230°C	Naphthalene, Phenol etc.
(c) Heavy oil	230° 270°C	Cresols, naphthalene
(d) Green oil	270° – 360°C	Anthracene
(e) Pitch	Residue	Carbon

2. Characteristic of Aromatic Compounds

[i] Aromatic compounds contain high percentage of carbon. They burn with smoky flame,

[ii] Aromatic compounds have the cyclic system and contain $(4n + 2)\pi$ electrons [Huckel rule].

Where $n = 0, 1, 2, 3, \dots$

Dipropylcyclopropenium perchlorate $n = 0$ 2π -electron


Benzene, pyridine, pyrrole, Furan, thiophen etc. $n = 1$ 6π -electron

Napthalene $n = 2$ 10π -electron

Anthracene $n = 3$ 14π -electron

Some Formulae of Benzene :

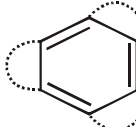
[a] Ladenberg's prism formula : 

[b] Claus-diagonal formula : 

[c] Dewar's parallel formula : 

[d] Armstrong and Baeyer's centric formula :



[e] Thiele's formula : 

Criteria for aromaticity :

Aromaticity means :

– **Unusual stability :**

Aromatic compounds are highly stable, as they have low heat of hydrogenation and low heat of combustion.

Compounds	Heat of hydrogenation (K.cal./mole)	Heat of Combustion (K.cal./mole)
Benzene	49.8	789.1
Cyclohexatriene	85.8	824.1

– Substitution reaction :

Aromatic compounds although contain double bond but give electrophilic substitution reaction (nitration, halogenation, sulphonation etc.)

– Resistant to oxidation :

Aromatic compounds are stable. Benzene ring is not affected by aq. KMnO_4 , HNO_3 etc.

Criteria : Mainly aromaticity is due to

- [i] Resonance energy
- [ii] Huckel rule
- [iii] Cyclic clouds of delocalised π -electrons

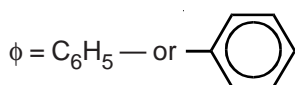
3. Few Groups

C_6H_5 – [Phenyl]

$\text{C}_6\text{H}_5\text{CH} <$ [Benzal] or [Benzylidene]

$\text{CH}_3 - \text{C}_6\text{H}_4$ – [o, m, p – Toly]

Few Compounds :



$\text{C}_6\text{H}_5\text{CH}_2$ – [Benzyl]

$\text{C}_6\text{H}_5\text{C} \equiv$ [Benzo] or [Benzylidyne]

Hydrocarbons :

$\phi - \text{CH}_3$

Toluene

$\phi - \text{C}(\text{CH}_3)_3$

t-Butyl benzene

$\phi - \text{C}_2\text{H}_5$

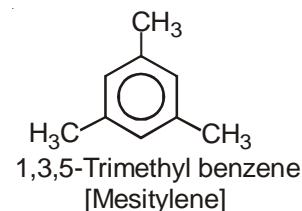
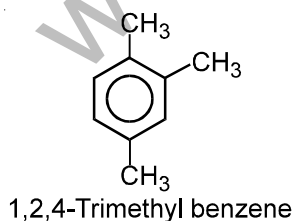
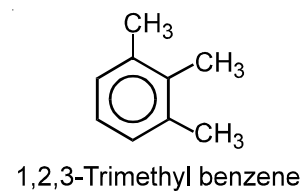
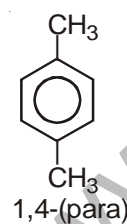
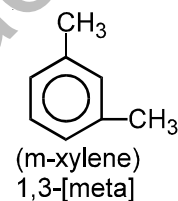
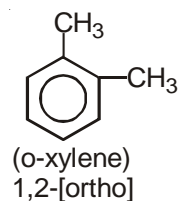
Ethyl benzene

$\phi - \text{CH}(\text{CH}_3)_2$

Isopropyl benzene

$\phi - \text{CH} = \text{CH}_2$

Vinyl benzene (Styrene)

**4. Benzene**

[i] **Discoverer :** Michael Faraday

[ii] C-hybridisation : sp^2

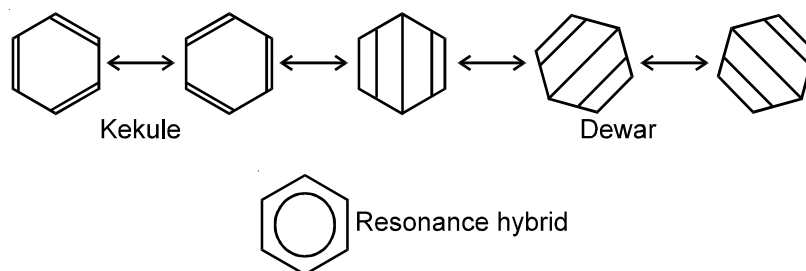
[iii] Geometry – Hexagonal

[iv] Bond angle : 120°

[v] C–C Bond length : 1.39 Å

[vi] C–H Bond length : 1.09 Å

[vii] Resonance in benzene :

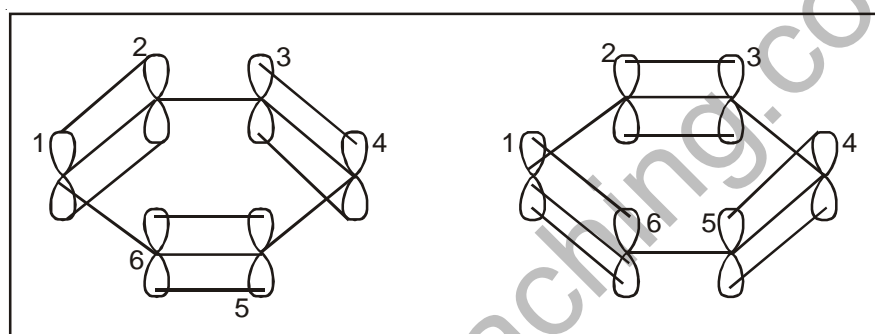


[ix] Number of angles of 120° : 18

[x] Localized and delocalized π -orbital

Localized π -orbital

Localized π -orbital

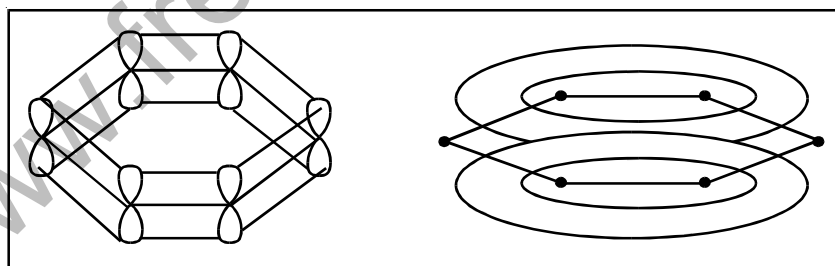


Partial overlapping
of p-orbital C_1-C_2 ,
 C_3-C_4 and C_5-C_6

Partial overlapping
of p-orbital C_2-C_3 ,
 C_4-C_5 and C_1-C_6

Obviously, each orbital formed in the partial overlapping is attracted by two carbon nucleus hence less stable.

Delocalized p-orbital :



4.1 Methods of Preparation of Benzene :

[1] Isolation From 'Light Oil Fraction – Industrial method :

In 'light oil', at least 60–65% benzene is present. Alkaline impurities (aniline, pyridine, quinolene, etc.) are removed by washing 'light oil' with cold and conc. H_2SO_4 . The acidic impurities are removed by washing with dilute NaOH solution. After that, NaOH is removed by washing with water. Three fractions are obtained at different temperature ranges by fractional distillation of the neutral sample of oil.

[i] 90% Benzol (90's benzol). $80-110^\circ$

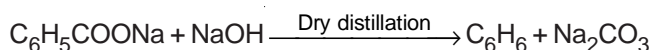
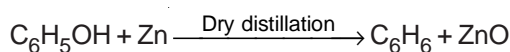
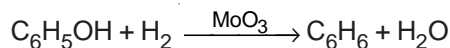
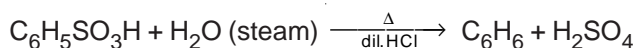
[ii] 50% Benzol (50's benzol). $110-140^\circ$

[iii] Solvent naphtha – $140^\circ-170^\circ$

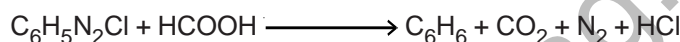
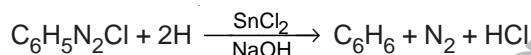
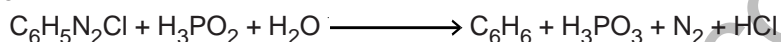
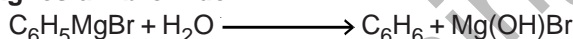
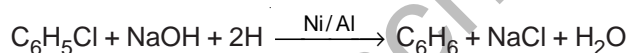
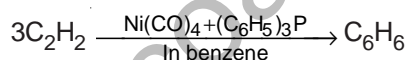
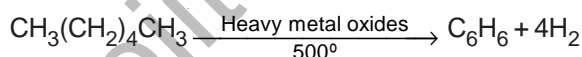
The 90% benzol contains about 70% benzene 24% toluene and remaining xylenes. Fractional distillation gives benzene at 80° , toluene at 110° and a mixture of all the three xylenes at $137-145^\circ$. Crystals are formed on cooling benzene from which pure benzene can be obtained by melting the crystals.

[2] Decarboxylation of Sodium Benzoate – Laboratory Method :

Benzene is formed on dry distillation of sodium benzoate with soda lime.

**[3] Reduction of Phenol :****[4] Reduction of Phenol – Fisher Method :****[5] Hydrolysis of Benzene sulphonic Acid :****[6] Reduction of Benzenediazonium Chloride :**

Hypophosphorus acid (H_3PO_2) or sodium stannite ($\text{SnCl}_2 + \text{NaOH}$) or formic acid can also be used for reduction in place of ethanol.

**[7] Hydrolysis of Phenylmagnesium bromide :****[8] Reduction of Chlorobenzene :****[9] Trimerisation of Acetylene :****[10] Hydroforming of n-Hexane :****4.2 Physical Properties :**

Benzene is a colourless liquid (boiling point, 80°), having a characteristic smell. It forms a colourless crystalline solid (melting point, 5.4°) on cooling. It burns with smoky or sooty flame. It is lighter than water (relative density, 0.8790) and is immiscible with water. Being nonpolar in nature. It is miscible with many organic solvents, like alcohol ether, acetone, acetic acid, carbon tetrachloride, carbon disulphide, etc.

4.3 Reaction :

Benzene is a compound having very low reactivity, because it remains unaffected by many common reagents, like HCl, KOH, NaOH, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc.

Benzene shows the following types of reactions :

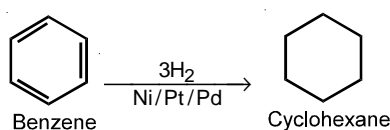
[a] Addition

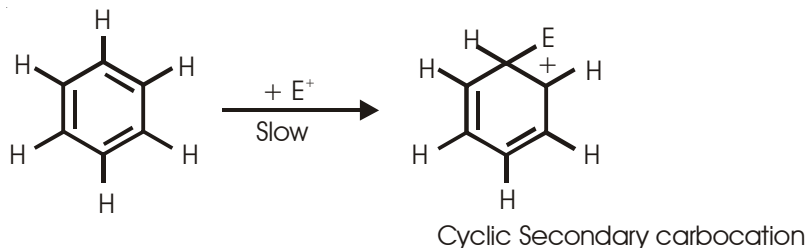
[b] Electrophilic substitution

[c] Oxidation

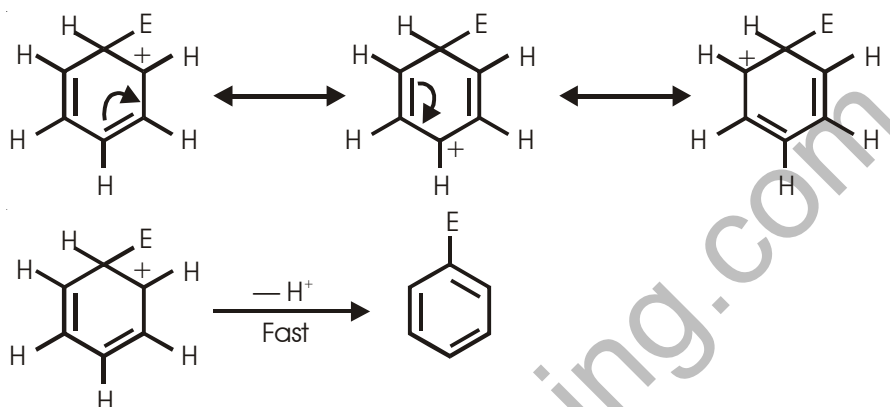
[d] Pyrolysis

[e] Pi complex formation

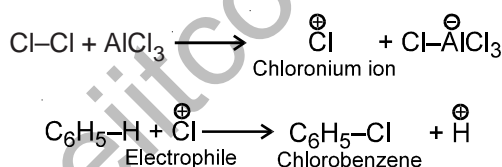
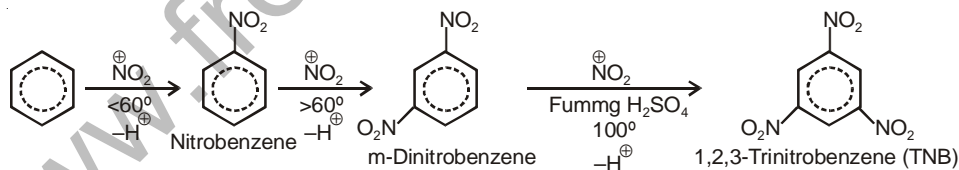
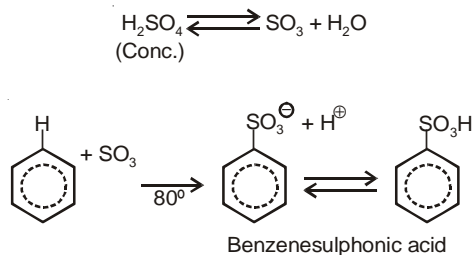
4.3.1 Addition Reaction :**1. Hydrogenation****[i] Catalytic Hydrogenation :**

Mechanism of Aromatic SE reaction :

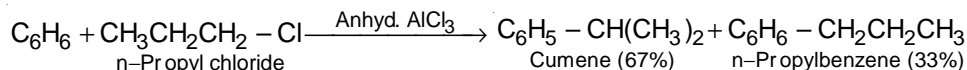
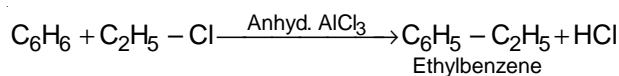
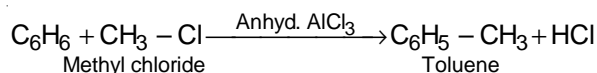
Cyclic secondary carboncation formed is satibilised by resonance.



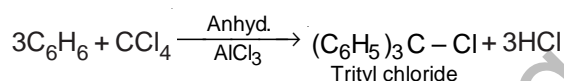
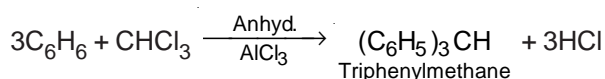
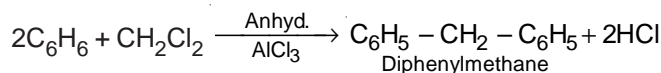
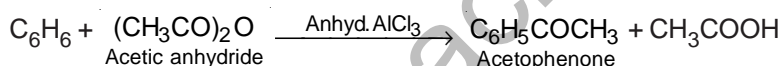
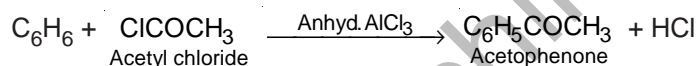
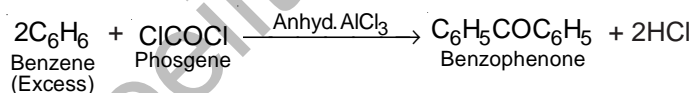
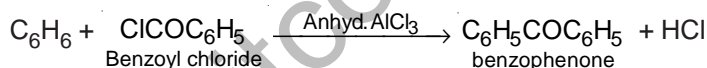
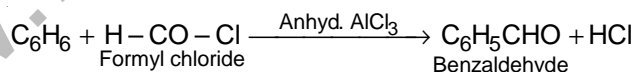
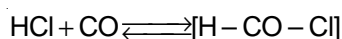
This is called as SE² mechanism i.e.; substitution electrophilic bimolecular reaction.

4. Halogenation :**5. Nitration :****6. Sulphonation :****7. Friedel-Crafts Reaction :**

Friedel-Crafts reaction involves replacement of hydrogen atom of an aromatic ring by a carbocation species obtained from a compound in the presence of anhydrous aluminium chloride. Friedel-Crafts reaction is always carried out in nitrobenzene (boiling point. 211°) medium and in the presence of anhydrous AlCl₃.

[i] Friedel-Crafts Alkylation :

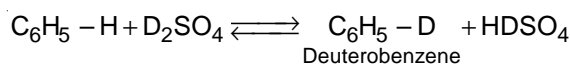
A mixture of cumene and n-propylbenzene is also obtained on taking propylene in place of n-propyl chloride in the above reaction.

**[ii] Friedel-Crafts Acylation :****[a] Acetylation :****[b] Benzoylation :****[iii] Formylation, or Gattermann-Koch Aldehyde Synthesis :**

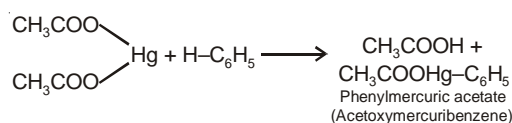
The above conversions can be carried out by taking many other compounds in place of anhydrous AlCl₃, e.g., FeCl₃, FeBr₃, SnCl₂, ZnCl₂, BF₃, etc.

8. Deuteration :

By using deuteriosulphuric acid a hydrogen atom of benzene can be substituted by deuterium.

**9. Mercuration :**

Benzene on heating with mercuric acetate forms **Acetoxymurcuribenzene**.

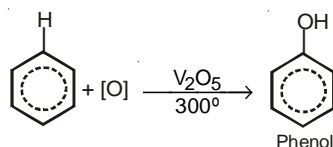


4.3.3 Oxidation :

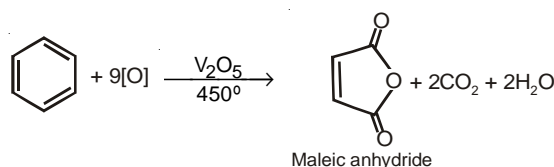
10. Catalytic Air Oxidation :

Oxidation of benzene by air in the presence of vanadium pentoxide can be carried out as follows :

[i] At 300° – Phenol is obtained as the major product

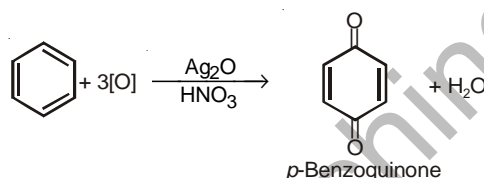


[ii] At 450° – Maleic anhydride is obtained as the major product.



11. Silver Oxide Oxidation :

Mainly *p*-benzoquinone is formed when oxidation of benzene is carried out by silver oxide and HNO₃.



12. Combustion :

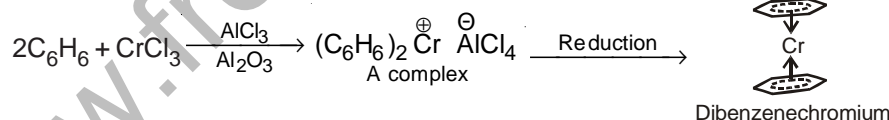


4.3.4 Catalytic Pyrolysis :

When the vapours of benzene are passed through red-hot copper or iron tube at 600° biphenyl is formed.

4.3.5 π Complex Formation :

A complex is obtained on heating benzene and chromic chloride with anhydrous AlCl₃ and Al₂O₃ at 180°, which on reduction forms dibenzenechromium (C₆H₅)₂Cr.



Dibenzenechromium is an organometallic compound.

Dibenzenechromium is a charge transfer complex or a π -complex or a sandwich compound. In this, electron charge of π clouds of two benzene rings is attracted towards the d-orbital of chromium atom. Here benzene behaves as a π base.

4.4 Uses of Benzene :

- [1] As an industrial solvent.
- [2] In dry cleaning.
- [3] As a constituent of power alcohol.
- [4] In the manufacture of an insecticide and pesticide.
- [5] In the manufacture of an explosive.
- [6] In the manufacture of dyes.
- [7] In the manufacture of medicines.
- [8] In the manufacture of perfumes.
- [9] In the synthesis of many aromatic compounds.
- [10] As a fuel.

5. Directive influence of substituent

(i) Directive influence of substituent 'S'

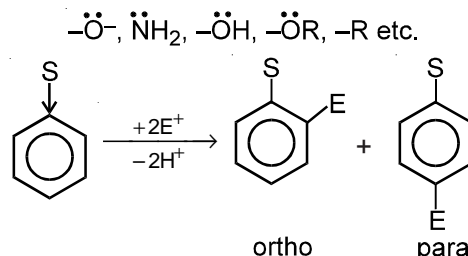
ϕ -S (Compound)

[i] S-Activates the benzene ring (Pumps in the electron density)

[ii] S-Exerts + M or + R effect

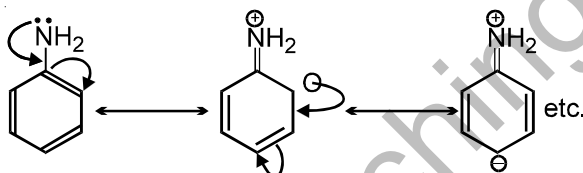
[iii] S-Either negatively charged or contains lone pair of electrons.

Examples :



Supposing S = NH_2

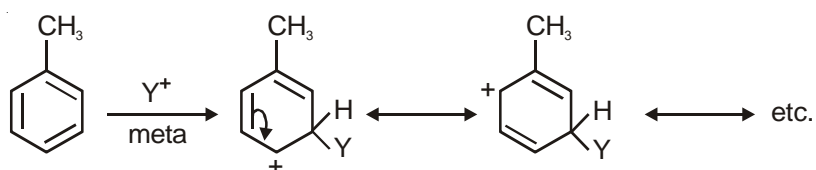
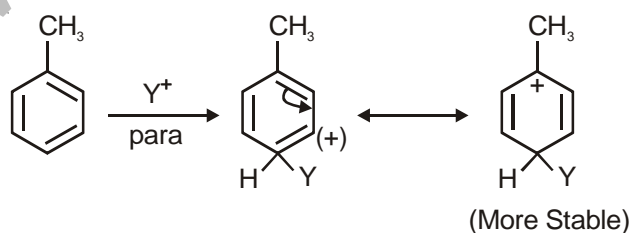
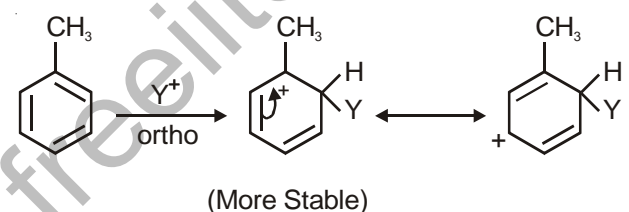
Lone pair of electrons present on the N-atom interact with delocalised p-orbital of benzene ring and increases the electron density at ortho and para positions. Obviously the electrophile attacks at o and p positions.



Decreasing order of o-, p-directing strength :

$-O^- > -NH_2 > -NHR > -NR_2 > -OH > -OR ; -NHCO > -COOR > -R > Ar > -X$

When an electrophile attacks at ortho and para positions of Toluene, the cyclic secondary carbocation formed is especially stable when compared with the carbocation formed by attack of electrophile at meta position.



In Toluene thus attack of electrophile takes place faster at ortho and para positions when compound with attack at meta position.

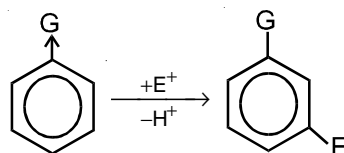
(ii) Directive influence of substituent 'G' ϕ -G (compound)

G-(m-directing)

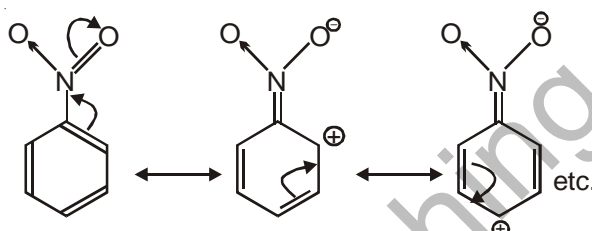
[i] G-Deactivates the ring [withdraws electron density]

[ii] G-Exerts -M or -R effect

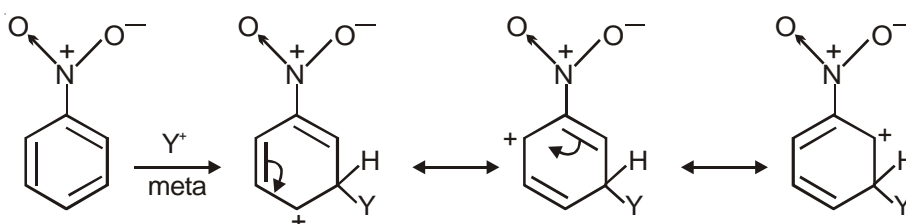
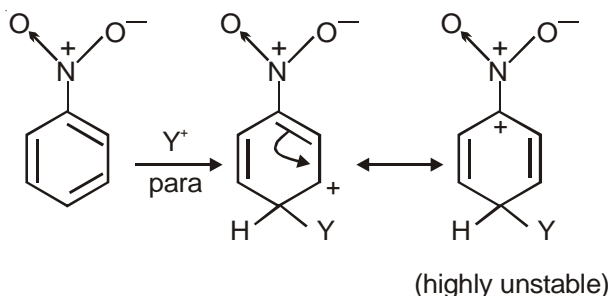
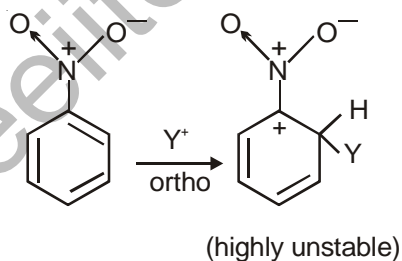
[iii] G-Either positively charged or electron attracting character.

Examples : $-\overset{\oplus}{\text{N}}\text{R}_3$, $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_2\text{OH}$, $-\text{CHO}$, $-\text{COOR}$ etc.

$-\text{NO}_2$, withdraws electron density from the benzene ring and makes the ortho and para positions as electron deficient centres. Obviously electrophile attacks at m-position, since it possesses a relatively high electron density.

**Decreasing order of m-directing strength :**
 $-\overset{\oplus}{\text{N}}\text{R}_3 > -\text{NO}_2 > -\text{CN} > -\text{SO}_2\text{OH} > -\text{CHO} > -\text{COR} > -\text{COOH} > -\text{COOR} > -\text{CONH}_2 > -\text{NH}_3$

When an electrophile attacks at meta position of nitrobenzene, the cyclic secondary carbocation formed is more stable than the carbocation formed by attack of electrophile at ortho and para position of nitrobenzene.



Toluene

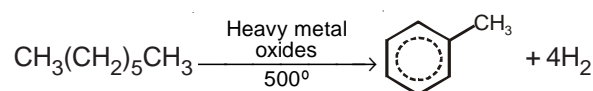
6. Toluene, $C_6H_5CH_3$

6.1 Methods of Preparation

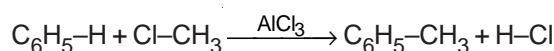
1. From 'Light Oil' Fraction – Industrial Method :

Toluene fraction can be collected by distillation at 110° after separation of benzene from 90% benzol.

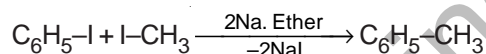
2. By Hydroforming of *n*-Heptane :



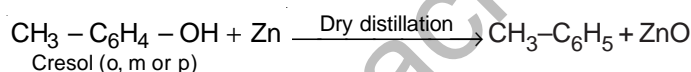
3. By Friedel–Crafts Methylation of Benzene :



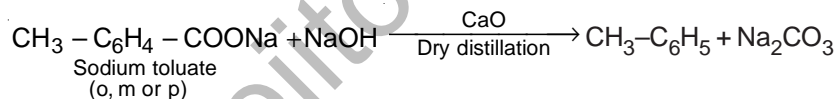
4. By Wurtz–Fitting Reaction :



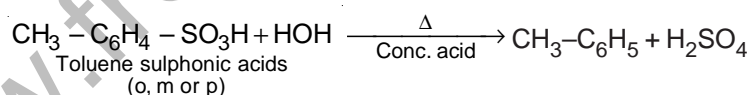
5. By Dehydroxylation of Cresols :



6. By Decarboxylation of Toluic Acids :



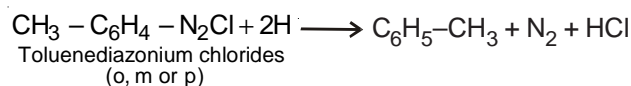
7. By Hydrolysis of Toluene Sulphonic Acids :



8. By Reduction of Benzyl Chloride :



9. By Reduction of Toluenediazonium Chlorides :



Ethanol, hypophosphorous acid (H_3PO_2), sodium stannite ($SnCl_2 + NaOH$) or formic acid can be used as the reducing agents.

6.2 Physical Properties :

Toluene is a colourless liquid (boiling point 111°). It has benzene-like smell. It is lighter than water and immiscible with water. It is miscible with organic solvents, like alcohol, ether, benzene, etc. It also burns like benzene with smoky and sooty flame.

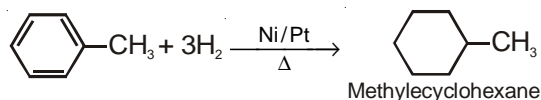
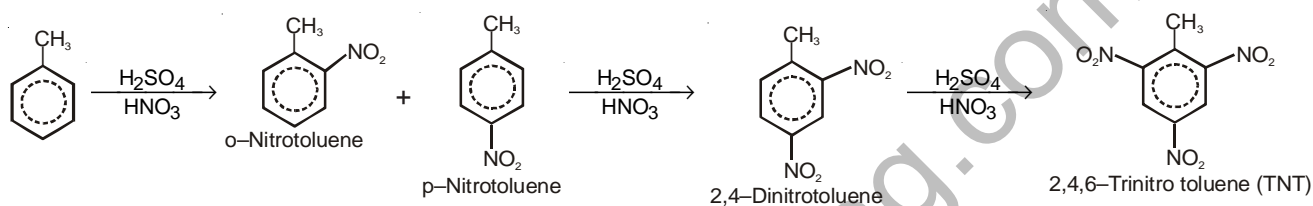
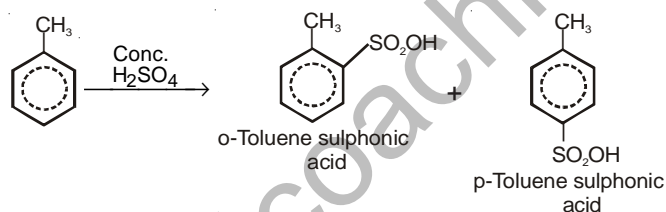
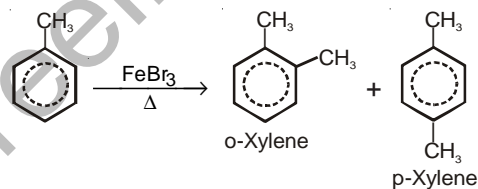
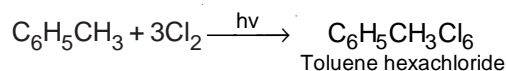
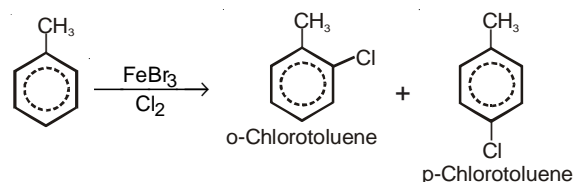
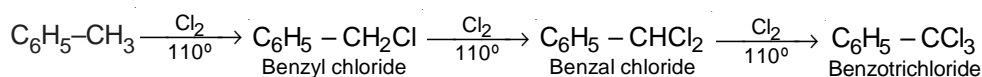
6.3 Reactions :

The following three types of reactions are shown by Toluene :

[A] Reactions due to benzene nucleus.

[B] Reactions due to methyl side chain.

[C] Reactions due to whole molecule (Combustion)

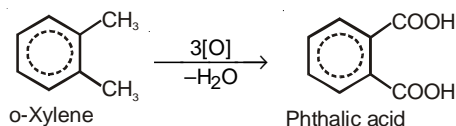
6.3.1 Reactions Due to Benzene Nucleus :**1. Catalytic Hydrogenation :****2. Nitration :****3. Sulphonation :****4. Alkylation :****5. Free Radical Nuclear Additive Chlorination :****6. Nuclear Electrophilic Substitutive Chlorination :****6.3.2 Reactions Due to Methyl Side Chain :****7. Free Radical Side Chain Substitutive Chlorination :**

8. Oxidation :

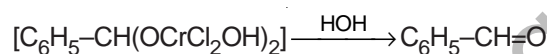
Benzoic acid is obtained on oxidation of toluene by **alkaline permanganate** or **acidified dichromate** or **dilute nitric acid**.



If more than one side chain is present, then the same number of COOH groups will be formed for example, phthalic acid is formed from o-xylene.

**9. Etard's Reaction :**

A complex is formed by the reaction of toluene and chromyl chloride in carbon tetrachloride solution. This complex gives benzaldehyde on hydrolysis.

**6.3.3 Reaction due to Whole Molecule :****10. Combustion :****6.4 Uses :**

- [1] As a constituent of aviation gasoline.
- [2] As a solvent.
- [3] In the manufacture of explosive.
- [4] In the manufacture of dyes.
- [5] In the manufacture of medicines.
- [6] In the manufacture of perfumes.
- [7] In the synthesis of many aromatic compounds.