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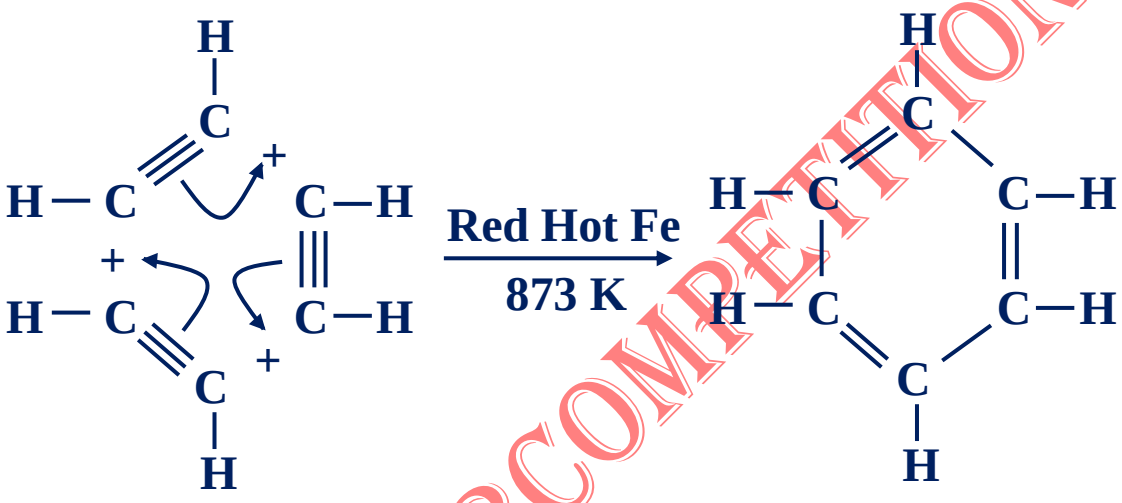
Aromatic Hydrocarbons

Benzene

Preparation Methods of Benzene

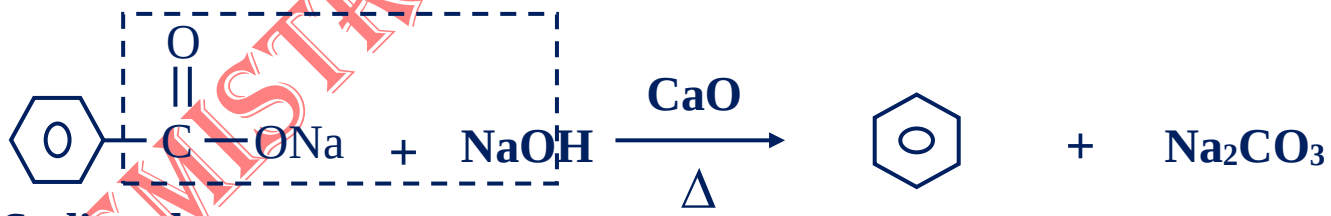
Benzene is an aromatic hydrocarbon that is commercially isolated from coal tar. It can be prepared in the laboratory by the following methods-

(1)By Cyclic Polymerization of Ethyne- When ethyne is passed through red hot iron tube at 873K temperature, it undergoes cyclic polymerization to form benzene. This reaction is also called aromatization.



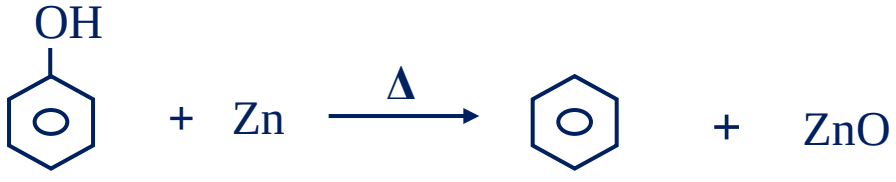
Ethyne (3 Molecules) → Benzene

(2)By Decarboxylation of Sodium benzoate- When Sodium salt of benzoic acid (Sodium benzoate) is heated with sodalime, it undergoes decarboxylation to form benzene.



Sodium benzoate → Benzene + Na_2CO_3

(3)By Reduction of phenol- When vapours of phenol is passed over heated zinc dust, it gets reduced to form benzene.



Phenol → Benzene + ZnO

Properties of Benzene

(a)Physical Properties

(1)Benzene is a colourless liquids with a characteristic aroma.
(2) It is immiscible with water, but is readily miscible with organic solvents.
(3) Like other aromatic compounds, it burns with sooty flame.

(b)Chemical Properties

Electrophilic substitution reactions are the most common reaction of benzene and its derivatives. However, under special conditions they give addition and oxidation reactions.

(A)Electrophilic substitution reactions

(1)Halogenation-When benzene is reacted with halogens (Cl_2 or Br_2) in the presence of a halogen carrier such as Fe, $FeCl_3$, $FeBr_3$ or $AlCl_3$, it undergoes halogenation to form haloarenes.

Benzene **Chlorobenzene**

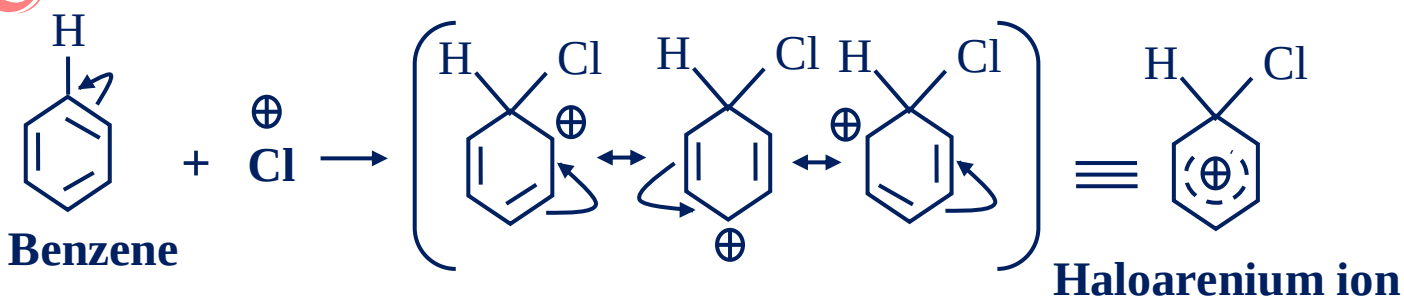
In this reaction $FeCl_3$ acts like Lewis acid and produces electrophile for the reaction.

Mechanism- It is an example of electrophilic substitution reaction and occurs in following three steps-

(1)Generation of Electrophile- First, Lewis acid ($FeCl_3$) attacks on halogen molecule to produce halonium ion (electrophile).

Chloronium ion

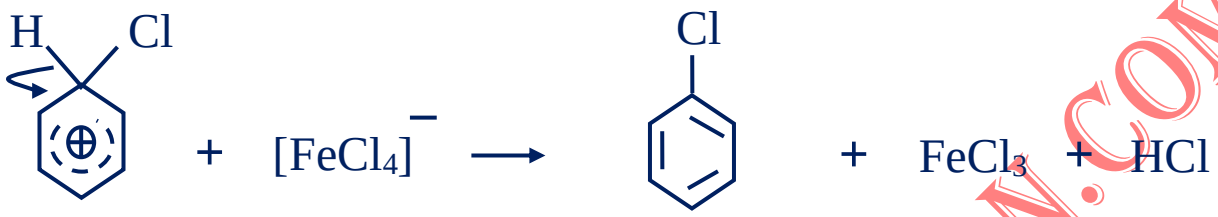
(2)Formation of Carbocation (Arenium ion)- In this step, halonium ion (electrophile) attacks on benzene ring to form resonance stabilized haloarenium ion (σ-complex) as reaction intermediate where, one of the carbon atoms of benzene ring is sp^3 hybridized.



Benzene **Haloarenium ion**

Here, sigma complex or haloarenium ion loses its aromatic character, because the delocalisation of π- electrons gets stopped at sp^3 hybridised carbon atom.

(3)Subtraction of proton from Haloarenium ion- Finally, $[FeCl_4]^-$ formed in first step subtracts a proton from sp^3 hybridised carbon atom of haloarenium ion to form halobenzene where, the aromatic character of benzene ring is restored.

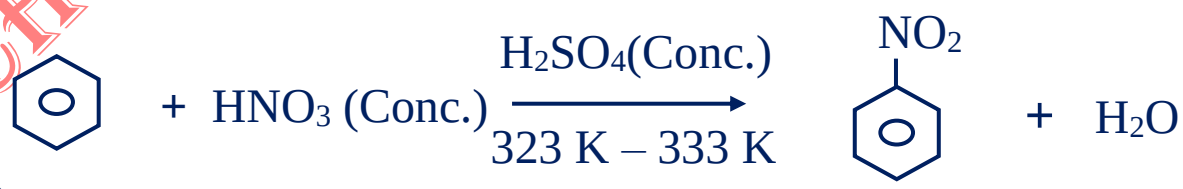


Haloarenium ion **Chlorobenzene**

If excess of electrophilic reagent is used, then further substitution reaction may take place, where other hydrogen atoms of benzene ring get successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ give hexachlorobenzene (C_6Cl_6) by its excessive chlorination.

Benzene **Hexachlorobenzene**

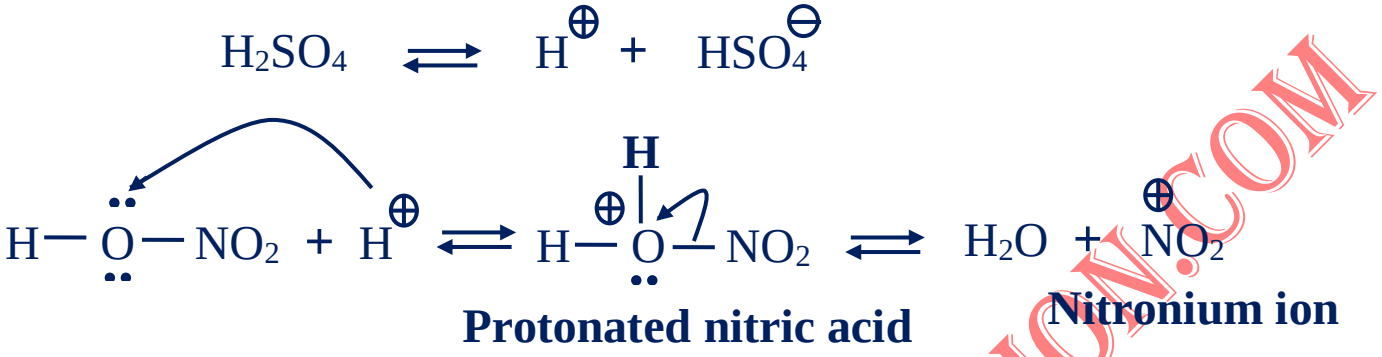
(2)Nitration- When benzene is reacted with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture) at about 323 K temperature, it undergoes nitration to form nitrobenzene.



Benzene **Nitrobenzene**

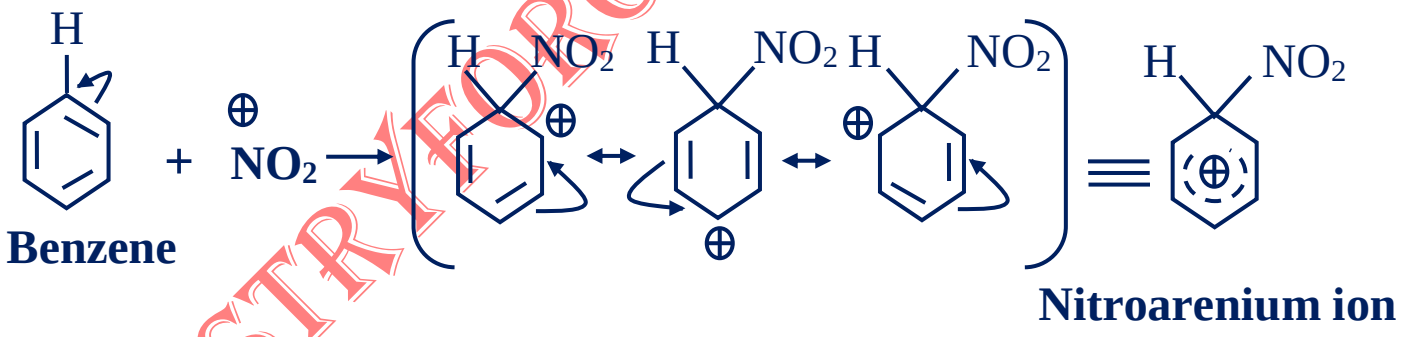
Mechanism- It is an example of electrophilic substitution reaction and occurs in following three steps-

(1)Generation of Electrophile- First, electrophile i.e. nitronium ion (NO_2^+) is produced by transfer of proton from sulphuric acid to nitric acid.



It is clear that, in nitrating mixture, sulphuric acid acts like Bronsted acid (gives proton) while, nitric acid acts like Bronsted base (takes proton) as well as Lewis base (gives lone pair of electron for protonation). Thus, it is a simple acid-base equilibrium.

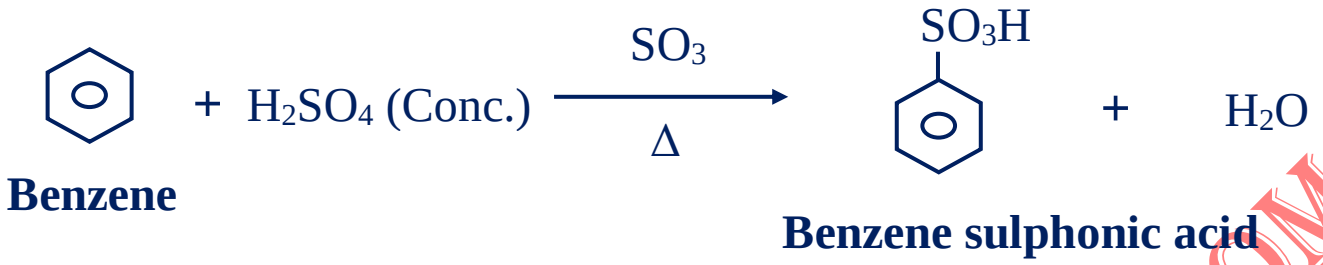
(2)Formation of Carbocation (Arenium ion)- In this step, nitronium ion (electrophile) attacks on benzene ring to form resonance stabilized nitroarenium ion (σ-complex) as reaction intermediate where, one of the carbon atoms of benzene ring is sp^3 hybridized.



Here, sigma complex or nitoarenium ion loses its aromatic character because the delocalisation of π- electrons gets stopped at sp^3 hybridised carbon atom.

(3)Subtraction of proton from Haloarenium ion- Finally, HSO_4^- formed in first step subtracts a proton from sp^3 hybridised carbon atom of nitroarenium ion to form nitobenzene where, the aromatic character of benzene ring is restored.

(4)Sulphonation-When benzene is heated with fuming sulphuric acid (conc. $H_2SO_4 + SO_3$), it undergoes sulphonation to form benzene sulphonic acid.



Benzene **Benzene sulphonic acid**

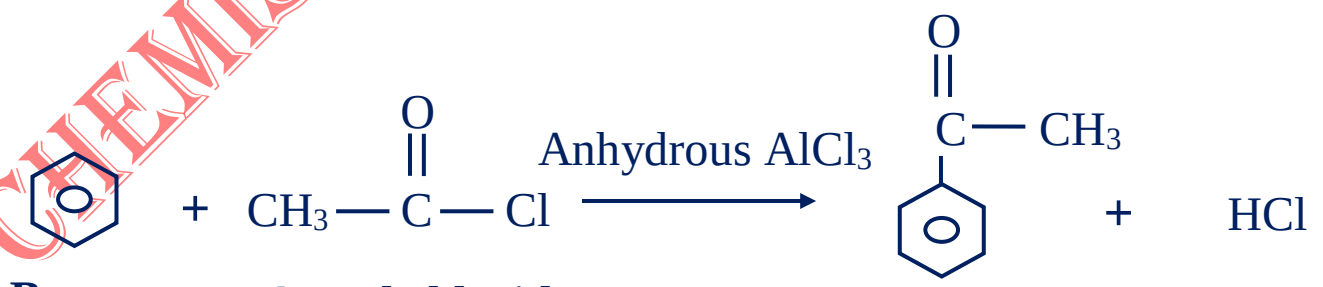
It is also an example of electrophilic substitution reaction where, SO_3 acts like electrophile.

(5)Friedel-Craft's Reaction-When benzene is reacted with alkyl halides in presence of anhydrous $AlCl_3$, alkyl benzene is obtained. This reaction is called Friedel-Craft's alkylation.

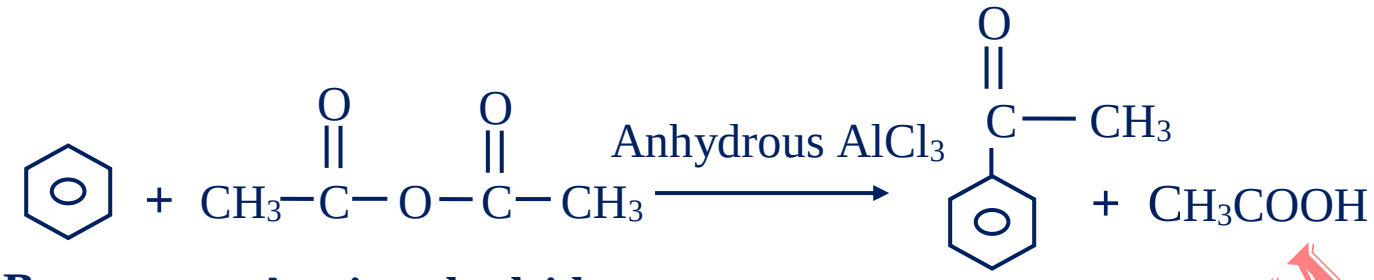
Benzene **Methyl chloride** **Methyl benzene**

It is also an example of electrophilic substitution reaction where, alkyl carbonium ions (CH_3^+) acts like electrophile.

Similarly, when benzene is reacted with acid halides or acid anhydrides in presence of anhydrous $AlCl_3$, acyl benzene is obtained. This reaction is called Friedel-Craft's acylation.



Benzene **Acetyl chloride** **Acetophenone**

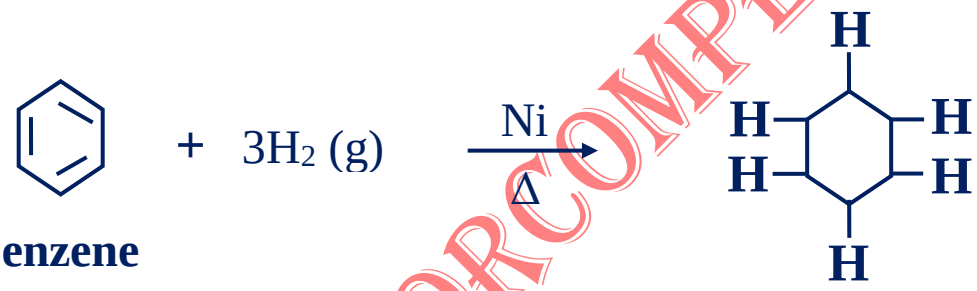


Benzene **Acetic anhydride** **Acetophenone**

It is also an example of electrophilic substitution reaction where, acylium ion (CH_3-C^+=O) acts like electrophile.

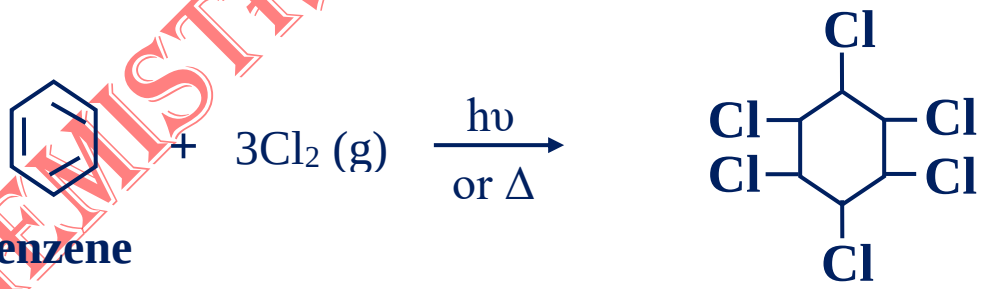
(B) Addition Reactions

(1)Hydrogenation-When benzene is reacted with hydrogen under vigorous conditions, *i.e.*, at high temperature and pressure in the presence of nickel catalyst, it undergoes hydrogenation to form cyclohexane.



Benzene **Cyclohexane**

(2)Addition of Chlorine-When benzene is reacted with chlorine in presence of uv light or at 500 K temperature, benzene hexachloride (BHC) is obtained.



Benzene

Benzene hexachloride
or
Gammexane or Lindane

Benzene hexachloride is a powerful insecticide and is sold under commercial name Gammaxane, Lindane or 666.

(C)Combustion-On heating in air, benzene burns with sooty flame producing CO_2 and H_2O.

$$C_6H_6 + \frac{15}{2} O_2\,(g) \xrightarrow{\Delta} 6CO_2 + 3H_2O\,(g)$$