

Benzene (C₆H₆).

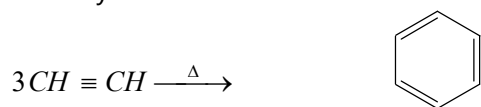
Benzene is the first member of arenes. It was first discovered by Faraday (1825) from whale oil. Mitscherlich (1833) obtained it by distilling benzoic acid with lime. Hofmann (1845) obtained it from coal tar, which is still a commercial source of benzene.

(1) **Structure of benzene:** Benzene has a special structure, which is although unsaturated even then it generally behave as a saturated compound.

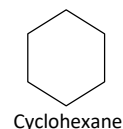
(i) **Kekule's structure:** According to Kekule, in benzene 6-carbon atoms placed at corner of hexagon and bonded with hydrogen and double bond present at alternate position.

(a) Evidence in favour of Kekule's structure

- Benzene combines with 3 molecules of hydrogen or three molecules of chlorine. It also combines with 3 molecules of ozone to form triozone. These reactions confirm the presence of three double bonds.
- Studies on magnetic rotation spectroscopy show the presence of three double bonds.
- The synthesis of benzene from three molecule of acetylene also favour'sKekule's structure.



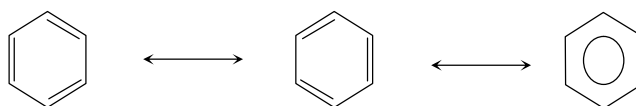
- Benzene gives cyclohexane by reduction by hydrogen. $C_6H_6 + 3H_2 \xrightarrow{Ni} C_6H_{12}$



(b) Objections against Kekule's formula

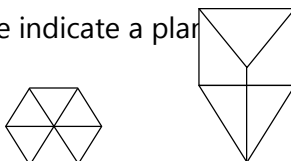
- Unusual stability of benzene.
- According to Kekule, two ortho disubstituted products are possible. But in practice only one ortho disubstituted product is known.
- Heat of hydrogenation of benzene is 49.8 kcal/mole, whereas theoretical value of heat of hydrogenation of benzene is 85.8 kcal/mole. It means resonance energy is 36 kcal/mole.
- C – C bond length in benzene are equal, although it contains 3 double bonds and 3 single bonds.

Kekule explained this objection by proposing that double bonds in benzene ring were continuously oscillating between two adjacent positions.

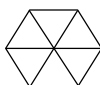


(ii) **Some other structures of benzene**

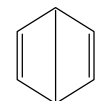
(a) Ladenberg's prism formula: This formula shows benzene three dimensional structure where X-ray studies of benzene molecule indicate a planar



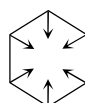
(b) Claus diagonal formula:



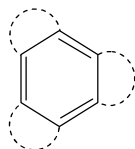
(c) Dewar's parallel formula:



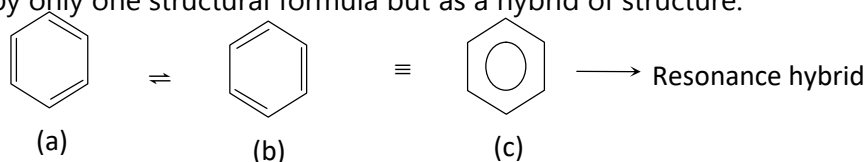
(d) Armstrong and Baeyer's centric formula:



(e) Thiele's formula:



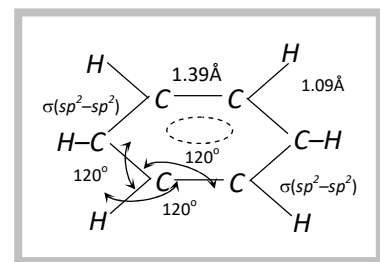
(iii) **Valence bond theory** [Resonance theory] : According to this theory, benzene cannot be represented by only one structural formula but as a hybrid of structure.



The resonance hybrid structure of benzene explain all the properties of benzene. The resonance structure of benzene is supported by the following facts,

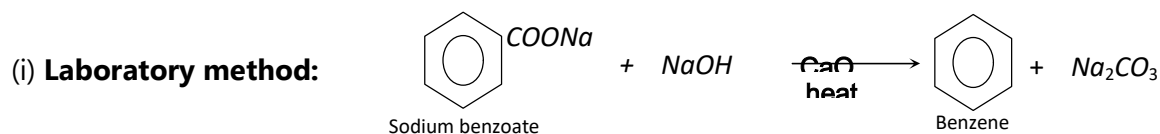
(a) The $C - C$ bond length in benzene is 139 pm which is intermediate between bond lengths for $C - C$ bond (154 pm) and $C = C$ (134 pm).

(b) Due to resonance the π electron charge in benzene get distributed over greater area. As a result of delocalisation the energy of resonance hybrid decrease as compared to contributing structure by about 50 kJ/mole . The decrease in energy is called resonance energy.

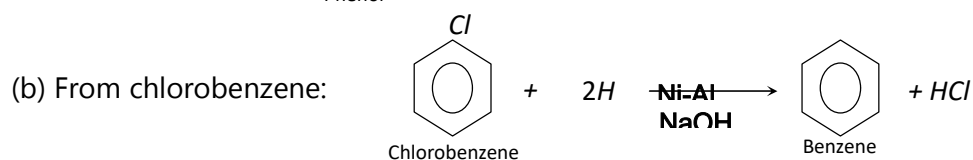
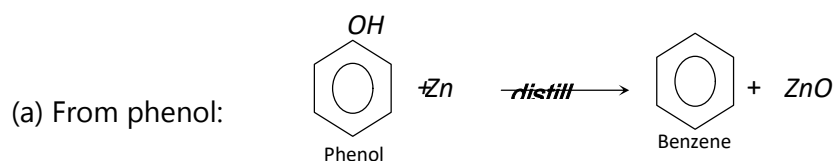


(iv) **M.O.T.** [Modern concept]: According to the orbital concept each carbon atom in benzene is sp^2 hybridised and one orbital remains unhybridised. Out of three hybrid orbitals two overlap with neighbouring carbon atoms and third hybrid orbital overlap with hydrogen atom for σ bonds. Thus benzene has a planar structure with bond angle of 120° each.

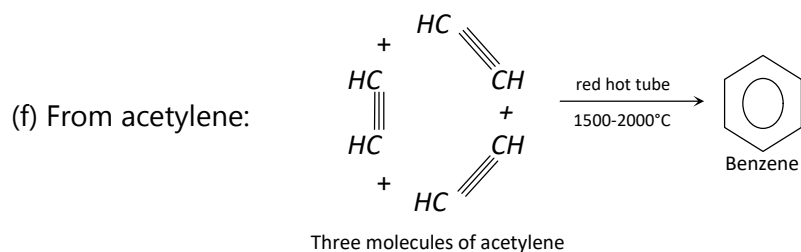
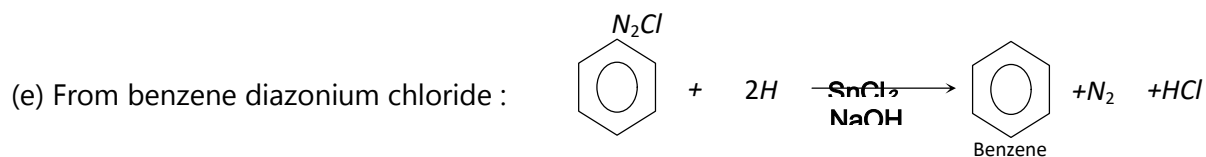
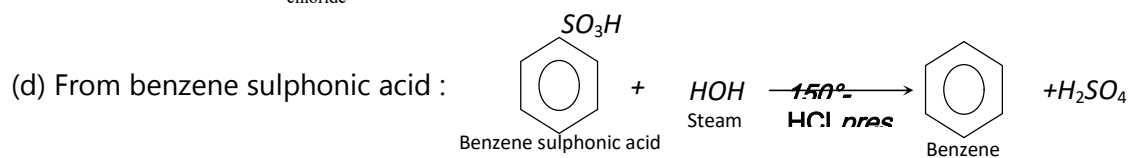
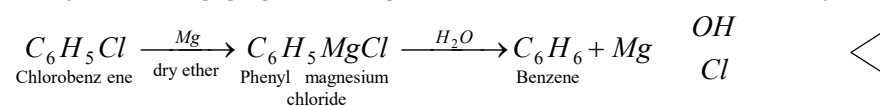
(2) Methods of preparation of benzene



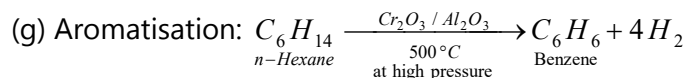
(ii) From benzene derivatives



(c) By preparing grignard reagent of chlorobenzene and then hydrolyzed



Note: Cyclic polymerization takes place in this reaction.



(3) Properties of benzene

(i) Physical properties

- (a) Benzene is a colorless, mobile and volatile liquid. Its boiling point is 80°C and freezing point is 5.5°C. It has characteristic odour.
- (b) It is highly inflammable and burns with sooty flame.
- (c) It is lighter than water. Its specific gravity at 20°C is 0.8788.
- (d) It is immiscible with water but miscible with organic solvents such as alcohol and ether.
- (e) Benzene itself is a good solvent. Fats, resins, rubber, etc. dissolve in it.
- (f) It is a non-polar compound and its dipole moment is zero.
- (g) It is an extremely poisonous substance. Inhalation of vapours or absorption through skin has a toxic effect.

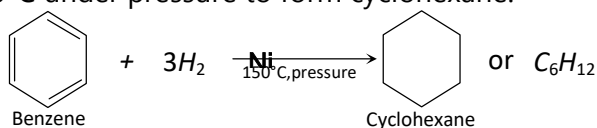
(ii) **Chemical properties:** Due to the presence of π electron clouds above and below the plane benzene ring, the ring serves as a source of electrons and is easily attacked by electrophiles (Electron loving reagents). Hence electrophilic substitution reaction are the characteristic reactions of aromatic compounds.

Substitution reactions in benzene rather than addition are due to the fact that in the former reactions resonance stabilized benzene ring system is retained while the addition reactions lead to the destruction of benzene ring. Principal reactions of benzene can be studied under three heads,

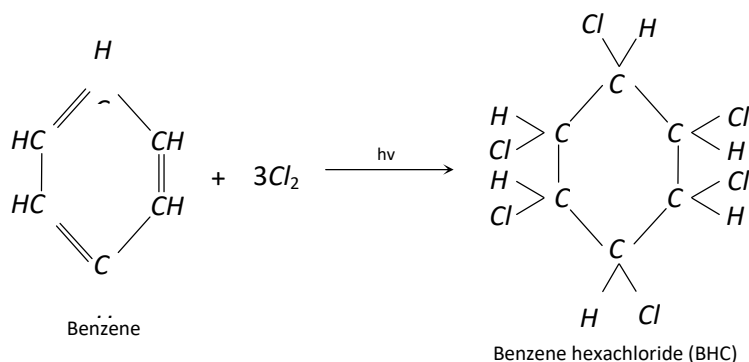
(a) Addition reactions (b) Substitution reactions (c) Oxidation reactions

(a) Addition reactions: In which benzene behaves like unsaturated hydrocarbon.

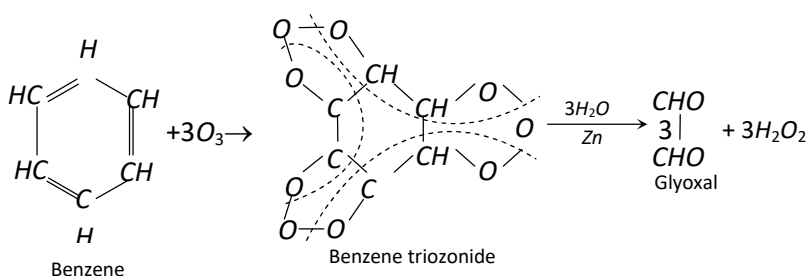
• Addition of hydrogen: Benzene reacts with hydrogen in the presence of nickel (or platinum) catalyst at 150°C under pressure to form cyclohexane.



- Addition of halogen :



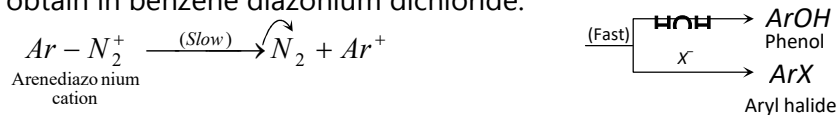
- Addition of ozone:



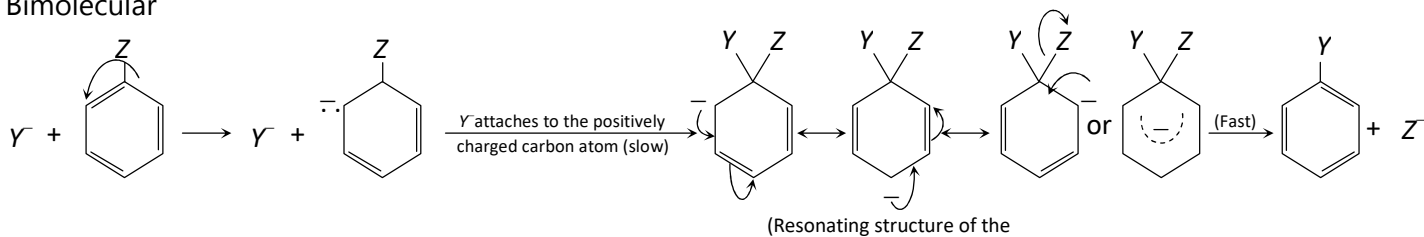
(b) Substitution reactions

- Nucleophilic mechanism

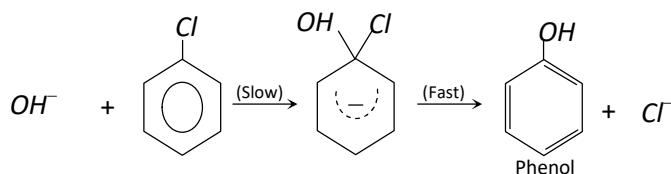
- Unimolecular: Mostly uncommon in aromatic substitution, there is only one example which obtain in benzene diazonium dichloride.



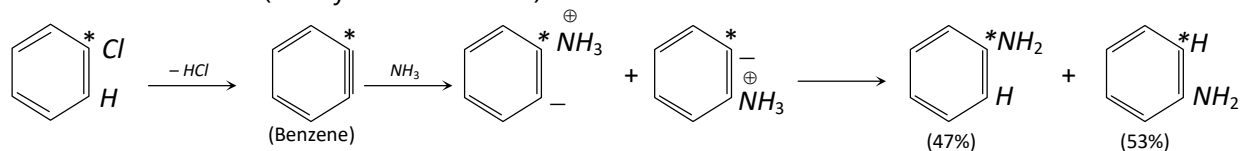
- Bimolecular



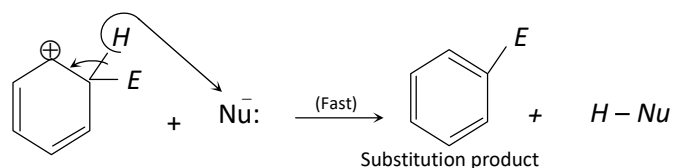
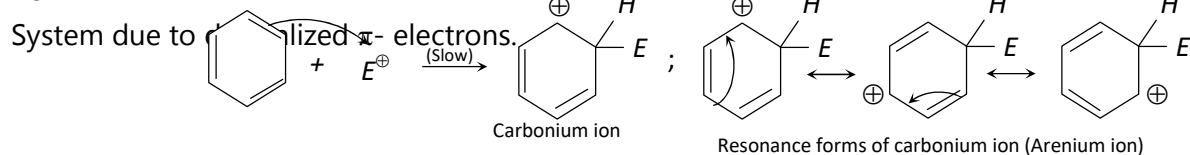
Example:



- Elimination-addition mechanism (Benzyne mechanism)

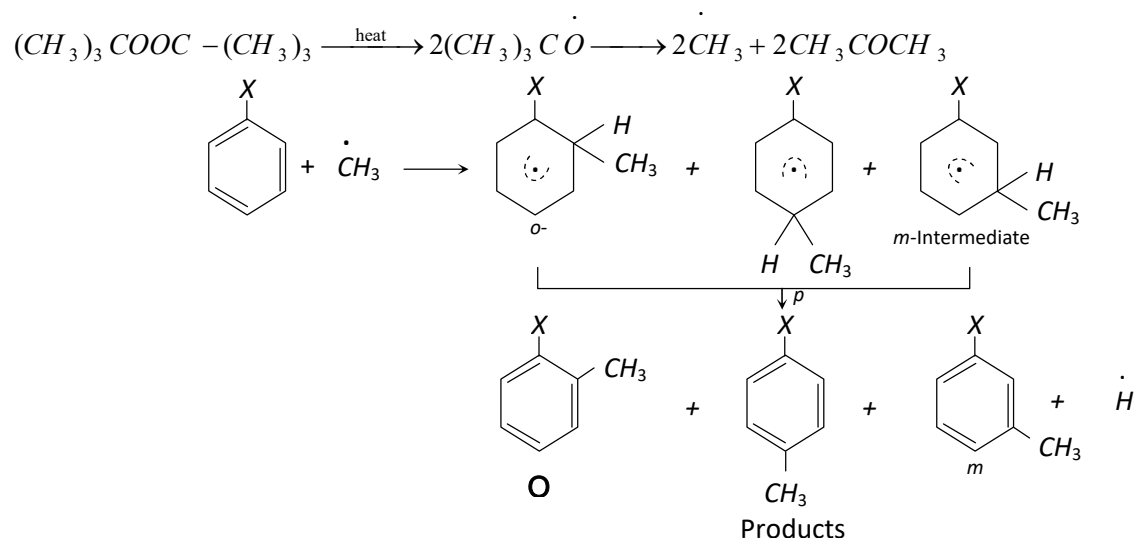


- Electrophilic substitution reaction: Benzene undergoes this reaction because it is an electron rich

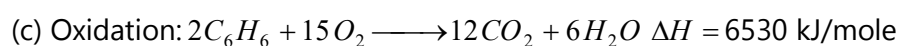
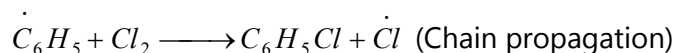
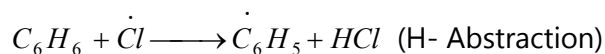
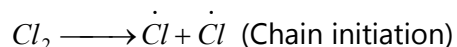


Electrophile (E^{\oplus})	Name	Source	Name of substitution reaction
Cl^+	Chloronium	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+	Bromonium	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
NO_2^+	Nitronium	$HNO_3 + H_2SO_4$	Nitration
SO_3	Sulphur trioxide	Conc. H_2SO_4 , Fuming sulphuric acid	Sulphonation
R^+	Alkyl carbonium	$RX + AlX_3$ ($X = Cl$ or Br), $ROH + H^+$	Friedel-Craft's (Alkylation)
$R-C^+=O$	Acyl carbonium	$RCOCl + AlCl_3$	Friedel-Craft's (Acylation)

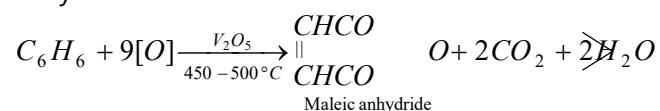
•Free radical aromatic substitution: The aromatic substitution reactions which follow free radical mechanisms are very few and have limited synthetic value. But some typical example of these reactions are:



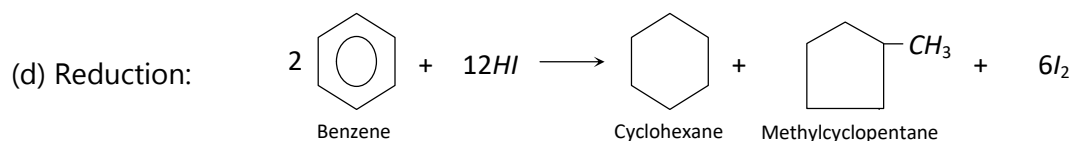
The mechanism of chlorination of benzene at high temperature is similar to that of the free radical aliphatic substitution



When vapours of benzene and air are passed over vanadium pentoxide at 450 – 500°C, maleic anhydride is obtained.



Note: Strong oxidising agents converts benzene slowly into CO_2 and water on heating.



(iii) **Uses:**(a) In dry cleaning (b) As a motor fuel when mixed with petrol. (c) As a solvent. (d) In the manufacture of gammexane (As insecticide). (e) In the preparation of nitrobenzene, chlorobenzene, benzene sulphonic acid, aniline, styrene, etc. Many of these are employed for making dyes, drugs, plastics, insecticides, etc.