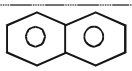
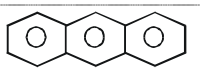
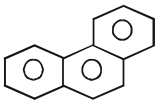
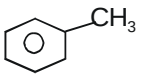
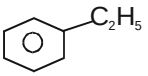
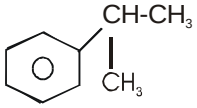
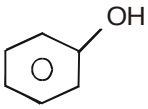
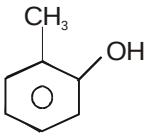
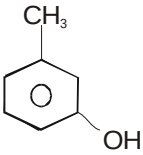
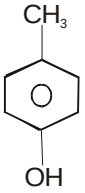
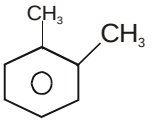
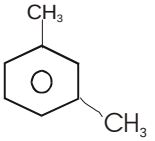
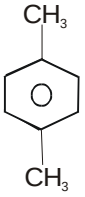
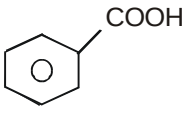
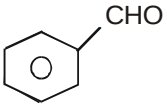
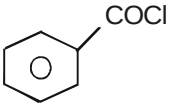
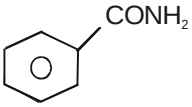
13. ORGANIC CHEMISTRY

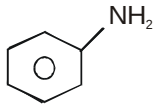
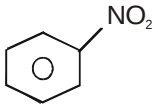
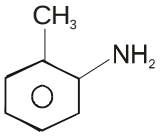
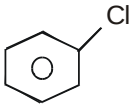
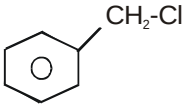
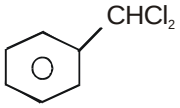
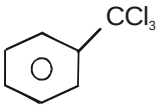
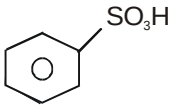
V) AROMATIC HYDROCARBONS (BENZENE)

- Benzene is the parent member of Aromatic compounds.
- The compounds which resemble benzene in structure and properties are called aromatic compounds.
- Aroma means fragrant smell (pleasant smell)
- Benzene was discovered by Faraday from illuminating gas cylinders
- Mitcherlich proposed the name benzene for it.
- Kekule discovered the structure of benzene.
- General molecular formula of monocyclic aromatic hydro carbons is C_nH_{2n-6}

Name of Aromatic compounds:

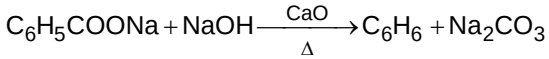
Common names of aromatic compounds are very popular than IUPAC names

 Benzene	 Napthalene	 Anthracene
 Phenanthrene	 Toulene	 Ethyl benzene
 Isopropyl Benzene	 Phenol	 O-Cresol
 m – cresol	 p - cresol	 o - xylene
 m - xylene	 p - xylene	 benzoic acid
 Benzeldehyde	 Benzoylchloride	 Benzamide

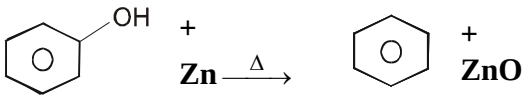
 Aniline	 Nitro benzene	 O–methylaniline
 Chlorobenzene	 Benzyl chloride	 benzal chloride
 Benzotrichloride	 benzene sulphonic acid	

Methods of preparation of benzene :

1. Decarboxylation of sodium salt of benzoic acid :



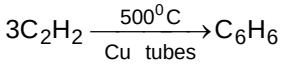
2. Reduction of phenol :



3. Hydrolysis of benzene sulphonic acid

$C_6H_5 - SO_3H + HOH \rightarrow C_6H_6 + H_2SO_4$

4. Polymerisation of Acetylene :



In the trimerisation of benzene, three pi bonds are broken and 3 sigma bonds are formed.

5. **Commercial preparation of Benzene :**

Benzene is prepared on large scale from coal.

Coal on destructive distillation gives 1. Coal gas 2. Coal tar 3. Ammoniacal liquor 4. Solid coke

Coal tar is black, viscous, oily liquid with unpleasant smell. Coal tar is separated from other 3 fractions and subjected to fractional distillation. The fractions collected at different temperatures and the aromatic compounds present in the respective fractions are

Light oil or crude naptha	upto 170^0C	Benzene, Toulene, xylene
Middle oil or carbolic oil	170 - 230^0C	Napthalene, Phenol, Pyridine
Heavy oil or cresote oil	230 – 270^0C	Napthalene, Cresol
Anthracene oil or green oil	270 – 400^0C	Anthracene, Phenanthrene

Residue left is called pitch and it is used in road making and varnishes.

- Light oil fraction is treated with H_2SO_4 to remove basic impurities like pyridine and then with NaOH to remove acidic impurities like phenol, cresol etc.

- Light oil fraction on further fractional distillation gives
  1) 1st fraction at 110^0C
  2) 2nd fraction upto 140^0C
- These two fractions are remixed and further distilled to give benzene between 80^0C – 81^0C.

Physical properties of benzene:

- It is colorless liquid with pleasant smell
- It's B.P. is 80^0C
- It is lighter than water.
- It is insoluble in water but soluble in alcohol, ether etc.
- It burns with sooty flame due to high percentage of carbon.

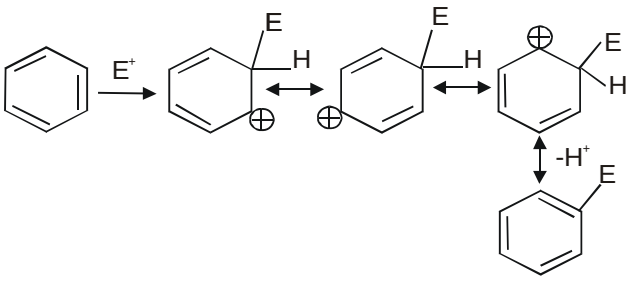
Chemical Reactions of benzene :

- Benzene is highly unsaturated, but it is less reactive because the benzene ring is stabilised by resonance.
- Benzene is expected to give normal addition reaction due to unsaturation. Because of unusual stability caused by resonance, it normally gives substitution reactions rather than addition reactions. Due to the presence of π - electron cloud, benzene ring easily attracts electrophilies.
- Thus, benzene normally gives electrophilic substitution reactions and under special conditions it also gives certain addition reactions.

Electrophilic substitution reactions:

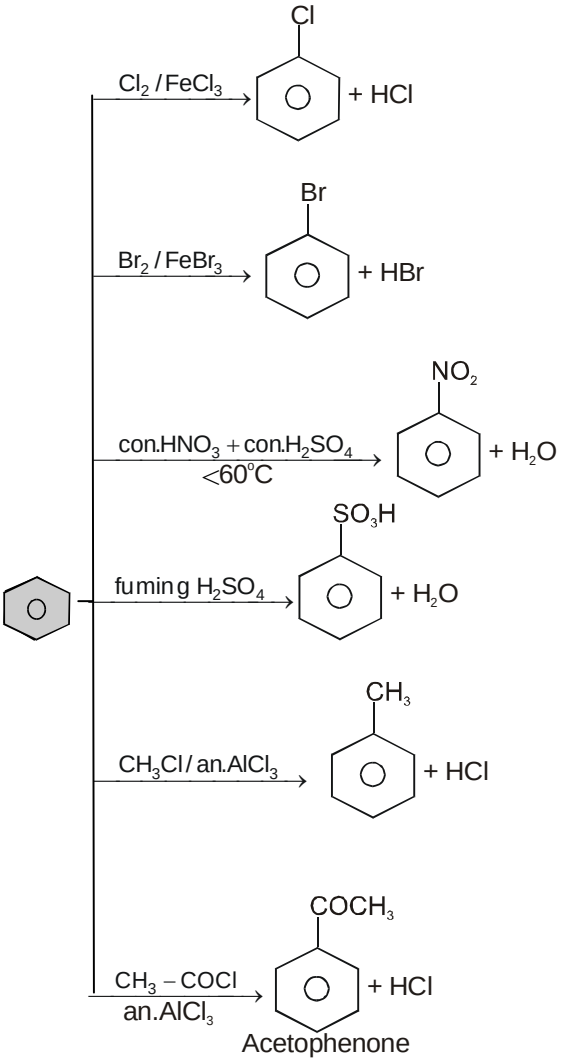
- In these reactions, benzene acts as nucleophile.
- Electrophile can attack any of six positions of Benzene.

Mechanism of electrophilic substitution:



- When, electrophile attacks the benzene, positive charge is developed at ortho position and then delocalises to para position thus, ortho and para positions carry the charge in case of electrophilic attack.

Reaction	**Reagent**	**Electrophilie**	**Product**
Chlorination	$Cl_2/FeCl_3$ or $AlCl_3$	Cl^+	C_6H_5-Cl
Bromination	$Br_2/FeBr_3$	Br^+	C_6H_5-Br
Nitration	$HNO_3+H_2SO_4$ /60^0C	NO_2^+	C_6H_5-NO_2
Sulphonation	$H_2SO_4 + SO_3$	SO_3	C_6H_5-SO_3H
Friedel – Craft's alkylation	R-Cl / anhydrous. $AlCl_3$	R^+	C_6H_5-R
Friedel – Craft's acylation	R – COX/ anhydrous. $AlCl_3$	R – CO^+	C_6H_5-COR



In the nitration of benzene, nitration mixture is con. HNO_3 and con.H_2SO_4 in 1:1 ratio . con.HNO_3 acts as base in the nitration reaction.

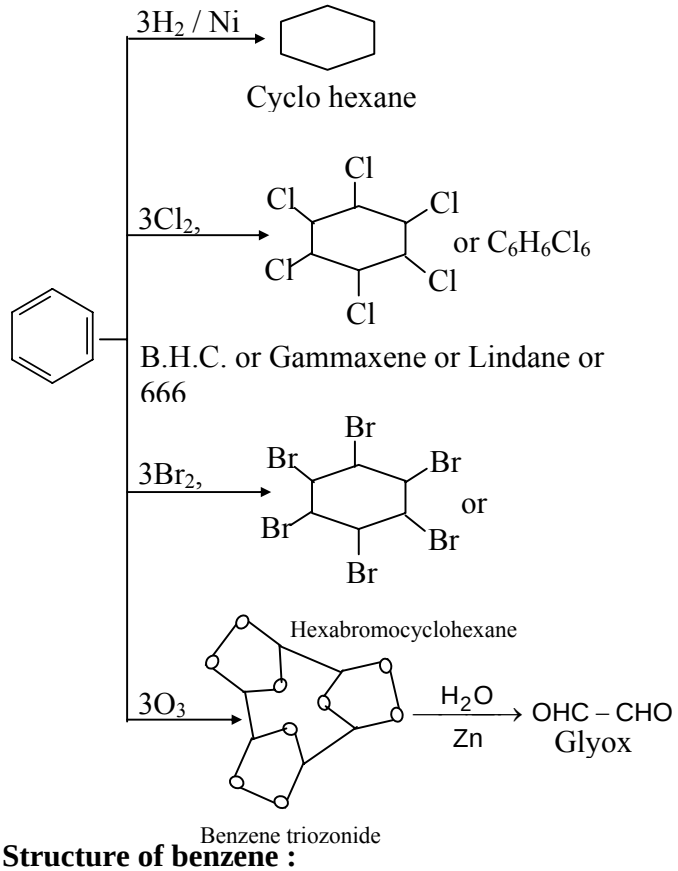
Uses of benzene :

- As solvent for fats, resins

- As motor fuel
- In dry cleaning
- As starting material in the manufacture of many compounds like aniline, oil of mirbane, insecticides, BHC, phenol, styrene etc.

II. Addition reactions :

Under special conditions, benzene gives certain addition reactions.



Structure of benzene :

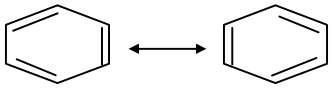
- It's molecular formula is C_6H_6 and empirical formula is CH.
- The ratio of carbon to hydrogen indicates, it is highly unsaturated. But the behaviour of benzene resembles saturated compounds.

Behaviour of unsaturated hydrocarbons	**Behaviour of benzene**
- More reactive - Less stable - Undergo additions - Decolorises alk. $KMnO_4$ and Br_2 water - Can be easily polymerized - Can be oxidized easily	- Less reactive - More stable - Undergo substitutions rather than additions - Will not decolorise alk. $KmnO_4$ and Br_2 water - Cannot be easily polymerised - Cannot be easily oxidised

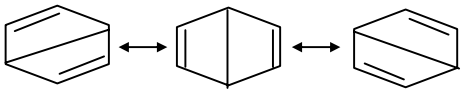
- Thus benzene looks like unsaturated but behaves like saturated.

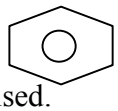
- **Resonance :** If the properties and structure of a compound can not be explained by a single structure but can be explained by two or more possible structures, it is called resonance and the different possible structures are called resonance structures or canonical forms.
- Chemically, resonance involves delocalisation (oscillation) of π - electrons or lone pairs of electrons.
- Delocalisation is possible only if the π - electron pairs, lone pairs or charge are at alternate positions.
- Because of resonance, some energy is lost by the compound and it is called resonance energy.
- Greater the number of resonance forms, more is the resonance energy and greater is the stability.
- Resonance structures are hypothetical and the real structure lies somewhere in between them.

  Kekule's structures of benzene :

  Dewar's structures of benzene :

- Kekule's structures will contribute about 80% and Dewar's structures will contribute about 20% towards the real structure of benzene.
- Benzene is stable because of resonance and greater resonance energy i.e. 150.48 KJ/mol.
- Normal representation of benzene: 
- In benzene each carbon is sp^2 hybridised.
- Due to resonance, all the six carbons are identical and all C – C bond lengths are identical the C – C bond length is 1.39 A° which is intermediate to that of C – C (single) and C = C (double), bond lengths.
- Number of sigma bonds :12
  Number of π - bonds: 3
  Number of C – C bonds: 6
  Number of C – H bonds: 6
- Number of bonds involving $sp^2 – sp^2$ overlapping: 6
- Number of bonds involving sp^2–s overlapping : 6
- Number of bonds involving sp^2–p overlapping : 0
- Number of bonds involving P – P overlapping : 3
- C – C bond order is 3/2.C – H bond order is 1.
- The number of hybrid orbitals involved in the formation of benzene molecule is 18.
- The number of all types of orbitals (hybrid and pure) involved in the formation of benzene molecule is 30.
- The ratio of s – character to p – character of all the orbitals together, involved in the formation of benzene molecule is 2 : 3.
- The number of mono substituted isomers of benzene : 1
- The number of di-substituted isomers of benzene: 3
- The number of tri-substituted isomers of benzene : 3

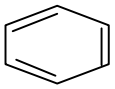
Aromaticity or aromatic character:

Aromatic compounds must possess the following properties.

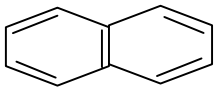
1. They must be cyclic and planar.
2. All Carbons must be sp^2 hybridised.
3. Alternate single and double bonds should be present.
   i.e. conjugation of π electrons.
4. Delocalisation of π electrons (Resonance) is required.
5. Normally they must undergo electrophilic substitutions.
6. They must obey Huckel's rule : According to which aromatic compounds must contain $(4n+2)\pi$ electrons, where n = 0, 1, 2, 3 … etc.

No fractional value or no negative value for 'n'.

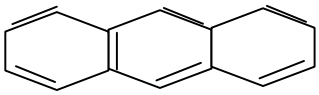
Illustration of Huckel's rule :

1. 

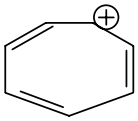
6π electrons (n =



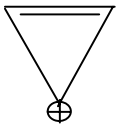
10π electrons (n =



14π electrons (n =



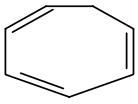
Tropelium ion



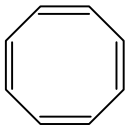
Cyclo propenyle cation

2π electrons (n = 0)

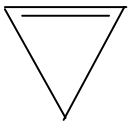
All the above are aromatic as they contain Huckel's number of delocalised π electrons.

2. 

6π electrons, not aromatic

3. 

8π electrons, non aromatic (no Huckel's no.)

4. 

2π electrons, non aromatic (no resonance)