ADV.M.N.DESHMUKH ART'S SCIENCE AND COMMERCE COLLEGE RAJUR

DEPARTMENT OF CHEMISTRY

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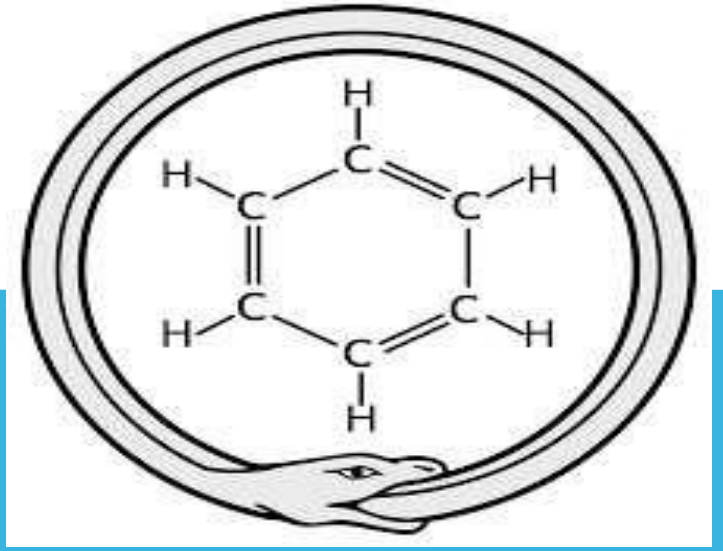
Discovery of Benzene

- The word "benzene" derives historically from "gum benzoin", sometimes called "benjamin" an aromatic resin known to European pharmacists and perfumers since the 15th century as a product of southeast Asia.
- Michael Faraday first isolated and identified benzene in 1825 from the oily residue derived from the production of illuminating gas, giving it the name bicarburet of hydrogen.

fall asleep while sitting in front of fire, dreamed about chains of atoms in form of twisting snakes. one of snake caught hold of its own tail , forming a whirling ring.

awoke , freshly inspired , spent remainder night working on his now-famous hypothesis.



CONDITIONS FOR AROMATICITY

The main essential for Aromaticity are:

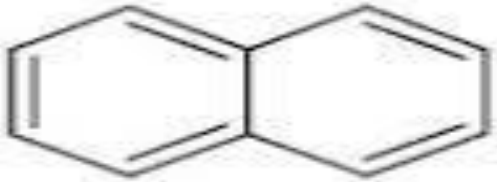
- **Delocalisation:** the molecule should contain a cyclic cloud of delocalized πelectron above and below the plane of the molecule
- **Planarity:** for the delocalisation of π-electron the ring must be planar to allow cyclic overlap of p-orbitals. Therefore, for a molecule to be aromatic, the ring must be planar.
- **(4n+2)π electron:** for Aromaticity, the π-electron could must contain a total of (4n+2)π electrons where n is an integer equal to 0,1,2,3.....n . This is known as Huckel Rule.

STRUCTURE OF BENZENE NAPHTHALENE

benzene

C_6H_6

m.w. 78.11



naphthalene

$C_{10}H_8$

128.17

Huckel Rule $(4n+2)\pi$ n=1

$(4x1+2)\ \pi$

$(6)\ \pi$

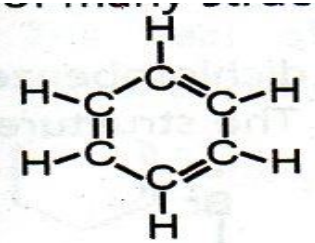
$(4n+2)\pi$ n=2

$(4x2+2)\ \pi$

$(10)\ \pi$

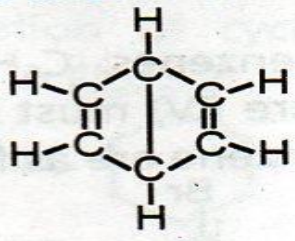
Both are aromatic compounds according to huckel rule

HISTORIC STRUCTURE OF BENZENE BY KEKULE



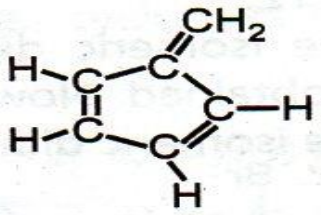
I

Kekule formula



II

Dewar formula



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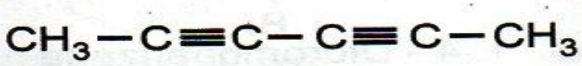
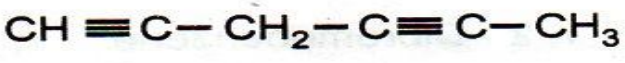
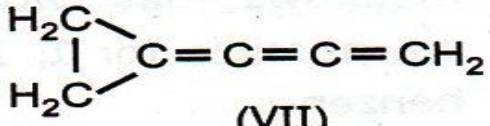


(IV)



(V)

(VI)



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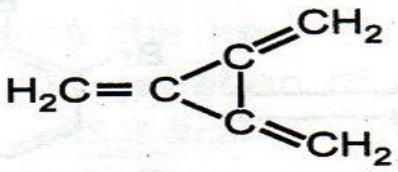

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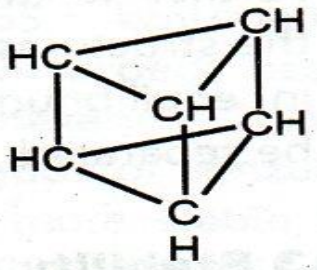
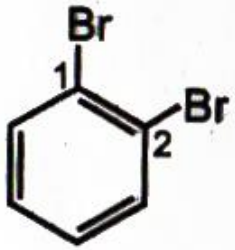
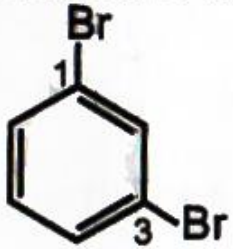


(IX)

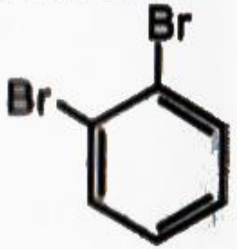




1, 2 - Dibromobenzene 1, 3 - Dibromobenzene 1, 4 - Dibromobenzene

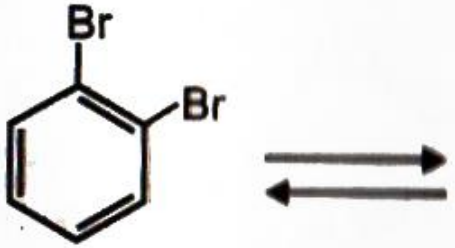
Closer examination of structure (I) shows that two structures are possible for 1, 2-dibromo-benzene.

(VI)



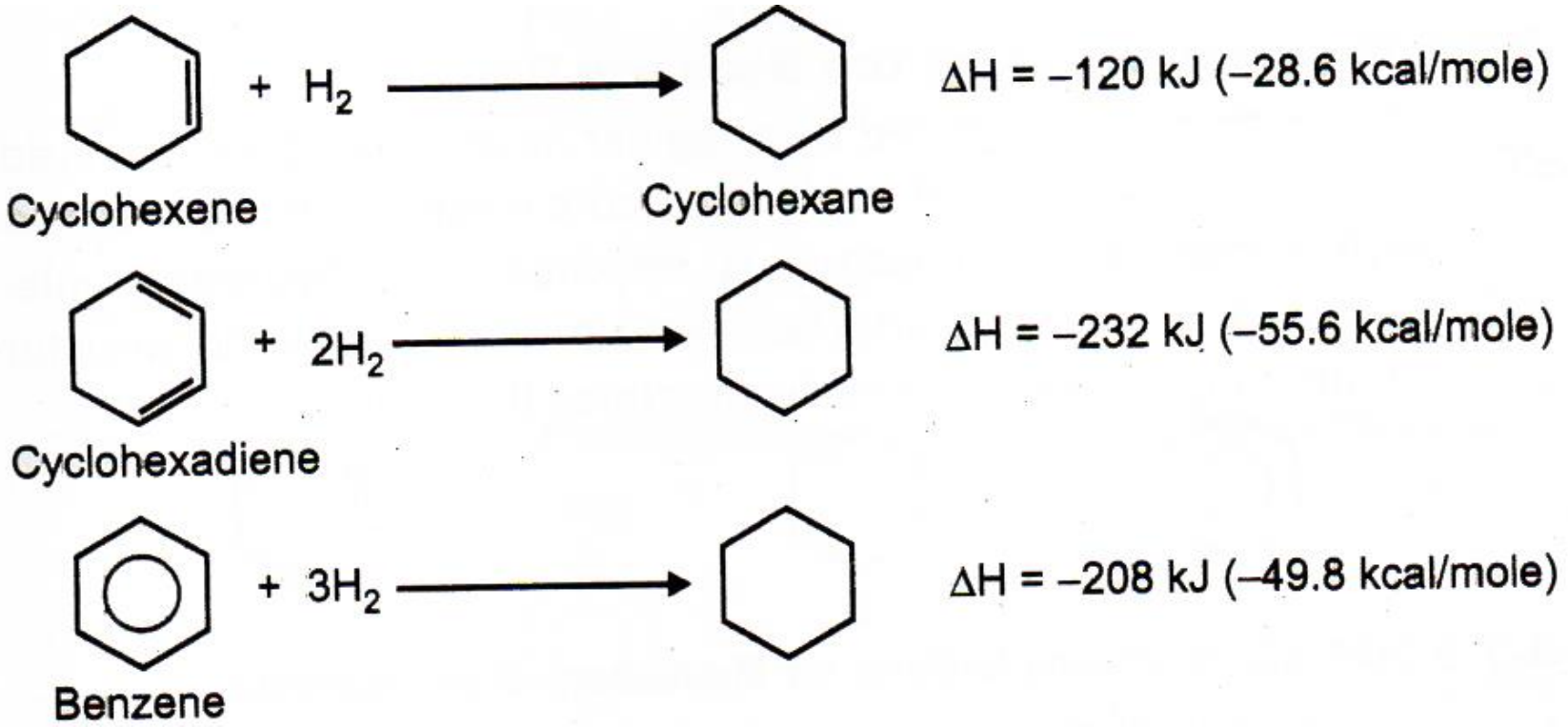
(VII)

Further Kekule proposed that the structures (VI) and (VII) are in equilibrium and could not be separated.



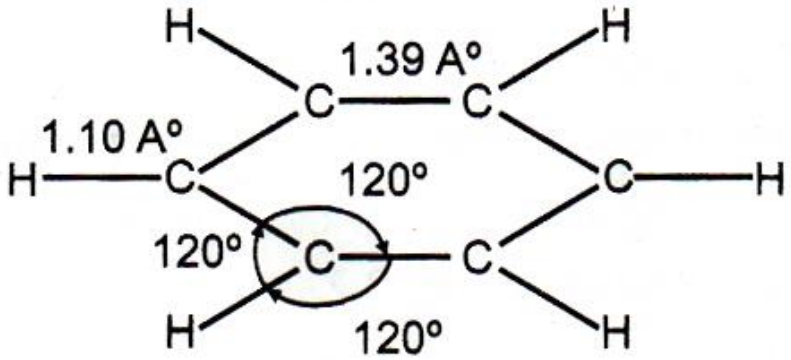
(VI) (VII)

HEAT OF HYDROGENATION
HEAT OF COMBUSTION

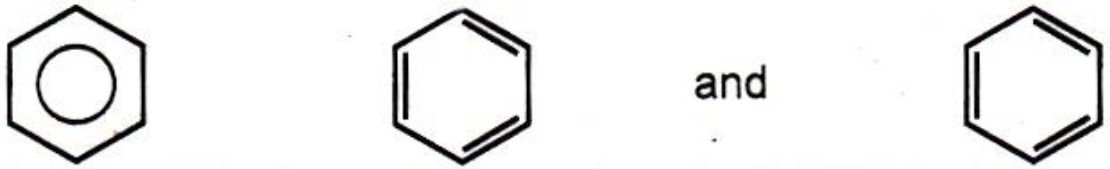


NEGATIVE HEAT HYDROGENATION = HEAT EVOLVED

C-C Bond length of benzene

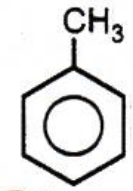


Representation of Benzene Ring

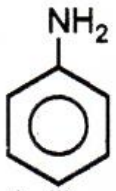


I II III

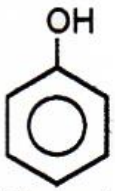
IUPAC NOMENCLATURE OF BENZENE DERIVATIVES



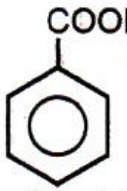
Toluene



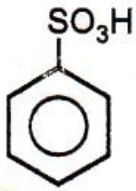
Aniline



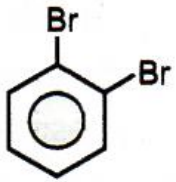
Phenol



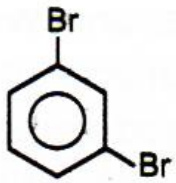
Bnzoic acid



Benzene sulphonic acid



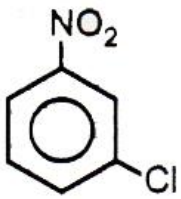
o-Dibromo benzene (ortho)



m-Dibromo benzene (meta)

p-Peradibromo benzene (para)

p-Bromoiodo benzene

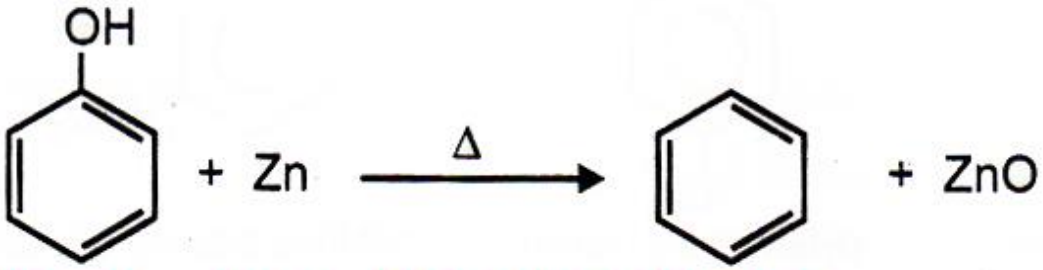


m-Chloronitro benzene

p-Chloro benzene sulphonic acid

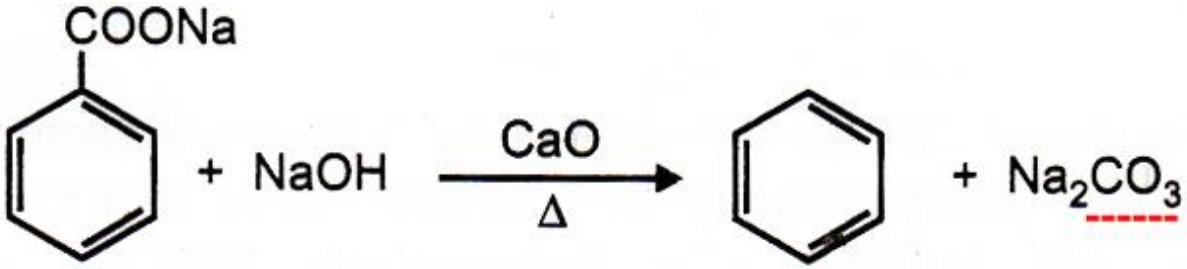
PREPARATION OF BENZENE

From - Phenol



Phenol Dust Reduction Benzene

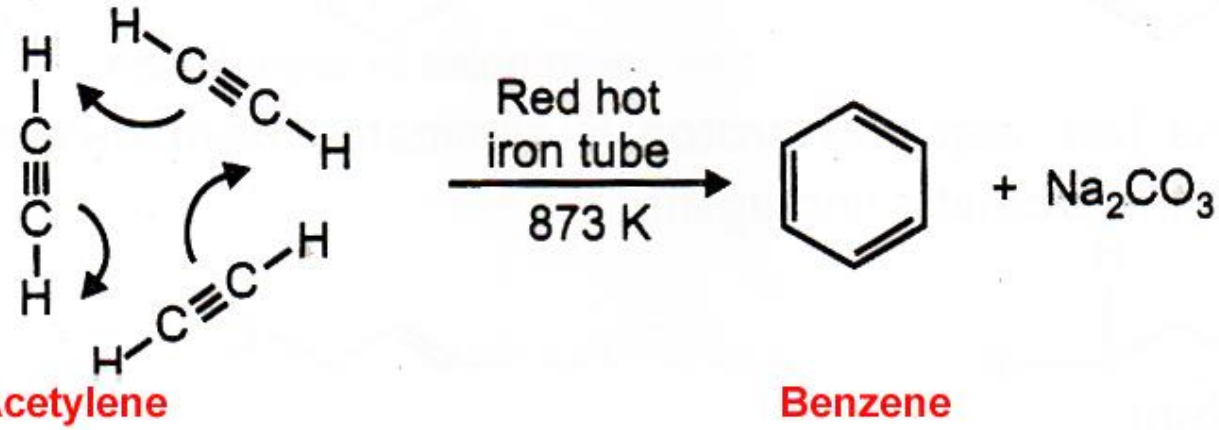
By - Decarboxylation



Sodium Benzoate Benzene

PREPARATION OF BENZENE

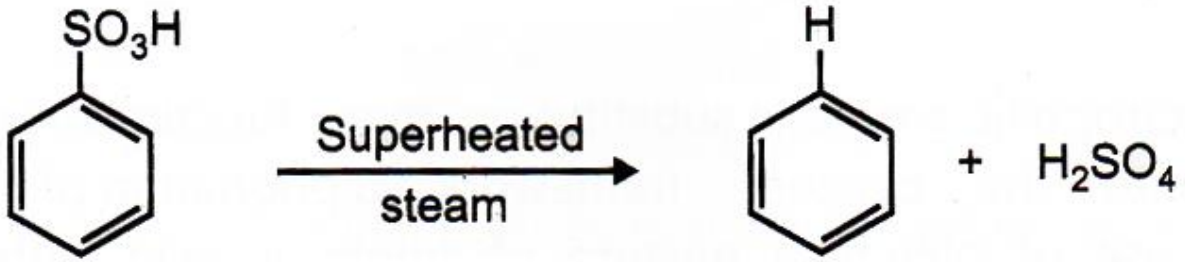
From - Acetylene



Acetylene

Benzene

From Benzene Sulphonic Acid

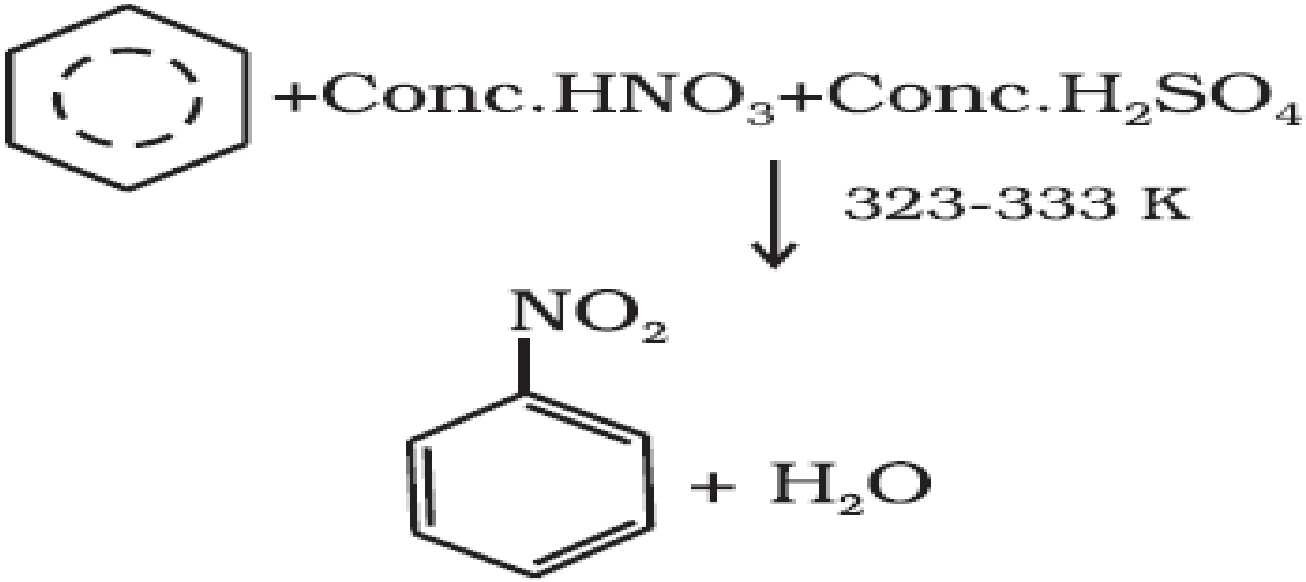


Sulphonic Acid

Benzene

NITRATION

- The replacement of a hydrogen atom in the ring by a nitro (-NO_2) group called nitration. It is carried out by heating benzene with the nitrating mix consisting of concentrated nitric acid and sulphuric acid



Nitrobenzene

MECHANISM OF NITRATION

The accepted mechanism for this reaction involves following sequence of reactions:

(i) $HONO_2 + 2\,H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + NO_2^+$

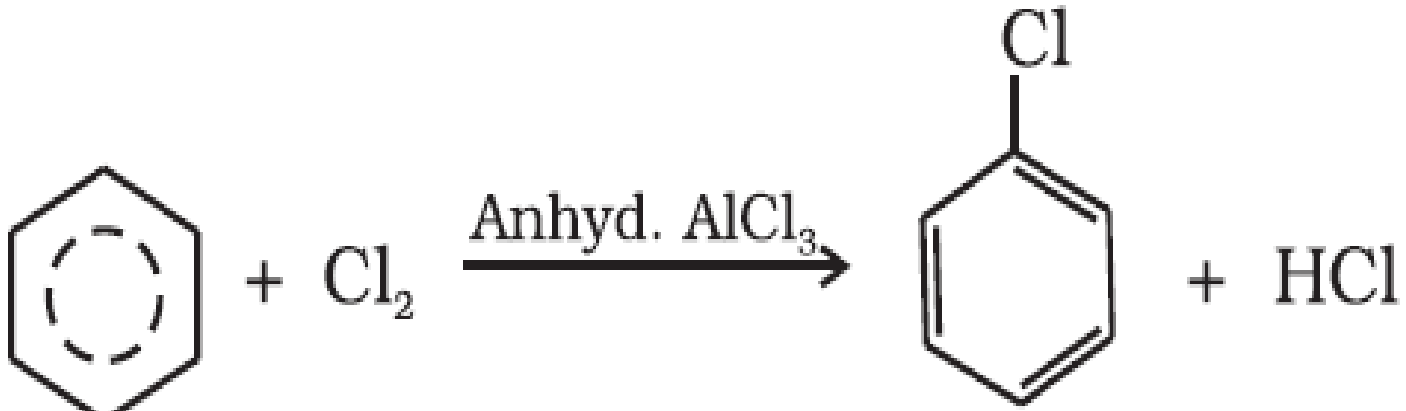
Nitronium ion

(ii) $NO_2^+ + C_6H_6 \rightleftharpoons C_6H_5^+(NO_2)$ slow step

(iii) $C_6H_5^+(NO_2) + HSO_4C_6H_5 \rightleftharpoons NO_2 + H_2SO_4$ fast step

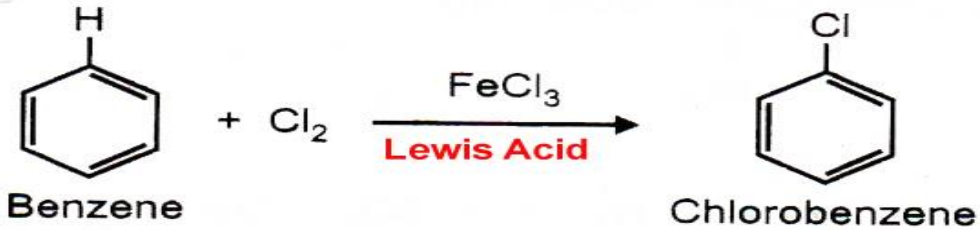
HALOGENATION

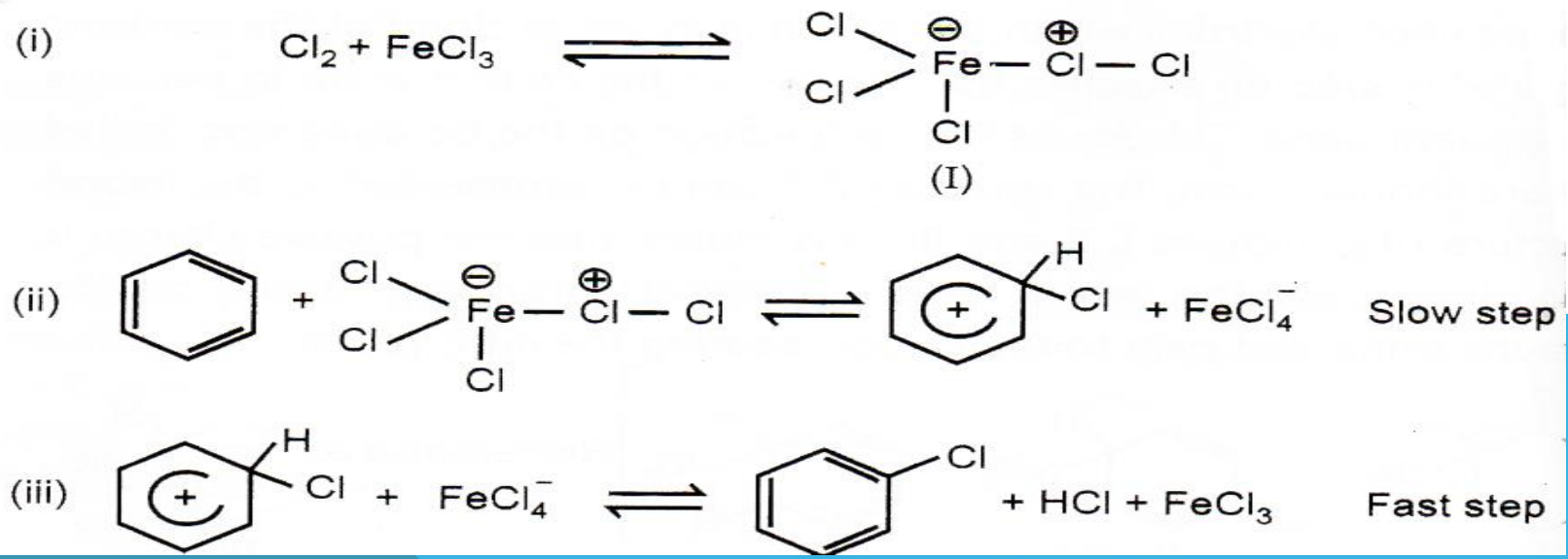
The replacement of a hydrogen atom in the ring by a halogen atom (F, Cl, Br or
I) is called halogenation. Arenes react with
presence of a Lewis acid like anhydrous haloarenes.



Chlorobenzene

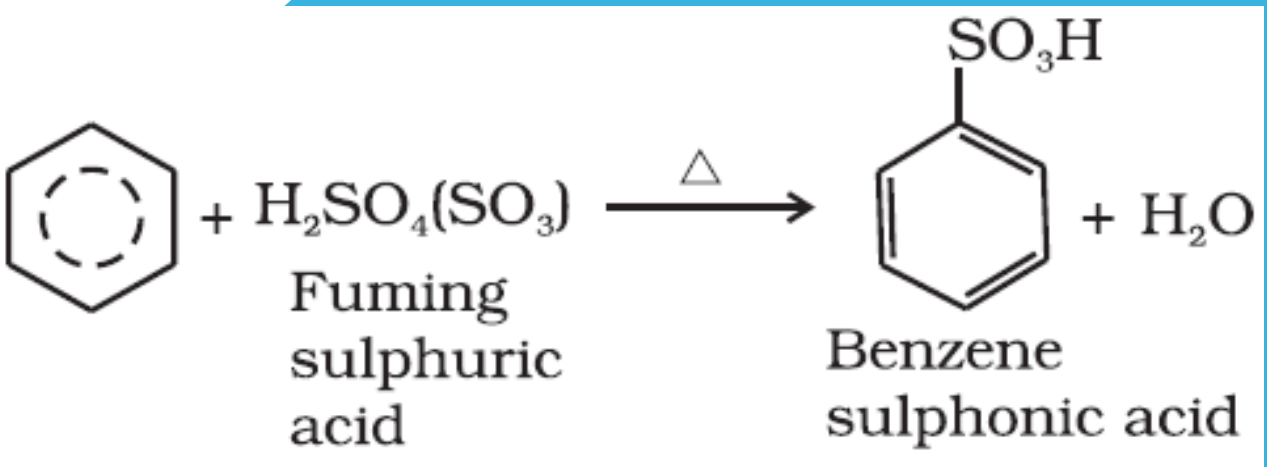
MECHANISM OF HALOGENATION





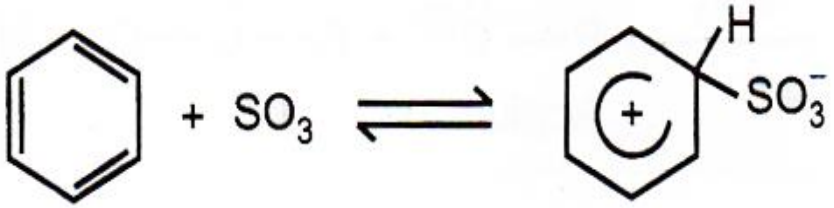
SULPHONATION

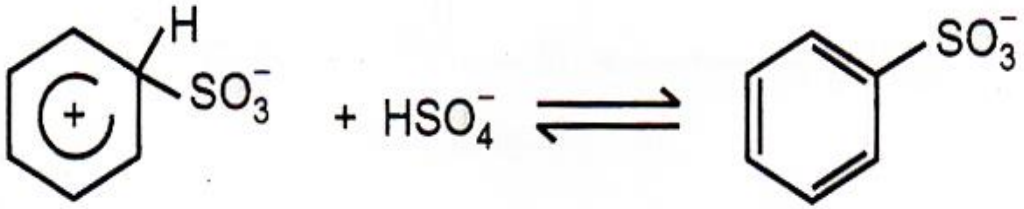
The replacement of a hydrogen atom in the ring by a sulphonic acid (-SO_3H) group is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid and oleum.

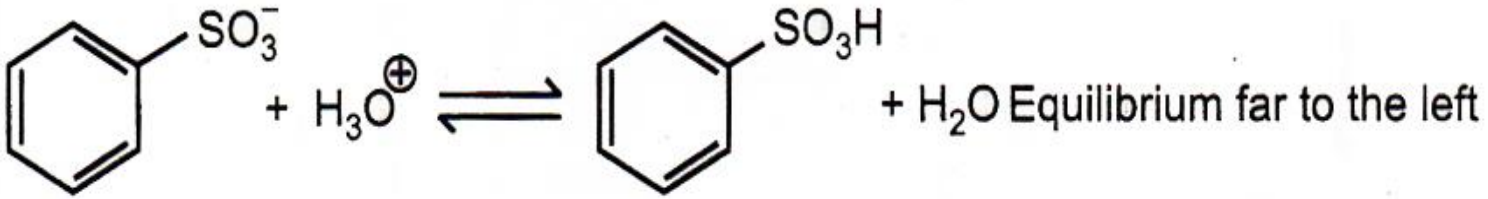


MECHANISM OF SULPHONATION

(i) $2\,H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$

(ii)  Slow step

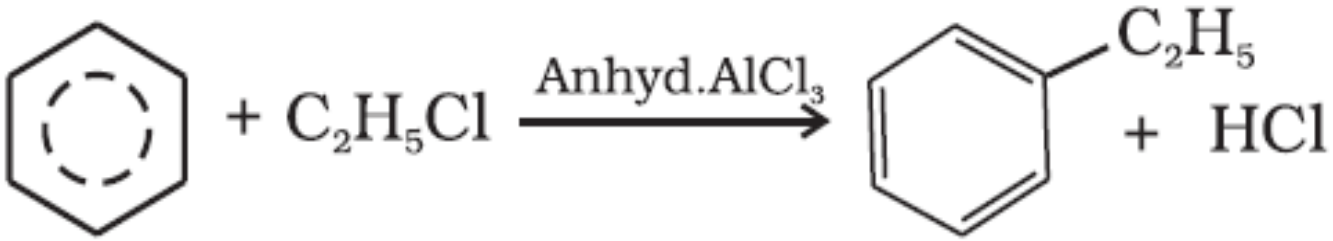
(iii)  Fast step

(iv) 

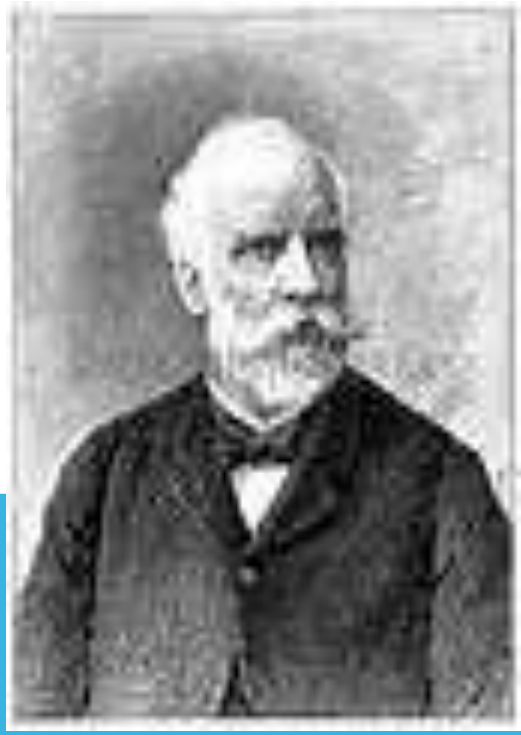
FRIEDEL CRAFTS ALKYLATION

ALKYLATION:-

- When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed

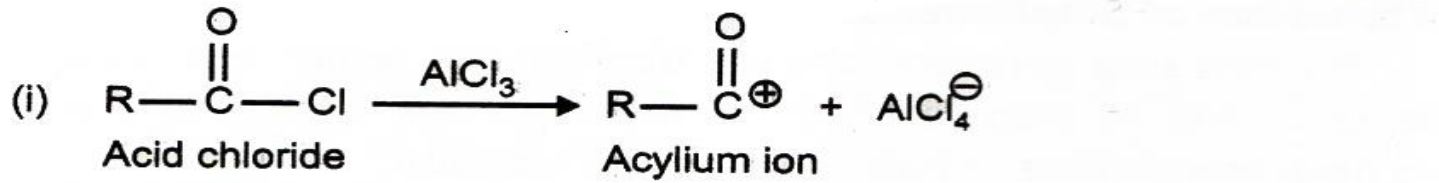


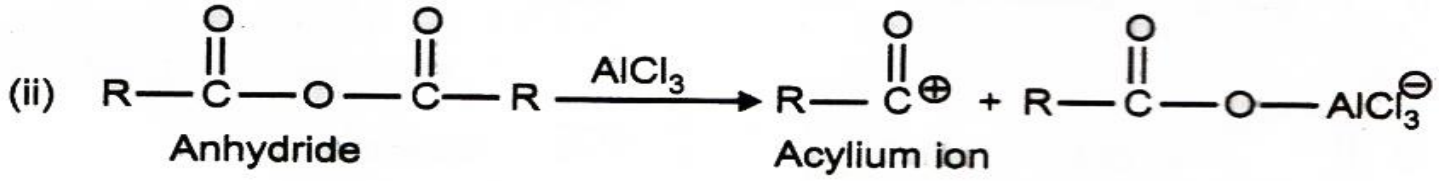
Ethylbenzene

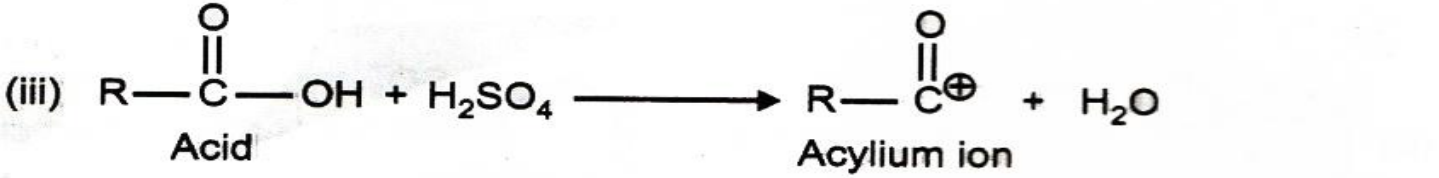


FREIDEL

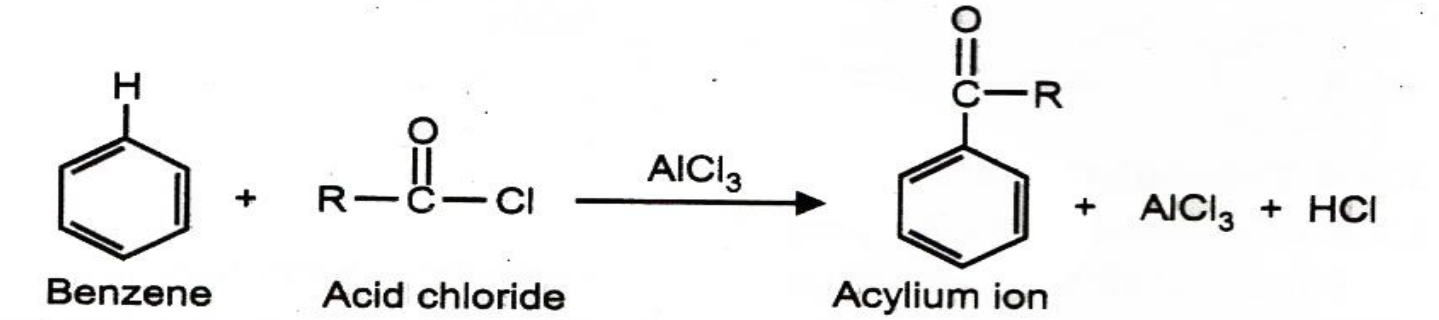
MECHANISM OF ACYLATION



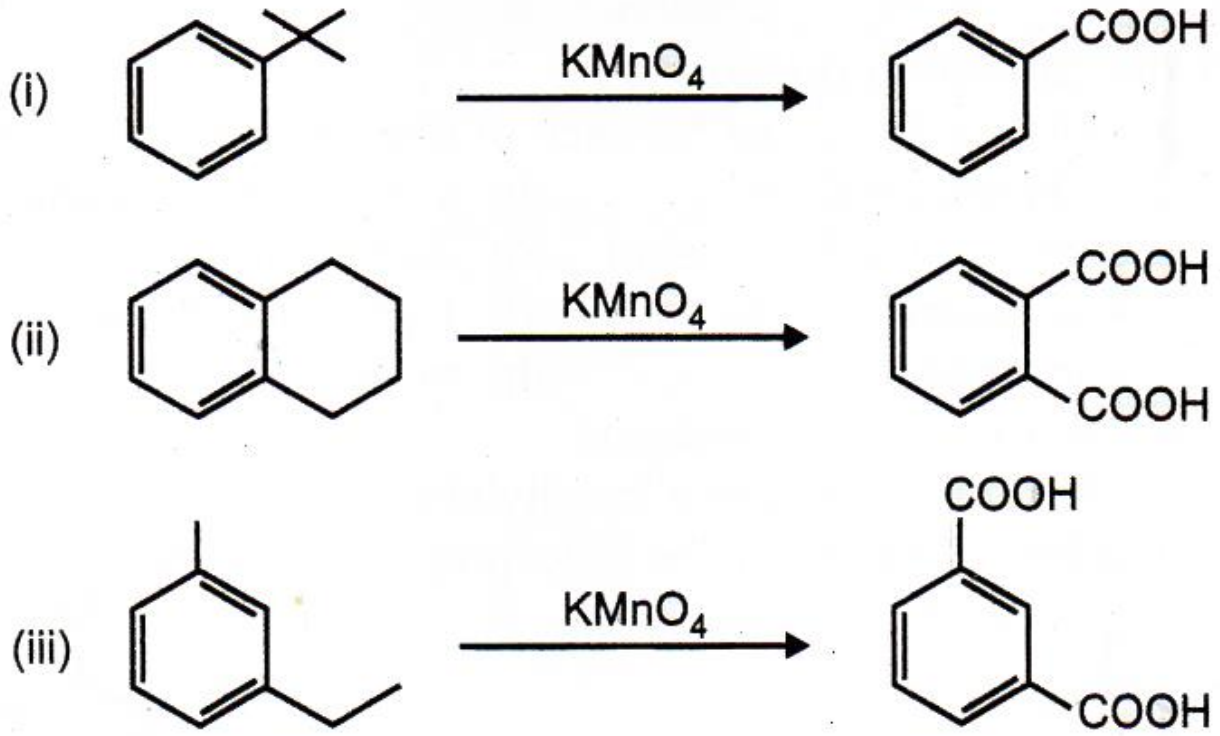




The reaction is as shown.



OXIDATION OF ALKYL BENZENE



MECHANISM OF ALKYL BENZENE