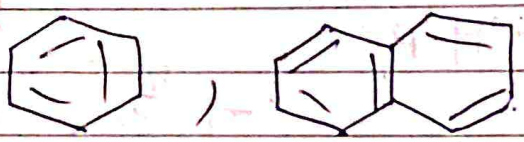
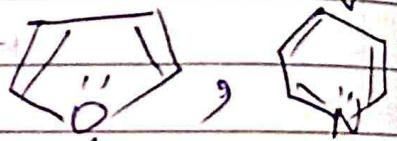
Aromatic hydrocarbon

* These hydrocarbon are known as 'arenes' as most of them smells pleasant, have aroma.

* Aromatic hydrocarbon

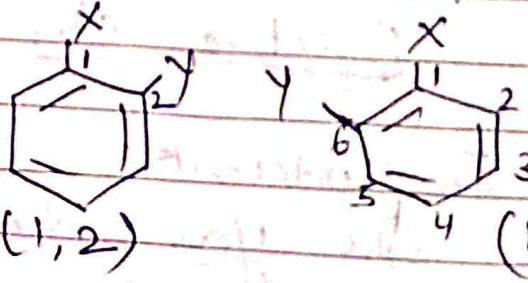
- Benzenoid (have Benzene Ring)
- Non-Benzenoid (don't contain Benzene Ring)

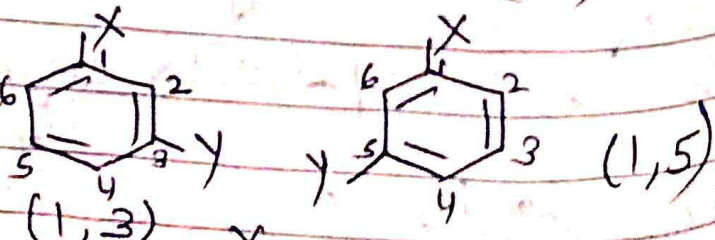
Eg:  Benzene C_6H_6, Naphthalene $C_{10}H_8$

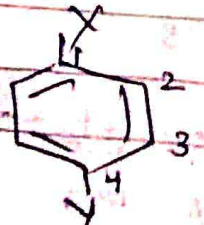
Eg:  Furan, Pyridine

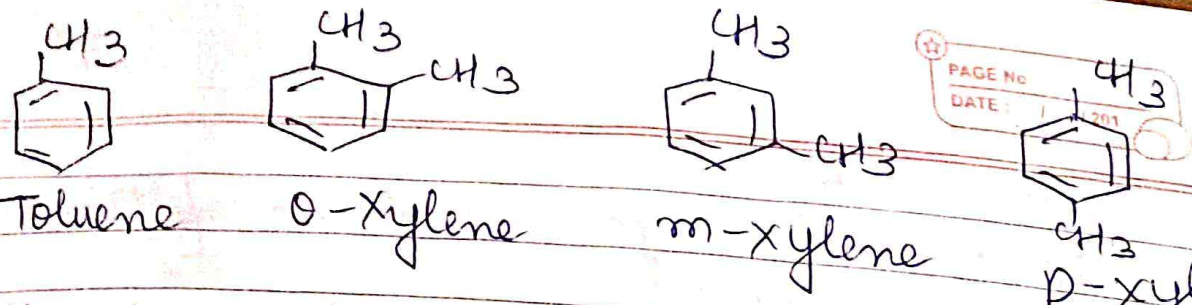
* Benzene ring is highly Unsaturated as it have three pi bonds.

* Benzenoid compound show three different position isomers

(o-) ortho-isomer  (1,2) (1,6)

(m-) meta-isomer  (1,3) (1,5)

(p-) para-isomer  (1,4)

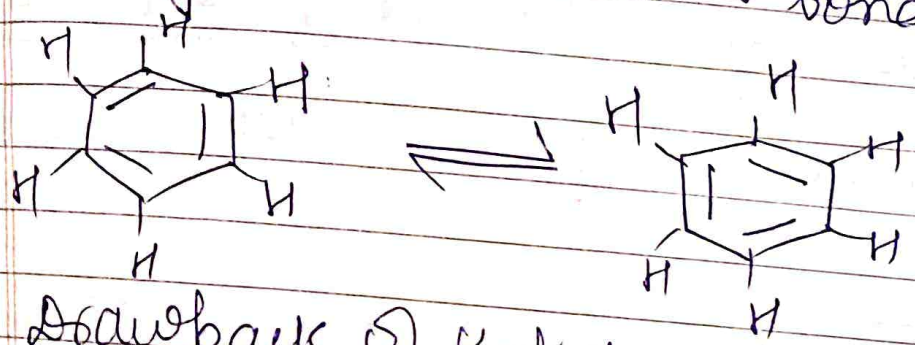


Eg Toluene o-Xylene m-Xylene p-Xylene

Structure of Benzene

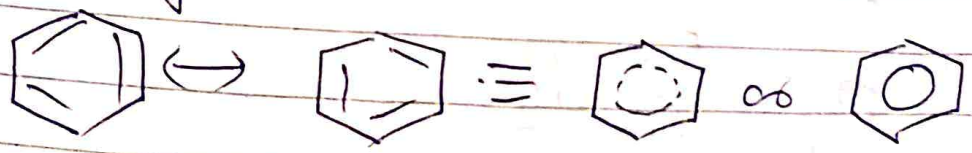
→ It was isolated by Michael faraday in 1825

→ August Kekule in 1865 have given structure for Benzene having alternate single and double bond



Drawback of Kekule structure are it fails to explain stability and preference to substitution reaction than addition reaction.

* Later, Resonance explain the concept of oscillating double bonds.



Benzene is a hybrid of various resonating structure.

All Carbon atoms are sp^2 hyberdised and they have one unhyberdised p-orbital ⊥ to the plane of ring

Aromaticity

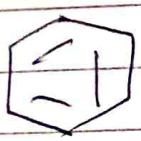
Aromatic compound have following characteristics

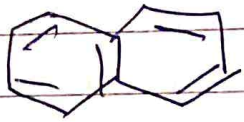
(i) Planarity

(ii) Complete deloralisation of π electrons in ring

(iii) Presence of $(4n+2)\pi$ electrons in ring where n is an integer

They are referred to as Huckel Rule

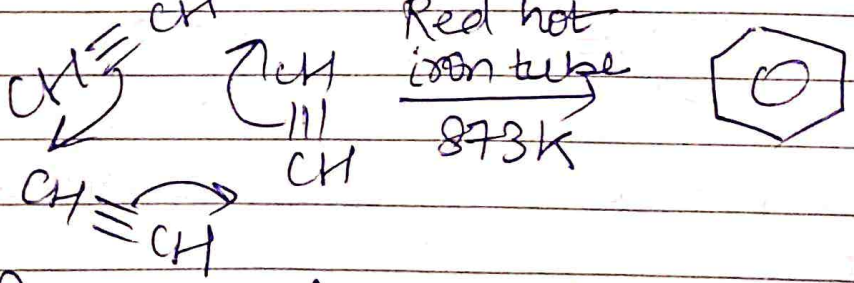
 Benzene [n=1, 6π electrons]

 Napthalene [n=2, 10π electrons]

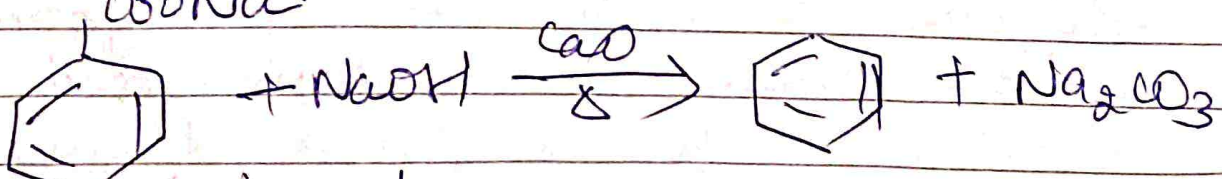
n is the no. of Ring

Preparation of Benzene

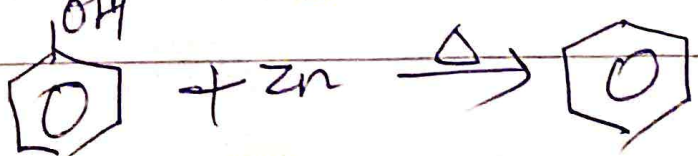
(1) Polymerisation of alkene



(2) Decarboxylation of Acids (Aromatic)



(3) From phenol

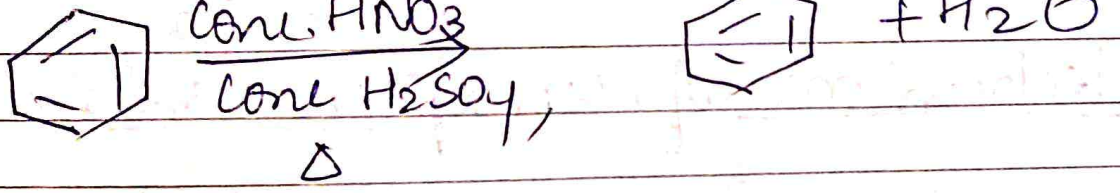


Aromatic compounds are non-polar molecules miscible with organic solvents and immisible with water & polar solvents.

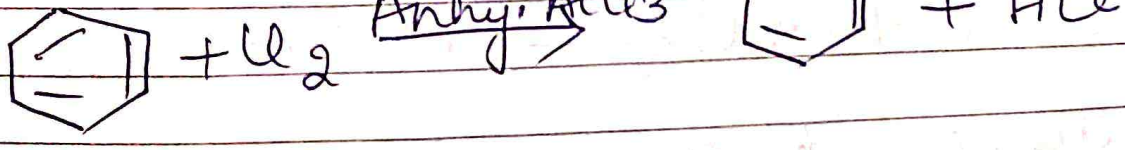
Electrophilic substitution - ~~are shown~~ is a chemical reaction in which electrophile (e^- loving species) replaces functional group / Hydrogen atom in organic reaction.

* Arenes show electrophilic substitution reaction and sometimes show addition and oxidation reaction.

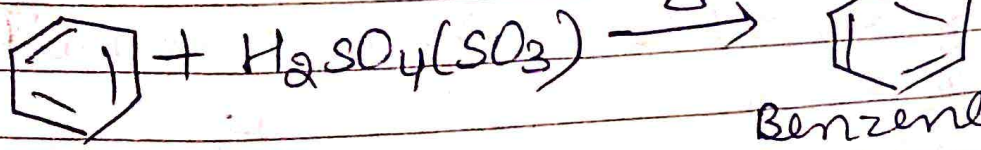
(1) Nitration



(2) Halogenation

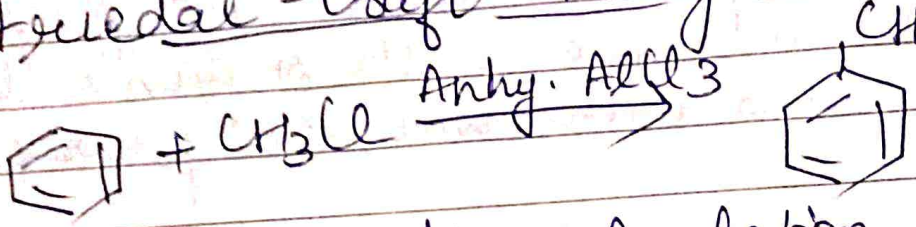


(3) Sulphonation

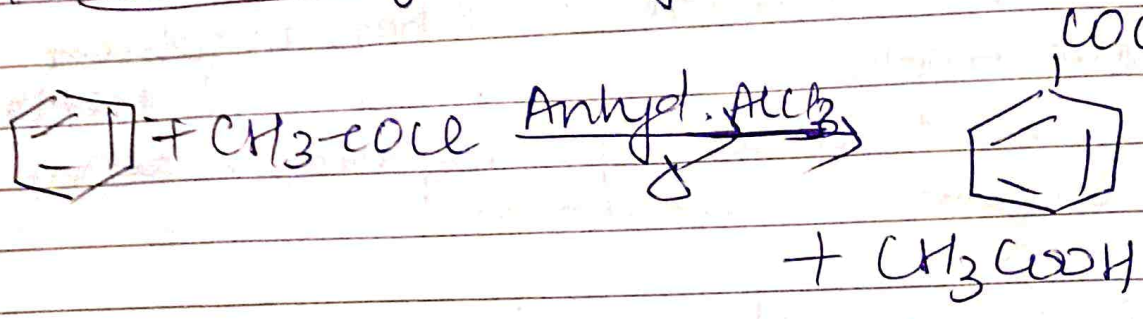


Benzene sulphonic acid

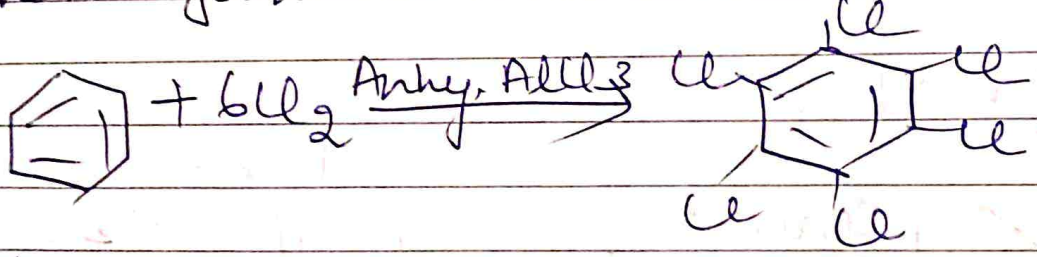
(4) Friedal-Craft Alkylation reaction



(5) Friedal Craft Acylation Reaction



If Excess electrophilic reagent is used, then further substitution takes plate



Mechanism of electrophilic substitution

(1) Generation of Electrophile, $E^{\oplus}$

$$Cl-Cl + AlCl_3 \longrightarrow Cl^+ + [AlCl_4]^-$$

or

$$CH_3-Cl + AlCl_3 \longrightarrow CH_3^+ + [AlCl_4]^-$$

or

$$CH_3-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow CH_3-\overset{+}{\underset{\underset{O}{\|}}{C}} + [AlCl_4]^-$$

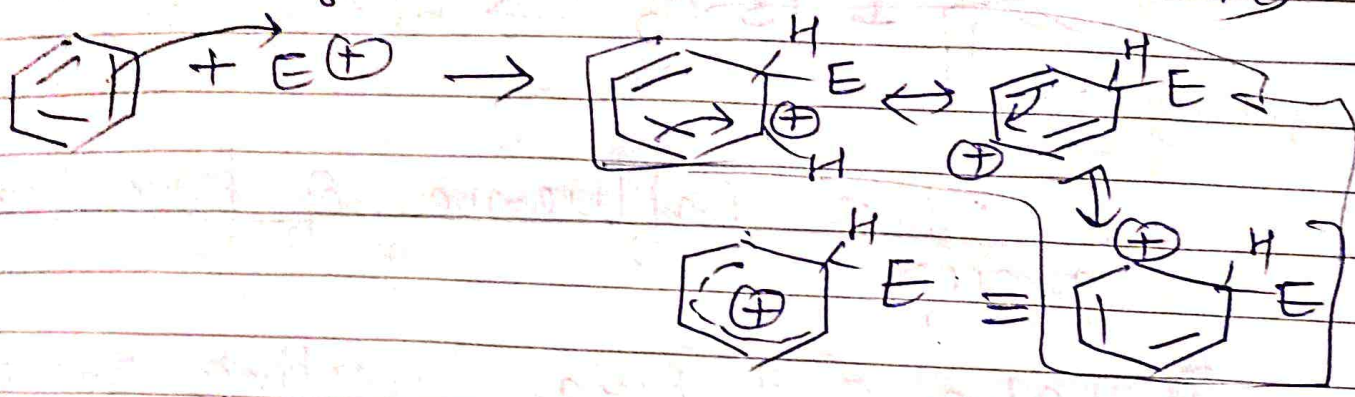
in Nitration,

$$HO_3SO-H + H-\ddot{O}-NO_2 \rightleftharpoons H-\overset{H}{\overset{+}{O}}-NO_2 + HSO_4^-$$

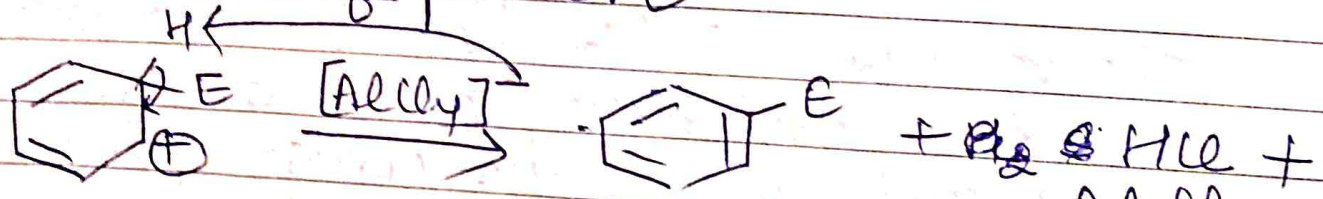
$$H-\overset{H}{\overset{+}{O}}-NO_2 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

(Nitronium ion)

(2) formation of carbocation (arenium ion)



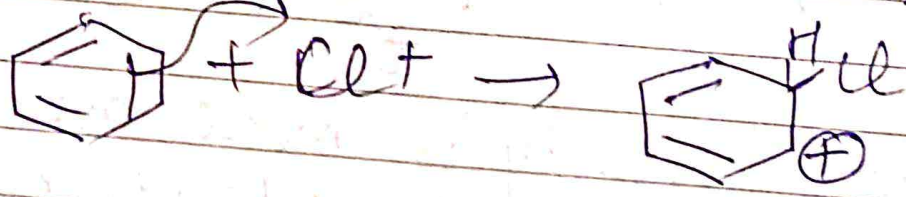
(3) Removal of proton



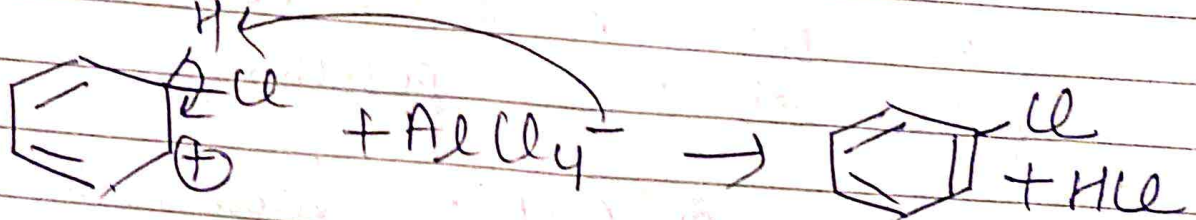
Eg:- Halogenation

Step-1:- $Cl-Cl + AlCl_3 \rightarrow Cl^+ + [AlCl_4]^-$

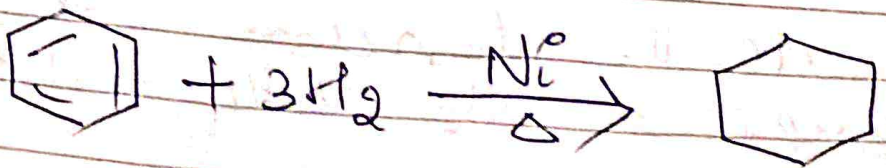
Step-2:-

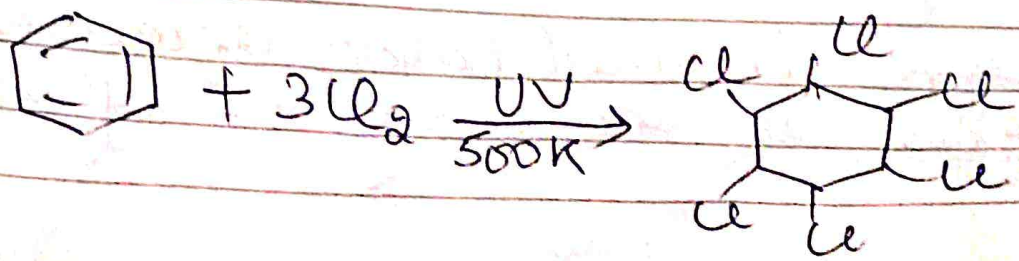


Step-3:-

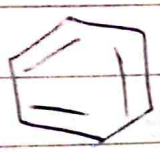


Addition reaction





Combustion Reaction

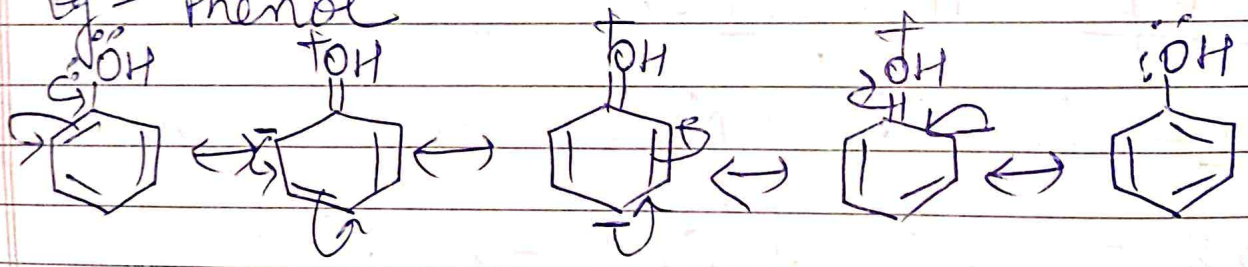
 $+ \frac{15}{2} O_2 \rightarrow 6CO_2 + 3H_2O$

Directive Influence of functional group

(1) Ortho and para directing groups

The Groups which direct incoming group to ortho and para positions are called ortho and para directing group.

Eg - Phenol



electron density is more on ortho, para position. ∴ substitution takes place at these positions.

-I effect of $\ddot{O}H$ is low ∴ overall e⁻ density is high.

∴ It activates the Benzene Ring.

Other Examples → $-NH_2$, $-NHR$, $-CH_3$, etc.

→ Halogens in aryl halides deactivates the ring due to strong -I effect.

DATE : / /201

(2) Meta directing Group

The Group which direct incoming group to meta position are called meta directing groups.

Eg :- $-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-SO_3H$

These groups show strong -I effect and hence decreases the overall electron density in ring ∴ these groups are 'deactivating group'

~~and incoming group attaches at meta~~