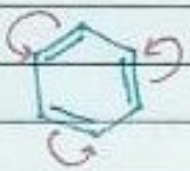
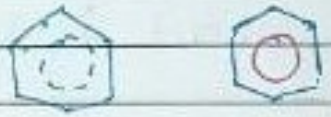
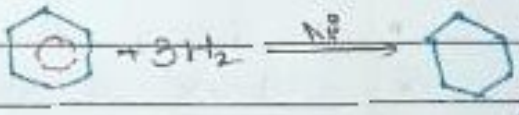
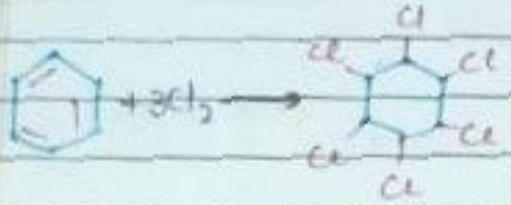
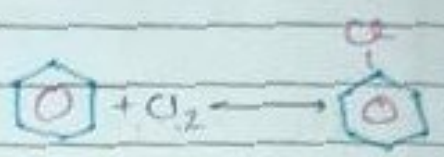
UNIT - I

Benzene & It's Derivative

Structure of Benzene & it's evidences
OR
Evidences for derivative of structure of Benzene

Kekule Structure	Actual structure
1. 	1. 
Cyclic structure C-C & C=C	Cyclic structure C=C bond exist due to delocalisation of πe^-
2.  + 120 kcal	2.  + 210 kcal
 + 360 kcal	Enthalpy of hydrogenation = -210 kcal.
Enthalpy of hydrogenation = -360 kcal	

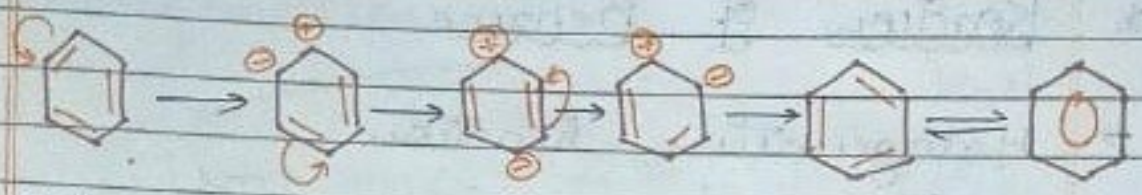
3. Benzene gives addⁿ. reaⁿ due to presence of three double bond (C=C bond)	3. Benzene gives substitution reaⁿ because the double bond (π-bond) is unstable due to delocalisation of e⁻.
4. 	4. 
Benene hexachloride (BHC)	Electrophilic substitution reaction
This reaⁿ confirms the presence of 3 double bond in benzene.	

* Resonance In Benzene :

→ for Resonance :

- σ-bond & π-bond at alternate position
- π-bond & +ve charge at alternate position
- σ-bond & -ve charge at alternate position
- σ-bond & ··(lone pair of e⁻) at alternate position
- σ-bond ·(free radical) at alternate position.

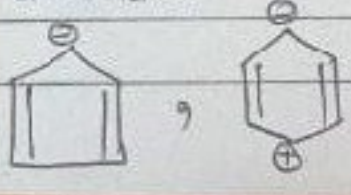
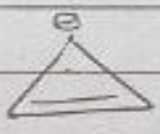
No. of Resonating Structure = No. of C=C bond



Resonance occurs due to delocalisation of π bond in benzene ring.

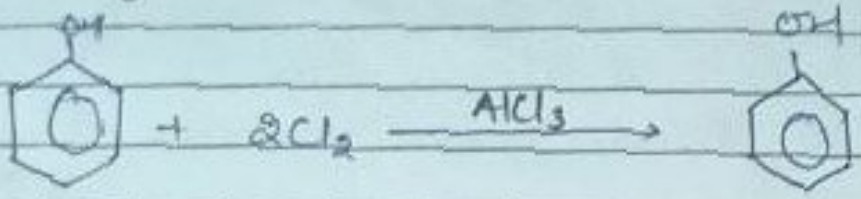
No. of Resonating Structure = 3

* Aromaticity (Aromatic Character):

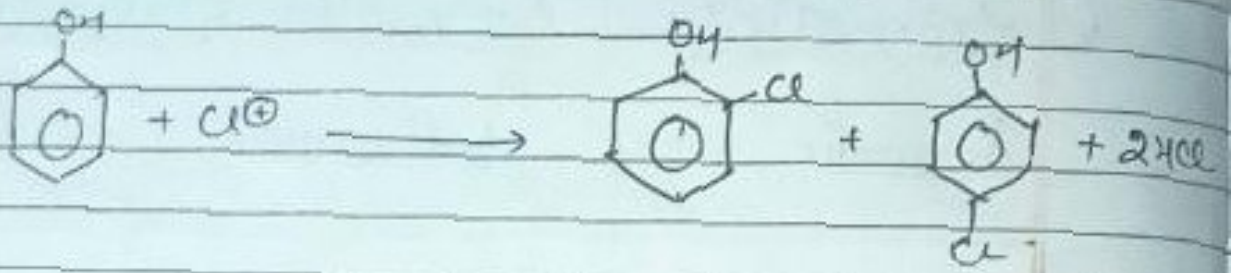
Aromatic	Antiaromatic	Non-Aromatic
Cyclic planer	Cyclic planer	If any of Characteristic necessary for aromatic & antiaromatic compound doesn't satisfied it will be non-aromatic
Resonance :-	Resonance :-	
π-π at alternate posⁿ	π-π at alternate posⁿ	
π-⊖ at alternate posⁿ	π-⊖ at alternate posⁿ	
π-⊕ at alternate posⁿ	π-⊕ at alternate posⁿ	
π-•• at alternate posⁿ	π-•• at alternate posⁿ	
π-• at alternate posⁿ	π-• at alternate posⁿ	
no. of π e⁻ = (4n+2) π (Huckel's Rule)	no. of π e⁻ = (4n) π e⁻	
Eg:  (4n+2) π e⁻ (4×1+2) = 6 π e⁻	 (4n) π e⁻ (4×1) = 4 π e⁻	 It is not planar so, it is non-aromatic
It satisfy all the Characteristics of aromatic.	It satisfy all the Characteristics of ~~non~~ anti aromatic	
		

* Reaction of Benzene

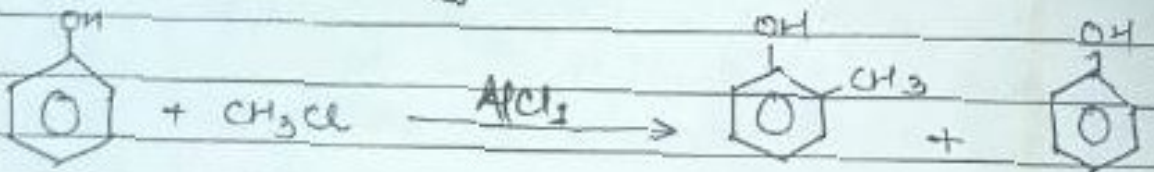
→ Halogenation Reaction



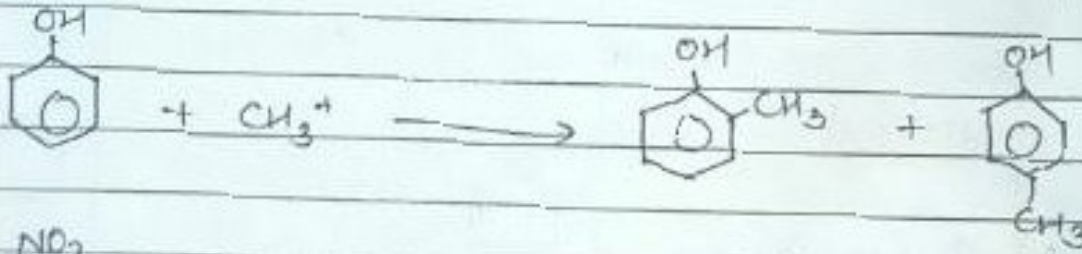
$$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4$$

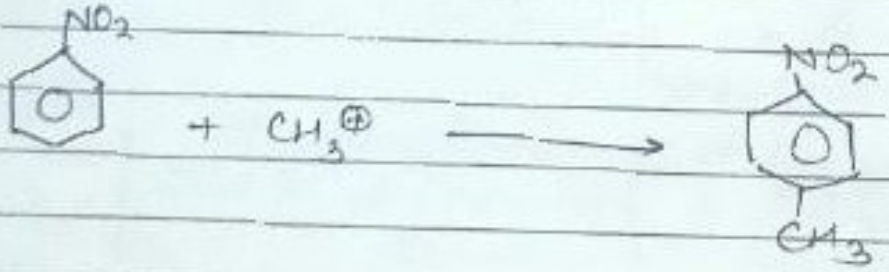


→ Friedalcraft Alkylation

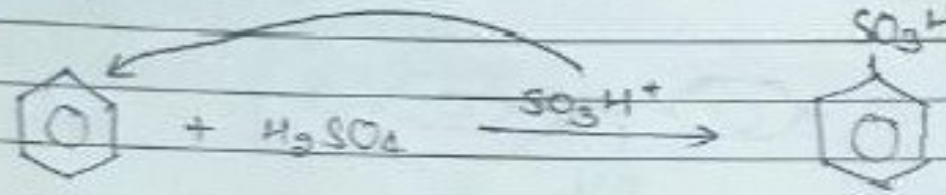


$$CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^\ominus$$

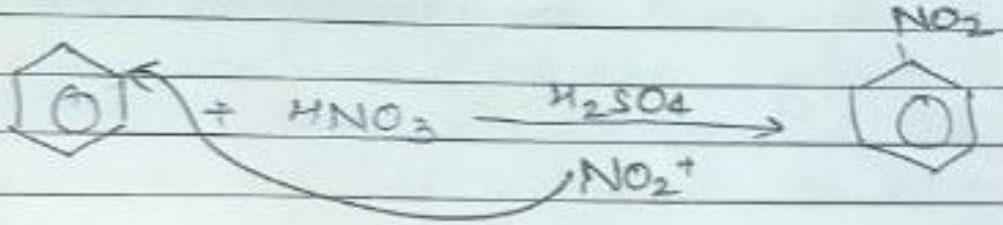




→ Sulfonation



→ Nitration

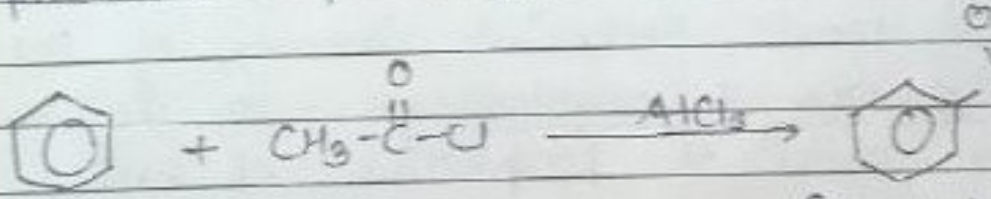


* Friedal Craft Acylation : An acyl group ($RCO-$) becomes attached to the Ar. ring thus forming a ketone the process is called acylation. As usual the friedal craft reaction

$$ArH + RCOCl \xrightarrow{AlCl_3} Ar\text{-}COR + HCl$$

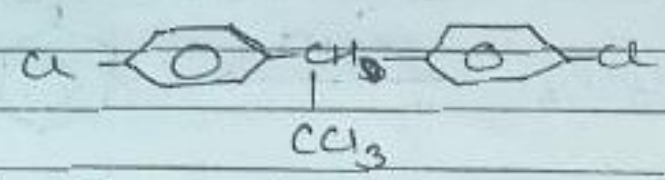
(Can acyl chlorides) (Ketone)

This involves the treatment of benzene with acetyl chlorides or acetic anhydride in the presence of $AlCl_3$.



(Acetophenone)

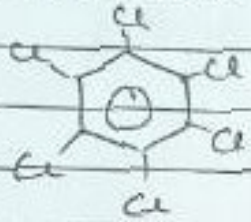
* DDT : Dichlorodiphenyltrichloromethane



→ Uses : •) Act as / used for insecticide in agriculture department.
•) It is used for the treatment of lice
•) It is used for control of mosquito including malaria.

*** DDT act upon in Na^+ ion channel in the neuron of insect causing spontaneous fising action potential, thus resulting death.

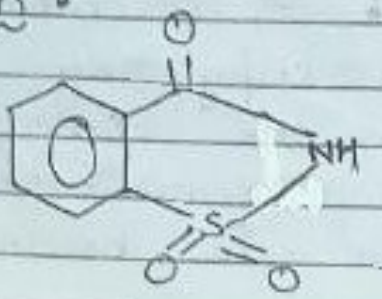
* BHC : Benzenehexachloride



→ Uses : •) It is used as insecticide & rodenticide.
•) It is used in pharmaceutics of treatment of lice.
•) It is used as agriculture, pesticide.

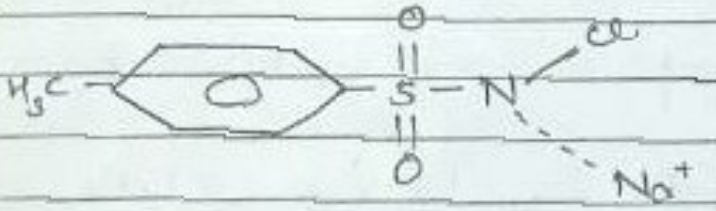
Note : The most potential isomer of BHC is γ-benzenehexachloride. It is responsible for most of properties of BHC.

* Saccharin :



→ Uses : •) It is used as sweetning agent.
•) It is 500 times more sweet than sugarcane.
•) It is genobiotic (those substance which is not naturally produced as that in the organism)
•) It contain '0' calorie.
•) Used as nucleating in the manufacturing of polyethylenepthalate.

* Chloramine-T : (Organic sodium salt of ~~Ethyl toluene~~ toluene-A sulphonamide)



→ Uses : •) Act as a anti-infective agent.
•) It is used as disinfectant.
•) It is used as indicator & reagent.
•) It is act as oxidant.

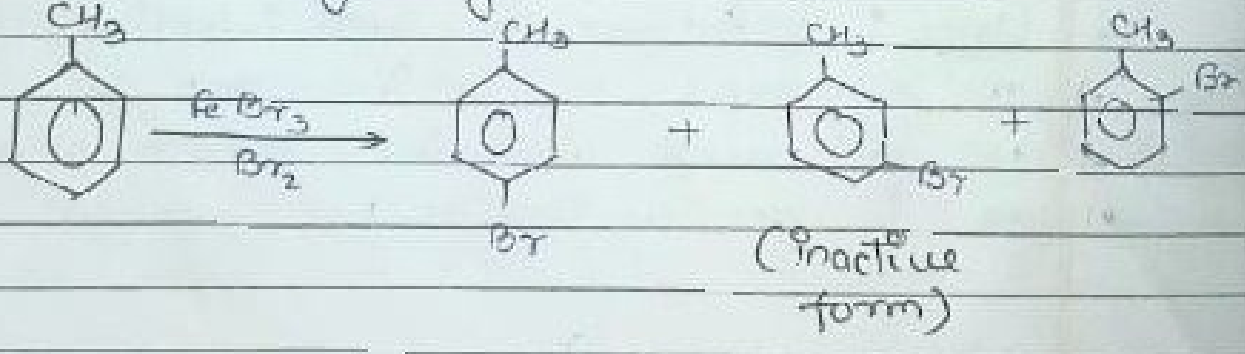
* Orientation : A second substitution can occupy any of the remaining 5 position in the monosubstituted benzene because of 1 substituted which are already present in benzene.

The position 2 & 6 are equivalent and give ortho product whereas 3 & 5 are equivalent & its give meta product, position 4 is unique and it give para product. These are 2 ortho, 2 meta & 1 para substitution with respect to substituent 1 para which is already present.

* On the basis of Direct Influence of Groups : All the Group can Be divided into 3 Classes :-

1) Ortho-para directing group : These groups direct the incoming grp to the ortho & para position

Eg : Alkyl (-R), Phenyl (C_6H_6), Hydroxyl (-OH), Amino ($-NH_2$)



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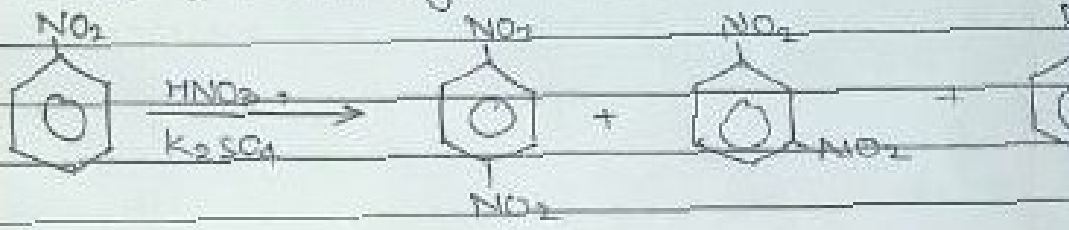
- Ortho - para directing are ring - activater.
- The CH_3 group is called as ortho - para director.
- The electron donating CH_3 group activate the benzene ring to electrophilic attack.

2) Meta directing group : This group direct the incoming group to meta - position.

Eg: Trialkyl ammonium ion, nitro (NO_2), cyno (CN), aldehyde (CHO), Carboxylic ($-COOH$),



- Meta directing group are ring - deactivator
- EWG (NO_2) deactivate the benzene ring to electrophilic attack.
- The NO_2 group is called as meta - director.
- Ortho - para directing & de-activating group

2) Ortho - para directing & de-activating group:

- Halogen are ortho & para directing but they de-activate the benzene ring.

Eg: Cl, F, Br, I

* Effect of Substituent :

Substituent : To benzene ring when any group replace H-atom & attach himself at this place, that process is known as substitution.

When any substituent attach on a ring it change the activity of ring & this is depends on the nature of substituent which attach on benzene.