

# Halalkanes & Haloarenes 09

## Properties of Haloarenes

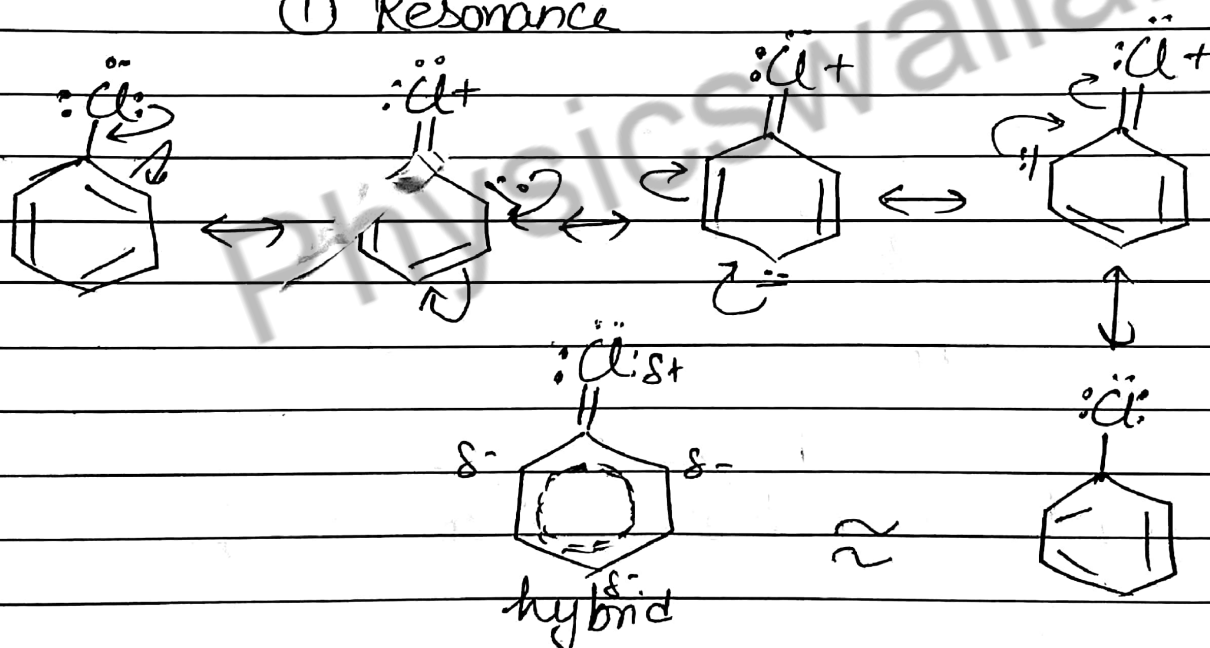
- Nucleophilic Substitution
- Reaction with Metals
- Electrophilic Substitution

## Nucleophilic Substitution

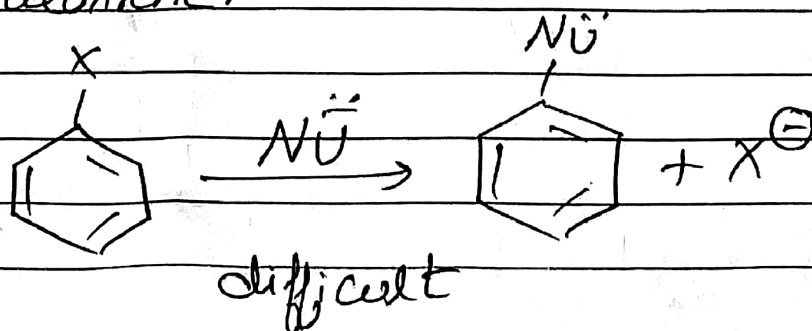
Haloarenes are chemically much less reactive than Halalkanes towards Nucleophilic Substitution reaction.

Reason:

① Resonance

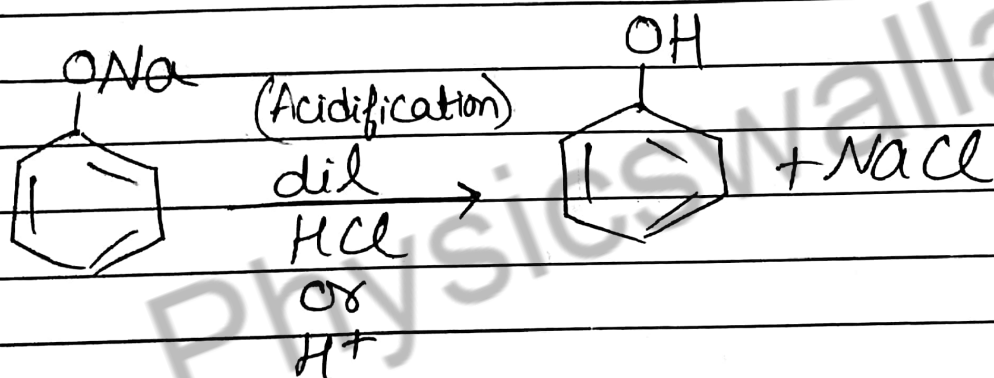
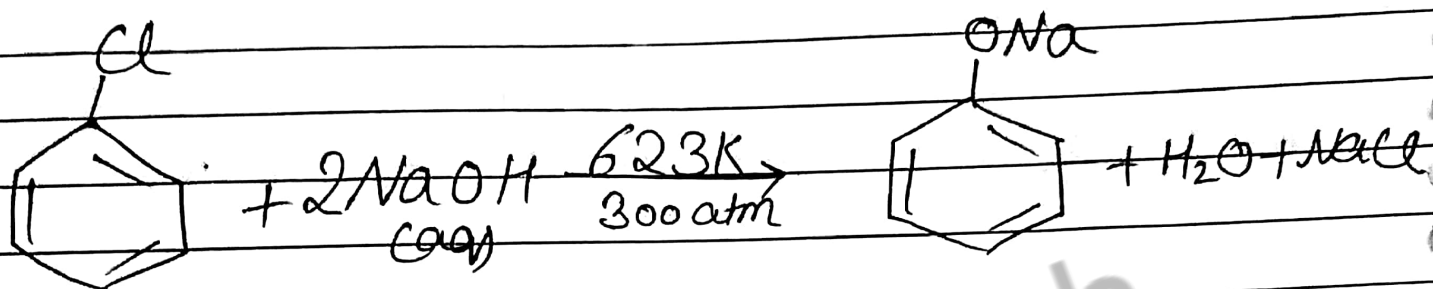


The C-Cl bond has partial double bond character due to Resonance, hence it is difficult to remove Cl (or halogen atom) of Haloarene.



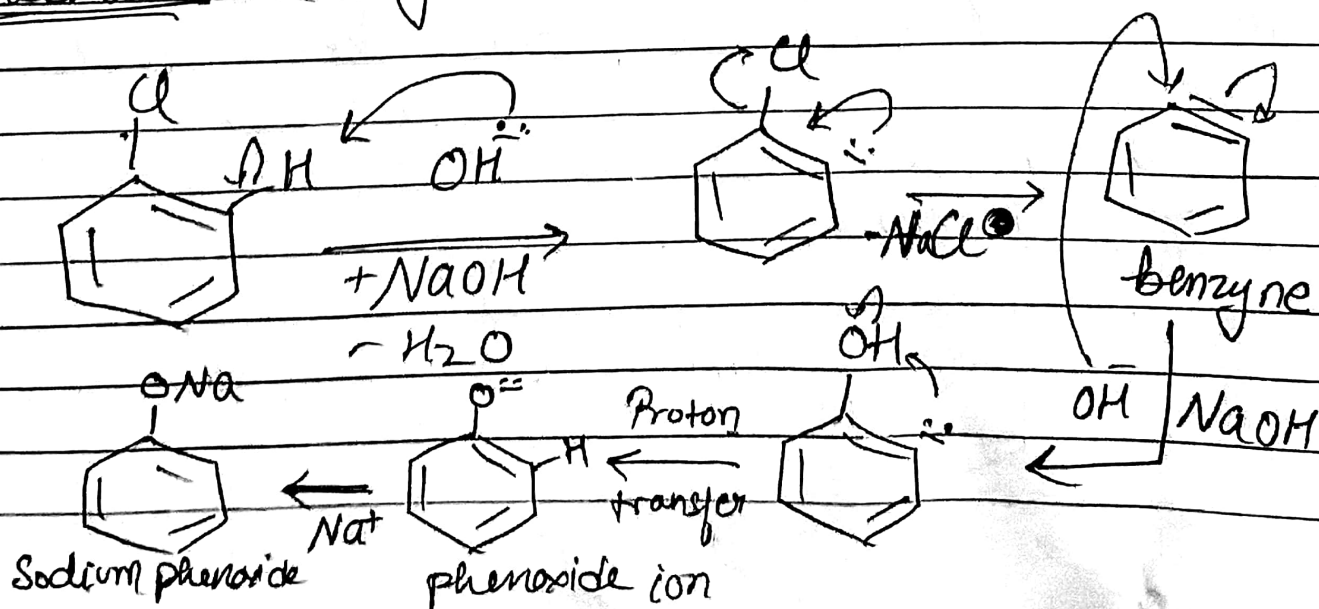
Still under drastic conditions, such as high Temperature or pressure, Halobenzenes can show Nucleophilic Substitution.

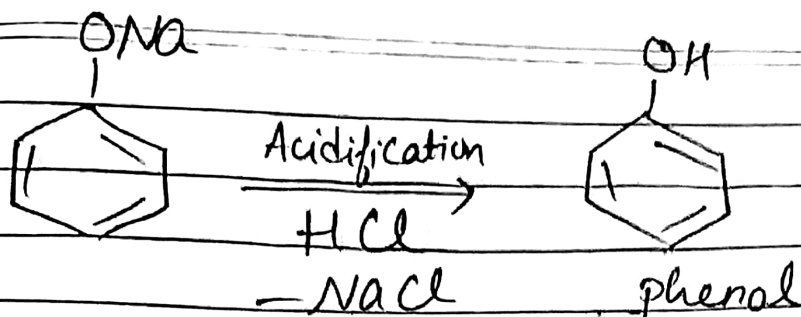
(i) Replacement by (OH) group  $\Rightarrow$  Formation of Phenol



Dow's Process  
Industrial Method for Manufacture of Phenol.

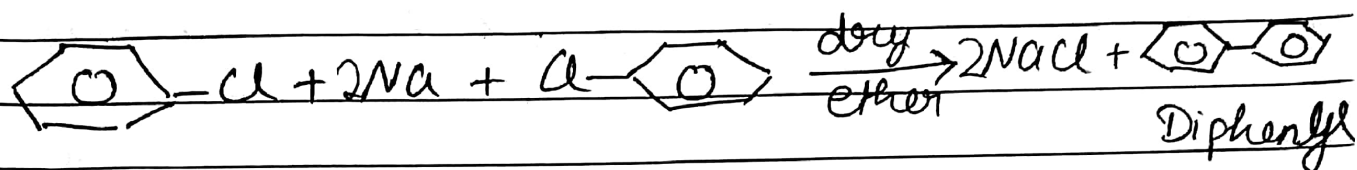
Mechanism: (Benzyne Intermediate)



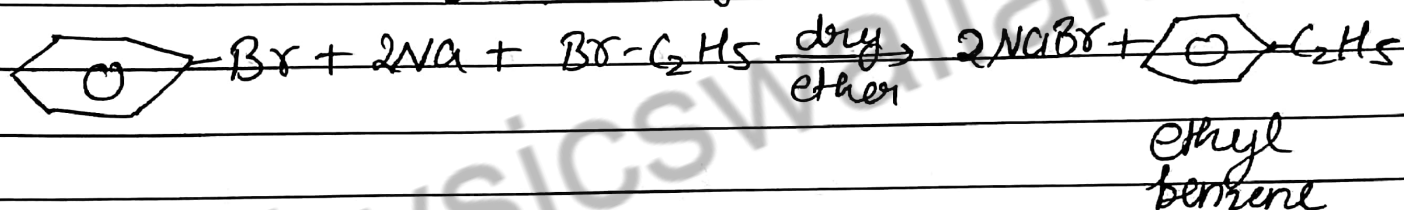


## Reaction with Metals

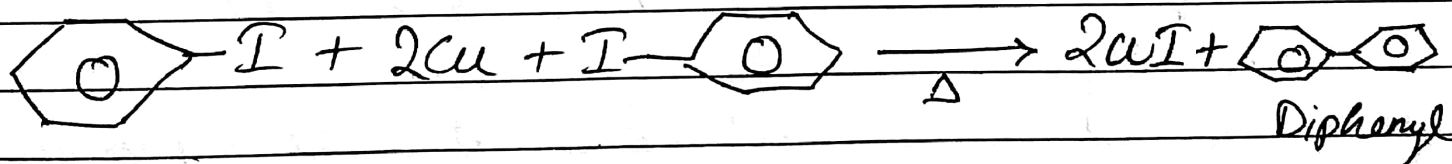
i) with sodium (Na)  $\rightarrow$  Fittig Reaction



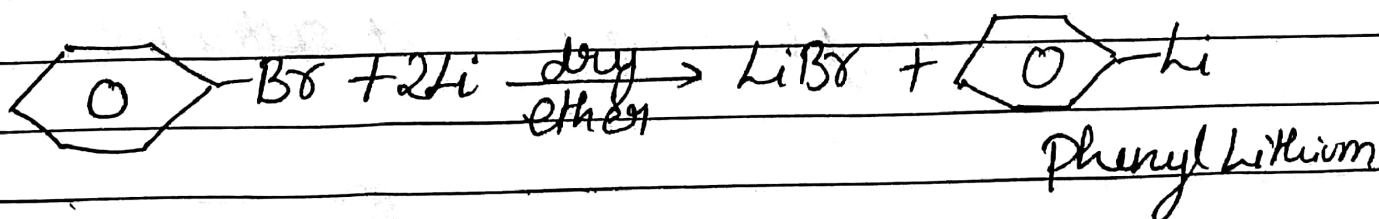
### Wurtz-Fittig Reaction



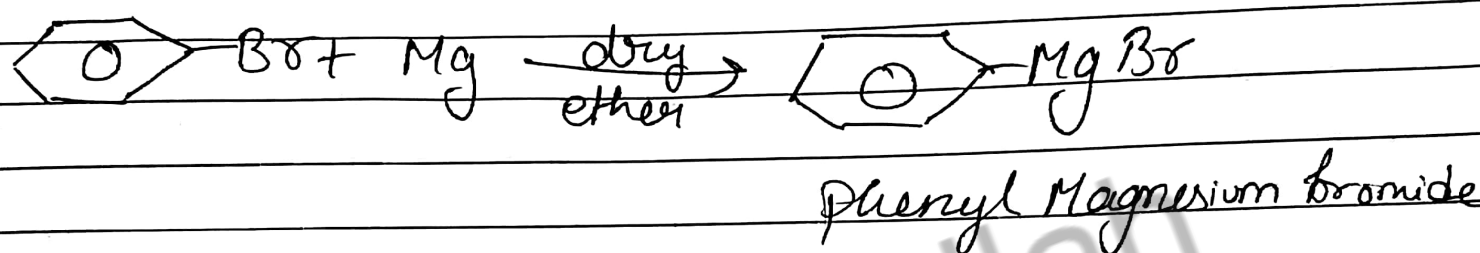
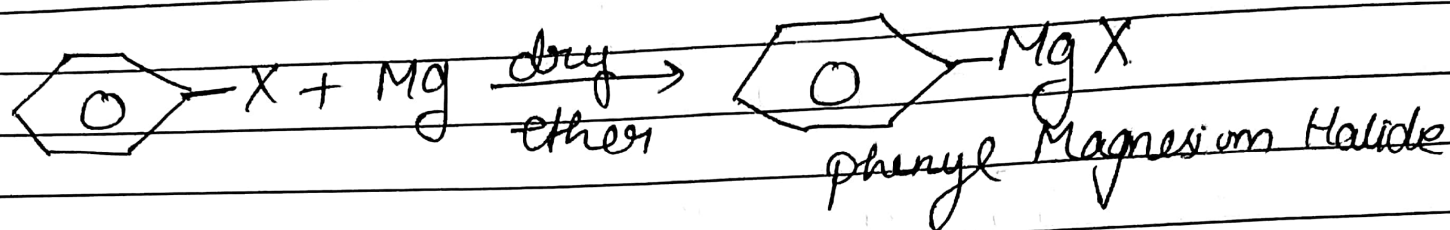
ii) with copper (Cu)  $\rightarrow$  Ullmann Synthesis (Reaction)



iii) with Lithium (Li)

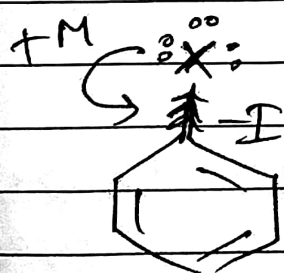


iv) with Magnesium (Mg)  $\Rightarrow$  Formation of Grignard's Reagent



### Electrophilic Substitution Reaction $\rightarrow$ (Ring Substitution)

Note: Halogens (Cl, Br, F, I) are deactivating groups  $\rightarrow$  They prevent Electrophilic Substitution  
 $\rightarrow$  they decrease  $e^-$  density of ring  
So  $E^+$  do not want to attack the ring

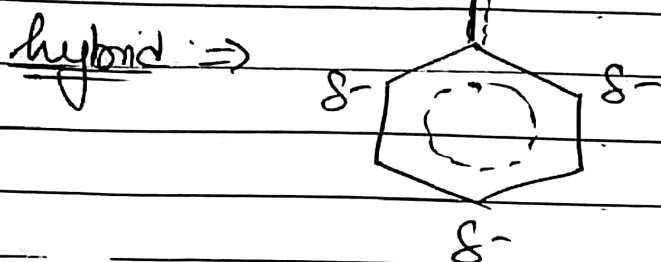
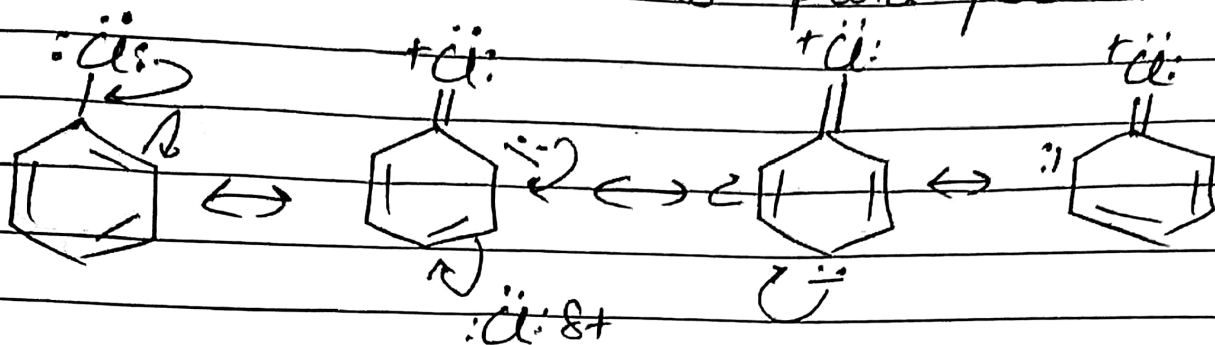


for halogens  $[-I > +M]$

overall  $e^-$  withdrawing from Ring  $\Rightarrow$  decreases  $e^-$  density of Ring

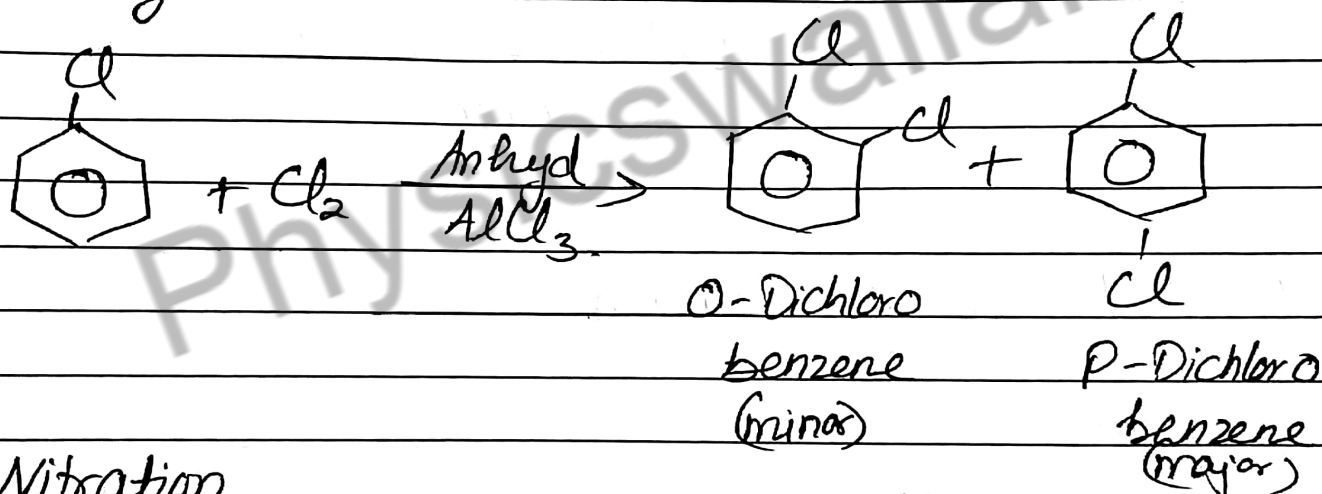
Incoming  $E^+$  do not get attracted.

but if  $E^+$  Substitution has to take place  $\rightarrow$   
 It occurs at ortho & para position  $\rightarrow$  why?

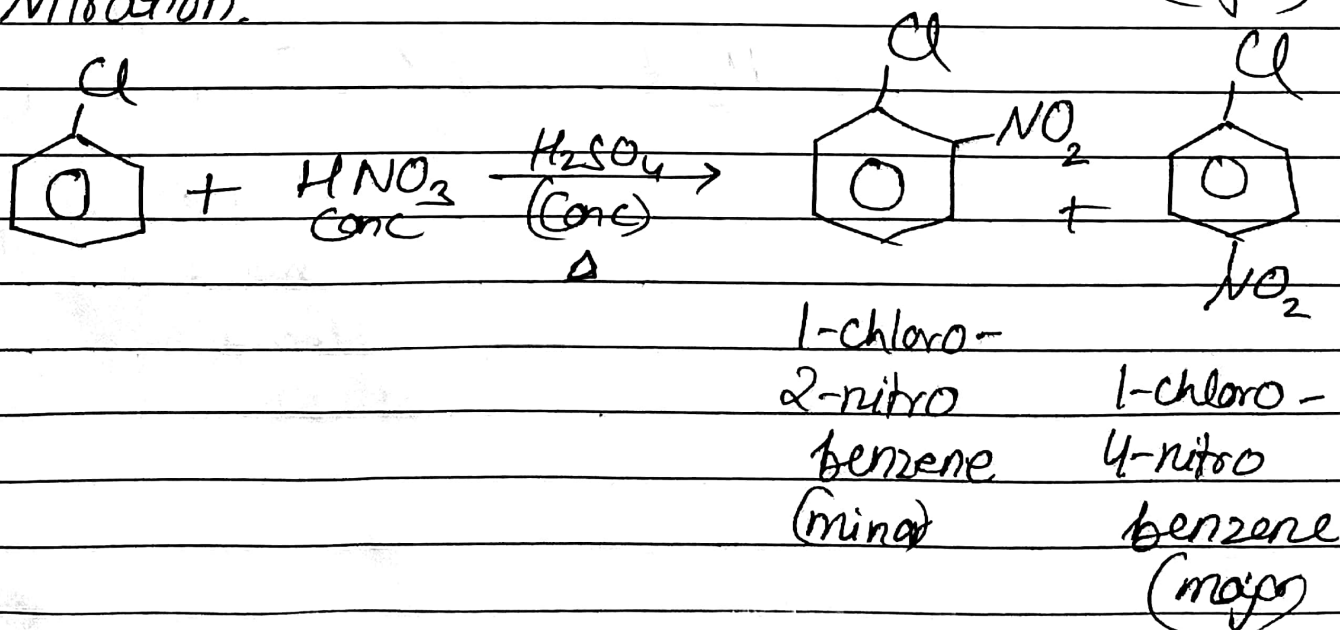


$e^-$  density is more on  
 ortho & para position.

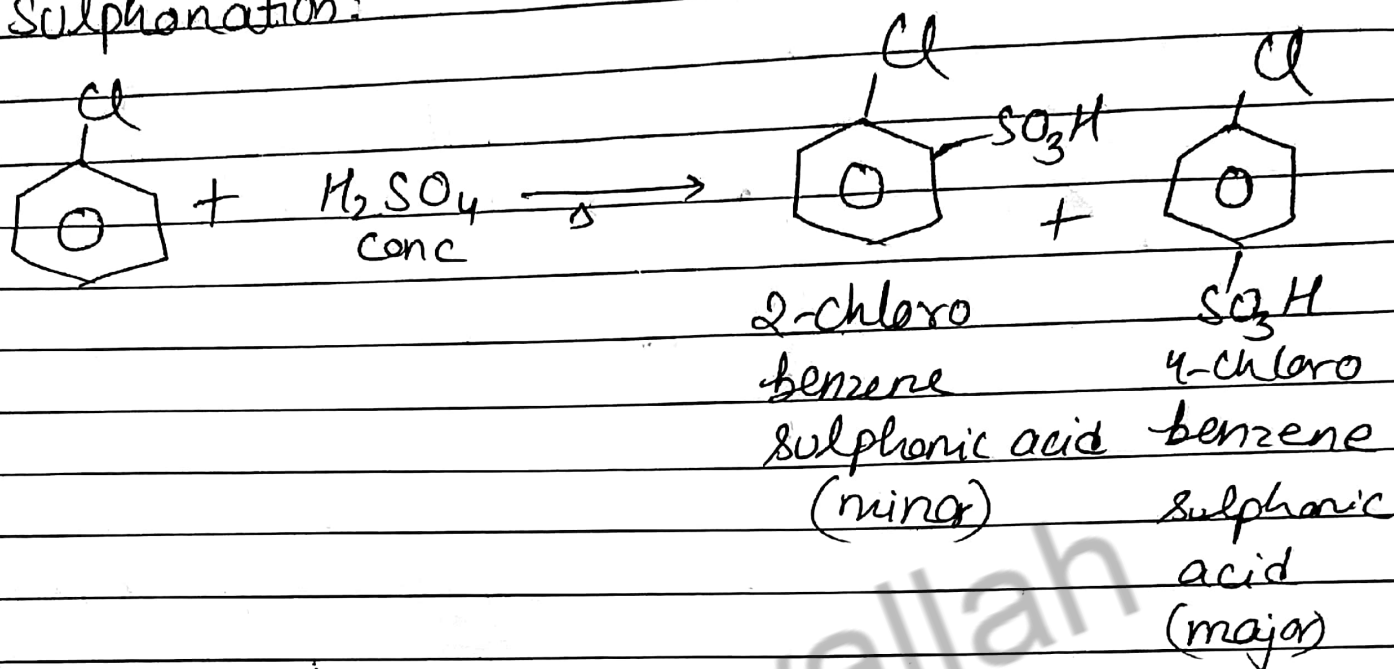
### ① Halogenation:



### ② Nitration.



### ③ Sulphonation:



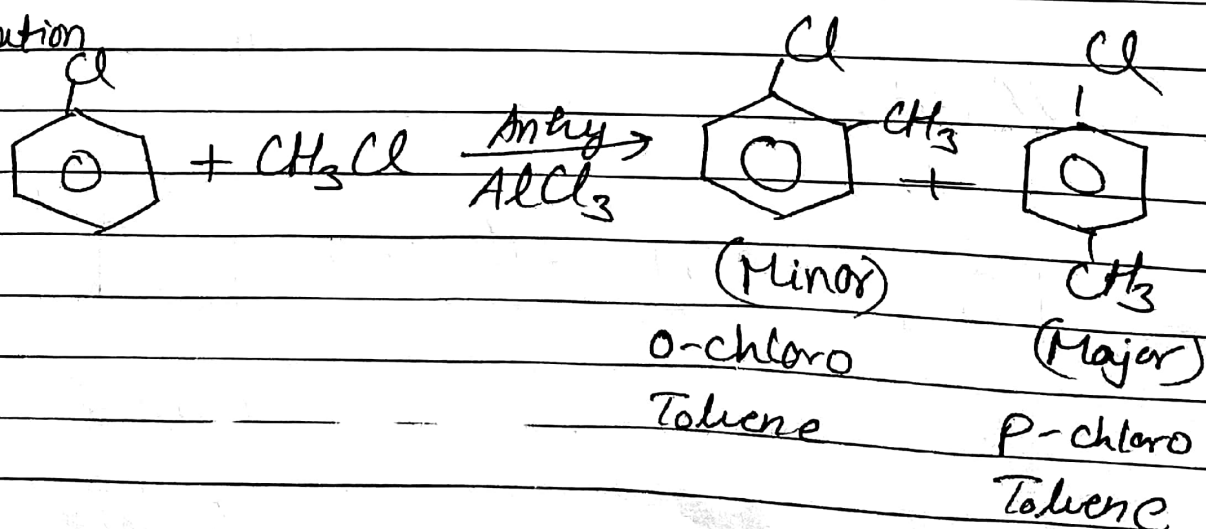
for detailed Mechanism →

Watch Reaction Mechanism Q.5

Chlorination, Nitration, Sulphonation  
in benzene "Physicewallah"

### ④ Friedel-Crafts Reaction

i) Alkylation



ii) Acylation.

