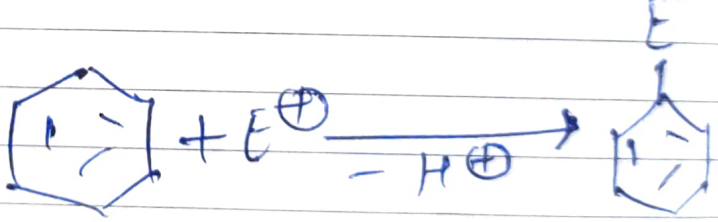
15 JUN MONDAY 2016

Aromatic Electrophilic Substitution

The Arenium ion mechanism :—

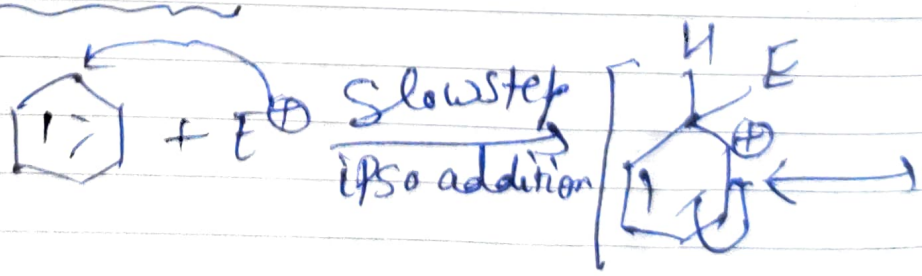
Electrophilic aromatic Substitution is the organic reaction in which an atom that attached to an aromatic system (typically hydrogen) is replaced by an electrophile. This is quite possible in aromatic system because there is π-electron density above and below the plane which is easily available for attacking electrophile and nucleophilic attack is opposed because of π-cloud shields the Carbon from such invasions.

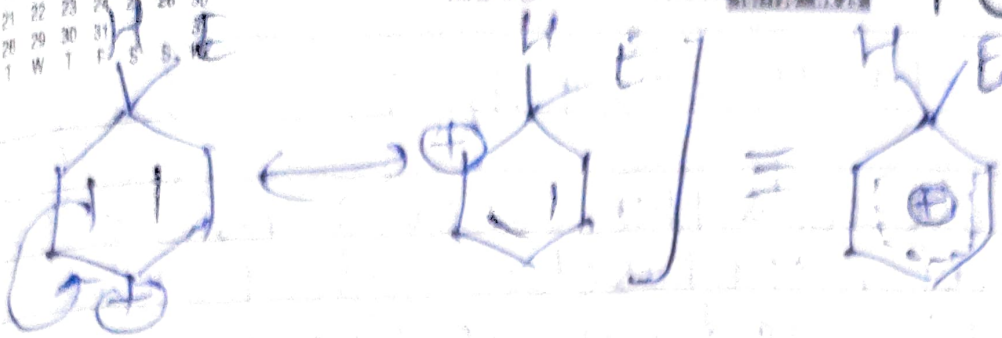
Example



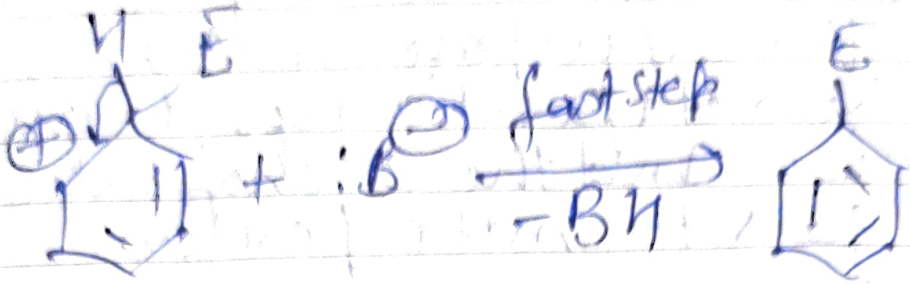
mechanism -

(I)





II)

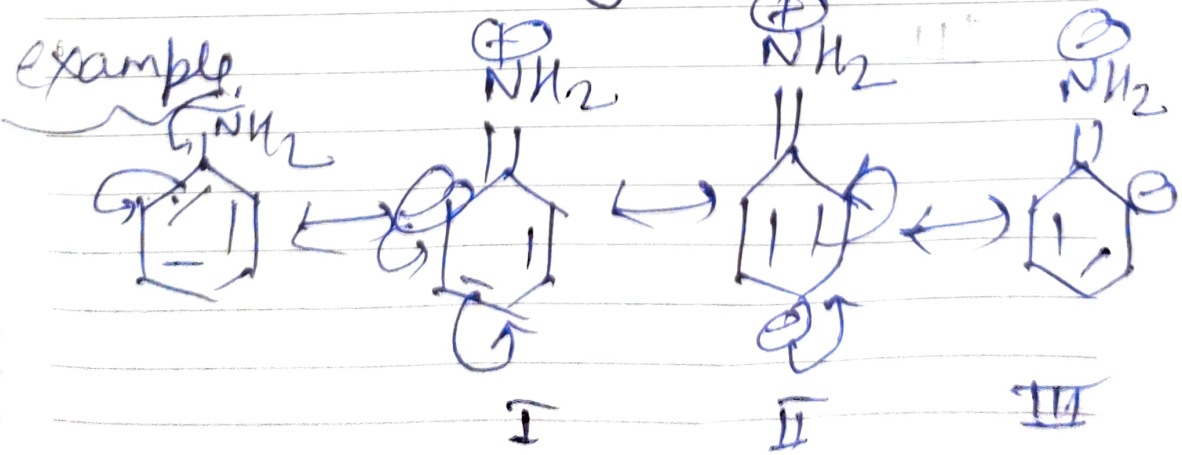


Product

ortho / para directing group

This group direct the incoming electrophile at ortho & para position this increases the electron density on the ortho & para position. Thus this creats room for attacking electrophile.

example



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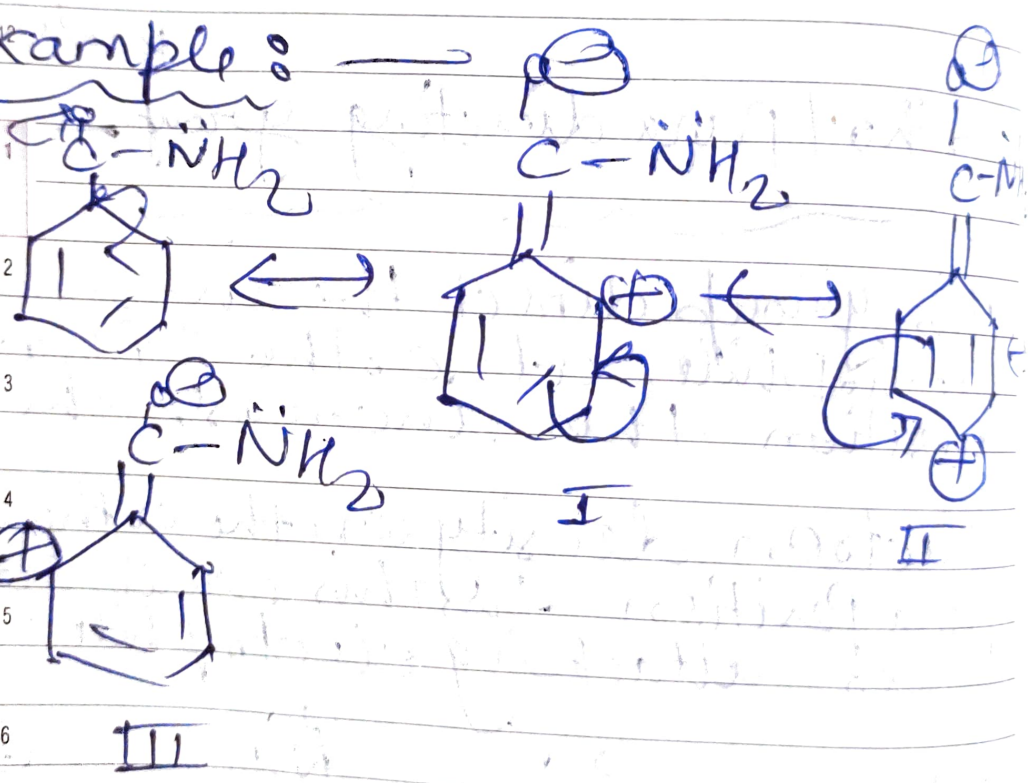
23	1	2	3	4	5	6
24	8	9	10	11	12	13
25	15	16	17	18	19	20
26	22	23	24	25	26	27
27	29	30				
Wk	M	T	W	T	F	S

meta directing gp :— This group directs the other substitution at meta position they withdraw the electron density from ortho & para position therefore the meta position is the electron rich and the electrophilic goes to meta position.

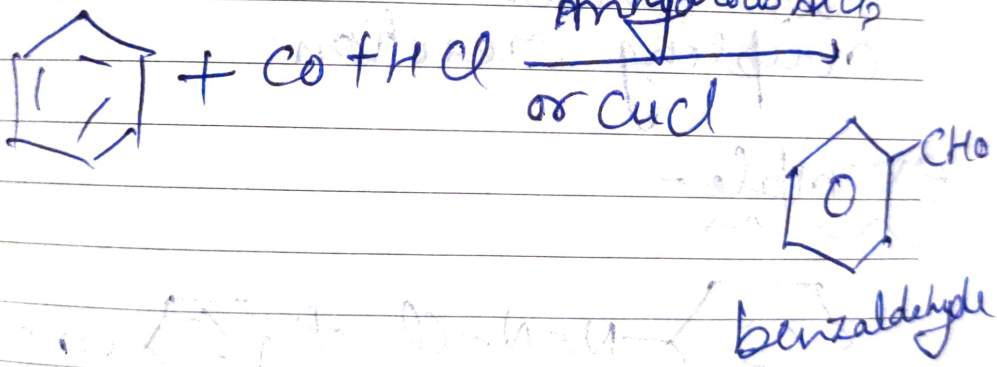
example :—



Gattermann Koch Reaction :-

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.

Example

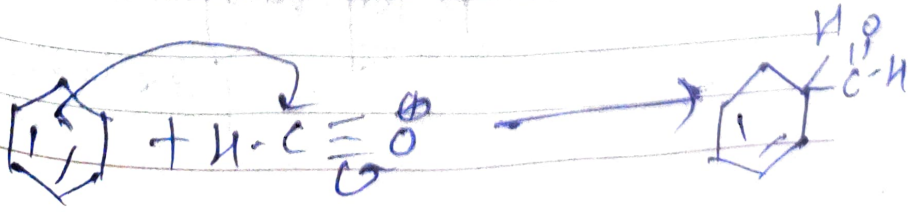


Mechanism -

I) $CO + HCl \longrightarrow H-\overset{\oplus}{C}=O \; AlCl_4^{\ominus}$

$H-C(=O)-AlCl_3 \xrightarrow{-AlCl_4} HC\equiv\overset{\oplus}{O}$

II)



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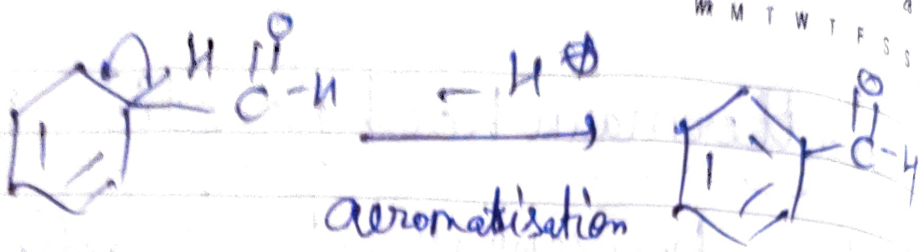
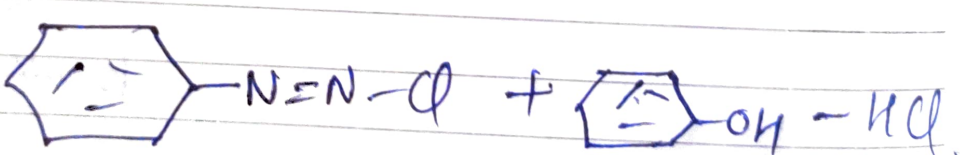
(III)



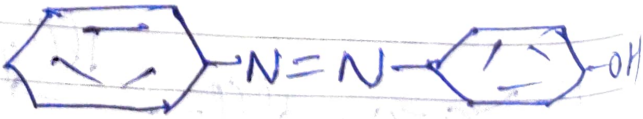
Diazonium Coupling Reaction:-

Reaction of Benzenediazonium Chloride with Phenol gives P-hydroxy azobenzene (orange dye) is known as diazonium coupling reaction

example -



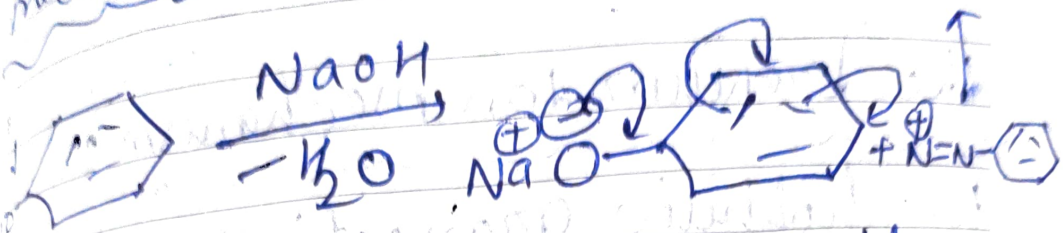
Benzenediazonium Chloride Phenol



P hydroxy azobenzene
(orange dye)

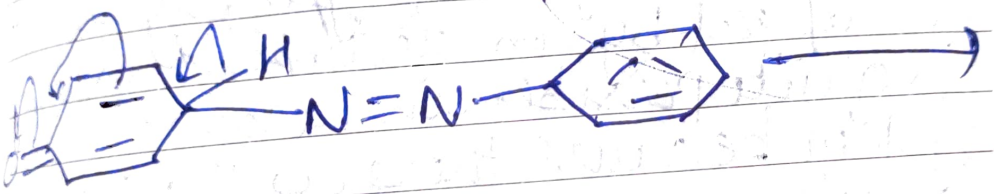
Mechanism :-

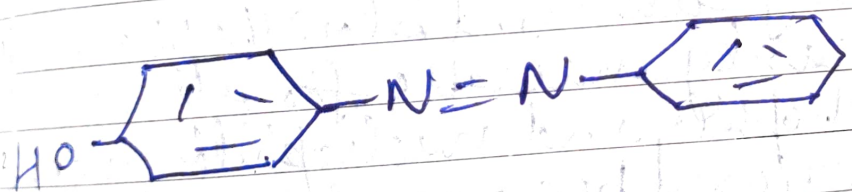
benzenediazonium ion



Phenol

Sodiumphenoxide

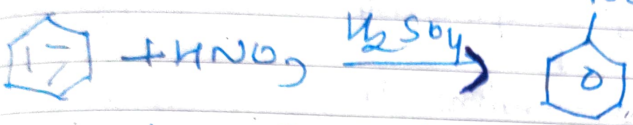




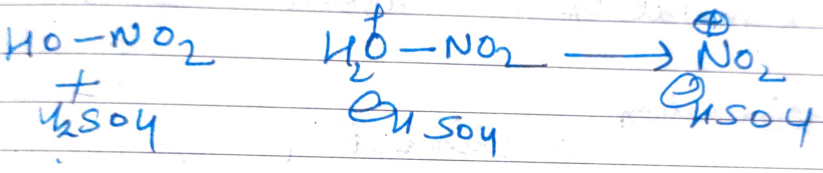
P-hydroxyazobenzene.

Nitration of benzene with Conc. HNO_3 and Conc. H_2SO_4 —

When benzene is treated with HNO_3 in presence of H_2SO_4 then Nitrobenzene is obtained. This reaction is R/a Nitration of benzene.



generation of electrophile —



mechanism: —