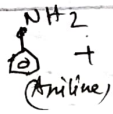
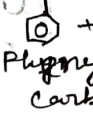
"Named organic reaction" "Jai Ram"
"Laboratory preparation" "Worksheet : 06"

1) **Carbylamine reaction :=**

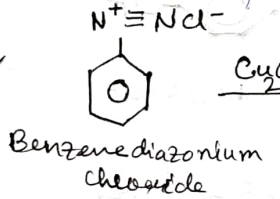
When an aliphatic or aromatic primary amine is heated with chloroform and alcoholic KOH, an isocyanide (carbylamine) having offensive (very unpleasant) smell is obtained.

(a) CH_3NH_2 (Methylamine) $+ CHCl_3 + 3KOH(alc.) \xrightarrow{Heat} CH_3-N\equiv C + 3KCl + 3H_2O$

(b)  (Aniline) $+ CHCl_3 + 3KOH(alc) \rightarrow$  $+ 3KCl + 3H_2O$

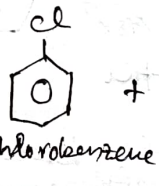
Phenyl carbylamine

2) **Sandmeyer reaction :=**

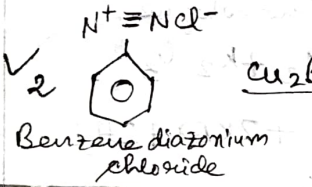


Benzenediazonium chloride

$\xrightarrow{Cu_2Cl_2/HCl}$

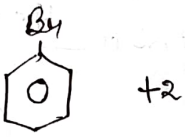


Chlorobenzene $+ N_2$



Benzene diazonium chloride

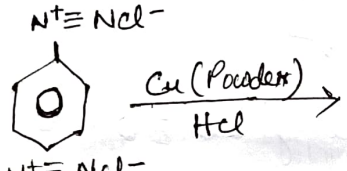
$\xrightarrow{Cu_2Br_2/HBr}$



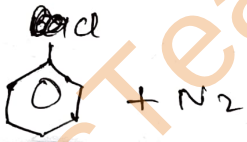
Bromobenzene $+ 2N_2 + Cu_2Cl_2$

3) **Gattermann reaction :=** * Modified version of sandmeyer reaction

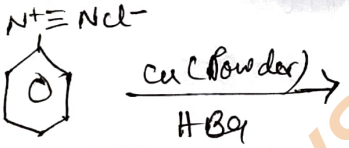
[In this reaction, diazonium salt is treated with copper powder and the corresponding Halogen acid]



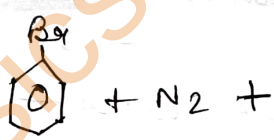
$\xrightarrow{Cu\ (Powder)/HCl}$



$+ N_2$

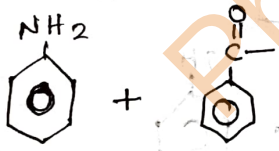


$\xrightarrow{Cu\ (Powder)/HBr}$



$+ N_2 + Cl^-$

4) **Schotten Baumann Reaction :=** (Benzoylation)

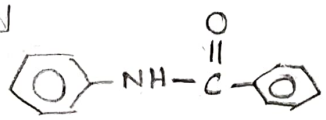


Aniline

$+$

$[C_6H_5COCl]$ (Benzoyl chloride)

$\xrightarrow[-HCl]{aq.\ NaOH\ (or\ Pyridine)}$



$+ HCl$

N-Phenylbenzenamide (Benzanilide)

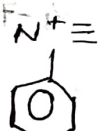
5) **Diazotisation Reaction :-** (conversion of an aromatic primary amine into a diazonium salt)

$NaNO_2 + HCl \rightleftharpoons NaCl + HNO_2$

Aniline.

$+ HNO_2 + HCl \xrightarrow[(or\ 0-5°C)]{273-278K}$

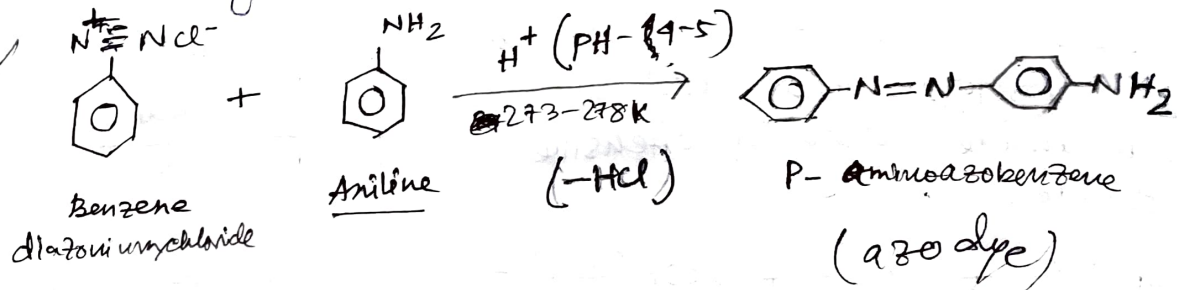
[Cold solution of nitrous acid.]

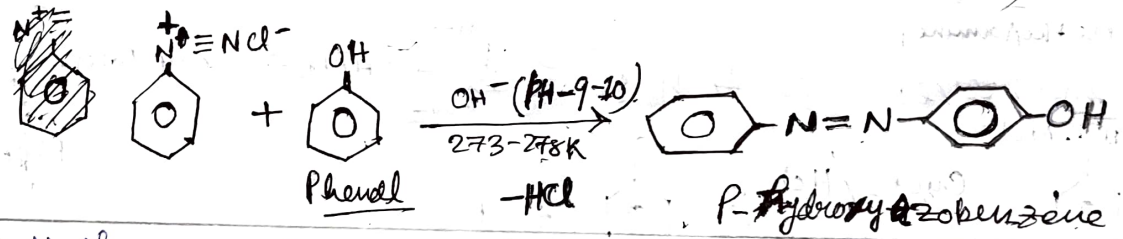


$+ 2H_2O$

Benzenediazonium Chloride.

6) Coupling reaction :-





7) Hoffmann Bromamide Reaction :-

(is very useful for converting a higher member of a family to a lower homologue.

$CH_3CONH_2 + Br_2 + 4KOH \xrightarrow{Heat} CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$

(Ethanamide) acetamide

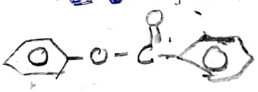
(Methanamine) Methylamine

* Hoffmann degradation reaction. (ex. Ethylamine to methylamine)

8) Schotten-Baumann Reaction :-

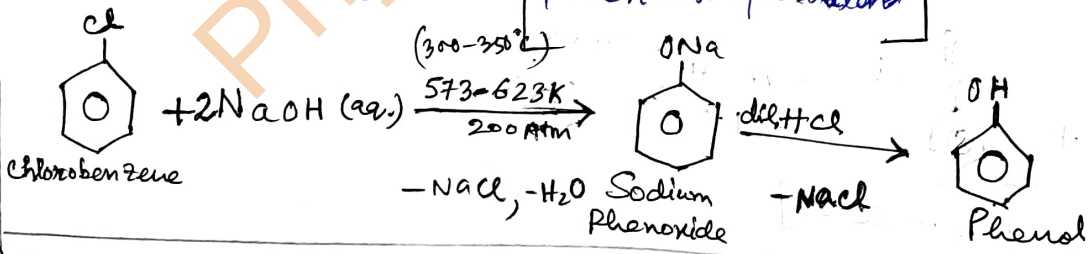
Note

Phenol + Benzoyl chloride → Phenyl benzoate

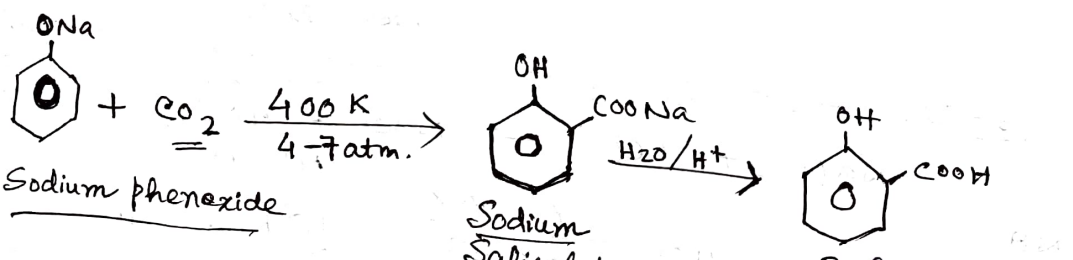
Aniline + " → ()

Alcohol + Benzoyl chloride →

9) Dow's Process :- [Phenol Preparation]

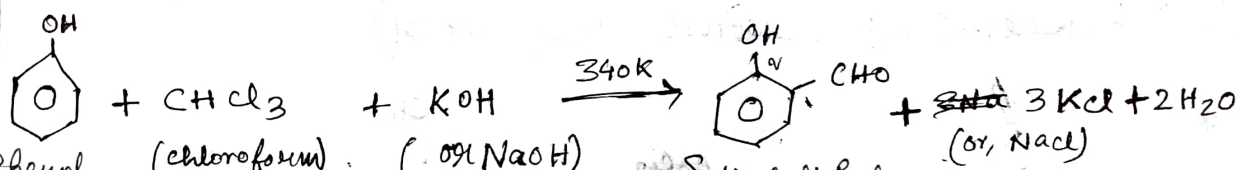


10) Kolbe's Reaction :-



Salicylic Acid Preparation

11) Reimer-Tiemann Reaction :- ✓ Salicylaldehyde preparation



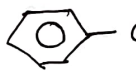
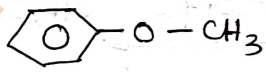
* [same as carbylamine reaction but phenol, instead of aniline]

12) Williamson's Synthesis [Best method for the preparation of ethers.]

An alkyl halide is treated with a suitable sodium alkoxide :

a) $CH_3Br + CH_3O^-Na^+ \longrightarrow CH_3-O-CH_3 + NaBr$

Methyl bromide — Sodium methoxide — (Dimethyl ether)

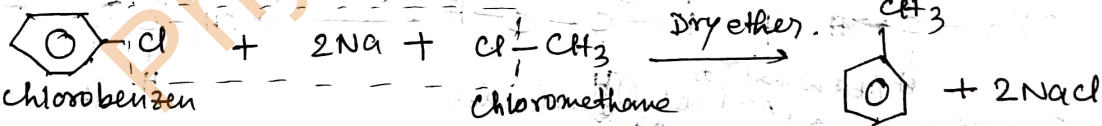
* b) CH_3Br +  →  + NaBr

Methyl bromide — Sodium phenoxide — Methyl phenyl ether (Anisole).

Anisole :- Methyl phenyl ether.

13) Wurtz-Fitting reaction * [Wurtz reaction + fitting reaction]

* [Haloarene + Haloalkane + Na]



11) A) Wurtz reaction.

[Haloalkane (alkyl halide) + Na $\xrightarrow{\text{dry ether}}$ Alkanes]

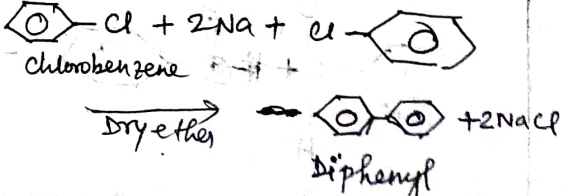
$CH_3I + 2Na + CH_3I \longrightarrow CH_3-CH_3 + 2NaI$

(Ethane)

* For the preparation of alkanes containing even number of carbon atoms

B) Fitting reaction.

Haloarene is heated with Na metal in the presence of dry ether diaryl is obtained.



Laboratory Method of Preparation

- **Bromoethane :–** (C_2H_5Br)

$$C_2H_5OH + KBr + \text{Conc. } H_2SO_4 \xrightarrow{\text{Heat}} C_2H_5Br + KHSO_4 + H_2O$$

- **Chloroform :–**

by heating ethanol (ethyl alcohol) or acetone with bleaching powder. (The reaction is called ~~haloform~~ reaction)

- **Iodoform :–**

ethanol is heated with iodine in the presence of an alkali.

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\text{Heat}} \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

- **Diethyl Ether :** (Ethoxy ethane)

By heating excess of ethyl alcohol with conc. H_2SO_4 at 413 K (140°C)

$$C_2H_5OH + HOC_2H_5 \xrightarrow[413\text{ K}]{\text{Conc. } H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

- **Acetone**

~~Acetaldehyde~~ : (~~Ethanal~~) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

~~by the dry distillation of calcium salts of carboxylic acids~~ by heating anhydrous calcium acetate

$$(CH_3COO)_2Ca \xrightarrow{\text{Heat}} CH_3COCH_3 + 2CaCO_3$$

calcium acetate. ~~calcium formate~~ Acetone.

- **Formaldehyde** ($HCHO$) (oxidation of methanol with oxygen)

$$2CH_3OH + O_2 \xrightarrow[825-875\text{ K}]{Cu} 2HCHO + 2H_2O$$

Methanol → Methanal (Formaldehyde)

* 5% aq. solution of Phenol : Carbolic acid.

* 40% aq. solution of methanal (formaldehyde) :– Formalin

- **Acetaldehyde** (Ethanal) CH_3CHO

by the oxidation of ethyl alcohol with

$$CH_3CH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3CHO + H_2O$$