"Worksheet – 02" (Named Organic reaction)

write the chemical equation for the following named organic reactions.

1. Haloform reaction

sample solution: This reaction is used for the preparation of haloform (generally $CHCl_3$ or CHI_3).

For example :- (preparation of iodoform)

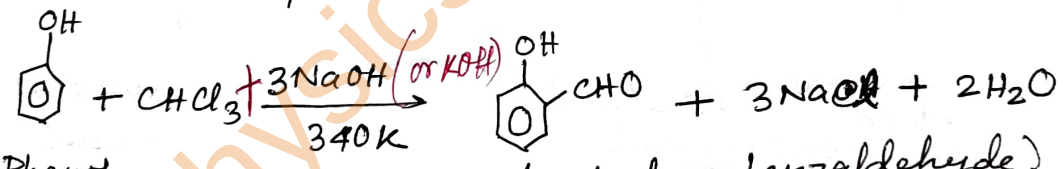
The reaction involves the heating of ethanol or acetone with iodine in the presence of an alkali.

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

Ethanol — (Iodoform) — Sod. formate

2. Reimer–Tiemann reaction

: In this reaction, phenol is treated with chloroform in presence of aq. sodium hydroxide (or alkali) at 340 K (followed by hydrolysis). This reaction is used for the preparation of o-hydroxybenzaldehyde (salicylaldehyde) as the major product.



Phenol — (2-hydroxybenzaldehyde) (main product)

*

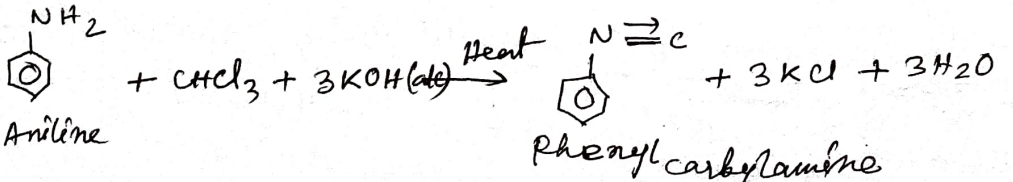
3. Carbylamine reaction:

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

a) $CH_3CH_2NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{Heat} CH_3CH_2-N\equiv C + 3KCl + 3H_2O$

Ethylamine — Ethyl carbylamine

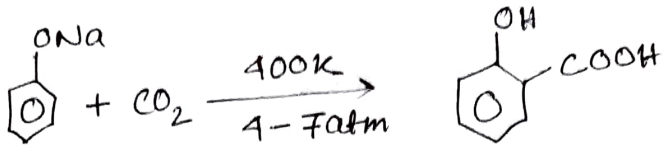
b)



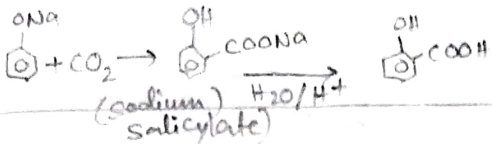
Aniline — Phenyl carbylamine (phenyl isocyanide)

4 Kolbe's-schmidt reaction or "Kolbe reaction"

In this reaction sodium phenoxide is heated with CO_2 at about 400K under a pressure of 4–7 atm, and 2-hydroxy benzoic acid (salicylic acid) is obtained as the major product.



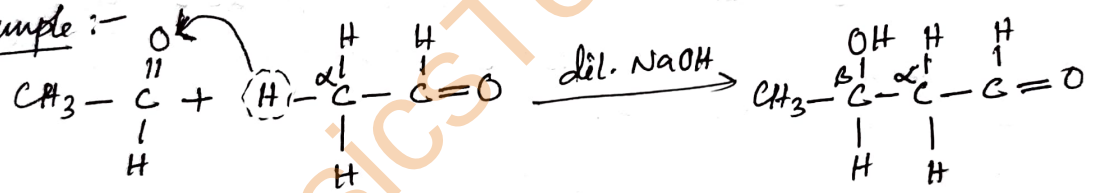
2-hydroxy benzoic acid (salicylic acid)



5 Aldol condensation

In this reaction, aldehydes and ketones containing at least one α-hydrogen atom when treated with dil. NaOH (or K_2CO_3), undergo self condensation to form β-hydroxy-aldehydes or β-hydroxy ketones [β-hydroxy aldehydes possess both aldehydic and alcoholic groups, they are commonly known as aldols]

Example :-



Ethanal (acetaldehyde) (two molecules)

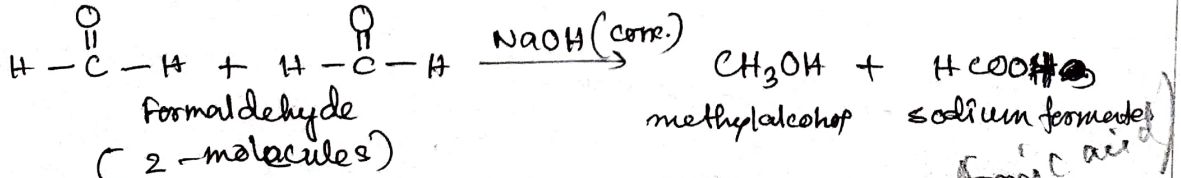
3-hydroxybutanal (aldol)

6 Cannizzaro reaction (also same for Benzaldehyde)

Self oxidation–reduction of an aldehyde containing no α-hydrogen atom in the presence of a conc. NaOH (or conc. KOH) is called Cannizzaro reaction. This reaction is shown [only by formaldehyde, benzaldehyde etc]

Example :-

Formaldehyde is heated with conc. NaOH, methyl alcohol and sodium formate are obtained.



Formaldehyde (2-molecules)

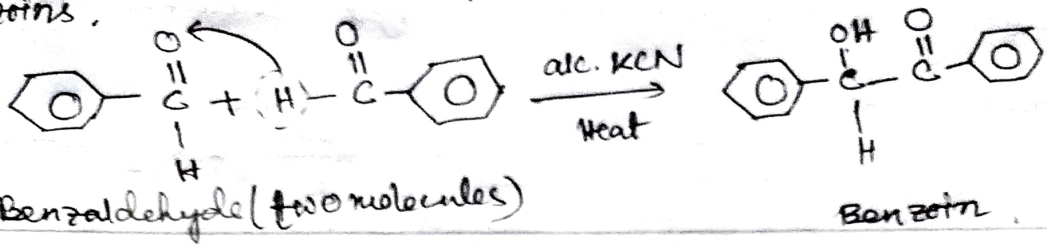
methylalcohol

sodium formate (from formic acid)

[One is reduced to CH_3OH while the other oxidised to $HCOOH$.]

7 Benzoin condensation (by two molecules of benzaldehyde)

Aromatic aldehydes (e.g. benzaldehyde), when heated with an alcoholic KCN, undergo self condensation to form benzoins.



Benzaldehyde (two molecules) → Benzoin

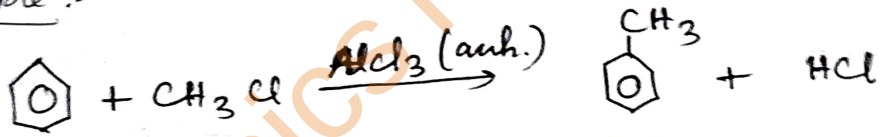
8 Friedel-Craft Reaction (alkylation)

The reaction involves the replacement of a hydrogen atom in benzene ring by an alkyl group or acyl group ($CH_3-\overset{O}{\overset{\|}{C}}-$)

- The replacement of hydrogen atom in benzene ring by an alkyl group is termed as friedel-craft alkylation.

In this reaction benzene is treated with an alkyl halide in the presence of anhydrous $AlCl_3$, an alkyl benzene (toluene) is obtained.

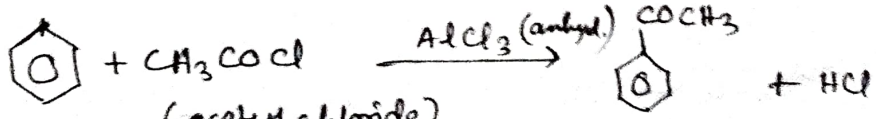
Example :-



Benzene + Methyl chloride → Toluene (methyl benzene) + HCl

9 Friedel-craft (acylation):

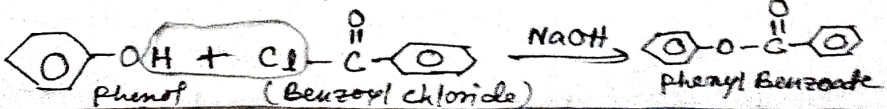
When benzene is treated with acetyl chloride in the presence of anhydrous $AlCl_3$, an acetyl benzene is obtained.



(acetyl chloride) Ethanoyl chloride + → Acetylbenzene (Acetaphenone) + HCl

10 Schotten-Baumann Reaction (Benzoylation of Phenol)

Benzoylation of phenols in the presence of alkali (NaOH) is known as Schotten-Baumann Reaction.

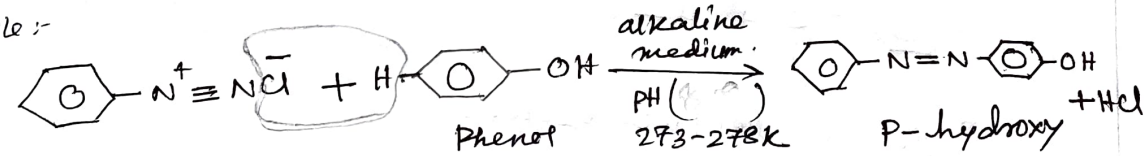


Phenol + (Benzoyl chloride) → Phenyl Benzoate + HCl

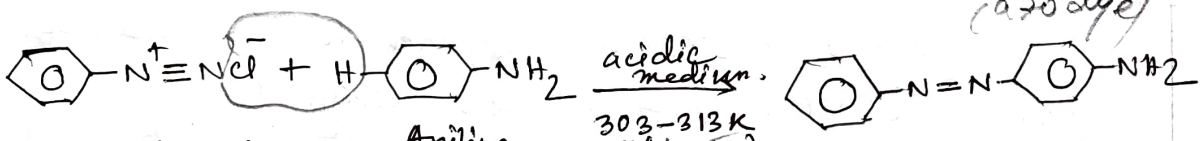
11 **Coupling Reaction**

This reaction involves the coupling of a diazonium salt at the para-position (p-position) of a phenol or aniline resulting in the formation of a bright coloured azo dye.

Example :-

(a) 

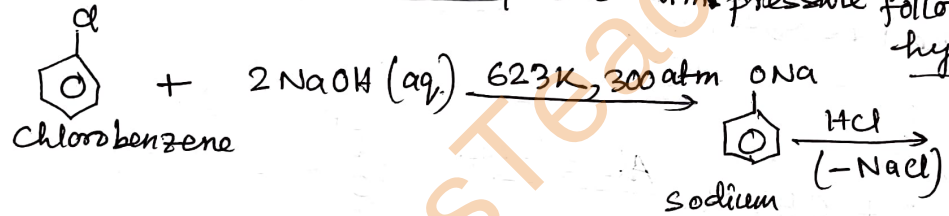
Phenol — p-hydroxy azobenzene

(b) 

Benzene diazonium Chloride — Aniline — p-aminoazobenzene

12 **DOW's process** [The process is used for the manufacture of 'Phenol']

Chlorobenzene is heated with an aq. solution of NaOH at 623K under ~~a pressure of~~ 300 atm pressure followed by hydrolysis.



Chlorobenzene — sodium phenoxide — phenol.

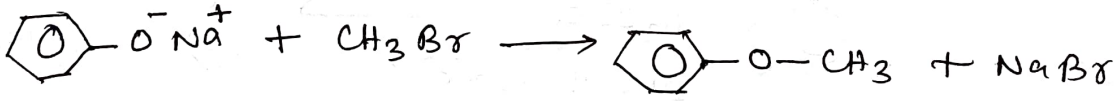
13 **Williamson's Synthesis** [This is one of the best method of preparation of 'Ethers'.

In this method, an alkyl halide is treated with a suitable sodium alkoxide.

~~Example~~-

(a) $C_2H_5ONa^+ + C_2H_5Br \longrightarrow C_2H_5-O-C_2H_5 + NaBr$

(Sodium ethoxide) (Bromoethane) (Diethyl ether)

(b) 

Methyl phenyl ether (Anisole)

14 **Esterification** [Ester preparation method]

Alcohol react with Carboxylic acid in the presence of Conc. H_2SO_4 to form esters.

Example :- $CH_3CH_2OH + CH_3-COOH \xrightarrow[(-H_2O)]{\text{conc. } H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

Ethyl acetate (Ethyl ethanoate)

15 HVZ reaction (Hell-Volhard-Zelinsky reaction)

Carboxylic acid (except formic acid which does not contain any alkyl group) react with chlorine or bromine in the presence of a small amount of phosphorus to give α-halogenated carboxylic acids.

$$\overset{\alpha}{C}H_3COOH \xrightarrow[(-HCl)]{Cl_2,\ Red\ P} CH_2ClCOOH \xrightarrow[(-HCl)]{Cl_2,\ Red\ P} CHCl_2COOH$$

(Acetic acid) (Ethanoic acid)

$$CCl_3COOH \xleftarrow[(-HCl)]{Cl_2,\ Red\ P}$$

(Trichloro acetic acid)

* $\overset{\beta}{C}H_3\overset{\alpha}{C}H_2COOH \xrightarrow{Br_2,\ Red\ P} CH_3-\underset{Br}{\overset{|}{\underset{|}{C}}}-COOH$

(Propanoic acid) 2,2-dibromopropanoic acid.

16 Mendius Reaction (Reduction) [Primary amine from alkyl cyanide]

The reaction involves the reduction of an alkyl cyanide in presence of sodium and alcohol. The product obtained is primary amine.

e.g. $CH_3CN + 4H \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$

Methyl cyanide (Ethane nitrile) → Ethylamine (1° amine)

17 Stephen's Reduction [Aldehyde from alkyl cyanide]

The partial reduction of an alkyl cyanide by $SnCl_2$ and HCl gas (at room temp) followed by hydrolysis give an aldehyde.

$$CH_3-C\equiv N \xrightarrow[\text{Ether, } 290-295K]{SnCl_2 + HCl\ (gas)} CH_3-CH=NH\cdot HCl \xrightarrow[\text{Boil}]{H_2O} CH_3CHO + NH_4Cl$$

Acetaldimine hydrochloride

Alternately

$$CH_3CN \xrightarrow[\text{Ether, } 290-295K]{SnCl_2 + HCl\ (gas)} CH_3CHO$$

(Acetaldehyde). Final product.

18 **Rosenmund's Reduction Reaction** [Aldehyde preparation from acetyl chloride]

This reaction involves catalytic hydrogenation of acid chloride (acetyl chloride) resulting in the formation of corresponding aldehydes.

e.g. $CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{(Boiling Xylene)}]{Pd/BaSO_4 + S} CH_3CHO + HCl$

(Acetylchloride) (Acetaldehyde)

19 **Clemmensen Reduction** [Hydrocarbon preparation from aldehyde and ketone]

When aldehydes and ketones are treated with zinc-amulgam and conc. HCl, they get reduced to the corresponding hydrocarbons.

a) $CH_3CHO + 4H \xrightarrow{Zn/Hg, HCl} CH_3CH_3 + H_2O$

Acetaldehyde — Ethane

b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 4H \xrightarrow{Zn/Hg, HCl} CH_3-CH_2-CH_3 + H_2O$

Acetone — Propane

20 **Swarts Reaction** [* Fluoro alkane preparation]

The replacement of chlorine (in organic compound) by fluorine through the action of antimony tri-fluoride (SbF_3) in the presence of antimony salts having antimony in the oxidation state of +5 (e.g. $SbCl_5$) is called Swarts reaction.

$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 3CF_2Cl_2 + 2SbCl_3$

Freon (chloro fluoro carbon) / (CFC)

21 **Finkelstein Reaction** [* Iodoalkane preparation]

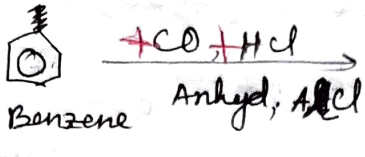
This reaction involves an exchange of chlorine (or bromine) present in chloro (or bromo) alkane with iodine.

$CH_3CH_2Cl + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} CH_3CH_2I + NaCl$

Chloroethane — Iodoethane.

* Halogen exchange method.

22 Gattermann-Koch Reaction :-



Benzene — Benzaldehyde.

* In this reaction benzene is treated with CO and HCl (gas) in the presence of anhyd. $AlCl_3$ or CuCl, benzaldehyde is obtained.

23 Hoffmann Ammonolysis :

When an excess of haloalkane is treated with alcoholic ammonia, a mixture of 1° amine, 2° amine, 3° amines and quaternary salt is obtained.

$$CH_3Br + NH_3 \xrightarrow{\text{(alc.)}} CH_3NH_2 + HBr.$$

Methylamine.

Reaction involved in the Test reaction

Test Reaction.

24 Lucas test :- [Lucas reagent : is a mixture of conc. HCl and anhydrous $ZnCl_2$ in the ratio 1:1]

Process : A small quantity of the unknown alcohol is added to the Lucas reagent at room temp. and the mixture is shaken.

The alcohol reacts with HCl to form an alkyl chloride which being insoluble in water, forms turbidity (cloudiness) in the test solution.

(a) A tertiary (3°) alcohol forms turbidity immediately.

(b) A secondary (2°) alcohol forms turbidity within five minutes.

(c) A primary (1°) alcohol shows no turbidity at room temp. The turbidity appears only upon heating. * $R-OH + HCl \xrightarrow{\text{Anhyd. } ZnCl_2} R-Cl + H_2O$

25 Hinsberg's Test :- [Hinsberg's reagent :- Benzenesulphonyl chloride ($C_6H_5SO_2Cl$)]

This test is used to distinguish primary (1°), secondary (2°) and tertiary (3°) amines.

Process: The unknown amine is shaken with hinsberg's reagent in the presence of excess of aq. KOH solution.

Different types of amines respond differently.

1° amine $\xrightarrow[KOH]{C_6H_5SO_2Cl}$ Clear solution $\xrightarrow{HCl}$ An insoluble substance.

2° amine $\xrightarrow[KOH]{C_6H_5SO_2Cl}$ An insoluble substance $\xrightarrow{HCl}$ No change

3° amine $\xrightarrow[KOH.]{C_6H_5SO_2Cl}$ No reaction. (insoluble) $\xrightarrow{HCl}$ Clear solution

26 Silver mirror Test :- [Tollen's reagent :- is an ammonical solution of silver nitrate]

$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$

$AgOH + NH_4OH \longrightarrow [Ag(NH_3)_2]^+ OH^- + 2H_2O$

[or benzaldehyde] Tollen's reagent

* Acetaldehyde, gives a silver mirror with Tollen's reagent [But acetone does not gives silver mirror with Tollen's reagent.]

$CH_3CHO + 2[Ag(NH_3)_2]^+OH^- \longrightarrow CH_3COONH_4 + 2Ag + 3NH_3 + H_2O$

Tollen's reagent — Silver mirror

* Formic acid gives silver mirror with Tollen's reagent.

27 Iodoform Test :- (Ethanol, Acetone, Acetaldehyde responds to iodoform test and gives a yellow ppt. of Iodoform when heated with I_2 and NaOH.

(a) $CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{Heat} \underset{\text{yellow ppt}}{CHI_3} + HCOONa + 5NaI + 5H_2O$ (Ethanol)

(b) $CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$ (Acetone)

* Acetic acid does not respond to this test.