Class 12 Organic Chemistry Important Topics

Named Reactions

- Sandmeyer Reaction:

The Sandmeyer reaction is a chemical reaction which is used to synthesize aryl halides from aryl diazonium salts. This reaction is a method for substitution of an aromatic amino group by preparing diazonium salt that is followed by its displacement and copper salts often catalyze it.

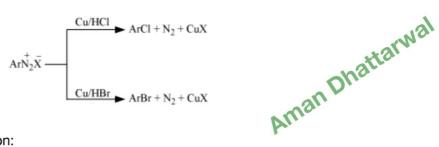
$$CuCl/HCl \longrightarrow ArCl + N_2$$

$$CuBr/HBr \longrightarrow ArBr + N_2$$

$$CuCN/KCN \longrightarrow ArCN + N_2$$

Gattermann Reaction:

Bromine and Chlorine can be present in the benzene ring by preparing the benzene diazonium salt solution with similar halogen acid present with copper powder. This is the Gattermann Reaction.



Balz-Schiemann Reaction:

When arene-diazonium chloride is prepared with fluoroboric acid, arene diazonium fluoroborate is precipitated and decomposes to yield aryl fluoride which on heating.

$$Ar \stackrel{+}{N_2}Cl^- + HBF_4 \longrightarrow Ar - \stackrel{+}{N_2}BrF_4^- \stackrel{Heat}{\longrightarrow} Ar - F + BF_3 + N_2$$
Eluoroboric acid

Finkelstein Reaction:

In the Finkelstein Reaction Alkyl iodides are prepared easily by the reaction of alkyl chlorides with Nal in dry acetone.

$$R - X + NaI \longrightarrow R - I + NaX$$

 $(X = Cl, Br)$

Swarts Reaction:

When alkyl chloride is heated in the presence of a metallic fluoride like AgF, Hg2F2, SbF3 or CoF2, we get alkyl fluorides.

$$H_3C-X + AgF \longrightarrow H_3C - F + AgX$$

 $(X = Cl,Br)$

Wurtz Reaction:

When Alkyl halides get reacted with sodium with dry ether, we get hydrocarbons that include the double number of carbon atoms present in the halide. This is known as the Wurtz Reaction

$$\begin{array}{ccc} CH_3Br+2Na+BrCH_3 & \xrightarrow{dry\ ether} CH_3-CH_3+2NaBr\\ Bromomethane & Ethane \\ C_2H_5Br+2Na+BrC_2H_5 & \xrightarrow{dry\ ether} C_2H_5-C_2H_5\\ Bromoethane & n\text{-Butane} \end{array}$$

Wurtz-Fittig Reaction:

When a mixture of alkyl halide and aryl halide gets treated with sodium in dry ether, we get an alkyl arene.

groups joined.

2
$$X + Na \xrightarrow{Ether} + 2NaX$$

Friedel-Crafts alkylation Reaction:

Benzene is prepared with an alkyl halide in the presence of anhydrous aluminum chloride to give Alkylbenzene.

+ CH₃Cl Anhyd. AlCl₃ + HCl Toluene (13.75)
$$C_2H_5Cl \xrightarrow{Anhyd.AlCl_3} C_2H_5 + HCl$$
 Ethylbenzene

Friedel-Crafts acylation reaction:

We get acyl benzene when an acyl halide is reacted with benzene in the presence of Lewis acids.

Reimer-Tiemann Reaction:

When preparing phenol with chloroform in the presence of sodium hydroxide, -CHO group is present at the ortho position of the benzene ring which results into salicylaldehyde.

$$\begin{array}{c|c}
OH \\
\hline
CHCl_3 + aq NaOH
\end{array}$$

$$\begin{array}{c|c}
\hline
O Na^+ \\
\hline
CHCl_2
\end{array}$$

$$\begin{array}{c|c}
NaOH
\end{array}$$

$$\begin{array}{c|c}
CHO \\
\hline
CHO
\end{array}$$

$$\begin{array}{c|c}
H^+ \\
\hline
Salicylaldehyde$$

Kolbe's Reaction:
Phenol reacts with sodium hydroxide to give sodium phenoxide which then reacts with carbon dioxide in acidic medium to give hydroxybenzoic acid. Aman

Rosenmund Reduction:

When Acyl chloride is hydrogenated to an aldehyde over a catalyst, known as Rosenmund catalyst which is either palladium or barium sulfate.

$$\begin{array}{c} O \\ II \\ Cl \\ \hline Pd-BaSO_4 \end{array} \begin{array}{c} CHO \\ Benzoyl \ chloride \end{array}$$
 Benzaldehyde

Stephen reaction:

Nitriles with stannous chloride in the presence of hydrochloric acid reduced to the corresponding imine and give the corresponding aldehyde after hydrolysis.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3 \overset{\circ}{O}} RCHO$$

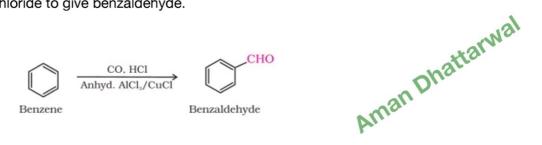
Etard reaction:

Chromyl chloride oxidizes methyl group to get chromium complex which on hydrolysis provides corresponding benzaldehyde.

$$CH_{3} + CrO_{2}Cl_{2} \xrightarrow{CS_{2}} CH(OCrOHCl_{2})_{2} \xrightarrow{H_{3}O^{+}} CHO$$
Toluene Chromium complex Benzaldehyde

Gatterman - Koch reaction:

Benzene is prepared with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminum chloride to give benzaldehyde.



Clemmensen Reduction:

In Clemmensen reduction, Carbonyl group of aldehydes and ketones on treatment with zincamalgam and concentrated hydrochloric acid reduced to CH2 group.

$$C=O \xrightarrow{Zn-Hg} CH_2 + H_2O$$
 (Clemmensen reduction)

Wolff Kishner Reduction:

Carbonyl group of aldehydes and ketones on treatment with hydrazine which on heating with sodium hydroxide in a high boiling solvent (ethylene glycol) reduced to CH2 group.

$$C=O \xrightarrow{NH_2NH_2} C=NNH_2 \xrightarrow{KOH/ethylene glycol} CH_2 + N_2$$
(Wolff-Kishner rduction)

Tollens' test:

Heating an aldehyde with fresh prepared ammoniacal silver nitrate solution produces a bright silver mirror due to the formation of silver metal.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3 \overline{O}H \longrightarrow RCOO + 2Ag + 2H_2O + 4NH_3$$

Fehling's test:

Fehling's solution A (aqueous copper sulfate) and Fehling solution B (alkaline sodium potassium tartrate) are mixed in equal amounts before the test. A reddish brown precipitate is obtained when an aldehyde is heated with Fehling's reagent.

R-CHO +
$$2Cu^{2+}$$
 + $5\overline{O}H \longrightarrow RCO\overline{O}$ + Cu_2O + $3H_2O$
Red-brown ppt

Aldol reaction:

Aldehydes and ketones having one α -hydrogen undergo a reaction in the presence of dilute alkali as the catalyst to produce β -hydroxy aldehydes or β -hydroxy ketones.

Aldol condensation:

Aldol and Ketol lose water to provide α,β -unsaturated carbonyl compounds which are aldol condensation products.

$$2 \text{ CH}_{3}\text{-CHO} \stackrel{\text{dil. NaOH}}{\longleftrightarrow} \text{CH}_{3}\text{-CH-CH}_{2}\text{-CHO} \stackrel{\Delta}{\longrightarrow} \text{CH}_{3}\text{-CH-CHO}$$
Ethanal
$$OH \qquad But-2\text{-enal}$$

$$3\text{-Hydroxybutanal} \qquad \text{(Aldol condensation product)}$$

$$(Aldol) \qquad \text{product}$$

$$2\text{CH}_{3}\text{-CO-CH}_{3} \stackrel{\text{Ba(OH)}_{2}}{\longleftrightarrow} \text{CH}_{3}\text{-C-CH}_{2}\text{-CO-CH}_{3} \stackrel{\Delta}{\longrightarrow} \text{CH}_{3}\text{-C-CH-CO-CH}_{3}$$

$$Propanone \qquad OH \qquad 4\text{-Methylpent-3-en-2-one} \qquad \text{(Ketol)} \qquad \text{(Aldol condensation product)}$$

Cross aldol condensation:

Aldol condensation is carried out between two different aldehydes and ketones. It gives a mixture of four products if both of them includes α -hydrogen atoms.

Cannizzaro reaction:

Aldehydes without α -hydrogen atom undergo self-oxidation and reduction reaction when prepared with concentrated alkali.

Kolbe electrolysis:

in Kolbe electrolysis, An aqueous solution of sodium or potassium salt of a carboxylic acid gives alkane containing an even number of carbon atoms on electrolysis.

$$\begin{array}{ccc} 2\text{CH}_3\text{COO} \ \text{Na}^+ + \ 2\text{H}_2\text{O} \\ \text{Sodium acetate} \\ & \downarrow \text{Electrolysis} \\ \text{CH}_3 - \text{CH}_3 + 2\text{CO}_2 + \text{H}_2 + 2\text{NaOH} \end{array}$$

Hell-Volhard-Zelinsky (HVZ)reaction:

Carboxylic acids having a α -hydrogen are halogenated at the α -position give α -halo carboxylic acids on treatment with chlorine or bromine in the presence of small amount of red phosphorus.

R-CH₂-COOH

(i)
$$X_2$$
/Red phosphorus

(ii) H_2 O

R-CH-COOH

X

X = Cl, Br

 α - Halocarboxylic acid

Gabriel phthalimide synthesis:

Phthalimide prepared with ethanolic potassium hydroxide produces potassium salt of phthalimide when heated with alkyl halide followed by alkaline hydrolysis forms the corresponding primary amine.

Hoffmann bromamide degradation reaction:

An amide with bromine in an aqueous solution of sodium hydroxide produces primary amines. Migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so produced include one carbon less than that present in the amide.

$$\begin{array}{c} O \\ || \\ R-C-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O \end{array}$$

Carbylamine reaction:

Aliphatic and aromatic primary amines when heated with chloroform and ethanolic potassium hydroxide produces isocyanides or carbyl amines which are foul smelling substances.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

Hinsberg's Test:

Benzenesulfonyl chloride (C6H5SO2CI) reacts with primary and secondary amines to produce sulphonamides.

1. The reaction of benzene-sulfonyl chloride with primary amine yields N-ethyl benzene-sulfonyl amide. The hydrogen attached to the nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulfonyl group. Hence, it is soluble in alkali.

2. In the reaction with a secondary amine, N, N-diethyl- benzenesulfonamide is formed. Since N, N- diethyl benzene sulphonamide does not contain any hydrogen atom attached to a nitrogen atom, it is not acidic and hence insoluble in alkali.

3. Tertiary amines do not react with benzene-sulfonyl chloride.

Coupling Reactions:

Benzene diazonium chloride gets reacted with phenol in which the phenol molecule at its para position is mixed with the diazonium salt to give p-hydroxyazobenzene.

p-Hydroxyazobenzene (orange dye)