NAMED REACTIONS

SANDMEYER'S REACTION

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by -Cl or -Br.

NUCLEOPHILIC SUBSTITUTION REACTIONS

In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen

$$N\bar{u} + - \stackrel{\backslash \delta^+}{C} \stackrel{\delta^-}{X} \longrightarrow C - Nu + \bar{X}$$

atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

SAYTZEFF RULE:

In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

$$H_3C-CH_2-CH=CH-CH_3 \stackrel{\overline{OH}}{\longleftarrow} H_3C-CH_2-CH_2-CH_2-CH_2 \stackrel{\overline{OH}}{\longrightarrow} H_3C-CH_2-CH_2-CH_2-CH_2$$
Pent-2-ene (81%) 2-Bromopentane Pent-1-ene (19%)

GRIGNARD REAGENT FORMATION:

The reagent obtained by the reaction of haloalkanes with magnesium metal in dry ether.

WURTZ REACTION

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.

$$2RX + Na \longrightarrow RR + NaX$$

FITTIG REACTION

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together.

$$2 \longrightarrow^{X} + \text{Na} \xrightarrow{\text{Ether}} + 2\text{NaX}$$

WURTZ-FITTIG REACTION

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether

$$X + Na + RX \xrightarrow{Ether} R + NaX$$

ESTERIFICATION

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/RO-H + R'-COOH \xrightarrow{H^+} Ar/ROCOR' + H_2O$$

 $Ar/R-OH + (R'CO)_2O \xrightarrow{H^+} Ar/ROCOR' + R'COOH$

LUCAS TEST:

Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl2) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature. $ROH + HX \rightarrow R-X + H_2O$

KOLBE'S REACTION

Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak

$$\begin{array}{c|c} \text{OH} & \text{ONa} & \text{OH} \\ \hline & \text{NaOH} & \begin{array}{c} \text{(i) CO}_2 \\ \text{(ii) H} \end{array} \end{array}$$

electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.

(Salicylic acid)

REIMER-TIEMANN REACTION

On treating phenol with chloroform in the presence of sodium hydroxide, a -CHO is introduced at ortho position of benzene

ring. This reaction is known as Reimer - Tiemann reaction.

WILLIAMSON SYNTHESIS

It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

$$R - X + Na - OR \rightarrow R - O - R + NaX$$

$$C_2H_5O - Na + I - CH_2CH_3 \rightarrow CH_3 - CH_2 - O - CH_2 - CH_3 + NaI$$
For propering 3° others, 3° alkeyide is treated with alked halide

For preparing 3° ethers, 3° alkoxide is treated with alkyl halide.

ROSENMUND REDUCTION:

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate

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

ETARD REACTION:

Chromyl chloride (CrO₂Cl₂) oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

$$\begin{array}{c} \text{CH}_3 \\ + \text{ CrO}_2\text{Cl}_2 \xrightarrow{\text{CS}_3} \end{array} \begin{array}{c} \text{CH(OCrOHCl}_2)_2 \\ \text{Chromium complex} \end{array} \begin{array}{c} \text{CHO}_2\text{CHO}_2 \\ \text{Benzaldehyde} \end{array}$$

GATTERMAN - 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.

CLEMMENSEN REDUCTION:

The carbonyl group of aldehydes and ketones is reduced to -CH₂-group on treatment with zinc amalgam and concentrated hydrochloric acid. $C = O \xrightarrow{\text{Zn-Hg}} CH_2 + H_2O$

The carbonyl group of aldehydes and ketones is reduced to CH2 group on

$$C = O \xrightarrow{NH_2NH_2} C = NNH_2 \xrightarrow{KOH/ethylene glycol} CH_2 + N_2$$

(Wolff-Kishner rduction) treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol

TOLLENS' TEST:

On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

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

FEHLING'S TEST:

Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

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

Red-brown ppt

HALOFORM REACTION:

Aldehydes and ketones having at least one methyl linked to the carbonyl carbon atom (methyl ketones) by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The is converted to haloform.

$$R \xrightarrow{C} CH_3 \xrightarrow{NaOX} R \xrightarrow{C} ONa + CHX_3 (X=CI, Br, I)$$
 group are oxidised $H \xrightarrow{CH_3} CH_3 \xrightarrow{NaOCI} H_3C \xrightarrow{NaOCI} H_3C \xrightarrow{NaOCI} ONa + CHCl_3$ methyl group

ALDOL CONDENSATION:

2 CH₃-CHO
$$\stackrel{\text{dil. NaOH}}{\longleftarrow}$$
 CH₃-CH-CH₂-CHO $\stackrel{\Delta}{\longleftarrow}$ CH₃-CH=CH-CHO

Ethanal OH But-2-enal

3-Hydroxybutanal (Aldol condensation product)

ketones (ketol), respectively. This is known as Aldol reaction. The aldol and ketol readily lose water to give

 α P-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol** Propanone condensation.

CANNIZZARO REACTION:

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

H C=O + Conc. KOH
$$\longrightarrow$$
 H CON + CON + H CON + H

HELL-VOLHARD-ZELINSKY REACTION:

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

R-CH₂-COOH

(i) X₂/Red phosphorus

R-CH-COOH

(ii) H₂O

I

GABRIEL PHTHALIMIDE SYNTHESIS

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

HOFFMANN BROMAMIDE DEGRADATION REACTION

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

CARBYLAMINE REACTION

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \rightarrow R-NC + 3KCl + 3H_2O$$

HINSBERG'S TEST:

Benzenesulphonyl chloride (C6H5SO2CI), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides. The property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide. The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

$$C_6H_5SO_2CI + R-NH_2 \rightarrow C_6H_5SO_2NHR + HCI$$

N-alkylbenzenesulphonamide

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide is formed. Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

$$C_6H_5SO_2CI + R_2-NH_2 \rightarrow C_6H_5SO_2NR_2 + HCI$$

N, N- dialkylbenzene sulphonamide

(c) Tertiary amines do not react with benzenesulphonyl chloride.

GATTERMAN REACTION.:

Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

$$Ar_{N_2X}^{+} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
 $Cu/HBr ArBr + N_2 + CuX$