SOME EMINENT NAMERICACIO

ARNDT-EISTERT REACTION

Arndt-Eistert synthesis is a convenient way of converting an aliphatic, aromatic, alicyclic or even a heterocyclic acid into the next higher homologue. The first step of the synthesis involves reaction between acid chloride and diazomethane to give a diazoketone. The diazoketone then undergoes Wolff rearrangement when warmed in the presence of water and Ag₂O (or with benzoate and triethylamine) to give the next higher homologous acid. Often photolysis gives better result than silver catalyst.

$$R \xrightarrow{\text{OH}} \xrightarrow{\text{SOCl}_2} R \xrightarrow{\text{C}} CH_2N_2$$

$$R \xrightarrow{\text{OH}} CH_2O R \xrightarrow{\text{C}} N^+$$

$$CH_2O R \xrightarrow{\text{N}^+} N^-$$

It must be ensured that R should not contain any functional group that is acidic enough to react with diazomethane.

CHICHIBABIN REACTION

Amination of pyridine and other heterocyclic compounds containing nitrogen using sodium amide is called Chichibabin reaction, named after Alexei E. Chichibabin.

$$\begin{array}{ccc}
& & & & & & & \\
\hline
N & & & & & & \\
\hline
N & & & & & \\
\hline
N & & & & \\
N & & & \\
N & & & \\$$

Actually sodium salts are formed, which when hydrolysed with water give amines.

CHUGAEV ELIMINATION

Pyrolysis of the xanthate to give olefin, carbonyl sulphide (COS) and the thiol is called Chugaev elimination.

DARZENS CONDENSATION

The condensation of aldehyde or ketone with an α -halo ester to produce an α , β -epoxy ester or a glycidic ester is the Darzens condensation. The reaction takes place in presence of very strong bases such as sodium ethoxide or sodamide.

$$\begin{array}{c} O \\ -\overset{||}{C} - + Cl - CH - COOC_2H_5 \xrightarrow{NaOEt} - \overset{||}{C} - \overset{||}{C} - COOEt \end{array}$$

ELBS PERSULPHATE OXIDATION

The Elbs persulphate oxidation is the chemical reaction of phenols with alkaline potassium persulphate to form p-diphenols.

OH
Phenol

1.
$$K_2S_2O_8/KOH$$

2. H_3O^+

HO

 p -Diphenol

(Quinol)

The reaction is generally carried out by adding an aqueous solution of K₂S₂O₈ to a cold alkaline solution of phenol followed by acidification.

HOUBEN-HOESCH REACTION

Condensation of cyanides with polyhydric phenols in presence of ZnCl2 and HCl to give ketones is called Houben-Hoesch reaction. Consider the reaction with resorcinol:

OH OH CO-R
$$+ RCN \xrightarrow{1. ZnCl_2, HCl} HO$$
HO HO

It is an extension of Gatterman's phenolic aldehyde synthesis.

LEDERER-MANASSE REACTION

Hydroxymethylation of phenols using formaldehyde in presence of acid or base catalyst is called Lederer-Manasse reaction.

OH
$$+ CH_2 = O \xrightarrow{\text{NaOH solution}} 6 \text{ days}$$

$$+ CH_2 = O \xrightarrow{\text{6 days}} 6 \text{ days}$$

$$+ CH_2 = O \xrightarrow{\text{6 days}} OH$$

$$+ CH_2 = O \xrightarrow{\text{6$$

The reaction is slow and takes place at low temperature.

QUELET REACTION

Passage of dry hydrochloric acid through a solution of a phenolic ether and an aliphatic aldehyde in ligroin in the presence or absence of a dehydration catalyst to yield α -chloroalkyl derivative by substitution in the *para*-position to the ether group or in the *ortho*-position in *para*-substituted phenolic ethers.

$$\begin{array}{c}
OMe \\
OMe \\
+ RCHO + HCl \xrightarrow{ZnCl_2} OMe \\
+ H_2O
\end{array}$$

Ligroin is a volatile fraction of petroleum used as solvent.

SKRAUP SYNTHESIS

The synthesis of quinoline by heating aniline with glycerol and H_2SO_4 , which acts as catalyst as well as dehydrating agent in presence of moderator Fe(II) sulphate is known as Skraup synthesis, named after Z. H. Skraup. Nitrobenzene acts as mild oxidant. Since the reaction can be violently exothermic, a moderator such as Fe(II) sulphate is usually added. Modern methods use Fe(III) sulphate instead of nitrobenzene as oxidant.

$$\begin{array}{c} \text{OH} \\ \text{NH}_2 \end{array} + \begin{array}{c} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \begin{array}{c} \text{PhNO}_2 \\ \text{H}_2\text{SO}_4, \Delta \end{array} \end{array} \begin{array}{c} \text{O} \\ \text{O} \\ \text{N} \end{array}$$
Aniline Quinoline

In a slightly different way than that of original Skraup synthesis, preformed acrolein is used instead of glycerol.

STRECKER SYNTHESIS

Preparation of α -amino nitriles by the treatment of an aldehyde and ketone with CN $^-$ and NH $_4$ Cl followed by hydrolysis is called Strecker synthesis, named after Adolph Strecker.

$$\begin{array}{c} O \\ R-C-H+NH_4Cl+NaCl \longrightarrow \\ R-CH-NH_2 \xrightarrow{H_3O^+} \Delta \\ CN & COO^- \\ \alpha\text{-Amino nitrile} \end{array}$$

Cyanide ion acts as the source of the acid portion and ammonia is the ultimate source of amino group. While usage of NH₄Cl gives unsubstituted amino acids, *pri*- and *sec*- amines give substituted amino acids successfully.

