MIND MAP

Carboxylic Acid & Amines

By Oxidation of Aldehydes

Aldehydes on oxidation with usual oxidizing agent give Carboxylic acid with same number of Carbon atoms as in the Aldehyde.

$$R-CHO + [O] \xrightarrow{\text{Tollen's Reagent}} R-COO^{-} \xrightarrow{H^{\oplus}} R-COOH$$

$$C_6H_5CHO + [O] \xrightarrow{\text{Tollen's Reagent}} C_6H_5COO^{\ominus} \xrightarrow{H^{\oplus}} C_6H_5COOH$$

By Oxidation of Alkenes

$$RCH=CHR' \xrightarrow[H_3O^{\oplus}]{\text{Conc. } KMnO_4 / OH^{\ominus}\ \text{Heat}} RCOOH + R'COOH$$

$$RCH=CHR' \xrightarrow[H_2O,\ \text{Distill.}]{O_3} RCOOH + R'COOH$$

By Carboxylation of Grignard Reagent

$$R-Br \xrightarrow[\text{Dry ether}]{Mg} RMgBr \xrightarrow{CO_2} R-\overset{O}{\overset{\|}{C}}-O^{\ominus}MgBr^{\oplus} \xrightarrow[-MgBr(OH)]{H_2O / H^{+}} R-\overset{O}{\overset{\|}{C}}-OH$$

By Hydrolysis of Acyl Derivatives of Carboxylic Acid

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2O \xrightarrow{H^{\oplus}} R-COOH + HCl$$

$$(R-CO)_2O + H_2O \xrightarrow{H^{\oplus}} R-COOH + R-\overset{O}{\overset{\|}{C}}-OH$$

$$R-COOR' + H_2O \xrightarrow{H^{\oplus}} R-COOH + ROH$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O \xrightarrow[\Delta]{H^{\oplus}} R-COOH + NH_4^{\oplus}$$

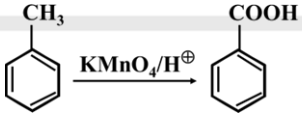
By Oxidation of Primary Alcohol with Acidic $KMnO_4$ or Acidic $K_2Cr_2O_7$

$$R-CH_2OH + [O] \xrightarrow[K_2Cr_2O_7 / H^{+}]{KMnO_4 / H^{+}} RCHO + H_2O \xrightarrow{[O]} RCOOH$$

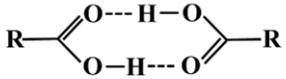
Cyanide Hydrolysis With Dilute Acids

$$R-CN \xrightarrow{H_3O^{\oplus}} RCOOH$$

By Oxidation of Alkyl Benzene



These are polar substances and can form H-bonds with each other to form dimer structures.



Melting Point

Melting point of the Carboxylic acid with even number of Carbon atoms is higher than acid with odd number of Carbon atoms.

Such effect is observed in first ten members of the Homologous series.

Reactions Involving –COOH Group

Soda Lime Decarboxylation

Carboxylic acid on heating with soda lime (NaOH and CaO) give Alkane with one Carbon atom less than the parent acid.

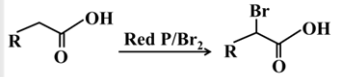
$$R-COOH \xrightarrow[\Delta]{\text{Soda lime}} R-H + CO_2$$

Hunsdiecker Reaction

$$R-COOH \xrightarrow{Ag_2O} R-COO^{-}Ag^{+} \xrightarrow[\text{in } CCl_4]{Br_2} R-Br + AgBr + CO_2$$

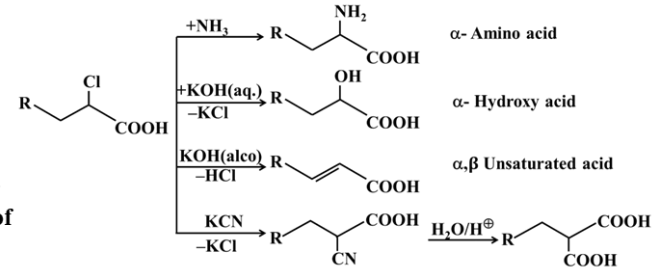
Hell-Volhard-Zelinsky Reaction

This is a-halogenation of a Carboxylic acid.



α-Bromo Acid

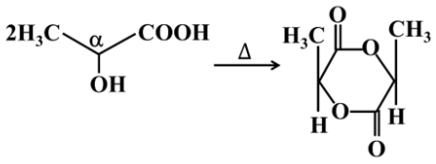
The reaction does not stop at mono substitution but continues till all a-Hydrogen are replaced.



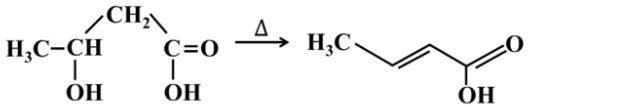
MIND MAP

Carboxylic Acid & Amines

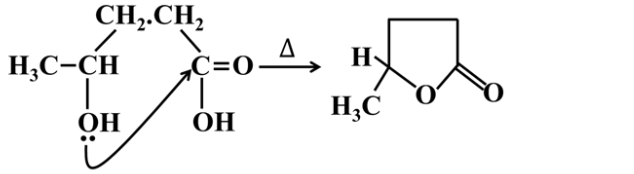
Heating of a, β And γ Hydroxy Acid



α- hydroxy acid — Lactides

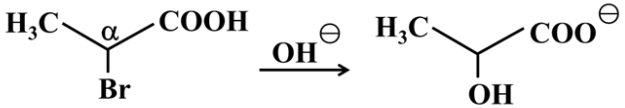


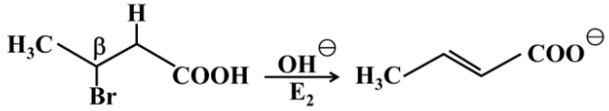
β- Hydroxy acid — α,β Unsaturated Carboxylic acid

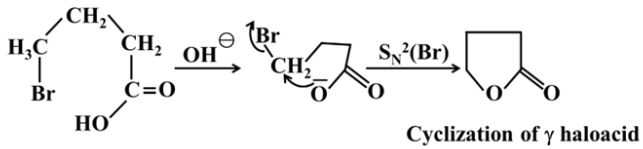


γ-Hydroxy Acid — 5-Methyldihydrofuran-2-one

Reaction of a, β And γ Halo Carboxylic Acid With Aq. NaOH

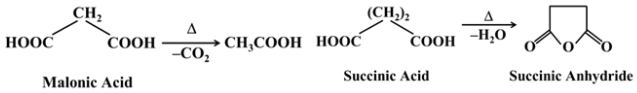




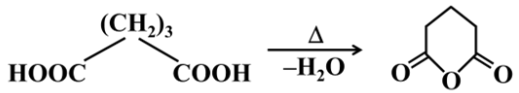


Cyclization of γ haloacid

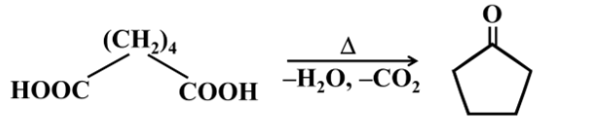
Heating of Dicarboxylic Acids



Malonic Acid — Succinic Acid — Succinic Anhydride



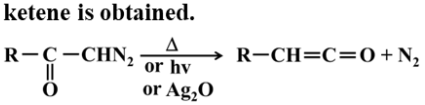
Glutamic Acid — Glutamic Anhydride



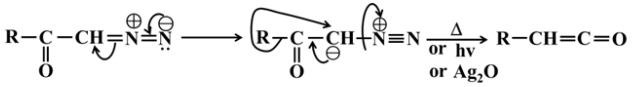
Cyclopentanone

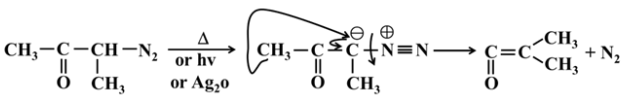
Wolff Rearrangement

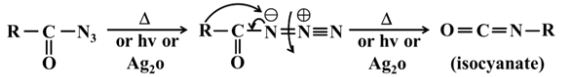
In this reaction, a-diazocarbonyl compound is treated with thermally, photochemically or catalytically so that ketene is obtained.

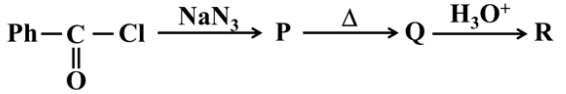


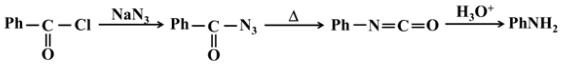
Mechanism





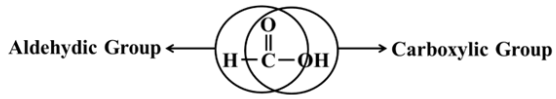






Abnormal Behaviour of Formic Acid

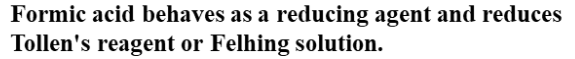
The behaviour of Formic acid is different from other Carboxylic acid due to presence of Aldehydic group.

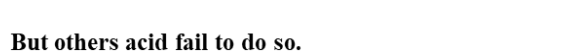


Reaction with a) Tollen's Reagents

Formic acid behaves as a reducing agent and reduces Tollen's reagent or Felhing solution.

But others acid fail to do so.





MIND MAP

Nitrogen Containing Compound

Amines

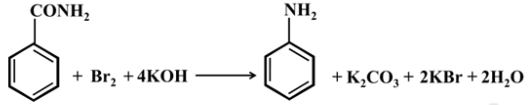
$NH_3 \xrightarrow[-H]{+R} R-NH_2 \xrightarrow[-H]{+R} R_2NH \xrightarrow[-H]{+R} R_3\ddot{N}$

p–amine (Amino) | s–amine (Imino) | t–amine (Nitrilo)

General Method of Preparation

Hoffmann's Bromamide Degradation

$R-CO-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$

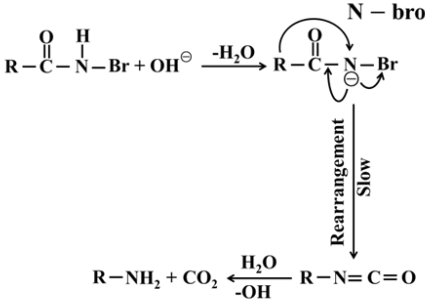


Mechanism

$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$

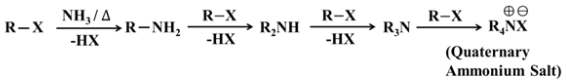
$R-\overset{O}{\overset{\|}{C}}-NH_2 + OH^- + Br_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-Br$

N – bromoacetamide



Ammonolysis of Alkyl Halides And Alcohol

a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis]



If ammonia is taken in excess, 1° amine is the main product.

By Reduction

a) With $RCONH_2$ $RCONH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$

b) With RCN $RCN \xrightarrow{Sn/HCl} RCH_2NH_2$ Mendius reaction.

$R-NC \xrightarrow[Or\ 4[H]]{C_2H_5OH/Na} RNHCH_3$

C) With Oximes

$R-CH=N-OH \xrightarrow[Na/C_2H_5OH]{LiAlH_4} RCH_2-NH_2 + H_2O$

D) With RNO_2 $RNO_2 \xrightarrow[Or\ 6[H]]{Sn/HCl} RNH_2 + 2H_2O$

By Hydrolysis of

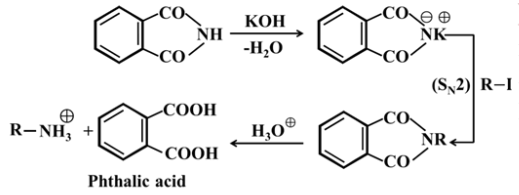
a) R–NC $R-NC + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$

From Grignard Reagent

$R-Mg-I + Cl-NH_2 \longrightarrow R-NH_2 + Mg\begin{matrix} I \\ Cl \end{matrix}$

Gabriel Phthalimide Synthesis

Phthalimide is first treated with Alcoholic KOH to obtain Potassium phthalimide which is then treated with Alkyl iodide.



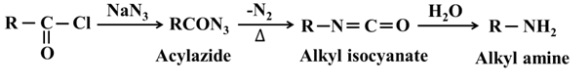
Phthalic acid

Note

i) Only 1° amine can be prepared

ii) Me_3CNH_2, $PhNH_2$ can not be prepared.

Curtius Degradation

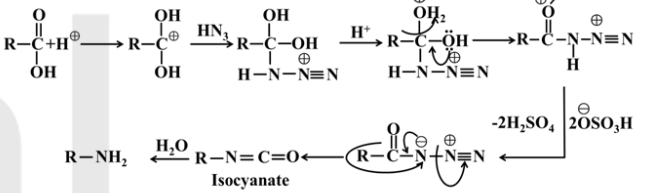


Schmidt Degradation

In presence of conc. H2SO4 Alkanoic acid reacts with Hydrazoic acid (N3H) to yield Alkylamine.

$R-COOH + N_3H \xrightarrow[\Delta]{Conc.\ H_2SO_4} R-NH_2 + N_2 + CO_2$

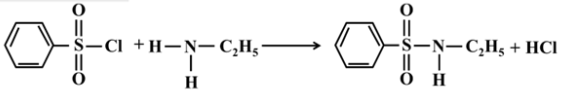
Mechanism



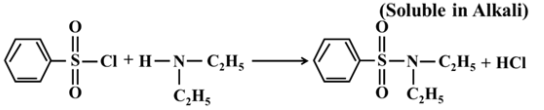
Chemical Properties

Separation of 1°, 2° and 3° amines

i) Hinsberg method



N-Ethylbenzenesulphonamide (Soluble in Alkali)



N,N-Diethylbenzenesulphonamide

$C_6H_5SO_2Cl$ + 1° amine ⟶ Product $\xrightarrow{KOH}$ Dissolve

$C_6H_5SO_2Cl$ + 2° amine ⟶ Product $\xrightarrow{KOH}$ Insoluble

3° Amine does not react with Benzenesulphonyl Chloride.

MIND MAP

Nitrogen Containing Compound

Hoffmann Method

1° Amine + Ethyl Oxalate ⟶ Solid product

2° Amine + Ethyl Oxalate ⟶ Liquid product

3° Amine + Ethyl Oxalate ⟶ No reaction

Acetylation

Acetylation takes place when Alkyl amine combines with Acetyl chloride or Acetic anhydride.

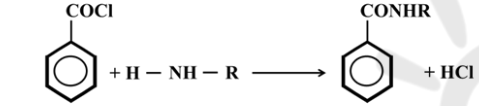
$$RNH_2 + ClCOCH_3 \longrightarrow RNHCOCH_3 + HCl$$

(N –alkyl acetamide)

$$RNH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

(N –alkyl acetamide)

Benzoylation (Schotten Baumann Reaction)



Benzoylchloride — N–alkyl benzamide

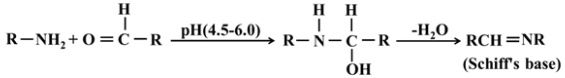
Acidic Nature

Amines are very weak acids only 1° and 2° Amines show Acidic nature.

$$R - NH_2 + Na \longrightarrow \overset{\ominus}{R}NH\overset{\oplus}{Na} + \frac{1}{2}H_2$$

N– alkyl sodamide

Reaction With Aldehydes

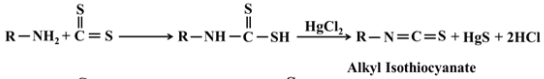


Carbylamine Reaction (Iso Cyanide Test)

$$R - NH_2 + CHCl_3 + 3\,KOH \longrightarrow R - N \equiv C + 3KCl + 3H_2O$$

Nucleophile RNH2 attacks electrophilic intermediate [:CCl2] dichlorocarbene.
This test is also given by Aniline. This is a test for p–Amines.

Hofmann's Mustard Oil Test



$$R_2NH + CS_2 \longrightarrow R_2NH - C(=S) - SH \xrightarrow{HgCl_2} \text{No reaction}$$

$$R_3NH + CS_2 \longrightarrow \text{No reaction}$$

Reaction With HNO_2 ($NaNO_2$ + HCl Or H_2SO_4)

Primary Amines react with Nitrous acid to produce Nitrogen gas [seen as bubbles]

$$R - NH_2 + HONO \longrightarrow R - OH + N_2\uparrow + H_2O$$

Diazotisation

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[-H_2O]{0^0 - 5^0\,C} C_6H_5N_2Cl$$

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl} + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$

Benzenediazonium Chloride

Note

Coupling between Arenediazonium Cations and Amines take place most rapidly in slightly acidic solution (pH 5 to 7).

Nitration

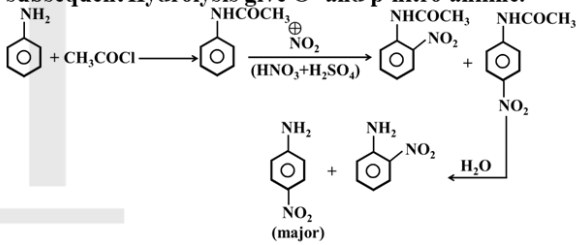
A) Direct Nitration

The direct Nitration of Aniline by conc. HNO_3 and conc. H_2SO_4 give Meta-nitroaniline.

Due to positively charged N, m-position becomes electron rich as compared to o, p–position.

B) Indirect Nitration

In indirect nitration Amino group is protected by acetylation to give Acetanilide, which on nitration and subsequent Hydrolysis give O- and p-nitro-aniline.



Tests of Aniline

Carbylamine Test

Aniline gives Carbylamine test or Isocyanide test.

$$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow C_6H_5NC$$

(Foul Smelling)

Dye Test

Aniline is first diazotised.
On adding Alkaline soln. Of b-naphthol to the diazotised product a scarlet red dye is formed.
On heating with Bromine water, a ppt. is formed.