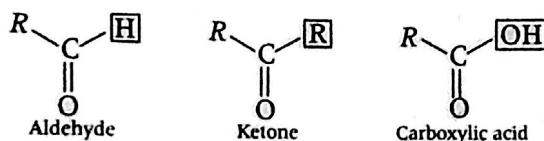


Aldehydes, Ketones and Carboxylic Acids

[TOPIC 1] Aldehydes and Ketones

Depending upon the atoms or group of atoms attached on either side of the carbonyl group, carbonyl compounds are divided into three major classes, i.e. aldehydes, ketones and carboxylic acids.



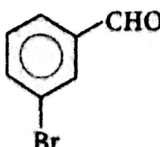
The compounds, which contain ' —C— ' group are called carbonyl compounds.

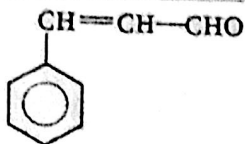
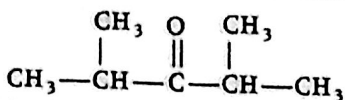
Aldehydes and ketones have same molecular formula $\text{C}_n\text{H}_{2n}\text{O}$ and are functional isomers of each other.

1.1 Nomenclature

The word 'al' and 'one' replaces the ending 'e' of corresponding alkanes while naming the open chain aliphatic aldehydes and ketones, respectively.

Common and IUPAC names of some aldehydes and ketones

Structural formula	Common name	IUPAC name
Aldehydes HCHO	Formaldehyde	Methanal
$\text{CH}_3\text{—CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{—CH}_2\text{—}\overset{\alpha}{\underset{\text{CH}_3}{\text{CH}}}\text{—CHO}$	α -methylbutyraldehyde	2-methylbutanal
	<i>m</i> -bromobenzaldehyde	3-bromobenzenecarbaldehyde or 3-bromobenzaldehyde

Structural formula	Common name	IUPAC name
$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$	Crotonaldehyde	But-2-enal
	Cinnamaldehyde	3-phenylprop-2-enal
Ketones CH_3COCH_3	Acetone	Propanone
	Diisopropyl ketone	2, 4-dimethylpentan-3-one

1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2 -hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in p -orbital where it forms a π -bond by overlapping with p -orbital of an oxygen. It possesses a trigonal coplanar structure with bond angle 120° . The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon.



1.3 Preparation of Aldehydes and Ketones

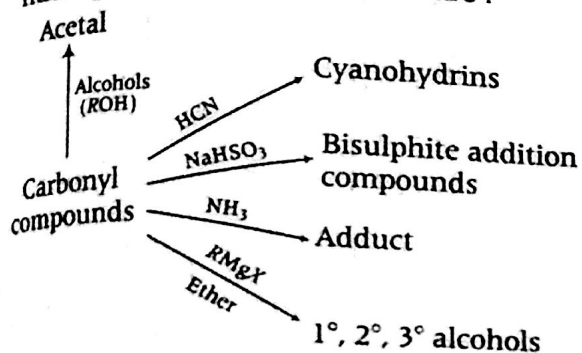
- Controlled oxidation of alcohols in the presence of $\text{K}_2\text{Cr}_2\text{O}_7 / \text{dil. H}_2\text{SO}_4$, $\text{KMnO}_4 / \text{dil. H}_2\text{SO}_4$ or Cu metal at 573 K result in the formation of aldehydes and ketones.
- Dry distillation of some calcium salts of acid gives simple ketones.
- Mixture of calcium salts of formic acid and calcium salts of any other carboxylic acid on dry distillation gives an aldehyde.
- Addition of Grignard's reagents to alkyl or aryl cyanides followed by hydrolysis with dil. acids gives ketones while with HCN, aldehydes are formed.
- Addition of H_2O on alkynes in presence of H_2SO_4 and HgSO_4 yields aldehydes (by terminal alkynes) and ketones (by non-terminal alkynes).

1.4 General Properties of Aldehydes and Ketones

- Boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
- The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water.
- Aldehydes and ketones generally undergo nucleophilic addition reactions.
- Aldehydes are more reactive than ketones toward nucleophiles due to more + I and steric effects in ketones.

1.5 Chemical Properties of Aldehyde and Ketones

(i) Aldehydes and ketones undergo a number of addition reactions due to the presence of polar carbonyl group (the carbonyl carbon bears partial positive charge, thus, undergoes nucleophilic addition reactions). Common nucleophilic addition reactions are :



(ii) Aldehydes and ketones also react with ammonia derivatives like:

(i) NH_2OH (hydroxylamine) to give oximes.

(ii) $\text{NH}_2\text{—NH}_2$ (hydrazine) to give hydrazones.

(iii) $\text{NH}_2\text{—NH—}$  (phenyl hydrazine)

to give phenyl hydrazones.

(iii) Reaction with 2, 4-DNP can be used to identify the presence of a carbonyl group.

(iv) **Clemmensen reduction** of aldehydes and ketones ($\text{Zn-Hg}/\text{conc. HCl}$) gives alkanes.

(v) **Wolff-Kishner reduction** The carbonyl group of aldehydes and ketones is reduced to —CH_2 group on treatment with

hydrazine followed by heating with KOH in ethylene glycol.

(vi) Aldehydes give positive **Tollen's test**, **Fehling's test**, **Benedict's test** and **Schiff's test**.

(vii) Aldehydes can be distinguished from ketones by **Tollen's reagent**, **Fehling's solution** and **Benedict's solution**.

(viii) **Tollen's reagent** is an ammoniacal silver nitrate ($\text{AgNO}_3 + \text{NH}_4\text{OH}$) solution. It is a mild oxidising agent.

(ix) Aromatic aldehydes do not reduce Fehling's solution.

(x) **Iodoform test** is given by $\text{CH}_3\text{CO—}$ or $\text{CH}_2\text{CH(OH)—}$ group containing compounds.

(xi) **Aldol condensation** is given by aldehydes and ketones that have α -hydrogen atom in the presence of dilute alkali. It involves carbanion as an intermediate.

(xii) **Cannizzaro reaction** is given by those aldehydes which do not have α -hydrogen atom (like $\text{C}_6\text{H}_5\text{CHO}$, HCHO) in the presence of concentrated alkali.

(xiii) Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.

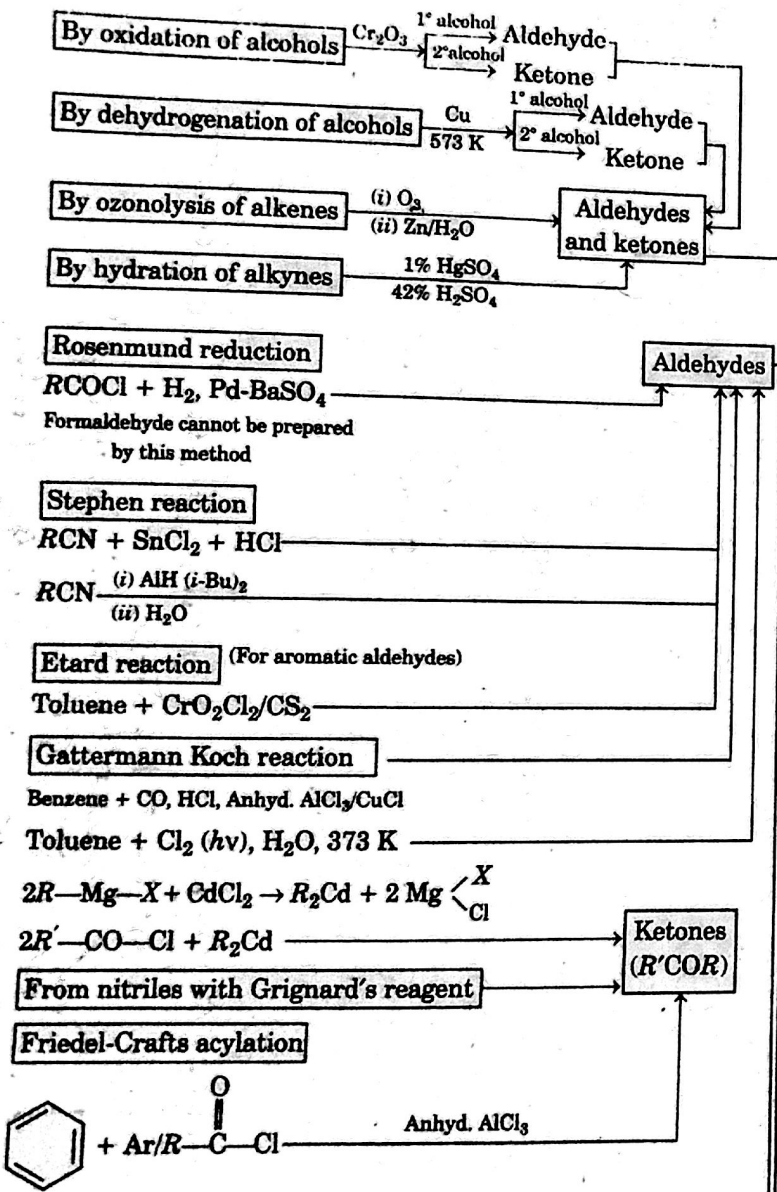
Uses

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare polymeric products. Benzaldehyde is used in perfumery and in dye industries.

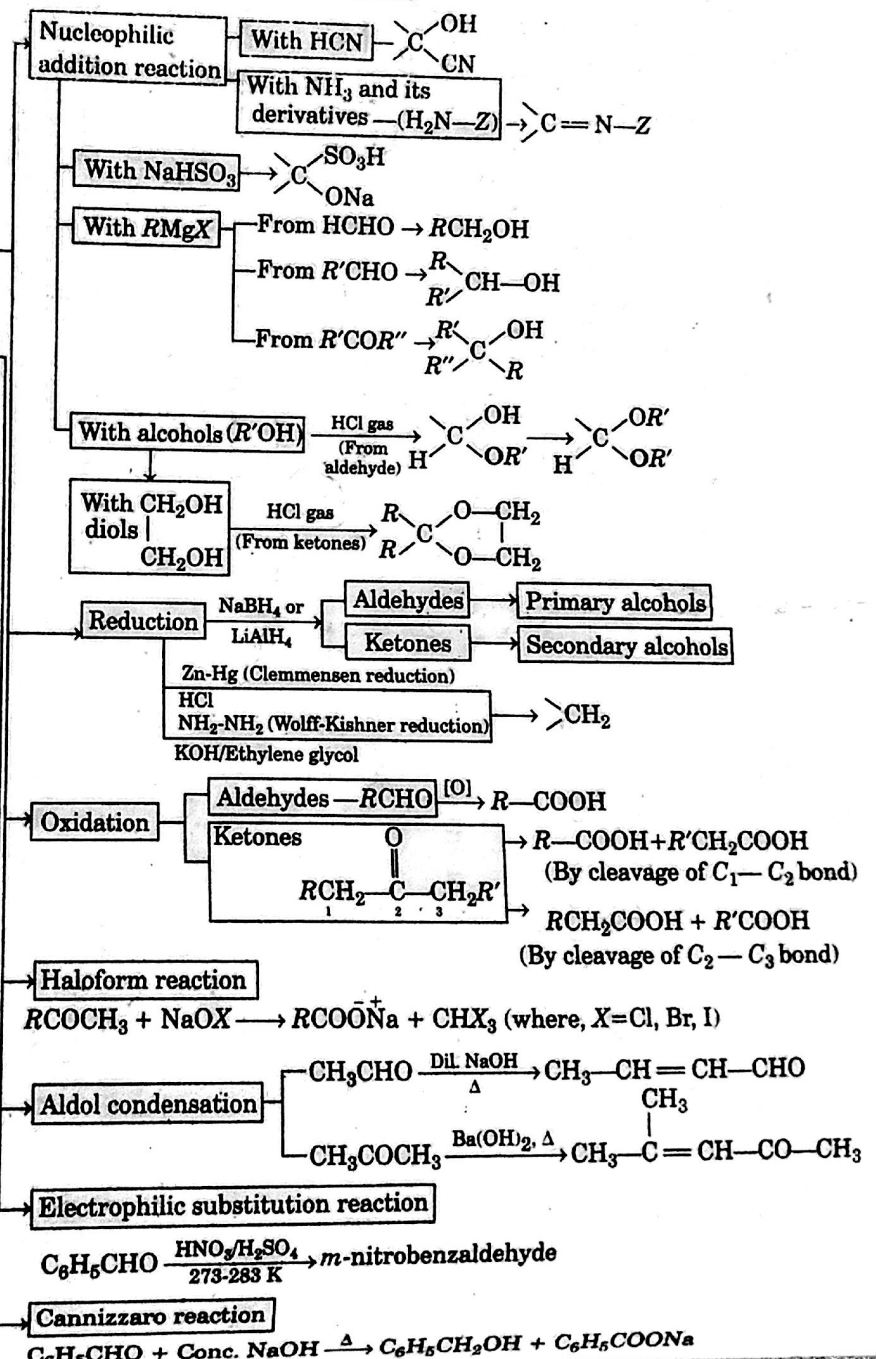
NOTE In Rosenmund's reduction, poisoning of Pd with BaSO₄ prevents reduction of RCHO to R-CH₂OH.

Flow Chart for the Preparations and Chemical Reactions of Aldehydes and Ketones

Preparations

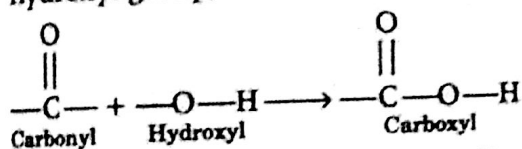


Chemical Reactions



[TOPIC 2] Carboxylic Acids

1. The carbon compounds containing " —C(=O)OH " group (—COOH) are known as carboxylic acids. The carboxyl group, consists of a carbonyl group attached to a hydroxyl group, hence it is named as carboxyl.



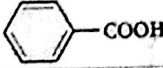
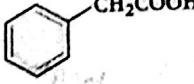
2. The general formula of carboxylic acid is $\text{C}_n\text{H}_{2n}\text{O}_2$.
3. Higher aliphatic acids are also known as fatty acids.

2.1 Nomenclature

Aliphatic carboxylic acids are named by replacing the ending —e in the name of the corresponding alkane with —oic acid .

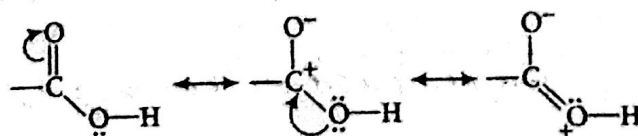
Names and structures of some carboxylic acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-methylpropanoic acid
HOOC—COOH	Oxalic acid	Ethanedioic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-phenylethanoic acid

2.2 Structure of Carboxyl Group

In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120° . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



2.3 Preparation of Carboxylic Acids

Carboxylic acids can be prepared by

- (i) oxidation of 1° alcohols and aldehydes.
- (ii) oxidation of alkyl benzenes.
- (iii) hydrolysis of alkyl cyanides and amides.
- (iv) carbonation of Grignard's reagent.
- (v) hydrolysis of acyl halides and anhydrides.
- (vi) Aromatic carboxylic acids are prepared by side chain oxidation of alkyl benzenes.

2.4 Properties of Carboxylic Acids

Carboxylic acids are weak acids, they give H^+ ions on ionisation. But they are stronger acids than phenols and alcohols, due to greater stability of carboxylate ion by two equivalent resonance structure in which the negative charge is at more electronegative oxygen atom. The acidity of carboxylic acids are effected by substituents which is directly attached with carboxylic carbon.

Electron withdrawing groups increase the acidity of carboxylic acids while electron donating groups decrease the acidity of carboxylic acids. Carboxylic acids has higher boiling points than aldehydes and ketones of comparable masses. This is due to intermolecular hydrogen bonding.

NOTE Benzoic acid has lesser acidic strength than formic acid.

2.4 Reactions of Carboxylic Acids

1. Reactions Involving Cleavage of O—H Bond

- (i) Carboxylic acids react with active metals like Na, K, Ca, Mg, Zn, etc, to form respective salts with evolution of H_2 gas
- (ii) They neutralise alkalis forming salts.
- (iii) They react with weaker bases such as carbonates and bicarbonates producing CO_2 gas.

2. Reactions Involving Cleavage of C—OH Bond

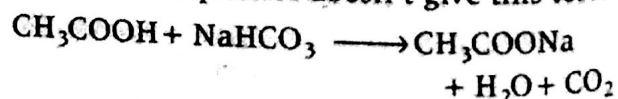
- (i) **Formation of anhydrides** When carboxylic acids are heated in presence of strong dehydrating agent such as P_2O_5 or conc. H_2SO_4 acid anhydrides are formed.
- (ii) **Formation of ester** When carboxylic acids are heated with alcohols or phenols in presence of a mineral acid such as conc. H_2SO_4 or HCl gas, esters are formed. This reaction is known as **esterification**.
- (iii) **Formation of acid chlorides** They react with $SOCl_2$, PCl_5 or PCl_3 to form acid chlorides by replacement of —OH group by Cl atom.
- (iv) **Formation of amides** They react with NH_3 to give ammonium salt which on further heating at high temperature give amides.

3. Reactions Involving —COOH Group

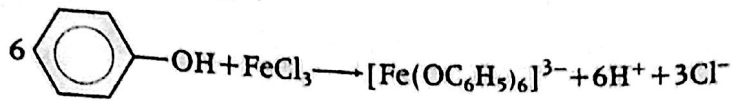
- (i) Carboxylic acids are reduced to 1° alcohols by $LiAlH_4$ or with B_2H_6 .
- (ii) They lose CO_2 to form hydrocarbons when their sodium salts are heated with sodalime ($NaOH + CaO$) in the ratio (3 : 1). This is known as **decarboxylation**.
- (iii) Alkali metal salts of carboxylic acid also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as Kolbe electrolysis.
- (iv) Carboxylic acid having an α -hydrogen are halogenated at the α -position with Cl_2 or Br_2 in presence of small amount of red phosphorous to give α -halocarboxylic acids. The reaction is known as **Hell- Volhard Zelinsky reaction**.

Test to Distinguish between a Phenol and a Carboxylic acid

- (i) **Sodium bicarbonate test** Carboxylic acids when treated with $NaHCO_3$ solution gives brisk effervescence due to evolution of CO_2 gas whereas phenol doesn't give this test.



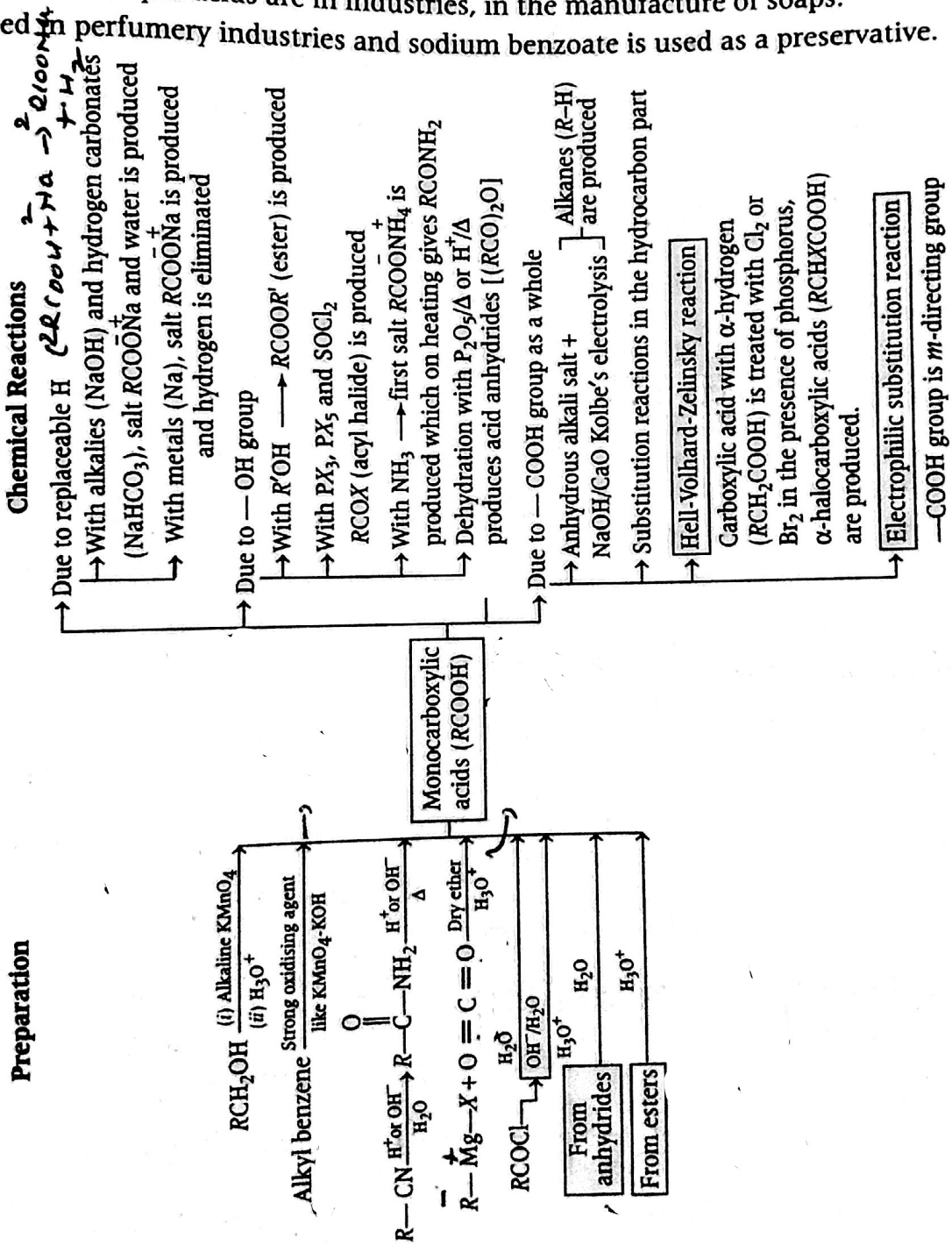
- (ii) **Ferric chloride test** Carboxylic acids give coloured ppt. when treated with neutral FeCl_3 solution whereas phenol give a violet coloured complex with FeCl_3 solution.
- $$3\text{CH}_3\text{COOH} + \text{FeCl}_3 \longrightarrow (\text{CH}_3\text{COO})_3\text{Fe} + 3\text{HCl}$$
- (Buff coloured ppt.)



Uses

- (i) The main use of carboxylic acids are in industries, in the manufacture of soaps.
 (ii) Esters are used in perfumery industries and sodium benzoate is used as a preservative.

Flow Chart for the Preparation and Chemical Reactions of Monocarboxylic Acid

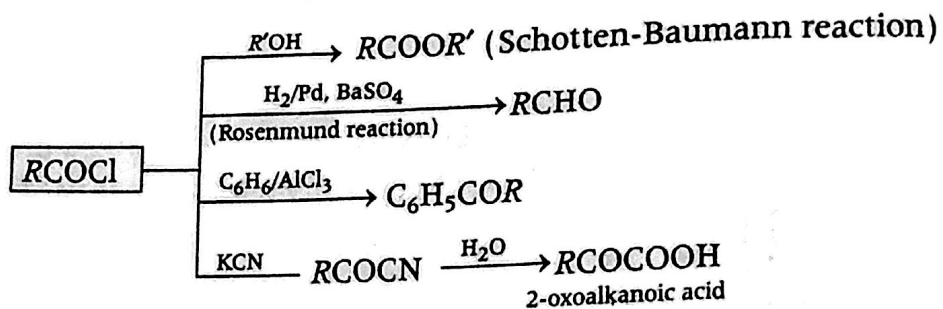


NOTE Carboxylate ions have more acidic strength than phenoxide ion due to delocalisation of lone pair of electrons over more electronegative two oxygen atoms.

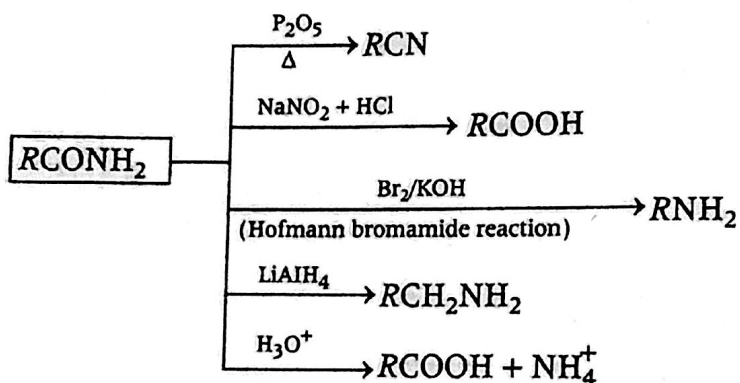
2.5 Derivatives of Carboxylic Acids

Esters, acid chlorides, amides and acid anhydrides are the derivatives of carboxylic acids. Some important reaction of its derivatives are as follows:

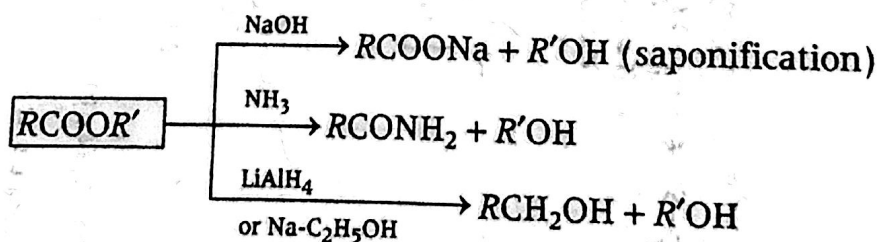
Chemical Reactions of Acid Chlorides



Chemical Reactions of Acid Amides



Chemical Reactions of Esters



Chemical Reactions of Anhydrides

