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Aldehyde, Ketones and Carboxylic Acid

3. Reactions with PCl_3, PCl_5 and $SOCl_2$: Carboxylic acids on treating with PCl_3, PCl_5 or $SOCl_2$, we get acid chlorides. Reaction with thionyl chloride ($SOCl_2$) is preferred because the byproducts are gases and are easily escaped from the reaction mixture so that we get pure acid chloride.

$$R\text{-}COOH + PCl_3 \longrightarrow R\text{-}COCl + H_3PO_3$$

$$R\text{-}COOH + PCl_5 \longrightarrow R\text{-}COCl + POCl_3 + HCl$$

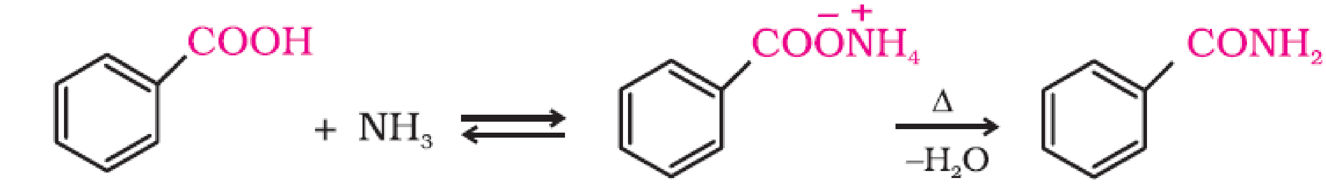
$$R\text{-}COOH + SOCl_2 \longrightarrow R\text{-}COCl + SO_2 + HCl$$

4. Reaction with ammonia: Carboxylic acids react with ammonia to give ammonium salts which on further heating at high temperature give amides.

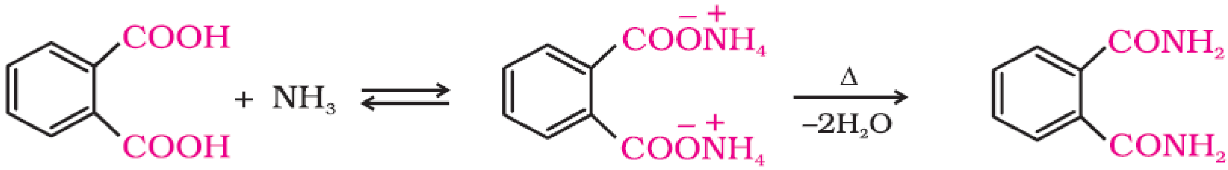
$$R\text{-}COOH + NH_3 \longrightarrow R\text{-}COO^-NH_4^+ \xrightarrow{\Delta} R\text{-}CONH_2 + H_2O$$

$$CH_3COOH + NH_3 \rightleftharpoons CH_3CO\overset{-}{O}\overset{+}{N}H_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$$

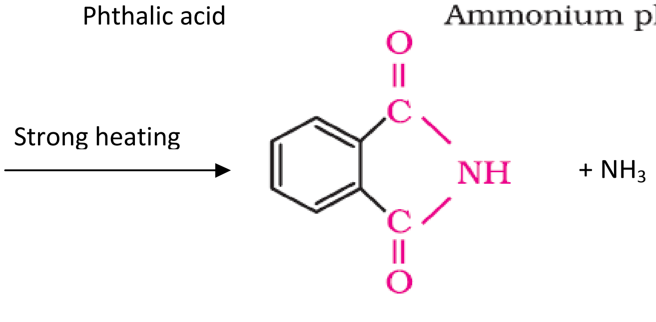
Ammonium acetate — Acetamide



Benzoic acid — Ammonium benzoate — Benzamide



Phthalic acid — Ammonium phthalate — Phthalamide



Phthalimide

C. Reactions Involving –COOH Group

1. Reduction: Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed. Diborane does not reduce functional groups like ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

$$R\text{-}COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) LiAlH4/ether or B2H6}} R\text{-}CH_2OH$$

$$CH_3\text{-}COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) LiAlH4/ether or B2H6}} CH_3\text{-}CH_2OH$$

2. Decarboxylation:

(i) When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation (elimination of CO_2) to form alkanes.

$$R\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} R\text{-}H + Na_2CO_3$$

$$CH_3\text{-}COONa + NaOH \xrightarrow{CaO/\Delta} CH_4 + Na_2CO_3$$

(ii) Kolbe's electrolysis: When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, we get alkanes having twice the number of carbon atoms that present in the alkyl group of the acid. This reaction is known as Kolbe electrolysis.

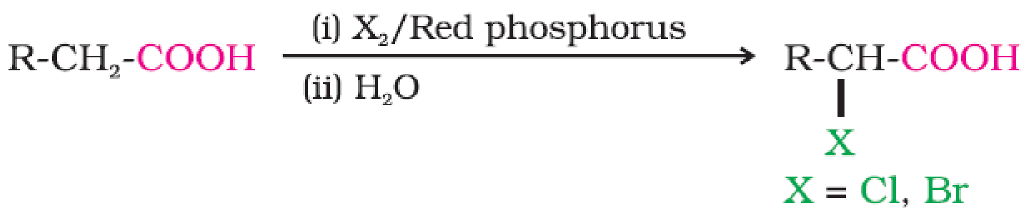
$$2\ R\text{-}COOK + 2H_2O \xrightarrow{\text{electrolysis}} R\text{-}R + 2KOH + H_2 + 2CO_2$$

$$2\ CH_3\text{-}\ COOH + 2\ H_2O \xrightarrow{\text{electrolysis}} CH_3\text{-}CH_3 + 2KOH + H_2 + 2CO_2$$

D. Substitution Reactions in the Hydrocarbon Part:

1. Halogenations [HVZ Reaction]

Carboxylic acids having an α-hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get α-halocarboxylic acids. This reaction is known as Hell-Volhard-Zelinsky(HVZ) reaction.



Carboxylic acid α-halo carboxylic acid

$$CH_3\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) Cl2/ Red P}} CH_3\text{-}CHCl\text{-}COOH + HCl$$

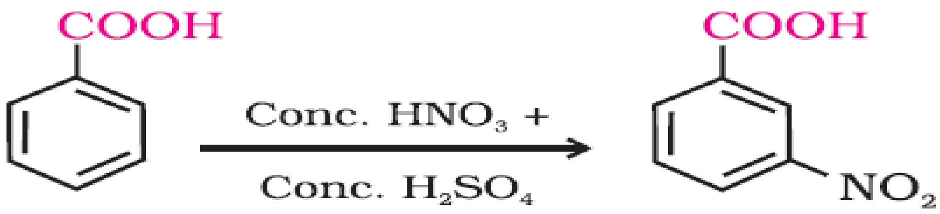
` Propanoic acid 2-chloropropanoic acid

This reaction is synthetically important since the halogen atom can be replaced by other groups.

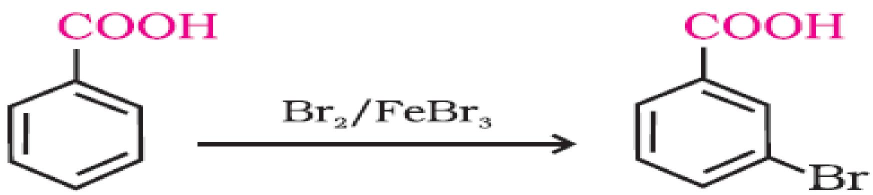
2. Electrophilic substitution reactions:

The –COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, we get meta derivatives.

e.g. 1. **Nitration**



2. Bromination



But *carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.*

5. Aldol condensation Reaction:

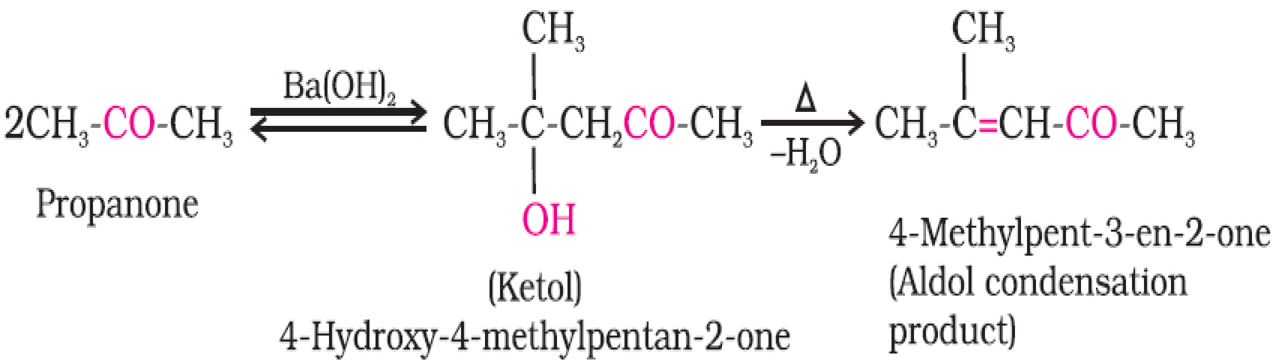
Aldehydes and ketones having at least one α-hydrogen atom when treated with dilute alkali, we get β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as Aldol reaction. The product formed contains both aldehydic (ketonic) and alcoholic group. So the name aldol or ketol is used.

The aldol or ketol on heated undergo dehydration to give α, β-unsaturated aldehyde or ketone. This reaction is called Aldol condensation.

$$2CH_3\text{-}CHO \xrightarrow{\text{dil. NaOH}} CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO \longrightarrow CH_3\text{-}CH{=}CH\text{-}CHO$$

Ethanal 3-Hydroxybutanal (aldol) But-2-enal

(Crotanaldehyde)



6. Cross aldol condensation: When aldol condensation is carried out between

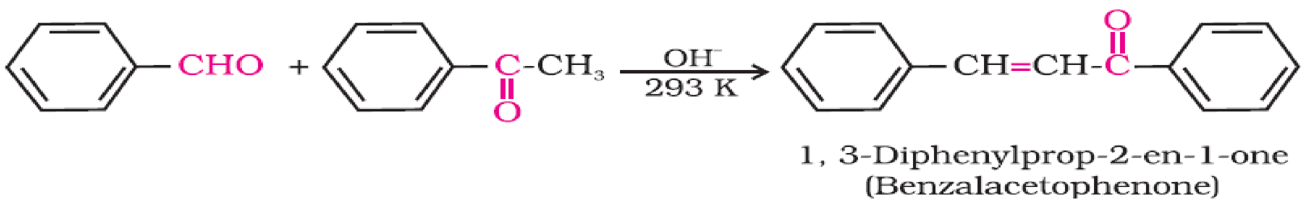
two different aldehydes or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, we get a mixture of four products.

$$CH_3\text{-}CHO + CH_2\text{-}CH_2\text{-}CHO \xrightarrow{NaOH/\Delta} CH_3\text{-}CH{=}CH\text{-}CHO +$$

Ethanal Propanal But-2-enal

$$CH_3\text{-}CH_2\text{-}CH{=}C(CH_3)\text{-}CHO + CH_3\text{-}CH{=}C(CH_3)\text{-}CHO + CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH$$

2-methylpent-2-enal 2-methylbut-2-enal Pent-2-enal



7. Cannizzaro Reaction:

Aldehydes having no α-hydrogen atom (e.g. HCHO, C_6H_5-CHO, CCl_3-CHO etc), when treated with Conc. alkali (NaOH or KOH) undergo self oxidation and reduction (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt. This reaction is called Cannizzaro reaction.

$$2\,HCHO \xrightarrow[KOH]{Conc.} CH_3\text{-}OH + H\text{-}COOK$$

Formaldehyde → Methanol + Potassium formate

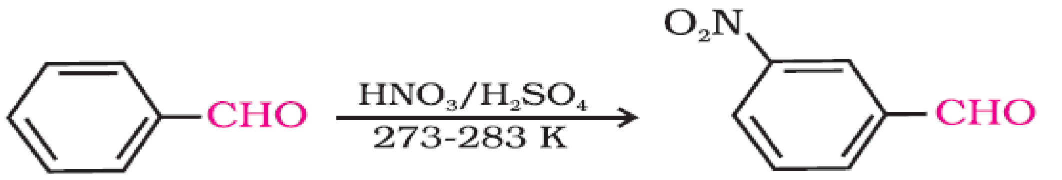
$$2\,C_6H_5\text{-}CHO \xrightarrow[KOH]{Conc.} C_6H_5\text{-}CH_2OH + C_6H_5\text{-}COOK$$

Benzaldehyde → Benzyl alcohol + Potassium benzoate

8. Electrophilic Substitution Reactions:

Aldehydic and ketonic groups are meta directing and deactivating. So on electrophilic substitution reactions, they give meta-derivatives.

e.g. Nitration:



Benzaldehyde → *m*-Nitrobenzaldehyde

Tests to distinguish Aldehydes and Ketones

1. Tollens' test:

Tollen's reagent is freshly prepared *ammoniacal Silver nitrate*. On warming Tollens' reagent, aldehydes give a bright silver mirror. During this reaction, the aldehyde is oxidised to corresponding carboxylate ion and silver nitrate is reduced to silver metal.

$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R\text{-}COO^- + 2\,Ag + 2\,H_2O + 4\,NH_3$$

2. Fehling's test:

Fehling reagent is a mixture 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).* On heating with Fehling's reagent, aldehyde gives a reddish brown precipitate of cuprous oxide (Cu_2O). Aromatic aldehydes do not give this test.

$$R\text{-}CHO + 2Cu^{2+} + 5OH^- \longrightarrow R\text{-}COO^- + Cu_2O + 3H_2O$$

(Cuprous oxide)

3. Benedict's test:

Benedict's solution is a mixture of *$CuSO_4$, sodium citrate and sodium carbonate*. Aliphatic aldehydes give reddish brown precipitate when heated with Benedict's reagent.

$$R\text{-}CHO + 2Cu^{2+} + 5OH^{-} \longrightarrow R\text{-}COO^{-} + Cu_2O + 3H_2O$$

The above tests are not answered by ketones.

CARBOXYLIC ACIDS

Carbon compounds containing a carboxyl functional group (–COOH) are called carboxylic acids. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Aliphatic carboxylic acids containing 12 to 18 C atoms are called fatty acids. They occur in natural fats as esters of glycerol.

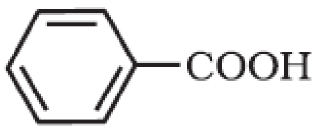
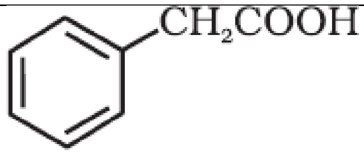
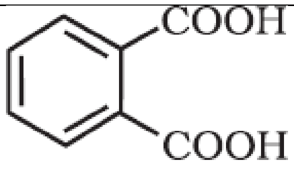
Nomenclature

The common names of carboxylic acids end with the suffix –ic acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: ormica means ant), acetic acid (CH_3COOH) from vinegar (Latin: acetum, means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin: butyrum means butter).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with – oic acid.

In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the ending –e of the alkane is retained. The number of carboxyl groups is indicated by adding the prefixes di, tri, etc. to the term oic.

Some examples are:

Compound	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid	Pentanoic acid
$CH_3CH_2CH_2CH_2CH_2COOH$	Caproic acid	Hexanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC -CH_2-COOH	Malonic acid	Propanedioic acid
HOOC -$(CH_2)_2$-COOH	Succinic acid	Butanedioic acid
HOOC -$(CH_2)_3$-COOH	Glutaric acid	Pentanedioic acid
HOOC -$(CH_2)_4$-COOH	Adipic acid	Hexanedioic acid
HOOC -CH_2-CH(COOH)-CH_2-COOH		Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

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