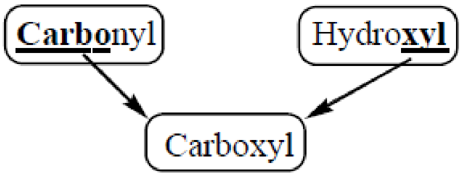
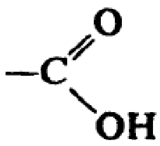
Carboxylic Acids

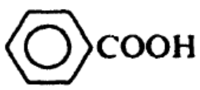
Of the organic compounds that show acidity, by far the most important are the carboxylic acids. These compounds contain the carboxyl group



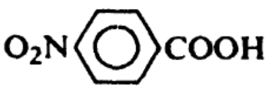


attached to either an alkyl group (RCOOH) or an aryl group (ArCOOH). for example:

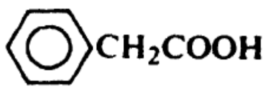
$HCOOH$	CH_3COOH	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Formic acid	**Acetic acid**	**Lauric acid**	**Oleic acid**
Methanoic acid	**Ethanoic acid**	**Dodecanoic acid**	***cis*-9-Octadecenoic acid**



Benzoic acid



***p*-Nitrobenzoic acid**



Phenylacetic acid

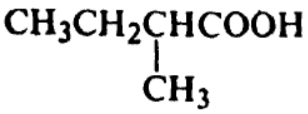
Whether the group is aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted, the properties of the carboxyl group are essentially the same.

Nomenclature:

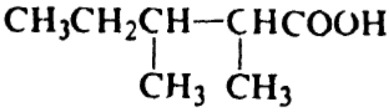
The aliphatic carboxylic acids have been known for a long time, and as a result have common names that refer to their sources rather than to their chemical structures. Formic acid, for example, adds the sting to the bite of an ant (Latin : formica, ant); butyric acid gives rancid butter its typical smell (Latin: butyrum, butter); and caproic, caprylic, and capric acids are all found in goat fat (Latin: caper، goat). Branched-chain acids and substituted acids are named as derivatives of the straight-chain acids. To indicate the position of attachment, the Greek letters, α, β, γ, δ, etc., are used; the α carbon is the one bearing the carboxyl group.

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-COOH$$ ***Used in common names***

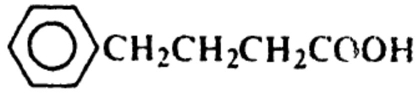
For example:



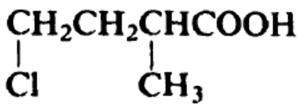
α-Methylbutyric acid



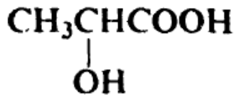
α,β-Dimethylvaleric acid



γ-Phenylbutyric acid



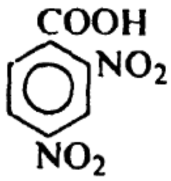
γ-Chloro-α-methylbutyric acid



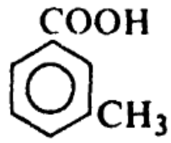
α-Hydroxypropionic acid
Lactic acid

Aromatic carboxylic acids as derivatives of benzoic acid are called as follows:

p-Bromobenzoic acid

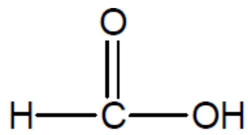


2,4-Dinitrobenzoic acid



m-Toluic acid

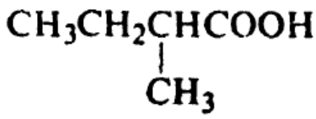
The **IUPAC** names follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the -e of the corresponding alkane with -oic acid. For example:



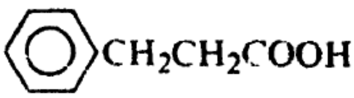
Methan~~e~~ + oic acid = Methan**oic acid**

$CH_3CH_2CH_2CH_2COOH$

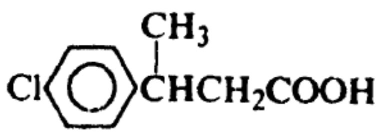
Pentanoic acid



2-Methylbutanoic acid



3-Phenylpropanoic acid

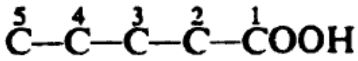


3-(*p*-Chlorophenyl)butanoic acid

$CH_3CH{=}CHCOOH$

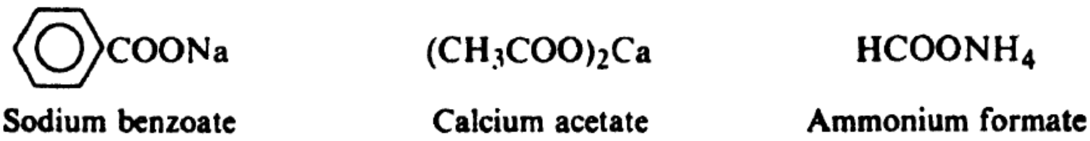
2-Butenoic acid

The position of a substituent is indicated as usual by a number. We should notice



Used in IUPAC names

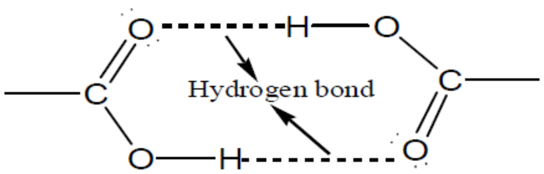
The name of a salt of a carboxylic acid consists of the name of the cation (sodium, potassium, ammonium, etc.) followed by the name of the acid with the ending -ic acid changed to -ate. For example:



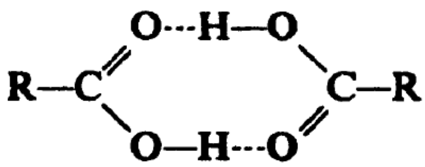
Physical properties:

As we would expect from their structure, carboxylic acid molecules are polar, and like alcohol molecules can form hydrogen bonds with each other and with other kinds of molecules. The aliphatic acids therefore show very much the same solubility behavior as the alcohols : the first four are miscible with water, the five- carbon acid is partly soluble and the higher acids are virtually insoluble. Water solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water. The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water. Carboxylic acids are soluble in less polar solvents like ether, alcohol،benzene, etc.

- The carboxylic acids are even higher boiling than alcohols. These very high boiling points are due to the fact that a pair of carboxylic acid molecules are held together not by one but by two hydrogen bonds:



OR



Note / Aliphatic acids with more than 8 carbons are solids at room temperature .Double bonds (especially cis) lower the melting point.

Acidity :

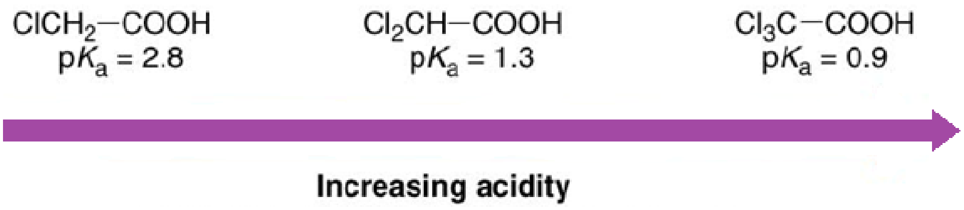
1- The acidity strength increases with the presence of **(Electron-withdrawing group)** because it works to increase the stability of the anion, as it reduces the concentration of the negative charge on the oxygen atom in the hydroxyl group.

....., -COOH , $-SO_3H$, -CN , $-NO_2$, Br , Cl ,F

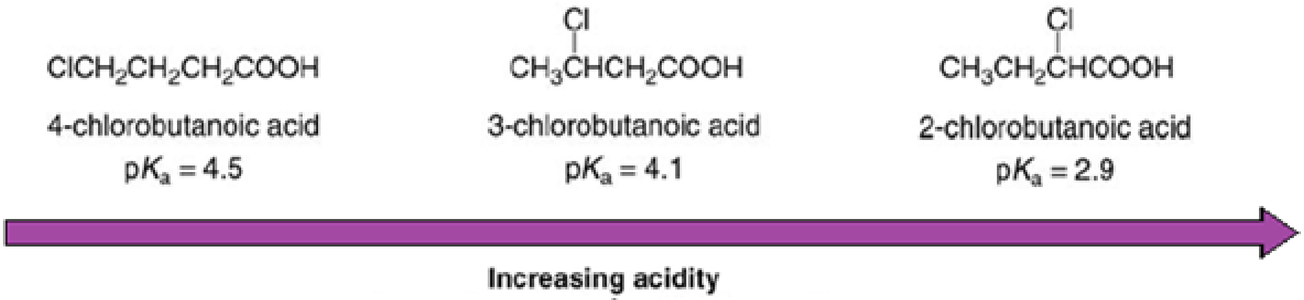
The acidity decreases with the presence of **(Electron-donating group)** as it increases the concentration of negative charge on the oxygen atom in the hydroxyl group.

-OH , $-NH_2$, $-OCH_3$, $-CH_3$

2- Increasing acidity when increasing number of electronegative Cl atoms.



3- Increasing acidity when increasing proximity of Cl to COOH



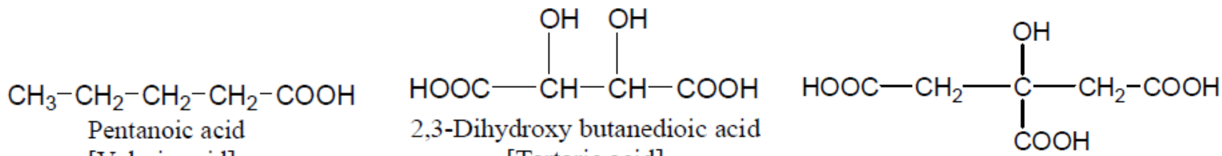
Classification of Carboxylic Acids: Carboxylic acids are classified on several basis:

1- Classification depends on the number of carboxyl groups present in their molecules to:

Monocarboxylic acid : It contains one carboxyl group

Dicarboxylic acid : It contains two carboxyl groups

Tricarboxylic acid : It contains three groups of carboxyl

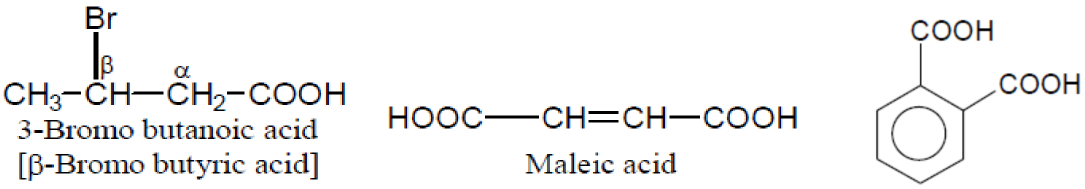


Pentanoic acid [Valeric acid] 2,3-Dihydroxy butanedioic acid [Tartaric acid] Citric acid

2- Classification depends on the type organic group related in a carboxyl group:

Aliphatic carboxylic acids (saturated and unsaturated)

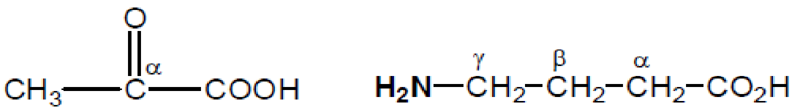
Aromatic carboxylic acids



3-Bromo butanoic acid [β-Bromo butyric acid] Maleic acid Phthalic acid

3- Classification depends on other functional groups present in their molecules:

Amino carboxylic acids contain an amine group and so on



α - Pyruvic acid γ- Amino butyric acid

Preparation Of Carboxylic Acids

1. Oxidation of primary alcohols.

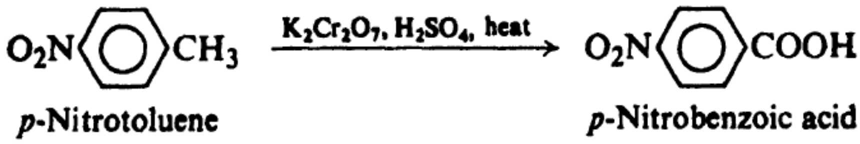
$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

Examples:

2. Oxidation of alkylbenzenes.

$$Ar{-}R \xrightarrow[K_2C_2O_7]{KMnO_4 \text{ or } K_2Cr_2O_7} Ar{-}COOH$$

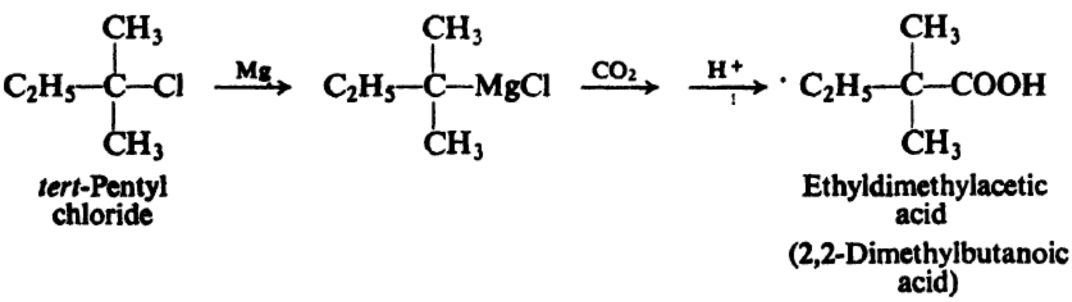
Examples:



3. Carbonation of Grignard reagents.

$$\underset{(\text{or } ArX)}{RX} \xrightarrow{Mg} RMgX \xrightarrow{CO_2} RCOOMgX \xrightarrow{H^+} \underset{(\text{or } ArCOOH)}{RCOOH}$$

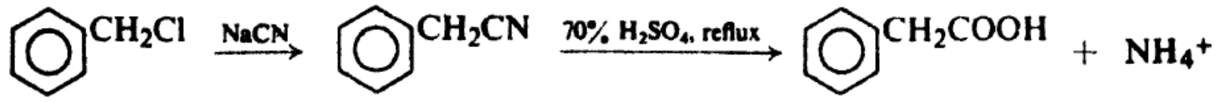
Example



4. Hydrolysis of nitrites.

$$R{-}C{\equiv}N \text{ or } Ar{-}C{\equiv}N + H_2O \xrightarrow{\text{acid or base}} R{-}COOH \text{ or } Ar{-}COOH + NH_3$$

Examples:



Benzyl chloride **Phenylacetonitrile** **Phenylacetic acid**

Reactions of Carboxylic Acids

1. Acidity. Salt formation.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

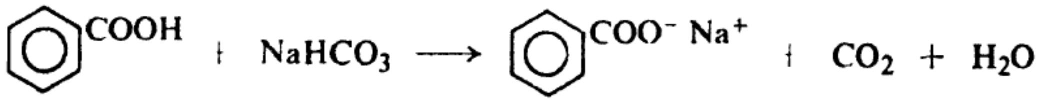
Examples:

$$2CH_3COOH + Zn \longrightarrow (CH_3COO^-)_2Zn^{++} + H_2$$

Acetic acid **Zinc acetate**

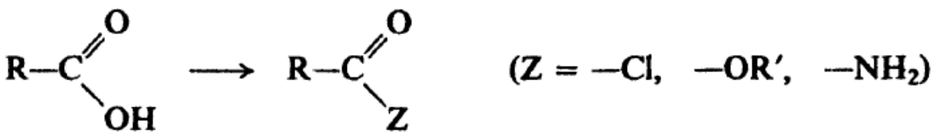
$$CH_3(CH_2)_{10}COOH + NaOH \longrightarrow CH_3(CH_2)_{10}COO^-Na^+ + H_2O$$

Lauric acid **Sodium laurate**

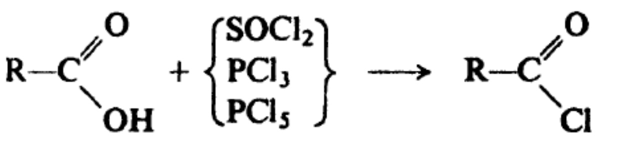


Benzoic acid **Sodium benzoate**

2. Conversion into functional derivatives.

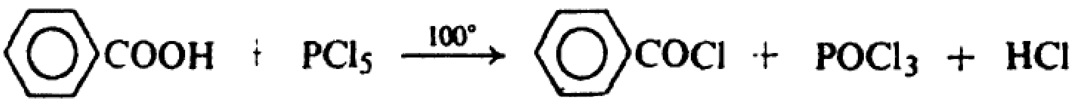


(a) Conversion into acid chlorides.



Acid chloride

Examples:

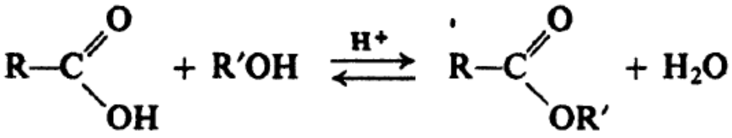


Benzoic acid **Benzoyl chloride**

$$n\text{-}C_{17}H_{35}COOH + SOCl_2 \xrightarrow{\text{reflux}} n\text{-}C_{17}H_{35}COCl + SO_2 + HCl$$

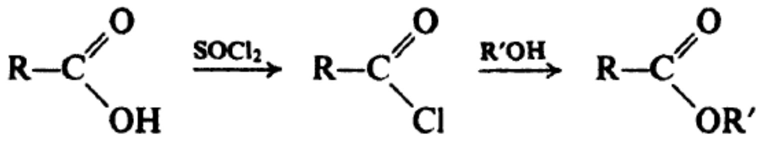
Stearic acid, Thionyl chloride, Stearoyl chloride

(b) Conversion into esters.

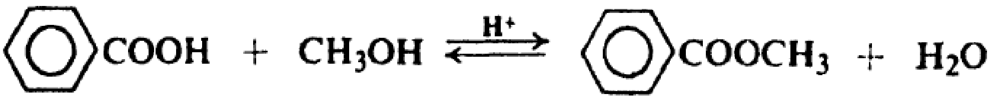


An ester

Reactivity of R′OH: 1° > 2° (> 3°)

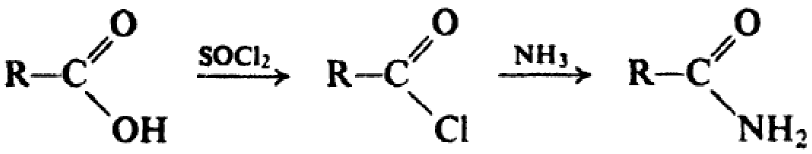


An acid chloride An ester



Benzoic acid Methanol Methyl benzoate

(c) Conversion into amides.



An acid chloride An amide

Example:

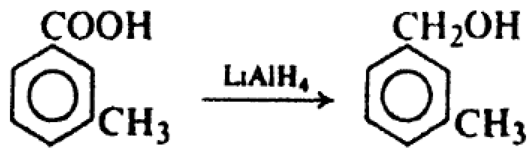
$$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow{NH_3} C_6H_5CH_2CONH_2$$

Phenylacetic acid, Phenylacetyl chloride, Phenylacetamide

3. Reduction.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

1° alcohol



m-Toluic acid → *m*-Methylbenzyl alcohol

4. Substitution in alkyl or aryl group

(a) Alpha-halogenation of aliphatic acids.

$$RCH_2COOH + X_2 \xrightarrow{P} \underset{\displaystyle X}{\underset{|}{RCH}}COOH + HX \qquad X_2 = Cl_2, Br_2$$

An α-haloacid

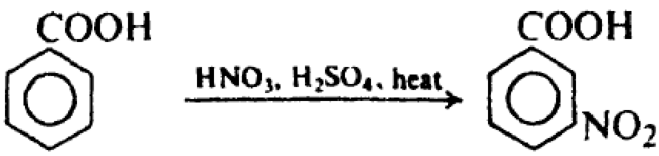
Examples:

$$CH_3COOH \xrightarrow{Cl_2,\ P} ClCH_2COOH \xrightarrow{Cl_2,\ P} Cl_2CHCOOH \xrightarrow{Cl_2,\ P} Cl_3CCOOH$$

Acetic acid, Chloroacetic acid, Dichloroacetic acid, Trichloroacetic acid

(b) Ring substitution in aromatic acids.

Example:



Benzoic acid → *m*-Nitrobenzoic acid