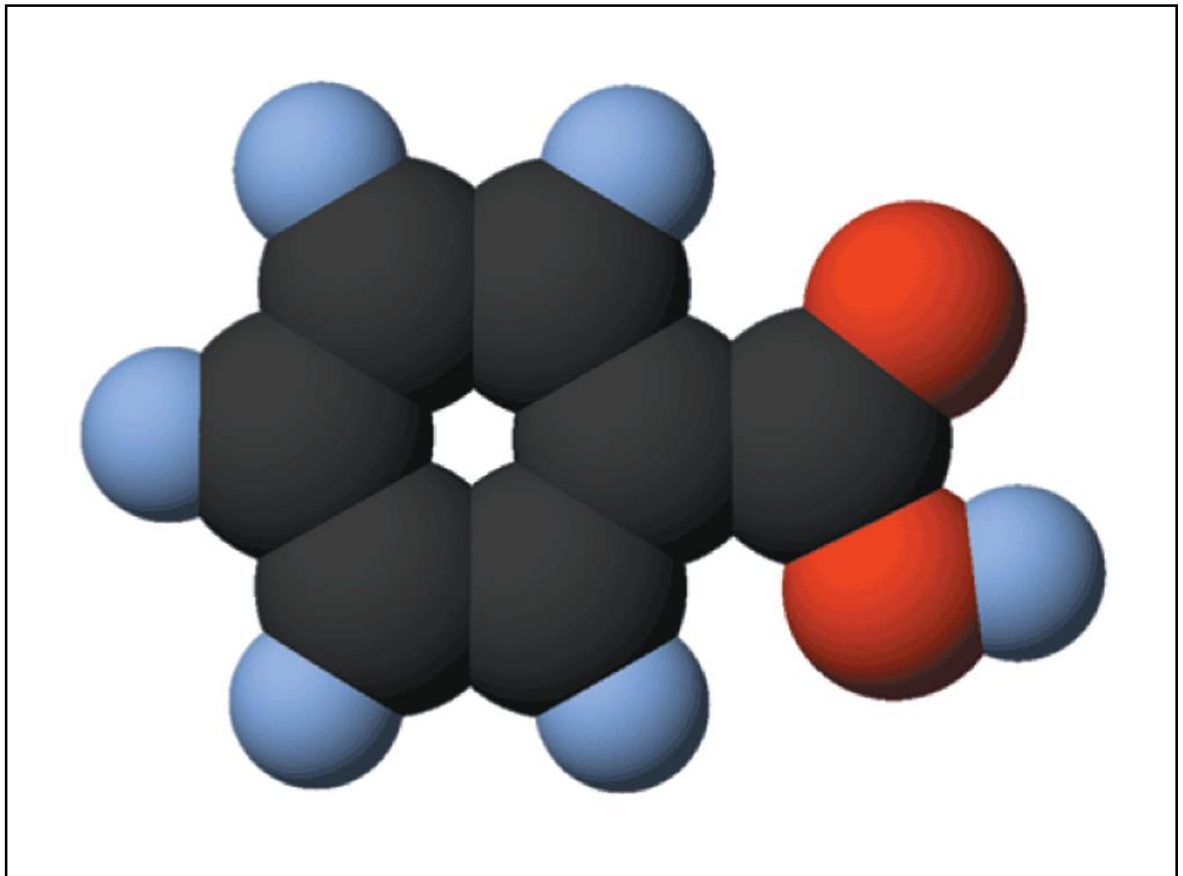
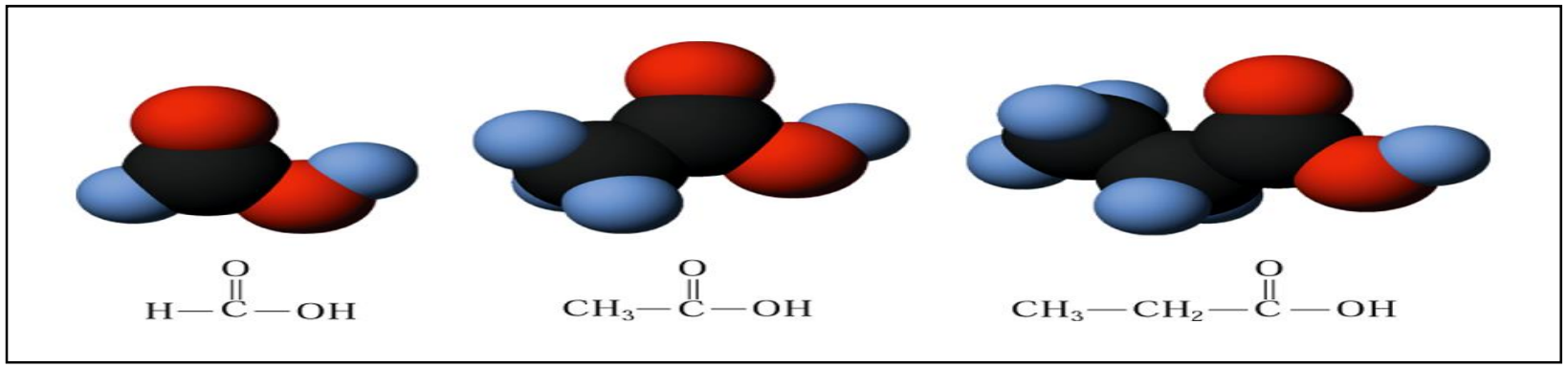
Carboxylic Acids and Carboxylic acid derivatives



Benzoic acid molecule

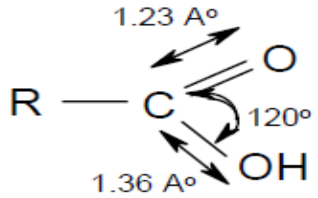
Lec.1 Carboxylic Acids

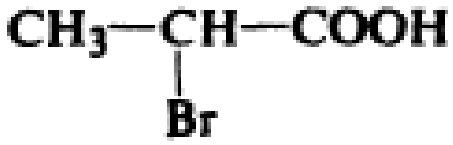
These compounds contain the carboxyl group attached to either an alkyl group(RCOOH , R-CO_2H , or an aryl group (ArCOOH).



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

Carboxylic Acids





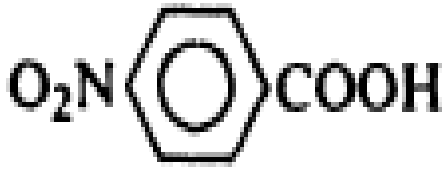
α-Bromopropionic acid
2-Bromopropanoic acid

Cyclohexanecarboxylic acid

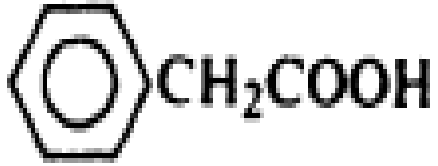
Acrylic acid
Propenoic acid

Carboxylic Acids

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.

2-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.

The common names of the more important acids are shown in Table1. 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)

Table 1: carboxylic acids

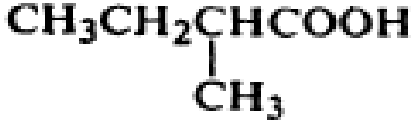
Common names:

HCO_2H	formic acid	*L. formica* ant
CH_3CO_2H	acetic acid	*L. acetum* vinegar
$CH_3CH_2CO_2H$	propionic acid	*G. "first salt"*
$CH_3CH_2CH_2CO_2H$	butyric acid	*L. butyrum* butter
$CH_3CH_2CH_2CH_2CO_2H$	valeric acid	*L. valerans*

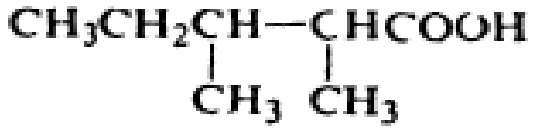
Branched-chain acids and substituted acids are named as derivatives of the straight-chain acids. To indicate the position of attachment, the Greek letters, α, β, γ, δ etc., are used; the α -carbon is the one bearing the carboxyl group:

Used in common names

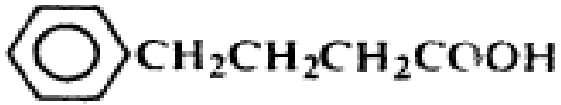
For example:



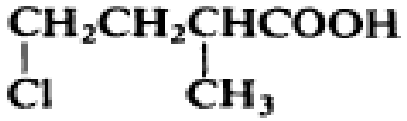
α-Methylbutyric acid



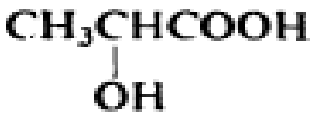
α,β-Dimethylvaleric acid



γ-Phenylbutyric acid



γ-Chloro-α-methylbutyric acid



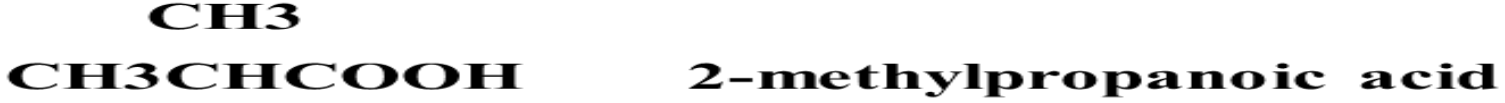
α-Hydroxypropionic acid
Lactic acid

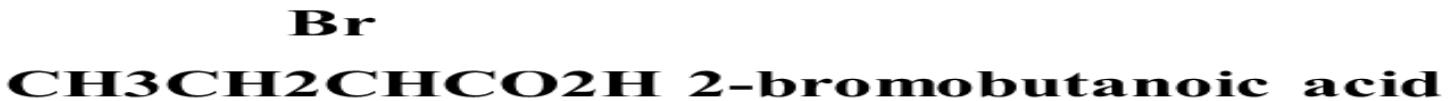
Generally the parent acid is taken as the one of longest carbon chain, although some compounds are named as derivatives of acetic acid.

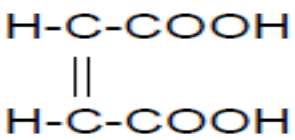
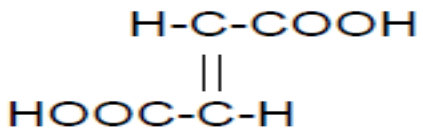
IUPAC nomenclature for carboxylic acids:

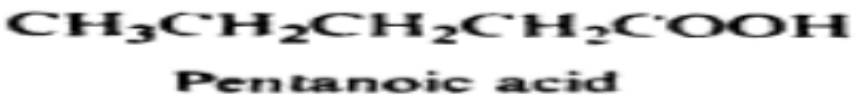
parent chain = longest, continuous carbon chain that contains the carboxyl group . alkane, drop –e, add –oic acid

Formula	IUPAC alkan -oic acid	Common prefix – ic acid
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

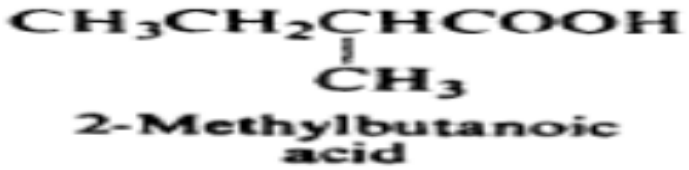




No.	Carboxylic acid	common name	IUPAC name
1.	$HCOOH$	Formic acid	Methanoic acid
2.	CH_3COOH	Acetic acid	Ethanoic acid
3.	$CH_3(CH_2)_3COOH$	Valeric acid	Pentanoic acid
4.	$CH_3(CH_2)_{16}COOH$	Stearic acid	Octadecanoic acid
5.	$CH_3CHOHCOOH$	Lactic acid	2-Hydroxypropanoic acid
6.	C_6H_5 –$CHOHCOOH$	Mandelic acid	2-Hydroxy-2-phenylethanoic acid
7.	$CH_2=CHCOOH$	Acryloic acid	2-Propenoic acid
8.	$PhCOOH$	Benzoic acid	Benzene carboxlic acid
9.	o- $C_6H_4(OH)COOH$	Salicylic acid	o-Hydroxybenzene carboxlic acid
10.	$HOOC\text{-}COOH$	Oxalic acid	Ethanedioic acid
11.	$HOOC.CH_2COOH$	Malonic acid	Propanedioic acid
12.	$HOOC.CH_2CH_2COOH$	Succinic acid	Butanedioic acid
13.	o- $HOOC.C_6H_4COOH$	Phthalic acid	1,2-benzenedicarboxlic acid
14.		Maleic acid	*cis*-2-butenedioic acid
15.		Fumaric acid	*trans*-2-butenedioic acid



Pentanoic acid



2-Methylbutanoic acid

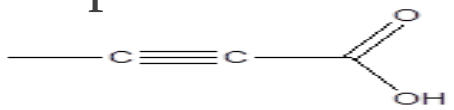
3-(4-chlorophenyl) butanoic acid

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

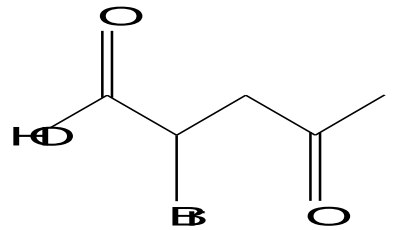
Used in IUPAC names

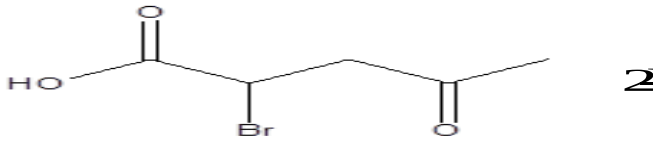
We should notice that the carboxyl carbon is always considered as C-l, and hence C-2 corresponds to α of the common names, C-3 to β, and so on. (Caution: Do not mix Greek letters with IUPAC names, or Arabic numerals with common names.)

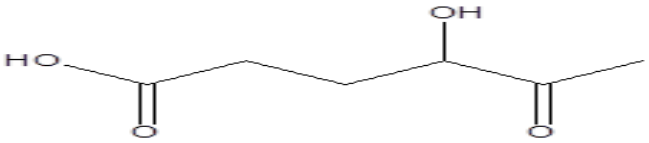
- The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming , in the latter cases , the prefix oxo- is used to locate the carbonyl group of the aldehyde or ketone , as in the example:

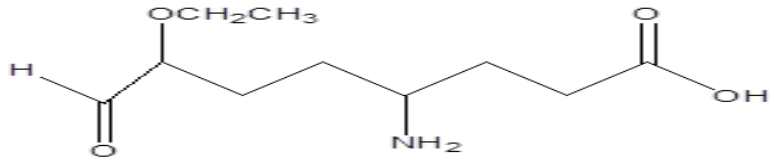


2-butynoic acid



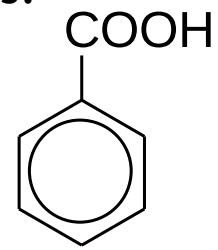




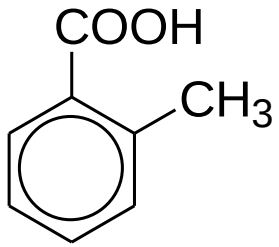


special names

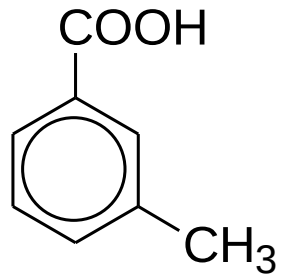
- Aromatic acids, ArCOOH, are usually named as derivatives of the parent acid, benzoic acid, C_6H_5COOH. The methylbenzoic acids are given the special acid of toluic acids.



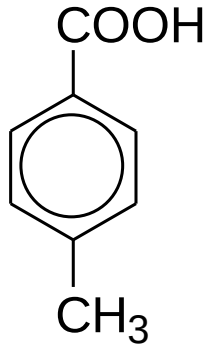
benzoic acid



o-toluic acid

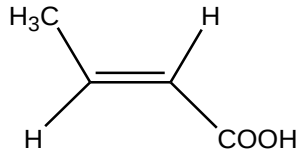


m-toluic acid

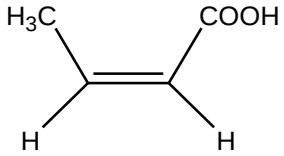


p-toluic acid

Unsaturated carboxylic acids



(z)-butanoic acid



(E)-butanoic acid

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:

$$\underset{\text{Stronger acid}}{\underset{\textit{Insoluble in } H_2O}{RCOOH}} + NaOH \longrightarrow \underset{\textit{Soluble in } H_2O}{RCOONa} + \underset{\text{Weaker acid}}{H_2O}$$

Sodium benzoate

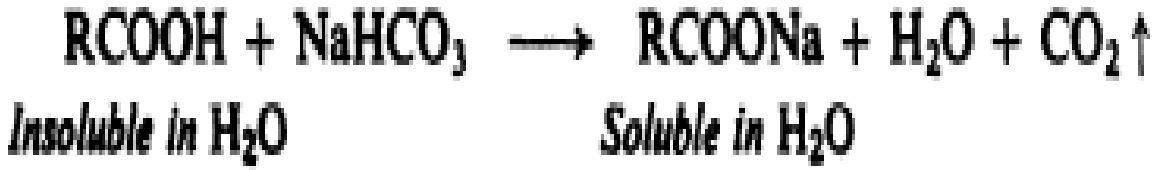
$(CH_3COO)_2Ca$

Calcium acetate

$HCOONH_4$

Ammonium formate

Potassium α,β-dibromopropionate
(Potassium 2,3-dibromopropanoate)

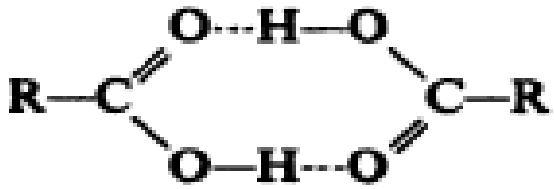

RCOOH + NaHCO3 → RCOONa + H2O + CO2↑
Insoluble in H2O
Soluble in H2O

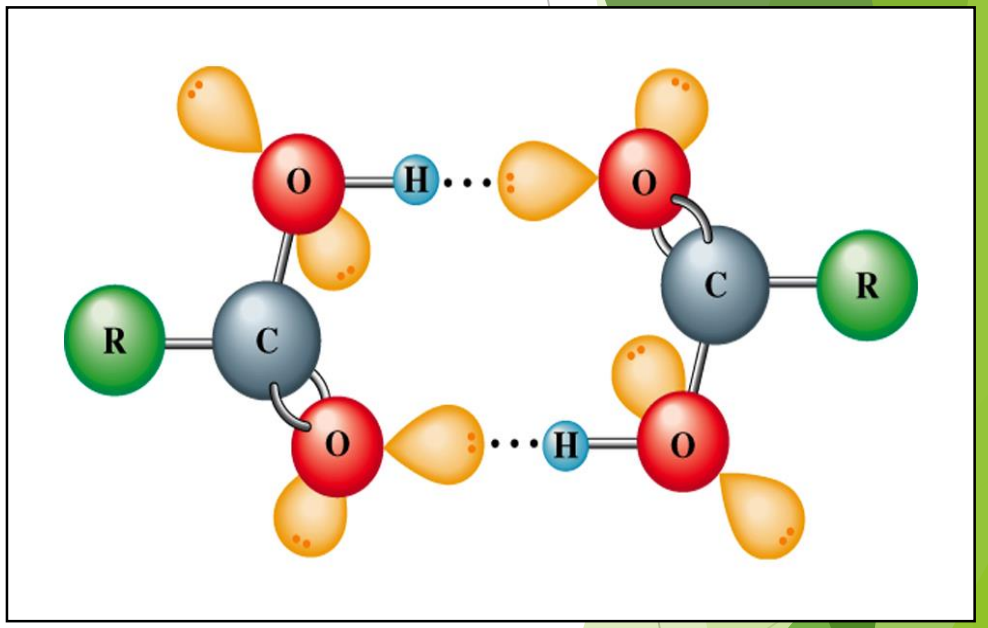
3-Physical properties

- carboxylic acid molecules are polar, and like alcohol molecules can form hydrogen bonds with each other and with other kinds of molecules.
- The first four are miscible with water.
- The five-carbon acid is partly soluble, and the higher acids are nearly insoluble.
- The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show noticeable solubility in water.
- Carboxylic acids are soluble in less polar solvents like ether, alcohol, benzene, etc.

Physical properties

The carboxylic acids are even higher boiling than alcohols. These very high together not by one but by two hydrogen bonds.





- boiling points are due to the fact that a pair of carboxylic acid molecules is held
- The odours of the lower aliphatic acids progress from the sharp, irritating odours, the higher acids have little odour because of their low volatility.

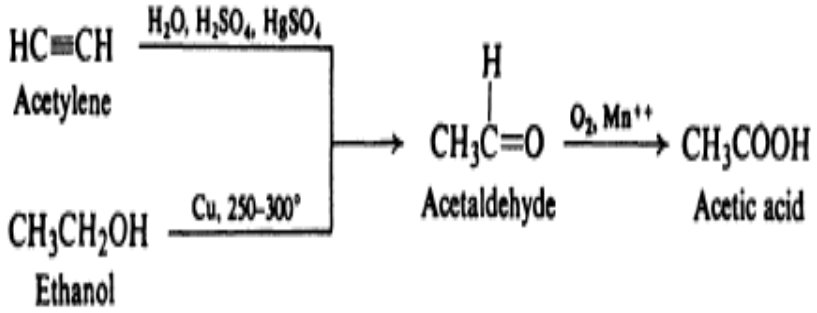
4 - Salts of carboxylic acids

Aqueous hydroxides therefore readily convert carboxylic acids into their salts; aqueous mineral acids readily convert the salts back into the carboxylic acids.

- Salts of carboxylic acid like all salts are crystalline non-volatile solids made up of positive and negative ions.
- The alkali metal salts of carboxylic acids (sodium, potassium, ammonium) are soluble in water but insoluble in non-polar solvent

Industrial source

- Acetic acid, by far the most important of all carboxylic acids, is prepared by air oxidation of acetaldehyde, which is readily available from the hydration of acetylene, or the dehydrogenation of ethanol.



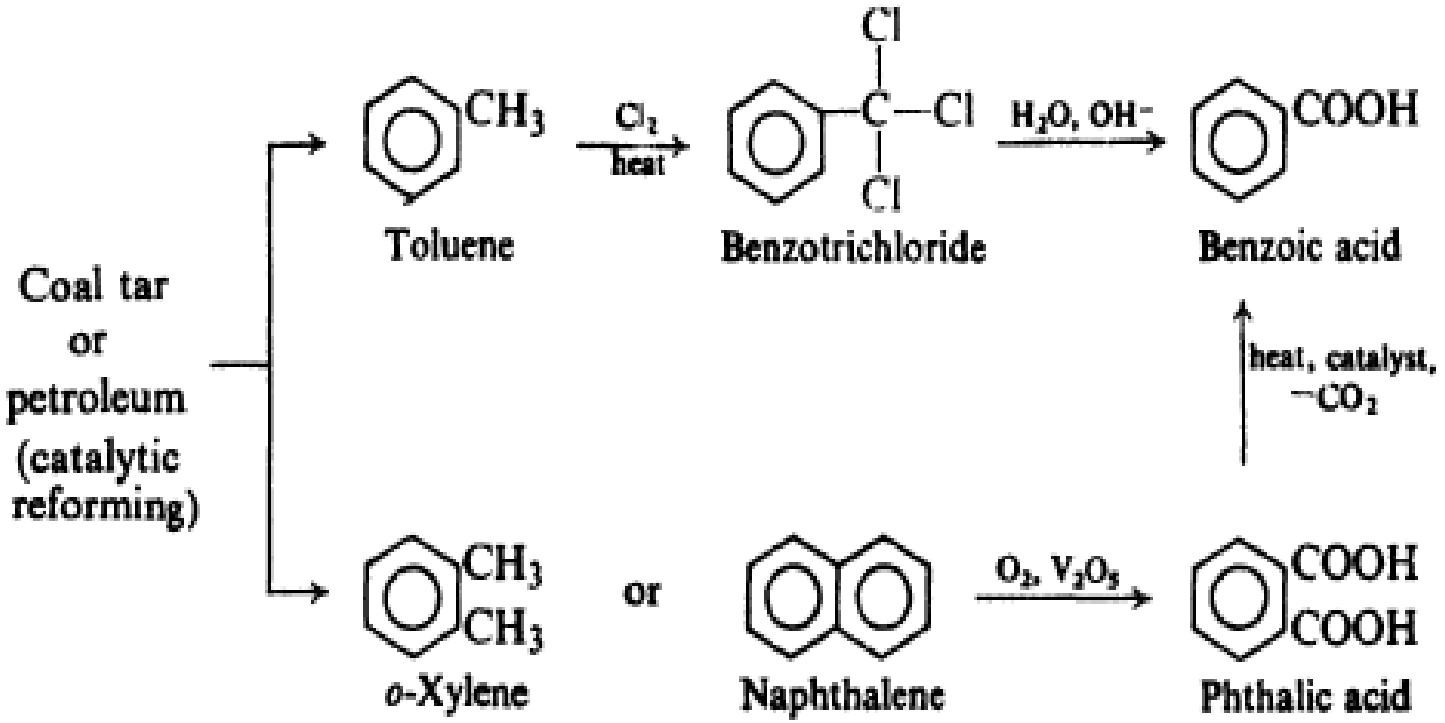
Industrial source

- Large amounts of acetic acid are also produced as the dilute aqueous solution known as vinegar.
- The acetic acid is prepared by air oxidation; the compound that is oxidized is ethyl alcohol, and the catalysts are bacterial (Acetobacter) enzymes.
- The most important of the aromatic carboxylic acids, benzoic acid and the phthalic acids, are prepared on an industrial scale by a reaction we have already

encountered: oxidation of alkylbenzenes

- The toluene and xylenes required are readily available from coal tar and, by catalytic reforming of aliphatic hydrocarbons, from petroleum.

Industrial source



Dicarboxylic acid

If the substituent is a second carboxyl group, we have a dicarboxylic acid.

- Malonic acid

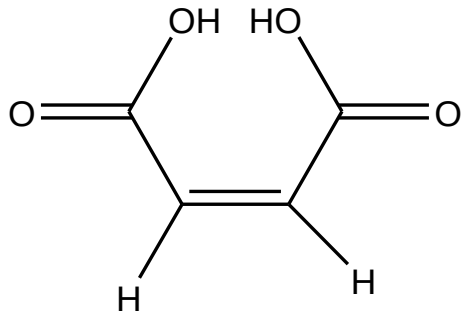
$HOOCCH_2COOH$

Propanedioic acid

benzenedicarboxylic acids

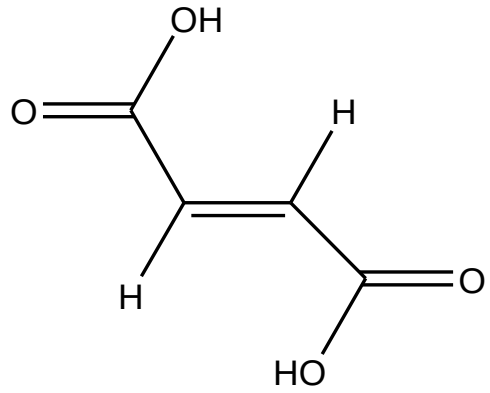
Phthalic	1,2-$C_6H_4(COOH)_2$
Isophthalic	1,3-$C_6H_4(COOH)_2$
Terephthalic	1,4-$C_6H_4(COOH)_2$

Unsaturated dicarboxylic acids



cis-butanedioic acid

Maliek acid



trans-butenedioic acid

fumaric acid