Carboxylic acid

carboxylic acid, any of a class of organic compounds in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group (−OH) by a single bond. A fourth bond links the carbon atom to a hydrogen (H) atom. The carboxyl (COOH) group is so-named because of the *carb*onyl group (C=O) and hydr*oxyl* group.

Nomenclature

IUPAC

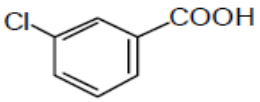
Alkanoic acid: cycloalkanecarboxylic acid

Take name of the alkane, drop the -e and add '–ic acid' or '-oic acid'. The acid functionality has the highest priority in organic nomenclature and always gets the lowest number

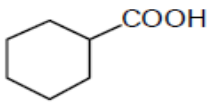
Common

There are some trivial names that must be memorized, e.g., Formic, Acetic, Propionic, Butyric, Acrylic, Crotonic, Cinnamic, etc., Acids.

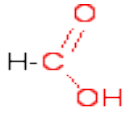
HCOOH	Methanoic Acid (Formic Acid)
CH_3COOH	Ethanoic Acid (Acetic Acid)
CH_3CH_2COOH	Propanoic Acid (Propionic Acid)
$CH_3CH_2CH_2COOH$	Butanoic Acid(Butyric Acid)



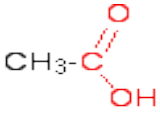
3-chlorobenzoic acid



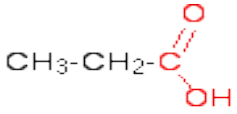
cyclohexanecarboxylic acid



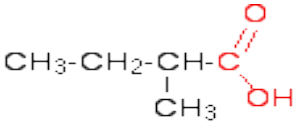
methanoic acid



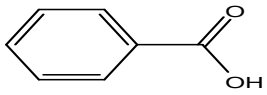
ethanoic acid



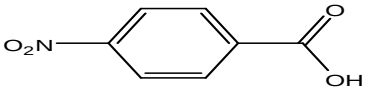
propanoic acid



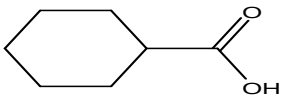
2-methylbutanoic acid



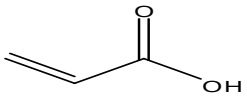
benzoic acid



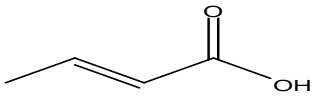
4-nitrobenzoic acid or p-nitrobenzoic acid



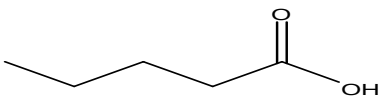
cyclohexanecarboxylic acid



acrylic acid



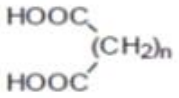
2-butenoic acid



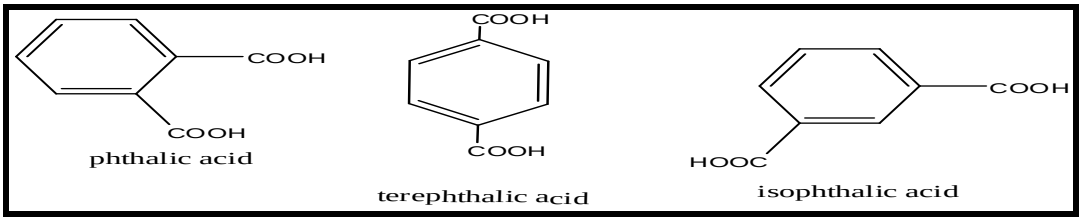
valeric acid

Dicarboxylic Acids:

IUPAC: Alkanedioic acid; cycloalkane-1,n-dicarboxylic acid
Common: All the common dicarboxylic acids have trivial names that must be memorized. One can use the mnemonic: "Oh my such good apple pie sweet as sugar."



ethanedioic acid	n = 0	oxalic acid
propanedioic acid	n = 1	malonic acid
butanedioic acid	n = 2	succinic acid
pentanedioic acid	n = 3	glutaric acid
hexanedioic acid	n = 4	adipic acid
heptanedioic acid	n = 5	pimelic acid
octanedioic acid	n = 6	suberic acid
nonanedioic acid	n = 7	azelaic acid

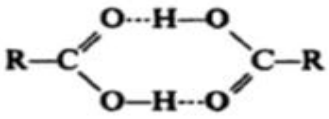


Physical properties

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.

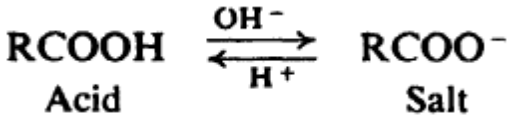
Carboxylic acids are soluble in less polar solvents like ether, alcohol, benzene, etc.

We can see from Table 18.1 that as a class the carboxylic acids are even higher boiling than alcohols. For example, propionic acid (b.p. 141°) boils more than twenty degrees higher than the alcohol of comparable molecular weight, *n*-butyl alcohol (b.p. 118°). 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:



Salts of carboxylic acid

Although much weaker than the strong mineral acids (sulfuric, hydrochloric, nitric), the carboxylic acids are tremendously more acidic than the very weak organic acids (alcohols, acetylene) we have so far studied; they are much stronger acids than water.

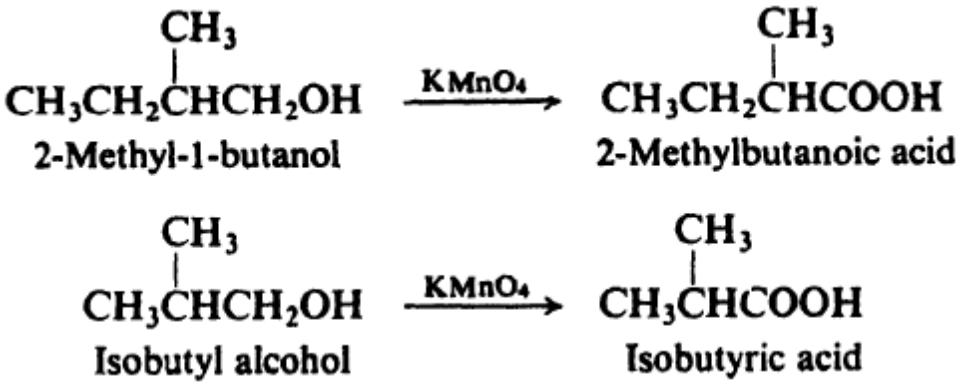


$CH_3CH_2COO^{\ominus}K$	$CH_3COO^{\ominus}Al^{\oplus}$
potassium propionate	aluminum(I) acetate aluminium ethanoate

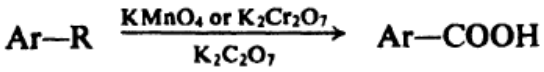
Preparation of carboxylic acid

1- Oxidation of primary alcohol

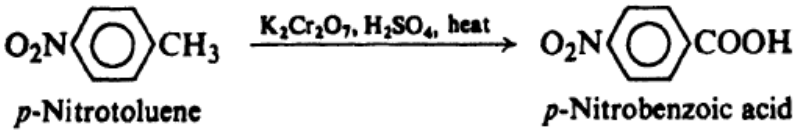
Examples

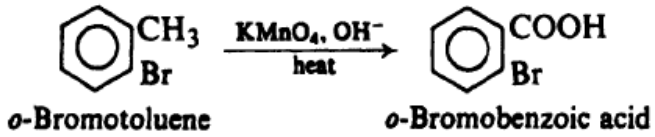


2- Oxidation of alkylbenzene

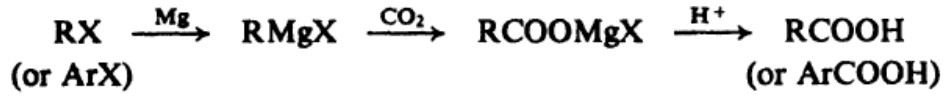


Examples:

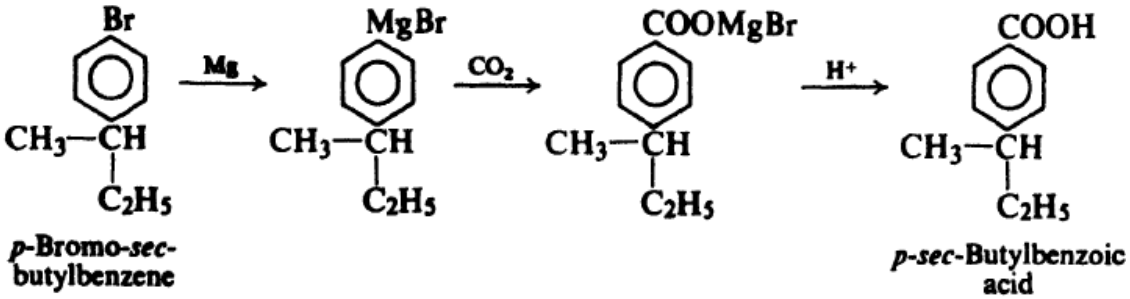




3- Carbonation of griniard reagents

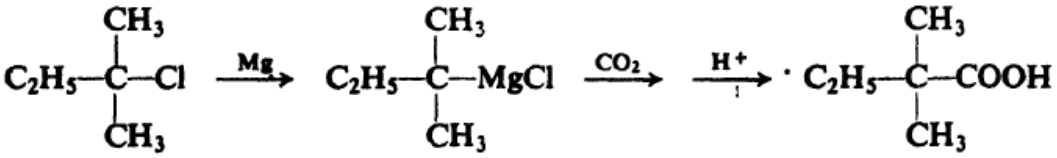


Examples:



***p*-Bromo-*sec*-butylbenzene**

***p*-*sec*-Butylbenzoic acid**

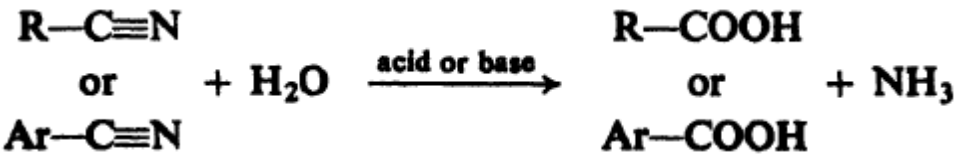


***tert*-Pentyl chloride**

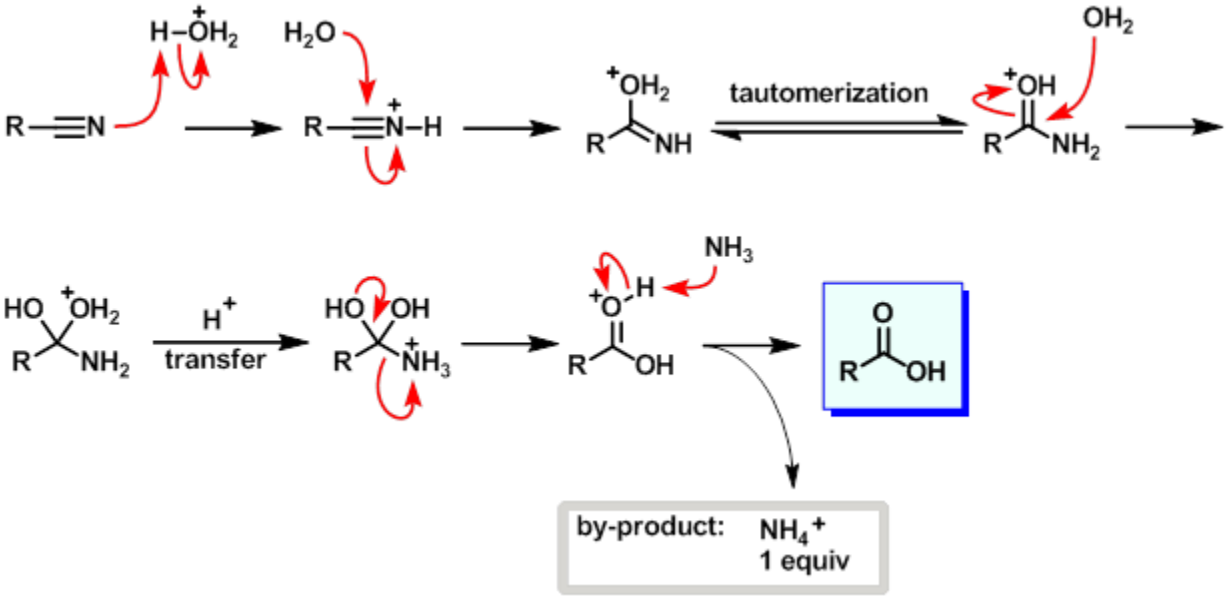
Ethyldimethylacetic acid

(2,2-Dimethylbutanoic acid)

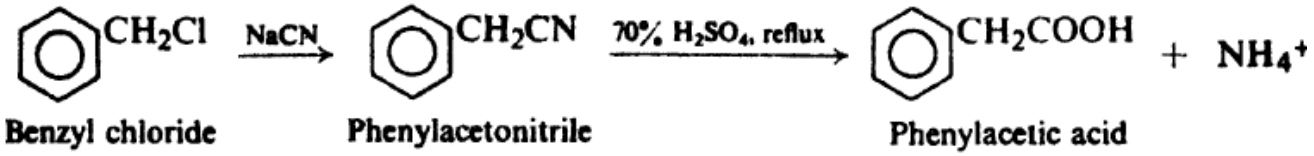
4- Hydrolysis of nitriles

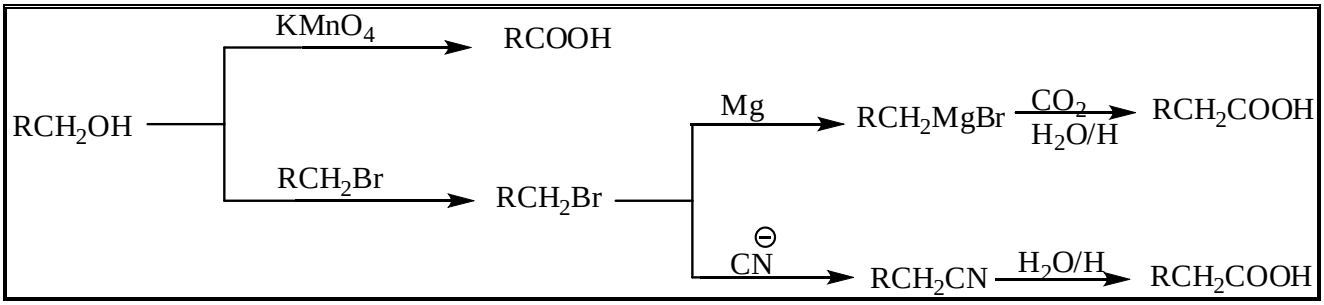


Mechanism



example





Reactions of carboxylic acids

The characteristic chemical behavior of carboxylic acids is, of course, determined by their functional group, **carboxyl**, —COOH. This group is made up of a carbonyl group (C=O) and a hydroxyl group (—OH). As we shall see, it is the —OH that actually undergoes nearly every reaction—loss of H^+, or replacement by another group.

1- Acidity salt formation

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

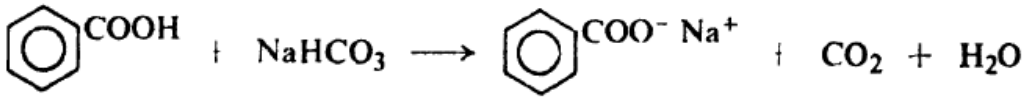
Examples:

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

Acetic acid — Zinc acetate

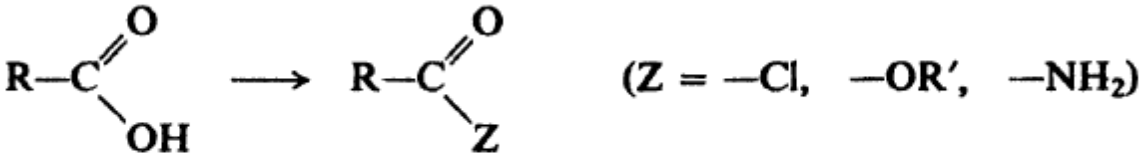
$$CH_3(CH_2)_{10}COOH + NaOH \longrightarrow CH_3(CH_2)_{10}COO^-Na^+ + H_2O$$

Lauric acid — Sodium laurate

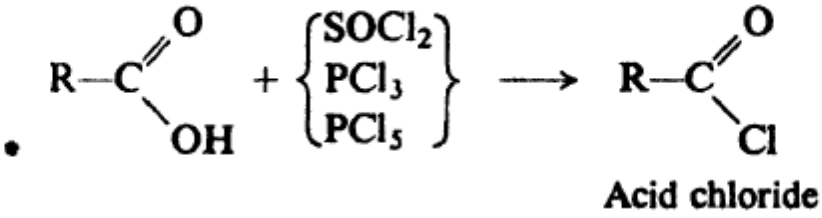


Benzoic acid — Sodium benzoate

2- Conversion into functional derivatives

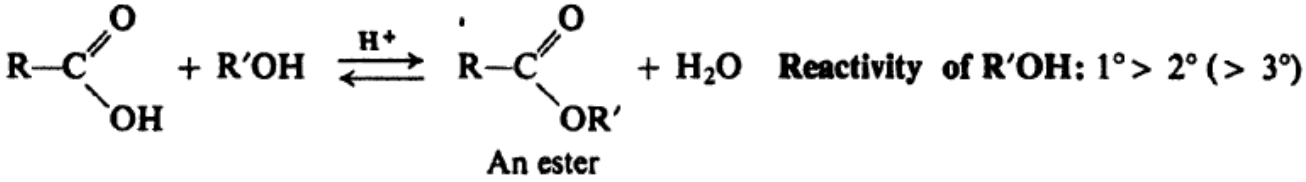


(a) Conversion into acid chlorides.

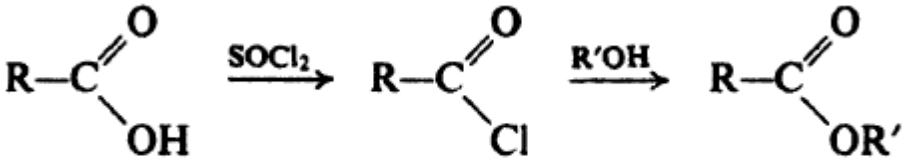


Acid chloride

Conversion into esters

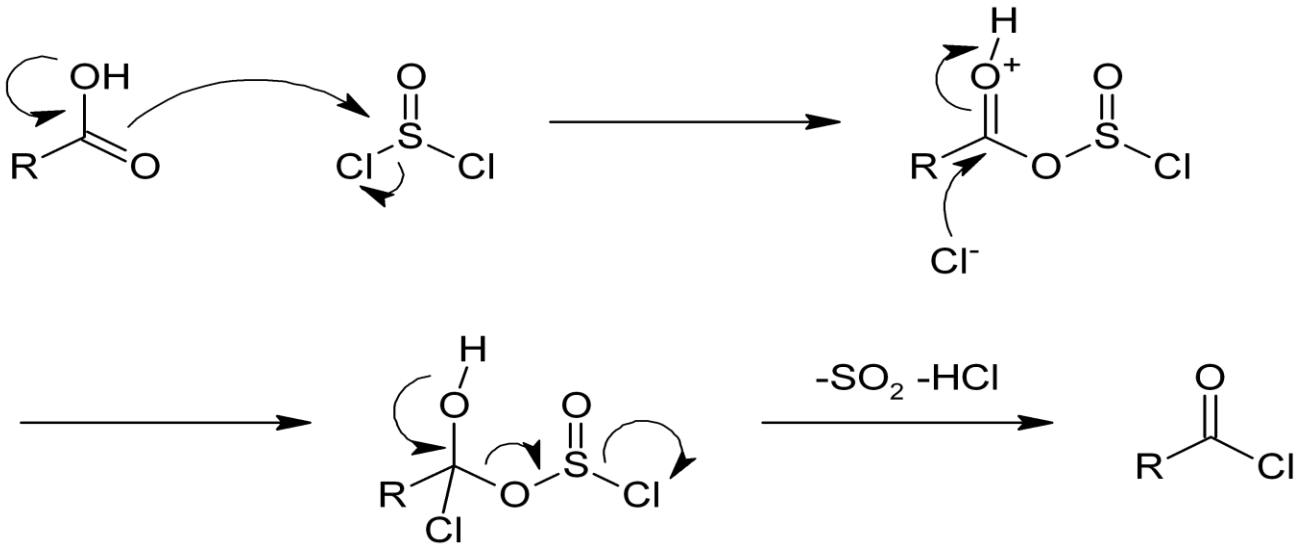


An ester

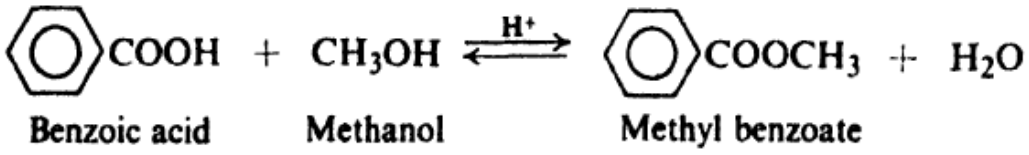


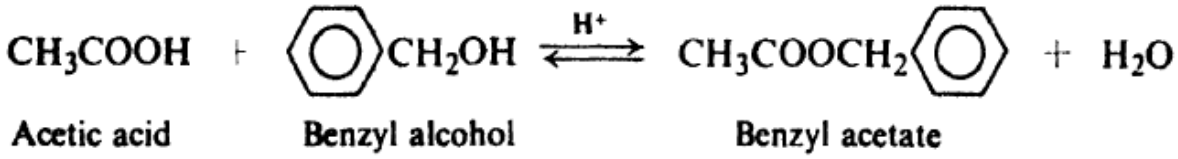
An acid chloride An ester

Mechanism (conversion into acid chloride)

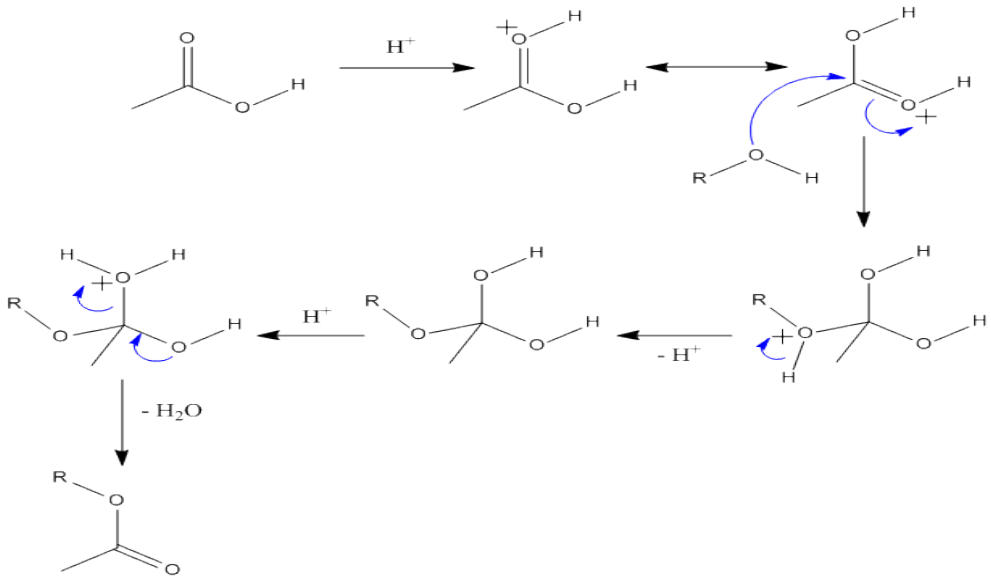


Examples:

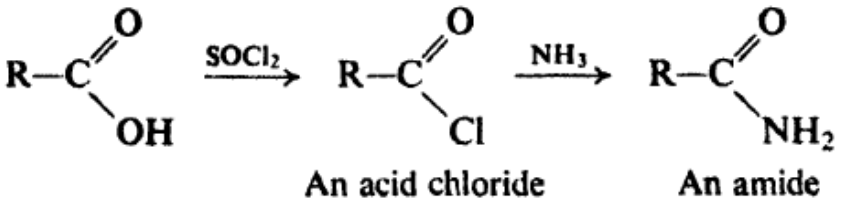




Mechanism



Conversion into amide



Example:

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

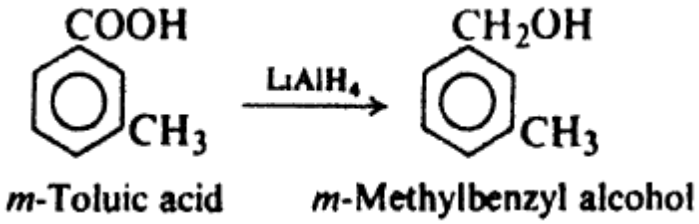
Phenylacetic acid — Phenylacetyl chloride — Phenylacetamide

Reduction of carboxylic acid

$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$

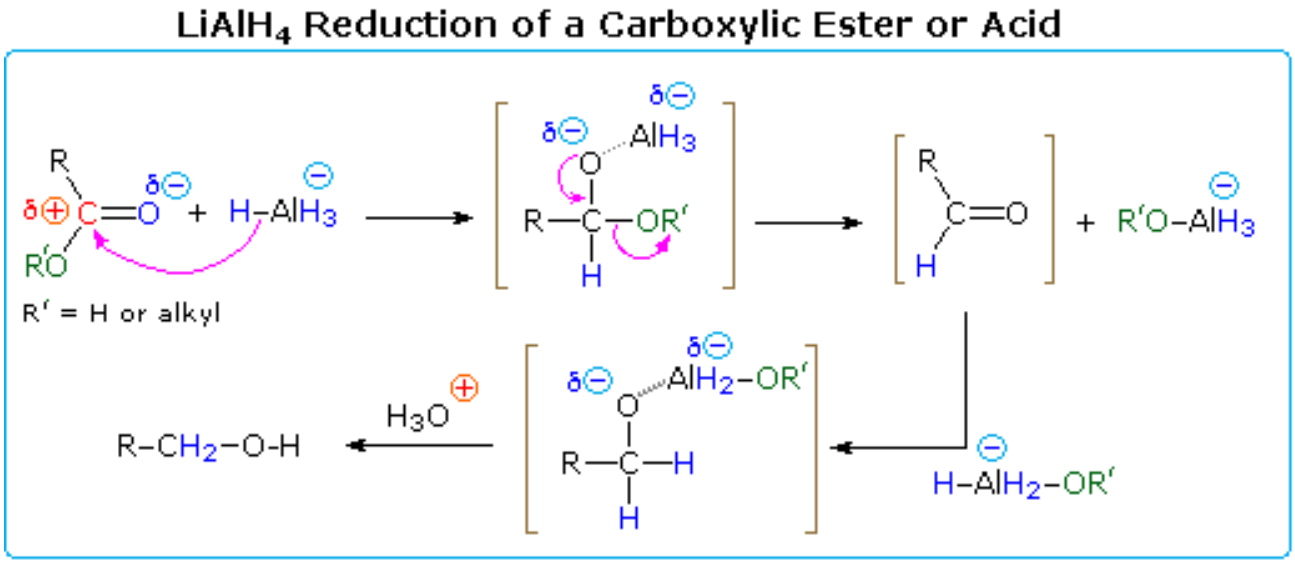
1° alcohol

Example



m-Toluic acid *m*-Methylbenzyl alcohol

Mechanism



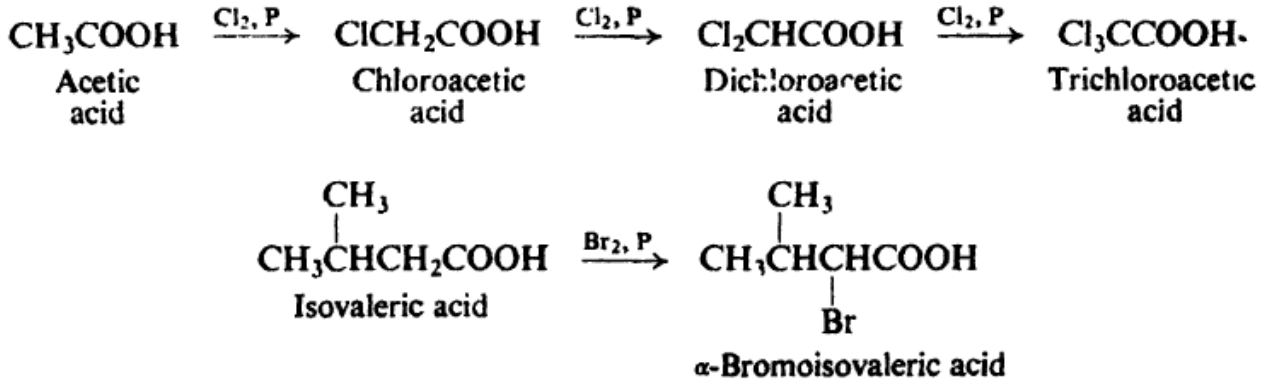
Substitution in alkyl or aryl groups

(a) Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction.

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

An α-haloacid

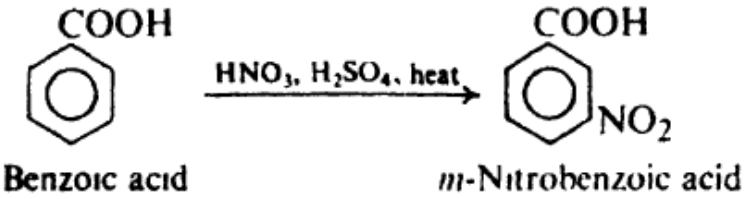
Examples:



Ring substitution in aromatic acids

—COOH: deactivates, and directs *meta* in electrophilic substitution.

Example:

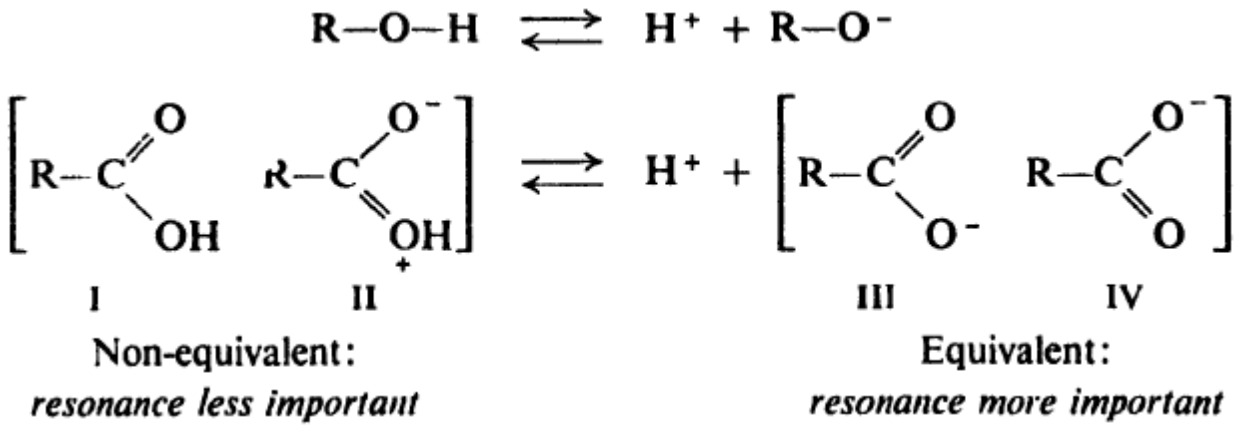


Acidity of carboxylic acid

Let us see how the acidity of carboxylic acids is related to structure. In doing this we shall assume that acidity is determined chiefly by the difference in stability between the acid and its anion.

First, and most important, there is the fact that carboxylic acids are acids at all. How can we account for the fact that the —OH of a carboxylic acid tends to release a hydrogen ion so much more readily than the —OH of, say, an alcohol? Let us examine the structures of the reactants and products in these two cases.

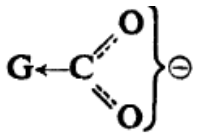
We see that the alcohol and alkoxide ion are each represented satisfactorily by a single structure. However, we can draw two reasonable structures (I and II) for the carboxylic acid and two reasonable structures (III and IV) for the carboxylate anion. Both acid and anion are resonance hybrids.



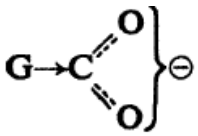
Effect of substituents on acidity

Electron withdrawing substituents

should disperse the negative charge, stabilize the anion, and thus increase acidity. Electron-releasing substituents should intensify the negative charge, destabilize the anion, and thus decrease acidity.



G withdraws electrons: *stabilizes anion, strengthens acid*



G releases electrons: *destabilizes anion, weakens acid*

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

$HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3COOH$