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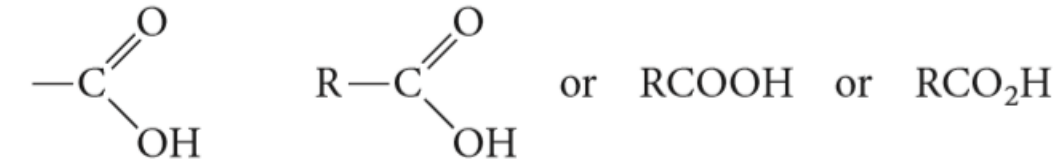
Chapter 7

Carboxylic Acids and their Derivatives

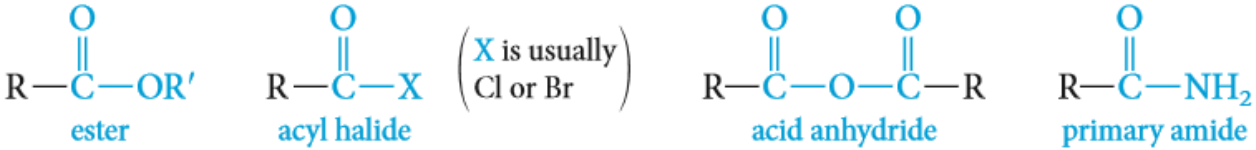
Structure of carboxylic Acids and their derivatives

- The combination of a carbonyl group and a hydroxyl on the same carbon atom is called a carboxyl group
- Carboxylic acids are strong organic acids which contain the carboxyl group.



carboxyl group — three ways to represent a carboxylic acid

- Carboxylic acid derivatives, in which the hydroxyl group of an acid is replaced by other functional groups.



- Carboxylic acids are classified as aliphatic or aromatic depending on whether R or an Ar is attached to the carboxylic group R-COOH or Ar-COOH
- Fatty acids: long straight-chain carboxylic acids with even numbers of carbons, which were first isolated from fats and waxes.

Nomenclature of carboxylic Acids

The IUPAC name:

- The root name is based on the longest continuous chain of carbon atoms bearing the carboxyl group.
- The *-e* is replaced by *-oic acid*.
- The chain is numbered starting with the carboxyl carbon atom.
- Cycloalkanes with carboxyl substituents are named as *cycloalkanecarboxylic acids*.

The Common name:

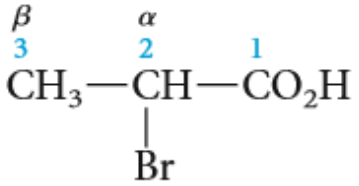
In common names, the positions of substituents are named using Greek letters (α, β, γ , δ…..) beginning with carbon next the carboxyl group.

Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, *formica*)	formic acid	methanoic acid
2	CH_3COOH	vinegar (Latin, *acetum*)	acetic acid	ethanoic acid
3	CH_3CH_2COOH	milk (Greek, *protos pion*, first fat)	propionic acid	propanoic acid
4	$CH_3(CH_2)_2COOH$	butter (Latin, *butyrum*)	butyric acid	butanoic acid
5	$CH_3(CH_2)_3COOH$	valerian root (Latin, *valere*, to be strong)	valeric acid	pentanoic acid

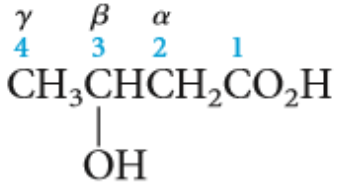
Dicarboxylic Acids:

Dicarboxylic acids are named as *alkanedioic acids* in the IUPAC system.

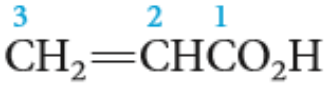
IUPAC name:
Common name:



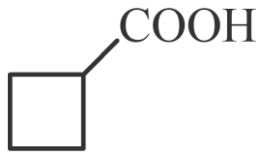
2-bromopropanoic acid
(α-bromopropionic acid)



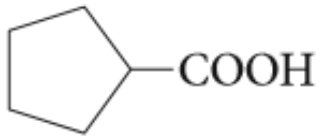
3-hydroxybutanoic acid
(β-hydroxybutyric acid)



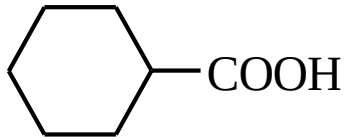
propenoic acid
(acrylic acid)



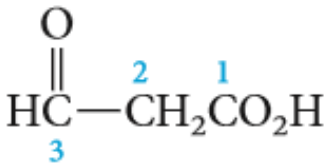
Cyclobutanecarboxylic acid



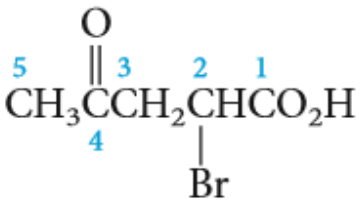
cyclopentanecarboxylic acid



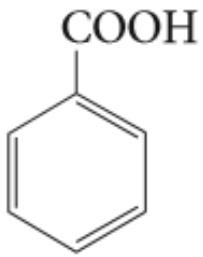
cyclohexanecarboxylic acid



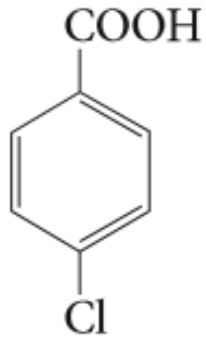
3-oxopropanoic acid



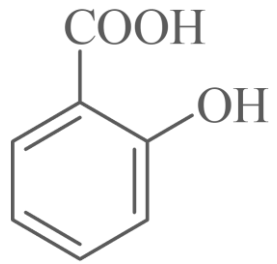
2-bromo-4-oxopentanoic acid



benzoic acid
Benzenecarboxylic acid

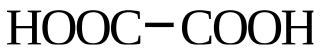


4-chlorobenzoic acid

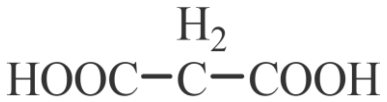


2-Hydroxybenzoic acid
Salicylic acid

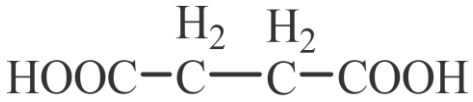
IUPAC name:
Common name:



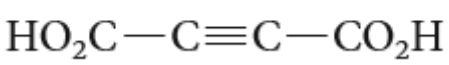
Ethanedioic acid
Oxalic acid



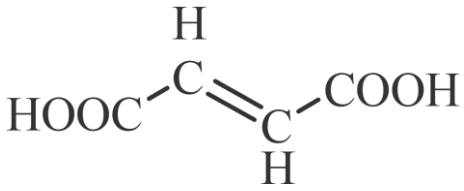
Propanedioic acid
Malonic acid



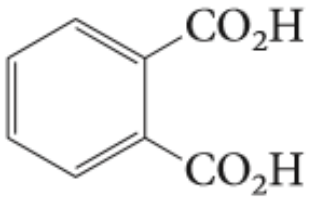
Butanedioic acid
Succinic acid



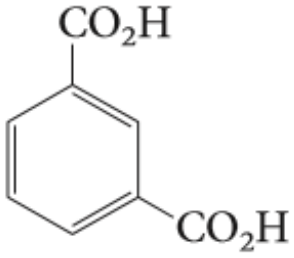
Butynedioic acid



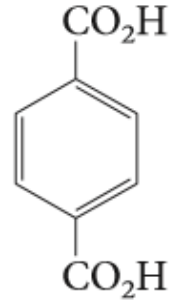
Butenedioic acid



1,2-Benzenedicarboxylic acid
phthalic acid



1,3-Benzenedicarboxylic acid
isophthalic acid

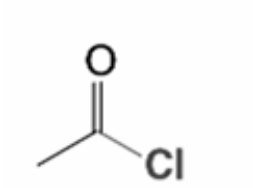


1,4-Benzenedicarboxylic acid
terephthalic acid

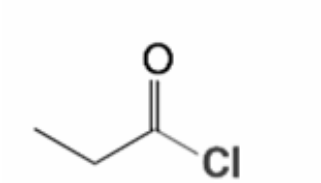
Nomenclature of carboxylic Acid derivatives

Nomenclature of Acyl Chlorides

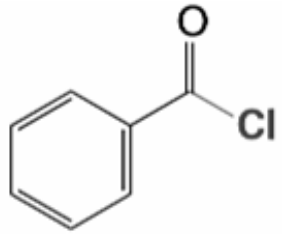
- Acyl chlorides are also called acid chlorides.
- They are named by dropping *-ic acid* from the name of the acid and then adding *-yl chloride*.



Ethanoyl chloride
Acetyl chloride



Propanoyl chloride

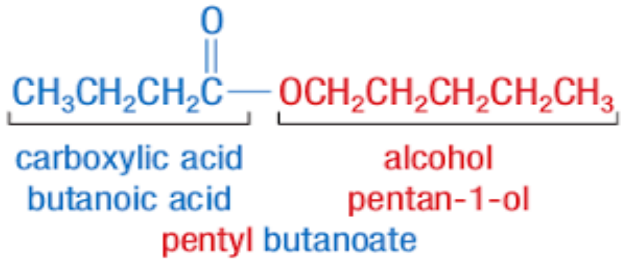


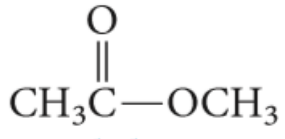
Benzoyl chloride

Nomenclature of carboxylic Acid derivatives

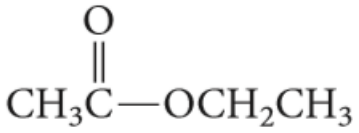
Nomenclature of Esters

- The names of esters are derived from the names of the alcohol (with the ending -yl) and the acid (with replacing of the ending *–ic acid* by *–ate*).

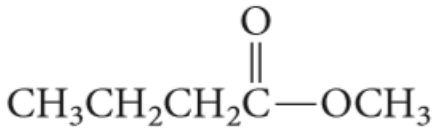




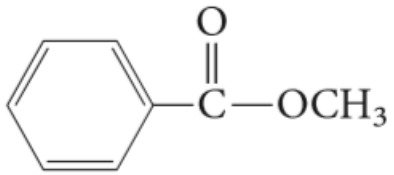
Methyl ethanoate
Methyl acetate



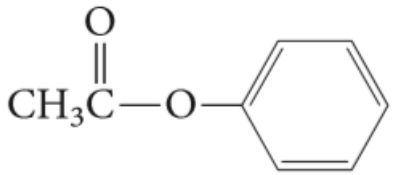
Ethyl ethanoate
Ethyl acetate



Methyl butanoate



Methyl benzoate

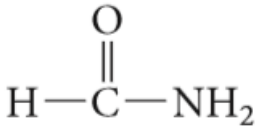


phenyl acetate

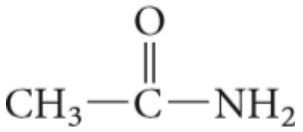
Nomenclature of carboxylic Acid derivatives

Nomenclature of Amides

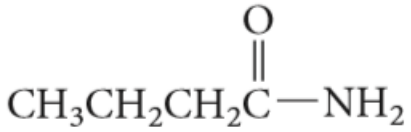
- Amides are named by replacing the *-oic acid* ending of the acid name, either the common or the IUPAC name, with the *-amide* ending.
- Alkyl groups on the nitrogen atom of amides are named as substituents, and the named substituent is prefaced by *N*- or *N*,*N*-



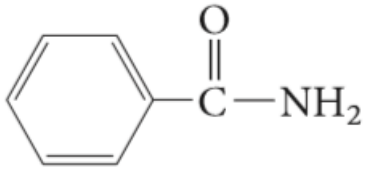
Methanamide
formamide



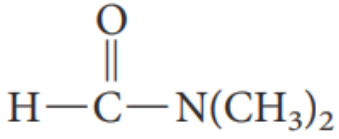
Ethanamide
actamide



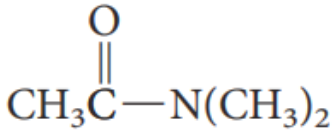
butanamide



benzamide
(benzenecarboxamide)



N,*N*-Dimethylmethanamide

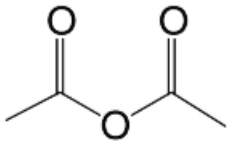


N,*N*-Dimethylethanamide

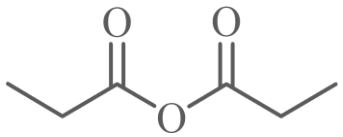
Nomenclature of carboxylic Acid derivatives

Nomenclature of Acid Anhydrides

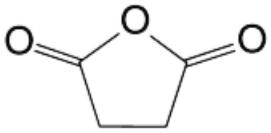
Most anhydrides are named by dropping the word *acid* from the name of the carboxylic acid and then adding the word *anhydride*



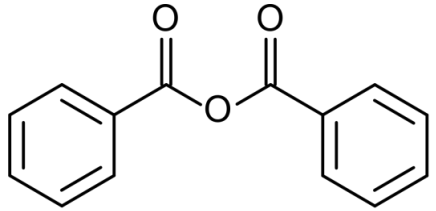
Ethanoic anhydride
acetic anhydride



Propanoic anhydride
Propionic anhydride



Butandioic anhydride
succinic anhydride

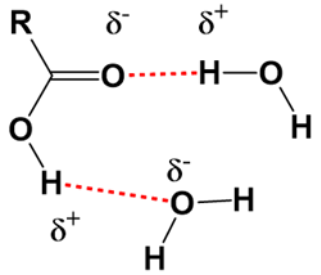


Benzoic anhydride

Physical Properties of Carboxylic acids

Solubility

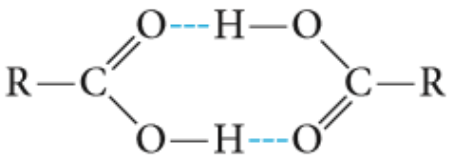
- Carboxylic acids interact with water molecules by hydrogen bonding through both the carbonyl and hydroxyl groups. Because of greater hydrogen bonding interactions, aliphatic carboxylic acids are more soluble in water than are alcohols, ethers, aldehydes, and ketones of comparable molecular weight.
- Aromatic acids are insoluble in water.

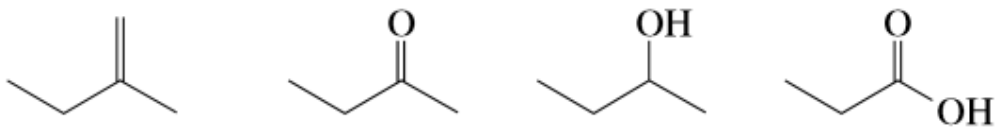


Physical Properties of Carboxylic acids

Boiling Point

- Carboxylic acids have significantly higher boiling points than other types of organic compounds of comparable molecular weight, such as alcohols, aldehydes, and ketones. This is due to carboxylic acids usually exist as dimers by forming two intramolecular hydrogen bonds in nonpolar media.



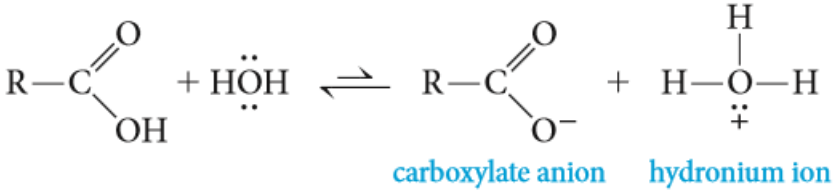


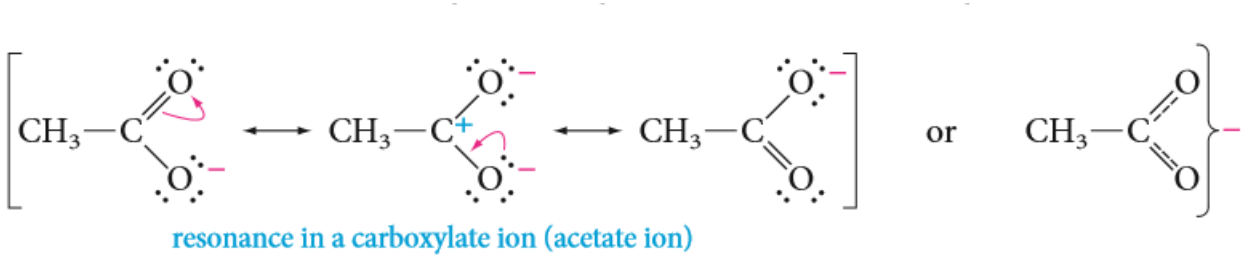
	2-Methyl-1-butene	2-Butanone	2-Butanol	Propanoic acid
bp (1 atm):	31°C	80°C	99°C	141°C

Physical Properties of Carboxylic acids

Acidity

- Carboxylic acids are the most acidic class of compounds, they are much stronger acids than water and alcohols.
- Dissociation of either an acid or an alcohol involves breaking an O-H bond, but dissociation of a carboxylic acid gives a carboxylate ion with the negative charge spread out equally over two oxygen atoms, compared with just one oxygen in an alkoxide ion .This charge delocalization makes the carboxylate ion more stable than the alkoxide ion; therefore, dissociation of a carboxylic acid to a carboxylate ion is less endothermic than dissociation of an alcohol to an alkoxide ion.

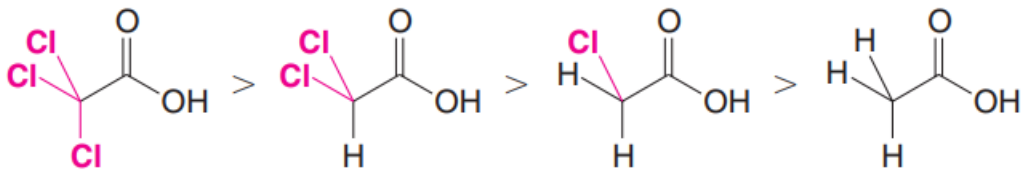


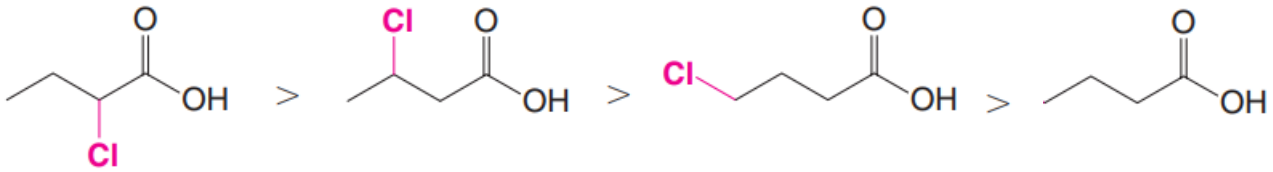


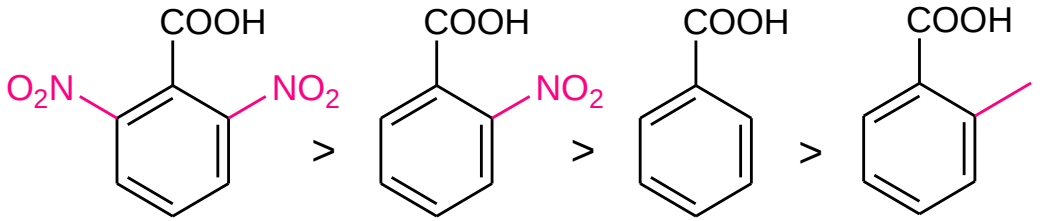
Physical Properties of Carboxylic acids

Effect of Structure on Acidity; the Inductive Effect Revisited

This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms. Recall that electron-withdrawing groups enhance acidity, and electron-donating groups reduce acidity.

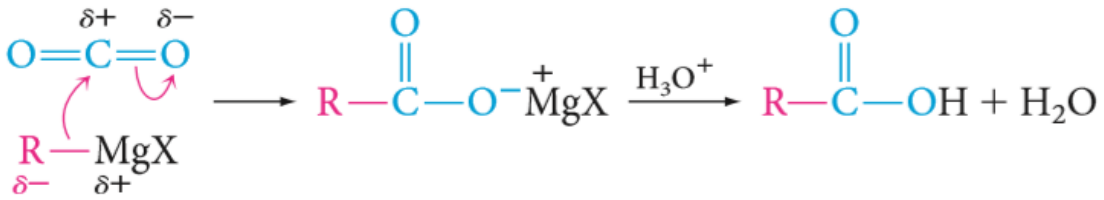


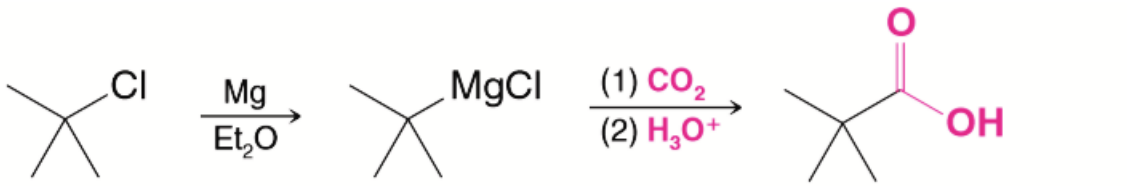




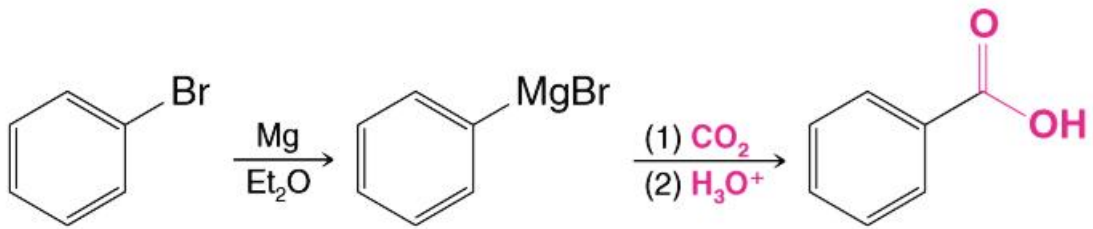
Preparation of Carboxylic Acids

1- Reaction of Grignard Reagents with Carbon Dioxide:





tert-Butyl chloride — 2,2-Dimethylpropanoic acid

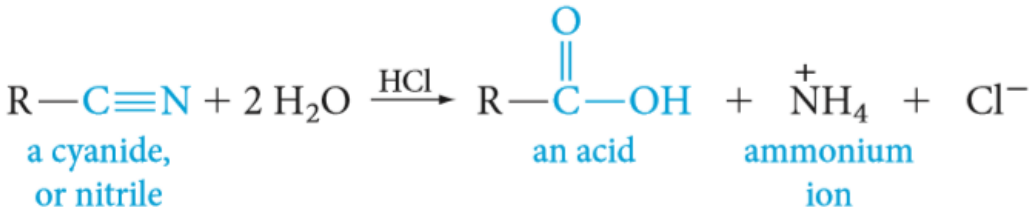


Bromobenzene — Benzoic acid

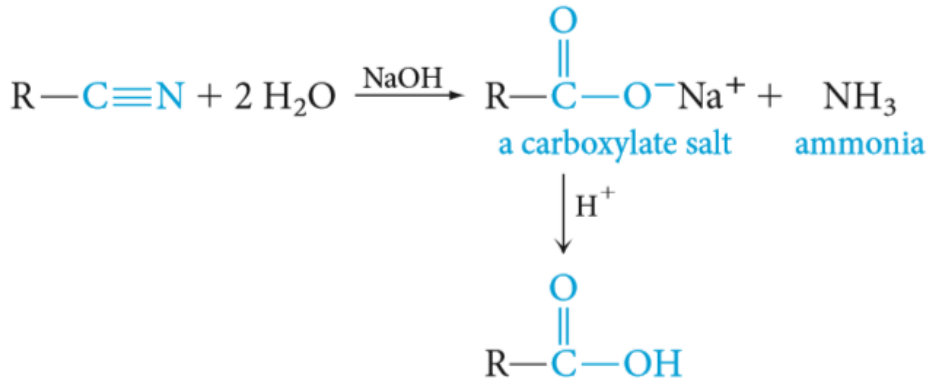
Preparation of Carboxylic Acids

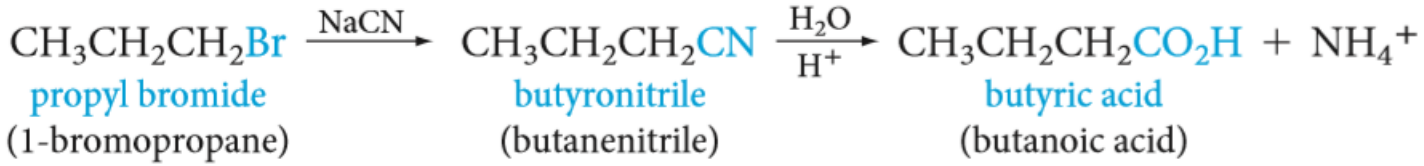
2- Hydrolysis of cyanohydrins and other nitriles:

In Acid:



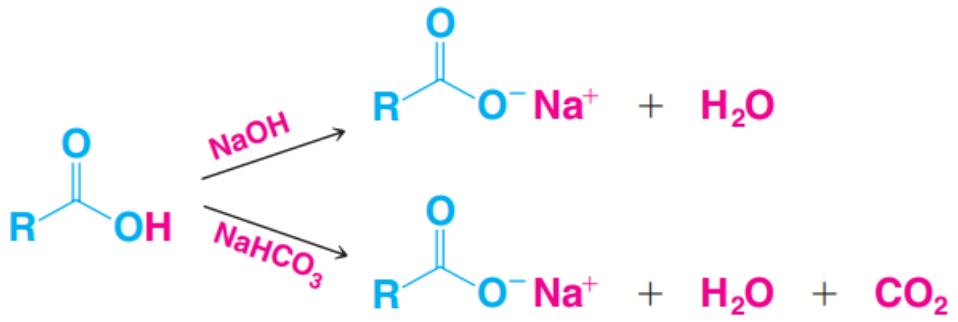
In Base:

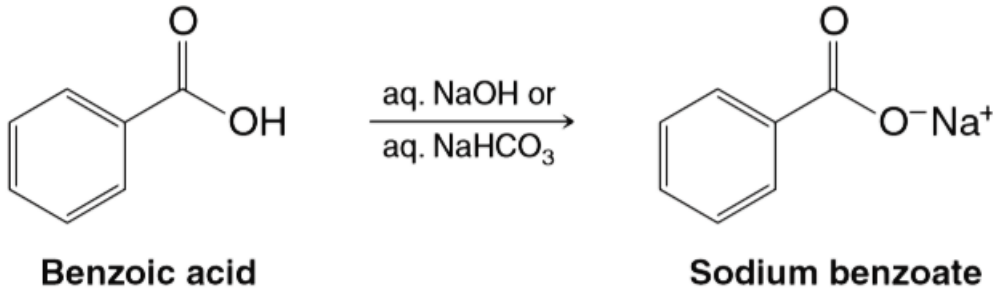




Reaction of Carboxylic Acids

1- Reaction with Strong Bases: NaOH , $NaHCO_3$ or NH_3

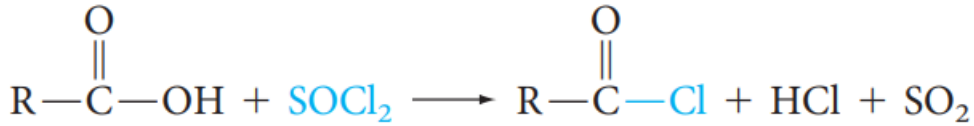


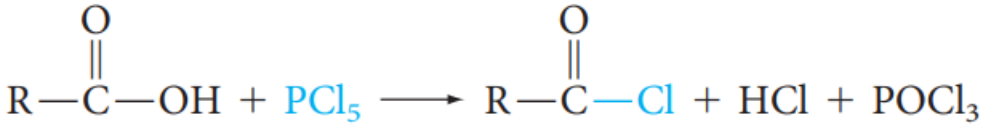


Reaction of Carboxylic Acids

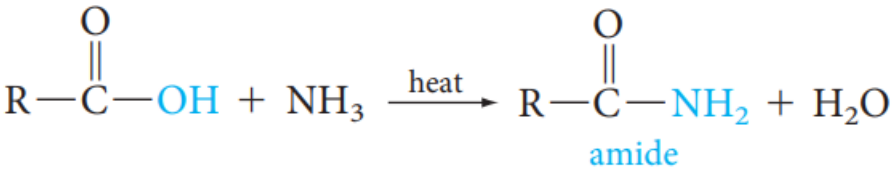
2- Nucleophilic Substitution of Hydroxyl Group

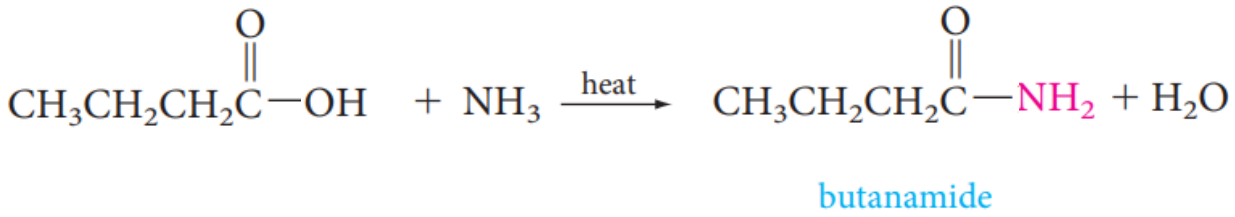
a) Conversion to acyl chlorides:



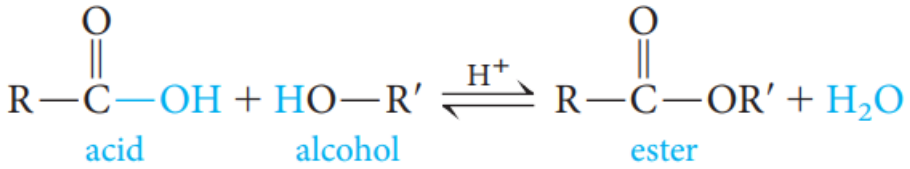


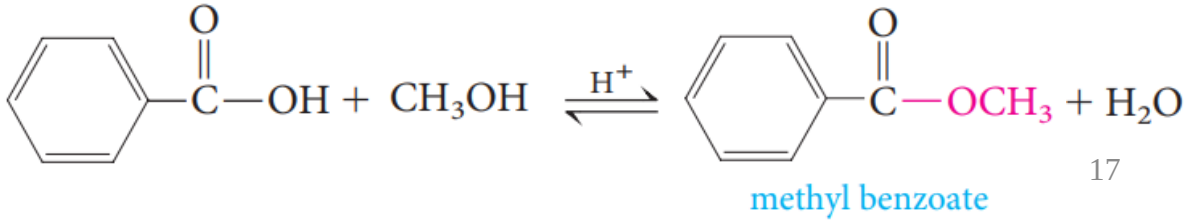
d) Conversion to amides:



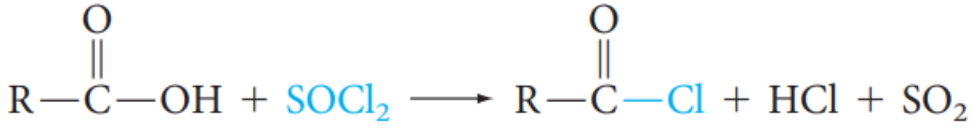


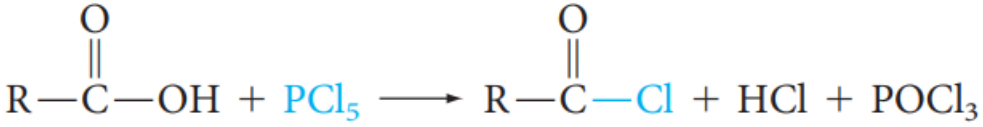
c) Conversion to esters:



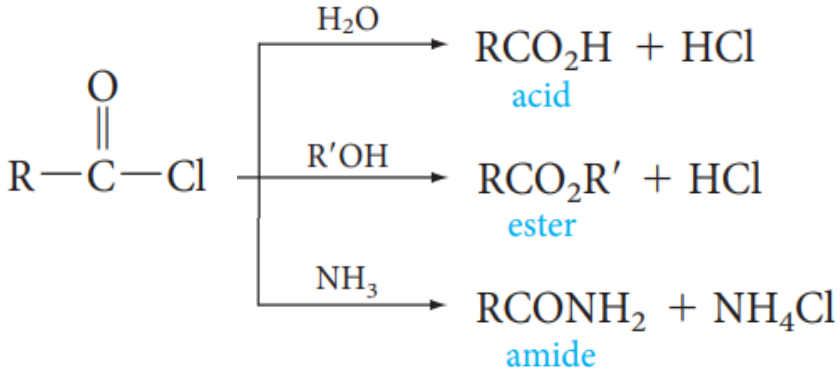


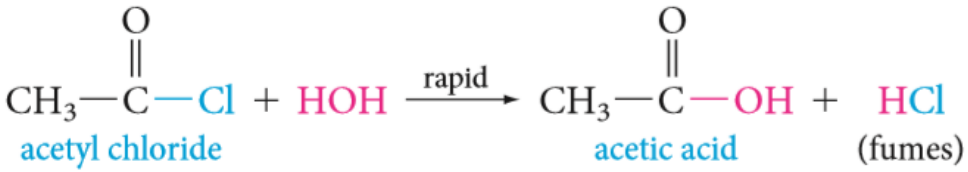
Preparation of Acyl Chlorides

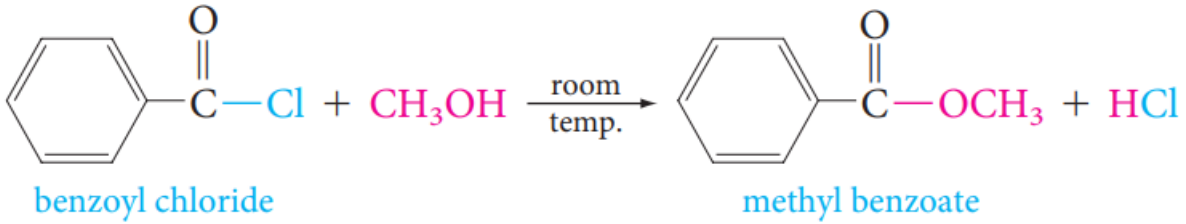


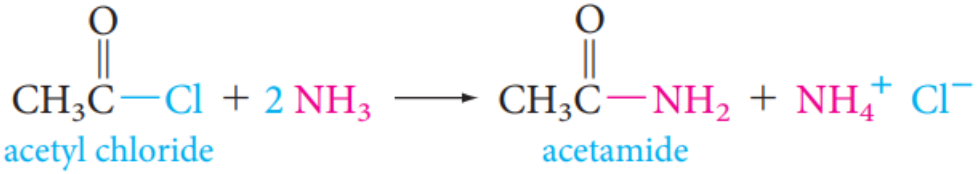


Reaction of Acyl Chlorides

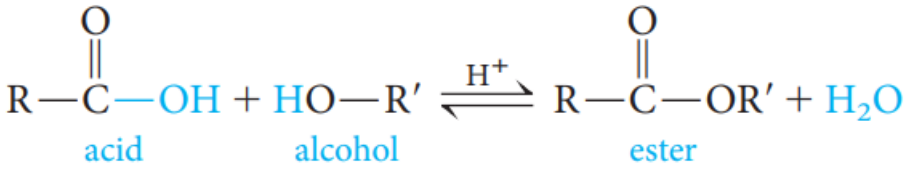




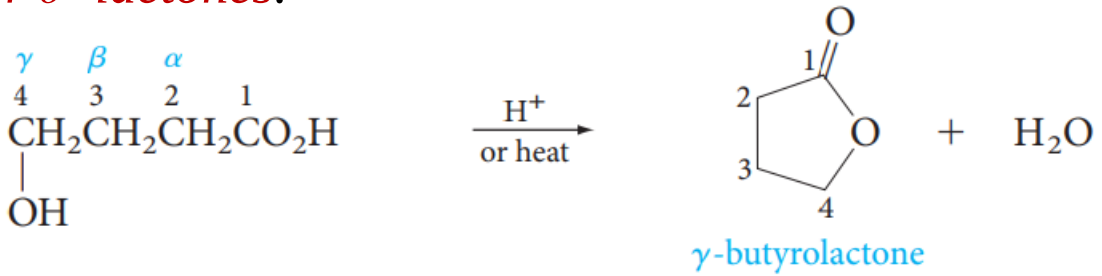




Preparation of Esters

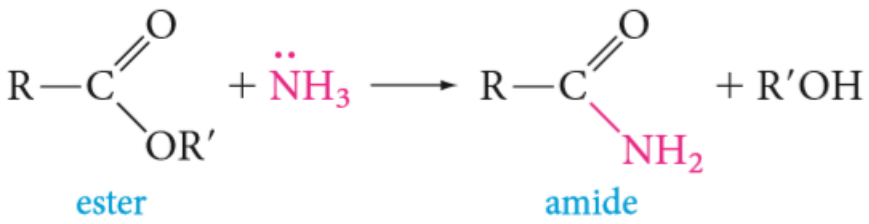


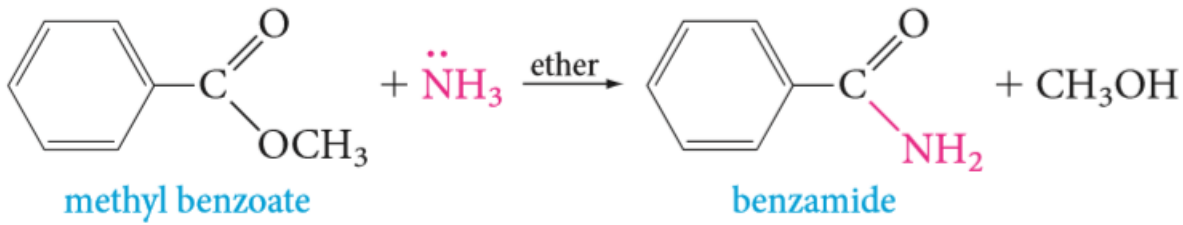
Carboxylic acids whose molecules have a hydroxyl group on a γ or δ carbon undergo an intermolecular esterification to give cyclic esters known as *γ - or δ -lactones*.



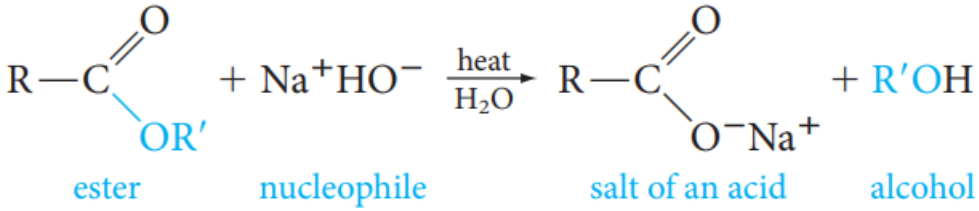
Reaction of Esters

Ammonolysis of Esters:

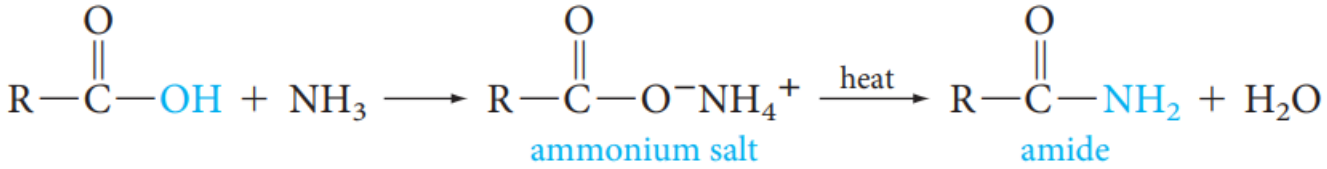




Saponification:

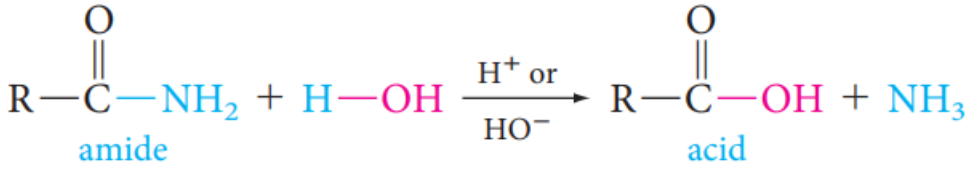


Preparation of Amides

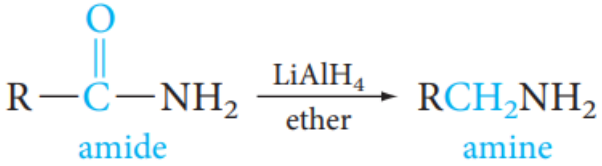


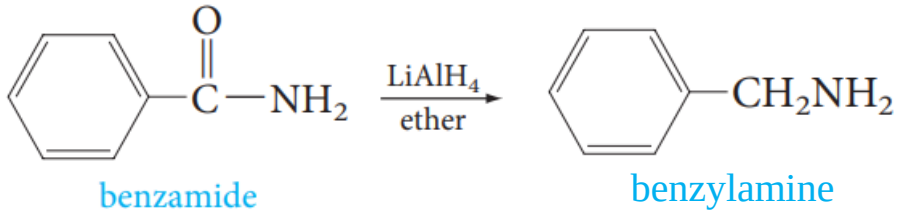
Reaction of Amides

Conversion to acids (hydrolysis):



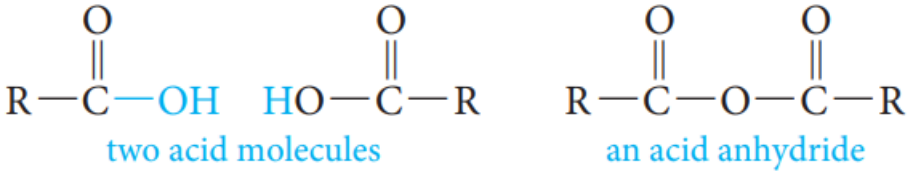
Reduction of Amides:



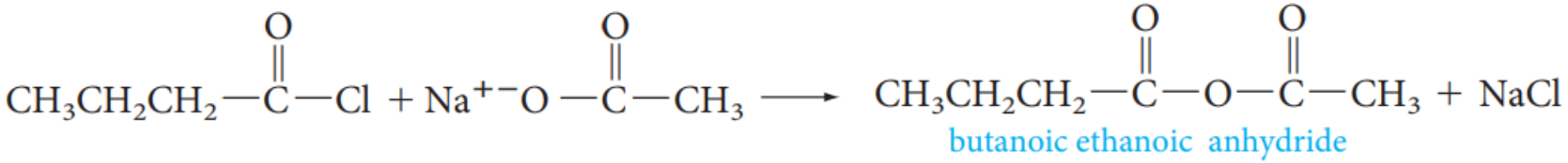


Preparation of Acid Anhydride

- Acid anhydrides are derived from acids by removing water from two carboxyl groups and connecting the fragments.



- Anhydrides can also be prepared from acid chlorides and carboxylate salts. This is a good method for preparing anhydrides derived from two different carboxylic acids, called mixed anhydrides.



Reaction of Acid Anhydride