Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

CHAPTER 7. CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Learning Objectives

At the end of this chapter, students will able to:

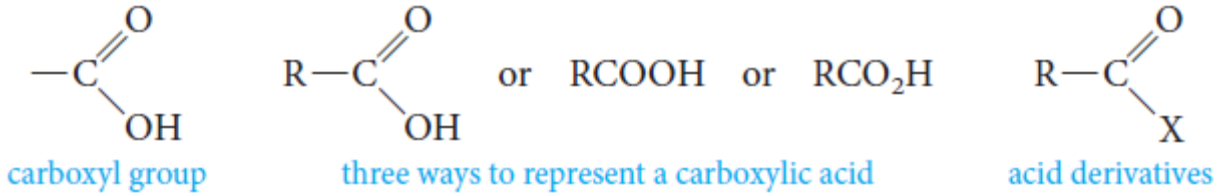
- Identify and name simple carboxylic acids.
- Recognize the properties (structure, physical and chemical properties) of carboxylic acid .
- Suggest preparation reactions from primary alcohols and from Grignard reagents and CO_2.
- Predict the product of the reduction of a carboxylic acid and give the reagents required to perform this reaction.
- Identify carboxylic acid derivatives as esters, amides, acid halides and acid anhydrides
- Predict the products that will be formed when a carboxylic acid derivative is treated with an alcohol or amine.
- Give the reagents required for the interconversion of carboxylic acid derivatives

Structure of Carboxylic Acids

- **The functional group common to all carboxylic acids is the carboxyl group.**

  The name is a contraction of the parts: the carbonyl and hydroxyl groups.

- **The general formula for a carboxylic acid can be written in expanded or abbreviated forms.**



carboxyl group — three ways to represent a carboxylic acid — acid derivatives

- **Depending on whether an R or an Ar.** residue is attached to the carboxyl group; **Carboxylic acids are classified** as;

  - **Aliphatic Carboxylic Acids.**

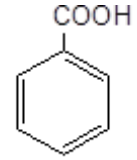
R–COOH (R = H or alkyl) CH_3–COOH

Aliphatic acid — Acetic acid

  - **Aromatic Carboxylic Acids.**

Ar—COOH (R = C_6H_5-)

Aromatic acid



Benzoic acid

- **Fatty acids.**

Long straight-chain carboxylic acids with even numbers of carbons, which were first isolated from fats and waxes.

Nomenclature of Carboxylic Acids

Common Names

- The **common names** of carboxylic acids all end in *-ic acid*.
- These names usually come from some Latin or Greek word that indicates the original source of the acid.
- **Common name**, substituents are located with Greek letters, beginning with the α– carbon atom.

IUPAC System

- We replace the final e in the name of the corresponding alkane with the suffix *-oic* and add the word *acid*.

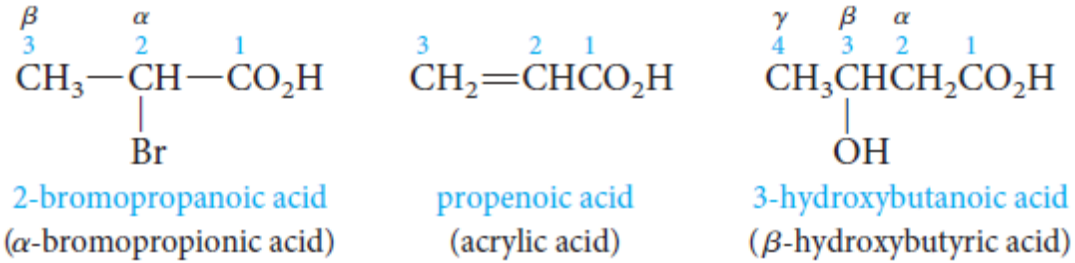
Alkane- e + *oic acid* = *Alkanoic acid*

- **IUPAC system**, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way.

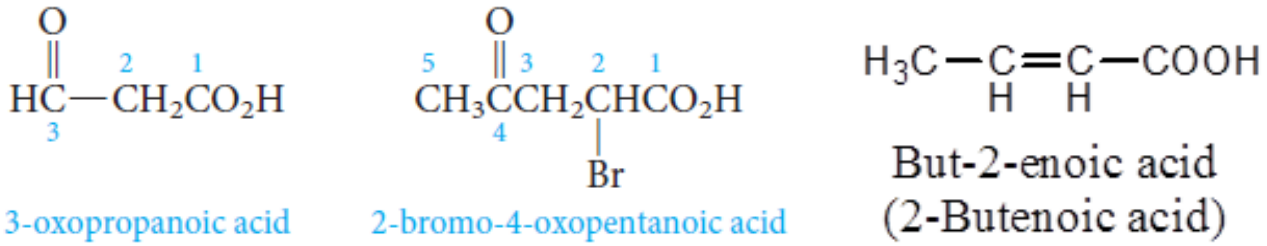
Nomenclature of Carboxylic Acids

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
6	$CH_3(CH_2)_4COOH$	goats (Latin, *caper*)	caproic acid	hexanoic acid
7	$CH_3(CH_2)_5COOH$	vine blossom (Greek, *oenanthe*)	enanthic acid	heptanoic acid
8	$CH_3(CH_2)_6COOH$	goats (Latin, *caper*)	caprylic acid	octanoic acid
9	$CH_3(CH_2)_7COOH$	pelargonium (an herb with stork-shaped seed capsules; Greek, *pelargos*, stork)	pelargonic acid	nonanoic acid
10	$CH_3(CH_2)_8COOH$	goats (Latin, *caper*)	capric acid	decanoic acid

Nomenclature of Carboxylic Acids



- **The carboxyl group has priority over alcohol, aldehyde, or ketone** functionality in naming.
- The prefix **oxo-** is used to locate the carbonyl group of the aldehyde or ketone.



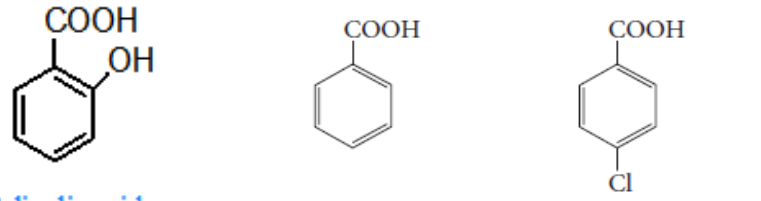
Nomenclature of Carboxylic Acids

- **Cycloalkane carboxylic acid**

  When the carboxyl group is attached to a ring, the ending ***-carboxylic acid*** *is added to the name of the parent* ***cycloalkane*****. (i.e.** ***Cycloalkanecarboxylic acid*****)**

Cyclopropanecarboxylic acid | Cyclobutanecarboxylic acid | Cyclopentanecarboxylic acid | Cyclohexanecarboxylic acid

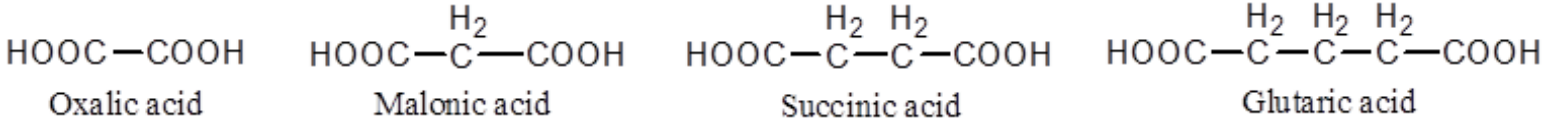
- **Aromatic acids** are named by attaching the suffix *-oic acid* or *-ic acid* to an appropriate prefix derived from the aromatic hydrocarbon.



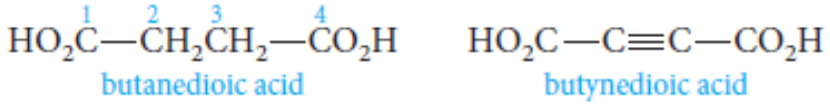
Common name:	Salicylic acid	benzoic acid	*p*-chlorobenzoic acid
IUPAC name :	2-Hydroxybenzenecarboxylic acid	(benzenecarboxylic acid)	(4-chlorobenzenecarboxylic acid)

Nomenclature of Carboxylic Acids

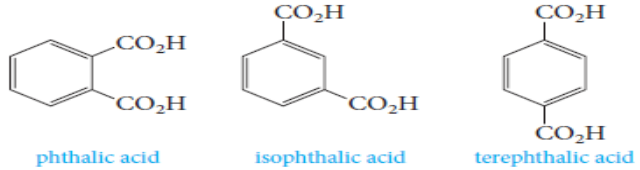
- **Dicarboxylic acids** (*acids that contain two carboxyl groups*) are known almost exclusively by their common names.



- **Aliphatic dicarboxylic acids** are given the suffix *-dioic acid* in the IUPAC system.



- The three **benzenedicarboxylic acids** are generally known by their common names.

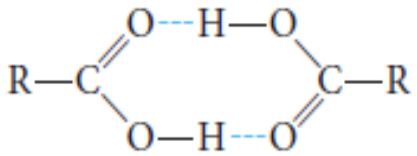


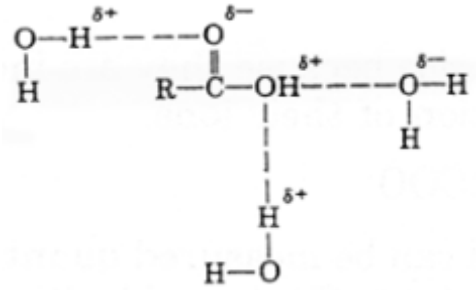
Common name:	phthalic acid	isophthalic acid	terephthalic acid
IUPAC name:	Benzene-1,2-dicarboxylic acid	Benzene-1,3-dicarboxylic acid	Benzene-1,4-dicarboxylic acid

Physical Properties of Acids

- **Carboxylic acids** are polar and they form hydrogen bonds with themselves or with other molecules.

- **Carboxylic acids form dimer**, with the individual units held together by two hydrogen bonds between electron-rich oxygens and electron-poor hydrogens.





Boiling Points

Therefore, they have high boiling points for their molecular weights-higher even those of comparable alcohols.

Solubility in water

Hydrogen bonding also explains the water solubility of the lower molecular weight carboxylic acids.

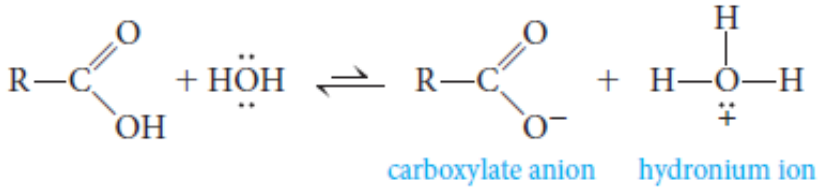
- The first four aliphatic acids (formic through butyric) are completely miscible in water.
- Aromatic acids are insoluble in water.

Physical Properties of Acids

Structure	Name	Mol. Wt.	b.p. °C	Solubility in H_2O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH_3CH_2OH	Ethyl alcohol	46	78	Very soluble
CH_3COOH	Acetic acid	60	118	Very soluble
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	60	97	Very soluble
$CH_3(CH_2)_3COOH$	Valeric acid	102	187	4.0 g/100 g H_2O
$CH_3(CH_2)_4CH2OH$	*n*-Hexyl alcohol	102	156	0.6 g/100 g H_2O
Ph-COOH	Benzoic acid	122	250	Insoluble
Ph-CH_2CH_2OH	3-Phenylethanol	122	250	Insoluble

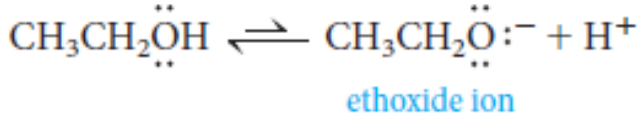
Acid Strength and Structure

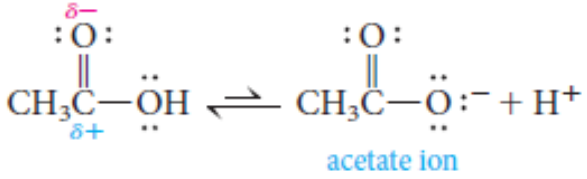
- **Carboxylic acids** (RCOOH) dissociate in water, yielding a carboxylate anion ($RCOO^-$) and hydronium ion.

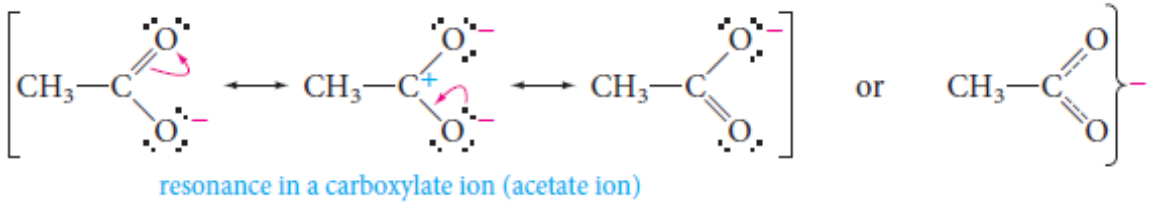


Why carboxylic acids are more acidic than alcohols?

- In ethoxide ion, the negative charge is localized on a single oxygen atom.
- In acetate ion, on the other hand, the negative charge can be delocalized through resonance.





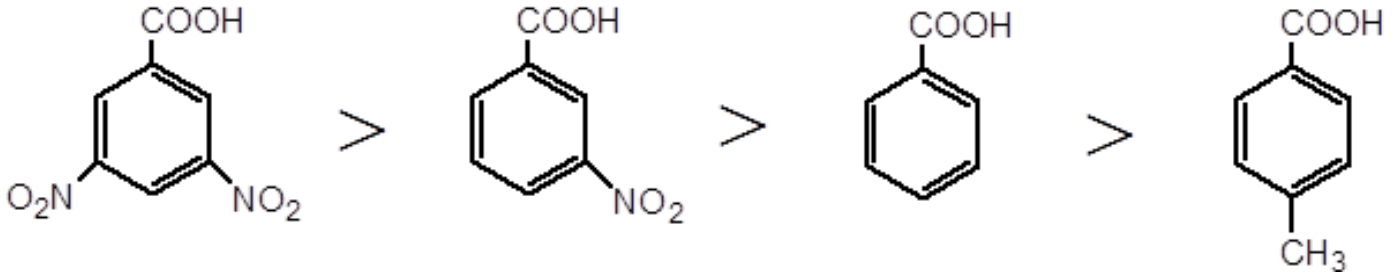


Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

- Acidities can vary depending on what other groups are attached to the molecule.

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



Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

- **Formic acid is a substantially stronger acid than acetic acid.**

  This suggests that the methyl group is more electron-releasing (hence anion-destabilizing and acidity-reducing) than hydrogen.

$$HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH$$

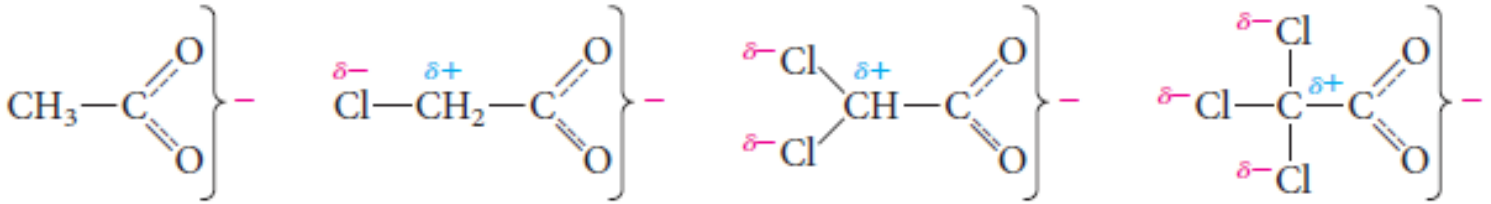
- **Example:** acetic acid with those of mono-, di-, and trichloroacetic acids.

  Comparison of acid strengths of acetic Acid and chlorinated acetic acids

$$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$$

Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect



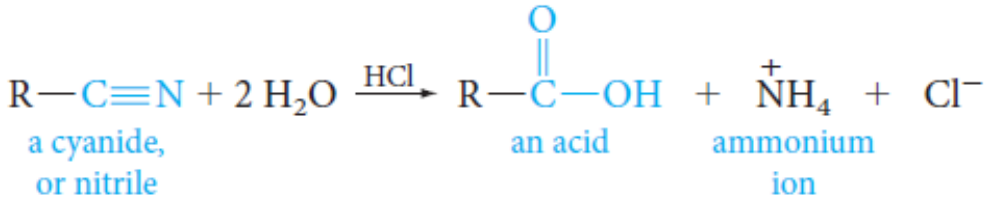
The more chlorines, the greater the effect and the greater the strength of the acid.

Preparation of Carboxylic Acids

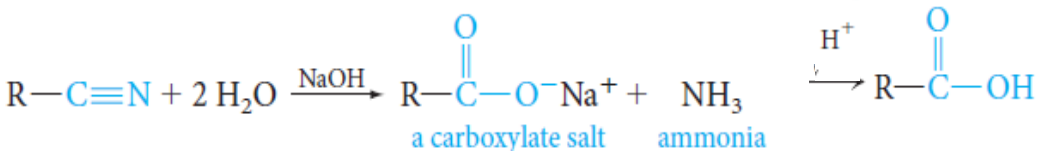
1) Hydrolysis of Cyanides (Nitriles)

- **The reaction requires either acid or base.**

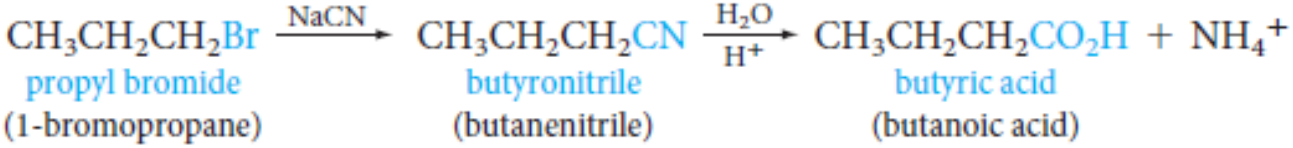
➢ **In acid**, the nitrogen atom of the cyanide is converted to an ammonium ion.



➢ **In base**, the nitrogen atom is converted to ammonia and the organic product is the carboxylate salt, which must be neutralized in a separate step to give the acid.



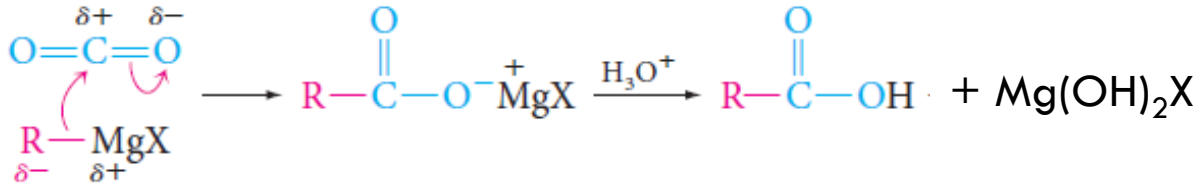
- **Alkyl cyanides** are generally made from the corresponding alkyl halide.



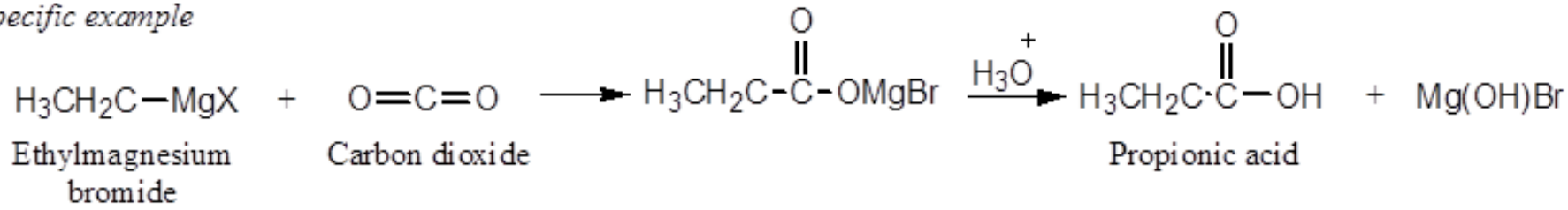
Preparation of Carboxylic Acids

2) Reaction of Grignard Reagents with Carbon Dioxide (Carbonation of Grignard Reagent)

- **Grignard reagents** add to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCl.
- **The acid obtained has one more carbon atom** (*the reaction provides a way to increase the length of a carbon chain*).



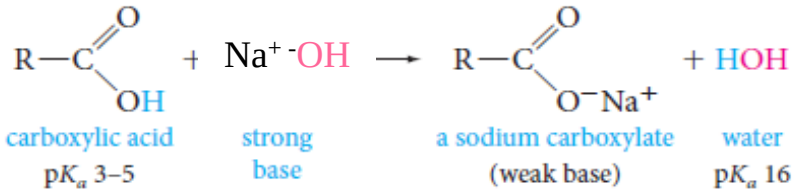
Specific example

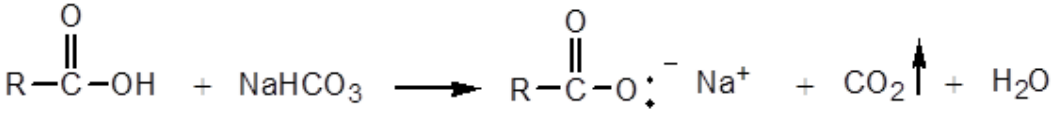


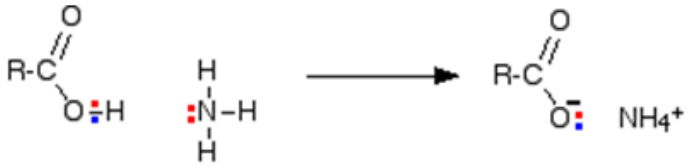
Reactions of Carboxylic Acids

1) Reactions with Bases: Salt Formation

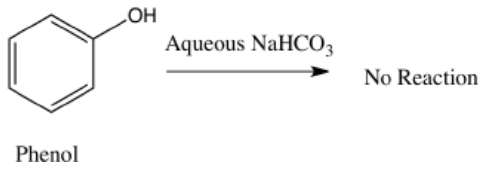
- **Carboxylic acids, when treated with a strong base, form carboxylate salts.**

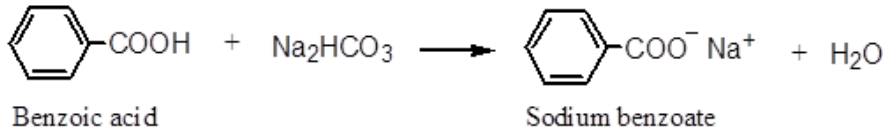






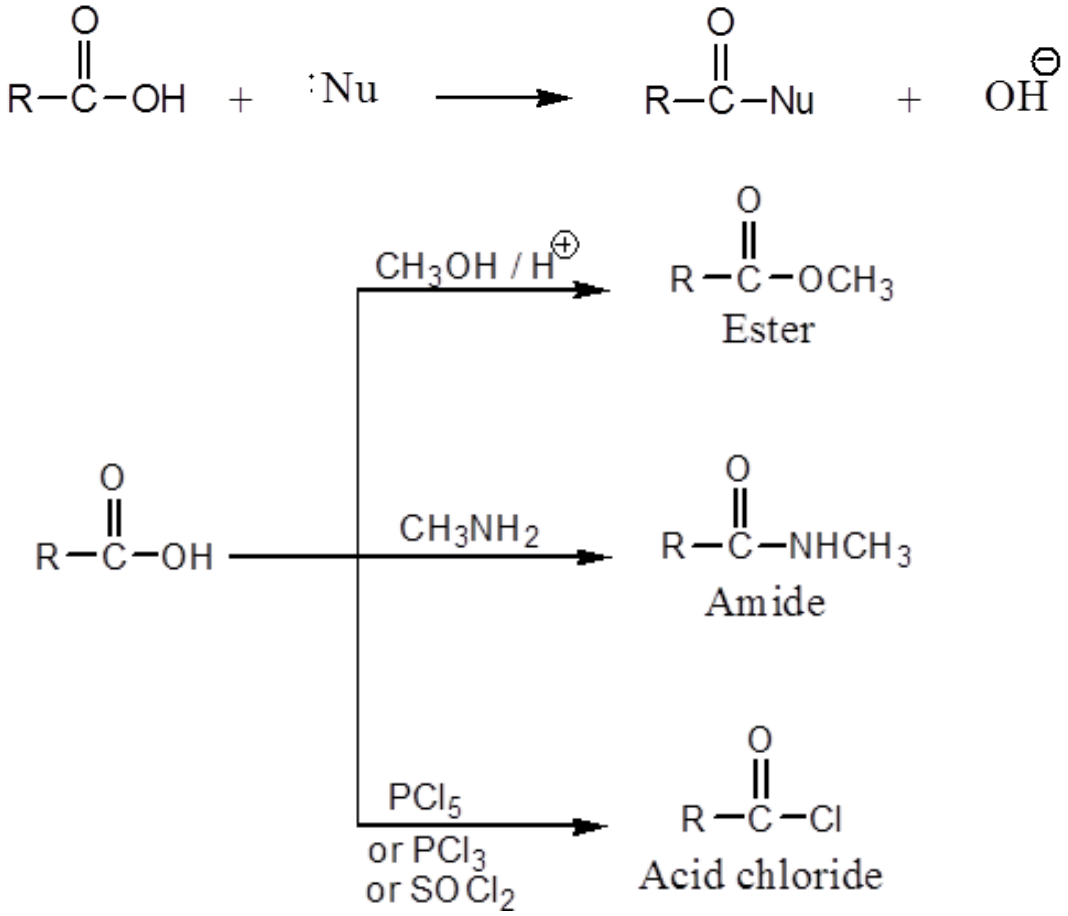
- **Examples.**





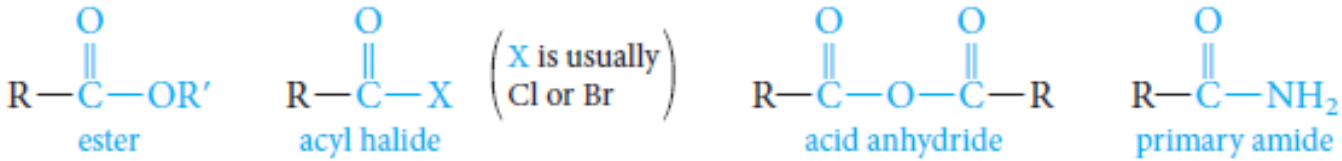
Reactions of Carboxylic Acids

2) Nucleophilic Substitution Reactions

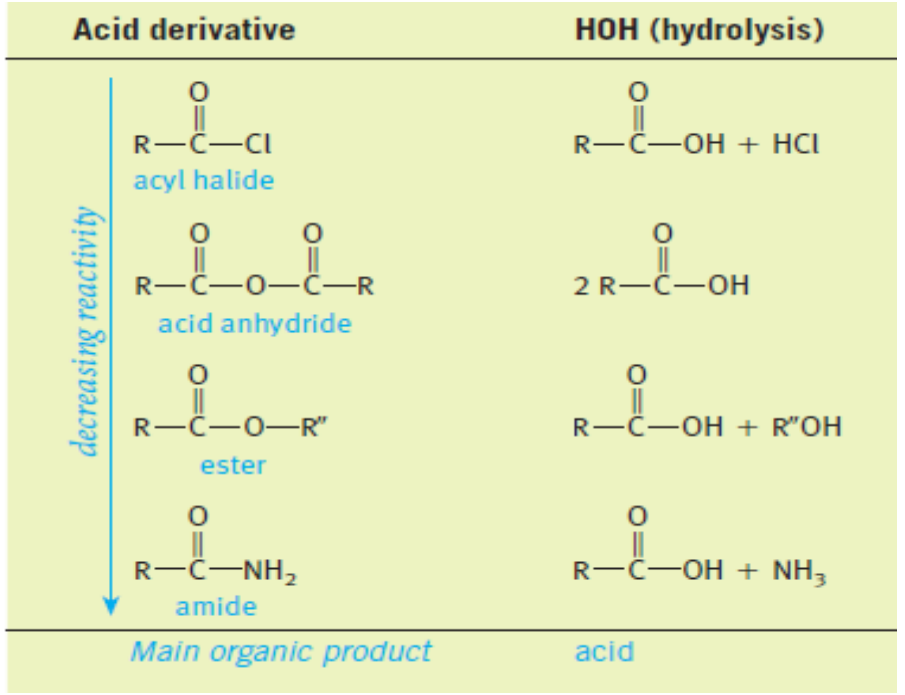


Carboxylic Acid Derivatives

- **Carboxylic acid derivatives** are compounds in which the hydroxyl part of the carboxyl group is replaced by various other groups.



- All acid derivatives can be hydrolyzed to the corresponding carboxylic acid.

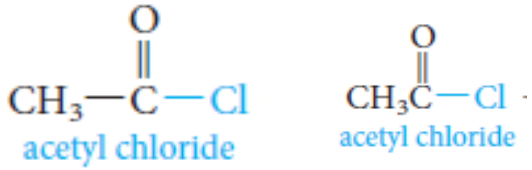


Carboxylic Acid Derivatives

Acid Chloride

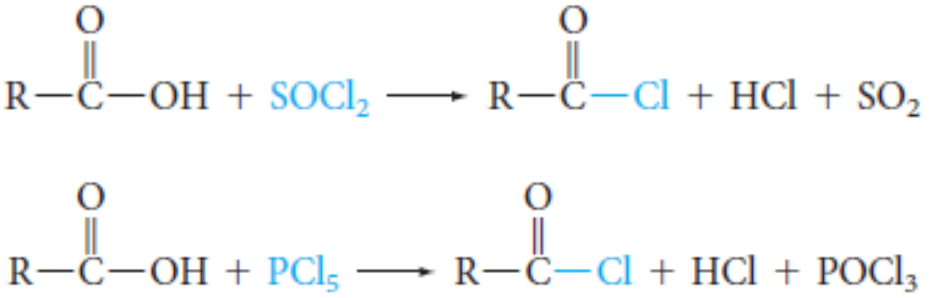
- **Acyl chlorides** have the general formula RCOCl.
- **Acyl chlorides** are more common and less expensive than bromides or iodides.
- **Nomenclature:**

  Acyl chlorides, or acid chlorides, are named by replacing the *-ic acid* ending of the parent acid by *-yl chloride*.



- **Preparation:**

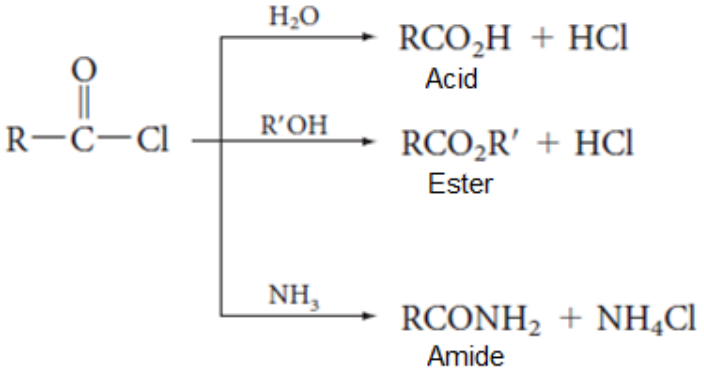
  They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.



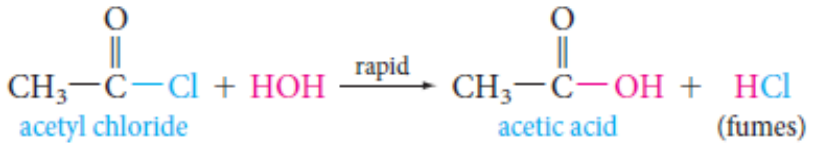
Carboxylic Acid Derivatives

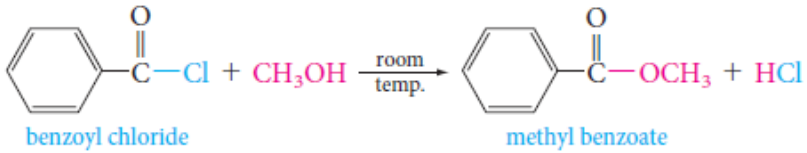
Acid Chloride

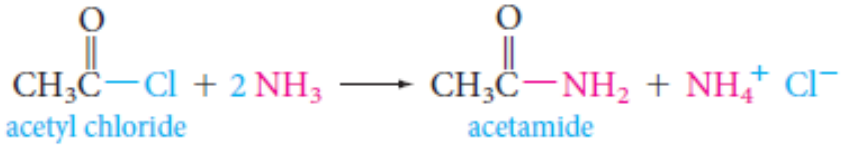
- **Reactions:** *They can react rapidly with most nucleophile.*



- **Examples:**



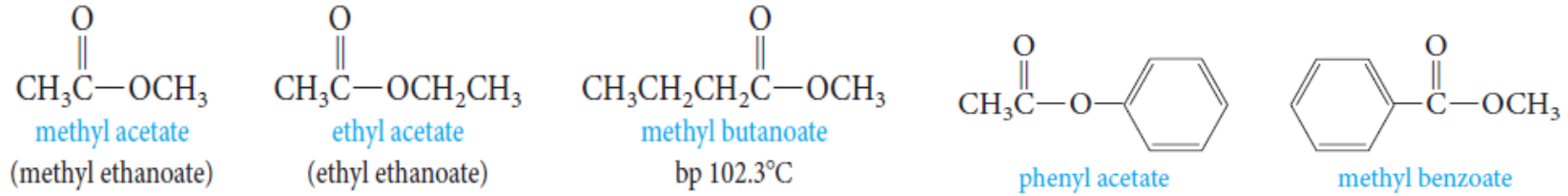




Esters

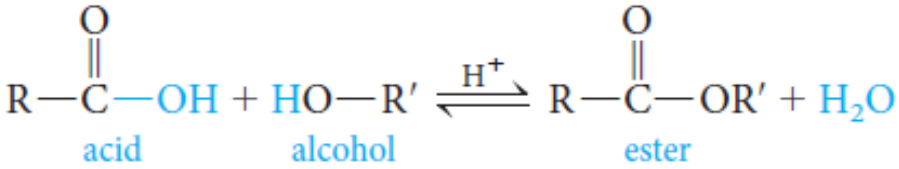
- **Esters** are derived from acids by replacing the –OH group by an –OR group and have the general formula R/COOR.

- **Nomenclature:**
  - They are named in a manner analogous to carboxylic acid salts.
  - The **R part of the –OR group is name first**, followed by the name of the acid, with the ***–ic acid*** ending changed to ***–ate***.



- **Preparation:**

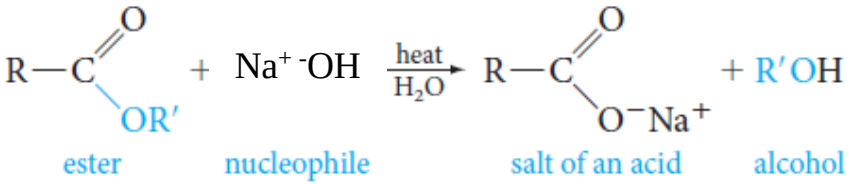
When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (HCl or H_2SO_4), an equilibrium is established with the ester and water.



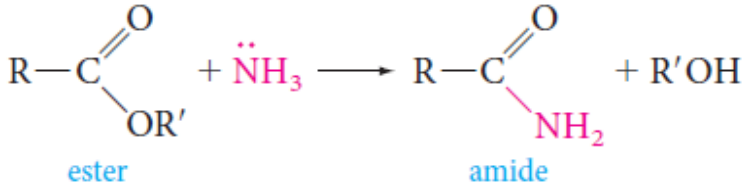
Esters

Reactions

- **Saponification;** esters are commonly hydrolyzed with base.



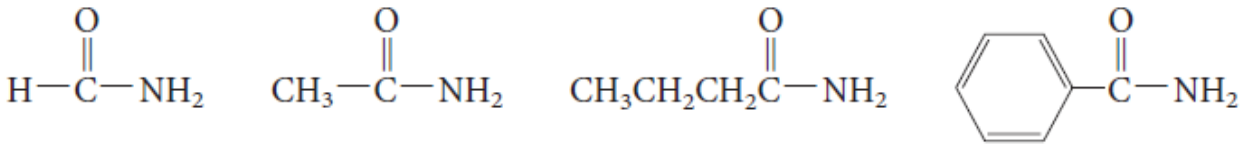
- Ammonia converts esters to **amides.**

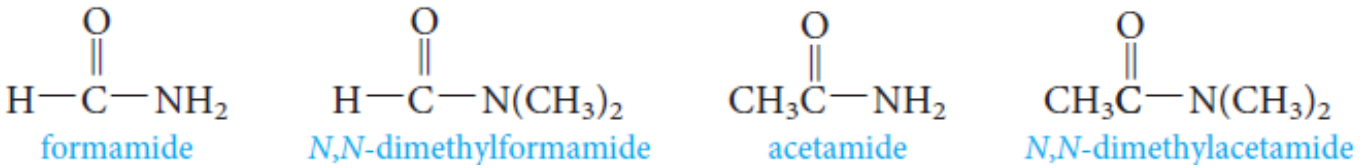


Amides

- **Amides** are the least reactive of the common carboxylic acid derivatives.
- Primary amides have general formula $RCONH_2$.
- **Nomenclature:**

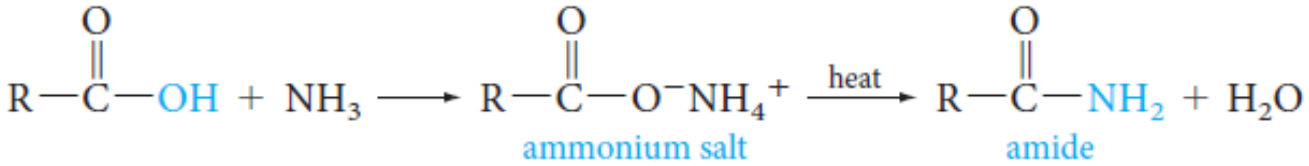
  Amides are named by replacing the *–oic acid* ending of the acid name with the *–amide* ending, This will be either for the common or the IUPAC name.



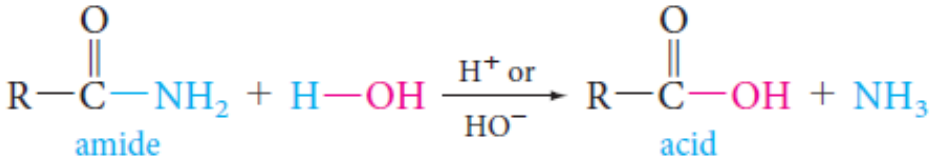


Amides

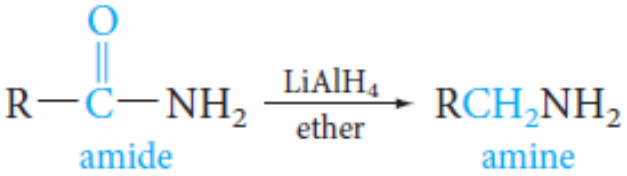
- **Preparation:**
  - They can be prepared by the reaction of ammonia with esters, with acyl halides, or with acid anhydrides.
  - Amides can also prepared by heating the ammonium salts of acids as shown in the following scheme.



- **Reactions**
  - **Amides** react with nucleophiles and they can be hydrolyzed by water.



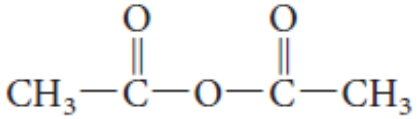
  - **Amides** can be reduced by lithium aluminums hydride to give amines.



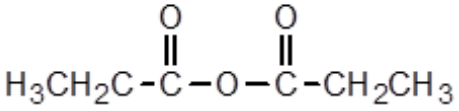
Acid Anhydrides

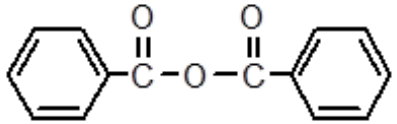
- **Acid anhydrides** have general formula RCOOCOR.
- **Nomenclature:**

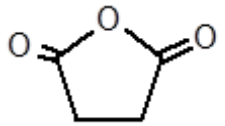
  The name of an anhydrides is obtained by naming the acid from which is derived and replacing the word acid with anhydride.



ethanoic anhydride or acetic anhydride





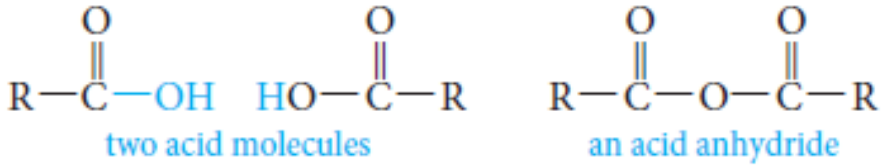


IUPAC name:	Propanoic anhydride	Benzoic anhydride	Succinic anhydride
Common name:	Propionic anhydride		

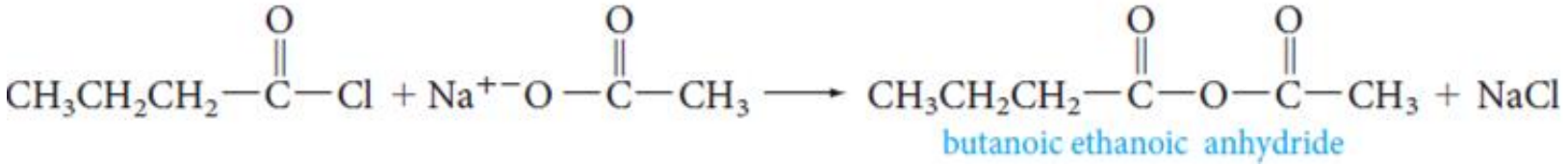
Acid Anhydrides

➢ Preparation

- **Acid anhydrides** are derived from acids by removing water from two carboxyl groups under heating and effect of suitable catalyst.



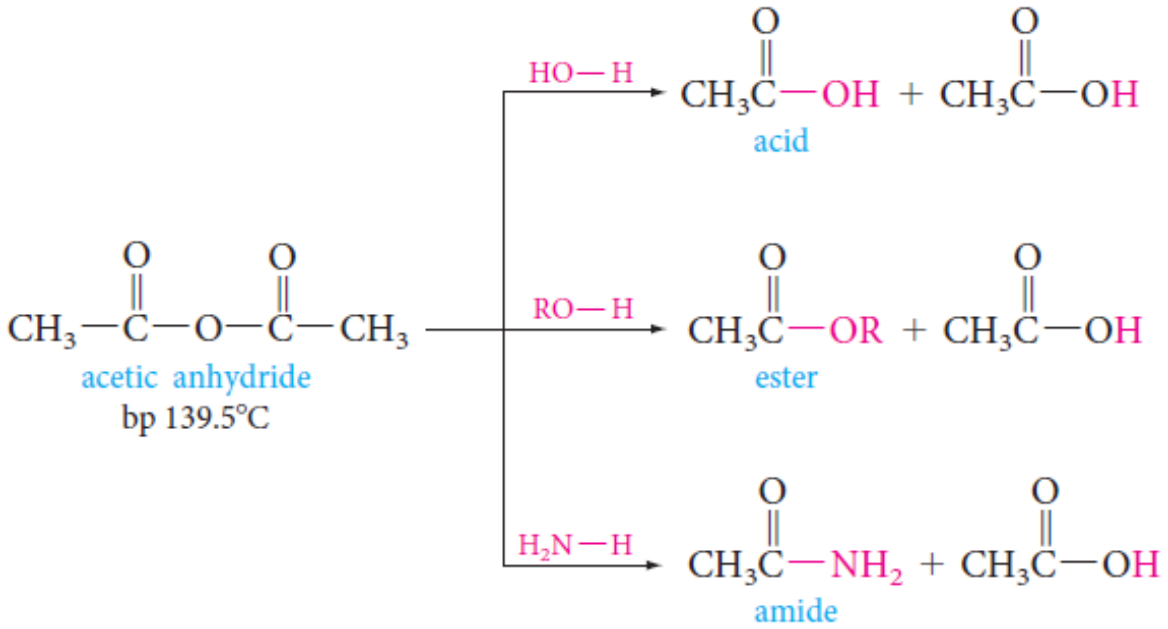
- **Anhydrides** can also be prepared from acid chlorides and carboxylate salts.
  This method is used for preparing anhydrides derived from two different carboxylic acids (mixed anhydrides).



Acid Anhydrides

➢ Reactions

- **Anhydrides** undergo nucleophilic acyl substitution reactions (*They are more reactive than esters, but less reactive than acyl halides*).



Uses of Carboxylic Acids

- **Salicylic acid**
  - It can be used to create acne medications.
  - Therefore, It is used frequently in cleansers, liquid foundations, moisturizers, anti-aging hydrating creams, eye gels, and sun screens.
- **Acetylsalicylic Acid in Aspirin**
  - Acetic acid acts as the precursor for the formation of an ester of salicylic acid which is used for aspirin (Acetyl Salicylic acid) production.
- **Citric Acid**
  - Citric acid has a sour taste and is often used to add flavor to sour candies (covered in a white powder).
  - Because citric acid is non-toxic and acidic, it is an ideal preservative. (it causes the pH to drop to a point where it is difficult for bacteria to survive).
- **Industrial uses**
  - Manufacturing of soaps and detergents (oleic acid, Palmitic acid and stearic acid).