Introduction to Organic Chemistry

CHEM 108

Credit hrs.: (3+1)

King Saud University

College of Science, Chemistry Department

CHAPTER 8: Carboxylic Acids

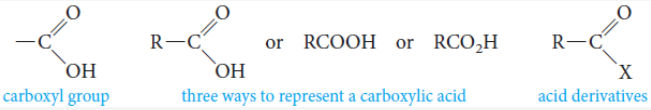
1

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.



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

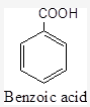
  - Aliphatic Carboxylic Acids.

    R–COOH (R = H or alkyl) Aliphatic acid

    CH_3–COOH Acetic acid

  - Aromatic Carboxylic Acids.

    Ar–COOH (R = C_6H_5-) Aromatic acid



Benzoic acid

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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.

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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

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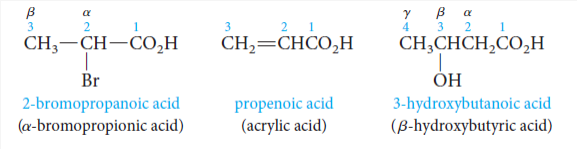
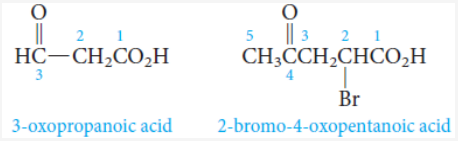
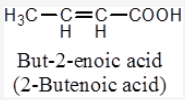
Nomenclature of Carboxylic Acids



- 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.





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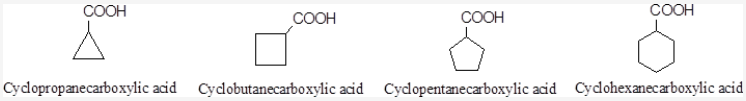
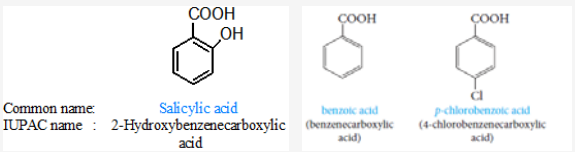
Nomenclature of Carboxylic Acids

- **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)



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



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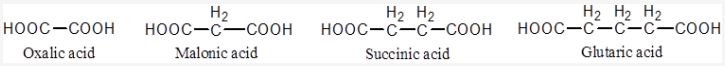
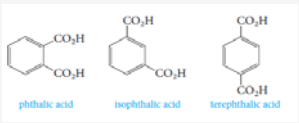
Nomenclature of Carboxylic Acids

- **Dicarboxylic acids** (*acids that contain two carboxyl groups*)
  - **Common names**.

    They are known almost exclusively by their common names.

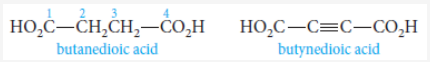




Common name:	Benzene-1,2-dicarboxylic acid	Benzene-1,3-dicarboxylic acid	Benzene-1,4-dicarboxylic acid
IUPAC name:			

  - IUPAC system

    They are given the suffix *-dioic acid* in the IUPAC system.



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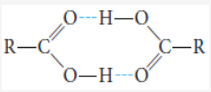
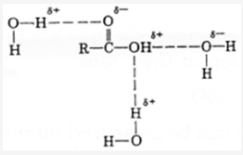
Physical Properties of Acids

- 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 the electron-rich oxygens and the 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.

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Physical Properties of Acids

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

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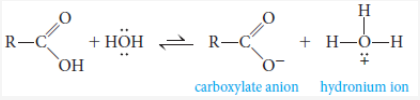
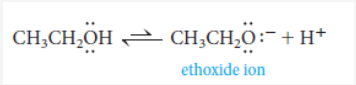
Acid Strength and Structure

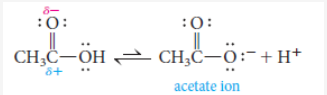
- Carboxylic acids (RCOOH) dissociate in water, yielding a carboxylate anion ($RCOO^-$) and hydronium ion.

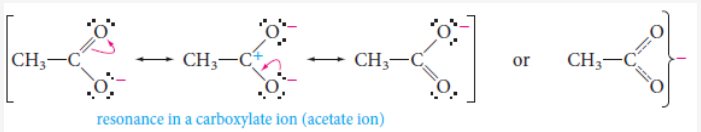


Why carboxylic acids are more acidic than alcohols?

- 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.







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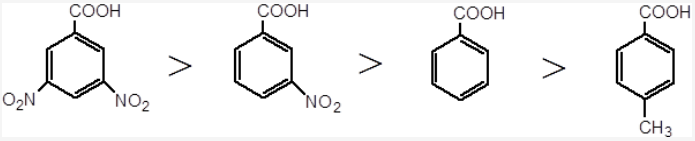
Acid Strength and Structure

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.



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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

$$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$$

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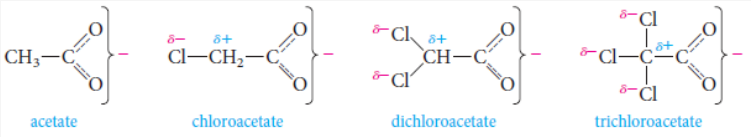
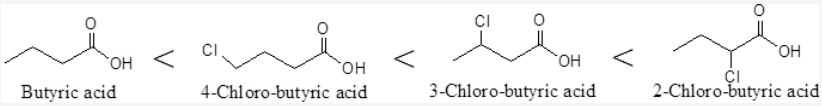
Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect



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

- Comparison of acid strengths of butyric acid and the monochlorinated acids.



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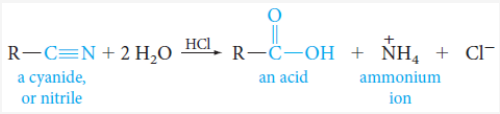
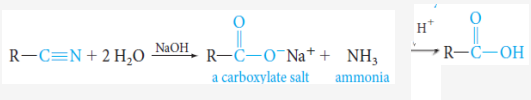
1) Hydrolysis of Cyanides (Nitriles)

Preparation of Acids

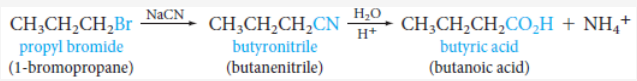
- The reaction requires either acid or base.
  - In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.



  - 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.



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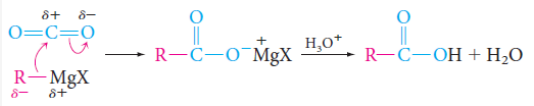
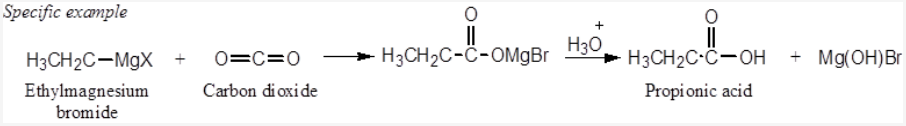
Preparation of Acids

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



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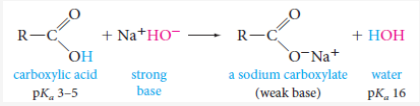
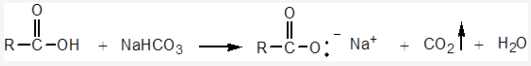
Reactions of Acids

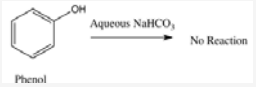
1) Reactions with Bases: Salt Formation

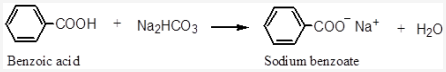
- Carboxylic acids, when treated with a strong base, form carboxylate salts.





- Examples.





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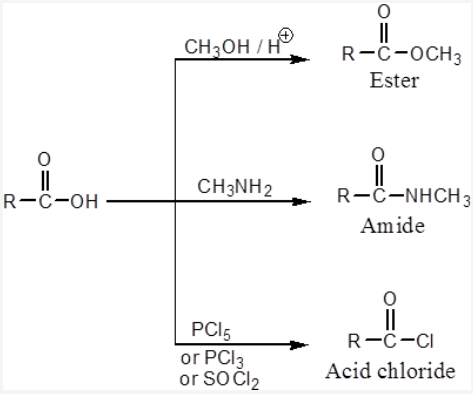
2) Nucleophilic Substitution Reactions

Reactions of Acids



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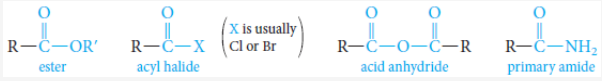
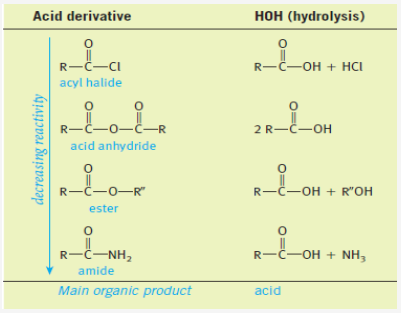
Carboxylic Acid Derivatives

- 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.



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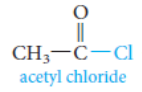
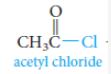
Acid Chloride

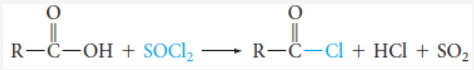
Carboxylic Acid Derivatives

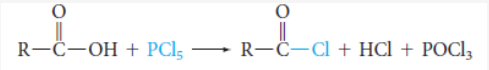
- Acyl chlorides have the general formula RCOCl.
- Acyl chlorides are more common and less expensive than bromides or iodides.
- **Nomenclature:**
  Acyl chlorides, or acid chlorides, are named by replacing the *-ic acid* ending of the parent acid by *-yl chloride*.





- **Preparation:**
  They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.





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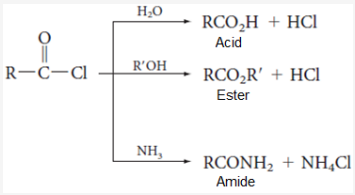
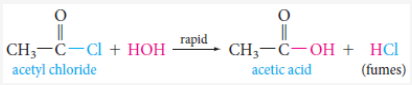
Acid Chloride

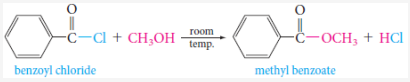
Carboxylic Acid Derivatives

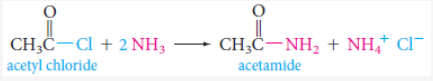
- **Reactions:** *They can react rapidly with most nucleophile.*



- **Examples:**







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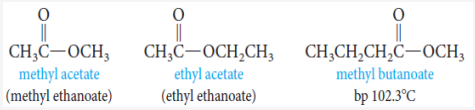
Esters

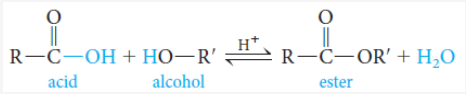
Carboxylic Acid Derivatives

- 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.



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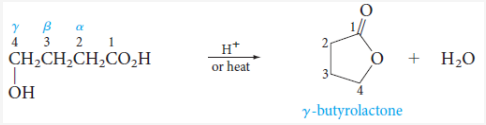
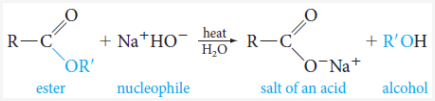
Esters

Carboxylic Acid Derivatives

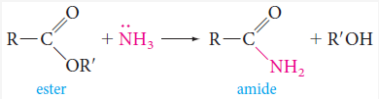
- **Reactions**
  - Cyclic esters (lactones) can be prepared from hydroxy acids if these groups can come in contact through bending of the chain.



  - Saponification; esters are commonly hydrolyzed with base.



  - Ammonia converts esters to amides.



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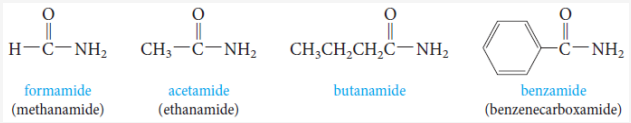
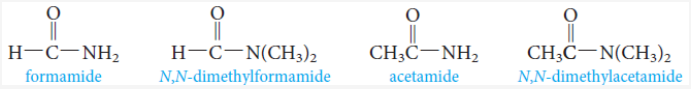
Amides

Carboxylic Acid Derivatives

- 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 *–ic or –oic acid* ending of the acid name, either the common or the IUPAC name, with the *–amide* ending.





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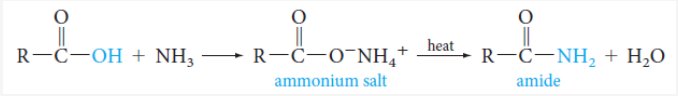
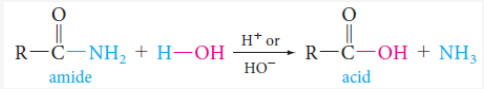
Amides

Carboxylic Acid Derivatives

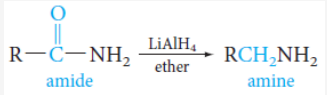
- **Preparation:**
  - They can be prepared by the reaction of ammonia with esters, with acyl halides, or with acid anhydrides.
  - Amides can also prepared by heating the ammonium salts of acids.



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



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



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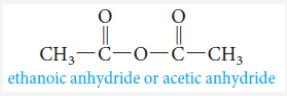
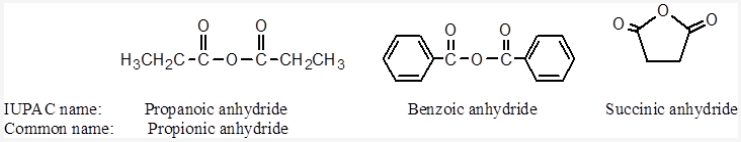
Acid Anhydrides

Carboxylic Acid Derivatives

- 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.





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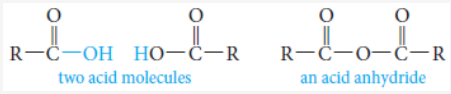
Acid Anhydrides

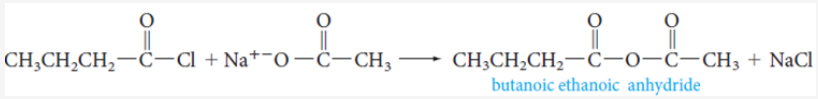
Carboxylic Acid Derivatives

- **Preparation**
  - 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 method is used for preparing anhydrides derived from two different carboxylic acids (mixed anhydrides).



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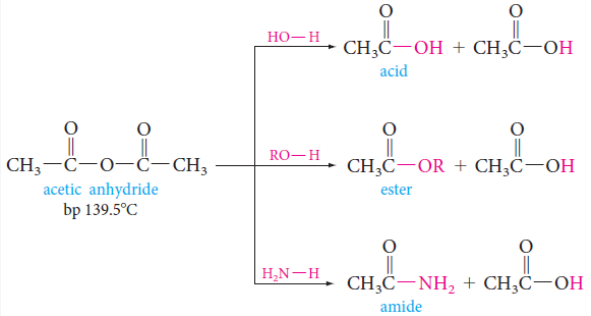
Acid Anhydrides

Carboxylic Acid Derivatives

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



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