

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

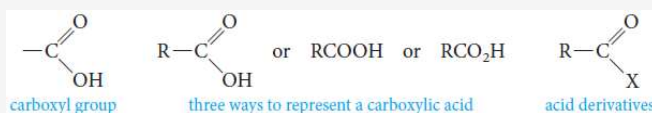
College of Science, Chemistry Department

CHAPTER 7: Carboxylic Acids

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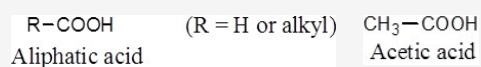
Structure of Carboxylic Acids

- 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.

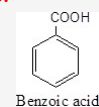
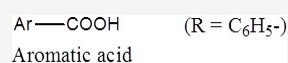


- Depending on whether an **R** or an **Ar** residue is attached to the carboxyl group; **Carboxylic acids are classified** as;

- Aliphatic Carboxylic Acids.**



- Aromatic Carboxylic Acids.**



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Nomenclature of Carboxylic Acids

Common Names

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

IUPAC System

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



- o **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, <i>formica</i>)	formic acid	methanoic acid
2	CH ₃ COOH	vinegar (Latin, <i>acetum</i>)	acetic acid	ethanoic acid
3	CH ₃ CH ₂ COOH	milk (Greek, <i>protos pion</i> , first fat)	propionic acid	propanoic acid
4	CH ₃ (CH ₂) ₂ COOH	butter (Latin, <i>butyrum</i>)	butyric acid	butanoic acid
5	CH ₃ (CH ₂) ₃ COOH	valerian root (Latin, <i>valere</i> , to be strong)	valeric acid	pentanoic acid
6	CH ₃ (CH ₂) ₄ COOH	goats (Latin, <i>caper</i>)	caproic acid	hexanoic acid
7	CH ₃ (CH ₂) ₅ COOH	vine blossom (Greek, <i>oenanthe</i>)	enanthic acid	heptanoic acid
8	CH ₃ (CH ₂) ₆ COOH	goats (Latin, <i>caper</i>)	caprylic acid	octanoic acid
9	CH ₃ (CH ₂) ₇ COOH	pelargonium (an herb with stork-shaped seed capsules; Greek, <i>pelargos</i> , stork)	pelargonic acid	nonanoic acid
10	CH ₃ (CH ₂) ₈ COOH	goats (Latin, <i>caper</i>)	capric acid	decanoic acid

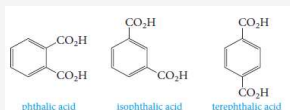
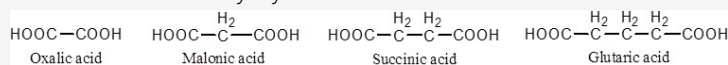
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Nomenclature of Carboxylic Acids

o Dicarboxylic acids (acids that contain two carboxyl groups)

▪ Common names.

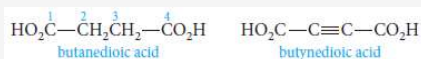
They are known almost exclusively by their **common names**.



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

▪ IUPAC system

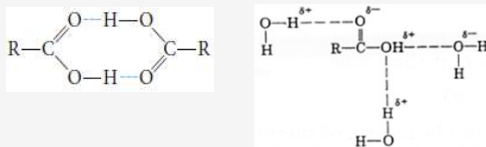
They are given the suffix *-dioic acid* in the IUPAC system.



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Physical Properties of Acids

- o Carboxylic acids are polar and they form hydrogen bonds with themselves or with other molecules.
- o 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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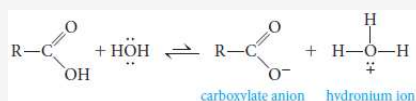
Physical Properties of Acids

Structure	Name	Mol. Wt.	b.p. °C	Solubility in H ₂ O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH ₃ CH ₂ OH	Ethyl alcohol	46	78	Very soluble
CH ₃ COOH	Acetic acid	60	118	Very soluble
CH ₃ CH ₂ CH ₂ OH	<i>n</i> -Propyl alcohol	60	97	Very soluble
CH ₃ (CH ₂) ₃ COOH	Valeric acid	102	187	4.0 g/100 g H ₂ O
CH ₃ (CH ₂) ₄ CH ₂ OH	<i>n</i> -Hexyl alcohol	102	156	0.6 g/100 g H ₂ O
Ph-COOH	Benzoic acid	122	250	Insoluble
Ph-CH ₂ CH ₂ OH	3-Phenylethanol	122	250	Insoluble

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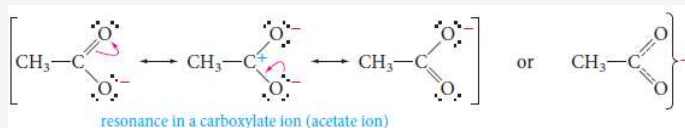
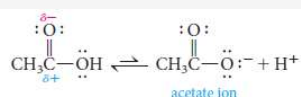
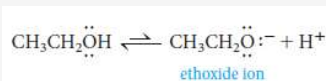
Acid Strength and Structure

- 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**.

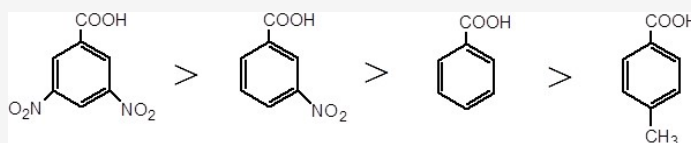


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Acid Strength and Structure

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.

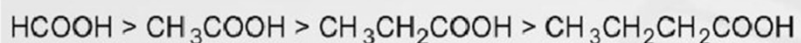


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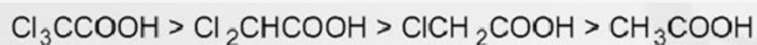
Acid Strength and Structure

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.



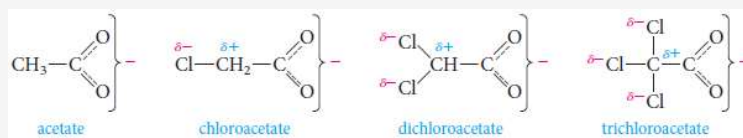
- Example:** acetic acid with those of mono-, di-, and trichloroacetic acids.
Comparison of acid strengths of acetic acid and chlorinated acetic acids



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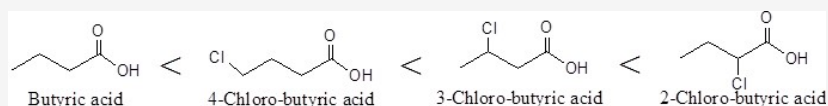
Acid Strength and Structure

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.

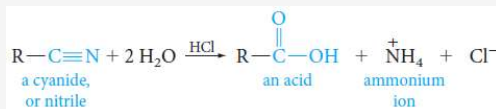


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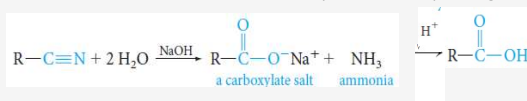
1) Hydrolysis of Cyanides (Nitriles)

Preparation of Acids

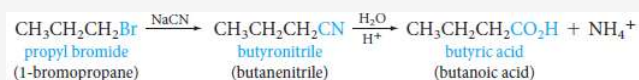
- The reaction requires either acid or base.
 - In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.



- 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.

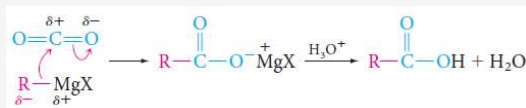


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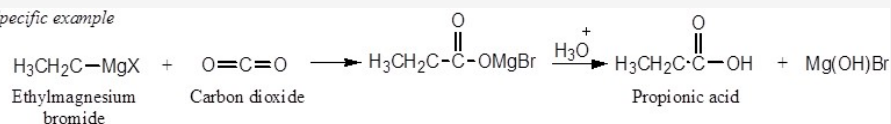
2) Reaction of Grignard Reagents with Carbon Dioxide (Carbonylation of Grignard Reagent)

Preparation of Acids

- 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

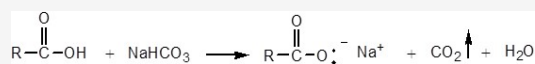
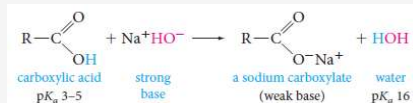


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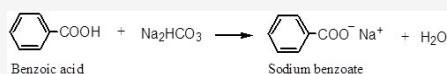
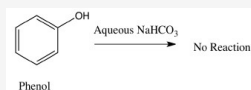
1) Reactions with Bases: Salt Formation

Reactions of Acids

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



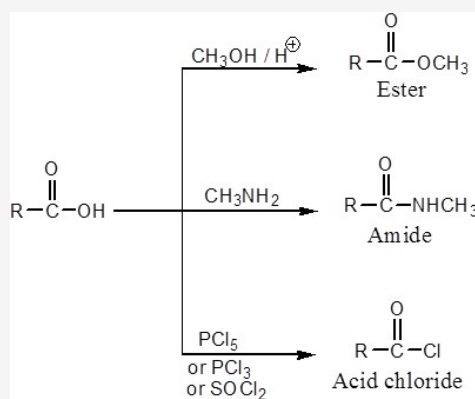
- Examples.



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2) Nucleophilic Substitution Reactions

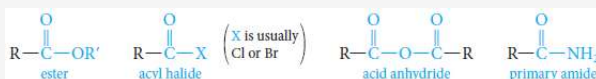
Reactions of Acids



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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.

Acid derivative	HOH (hydrolysis)
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ acyl halide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{HCl}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ acid anhydride	$2 \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$ ester	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{R}'\text{OH}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ amide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{NH}_3$
Main organic product	acid

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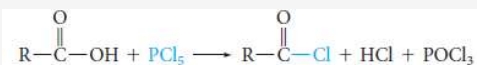
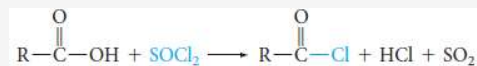
Acid Chloride

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.

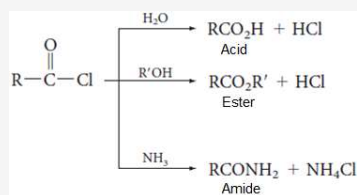


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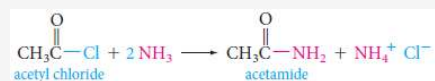
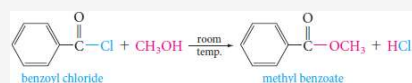
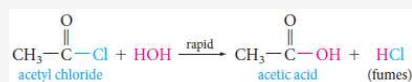
Acid Chloride

Carboxylic Acid Derivatives

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



- **Examples:**

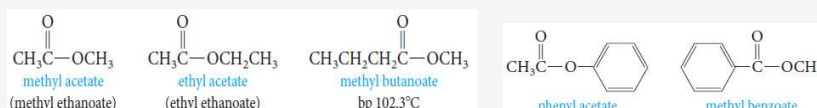


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Esters

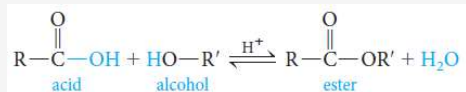
Carboxylic Acid Derivatives

- **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 H₂SO₄), an equilibrium is established with the ester and water.



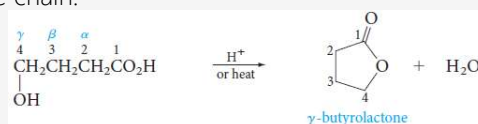
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Esters

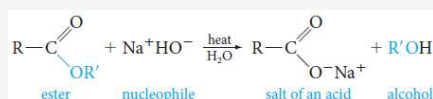
Carboxylic Acid Derivatives

- **Reactions**

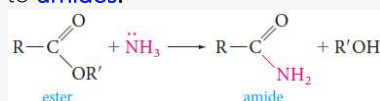
- **Cyclic esters (lactones)** can be prepared from hydroxy acids if these groups can come in contact through bending of the chain.



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



- Ammonia converts esters to **amides**.



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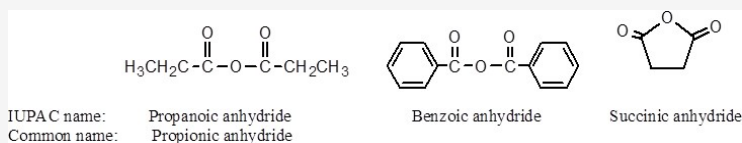
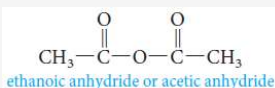
Acid Anhydrides

Carboxylic Acid Derivatives

- Acid anhydrides have general formula RCOOCOR .

- **Nomenclature:**

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



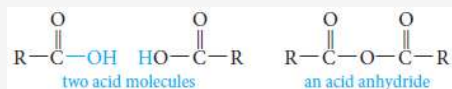
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Acid Anhydrides

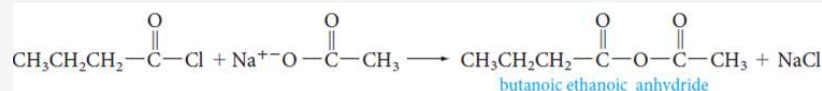
Carboxylic Acid Derivatives

- **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).



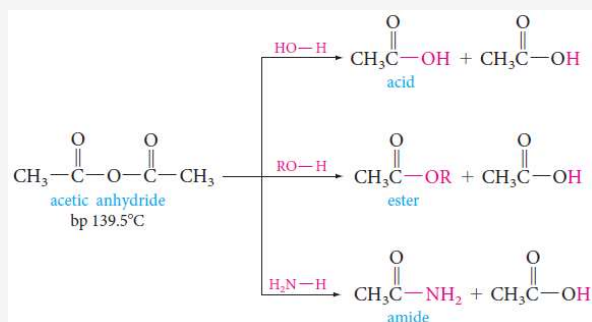
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Acid Anhydrides

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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