



# Fundamentals of Organic Chemistry

**CHEM 109**

*For Students of Health Colleges*

Credit hrs.: (2+1)

*King Saud University*

College of Science, Chemistry Department

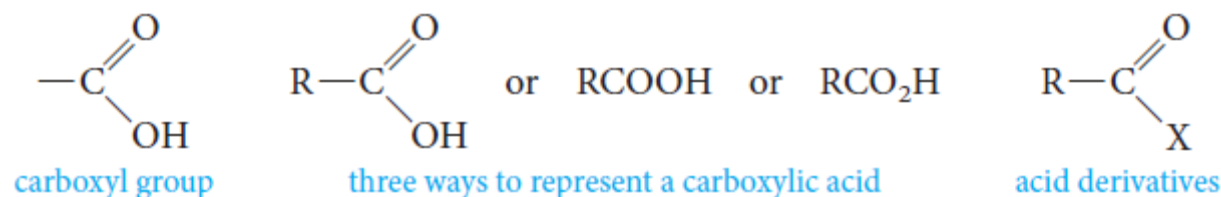
# Structure of Carboxylic Acids

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

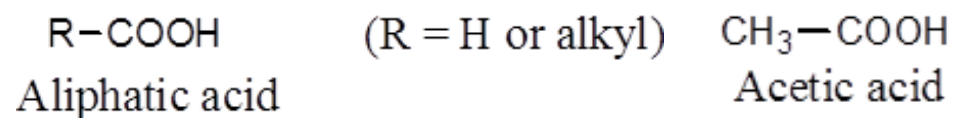
*The name is a contraction of the parts: the **carbonyl** and **hydroxyl** groups.*

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

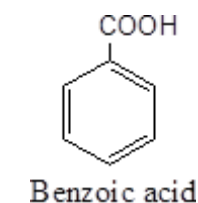
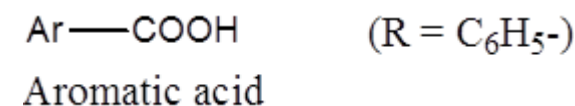


- Depending on whether an **R** or an **Ar** residue is attached to the carboxyl group; **Carboxylic acids are classified** as;

- Aliphatic Carboxylic Acids.**



- Aromatic Carboxylic Acids.**



- 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  $\alpha$ -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*.

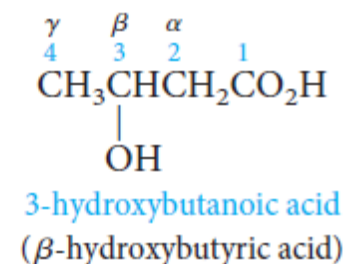
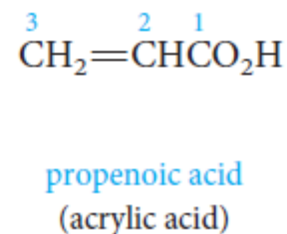
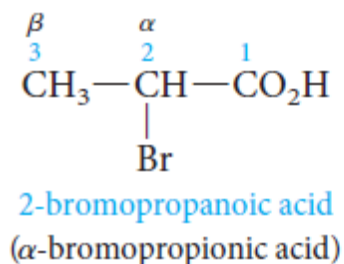
**Alkane- e + oic acid = Alkanoic acid**

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

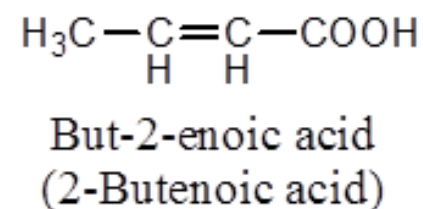
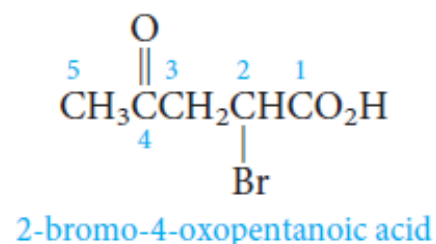
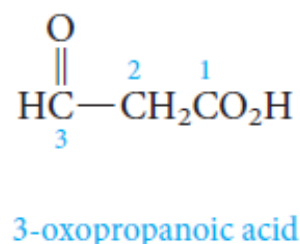
# Nomenclature of Carboxylic Acids

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

# Nomenclature of Carboxylic Acids



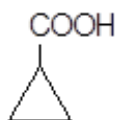
- The **carboxyl** group has **priority over alcohol, aldehyde, or ketone** functionality in naming.
- The prefix **oxo-** is used to locate the carbonyl group of the aldehyde or ketone.



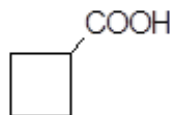
# Nomenclature of Carboxylic Acids

## ➤ Cycloalkane carboxylic acid

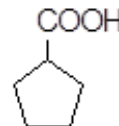
When the carboxyl group is attached to a ring, the ending **-carboxylic acid** is added to the name of the parent **cycloalkane**. (i.e. **Cycloalkanecarboxylic acid**)



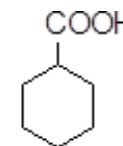
Cyclopropanecarboxylic acid



Cyclobutanecarboxylic acid

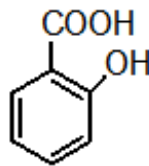


Cyclopentanecarboxylic acid

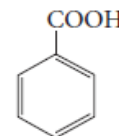


Cyclohexanecarboxylic acid

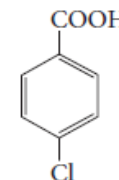
➤ **Aromatic acids** are named by attaching the suffix **-oic acid** or **-ic acid** to an appropriate prefix derived from the aromatic hydrocarbon.



Common name: **Salicylic acid**  
IUPAC name : 2-Hydroxybenzenecarboxylic acid



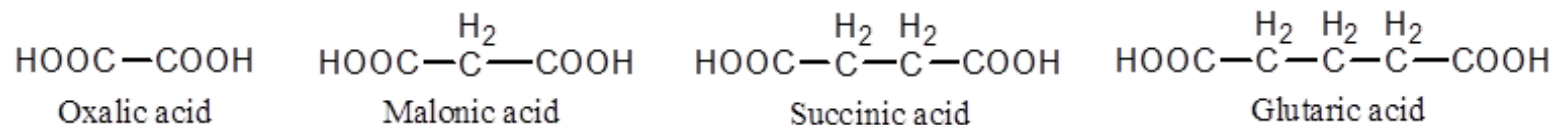
benzoic acid  
(benzenecarboxylic acid)



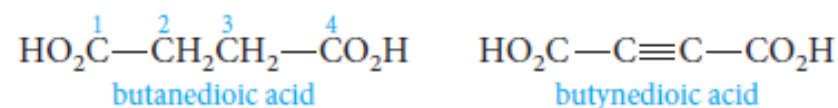
*p*-chlorobenzoic acid  
(4-chlorobenzenecarboxylic acid)

# Nomenclature of Carboxylic Acids

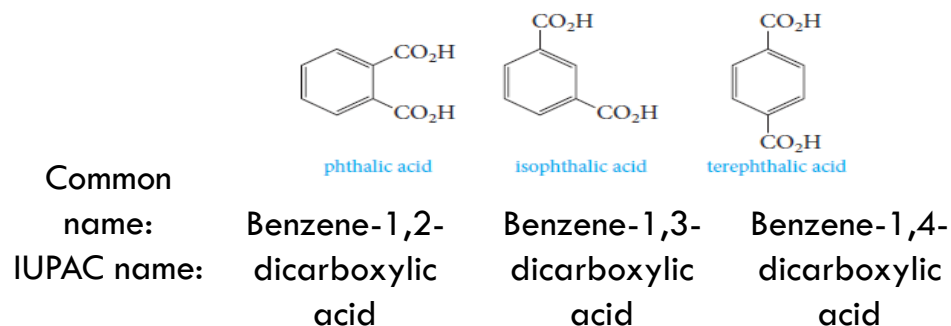
- **Dicarboxylic acids** (*acids that contain two carboxyl groups*) are known almost exclusively by their common names.



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



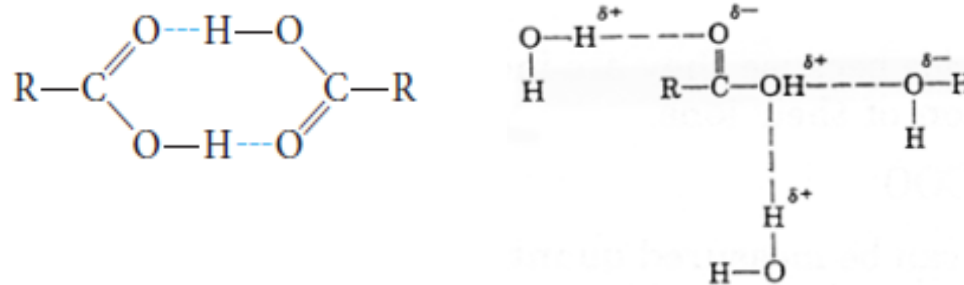
- The three **benzenedicarboxylic acids** are generally known by their common names.



# Physical Properties of Acids

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- **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**.

# Physical Properties of Acids

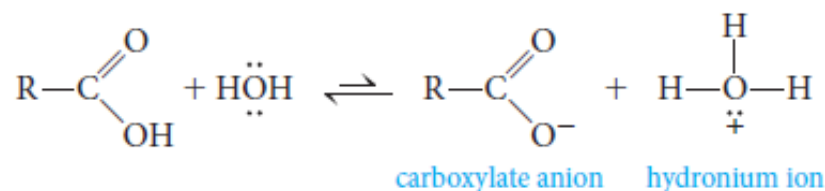


Structure	Name	Mol. Wt.	b.p. °C	Solubility in H <sub>2</sub> O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH <sub>3</sub> CH <sub>2</sub> OH	Ethyl alcohol	46	78	Very soluble
CH <sub>3</sub> COOH	Acetic acid	60	118	Very soluble
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	<i>n</i> -Propyl alcohol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

# Acid Strength and Structure

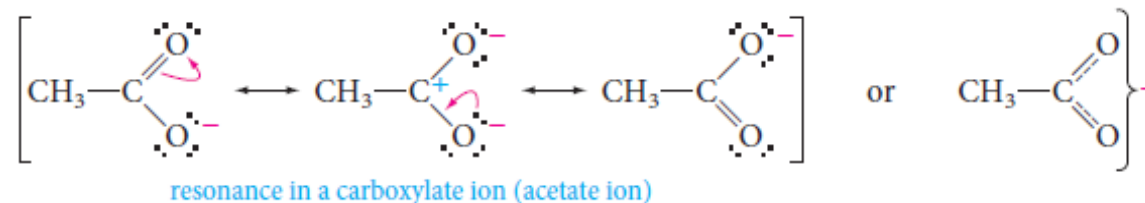
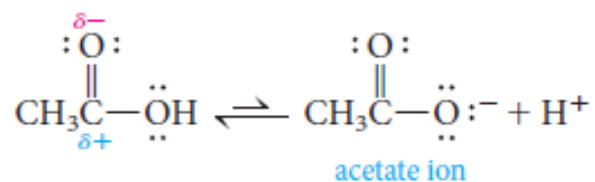
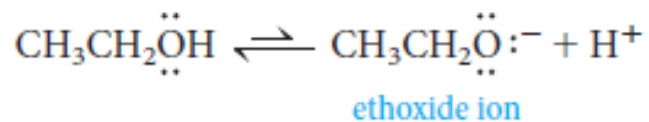


- **Carboxylic acids** (RCOOH) dissociate in water, yielding a carboxylate anion (RCOO<sup>-</sup>) and hydronium ion.



## 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**.

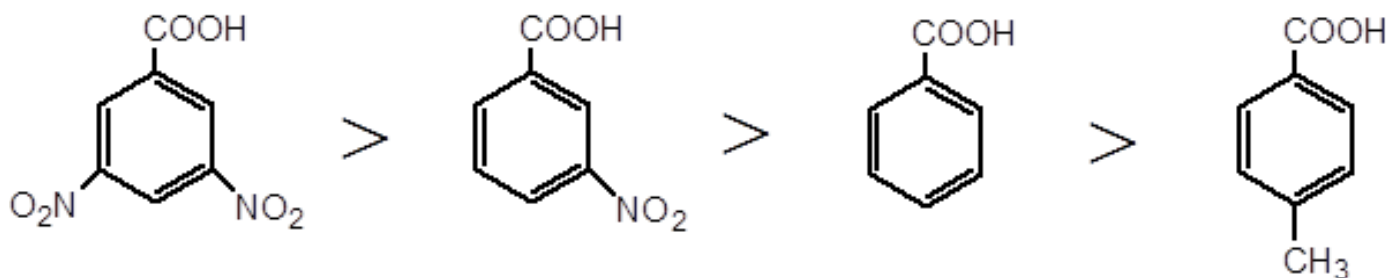


# Acid Strength and Structure

## 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

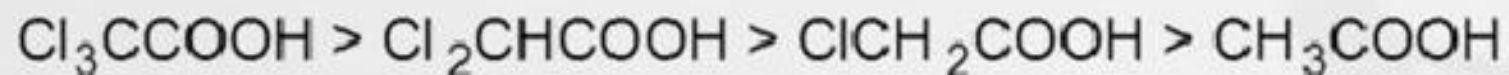
- **Formic acid is a substantially stronger acid than acetic acid.**

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



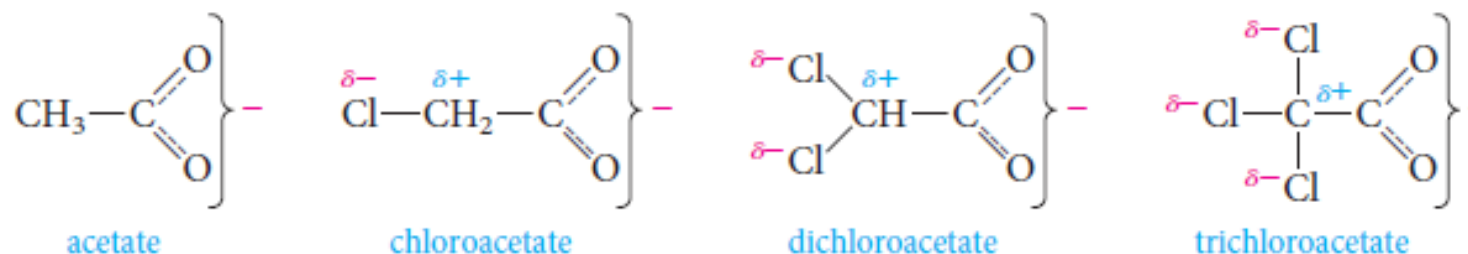
- **Example:** acetic acid with those of mono-, di-, and trichloroacetic acids.

*Comparison of acid strengths of acetic Acid and chlorinated acetic acids*



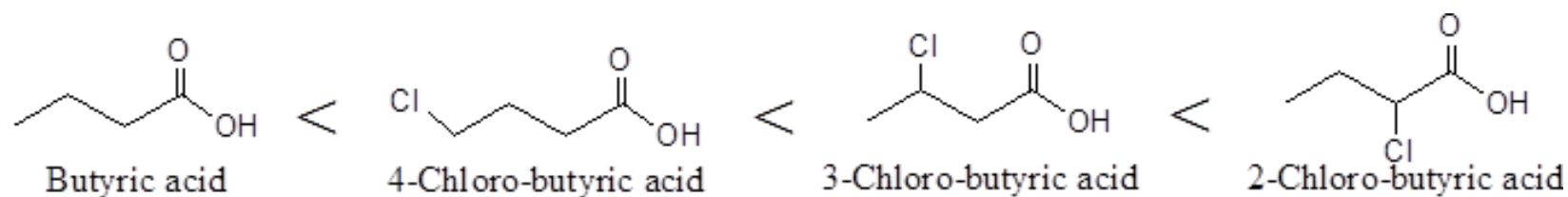
# Acid Strength and Structure

## 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.

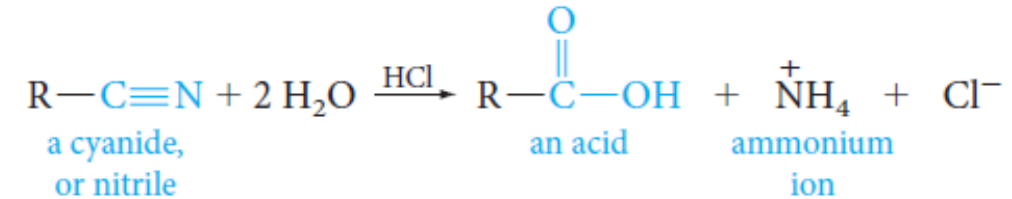


## 1) Hydrolysis of Cyanides (Nitriles)

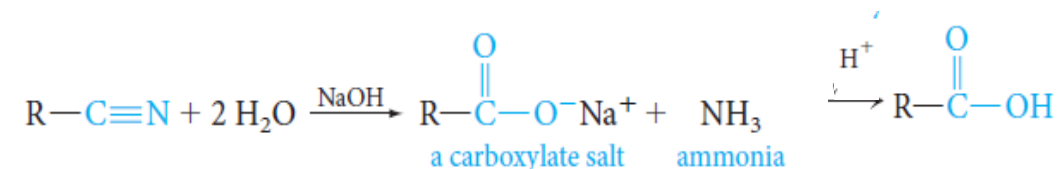
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- The reaction requires either acid or base.

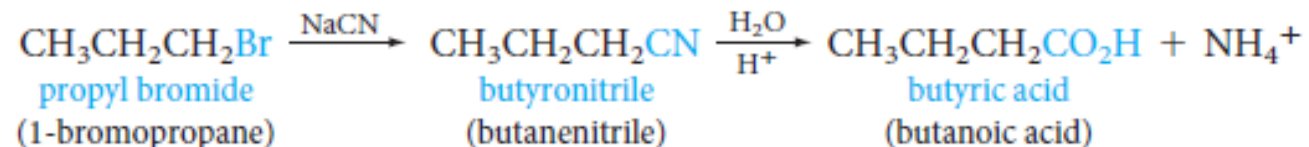
➤ In acid, the nitrogen atom of the cyanide is converted to an ammonium ion..



➤ 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.

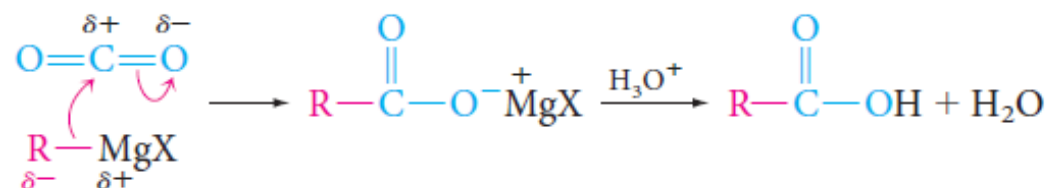


## 2) Reaction of Grignard Reagents with Carbon Dioxide (Carbonation of Grignard Reagent)

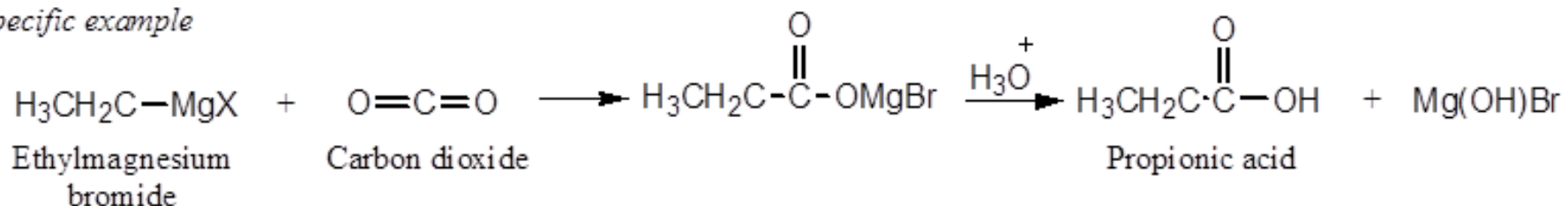
# Preparation of Carboxylic Acids

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- **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*).



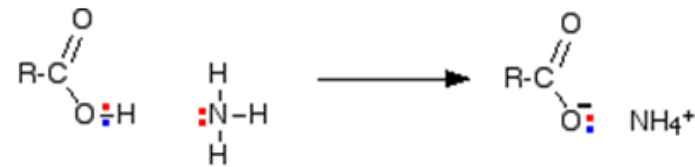
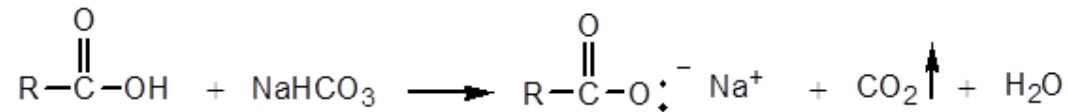
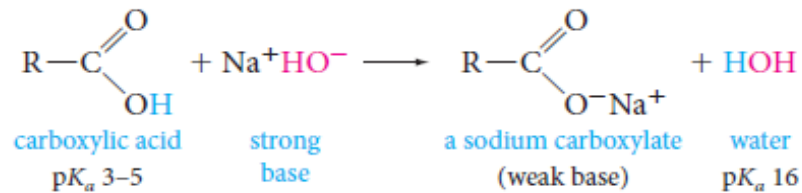
*Specific example*



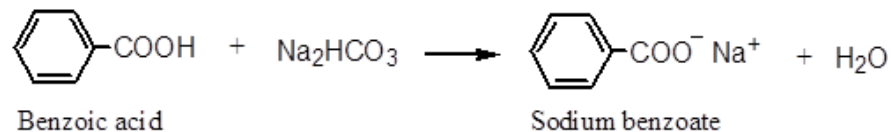
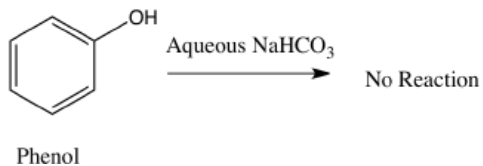
## 1) Reactions with Bases: Salt Formation

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

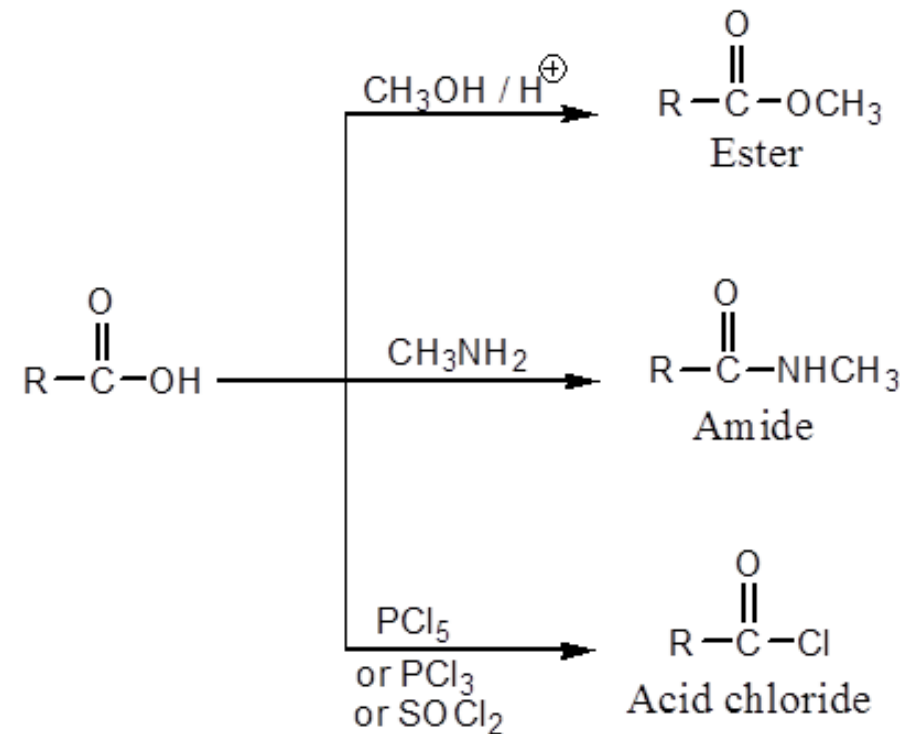
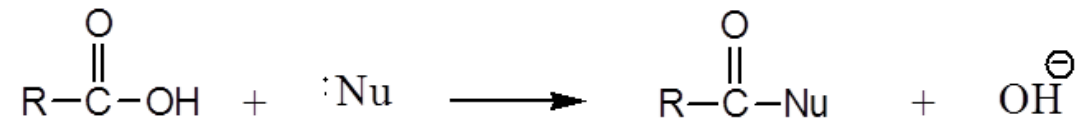


- Examples.**



## 2) Nucleophilic Substitution Reactions

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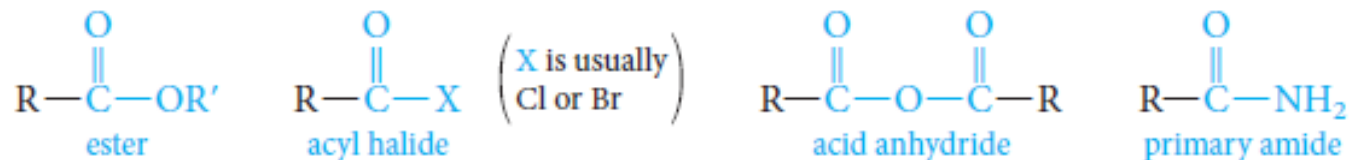


# Carboxylic Acid Derivatives



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- **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.

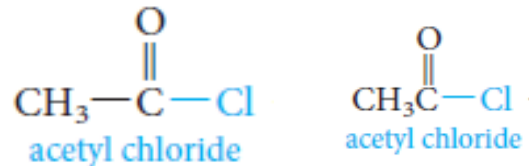
Acid derivative	HOH (hydrolysis)
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ acyl halide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{HCl}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ acid anhydride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

## Acid Chloride

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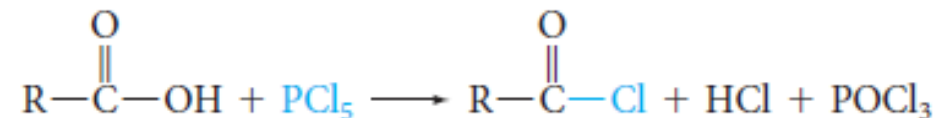
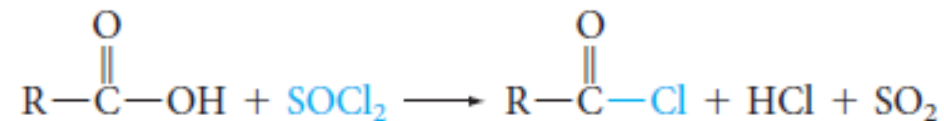
- **Acyl chlorides** have the general formula  $\text{RCOCl}$ .
- **Acyl chlorides** are more common and less expensive than bromides or iodides.
- **Nomenclature:**

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



- **Preparation:**

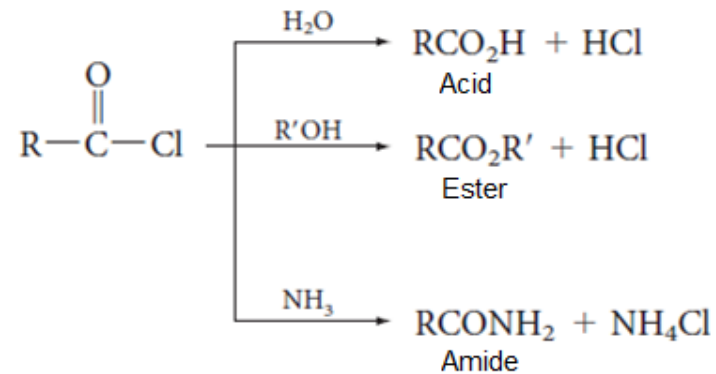
They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.



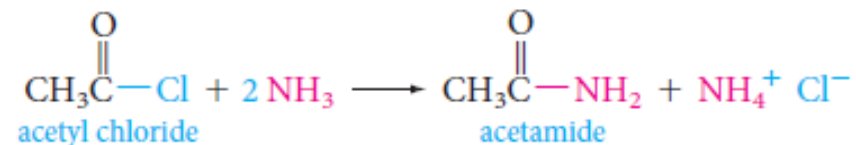
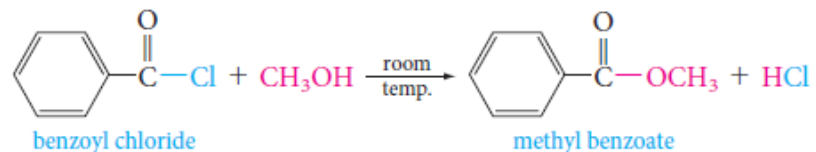
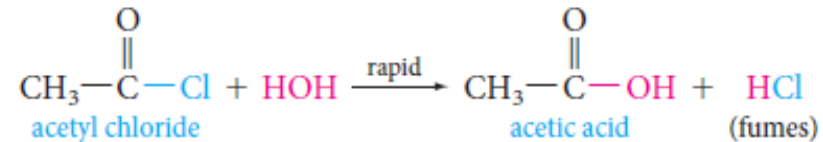
## Acid Chloride

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



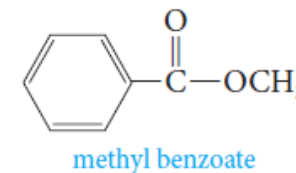
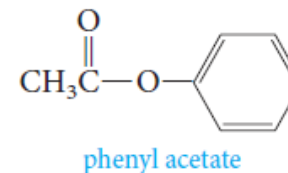
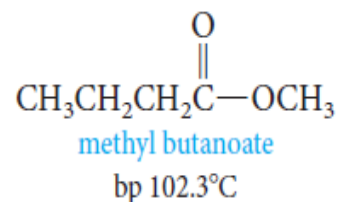
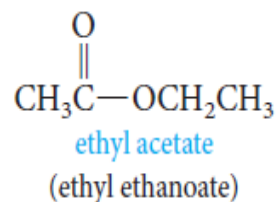
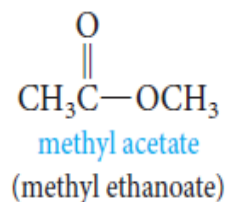
- **Examples:**



## Esters

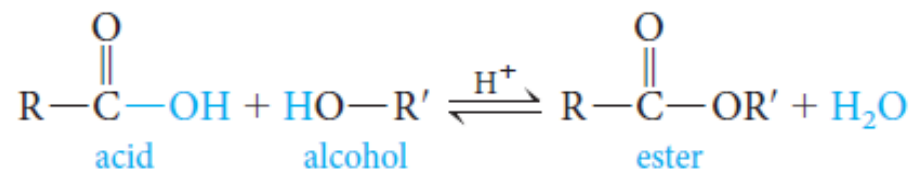
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- **Esters** are derived from acids by replacing the  $\text{-OH}$  group by an  $\text{-OR}$  group and have the general formula  $\text{R}/\text{COOR}$ .
- **Nomenclature:**
  - They are named in a manner analogous to carboxylic acid salts.
  - The **R part of the  $\text{-OR}$  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 ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ), an equilibrium is established with the ester and water.

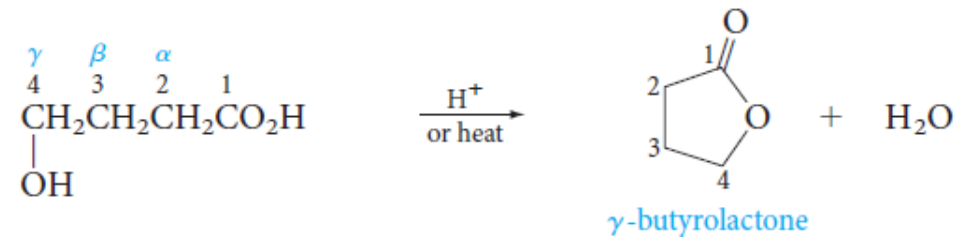


## Esters

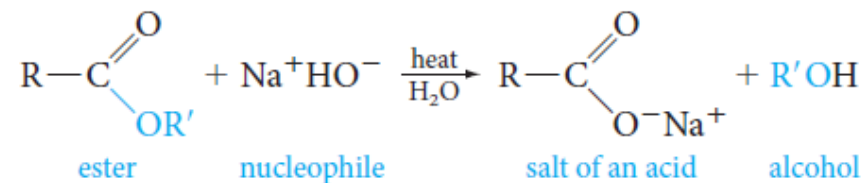
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### ○ Reactions

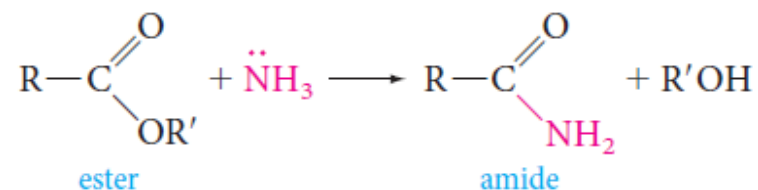
- **Cyclic esters (lactones)** can be prepared from hydroxy acids if these groups can come in contact through bending of the chain.



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



- Ammonia converts esters to **amides**.



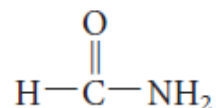
## Amides

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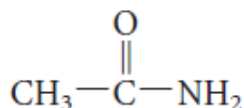
- **Amides** are the least reactive of the common carboxylic acid derivatives.
- Primary amides have general formula  **$\text{RCONH}_2$** .

### ➤ Nomenclature:

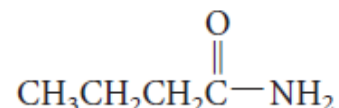
Amides are named by replacing the  $-ic$  or  $-oic$  acid ending of the acid name, either the common or the IUPAC name, with the  $-amide$  ending.



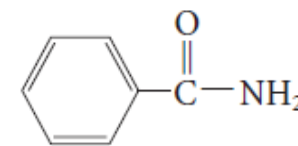
formamide  
(methanamide)



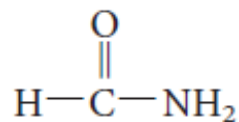
acetamide  
(ethanamide)



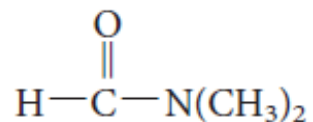
butanamide



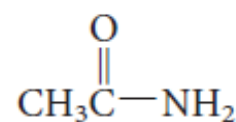
benzamide  
(benzenecarboxamide)



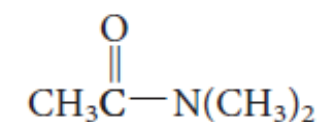
formamide



*N,N*-dimethylformamide



acetamide



*N,N*-dimethylacetamide

- ## ○ Reactions

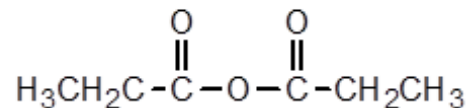
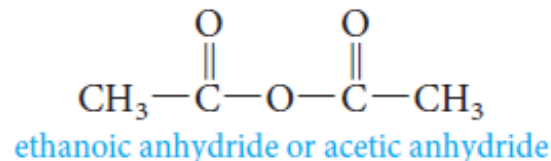
## Acid Anhydrides

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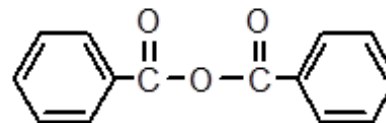
➤ **Acid anhydrides** have general formula  $\text{RCOOCOR}$ .

➤ **Nomenclature:**

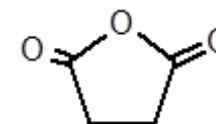
The name of an anhydrides is obtained by naming the acid from which is derived and replacing the word acid with anhydride.



IUPAC name: Propanoic anhydride  
Common name: Propionic anhydride



Benzoic anhydride



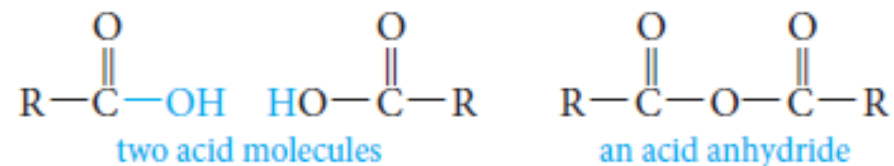
Succinic anhydride

## Acid Anhydrides

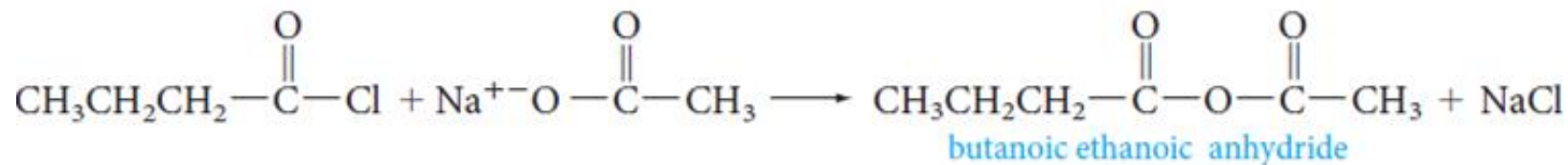
32

### ➤ 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).*



## Acid Anhydrides

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### ➤ Reactions

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

