

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

Learning Objectives

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At the end of this chapter, students will be 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

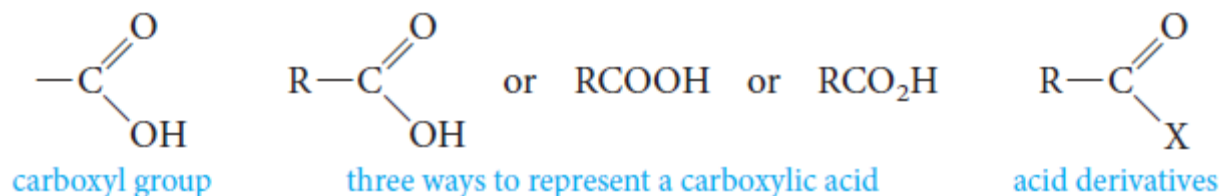
Structure of Carboxylic Acids

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

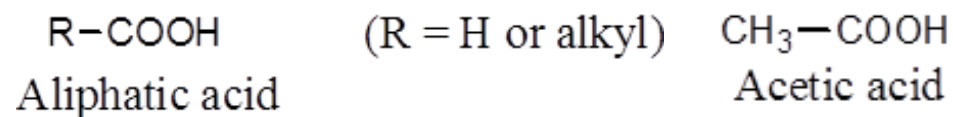
*The name is a contraction of the parts: the **carbonyl** and **hydroxyl** groups.*

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

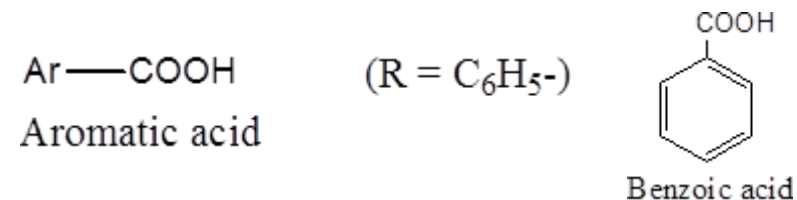


- Depending on whether an **R** or an **Ar** residue is attached to the carboxyl group; **Carboxylic acids are classified** as;

- 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 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**.



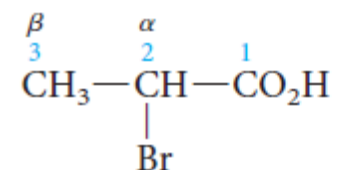
- **IUPAC system**, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way.

Nomenclature of Carboxylic Acids

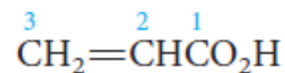


Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, <i>formica</i>)	formic acid	methanoic acid
2	CH ₃ COOH	vinegar (Latin, <i>acetum</i>)	acetic acid	ethanoic acid
3	CH ₃ CH ₂ COOH	milk (Greek, <i>protos pion</i> , first fat)	propionic acid	propanoic acid
4	CH ₃ (CH ₂) ₂ COOH	butter (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

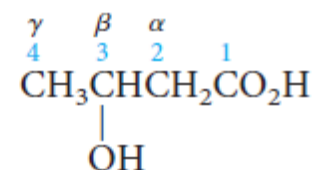
Nomenclature of Carboxylic Acids



2-bromopropanoic acid
(α -bromopropionic acid)

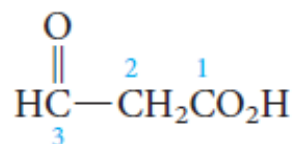


propenoic acid
(acrylic acid)

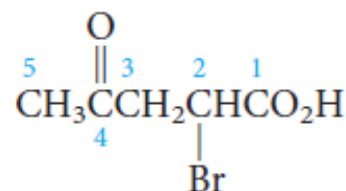


3-hydroxybutanoic acid
(β -hydroxybutyric acid)

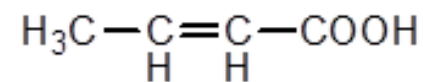
- The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming.
- The prefix **oxo-** is used to locate the carbonyl group of the aldehyde or ketone.



3-oxopropanoic acid



2-bromo-4-oxopentanoic acid



But-2-enoic acid
(2-Butenoic acid)

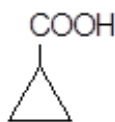
Nomenclature of Carboxylic Acids



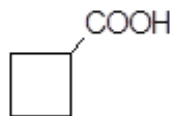
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➤ Cycloalkane carboxylic acid

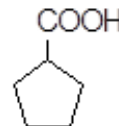
When the carboxyl group is attached to a ring, the ending **-carboxylic acid** is added to the name of the parent **cycloalkane**. (i.e. **Cycloalkanecarboxylic acid**)



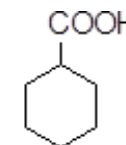
Cyclopropanecarboxylic acid



Cyclobutanecarboxylic acid

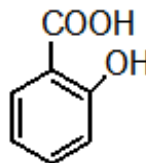


Cyclopentanecarboxylic acid

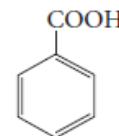


Cyclohexanecarboxylic acid

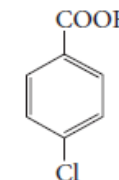
➤ **Aromatic acids** are named by attaching the suffix **-oic acid** or **-ic acid** to an appropriate prefix derived from the aromatic hydrocarbon.



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



Common name: **benzoic acid**
(benzenecarboxylic acid)

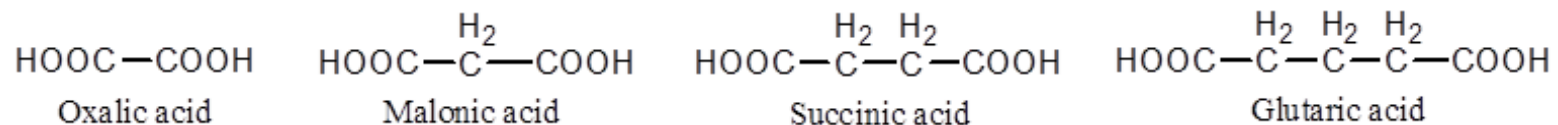


Common name: **p-chlorobenzoic acid**
(4-chlorobenzenecarboxylic acid)

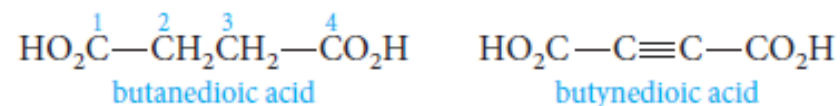
Nomenclature of Carboxylic Acids



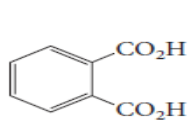
- **Dicarboxylic acids** (acids that contain two carboxyl groups) are known almost exclusively by their common names.



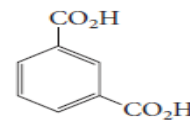
- **Aliphatic dicarboxylic acids** are given the suffix *-dioic acid* in the IUPAC system.



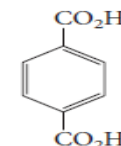
- The three **benzenedicarboxylic acids** are generally known by their common names.



phthalic acid



isophthalic acid



terephthalic acid

Common name:

IUPAC name:

Benzene-1,2-
dicarboxylic
acid

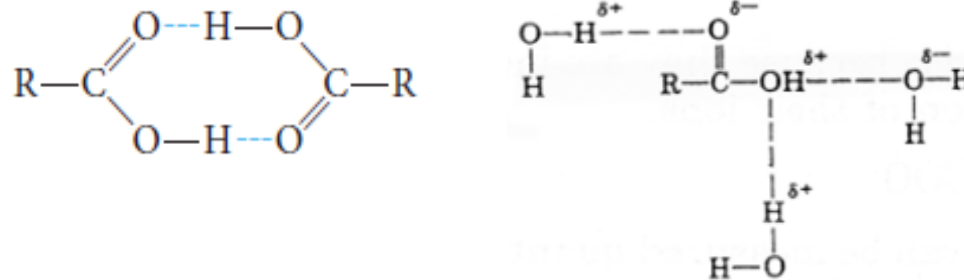
Benzene-1,3-
dicarboxylic
acid

Benzene-1,4-
dicarboxylic
acid

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 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

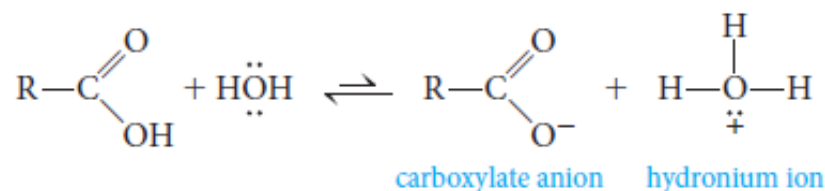


Structure	Name	Mol. Wt.	b.p. °C	Solubility in H ₂ O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH ₃ CH ₂ OH	Ethyl alcohol	46	78	Very soluble
CH ₃ COOH	Acetic acid	60	118	Very soluble
CH ₃ CH ₂ CH ₂ OH	<i>n</i> -Propyl alcohol	60	97	Very soluble
CH ₃ (CH ₂) ₃ COOH	Valeric acid	102	187	4.0 g/100 g H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

Acid Strength and Structure

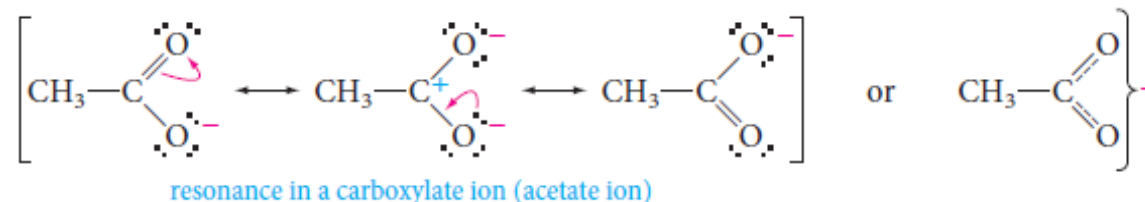
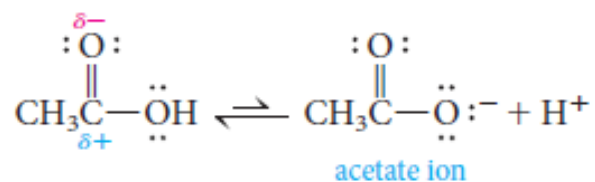
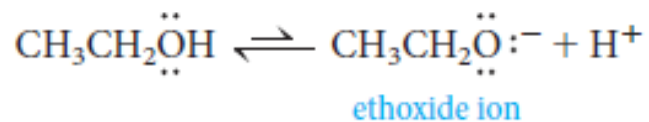


- **Carboxylic acids** (RCOOH) dissociate in water, yielding a carboxylate anion (RCOO⁻) and hydronium ion.



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**.



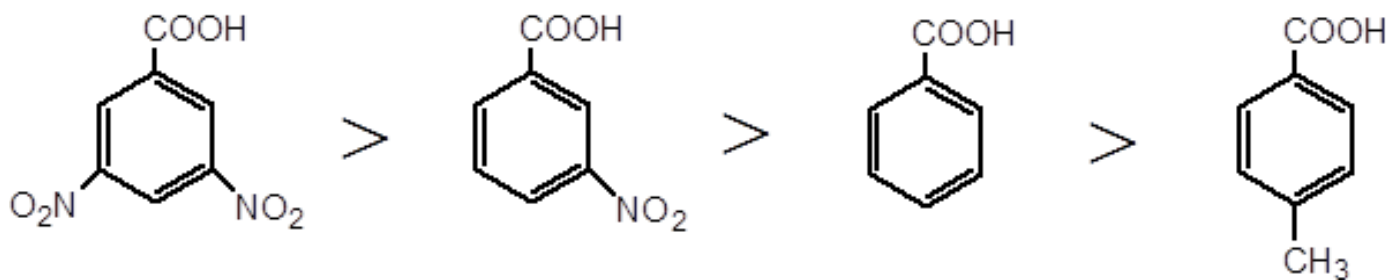
Acid Strength and Structure



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



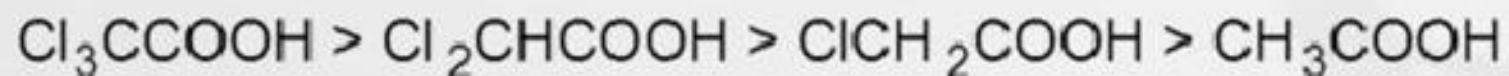
Effect of Structure on Acidity; the Inductive Effect

- **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.



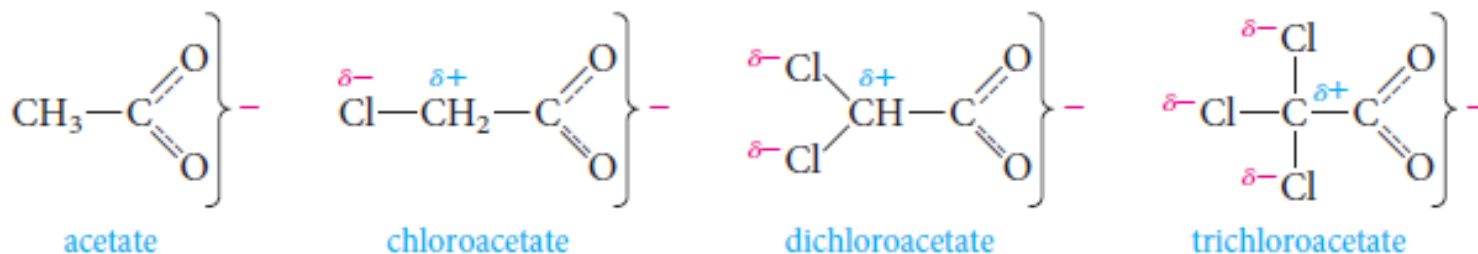
- **Example:** acetic acid with those of mono-, di-, and trichloroacetic acids.
Comparison of acid strengths of acetic Acid and chlorinated acetic acids



Acid Strength and Structure



Effect of Structure on Acidity; the Inductive Effect



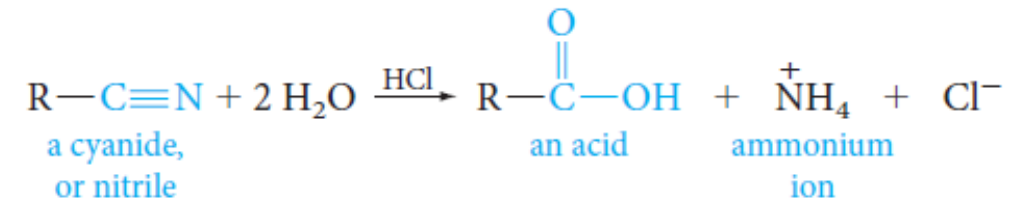
The more chlorines, the greater the effect and the greater the strength of the acid.

1) Hydrolysis of Cyanides (Nitriles)

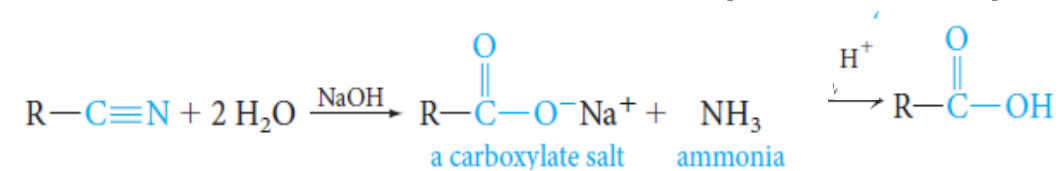
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- The reaction requires either acid or base.

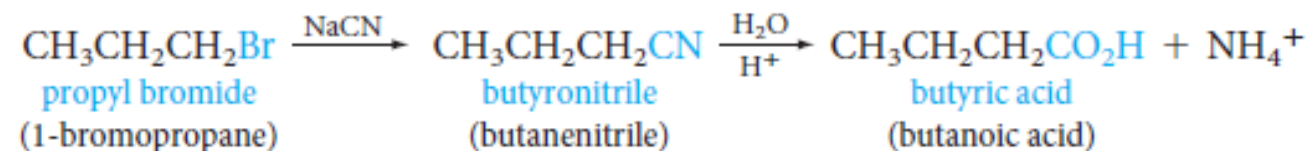
➤ **In acid**, the nitrogen atom of the cyanide is converted to an ammonium ion.



➤ **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.

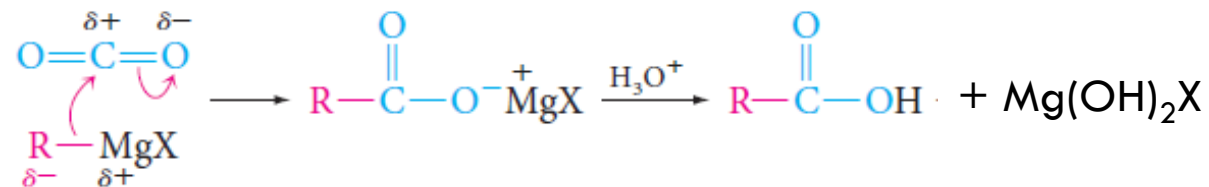


2) Reaction of Grignard Reagents with Carbon Dioxide (Carbonation of Grignard Reagent)

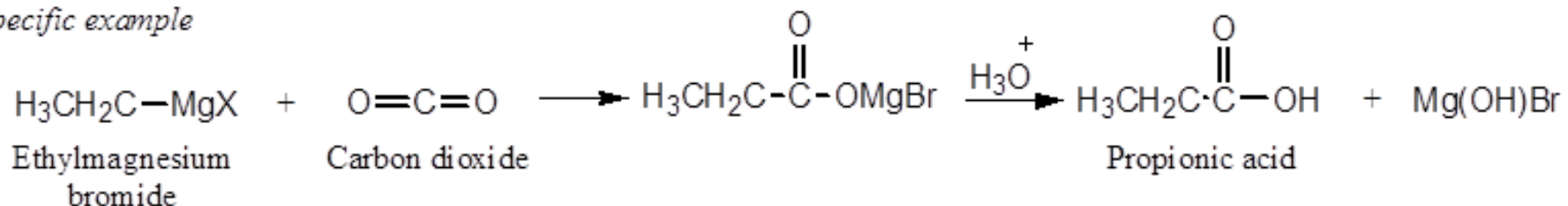
Preparation of Carboxylic Acids

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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).



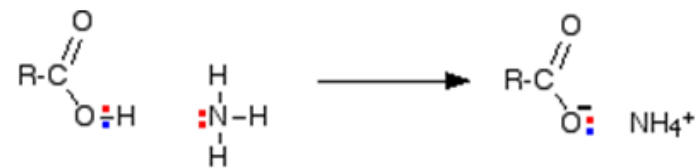
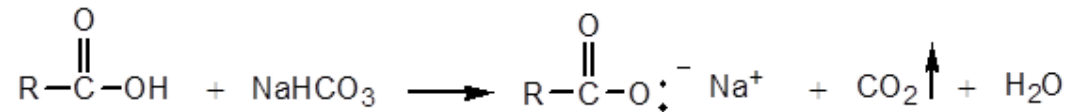
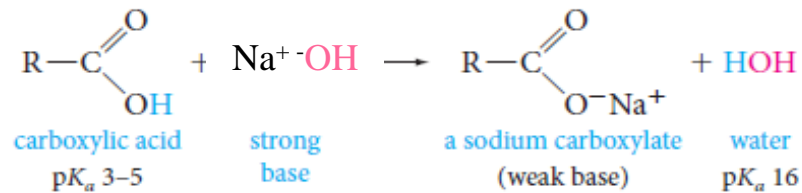
Specific example



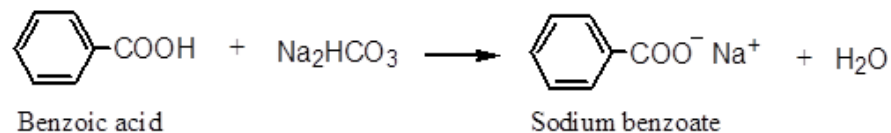
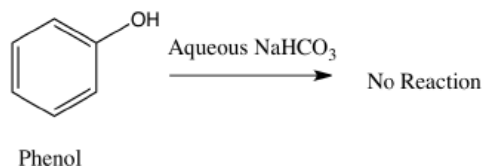
1) Reactions with Bases: Salt Formation

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

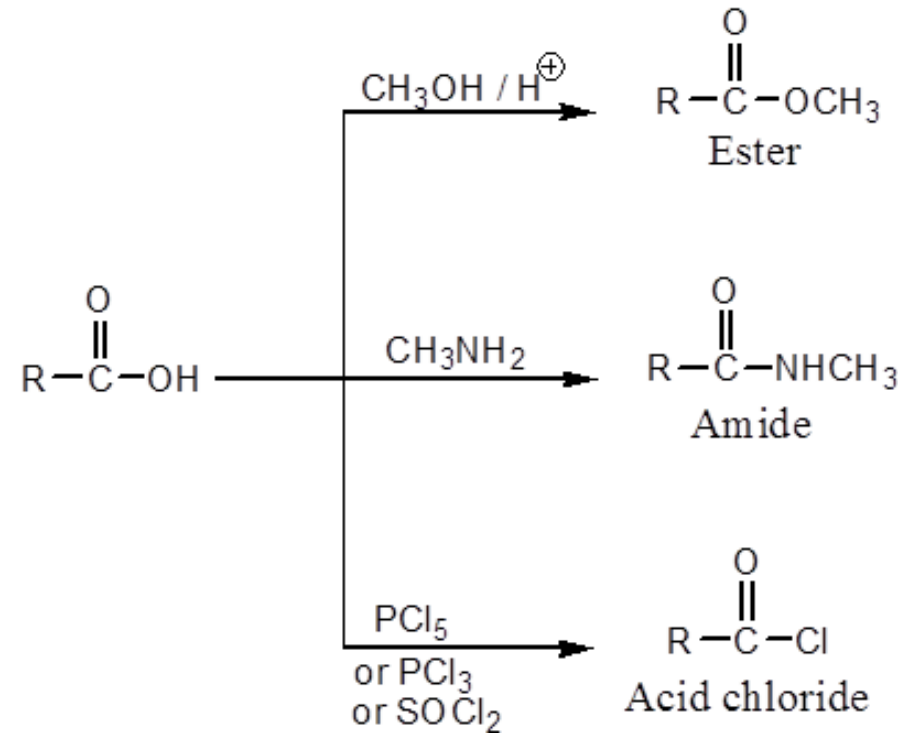
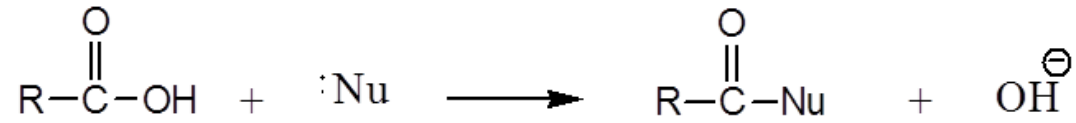


- Examples.**



2) Nucleophilic Substitution Reactions

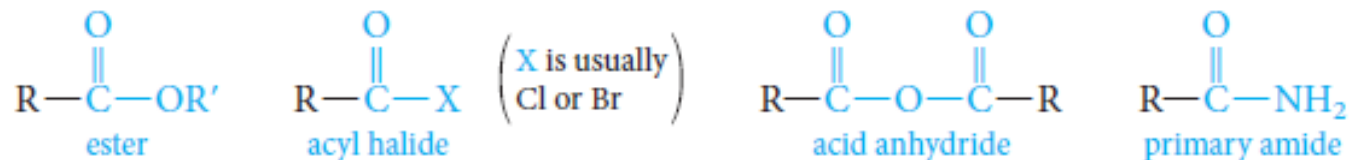
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Carboxylic Acid Derivatives



- **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.

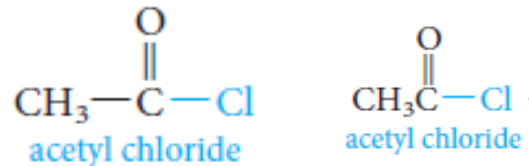
Acid derivative	HOH (hydrolysis)
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \\ \text{acyl halide} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} + \text{HCl} \end{array}$
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \\ \text{acid anhydride} \end{array}$	$2 \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \\ \text{ester} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} + \text{R}'\text{OH} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \\ \text{amide} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} + \text{NH}_3 \end{array}$
<i>Main organic product</i>	<i>acid</i>

Acid Chloride

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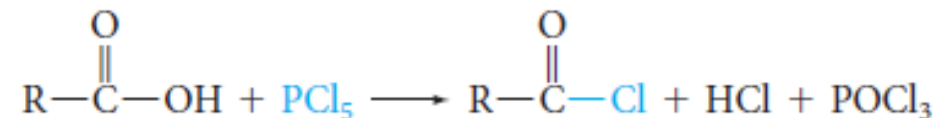
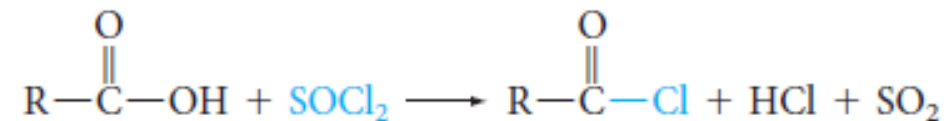
- **Acyl chlorides** have the general formula RCOCl.
- **Acyl chlorides** are more common and less expensive than bromides or iodides.
- **Nomenclature:**

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



- **Preparation:**

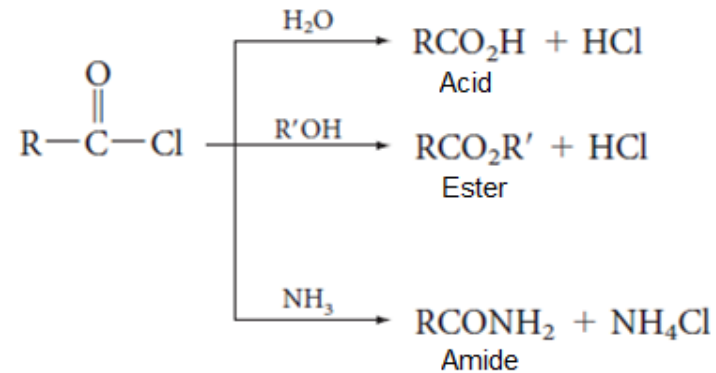
They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.



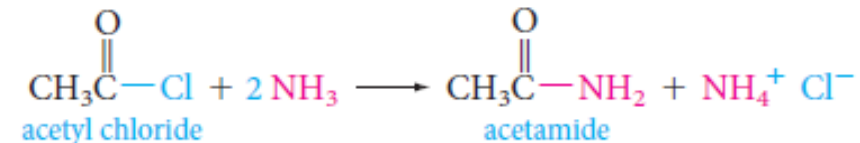
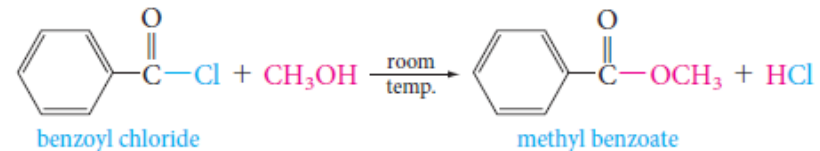
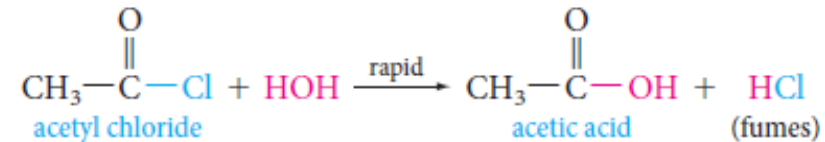
Acid Chloride

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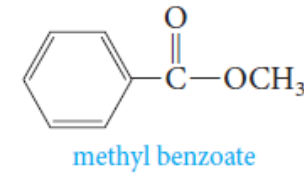
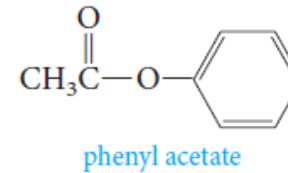
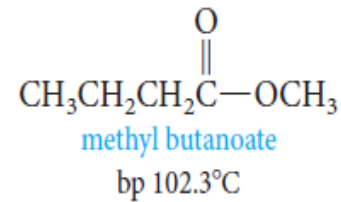
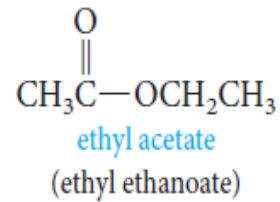
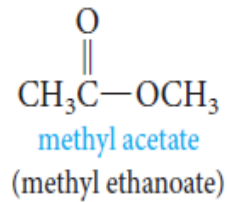
- **Reactions:** They can react rapidly with most nucleophile.



- **Examples:**

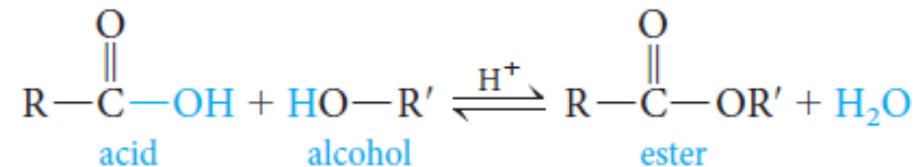


- **Esters** are derived from acids by replacing the -OH group by an -OR group and have the general formula $\text{R}'\text{COOR}$.
- **Nomenclature:**
 - They are named in a manner analogous to carboxylic acid salts.
 - The **R part of the -OR group is name first**, followed by the name of the acid, with the **-ic acid** ending changed to **-ate**.



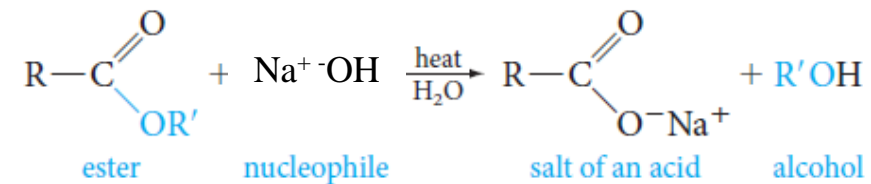
- **Preparation:**

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.

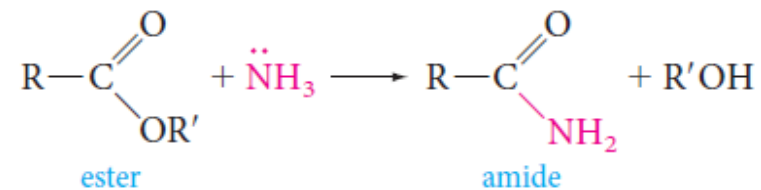


○ Reactions

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



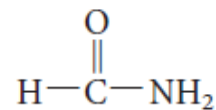
- Ammonia converts esters to **amides**.



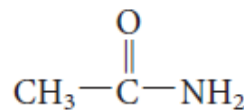
- **Amides** are the least reactive of the common carboxylic acid derivatives.
- Primary amides have general formula RCONH_2 .

➤ Nomenclature:

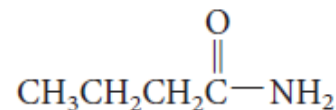
Amides are named by replacing the -oic acid ending of the acid name with the -amide ending, This will be either for the common or the IUPAC name.



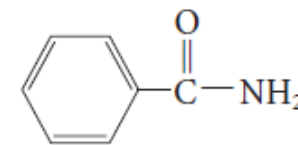
formamide
(methanamide)



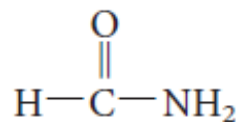
acetamide
(ethanamide)



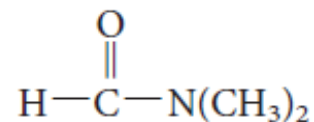
butanamide



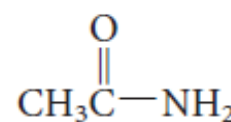
benzamide
(benzenecarboxamide)



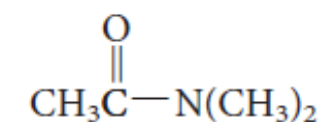
formamide



N,N-dimethylformamide



acetamide



N,N-dimethylacetamide

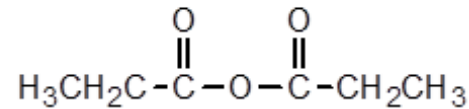
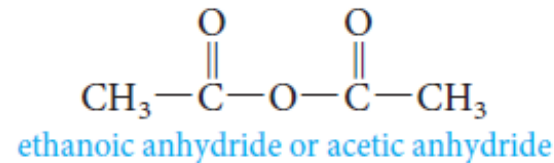
Acid Anhydrides

31

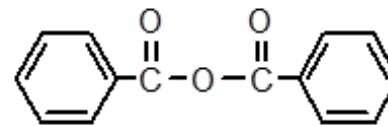
➤ **Acid anhydrides** have general formula **RCOOCOR**.

➤ **Nomenclature:**

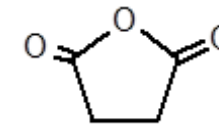
The name of an anhydride is obtained by naming the acid from which it is derived and replacing the word acid with anhydride.



IUPAC name: Propanoic anhydride
Common name: Propionic anhydride



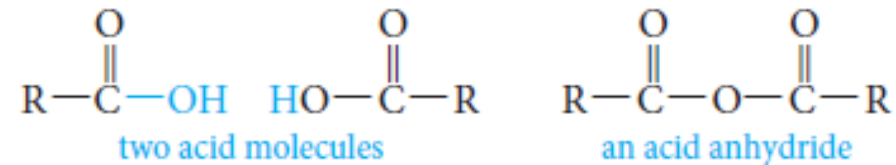
Benzoic anhydride



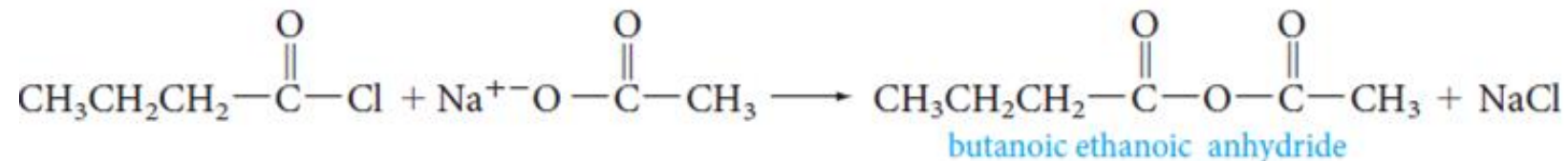
Succinic anhydride

➤ 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).*

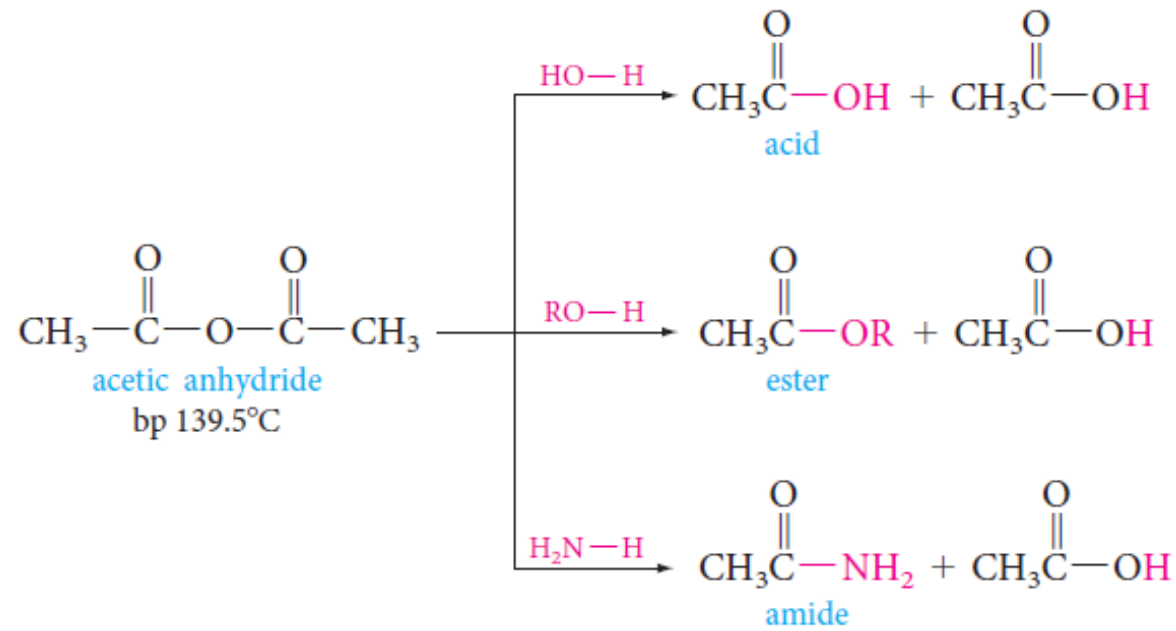


Acid Anhydrides

33

➤ Reactions

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



Uses of Carboxylic Acids

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➤ 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).