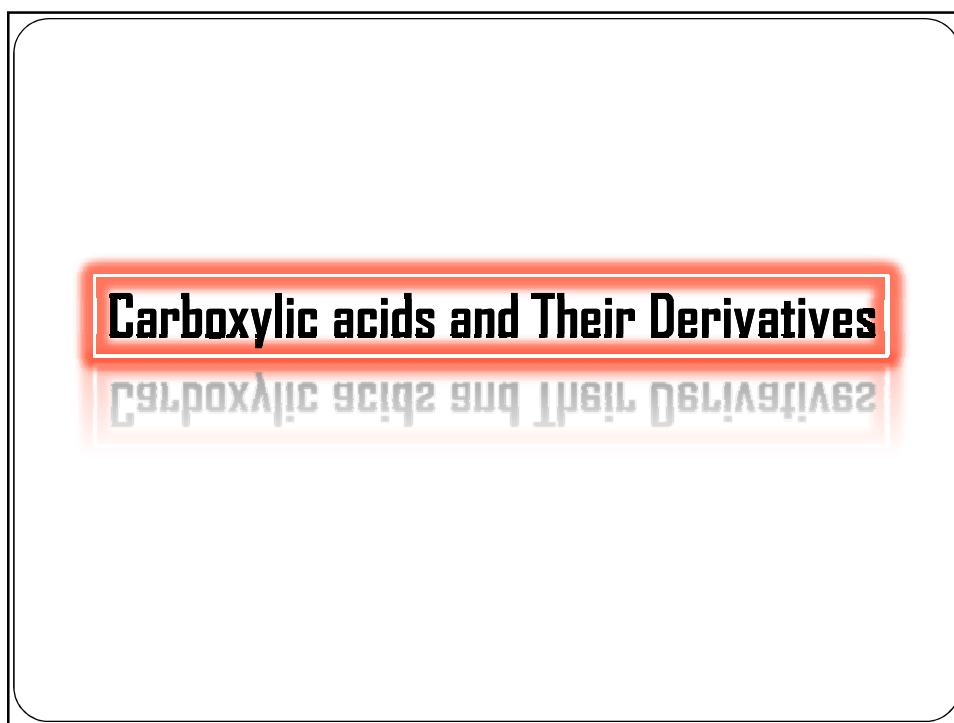


The book cover features a blue background with various chemical structures and molecular models. In the top right corner, there is a logo for King Saud University in Arabic and English. The title "Organic Chemistry" is written in a large, white, serif font on a dark blue horizontal band. Below the title, the author's name "Dr. Mohamed El-Newehy" is displayed in white on a green rectangular background. Underneath the name, the author's affiliation "Chemistry Department, College of Science, King Saud University" and a website URL "http://fac.ksu.edu.sa/melnewehy" are listed in a smaller white font.

جامعة الملك سعود
King Saud University

Organic Chemistry

By
Dr. Mohamed El-Newehy
Chemistry Department, College of Science, King Saud University
<http://fac.ksu.edu.sa/melnewehy>



The slide content is centered within a rounded rectangular frame. The title "Carboxylic acids and Their Derivatives" is presented in a bold, black, sans-serif font, enclosed in a red-bordered box. Below this, the same title is repeated in a lighter, semi-transparent font.

Carboxylic acids and Their Derivatives

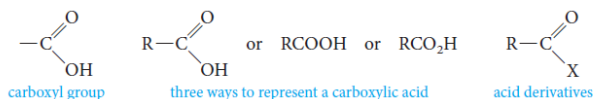
Carboxylic acids and Their Derivatives

Structure of Carboxylic Acids

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

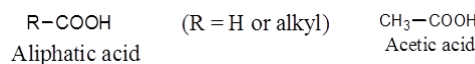
*The name is a contraction of the parts: the **carbonyl** and **hydroxyl** groups.*

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

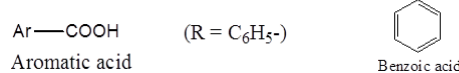


- Depending on whether an **R** or an **Ar** residue is attached to the carboxyl group; **Carboxylic acids** are classified as **aliphatic** or **aromatic**.

- **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 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.

IUPAC System

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

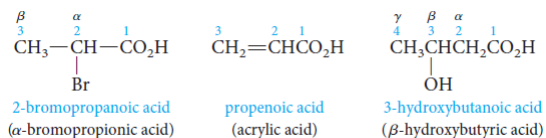
Alkane- e + oic acid = Alkanoic acid

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

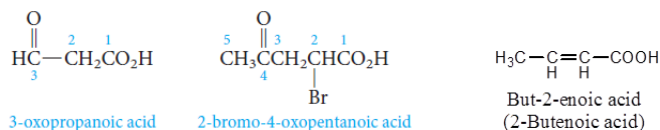
Nomenclature of Acids

Substituted acids are named in two ways;

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



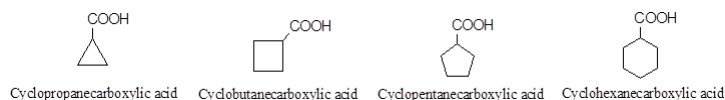
- The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming.
- The prefix *oxo-* is used to locate the carbonyl group of the aldehyde or ketone.



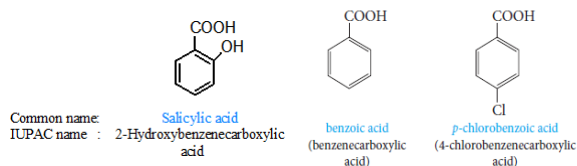
Nomenclature of Acids

- 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*)

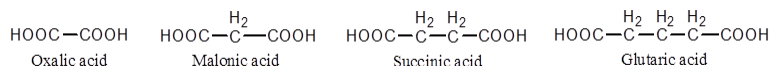


- **Aromatic acids** are named by attaching the suffix *-oic acid* or *-ic acid* to an appropriate prefix derived from the aromatic hydrocarbon.

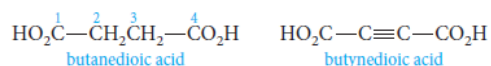


Nomenclature of Acids

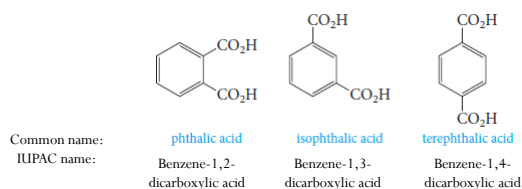
- **Dicarboxylic acids** (*acids that contain two carboxyl groups*) are known almost exclusively by their common names.



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

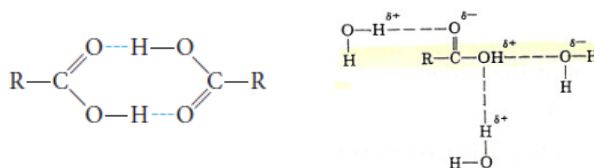


- The three **benzenedicarboxylic acids** are generally known by their common names.



Physical Properties of Acids

- 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 than 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.

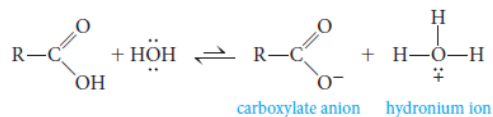
Physical Properties of Acids

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

- The first nine aliphatic acids are colorless liquids.
- Pure acetic acid is called glacial acetic acid because it solidifies into ice-like crystals at temperatures slightly below normal room temperature (about 17°C).
- Acids of five to ten carbons have goat-like smells because they are present in the skin secretion of goats.
- Higher acids are wax-like solids and are practically odorless.
- Aromatic acids are also high-melting odorless solids.

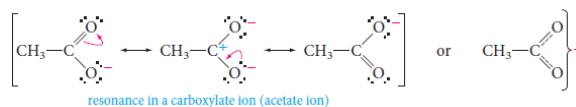
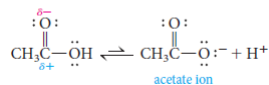
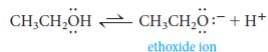
Acid Strength and Structure

- 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.

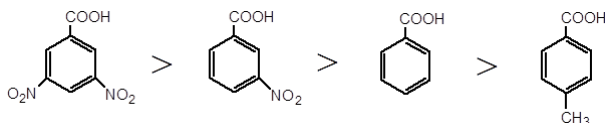


Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

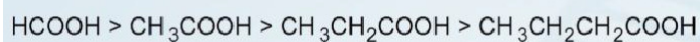
- Acidities can vary depending on what other groups are attached to the molecule.
- Recall that *electron-withdrawing groups (-I) enhance acidity, and electron-releasing groups (+I) reduce acidity.*

This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms.



- **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.

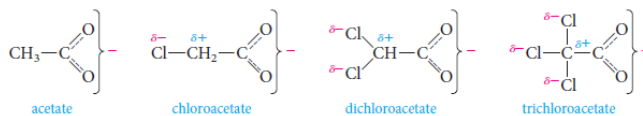


Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

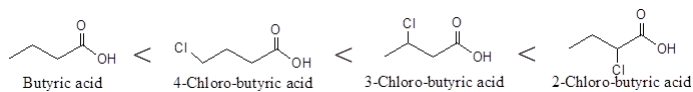
- **Example:** acetic acid with those of mono-, di-, and trichloroacetic acids.

Comparison of acid strengths of acetic acid and chlorinated acetic acids



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

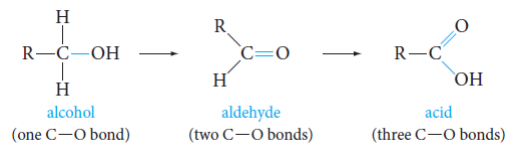
- Comparison of acid strengths of butyric acid and the monochlorinated acids.



Preparation of Acids

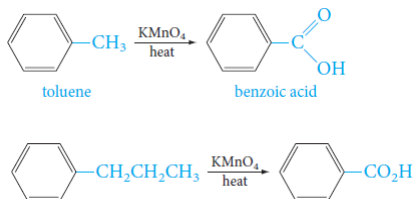
1) Oxidation of Primary Alcohols and Aldehydes

- Primary alcohols are oxidized to carboxylic acids by potassium permanganate, KMnO_4 , or by a mixture of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, and sulfuric acid.



2) Oxidation of Alkyl Benzenes

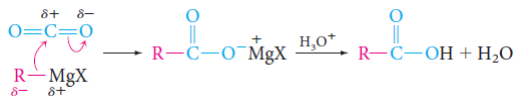
- Aromatic acids can be prepared by oxidizing an alkyl side chain on an aromatic ring.



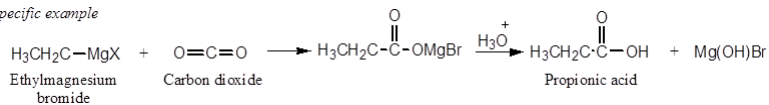
Preparation of Acids

3) 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*).



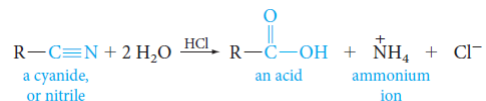
Specific example



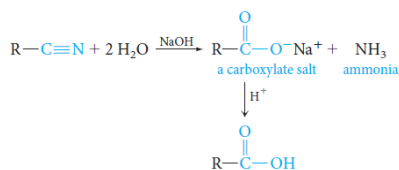
Preparation of Acids

4) Hydrolysis of Cyanides (Nitriles)

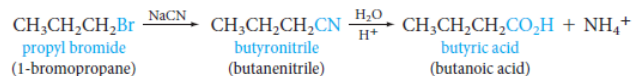
- The reaction requires either acid or base.
- **In acid**, the nitrogen atom of the cyanide is converted to an ammonium ion.



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



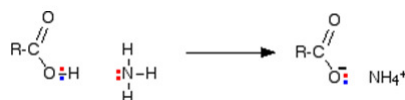
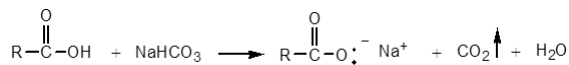
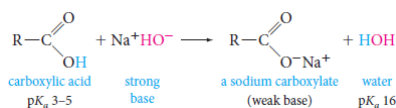
- Alkyl cyanides are generally made from the corresponding alkyl halide.



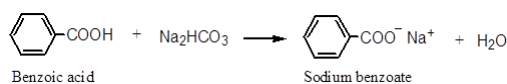
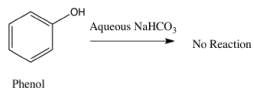
Reactions of Acids

1) Reactions with Bases: Salt Formation

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

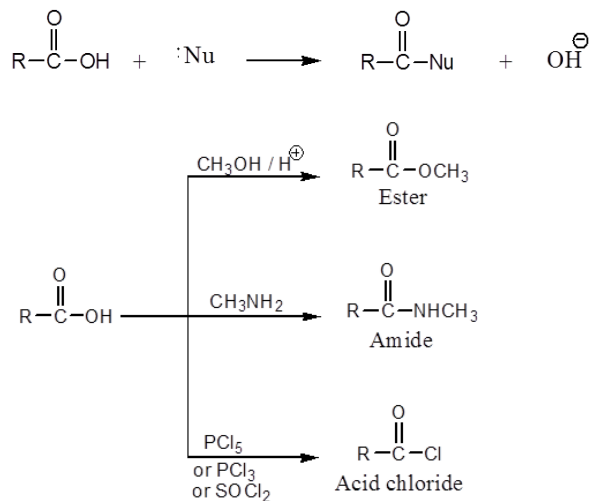


- Examples.



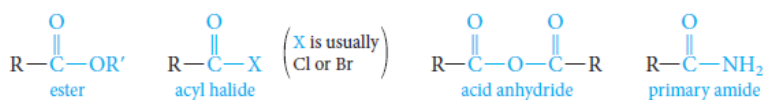
Reactions of Acids

2) Nucleophilic Substitution Reactions



Carboxylic Acid Derivatives

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



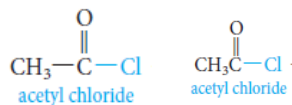
- All acid derivatives can be hydrolyzed to the corresponding carboxylic acid.

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>	acid

Carboxylic Acid Derivatives

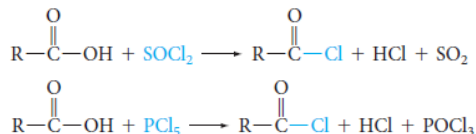
Acid Chloride

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



- Preparation:

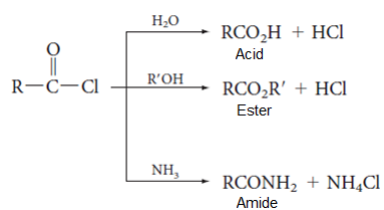
They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.



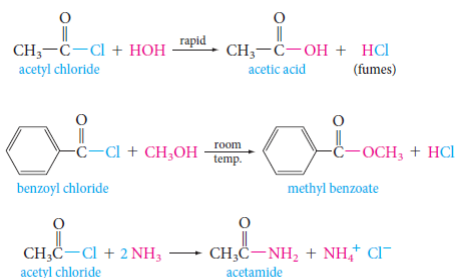
Carboxylic Acid Derivatives

Acid Chloride

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



- Examples:



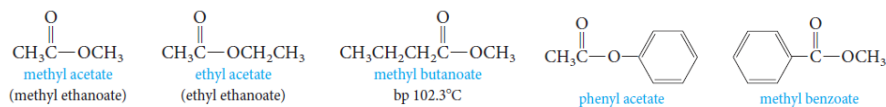
Carboxylic Acid Derivatives

Esters

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

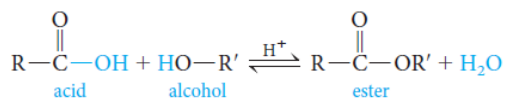
- Nomenclature:

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



- Preparation:

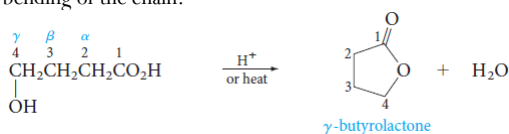
When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (HCl or H_2SO_4), an equilibrium is established with the ester and water.



Carboxylic Acid Derivatives

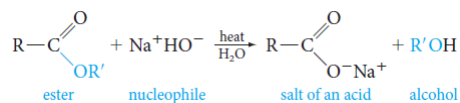
Esters

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

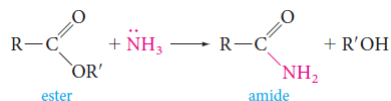


- Reactions

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



- Ammonia converts esters to amides.



Carboxylic Acid Derivatives

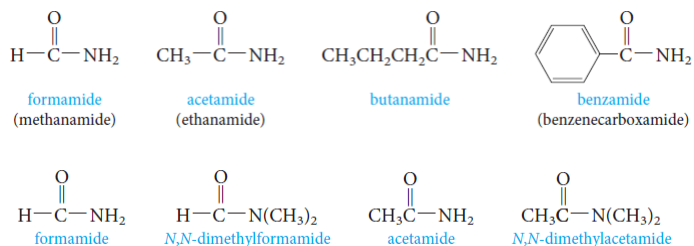
Amides

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

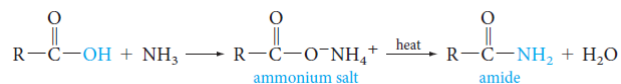


Carboxylic Acid Derivatives

Amides

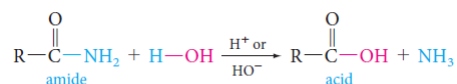
- Preparation:

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

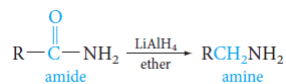


- Reactions

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



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



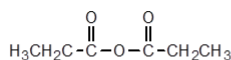
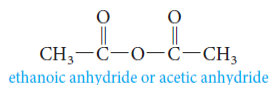
Carboxylic Acid Derivatives

Acid Anhydrides

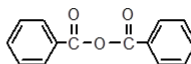
- Acid anhydrides have general formula RCOOCOR .

- Nomenclature:

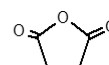
The name of an anhydride is obtained by naming the acid from which it is derived and replacing the word acid with anhydride.



IUPAC name: Propanoic anhydride
Common name: Propionic anhydride



Benzoic anhydride



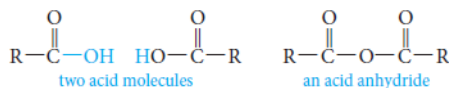
Succinic anhydride

Carboxylic Acid Derivatives

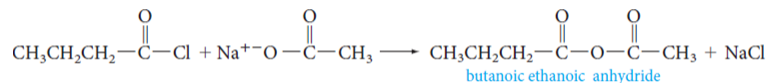
Acid Anhydrides

- 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).



Carboxylic Acid Derivatives

Acid Anhydrides

- Reactions

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

