CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

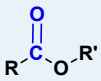
CREDIT HOURS; 4 (3+1)

Chemistry Department, College of Science, King Saud University

CHAPTER 7

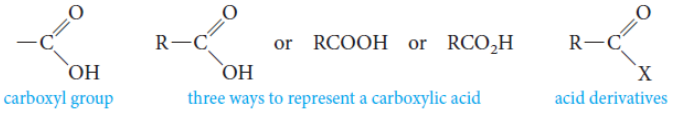
CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	

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.**

    R–COOH (R = H or alkyl) CH_3—COOH
    Aliphatic acid Acetic acid

  - **Aromatic Carboxylic Acids.**

    Ar—COOH (R = C_6H_5-)
    Aromatic acid

Benzoic acid

- **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.
- Common name, substituents are located with Greek letters, beginning with the α–carbon atom.

IUPAC System

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

Alkane- e + *oic acid = Alkanoic acid*

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

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Nomenclature of Acids

Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, *formica*)	formic acid	methanoic acid
2	CH_3COOH	vinegar (Latin, *acetum*)	acetic acid	ethanoic acid
3	CH_3CH_2COOH	milk (Greek, *protos pion*, first fat)	propionic acid	propanoic acid
4	$CH_3(CH_2)_2COOH$	butter (Latin, *butyrum*)	butyric acid	butanoic acid
5	$CH_3(CH_2)_3COOH$	valerian root (Latin, *valere*, to be strong)	valeric acid	pentanoic acid
6	$CH_3(CH_2)_4COOH$	goats (Latin, *caper*)	caproic acid	hexanoic acid
7	$CH_3(CH_2)_5COOH$	vine blossom (Greek, *oenanthe*)	enanthic acid	heptanoic acid
8	$CH_3(CH_2)_6COOH$	goats (Latin, *caper*)	caprylic acid	octanoic acid
9	$CH_3(CH_2)_7COOH$	pelargonium (an herb with stork-shaped seed capsules; Greek, *pelargos*, stork)	pelargonic acid	nonanoic acid
10	$CH_3(CH_2)_8COOH$	goats (Latin, *caper*)	capric acid	decanoic acid

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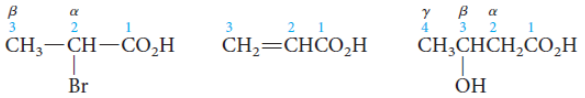
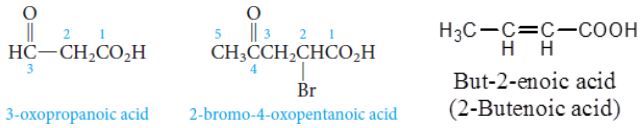
Nomenclature of Acids

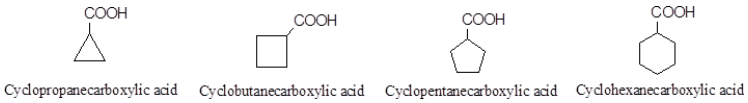


- The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming.
- The prefix *oxo-* is used to locate the carbonyl group of the aldehyde or ketone.



- **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)



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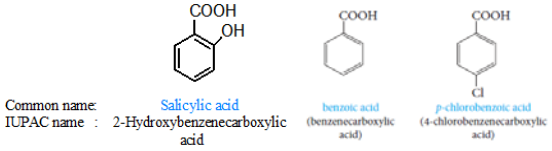
Nomenclature of Acids

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



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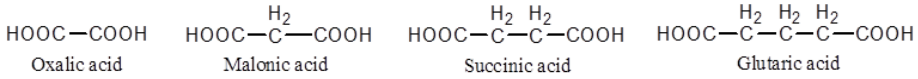
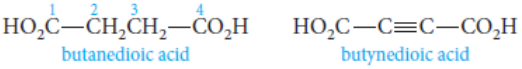
Nomenclature of Acids

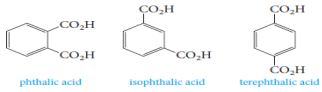
- **Dicarboxylic acids** (*acids that contain two carboxyl groups*) are known almost exclusively by their common names.



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



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



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

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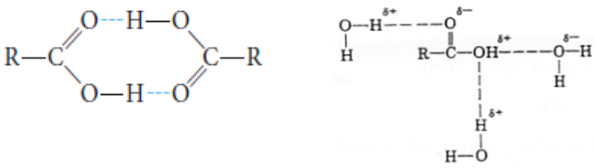
Physical Properties of Acids

- **Carboxylic acids** are polar and they form hydrogen bonds with themselves or with other molecules.
- **Carboxylic acids form dimer**, with the individual units held together by two hydrogen bonds between the electron-rich oxygens and the electron-poor hydrogens.



Boiling Points

Therefore, they have high boiling points for their molecular weights-higher even those of comparable alcohols.

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Physical Properties of Acids

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.

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

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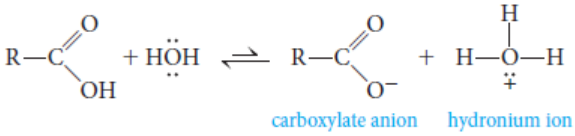
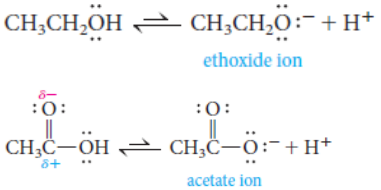
Acid Strength and Structure

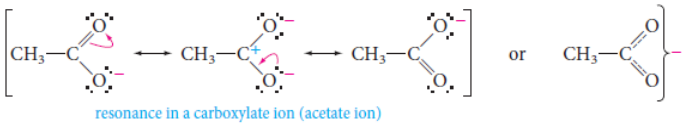
- Carboxylic acids (RCOOH) dissociate in water, yielding a carboxylate anion ($RCOO^-$) and hydronium ion.



Why Carboxylic Acids Are More Acidic Than Alcohols?

- In ethoxide ion, the negative charge is localized on a single oxygen atom.
- In acetate ion, on the other hand, the negative charge can be delocalized through resonance.





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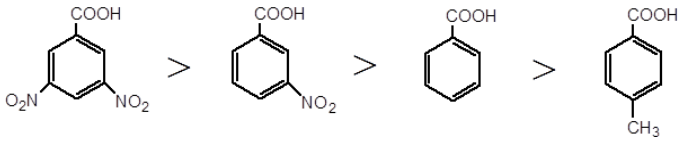
Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

- Acidities can vary depending on what other groups are attached to the molecule.
- Recall that *electron-withdrawing groups (-I) enhance acidity, and electron-releasing groups (+I) reduce acidity*.
  This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms.



- **Formic acid is a substantially stronger acid than acetic acid.**
  This suggests that the methyl group is more electron-releasing (hence anion-destabilizing and acidity-reducing) than hydrogen.

$$HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH$$

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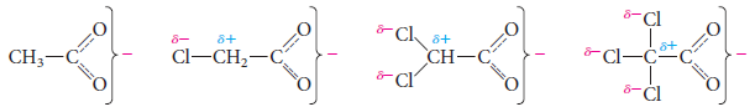
Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

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

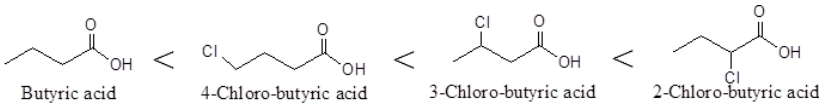
Comparison of acid strengths of acetic Acid and chlorinated acetic acids

$$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$$



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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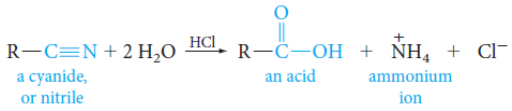
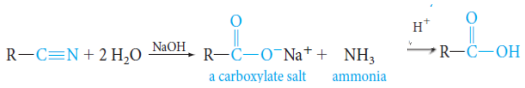
Preparation of Acids

1) Hydrolysis of Cyanides (Nitriles)

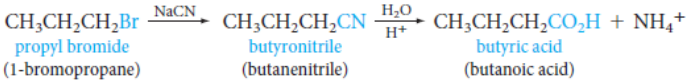
- The reaction requires either acid or base.
  - In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.



  - 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.



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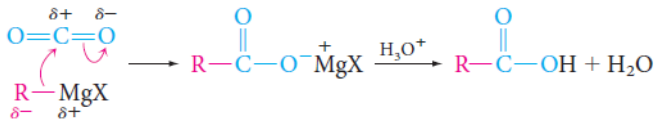
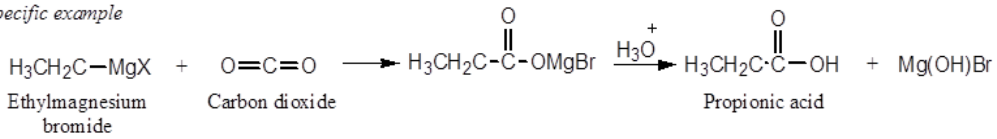
Preparation of Acids

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

- Grignard reagents add to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCl.
- The acid obtained has one more carbon atom (*the reaction provides a way to increase the length of a carbon chain*).



Specific example



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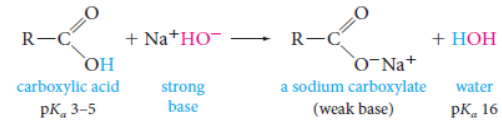
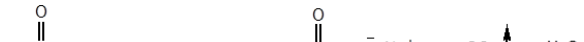
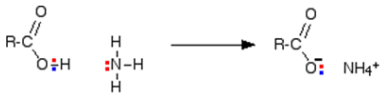
Reactions of Acids

1) Reactions with Bases: Salt Formation

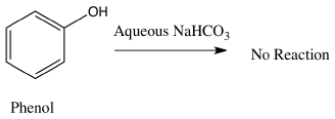
- Carboxylic acids, when treated with a strong base, form carboxylate salts.

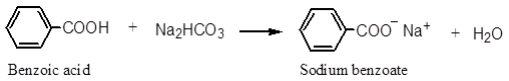






- Examples.





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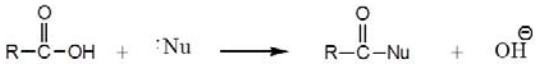
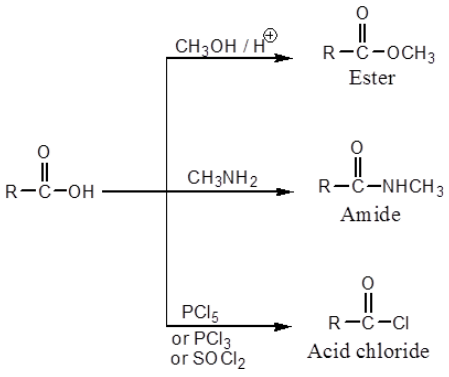
Reactions of Acids

2) Nucleophilic Substitution Reactions





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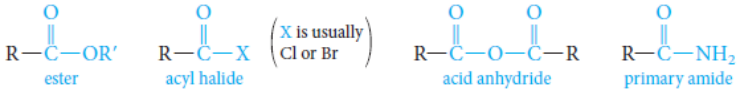
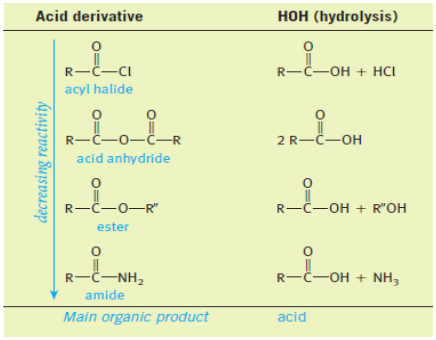
Carboxylic Acid Derivatives

- 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.



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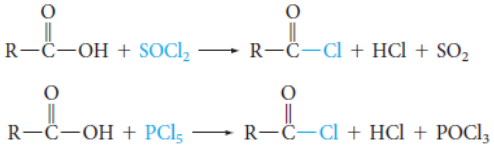
Carboxylic Acid Derivatives

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.



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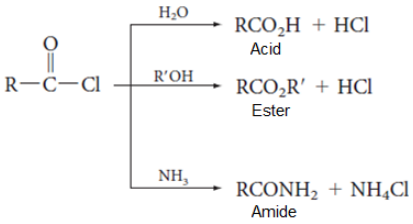
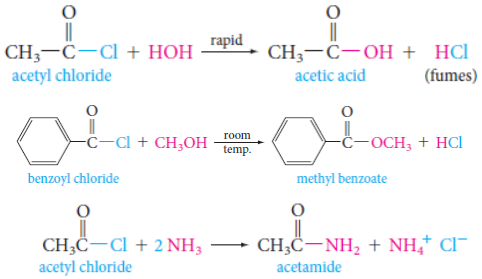
Carboxylic Acid Derivatives

Acid Chloride

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



- **Examples:**



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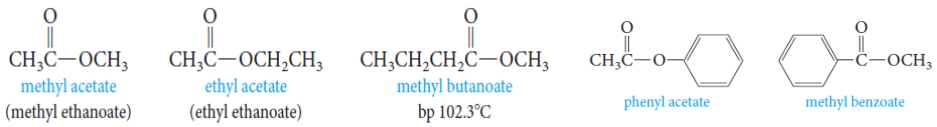
Carboxylic Acid Derivatives

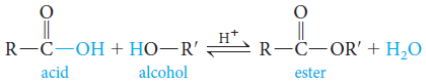
Esters

- **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.



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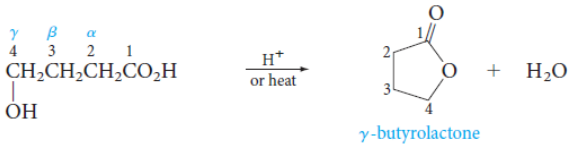
Carboxylic Acid Derivatives

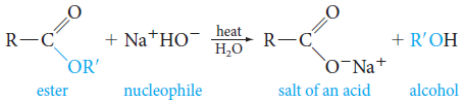
Esters

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



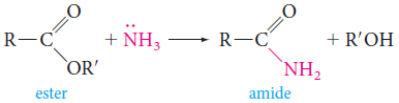
γ-butyrolactone

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



ester nucleophile salt of an acid alcohol

  - Ammonia converts esters to amides.



ester amide

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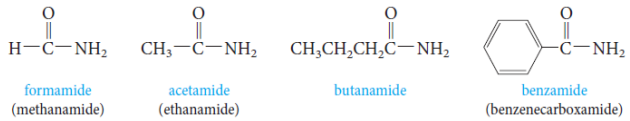
Carboxylic Acid Derivatives

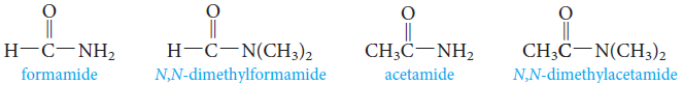
Amides

- 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.



formamide (methanamide) acetamide (ethanamide) butanamide benzamide (benzenecarboxamide)



formamide *N,N*-dimethylformamide acetamide *N,N*-dimethylacetamide

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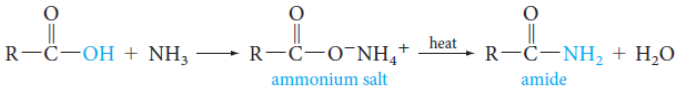
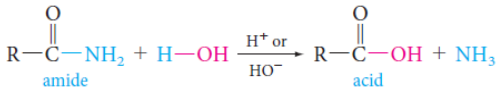
Carboxylic Acid Derivatives

Amides

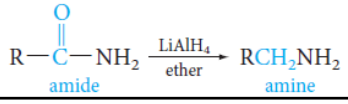
- **Preparation:**
  - They can be prepared by the reaction of ammonia with esters, with acyl halides, or with acid anhydrides.
  - Amides can also prepared by heating the ammonium salts of acids.



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



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



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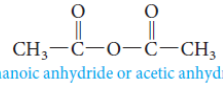
Carboxylic Acid Derivatives

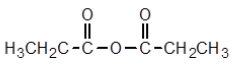
Acid Anhydrides

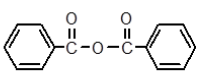
- **Acid anhydrides** have general formula RCOOCOR.
- **Nomenclature:**

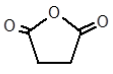
  The name of an anhydrides is obtained by naming the acid from which is derived and replacing the word acid with anhydride.



ethanoic anhydride or acetic anhydride







IUPAC name:	Propanoic anhydride	Benzoic anhydride	Succinic anhydride
Common name:	Propionic anhydride		

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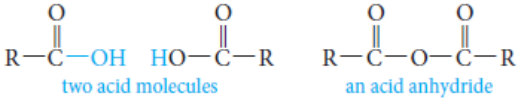
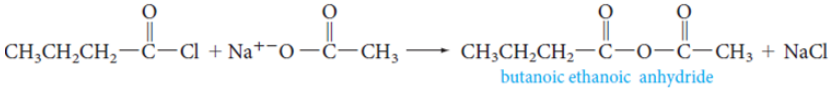
Carboxylic Acid Derivatives

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).



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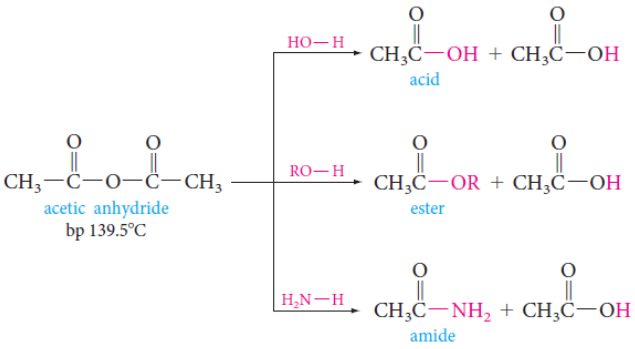
Carboxylic Acid Derivatives

Acid Anhydrides

- Reactions

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



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