

## 3.14: THE CARBOXYLIC ACID DERIVATIVES

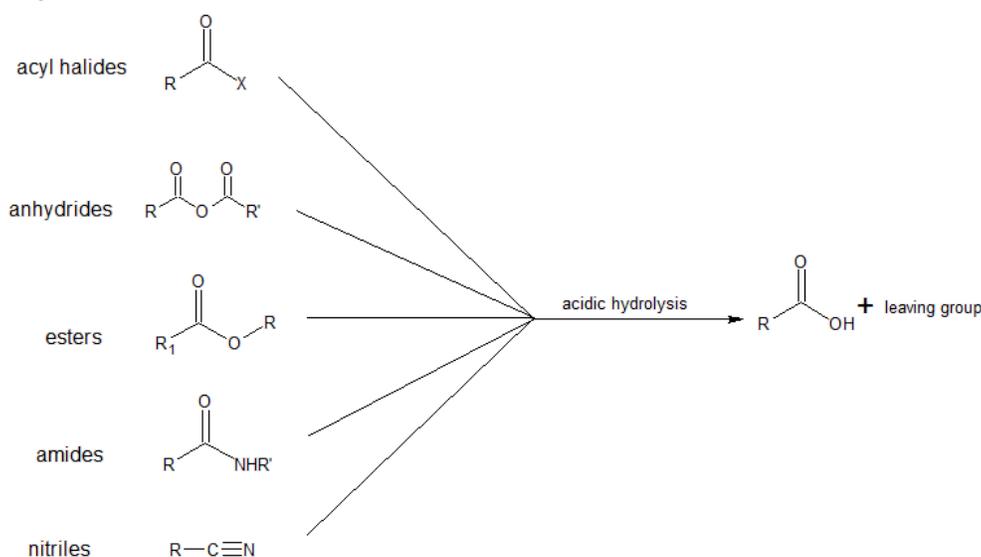
### learning objectives

- name acid halides, anhydrides, esters, amides, nitriles, and dicarboxylic acids using IUPAC (systematic) and selected common name nomenclature
- draw the structure of acid halides, anhydrides, esters, amides, and nitriles from IUPAC (systematic) and selected common names

Note: Nomenclature of thioesters and phosphoesters is also discussed. Ask the professor if this information is required for your course.

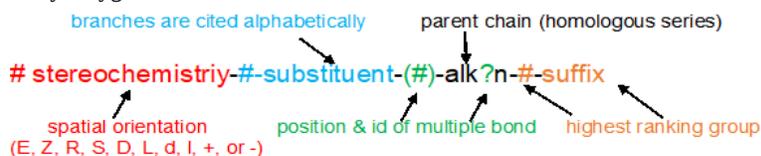
### INTRODUCTION

The important classes of organic compounds known as alcohols, phenols, ethers, amines and halides consist of alkyl and/or aryl groups bonded to hydroxyl, alkoxy, amino and halo substituents respectively. If these same functional groups are attached to an **acyl group** (RCO-) their properties are substantially changed, and they are designated as **carboxylic acid derivatives**. Carboxylic acids have a hydroxyl group bonded to an acyl group, and their functional derivatives are prepared by replacement of the hydroxyl group with substituents, such as halo, alkoxy, amino and acyloxy. The carboxylic acid derivatives can all be hydrolyzed to carboxylic acids. The specific reaction conditions are discussed in the corresponding chapter later in this text, however, the shared pattern of chemical reactivity is summarized in the diagram below.



### IUPAC NOMENCLATURE - ONE PATTERN, SO MANY VARIATIONS

Apply the IUPAC nomenclature format to carboxylic acid derivatives as summarized below using the suffix or substituent names listed in the table. Some students find esters challenging to name. Carboxylates can be described as independent ions, but require a cation to form compounds. It can be helpful to think of esters as "alkylated carboxylates": identify and name the carboxylate, this name is preceded by the alkyl group branch on the carboxyl oxygen.



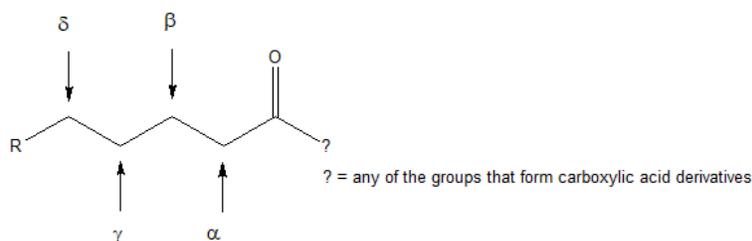
Functional Group	Structure	Suffix Name	Substituent Name
carboxylic acid		-oic acid	carboxy-
carboxylate		-oate	see above
ester		-oate	alkoxycarbonyl-
dicarboxylic acid		-dioic acid	not applicable
acyl halide		-oyl halide	not applicable
anhydride		-anhydride	not applicable
amide		-amide	amido-
nitrile		-nitrile	cyano-

### Common names

Most common names were derived from older systems of nomenclature that some may argue were "not systematic at all". However, it is helpful to note that the older systems of nomenclature were often based on shared structural features and/or chemical reactivity. Understanding the older nomenclature systems can offer insights into chemical reactivity and structural patterns. There are some common names that are so prevalent, they need to be memorized. Common names frequently exist when the group bonded to the carbonyl carbon is a methyl group (indicated with "acet" or "acetyl" in the common name) or a hydrogen atom (indicated with "formyl" or "form"). For example  $\text{CH}_3\text{C}\equiv\text{N}$  is ethanenitrile (or acetonitrile) and  $\text{HCONH}_2$  is methanamide (or formamide).

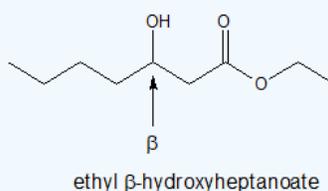


The common names for compounds with carbonyl groups often use Greek letters to specify the carbon position relative to the carbonyl carbon.



### Example

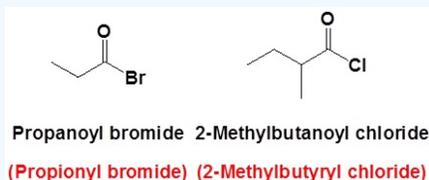
In this text, we will learn about the patterns of reactivity for compounds with for beta-hydroxy carbonyl structures like the one shown below.



## NOMENCLATURE OF ACID HALIDES

The nomenclature of acid halides starts with the name of the corresponding carboxylic acid. The **-ic acid** ending is removed and replaced with the ending **-yl** followed by the name of the halogen with an **-ide** ending. This is true for both common and IUPAC nomenclature. The carbonyl carbon is given the #1 location number. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain.

### Example

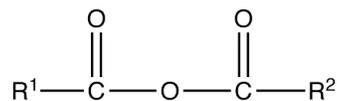


## NOMENCLATURE OF ANHYDRIDES

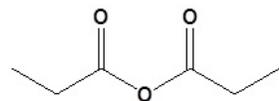
The acid anhydride functional group results when two carboxylic acids combine and lose water (anhydride = without water). Symmetrical acid anhydrides are named like carboxylic acids except the ending **-acid** is replaced with **-anhydride**. This is true for both the IUPAC and Common nomenclature.

### SYMMETRICAL ANHYDRIDES

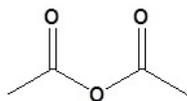
A symmetrical anhydride is a carboxylic acid anhydride that has the following general structural formula.



where  $R^1=R^2$ = hydrogen atoms, alkyl groups, aryl groups



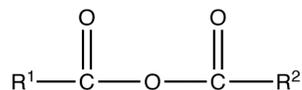
Propanoic anhydride  
 (Propionic anhydride)



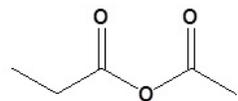
Ethanoic anhydride  
 (Acetic anhydride)

### UNSYMMETRICAL ANHYDRIDES

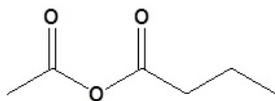
A mixed or unsymmetrical anhydride is a carboxylic acid anhydride that has the following general structural formula.



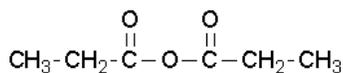
where  $R^1 \neq R^2$ , but are hydrogen atoms, alkyl groups, aryl groups. When naming unsymmetrical acid anhydrides, name both using alkanoid general method and then put the two names *alphabetically*. Hence, first name each component and alphabetically arranged them followed by spaces and then the word anhydride.



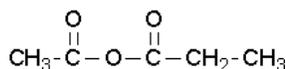
Ethanoic propanoic anhydride  
 (Acetic propionic anhydride)



Butanoic ethanoic anhydride  
 (Acetic butyric anhydride)



propanoic anhydride

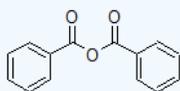


ethanoic propanoic anhydride

### Exercises

1. Draw the bond-line structure for benzoic anhydride.

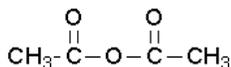
Solution:



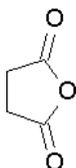
2. What is the common name for the compound below?

Solution: acetic benzoic anhydride

### COMMON ANHYDRIDE NAMES TO KNOW



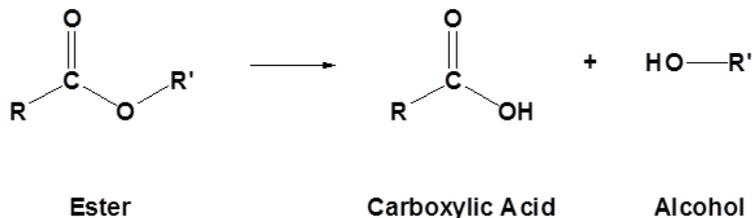
acetic anhydride (Try to name this anhydride by the proper name. J )



succinic anhydride (Try to name this anhydride by the proper name. J )

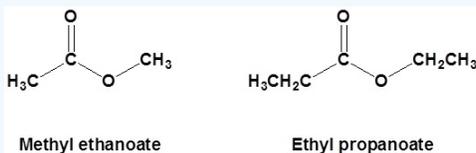
### NOMENCLATURE OF ESTERS

Esters are made from a carboxylic acid and an alcohol.



Esters are named as if the alkyl chain from the alcohol is a substituent. No number is assigned to this alkyl chain. This is followed by the name of the parent chain from the carboxylic acid part of the ester with an **-e** remove and replaced with the ending **-oate**.

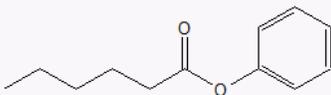
### Example



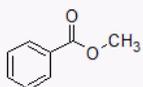
### Exercises

3. Draw the bond-line structure for phenyl hexanoate.

Solution



4. What is the IUPAC name for the compound below?



Solution

methyl benzoate

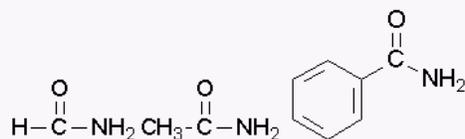
### NOMENCLATURE OF LACTONES (CYCLIC ESTERS)

Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carboxyl carbonyl group.

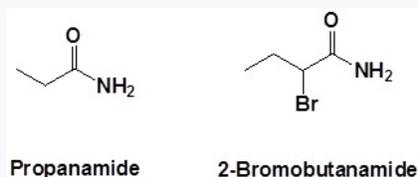
### NOMENCLATURE OF AMIDES

#### PRIMARY AMIDES

Primary amides are named by changing the name of the acid by dropping the -oic acid or -ic acid endings and adding -amide. The carbonyl carbon is given the #1 location number. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain.



methanamide or formamide (left), ethanamide or acetamide (center), benzamide (right)



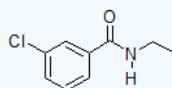
Propanamide

2-Bromobutanamide

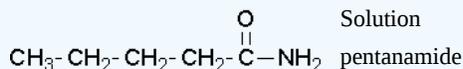
#### Exercises

5. Draw the bond-line structure for 3-chloro-N-ethylbenzamide.

Solution

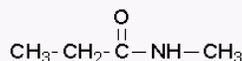


6. What is the IUPAC name the compound below?

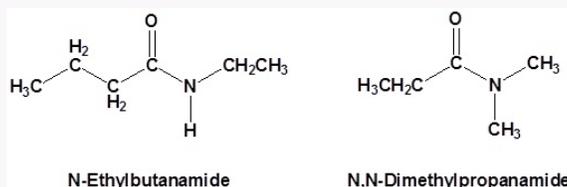


#### SECONDARY AMIDES

Secondary amides are named by using an upper case N to designate that the alkyl group is on the nitrogen atom. Alkyl groups attached to the nitrogen are named as substituents. The letter N is used to indicate they are attached to the nitrogen. Tertiary amides are named in the same way.



N-methylpropanamide



N-Ethylbutanamide

N,N-Dimethylpropanamide

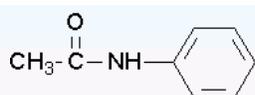
#### Exercises

7. Draw the bond-line structure for N,N-dimethylformamide.

Solution

8. What are the IUPAC and common names the compound below?

Solution



N-phenylethanamide and N-phenylacetamide, respectively

Cyclic amides are called lactams. A Greek letter identifies the location of the nitrogen on the alkyl chain relative to the carboxyl carbonyl group.



$\beta$ -lactam



$\gamma$ -lactam



$\delta$ -valerolactam

### Nomenclature of Nitriles

Name the parent alkane (include the carbon atom of the nitrile as part of the parent) followed with the word -nitrile. The carbon in the nitrile is given the #1 location position. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain. A nitrile substituent, e.g. on a ring, is named carbonitrile.

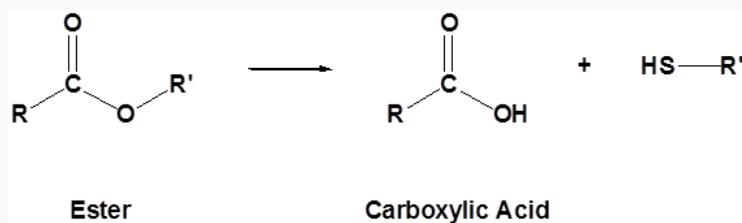
include the location number in the name because it is assumed that the functional group will be on the end of the parent chain.

### Example

(3-methylbutanenitrile (or isovaleronitrile) cyclopentanecarbonitrile

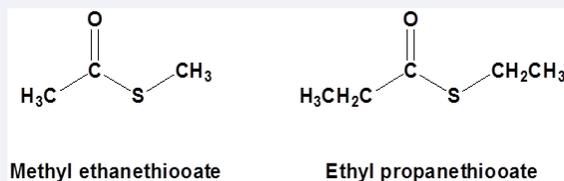
## NOMENCLATURE OF THIOESTERS

Thioesters are made from a carboxylic acid and a thiol.



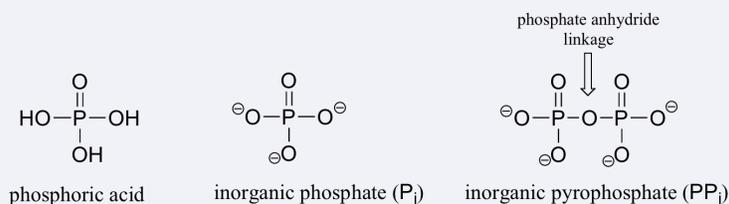
Thioesters are named as if the alkyl chain from the alcohol is a substituent. No number is assigned to this alkyl chain. This is followed by the name of the parent chain from the carboxylic acid part of the thioester named as an alkane with the ending **-thioate**.

### Example

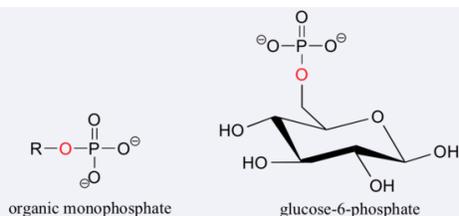


## NOMENCLATURE OF PHOSPHATES

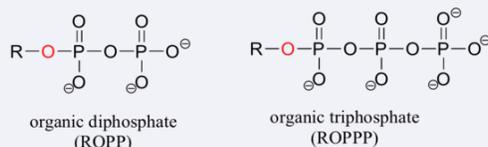
**Phosphoryl groups** are derivatives of phosphoric acid, a strong acid that is commonly used in the laboratory. The fully deprotonated conjugate base of phosphoric acid is called a phosphate ion, or inorganic phosphate (often abbreviated 'P<sub>i</sub>'). When two phosphate groups are linked to each other, the linkage is referred to as a 'phosphate anhydride', and the ion is called 'inorganic pyrophosphate' (abbreviation PP<sub>i</sub>).



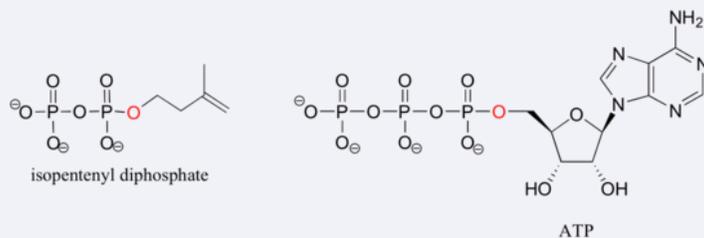
When a phosphate ion is attached to a carbon atom on an organic molecule, the chemical linkage is referred to as a phosphate ester, and the whole species is called an organic monophosphate. Glucose-6-phosphate is an example.



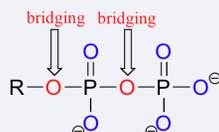
If an organic molecule is linked to two or three phosphate groups, the resulting species are called organic diphosphates and organic triphosphates.



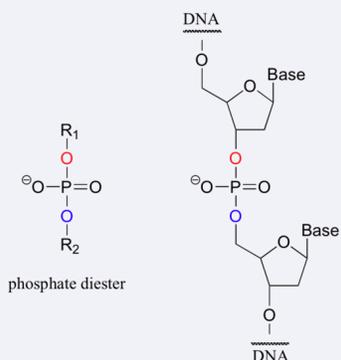
Isopentenyl diphosphate and adenosine triphosphate (ATP) are good examples:



Oxygen atoms in phosphate groups are referred to either 'bridging' and 'non-bridging', depending on their position. An organic diphosphate has two bridging and five non-bridging oxygens.

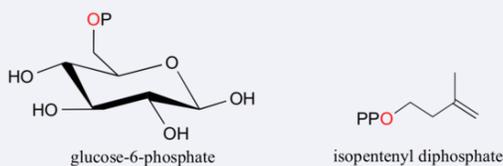


When a single phosphate is linked to two organic groups, the term 'phosphate diester' is used. The backbone of DNA is composed of phosphate diesters.



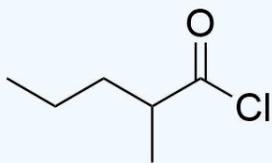
The term 'phosphoryl group' is a general way to refer to all of the phosphate-based groups mentioned in the paragraphs above.

Recall that phosphate groups on organic structures are sometimes abbreviated simply as 'P', a convention that we will use throughout this text. For example, glucose-6-phosphate and isopentenyl diphosphate are often depicted as shown below. Notice that the 'P' abbreviation includes the oxygen atoms and negative charges associated with the phosphate groups.

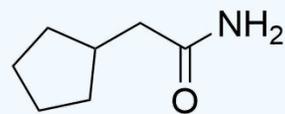


Exercise

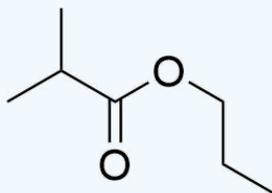
1. Name the following compounds using IUPAC conventions



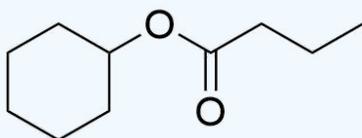
(a)



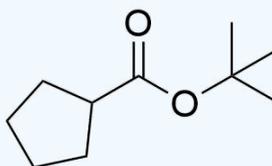
(b)



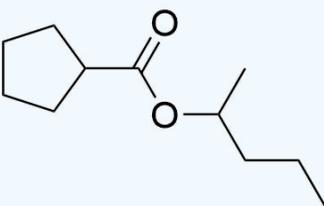
(c)



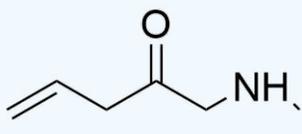
(d)



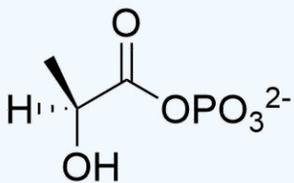
(e)



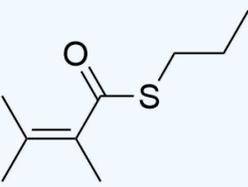
(f)



(g)



(h)



(i)

**Answer**

1.
  - a) 3-methylpentanoyl chloride
  - b) 2-cyclopentylacetamide
  - c) propyl 2-methylpropanoate
  - d) cyclohexylbutanoate
  - e) tert-butylcyclopentanecarboxylate
  - f) 1-methylbutylcyclopentane carboxylate
  - g) N-methyl-3-butenamide
  - h) (S)-2-hydroxypropanoyl phosphate
  - i) propyl 2,3-dimethyl-2-butenethioate

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