Chapter 11. Carbonyl compound I

Learning objectives:

1. Provide both IUPAC and common names carboxylic acids and acid salts.
2. Recognize the physical properties of for carboxylic acids.
3. Provide the reagent for the transformation of carboxylic acids to acyl chlorides.
4. Write the electron-pushing (arrow-pushing) mechanism for Fisher esterification.
5. Provide the names for the following compounds: acyl halides, acid anhydrides, esters and amides.
6. Write the electron-pushing (arrow-pushing) mechanisms for the nucleophilic acyl substitution of acid halide, acid anhydride, ester, and amide.
7. Explain the order of reactivity toward nucleophilic acyl substitution among acyl halide, acid anhydride, ester, and amide based on the pKa of the conjugate acid of the leaving groups on these four acid derivatives.
8. Provide appropriate reagents and reaction conditions for the interconversions among acyl halide, acid anhydride, carboxylic acid, ester, and amide.
9. Be able to describe the structures of fats, oils, and soaps, and be able to explain how detergents and surfactants work.

Sections to be covered:

11.1 Nomenclature of Carboxylic Acids and Carboxylic Acid Derivatives
11.2 Structures and Properties of Carboxylic Acids and Carboxylic Acid Derivatives
11.3 How Class I Carbonyl Compounds React
11.4 Soaps, Detergents, and Micelles
11.5 Reactions of Carboxylic Acids

11.1 Nomenclature of Carboxylic Acids and Carboxylic Acid Derivatives

- $R$: alkyl group
- $Ar$: aryl group

- carbonyl group
- acyl group
A. General Nomenclature

B. Examples

(i) Carboxylic acids

\[ \text{RCOOH} \quad \text{RCO}_2\text{H} \quad \overset{\text{+ } \text{M}^+\text{OH}^-}{\leftrightarrow} \quad \text{RCO}_2\text{O}^-\text{M}^+ \quad \overset{+ \text{H}_2\text{O}}{\leftrightarrow} \]
(ii) Acyl halides

\[ \text{acyl halide} \]

(iii) Acid anhydride and acid salts

\[ \text{acid anhydride} \]
\[ \text{acid salt} \]
(iv) Esters

\[
\text{ro} \quad \text{ro} \quad \text{ro}
\]

Cyclic esters

\[
\text{ro} \quad \text{ro}
\]

(v) Amides

\[
\text{ro} \quad \text{ro} \quad \text{ro} \quad \text{ro}
\]
Cyclic amides

C. Self-assessment Questions

- Can you provide both IUPAC and common names carboxylic acids and acid salts?
- Can you provide the names for the following compounds: acyl halides, acid anhydrides, esters and amides?
- Can you recognize the structures of lactones and lactams?
- Can you recognize the structures of acyl and carbonyl groups?

11.2 Structures and Properties of Carboxylic Acids and Carboxylic Acid Derivatives
A. Resonance of Carboxylic Acids and Carboxylic Acid Derivatives

B. Relative B.P. of Organic Molecules with Similar Molecular Weight
C. Self-assessment Questions

- Can you describe the physical properties of carboxylic acids, acyl halides, acid anhydrides, esters and amides?
- Can you provide the resonance structures of carboxylic acids, acyl halides, acid anhydrides, esters and amides?
- Can you explain the tendency of boiling point for carboxylic acids, acyl halides, acid anhydrides, esters and amides, and compare that with other functional groups?

11.3 How Class I Carbonyl Compounds React

A. Analysis of Structure

B. Class I vs. Class II Carbonyl Compounds
C. Relationship among Nucleophiles, Bases and Leaving Groups

*Know how to use the acidity (pKa) of conjugate acid as the guideline.*

D. Nucleophilic Acyl Substitution (Class I)
Know how to predict the direction of the equilibrium.

Know how to explain the tendency of pKa.
E. Relative Reactivity of Class I Carbonyl Compounds

F. Reaction of Acyl Halides

(i) Formation of acid anhydrides
Mechanism

(ii) Formation of esters and carboxylic acids
Mechanism

(iii) Formation of amides
Formation of esters vs. formation of amides

Use of $3^\circ$ amines in the formation of amides
Use of 3° amines in the formation of esters

G. Reaction of Acid Anhydrides

(i) Formation of esters and carboxylic acids
**Mechanism**

(ii) Formation of amides
Mechanism

H. Reaction of Esters

(i) Formation of esters and carboxylic acids with acid catalyst
In the presence of acid catalyst:

Mechanism
Base-promoted hydrolysis of esters, formation of carboxylate

Mechanism
Base-promoted hydrolysis of ester for soap preparation (saponification)

Trans-esterification and Biodiesel
Mechanism of Trans-esterification of Esters

(ii) Formation of amides
Mechanism

I. Reaction of Amides

(i) Formation of carboxylic acids or carboxylates
(ii) Mechanism of acid-catalyzed hydrolysis of amides

(iii) Mechanism of base-promoted hydrolysis of amides
J. Self-assessment Questions

- Can you write the electron-pushing (arrow-pushing) mechanisms for the nucleophilic acyl substitution of acyl halide, acid anhydride, ester, and amide?
- Can you explain the order of reactivity toward nucleophilic acyl substitution among acyl halide, acid anhydride, ester, and amide based on the pKa of the conjugate acid of the leaving groups on these four acid derivatives?
- Can you provide appropriate reagents and reaction conditions for the interconversions among acid halide, acid anhydride, carboxylic acid, ester, and amide?

11.4 Soaps, Detergents, and Micelles

A. Amphiphiles and Amphiphilic Compounds

B. Saponification (Making of Soap)
C. How Does Soap Work?

*Recognize amphiphilic compounds (compounds that posses both hydrophilic and lipophilic (hydrophobic) properties.)*

C. Micelles, Vesicle and Lipid Bilayer
D. Self-assessment Questions

- Can you write the electron-pushing (arrow-pushing) mechanisms for saponification?
- Can you describe the structures of fats, oils, and soaps, and be able to explain how detergents and surfactants work?
- Can you describe what are micelles, vesicle and lipid bilayer?

11.5 Reactions of Carboxylic Acids

Carboxylic acids are difficult to undergo nucleophilic addition.
A. Fisher esterification

(i) Mechanism
(ii) Artificial flavors and esters

(iii) Converting carboxylic acids into amides

C. Converting Carboxylic Acids into Acyl Chlorides

\[ \text{RCOOH} + \text{SOCl}_2 \]
D. Overview

\[
\begin{align*}
&\text{SOCl}_2, \\
&\text{PCl}_3, \\
&(\text{COCl})_2, \\
&[\text{PBr}_3]
\end{align*}
\]

\[
\begin{align*}
\text{R'}\text{CO}_2^- & \rightarrow \text{R'OH} \\
\text{R'O} & \rightarrow \text{R'O'} \\
\text{H}_2\text{NR} & \rightarrow \text{H}_2\text{NR} \\
\text{H}_2\text{SR} & \rightarrow \text{H}_2\text{SR}
\end{align*}
\]

\[
\begin{align*}
\text{P}_2\text{O}_5, \text{heating} & \rightarrow \text{OH}^- \\
\text{H}_2\text{O}, \text{H}^+, \text{heating} & \rightarrow \text{OH}^- \\
\text{H}_2\text{O}, \text{DCC} & \rightarrow \text{OH}^- \\
\text{H}_2\text{O}, \text{H}^+, \text{heating} & \rightarrow \text{OH}^-
\end{align*}
\]
E. Self-assessment Questions

- Can you provide the reagent for the transformation of carboxylic acids to acyl chlorides?
- Can you write the electron-push (arrow-pushing) mechanism for Fisher esterification?
- Can you provide appropriate reagents and reaction conditions for the interconversions among acyl halide, acid anhydride, carboxylic acid, ester, and amide?