

Chapter 17: Carbonyl Compounds I

Learning Objectives:

1. Recognize the general structures of carboxylic acids, acyl halides, acid anhydrides, esters, amides, and nitriles, and be able to assign names to simple members of these compound families.
2. Identify and be able to write the general mechanism for nucleophilic acyl substitution, and be able to judge the relative reactivities of carbonyl compounds in this reaction.
3. Identify and be able to write the mechanisms for nucleophilic substitutions of acyl halides, and esters.
4. Identify and be able to write the mechanism for the acid-catalyzed hydrolysis of an ester and of a nitrile.
5. Identify and be able to write the mechanism for the hydroxide-promoted hydrolysis of an ester.
6. Identify and be able to write the mechanisms for the acid-catalyzed and the hydroxide-promoted hydrolysis of amides.
7. Identify and be able to write the mechanism for the Fischer esterification of a carboxylic acid
8. Be able to describe the structures of fats, oils, and soaps, and be able to explain how detergents and surfactants work.
9. Be able to describe how to use chemical reagents for the desired transformation among acid derivatives.

Sections:

- 17.1 Nomenclature
- 17.2 Structures of Carboxylic Acids and Carboxylic Acid Derivatives
- 17.3 Physical Properties of Carbonyl Compounds
- 17.4 Naturally Occurring Carboxylic Acids and Carboxylic Acids Derivatives[#]
- 17.5 How Class I Carbonyl Compounds React*
- 17.6 Relative Reactivities of Carboxylic Acids and Carboxylic Acid Derivatives*
- 17.7 General Mechanism for Nucleophilic Acyl Substitution Reactions*
- 17.8 Reactions of Acyl Halides
- 17.9 Reactions of Acid Anhydrides
- 17.10 Reactions of Esters
- 17.11 Acid-Catalyzed Ester Hydrolysis*
- 17.12 Hydroxide –Ion Promoted Ester Hydrolysis*
- 17.13 Soaps, Detergents, and Micelles
- 17.14 Reactions of Carboxylic Acids
- 17.15 Reactions of Amides
- 17.16 Acid-Catalyzed Hydrolysis of Amides*
- 17.17 Hydrolysis of an Imide: The Gabriel Synthesis
- 17.18 Hydrolysis of Nitrile*
- 17.19 Designing a Synthesis IV: The Synthesis of Cyclic Compounds
- 17.20 Synthesis of Carboxylic Acid Derivatives*
- 17.21 Dicarboxylic Acids and Their Derivatives

* Sections that will be focused

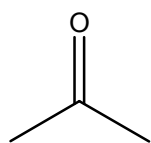
[#] Sections that will be skipped

Recommended additional problems

17.38 – 17.46, 17.49 – 17.51, 17.53-17.55, 17.64 – 17.75

Class Note

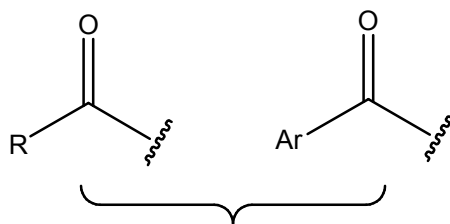
17.1 Nomenclature



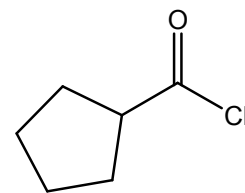
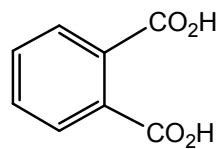
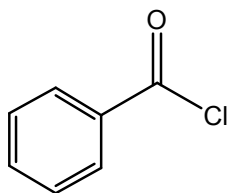
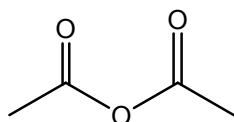
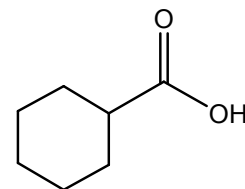
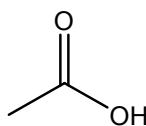
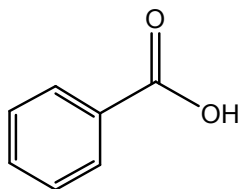
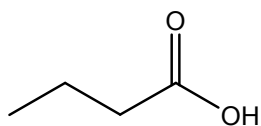
carbonyl group

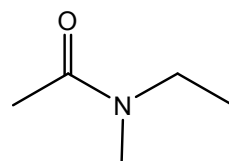
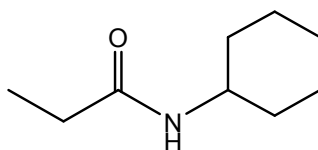
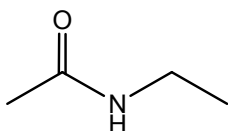
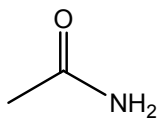
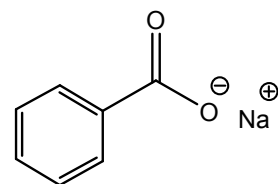
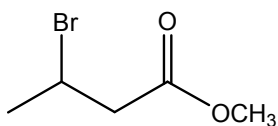
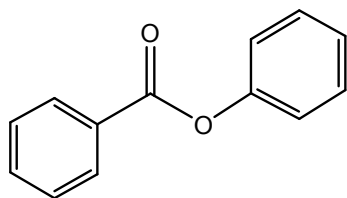
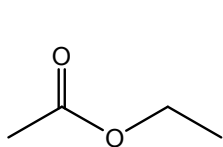
R: alkyl group

Ar: aryl group



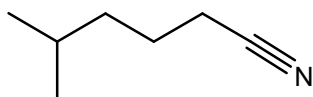
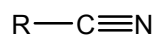
acyl group





Lactone

Lactam



17.2 Structures of Carboxylic Acids and Carboxylic Acid Derivatives

17.3 Physical Properties of Carbonyl Compounds

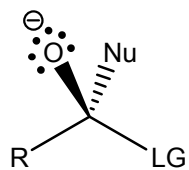
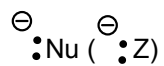
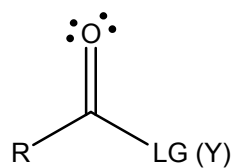
17.5 How Class I Carbonyl Compounds React, 17.6 Relative Reactivities of Carboxylic Acids and Carboxylic Acid Derivatives, and 17.7 General Mechanism for Nucleophilic Acyl Substitution Reactions

A. General mechanism

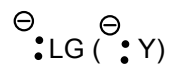
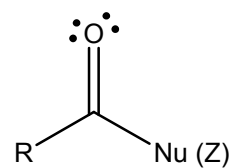
(i) Nucleophile (nucleophilicity) and leaving group

(ii) Nucleophilicity, basicity, and pK_a

(iii) Nucleophilic acyl substitution reaction (an addition-elimination reaction)

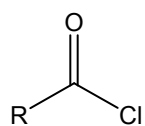


tetrahedral
intermediate

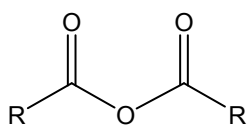


(iv) Molecular orbital view of nucleophilic acyl substitution reaction

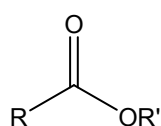
B. Relative reactivities of carboxylic acid derivatives



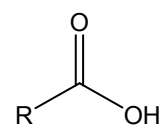
acyl chloride



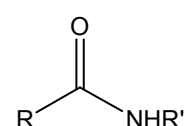
acid anhydride



ester



carboxylic acid



amide

(i) Inductive effect vs. resonance effect

(ii) Nucleophilicity, basicity, and pK_a

17.8 Reactions of Acyl Halides

A. Reactions

B. Why two equivalents of amine are needed for the formation of amide?

17.9 Reactions of Acid Anhydrides

17.10 Reactions of Esters

17.11 Acid-Catalyzed Ester Hydrolysis

17.12 Hydroxide –Ion Promoted Ester Hydrolysis

A. Comparison of hydrolysis of ester in acidic and basic conditions

B. Mechanistic studies using isotope

17.13 Soaps, Detergents, and Micelles

17.14 Reactions of Carboxylic Acids

A. Fisher esterification

B. Other reactions

17.15 Reactions of Amides and 17.16 Acid-Catalyzed Hydrolysis of Amides

17.17 Hydrolysis of an Imide: The Gabriel Synthesis

A. Gabriel synthesis

17.18 Hydrolysis of Nitrile

17.19 Designing a Synthesis IV: The Synthesis of Cyclic Compounds

17.20 Synthesis of Carboxylic Acid Derivatives

A. Use of SOCl_2 , PCl_3 , PBr_3

B. Use of P_2O_5

17.21 Dicarboxylic Acids and Their Derivatives