CHEMISTRY 263 - Section A2

Lecture Outline 4 and Assignment 4

TR 12:30-13:50 **November 2016**
Dr. J. C. Vederas **Office: W5-09A**

Assignment 4: Carboxylic Acids and Their Derivatives

Read: TWG Solomons and CB Fryhle "Organic Chemistry" 11th Edition (2014)

Functional Group List on pp 76 and
Periodic Table Inside front Cover (One page back from Inside Back Cover earlier Editions)
Relative **Strength of Acids** and Bases on Inside Front Cover - same table page 111 (page 101 9th Edition & page 105 - 8th Edition)

Chapter 17 – Carboxylic Acids and the Derivatives

Chapter 18 – Reactions at α-Carbon of Carbonyl

Chapter 23 - Lipids

Problems: do review problems, answers in "Solutions Manual for Organic Chemistry"

Chapter 17: 17.1; 17.3 to 17.6; 17.8; 17.10; 17.18; 17.19; 17.22; 17.23; 17.25; 17.26; 17.28; 17.33

Chapter 18: 18.2; 18.3; 18.15; 18.18;

Chapter 23: 23.1; 23.2; 23.3; 23.6; 23.7; 23.8; 23.9

Lecture Outline 4: Carboxylic Acids and Their Derivatives

I. Structure and Nomenclature - The Acyl Group
- A. Acids - RCOOH
- B. Acid Halides - RCOX
- C. Anhydrides - $(RCO)_2O$
- D. Esters - RCOOR'
- E. Amides - $RCONH_2$, RCONHR, $RCONR_2$

II. Carboxylic Acids
- A. Acidity and Physical Properties
- B. Preparation
  1. Oxidation of Alkenes
  2. Oxidation of Alcohols and Aldehydes
  3. Oxidation of Alkylbenzenes
  4. Oxidation of Methyl Ketones (Haloform reaction)
  5. Hydrolysis of Nitriles
  6. Carbonation of Grignard Reagents ($RMgX + CO_2$)
- C. Reactions
  1. Salt formation
  2. Ester formation
  3. Reduction

III. Acid Halides
- A. Physical Properties and Reactivity
- B. Preparation from Carboxylic Acids

III. Acid Halides (cont'd)
- C. Reactions on Carbonyl Carbon - (Nucleophilic Substitution)
  1. Hydrolysis to Carboxylic Acids
  2. Anhydride Formation with Carboxylates
  3. Alcoholysis to Esters
  4. Ammonolysis to Amides
  5. Reduction to Alcohols or Aldehydes
  6. Friedel Crafts Acylations
- D. Reaction on α-carbon - Halogenation

IV. Anhydrides
- A. Physical Properties
- B. Preparation
  1. From Acid Halides and Carboxylates
  2. Cyclic Dehydration of Diacids
- C. Reactions on Carbonyl Carbon
  1. Hydrolysis to Carboxylic Acids
  2. Alcoholysis to Ester and Acid
  3. Ammonolysis to Amide and Salt of Acid
  4. Reduction to Alcohols
  5. Friedel Crafts Acylations
- D. Reaction on α-carbon - Perkin Reaction

V. Esters
- A. Physical Properties
- B. Preparation
  1. Alcoholysis of Acid Halides
  2. Alcoholysis of Anhydrides
  3. Esterification of Carboxylic Acids
     a. Primary and Secondary ROH
     b. Tertiary ROH
     c. Lactone formation
- C. Reactions at Carbonyl Carbon
  1. Acidic Hydrolysis - Acyl - Oxygen and Alkyl - Oxygen Cleavage
  2. Alkaline Hydrolysis - Acyl - Oxygen Cleavage
  3. Transesterification with Alcohols
  4. Ammonolysis to Amide and Alcohol
  5. Reduction to Alcohols
  6. Grignard Reaction
- D. Reactions at α-carbon
  1. Ester-Ester Condensation - Claisen and Dieckmann
  2. Ester-Ketone and Ester-Aldehyde Condensation
- E. Fats, Waxes, and Soaps

VI. Amides
- A. Physical Properties
- B. Preparation
  1. Ammonolysis of Acid Halides, Anhydrides, Esters
  2. Partial Hydrolysis of Nitriles
- C. Reactions at Carbonyl Carbon
  1. Hydrolysis
  2. Reduction to Amines