

Prepared by the Department of Natural Sciences & Applied Technology

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Effective: Fall 2014

- 1. Course Number:** CHM 252 / CHM 252L  
**Course Title:** Organic Chemistry II / Organic Chemistry II Laboratory
- 2. Description:** Continues CHM 251 Organic Chemistry I. It includes nomenclature, reaction mechanisms, name reactions, synthesis, organic qualitative analysis, carbanions, oxygen and nitrogen containing functional groups, spectroscopy and biochemical processes. In the laboratory, organic qualitative analysis, synthesis and spectroscopy for organic compounds are taught. (3 class hours/ 4 laboratory hours)
- 3. Student Learning Outcomes:** Upon successful completion of this course, students are able to do the following.
  - Identify the reliable characteristic peaks when given an IR spectrum
  - Identify functional groups from IR spectra
  - Identify conjugated and strained C=O and conjugated and aromatic C=C bonds from their absorptions in the IR spectrum
  - Determine molecular weights from mass spectra
  - When given a structure, determine which protons are equivalent and which are nonequivalent; predict the number of signals and their approximate chemical shifts
  - Suggest likely types of protons when given the chemical shifts of absorptions
  - Use integral trace to determine the relative numbers of different types of protons
  - Use proton spin-spin splitting patterns to determine the structure of alkyl and other groups
  - Combine the chemical shifts, integrals, and spin-spin coupling patterns in the NMR spectrum with information from IR and mass spectra to determine the structures of organic compounds
  - Interpret the spectra of acid derivatives and use the spectral information to determine the structures
  - Demonstrate the conversion of acid derivatives by nucleophilic acyl substitution from more reactive derivatives to less reactive derivatives
  - Propose mechanisms for reactions involving acid catalysis in the synthesis of acid derivatives (e.g., Fischer esterification)
  - Propose mechanisms for the hydrolysis of acid derivative
  - Indicate the reagents used in reduction of acid derivatives, indicate the products resulting from addition of Grignard and organolithium reagents to acid derivatives; propose mechanisms for these reactions
  - Show how enols and enolate ions act as nucleophiles; give mechanisms for acid-catalyzed and base-catalyzed keto-enol tautomerisms
  - Indicate mechanisms for acid-catalyzed and base-promoted alpha halogenation of ketones and acid-catalyzed halogenation of acids
  - Predict the products of aldol and crossed aldol reactions before and after dehydration of the aldol products. Give mechanisms for the acid- and base-catalyzed reactions
  - Predict the products of Claisen and crossed Claisen condensations and propose mechanisms
  - Show how the malonic ester synthesis and the acetoacetic ester synthesis are used to make substituted acetic acids and substituted acetones; give the mechanism of the Robinson annulation and use it to form cyclohexenone ring systems
  - Recognize reactions that are enhanced by resonance stabilization of the intermediates, such as free-radical reactions and cationic reactions; draw resonance forms of the stabilized intermediates
  - Predict the products of Diels-Alder reactions; including the orientation of cycloaddition with unsymmetrical reagents and the stereochemistry of the products
  - Use values of  $\lambda_{\text{max}}$  from UV spectra to estimate the length of conjugated system, and compare compounds with similar structures
  - Use Huckel's rule to predict whether a given annulene, heterocycle, or ion will be aromatic, antiaromatic, or nonaromatic
  - Name aromatic compounds and draw their structures from the names
  - Use IR, NMR, UV, and mass spectra to determine the structures of aromatic compounds

- Predict products and propose mechanisms for the common electrophilic aromatic substitutions; halogenation; nitration; sulfonation; and Friedel-Crafts alkylation and acylation
- Draw resonance structures for the intermediates resulting from electrophilic attack on substituted aromatic ring; explain which substituents are activating and which are deactivating; show why they are ortho/para directing or meta directing
- Design syntheses that use the influence of substituents to generate the correct isomers in multisubstituted aromatic compounds
- Explain how the reactions of side chains are affected by the presence of the aromatic ring
- Predict the product of oxidation and substitution of phenols, and use the reactions in syntheses
- Name ketones and aldehydes; draw structures from their names
- Interpret IR, NMR, UV, and mass spectra of ketones and aldehydes; use spectral information to determine structures
- Write equations for syntheses of ketones and aldehydes from alcohols, alkenes, alkynes, carboxylic acids, nitriles, acid chlorides, and aromatic compounds
- Propose effective single-step and multi-step syntheses of ketones and aldehydes
- Predict the products of reactions of ketones aldehydes with the following types of compounds (give mechanisms where appropriate); hydride reducing agents (Clemmensen and Wolff-Kishner reagents); Grignard and organolithium reagents; phosphorus ylides; water; hydrogen cyanide; ammonia and primary amines; hydroxylamine and hydrazine derivatives; alcohols; oxidizing agents
- Convert ketones and aldehydes to other functional groups
- Use retrosynthetic analysis to propose effective multi-step syntheses using ketones and aldehydes as intermediates and protecting the carbonyl group if necessary
- Name amines and draw structures from names
- Interpret IR, NMR, and mass spectra amines
- Explain how the basicity of amines varies with hybridization and aromaticity
- Contrast the physical properties of amines with those of their salts
- Predict the products of reactions of amines with the following types of compounds (propose mechanisms where appropriate): ketones and aldehydes; alkyl halides and tosylates; acid chlorides; sulfonyl chlorides; nitrous acid; oxidizing agents; arylamines with electrophiles
- Give examples of the use of arenediazonium salts in diazo coupling reactions and in the synthesis of aryl chlorides, bromides, iodides, fluorides, and nitriles
- Illustrate the uses and mechanisms of the Hofmann and Cope eliminations, and predict the major products
- Name carboxylic acids and draw the structures from their names
- Show how the acidity of acids varies with their substitution
- Contrast the physical properties of carboxylic acids and their salts
- Interpret the IR, UV, NMR, and mass spectra of carboxylic acids, and use the spectral information to determine the structures
- Devise syntheses of carboxylic acids from oxidation of alcohols and aldehydes, carboxylation of Grignard reagents, hydrolysis of nitriles, and oxidation of alkylbenzenes
- Propose mechanisms for the nucleophilic acyl substitutions of carboxylic acids in their conversion to esters and amides using acid chlorides as intermediates
- Give mechanism of the Fischer esterification
- Predict the products of reactions of carboxylic acids with the following reagents and give mechanisms where appropriate; diazomethane; amines, followed by heating; lithium aluminum hydride; excess alkyllithium reagents
- Name carboxylic acid derivatives and draw structures from their names
- Compare the physical properties of acid derivatives, explaining the unusually high boiling points and melting points of amides

4. **Credits:** 5 credits

5. **Satisfies General Education Requirement:** No.

6. **Prerequisite:** Grade of C or better in CHM201 or CHM251

7. **Semester Offered:** Spring

**8. Suggested General Guidelines for Evaluation:** Course grading procedures are detailed on a student handout. In summary, grades will be based on quizzes, hourly exams, final exam, laboratory reports and notebook, and an oral laboratory final exam.

**9. General Topical Outline:**

**CHM252 Organic Chemistry II Course Outline**

A. Aromaticity - Benzene

1. Aliphatic and Aromatic Compounds
2. Structure of Benzene
3. Molecular Formula. Isomer Number. Kekulé Structure.
4. Stability of the Benzene Ring
  - a. Reactions of Benzene
  - b. Heats of Hydrogenation and Combustion
5. Carbon-Carbon Bond Lengths in Benzene
6. Resonance Structure of Benzene
7. Orbital Picture of Benzene
8. Aromatic Character. The Hückel  $4n + 2$  Rule
9. Nomenclature of Benzene Derivatives
10. Polynuclear Aromatic Hydrocarbons

B. Electrophilic Aromatic Substitution

1. Effect of Substituent Groups
  - a. Orientation
  - b. Relative Reactivity
2. Classification of Substituent Groups
3. Orientation in Disubstituted Benzenes
4. Mechanism of
  - a. Nitration
  - b. Sulfonation
  - c. Halogenation
  - d. Friedel-Crafts
    - i. Alkylation
    - ii. Acylation
5. Theory of Reactivity and Orientation
6. Electron Release via Resonance

C. Aromatic-Aliphatic Compounds - Arenes and Their Derivatives

1. The Aromatic Ring as a Substituent
2. Arenes
3. Structure and Nomenclature
4. Physical Properties
5. Preparation
  - a. Industrial
  - b. Laboratory
6. Limitations of the Friedel-Crafts Reaction
7. Reactions of Alkyl Benzenes
  - a. Oxidation
  - b. Electrophilic Aromatic Substitution
  - c. Side Chain Halogenation
8. The Benzyl Radical
9. The Benzyl Carbocation
10. Addition to Conjugated Alkylbenzenes

D. Spectroscopy and Structure

1. The Mass Spectrum
2. The Infrared Spectrum
3. The Ultraviolet and Visible Spectrum
4. The Nuclear Magnetic Resonance Spectrum
5. Interpreting Spectra

E. Aldehydes and Ketones - Nucleophilic Addition

1. Structure
2. Nomenclature
3. Physical Properties

4. Preparation
  - a. Friedel-Crafts Acylation
  - b. Organocopper Compounds
  - c. Nucleophilic Addition
  - d. Oxidation
  - e. Reduction
  
5. Reactions
  - a. Oxidation
  - b. Reduction
  - c. Addition Reactions
    - i. Cyanide
    - ii. Ammonia Derivatives
    - iii. Alcohols
    - iv. Grignard Reagents
  - d. Cannizzaro Reaction
6. Limitations of the Grignard Synthesis
7. Analysis of Aldehydes and Ketones
  - a. Iodoform Test
  - b. Periodic Oxidation
8. Spectroscopic Analysis

#### F. Carboxylic Acids

1. Structure
2. Nomenclature
3. Physical Properties
4. Salts of Carboxylic Acids
5. Preparation
  - a. Industrial
  - b. Laboratory
    - i. Oxidation
    - ii. Grignard Synthesis
    - iii. Nitrile Synthesis
6. Reactions
  - a. Acidity Constant
    - i. Ionization
    - ii. Effect of Substituents
    - iii. Strengths of Acids
  - b. Conversion to
    - i. Acid Chlorides
    - ii. Esters
    - iii. Amides
    - iv. Acid Anhydrides
  - c. Reduction
7. Halogenation of Aliphatic Acids
8. Dicarboxylic Acids
9. Analysis of Carboxylic Acids
10. Spectroscopic Analysis

#### G. Functional Derivatives of Carboxylic Acids - Nucleophilic Acyl Substitution

1. Structure
2. Nomenclature
3. Physical Properties
4. Nucleophilic Acyl Substitution - Role of the Carbonyl Group
5. Acid Chlorides
  - a. Preparation
  - b. Reactions
  - c. Conversions to Other Derivatives
6. Acid Anhydrides
  - a. Preparation
  - b. Reactions
7. Amides
  - a. Preparation
  - b. Reactions
  - c. Hydrolysis
  - d. Imides

8. Esters
  - a. Preparation
  - b. Reactions
  - c. Hydrolysis
    - i. Acidic
    - ii. Basic
  - d. Ammonolysis
  - e. Transesterification
  - f. Grignard Reactions
  - g. Reduction
9. Analysis of Carboxylic Derivatives
10. Spectroscopic Analysis

#### H. Carbanions I - Aldol and Claisen Condensations

1. Acidity of  $\alpha$ -Hydrogens
2. Reactions Involving Carbanions
3. Halogenation of Ketones
  - a. Acid Catalyzed
  - b. Base Catalyzed
4. Aldol Condensation
  - a. Dehydration of Products
  - b. Use of in Synthesis
  - c. Crossed Aldol
  - d. Similar Reactions
5. Claisen Condensation
  - a. Formation of  $\beta$ -Keto Esters
  - b. Crossed Claisen
6. Wittig Reaction

#### I. Amines I. Preparation and Physical Properties

1. Structure
2. Classification
3. Nomenclature
4. Physical Properties
5. Salts of Amines
6. Stereochemistry
7. Preparation
  - a. Industrial
  - b. Laboratory
    - i. Reduction of Nitro Compounds
    - ii. Ammonolysis of Halides
    - iii. Reductive Amination
    - iv. Hofmann Degradation of Amides
8. Synthesis of Secondary and Tertiary Amines
9. Heterocyclic Amines
10. Hofmann Rearrangement
  - a. Migration to Electron-Deficient Nitrogen
  - b. Stereochemistry at the Migrating Group
  - c. Timing of the Steps

#### J. Amines II. Reactions

1. Reactions
2. Basicity
3. Structure and Basicity
4. Effect of Substituents on Basicity of Aromatic Amines
5. Quaternary Ammonium Salts - Hofmann Elimination
6. Conversion of Amines into Substituted Amines
7. Ring Substitution in Aromatic Amines
8. Sulfonation of Aromatic Amines
9. Reactions of Amines with Nitrous Acid
10. Diazonium Salts
  - a. Preparation
  - b. Replacement by Halogen
  - c. Replacement by -CN
  - d. Replacement by -OH
  - e. Replacement by -H
11. Synthesis Using Diazonium Salts

12. Coupling and Azo Dyes
13. Analysis of Amines - Hinsberg Test
14. Analysis of Substituted Amides
15. Spectroscopic Analysis

#### K. Phenols

1. Structure and Nomenclature
2. Physical Properties
3. Salts of Phenols
4. Preparation
  - a. Industrial - Rearrangement of Hydroperoxides
    - i. Migration to Electron-Deficient Oxygen
    - ii. Migratory Aptitude
  - b. Laboratory
5. Reactions
  - a. Acidity
  - b. Ester Formation - Fries Rearrangement
  - c. Ring Substitution
  - d. Kolbe Reaction - Synthesis of Phenolic Acids
  - e. Reimer-Tiemann Reaction - Synthesis of Phenolic Aldehydes
  - f. Formation of Aryl Ethers
6. Analysis of Phenols
7. Spectroscopic Analysis

#### L. Carbanions II - Malonic Ester and Acetoacetic Ester Syntheses

1. Carbanions in Organic Synthesis
2. Malonic Ester Synthesis of Carboxylic Acids
3. Acetoacetic Ester Synthesis of Ketones
4. Decarboxylation of  $\beta$ -Keto Acids and Malonic Acids
5. Direct and Indirect Alkylation of Esters and Ketones
6. Organoborane Synthesis of Acids and Ketones
7. Alkylation of Carbonyl Compounds via Enamines

#### M. Aryl Halides - Nucleophilic Aromatic Substitution

1. Structure
2. Physical Properties
3. Preparation
4. Reactions
5. Low Reactivity of Aryl and Vinyl Halides
6. Nucleophilic Aromatic Substitution
  - a. Bimolecular Displacement
    - i. Mechanism
    - ii. Reactivity
    - iii. Orientation
    - iv. Electron Withdrawal by Resonance
    - v. Evidence for the Two Steps
  - b. Elimination-Addition Mechanism. Benzyne
7. Aliphatic vs Aromatic Nucleophilic Substitution
8. Analysis of Aryl Halides
9. Spectroscopic Analysis

#### N. $\alpha,\beta$ -Unsaturated Carbonyl Compounds - Conjugate Addition

1. Structure and Properties
2. Preparation
3. Interaction of Functional Groups
4. Electrophilic Addition
5. Nucleophilic Addition
6. The Michael Addition
7. The Diels-Alder Reaction
8. Quinones