CHEM 5110 – Organic Chemistry III
Structure, Reactivity, and Mechanism
Fall 2016

MWF 9:00–9:50, Chemistry Room 305

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Course Description

In undergraduate Organic Chemistry you learned about basic structural concepts, the major functional groups found in organic molecules, their reactivity, and the fundamental reaction mechanisms that underlie that reactivity. This basic knowledge is necessary for understanding and predicting the outcomes of all organic reactions, but often not sufficient to explain some results that are encountered in the practice of organic chemistry, for example when starting materials and products are more structurally complex or are stereochemically intricate. The goal of this course is for you to develop a more sophisticated understanding of structural and mechanistic organic chemistry that will provide a framework for understanding reaction outcomes that cannot be explained by what you already know.

Prerequisites

You are expected to have completed a standard Organic Chemistry sequence at your undergraduate institution (UVa equivalent is 2410/2420 or the 800 series). You should be comfortable with the reaction types covered in undergrad Organic and in particular their mechanisms. We will briefly review some of these reactions as necessary, however I encourage you to work on your own to ensure you are up to speed as we encounter them in class.

Molecular Modeling Kit

A molecular modeling kit (Maruzen HGS 1003A, available at the UVa bookstore) is **required** for the course. We will be using these in class and you will likely find them very helpful for problem sets and exams.

Textbooks

The following textbooks are **recommended, but optional**. Copies will be available on reserve in the Chemistry library. Supplemental reading will be assigned from these books.

F.A. Carey and R. J. Sundberg, *Advanced Organic Chemistry Part A: Structure and Mechanisms (5th edition)*

I. Fleming, *Molecular Orbitals and Organic Chemical Reactions (Student Edition)*

Primary Literature

You will be provided references to manuscripts throughout the semester and are encouraged to download and read as many of the articles as you can. While in principle you can succeed in this course by simply studying the lecture notes (which are frequently derived from the primary literature), reading these articles will provide important perspectives on the material and are vital to developing a deep comprehension.

Learning Objectives

As you progress through this course, you will:

- Master the critical thermodynamic and kinetic "toolbox" information that governs organic molecules and their reactions.
- Acquire an advanced understanding of conformational analysis and use what you learn to predict favored conformations and reaction outcomes.
- Understand the effect of molecular orbitals on the outcome of reactions and apply this knowledge to understand certain fundamental reaction types, such as pericyclic reactions and carbonyl additions.
- Acquire strategies to propose reasonable mechanisms for even the most complex organic reactions, including those that occur stereoselectively.

Problem Sets

Problem sets will be periodically assigned. These will not be collected, but I highly encourage you to work through them in a timely fashion. Concepts will be introduced in lecture, but only by practicing their application will you gain the depth of understanding necessary to pass the exams (and to apply the concepts in your research and future careers). Detailed solutions will be posted on Collab, but not right away so as to give you some time to work the problems without the temptation to just looks at the answer. You may collaborate on the problem sets. Do not use SciFinder, Reaxys, or consult the literature to find the answers, unless specifically directed to do so.

Exams

Midterm I: 30% of grade (tentatively 9/28)
Midterm II: 30% of grade (tentatively 11/2)
Final Exam: 40% of grade (12/10, 2-5 pm in Chem 305)

Academic Integrity

All students are expected to abide by UVa's Honor Code. In this course, this especially pertains to the use of only allowed materials for help on problem sets and exams.

Course Outline (General overview: deviations may ensue)

I. Fundamentals: Bonding, Electronic Structure, Thermodynamics, and Kinetics

- Review of bonding and hybridization
- Molecular orbitals
- Carbocations
- Aromaticity

- Reaction types; Bond enthalpies and pKa
- Fundamental mechanistic concepts
- Kinetic vs. thermodynamic control
- Diastereoselective and enantioselective reactions
- Universal effects governing chemical reactions
- MO explanations for some fundamental reaction types

II. Conformational analysis
- Acyclic compounds
- Cyclic compounds
- The anomeric effect
- Stereoelectronic effects for acyclic compounds
- Nucleophilic addition to π bonds (cyclic substrates)
- π-Cation cyclizations

III. Pericyclic Reactions
- Types of pericyclic reactions
- Woodward-Hoffman rules
- Frontier Molecular Orbital theory
- The Diels-Alder reaction
- [2+2] Cycloadditions
- Cope and Claisen rearrangements

IV. Carbonyl Chemistry
- Enolate formation
- Alkylation
- Aldol reactions
- Additions to chiral aldehydes and ketones
- Olefinations