

SYLLABUS
CHEM 395-003/ CHEM 420-001

Advanced Organic Chemistry: Rearrangements, Structure, & Mechanisms

Fall Semester, 2010

Mon. & Wed., 5:30 to 6:45 p.m., FH-105

Instructors: J. Babler and D. Crumrine

Textbook: None required, but suggested readings can be found in the following texts: Organic Chemistry: An Intermediate Text, 2nd Edition, by R.V. Hoffman (available at the bookstore); and March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 6th Edition, by M.B. Smith and J. March.

Prerequisites: Elementary aliphatic and aromatic organic chemistry

Examinations: Both of the instructors will give an exam (each worth 100 points) after presenting his segment of the course. The first of these exams (covering acids and bases, as well as rearrangements) is tentatively scheduled for Wednesday, Oct. 13. The second exam will be administered in late November/ early December. There will be no comprehensive final exam for this course.

Content: The topics to be covered are as follows:

Part I of the course:

- (a) Acids and Bases: The topics in Smith and March's textbook that are presented in chapter 8 (pp. 356-394) on acid-base theories: e.g., hard and soft acid-base theory; the effects of structure on the strengths of acids and bases; and the effects of the solvent on acid and base strength. [Note: A more succinct discussion of acid-base theories can be found in Hoffman's textbook, chapter 3 (pp.47-68).] Other topics to be discussed are "non-ionic organic superbases" and the development of Lewis acid catalysts for selective organic reactions in aqueous media.
- (b) A brief review of transition-state theory, along with the types of intermediates generated during organic reactions [discussed in detail in Chapter 5 of Smith and March's textbook; as well as in Chapter 4 (pp. 69-85) and part of Chapter 5 (pp. 86-99) in Hoffman's textbook].
- (c) A variety of "name reactions" extensively used in organic chemistry that are classified as "polar rearrangements" will be surveyed from a mechanistic as well as a synthetic viewpoint. To expose students to as many diverse mechanisms as possible, the rearrangements selected will illustrate all types of intermediates one might encounter in rate-determining steps including carbenes and nitrenes. Depending on how much lecture time is available, a brief discussion of "pericyclic rearrangements", in which a reactant is converted to a product without intervention of a reactive intermediate, will be presented. More specifically, sigmatropic and electrocyclic reactions involve rearrangements that proceed via pericyclic mechanisms (i.e. concerted

processes with cyclic transition states). Since they are not classified as rearrangements there will be no discussion of another class of pericyclic reactions --- cycloadditions [e.g., the Diels-Alder reaction and 1,3-dipolar cycloadditions which you can read about, if you wish, in Chapter 10 (pp. 312-323) of Hoffman's textbook]. Note: An exhaustive survey of both polar and pericyclic rearrangements can be found in chapter 18 of Smith and March's textbook.

Part II of the course (tentatively scheduled to begin on Monday, Oct. 18) will cover topics such as chemical bonding; various types of reaction mechanisms and how electronic, structural, and stereochemical results bear on these mechanisms; linear free energy relationships; and solvent effects.