

Chemistry 675
Advanced Organic Chemistry
Fall Semester 2009

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Office hours: by appointment
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Lectures: MWF 10:40-11:35 am
Room: 200 LSB
Credits: 3
Prereq: 1 yr each, elem. org. and phys. chem.

Book: Anslyn & Dougherty (A&D), *Modern Physical Organic Chemistry* (required)
Sponsler, Anslyn, and Dougherty, *Student Solutions Manual* (required)

Supporting texts are on reserve at the Science and Technology Library: Lowry and Richardson, *Mechanism and Theory in Organic Chemistry*; Carey and Sundberg, *Advanced Organic Chemistry, Part A* (the most recent edition is available electronically: http://www.knovel.com/web/portal/basic_search/display?_EXT_KNOVEL_DISPLAY_bo okid=2053); Carroll, *Perspectives on Structure and Mechanism in Organic Chemistry*; and Miller, *Advanced Organic Chemistry: Reactions and Mechanisms*. These texts present some of the same material from a somewhat different perspective. Collman, Hegedus, Norton, and Finke, *Principles and Applications of Organotransition Metal Chemistry* is a supporting text for A&D Ch 12.

Course Description: Chemistry 675 is a graduate-level organic chemistry course that may be continued in the Spring Semester as Chemistry 685 (Organic Mechanisms). The sequence, which could also be called Physical Organic Chemistry, deals with the structure and reactivity of organic species in more detail than undergraduate-level organic chemistry. Chemistry 675 will begin with an introduction/review of bonding concepts, structure, and energetics. Experimental methods for probing mechanisms will then be surveyed. Other topics will include mechanistic organometallic chemistry, theoretical calculation methods, pericyclic reactions, photochemistry, and electronic organic materials.

Learning Outcomes: After completing this course, a student should

- Understand the structure of organic molecules and intermediates on multiple levels (bonding theory, conformational flexibility, sources of strain, reactivity, etc.) and be able to predict various issues relating to geometry and energetics.
- Be able to suggest reasonable mechanistic pathways for some types of organic reactions.
- Be able to interpret results from a variety of mechanistic experiments.
- Be able to devise experiments that address particular mechanistic issues.
- Recognize the value of physical organic methods to other areas of chemistry, including theoretical understanding, synthetic efforts, design of various materials, and organometallic chemistry.

Academic Honesty: Complete academic honesty is expected of all students. Any incidence of academic dishonesty, as defined by the SU Academic Integrity Policy (see <http://academicintegrity.syr.edu>), will result in both course sanctions and formal notification of the College of Arts & Sciences. In this course, students are allowed and encouraged to work and study together, but all assignments turned in must be the work of

the individual student and may not be copied from another student's work, the text, or any other source, except for short quotations with proper attribution. Realize that plagiarism does not necessarily mean copying word-for-word but also applies to unattributed use of ideas. If you are unsure, check <http://www.plagiarism.org/>.

Reading Assignments: The A&D textbook assignments listed on the syllabus are required reading; you will be responsible for this material on the exams. Additional required reading may be given in the form of handouts. Literature references given in class are offered so that interested students can follow up, but these are not required readings. The exams will cover required readings and lectures.

Literature Reports: One literature report will be required, due Friday, November 6. The report should be 1000-1500 words (about 3-5 pages, double spaced, no longer!), typed, on the topic of a recent (2009) paper or communication. Select a paper that has new data (not a review) about a novel organic structure or an organic reaction mechanism. The report should very briefly summarize the experiments done; however, most of the report should describe two or three other experiments that could be done to verify and/or extend the results. A copy of the paper should be attached to the report. If you are in doubt about the appropriateness of a particular paper for the assignment, get prior approval from me. The purpose of this report is to give you the opportunity to apply the course material to actual research that is being done. Grading will be based upon the viability of the proposed experiments to provide the desired information, and conciseness (ability to clearly describe in a short space the experiments and the information to be obtained).

Office Hours: My schedule is erratic enough this semester that to avoid having to announce multiple cancellations I am doing office hours by appointment. Please feel free to make an appointment by email. You are also welcome to just stop by my office or lab to see if I am there.

Grading: Four examinations will be given in the normal class period, and the average of the four test scores will represent 75% of the final grade. The literature report will count for 10%. Problem sets (handed out one week before due) will be graded and will account for the remaining 15%. No final examination will be given. Examinations will principally test understanding of the material and problem-solving ability.

Exam dates: Friday, September 25 No makeup exams will be given.
 Wednesday, October 21
 Wednesday, November 18
 Monday, December 14

Disability Accommodation: Students who may need academic accommodations due to a disability are encouraged to discuss their needs with the instructor at the beginning of the semester. In order to obtain authorized accommodations, students should be registered with the Office of Disability Services (ODS), 804 University Avenue, Room 309, 315-443-4498 and have an updated accommodation letter for the instructor. Accommodations and related support services such as exam administration are not provided retroactively and must be requested in advance.

Course Calendar (approximate): Reading (C&S)

Aug.	31	Bonding concepts	Ch 1
Sept.	2	Polarity and resonance	
	4	Molecular Orbital Theory, group orbitals	
	7 <i>No class (Labor Day)</i>	
	9	Reactive intermediates; inorganic bonding	
	11	Strain and stability; bond dissociation energies; energy surfaces	Ch 2
	14	Group increments; thermochemistry of reactive intermediates	
	16	Conformational analysis	
	18	Ring conformational analysis, electronic effects	
	21 <i>No class (Eid Ul-Fitr)</i>	
	23	Highly strained molecules, molecular mechanics	
	25 First Examination	
	28 <i>No class (Yom Kippur)</i>	
	30	Energy surfaces, transition state theory	Ch 7
Oct.	2	Kinetic analysis and experiments	
	5	Kinetics and mechanisms; kinetic methods	
	7	Calculating rate constants; multiple reaction coordinates	
	9	Isotope effects	Ch 8
	12	Substituent effects; Hammett plots	
	14	Other linear free energy relationships; acid-base effects	
	16	Basis of LFERs; mechanistic experiments	
	19	Mechanistic experiments	
	21 Second Examination	

	23	Stereochemistry vocabulary; Basics of organometallic complexes	6 to 6.1.1, Ch 12
	26	Ligand exchange, oxidative addition, reductive elimination	
	28	α - and β -elimination, migratory insertion, addition to ligands	
	30	Electronic structure theory; calculational methods	Ch 14
Nov.	2	SCF theory; secular determinants; semi-empirical methods; DFT	
	4	Hückel MO theory; perturbation theory	
	6	MO insights	Literature report due
	9	Pericyclic reactions; [2+2] and [4+2] cycloadditions	Ch 15
	11	More cycloadditions	
	13	Electrocyclic reactions; sigmatropic reactions	
	16	Chelotropic reactions	
	18 Third Examination	
	20	Photochemistry; photophysical processes	Ch. 16
	23	Bimolecular photophysical processes	
	25 <i>No class (Thanksgiving Vacation)</i>	
	27 <i>No class (Thanksgiving Vacation)</i>	
	30	Photochemistry of alkenes	
Dec.	2	Photochemistry of aldehydes and ketones; elimination of N ₂	
	4	Chemiluminescence; singlet oxygen	
	7	Electronic organic materials	Ch. 17
	9	Conducting polymers; magnetic materials	
	11	Superconductivity; non-linear optics; photoresists	
	14 Fourth Examination	