

Clemson University

Organic Chemistry: **CH 822**

SEMESTER II, SPRING 2008

Lectures: Times 9:05-9:55 MWF, Hunter 470. Office hours by arrangement.
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Students are expected to wait for 15 minutes before leaving if the instructor fails to appear on time. There is no formal **Attendance Policy**, but examination questions will be taken from classroom lectures, and classroom participation counts toward the final grade.

Course Objectives: It is the objective of this course to acquaint the student with the enormous volume of knowledge and information necessary to successfully carry out organic reactions in the laboratory, and to integrate that knowledge with guiding and organizing principles and concepts. To this end, the course will utilize lecture delivered content via instructor expertise and breath of knowledge coupled to student self study revolving around assigned reading, homework problems, homework quizzes, and independent student reading as required to achieve mastery. It is the aim of the course to help students develop their own protocol for navigating back-and-forth between theory and experiment, concept and detail in a seamless pattern of reiteration.

Textbook: Francis A. Carey and Richard J. Sundberg, "Advanced Organic Chemistry, Part B: Reactions and Synthesis", 3rd Ed., Plenum Press, New York, N.Y., 1983 (required). In addition to this textbook, students will be responsible for specified chapters in "Organic Reactions". Lecture material will be taken from the above sources as well as additional texts, monographs, review articles, and original research papers. It is to be understood that at the 800 level, the student is expected to acquire a working understanding of the subject material irrespective of the level presented in the assigned textbooks or the lecture. The student is expected to engage in additional reading which should not be limited to sources listed by the instructor. The textbook and lecture presentations represent a minimum level of understanding expected in this course.

Examinations: There will be two-hour exams (50% of grade), and a final exam (25% of the final grade). The final exam will be cumulative. A passing grade of B will be given for performance at a first year graduate level which is interpreted to mean sufficient knowledge of organic reactions and mechanisms so that the student could readily choose reactions and reagents to carry-out short synthetic sequences for the preparation of starting materials that an advisor might suggest for a research project.

Work below an acceptable level for a graduate student will receive a grade of C or lower.

Grades:

Grades will be determined by examinations (75%), assigned "electron pushing" mechanistic problems (10%), responses to in class questions (up to 5% extra credit), handed in summaries for 10 chapters (5%) in the textbook (5) and *Organic Reactions* (5), and by a proposed synthesis of an organic target molecule (10%). Handed in homework will measure the class's dedication and hence influence the instructor's grading scale.

Assumed Knowledge:

It is assumed that students will have a working knowledge of basic stereochemistry including enantiomeric (*R,S* nomenclature, Fischer, Newman, and sawhorse projections, chirality in the absence of chiral centers) and diastereomeric (resolutions, olefins, multiple chiral centers and descriptors of relative stereochemistry, cyclic systems and chiral molecules which lack chiral centers) relationships as well as conformational analysis of mono and polycyclic cyclohexanes. It is expected that the student will have a good understanding of acid-base chemistry, organic functional groups, electronegativity, bonding and structure, valence bond theory (resonance) and molecular orbital theory as applied to the routine daily practice of organic chemistry (CH 421/621 and 821 should provide a good background). For review of these concepts consult a basic text, Part A of Cary and Sundberg, undergraduate texts, and/or notes from CH 421/621 and 821.

Academic Integrity:

"As members of the Clemson University community, we have inherited Thomas Green Clemson's vision of this institution as a "high seminary of learning." Fundamental to this vision is a mutual commitment to truthfulness, honor, and responsibility, without which we cannot earn the trust and respect of others. Furthermore, we recognize that academic dishonesty detracts from the value of a Clemson degree. Therefore, we shall not tolerate lying, cheating, or stealing in any form. In instances where academic standards may have been compromised, Clemson University has a responsibility to respond appropriately and expeditiously to charges of violations of academic integrity."

"When in the opinion of a faculty member, there is evidence that a student has committed an act of academic dishonesty, the faculty member shall make a formal written charge of academic dishonesty including a description of the misconduct, to the Dean of the Graduate School. At the same time, the faculty member may, but is not required to, inform privately the student charged of the nature of the allegation."

Disability Access:

"It is University policy to provide, on a flexible and individualized basis, reasonable accommodations to students who have disabilities. Students are encouraged to contact Student Disability Services to discuss their individual needs for accommodation."

Topics

Subject	Chapter (C&S)
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Introduction to the Forest	
Alkylation of Nucleophilic Carbon. Enolates and Enamines.....	1
Reactions of Carbon Nucleophiles with Carbonyl Groups.....	2
Functional Group Interconversion by Nucleophilic Substitution.....	3
Electrophilic Addition to Carbon-Carbon Multiple Bonds.....	4
Reduction of Carbonyl and Other Functional Groups.....	5
Organometallic Reagents (plus organocopper & Pd cpds 8.1-2).....	7
Cycloadditions and Unimolecular Rearrangements and Eliminations... .	6
Organoboron, Silicon, and Tin Chemistry.....	9
Reactions of Electron Deficient Intermediates.....	10
Oxidations.....	12
Photochemistry.....	13 (Part A)
Multistep synthesis.....	13

The material in chapters 1,2,6,7 and 9 (Part B) and chapter 13 (Part A) will be strongly emphasized in class. Chapters 5, 10, and 12 will receive little or no class coverage. Chapter 13 (Part B) will depend upon amount of time available.

IMPORTANT DATES:

First day of class	January 9
Last day students can add class	January 15
Last day to drop without a W	January 23
Last day to drop without final grade	February 29
Last day of class	April 25
Final Examination	Monday April 28 (8-11:00 a.m.)

READINGS IN ORGANIC REACTIONS FOR CH 822 (Vols > 42 at Cooper Lib.)

For each topic know the scope, mechanism and limitations.

Carbonyl Reactions

Acetoacetic Ester Synthesis	1	Tin Enolates	46
Acylation of Ketones	8	Asy Reduction	52
Aldol Condensation	16,51	[O] with hypervalent	
Directed Aldol	28	iodine reagents	54,57
Stobbe Condensation	6	TosMIC	57
With Hydrogen Cyanide	25		
Conjugate Addition of Organocuprates	19,41		
Synthesis of Cyclic Ketones	1,2,15,23		
Darzens Synthesis	5		
Organolithium Reactions with Acids	18		
Knoevenagel Reaction	1,15		
Mannich Reaction	1,7		
Michael Reaction	10,15,19,20,47		
Perkin Reaction	1		
Reformatsky	1,22		
Wittig/alkylidenations	14,20,43		

Alkene synthesis

From α -Halosulfones	25	Stille Reaction	50
From Tosylhydrazones	23,39		
From Diols	30		
Diels-Alder reaction	32,52,53		
Alkenyl & alkynylaluminum cpds	32		
Allyl & vinyl silanes	37		

Oxidations and Reductions

Meerwein-Pondorff-Verley	2	Reduction with SmI ₂	46
Oppenauer	6	Sharpless epoxidation	48
Hydroboration	13		
Baeyer-Villiger	9,43		
Birch Reduction	23, 42		
Clemmensen Reduction	1,22		
Desulfurization	12		
Homogeneous Hydrogenation	24		
Reductions of α,β -unsaturated ketones	23		
Decarboxylation with Lead Tetraacetate	19		
Wolff-Kisher	4		
Sulfide Reduction of Nitroarenes	20		
Aluminum Hydrides	34		

Miscellaenous

Arndt-Eistert	1	Baylis-Hillman	51
Curtius Rearrangement	3	Cycloadditions	49, 51
Beckmann Rearrangement	11	Anion rearrangements	43
Simmons-Smith Cyclopropanation	20,57	Selenoxide Elimination	44
Schmidt Reaction	3	Enone hv [2 +]	44

Lithiations	6,7,18,26,27,39	Nucleosides	55
Sandmeyer	2	Hydroformylations	55
Sommelet-Hauser	18	Nazarov cyclizations	45
Organoboranes & borates	32	Ketene cycloadditions	45
Pummerer reaction	40	[2,3]-Wittig	46
Palladium Catalyzed Vinylation	27	Radical cyclizations	48
Alkenyl/Alkynyl Aluminum Compounds	32	Vilsmeier	49,56
Mitsunobu Reaction	42	Aryl S _{RN} 1	54