CEM311

Advanced Organic Chemistry

Spring 2012

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Meetings: 9:30-11 AM TR. There will be no class on March 1 (midterm examination, see below). Spring Break is March 5-9. The last day of class is Tuesday, April 24.

Office hours: 10 AM-noon Monday, 10 AM-noon Wednesday, 2-4 PM Friday

Drop-ins are welcome; appointments made by telephone or E-mail messages **will** be honored subject to my posted schedule (www.bluffton.edu/~bergerd/classes/sched.html) and prior commitments.

Required Texts

Advanced Organic Chemistry: Reactions and Mechanisms, 2nd Ed. by Bernard Miller

Reserve Texts

Electron Flow in Organic Chemistry by Paul H. Scudder. This book is Dr. Berger's personal copy and will be kept in **Shoker Science Center**. This book is helpful for reviewing how to write organic reaction mechanisms.

Basic Skills for Organic Chemistry: A Toolkit by Stuart Rosenfeld. This book is Dr. Berger's personal copy and will be kept in **Shoker Science Center**. You should use this as a review text for organic chemistry.

Organic Chemistry as a Second Language, v. 1 and 2 by David R. Klein. Dr. Berger's personal copies will be kept in **Shoker Science Center**. You should use this as a review text for organic chemistry.

A Handbook of Computational Chemistry by Tim Clark. This book is Dr. Berger's personal copy and will be kept in **Shoker Science Center**. Section 3.6 of this book is an excellent, brief discussion of qualitative molecular orbital theory as presented in Miller, Section 2.3. If you are interested in more depth, get a copy of B.M. Gimarc's *Molecular Structure and Bonding: The Qualitative Molecular Orbital Approach*, or his article in *Accounts of Chemical Research*, **1974**, *7*, 384-392.

Online resources

The local web page http://www.bluffton.edu/~bergerd/classes/CEM311/ will contain or link to all online materials relevant to this course. The Moodle page will be used only as a convenient link-back point and a place to keep track of your grade, unless it becomes apparent that online discussions would be valuable. I will distribute announcements by E-mail to your Bluffton College accounts, and you are encouraged to use E-mail to ask questions.*

Prerequisite: CEM 222 (Organic Chemistry II).

* E-mail questions will be distributed to your coursemates or discussed in class. **All identifying information will be removed before distribution.**

Overview

CEM 311 will explore molecular orbital (MO) theory by considering organic reactions that require MO theory to be understood. We will discuss chemical bonding and reactivity using a variety of theoretical descriptions, and learn the fine art of proposing organic reaction mechanisms.

Your money's worth. This course is intended to be the equivalent of a 3-credit advanced course, and we will do our best to give you your money's worth and more. However, this will require a great deal of work on your part. We will schedule an extra, weekly meeting at your convenience to work on problems from the text. *Minimum* coverage will be Chapters 1 through 8, according to the schedule in this syllabus; but we will move faster if we can, because some of the most interesting material for biological chemistry is found in Chapters 10-12. *This will require that we move through the text at about a chapter per week.*

Integration of Ideas. The theories and ideas used in this course are not unique to organic chemistry. Students should notice how the ideas and techniques used in this course are useful in other courses, and how they may be useful in daily life or global citizenship. The professor will attempt to point out these connections. Students are encouraged to note them themselves, and to point out connections as they notice them. Please ask questions as they arise.

Students with disabilities, including learning disabilities, who wish to request accommodations in class, should register with the Counselor for Disability Services early in the semester. This allows time for appropriate arrangements to be made. In accordance with federal laws, students requesting special accommodations must provide documentation of their disability to the Counselor for Disability Services, Jacqui Slinger, 2nd floor College Hall, extension 3215.

Course Expectations and Grading

Examinations. Exams are worth 80% of your course grade, with the lower of your two exam scores adjusted as explained below. There will be a mid-term and a final examination, each of which will be two hours in length.[*] Reasonable efforts will be made to accommodate emergencies and other schedule problems. You are reminded that the final examination may not be rescheduled except through the Registrar's office.

March 1	**Mid-Term Examination**
May 3, 1:30 PM	**Final Examination**

Readings and problem sets. You are expected to keep up with the reading **and the text problems**. We will spend class time discussing[†] the assigned material for each day. Reading assignments and problem sets will be given at each lecture, for the following meeting. Late problem sets will **not** be accepted. Problem sets will be worth 20% of your grade. Each problem will be graded either 0 or 1, where 1 = "a reasonable attempt to solve," and selected problems will be graded on a scale from 0 = "no attempt to solve" to 4 = "correct solution." Problem sets will be returned to you at the next class session.

Attendance: Because this is NOT a lecture course, your attendance is expected at *every* class session. Failure to attend will result in your course grade being lowered by 1% for each absence beyond two.

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[*] Because the scheduled class period is 1.5 hours, you may take the mid-term during any available two-hour time block between 8:30 AM and 5:30 PM.

[†] This is **NOT** a euphemism for lecture; you are expected to participate and to be on top of the material! Obvious lack of preparation will result in your being marked absent for the day.

There is no such thing as an excused absence, so no excuses need to be made. Emergencies or extra-curricular activities requiring more than two absences will be dealt with on a case-by-case basis.

Your final grade will be assigned based on the following percentage scale:

	A (90%)	A- (85%)	B+ (80%)	B (75%)	B- (70%)
C+ (65%)	C (60%)	C- (55%)	D+ (50%)	D (45%)	D- (40%)

Academic Integrity

The Bluffton College Honor System will be followed in this course. You are expected, on your honor, to refrain from violating the Honor System. However, you are encouraged and expected to work closely with the instructor on all coursework.

Exams will be closed-book. No aids other than brains and writing implements are allowed.

Assigned problem sets are expected to represent **your own work**, although you are encouraged to consult with the instructor and with each other.

Uncontested academic dishonesty will result in the *minimum* penalty of receiving a zero for the examination, homework or project during which the infraction took place. In most cases penalties will be more severe than those for failure to complete the work. Sufficiently serious violations will result in referral to the Dean's office for further action.

Tentative schedule

The following is based on the schedule we followed in 2011, with two meetings per week.

Week of…	Chapters	Topics
January 9	1	Reaction mechanisms, acid-base reactions, nucleophiles and electrophiles, resonance, curly arrows.
January 16	2	Electrocyclic reactions. Thermal conrotatory and disrotatory ring-openings and ring-closings and the molecular-orbital explanations for them. Qualitative MO theory and bonding. Electrocyclic reactions of formally-charged species. Photochemical electrocyclic reactions.
January 23	3	Cycloaddition and cycloreversion reactions. Suprafacial and antarafacial are the same as conrotatory and disrotatory.
January 30	3	The Woodward-Hoffman rules and the MO explanation for them. Thermal and photochemical cycloadditions.
February 6	3,4	Finish Chapter 3. Chapter 4: Sigmatropic shifts (rearrangement reactions), theory and observations.
February 13	4	Sigmatropic shifts (rearrangement reactions). Theory and observations. Sigmatropic shifts in neutral and charged systems.
February 20	4,5	Finish Chapter 4. Chapter 5: Linear free-energy relationships. The Hammett Equation as a way of quantifying electron-donating and electron-withdrawing effects.
February 27	5	Catch-up and review; mid-term exam.
March 5		Spring Break
March 12	6	Migrations to electron-deficient centers as a special case of sigmatropic shifts; some migrations are "nucleophilic." Migratory aptitudes, rearrangements of carbocations, long-distance migrations, migrations to nitrogen or oxygen.
March 19	6, 7	Finish Chapter 6, begin Chapter 7
March 26	7	Neighboring group effects that stabilize carbocations; "non-classical" cations. Various phenomena associated with neighboring groups and how they can be explained.
April 2	8	Rearrangements of carbanions and free radicals. How such rearrangements can be folded into the concepts seen previously: sigmatropic shifts and electrophile/nucleophile reactions.
April 9	8,9	Finish Chapter 8; begin Chapter 9
April 16	9	Carbenes and nitrenes. How they react and how these reactions may be explained. The differences between carbenes and carbenoids.
April 23		Last day of class; catch-up
May 3		1:30 PM Final Exam

"Your money's worth" schedule

The following is a tentative schedule for covering all of Miller, at a rate of one chapter per week. This will *absolutely require* an extra meeting each week.

Week of…	Chapters	Topics
January 9	1	Reaction mechanisms, acid-base reactions, nucleophiles and electrophiles, resonance, curly arrows.
January 16	2	Electrocyclic reactions. Conrotatory and disrotatory ring-openings and ring-closings and the molecular-orbital explanations for them. Qualitative MO theory and bonding. Thermal and photochemical electrocyclic reactions.
January 23	3	Cycloaddition and cycloreversion reactions. Suprafacial and antarafacial are the same as conrotatory and disrotatory. The Woodward-Hoffman rules and the MO explanation for them. Thermal and photochemical cycloadditions.
January 30	4	Sigmatropic shifts (rearrangement reactions). Theory and observations. Sigmatropic shifts in neutral and charged systems.
February 6	5	Linear free-energy relationships: the Hammett Equation as a way of quantifying electron-donating and electron-withdrawing effects.
February 13	6	Migrations to electron-deficient centers as a special case of sigmatropic shifts; some migrations are "nucleophilic." Migratory aptitudes, rearrangements of carbocations, long-distance migrations, migrations to nitrogen or oxygen.
February 20	7	Neighboring group effects that stabilize carbocations; "non-classical" cations. Various phenomena associated with neighboring groups and how they can be explained.
February 27		Catch-up and review; mid-term exam.
March 5		Spring Break
March 12	8	Rearrangements of carbanions and free radicals. How such rearrangements can be folded into the concepts seen previously: sigmatropic shifts and electrophile/nucleophile reactions.
March 19	9	Carbenes and nitrenes. How they react and how these reactions may be explained. The differences between carbenes and carbenoids.
March 26	10	Photochemistry. The photophysical process of energy absorption. Photoreactions of carbon-carbon and carbon-oxygen double bonds.
April 2	11	Six-membered heterocyclic rings. Nomenclature and bonding in aromatic heterocycles. Reactions of pyridine and its analogs. Synthesis of six-membered heterocycles.
April 9	12	Five-membered heterocyclic rings. Aromaticity in 5-membered heterocycles. Reactions and synthesis of 5-membered heterocycles.
April 16	13	Organophosphorus and organosulfur chemistry. Conventional compounds and their properties. Hard and soft acids and bases. Oxygenated compounds of phosphorus and sulfur. Phosphorus and sulfur ylides.
April 23		Catch-up and review. There is only one scheduled meeting, but we may schedule a meeting on Friday, April 27, at your convenience.
May 4		1:30 PM Final Exam