

**Lycoming College**

**Chem 440  
Advanced Organic Chemistry**

**Fall 2014**

Course description - This course is designed to further your understanding of modern organic chemistry. The laboratory component of the class is meant as an introduction to typical experiments within the discipline.

Instructor - Dr. Chriss McDonald, phone: 321-4186 (work), 998-8647 (home, call up to 10 pm)  
Email: mcdonald@lycoming.edu

Texts and other stuff

- no textbook per se, I will supply readings from the primary and secondary literature.*
- Your 200-level organic chemistry text (McMurry)
- Bound laboratory notebook by Freeman
- Calculator (add, subtract, multiply, divide, logs, exponents),
- Chem 220-221 lab manual (your old one, whichever year it happens to be)

Course objectives:

- To understand how different experimental techniques are used to elucidate organic reaction mechanisms;
- To become more familiar with the three main mechanistic classes (polar, radical, pericyclic) of organic reactions;
- To become familiar with more advanced laboratory techniques for physical and synthetic organic chemistry;
- To understand the key issues involved in natural product synthesis.

Department of Chemistry learning goals that are supported by this course:

- Exhibit proficiency in the major sub-disciplines of chemistry;
- Perform wet laboratory techniques that are appropriate to organic chemistry;
- Understand and use modern chemical instrumentation;
- Exhibit integrative problem-solving skills, such as experimental design, data manipulation, and data interpretation.

This course supports the Mission of the College

The mission of Lycoming College is to provide a distinguished baccalaureate education in the liberal arts and sciences within a coeducational, supportive, residential environment.

Learning differences and disabilities

Lycoming College provides academic support for students who officially disclose diagnosed learning, physical and psychological disabilities. If you have a diagnosed disability and would like to seek accommodations, please contact Jilliane Bolt-Michewicz, Assistant Dean of Academic Services / Director of the Academic Resource Center. Dean Bolt-Michewicz will help you arrange for appropriate academic accommodations. She can be reached by calling 570-321-4050, emailing

[michewicz@lycoming.edu](mailto:michewicz@lycoming.edu), or visiting her office (Academic Resource Center, 3rd Floor of Snowden Library).

#### Course format

Lectures - MWF, 2:00 PM, HBC 215

Recitations - None scheduled, if you guys want some, let me know and we'll find a time to get together. We do have a few in class problem sessions scheduled. As always, questions are welcome at any time.

Assigned homework - problems designed to enhance your understanding and prepare you for testing situations. Some of these questions will be taken from the literature (which means you can go look up the answers!). A key will be posted immediately after class. No late homework will be accepted. There will also be individually assigned mechanistic problems for you to present in class.

Laboratory - 8:00 - 11:50 AM, Tuesday, in the *Swing Lab*, the labs will be designed to probe mechanistic problems in organic chemistry.

Exams - Exams will occur during the lab period of the indicated week. They should be both fun and challenging.

Colloquium – Almost all of our colloquia have some synthetic/mechanistic chemical content. Therefore a small portion of your grade is based on your attendance at colloquium. You must attend 7 colloquia to obtain full credit. If you are unable to attend colloquium due to a scheduling conflict, you may obtain the points by summarizing appropriate articles from the chemical literature. You should discuss this with me before begin summarizing articles.

#### Grading scheme

- a. The final grade is based on the number of points obtained out of a possible 660 points. The points will be distributed as follows:

quizzes	45 points
mechanistic problem for each	10 points
exam 1	100 points
exam 2	100 points
exam 3	100 points
final exam (cumulative)	124 points
laboratory	130 points
homework	50 points
colloquium	<u>21 points</u>
<b>total</b>	<b>680 points</b>

- b. Assignment of letter grades is based on the following scale: 680 -612 **A**, 611 - 544 **B**, 543 - 476 **C**, 475 - 408 **D**, < 407 **F**. I reserve the right to curve the grades in your favor if deemed appropriate based upon overall class performance and a qualitative assessment

of the difficulty of quizzes and exams. Also, if you score a higher *percentage* on the final exam than one of your hour exams, I'll replace the lower score with the higher (appropriately weighted). The assignment of the final grade is also influenced by attendance and class participation. This is especially true in the case of a student with a borderline average.

Policy on attendance for exams and quizzes Makeups will be administered only if I deem the reason for absence to be legitimate (illness, death in the family....). Absence due to transportation difficulties is not considered legitimate.

### Chem 44014 Schedule

Week	Date	Topic	Reading Assignment	Q/E/MP	
1	8/25	this is advanced organic chemistry	1. Buskirk, Baradaran, "Can Reaction Mechanisms be Proven?", <i>JCE</i> <b>2009</b> , 551-8		
	8/27	enantiomerism	2. <i>C&amp;S A</i> 5 <sup>th</sup> 119-141		
	8/29	diastereomerism and resolution	3. <i>C&amp;S A</i> 5 <sup>th</sup> 119-141; Whitesides, Lewis, "The Determination of Enantiomeric Purity..." <i>JACS</i> <b>1971</b> , 93, 5914-5915, 4. <i>C&amp;S A</i> 5 <sup>th</sup> 208-210		
2	9/1	diastereomerism and resolution	5. Gawley, "Do the Terms % ee" and % de"... " <i>JOC</i> <b>2006</b> , 71, 2411-2416		
	9/3	dynamic stereochemistry	6. <i>C&amp;S A</i> 5 <sup>th</sup> 169-198; 7. Masamune, "Organoborane Compounds in Organic..." <i>JACS</i> <b>1985</b> , 107, 4549-4551; 1. <i>C&amp;S A</i> 5 <sup>th</sup> 119-141		Quiz 1
	9/5	prochirality	as above		MP1
3	9/8	acyclic conformational analysis	8. <i>C&amp;S A</i> 5 <sup>th</sup> 142-51		
	9/10	conformational analysis of cyclic compounds	9. <i>C&amp;S A</i> 5 <sup>th</sup> 152-169; 10. <i>C&amp;S A</i> 4 <sup>th</sup> 149-151		MP2
	9/12	conformation and reactivity	6. <i>C&amp;S A</i> 5 <sup>th</sup> 169-198		
4	9/15	conformation and reactivity	as above		
	9/17	Baldwin's rules	11. <i>C&amp;S A</i> 4 <sup>th</sup> 166-171, 12-14. Baldwin, "Rules for Ring Closure" <i>JCSCC</i> <b>1976</b> 734-741 (3 articles)		MP3
	9/19	Baldwin's rules	as above		Quiz 2
5	9/22	kinetic isotope effects	1. <i>C&amp;S A</i> 5 <sup>th</sup> 332-335		
	9/23	Exam 1	-		Exam 1
	9/24	labwork	-		
	9/26	TBA	-		
6	9/29	acid/base catalysis, solvent effects	2. <i>C&amp;S A</i> 5 <sup>th</sup> 345-368		
	10/1	linear free energy relationships	3. <i>C&amp;S A</i> 5 <sup>th</sup> 335-344		MP 4
	10/3	linear free energy relationships	as above		

<b>7</b>	10/6	redox conventions	<b>4.</b> Kjonaas, "Number of Oxidations..." <i>JCE</i> <b>1986</b> , 63, 311-314	
	10/8	NaBH <sub>4</sub> /LiAlH <sub>4</sub>	<b>5.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 262-273	<b>MP 5</b>
	10/10	stereochemistry of hydride reduction	<b>6.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 273-280	
<b>8</b>	10/13	reduction of other functionality	<b>7.</b> Grabowski, "A Practical Process for the Preparation..." <i>JOC</i> <b>1993</b> , 58, 2880-2888;	<b>MP 6</b>
	10/15	other sources of hydride	<i>C&amp;S B</i> 4 <sup>th</sup> 273-280, <b>8.</b> Stryker, "Selective Hydride-Mediated..." <i>JACS</i> <b>1988</b> , 110, 291-293	
	10/17	Long Weekend 2014	<i>C&amp;S B</i> 4 <sup>th</sup> 273-280	<b>Quiz 3</b>
<b>9</b>	10/20	α deprotonation of carbonyls	<b>9.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 1-10	
	10/22	alkylation of enolates	<b>10.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 11-31	<b>MP 7</b>
	10/24	more alkylation issues	<b>11.</b> Negishi, "Highly Regioselective Generation..." <i>TL</i> <b>1983</b> , 24, 1341-1344; <b>12.</b> Holton, "Regiospecific Preparation of Thermodynamic..." <i>TL</i> <b>1983</b> , 24, 1345-1348; <b>13.</b> Nakamura, "Alkylation of Magnesium..." <i>JACS</i> <b>2005</b> , 127, 14192-14193	
<b>10</b>	10/27	radicals: initiation and structure	<b>1.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 965-970; <b>2.</b> 976-992	
	10/28	<b>Exam 2</b>	-	<b>Exam 2</b>
	10/29	TBA	-	
	10/31	Bu <sub>3</sub> SnH and SmI <sub>2</sub> reduction of RX	<b>3.</b> P,F,&S 1-15; <b>4.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 288-290; <b>5.</b> Inanaga, "A Mild and Convenient..." <i>CL</i> <b>1987</b> , 1485-1486	
<b>11</b>	11/3	addition of radicals to alkenes	<b>6.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 651-657; <b>7.</b> Giese, "Synthesis of δ-Lactones..." <i>JOC</i> , <b>1986</b> , 51, 3726-3729,	
	11/5	addition of radicals to alkenes	<b>8.</b> <i>C&amp;S B</i> 4 <sup>th</sup> 657-674; <b>9.</b> Curran, Rakiewicz, "Tandem Radical Cyclization..." <i>JACS</i> <b>1985</b> , <b>MP 8</b> 107, 1448-9; <b>10.</b> Curran, "A Samarium(II) Promoted..." <i>JACS</i> <b>1988</b> , 110, 5064-5067; <b>11.</b> Parker, "Total Synthesis of Bisabosqual A" <i>JACS</i> <b>2012</b> , 135, 582-585; <b>12.</b> Procter, Pleuromutilin <i>Chem. Eur. J.</i> <b>2013</b> , 19, 6718-6723; <b>13.</b> Bode, "SnAP Reagents..." <i>ACIED</i> <b>2013</b> , 52, 1705-8.	
	11/7	Huckel MO theory for polyenes	<b>1-3.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 27-391; 713-718; 725-735	
<b>12</b>	11/10	intro to pericyclic reactions	<b>4.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 833-6	<b>MP 9</b>
	11/11	<b>Exam 3</b>		<b>Exam 3</b>
	11/12	electrocyclic reactions	<b>5.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 892-906	
	11/14	electrocyclic reactions	as above	
<b>13</b>	11/17	sigmatropic rearrangements	<b>6.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 911-921	<b>MP 10</b>
	11/19	Diels-Alder reaction	<b>7.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 834-848	
	11/21	more DA	<b>8.</b> <i>C&amp;S A</i> 5 <sup>th</sup> 860-873	

<b>14</b>	11/24	Diels-Alder reaction	<b>9.</b> Stork, "The Temporary Silicon Connection..." <i>JACS</i> <b>1992</b> , <i>114</i> , 7578-7579; <b>10.</b> Padwa, "Application of Furanyl Carbamate..." <i>JOC</i> <b>2001</b> , <i>66</i> , 3119-3128 <b>11.</b> Hudlicky, "Short Chemoenzymatic Total..." <i>ACIED</i> <b>2014</b> , <i>53</i> , 4355-4358
	11/26	Thanksgiving 2014	
	11/28	Thanksgiving 2014	-
<b>15</b>	12/1	natural product synthesis	<i>C&amp;S B</i> 4 <sup>th</sup> 821-848
	12/3	same	TBA
	12/5	same	TBA
	12/8-12	finals week	

### Literature code:

**ACIED** = *Angewandte Chemie International Edition*

**C&S A 5<sup>th</sup>** = Carey and Sundberg, Part A, "Advanced Organic Chemistry", 5<sup>th</sup> edition, 2007 (also one reading from the 4<sup>th</sup> edition)

**C&S B 4<sup>th</sup>** = Carey and Sundberg, Part B, "Advanced Organic Chemistry", 4<sup>th</sup> edition, 2001

**CL** = *Chemistry Letters*

**CEJ** = *Chemistry A European Journal*

**JACS** = *Journal of the American Chemical Society*

**JCE** = *Journal of Chemical Education*

**JCSCC** = *Journal of the Chemical Society, Chemical Communications*

**JOC** = *Journal of Organic Chemistry*

**P,F&S** = Procter, Flowers, Skydstrup, "Organic Synthesis using Samarium Diodide", 2010

**TL** = *Tetrahedron Letters*