CHEMISTRY 234 - ORGANIC CHEMISTRY LAB II

SPRING 2015

Instructor: Professor Mo Hunsen
Office: Tomsich 310
e-mail: hunsenm@kenyon.edu
Office Hours: T 4-6 PM, W 12-2 PM, or by appointment
Office Tel.: 740-427-5091

Texts: Mayo, Dana W.; Pike, Ronald M. and Trumper, Peter K. "Microscale Organic Laboratory: With Multistep and Multiscale Syntheses," 5th edition

Zubrick, James W. "The Organic Chem Lab Survival Manual," 8th edition
Handouts: Moodle

Required Material: The Hayden-McNeil Student Lab Notebook & goggles.

Point Distribution:

1 Full Laboratory Report + Draft/Peer editing	90
6 Data sets @ 40 points each	240
Notebook/ Laboratory Technique/ Safety	30
Exam (see Lab Schedule)	80
Quizzes	60

Total	500

Rules for the Course:

Goals: Chemistry 234 provides a technical foundation for first-hand experimental work in organic chemistry. The course emphasizes techniques and skills that will be used in other courses and any research projects requiring material manipulations. The techniques and reactions involved integrate and illustrate Chemistry 231 and 232 (the classroom course) material.

Attendance: Organic chemistry is a science that continually builds upon itself, and it is quite easy to get behind if you miss a particular lab period. Therefore, attendance to your assigned laboratory section is mandatory. I strongly discourage you from switching lab sections during the semester. If it is absolutely imperative that you perform an experiment during another lab section for a particular week, you must obtain permission from me and the instructor of the section you are attempting to switch into.

Course Meeting Time: We will meet in Tomsich Hall 207 for a pre-lab discussion during the first week of a particular experiment. This meeting should last about 20 minutes and may begin with a 5 minute quiz which will be germane to the experiment at hand. You will have only your laboratory notebook to help you during the quiz, so you will need to prepare a preliminary write-up in your notebook. Planning your lab work ahead of time will increase your efficiency in lab. Afterwards, we will walk down to Tomsich Hall 209 and start working. If we are in the second (and last) week of an experiment, you can begin working promptly at 1:10 pm in Tomsich Hall 209. You should confine your lab work to the scheduled hours.

Evening Analysis Sessions: The lab will be open, as needed, Sunday or Thursday nights from 7 – 9 pm, staffed by an undergraduate assistant and disco ball. You may perform analytical techniques such as melting point

analysis and the various spectroscopies. No other experiments are allowed. As a guideline, if all you had was your sample and sample prep material, you may not do anything that would require opening your drawer.

***Late Work**:* For late work, you will lose points as follows: 0.1%/min (1-10 min late), 1%/min (11-20 min late), 5%/min (21-30 min late), 10%/min (31-40 min late).

Safety: The safety rules for the course are stated in Mayo, Chapter 2 and in Zubrick, Chapter 1. In the laboratory, the most important rules are: 1. Wear safety **goggles at all times** -- – being in the lab without goggles will cost you 5 points per incident; 2) Long pants and shoes that cover the entire foot must be worn at all times; 3) No eating or drinking; 4) Be mentally alert to hazards and prepared for emergencies. If you are uncertain whether something is safe, consult with me.

***Reading**:* The location of an experiment in your laboratory text is listed in the schedule. The beginning of each experiment in MOL lists Prior Reading. I will assume you have read this material as well as any relevant discussions and introductions, even if they are not immediately proximate to the experiment in question.

Laboratory Notebooks: You are required to purchase and maintain a laboratory notebook. Learning to keep an accurate and detailed lab notebook is critical -- as it is your only source of information to help you remember what you actually did in lab when writing a lab report in the days ahead. The notebook for this course contains white pages and carbon copies of the white pages. After you have finished for the day, your notebook will be signed and dated by me or the laboratory teaching assistant and the relevant pages will be submitted with the lab report.

There is no one right style for writing in a laboratory notebook; everyone has his or her own style. A good template is in Mayo and in Zubrick, Chapter 2. For this course I expect you to follow the format shown on the attached page. The most important rules are: 1. Your lab notebook is your scratch paper -- data and observations should be recorded directly into your notebook at the time the observations or measurements are made; 2. The writing should be done with indelible ink; 3. After you are finished with your experiment, your lab notebook should contain sufficient information for another investigator, familiar with the field, to be able to reproduce your work, using only your notebook as a guide.

***Data Sets**:* After finishing each experiment you will prepare a data set. Data sets are your proof that you have completed the experiment and will be the primary basis of your grade. Data sets are due at the beginning of lab on the dates indicated on the schedule of experiments. Each data set will include the following items:

1. Product Cards: This is a summary card of the data collected and is attached to the top of your written experimental. While once actual cards, these are now electronic. Fill out all pertinent sections and, in the remarks section, indicate what else will be handed in (e.g. – 'Included with experiment: experimental section, 1H NMR spectrum, 13C NMR spectrum, IR spectrum, product vial, and lab notebook pages') or other important information.

2. Experimental Section: For each experiment you should write an experimental section in prose suitable for publication in an ACS journal (links to representative papers and the ACS Style Guide may be found on the course webpage). General guidelines for scientific writing should be followed.

3. Annotated Analytical Data: All your analytical data should be interpreted and clearly annotated. Annotation includes carefully drawing the structure of the compound under analysis and clearly correlating spectral signals with that structure. The course webpage has examples of annotated spectra. All spectra should have the following information: compound structure, compound name, compound ID number (YDG-3-113B, initials - lab book number – page[letter tracking isolations]) and method of sample preparation (i.e. KBr pellet, ATR, CDCl3, etc). For IR, only major features are labeled. For NMR, every peak is labeled.

4. Labeled Product Vial: Place your product into a 1 dram (4 ml) vial labeled with the compound name, compound ID number, and your name. The vial should be placed in the appropriate location in the sample rack.

5. Lab Notebook Carbons: Attach the originals from your laboratory notes for the experiment.

Laboratory Reports: A combined lab report for experiments for the convergent synthesis of hexaphenylbenzene (approximately 3-6 typewritten pages excluding attached spectra and chromatograms), written in your own words is required. The written lab report should be divided into the following sections: Abstract, Introduction, Results and Discussion, Sample Calculations, Experimental, Questions, References, and Supplemental information (Spectra, Notebook copies, etc.). All structures must be drawn using ChemDraw which as a free download at http://scistore.cambridgesoft.com/sitelicense.cfm. Chemical structures which are scanned, hand-drawn, copied from the web, etc. are not acceptable.

Following the completion of the convergent synthesis of hexaphenylbenzene, we will hold a lab report workshop in class. **You must have a draft submitted by midnight the night before the workshop in order to participate and get credit for this assignment.**

Please refer to "*A Brief Guide to Writing in Chemistry"* for guidance in writing your report. Brief descriptions of expectations for each section are included below:

> *Abstract*: This is a summary of your results and the methods used to obtain them. It varies from 1-5 sentences, but never exceeds 110 words (approximately 8 lines). Abstracts must include a graphical summary no larger than 3.25" by 1.75".
>
> *Introduction*: This is a statement describing the theoretical background, purpose and goals of your work. Give the reader a reason to care. You should describe (in words, pictures, balanced chemical equations, mathematical equations, etc.) the new method(s) and/or chemical reaction(s) that you have investigated for this report.
>
> *Results and Discussion*: This includes your data (results) and the interpretation/explanation of your data (discussion). Your data are most effectively presented using tables, graphs, lists, etc. Spectra are included as appendices that are referenced in the text. You should interpret and discuss your data in terms of what you learned from them, and how the data reinforce or contradict the principles taught in this and other courses. Typically, this is the main body of text in your report.
>
> *Sample Calculations*: This contains a detailed account of how you arrived at a certain number or result during a calculation. You should show one sample calculation for each type calculation (i.e. one each for % recovery, theoretical yield, % yield, optical rotation, etc.) that you performed for a particular experiment. Pay attention to significant figures.
>
> *Experimental*: This is a description of what you actually did in the laboratory according to your notebook and not necessarily what is described in MOL. The experimental is written in the third person, the past tense, and in the passive voice.
>
> *References*: These are the sources of information that were used in the report (MOL, Zubrick, CRC Handbook of Chemistry and Physics, Science, Journal of Organic Chemistry, etc.). This is a critical and oft overlooked section of a lab report. On what are you basing your statements? A book, a journal article, a website (be careful!), your own imagination? All references should be according to the ACS Style Guide, using the Acc. Chem. Res. style with full article titles.[1] You may find Table 14-2 particularly useful.

[1] Dodd, J. S.; Solla, L.; Bérard, P. M. References. In *The ACS Style Guide: Effective Communication of Scientific Information* [Online]; Coghill, A. M.; Garson, L. R., Eds.; Oxford University Press: 1996; Chapter 14, pp. 287-341. http://pubs.acs.org/doi/abs/10.1021/bk-2006-STYG.ch014 (accessed April 9, 2013).

Quizzes: As noted above, a five-minute quiz will be given at the beginning of each experiment (on the first week of two-week experiments). The content of the quiz will be germane to the experiment at hand and may include questions about technique as discussed in Zubrick, suggested questions assigned from Mayo, spectral interpretation, or questions about material you should know in preparation for the experiment.

Exam: In lieu of final exam, the electronic data set of your last experiment will be due at the designated time. However, there will be one exam covering the experiments in the hexaphenylbenzene synthesis in early April (see Schedule). The full report for Convergent Synthesis of Hexaphenylbenzene (final version) is due during the final exams week (see schedule).

Grading: Your performance will be evaluated over the entire semester based upon the following absolute scale: A (+/-) = 100-90%; B (+/-) = 89-80%; C (+/-) = 79-70%; D (+/-) = 69-60%; F <60%.

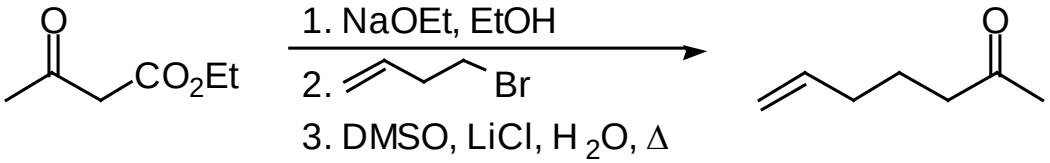
Statement of Academic Integrity: At Kenyon we expect all students, at all times, to submit work that represents the highest standards of academic integrity. It is the responsibility of each student to learn and practice the proper ways of documenting and acknowledging those whose ideas and words they have drawn upon (see Academic Honesty and Questions of Plagiarism in the Course Catalog). Ignorance and carelessness are not excuses for academic dishonesty. If you are uncertain about the expectations for this class, please ask for clarification.

Statement on Disability Accommodations: Students who anticipate they may need accommodations in this course because of the impact of a learning, physical, or psychological disability are encouraged to meet with me privately early in the semester to discuss their concerns. In addition, students must contact Erin Salva, Director of Student Accessibility and Support Services *(740-427-5453* or *salvae@kenyon.edu*), as soon as possible, to verify their eligibility for reasonable academic accommodations.

Title IX Responsibilities: Kenyon faculty are committed to supporting our students and upholding gender equity laws as outlined by Title IX. Therefore, if a student chooses to confide in a member of Kenyon's faculty regarding an issue of sexual misconduct, that faculty member is obligated to tell Kenyon's Title IX Coordinator. The Title IX coordinator will assist the student in connecting with all possible resources both on and off campus. . For more information about your options at Kenyon, please go to: http://www.kenyon.edu/directories/offices-services/office-of-equal-opportunity/sexual-assault-and-harassment/

Withdraw Late: Co-requisite for this course is CHEM 232, but withdrawing late (WL) from the lab does not also withdraw you from the associated lecture course – they are separate courses with separate grades.

Sample Experimental



6-Hepten-2-one. Na (25.0 mg, 1.09 mmol) was added to a solution of ethyl acetoacetate (130 mg, 1.00 mmol) in ethanol (1.0 mL) in a 3-mL conical vial equipped with a reflux condenser and a drying tube. The mixture was allowed to stir until all of the Na had dissolved. 4-Bromo-1-butene (150 mg, 1.11 mmol) was added, and the mixture was heated to reflux until it was no longer basic to litmus. The reaction mixture was cooled, filtered, and the solvent was removed by distillation. The resulting oil (153 mg, 83% crude) was dissolved in dimethyl sulfoxide (0.5 mL). H_2O (40 μL, 2.2 mmol) and LiCl (63.6 mg, 1.50 mmol) were added, and the solution was heated to reflux

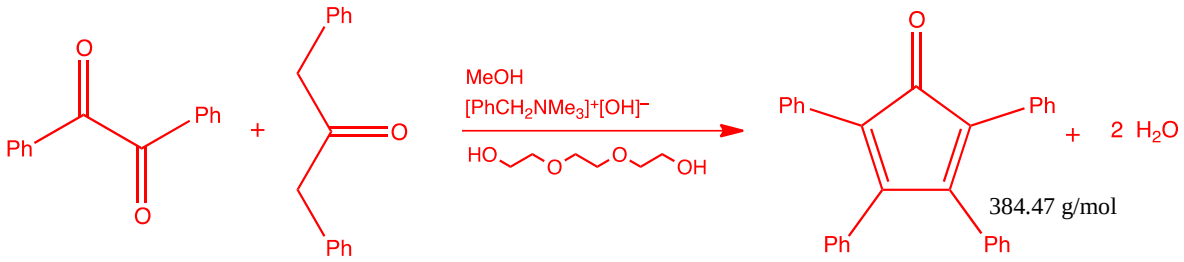
for 1 h. The resulting dark brown solution was diluted with saturated aqueous NaCl (1.5 mL), extracted with ether (3 x 0.5 mL), dried over excess $MgSO_4$, filtered, and the solvent removed by warming the flask under a stream of nitrogen in a warm sand bath. The resulting residue was distilled into a Hickman still head, and the fraction boiling in the range of 145-148 °C was collected to give 76.7 mg (68.5%) of 6-hepten-2-one as a colorless liquid.

Notice the use of common abbreviations (i.e. volumes in mL; weights in mg or g; molar amounts in mmol; temperature in °C; time in s, min, h, or d; distance in mm or cm; etc.). Make use of them. Also notice that a simple chemical formula is used instead of the compound's name whenever possible. For example "Na" is written instead of "sodium," or "H_2O" instead of "water," because these formulae can only describe these particular compounds. However, "C_2H_6O" cannot be written for ethanol, since another compound, dimethyl ether, has the same formula. Therefore, the word "ethanol" is written instead.

This syllabus, constructed over multiple years with contributions from several instructors, is subject to change at my discretion. I will notify you of any changes in class and/or by email.

EXAMPLE LAB NOTEBOOK PAGE

01/17/2007



(cf: Mayo; Pike; Trumper, 436 – 437)

chemical	Benzil	1,3-diphenylacetone	triethylene glycol	[BnNMe$_3$][OH]
source	Aldrich, 98%	Aldrich, 98%	Akros, reagent	stockroom
purification	UAR*	UAR	UAR	UAR
MW	210.23	210.27		153.22
d(g/ml)	N/A (solid)			40% in MeOH
amount	0.401 g	0.406 g	2 ml	0.4 ml
mmol	1.91	1.93		1.
eq.	1.00	1.01		0.5

(0.4 ml BnNMe$_3$OH soln)*(0.4 g BnNMe$_3$OH/1 ml BnNMe$_3$OH soln)*(1 mol BnNMe$_3$OH/153 g BnNMe$_3$OH) = 1 mmol BnNMe$_3$OH

- benzil, diphenylacetone and triethylene glycol added to 5 ml conical vial (equipped w/air-condenser + spin vane)
- heated until sol'n homogeneous (sand bath ~150 °C, ~10 min)
- added 0.4 ml benzyltrimethylamonium hydroxide sol'n
- as sol'n cooled, deep purple/brown x-tals began to precipitate
- poured rxn into 15 ml Erlenmeyer, rinsed remaining material into Erlenmeyer w/~5 ml *cold* MeOH (reagent)
  spilled some of sol'n, lost some x-tals
- cooled flask in ice bath (~10 min)
- isolated w/Hirsch funnel, rinsed 3 x w/small minimum cold MeOH
- x-tals are mottled, dark purple
- sample (YDG-075A) left to dry until next lab

1/25/07
yield: 0.80 g (2.1 mmol, >100 %!!?)
mp: 200 –219 (lit: 220–221)
damn! – must re-xtalize
- in 15 ml Erlenmeyer, dissolved YDG-075A in min. hot acetone & added MeOH until ppt began to appear
- added touch more acetone, covered w/parafilm & placed in ice bath for 1.5 hrs
- x-tals (isolated as above) are unblemished dark purple
- covered funnel w/kimwipe & drew air through for ~1/2 hr; x-tals look dry → YDG-4-075B

yield: 0.43 g (1.1 mmol, 48 %)
mp: 218 –220 (lit: 220–221)

IR – KBr pellet (see attached spectrum with relevant peaks labeled)
NMR – ^{1}H CDCl$_3$ (see attached spectrum with *all* peaks labeled } all look good!

* UAR = used as received

CHEM 234: ORGANIC CHEMISTRY Lab Schedule (SPRING 2015)

Week of	Experiment	Reference/Week Due	Questions (Ch. 7)
1/12 & 1/19	*Experiment [A1$_a$] The Benzoin Condensation of Benzaldehyde* Methods: Macroscale (Kem Kits), Reflux, Filtration, Recrystallization, mp, IR Scale: 2 ml benzaldehyde	Mayo pp. 429 **Week Due: 2/2**	1, 2, 3, 5
1/26 & 2/2	*Experiment [A2$_a$] HNO_3 Oxidation of Benzoin: Synthesis of Benzil* ***Note: Alternative Protocol (HNO_3 Oxidation) – see handout*** Methods: Reflux, Filtration, Recrystallization, mp, IR, TLC, Chromatography (if needed); Scale: ≥800 mg	Handout Mayo pp. 433 ***Week Due: 2/23***	6, 8a, 9, 10
2/9	*Experiment [A3$_a$] Tetraphenylcyclopentdadienone* via *Aldol Condensation* Methods: Filtration, Recrystallization (if needed), NMR; Scale: >400 mg	Mayo pp. 438 **Week Due: 2/23**	12, 13, 14, 15
2/16 & 2/23	*Experiment [A2$_b$] A Greener Bromination of Stilbene* ***Note: Alternative Protocol (HBr/H_2O_2 Bromination) – see handout*** Methods: Reflux Filtration, mp, IR, Recrystallization (if needed); Scale: See Handout	Handout Mayo pp. 444 **Week Due: 3/30**	23, 24, 25, 26
¡SPRING BREAK! – 3/2 to 3/15		**Lab Report Draft - Week Due 4/13**	
3/16 & 3/23	*Experiment [A3$_b$] Dehydrohalogenation of* meso-*Stilbene Dibromide: Diphenylacetylene* Methods: Filtration, Recrystallization, mp, IR, NMR; Scale: 400 mg	Mayo pp. 450 **Week Due: 3/30**	28, 29, 30
3/30 & 4/6	*Experiment [A4$_{ab}$] Hexaphenylbenzene* via *Diels-Alder* Methods: thermolysis, IR, TLC (3:1 hexanes:CH_2Cl_2) Scale: whatever you've got! **Lab Report: Convergent Synthesis of Hexaphenylbenzene** (no data set)	Mayo pp. 453 **Draft: Week of 4/13** **Final: Week of 5/4** Word Limit: 2,400	32, 33, 34
4/13	***Exam and Peer Review***		
4/20 & 4/27	*Stepwise Synthesis of Nylon-6,6 with Green Oxidation Modification* ***Lab Check Out***	Handout, Mayo pp. 457 **Week Due: 5/4**	Handout; 35, 37, 42, 45, 46, 47

Notes: All questions are from *MOL*, Chapter 6. You may find it useful to read relevant sections of Zubrick multiple times. All Experimental written text will be submitted through TurnItIn and will be due at 11:59 pm on the day preceding your lab section. Hardcopy Data Sets and product vials are due at the beginning of lab on the day the data set is due. For example, if you are in the Thursday section, your first Experimental will be due at 11:59 on Wednesday, February 4th.