

Course Organization for Chemistry 3520

- **Prerequisite.** The prerequisite for Chemistry 3520 is Chemistry 3510/51.
- **Grading and Examination Practices.**
- **Course Objectives**
 - **Learn the fundamental reactions and properties of various compounds**
 - **Understand and work with stereochemical problems**
 - **Understand and formulate mechanisms for simple organic reactions**
 - **Devise simple organic synthetic schemes**
 - **Master simple laboratory techniques**
 - **Understand and interpret nmr, ir and mass spectroscopy**
- **The Final Grade.** The grade will be determined as follows:
 - **Recitation Grade 25%**
 - **Laboratory Grade 25%**
 - **Lecture Examinations 25%**
 - **Final Examination 25%**

Final letter grades for the course will be assigned by a course grading committee. It is the recitation instructor's responsibility to keep a record of all of the student's grades. To receive your grade after the course ends, either visit the [Brooklyn College web site](#) or give a stamped post card or envelope to your recitation teacher.

Recitation Grade. This grade will be based on the student's average score on recitation quizzes and may also include the instructor's evaluation of the student's class participation. All recitations must be attended. Absence from recitation is subject to penalties.

Laboratory Grade. The laboratory instructor is responsible for determining the laboratory grade and will include his assessment of your advance preparation, comprehension of the experiment, aptitude for laboratory work, and your compliance with safety regulations among other criteria which will be explained to you by the laboratory instructor. Penalties will be assigned for failure to attend lab and do all of the assigned experiments.

Lecture Examinations. There will be two lecture examinations given to students in all sections. Questions based on the reading assignments, the lectures, and the laboratory experiments will be included. The examinations will be held during the regular lecture hour. The dates of these examinations are shown in the lecture schedule; the location of the examination rooms will be announced by the lecturer.

Final Examination. This examination will cover the assignments of the ENTIRE semester including the laboratory work. There are no exemptions from the final examination.

Illness During Examinations. If you become ill during any examination and feel that you are unable to complete it, notify a proctor immediately, write the words "I am sick", and hand in you paper. Your paper will not be graded and you will be considered absent

from the examination. If you complete the exam, your paper will be graded and your grade will not be changed by a later claim of illness.

Absence from Examinations. No make up examinations are given to students who are absent from the lecture examinations. Students who miss one of the exams with a valid excuse, will be assigned a score for the exam missed on the basis of their performance on the other lecture exam and on the final. A grade of zero for lecture will be given if both lecture exams are missed. In the event of absence from the final exam, you will need to apply to the academic Advisement Center for permission to take the make up final examination given the following semester. If the recitation instructor has recorded an ABS 50 grade or lower, permission will be denied.

Cheating. Any student found cheating on any laboratory exercise, quiz or exam will be given a failing grade for the course.

Exposure to Chemicals. During the laboratory exercises you will inevitably be exposed to a variety of chemical reagents. This may pose a hazard to some people: those who are particularly sensitive and those that are pregnant. In particular, I strongly recommend that if you are pregnant you not take the course. If you become pregnant during the course consult with me. We may be able to allow you to continue in the lecture portion of the course, receive an INC, and complete the laboratory when the pregnancy is completed.

Safety Goggles. Note that students **must** wear approved safety goggles whenever any laboratory work is being performed in the laboratory.

Sample Exams and Quizzes. Previously used testing items are available on my BC web site: <http://academic.brooklyn.cuny.edu/chem/howell/jhowell.htm>

• **Required textbooks:**

- **Organic Chemistry**, 5th Edition, W. Brown, C. S. Foote, B. L. Iverson, E. V. Anslyn, Thomson Brooks/Cole, Belmont, CA, 2009
- **Techniques & Experiments in Organic Chemistry**, 2nd Edition, L. B. Gortler and R. C. Tripp, Avery Publishing Group, Wayne, NJ, 1977
- **Supplement for Organic Chemistry 51 and 52**, Brooklyn College Press, 1987. (Available only at the Brooklyn College Bookstore)

• **Recommended**

- **Molecular Model Set for Organic Chemistry**, HGS, Maruzen

Chemistry 3520 Calendar

Fall 2010

	Date	Subject	Reading in BFI	Suggested Problems BFIA
1	Aug. 30	Carboxylic Acids	17.1 – 17.4	Ch. 17 (7, 8, 9, 12, 14, 15, 17, 18, 20, 22, 24, 25, 26, 27, 30, 32, 34, 37, 41, 43)
2	Sept. 1	Carboxylic Acids	17.5 – 17.0	
3	Sept. 8 (no lab)	Acid Derivatives	18.1 – 18.5	Ch. 18 (12, 13, 14, 16, 17, 18, 21, 26, 27, 30, 32, 34, 36, 38, 40, 43, 45, 47, 49, 52, 56, 58)
4	Sept. 13	Acid Derivatives	18.6 – 18.10	
5	Sept. 15	Enolates, Enamines	19.1 – 19.4	Ch. 19 (18, 21, 22, 24, 27, 31, 34, 38, 40, 43, 44, 46, 49, 50, 51, 53, 58, 63, 66, 78)
6	Sept 20	Enolates, Enamines	19.5 – 19.7	
7	Sept. 22	Enolates, Enamines	19.8 – 19.9	
8	Sept. 27	Conjugated Systems	20.1 – 20.3	Ch. 20 (6, 7, 8, 11, 12, 14, 15, 16, 19)
9	Sept. 29	Benzene and Aromaticity	21.1 – 21.3	Ch. 21 (8, 9, 10, 11, 14, 15, 17, 18, 21, 22, 30, 32, 34, 35, 38, 42, 47, 49, 51, 52, 54, 58)
10	Oct. 4	Benzene and Aromaticity	21.1 – 21.5	
11	Oct. 6	Exam 1	3.5 - 3.9	
12	Oct. 13	Reactions of Aromatic Compds	22.1 – 22.2	Ch. 22 (7, 8, 9, 10, 14, 15, 17, 19, 21, 23, 24, 27, 29, 33, 36, 41, 42, 50, 54, 58, 61)
13	Oct. 18	Reactions of Aromatic Compds	22.3	
14	Oct. 20	Amines	23.1 – 23.5	Ch. 23 (16, 17, 18, 19, 21, 22, 24, 25, 27, 28, 30, 31, 34, 36, 39, 44, 48, 54, 56, 58, 60, 69)
15	Oct. 25	Amines	23.6 – 23.10	

16	Oct. 27	C-C Bond Formation and Synth.	24.1 – 24.4	Ch. 24 (10, 12, 15, 19, 23, 25, 28, 30, 33, 34, 35, 36, 39, 46, 48, 49, 51, 52)
17	Nov. 1	C-C Bond Formation and Synth.	24.5 – 24.8	
	Nov. 3	No lecture Afternoon lab meets		
18	Nov. 8	Carbohydrates	25.1 – 25.3	Ch. 25 (7, 9, 15, 16, 20, 21, 24, 29, 33, 35, 36, 38, 41, 45, 46)
19	Nov. 10	Carbohydrates	25.4 – 25.6	
20	Nov. 15	Exam 2		
21	Nov. 17	Lipids	26.1 – 26.3	Ch. 26 (2, 7, 10, 12, 14, 16, 18, 19, 21, 23, 25, 27, 30, 31, 33)
22	Nov. 22	Lipids	26.4 – 26.6	
23	Nov. 24	Amino Acids and Proteins	27.1 – 27.3	Ch. 27 (8, 10, 12, 13, 16, 19, 21, 22, 24, 29, 32, 35, 39, 40, 41, 44, 48, 49, 51, 53, 56)
24	Nov. 29	Amino Acids and Proteins	27.4– 27.6	
25	Dec. 1	Nucleic Acids	28.1 – 28.3	Ch. 28 (7, 11, 13, 14, 17, 20, 21, 25, 28, 34, 38, 39, 41, 42)
26	Dec. 6	Nucleic Acids	28.4 – 28.5	
27	Dec. 8	Polymers	29.1 – 19.3	Ch. 29 (5, 7, 9, 14, 16, 19, 21, 24, 28, 33, 34, 35, 37, 38)
28	Dec. 13	Polymers	29.4 – 19.6	

Schedule of Laboratory Experiments:

<u>Lab Period</u>	<u>Experiment</u>	<u>Page</u>
1	Sodium p-Toluenesulfonate	103
2	Anthraquinone	supplement
3	p-Nitrobenzoic Acid	supplement
4	Methyl p-nitrobenzoate	supplement
5	Identification of unknowns (3)	135
6	Identification of unknowns (3)	135
7	Identification of unknowns (3)	135
8	Identification of unknowns (3)	135
9	Identification of unknowns (3)	135
10	Identification of unknowns (3)	135
11	Identification of unknowns (3)	135
12	Identification of unknowns (3)	135
13	Identification of unknowns (3)	135
14	Check-out	

* Note that the starting material in this experiment is your own product from an earlier experiment (3)

Required Materials for Laboratory (These should be obtained by the first laboratory period if possible.)

1. Padlock (required for first lab period.)
2. Safety glasses (State Law, as well as common sense, requires that these be worn in the laboratory at all times.)
3. Laboratory manual (L. B. Gortler and R. C. Tripp, "Techniques and Experiments in Organic Chemistry", second edition, second printing, 1977)
4. Laboratory notebook
5. Laboratory coat or apron
6. Towel
7. Soap, detergent, and/or scouring powder
8. Pocket knife or single edge razor blade
9. Matches or flint lighter
10. Assorted tin cans (to be used for ice baths.)
11. Box of labels or small roll of one inch wide masking tape to be used for labels

Before beginning any laboratory work the student must be familiar with the safety precautions and regulations (section 1.2 in the laboratory manual) and with regulations concerning laboratory cleanliness (section 1.3).

Students are expected to have the laboratory work planned and to have part of the notebook write-up done in advance. Otherwise the instructor may ask the student to comply before beginning the experiment.

The laboratory instructor will issue instructions on the format to be used in the notebook.

Organic Chemistry Laboratory Policies

Required Materials for Laboratory. As many as possible of the items listed in section 1.8 should be brought to the first laboratory period (except for lab fee, which is no longer required).

Laboratory Rules. Before beginning any laboratory work the student must be familiar with the safety precautions and regulations (section 1.1 in the laboratory manual) and with regulations concerning laboratory cleanliness (section 1.3).

Students are expected to have the laboratory work planned and to have part of the notebook write-up done in advance for each experiment. Otherwise, the instructor may ask the student to comply before beginning the experiment.

Care of Equipment. Students are responsible for all the equipment in their lockers after they have been checked in and will be billed for any equipment which has been broken or lost. Students are urged to check carefully at the end of each laboratory period to make certain that everything has been returned to the drawer and that the lock has been secured.

Students who drop the course before the end of the semester must check out of the laboratory immediately.

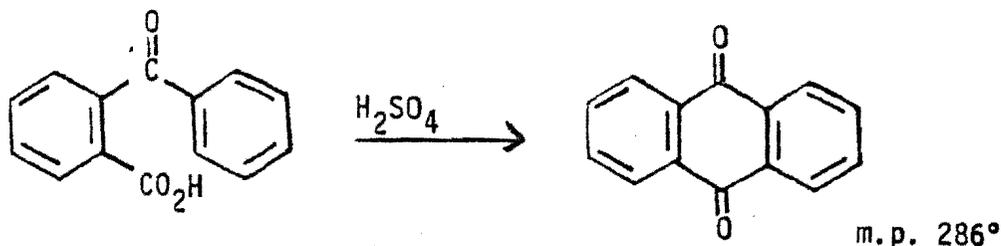
Make-up Laboratories. Students who need to make up laboratory work missed may do so in other scheduled laboratories only under the following conditions:

1. The student must have written permission from his own laboratory instructor. Permission is ordinarily granted only if the student has been absent for a valid reason or has fallen behind because of extenuating circumstances. Laboratory make-up permission forms are available at the stockroom window. The instructor in the make-up lab will sign and return the form to the student's own lab instructor to confirm the student's presence.

2. The student must obtain the permission of the instructor in charge of the laboratory during the period when he wishes to make up the lab. The instructor is free to deny permission for any reason, but particularly if he feels that the laboratory will become dangerously crowded.

3. Students should not expect lab instructors to take time away from their own students to find chemicals for or answer questions from students making up labs.

4. Students making up labs must be especially careful to observe all the safety rules and to clean up their working space.



Place 5.0 g. of o-benzoylbenzoic acid in a dry 250 ml round bottomed flask, add 25 ml of conc. sulfuric acid, and heat on the steam bath and swirl until the solid is dissolved. Then clamp the flask, immerse the bulb of a thermometer into the solution (clamp the top of the thermometer) and heat the flask over a microburner or over the small flame of a Bunsen burner.

Raise the temperature to 150° and maintain it at 150° - 155° for 5 minutes. Let the solution cool to 100°, remove the thermometer after letting it drain, and with a dropper add 5 ml. of water, drop by drop. Swirl during this addition to keep the initially precipitated material dissolved as long as possible so that it will separate as small but easily filtered crystals. Cool the mixture to room temperature and add 100 ml of water, cool again and collect the crystals by suction filtration. Wash the crystals with 2 or 3 50 ml. portions of water.

Pour out the filtrate, rinse the filter flask with water, and then return the funnel containing the product but do not apply suction. Now test for unreacted starting material as follows. Dilute 10 ml of conc. ammonia with 50 ml. of H₂O (makes approx. 3 M of 6% ammonia), pour this solution onto the funnel and loosen the filter cake so that it is well leached. Then apply suction and wash with water. Acidify a few ml. of the filtrate. If no precipitate forms on acidification the yield of anthraquinone should be close to 100% since it is insoluble in water.

Questions

1. Write a detailed mechanism for the formation of anthraquinone from o-benzoylbenzoic acid showing all intermediates.
2. What is the compound in the ammoniacal wash of the anthraquinone and why does it form a ppt. on acidification? Write an equation for this transformation.

18.4--4-Nitrobenzoic Acid. Oxidation of 4-Nitrotoluene with Potassium Permanganate

Prepare a solution of 6.4 g of potassium permanganate in 75 mL of water in a 250 mL round-bottom flask. Add 2.74 g of 4-nitrotoluene, 1 mL of 2 M NaOH and two boiling stones to the flask, and heat the mixture under reflux until most of the purple color has disappeared (from 1 to 2.5 hours).

After 45 minutes, stop the reflux and check for the presence of unreacted potassium permanganate. Dip a glass stirring rod into the reaction mixture and touch the rod to a piece of filter paper. A pink color in the ring around the brown manganese dioxide indicates the presence of potassium permanganate. Check again every 10 to 15 minutes to see if the color is getting lighter.

When only a trace of potassium permanganate remains in the mixture (as indicated by only a light pink ring), filter the hot solution by vacuum filtration. The product should be in the filtrate, but save the filter cake (the brown material on the filter paper) until you have isolated the product. Cool the filtrate. If the filtrate is pink, add 0.1 g of sodium hydrogen sulfite and heat the solution for a minute or two to destroy excess permanganate. Cool the solution to room temperature once more.

Check the now colorless solution with red litmus paper to be certain it is basic.¹ If there is any undissolved solid in the flask, filter it off by gravity filtration. Cool the clear solution in an ice bath and slowly add 10% sulfuric acid. Check with red litmus paper to see when the solution turns acidic. Add 1 mL more acid after the solution turns acidic.

Collect the precipitated 4-nitrobenzoic acid by suction filtration. Wash it with 10 mL of water and dry as much as possible under suction. Finally, dry the product in the open air on some absorbent paper for at least a day before determining the melting point. Weigh the product and determine the percentage yield.

If time permits, extract the filter cake of MnO_2 with 5 to 10 mL of hot ethanol. Stir the MnO_2 with the hot ethanol and then filter by suction filtration. Cool the ethanol and isolate any precipitated solid. Dry, weigh and take a melting point of this solid. What is it? How does this affect the yield of your 4-nitrobenzoic acid?

¹ To check the acidity of the solution, DO NOT dip an entire piece of litmus paper into the solution. Dip a fine stirring rod (a melting point capillary tube is ideal) into the solution, and then touch the stirring rod to the litmus paper. A single piece of litmus paper can be used for several determinations using this technique.

18.5--Questions

1. Write a balanced equation for the oxidation of 4-nitrotoluene with permanganate in a basic medium.
2. Why do the directions say to keep the filter cake until after you have the product?
3. Carboxylic acids are often recrystallized from ethanol in the usual manner. Describe another way of purifying the product that takes advantage of its acid properties.

16.3-The Preparation of Methyl 4-Nitrobenzoate

Weigh 1.67 g (0.01 M) of 4-nitrobenzoic acid (the thoroughly dried product obtained from the oxidation of 4-nitrotoluene).¹ Transfer the acid to a 50 mL round-bottom flask containing one or two small boiling stones. Measure 4.8 mL of a methanol-sulfuric acid solution² (containing 0.55 mL of concentrated sulfuric acid dissolved in 4.55 mL of anhydrous methanol) into a clean, dry, 10 mL graduated cylinder. Transfer this solution to the 50 mL reaction flask, attach a reflux condenser equipped with a drying tube containing calcium chloride, and heat gently under reflux for one hour on a steam bath with no steam escaping (Item 12, . 3 of the lab manual) or with a very small flame. Make a note of how long it takes for the contents of the flask to become homogeneous.

At the end of the reflux, stopper the flask with a rubber stopper, clamp the flask in an upright position and surround it with an ice water bath for at least 10 minutes. The product precipitates rapidly after heating is discontinued. Remove the stopper and add 40 mL of water which has been chilled to 0° to 2°. Break up the precipitate in the flask with a spatula so there are no lumps suspended in the liquid.

Collect the product by suction filtration. Wash the product three to five times with cold water (using a total of at 20-25 mL of water), then three to five times with saturated aqueous sodium bicarbonate solution (using a total of 20-25 mL of this solution), and finally five times with cold water (using a total of 30-35 mL of water). Air dry the precipitate on a sheet of white paper for at least a day. Determine the yield and the melting point of the product.

16.3-Questions

1. Why must the apparatus and chemicals used in this preparation be thoroughly dry, and why must the reaction be conducted under anhydrous conditions?
2. Would you expect variations in the concentration of sulfuric acid used in this reaction to affect the yield of product significantly if the reaction were heated under reflux for a very long period of time? Explain how the concentration of sulfuric acid does affect the yield.
3. Explain why the reaction mixture for this reaction and for similar esterifications using ethanol and butanol are heterogeneous initially but later become homogeneous. What factors would be expected to affect the length of time it takes for complete solution to occur?
4. Describe how you would recover unreacted 4-nitrobenzoic acid from the reaction mixture.

1 If you have less than 1.67 g, use whatever you have. Do not decrease the quantities of the other reagents in this procedure.

2 Since this reagent is hygroscopic, its exposure to the atmosphere should be as brief as possible. The reagent bottle should be closed tightly as soon as your sample has been withdrawn.

¹H NMR Experiment:

Organic chemists rely heavily on NMR (Nuclear Magnetic Resonance) to assist in assigning structures to unknown organic compounds. You learned about NMR in chem. 51; for a more in depth review of ¹H NMR spectroscopy as well as a list of common chemical shifts, refer to Chapter 13 and Appendix 4 in your textbook.

Brief review

Three pieces of information should be used when assigning structures to unknown compounds: 1) chemical shift, 2) peak multiplicity, and 3) peak integration. The chemical shift provides information about the electronic environment of the proton at which you are looking. Electron rich protons will appear more upfield (i.e. more towards 1-2 ppm); electron deficient protons will appear more downfield (i.e. more towards 10-11 ppm). The peak multiplicity provides information about the number of neighboring protons. Recall that peak multiplicity obeys the following formula: multiplicity = # of protons on adjacent carbon atoms + 1. The peak integration provides information about the number of protons at which you are looking relative to all other protons in the molecule.

As an example, let's look at the chemical shift, multiplicity, and integration of protons labeled H_A of ethyl acetate (see Figures 1 and 2). The protons labeled H_A are connected to a carbon that is bound only to an sp₃ carbon. sp₃ carbons are not as electronegative as sp₂ carbons or as oxygen atoms, which is why H_A appear farthest upfield. The protons labeled H_B are connected to a carbon that is bound to a carbon with two protons, labeled H_C, on it. In other words, the H_B protons have two "neighboring" protons, so the H_B protons will appear as a triplet. Finally, the peak corresponding to the H_C protons integrates to three, indicated by the "3H", because there are three H_C protons.

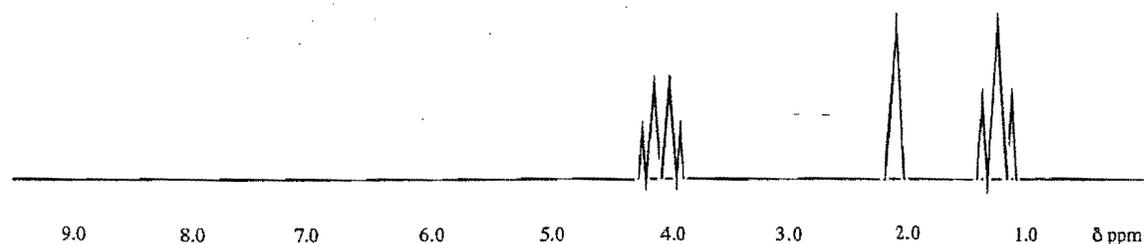
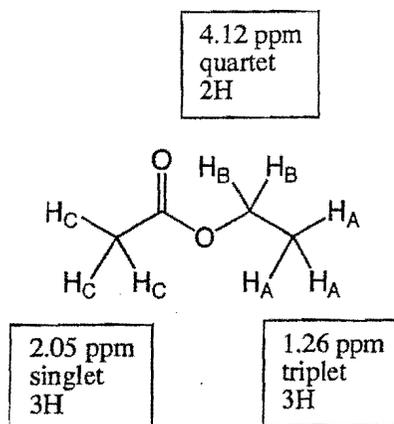
Figure 1: Representative ¹H Spectrum of Ethyl Acetate

Figure 2: Peak Assignment of Ethyl Acetate



To prepare your sample

- 1) It is very important that you use only clean and dry glassware in this experiment.
- 2) Weigh out 10 mg of your unknown into a small test tube.
- 3) If your unknown is soluble in water, dissolve your unknown in 1 mL of D₂O (deuterated water). If your unknown is insoluble in water, dissolve your unknown in 1 mL of CDCl₃ (deuterated chloroform).
- 4) If your unknown dissolves completely in the deuterated solvent, proceed to step 5.

If your unknown is mostly dissolved in the deuterated solvent, but some solid remains undissolved, you must filter your solution. Prepare a filter-pipette by placing a small piece of cotton firmly inside a disposable pipette. Pipette your sample into the filter pipette, and collect the liquid in a small, clean test tube or a small Erlenmeyer flask.

If your unknown is mostly undissolved in the deuterated solvent you chose, you may wish to try weighing out another 10 mg of your unknown and dissolving it in 1 mL of the other deuterated solvent.

- 5) Pipette about half your sample into the NMR tube. (You need about 1.5-2" of liquid in the tube.)
- 6) **CAREFULLY** place the cap on the NMR tube. NMR tubes are very fragile, and are easily broken when placing or removing their caps.

- 7) Make a label for your sample. The label should have the name of the deuterated solvent in which your sample was prepared (either D₂O or CDCl₃). You should also choose a short name for your sample. This could be a combination of you and your lab partner's initials, etc.
- 8) When your lab instructor tells you to, head over to the NMR room, which is located at 349NE. The NMR instructor will acquire a ¹H NMR spectrum of your unknown for you.
- 9) Keep the printout of your ¹H NMR spectrum, as you will need to attach it to your lab report at the end of the semester. In your lab report, you will also need to discuss how the ¹H NMR spectrum supports the structure you identified as your unknown.
- 10) When you return to lab, place the NMR tube in the appropriate container in the fume hood.