Welcome to CHEM 22300 Lab – Introduction & Common Policies

COURSE DESCRIPTION & GRADING OVERVIEW

In this course, you will first learn how to separate and purify organic compounds. You will then synthesize a number of organic compounds yourself and employ the techniques that you have learned earlier (as well as learn some new ones) to separate, purify, and study your reaction products.

Your grade will be assigned on a 1350-point schedule. Your point totals will be based on pre-lab quizzes, your lab performance, written lab reports and recitation class assessments. Keep in mind that good execution of laboratory techniques, adherence to safe laboratory practices (including cleanliness and proper disposal), the quality & quantity of the products you hand in, the organization of your work (including how well you have planned your work beforehand) and how well you understand the chemical processes that occur are all factored into your grade!

REQUIRED TEXT: Pavia, Kriz, Lampman, and Engel: A Small Scale Approach to Organic Laboratory Techniques, Fourth Edition. (This lab manual will refer to this textbook as "Pavia")

PLANNING AND EXECUTION

In the Organic Chemistry laboratory, you will plan and execute your work more independently than in previous laboratory courses that you have taken so far. You must do a lot of preparation work before you work on an experiment. In addition to reading the text, you must attend the lab recitation class. Take good notes in the lab recitation and review them carefully when planning each experiment. **The pre-laboratory assignments for each experiment must be completed BEFORE you come to class!**

Many of the experiments that you will complete this semester are not taken directly from the Pavia textbook though you may find many similarities. Part Six of the Pavia textbook (starting at page 548) should be especially helpful to you as it contains descriptions of the techniques you will use throughout the term. The importance of studying the recitation material and applying what you have learned cannot be exaggerated. The key to success is planning your work carefully before you enter the laboratory!

It is essential that you start working promptly as soon as possible, rather than socialize with other students. You will be so busy in some experiments that you probably won't have time to talk at length to anyone. Sometimes, you will need to work on different parts of an experiment at the same time in order to finish on time. It is very important that you finish all work within the scheduled class time and within the total time allotted for the experiment (if more than one class session is dedicated for an experiment). **No work will be allowed outside the scheduled class time, including washing glassware and taking melting points. Everybody must physically leave the laboratory by the scheduled end of class time!** No additional time will be given to any student who falls behind on work.

You will work individually on some procedures, but there are also some procedures in an experiment that you will perform in pairs or as a small group. Your instructor will let you know about the working arrangement on the day of the experiment. One set of equipment will be issued to a pair of students – you and your assigned partner will be responsible for keeping them in good condition throughout the semester (even if the two of you don't necessarily work together on any experiment).

When you hold a flask in front of your instructor to ask a question about the contents, you must be able to describe exactly what you put in the flask, and the exact sequence of operations you have carried out in arriving at that point. Your lab instructor will not simply provide answers! You should always be prepared to intelligently discuss what you are doing and try to arrive at a solution to your own problem

compound is considered a trace amount on the small ends of your spatula tips. In preparing sample solutions, the concentration must be adjusted so that isolable, discrete spots can be developed. A solution that is too low in concentration results in very faint spots, which can be difficult to visualize, while streaking and poor separation is observed when the concentration is too high.

HINT: Methylene chloride (dichloromethane) evaporates **VERY QUICKLY**! You must work very quickly as soon as you pour the methylene chloride from its glass container to the watch glass.

Spot the plate, by dipping either end of the capillary tube into the solution. The solution will be drawn up by capillary action. You then empty the capillary tube by touching it **lightly** on the surface of the TLC plate. This will transfer the solution to the plate as a small spot. You should only hold the micropipette in contact with the plate very briefly, otherwise, the entire contents may be delivered to the plate and your spot will be too large. It may be a good idea to gently blow on the plate as the sample is applied. This will help the solvent to evaporate quickly, keeping the spot small.

Developing the TLC Plate

Choose a solvent or solvent mixture (preferably a mixture of ethyl acetate, $CH_3CO_2C_2H_5$, and hexane. Petroleum ether can be used as a substitute for hexane) and prepare the developing chamber as shown in the illustration on page 13. Start by developing one plate with pure petroleum ether and another with pure ethyl acetate. Then use a one to one mixture of ethyl acetate and hexane. By examining these TLC plates, you can decide whether to increase or decrease the polarity as needed by adding more of either solvent. Be sure that you know what proportions of the solvents are used as you adjust the polarity of the mixture. The level of the solvent in the jar must be below the level of the spots, and the atmosphere in the jar should be saturated with solvent vapors. (If the jar is not saturated with solvent vapors, the solvent will not run all the way up the plate!). When the solvent front is near the top of the plate, immediately remove the plate from the beaker with forceps, and mark the solvent front with a pencil, before the solvent completely evaporates.

Visualizing the Spots on the TLC Plate

Allow the TLC plates to dry. First, check your plate with the UV lamp (short-wave). Lightly outline the spots which you observe with a pencil, and make a sketch of the TLC plate in your notebook. Note any differences in the appearance of the spots. **CAUTION:** Do not look directly at the UV lamp, or shine it at anyone else! If the spots are not visible under UV light, place the slide inside an iodine chamber and allow it to sit until the subliming iodine coats the TLC plate. Mark any new spots that become visible.

Calculating the R_f Values

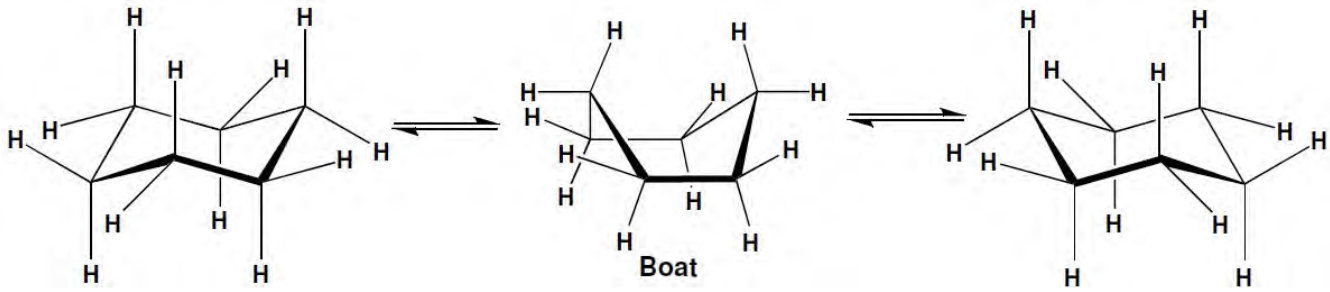
Next, measure the position of the original spotting to the spot (baseline), and of the solvent front. Calculate the R_f values. For each compound record in tabular form, the solvent (or solvent mixture) and the R_f value.

Part II. Column Chromatography

Packing the Micro-column

Silica gel should always be transferred inside the hood, since the small particle size makes it very hazardous to the respiratory system if it is breathed in. Prepare a column from a Pasteur pipette by carefully pushing a small piece of cotton down to the narrow part. Clamp the pipette with a thermometer clamp and add about 1/4 inch of sand (use weighing paper as a funnel). Then add about 2-1/2 inches of silica gel. Get a small quantity (just a spatula tip full) of the mixture of ferrocenes and add it directly to the top of the silica gel in your column. Then add another quarter of an inch of sand.

Draw a Newman Projection of your model of the chair conformation, sighting along the two parallel axes on either side. Grasp your model firmly by two of the parallel carbon-to-carbon bonds and push either end up or down to make the boat conformation. Compare and contrast the boat and chair conformations in terms of symmetry, torsional strain, steric strain, angle strain and overall energy. Draw the Newman Projection of the boat conformation, sighting down the two parallel carbon-to-carbon bonds. Now push the opposite end of the molecule up or down to convert it to the completely interconverted chair conformation as illustrated below.



Repeat this chair-to-chair interconversion (ring flip) several times. Make note of the relationship between axial and equatorial hydrogens as you do so. An actual sample of cyclohexane is a mixture of these rapidly interconverting chair conformations. Since both forms of the chair are equal in energy they contribute equally to the composition of their equilibrium mixture.

B. Constitutional Isomers and Conformations of Dimethylcyclohexane

Replace one of the axial hydrogen atoms on your model of cyclohexane with a methyl group. Then replace another axial hydrogen atom in position #3 on the same side of the ring to make *cis*-1,3-dimethylcyclohexane. Analyze the different symmetry elements of this molecule. When a non-hydrogen substituent is in an axial position on a chair conformation, it comes close enough to other substituents or axial hydrogens to interfere with them sterically. This produces a type of strain known as a **1,3-Diaxial Interaction**. As shown in *Table 1*, the 1,3-Diaxial interaction between a methyl group and one axial hydrogen increases the molecule's energy by 3.8 kJ/mol. Perform a ring flip to convert *cis*-1,3-dimethylcyclohexane to the opposite chair conformation. Observe the orientation of the two methyl groups in each conformation. Describe their relative energies in terms of torsional strain, steric strain and 1,3-diaxial interactions.

Keeping one methyl group in a fixed position, move the second methyl group to the other bond on position #3 to make *trans*-1,3-dimethylcyclohexane. Execute a ring flip and draw the chair and Newman Projection of both conformations. Perform the same analysis of this isomer in terms of its symmetry and energy that you did with *cis*-1,3-dimethylcyclohexane. Now move the second methyl group to different points around the ring until you have made all of the *cis* and *trans* isomers of dimethylcyclohexane. How many different constitutional isomers are there? Do a ring flip with each isomer that you make. Set up a table to include your illustrations of each isomer **and** its ring flipped conformation as **both** a chair and Newman Projection. Describe the relative energy of each pair of conformers.

WRITING YOUR LAB REPORT

Write your Lab Report following the format written on the "ORGANIC CHEMISTRY LAB 223 & 225 GENERAL NOTEBOOK FORMAT" sheet (Items 1 to 4 for Pre-Lab and 5 to 9 for Post-Lab).

Appendix III
MICROSCALE RECRYSTALLIZATION

Dissolving the solute: Before you dissolve the solute, prepare a Pasteur pipette for filtering. Shorten the stem of the pipette to about 1/2", by etching the glass with a file, and snapping it while holding with a piece of cloth. Insert a tiny cotton plug into the pipette, and add a small amount of celite (~1/4" high).

To a sample of the solute in a small test tube, carefully add dropwise via a pipette a small volume of hot solvent. Add a boiling chip, and maintain boiling of the solution while adding small portions of solvent. Swirl the test tube between additions to prevent bumping of the solution. Use a sand or water bath for heating. **Remember the aim is to use the minimum volume of solvent to dissolve the solute.**

Decolorizing the Solution and Removing Suspended Solids: Remove the boiling solution from the heating bath, and after boiling has subsided, add gradually a small amount of decolorizing carbon, (Norite) (caution-frothing), and swirl the solution gently. Heat the solution to boiling, gently, for approximately 5 minutes. Record the weight of a second clean, dry, small test tube to the nearest 0.0001g. Flush the Pasteur pipette prepared above, with hot solvent, and quickly filter the hot solution into the test tube, (Fig 1). Use a small amount of hot water, to ensure complete transfer of the solution. It is important that the filtration equipment is as hot as possible, and filtration carried out quickly, otherwise, cooling of the solution may lead to crystallization and blockage of the plug in the pipette.

Crystallizing the solute: Cover the mouth of the test tube containing the hot filtrate, by loosely replacing the cap, and allow to cool first to room temperature, then undisturbed, in an ice water bath. When the product has crystallized completely, collect, wash and dry the crystals according to Method I or II.

Method I - Filtration Using the Pasteur Pipette: The ice-cold crystalline mixture is stirred with a Pasteur pipette, and while air is being expelled from the pipette, it is forced to the bottom of the test tube. The bulb is released and the solvent is drawn into the pipette through the very small space between the square tip of the pipette and the curved bottom of the tube (Fig. 2). When all the solvent has been withdrawn it is expelled into another test tube held next to the tube containing the crystals. It is sometimes useful to rap the tube containing the wet crystals against a hard surface to pack them so that more solvent can be removed. The tube is returned to the ice bath, and a few drops of cold solvent are added to the crystals. The mixture is stirred to wash the crystals, and the solvent is again removed. This process can be repeated as many times as necessary.

Dry the product by connecting the test tube to the water aspirator (Fig. 3). If the tube is clamped in a beaker of hot water, the solvent will evaporate more rapidly under vacuum, but take care not to melt the product. Water, which has a high heat of vaporization, is difficult to remove this way. This may require taking the m.p. in the next lab period so that the crystals can air-dry over the week. Drying of the product may be hastened by scraping onto a filter paper and remove the last bit of solvent by squeezing the crystals between sheets of filter paper before drying them in air. Be careful with losses in transferring the crystals since you have to determine your percent recovery.

Determine the weight, % recovery and m.p.'s of the recrystallized material.

REFER TO FIGURES 1-3 ON THE NEXT PAGE