

Macroscale Esterification

BEFORE YOU COME TO LAB, YOU MUST PLAN AND WRITE OUT A PROCEDURE FOR THE SYNTHESIS, ISOLATION, AND PURIFICATION OF YOUR ASSIGNED ESTER (see below). FOR THIS EXPERIMENT, YOU WILL WORK ONLY FROM YOUR PRELAB OUTLINE. IF YOU DO NOT HAVE AN ADEQUATE PLAN AND PRELAB OUTLINE, YOU WILL NOT BE ABLE TO DO THE EXPERIMENT. If you have trouble with planning the synthesis or finding the entries in the handbook, see your TA BEFORE the day of your lab. As always, a table of reactants and products (sample table on moodle) should always be completed as part of the prelab outline for a synthesis experiment such as this. As always, the report will include an "Experimental" section and be written in the style of *JACS* or *JOC*.

This experiment is done on a macro scale. Consequently, new techniques and apparatus will be used. It is therefore imperative that you read the macroscale sections in the chapter on "Distillation" and review macroscale "Extraction," referred to in the "Schedule of Experiments".

Esters will be assigned by last name in a separate document.

In this synthesis, the ester is made from reaction of a carboxylic acid and an alcohol. To know what starting materials to use, you must write out the reaction that produces your ester. You will need to know the BPs, densities, and other physical properties of the reactants and products. In looking up esters in the Handbook, look up the name of the carboxylic acid and then, under that, the alkyl ester. For example, methyl hexanoate would be found under hexanoic acid, - methyl ester. As stated in the "Schedule of Experiments," plan to synthesize 0.080 mol of your ester, using an 8-fold excess (0.64 mol) of the alcohol. Use the procedure (but with your reactants and quantities, NOT those in the book) given for the synthesis of methyl benzoate (Experiment 40-4).

Caution: concentrated sulfuric acid is extremely dangerous. If you accidentally come into contact with it, immediately wash the contaminated skin with copious amounts of water and soap and water. Clean up spills immediately so others do not become accidentally contaminated.

Procedural notes: Exp 40-4, 2nd paragraph: use simple distillation to remove the t-butyl methyl ether. During extraction with bicarbonate, CO₂ evolution will cause pressure build-up. Vent the separatory funnel frequently.

Experimental Details:

Measure carboxylic acid by weight, alcohol by volume. Conc. sulfuric acid – use extreme CAUTION.

Condenser water: to ensure that the cooling water is cool, set up the condenser as soon as possible and begin a slow flow of water through it. By the time you are ready to begin heating the reaction, the water should be cool.

Mixing reactants: be sure to carefully swirl the contents of the RB flask as soon as you add the H₂SO₄, to completely mix the reagents. Allowing the conc H₂SO₄ to remain in contact with the reagents without mixing may cause decomposition of the reagents. Some darkening is not a problem.

Reflux: check for cracks in round-bottomed (RB) flask – replace if necessary. No grease on ground glass fittings. Place the heating mantle (without sand) onto a ring clamped to a ring stand and set it a few inches above the base of the stand. This will allow you to drop the heat quickly if overheating occurs. Securely clamp the RB flask but not the condenser (one clamp is all that is needed – using a clamp on the condenser may lead to a poor connection with the RB flask). Water in bottom of condenser, out top. VERY LOW

FLOW. Exit water into sink drain. Use boiling chips. Heat carefully so that vapors condense no higher than about 1/3 of the way up the condenser.

Extraction with separatory funnel: while reflux takes place, check sep funnel and operation first with plain water for practice. For each extraction, shake for a few minutes each time, venting often at first (don't point exit toward anyone – the bicarbonate extraction produces CO₂ and a build-up of pressure – vent right away). Collect aqueous washings in a large beaker for later disposal. After draining saturated sodium chloride (last wash), carefully pour org layer out the top of the sep funnel into Erlenmeyer, leaving behind droplets of water stuck to funnel.

Larger-Scale Distillation

In setting up a distillation apparatus using larger, ground-glass equipment, it is important to do it in the right order, and to take special precautions, which will help to make sure all connections are tight.

- Place the dried ester/t-butyl methyl ether solution into RB flask, along with a few boiling stones and clamp this to a ring stand, with the bottom of the flask about 3.5 – 4 inches above the base of the ring stand. The heating mantle (without sand) should be placed on an iron ring clamped to the ring stand. The idea is to be able to move the mantle up to the flask, so if overheating occurs, the mantle can be quickly lowered and moved away. (with the microscale distillation apparatus it was easy to move the entire apparatus up away from the heat if necessary but with the larger apparatus, it is not easy to do, so moving the heat down and away is better.)
- Place the distilling head onto the RB flask.
- Connect rubber tubing to a condenser, and using a second ring stand and large three-pronged clamp (double prong at bottom), clamp the condenser at approximately the same angle as the exit from the distilling head, and at approximately the height necessary to connect it to the distilling head. Slip a rubber band over the tubing going to the lower end (exit end) of the condenser.
- Move the condenser and ring stand close to the first ring stand, and using a combination of adjustments of the clamp (height, angle) and position of the ring stand, move the condenser up to make the connection with the distilling head, being sure that the angle and height are correct, so that there are no strains on the connection and the connection is tight. (this is tricky – the connections tend to separate easily unless the angle and position is just right).
- Attach the condenser adaptor to the lower end of the condenser and hold it in place with the rubber band slipped over the sidearm. Place a receiving flask under the adaptor to collect distillate.
- Carefully insert the thermometer into the thermometer adapter. Always be careful whenever inserting a glass tube such as a thermometer into an aperture, especially if the fitting is tight. ALWAYS HOLD THE THERMOMETER CLOSE TO THE ADAPTOR SO YOU ARE NOT PUTTING TOO MUCH LEVERAGE ON THE GLASS AND ALSO SO IF BREAKAGE OCCURS, THERE WILL JUST BE A SHORT PIECE OF BROKEN GLASS AND NOT A LONG DAGGER-LIKE PIECE FLYING AROUND UNCONTROLLED. Hold the thermometer very close to the adaptor as you push gently and twist away from yourself or anyone else, until the correct position is reached (the top of the liquid-filled bulb should be slightly below the bottom of the exit on the distilling head (you want the vapors which are just creeping over to completely engulf the bulb).

- Turn on the condenser water SLOWLY to produce a SLOW flow and make sure the exit water goes directly into the sink. Check the flow during the distillation to be sure it has not stopped. Generally, feeling the condenser will tell you if flow is ok – it should be cool.
- Because the ether is low boiling, the heating must be done gently. With the heating mantle set to about 3 and preheated, move it up towards the RB flask but not touching it. Leave a space between the flask and mantle. It will take minutes before the large volume of ether heats to the BP, so give it time. If more heat is needed, move the mantle up a bit more and wait. Distillation of the ether does not have to be done too slowly. When the distillation slows considerably and/or the temp rises well above the BP of the ether (52° C), stop. If heating becomes too rapid, just lower the mantle and swivel it to the side, away from the flask.
- Follow your prelab outline (instructions from the text) to further dry and distill the ester. Cooling water must NOT be used for the final ester distillation because it is not needed and the high-boiling ester may crack the condenser if the condenser is too cool. Distillation should be done at a rate of about one drop per second. Distill into a clean, dry, tared container, collecting as product material that distills at the correct temperature (+/-).
- Calculate % yield. Save the product for IR, GC, and NMR.

Waste Disposal: Place the aqueous layers from the three separatory funnel extractions and all other liquid wastes into the “Liquid Waste” container. Dispose of calcium chloride pellets in the container labeled as such.

Note the odor of the alcohol, the carboxylic acid, and the ester product and describe the odors in your notebook. Check the odor of other esters prepared by your colleagues and describe those as well. Analyze the product by GC and IR. Calculate a % yield. Save the sample for NMR analysis later in the semester.

Postlab Questions: (use ChemDraw for structures)

- 1.) Using structural formulas, write out a different synthesis of your ester, starting with the same starting materials (alcohol and carboxylic acid). Hint: look at the refs to Wade.
- 2.) Write out the detailed mechanism for your esterification reaction.
- 3.) Draw a predicted proton NMR spectrum for your product. Note that in most cases, simple first-order (n+1) rules will not apply for all of the H's in the molecule. For H's that have very similar chemical shifts, just describe those peaks as complex multiplets.