Experiment 9 —

Recrystallization

Pre-lab preparation. (1) Read the supplemental material from Zubrick, *The Organic Chem Lab Survival Manual*. (2) Draw the structure of acetanilide and report relevant physical data. Be sure to cite the source of the data. You should be able to figure out what's relevant by reading the procedure. (3) Find and report the boiling points of the solvents you will be using for this experiment. (4) Outline the steps in the recrystallization of acetanilide.

Recrystallization involves dissolving a solid in a solvent and crystallizing it again, taking the opportunity to discard impurities along the way. One normally chooses a solvent in which the solubility increases significantly with temperature. The solid is dissolved in a minimal amount of hot solvent, and the solution is filtered to remove *insoluble* impurities. Upon cooling the solution, the desired compound crystallizes, leaving *soluble* impurities in solution. Alternatively, a mixed solvent system can be used to modify the solubility — the key is to get the compound into solution then get it back out of solution.

Ideally, one would like to recover all of the desired solid completely free of contaminants. Unfortunately, this is rarely possible. Usually, if most of the material is recovered, it is not very pure, and extremely pure material can be obtained only in low yield. The trick is to find the proper balance between yield and purity.

Now to the specifics of the problem at hand. Over the summer, certain stockroom personnel had an unauthorized juggling contest and accidentally dumped all the acetanilide on the floor. Unfortunately, the floor wasn't very clean, now the material is contaminated with what appears to be rodent hair, gravel, dead spiders, etc. They were able to remove most of the dead roaches. Your mission, should you decide to accept it... well, you really have no choice but to accept it, do you?... is to clean up the acetanilide by recrystallizing it.

Part A — acetanilide. Fetch about 1 g of dirty acetanilide. Don't fool around adjusting the mass to 1.000g — it's not that important — just *record* ***in your notebook*** *exactly how much you used*. Place your weighed sample in a 125-ml Erlenmeyer flask and add a boiling chip. Heat about 50 ml of water to boiling in a separate flask (+ boiling chip!) using a hot plate.

Note: Always add a boiling chip *before* heating any solvent or solution. *Never* add any solid to a liquid that is at or near its boiling point. Suddenly creating nucleation sites is likely to cause anything from a simple boil-over to something resembling a volcano.

Now, dissolve the solid in a minimal amount of boiling water. This is done by adding the solvent to the solute (*not* the other way around!) in small increments and bringing the solution to a boil. Start out with about 10 - 15 ml of water and add a few ml at a time until all the soluble stuff dissolves. (Don't measure it out, just estimate!) Watch how much solid dissolves each time — this will give you an idea how much water you'll need to add to dissolve it all. Just be careful not to add way too much water, or you'll have to reduce the volume later. And keep in mind that there may be insoluble junk remaining after all the good stuff has dissolved. How do you tell the difference? One bit of information is the color. What color is acetanilide? What color is the stuff that's not dissolving? One final bit of advice — solids with melting points below the boiling point of the solvent will melt and form what look like oil droplets. If you see this, you need to add more solvent until the droplets dissolve. Even solids that melt above the solvent bp may do this if they are very impure (remember mp depression?) or if the hot water can infiltrate the crystal lattice

To get rid of the insoluble bits, filter the hot solution by gravity through a pre-warmed funnel containing fluted filter paper. *The tricky part is to keep the solution hot during this operation*. This is important — if you heat the solution, then remove it from the hot plate and try to do the filtration on the benchtop, everything's going to cool down, right? Solid will precipitate all over the place and make a terrible mess. Rinse the filter paper with a little hot solvent to dissolve any crystals that may have formed.

Slow crystallization is the key to getting high purity product. Plunging the hot solution into ice may cause tiny crystallites to crash out of solution (if it doesn't break the flask), and lots of impurities will end up trapped in the crystal lattice. So don't do that. Instead, allow the

filtrate to cool sllloooooooowwwwly. Be patient. If the solution was close to the saturation point when it was hot, the compound should be eager to crystallize as the solution cools. If no crystals form, this could be because (1) the solution is too dilute (i.e. the solid is completely soluble so it doesn't want to come out of solution), or (2) the solution is supersaturated (i.e. the solid would like to crystallize but can't quite decide how to get started. If the problem is too much solvent, the only remedy is to boil off the excess. If the solution is supersaturated, try scratching the flask with a glass stirring rod — the scratches and glass chips may provide nucleation sites that get crystal formation started. If that doesn't work, try adding a tiny seed crystal. The best seed crystal is a tiny speck of someone else's clean solid. If you're not too fussy about product purity, those white flakes in your instructor's beard can probably also be used as seed crystals. Once crystal formation appears to have stopped, cool the flask in ice to complete the crystallization. Collect the crystals by suction filtration using a Büchner funnel. Wash the crystals with a few milliliters of *cold* water, and press them down with a clean spatula or small beaker.

Dry the crystals by pressing them between two pieces of clean filter paper, and let them dry until your next lab period. You will then determine the mass, the % recovery, and the melting range.

Part B — solids from Extraction lab. You've saved samples of benzoic acid, benzocaine, and fluorenone that we separated by extraction several weeks ago. Now we're going to purify these by recrystallization. So that we have plenty of material to work with we're going to start by consolidating samples with other groups.

Get together with two other groups, and combine your three samples of benzoic acid, (*separately!*) combine your three samples of benzocaine, and combine your three samples of fluorenone. (If you misread this and mix everything together, no worries, you can just repeat the extraction to separate them again.)

Now, one group is going to recrystallize the benzoic acid from water, one group is going to recrystallize the benzocaine from ethanol and water, and one group is going to recrystallize the fluorenone from hexanes.

You'll have to figure out how much solvent to use. Hot filtration should probably not be necessary unless you have to sweep the solid up off the floor. The procedure for the mixed solvent crystallization can be found in the supplemental reading from Zubrick.

Your purified solids will be dry enough by next week for a final melting point. Next semester we'll measure their infrared spectra.

Your report for this lab consists of your data and observations for both parts that you did. Also include a brief synopsis of the procedures used by the two groups with whom you collaborated. For example, "W. Fu and G. Snyder recrystallized 4.27g of impure Lipitor that they swept up off the floor. 15 ml of boiling benzene was used to dissolve the solid, and the hot solution was filtered by gravity. Upon cooling... [describe the crystals and how they were isolated]" If the solid is dry, you can measure the mass and % recovery now.

Turn this in before you leave, *not next week, please*. The management appreciates your cooperation.