

EXPERIMENT #2 - SYNTHESIS AND RECRYSTALLIZATION OF DIBENZALACETONE

Introduction and Purpose

Recrystallization is, by far, the most common way in which solid organic compounds are purified. Since experimental chemistry can be a challenge under the best of circumstances, most practitioners try to operate under those circumstances. This means, among other things, working with pure compounds. Consequently, solid products of reactions are routinely recrystallized before subsequent use. The main purpose of this experiment is to give you some understanding of the process of purification of solids by recrystallization and to give you some practical experience in carrying out this process.

Theory

The problem at hand is that you have a solid substance that contains relatively small, but significant, amounts of impurities, and you want to dispose of the impurities but keep as much of the compound as you can. [Recrystallization is less likely to be successful if there are really large amounts of impurity. See if you can figure out why, after you have read this.] The solution to this problem is to find a solvent that has the following properties:

- ☞ your compound is soluble in the hot solvent,
- ☞ your compound is insoluble, or only slightly soluble, when the solvent is cold, and
- ☞ the impurities are either completely soluble when the solvent is cold, or completely insoluble when the solvent is hot.

This set of properties, combined with some work on your part, will enable you to clean up impure solids by separating out the impurities and throwing them away. The idea, then, is to place the material to be recrystallized in an Erlenmeyer flask, add a small amount of solvent that has the properties described above, and warm the mixture, bringing it to a boil. If all of the compound does not dissolve after a few minutes of boiling, you slowly add more solvent, keeping the mixture at a gentle boil, until all of the compound has dissolved. *If* any insoluble impurities – rust, dandruff, floor sweepings, *etc.* – are observed, use gravity filtration (conical funnel and folded filter paper, not Buchner funnel with vacuum and flat filter paper) to remove them and discard. After you have done this, or if there were no insoluble impurities, allow the filtrate to cool and collect the crystals of product that form, on a Buchner funnel. The soluble impurities are now in the filtrate, which is discarded. The solvent adhering to the crystals in the Buchner funnel is allowed to evaporate. The product is now pure.

The Art of Recrystallization

O.K., in practice, things get a *little* more complicated than suggested above. But we're definitely not talking about brain surgery here. Even a Hartwick student can perform a successful recrystallization (well..., some of them).

The Solvent

If you are not told what solvent to use the first thing you will have to do is select one. If the compound you are trying to recrystallize is listed in a handbook such as the CRC

"Handbook of Chemistry and Physics" or "The Merck Index", that source may provide a suggestion. In the absence of specific information you'll be on your own. What properties should you look for? First, the solvent should not react with your sample. Secondly, the solvent should have the properties described above in regard to the compound and its impurities. Thirdly, the solvent should not have low volatility because it will adhere to the crystals after recrystallization. For this reason, solvents with boiling points much in excess of 100° C are rarely used. Fourthly, the boiling point should not be below about 50° C for the solubility of the compound to be substantially greater at the boiling point than it is at room temperature. Finally, it is usually unwise to use a solvent that has a boiling point that is higher than the melting point of the substance being recrystallized, as doing this is likely to result in the formation of an oil rather than crystals. What this boils down to is that you will have to test the sample solubility characteristics in a series of solvents that are fairly inert and boil between ~50° and ~100°. Some common solvents are listed below.

To test the solubility suitability of the solvent, place 0.10 gram of your solid in a small test tube. Add 3 milliliters of a solvent, cork the tube, and shake. If the sample dissolves, it is too soluble in this solvent; try another. If the sample is insoluble or slightly soluble, place a boiling stick into the test tube to prevent "bumping" and heat the tube in a BB bath until the contents boil gently. Stir using the stick. If the sample does not dissolve at all, try another solvent; if a substantial amount dissolves, this may prove to be a good solvent. Try cooling the test tube in an ice/water bath. If crystals do not form, try scratching the bottom of the test tube on the inside with a glass stirring rod. If you get crystals, with or without scratching or incantations, you have found a solvent. If you do not get crystals, try another solvent. If you cannot find a suitable solvent, you may have to perform a *mixed-solvent recrystallization*. In this situation, you employ a mixture of two solvents, one in which the compound is quite soluble and the other in which the compound is almost insoluble. This is described later on.

Solvent	Boiling Point, °C	Comments
water	100	Good for polar compounds, difficult to remove from crystals.
ethanol (<i>aka</i> alcohol, Reagent Alcohol)	78	Very common - often tried first, fairly polar, easily removed, may react with acids and esters.
2-butanone (<i>aka</i> methyl ethyl ketone)	80	Moderately polar, easily removed.
ethyl acetate	78	Moderately polar, easily removed.
toluene	110	Low polarity, not easily removed, unreactive.
Ligroin/petroleum ether	60-90/30-60	Non-polar, unreactive hydrocarbons. Ligroin is commonly used.

Performing a Typical Recrystallization

Put the material to be recrystallized in a reasonable sized Erlenmeyer flask (or test tube, for small samples); as a rule of thumb the solid should occupy between 10 and 25% of the volume of the vessel. Add a boiling chip to the flask (or an applicator stick to the test tube) so the liquid in the flask doesn't "bump" when it boils. [The boiling chip or wood provides places where bubbles can form. The smooth glass surface of the vessel does not provide places for this *nucleation*. This can lead to the liquid becoming *superheated* – remaining a liquid above its boiling point. When a bubble does form in this circumstance, it can undergo a very rapid expansion, pushing the liquid out of the vessel ahead of it.] (If you remember to add the boiling aid after you have heated the mixture, remove the vessel from the heat until it cools a little, then add it.) Add enough solvent to just form a slurry with the crystals. Warm the flask or test tube using a safe source of heat; do *not* use a flame if the solvent is flammable. (The only common non-flammable recrystallization solvent is water. A safe source of heat would be a heating mantle containing BB's, hot plate, or steam bath. If you use a BB bath, plug the heater into the voltage controller and the controller into the 120 volt outlet. The voltage controller will give you some control over the temperature of the BB bath.) As some of the solid dissolves with heating, slowly add more solvent (a Pasteur pipet or eye dropper works well for a test tube; you can slowly pour liquid into a flask from time to time) and continue heating to keep the solution at or near its boiling point. Continue doing this – adding solvent and heating – until all of the material that is soluble dissolves. If there are no insoluble impurities, everything will have dissolved. If there are insoluble impurities, there will be flotsam and jetsam in the solution – not everything will have dissolved. If you pay attention to what is going on, it is usually easy to tell the difference between undissolved compound and the flotsam and jetsam of insoluble impurities. If you have no insoluble impurities, continue with the next paragraph. If you do have insoluble impurities (this is not very common) see the section below that deals with this, now; then come back to the following paragraph.

Allow the solution to cool to room temperature. If crystals do not form, scratch the inside of the vessel with a *glass* stirring rod. The scratches you make on the glass provide a place for crystal growth. If this does not work, and a small amount of the solid compound is available, you can add a few *seed crystals* to the solution to initiate crystallization. Cooling the flask in an ice/water bath will cause some more of your product to crystallize from solution. The downside is that doing this can sometimes cause impurities to crystallize out, but that doesn't usually happen.

If you will be collecting more than about a gram of product, collect it using a clean Buchner funnel. To do this, fit the funnel with filter paper that covers the holes and lies flat on the bottom of the funnel. Using the attached rubber stopper, insert the funnel into a clean filter flask that has a neck of such diameter that the stopper will not be sucked into the flask when vacuum is applied. Fit the bottom of an aspirator with a splash arrester (do not push the splash arrester all the way onto the aspirator as doing this will partially block the flow of water). Attach a piece of black, thick-walled rubber tubing to the side-arm of the aspirator and to the side-arm of the filter flask. Open the valve on the faucet all the way. The vacuum should be sufficient to hold the filter paper to the Buchner funnel. Swirl the contents of the flask and pour them into the funnel. If not all the crystals have been transferred to the funnel, you may rinse out the remaining ones with a little cold recrystallization solvent. (Depending on how impure your sample was, it may be advantageous to *wash* the crystals in the Buchner funnel with a little cold solvent to remove impurities adhering to their surfaces. The tradeoff here is that you will dissolve some

product and this will be lost.) Allow the solvent to evaporate from the product. If you have recovered most of the material you started with store it in a *labeled* vial. [Recrystallization always results in some loss of product. The filtrate that you discard contains the soluble impurities, but it is also saturated with your product. This is why, of course, that we use a solvent in which the compound is only slightly soluble at room temperature.] If you are submitting the material to your instructor, include the following on the label: your name, name of the compound, melting point of the compound, and yield (weight of the compound).

If you think you had a lot more product before recrystallization than you have now, you can try to collect a second crop of crystals. To do this, place the filtrate into a beaker, add a boiling chip, and boil the solution down to about half its initial volume. Allow the solution to cool and collect the crystals on a Buchner funnel, as above. Keep the first and second crops of crystals separate, as the second crop may be less pure than the first. If you are submitting the product to your instructor, use two vials and label each with your name, name of the compound, melting point of the compound, weight of the material in the vial, and "First Crop" or "Second Crop".

How To Deal With Insoluble Impurities

The idea is to remove these impurities, by filtering them out, while the solvent is hot and the compound you're recrystallizing is, therefore, in solution. In practice, the trouble with doing this is that as you try to filter the mixture, it cools. Since it is saturated with your compound, the compound begins to crystallize in the filter. This plugs the pores of the filter paper, slowing the filtration. This slower filtration gives even more opportunity for cooling, resulting in even greater deposition of crystals in the paper – a vicious cycle, the result of which is that most of the compound winds up deposited in and on the filter paper along with the insoluble impurities.

This problem is easily solved. At the point in the recrystallization procedure where you are heating the mixture and everything but the insoluble impurities have dissolved, add about 33% more solvent to the flask and remember how much you are adding at this point. For example, if there are 100 ml of solvent in the flask already, add an additional 33 ml. Bring the mixture back to boiling, then carry out a gravity filtration of the mixture. Now the mixture is not saturated at its boiling point, so if it cools somewhat as it is being filtered crystals do not precipitate out. Nevertheless, you will want to filter the mixture as quickly as possible. Unfortunately, vacuum filtration does not work well; the holes in the Buchner funnel become plugged owing to evaporation of solvent under vacuum. This leaves trying to accomplish a gravity filtration as rapidly as possible. This means that we do not fold the filter paper in quarters, as you may have done in general chemistry. If you do that, you use only half of the filtering capacity of the filter paper. What you should do, is use *fluted filter paper*. Fluting filter paper involves some origami and a live

Try to move the apex of your folds across the diameter of the circle so you do not wear a hole in the center of the paper.

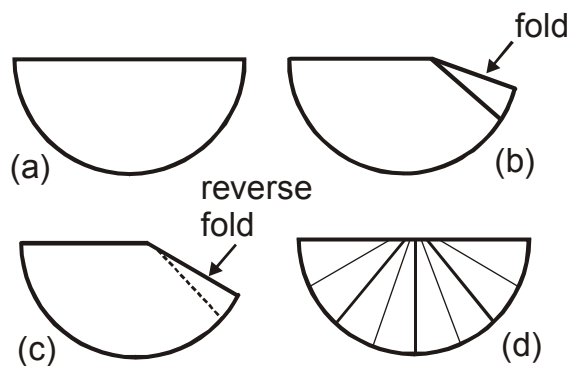


Figure 1 - Fluting the Filter Paper

demonstration helps. The basic idea is that you want to make the filter paper fold like a paper fan or an accordion. An easy way to do this, is to fold a circle of filter paper in half (Fig. 1a). Then, starting about one-third the way along the folded edge, fold over a narrow pie shaped wedge (Fig. 1b). Then fold a similar wedge next to the one you just made, but fold the paper in the opposite direction to make pleats or fan-like folds (Fig. 1c). Continue doing this, folding back and forth, until the whole circle is pleated. As you are folding, try to move the apex of the folds down the length (the diameter) of the first fold you made (the one in which the circle was folded in half), winding up about two-thirds the way from the end at which you started (Fig 1d). Open the filter paper. Find a stemless or short-stemmed conical funnel. [You do not want to give the crystals the opportunity to form in the stem of a funnel.] Set the funnel into the neck of an Erlenmeyer flask, insert the fluted filter paper, and filter the mixture. If crystals of product do not form in the filter paper, discard it. Put the filtrate into a *beaker* and boil off the 33% additional solvent you added. Allow the solution to cool and collect the crystals as described above.

Mixed Solvent Recrystallizations

Sometimes you cannot find a solvent that has just the properties you need for a recrystallization; the compound is too soluble in some and insoluble in the others when they are hot. In a case like this it is sometimes possible to carry out the recrystallization using a mixture of two solvents. The two solvents you use must be completely miscible with each other; you definitely do not need the complication of two liquid phases. Usually, you would employ one solvent in which your compound is soluble and one in which it is not. Ethanol - water is probably the most commonly used solvent pair. For the most part, you proceed as you would for a one solvent recrystallization, except at the beginning –

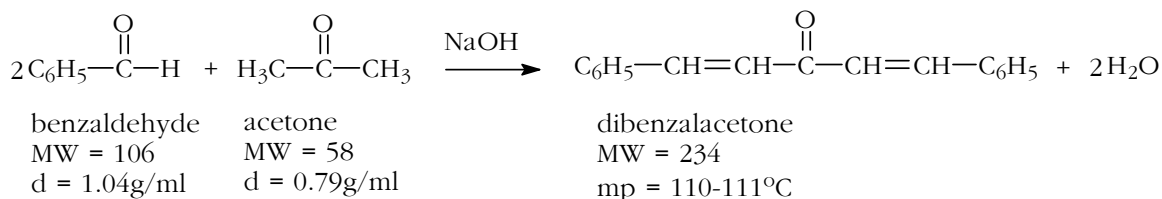
Add enough of the solvent in which the material is insoluble to make a slurry. Warm the mixture and begin to add some of the solvent in which the compound is soluble. Continue to add this solvent, slowly with warming, until your compound has just dissolved. At this point proceed as you would in any other recrystallization.

Mixed solvent recrystallizations are usually a desperation measure. The reason is that these crystallizations are more likely to form oils (rather than crystals) than single solvent crystallizations. While crystals are usually fairly pure – the impurities are insoluble in your crystalline compound – the same cannot be said for oils. If your compound oils out, the impurities are likely to dissolve in the oil. The oil may solidify as it cools down, but that doesn't make it any purer. What can you do if you get an oil rather than crystals?

- 1) Try changing the composition of the solvent. Use less solvent richer in the component in which your compound is more soluble, or more solvent richer in the component in which your compound is less soluble.
- 2) Evaporate off all the solvent and again look for a single solvent that will do the job.
- 3) Pray.
- 4) *Triturate* some of the oil with some solvent or other. Place some of the oil on a watch glass, add a drop or two of solvent, and scratch the mixture with a stirring rod. Maybe you can beat the oil into submission, causing it to crystallize.
- 5) Ask your instructor for help. He will be sympathetic, knowing that oiling can be very frustrating, but he may not be able to help much.

Synthesis of Dibenzalacetone

Introduction



The synthesis of dibenzalacetone is an example of a type of reaction known as a Claisen-Schmidt condensation. The details of how this reaction takes place – its *mechanism* – may be discussed in lecture. For our present purpose – developing skill at recrystallization – it is sufficient to note that this reaction gives a solid product, which is impure when first isolated, but which can be purified by recrystallization.

Procedure

Mix 0.05 mole of benzaldehyde (0.05 mole x 106 g/mole = 5.3 g; 5.3 g/1.04 g/ml = 5.1ml) with 0.025 mole of acetone [Acetone: MW = 58.1, density = 0.790 g/ml.] in a 25 or 50-ml Erlenmeyer flask. Set the flask (flask #1) aside.

In a 125 or 250-ml Erlenmeyer flask (flask #2) dissolve 5 g of sodium hydroxide in 50 ml of water, add 40 ml of ethanol, and cool this solution to 20° C.

Add *half* of the benzaldehyde-acetone solution (flask #1) to the sodium hydroxide solution (flask #2) and swirl the mixture frequently for 15 minutes. The mixture should turn cloudy within a couple of minutes of mixing and a yellow precipitate should form. After 15 minutes add the second half of the benzaldehyde-acetone mixture (flask #1) to the basic mixture (flask #2). Rinse flask #1 with a little ethanol and add this to the basic mixture (flask #2) also. Continue swirling frequently for 30 minutes. Collect the yellow precipitate by suction filtration in a Buchner funnel. (The aqueous filtrate may be discarded in the sink.) Transfer the yellow solid to a large beaker and add 300 ml of water. Stir this mixture to break up clumps of the product so the water can dissolve the remaining sodium hydroxide; the dibenzalacetone is insoluble in water. Collect the crude product by suction filtration on a Buchner funnel using a fresh piece of filter paper. While the aspirator is on, press the filter cake with a cork to express as much water as possible. (Again, the aqueous filtrate may be discarded in the sink.)

To recrystallize the crude product place it in an Erlenmeyer flask of appropriate size and add enough ethanol to make a thick slurry of the crystals. Place a boiling chip in the flask (to prevent “bumping”) and warm the mixture on a hot plate. While it is boiling gently, *slowly* add ethanol until the crystals just dissolve. Allow the solution to cool until crystals have formed and it is no longer hot. You may cool the mixture in ice at this point. After crystals have stopped forming, collect the recrystallized dibenzalacetone in a Buchner funnel and wash the crystals with a little *cold* ethanol. Transfer the crystals to a beaker, label the beaker “recrystallized dibenzalacetone,” and allow the crystals to air dry until the next lab period. (Discard the filtrate in the container labeled “Filtrate from Recrystallization of Dibenzalacetone.”) Determine the melting point and weight of the crystals and record this information on the report form along with the percent yield. Submit your product in a 4 dram, or larger, vial, labeled as shown on the report sheet, along with the report.