

CH 241 EXPERIMENT #5

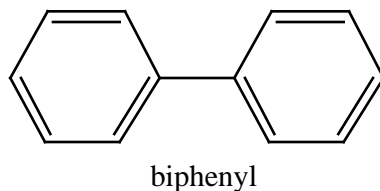
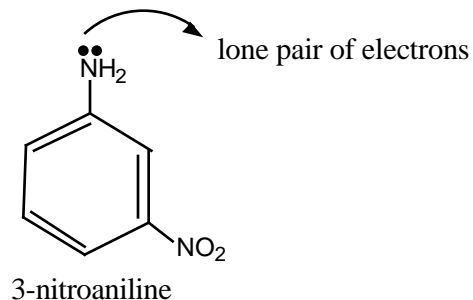
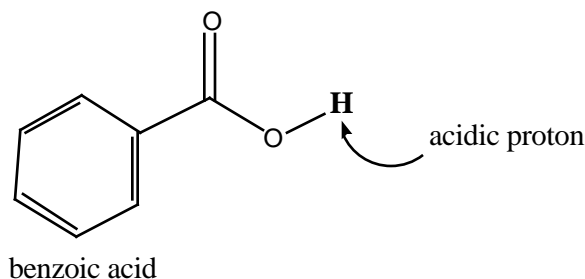
WEEKS OF OCTOBER 29 AND NOVEMBER 5, 2001

CHEMICALLY ACTIVE EXTRACTION INFRARED SPECTROSCOPY

A. Background

In this experiment you will use extraction and acid-base chemistry to separate reactive organic compounds from a crude sample that potentially contains biphenyl (or diphenyl), benzoic acid and 3-nitroaniline (or m-nitroaniline). In the interest of time, only two of those components will actually be in the mixture, but you will not know which two until you work up the extracts. The recovered crude products will then be further purified, if necessary, by recrystallization in Week 2 of this experiment. You will be using melting points and tlc, with which you are already familiar, and a new technique, infrared spectroscopy (IR), to determine the purity of your products. Infrared spectroscopy will be discussed in class prior to the beginning of Week 2.

Benzoic acid is a carboxylic acid; it has a proton that can be abstracted by a base such as sodium hydroxide or sodium bicarbonate. The 3-nitroaniline is an organic base; there is a lone pair of electrons on the nitrogen atom of the amino group, making 3-nitroaniline a Lewis base (an electron pair donor). Under these conditions biphenyl has neither an acidic proton nor a lone pair of electrons to donate, and is considered a neutral compound.



These three compounds are very soluble in dichloromethane (also commonly called methylene chloride), but not appreciably soluble in water. Therefore, if you were to dissolve these compounds in dichloromethane and try to extract them into water by shaking the layers in a separatory funnel, most of all three of the compounds would remain in the dichloromethane layer. However, if you selectively change the structure of the compounds,

one at a time, separation is possible. Benzoic acid is an acid; if you react it with a base, such as sodium hydroxide or sodium bicarbonate, the result would be a charged species, an anion. Charged species partition preferentially and readily into the highly polar aqueous phase (remember that a sodium hydroxide or sodium bicarbonate solution is just "basic" water), so you have effectively removed benzoic acid from the dichloromethane layer and into the aqueous layer as its charged anionic form. Similarly, if you react the base 3-nitroaniline with an acid, like HCl, the result is again a charged species, this time a cation, which will partition into the acidic aqueous phase. Since biphenyl has neither an acidic proton nor a lone pair of electrons, it will remain in the dichloromethane layer throughout the extraction procedure. **Use this information to help you complete your flow diagram (see Section D.)**

B. Experiment--Week One

Be sure to record all pH measurements, all weights of isolated products and all melting point ranges in your notebook. Be sure compounds are dry before weighing, taking melting points or performing tlc and IR analysis.

1. Dissolution of Sample.

Weigh out approximately 8 g of the Crude CAE (for chemically active extraction) Mixture, which contains a 1:1 weight mixture of biphenyl and/or benzoic acid and/or 3-nitroaniline. Save a few milligrams of the mixture for tlc analysis. Dissolve the mixture in 100 mL of dichloromethane (CH_2Cl_2). If any solid does not dissolve, filter (by gravity) the solution directly into a separatory funnel. Otherwise, pour the solution into the separatory funnel.

2. Acid Extraction.

Extract the CH_2Cl_2 solution *two times* with 30 mL aliquots of **2.5 M HCl** (i.e. *separate* the layers after the first extraction, return the CH_2Cl_2 solution to the separatory funnel and extract it again with a fresh 30 mL portion of **2.5 M HCl**). Combine the aqueous layers from both extractions in a *labeled* 250 mL beaker and test the pH of the aqueous solution. It should be acidic.

3. Basic Extraction.

Extract the CH_2Cl_2 solution resulting from step 2, *two times* with 30 mL aliquots of 10% NaHCO_3 . Be sure to open the stopcock frequently to "vent" the separatory funnel since CO_2 gas will be evolved during these extractions. Combine the aqueous layers in a *labeled* 400 mL beaker and test the pH of the aqueous solution. It should be basic.

4. Recovery of the Compounds.

a. CH_2Cl_2 solution:

Dry the CH_2Cl_2 solution resulting from step 3 with *anhydrous* Na_2SO_4 . Let this mixture stand for about 5 minutes, swirling it frequently. Remove the drying agent by gravity filtration or by decanting, add a boiling stone and evaporate the solvent using a rotary evaporator or by a simple distillation using your steam bath as the heat source. Be sure to put the recovered CH_2Cl_2 into the appropriate container. If a solid is present after the evaporation of the solvent, transfer it to a large filter paper with the sides turned up and air-dry the solid *until the end of the period* (see section d).

b. Acid Extracts:

While the CH_2Cl_2 is evaporating, cool the acid solution in an ice-water bath and then make the solution basic by adding **6 M** NaOH until the solution tests strongly basic with pH paper. A precipitate should form during the addition of NaOH if a compound is present in this extract. Collect the solid by vacuum filtration and wash the solid on the filter with ice cold water. Transfer the compound to a large filter paper and allow it to dry (see section *d*).

c. Base Extracts:

Cool the basic solution in an ice-water bath and then make the solution acidic by **slowly** adding **6 M** HCl with stirring (CAUTION: CO_2 evolution may cause the solution to foam) until it tests strongly acidic with pH paper. Collect any precipitated solid by vacuum filtration and wash the solid on the filter with ice cold water. Transfer the compound to a large filter paper and allow it to dry (see section *d*).

NOTE: A tip to speed filtrations: Finely divided precipitates often clog the filter paper of a Büchner or Hirsh funnel and can take a very long time to filter. To avoid this, try to decant the bulk of the liquid through the filter before much solid is transferred to the funnel and try *not* to let the filter paper go dry until the end of the filtration. If the funnel does clog, *gentle* scraping of the filter paper with a spatula may help. If that doesn't work, then change to a fresh filter paper. When transferring the solid to the funnel, use a rubber policeman to scrape the walls of beakers or Erlenmeyer flasks. Stirring rods or scoop shaped spatulas are less effective.

d. Drying Procedures and Data:

The "recovered crude biphenyl"* should be crushed to small particle size and allowed to dry for a total of about one hour. It will dry quickly since it was isolated from a low boiling solvent. At other times, keep it in a closed vial since it sublimes. Because your crude biphenyl dries quickly, it should be possible to weigh it and take its melting point during the first week. Take its melting point side by side with pure biphenyl.

The benzoic acid* and 3-nitroaniline* should be allowed to air dry in the student sample drawer until the next period. At the end of the day, transfer the compounds to vials, but leave the vials open. These compounds were isolated from water, and water evaporates slowly from these polar compounds.

*Of course, you will have only two of the three possible compounds.

C. Prelab Assignment--Week 1:

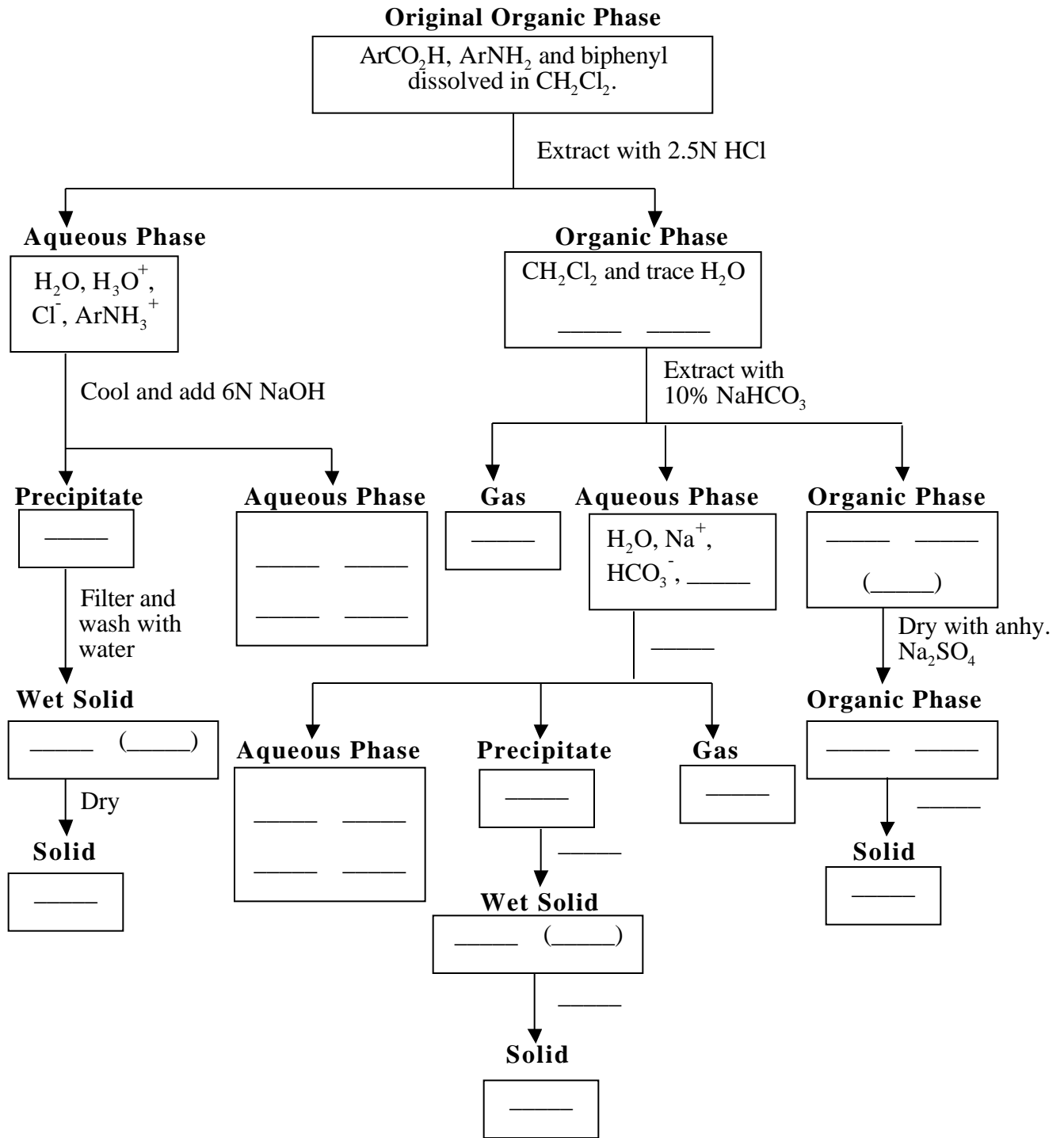
1. Prepare a table of compounds listing:
 - a. the boiling point and density of dichloromethane
 - b. the melting points, water solubility and the solubility in organic solvents of 3-nitroaniline, benzoic acid and biphenyl
2. Write the equations (there should be four of them) to illustrate the reactions taking place in this experiment. Use **structural formulas** and **indicate clearly which atoms in the structures gain or lose protons** in the reactions.
3. Read a treatment about extractions, the use of a separatory funnel and the use of drying agents in one of the laboratory texts in the Science Library.
 - a. In this experiment, will the organic phase be the top layer or the bottom layer?
 - b. Explain briefly how a drying agent works.

D. Flow Diagrams

Flow diagrams are often used to summarize procedures for the separation and purification of the components of complex mixtures. A flow diagram consists of a series of boxes connected by arrows. Each box represents a *phase* (solid, liquid or vapor) and connecting arrows represent *operations* (e.g. filter, extract, boil, etc.) or addition of reagents. The name of the phase is written above each box and symbols, formulas, etc. for *all of the important* components of the phase are written inside each box. Operations and/or reagents are written under or next to appropriate arrows. Separation of phases is shown by a split in the arrow, giving two boxes.

An **incomplete** flow diagram for this extraction experiment is given on the next page. It contains all of the arrows and boxes needed, but lacks some operations and compounds. You should refer to this flow diagram as you proceed with the experiment during Week 1. A completed diagram is required as part of the prelab for Week 2. Use ArCO_2H for benzoic acid, ArCO_2^- to represent deprotonated benzoic acid, ArNH_2 for 3-nitroaniline, ArNH_3^+ for protonated 3-nitroaniline and Ph-Ph for biphenyl.

**Incomplete Sample Flow Diagram
(Fill in the blanks)**



Abbreviations: ArCO₂H = benzoic acid; ArNH₂ = 3-nitroaniline; Ph-Ph = biphenyl

E. Experiment--Week 2

1. If you did not weigh and take the melting point (m.p.) of your crude biphenyl* side by side with pure biphenyl, do so.
2. Weigh your crude benzoic acid* and take its m.p. side by side with pure benzoic acid.
3. Weigh your crude 3-nitroaniline* and take its m.p. side by side with pure 3-nitroaniline.
4. Save a few milligrams of each product for tlc analysis. At this point, you should have a sample of the original mixture from the beginning of Week 1 and the two recovered compounds. Every plate you run must include authentic samples as well so that the R_f values of these compounds can be compared to the R_f values of the spots you find using your experimental compounds. Therefore, the origin of your tlc plate should have five lanes. If you don't think that five spots will fit, run two separate plates, but make sure the authentic compounds are on each plate. Use dichloromethane as the solvent to elute the plates. Place the developed plate under a UV light to see if you can visualize your compounds. Some compounds fluoresce themselves, and you will see a spot that is brighter than the background, and some compounds quench the fluorescence of the plate, in which case you will see a dark spot where the compound is located. It is also possible to visualize many organic compounds by placing them in an iodine chamber. This method should be used only after you have used the UV light. Calculate the R_f values for each of the spots you see.
5. Based on your melting point data and tlc results, decide whether recrystallization of one or both of your compounds is necessary. If you decide it is, proceed with the recrystallization. If you recrystallize your crude products, run another tlc plate and take the melting points of the purified compounds so that you will be able to analyze the purification process.
6. Perform IR analysis on your crude samples.

F. Prelab Assignment--Week 2

1. Complete the flow diagram (Section D of the handout) for all of the steps you would have done in the lab to isolate 3-nitroaniline, benzoic acid and biphenyl from the mixture. A copy of your flow chart should be in your notebook as well.
2. Decide on a solvent that you feel would be appropriate for recrystallization of each compound. Complete this exercise only for the two compounds you actually recovered during Week 1. Explain why you chose those particular solvents.
3. If you have not already done so, read Section 14.3 in your text and a treatment of IR spectroscopy in one of the laboratory texts in the Science Library. Then answer the following:
 - a. Why are KBr and NaCl used for sample cells?
 - b. Explain briefly how you could easily differentiate among methanol, acetic acid and ethyl acetate using IR spectroscopy.

Report

1. Prepare a summary table that includes the yields of crude and recrystallized products. Also include the melting point data (crude, recrystallized and authentic samples) for each product. If you chose not to recrystallize one or both of your products, clearly explain your reasons for omitting the recrystallization.
2. Submit the results of your tlc analyses. Include R_f values for all spots. Sketches of your tlc plates may make your results clearer, but don't attach the actual tlc plates; they should be in your notebook.
3. In a few sentences discuss, for each product, the results of this experiment. Include a discussion of yield, melting point, tlc analysis and IR results. Be sure to address the consistency of your results.
4. In the experiment that you have just completed, you extracted a CH_2Cl_2 solution first with an acidic solution and then with a basic one. Considering the characteristics of the components involved, could the separation desired in this experiment have been accomplished by extracting first with base and then with acid? Explain, briefly.
5. Also, the basic extraction in this experiment employed NaHCO_3 as the base. Could this extraction have been satisfactorily accomplished with a NaOH solution? Explain.
6. A compound with the formula $\text{C}_4\text{H}_7\text{N}$ has an IR spectrum that includes peaks, among others, between $2900\text{-}3000\text{ cm}^{-1}$. There is also a strong peak at $\sim 2250\text{ cm}^{-1}$. The ^1H NMR spectrum of this compound shows only two peaks, a doublet at $\sim 1.3\text{ ppm}$ and a multiplet centered at $\sim 2.7\text{ ppm}$. The intensity of the doublet is six times that of the multiplet. The ^{13}C NMR shows two peaks almost overlapping at $\sim 20\text{ ppm}$ and a peak at $\sim 124\text{ ppm}$. What is the identity of this compound? Clearly show your reasoning by assigning the spectral peaks.
7. A compound with the formula $\text{C}_4\text{H}_8\text{O}$ has an IR spectrum that includes peaks, among others, between $2800\text{-}3000\text{ cm}^{-1}$. There is also a strong peak at $\sim 1070\text{ cm}^{-1}$, and a broad, strong peak at $\sim 900\text{ cm}^{-1}$. The ^1H NMR spectrum shows two peaks of equal intensity at $\sim 1.6\text{ ppm}$ and $\sim 3.6\text{ ppm}$. Both peaks look essentially like triplets. The ^{13}C NMR also shows two peaks between 20 and 30 ppm. What is the identity of this compound? Clearly show your reasoning by assigning the spectral peaks.