Alcohol or Amine Unknowns

Overview:
You will receive either an alcohol or an amine as an unknown. Your job will be to both identify your compound and prepare a derivative. Several pieces of information will be useful:

- Water solubility tests (big or small? Aromatic or not?)
- Solubility in acid-water. (Amines sometimes dissolve)
- Cupric Sulfate Test (For amines)
- Boiling point or melting point of starting material (optional)
- The melting point of the derivative (required)
- NMR information on the starting material.

Classifying Tests

1. Water Solubility Test (Helpful, but not always decisive or clear-cut. Use, but don't depend on it too much?!)

- Add 15 drops of water to a small test tube, and then add 2 drops of sample. Shake vigorously. Is it homogeneous or heterogeneous? If heterogeneous, do the droplets float or sink?
- Interpretation:
    a. Alcohols/amines with <4 carbons have ≥10% solubility (soluble).
    b. Alcohols/amines with >5 carbons have ≤5% solubility (insoluble)
    c. Alcohols/amines with 4,5 C's, borderline; may dissolve or may not. Usually adding some more water will dissolve, if doesn't initially.
    d. An insoluble Alcohols/amines that floats is nonaromatic.
    e. An insoluble Alcohols/amines that sinks has an aromatic ring present

2. HCl/Water Solubility Test
    - Same procedue as above, except using acid-water
    - Interpretation: Some amines (not all) will be protonated and become soluble. If you had a sample that didn't dissolve in regular water, but does dissolve easily in acid-water, it is likely to be an amine.
3. Copper Sulfate Test
    - Add 10 drops of $CuSO_4$ reagent, then 2 drops of unknown. If the solubility is poor, add an additional 10 drops of ethanol to try to improve the solubility.
    - Interpretation: Alcohols should not react, but amines should change the color, and may cause a precipitate

Derivatives:
A. Alcohols: See p. 766-767 for Derivative Table: Use the "3,5-Dinitrobenzoate" Column

To a large test tube add about 0.3 g of 3,5-dinitrobenzoyl chloride and then 10 drops of your alcohol. Heat the mixture so that the solid material melts, using a Bunsen burner, and keep it warm enough over a 5-minute period so that it stays in the liquid form without solidifying. Do not overheat! Warm it up enough to melt, but otherwise try to keep it as cool as possible. Allow the melt to cool and solidify. Cut up the crystalline mass with a spatula, add 2-3 mL of sodium hydroxide solution, and stir/grind the mixture vigorously with a glass rod, then add a stir bar and vigorously stir for 5 minutes. Collect it by filtration on a Hirsch funnel, and wash it with 3 x 3 mL of water. The solid/powder is your derivative.

Recrystallize/digest the derivative in a small Erlenmeyer or beaker by adding 3 mL of ethanol, and heat the solution at ~80˚C for 5 minutes. Let cool to room temp, further cool on ice, and filter and dry as usual. If you have no crystals, boiling off some ethanol and/or adding drops of water may help. You may wish to recrystallize again to get a more perfect product, but this may not be necessary.

Disposal: Filtrates down the drain.

Note: Some hindered alcohols have trouble making this derivative.

Phenylurethanes: See p. 766-767 for Derivative Table

Flame dry a large test tube, and add a stir bar. Add 10-drops of your alcohol, then add 10 drops of phenyl isocyanate. Heat this solution in a hot-water bath for 5 minutes, then dilute with 3 mL of hexane or ligroin while stirring, cool, and let crystallize while stirring. (The stirring helps to get oils to solidify). The crude crystals may be satisfactory. To recrystallize, either use hexane (or ligroin), or else ethanol/water.

B. Amines See p. 769-771 for Derivative Table: Use the "Benzamide" Column

-Add about 15 drops of benzoyl chloride in small portions with vigorous shaking and cooling to a suspension of about 15 drops of amine (if it is a liquid) or about 0.10 g (if it is a solid) in 2 mL of aqueous sodium hydroxide solution. After about 10 minutes of shaking, acidify with aqueous HCl. (Use litmus or pH paper to confirm that the pH is on the acidic side of 7.) Cool on ice, filter the lumpy product through the Hirsch funnel, and wash with 3x3 mL of cold water. Recrystallize using a minimum of ethanol-water.

Unknown Report Sheet-Amines/Alcohols

Unknown No. Name

1. Physical Examination of Starting Material

a) Physical State_____b) Color_____c) Odor_____

2. Solubility Tests on Starting Material

Solubility in Water: _____ If Insoluble, Does it Float or Sink?

Solubility in HCl/Water: _____ If Insoluble, Does it Float or Sink?

Conclusion:

3. Chemical Tests Result Conclusion

Copper Sulfate

4. Boiling point or melting point for starting material: Book value:

5. Derivative

	observed mp	literature mp
Crude		
Recrystallized		

6. NMR (attach)

7. What is My Actual Unknown? (Letter, Structure and Name)

8. Comments, difficulties, complaints, etc..