

Alcohol or Amine Unknowns

Overview:

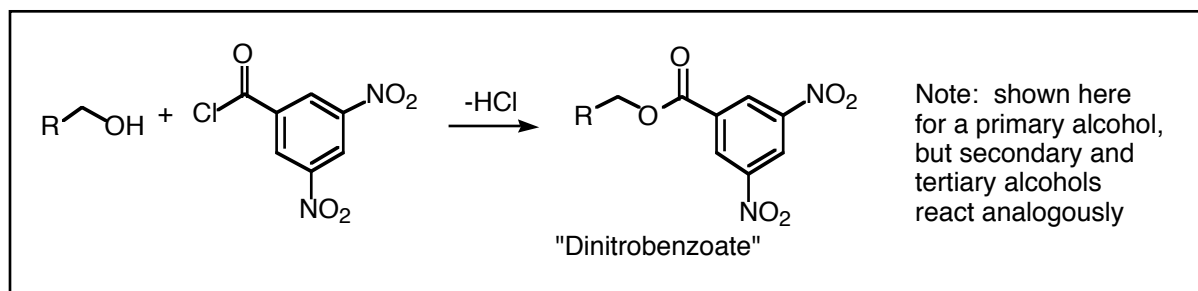
You will receive either an alcohol or an amine as an unknown. Your job will be to both identify your compound and prepare a derivative. Several pieces of information will be useful:

- Water solubility tests (big or small? Aromatic or not?)
- Solubility in acid-water. (Many basic amines ionize and dissolve in acid-water)
- Cupric Sulfate Test (For amines. Note: this is not entirely reliable...)
- Boiling point or melting point of starting material (optional, if bp doesn't work...)
- 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.)
 - 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 $\geq 10\%$ solubility (always dissolve).
 - b. Alcohols/amines with >7 carbons have $\leq 5\%$ solubility (never dissolve)
 - c. Alcohols/amines with 4-7 C's are borderline; some dissolve, some don't. Adding more water may help dissolve? Amines are more soluble than alcohols; some 7-C amines dissolve, whereas no 7-C alcohols do.
 - d. An insoluble alcohol/amine that sinks has an aromatic ring present. (Although not all aromatic compounds sink. Some floaters also have an aromatic ring, although most floaters are nonaromatic).
2. HCl/Water Solubility Test
 - Same procedure as above, except use a large test tube, use acid-water, add a stir-bar, and use 25 drops of acid-water instead of 15. Use magnetic stirring.
 - Interpretation: Most amines with normal basicity will be protonated and become soluble. If you had a sample that didn't dissolve in water, but does dissolve easily in acid-water, it is likely to be an amine. Caution: solid amines sometimes take a while to ionize and dissolve, and amines in which the nitrogen is conjugated and has the nitrogen lone-pair in a p orbital may be relatively nonbasic and may not dissolve.
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
 - Caution: the color change is often modest, some green or brown formation. And it isn't always automatic. It also doesn't always work for low-basic amines (in which the nitrogen is sp^2 hybridized and has a p lone pair).
4. Amines Smell Rancid
5. Many Amines are Solids

Suggestion: Use Tests and/or NMR to try to assess whether you have an alcohol or amine. Confirm with instructor before proceeding with derivative.

Derivatives:**A. Alcohols:****3,5-Dinitrobenzoate Derivatives**

Place a small stirring bar into a large test tube. Add about 0.3 g of 3,5-dinitrobenzoyl chloride and then 30 drops of your alcohol. Gently heat the mixture on a hot plate while stirring so that the solid material melts, and maintain heat and stirring for 5 minutes. Keep it minimally hot enough to keep the solid from freezing; as long as it's in liquid state, you don't need to heat it longer or harder. After the heating process, allow the mixture to cool (while stirring if it hasn't already solidified). If the mixture hardens, try to cut up the crystalline mass with a spatula or grind with a rod. After it isn't too hot, add 5 mL of NaOH/water solution, and stir/grind/pulverize the mixture vigorously. If there are still big blocks of solid, again try to cut them up with spatula and crush them with a glass rod. Stir vigorously for 5 minutes. Collect the solid by filtration on a Hirsch funnel, and wash it with 2 x 5 mL of NaOH/water, then 2 x 5 mL water (or more if there is residual purple type color), and then 1 x 5 mL of HCl/water. Then wash/rinse with 2 x 2mL of ice-cold ethanol. If it turns purple, wash with additional water again, followed by ice-cold ethanol again, until it remains purple-free. The solid/powder is your derivative.

Recrystallize the derivative in a small, 25-mL Erlenmeyer. Depending on your yield, 2 mL of ethanol may be a good starting guess. (But this may be too much if your yield is poor, or too little depending on your substance.) Improvise as needed, by adding more ethanol if the solid doesn't dissolve in the boiling solvent, or by spiking the boiling solution with drops of water if the solid dissolves too easily. If you have no crystals, boiling off some ethanol and/or adding drops of water may help. If after cooling you don't harvest any or many crystals, adding an ice chip (or more than one) will often stimulate crystallization.

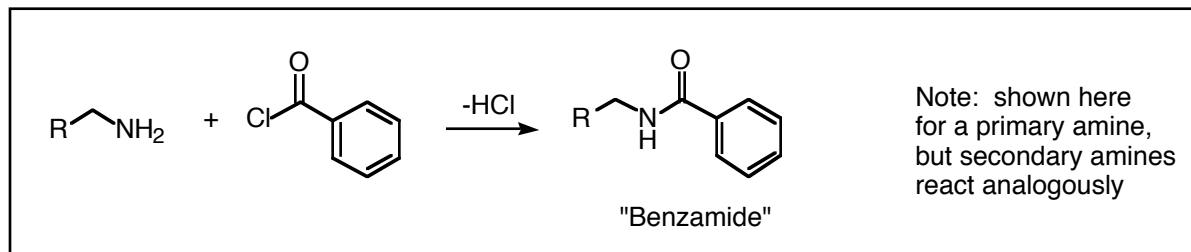
Note: be sure that you use enough solvent. If the solubility is quite high in ethanol, then add water to reduce the solubility. If you're using very little solvent, the impurities may have no place to go!

If the aqueous washes did not succeed in washing out all of the dinitrobenzoyl chloride side products, there may possibly be a small amount of an ionic, ethanol-insoluble solid. So if there is a little bit of white solid, and adding more hot ethanol doesn't seem to make it go away, you'll need to do an extra hot filtration. Filter your hot solution through filter paper into a clean filter flask. The solid filtered off is junk; the solution that passed through into the filter flask has your product. You can then recrystallize that again, with some additional ethanol, if all of the ethanol gets sucked off during the hot filtration process.

Disposal: Water filtrates from the crude material down the drain. Ethanol from the recrystallization into the ethanol waste.

Note: Some hindered alcohols have trouble making this derivative.

B. Amines: Benzamide Derivatives



Place a small stir-bar and 2 mL of aqueous sodium hydroxide solution into a large test tube. Add the amine, about 15 drops if it's a liquid, about 0.20 g if it's a solid. Stir the solution vigorously, and add about 15 drops of benzoyl chloride. Stir vigorously for 10 minutes, then acidify with aqueous HCl (this helps the amide to crystallize). (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 3x5 mL of cold water, then 2 x 3 mL of HCl/water (to wash off unreacted amine), and then 2 x 3 mL of NaOH/water (to wash off unreacted benzoyl chloride). Recrystallize using a minimum of ethanol, perhaps adding water as necessary.

Alcohol Candidates

Bp of Starting Alcohol	Unknown	mp of 3,5-dinitrobenzoate Derivative	mp of phenylurethane Derivative
65	Methanol	108	47
78	Ethanol	93	52
82	2-propanol	123	88 (75)
83	2-methyl-2-propanol	136	136
97	2-propen-1-ol	49	70
97	1-propanol	74	57
99	2-butanol	76	65
102	2-methyl-2-butanol	116	42
108	2-methyl-1-propanol	87	86
115	3-pentanol	101	48
118	1-butanol	64	61
119	2-pentanol	62	oil
123	3-methyl-3-pentanol	96	43
130	2-methyl-1-butanol	70	31
132	4-methyl-2-pentanol	65	143
137	1-pentanol	46	46
140	cyclopentanol	115	132
140	2-hexanol	39	oil
157	1-hexanol	58	42
160	cyclohexanol	113	82
176	1-heptanol	47	60
178	2-octanol	32	oil
195	1-octanol	61	74
204	benzyl alcohol (PhCH ₂ OH)	113	77
204	1-phenylethanol	95	92
220	2-phenylethanol	108	78
231	1-decanol	57	59

Amine Candidates

Bp of Starting Amines (Liquids)	Unknown	mp of Benzamide Derivative
48	Propylamine	84
55	Diethylamine	42
78	Butylamine	42
159	Dibutylamine (Bu ₂ NH)	oil
182-185	Benzylamine (PhCH ₂ NH ₂)	105
184	Aniline	163
187	PhCH(CH ₃)NH ₂	120
196	N-Methylaniline (PhNHCH ₃)	63
200	2-Methylaniline	144
204	3-Methylaniline	125
208	2-Chloroaniline	99
210	2-Ethylaniline	147
216	2,6-Dimethylaniline	168
218	2,4-Dimethylaniline	192
218	2,5-Dimethylaniline	140
225	2-Methoxyaniline	60
230	3-Chloroaniline	120

Mp of Starting Amines (Solids)	Unknown	mp of Benzamide Derivative
35-38	PhCH ₂ NHPh	107
41-48	4-methylaniline	158
49-51	2,5-dichloroaniline	120
52-55	Diphenylamine (Ph ₂ NH)	180
57-60	4-methoxyaniline	154
57-60	2-aminopyridine	165
58-66	4-bromoaniline	204
71-73	2-Nitroaniline	110
112-114	3-nitroaniline	157
115-116	4-methyl-2-nitroaniline	148
138-140	2-methoxy-4-Nitroaniline	149
148-149	4-Nitroaniline	199

Note: amines are hydrophilic, and tend to absorb some water from the air. Some of the starting amines may also have trace isomeric impurities. The result of moisture and/or impurities means that some of the starting materials may have melting points that are a little bit depressed.

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 mpliterature mp

Crude

Recrystallized

6. H-NMR of starting unknown (attach, with assignments/interpretation)

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

8. Comments, difficulties, complaints, etc..

