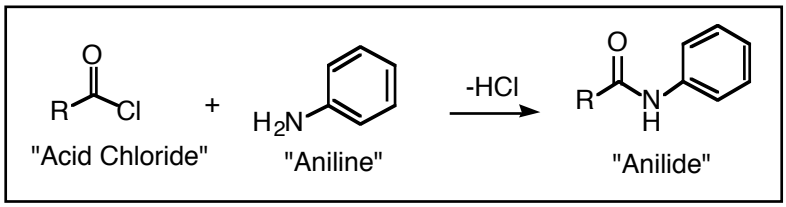
CARBOXYLIC ACID UNKNOWN

A. Anilide Derivative



Place 10 drops (or 0.10 grams, if it's a solid) of the acid chloride into a large test tube. Add a stir bar, and add 1 pipet of ether. To this solution add 20 drops of aniline, dropwise (may spatter if you add it all at once) and stir for 1 minutes if it's not already solid. The primary precipitate that forms is the aniline hydrochloride salt. If your reaction is so exothermic that the ether boils away and you end up with an unstirrable solid, then add another pipet of ether.

After the one minutes is up, add 2 pipets of aqueous NaOH, and continue stirring for an additional two minutes. If some precipitate remains it is the derivative itself.

Use a long pipet to remove the aqueous layer from the bottom of the test tube. (Any unreacted acid chloride should be removed by the basic water.)

Then add 2 pipets of aqueous HCl, and stir vigorously.

Use a long pipet to remove the aqueous layer. (The aniline should be removed in the process.) Cool your solution in an ice-bath for at least a minute.

If you have a significant amount of precipitate at this point, it is the desired derivative. If so, then filter directly over a Hirsch funnel, after which you'll recrystallize the sample.

- However, if you *don't* have a significant amount of precipitate, call instructor over and/or skip down to the instructions in bold.

Assuming you did have a significant amount of precipitate, Recrystallize the crude derivative from ethanol. Ideal volumes will vary depending on your unknown, but a suggested starting point is 2mL of ethanol and 10 drops of water. But the solubilities will vary greatly from unknown to unknown, so you need to make whatever adjustments are appropriate for your particular sample. You shouldn't need these anymore, but several recrystallization reminders:

- Use a small Erlenmeyer, not a beaker, to reduce solvent evaporation.
- Make all your adjustment decisions while the solution is boiling hot.
- Heating your Erlenmeyer in a hot-water beaker is convenient, to provide more even heating than if you just stand it on a hot plate, and to avoid overheating on the hot-plate surface.
- You and your hood partner should also warm up some ethanol in case you need to add some
- Other than when you're just starting, never add cold solvents.
- During cooling, cover the flask to avoid evaporation of the hot solvent.
- Supersaturation is quite common. If you think you're at 50% water, probably stop and cool and see whether crystals will form.
- If no crystals form even after slowly cooling and then icing, try adding ice chip(s).
- Your rinse solvent should be very similar to what you think your actual solvent blend is.

If following the acid wash you do not have a precipitate (or don't have very much precipitate), then much/all of the derivative is dissolved in the ether. Add a boiling stick and heat your test-tube to boil off the ether, either with a heat gun or in a hot-water bath. place it in an ice-bath. (Maybe consult with the instructor for fast help.) The residue will probably then crystallize. If not, try to add an ice chip and scrape it with a rough stick. Whether it

actually crystallized or not, just recrystallize right in the large test tube. Start with around 1 mL of water. Heat it up in a hot water bath, and add as much hot ethanol as it takes to just barely get the product to just barely dissolve. Cool slowly, and perhaps stimulate crystal formation with an ice chip if necessary. Then harvest your crystals. Your wash solvent should probably be at least 50% water.

C. Titration/Neutralization Equivalence→Molecular Weight Determination

Weigh, as accurately as possible, around 200 mg (0.200g) of your acid into a 125 mL Erlenmeyer flask. Use the balance nearest the acetone-hood. (You want 3-4 significant figures after the decimal for this, so the other balances are unacceptable.) Pre-tare the flask, then add sample directly into the flask and record the mass to avoid inaccuracy. (Adding to a boat, recording, and then pouring into Erlenmeyer will introduce error.) Whether you have 200 mg or 220 or 180 doesn't matter, so long as you know exactly what your original mass is. Dissolve your material in around 25 mL of ethanol. [Logic: It is vital that the solution be homogeneous, so you need ethanol to keep it dissolved. But the indicator needs water to work right.] Add 2 drops of phenolphthalein indicator solution. Titrate the solution with _____ M NaOH. (Copy the concentration down from the bottle!)

Summary of titration logic: Molecular weight (or "formula weight", FW) is the ratio of mass per mole. Having weighed your acid, you know the mass very precisely; but how do you know how many moles? By titrating against the precisely standardized base! From the precisely known volume of base and the molarity of the base, you can determine the # of moles of base used. Since the mole/mole stoichiometry is 1 mole of base per 1 mole of acid, the # of moles of base tells the # of moles of acid. Knowing mass of acid and moles of acid, the ratio gives you the formula weight.

Note: Do your titration once, and check the molecular weight value with me. If you get within 5 g/mol, I'll tell you and you won't need to repeat. If you don't get within 5 g/mol, then you'll need to do it again. (Normally several repeats for reproducibility would be in order.)

Molecular weight calculations like this are not perfectly reliable (even if you calculate right!). In general an error of up to five grams/mole is acceptable. Logical reasons for errors are shown below:

- Reason 1: If you don't see the color change right away and "overshoot" the amount of NaOH added, you will have added more moles of NaOH than necessary. The calculation assumes that the number of moles of acid is exactly the same as the number of moles of NaOH added; but if you overshoot the NaOH, this won't actually be true. Your moles of acid will actually be slightly less than the number of moles of base. So when you are dividing mass of acid by moles of acid, you will have a slightly exaggerated number for the denominator. This will result in an underestimation of the grams/mole ratio, and will underestimate the actual molecular weight.
- Reason 2: Not all of the acids are perfectly pure. For example, if the solid sample is only 95% pure, this will cause an error in the calculation! Since acids are somewhat hydrophilic, it's not uncommon for acids to be somewhat wet and to give somewhat exaggerated molecular weight numbers.
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Example of Molecular Weight Calculation:

Measured data:

- Weight of acid: 0.2015 g
- Molarity of NaOH: 0.1005 M
- Volume of NaOH to reach the titration end-point: 14.50 mL

Mathematical Calculation of Molecular Weight:

- Moles of NaOH = $(14.50mL)\left(\frac{1L}{1000mL}\right)\left(\frac{.1005mol}{1L}\right)$ = 0.001457 mol NaOH
- Moles of acid = moles of base = 0.001457 mol acid

- Molecular weight of acid = $\frac{0.2015 g}{0.001457 mol}$=138.3 g/mol

B. Melting Point/Boiling Point

If your carboxylic acid is a solid, take its melting point. If it is a liquid, take its micro-boiling point.

E. NMR ^{1}H will be useful. Don't bother with a ^{13}C NMR, since solubility will probably be too low to get anything worthwhile. The OH hydrogen is often very broad, due to H-bonding, sometimes so broad that you won't see it at all.

- Aromatic hydrogens ortho to a carbonyl are typically pushed downfield, toward 8 ppm. This is because a carbonyl group is a strong electron withdrawer, so it makes the ortho carbons more electron poor, which "deshields" the ortho hydrogens.
- A carboxylic acid hydrogen will normally be invisible, so don't look for it. They are so broadened by hydrogen-bonding that they often just blend into the baseline. Even if you could see them, they appear down at 11-14 ppm, which is off-scale from our plots.
- Some solid carboxylic acids will have low solubility in CDCl3. If your sample is not completely soluble, you can run it anyway. But sometimes when there isn't that much sample dissolved, background lines from components in the CDCl3 solvent can be misinterpreted for real sample lines. The two most common candidates are a line at 0.00 ppm (tetramethylsilane) and a singlet at 7.26 (CHCl3). These two components are always present when you use CDCl3 solvent, but their height in a printed spectrum looks much taller relative to other signals if the real sample is very dilute versus if the real sample is more concentrated.

Carboxylic Acid Candidates

Liquid Acid Unknowns	bp of Acid	mw of Acid (g/mol)	mp of Anilide Derivative
Ethanoic Acid	118	60	47
Propanoic Acid	141	74	103
Butanoic Acid	162	88	95
Pentanoic Acid	185	102	63
2,2-Dichloroethanoic Acid	194	129	118
Hexanoic Acid	202	116	95
Octanoic Acid	237	140	57

Solid Acid Unknowns	mp of Acid	mw of Acid (g/mol)	mp of Anilide Derivative
Decanoic Acid	31-32	164	70
Bromoethanoic Acid	47-49	139	131
3-Phenylpropanoic Acid	47-49	150	92-98
2,2,2-Trichloroethanoic Acid	54-58	163.4	97
2-Chloroethanoic Acid	61-62	94.5	137
2-Butenoic Acid ($CH_3CH{=}CHCO_2H$)	71-73	86	118
2-Phenylethanoic Acid	76-79	136	118
3-Methylbenzoic Acid	108-110	136	126
Benzoic Acid	122-123	122	163
2-Benzoylbenzoic Acid ($PhCOC_6H_4CO_2H$)	127-128	226	195
Cinnamic Acid ($PhCH{=}CHCO_2H$)	133-135	148	153
2-Chlorobenzoic Acid	138-142	156.5	118
3-Nitrobenzoic Acid	140-142	167	155
2,2-Diphenylethanoic Acid	147-149	212	180
2-Bromobenzoic Acid	150	201	141
2,2-Dimethylpropanoic Acid	163-164	102	127
3,4-Dimethoxybenzoic Acid	179-182	182	154
4-Methylbenzoic Acid	180-182	136	145
4-Methoxybenzoic Acid	182-185	152	169-171
3-Hydroxybenzoic Acid	201-203	138	157
3,5-Dinitrobenzoic Acid	203-206	212	234
4-Nitrobenzoic Acid	239-241	167	211-217

- Note: Carboxylic acids 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- **Carboxylic Acid**

Unknown No. Name

1. Physical Examination of Starting Material

   a) Physical State_____ b) Color_____

2. Solubility Tests on Starting Material

Solvent:	Water	If Insoluble in Water, Does it Float or Sink?	Aq NaOH	Aq NaHCO
Solubility:	_____	_____	_____	_____

3. Melting point or boiling point for starting material: List value:

4. What is the approximate molecular weight (mw) of my sample, based on my titration?

   _____ g/mol. (Attach a separate sheet that details your weights, calculation!)
   *Beware of ridiculous significant figures.

5. Derivative

	observed mp	literature mp
Crude (optional)		
Recrystallized		

6. H-NMR (attach, with assignments/interpretation. Do analyze aromatic H's)

- **On the proton spectrum, create a standard 4-column summary table of your H-NMR data, detailing chemical shifts, integrations, and splittings, and "source".**
- Draw the structure of your molecule, with identifiers by each carbon (a, b, c…).
- Then on your standard summary table add a "source" column in which you explain which hydrogens (a, b, or c, etc…) are responsible for which signals. Note: if the sample is too concentrated, the splitting may in some cases get broadened and become problematic.
- Do analyze aromatic H's for solid samples. For liquid samples with aromatics, the aromatic H's will have overlapping so won't be useful to detail.

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

8. Comments, difficulties, complaints, etc..