UNKNOWN UNKNOWNS

Candidates: ACIDS, ALCOHOLS, AMINES, CARBONYLS (ALDEHYDES/KETONES)

Requirements: You will be given two unknowns. Identify your unknowns. Try to make a successful derivative of each of them, but be sure to succeed on at least two of them. Get melting point/boiling point on both starting material and derivative. Titrate and get molecular weight if a sample is an acid. Include H-NMR's for starting material. Do whatever solubility/chemical tests you find useful. For a liquid sample (which will have good solubility), taking a C-13 NMR may also be quite helpful.

General Strategy: The strategy simplifies into two major levels. The first level is to **classify your feature functional group**, as quickly as possible. (Alkene, halogen, nitro, and aromatic functional groups are also possible.) Chemical tests (including solubility tests) and NMR are both useful for this purpose. Until you know your functional group, a melting point or boiling point alone is of limited use. And until you know your functional group, you can't know how to make the right derivative.

The second level is to make derivatives and specifically identify your materials. NMR's, mp/bp on starting material, mp on derivative, and titration information for acids should provide adequate information!

A. Review of Chemical Tests

1. Solubility Tests, especially for Amines or Carboxylic Acids

Procedure: Add 2 drops of sample if it is a liquid or a little spatula quantity (0.030 g) if you have a solid to a test tube. Then add 15 drops of water solution (neutral water, HCl/water, NaOH/water, or $NaHCO_3$/water) if your unknown sample is a liquid, add 30 drops of water solution if your unknown is a solid. When testing solids with either HCl/water, NaOH/water, or $NaHCO_3$/water, it is desirable to use a large test tube and stir with a stir bar for 5 minutes or longer. For any unknown that you suspect may be partially soluble, the addition of additional aqueous solution may be able to provide additional information by enabling complete dissolving.

- For each unknown, test its solubility in each of the following four water solutions:
  a. in neutral water
  b. n HCl/water (amines may be ionized and dissolved)
  c. in NaOH/water (acids may be ionized and dissolved)
  d. in $NaHCO_3$/water (acids may be ionized and may cause bubbling and perhaps dissolve)

Interpretation Notes:

a. If the sample is soluble in neutral water, it may not have very many carbons. For alcohols, acids, aldehydes, and ketones, the most possible carbons in a water-soluble sample is 6-carbons. And many substances with 3-6 carbons will still be insoluble. For amines, the most possible carbons in a water-soluble sample is 7-carbons.
b. If a sample is insoluble in neutral water and it sinks, it has an aromatic ring present. (Although not all aromatic compounds sink. Some floaters also have an aromatic ring, although most floaters are nonaromatic).
c. If a sample is insoluble in neutral water but is soluble in HCl, that is good evidence that it may be an amine. (Although there are some exceptions, both amines with p-orbitals that still don't dissolve in acid, and an occasional non-amine which is more soluble in acid than in neutral water.)
d. If a sample is insoluble in neutral water but is soluble in either NaOH or $NaHCO_3$, that is good evidence that the unknown is a carboxylic acid. (However, not all carboxylic acids dissolve completely or quickly or easily in these basic solutions.)

e. If a sample bubbles in $NaHCO_3$ solution, then it is an acid for sure. (However, not all carboxylic acids bubble visibly or quickly in $NaHCO_3$ solution).
f. Note: The NaOH and $NaHCO_3$ tests are really the only tests for acids.

2. Chromic Acid Test ("Jones' Test") for **Alcohols or Amines (sometimes) or Aldehydes (sometimes)**. Cr^{+6} oxidizes 1° alcohols (to carboxylic acids) and 2° alcohols (to ketones), but does not oxidize 3° alcohols. Cr^{+6} (red-orange) gets reduced to Cr^{+3} (blue-green) in the process. Aldehydes also are oxidized, but more slowly. Some amines are oxidized as well.
Procedure: Put 20 drops of acetone (solvent) and 1 drop or one small spatula tip of unknown into a test tube. Add 1 drop of chromic acid solution and mix well. Note: Amines are oxidized as well, so they too give a gross response.
   - Interpretation: a positive test involves both a rapid color change, from orange → green/brown/black, and formation of a precipitate. Primary or secondary alcohols always do this, quickly; amines and aldehydes often react also, although not always with the same intensity or speed.

3. Copper Sulfate Test for **Amines, not Alcohols**
   - Procedure: Add 10 drops of $CuSO_4$ reagent, then 2 drops or a small spatula tip of unknown.
   - Interpretation: Alcohols should not react, but amines should change the color, and may cause a precipitate. Some liquid amines cause an immediate precipitate that is only a slightly different color of blue.
   - Caution: the color change is often modest, some green or brown formation, or for some liquid amines perhaps just a slightly different shade of blue. 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. "DNP" Test for **Aldehydes and Ketones**. (2,4-Dinitrophenylhydrazine test.)
   - Procedure: Put 10 drops of DNP solution into a test tube. Add 3 drops or a small spatula tip of unknown and mix.
   - Interpretation: a positive test involves formation of a new, thick precipitate.
   - Saturated carbonyl derivatives usually are **yellow**, unsaturated are usually **orange/red**.
   - Note: If you end up with an aldehyde or ketone, you can make your derivative in this same test tube. Just add the rest of the recipe into the same tube and proceed.
   - Note: False positives are sometimes observed under four circumstances:
     - With a tube that has been washed with acetone! Acetone will give a DNP precipitate!
     - With 2º alcohols. Sometimes 1-10% of a 2º alcohol air-oxidizes to ketone, and the small amount of contaminating ketone can give positive DNP response. (But not as much).
     - With solid unknowns. If an unknown is insoluble, a precipitate will be seen even if the unknown doesn't react. Real derivatives give a very thick mixture, almost turning the whole concoction into a solid paste.
     - Some liquid amines, are protonated and form an ammonium precipitate in the acidic DNP solution. Again, if a really thick mixture doesn't form, it's probably not really a DNP derivative.

5. NMR Test to Distinguish **Aldehydes from Ketones**: Aldehydes give a signal in the 9-10 region of the H-NMR.

Summary of Chemical Tests:

Family	Jones (H_2CrO_4)	$CuSO_4$	DNP	HCl	HO^-/HCO_3^-
Acid	NO	NO	NO (but may not be soluble, so some ppt. may be seen)	NO	**YES**
Alcohol	**YES** (fast color change)	NO	NO (but trace ketone impurities may give a little bit of DNP derivative)	NO (but maybe)	NO
Aldehyde	**YES** But not always as intense as for alcohols	NO	**YES**	NO (but maybe)	NO
Amine	Maybe, Sometimes **YES**, sometimes no	**YES**	NO (but either amine or ammonium ion may not be soluble, so some ppt. may be seen)	**YES**	NO
Ketone	NO	NO	**YES**	NO (but maybe)	NO

B. Titration/Neutralization: Molecular Weight Determination of a Carboxylic Acid

Weigh, as accurately as possible, around 200 mg (0.200g) of your acid into a 125 mL Erlenmeyer flask. You want 3-4 significant figures after the decimal for this, so the usual balances are unacceptable. Whether you have 200 mg or 220 or 180 doesn't matter, so long as you know exactly what your original mass is. If you have a liquid, add drops until you get to about the same mass. 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!)

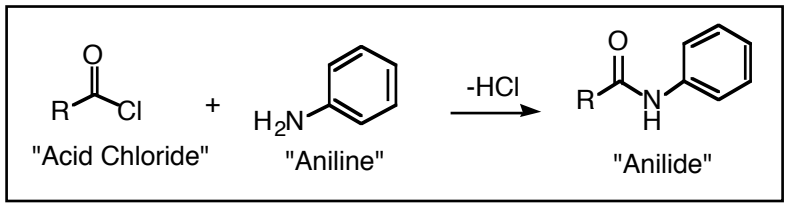
Summary of titration logic: Molecular weight (or "formula weight", FW) is the ratio of mass per mole. Having weighed your acid, you know the mass very precisely; but how do you know how many moles? By titrating against the precisely standardized base! From the precisely known volume of base and the molarity 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. See the next page for an example of a molecular weight calculation.

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, this will result in an underestimation of the grams/mole ratio, and you will underestimate the actual molecular weight.
- Reason 2: Not all of the acids are perfectly pure. Since acids are somewhat hydrophilic, it's not uncommon for acids to be somewhat wet and to give somewhat exaggerated molecular weight numbers.

C. DERIVATIVES

1. Carboxylic acids: 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 5 minutes. 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 five minutes is up, add 2 pipets of aqueous NaOH, and continue stirring for an additional five 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.

If you have a significant amount of precipitate at this point, it is the desired derivative. Filter directly over a Hirsch funnel. Rinse with some HCl/water and then some water to get your crude derivative.

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. Heat your test-tube to boil off the ether, either with a heat gun or in a hot-water bath. Add two pipets of HCl/water, swirl it around, and place it in an ice-bath. The residue will probably crystallize. If not, try to add an ice chip or scrape it with a rough stick. Scrape the residue out onto a Hirsch funnel, and rinse with some HCl/water and then some water to get your crude derivative. When you recrystallize, you will probably not need very much ethanol, and will probably need ice chips to help induce crystallization. But it should still work.

Recrystallize the crude derivative from ethanol. Ideal volumes will vary depending on your unknown, but normally a good starting guess will be only 2 mL of ethanol. Add more as needed (which will be true in many cases). If no crystals form even after cooling, try adding an ice chip. (Or more than one ice chip.)

Example of Molecular Weight Calculation:

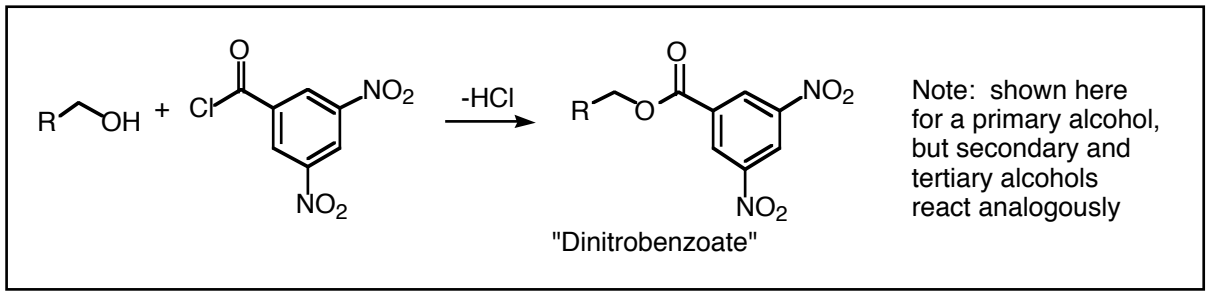
Measured data:

- Weight of acid: 0.2015 g
- Molarity of NaOH: 0.1006 M
- Volume of NaOH to reach the titration end-point: 14.50 mL

Mathematical Calculation of Molecular Weight:

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

2. Alcohols: 3,5-Dinitrobenzoate Derivatives



Place a small stirring bar into a large test tube and flame dry. Add about 0.3 g of 3,5-dinitrobenzoyl chloride and then 30 drops of your alcohol. In a hot-water bath (or by using a Bunsen burner), gently heat the mixture so that the solid material melts, and maintain heat and stirring for 5 minutes. (If you use a Bunsen burner, heat very lightly, just enough to keep the solid melted! If the solution starts to turn brown or black, that isn't good!) 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 2 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, 3 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.

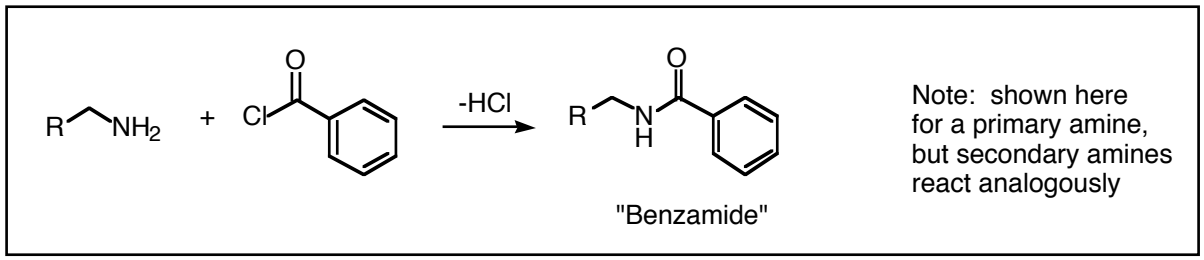
Note: be sure that you use enough solvent. If the solubility is quite high in ethanol, then add water to reduce the solubility. If you're using very little solvent, the impurities may have no place to go!

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.

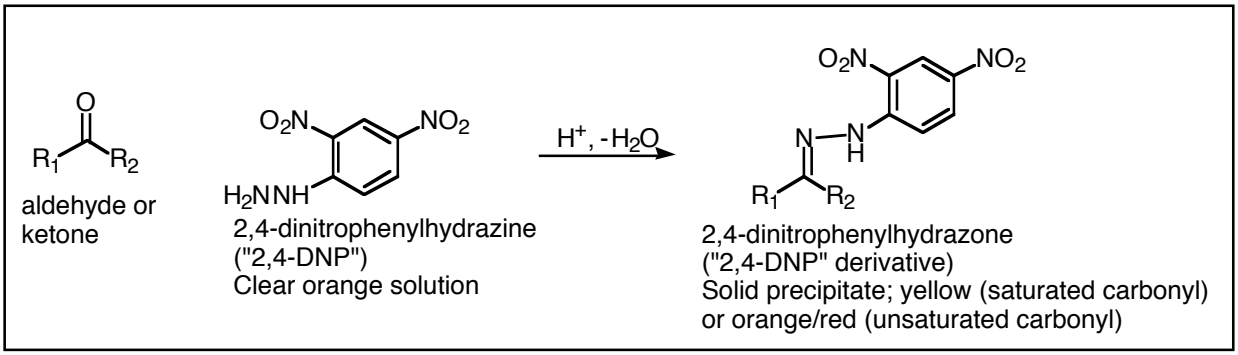
Note: Some hindered alcohols have trouble making this derivative.

3. Amines Benzamide Derivatives



Place a small stir-bar and 2 mL of aqueous sodium hydroxide solution into a large test tube. Add the amine, either about 15 drops if it's a liquid, or about 0.30 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. If after cooling you don't harvest any or many crystals, adding an ice chip (or more than one) will often stimulate crystallization.

4. Ketone/Aldehyde Unknowns: Making a 2,4-DNP Derivative of an Aldehyde or Ketone



Put 4 pipets of 2,4-DNP solution into a large test tube, add a magnetic stir bar, and to a well-stirred solution add 30 drops of your unknown. After 5 minutes, cool, add 2 pipets of cold water, filter, wash with cold water, and wash with a small amount (three pipets) of cold ethanol. Aspirate thoroughly, and hopefully get a crude mp. Recrystallize (or "digest") from anhydrous ethanol, using a 125-mL Erlenmeyer.

In some cases, it takes a lot of ethanol to get the crystals dissolved. The amount of ethanol required will vary from one unknown to another; saturated alkyl ones usually dissolve more easily, the longer the alkyl chains the easier. Aromatic aldehydes/ketones are often much harder to dissolve and require a lot of ethanol, or else simply will never dissolve completely. In the latter case, simply boiling the mixture for a while enables the impurities to get free, even if not all of the crystal is completely dissolved at any one time.

Disposal: Into DNP waste container.

NOTE: Saturated carbonyl derivatives usually are **yellow**, unsaturated are usually **orange/red**.

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.

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 ($PhCH_2OH$)	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_2NH)	oil
182-185	Benzylamine ($PhCH_2NH_2$)	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	$PhCH_2NHPh$	107
41-48	4-methylaniline	158
49-51	2,5-dichloroaniline	120
52-55	Diphenylamine (Ph_2NH)	180
57-60	4-methoxyaniline	154
57-60	2-aminopyridine	165
58-66	4-bromooaniline	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.

Carbonyl (Aldehyde/Ketone) Candidates

Bp of Starting Carbonyl	Unknown	mp of 2,4-DNP Derivative
48	propanal	148
56	acetone	126
63	2-methylpropanal	187(183)
75	butanal	123
80	2-butanone	117
91	3-methylbutanal	123
92	2-methylbutanal	120
100	2-pentanone	143
102	3-pentanone	156
103	pentanal	107(98)
115	4-methyl-2-pentanone	95
128	5-hexen-2-one	108
129	4-methyl-3-penten-2-one	205
131	cyclopentanone	146
131	hexanal	104(107)
145	4-heptanone	75
145	5-methyl-2-hexanone	95
146	2-heptanone	89
147	3-heptanone	81
153	heptanal	108
156	cyclohexanone	162
169	3-methylcyclohexanone	155
173	2-octanone	58
179	benzaldehyde (PhCHO)	237
200	o-methylbenzaldehyde	194
204	p-methylbenzaldehyde	234
202	ethanoylbenzene	244
216	1-phenyl-2-propanone	156
217	(2-methylpropanoyl)benzene	163
218	propanoylbenzene	191
226	p-methylacetophenone	258
232	butanoylbenzene	191
235	4-phenyl-2-butanone	127
248	p-methoxybenzaldehyde	253

Unknown Report Sheet Name

Unknown No.

1. Physical Examination of Starting Material: Solid or Liquid?

2. Solubility Tests on Starting Material

Solvent:	Neutral Water	(Float or Sink?)	Aq. HCl	Aq NaOH	Aq NaHCO
Solubility:	_____	_____	_____	_____	_____

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

4. Chemical Tests	Result	Conclusion
Jones Reagent (Chromic Acid)		
$CuSO_4$ Test		
2,4-Dinitrophenylhydrazone		

5. If I have an acid, what is the approximate molecular weight (mw) of my sample, based on my titration?

Approximately _____ g/mol. (Attach a sheet with calculations!)

6. Derivative

	observed mp	literature mp
Crude		
Recrystallized		

7. H-NMR (attach, with assignments/interpretation). (Attach C-NMR if taken).

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

9. Comments, difficulties, complaints, etc..

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Unknown No.

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2. Solubility Tests on Starting Material

Solvent:	Neutral Water	(Float or Sink?)	Aq. HCl	Aq NaOH	Aq NaHCO
Solubility:	_____	_____	_____	_____	_____

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