Identification of an Unknown Organic Compound

Background:

Organic chemists often need to identify unknown compounds. This is quite common in the course of organic chemistry research, but organic chemists may also be consulted by specialists in other areas: Organic chemists may be needed to analyze a substance found in a crime scene or a pollutant found on the site of an environmental cleanup. Organic chemists may be asked to determine the identity of a metabolic byproduct from an experimental drug that is causing liver damage in clinical trials.

You have already studied some of the ways to prove the identity of a product you obtain from a well-understood reaction: physical constants and spectroscopic analysis may be compared with the literature data to establish identity. When presented with an unknown compound, however, there may be no knowledge of the history of the sample, and no knowledge of the reactants that were used to make it. The physical constants and spectroscopic data may be gathered as usual, but there are several million organic compounds in the literature with which to compare your data. Finding which one of these is your unknown becomes an entertaining problem of logical deduction, a tangled web of a puzzle which is best navigated with a systematic approach.

In this experiment, you will determine the identity of an unknown compound using a combination of physical properties, chemical tests and spectroscopic data. Your compound will be chosen at random; each student will have a different compound. With deductions gathered from the analytical procedures you choose, you will apply a logical process to gradually eliminate functional group classes, then rule out specific compounds until there is only one left that is consistent with the data you've collected.

Beware! There is no universally applicable set of instructions for solving the structure of an unknown. The first steps may be the same for everyone, but then you will need to think for yourself and choose the tests and procedures which are best suited to your unknown. Be prepared to mentally review your logic if you reach a dead end. You may need to continually modify your process of elimination as new information becomes available. It is a good idea to think very carefully about what you will do each day <u>before</u> you arrive, and have a backup plan in case of inconsistencies in the experimental results.

It is crucial to keep a good written account of each step, and to record your results and observations clearly. You'll need these observations in order to evaluate the relative importance of contradictory pieces of information. There are "false positives" and "false negatives" commonly observed, so that the results from two tests may not be in agreement. If you recorded in your notebook that one of these tests gave an ambiguous result (perhaps a color change was not as dramatic as you expected), then you may be able to use this to decide which data should be given more weight in your analysis. Also, note that the quality of your instructor's advice will depend on the completeness of the observations in your notebook.

Procedure:

The following discussion outlines the general steps to be followed in the determination of your unknown. Remember, every case is different, and you should be prepared to modify the steps as needed once you begin to accumulate information.

1. Get Sample. Obtain the randomly assigned unknown sample from your TA. Note the unknown # in your notebook.

2. Physical State. Note the physical state (e.g., solid or liquid) and its appearance and color.

3. Melting or Boiling Point. Obtain either a melting point or a micro-boiling point for your sample. Be aware of the uncertainty of these values, particularly with regard to the micro-boiling points. When considering possible structures for your unknown, add ± 5–10 °C to the melting point range, and ± 10–20 °C to the micro-boiling point. The micro-boiling points become increasingly unreliable above about 200 °C. Be careful not to heat the sample too quickly. Note: More reliable data can be obtained if the mp/bp measurement is repeated. Liquid samples should be saved after this procedure to provide a backup in the event that you run out of sample. However, these recovered samples should be used as a last resort because of the possibility of impurities from decomposition during micro boiling point determination.

4. Solubility. Conduct solubility tests to identify the major functional group(s) present.

5. Infrared Spectrum. Obtain a GOOD, CLEAN IR of the unknown to identify the major functional groups present. If more than one peak reaches down to 0% transmittance, then you have too much sample on the salt plates; take the plates apart, wipe one off, put them back together and obtain the spectrum again. If the sample is a solid, obtain the spectrum on a solution of your compound in the minimum amount of $CHCl_3$. If the solid is insoluble in $CHCl_3$, prepare a nujol mull by mixing nujol with very finely ground solid. Note that $CHCl_3$ and nujol have their own peaks in the IR. If these interfere in your analysis, they may be subtracted by running the background with the $CHCl_3$ or nujol alone.

6. Functional Group Tests. Conduct chemical tests for functional group properties that are <u>necessary</u> to confirm or determine the nature of the functional groups present. Be wary of false positives and/or false negatives. Every functional group test should be run with two samples side-by-side; one should be a known compound as a positive control experiment to compare with your unknown. In this way you'll know exactly what the positive test will look like. Negative controls or "blank" experiments may also be useful in some cases, and can be done by simply leaving out the unknown. You will probably not have to run all of the possible tests on your sample, but you must run at least three.

Confirming the functional group narrows your list of compounds from several hundred down to about 50–100. Your melting or boiling point should then restrict your unknown's identity to a list of about 5–10 compounds. Quick, simple tests for aromaticity and halogen can rule out a few more possibilities.

7. Flame Test. Burn a small sample of the unknown in the hood to determine if aromatic rings are present.

8. Beilstein Test. Conduct the Beilstein test (copper wire) to determine if halogen is present.

9. Short List. Using your experimental data (mp/bp, functional group tests), develop a list of 3–5 possible structures from the tables available in your laboratory and on the web. If these are not all the same functional group, you may need to go back to solubility and IR data to be sure of what functional group you have. Submit this list of 3–5 possibilities to the person designated by the instructor to distribute NMR data.

10. Feedback. If your list of 3–5 compounds contained your actual unknown, you may receive an NMR spectrum. If your list did not contain your unknown, you will receive feedback on whether you are on the "right track" or not, and you will be able to submit a second list later at no penalty.

11. Derivative. The melting point of an appropriate derivative can distinguish between alternative structures. Synthesize a derivative of your unknown, recrystallize it, and obtain its melting point. Recall that impure compounds exhibit melting point depression as well as broader range. A melting range of 2.0 °C or less is indicative of a reasonably pure compound. If the range is greater than 2.0 °C,

or if the mp doesn't match any of the literature values from the tables, purify by recrystallizing it again, and get a more accurate melting point.

12. Propose Structure. Using your accumulated information, propose a structure for your unknown.

13. Write Report. Discuss the logical process of elimination and explain how inconsistencies in the data (if any) were resolved.

CAUTION! Additional allotments of unknown will result in a penalty. Work carefully, don't waste the unknown on unecessary tests, and keep your sample safe and tightly sealed! If you need to repeat some procedures, it's worth noting that most of the tests and derivatives can be done on smaller scale, as long as all the other reactants and solvents are scaled accordingly.

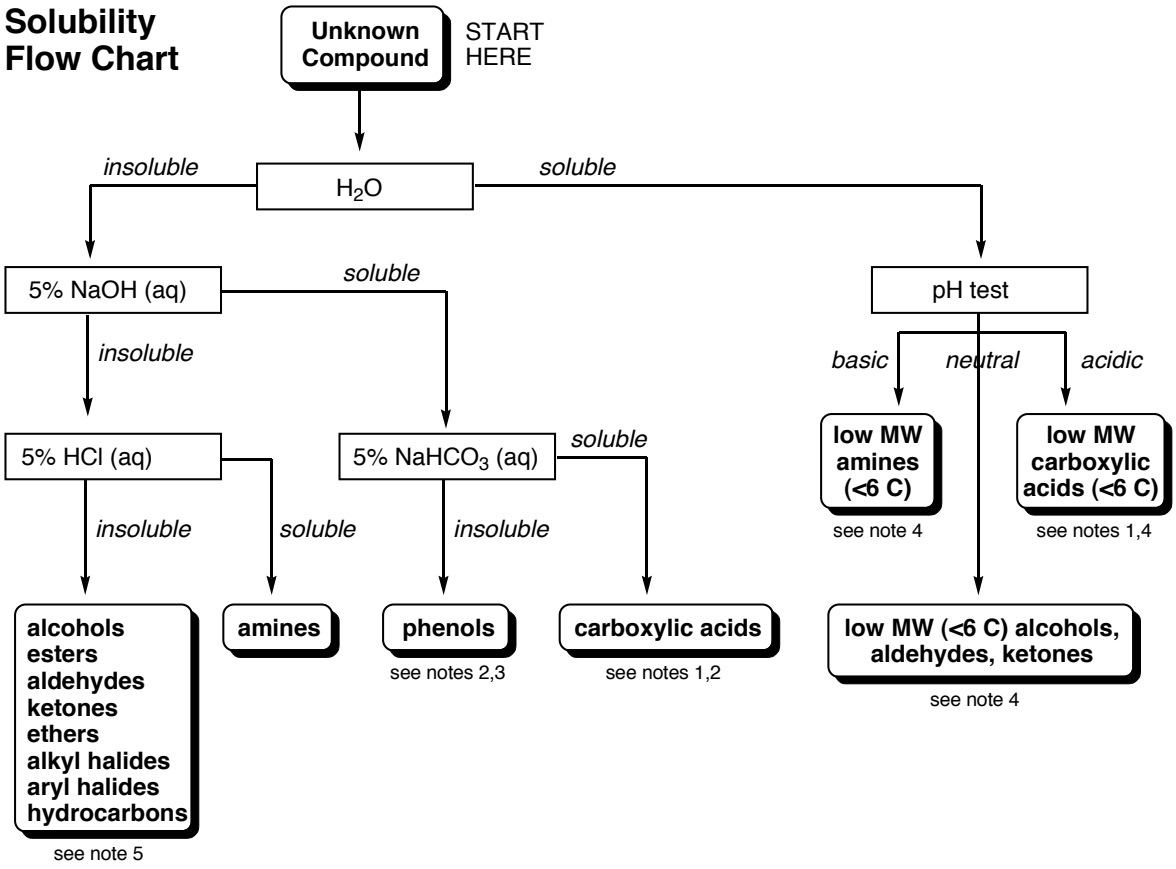
Solubility Tests:

The solubility characteristics of an organic compound in water, aqueous base, and aqueous acid can often be enough to identify the most reactive functional group in the compound. Additionally, solubility may provide some information regarding the molecular weight or the presence or absence of other functional groups. There are four standard solubility tests which are most useful: You will test the solubility in water, 5% aqueous sodium hydroxide, 5% aqueous sodium bicarbonate, and 5% aqueous hydrochloric acid.

Procedure: Prepare a hot water bath with about 1 inch of water in a beaker. A fresh sample of the unknown should be used for each solubility test. Place 0.1 g of a solid or 0.2 mL of a liquid in a test tube with 3 mL of the solvent. Mix the sample well and set it aside for a few minutes while you prepare tubes for the other solubility tests. If the unknown is not dissolved after a few minutes at room temperature, dip it briefly (less than 10 seconds) in the hot water bath. Check solubility after the tube reaches room temperature. Do not heat the acid or base solubility tests for more than a few seconds; false positives can occur upon heating, especially with functional groups that can be hydrolyzed.

Smaller amounts of unknown may be used, but to avoid false positives the solvent must be scaled down accordingly (for example, use 10 mg unknown in 0.3 mL solvent). The amounts of sample and solvent do not need to be exact. They may be measured for the first test and estimated thereafter.

Interpretation: For the purpose of functional group classification, a substance is said to be soluble in H_2O if 30 mg or more of the solute dissolves completely in 1 mL of water. The solubility in acidic or basic solutions should be determined by comparison to the water solubility. If the compound is noticeably more soluble in acid (or base) than in water alone, it is then considered to be soluble, even if not completely dissolved. Occasionally, compounds may have inconclusive or misleading solubility data because of electronic influences of a second functional group. For example, phenols bearing nitro groups may be soluble in $NaHCO_3$ because the electron-withdrawing nitro group decreases the pKa of the phenolic OH group sufficiently to make it behave as a carboxylic acid. Therefore, the solubility data should be accompanied by additional evidence, such as the IR spectrum or functional group tests, before making a final decision on the identity of the functional group.



Further Important Notes About the Interpretation of Solubility Data

1. If the compound is water-soluble, most of the other solubility tests are not useful because they are aqueous and may therefore be false positives. One important exception is water-soluble acids; these will cause vigorous gas evolution (CO_2) with the 5% $NaHCO_3$ (aq).
2. Phenols with strong electron-withdrawing groups (especially ortho or para) may have solubility behavior of carboxylic acids.
3. Beta-dicarbonyl compounds may have solubility behavior of phenols.
4. Compounds with more than one hydrophilic functional group may be water soluble, even with six carbons or more.
5. It is possible to distinguish the organic halides and hydrocarbons from neutral oxygen-containing compounds by testing the solubility in concentrated H_2SO_4. This will rarely be needed in this course.
6. Liquid aldehydes which have been exposed to air will usually contain some of the corresponding carboxylic acid (produced by air-oxidation). This may show up as a false positive for solubility in $NaHCO_3$. Distilling a portion of the unknown can resolve this problem, which is less common with solid aldehydes.

Functional Group Tests

The following tests may be used for the identification of functional groups in your unknown. Please note that only the reagents listed here will be available in the laboratory.

Tests for Alkenes:

• Bromine/CCl_4 Test: Harwood and Moody, pg. 245.

Procedure: In a small test tube, dissolve 10-20 mg of your unknown in *ca*. 2 mL THF or CH_2Cl_2. Add a solution of 5% bromine in CCl_4 dropwise, with shaking, and observe the results.

Interpretation: A positive test for unsaturation results in a discharge of the bromine color (decolorization of the solution).Some alkenes react very slowly with this reagent, if at all. Also, the results of the test must be observed immediately since the solution may decolorize in time due to evaporation of bromine.

Tests for Aromatic Compounds:

• Flame Test: Harwood and Moody, pg. 232.

Procedure: Place 10–20 mg of your unknown on a spatula, and briefly place it in the flame of a Bunsen burner (in the hood). Pull the spatula away from the flame and observe the nature of combustion, the color of the flame, and presence or absence of smoke. Try toluene, hexane, and 2-propanol as control experiments for comparison with your unknown.

Interpretation: A black, sooty smoke is indicative of an aromatic species. Some unsaturated molecules (alkenes, alkynes) and very long-chain alkanes may also give positive tests. The absence of sooty smoke suggests the presence of an aliphatic compound. Compounds with multiple functional groups or combined aromatic/aliphatic structures may give ambiguous results. The results are not strong evidence on their own, but may be useful in conjunction with other observations.

Nature of combustion:
Rapid and instantaneous combustion -- high oxygen content
Explosive (sparks) -- high nitrogen content, or nitro groups

Color of the flame:
Yellow smoky flame -- aromatic, unsaturated, or high MW aliphatic compounds
Yellow non-smoky flame -- lower MW aliphatic organic compounds
Clear bluish flame -- oxygen-rich compounds (ethanol):

This test may provide additional evidence for the presence of some functional groups in structure, but should not be given more weight than the data from solubility tests or infrared spectroscopy.

Tests for Alkyl or Aryl Halides:

• Beilstein Test: Ault, p. 242

Procedure: Form a small coil in the end of a copper wire by making a couple of turns around a nail or glass rod or similar object. Heat the tip of a copper wire in a Bunsen burner flame until no further coloration of the flame is noticed. Allow the wire to cool slightly, then dip it into a small sample of the unknown (solid or liquid), and place the wire into the flame again.

Interpretation: A transient green color forms in the flame when traces of copper are made volatile in the presence of the halogenated organic compounds. The green flash, which may be very brief, constitutes a positive test for halogen, indicating the presence of chlorine, bromine or iodine. Fluorine is not detected. Alkyl and aryl halides are not distinguished; both give positive tests.

• Silver Nitrate Test: Harwood and Moody, pp 247-248.

Procedure: Add 1 drop of the unknown to 2 mL of a 0.1M solution of silver nitrate in ethanol. Let stand for 5 min at room temperature. If no precipitate is observed after this time, heat the solution in a water bath and observe any change. Note the color of any ppt that is formed.

Interpretation: This reaction exhibits relative reactivities typical of S_N1 reactions. Benzylic, allylic and tertiary alkyl halides give an immediate precipitate at room temperature. Primary and secondary

alkyl halides give a precipitate upon heating. Aryl and alkenyl halides do not react, even with heating. The color of the precipitate (ppt) may suggest which halogen is present: White ppt = Cl; pale yellow ppt = Br, yellow ppt = I. Carboxylic acids may give a false positive, a precipitate which is the silver carboxylate salt (RCO_2Ag). To detect this false positive, add two drops of 5% nitric acid; silver carboxylates will dissolve but silver halides will not.

Tests for Alcohols:

- Chromic Acid Test: Shriner et al. pp. 149–150

  Procedure: Dissolve 1 drop of a liquid or *ca*. 10 mg of a solid unknown in 1 mL of reagent grade acetone. In a second tube, place only the acetone as a blank or negative control. Add 1 drop of the chromic acid reagent to each tube and immediately examine the colors of both tubes.

  Interpretation: A positive test for a primary or secondary alcohol is the immediate appearance of a blue-green color within 2 seconds. Tertiary alcohols do not react within that time period, and the color remains orange. Note that aldehydes can also be oxidized with chromic acid, and will give a positive in this test. Acetone may contain trace amounts of isopropanol leading to a false positive which can be detected in the blank test tube. The yellow-orange color should persist in the blank for at least 3 seconds. If the acetone gives a positive test, inform your TA or instructor, and request pure acetone.

- Lucas Test: Harwood and Moody, pg. 245.

  Procedure: Lucas reagent is an equimolar solution of anhydrous $ZnCl_2$ and concentrated HCl prepared by the prep room staff. Combine 0.5 mL unknown with 3 mL Lucas reagent (caution! strong acid!). Stopper the tube, shake for 15 sec, then allow the mixture to stand. After 5 min, observe whether there is a precipitate (usually the precipitate will be a liquid).

  Interpretation: This test is dependent on ease of formation of carbocation intermediates, leading from the alcohol to the corresponding alkyl chloride. A positive test usually appears as a liquid precipitate or separate liquid layer; how rapid this ppt forms gives an indication of structure. Because one looks for a precipitate, the test works well for those alcohols which are initially soluble in the reagent (generally liquid alcohols of low molecular weight).

  Formation of ppt within 2 minutes: benzylic, allylic, or tertiary alcohol
  Formation of ppt after 10 minutes: secondary alcohol
  No ppt: primary alcohol

Tests for Phenols:

- Ferric Chloride Test: Harwood and Moody, pg. 251.

  Procedure: Add 1 drop of liquid or *ca*. 10 mg of solid unknown to 2 mL of water. Add several drops of ferric chloride solution and observe the color immediately.

  Interpretation: Most phenols produce an intense red, blue, purple, or green color. Some colors are transient and must be viewed immediately upon mixing. Some phenols, especially sterically hindered ones, do not give a positive test, so a negative test is unreliable evidence. Esters and 1,3-dicarbonyl compounds sometimes also show intense coloration (false positive).

- Bromine-Water Test: Harwood and Moody, pg. 269.

  Procedure: Dissolve 1 drop of liquid or *ca*. 10 mg of solid unknown to 1 mL of EtOH. Add the bromine reagent dropwise until the yellow color persists, shaking the reaction mixture after each addition. Moisten a piece of litmus paper and hold it at the mouth of the test tube, watching for color change.

  Interpretation: The disappearance of the yellow bromine coloration is indicative of the consumption of bromine, and this suggests that a bromination of the electron-rich aromatic ring of a phenol. The color of the litmus paper turns pink in a positive test due to the evolution of HBr. A precipitate may

form in some cases, and on larger scale this could be a useful derivative. Other highly activated aromatic compounds, aromatic ethers for example, could also give a positive result.

Tests for Aldehydes & Ketones:

- 2,4-Dinitrophenylhydrazine (DNP) Test: Harwood and Moody, pp 241-242.

  Procedure: The DNP reagent is a solution of 2,4-dinitrophenylhydrazine and sulfuric acid in aqueous ethanol, prepared by the prep room staff. Dissolve 2-3 drops or *ca*. 50 mg unknown in a few drops of methanol. Add 1 mL of the DNP reagent and shake. If no ppt is formed, boil the mixture for 1 min and cool in ice.

  Interpretation: The appearance of a red, orange, or yellow precipitate indicates the presence of an aldehyde or ketone. The color of the precipitate can distinguish conjugated carbonyls (directly attached to alkene or aromatic ring) from non-conjugated carbonyls; a yellow ppt indicates the carbonyl is non-conjugated, while orange or red ppt indicates conjugation. Positive or negative for precipitate is the strongest evidence from this test; the color can sometimes be misleading. The precipitate is the DNP derivative, but the amount may be too small to recrystallize conveniently. The derivative procedure should be used to make the product on larger scale.

- Tollens Test: Harwood and Moody, p. 242.

  Reagent: The Tollens reagent must be freshly prepared. To a NEW test tube, add 2 mL of 5% $AgNO_3$ solution and one drop of 10% NaOH solution. Slowly add 2% NH_4OH solution dropwise, with thorough mixing between each drop added, until the precipitate of silver oxide is almost disappeared, but not completely gone (too much ammonia will decrease the sensitivity of the reagent). Use only the supernatant solution in the following test procedure; transfer by pipet and leave the solid behind.

  Procedure: To 5-6 drops of the unknown liquid (or *ca*. 0.1 g of solid) in a NEW test tube, add 1 mL of freshly prepared Tollens reagent. Look for the formation of a silver mirror on the walls of the test tube, or a black precipitate. If there is no black precipitate or silver mirror forming after 10 minutes, warm the tube by immersing in a hot water bath (>70 °C) for at least 10 minutes, then check again.

  Interpretation: The formation of Ag metal coating (silver mirror) inside the test tube, or a black ppt of finely divided Ag metal, constitutes a positive test, indicating the presence of an aldehyde. The Ag(I) in the reagent produces Ag(0) as it oxidizes the aldehyde to a carboxylate salt. Ketones are not oxidized under these conditions and give a negative test. Used or dirty test tubes may result in a black precipitate instead of the silver mirror. Some aromatic amines and phenols give a false positive in this test. Liquid aldehydes are likely to be contaminated by carboxylic acids due to air oxidation; a distilled sample of such aldehydes may give more reliable results in the Tollens test.

- Iodoform Test: Shriner et al., p. 167.

  Reagent: The iodoform test reagent is a solution of KI and I_2 in water, prepared by the prep room staff. This is a deep brown solution.

  Procedure: Have a 60 °C water bath ready. In a test tube dissolve 2–3 drops or *ca*. 50 mg unknown in 2 mL tetrahydrofuran (for water-insoluble unknowns) or 1 mL water (for water-soluble unknowns) and add 1 mL 10% NaOH solution. Add the iodoform test reagent dropwise, taking note of the color and the volume of the reagent added. As each drop is added, the color should disappear upon mixing (if not, immerse the test tube in the 60 °C water bath). Continue adding and shaking the test tube until the the dark color persists for more than 2 min at 60 °C. Add a couple of drops of 10% NaOH to decolorize the excess reagent. Fill the tube with water and allow to stand for 15 min, noting the presence or absence of yellow precipitate.

  Interpretation: Formation of a pale yellow ppt indicates that the unknown contains a methyl ketone, $RCOCH_3$. Disappearance of the brown coloration as the reagent is added is consistent with the alpha-iodination of the ketone via a ketone enolate. With a methyl ketone, this reaction happens three times in succession to afford $RCOCI_3$, then CHI_3 (iodoform) is released by nucleophilic acyl

substitution of $RCOCI_3$ by OH^-. Iodoform is a pale yellow solid (mp 119°C) with a foul odor. Ethanol and other alcohols of the type $CH_3CH(OH)R$ will give a false positive, as they are oxidized to methyl ketones under the reaction conditions. Acetaldehyde also gives a positive result.

Tests for Carboxylic Acids:

- Sodium Bicarbonate Test: Harwood and Moody, pg. 250.

  Procedure: This is simply the solubility test using $NaHCO_3$. Observe whether bubbles form. If no bubbles form, immerse the tube in a hot water bath for several minutes and examine it again. Some solid carboxylic acids react quite slowly, and may not dissolve entirely.

  Interpretation: The formation of bubbles suggests the evolution of CO_2 gas. This is expected when $NaHCO_3$ is mixed with an acid stronger than H_2CO_3. In such cases the HCO_3^- ion is protonated to make H_2CO_3, which then decomposes to afford H_2O and CO_2. Carboxylic acids (pKa of about 4) protonate the HCO_3^- ion and produce CO_2, but most phenols (pKa of about 10) do not. However, phenols bearing strongly electron-withdrawing groups may give a false positive. Liquid aldehydes are likely to be contaminated by carboxylic acids due to air oxidation, and may give a false positive. If other evidence suggests an aldehyde, then a false positive here can be ruled out by repeating the test on a distilled sample of the unknown.

Tests for Amines:

- Hinsberg Test: Shriner et al., pp. 230-232

  Procedure: Combine 0.2 mL of liquid unknown (or 0.2 g of solid unknown) with 5 mL 10% NaOH solution. Add 0.4 mL benzenesulfonyl chloride. Stopper the tube and shake vigorously for 5–10 min, cooling in a water bath if it becomes hot. Test the solution with pH paper to see if it is still basic. If not, add another 1 mL 10% NaOH and shake for 5 min. Separate any insoluble material ("Fraction A", may be liquid or solid) by decanting or filtering and test its solubility in 5% HCl. Acidify the filtrate ("Fraction B") by dropwise addition of concentrated HCl (check with pH paper) and promote crystallization by cooling and scratching the inside of the test tube.

  Interpretation: Primary amines afford a secondary sulfonamide ($RNHSO_2Ph$) with relatively acidic N–H bond; it is therefore soluble in NaOH solution and will precipitate or crystallize only after acidifying "Fraction B". Secondary amines afford a tertiary sulfonamide (R_2NSO_2Ph) which has no N–H to deprotonate, so it will be insoluble in NaOH solution and detected as "Fraction A", insoluble in 5% HCl. Tertiary amines will not react with $PhSO_2Cl$, and the unreacted amine should be insoluble in NaOH, so it will be detected as a "Fraction A" which is soluble in 5% HCl. Some secondary amines react slowly, and may require warming of the reaction mixture. Use the Hinsberg test only after establishing with some certainty that the unknown is an amine.

Tests for Esters:

- Hydroxyl Amine/Ferric Chloride Test: Harwood and Moody, pp. 243-244.

  Procedure: To 2–3 drops or *ca*. 50 mg unknown add 10 drops of a saturated ethanolic solution of hydroxylamine hydrochloride and 10 drops of 20% ethanolic KOH. Heat the mixture to boiling, acidify with 5% HCl, then add a 5% solution of $FeCl_3$ dropwise. Examine the color.

  Interpretation: Formation of a deep red or purple coloration (a positive result) suggests the presence of an ester. Do this test only if the compound is insoluble in NaOH, as phenols and carboxylic acids will give a false positive. If a positive result is observed, repeat the test without using hydroxylamine hydrochloride, positive in this case indicates a phenol, not an ester.

Tests for Nitro Compounds:

- Iron(II) Hydroxide Test: Harwood and Moody, pp. 248-249.

  Procedure: Add 2-3 drops or *ca*. 50 mg unknown to 2 mL of freshly prepared aqueous solution of 5% iron(II) ammonium sulfate. Add 3 drops 1M H_2SO_4, followed by 1 mL of 2M ethanolic KOH. Stopper the tube and shake well. Check for a precipitate and examine its color immediately, and also after 1 min.

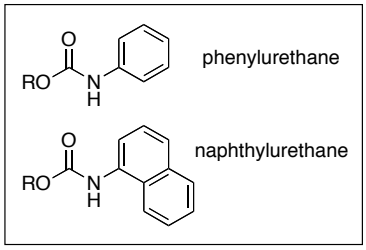
  Interpretation: The presence of a red-brown or brown precipitate within 1 minute constitutes a positive test for nitro groups. The precipitate may initially appear blue, then turn brown within 1 min. A slight darkening of the solution or appearance of a greenish color does not constitute a positive test.

Derivatives

The following derivative preparations will be available for your use in the laboratory. Please note that only the reagents listed here will be available in the laboratory. Also note that the amounts of compounds used in making these derivatives can be scaled to fit the amount of material you would like to use. The melting point should be determined when the product is thoroughly dry. In all cases, a melting point range greater than 2.0 °C is unsatisfactory and calls for recrystallization.

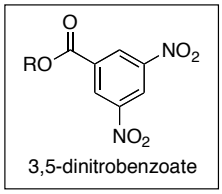
Derivatives from Alcohols

- Phenyl Urethane or 1-Naphthyl Urethane: Shriner et al., p. 156



  Procedure: Place 0.6 g of the anhydrous alcohol or phenol in a dry test tube and add 0.3 mL of phenyl isocyanate (alcohols) or α-naphthylisocyanate (phenols). If the compound is a phenol, add 2 or 3 drops of pyridine to catalyze the reaction. If the reaction is not spontaneous, heat the mixture in a hot water bath for 30 min, taking care to keep moisture out of the tube. While the mixture is still hot, remove insoluble byproducts by gravity filtration (moisture leads to a diarylurea byproduct). Cool the filtrate and scratch the inside of the tube with a glass rod to induce crystallization, then collect the product by vacuum filtration. A second recrystallization from hot petroleum ether, including another hot filtration, may be necessary to remove all of the diarylurea byproduct.

- 3,5-Dinitrobenzoate: Harwood and Moody, pg. 263.



  Procedure: Combine *ca*. 0.5 mL (0.5 g) alcohol, 1 g 3,5-dinitrobenzoyl chloride, and 2 mL pyridine in a dry test tube. Heat the mixture in a hot water bath for 15 min (30 min if the unknown is believed to be a 3° alcohol), taking care to keep moisture out of the tube. Pour the mixture into 10 mL ice-water while stirring, then acidify by cautious addition of concentrated HCl (check with pH paper). Decant the water and thoroughly triturate the residue (solid or oil) twice with 5 mL of 5% sodium carbonate solution. Collect the solid by vacuum filtration and recrystallize from petroleum ether or aqueous ethanol.

Derivatives from Phenols

- Phenyl Urethane or 1-Naphthyl Urethane: Harwood and Moody, pp 262-263.

  Same procedure as for alcohols (see above).

- 3,5-Dinitrobenzoate: Harwood and Moody, pg. 263.

  Same procedure as for alcohols (see above).

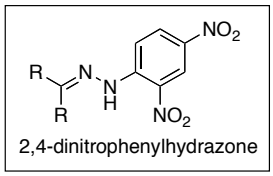
- Brominated derivatives: Harwood and Moody, pg. 269.

  Procedure: Dissolve 0.5 g phenol in 5 mL ethanol and add the aqueous bromine reagent dropwise, shaking the reaction mixture until a yellow color persists. Add 20 mL ice-water and isolate the ppt via vacuum filtration. If the ppt is yellow, rinse with 5 mL saturated aqueous $NaHSO_3$ then water (3 x 15 mL). Recrystallize the crude product from ethanol or aqueous ethanol. *Note: If an unknown gives no precipitate in the bromine water test for phenols, this is not likely to be a useful derivative procedure.*

Derivatives from Aldehydes & Ketones

- 2,4-Dinitrophenylhydrazone: Harwood and Moody, pg. 260.

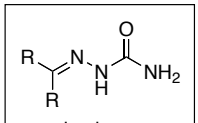
  Procedure: Combine *ca*. 0.20 g unknown with 5 mL 2,4-DNP reagent. Swirl to mix. If a solid does not form immediately, warm briefly in a water bath, then allow to stand for 10 min. If precipitation still does not occur, add water dropwise until a ppt forms. Isolate the solid by vacuum filtration. Wash successively with 5% $NaHCO_3$, and aqueous methanol (1:1). Recrystallize from ethanol or ethyl acetate.



2,4-dinitrophenylhydrazone

- Semicarbazone: Harwood and Moody, pg. 261.

  Procedure: Dissolve 1.0 g semicarbazide hydrochloride and 2.0 g sodium acetate in 5 mL distilled water, then add *ca*. 0.5 g of the unknown. If the unknown is not soluble, add ethanol dropwise until solution occurs. Swirl the mixture with warming in a water bath for 10 min, then cool in ice. Collect the solid by vacuum filtration and recrystallize from ethanol, ethyl acetate, or aqueous ethanol.



semicarbazone

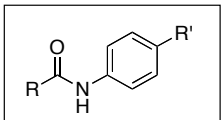
Derivatives from Carboxylic Acids

Carboxylic acids are first converted to the acid chloride (step 1), with subsequent reaction leading to the amide derivative (step 2).

- Anilides and *p*-Toluidides: Ault pp. 286–287

  Procedure, Step 1: Prepare the acid chloride. You will need a 50 mL round bottomed flask with a reflux condenser and a drying tube with fresh anhydrous calcium chloride. Place 0.3 g unknown acid, 1.8 mL thionyl chloride, and 1 drop of dimethylformamide (DMF) in the flask (the reaction may be exothermic). Attach the condenser with the drying tube on top, and heat under reflux for 30 min, taking care to exclude moisture. Allow the mixture to cool before proceeding to the second step.

  Procedure, Step 2: Dissolve 5 mmol of the aromatic amine (aniline or *p*-toluidine) in 20 mL toluene. Slowly add this solution to the acid chloride prepared in step 1 (*caution: there may be considerable fuming and a vigorous reaction*). Heat under reflux for 15 minutes. Cool to room temperature, transfer to a separatory funnel, and extract with 2 mL water, 5 mL 5% HCl, 5 mL 5% NaOH, and 2 mL water. Concentrate on the rotary evaporator, and recrystallize from ethanol or aqueous ethanol.

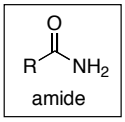


anilide (R' = H)
p-toluidide (R' = CH_3)

- Amides ($RCONH_2$): Ault pp. 285–286

  Procedure, Step 1: Prepare the acid chloride (see above).

  Procedure, Step 2: Pour the acid chloride cautiously into 5 mL ice-cold concentrated ammonium hydroxide (*caution: there may be considerable fuming and a vigorous reaction*). Collect the product by vacuum filtration and recrystallize from water or aqueous ethanol.



amide

Derivatives from Esters

Esters can be hydrolyzed, or saponified, into alcohol and carboxylic acid components; either of these components, if solid, can serve as the derivative. If the component of interest is a liquid, then it will have to be made into an appropriate solid derivative, as described under alcohols and carboxylic acids. Note that the component of interest will depend on whether it distinguishes between the possible structures of your unknown. For example, if you are trying to distinguish methyl *o*-chlorobenzoate or methyl *m*-chlorobenzoate, the alcohol component (methanol) will be the same for both. If the acid is the component of interest and is water-soluble (i.e., <6 carbons, such as acetic acid), saponification is not recommended because of the difficulty in recovering the product.

- Saponification of Esters: Harwood and Moody, pp 272-273.

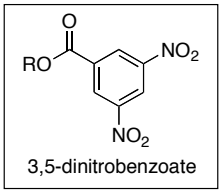
  This procedure can produce liquid alcohols and/or carboxylic acids which are not water-soluble.

  Procedure: In a 25 mL round bottomed flask equipped with reflux condenser, dissolve 1 g KOH in 3 mL diethylene glycol. Add *ca*. 1 mL (1 g) unknown ester and a boiling stone, then warm to reflux. Heat until a single liquid phase is visible. Cool to room temperature, then distill the alcohol from the reaction mixture. Do not collect diethylene glycol (bp 245°C). Note the temperature at which the alcohol distills to assist in a preliminary identification. When distillation is complete, cool the residue, add 10 mL water, and acidify with 20% H_2SO_4. If at this point the carboxylic acid precipitates, collect by vacuum filtration, wash with cold water (3 x 5 mL) and recrystallize. If a solid does not form, extract with ethyl acetate, dry the organic phase over Na_2SO_4, and concentrate on the rotary evaporator to obtain the carboxylic acid. Recrystallize or prepare a solid derivative.

- Transesterification: 3,5-Dinitrobenzoates. Ault, pp. 290-291

  This is a method to obtain a derivative of the alcohol component directly, without the saponification. It is not effective for esters of alcohols which are unstable to strong acid, such as tertiary alcohols or unsaturated alcohols. Higher molecular weight esters may react slowly.

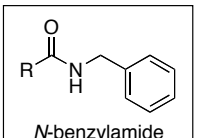
  

  3,5-dinitrobenzoate

  Procedure: In a 25 mL round bottomed flask equipped with reflux condenser, mix 0.5 g of the ester with 0.5 g of powdered 3,5-dinitrobenzoic acid, add a drop of concentrated sulfuric acid, and heat under reflux (or to 150 °C if the ester boils above 150 °C) until the 3,5-dinitrobenzoic acid dissolves, and then for an additional 30 min. Pour the mixture into a beaker containing ice and water (10 mL). Add 5% $NaHCO_3$ solution (caution: foaming will occur) until the evolution of CO_2 no longer occurs. Transfer the mixture to a separatory funnel, using 5 mL ethyl acetate to rinse product residues from the beaker into the separatory funnel. Extract with ethyl acetate (10 mL), concentrate the organic phase on the rotary evaporator, and recrystallize the residue from ethanol or aqueous ethanol.

- N-Benzylamides: Ault, p. 290

  This is a method to obtain a derivative of the acid component directly, without saponification. The procedure is effective for methyl and ethyl esters; higher esters may react very slowly.

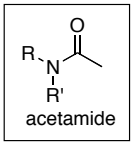
  

  N-benzylamide

  Procedure: In a 25 mL roundbottomed flask equipped with reflux condenser, mix 0.5 g of the ester with 1.5 mL benzylamine ($PhCH_2NH_2$) and 50 mg ammonium chloride. Heat under reflux for 1 hour. Pour, while stirring, into a mixture of 5% HCl (5 mL) and ice-water (10 mL). Collect the solid by suction filtration and recrystallize from aqueous ethanol.

Derivatives from Primary & Secondary Amines

- Acetamide: Ault, pp. 280-281

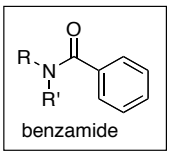
  

  acetamide

  Procedure: Prepare a solution of 5 g sodium acetate trihydrate in 5 mL water and set this aside for later. In a separate flask, dissolve about 0.5 g of the amine in 5% HCl solution

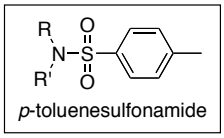
(25 mL). Add 5% NaOH solution dropwise until the mixture just begins to become cloudy from precipitation of the amine. Add a couple drops of 5% HCl, only as much as required to remove the cloudiness. Add 10 g ice and 5 mL acetic anhydride. With stirring, add the previously prepared sodium acetate solution in one portion. Cool the mixture in an ice bath. If no crystallization occurs after 30 min, cover the flask and allow it to stand until the next lab period. Collect the solid by vacuum filtration, wash with 5 mL water and recrystallize from aqueous ethanol.

- Benzamide: Harwood and Moody, pp 279-280.



Procedure: Combine 0.2 mL (0.2 g) amine with 3 mL 10% NaOH in a small flask. Add *ca*. 0.4 mL benzoyl chloride in 4 portions, stoppering the flask securely (use a glass stopper) and shaking vigorously for 2 min between each addition. After all the benzoyl chloride has been added, let the mixture stand for 10 min, then destroy and reagent residue with an ammonium hydroxide wash. Check to see if the reaction mixture is still alkaline (add more ammonium hydroxide if necessary), and collect the precipitate by vacuum filtration. Wash the residue with 10 mL water, then recrystallize from aqueous ethanol.

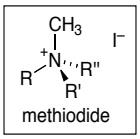
- *p*-Toluenesulfonamide: Ault, p. 282



Procedure: In a 25 mL roundbottomed flask equipped with reflux condenser, mix 0.5 g of the amine, 1.5 g *p*-toluenesulfonyl chloride, and 3 mL pyridine. Heat under reflux for 30 minutes. Pour the reaction mixture into 5 mL cold water adn stir until the product crystallizes. Collect the precipitate by vacuum filtration, wash with water, and recrystallize from ethanol or aqueous ethanol.

Derivatives from Tertiary Amines

- Quaternary Ammonium Salt: Methiodide Ault p. 285



Procedure: This derivative must be made in the hood! Prepare solutions of 0.5 g of the unknown amine in 1 mL acetonitrile, and 1 g methyl iodide in 1 mL acetonitrile. In a round-bottomed flask, combine the two solutions and allow the mixture to stand for 1 h, then carefully heat the mixture in a boiling water bath for 30 min. If the methiodide salt crystallizes on cooling, collect the product by vacuum filtration. If crystallization does not occur, remove the solvent on the rotary evaporator. Recrystallize from ethanol or ethyl acetate.

References

Z. Rapoport, Ed. "CRC Handbook of Tables for Organic Compound Identification", 3rd ed.; CRC Press, Inc.: Boca Raton, FL, 1988.

D.L. Pavia, G.M. Lampman, and G.S. Kriz, "Introduction to Organic Laboratory Techniques", 3rd ed.; Saunders College Publishing Co.: Philadelphia, PA, 1988, pp 682-690 (other editions available as well).

L.M. Harwood and C.J. Moody, "Experimental Organic Chemistry: Principles and Practice"; Blackwell Scientific Publications: Oxford, England, 1989, pp 232-233.

A. Ault, "Techniques and Experiments for Organic Chemistry"; University Science Books: Sausolito, CA, 6th Edition, 1998.

R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. C. Morrill, "The Systematic Identification of Organic Compounds", Wiley: New York, 6th Edition, 1980.

FIRST ATTEMPT

Name: _____ Section: _____

ID #: _____ Date: _____

In order to receive an ^{1}H NMR spectrum and mass spectrum of your unknown, submit a list of at least three, but no more than five, possibilities. In addition to the compound names, include the structure of each compound and its mp/bp.

Unknown #: _____

Physical properties: _____

Boiling Point: _____ Melting Point: _____

Possible Compounds (include name, structure and mp/bp):

1: _____

2: _____

3: _____

4: _____

5: _____

SECOND ATTEMPT

Name: _____ Section: _____

ID #: _____ Date: _____

In order to receive an ^{1}H NMR spectrum and mass spectrum of your unknown, submit a list of at least three, but no more than five, possibilities. In addition to the compound names, please include the structure of each compound and its mp/bp. If you have made a derivative, include its name and mp.

Unknown #: _____

Physical properties: _____

Boiling Point: _____ Melting Point: _____

Possible Compounds (include name, structure and mp/bp):

1: _____

2: _____

3: _____

4: _____

5: _____

Derivative Prepared: _____

Melting Point: _____

Pre-lab Flow Sheet: Unknown Experiment

Name: _____ Section: _____

ID #: _____ Date: _____

Indicate with an X the Infrared (IR) absorbances you would expect to see for each of the major functional groups listed below. Record any comments that you think might be helpful in identifying each group. Also, indicate in the comments column the IR absorbances you would expect to see if a nitro group was present in your unknown compound.

	IR Absorbance(s) Expected			
Functional Group	**-NH**	**-OH**	**C=O**	**comments**
Carboxylic Acid				
Ester				
Aldehyde				
Ketone				
Alcohol				
Phenol				
1° Amine				
2° Amine				
3° Amine				
Nitro Group				

Frequency (cm-1)	Bond	Functional Group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	primary, secondary amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C(triple bond)C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C(triple bond)N stretch	nitriles
2260–2100 (w)	–C(triple bond)C– stretch	alkynes
1760–1665 (s	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	alpha,beta–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	alpha,beta–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	primary amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1300–1150 (m)	C–H wag (–CH2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	primary, secondary amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C(triple bond)C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

Experiment #9: Unknown -- Short Report Form CHEM 141

Name: _____ **Date:** _____

Unknown Compound, Name: _____

Unknown #: _____ **Unknown Compound, Structure:**

1. . Physical Constants

a. melting point, observed: _____(Literature: _____)

b. boiling point, observed: _____(Literature: _____)

2. Solubility Tests

(indicate + or –, include comments if relevant)

	H_2O	aq NaOH	aq $NaHCO_3$	aq HCl	conc. H_2SO_4
observed:					
comments:					

3. Functional Group Classification Tests

Reagent or Test	Results	Inferences

4. Spectroscopic Examination
(list absorbances and assignments; show structure with C's and H's labeled, attach labeled spectra)

a. infrared:
format: xxxx cm^{-1} (functional group)
example: 1690 cm^{-1} (α,β-unsaturated ketone)

b. ^{1}H NMR:
format: x.xx ppm (multiplicity, integration, assignment)
example: 1.22 ppm (triplet, 3H, H's of methyl group)

c. ^{13}C NMR:
format: xxx.x ppm (DEPT, assignment)
example: 131.2 ppm (up, ortho carbon of Ph), 202.3 ppm (none, C=O)

5. Preparation of Derivative

Derivative type	observed mp	literature mp

6. Discussion (attach to this form). No more than one page from your lab notebook, handwritten. In two or three sentences, briefly explain the logic which led you to the compound you concluded was your unknown. Identify results of tests which were inconsistent with this conclusion, such as false positive tests or inaccurate physical properties, and explain why you disregarded them. If the derivative procedure failed, briefly indicate what was observed.