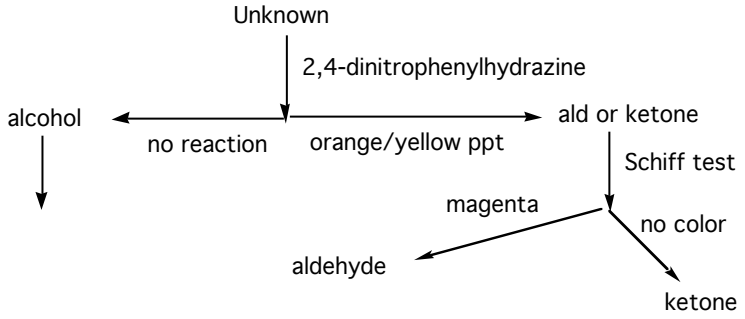
CHEMISTRY 268. Identification of an Unknown.

THE EXPERIMENT DONE OVER THE NEXT TWO WEEKS REQUIRES A LOGICAL APPROACH AND A COHERENT PLAN. IF YOU TRY TO USE THE SHOTGUN APPROACH AND DO EVERY TEST AVAILABLE YOU WILL NOT HAVE ENOUGH TIME OR SAMPLE AND THE RESULTS WILL BE CONFUSING. CAREFUL PREPARATION IS ESSENTIAL TO SUCCESS. The actual procedure that you follow will need to be revised as you gather data. Each unknown is different so each person's approach will differ. There is no set procedure given. You must prepare this yourself from these notes and the text (Chapt 36 and the copy of Chapt 70 from the previous text, available on the Chem 268 website – call this the "large handout"). These experiments are challenging and satisfying in that they put together much of what you have learned and practiced in this course over the past two semesters and they require the use of the chemical knowledge gained in lecture and lab. Writing out a flow diagram (or branch diagram) showing your general approach will help guide you. A **partial** example follows:



Given: a liquid unknown that will be either an alcohol, an aldehyde, or a ketone taken from the large unknown list available in lab (NOT the tables at the end of the large handout). Task: using physical properties (MP of a solid derivative, BP of the unknown), chemical reactions, other observations, and spectra, identify the unknown. Caution: As with all laboratory chemicals, assume that all of the unknowns and reagents are toxic. Many of them are. Keep them off of your skin and avoid breathing their dust or vapors. You will be issued a limited amount of unknown (about 2 g or 2 mL) so use it sparingly. A re-issue will cost you one point. It is important to learn to work with small quantities of materials and to not be wasteful. Some unknowns are quite volatile and will evaporate if left uncapped. Others, such as aldehydes, react with oxygen in the presence of light. To keep the unknowns from evaporating or reacting, keep them tightly capped and keep them dark by wrapping aluminum foil around their containers. If you have a volatile compound or one that is air and light sensitive, and you do not complete all tests during the first week, ask your TA to store it in the refrigerator at the end of the period so you can continue with it the following week. Many unknowns have a disagreeable odor so keep them contained and work with them in the fume hood. Pipets that have come into contact with an unknown should be rinsed with acetone into the waste and left in the container in the waste hood, not thrown into the glass waste.

Make careful, detailed observations and keep thorough records. Identifications should be based on an analysis of your entire set of data. Occasionally a test will not work well or the results will contradict other data. Verify that a questionable result is indeed reproducible and consider that in your final analysis. Some unknowns will simply not behave as expected. Do not jump to conclusions. Know what each test tells you.

Purity. For a truly unknown sample it would be essential to test for purity using spectroscopy and/or chromatography and if necessary to purify it by distillation if a liquid, or recrystallization if a

solid Working with an impure sample could be very misleading. Assume however that this unknown is sufficiently pure.

General Approach. Because of the many tests being done there will be several waste containers. Be especially careful to use the correct ones. Mixing wastes can lead to expensive waste disposal costs. Make as many initial observations as possible - color, odor (carefully), anything else that may be useful. Equipment and reagents for the various tests will be located throughout the lab and will be well labeled for easy navigation. Please leave reagents at their designated stations. There is no need to wait in line to do any test. The tests do not necessarily have to be done in the order shown here. The ignition test and Beilstein test may be observed at the same time and will be done in the unused lab area, away from flammable mcompounds, as before. Determine the BP. The method used here for taking a BP on a small scale is similar to that given on p. 59, 60, "Using a 3- to 5- mm Tube". The difference is that you will use a MP capillary in a MelTemp apparatus. The observations will be the same only on a smaller scale. Omit the sodium fusion test. Solubility tests are indispensible for making a preliminary classification of compound type, however because of the limited number of possible compound types the only solubility test done here will be water solubility. Classification tests provide more detailed information about compound type (functional groups present). Derivative formation is used to provide additional physical constants (MPs) which can be checked in the Tables of possible compounds. Infrared spectroscopy should be done only after you have made a preliminary identification of functional groups based on chemical tests. Report your initial results to your TA before taking an IR. After you have made a preliminary assignment of structure, you will be given a copy of a 60 MHz ^{1}H NMR spectrum.

Classification tests are used to classify compounds by functional group type. At the same time that a classification test is run on the unknown, it should also be run side-by-side on a compound known to give a positive test (control) and one known to give a negative test (blank). The control will show you what a positive test looks like and will also confirm that the reagents and conditions are correct. The blank will show what a negative test looks like. Solid derivatives are made so that you will have an additional physical constant (MP), which will help in your analysis. MPs of solid derivatives are found in the table. You should plan on making two derivatives for your unknown. Occasionally a derivative will be an oil and/or will not crystallize. This often means that the MP of that derivative is low or that the derivative is impure. That information alone may be useful (e.g., low MP). Remember that a compound with a wide MP range (> 2 deg C) should be considered to be impure, and that the actual MP of the compound would be somewhat higher that that found. In other words, unless a derivative is pure, its MP will be of limited value in identification of the unknown. Ideally, compounds must be recrystallized repeatedly, to constant MP, for their MPs to be considered dependable. Practically speaking, derivatives must be recrystallized at least once before a reliable MP can be obtained. Derivatives must also be completely dry before a reliable MP can be obtained.

The strategy then is to approach this in a logical way and to gather as much information as needed to identify the unknown (BP of unk, MP of derivatives, results of classification tests, other observations). Some tests and derivatives shown in the textbook will not be available. For this unknown, the following classification tests will be available: the Cerium(IV) Nitrate Test, the 2,4-Dinitrophenylhydrazone Test, the Schiff Test, and the Iodoform Test. For the first unknown, the derivatives available to you are, for alcohols, the 3,5-dinitrobenzoates and phenylurethanes, and for aldehydes and ketones, 2,4-dinitrophenylhydrazones and semicarbazones. If you obtain a positive 2,4-dinitrophenylhydrazone classification test, simply filter the solid, recrystallize it, and use it as one of your derivatives. It will then be unnecessary to do a separate preparation of the

2,4-dinitrophenylhydrazone derivative. Your unknown will be water soluble or water insoluble. Some tests make provisions for each case. In most cases, if your MPs are accurate, you will be able to make a definite identification based only on the chemical tests, the BP, and derivative MPs. In some cases however, a final determination may require interpretation of the NMR spectrum. In all cases, interpretation of the IR and NMR spectra are required for the write-up.

Notes on procedure: (see comment on stink under Waste Disposal below!)

The "large handout" covers the approach used to analyze an unknown that may be one of many different functional groups. Because your unknown is limited to only alcohols, aldehydes and ketones, much of the large handout may be ignored. In other words, in the large handout, skip over discussion of acids, amides, and any other functional groups besides alcohols, aldehydes and ketones.

These tests are qualitative and in most cases the reagents are used in excess. Therefore it is unnecessary and a waste of time to measure amounts exactly. Assume that 1-2 drops of liquid unknown is equal to 0.2 mmol or 20 mg. Many of the reagents will have, attached to the bottle, Pasteur pipets which are marked off at a certain volume. In other cases, measuring amounts by counting drops with a pipet calibrated in drops/mL will be sufficient.

Solubility tests: again, you will do only a water solubility test for this unknown.

For preparation of the 3,5-dinitrobenzoates use 100 mg of dinitrobenzoyl chloride as stated but use 4 drops of liquid unknown (about 50 mg). Do not overheat.

A Note on Semicarbazone Derivatives: Pyridine = stench. Use in fume hood only. Sometimes, a semicarbazone forms immediately, even before addition of pyridine, and thus can be confused for unreacted unknown. The temptation in such a case is to add methanol until the solid dissolves to produce a clear solution as described in the book. In no case should you add more than 0.5 mL of methanol. In some other cases, the semicarbazones do not crystallize well. Try the usual methods - scratching, cooling, letting it stand for a long time on ice. If it still does not crystallize, try saturating the hot solution with a little warm water or try running the reaction again, this time using less methanol. If all else fails, try this alternate method: For HOH sol unk, add 3 drops unk to 0.4 mL reagent and 0.1 g sodium acetate. Mix well, heat, cool to crystallize. For HOH insol unk, dissolve 3 drops of unk in 0.7 mL ethanol, add HOH dropwise to produce cloudiness, add 0.4 mL reagent and 0.1 g sodium acetate, heat, and cool to crystallize.

When looking up MPs of derivatives in the table, remember that your MP determination may not be perfect (the derivative may not be absolutely pure or dry, the thermometer is only accurate to ± 2°). Therefore, as a first approximation, consider all compounds from the table that have derivatives which melt within several degrees of the MP of your unknown derivative (e.g., if you find a MP range of 154-156° C, consider compounds melting between 154 and 160, or even more if necessary, in the first pass). You can fine tune your conclusions based on other data afterward. Note that in the tables some derivatives may be listed with two MPs. This is because the literature shows reports of both. The difference is sometimes due to different crystal forms having different MPs and sometimes simply as a result of error. Care should be exercised in interpretation in such situations.

IR spectroscopy. Clean the salt plates after use and return them to their containers. Do not leave them in the instrument. As good practice, you should clean them before use as well. Assuming that the previous person cleaned them well may be a bad assumption. Methylene chloride (dichloromethane) is used to clean the plates in the fume hood. At no time should water come in contact with the plates. Liquids will be taken as a thin film between two NaCl plates.

NMR spectroscopy. Once you have narrowed down the unknown to no more than a few possibilities, draw the structures of the possible compounds and sketch out predicted NMRs or portions of NMRs. Present your findings to your TA and you will be given a copy of the NMR spectrum. **By giving you the NMR, the TA is not implying that your proposed possibilities are correct.**

Warnings: (1) Acetone is a ketone. If glassware is contaminated with acetone, you will get false positive results for ketones and methyl ketones. (2) Some unknowns may contain two functional groups.

SAFETY: As is true with any laboratory chemicals, the reagents and unknowns in this experiment should be considered to be toxic and should not be inhaled or allowed to come into contact with the skin. Remember that many organic chemicals pass quickly through the skin to cause systemic poisoning.

WASTE DISPOSAL: Be sure to place wastes in the proper containers. The following containers will be available: Nonhalogenated Liquid Waste (nonhalogenated organic solvents and solutions), Halogenated Liquid Waste (any liquid containing halogenated compounds or solvents – e.g., Iodoform Test waste), Acidic Waste (2,4-DNP Test waste), Solid Waste. Many unknowns stink. Do not dispose of pipets contaminated with unknowns or reagents directly in the glass waste box (they will stink up the entire room!) - rinse them with a little acetone first, then leave them in the hood in the container labeled as such.

CLEAN-UP: Reminder. As always, do not leave chemical spills unattended. Leaving spills puts your fellow students and the lab personnel at risk. Clean up balance and hood areas immediately after using them. Cap all reagent bottles after use. Dispose of glass in the glass waste containers only.

ID of Alcohols, Aldehydes, and Ketones – some further tips

- general tests – BP, solubility do not have to be done in order or even right away. Don't waste time waiting for a set-up for these. If set-ups are busy begin with the 2,4-dinitrophenylhydrazine test and proceed from there and do the general tests when the set-ups are free and when you have a break in the action.

- do chemical tests in logical order, isolate derivatives and recrystallize. Making and purifying the derivatives early in the afternoon may result in samples that are dry enough for MPs. Make careful observations and gather as much data as possible.

- when you have done all chem tests report your preliminary results to your TA. Once your TA gives the go ahead, take an IR (don't wait around for this either – go do something else if the IRs are busy)

- when and only when the derivative is fully dry, take the MP and find possible compounds on the list. Draw the structures and see if any can be eliminated by considering the test results (e.g., if you have a neg. iodoform, you can eliminate all ket's or ald's in which one of the R groups is a methyl group – so-called methyl ket or ald. Color of DNP – yellow: probably non-conj C=O. Orange/red: likely conj C=O.)

- when you have narrowed the possibilities to one or two compounds report your findings to your TA. Your TA will then give you a copy of the 60 MHz NMR spectrum.

Even if you think you have the correct compound, interpret the NMR as best you can as part of the write-up. Careful researchers don't jump to conclusions so consider all data as a whole before making a final conclusion.

Don't ask your TA if you have the correct compound. Just write up the report based on your careful observations and conclusions. (rev, pws, apr12)