Experiment 10 —

Qualitative Analysis

Pre-lab preparation. (1) Find and carefully record in your notebook the structure of each of the 8 unknown compounds you will be working with. If you can't find the data in Wikipedia, try ChemSpider or another source. Also find and draw the structures of the 5 compounds to be used as controls in the DNP, chromic acid and permanganate tests. Not any information that you happen to find regarding physical appearance or odor — this may help you identify the compounds. (2) Based on its functional group, to which class does each compound belong? Be sure you get this right — there are lists of functional groups in your text. (3) Write a flow chart for the sequence of tests that you will be able to follow as you work. At each stage, indicate which compounds give positive and which give negative tests, and what positive and negative results look like. The order of the tests and a sample flow chart is below. Because this is so important, the pre-lab write-up for this lab is worth 10 points (and the write-up is worth 10).

Chemists frequently use qualitative patterns of reactivity to identify the functional groups of unknown compounds. This technique, called *qualitative analysis*, was an especially important tool for structure determination in the early days of organic chemistry. An alkene, for example, can be identified by its reaction with Br_2 — disappearance of the red-brown color of the bromine provides clear visual evidence that a reaction has occurred. Similarly, upon treatment with chromic acid, certain functional groups are oxidized, and this is accompanied by reduction of the orange Cr(VI) to the blue-green Cr(III) — an obvious change.

Since the development of powerful spectroscopic methods for structure determination, including infrared (IR), and especially nuclear magnetic resonance (NMR, which we will study next semester), most of these qualitative chemical tests have become less important than they once were. However, these tests are quick and easy, and they are still useful for identifying functional groups or confirming the presence of functional groups identified spectroscopically.

Perhaps more important for our purposes, these tests will familiarize us with the chemical behavior of a variety of different compounds, they'll give us a chance to learn some new chemistry, and — gosh darn it — they're just plain old fashioned *fun*.

In this lab you will use qualitative chemical tests to identify eight compounds. These have been placed in plain brown bottles labelled "A" - "H" to protect their identities. Fortunately, you will not have to determine the entire structure of each compound (you couldn't do that at this point in the course even if you wanted to). The compounds are **1-butanamine**, **butanone**, **1-butanol**, **butanal**, **propanoic acid**, **1-chloropropane**, **pentane**, and a **2-pentene** (a mixture of *cis* and *trans*). Since each compound has a different functional group (or none), you will be able to determine which compound is in which bottle by determining what functional group is present.

Caution: Most of the unknown liquids are flammable, and their vapors may be harmful. Some can cause irritation on contact with eyes or skin. Keep them away from open flames and avoid unnecessary contact or inhalation of vapors.

Chemical tests. A combination of physical and chemical tests will be used to determine what functional groups are present. Each of these tests should give an easily visible result. The different tests are explained in detail and the procedures are described below. The section that follows the individual tests will guide you through the process of putting it all together and developing a scheme that you can use to identify each of the compounds. If you work this out before you come to lab, the experiment should be go very quickly and you'll be out early; if you don't you're unlikely to finish before the end of the period.

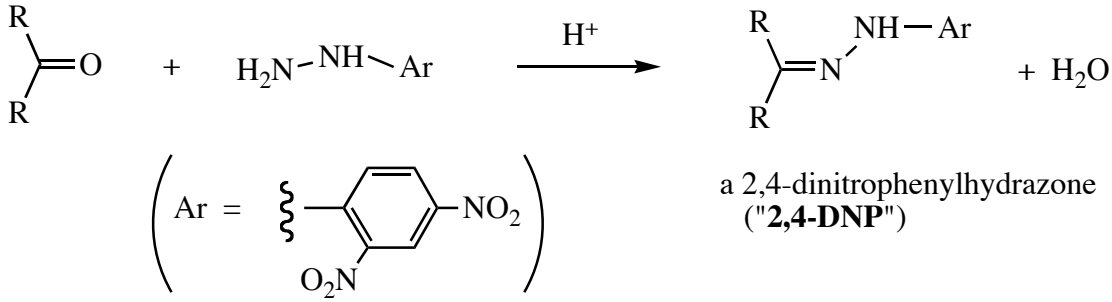
(a) **Water solubility** and **litmus tests.** Because the molecules in our set of 8 are relatively small, a polar functional group — especially one capable of hydrogen bonding — will probably make the compound miscible with, or at least soluble in, water.

Procedure. To get an idea of the water solubility of each compound, add about one ml of water to 10-drops of compound in a test tube, stopper the tube and shake it vigorously. If a homogeneous solution results, the compound is extremely soluble or miscible in water. If the compound does not completely dissolve, dilute the mixture with water to a total volume of 10 ml

and shake. If the compound completely dissolves, we'll call it "soluble"; if not, we'll call it "insoluble".

Test the pH of all the homogeneous solutions by placing a drop on pH paper (don't dip the paper into the solution — oink, oink — that's kind of like dipping your fettuccini into your cabernet sauvignon.) One of the compounds in the set should test acidic; one should test basic. Which ones? Note that it's not necessary for a compound to be completely protonated or deprotonated by water to alter the pH (think gen-chem pH calculations here). Now, for the compounds that didn't dissolve at all, it's pointless to test the pH of the water, so don't do that. Discard these solutions and mixtures when you're finished — the remaining tests must be done starting with the pure compounds.

(b) **DNP test.** Ketones and aldehydes react with hydrazines to form compounds called hydrazones. For example, the reaction of 2,4-dinitrophenylhydrazine ("2,4-DNPH") with a generic ketone is shown below.



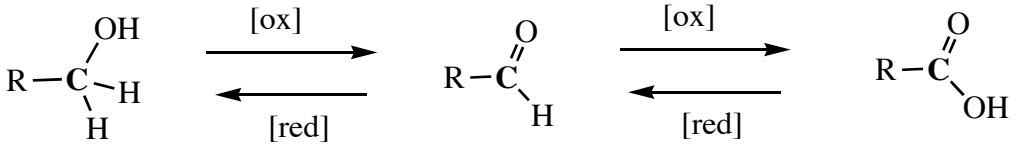
Although this is a reaction you haven't seen before, you can write the mechanism. There are two steps and some "proton shuffling". The N attached to the aromatic ring is not nucleophilic because its lone pair is delocalized by resonance; the "end" nitrogen is the nucleophilic one. This N attacks the carbonyl C, displacing the π-electrons onto O — that's step 1 — formation of the CN bond. Next, the negative O is protonated and the positive N is deprotonated (H^+ is transferred to the solvent). The resulting "carbinolamine" then undergoes an acid-catalyzed dehydration (you already know that mech!) to form the CN π-bond of the product — O is protonated, then water is lost (that's "step 2" — cleavage of the CO bond), the resonance-stabilized cation spits out a proton and... congratulations, you've just made a hydrazone!

2,4-Dinitrophenylhydrazones ("2,4-DNPs") are typically yellow or orange crystalline solids. The hydrazones derived from simple aldehydes and ketones are usually yellow; those derived from conjugated carbonyl compounds are usually orange or red-orange. Hydrazones of simple aldehydes and ketones normally form quite easily. (Complications are sometimes encountered as a result of impurities, formation of colored complexes with certain compounds, and side-reactions that can give false positive tests, but these complications should not be a major concern for us. However, this is why we also need to run *control experiments* so we can see what authentic positive and negative results look like!)

Procedure. Dissolve 1 drop of compound in about 1 ml of 95% aq ethanol, and add 2 ml of the 2,4-DNPH reagent (this is a solution of the hydrazine (about 2%) in EtOH (50%), H_3PO_4 (40%), and H_2O (10%) — ***Caution: this solution is toxic and corrosive***.) Gently shake the mixture and let it stand. Also run three controls: cyclohexanone, benzaldehyde, and 1-pentanol so that you can see what authentic positive and negative results look like.

(c) **Chromic acid test.** Certain alcohols, aldehydes, and a few other types of compounds can be oxidized with aqueous chromic acid, H_2CrO_4. Oxidation of the organic compound is accompanied by reduction of the chromium from the soluble orange Cr(VI) reagent to an insoluble blue-green Cr(III) product.

Most oxidations of organic compounds involve loss of hydrogens and/or gain of oxygens or gain of bonds to oxygen. For example, a primary alcohol — one whose –OH group is attached to a primary C — can be oxidized Cr(VI) (as well as other reagents) to an aldehyde; most oxidants, including aqueous chromic acid, will further oxidize the aldehyde to a carboxylic acid. At this stage the C has no more Hs, so that's the end of the road — carboxylic acids cannot (easily) be oxidized further. Note the exchange of C–H bonds for C–O bonds in each step. (To recognize oxidations and reductions, you need to focus on what's happening to the **C** not the O!)



Secondary alcohols are oxidizable (to ketones), but tertiary alcohols are not. Draw these and you'll see why — the key is whether the C bearing the hydroxyl group has an H or not — if

not, that C is not oxidizable. To take this idea one step further, unlike all other carboxylic acids, formic acid, H–CO_2H *can* be oxidized to CO_2 (or to the "hydrate" of CO_2, H_2CO_3). Formic acid is the only oxidizable carboxylic acid because it's the only one with an H on the carboxyl C!

Alcohols are normally oxidized rapidly with chromic acid, H_2CrO_4; aldehydes are oxidized a bit more slowly, possibly because their oxidation occurs via an intermediate hydrate ($RCH(OH)_2$, formed by addition of water to the CO π-bond). In addition, chromic acid will oxidize phenols and may also oxidize amine nitrogens and even alkenes, alkynes, and certain ketones under more extreme conditions. The amine should be out of the picture by the time you get to this test, but you should run controls on the other functional groups.

Procedure. Dissolve 1 drop of compound in about 1 ml of reagent grade acetone. Add one drop of the chromic acid reagent (this was made by combining 20 g of $Na_2Cr_2O_7$, 14 ml of H_2SO_4, and 100 ml of H_2O — ***Caution: this solution is toxic and corrosive. Chromic acid is a suspected carcinogen***). Gently swirl the mixture and let it stand. Note the time required for reaction. A positive result should be visible within a few minutes. Run the same three controls that you did for the DNP test, plus *tert*-butyl alcohol and cyclohexene.

(d) **Permanganate test.** In basic solution at room temperature $KMnO_4$ will hydroxylate an alkene (i.e. add two –OH groups to the π-bond, like the OsO_4 reaction we learned in lecture); in neutral or acidic solution, it will chop an alkene into two pieces by cleaving both σ- and π-bonds (like ozonolysis, but messier). Both of these reactions are oxidations of the organic compound; the manganese is reduced from Mn(VII) to Mn(IV) in the process. This reduction changes the purple permanganate solution to a brown precipitate of MnO_2.

Under the relatively mild conditions of our test (dilute, neutral permanganate solution), only alkenes and alkynes should react. However other oxidizable compounds may react as well, e.g. amines, phenols, aldehydes, and alcohols (surprisingly, most alcohols are not oxidized under these conditions). Also, be aware that a tiny amount of oxidizable impurity might cause a false positive with the first drop of permanganate added. Again, these are the reasons that we run controls — so we can see what authentic positive and negative test results look like.

Procedure. Dissolve 1 drop of the pure compound in 2 ml of 95% aq EtOH, and add 5 drops of 0.1M aqueous $KMnO_4$ solution. (***Caution: this is likely corrosive***.) Remember, decolorization of just the *first drop* may be due to an oxidizable contaminant rather than the compound of interest. If a reaction does not take place immediately, shake the mixture and let it stand for 5 min. This should be sufficient time for even the most stubborn alkene to decide to react; anything that happens after this time is probably due to oxidation of a less reactive functional group. Even alcohols tend not to react within 5 min under these conditions (strange, but true). Also run cyclohexene, 1-pentanol, and *tert*-butyl alcohol as controls (we'll find out if alcohols really fail to react!). Also test any of the other controls that you think might be relevant. (i.e. if you think you may have an aldehyde, then see what the reaction of an authentic aldehyde looks like. Does it turn brown? Green? Start smoking? Grow hair?)

(e) **Beilstein test.** This is a classic test for halogenated compounds. When red-hot Cu is placed in contact with an organo-halide, some CuX is formed. Cuprous halides are volatile enough that placing them in a flame will generate a green color in the flame from the vaporized CuX. The green is a characteristic of the copper atoms.

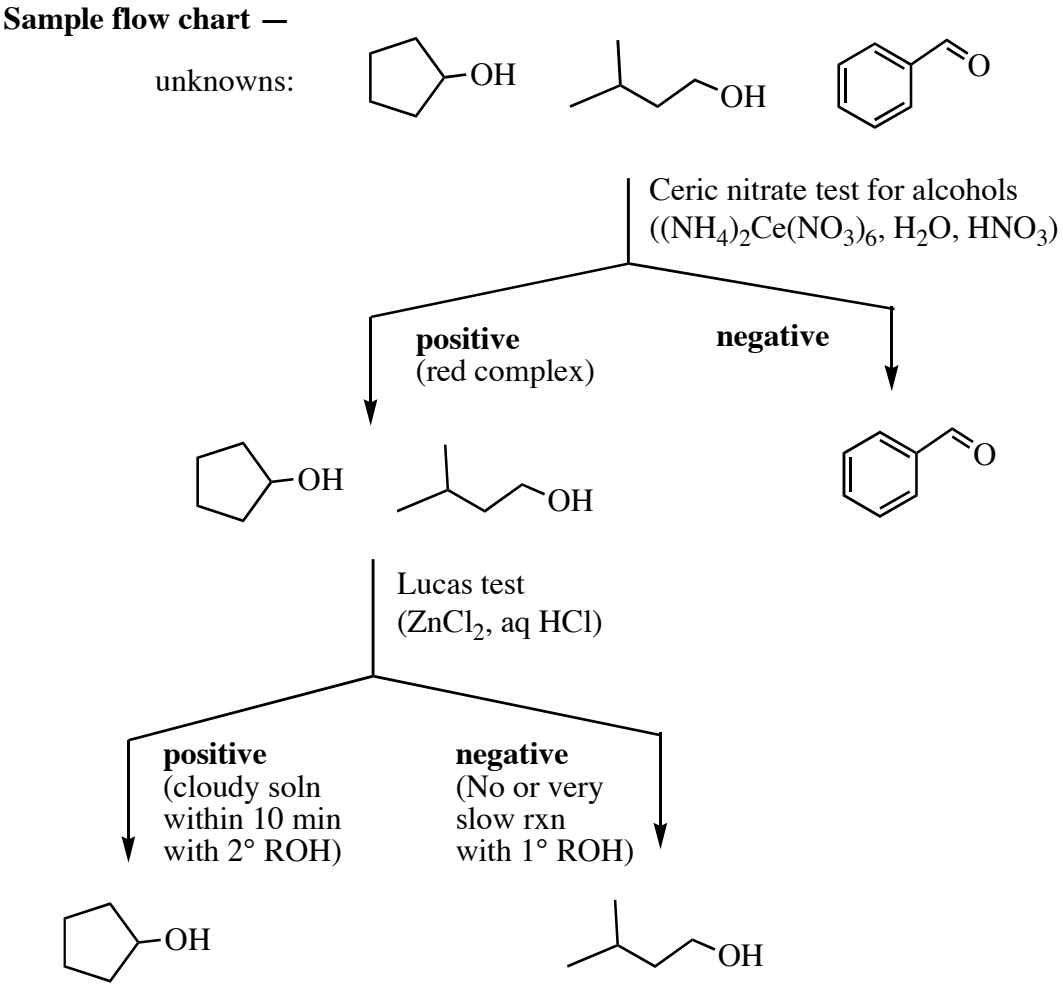
Procedure. Get about 10 cm of copper wire and make a small loop at the end. Heat the loop in a flame, in the fume hood, until it's glowing red. Plunge the red-hot Cu loop into about 0.5 ml of the compound to be tested (seriously), then return it to the flame and watch carefully. Note that Bunsen burners have an air intake that may need to be adjusted — a yellow flame (too much gas, not enough air) is too cool and too bright; you need a blue flame for this experiment. ***Caution: Be careful not to set fire to the compounds, your notebook, paper towels, yourself, your partner, the instructors, or anything else.*** No controls this time; at this point you should be down to two compounds, one that creates fireworks and one that doesn't.

Putting it all together. To do this lab quickly and sensibly you need to do a little preparation before you start. At this point you've written down the structures of the eight unknowns and the five knowns and categorized them according to functional groups. If you haven't done that yet, now would be a good time.

Write a flow chart that shows which compounds should give positive and negative results for each of the tests in the following sequence: **litmus test** (here there are three options, of course

— neutral, acidic, or basic)**, DNP test, H_2CrO_4 test, $KMnO_4$ test, and Beilstein flame test**. Once you've positively identified a compound, you can set that aside — don't continue running tests. For example, if one compound tests acidic with litmus, you know which one that is, right? Don't bother running the other tests on that one. As an example, a flow chart for a completely different series of compounds and tests is shown below.

Sample flow chart —



Your flow chart is the most important part of your pre-lab write-up. You *must* do this carefully and thoughtfully before you can start the experiment. Your TA will check the flow charts early in the lab so potential points of confusion can be identified before anyone gets completely off track.

Experimental procedure. Each partner should participate in *each part* of this experiment and *independently record observations in his or her notebook*. *Do not* split the tasks and exchange data later!

Start by obtaining 10 drops of each unknown in dry, labelled, stoppered test tubes. Carefully observe the physical characteristics, including the odor. Smell each compound by holding the test tube about six inches from your face and fanning the vapors toward your nose with your hand. Never hold a container with a volatile liquid directly under your nose and inhale! Characterize each odor and its intensity as best you can. The physical characteristics and odor may allow you to make a tentative assignment by comparison with the data you dug up before lab. However, you probably won't be able to draw any firm conclusions about any of the compounds from appearance or odors alone.

Next, do the water solubility test. Based on their structures, which compounds do you expect to be water-soluble and which insoluble? Again, this may give you some ideas about which is which, but you'll still need to carry on with the litmus test and then follow the sequence dictated by your flow chart.

Your report, due at the end of the lab period (no later, please!) should include everything you did and observed, and the compound assignments you were able to make at every step of the process. Be sure to carefully note any unclear or anomalous results (there are bound to be some things that are less than clear in these tests). Your TA will appreciate a final summary of the compound structures that correspond to your section's unknowns A - H.

Also, determine the mass and % recovery of your acetanilide and the other compound you and your partner recrystallized in the last lab, and measure their melting ranges. How does the melting range of the recrystallized fluorenone, benzocaine, or benzoic acid compare with the melting ranged of the crude solid that you (or your partner groups) measured previously? How does this compare with the literature mp of that compound? ***Please include this info in your report.*** Hang onto the sample — we're going to run IRs of these next semester.

No check-out; you'll get your same drawer back for Chem 22. If you're not planning to continue to Chem 22, please see the stockroom staff about checking out, and don't forget to return your key.

Expt adapted from *Operational Organic Chemistry*, by J. W. Lehman, Allyn and Bacon, Boston (1981), pp. 54–65.