EXPERIMENT 1 - Identification of a Single Unknown

In this dry lab exercise, you will identify an unknown organic compound using IR spectroscopy, chemical tests, and ^{1}H-NMR spectroscopy. Each unknown contains nine carbon atoms or less and will have one of the following functional groups: alcohol, alkyl halide, aldehyde, ketone, carboxylic acid, or ester. In addition, the unknown may have an ether and/or arene group, though no chemical test will confirm that.

You will be given a packet containing the IR spectrum, chemical test results, and ^{1}H NMR spectrum for an unknown. You are required to fully interpret the data and ***solve the unknown before leaving the lab on the same day***. As always, the TA will be there to assist you and to clarify any questions, especially about ^{1}H-NMR. You should come to the lab very well prepared with a good working knowledge of IR and, above all, ^{1}H-NMR.

Notebook Preparation

Prepare 2 blank tables on separate pages: (1) IR – bond, functional group, and stretching frequency - and (2) ^{1}H NMR Spectroscopy - chemical shift, integration, splitting, and assignment. Don't forget to add each page to the table of contents.

Pre-lab Questions – Read the chemical test descriptions on the following page and consider the questions below. Concise responses should be written in passive voice without personal pronouns, typed and in-hand at the beginning of lab. Draw all structures by hand. Do not copy/paste from other sources. You may use ChemDraw if you know how, but this may be overly tedious for mechanisms.

1. What are the expected IR stretches for each of the functional groups that may be present in the unknown? Present your responses in table format.

2. Give an example of the balanced reaction and mechanism for a molecule that gives a positive Lucas test.

3. Give an example of the balanced reaction and mechanism for a molecule that gives a positive 2,4-dinitrophenylhydrazine test.

4. What is the full balanced reaction for the oxidation of a generic aldehyde (R-CHO) to a carboxylate and the reduction of Cu^{2+} to Cu_2O? No mechanism.

5. What is a chelating agent? Look up the structure of tartrate (the conjugate base of tartaric acid) and propose a structure for copper II tartrate.

6. Give an example of the balanced reaction and mechanism for a molecule that gives a positive sodium iodide in acetone test.

7. Give an example of the balanced reaction and mechanism for a molecule that gives a positive silver nitrate in ethanol test.

8. What are the characteristic ^{1}H NMR chemical shifts for each possible functional group? Present your responses in table format.

EXPERIMENTAL PROCEDURE

The ***Lucas test*** is based on the reaction of alcohols with HCl that leads to the formation of alkyl chlorides. The reaction takes place by an S_N1 mechanism. Tertiary alcohols are the most reactive, followed by secondary alcohols. Primary alcohols do not react with Lucas reagent at room temperature.

The test is useful only for alcohols soluble in the Lucas reagent (small alcohols with fewer than six carbons). Tertiary alcohols soluble in the Lucas reagent ($ZnCl_2$ in $HCl_{(c)}$) react immediately and give an insoluble tertiary alkyl chloride that separates as an immiscible layer or as an emulsion. Secondary alcohols soluble in the Lucas reagent react more slowly than tertiary alcohols and cloudiness, or an immiscible layer, forms within 5-10 minutes.

The ***2,4-dinitrophenyldrazine test*** is based on the nucleophilic addition of a hydrazine derivative (H_2N-NH-R), to the carbonyl group of aldehydes and ketones. A positive result is the formation of an insoluble 2,4-dinitrophenylhydrazone. This has a more extended system of conjugation than the original hydrazine and absorbs visible light at longer wavelengths (blue) than the original 2,4-dinitrophenylhydrazine (absorbs violet). The resultant product tends to be orange (the complementary color of blue). Aldehydes and ketones react almost immediately and give a yellow-orange (sometimes red) precipitate when treated with 2,4-dinitrophenylhydrazine.

Esters do not react; they give a negative test as evidenced by the lack of a precipitate. If the 2,4-nitrophenylhydrazine test was positive, the ***Fehling's test*** is performed as well. Aliphatic aldehydes give a positive test (the formation of a brown-reddish precipitate of cuprous oxide) with the Fehling's reagent. Ketones and aromatic aldehydes do not react.

Fehling's test is a redox reaction accompanied by a drastic change in color. Cu^{2+} under basic conditions is deep blue, and the product of the reaction, usually Cu_2O rather than metallic copper, is a reddish precipitate. The reaction is performed in the presence of tartrate to keep the Cu^{2+} in solution under basic conditions. Tartrate is a chelating agent.

Aldehydes, especially aliphatic aldehydes, can be easily oxidized with Cu^{2+}. The aldehyde gets oxidized to a carboxylic acid (or a carboxylate under the basic conditions of the test) and the copper gets reduced to Cu^{+} (in the form of Cu_2O) and occasionally to Cu^{0} (metallic copper). Esters do not react with the Fehling reagent.

The ***sodium-iodide-in-acetone*** and ***silver-nitrate-in-ethanol test*** are based on substitution reactions and allow one to distinguish between primary and tertiary alkyl halides.

Sodium iodide in acetone test

Alkyl chlorides and bromides react with NaI in acetone to give an alkyl iodide and sodium chloride or sodium bromide, respectively. The reaction typically takes place by an S_N2 mechanism. Primary alkyl bromides and chlorides react faster than secondary halides. Primary alkyl bromides react at room temperature. Primary and secondary alkyl chlorides and secondary and tertiary alkyl bromides react upon heating at 50°C. Tertiary alkyl chlorides, aryl halides, and vinylic halides do not react even after heating. The formation of a white precipitate of NaCl or NaBr is considered a positive test. This test is based on the limited solubility of sodium chloride and sodium bromide in acetone. NaI (the reagent) is soluble in acetone, while NaCl and NaBr (the possible side products) are not.

Alkyl halides react with silver nitrate in ethanol to give silver halide which separates as a precipitate. The formation of this precipitate is considered a positive test. The by-products are nitric acid and an ether. The reaction takes place by an S_N1 mechanism so tertiary alkyl halides react faster than secondary. Primary alkyl halides react slowly and give a precipitate only upon heating.

After interpreting the IR spectrum and chemical tests, ***check the results with a TA or instructor***. If you are on the right track, move on to ^{1}H-NMR interpretation, otherwise we will help you reorient. The interpretation of the NMR should be done in the lab. These are the recommended steps to follow for structural elucidation:

- Fill in the table with all NMR peaks: chemical shift, integration, splitting, and assignment.

- Notice the solvent used to obtain the NMR and make sure that you do not assign solvent or impurity signals, such as ***water***, to your sample. Check the table provided at the end of this manual for a list of commonly used solvents and their NMR signals, including water.

- Interpret the integration values in the ^{1}H-NMR spectrum. Since you do not know the molecular formula, your integration will be in relative terms. However, you should try to anchor the integration by making a reasonable assumption about the number of hydrogens under a certain peak. Your assumption should be based on the functional group present in your molecule and knowing that the unknown is a relatively small molecule with 9 or fewer carbons. For example, if you suspect an aldehyde, locate the aldehyde hydrogen. That peak should integrate to 1H.

- Interpret the multiplicity of the peaks following the n+1 rule. This will tell you not only the number of neighbors for each type of hydrogen, but it may also be helpful in anchoring the integration. For example, if your spectrum shows two triplets and no other multiplet (doublet, triplet, quartet, etc.), it is likely that each triplet integrates for 2H (the 2H that split the neighbor's signal into a triplet).

- Pay attention to the chemical shifts to determine the environment of each hydrogen (shielded or deshielded). Use the correlation tables provided at the end of this manual to narrow down the possible functional groups or atoms nearby.

- Keep in mind that contrary to IR, every peak of the NMR spectrum should be accounted for (except for very small peaks that may belong to impurities). If you leave a peak without interpretation, it's very likely that your proposed structure is wrong.

- *Check your structure yourself before checking with the TA:* calculate the expected chemical shifts of your structure using the correlation tables online or use an online NMR predictor tool. Check for any large discrepancies in chemical shift and splitting.

- ***Before leaving the lab, present the name and structure of the unknown to your TA and explain your reasoning.***

EXPERIMENT 1 REPORT GUIDELINES

- Read and apply info from ***Appendices 1* & *2*** in the lab manual.
- Include the unknown number as a Header – appears at the top of every page.
- The structures of the unknown should be provided at least twice in the report (abstract & results sections). Look up the name/structure online. Use common name if applicable.
- Keep as concise as possible while still being descriptive.

The lab report will consist of the following sections with the cover page available online.
Abstract – one paragraph summary of the experiment in this order:
(1) Purpose – "The purpose of this experiment was to…"
(2) Methods – list the methods used to determine the unknown, NOT procedures (IR, names of chemical tests, and ^{1}H NMR)
(3) Results – results of *pertinent* chemical tests only (Lucas test was positive for …), one or two distinctive IR stretch(es) and one or two distinctive NMR peak(s)
(4) Conclusion - state the identity of the compound (acceptable name).
Include the structure of the unknown below this abstract – no Figure heading necessary in abstract only. Use ChemDraw to present the structure here.

Results – Briefly introduce only pertinent chemical tests in one-to-two sentences: <u>what *general* information one could / would get from that part of the experiment?</u> Do not explain the history or inner workings of IR or ^{1}H NMR spectroscopy. State the facts, include all pertinent results for each part of the experiment with <u>limited interpretation</u>, and present the structure at the end of this section. Text should be interspersed with tables, where the text appears before it with a clear parenthetical reference to it (**Table x**). You will likely not list every result from the tables in the text. Instead, re-state a few key findings and refer the reader to the table. Save the logical description of how you solved the structure for the discussion section. Stick to the facts and initial interpretation in the results section. An example of how to organize the results section follows:

- Utility of IR spectroscopy and main findings
    - IR table: Functional group, bond, expected stretch, observed stretch
        - Include each IR active bond in your solved unknown structure (ignoring the fingerprint region)
- Description of each *pertinent* chemical test and results
    - Chemical test table: include ALL given chemical test results. Include a column for the functional group interpretation of each
- Utility of ^{1}H NMR Spectroscopy and main findings
    - Use ChemDraw to present the solved structure above the NMR table. Add letters corresponding to each set of H's on the structure.
    - NMR Table: Assignment (letter corresponding to labeled structure), observed chemical shift, expected chemical shift (use predictor tool or calculate values of solved structure), integration, and splitting.

Discussion – Re-state the goal of the experiment, initial IR findings, and a brief summary of the results obtained in the chemical tests (functional group assignment). Your analysis should be critical, showing how you deduced the structure of your unknown. Include the complete interpretation of IR and ^{1}H-NMR with the chemical shifts, integration, and splitting, comparison with table values and assignments (which bonds gave rise each IR band in the table and to which H does each NMR signal belong?). Students should refer to tables from the results section and peaks within (ex. the 3H singlet at 2.0 ppm was assigned to signal A, **Table 1**) rather than reproducing the entire table and structure. Conclude with a statement of the methods used and the unknown name.

Exp 1 – Unknown Identification Name _____

Attach this as the cover page to your report.

***Refer to specific writing guidelines online when preparing the final report*

CHEM 146A GRADING RUBRIC

SECTION	EDITOR COMMENTS	POINTS ASSIGNED
LAB REPORT – Staple the report together in this order		
ABSTRACT One paragraph, six sentences max: Purpose, procedure, main result(s), and conclusion(s). Unknown structures included.		/ **20**
PRE-LAB QUESTIONS Enumerated responses given in complete sentences		/ **25**
RESULTS Brief introduction, results with limited interpretation, text interspersed with tables, all tables have headings & descriptions and are referenced within the text.		/ **35**
DISCUSSION Logical explanation for structural elucidation including relevant chemical test results and IR absorbances as well as detailed ^{1}H NMR analysis and assignments. Conclusion statement with methods and unknown identification.		/ **30**
NEATNESS AND ORGANIZATION Proper grammar, order, and format per instructor announcements and guidelines in lab manual. Tables and figures numbered and given descriptive titles, referred to in text.		/ **20**
LAB NOTEBOOK Up-to-date table of contents; 3 tables with given chemical test results, IR stretches, and ^{1}H NMR signals.		/ **20**
	LAB REPORT TOTAL	**/ 150**