27. Qualitative Analysis 3

Last week the functional group present in an unknown sample was identified using wet chemical tests. In today’s experiment the same sample will be analyzed using two instrumental analysis techniques; IR and $^1$HNMR. A boiling point range and $^{13}$C NMR spectrum will be provided. An extensive list of possible compounds will be made available. The objective of this lab is to determine the exact chemical structure of the unknown substance based on the $^1$HNMR, $^{13}$CNMR, boiling point and IR.

PRE-EXPERIMENT ASSIGNMENT

Review the material for Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy within this manual and in the on-line notes found within the Organic Chemistry web page.

A student who has prepared for the Qualitative Analysis 3 experiment should be able to:
1. Know how to analyze a sample using an Infrared Spectrometer.
2. If given an IR spectrum be able to identify functional groups present.
3. Know how to prepare and dispose of NMR samples.
4. Be able to predict the IR spectrum if given a chemical structure.
5. Know how to interpret a $^1$H NMR spectrum. If given a spectrum know how many nonequivalent sets of hydrogen are present, the environment of each of these sets of hydrogen, the number of adjacent hydrogen and the relative numbers of each.
6. If given a compound be able to predict the $^1$H NMR spectrum including number of signals, shift, splitting pattern, and relative size.
7. If given a chemical structure, be able to predict the $^{13}$C NMR spectrum.
8. If given a $^{13}$C NMR spectrum, choose possible responsible compounds.
9. Know how to prepare a sample in an NMR tube for analysis.

Quizzes given after the experiment has been performed may also include:

10. If given IR, $^1$H NMR, boiling points and $^{13}$C NMR be able to choose the correct identity of an unknown.

Safety Considerations

The unknown compounds include phenols and carboxylic acids. Most phenols are toxic and may be absorbed through the skin. Carboxylic Acids are corrosive. Some of the other unknowns are irritants. Be very careful when handling chemicals. Wear gloves. Wipe up all spills immediately. Keep chemicals away from skin. If accidental contact is made, wash immediately with copious amounts of soap and water. Wash hands thoroughly at end of lab.
The solvent used to prepare $^1$H NMR samples is CDCl$_3$ or deuterated chloroform. Deuterated chloroform has the same physical properties as regular chloroform, namely it is a central nervous system (CNS) depressant and will cause lightheadedness, nausea and even loss of consciousness if inhaled in sufficient quantities. Handle CDCl$_3$ in hood.

**EXPERIMENTAL**

Retrieve the unknown you used last week during Qualitative Analysis 2. Analyze the sample on one of the infrared spectrometers. Prepare a NMR sample by following the below sample preparation instructions. Run a $^1$H NMR on your sample. Obtain spectrum.

Your instructor will provide you with a boiling point range and a $^{13}$C NMR spectrum of your compound. A list of approximately 150 possible compounds along with their boiling points will be made available. Combine this information with the $^1$H NMR and IR of your sample to determine your compound identity.

A useful approach to determining the structure is to first use the boiling point range to eliminate a substantial number of the possible candidates. The functional group identification will further reduce the number of possible structures. The $^{13}$C NMR and $^1$H NMR can then be used to select the proper compound identification from the remaining candidates.

**NMR sample preparation and disposal**

NMR tubes are precision made and fairly expensive. Handle these with care. Deuterated chloroform is expensive, be careful not to spill or contaminate contents of bottle. The deuterated chloroform solvent contains 0.10% tetramethylsilane (TMS), so no external reference material needs to be added. Obtain a clean NMR tube. Using a new clean pipette, transfer approximately ¾ mL of CDCl$_3$ into NMR tube. This should fill the tube to about 5 cm or three fingers width. This does not have to be exact. Add 2-3 drops of unknown material to tube. Do not add more sample or a poor NMR spectrum will result. Cap tube and invert to mix. The sample is ready. Take this to NCF 371 and obtain a spectrum on the 60 MHZ NMR.

After you are finished obtaining a $^1$HNMR spectrum, carefully remove cap from the fragile NMR tube. Empty contents of tube into the halogenated organic liquid waste bottle. Using a wash bottle fill NMR about half way with acetone. Empty contents into halogenated organic waste bottle. Rinse with acetone once more. Place NMR tube upside down in beaker in hood labeled “Used NMR Tubes”.

**CLEANUP**

Cap unknown and return to instructor. Discard used Pasteur pipettes. Rinse IR salt plates with acetone and return them to the envelopes within jar. Place jar in desiccator. Place used kim-wipes in trash can.
POST-EXPERIMENT ASSIGNMENT

Complete datasheet and turn into instructor by specified time. Prepare for the final exam.

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