

**CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012**  
**Lab #5: Identification of an unknown –MP, IR, and NMR spectroscopy**

You will be performing an abbreviated experiment from an article published in the 2005 Journal of Chemical Education (page 1382-84). Each pair of students will identify an unknown solid organic compound from an extensive list of carboxylic acids, aldehydes, ketones, and amines. You will need to perform an accurate mp analysis and then analyze your sample by IR, proton, and carbon NMR spectroscopy. This will enable you to interpret your spectra and determine the identify of your unknown.

**You will be deducted heavily for requesting more of your unknown. So use your sample sparingly.**

**Pre-lab Reading:** You are expected to read the posted pdf (JCE, 82, 9, 1382-84.) and this lab packet. Refer to the sections of your text (chapters 2 and 9) for background information on the IR and NMR spectroscopy techniques and analysis of spectra. You will not need to include any pre-lab or lab information in your lab notebook, but you must fully complete the lab packet and report sheets.

You **must proceed with extreme caution when handling the unknowns** since you are unable to look up the toxicity of the substance prior to knowing its identity. Treat each unknown as if it was a serious human hazard and use gloves, goggles, and appropriate lab techniques to handle the samples. Any contact with your skin should result in immediately rinsing with water.

Throughout the lab report, points will be distributed for both your written interpretation of your elucidation process as well as the accurate determination.

The **melting point and IR analysis should be conducted carefully** as they serve as your primary starting points for the unknown determination. Once you have completed the MP and IR determination, you must check with your instructor to find out if you are on target, (see the report sheet)

At the completion of the assignment, **each student is required** to turn in their own **IR spectra, proton NMR spectra, and  $^{13}\text{C}$  NMR spectra** with the lab report to their instructor.

Review the journal article associated with this lab, read the conclusion and list the five valuable aspects the authors feel that this exercise provides for the undergraduate organic student: **(2pt)**

- 1.
- 2.
- 3.
- 4.
- 5.

**CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012**

**Lab #5: Identification of an unknown –MP, IR, and NMR spectroscopy**

(INFORMATION ON THIS PAGE SHOULD GO IN YOUR LAB BOOK AND THE SHEET BELOW)

Name: \_\_\_\_\_

Lab Partner: \_\_\_\_\_

Record your unknown number: \_\_\_\_\_ (2 pt)

**You will be deducted heavily for requesting more of your unknown. So use your sample sparingly.**

Record the physical appearance of your unknown: \_\_\_\_\_ (2 pt)

Prepare a capillary tube and conduct a melting point determination of your unknown. Always quote a range and realize that a melting point range of more than 2 degrees is possible, but would likely indicate impurities

Record your unknown melting point range: \_\_\_\_\_ (2 pt)

Now add +/- 4°C and record the expanded range with this error margin. \_\_\_\_\_ (2 pt)

(If you have accurately determined your mp, then your unknown will fall within this expanded range)

Perform an IR experiment on your unknown compound. Study your IR spectra and reference your list of IR absorptions (two sided pink page). Describe the functional groups, (include the wave number for the absorptions), that seem to be **present and** what groups seem to be **absent**. (3 pt)

Briefly describe how comfortable you are with your mp accuracy and the IR spectra you have obtained. (3 pt)

Each unknown will be an aldehyde, amine, carboxylic acid, or ketone and not mixtures of these functional groups, (in addition you may also have a hydroxyl, halogen, nitro group, or other functionality). After determining which of these 4 species you believe to be in your unknown, you will consult the appropriate functional group unknown table and narrow down your unknown choice based upon your IR data and melting point, (see the report sheet).

Report Sheet for Lab #5 (Identification of an unknown –MP, IR, and NMR spectroscopy)

Name: \_\_\_\_\_

Lab Partner: \_\_\_\_\_

Record your *unknown number*: \_\_\_\_\_ (2 pt)

(Fill in this IR table referencing your IR spectra and staple your spectra to this report) (4 pt)

IR Absorption Peak (cm-1)	Meaning of the absorption

*Functional Group (aldehyde, amine, carboxylic acid, or ketone) selected*: \_\_\_\_\_ (2 pt)

Record your *melting point range*: \_\_\_\_\_ (2 pt)

Write the melting point range with the +/- 4° C error margin: \_\_\_\_\_ °C (2 pt)

Complete the above sections and then show your instructor your report sheet to verify the accuracy of your mp and functional group selection: \_\_\_\_\_ (initials) (3 pt)

---

Everything above this line must be completed before moving on to the remainder of the lab

List the 4 most plausible unknown candidates from the appropriate functional group table that fall within your melting point range: (include at least 4) (4 pt)

Compound	Melting point ( degrees C)

---

Prepare an NMR sample of your unknown by placing a tiny scoop, (the end of a microspatula), in the NMR tube. Then add 1.5 inches roughly of CDCl<sub>3</sub>, (deuterated chloroform solvent). MAKE SURE you add CDCl<sub>3</sub> and not the wrong solvent! (your instructor will show you how to prepare the sample in pre-lab)

Perform a proton NMR experiment on your unknown with your instructors assistance  
Perform a carbon-13 NMR experiment on your unknown with your instructors assistance.

Report Sheet for Lab #5 (Identification of an unknown –MP, IR, and NMR spectroscopy)

Name: \_\_\_\_\_

Lab Partner: \_\_\_\_\_

Draw the structures of these 4 candidates and fill in the table with expected NMR data for each.  
(Use ChemDraw or the internet to get the structures) (Do not group in-equivalent aromatic protons) **(25 pt)**

Name of candidate 1: <b>Structure of candidate 1</b>	number of proton signals = number of carbon 13 nmr signals =
circle and indicate the multiplicity on each proton set, (singlet, doublet, triplet, quartet, or multiplet	

Name of candidate 2: <b>Structure of candidate 2</b>	number of proton signals = number of carbon 13 nmr signals =
circle and indicate the multiplicity on each proton set, (singlet, doublet, triplet, quartet, or multiplet	

Name of candidate 3: <b>Structure of candidate 3</b>	number of proton signals = number of carbon 13 nmr signals =
circle and indicate the multiplicity on each proton set, (singlet, doublet, triplet, quartet, or multiplet	

Name of candidate 4: <b>Structure of candidate 4</b>	number of proton signals = number of carbon 13 nmr signals =
circle and indicate the multiplicity on each proton set, (singlet, doublet, triplet, quartet, or multiplet	

Explain in detail how your  $^1\text{H}$  NMR spectra and your  $^{13}\text{C}$  NMR spectra enabled you to indentify your unknown. For the proton NMR, be sure to address the number of signals, the chemical shifts of those signals, the integration of the signals, and the multiplicity of the signals.  
(You should draw the molecule as a reference when addressing each of theses topics) **(15 pt)**

For the  $^{13}\text{C}$  NMR, be sure to indicate the number of signals observed and the chemical shifts. **(5 pt)**

My unknown # \_\_\_\_\_ is determined to be: \_\_\_\_\_ **(20 pt)**

If you are not convinced that your identification is 100% accurate, you can add a discussion below that addresses any conflicting data or interpretations, (this will be used to assign partial credit on incorrect unknown identifications – you can earn up to 10 of the 20 pts on an incorrect answer)

\* Re-visit your IR table, (page 3) and list the absorptions for all of your molecules functional groups.

### Aldehydes

<u>Compound</u>	<u>Melting Point (°C)</u>
ortho-iodobenzaldehyde	37
piperonaldehyde	37
ortho-anisaldehyde	38
acetylsalicylaldehyde	39
ocatadecanal	39
meta-iodobenzaldehyde	57
meta-nitrobenzaldehyde	58
veratraldehyde	58
2,5-dichlorobenzaldehyde	59
2-naphthaldehyde	60
3-hydroxybenzaldehyde	104
9-anthraldehyde	105
para-nitrobenzaldehyde	106
2,3,4-trichlorobenzaldehyde	106
2,3-dihydroxybenzaldehyde	108

### Amines

<u>Compound</u>	<u>Melting Point (°C)</u>
para-toluidine	45
3-bromo-4-ethoxyaniline	47
3,4-dimethylaniline	49
2,5-dichloroaniline	50
4-chloro-2-methoxyaniline	52
3,4-dimethyl-2-nitroaniline	66
2,4,5-trimethylaniline	68
2-bromo-4-chloroaniline	69
para-chloroaniline	71
ortho-nitroaniline	71
para-phenylenediamine	140
2-methoxy-4-nitroaniline	140
3,4-dimethyl-6-nitroaniline	140
2,5-dimethyl-4-nitroaniline	145
4-chloro-2,6-dinitroaniline	146
para-nitroaniline	147

### Carboxylic acids

<u>Compound</u>	<u>Melting Point (°C)</u>
Dibromoacetic acid	48
3-phenylpropionic acid	48
tert-butylpropionic acid	49
hydrocinnamic acid	49
4-phenylbutyric acid	52
4-bromocrotonic acid	74
3-ketocyclohexanecarboxylic acid	76
phenylacetic acid	77
3-(3-chlorophenyl)propionic acid	78
glycolic acid	79
ortho-bromobenzoic acid	150
benzylic acid	150
2,6-dibromobenzoic acid	151
adipic acid	153
phenylmalonic acid	153
meta-bromobenzoic acid	155

### Ketones

<u>Compound</u>	<u>Melting Point (°C)</u>
1,3-dichloro-2-propanone	45
2,2'-dichlorobenzophenone	47
benzophenone	48
phenacyl bromide	50
para-bromoacetophenone	51
methyl 3-naphthyl ketone	53
para-methylbenzophenone	54
4-aminopropiophenone	140
3,3'-dibromobenzophenone	141
2-acetylphenanthrone	143
4,4'-dimethoxybenzophenone	143
2,4-dihydroxybenzophenone	144