Massachusetts Institute of Technology
Organic Chemistry 5.13

Wednesday, September 29, 2004 Prof. Timothy F. Jamison

Hour Exam #1

Name _____

(please both **print** and **sign** your name)

Official Recitation Instructor _____

Directions: *Closed book exam, no books, notebooks, notes, etc. allowed. However, calculators, rulers, and molecular model sets **are** permitted.*

Please read through the entire exam before beginning, in order to make sure that you have all the pages and in order to gauge the relative difficulty of each question. Budget your time accordingly.

Show all of your work if you wish to receive partial credit.

You should have **12** pages total: **6** exam pages including this page, **4** pages of reference information, and **2** blank pages for scratchwork.

Question:		**Grader:**
1. _____/	**36 points**	_____
2. _____/	**20 points**	_____
3. _____/	**20 points**	_____
4. _____/	**24 points**	_____
Total: _____/	**100 points**	

1. **(36 points total**) Use the information provided below and the IR and NMR spectra on the next page to answer the following questions.

a. (10 points) Determine the **molecular formula** that satisfies the following data (**circle** your final answer): EA (found): C, 61.85; H, 5.19; **and** M^+ = 194.

b. (6 points) Calculate the **Index of Hydrogen Deficiency** (IHD) for the molecule in **a**, above (**circle** your final answer).

c. (5 points) An IR spectrum of the molecule in **a** appears on the following page. What functional group or groups correspond(s) to the peak at 1731 cm^{-1} in the spectrum? **Draw** the structure of this/these group(s), **showing all bonds** (i.e. single, double, triple).

d. (10 points) Using the information in **a**, **b**, and **c**, above, and the ^1H NMR and ^{13}C NMR spectra on the next page, determine a structure of this unknown molecule that is consistent with **all** data. **Draw the structure of this molecule below** (**circle** your final answer).

e. (5 points) **Provide an explanation** for the fact that the triplet at 8.7 ppm in the ^1H NMR spectrum appears so far downfield.

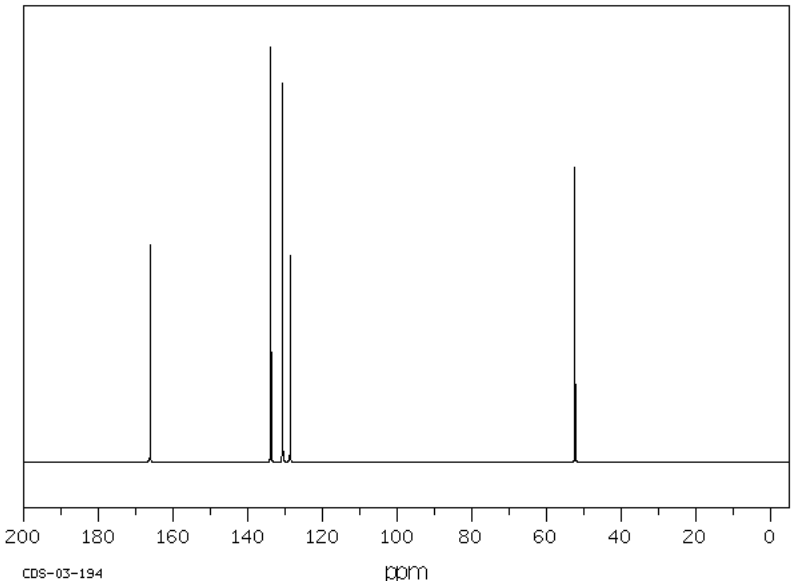
f. (EXTRA CREDIT, 3 points, 2 points): What type of bond (e.g. P–N double bond) and what vibrational mode (stretch, bend, or wag) are indicated by the strong peak at 1244 cm^{-1} in the IR spectrum for this compound (next page)? Be specific.

(IR, ^{1}H NMR and ^{13}C NMR spectra for the molecule in problem 1 on the previous page)

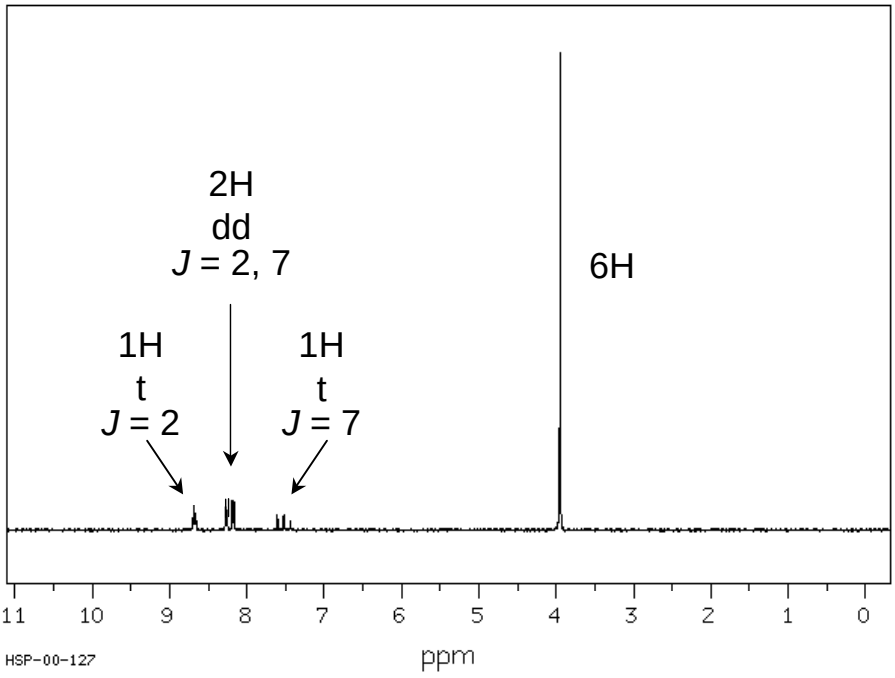
IR

1731 cm^{-1} 1244 cm^{-1}

^{13}C NMR



^{1}H NMR



2. **(20 points**) Sometimes it is possible to determine the structure of an organic molecule without using the three-step process we discussed in class. An unknown organic molecule containing **only carbon, hydrogen, and fluorine** was analyzed by ^{1}H NMR spectroscopy, providing the following data:

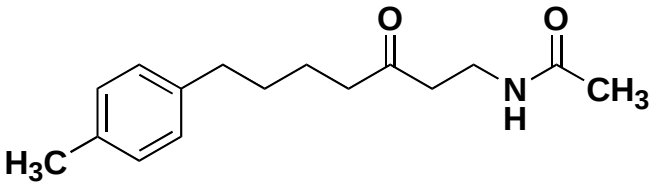
^{1}H NMR: 7.45 (dd, *J* = 8.0, 1.3, 1H), 7.14 (dd, *J* = 7.6, 1.7, 1H), 7.10 (ddd, *J* = 7.6, 7.5, 1.3, 1H), 6.95 (ddd, 8.0, 7.5, 1.7, 1H), 2.38 (s, 3H).

What is the structure of this molecule? Clearly draw your answer (**one and only one**) below and **circle** it.

3. (20 points) An unknown compound **X** (C_5H_8) with a signal at 2107 cm^{-1} in the IR was treated with a reagent (**A**) and added to another unknown compound **Y** with the following in the ^1H NMR spectrum (in ppm relative to tetramethylsilane): 9.67 (s, 1H), 7.1-7.4 (m, 5H). After an acidic work-up and purification, the product of the reaction (**Z**) was analyzed by ^1H NMR spectroscopy. The singlet at 9.67 ppm for compound **Y** was no longer present, but the 5H multiplet was. The other new peaks in the NMR spectrum of **Z** were a 1H septet at 2.01 ppm, a singlet at 3.45 ppm, also integrating to 1H, and finally a 6H doublet at 1.05 ppm.

What are the structures of compounds **X**, **Y**, and **Z**? Clearly **draw and label** all 3 below. Also propose an effective reagent **A** for this transformation and label it clearly below.

4. **(24 points**) Mass spectrometry was performed on the structure shown in the box below, and several signals corresponding to **fragments** (M_f^+) were observed in the spectrum. Write the *m/z* value observed for $\mathbf{M^+}$ **in the box provided** (3 points). In each question below the *m/z* value for M_f^+ is provided. **Draw the structure** of M_f^+ in the corresponding box (3 points each). Also, **write** the **molecular weight** of the **neutral** species ($M_{neutral}$) formed in each fragmentation in the boxes on the right (1 point each). Finally, **draw the structure** of each ($M_{neutral}$) in the boxes on the right (3 points each). **BE SURE TO INDICATE WHETHER EACH** M_f^+ and **EACH** $M_{neutral}$ is a **radical** (i.e. has an unpaired electron).



$\mathbf{M^+ =}$ _____

a.

(Write the structure of $\mathbf{M_f^+}$ here.)

m/z for $\mathbf{M_f^+ = 105}$

(Write the structure of $\mathbf{M_{neutral}}$ here.)

mass of $\mathbf{M_{neutral} =}$ _____

b.

(Write the structure of $\mathbf{M_f^+}$ here.)

m/z for $\mathbf{M_f^+ = 129}$

(Write the structure of $\mathbf{M_{neutral}}$ here.)

mass of $\mathbf{M_{neutral} =}$ _____

c.

(Write the structure of $\mathbf{M_f^+}$ here.)

m/z for $\mathbf{M_f^+ = 72}$

(Write the structure of $\mathbf{M_{neutral}}$ here.)

mass of $\mathbf{M_{neutral} =}$ _____

Characteristic Functional Group Chemical Shifts in ^{13}C NMR (ppm)

Alkanes	
Methyl (RCH_3)	0-30
Methylene (RCH_2R')	15-55
Methine (RCH(R')(R"))	25-55
Quaternary (RC(R')(R")(R"'))	30-40
Alkenes	100-150
Aromatic	120-160
Alkynes	70-90
Nitriles	110-125
Alcohols, Ethers	50-90
Amines	40-60

Organohalogen	
C–F	70-80
C–Cl	25-50
C–Br	10-40
C–I	–20-10
Ketones, Aldehydes	185-220
Carboxyl Derivatives	
Acids	150-185
Esters	155-180
Amides	150-180
Carbamates	150-160