Massachusetts Institute of Technology
Organic Chemistry 5.13

Friday, September 26, 2003 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, 37.02; H, 2.22; N, 18.50; **and** $M^+ = 227$

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

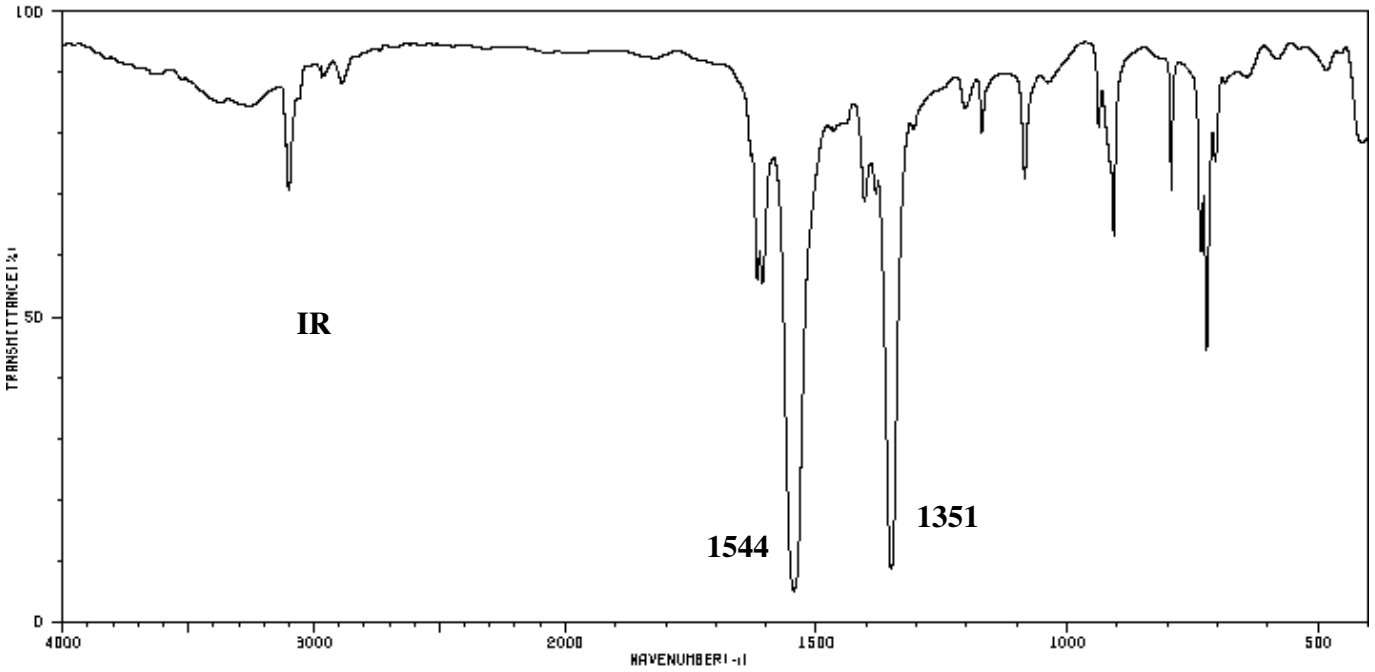
c. (5 points) An IR spectrum of the molecule in **a** appears on the following page. What functional group or groups correspond(s) to the **2 most intense** peaks in the spectrum? **Draw** the structure of this/these group(s), **showing all bonds** (i.e. single, double, triple).

d. (10 points) Using the information in **a**, **b**, and **c**, above, and the ^{1}H 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).

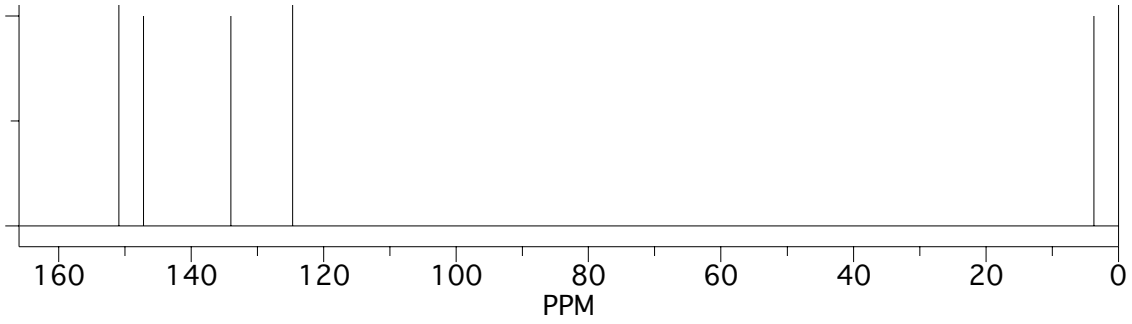
e. (5 points) **Provide an explanation** for the fact that the singlet at 9.4 ppm in the ^{1}H NMR spectrum appears so far downfield.

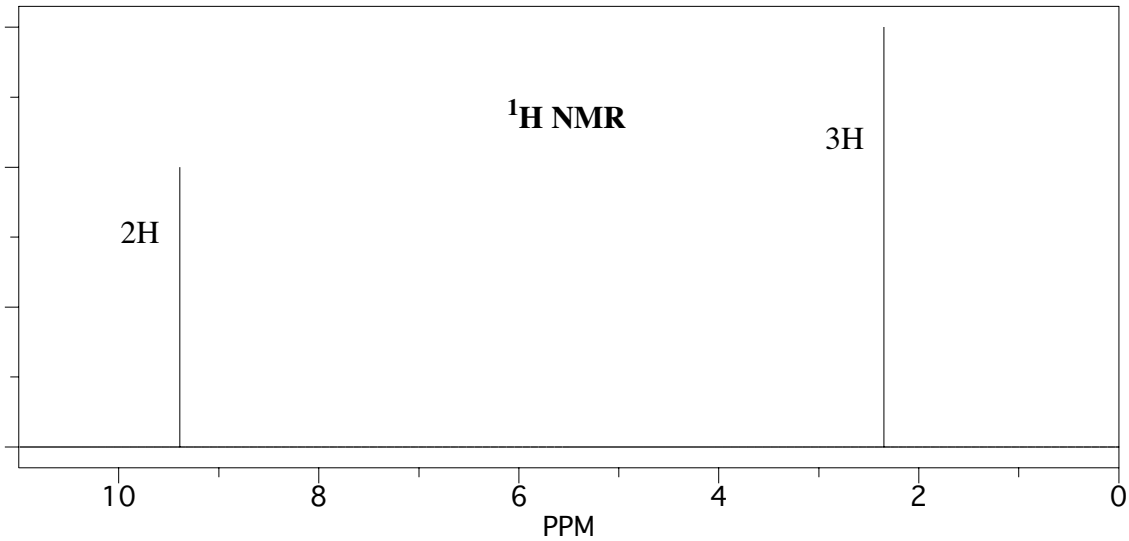
f. (EXTRA CREDIT, 5 points): What is this compound, and what is its most notorious physical property?

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

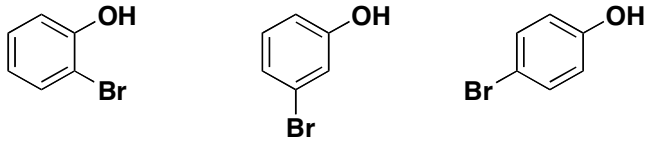


^{13}C NMR

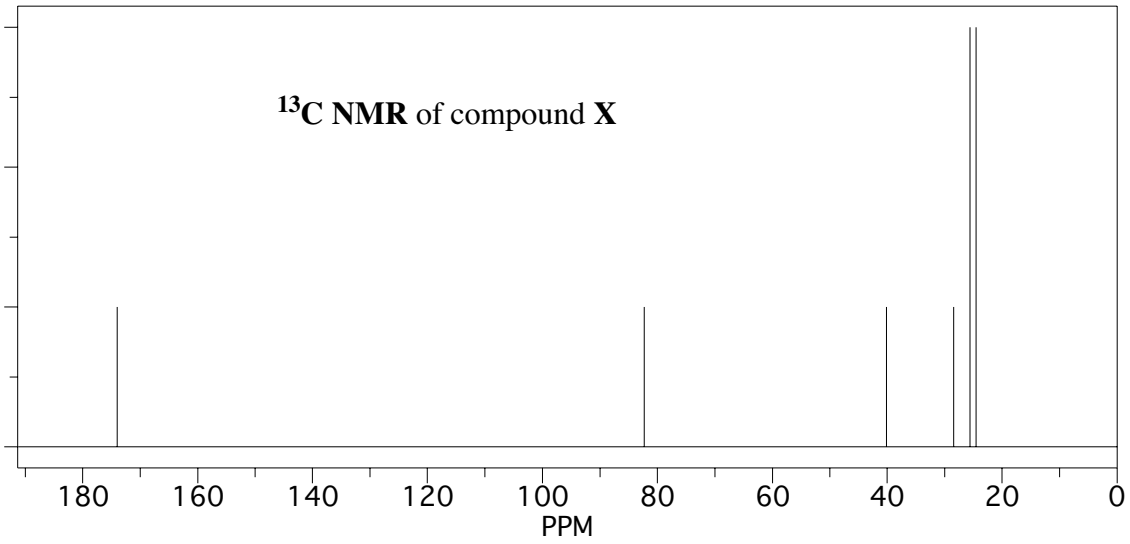


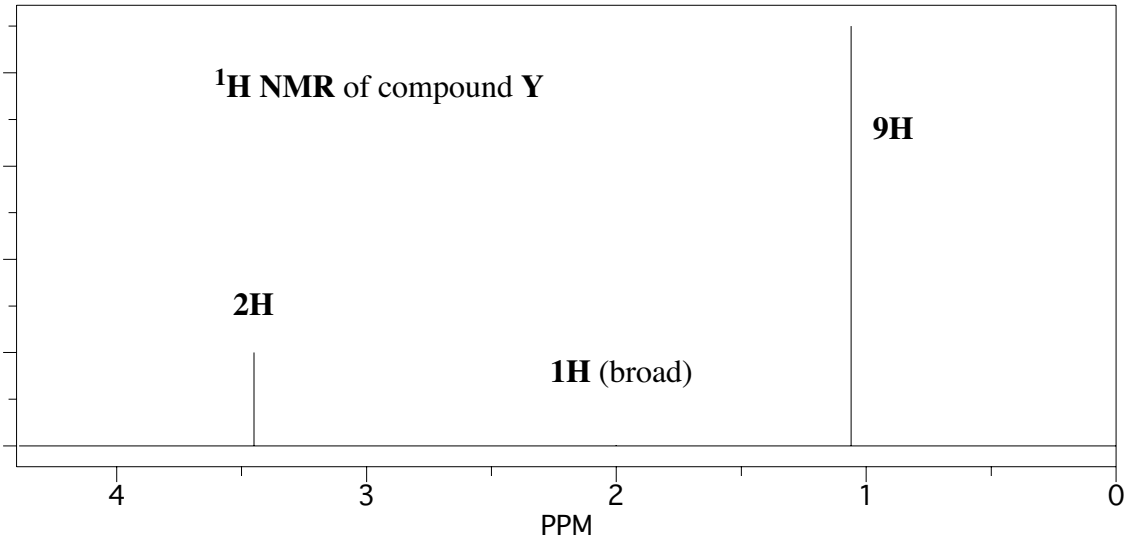


2. (**20 points**) Using **only ^{1}H NMR spectroscopy**, how would you **conclusively** distinguish between ***all* 3 isomers** (*ortho, meta, and para*) of **bromophenol**? **Be as specific as necessary in order to differentiate *ortho* from *meta*, *meta* from *para*, *and* *ortho* from *para*.** (Suggestion: Use chemical structures as part of your answer.)

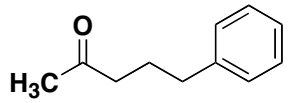


3. (20 points) An unknown compound **X** (containing **only** carbon, hydrogen, and oxygen) has **m/z = 172** (M^+) and **115**, and its **^{13}C NMR spectrum** below. When treated with lithium aluminum hydride in ether, a **single** compound **Y** is produced, and its **^{1}H NMR spectrum** is given below. In the space below the NMR spectra at the bottom of the page, **draw the structures of X** and **Y**. Circle your final answers and **clearly** indicate which is compound **X** (12 points) and which is compound **Y** (8 points).





4. **(24 points**) Mass spectrometry was performed on 5-phenyl-2-pentanone (below), and several signals corresponding to **fragments** (M_f^+) were observed in the spectrum. Write the *m/z* value observed for **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).



M^+ = ____

a.

(Write the structure of **M_f^+** here.)

m/z for **M_f^+ = 147**

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

mass of **$M_{neutral}$ =** ____

b.

(Write the structure of **M_f^+** here.)

m/z for **M_f^+ = 91**

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

mass of **$M_{neutral}$ =** ____

c.

(Write the structure of **M_f^+** here.)

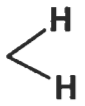
m/z for **M_f^+ = 58**

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

mass of **$M_{neutral}$ =** ____

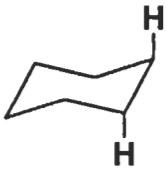
^{1}H NMR Coupling Constants (Expanded)

vicinal 6-8 Hz
(averaged by free rotation)

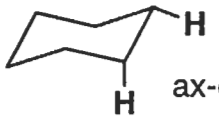


geminal 12-15 Hz
acyclic
can be 0-25 Hz in cyclic systems

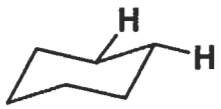
In rigid systems, vicinal coupling can range from 0 to15 Hz. For example:



ax-ax 6-14 Hz

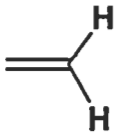


ax-eq 0-5 Hz



eq-eq 0-5 Hz

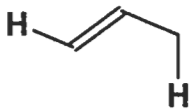
Spin-spin coupling in **alkenes**:



geminal 0-3 Hz

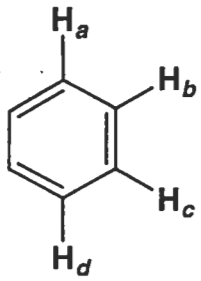
cis 6-12 Hz

trans 12-18 Hz



allylic 0-3 Hz

Spin-spin coupling in **arenes**:



J_{ab} (ortho) 6-10 Hz
J_{ac} (meta) 1-3 Hz
J_{ad} (para) 0-1 Hz

Note: Structures shown above represent generic coupling situations and not the specific molecules depicted (in which the labeled protons would be chemically equivalent and would not couple).

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