Massachusetts Institute of Technology
Organic Chemistry 5.13

Friday, September 26, 2003 Prof. Timothy F. Jamison

Hour Exam #1

Name SUGGESTED SOLUTIONS (OTHER ANSWERS POSSIBLE IN SOME CASES; PARTIAL CREDIT POSSIBLE IN MOST CASES.)

(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** $M^+ = 227$

   $C_7H_5N_3O_6$

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

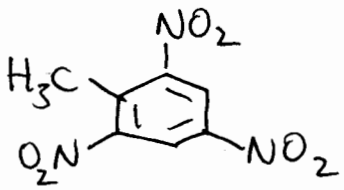
   7

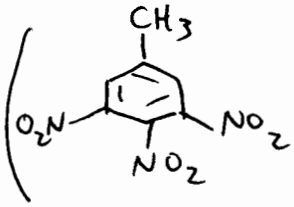
   c. (5 points) An IR spectrum of the molecule in **a** appears on the following page. What functional group or groups correspond(s) to the **2 most intense** peaks in the spectrum? **Draw** the structure of this/these group(s), **showing all bonds** (i.e. single, double, triple).

   NITRO GROUPS

   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).

   ALSO SATISFACTORY

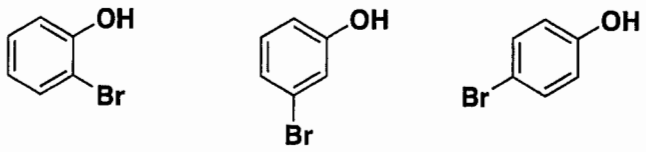
   e. (5 points) **Provide an explanation** for the fact that the singlet at 9.4 ppm in the ^{1}H NMR spectrum appears so far downfield.

   2 NO_2 (e^--WITHDRAWING) DESHIELD PROTONS ON AROMATIC RING SIGNIFICANTLY.

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

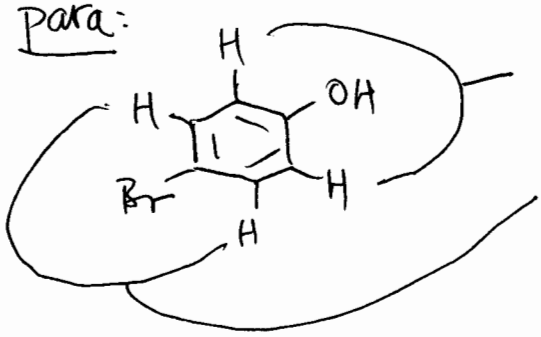
   (2,4,6)-TRINITROTOLUENE (TNT). EXPLOSIVE.

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.)



SPIN-SPIN COUPLING CAN DIFFERENTIATE ALL 3 FROM ONE ANOTHER

para:

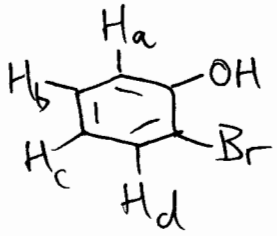


each 2H, d (or dd, J = 7-8, 2) ← (meta coupling)

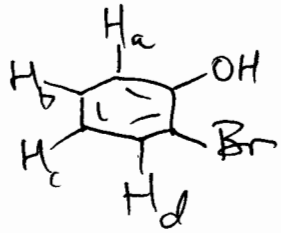
J = 7-8

DEPENDING ON STRENGTH OF MAGNET USED, THIS COUPLING MAY OR MAY NOT BE EVIDENT IN ^{1}H NMR SPECTRUM.

ortho:



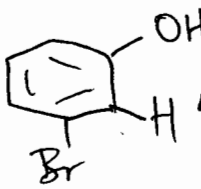
or



- J_{Ha-Hb} : 7-8 Hz } Ha : d
- J_{Hb-Hc} : 7-8 Hz
  J_{Hb-Hc} : 7-8 Hz } Hb : dd
- Hc : SAME PATTERN AS Hb : dd
- Hd : " " " Ha : d

IF META COUPLINGS DETECTABLE, THEN EACH PROTON HAS 1 ADDITIONAL 2 Hz-COUPLING, i.e. J_{Ha-Hc}, J_{Hb-Hd}, etc.

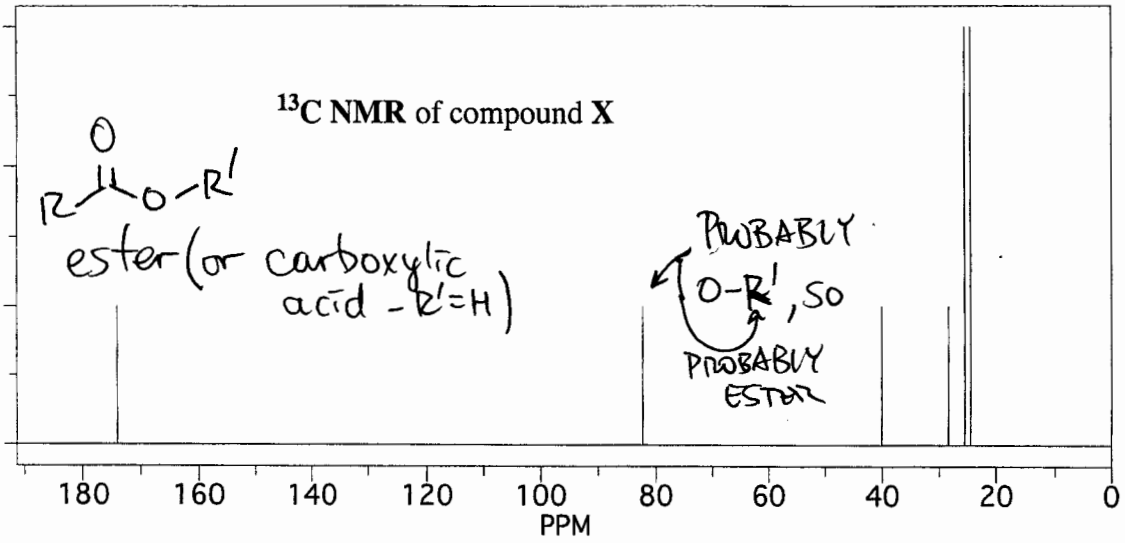
meta:

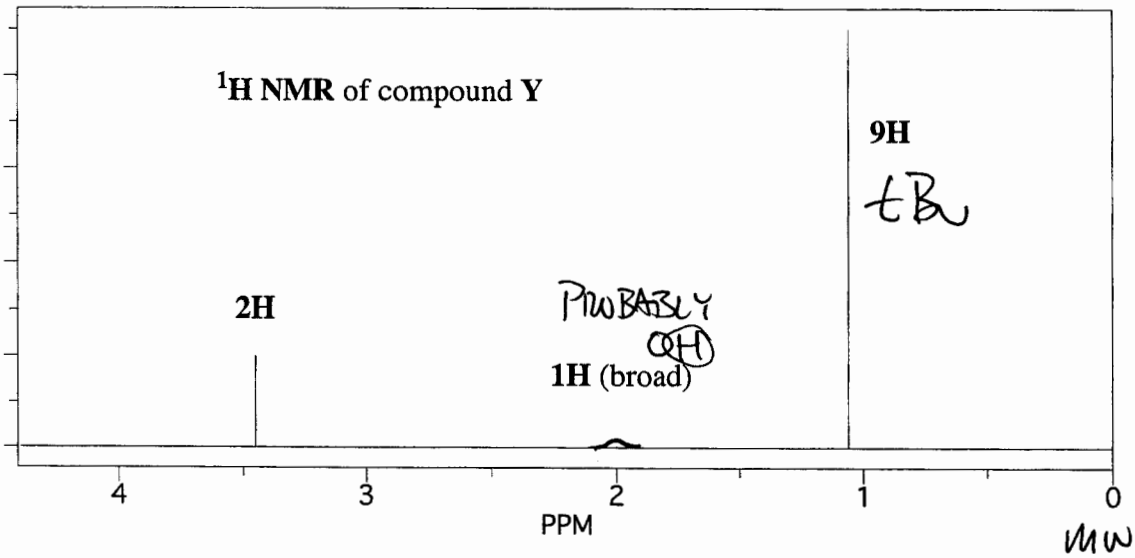


← WILL BE SINGLET (ONLY ONE)

(OR dd or t, J ≅ 2, 2 IF MAGNET OF HIGH ENOUGH FIELD)

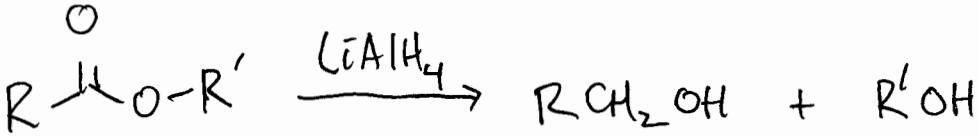
3. **(20 points)** An unknown compound **X** (containing **only** carbon, hydrogen, and oxygen) has **m/z = 172** (M^+) and **115**, and its **^{13}C NMR spectrum** below. When treated with lithium aluminum hydride in ether, a **single** compound **Y** is produced, and its **^{1}H NMR spectrum** is given 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).





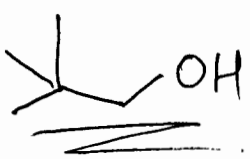
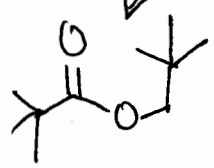
DOUBLE-CHECK: $C_{10}H_{20}O_2$ MW = 172

SO:



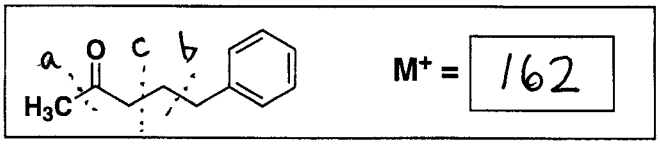
$R\text{-}C(=O)\text{-}O\text{-}R' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$

BUT $RCH_2 = R'$, BECAUSE BOTH ALCOHOLS ARE "Y"

$\therefore$ Y = RCH_2OH =  | X = 

tBu (9H) 2H's 1H

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^+ = 162

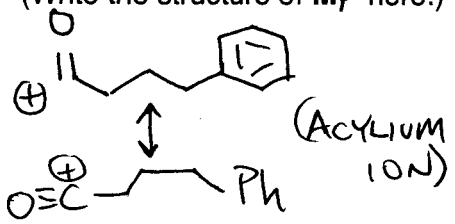
$C_{11}H_{14}O$

MW = 162

M^+ = 162

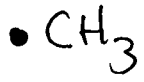
a.

(Write the structure of M_f^+ here.)



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

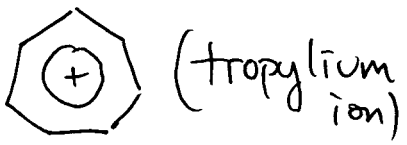
(Write the structure of $M_{neutral}$ here.)



mass of $M_{neutral}$ = 15

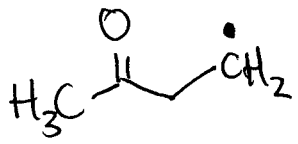
b.

(Write the structure of M_f^+ here.)



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

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

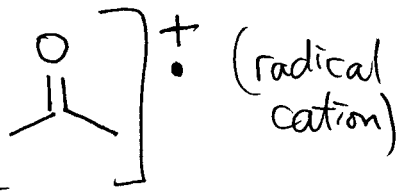


mass of $M_{neutral}$ = 71

c.

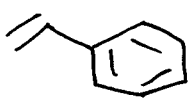
McLAFFERTY REARRANGEMENT

(Write the structure of M_f^+ here.)



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

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



mass of $M_{neutral}$ = 104