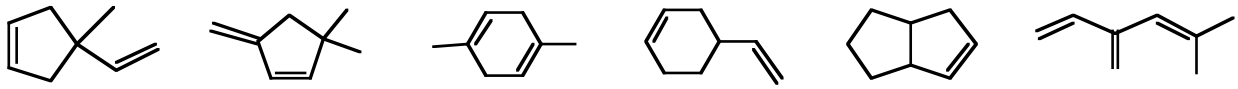
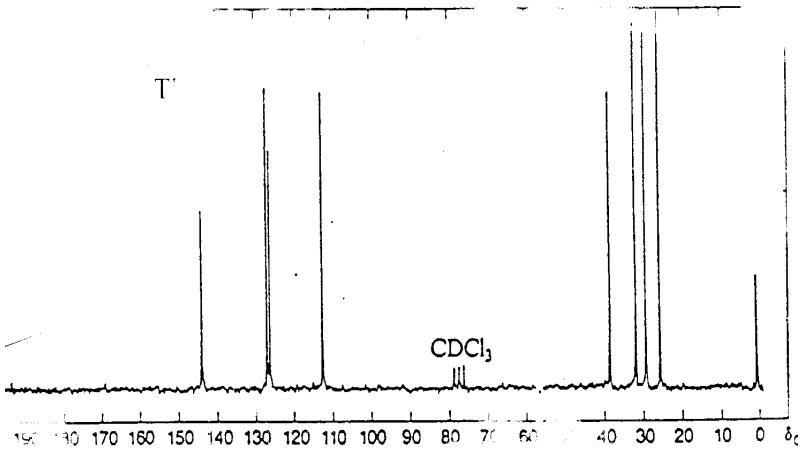
Chem 22 **Homework set 3**

1. (a) How many lines (peaks) would be observed in the proton-decoupled ("normal") ^{13}C NMR spectrum of each of the isomeric C_8H_{12} hydrocarbons below?

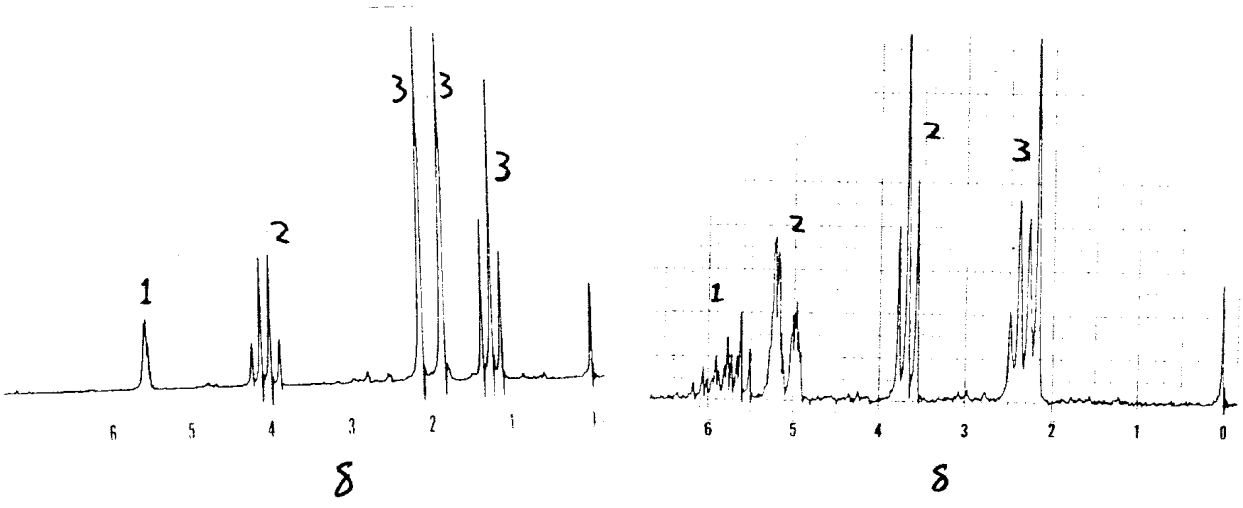


(b) The ^{13}C NMR spectrum at right belongs to one of these 6 compounds. Which one?

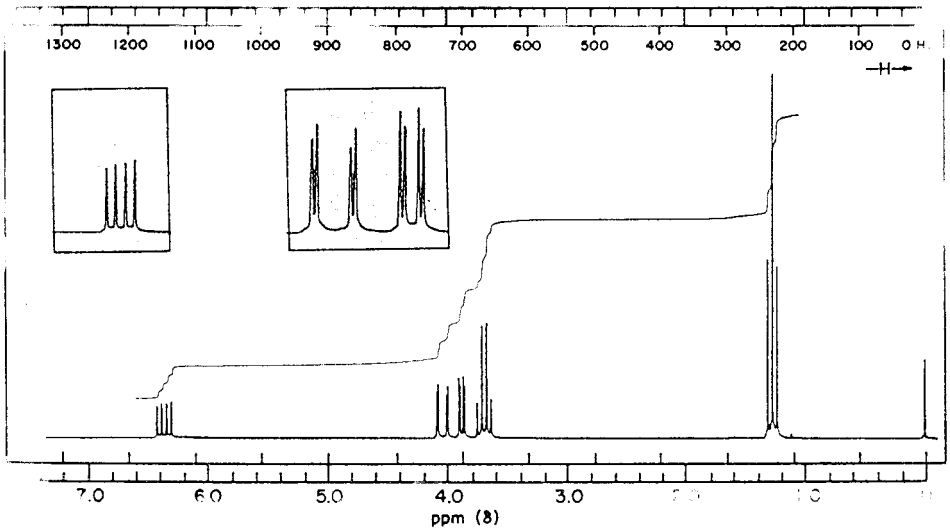
(c) In an off-resonance decoupled ^{13}C NMR spectrum, the peaks at δ 145 and 128 all appear as doublets; the one at δ 112 appears as a triplet. Use this information and some "chemical intuition" to assign these lines to the vinylic Cs.



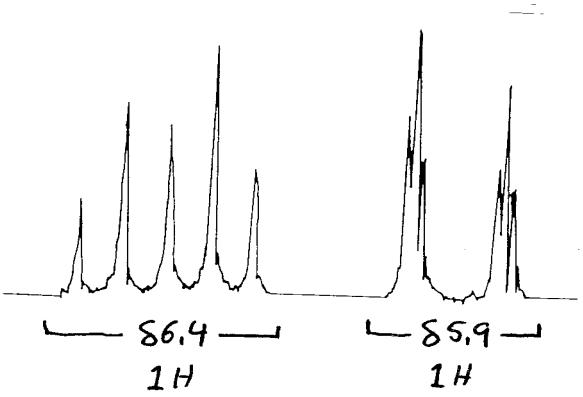
2 (a) An ester **$C_7H_{12}O_2$** has the 60-MHz ^1H NMR spectrum shown below left. Draw the structure. (b) A compound with the formula **C_4H_8O** has the 60-MHz ^1H NMR spectrum below right. When a drop of D_2O is added to the sample, the 3-H signal at δ 2.3 becomes a 2-H quartet (1:3:3:1), and an HOD peak appears around δ 1.6. Draw the structure.



3. A compound $\mathbf{C_4H_8O}$ has the 180-MHz ^{1}H NMR spectrum shown below. (a) Although the chemical shift is a bit unusual, based on the splitting patterns, what type of Hs are likely responsible for the signals near δ 4 (enlarged in the inset)? (b) Draw the structure. (c) Why have these Hs strayed so far (about 1 ppm) from their normal δ range? (Hint: think resonance structure...)



4. At right are the vinylic ^{1}H NMR signals of one stereoisomer of 1-iodohexene,
I—CH_a=CH_b—CH_2–$CH_2CH_2CH_3$.
(a) Which one belongs to $\mathbf{H_a}$ and which one to $\mathbf{H_b}$? (b) Draw a tree diagram for each H to account for the appearance of the signals. (c) Based on your analysis, is the compound E or Z?

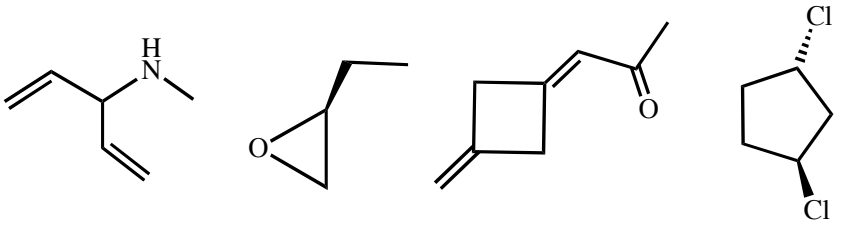


5. (a) The *o*, *m*, and *p* protons of nitrobenzene appear at δ 8.22, 7.53, and 7.65, respectively. Explain why the *o* and *p* appear downfield of the *meta*.

(b) The *o*, *m*, and *p* protons of aniline appear at δ 6.52, 7.02, and 6.62, respectively. Explain why the *o* and *p* appear upfield of the *meta*.

Chem 22
Spring 2010 *Name* _____
HW set 3
25 points; due Wed, Feb 10 at the beginning of class.

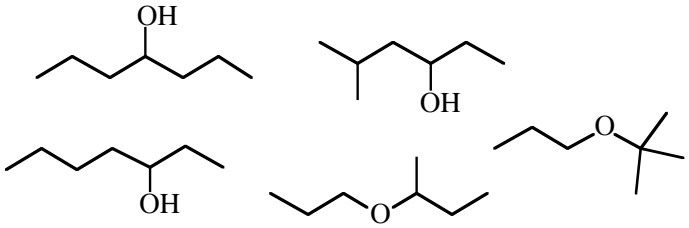
1. (a) For each compound below, how many separate signals would you expect to see in a (room temp) proton-decoupled ^{13}C NMR spectrum, and how many in a ^{1}H NMR spectrum? (In other words, how many different sets of equivalent Cs and Hs are present?) Write the numbers in the spaces provided.

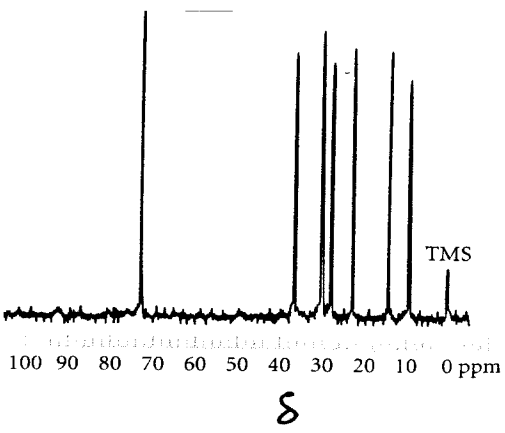


^{13}C NMR signals: _____ _____ _____ _____

^{1}H NMR signals: _____ _____ _____ _____

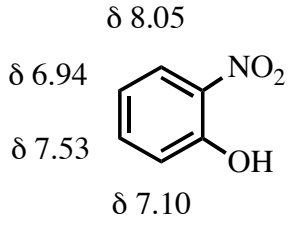
2. The proton-decoupled ^{13}C NMR spectrum at right belongs to one of the compounds shown. (a) Which one? Please circle your choice. (You do not need a table of ^{13}C δ values.)



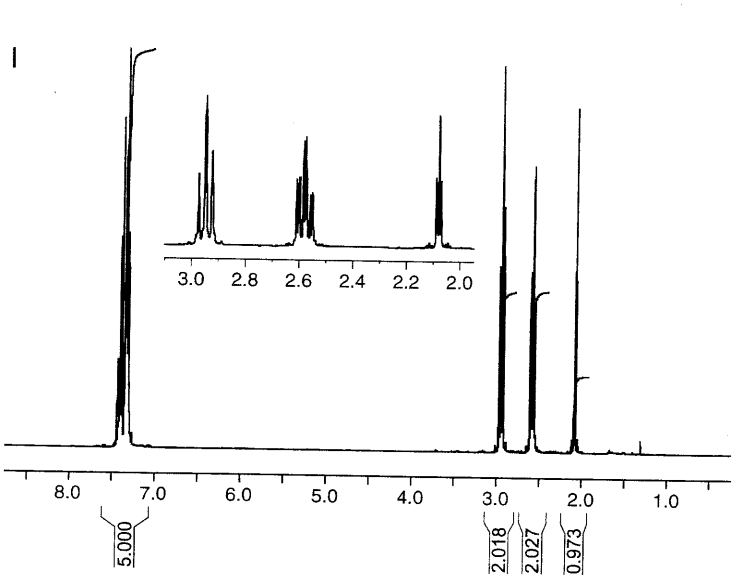


(b) In the structure you chose, draw a box around the C that is responsible for the signal at δ 73.

3. Two NMR signals of *o*-nitrophenol are upfield (δ7), and the other two are downfield (δ7.5 - 8) within the aromatic region. Why?



4. A compound with the formula $\mathbf{C_{10}H_{10}}$ displays IR stretches at about 3300 and 2150 cm^{-1}. The compound's ^1H NMR spectrum is shown. The number printed below the chemical shift scale are digital integrals. (a) Draw the structure. (b) Draw a tree diagram to account for the splitting pattern of the δ2.0 signal.



5. The ^1H NMR spectrum of an ester with the formula $\mathbf{C_{12}H_{14}O_3}$ is shown below. (a) Draw the structure. (b) Explain the dramatic downfield shift of the signal at δ7.7.