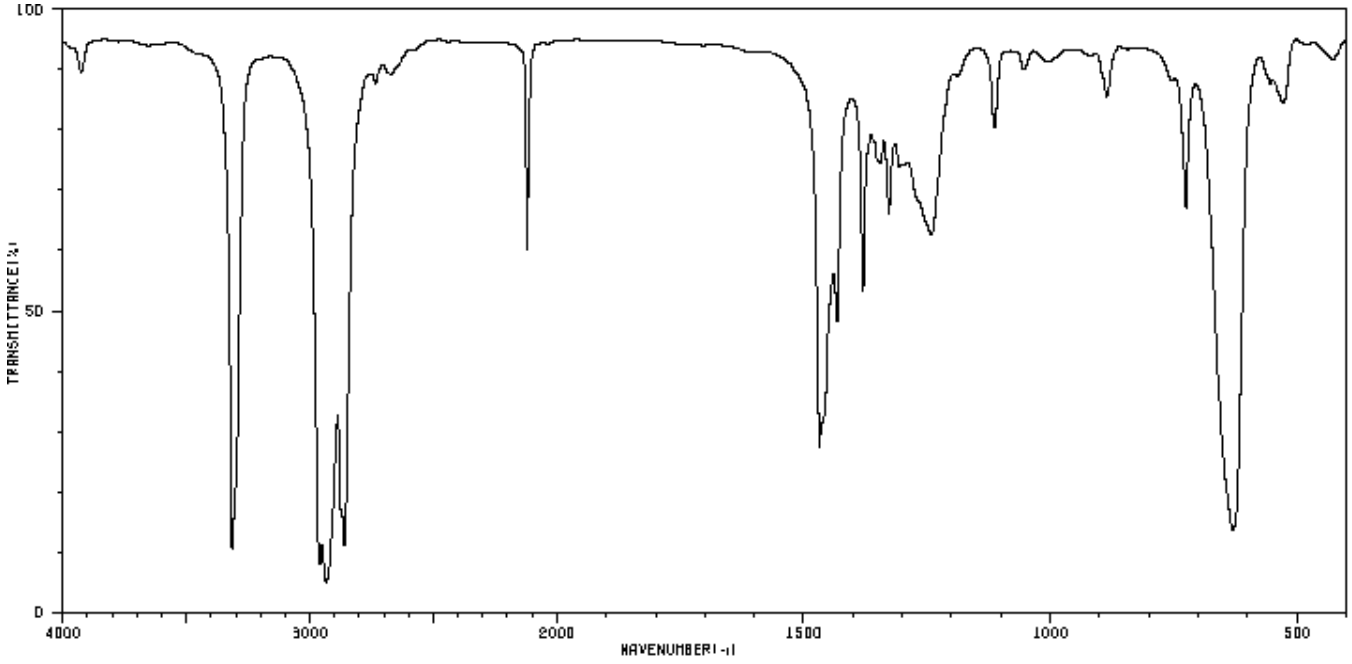
Chemistry 125 Seventh Examination Name _____

April 7, 2006

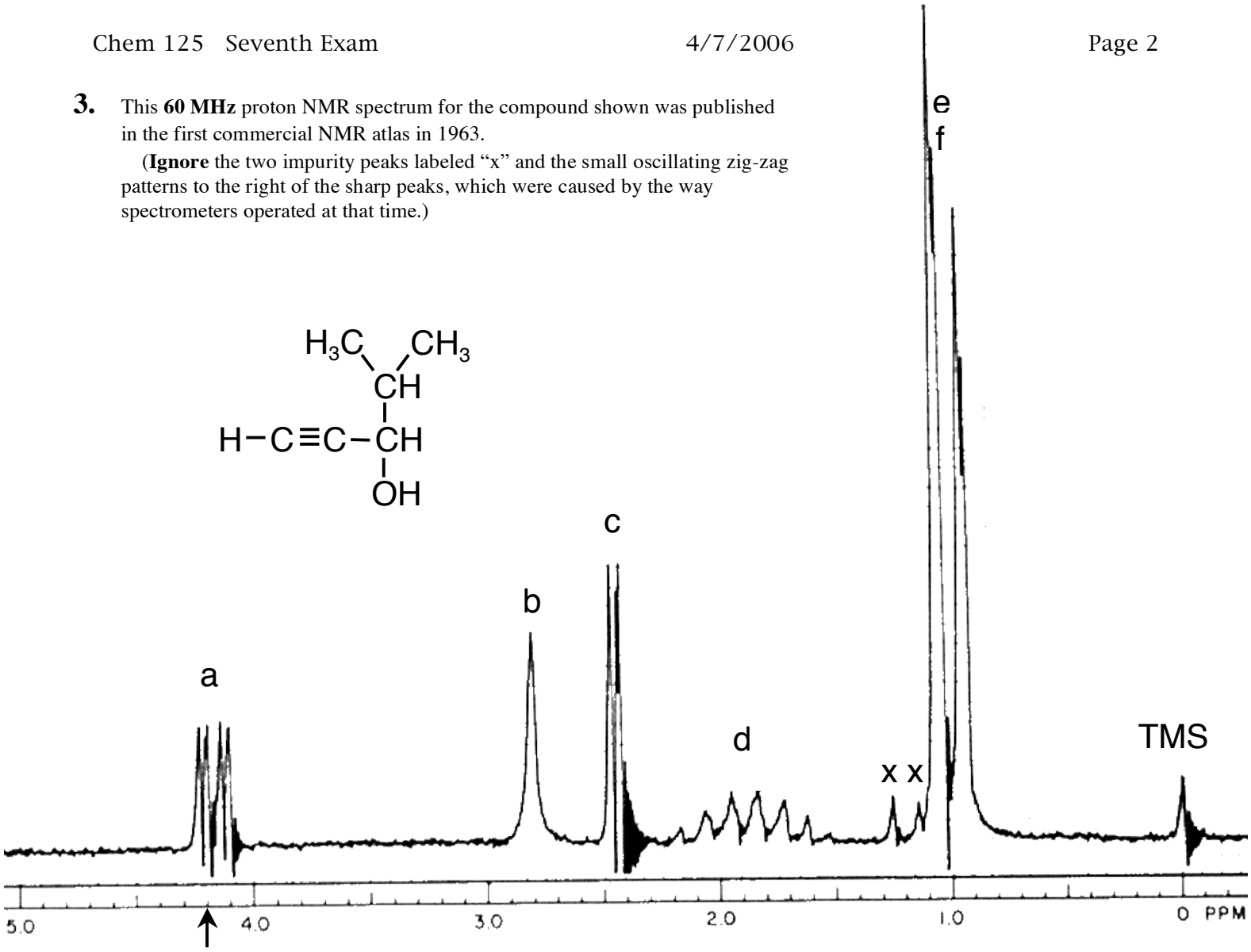
1. (4 min) Explain why light can cause a *1s* electron to become a *2p* electron, but cannot cause a *1s* electron to become a *2s* electron.

2. (6 min) **Circle and explain** the **THREE** peaks that allow using this spectrum to discriminate among n-octane, (Z)-3-octene, (E)-3-octene, 1-octyne, or 3-octyne for the identity of this hydrocarbon sample.



3. This **60 MHz** proton NMR spectrum for the compound shown was published in the first commercial NMR atlas in 1963.

(**Ignore** the two impurity peaks labeled "x" and the small oscillating zig-zag patterns to the right of the sharp peaks, which were caused by the way spectrometers operated at that time.)



A. (1 min) **Draw a second arrow** beneath the ppm scale that is **7 Hz** from the arrow at 4.2 ppm.

B. (5 min) **Label** the protons in the **chemical formula** with the letters **a-f** to correspond to the labeled groups of peaks.

C. (3 min) Explain why the **chemical shift** of the peak labeled "**b**" is strongly **dependent on concentration** and **temperature**.

(Continued on next page)

Question 3 (cont)

D. (3 min) Explain the **spin-spin splitting** of the proton at "**a**".

E. (3 min) **Describe TWO** competing factors that determine the **chemical shift** of the peak labeled "**c**".

4. (4 min) Explain **briefly** how the rarity of ^{13}C can be a ***benefit*** for ^{13}C nmr.

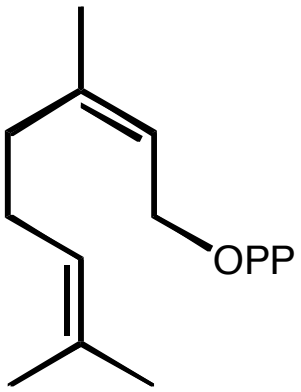
5. (5 min) Explain how comparing the rate constants for nucleophilic substition on R-L using a range of R groups and a single leaving group helps choose between Dissociation/Association and Concerted (or Association/Dissociation) mechanisms.

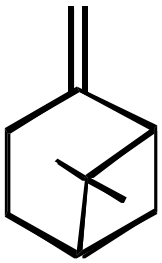
6. (5 min) **Explain ONE** (1 only) of the following:

(A) How BOLD imaging works to study brain function

(B) The utility of the "rotating frame" for understanding nmr.

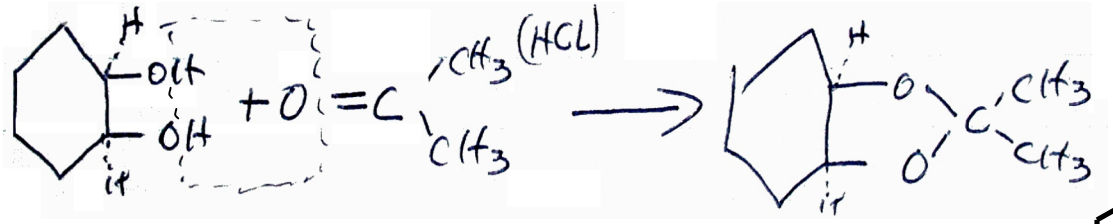
7. (5 min) Use **curved arrows** to show how neryl pyrophosphate (on the left) transforms to β-pinene (on the right). Two intermediate structures are necessary. [In lecture one of these intermediates was drawn in two different ways.]



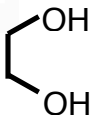


8. (6 min) The following naive figure is from my class notes when I studied elementary organic chemistry in 1960.

What passed for giving the "mechanism" of **acid-catalyzed** formation of a ketal from a diol and a ketone was drawing a dotted "lasso" around the atoms to be lost as water, and then drawing the product.



Draw a mechanism with **curved arrows** to explain this transformation. **Abbreviate** 1,2-cyclohexanediol as



[Hint: analogous to the **reverse** of the last step of ozonolysis]