Chemistry 125 Seventh Examination Answers **April 7, 2006**

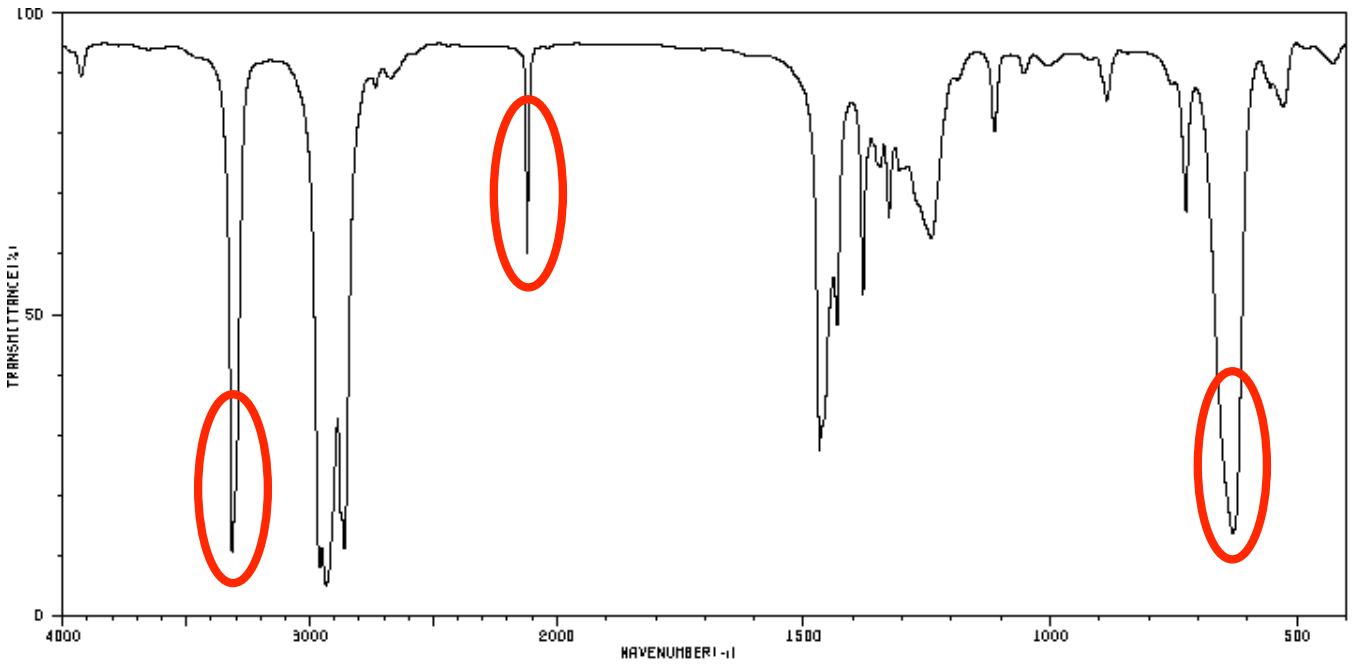
	This Exam	Sum of 3 Hr. Exams
Average	74.7	217.9
1/3 of scores greater than	81	240
2/3 of scores greater than	70	200

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.

In the presence of an electron field the electrons on an atom shift in one direction (and the heavy nucleus a very small distance in the opposite direction). Mixing a *1s* orbital with a *2p* orbital shifts the electrons in this way, but mixing it with a *2s* orbital just makes it expand evenly in all directions. Thus the oscillating electric field of light has a "handle" on the *1s-2s* transition, but not on the *1s-2s* transition.

[Note that the electric field of the light must stay in phase with the direction of polarization of the mixed state as its *1s* and *2p* components oscillate in- and out-of-phase, so that the electron polarization shifts back and forth at the frequency of the difference in energy between the two components. That is, the light must have the proper frequency. But even if it had the correct frequency to match the 1s-2s energy difference, its electric field could not mix these two states.]

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.



3315 cm^{-1} C-H stretch of terminal acetylene (1-octyne) Very high frequency because of lightness of H and strength of bond involving sp hybridized carbon atom.

2120 cm^{-1} CC triple bond stretch. High frequency for bond between heavy atoms because of bond strength. [An internal CC triple bond is much weaker in intensity, because it is more symmetrical and less polar. A CC double bond comes at about 1655 cm^{-1}]

630 cm-1 CC-H bend of terminal acetylene. Low frequency because no other substituents to "run into"

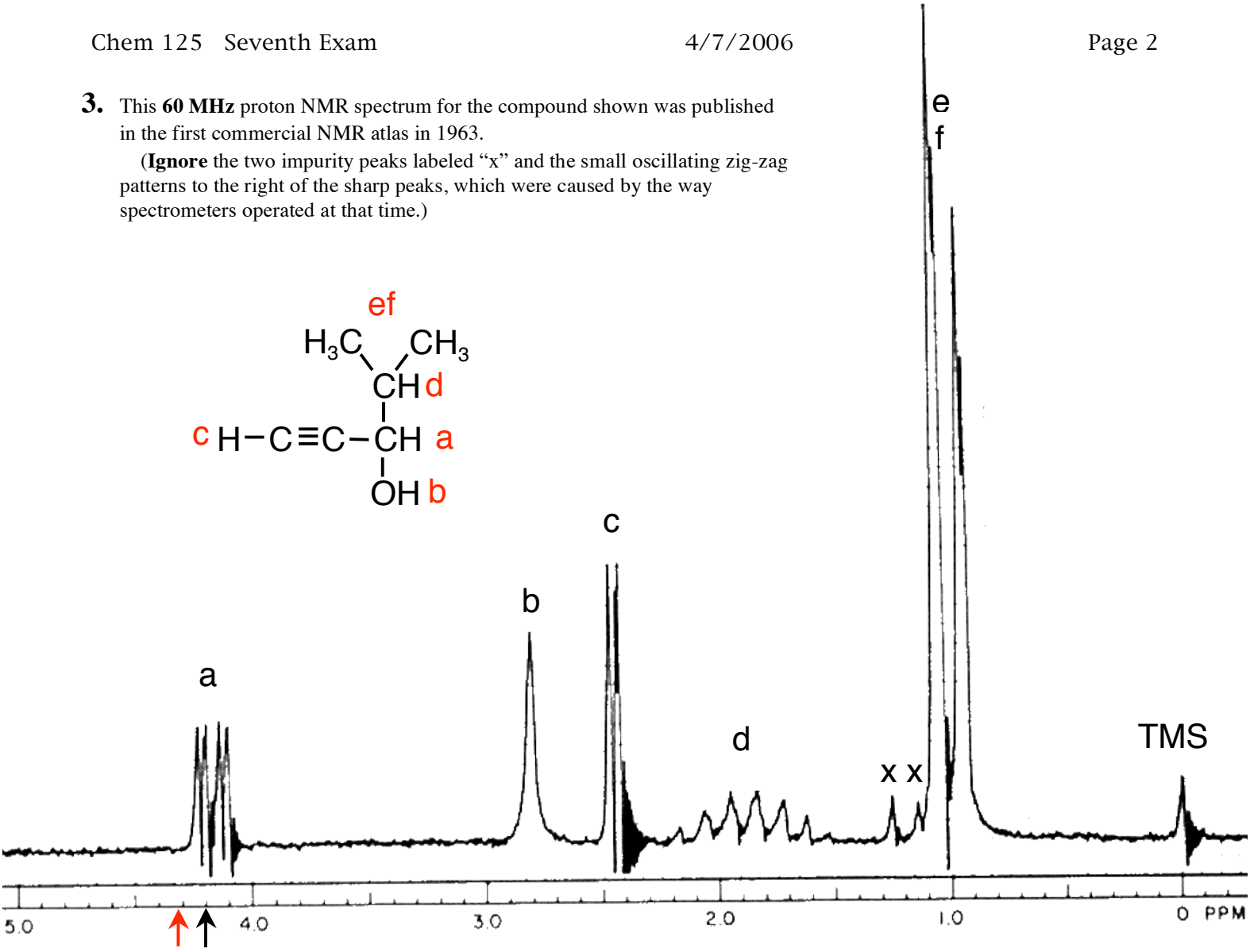
Note that all of these bonds are characteristic because they do not mix with nearby vibrations (which have much different frequencies.

The other peaks do not provide an easily interpreted distinction among these hydrocarbons.

[See slide 6 in the lecture powerpoint for 3/22/06]

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.

[Everyone got this correct. Congratulations]

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**.

This is the OH signal. The proton is rapidly exchanging among differently hydrogen-bonded environments and thus appears at the average of their chemical shifts. The equilibrium distribution of environments changes with concentration (higher concentration : more H-bonding) and temperature (higher temperature : less H-bonding).

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

Proton "a" is split into a double doublet first by proton "d" (normal 7 Hz splitting for protons on adjacent carbons) and second by proton "c" (small 2 Hz splitting through 3 carbons. Normally such splittings are smaller and not observed, but here there is unusually strong electronic communcation through hyperconjugation with the pi orbitals of the acetylene). Note that there is no splitting by the OH proton "b" because that proton is rapidly exchanging and one sees the average value of zero.

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

It is shifted downfield by *sp* hybridiztion of the acetylenic carbon (electron withdrawal), but upfield by diamagnetic anisotropy of the triple bond (H above the circulation that is allowed when CC is parallel to magnetic field).

[Incidentally, the methyl doublets e and f are diastereotopic and have very slightly different chemical shifts.]

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

It allows one to introduce magnet nuclei in selected positions by intentional synthesis, and thus to trace the source of particular carbon atoms in a product from labeled positions in a starting material by CMR. In a more sophisticated experiment it allows dilute double labeling of adjacent carbons in a starting material to show that there is rearrangement that separates these carbons in the product, as in the proof of the mechanism of squalene polycyclization to lanosterol.

[also it makes PMR spectra simpler, since there is very little splitting of proton signals by ^{13}C]

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.

Making the R group bulkier (methyl to ethyl to isopropyl to neopentyl) successively slows the S_N2 reaction. This is consistent with steric hindrance to formation of the more crowded pentavalent transition state (or intermediate) of the concerted (or A/D) process, but greater bulk would have been expected to accelerate loss of the leaving group in the D/A process, both through steric hindrance and through stabilization of a more substituted carbocation intermediate.

[had the question asked for specifics, it would have been important to specify the rate ratios]

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

(A) How BOLD imaging works to study brain function

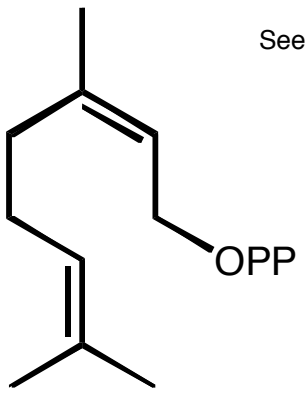
BOLD imaging uses the normal inhomogeneous-field of MRI to see where proton signals of water are coming from. The special feature is that the signals are enhanced by relaxation, which maintains an excess of protons in the favorable orientation, despite the constant pumping of protons to the unfavorable orientation by the rf field that measures the signal. The relaxation is cause by nearby magnetic O_2 molecules. When neurons are active, blood flow to them increases bringing with it an increase in the local O_2 concentration. Thus comparing images before and after the neurons fire show a increase in the proton signals in the vicinity of these neurons

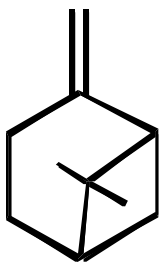
(B) The utility of the "rotating frame" for understanding nmr.

By thinking of how a magnetic nucleus would appear in a frame rotating about the large applied field at the precession frequency, one can ignore the influence of this field. This allows one to treat the influence of a weak rf magnetic field perpendicular to the permanent applied field, and oscillating at the precession frequency, as if it were the only game in town. Its direction would be constant in the rotating frame, so the proton would precess slowly about it (slowly, because it is so weak). This results in protons changing periodically from being oriented with the applied field to being oriented against the applied field

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.]

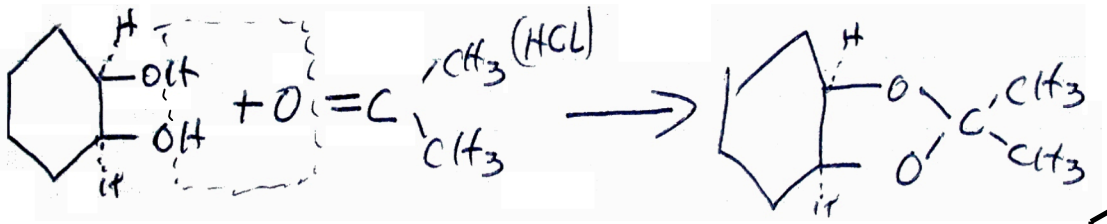
See the animation in slide 27 of the lecture powerpoint for 3/31/2006

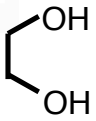




8. (6 min) The following naive figure is from my class notes when I studied elementary organic chemistry in 1960.

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]

This is precisely the *reverse* of the mechanism for "ketal hydrolysis" shown in Slide 12 of the lecture powerpoint for 3/1/2006, except that the two R groups of separate alcohols are linked together to form a diol.

A particularly important feature of this mechanism is that it begins by protonation of the double bonded O atom of the O=C to give an unusually stable carbon cation (its vacant orbital stabilizes an electron pair of the adjacent OH group). This cation is then attacked by the unshared pair of an OH group of the diol, which subsequently loses a proton to establish the first ether linkage. The new OH group (from protonating the oxygen of the O=C group), is then protonated again and lost as water to give a tertiary carbon cation (stabilized again by adjacent oxygen). The second OH of the original diol now adds and loses a proton to give the product.

This is an important mechanism, and we will go over it again in class.