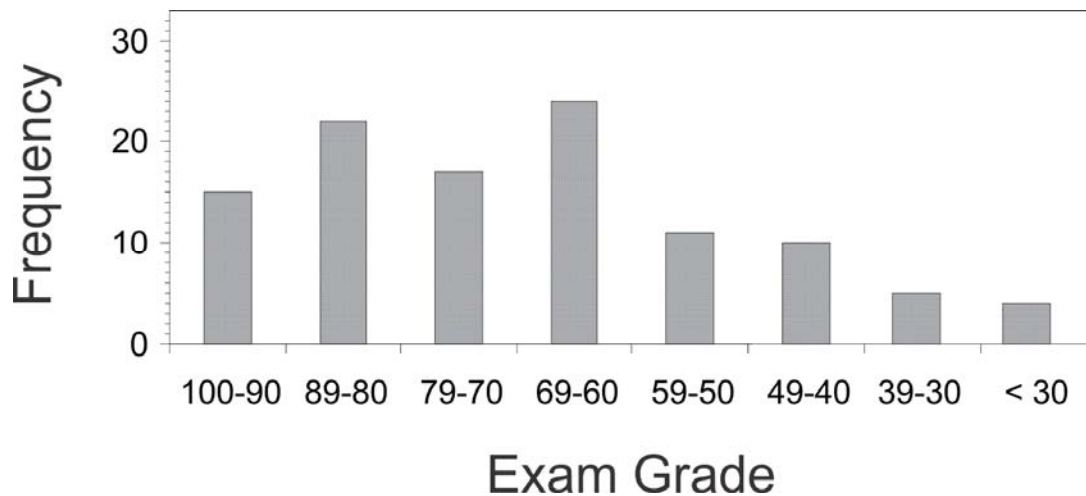
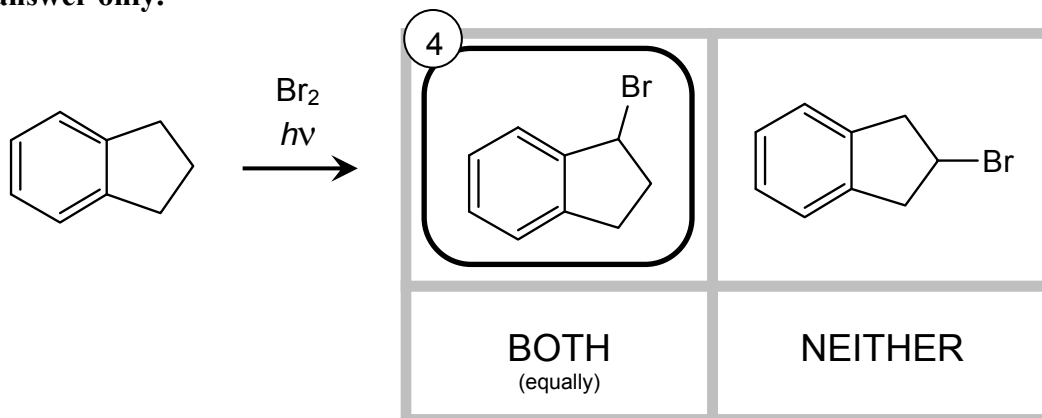


**Exam 4  
Answer Key**

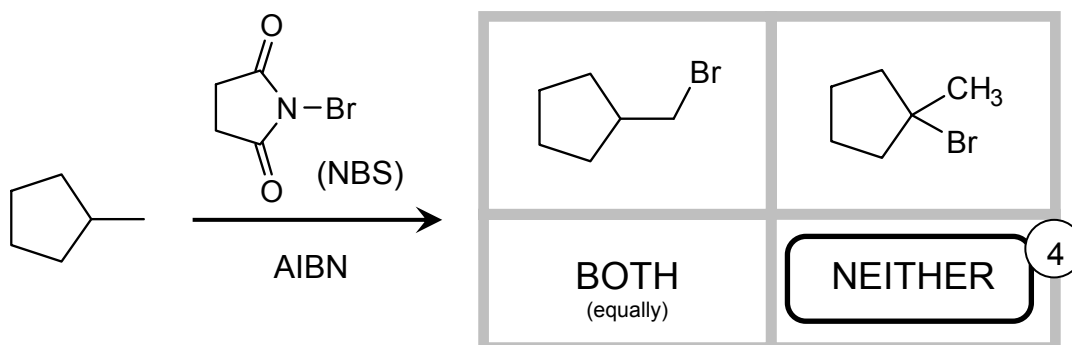
Exam 4 Mean: 69  
Exam 4 Median: 70  
Exam 4 St. Dev.: 20



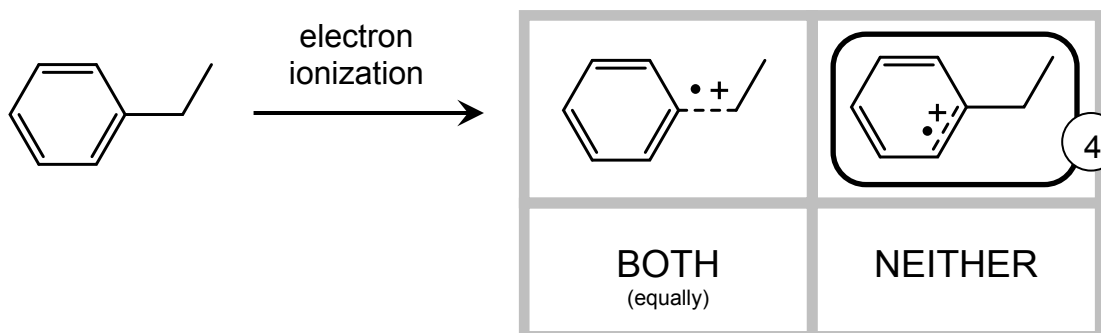
1. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



Benzylic halogenation is preferred, due to the enhanced stability of the benzylic radical.



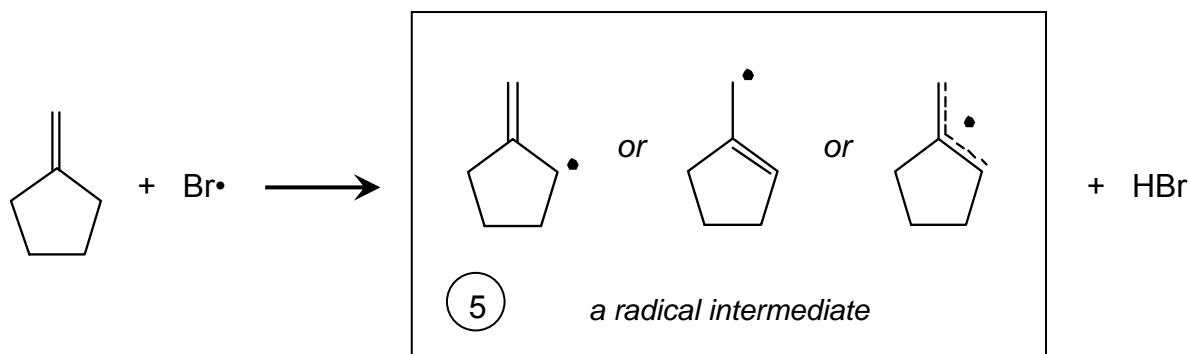
NBS performs allylic and benzylic halogenation, selectively, by generating an extremely low but steady concentration of  $\text{Br}_2$ . This has an upside and a downside. The upside is that



Electron ionization (in a mass spectrometry experiment) preferentially removes the highest-energy electron a molecule has. That's usually a lone-pair electron, followed by a multiple-bond electron, and finally (if these others aren't available) a  $\sigma$ -bond electron.

2. (15 pts)

- a) Radical bromination of ethylenecyclopentane goes predominantly through a single radical intermediate  $R\cdot$ . **What is the structure of the radical intermediate?**



With radical halogenation, the first question you have to ask is, which hydrogen is abstracted, to form which radical? Radical bromination proceeds through the most stable radical intermediate. Here, that will be the resonance-stabilized allylic radical, which is generated by abstracting a hydrogen on a carbon next-door to the double bond.

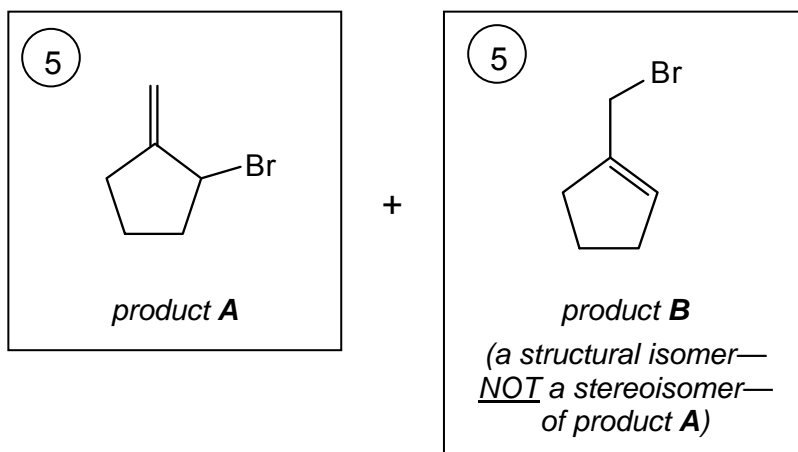
Rubric:

5 points for any of these correct structures.

1 points partial for any radical. (But not for a cation or anion.)

-2 points for each clearly trivial structure mistake.

- b) This radical intermediate then reacts with  $Br_2$  to give two different monobrominated products. What are the structures of these products?



Rubric:

5 points for each product.

Full credit for each product derived from incorrect answer to part (a). If that radical doesn't have resonance structures, then there can be only one derived product (and maximum 5 points total for this part).  
 -2 points for each clearly trivial structure mistake.

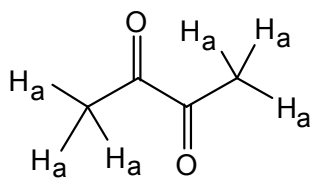
NOTE: As we discussed in class, a chemist wouldn't ordinarily do allylic hydrogenation this way, because of non-radical (electrophilic addition) side products that would also be formed; normally this would be done with NBS.

3. (37 pts)

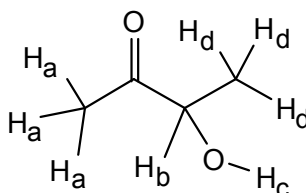
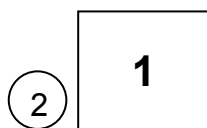
The actual causative agent in the cases of "popcorn lung" investigated by NIOSH was diacetyl, which has been eliminated from all U.S.-branded microwave popcorn. Although most of the cases of popcorn lung involved food plant workers, one well-publicized case did involve a man who had eaten several bags of microwave popcorn every day for 10 years; the FDA concluded that, like the factory workers, the man had likely been overexposed to diacetyl by inhalation in his kitchen.

But, as the problem points out, the answer to this problem is not the toxic agent (diacetyl). What is it?

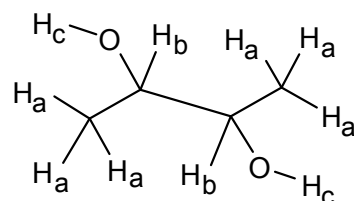
a. In each drawing, equivalent protons have the same letter subscript:



diacetyl



acetoin



2,3-butanediol



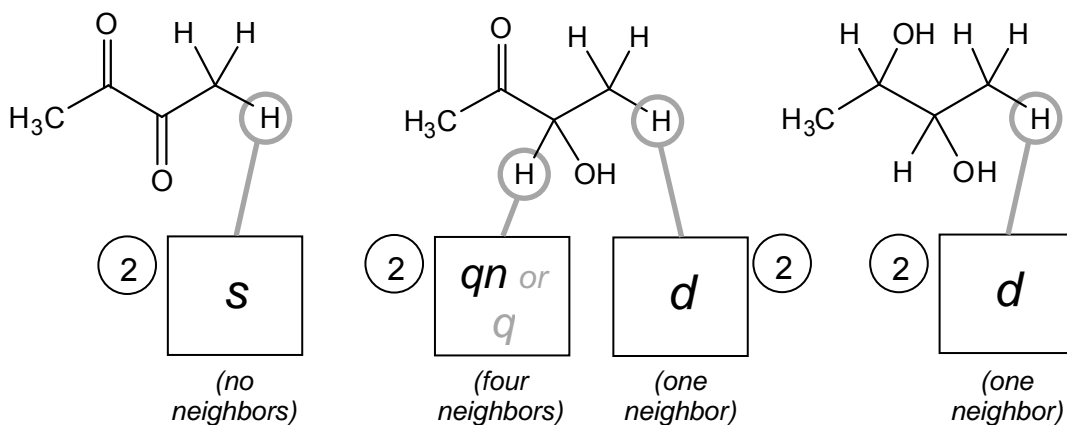
# <sup>1</sup>H NMR resonances expected

Why do the second and third boxes have greyed-out, alternative answers? In the presence of acidic or basic impurities, -OH and -NH protons can experience rapid exchange that makes them lose coupling with neighbors, broaden, and occasionally disappear entirely. This might mean that Hc doesn't show up for these molecules. On the other hand, if the solution is rigorously pure of acidic or basic impurities, these protons show up as sharp signals, and can split their neighbors. (That's unusual though.)

b. Multiplicities:

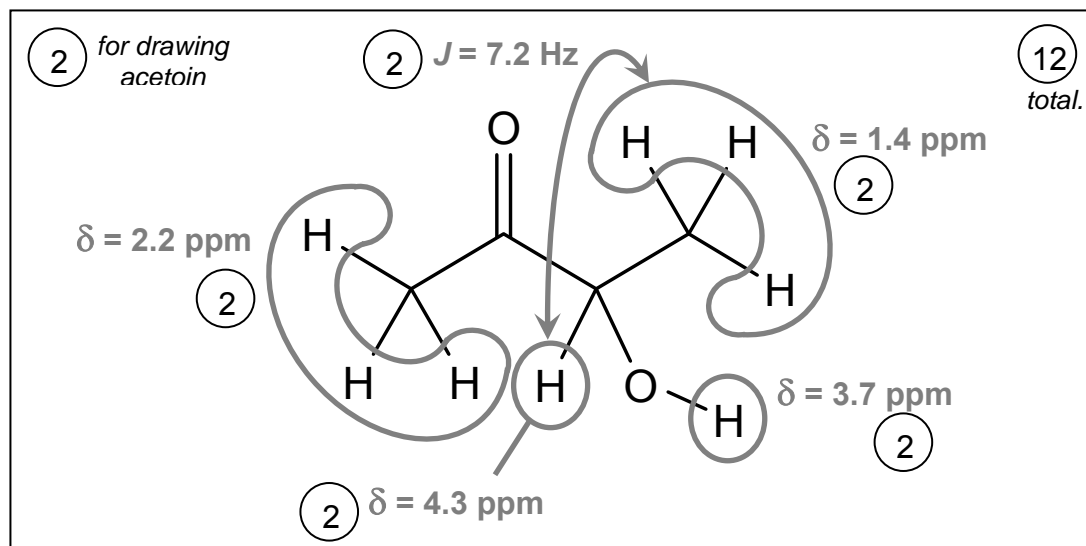
abbreviations for multiplets

<i>s</i> : singlet	<i>q</i> : quartet
<i>d</i> : doublet	<i>qn</i> : quintet
<i>t</i> : triplet	<i>sx</i> : sextet



c.  $^1\text{H}$  NMR assign  $^{13}\text{C}$  spectra for the isolated molecule are shown on the next page. Is the molecule diacetyl, acetoin, or 2,3-butanediol? On the unfinished skeleton in the box below, indicate your choice by drawing in the functional groups on the two center carbons, as well as all hydrogens. Then,

- Circle each group of equivalent H's;
- Assign a  $^1\text{H}$  chemical shift ( $\delta$ ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant ( $J$ ).



Rubric for part (c):

2 points for drawing acetoin (the correct molecule choice).

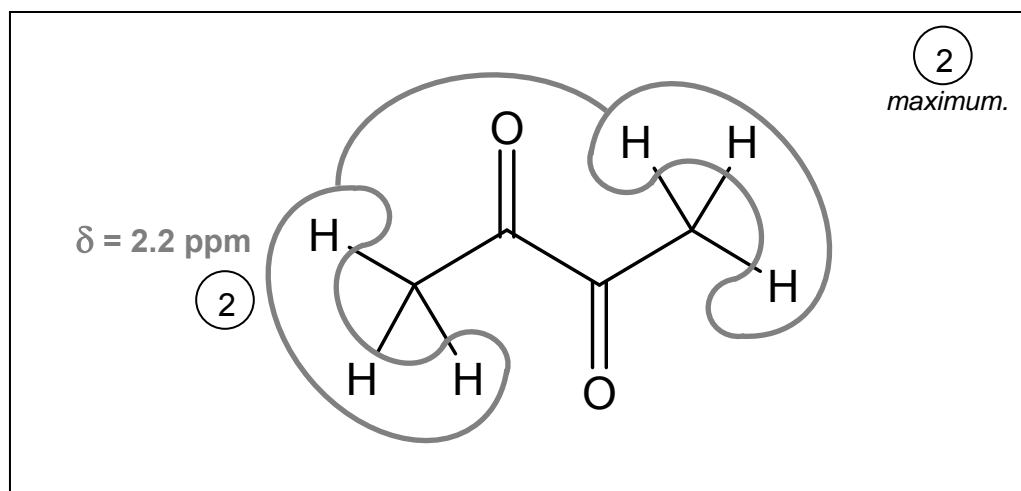
2 points for each set of circled protons and  $\delta$  values. (8 points total for chemical shift assignment.) To get 2 points, the circle must be perfect (include all the right hydrogens, no less, no more), and the  $\delta$  value must be correct within 0.1 ppm.

*1 point partial for each  $\delta$  assigned correctly to one correct proton. You get this if circle is incorrect, but  $\delta$  is correctly associated with one of the protons in the circle.*

*1 point partial for each circle that is perfectly correct but has incorrect  $\delta$  assignment.*

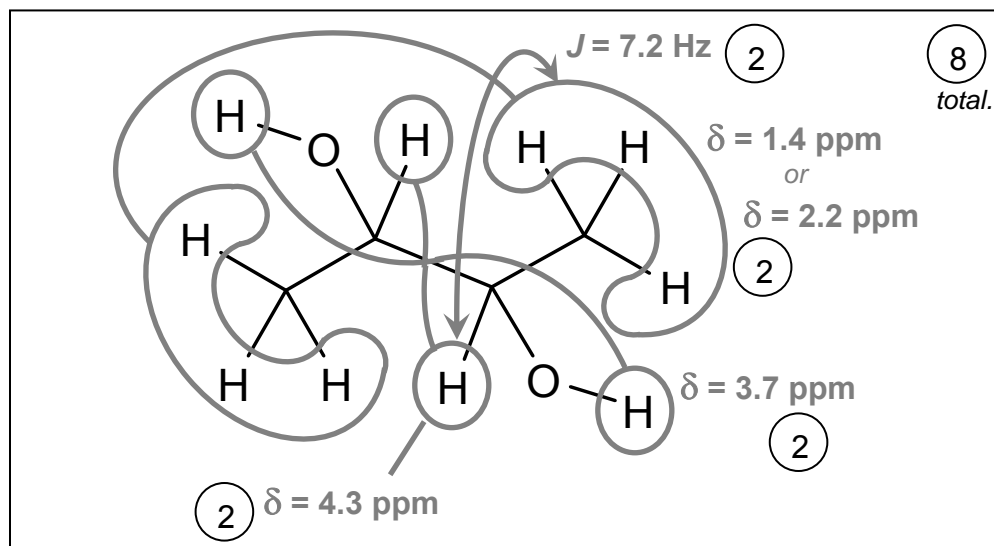
2 points for  $J$  assignment. Circles need not be correct to get these points; curved arrow only needs to connect one correct proton with one correct partner. But, both partners need to be correct to get the points.

If you drew diacetyl:



(The spectra were very inconsistent with diacetyl as an answer—not much partial credit available to assign here.)

If you drew 2,3-dihydroxybutane:

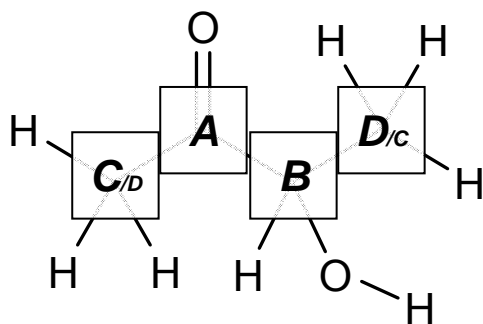


For these two cases, the rubric is the same as on the previous page.

d.  $^{13}\text{C}$  NMR assignments:

Rubric: 1 point per letter.

If you drew acetoin:

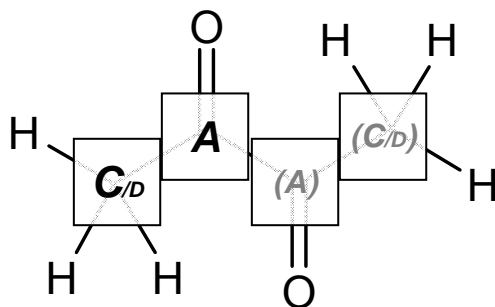


(2) point each box,

(8) points total.

*C and D are interchangeable (but can't put same letter for both; only 1 point out of 2 awarded for that case)*

If you drew diacetyl:

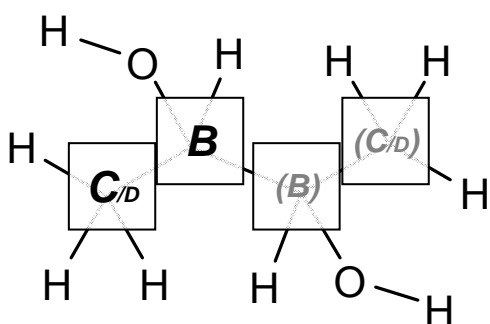


2 point each box,

4 points total.

(Only two of the four peaks in the <sup>13</sup>C spectrum can be explained by the two inequivalent carbons of diacetyl.)

If you drew 2,3-dihydroxybutane:



2 point each box,

4 points total.

(Only two of the four peaks in the <sup>13</sup>C spectrum can be explained by the two inequivalent carbons of 2,3-dihydroxybutane.)

e. Is the <sup>1</sup>H resonance of CHCl<sub>3</sub> at  $\delta = 7.26$  ppm the farthest

upfield

or

downfield

3

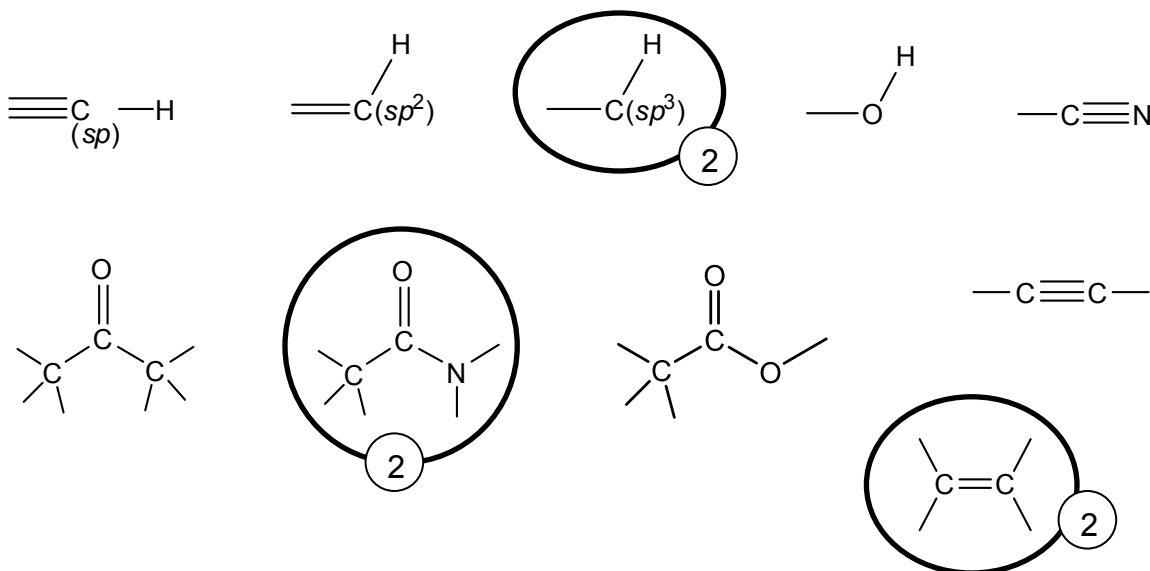
?

4. (36 pts) The spectra on pages 8-9 correspond to a pure solvent molecule, collected from the waste stream of a chemical plant. High-resolution mass spectrometry determined an exact mass of 101.0841 amu for the highest-mass (parent,  $M^+$ ) peak in the MS spectrum, which corresponds to a molecular formula of C<sub>5</sub>H<sub>11</sub>NO.

To help you solve this problem, tables of typical IR frequencies and NMR chemical shifts are provided on pages 17-21 of the exam. Use these tables.



- a. Based on the features above  $1600\text{ cm}^{-1}$  in the IR spectrum, what functional groups could the unknown molecule possibly have? **Circle all answers that apply.**



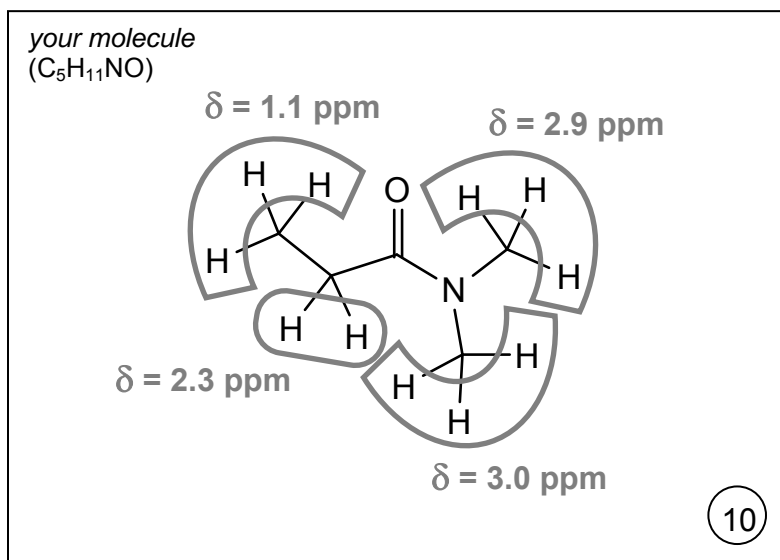
This was hopefully pretty simple; there are no peaks to the left of  $n = 3000\text{ cm}^{-1}$ , so there's no alkene or alkyne protons, and no alcohols; there are no peaks between  $2000\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$ , so there's no triple bonds. But the peak at  $1656\text{ cm}^{-1}$  could be an amide or a double bond--the IR spectrum alone doesn't tell us which.

Rubric (for this part):

2 points for each correct circle.

-2 points for each incorrectly circled group.

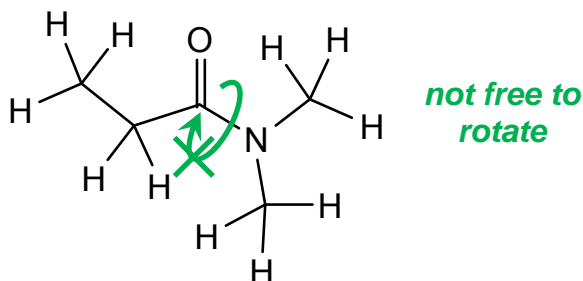
- b. **What is the structure of the molecule?** In the box at right, draw your molecule's structure, including all hydrogens. Then, considering the  $^1\text{H}$  NMR spectrum, circle each set of equivalent H's, and label each circle with its unique  $^1\text{H}$  NMR chemical shift. (You do not need to label coupling constants  $J$ .)



In the  $^1\text{H}$  NMR, there is one obvious feature and one not-so-obvious feature. The obvious feature is the coupled pair of resonances at  $\delta = 1.1$  and  $2.3$  ppm. The first is 3 protons, coupled to two neighbors; and the second is 2 protons, coupled to three neighbors. That sounds a lot like an ethyl group. The chemical shift of the  $-\text{CH}_2-$  protons in that ethyl group,  $2.3$  ppm, means that the group is attached to something electron-withdrawing, possibly the carbonyl or a nitrogen atom.

The not so obvious feature is the two peaks at  $\delta = 2.9$  and  $3.0$  ppm. These look like they might be a 6H doublet, but after accounting for the ethyl group, there are no possible coupling partners for these 6 protons. The key is that the two peaks actually represent 3 inequivalent protons each—that this is two singlets, not one doublet. That represents two inequivalent methyl groups.

So wait—for the molecule above, why are the two methyl groups inequivalent? Resonance between the nitrogen lone pair and the  $\text{C}=\text{O}$  double bond means that the  $\text{N}-\text{C}$  bond is **not** free to rotate. So, one of the methyl groups will stay near the carbonyl oxygen, and the other will stay near the ethyl group. Those different environments lead to different chemical shifts (albeit only slightly different).



Rubric (for this part):

2 points for correct structure (which is not only consistent with the NMR, but is also the only structure consistent with the MS fragmentation).

*Structure need not be correct to receive the other 8 points in this problem.*

2 points for each  $\delta$  value. (8 points total this box.) *To get full credit, circle must include all equivalent protons for your structure, match the integration intensity of the peak, match the type of proton that would appear at that frequency, and  $\delta$  value must be within  $\pm 0.1$  ppm of value shown above.*

1.1 ppm: A methyl group next to any  $-\text{CH}_2-$  group.

2.3 ppm: A  $-\text{CH}_2-$  group attached to a  $-\text{CH}_3$  on one side and an electron-withdrawing group (O atom, N atom,  $\text{C}=\text{O}$  carbon) on the other.

2.9 ppm: A methyl group attached to an electron-withdrawing group.

*Exception to note above: You get these 2 points also if you circled 6 methyl protons together, as if they were equivalent. You get them whether they were actually equivalent or not.*

3.0 ppm: A methyl group, not equivalent to methyl group above, attached to an electron-withdrawing group.

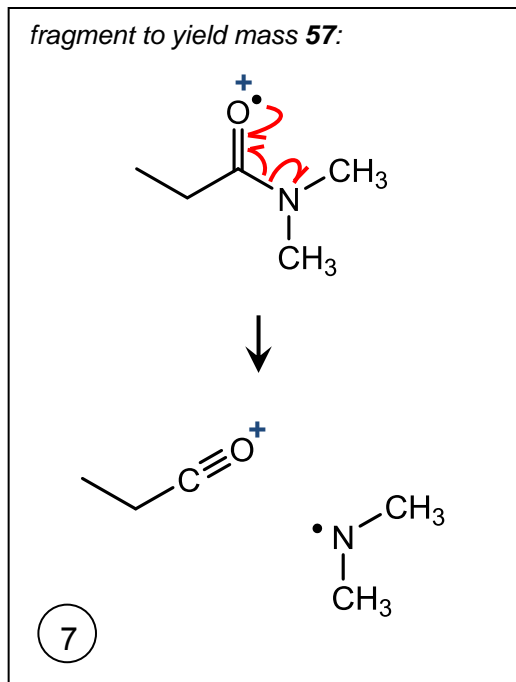
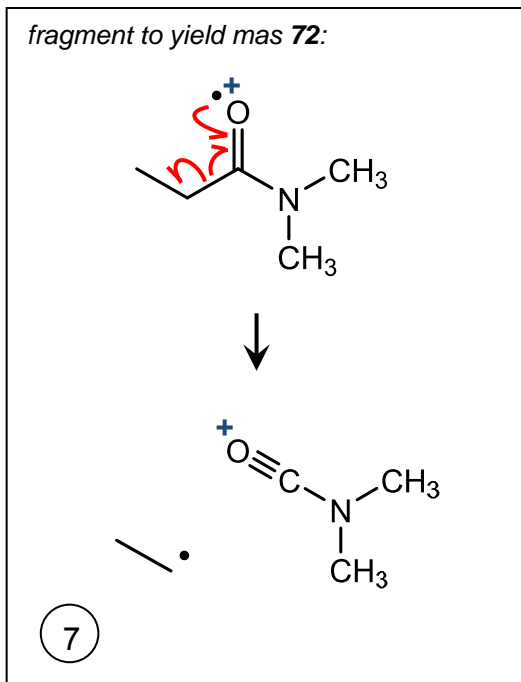
*You only get these points if the three methyl groups are each circled separately.*

*If the two downfield methyl groups are labeled with the same  $\delta$  value—say both are labeled  $3.0$  ppm, or both are labeled  $2.9$  ppm—this is fine. Both of the values are within  $0.1$  ppm of the real value.*

- c. How many resonances would you expect to see in the  $^{13}\text{C}$  NMR of your molecule?

2 for any answer consistent with your answer to part (b).

- d. The mass spectrum shows two high-mass fragment peaks at  $m/z = 72$  and  $m/z = 57$ . In each of the two boxes below, draw a mechanism (via “electron pushing”) that shows how the radical cation of the parent molecule you drew in part (c) could yield these fragments.



Rubric (for this part): 7 points each box (14 total).

- 2 points for any lone-pair ionized, radical cation from the neutral drawn in part (b).
- 3 points for drawing any cation fragment of this molecule with the correct mass.
- 2 points for illustrating a reasonable fragmentation mechanism.

- e. In the mass spectrum, adjacent to the  $m/z = 44$  and 101 peaks, there are smaller peaks that are one mass unit higher (at  $m/z = 45$  and 102). In class, we said that  $[\text{M}+1]^+$  peaks could correspond to ions that had one  $^{13}\text{C}$  atom in place of a  $^{12}\text{C}$ . Looking at the mass spectrum, is this a plausible explanation for the  $m/z = 45$  and 102 peaks? (Circle one each line.)

The peak at  
 $m/z = 45$

could

or

could not

be due to  $m/z = 44$  ions bearing one  $^{13}\text{C}$ .

2

The peak at  
 $m/z = 102$

could

or

could not

be due to  $m/z = 101$  ions  
bearing one  $^{13}\text{C}$ .

2

Molecules, and fragments of molecules, can have a  $^{13}\text{C}$  in place of a  $^{12}\text{C}$ , but because the natural abundance of  $^{13}\text{C}$  is low (~1% of all carbon), the fraction of molecules that have one  $^{13}\text{C}$  will be low. In the case of the parent  $\text{C}_5\text{H}_{11}\text{NO}$ , there are 5 carbons that could each get replaced, and so the probability of a molecule having one  $^{13}\text{C}$  is ~5%. That roughly matches the intensity of the  $m/z = 102$  peak, but definitely not the  $m/z = 45$  peak, which is almost as tall as the  $m/z = 44$  peak (and has fewer carbons than the parent to boot). So this cannot explain the 45 peak.