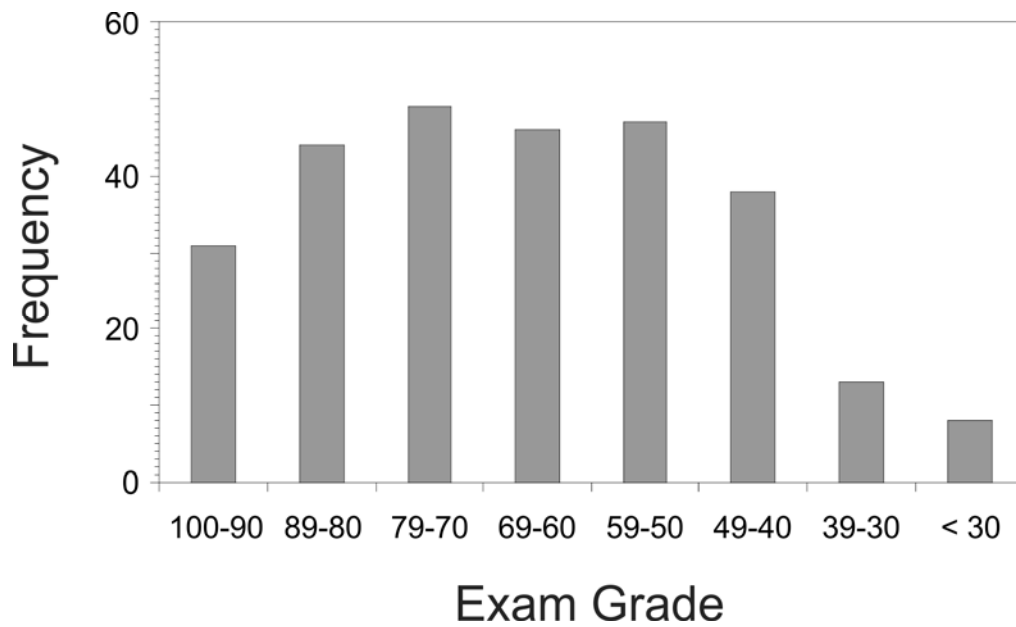**Exam 4**
**Answer Key**

Exam 4 Mean:          66
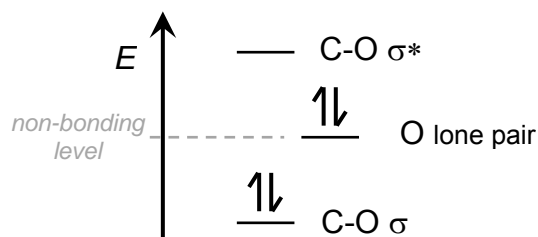Exam 4 Median:        67
Exam 4 St. Dev.:       19

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 <u>equally</u>, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

$Cl_2$
$h\nu$

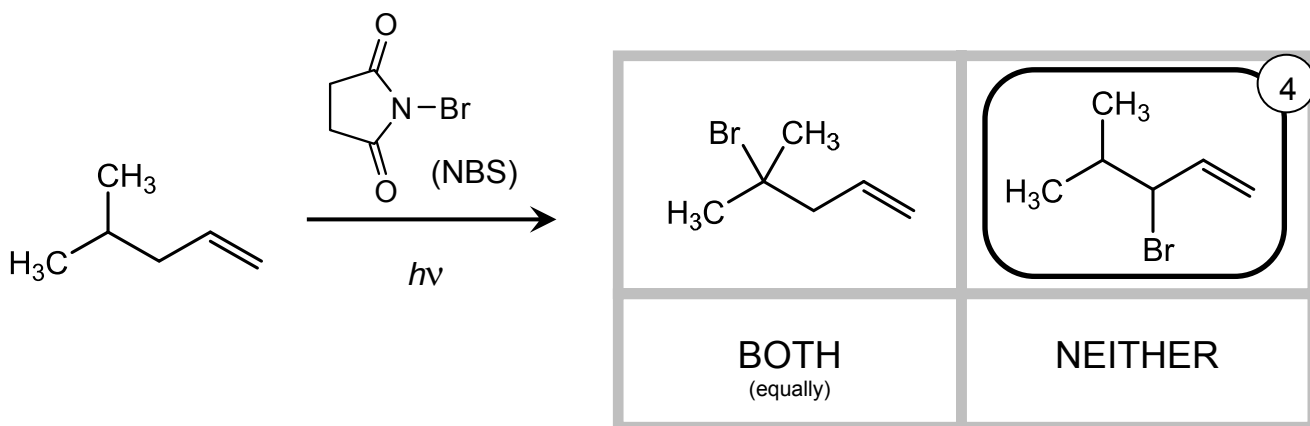| 4 (Cl) | (Cl) |
|---|---|
| BOTH (equally) | NEITHER |
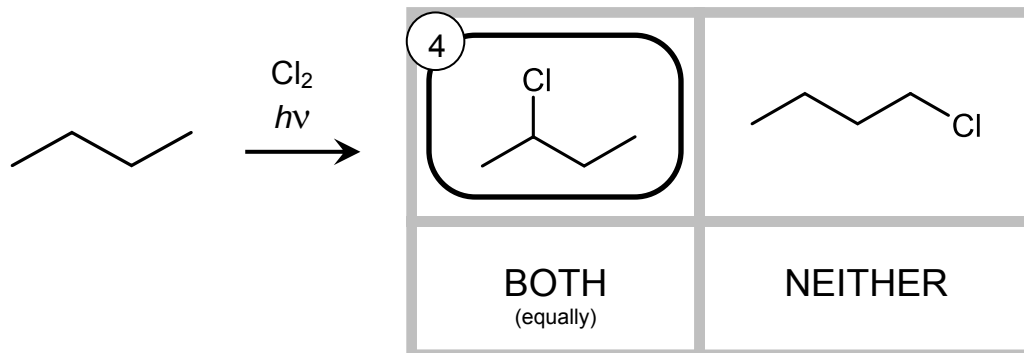
Radical halogenation is typically selective for the most substituted carbon, because the most substituted radical intermediate formed in the rate-determining step is the most stable radical.

electron ionization

| •+ | 4 •+ |
|---|---|
| BOTH (equally) | NEITHER |
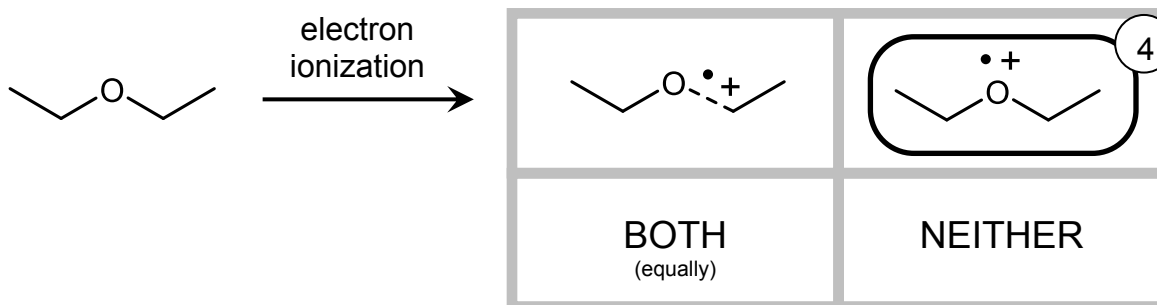
Electron ionization preferentially removes the highest-energy, easiest electron to remove—a lone-pair electron.

$E$

—— C-O σ*

⇅ O lone pair

*non-bonding level*

⇅ C-O σ

The reaction: 4-methyl-1-pentene + NBS, hv. Product options:

Br, CH₃ / H₃C (BOTH equally) / [circled 4] CH₃, H₃C, Br / NEITHER

NBS bromination—in fact, all radical bromination—preferentially goes through the most stable radical intermediate. In class, we discussed two effects that stabilize radicals: substitution, and resonance. Out of those two, resonance is usually more important. As a result, even though the product on the left is a less substituted bromide, it is generated from an *allylic*, resonance-stabilized radical in the rate-determining step, and so it is favored.
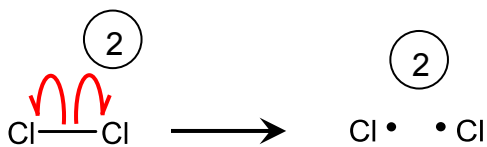


*allylic,*
*resonance-stabilized*
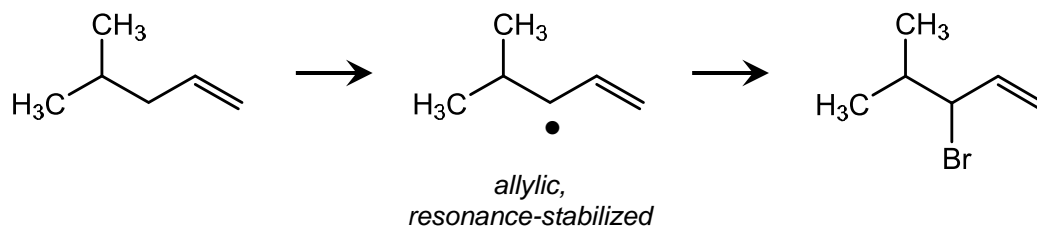
2. (22 pts)
   a. Draw a mechanism (using "electron pushing") for the radical reaction shown below. Draw each mechanistic step explicitly, in its own box, and label each step as an initiation or propagation step. (Do not draw any termination steps in this part.) Use only the molecules shown in the problem; don't invoke generic species.



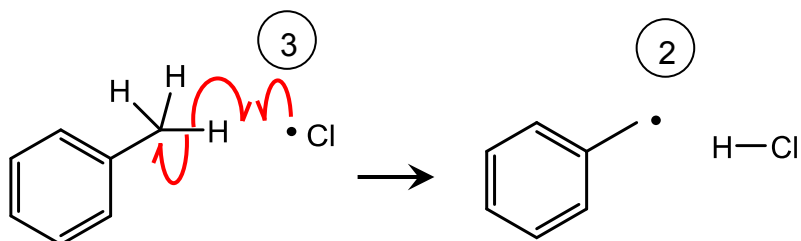toluene + Cl₂, hv → benzyl chloride

---

*Mechanism, step 1:*

② Cl——Cl → Cl• •Cl  ②
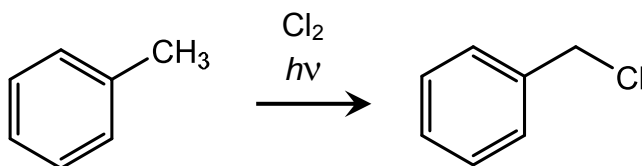
[circled 1] **initiation**

*or*

**propagation**

---

3
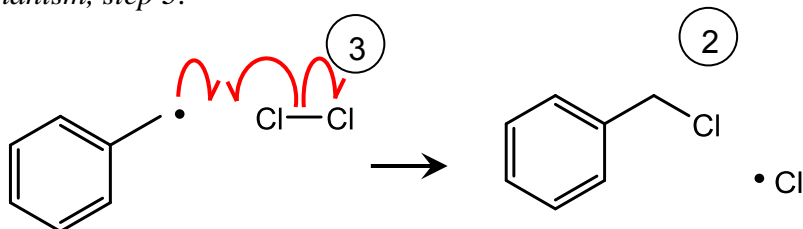
*Mechanism, step 2:*



③ ②

initiation

*or*

**propagation** ①

*Mechanism, step 3:*



③ ②

initiation
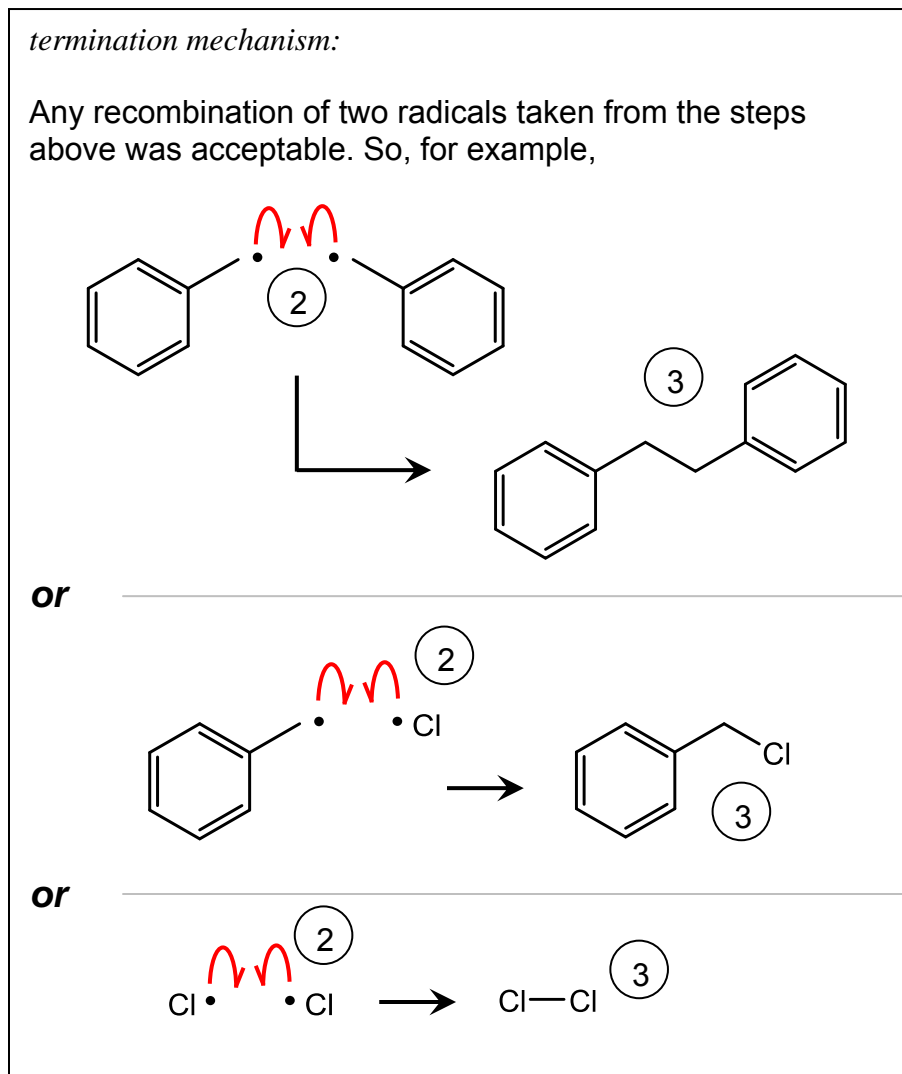
*or*

**propagation** ①

Rubric for electron pushing:
Overall notes:

*Overall, the minimum score for each graded element is zero; errors in a step cannot earn you negative points that count against another, correct step.*

*Things that have left and spectators may be omitted after the step they are made.*

*-1 point, for each arrow in each step, for errors (including omission) in drawing arrows. Each arrow in this problem must be \*single-barbed\*. Double-barbed arrows earn no partial credit. Arrow must start at an unpaired electron or an electron pair, and end at a nucleus or newly formed bond.*

*-1 point for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.*

2 or 3 points (as marked) for each arrow-pushing step.
2 or 3 points (as marked) points for each set of step products.

b.  In the box on the right, draw the mechanism of a termination step that you would expect for the reaction on the previous page.

*termination mechanism:*

Any recombination of two radicals taken from the steps above was acceptable. So, for example,



*or*



*or*



Rubric: Same criteria as part (a).
2 points for electon pushing.
3 points for drawing a termination product.
   *Arrows don't have to be correct to get points for correct product.*

3. (38 pts) The spectra on page 6 correspond to a pure molecule; high-resolution mass spectrometry determined an exact mass of 110.0732 amu for the highest-mass (parent, $\mathbf{M}^+$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_7H_{10}O}$.

a. Considering only the features in the IR spectrum, what functional groups might the unknown molecule possibly have? **Circle all answers that apply.**
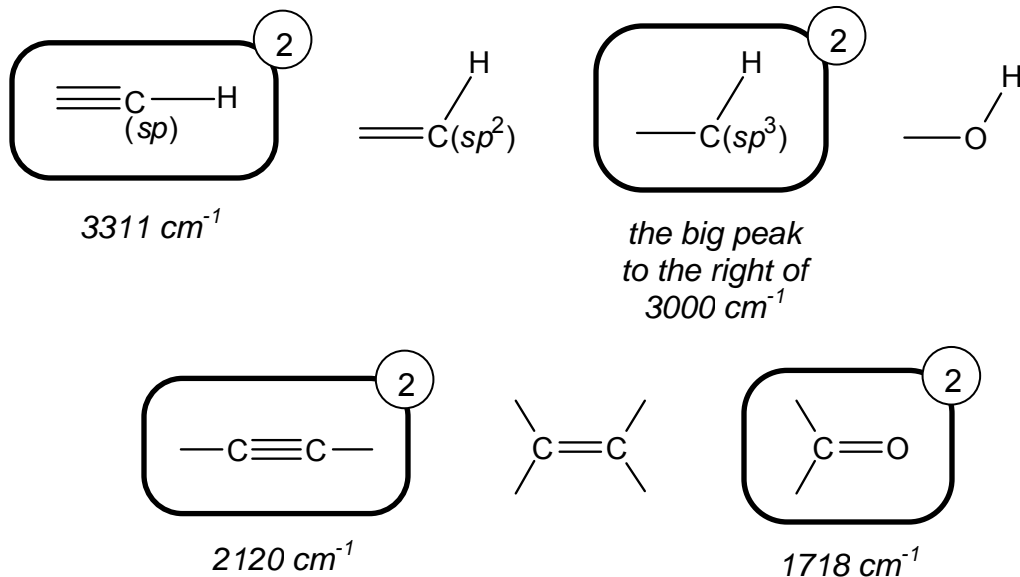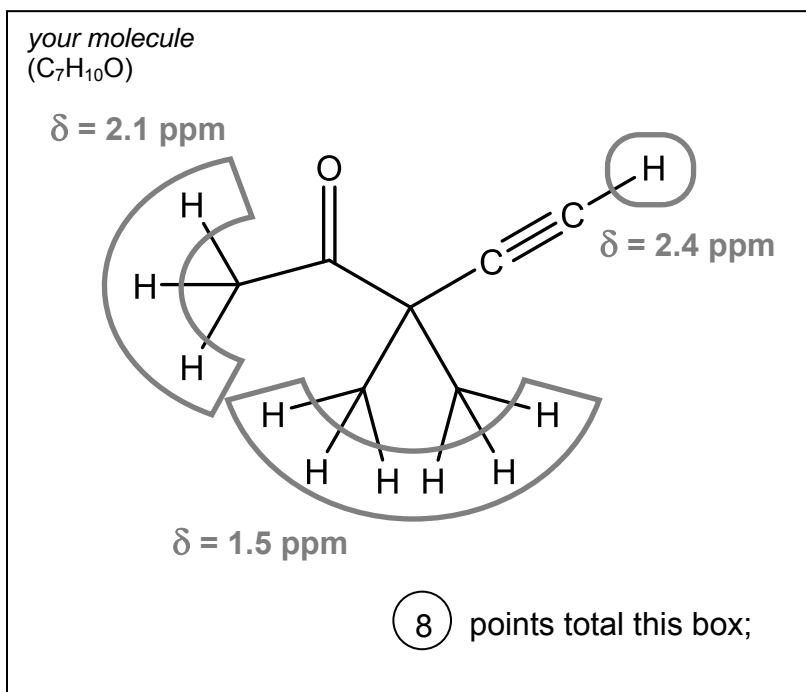


Rubric:
2 points for each correctly circled functional group.
-2 points for each underlined incorrectly circled functional group.

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



your molecule
$(C_7H_{10}O)$

$\delta$ = 2.1 ppm

$\delta$ = 2.4 ppm

$\delta$ = 1.5 ppm

8 points total this box;

6

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 6 points in this problem.*
2 points for each $\delta$ value. (6 points total for $\delta$ assignments.) *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 ±0.1 ppm of value shown above.*
  2.4 ppm: A single H, not coupled to any partners, either attached to a triple bond or allylic to a multiple bond.
  2.1 ppm: A methyl group attached to a somewhat electron-withdrawing group, with no proton neighbors.
  1.5 ppm: Two equivalent methyl groups with no neighbors (and no other equivalent methyl groups).

c. Is the $^1$H resonance at $\delta = 1.4$ ppm the farthest **upfield** ② or **downfield** ?

d. Are the protons at $\delta = 1.4$ ppm the most **shielded** ② or **deshielded** ?

e. Do the spins at $\delta = 1.4$ ppm precess ("wobble") the **fastest** or **slowest** ② ?

f. The parent mass peak at $m/z = 110$ corresponds to a radical cation ($\mathbf{M}^{\bullet+}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw $\mathbf{M}^{\bullet+}$; re-draw the structure you drew in part (b), but specifically indicate which electron is removed by drawing the molecule with one less electron. *Feel free to omit the hydrogens you drew in part (b).*



$\mathbf{M}^{\bullet+}$
$(C_7H_{10}O^+)$ ③
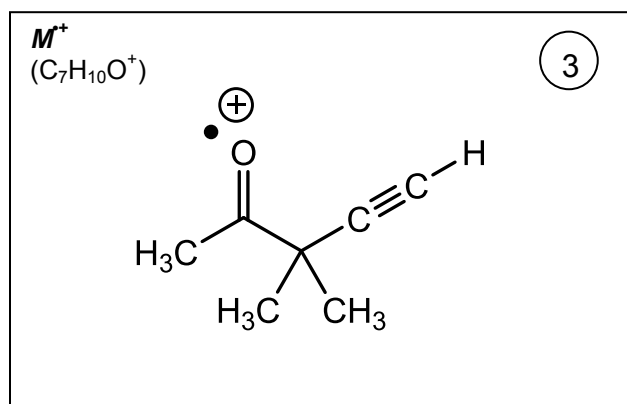
The electrons that have the highest energy are the easiest for electron ionization to remove--and those are the lone-pair electrons, which haven't been stabilized in a bond.

g. The parent ion fragments to form a daughter ion with $m/z = 95$. In the box on the next page, draw a mechanism (using "arrow pushing") that shows how fragmentation of the parent you drew in part (f) generates this ion, and that identifies the structure of this ion.

*fragmentation to m/z = **95**:*
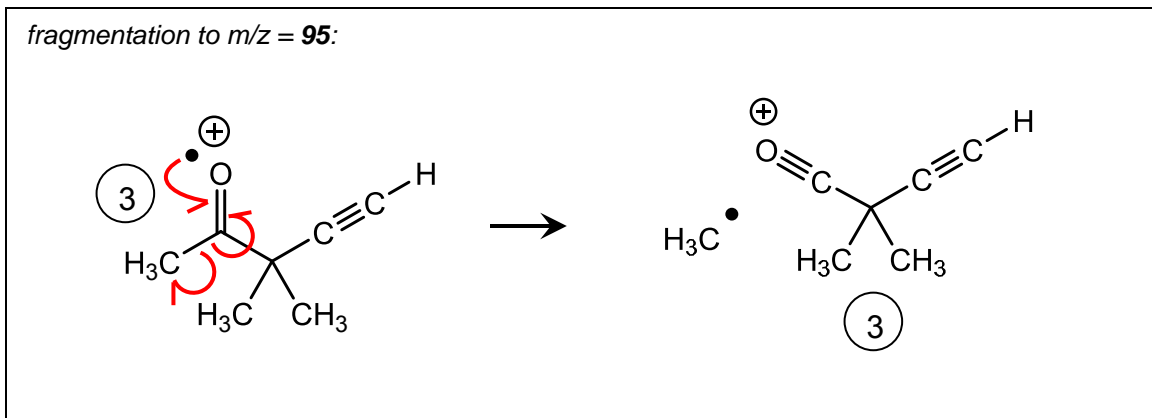


Rubric for part (g):
3 points for $\alpha$-cleavage electron-pushing.
*In order to earn these points, the electron pushing needs to make sense, both in terms of the mechanism and in terms of the starting ion. But your starting ion doesn't have to match mine, and neither does your product, to get these points.*
3 points for drawing a $m/z = 95$ cation fragment of your answer to (f).
*The mechanism does not have to be correct to receive these points, and neither does (f). But the structure does have to have m/z = 95, it must be a cation, and it must be related to (f).*

h. Draw structures for the $m/z = 67$ and $m/z = 15$ ions. You do not need to draw any mechanisms in this part.

*m/z = **67**:*

*m/z = **15**:*
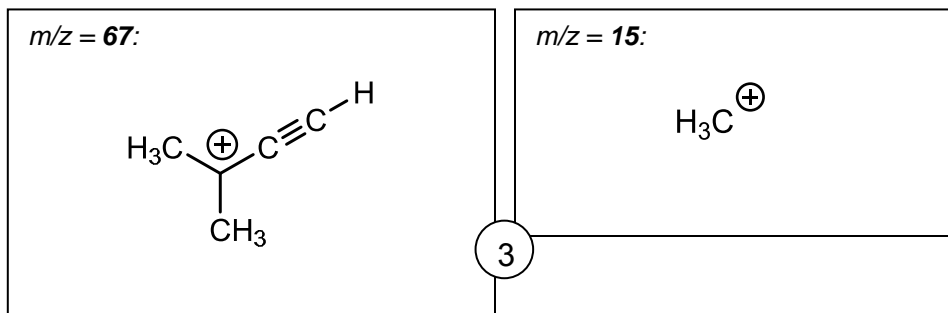


Rubric for part (h):
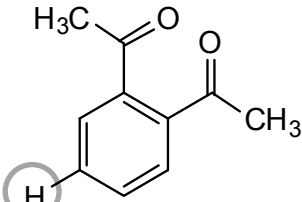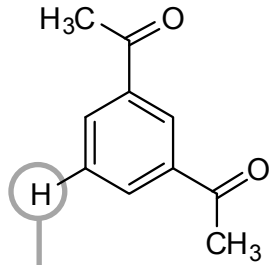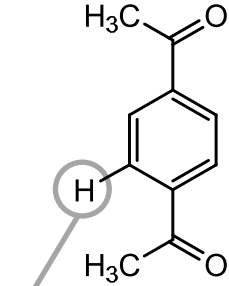3 points for *either* of these correct.

I did the math wrong when I assigned points to this problem, so

**+ 4 AUTOMATIC POINTS.**

4. (28 pts) When acetophenone is combined with acetyl chloride and a Lewis acid catalyst—in a reaction that you will learn about in CHEM 2302—three different diacetylbenzenes could be generated as products. Normally this reaction doesn't work, but in this problem, we will imagine that you are a chemist that has performed this reaction, and that you have isolated one of these three products. You have performed $^1$H and $^{13}$C NMR spectra on this product, shown on page 9. In the questions that follow, you will decide which of the three products you have isolated.
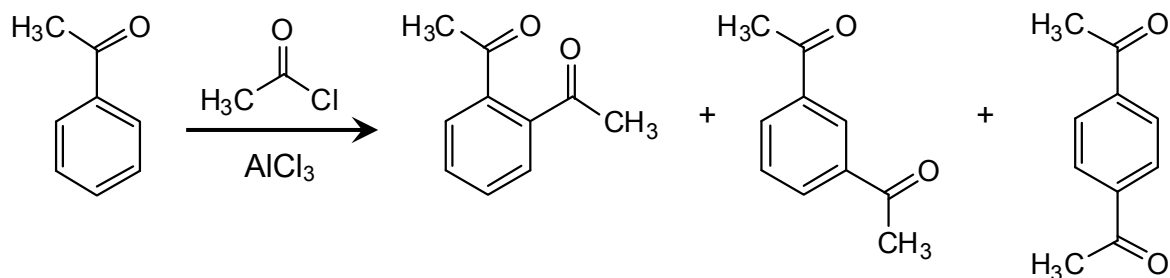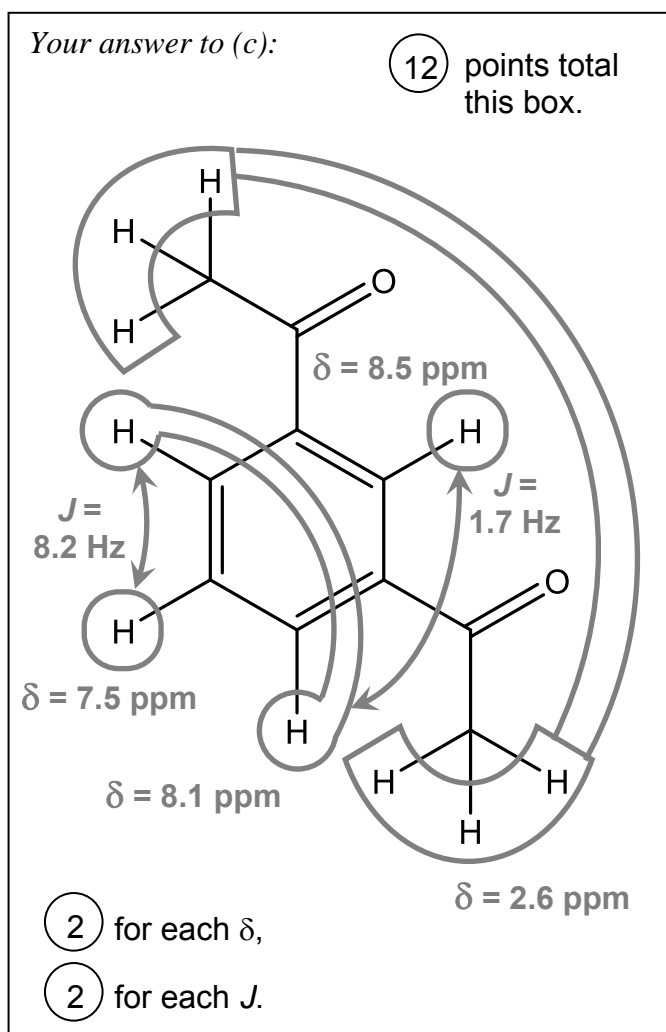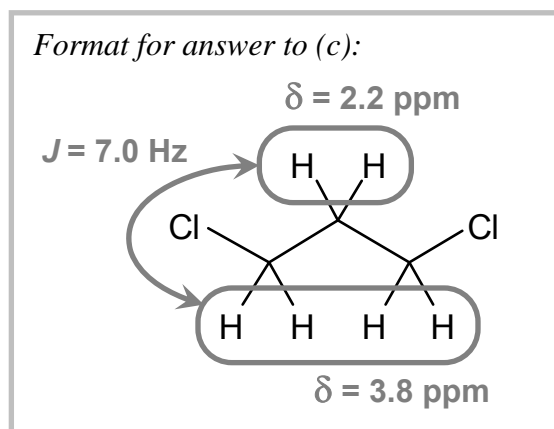


a. How many resonances would you expect to see in the $^1$H NMR of each of these products? In other words, how many inequivalent sets of protons are there in each structure? Write your answers in the boxes below.

# $^1$H NMR resonances expected



| | | |
|---|---|---|
| ②  **3** | ②  **4** | ②  **2** or **3** |

type of multiplet for this proton



| ②  **d** | ②  **t** | ②  **s** |
|---|---|---|

b. Each proton highlighted in the structures above could be split by neighboring protons. What kind of multiplet should each proton produce in a $^1$H NMR spectrum? (Assume that there is no long-range coupling for the circled proton. But there might be for the others!) Use the abbreviations on the chart on the right, and write your answers in the boxes above.

abbreviations for multiplets

s: singlet
d: doublet
t: triplet
q: quartet
dd: doublet of doublets

9

*Format for answer to (c):*

δ = 2.2 ppm

J = 7.0 Hz

H   H

Cl          Cl

H   H   H   H

δ = 3.8 ppm

*Your answer to (c):*

⑫ points total
this box.

H

H

H

O

δ = 8.5 ppm

H          H

J =
8.2 Hz

J =
1.7 Hz

H

O

δ = 7.5 ppm

H

H          H

H

δ = 8.1 ppm

δ = 2.6 ppm

② for each δ,

② for each J.

c.  $^1H$ and $^{13}C$ spectra for the isolated molecule are shown on the next page. Which of the three products did you isolate? On the unfinished skeleton in the box at right, indicate your choice by drawing in any appropriate functional groups, as well as all hydrogens. Then,

- Circle each group of equivalent H's;
- Assign a $^1H$ chemical shift (δ) 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):

*Structure need not be correct to receive partial credit in this problem. However, other structures are inconsistent with the data, and this will make your individual answers not match the spectra, and cost you points that way.*

2 points for each set of circled protons and δ values. (**8 points total for chemical shift assignments and circles.**) To get 2 points, circle must include all equivalent protons for your structure, match the integration intensity of the peak, and match the type of proton that would appear at that frequency within 0.2 ppm.

--------

*1 point partial for assigning each ppm value to the wrong number of H's, but the correct type. If multiple inequivalent H's are labeled with the same δ value, you get maximum 1 point partial credit for that δ value.*

*-------*

<u>8.5 ppm:</u> Must be one aromatic proton, not equivalent to any others.
 *1 point for assigning this value to proton on opposite end of benzene ring.*
<u>8.1 ppm:</u> Must be two aromatic protons, with two neighbors.
<u>7.5 ppm:</u> Must be one aromatic proton, not equivalent to any others.
 *1 point for assigning this value to proton on opposite end of benzene ring.*
<u>2.6 ppm:</u> Must be two methyl groups, regardless of structure.
 *2 points partial if methyl group has neighboring H's.*
2 points for each *J* assignment.
 *Curved arrow only needs to connect one proton with one partner.*
 <u>8.2 Hz:</u> *Any vicinal (three-bond) aromatic pair.*
 <u>1.7 Hz:</u> *Any long-range pair.*

d. The $^{13}C$ NMR spectrum of the isolated product showed 6 peaks, which appear in three distinct regions of the spectrum. I've labeled these regions **A**, **B** and **C** on the $^{13}C$ spectrum on the next page. As you did above, re-draw your proposed product structure on the right (though this time you can omit H's). Then, in each empty box, write the letter **A**, **B**, or **C** to indicate the region of the $^{13}C$ NMR you would expect to find that carbon resonance. **Fill all boxes.**
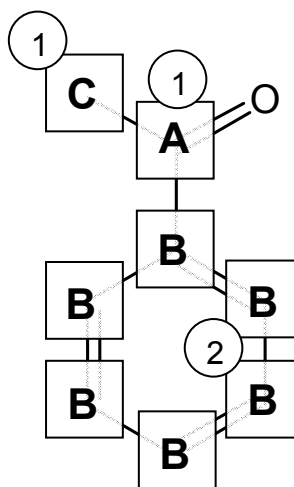


<u>Rubric for part (c):</u> 4 points total this part.
 *Structure need not be correct to receive credit in this problem.*
1 point for assigning "**A**" to carbonyl carbon.
2 points for assigning "**B**" to <u>all</u> aromatic carbons.
 *1 point partial for assigning "B" to any aromatic carbon.*
1 point for assigning "**C**" to methyl group carbon.