NAME:_____ Section:_____ Student Number:_____

Fall 2018 **Chemistry 2600 Midterm** ____/ 60 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 7 pages of questions in addition to this cover page and a periodic table.
2) You have also been given a 6 page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE!** If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) You may use a molecular model kit and ruler. You may not have any papers or other written materials in your model kit.
4) You may use a calculator. It may not have wireless capability. You may not have any other electronic devices (phone, iPod, etc.) with you when you write the exam.
5) If your work is not legible, it will be given a mark of zero.
6) Marks will be deducted for incorrect information added to an otherwise correct answer.
7) You have 2 hours to complete this test.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on Wednesday, October 10th, 2018. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/60 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____

Course: CHEM 2600 (Organic Chemistry II)
Semester: Fall 2018
The University of Lethbridge

Question Breakdown

Q1	/ 12
Q2	/ 10
Q3	/ 6
Q4	/ 6
Q5	/ 6
Q6	/ 20
Total	/ 60

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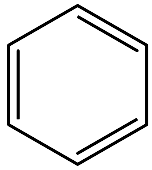
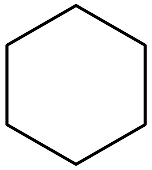
1. For each of the following pairs of molecules, explain how you would use **<u>two</u>** spectroscopic methods to distinguish between them. Be specific. What peak(s) are you looking for? Where are they? Give numbers or ranges where possible. **[12 marks]**
You may choose from ^{1}H NMR, ^{13}C NMR, IR and MS. You may choose different spectroscopic methods for each pair of molecules. It must be clear which methods you have chosen.

(a)



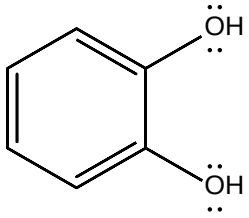
vs.



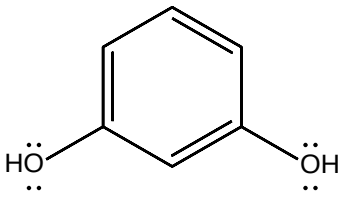
IR	$C(sp^2)-H$ stretch just above 3000 cm^{-1} $C=C$ stretch in 1500-1650 cm^{-1} region	$C(sp^3)-H$ stretch just below 3000 cm^{-1} no $C=C$ stretch in 1500-1650 cm^{-1} region
^{13}C NMR	1 signal in aromatic region (110-150 ppm)	1 signal in aliphatic region (~25-45 ppm for CH_2)
^{1}H NMR	1 singlet in aromatic region (7.26 ppm)	1 singlet in aliphatic region (~1.3 ppm for CH_2)
MS	Molecular ion is m/z 78	Molecular ion is m/z 84

- *Aliphatic is the technical term for carbon rings/chains/etc. that contain only $C-C$ single bonds.*
- *Remember that not all rings are aromatic! The important difference between these two molecules is that the one on the left contains double bonds while the one on the right does not.*

(b)



vs.



^{13}C NMR	3 signals in aromatic region (110-150 ppm)	4 signals in aromatic region (110-150 ppm)
^{1}H NMR	2 peaks in aromatic region (6.5-9 ppm) plus one OH peak	3 peaks in aromatic region (6.5-9 ppm) plus one OH peak

- *Neither IR nor MS will be much use for distinguishing between these two isomers (unless you look at certain peaks in the fingerprint region of the IR which we did not discuss in class).*

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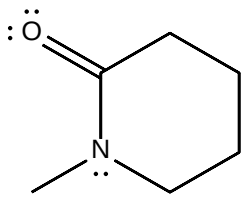
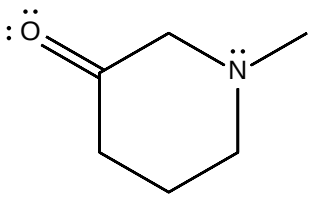
(c)



vs.



IR	(tertiary) amide $C=O$ stretch between 1630 and 1670 cm^{-1}	ketone $C=O$ stretch between 1705 and 1725 cm^{-1}
^{13}C NMR	signal for amide $C=O$ carbon is expected to be between 160 and 180 ppm	signal for ketone $C=O$ carbon is expected to be between 180 and 220 ppm
^{1}H NMR	5 signals are predicted to be: • singlet (3H) • triplet (2H) • pentet (2H) • pentet (2H) • triplet (2H)	5 signals are predicted to be: • singlet (3H) • singlet (2H) • triplet (2H) • pentet (2H) • triplet (2H)

- *The key difference between these two molecules is that the two carbonyl groups are in different functional groups (amide vs. ketone) which are easily distinguished via IR or ^{13}C NMR. While you could use ^{1}H NMR splitting patterns, it is very likely that some of the peaks overlap and that it will be difficult to identify the exact splitting pattern for each peak.*

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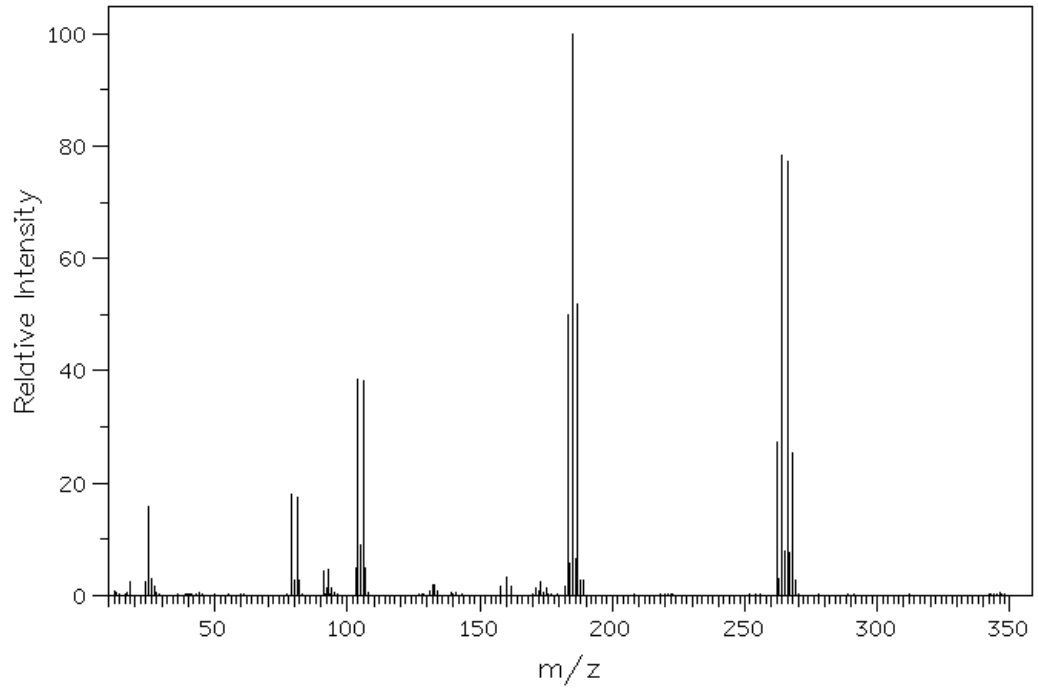
2. Consider the following mass spectrum for Unknown A: **[10 marks]**



The following table lists the heights of all peaks with relative intensity higher than 10:

m/z	intensity		m/z	intensity		m/z	intensity		m/z	intensity		m/z	intensity
25	15.9		79	18.0		104	38.4		183	50.0		262	27.2
			81	17.4		106	38.3		185	100.0		264	78.4
									187	51.8		266	77.2
												268	25.4

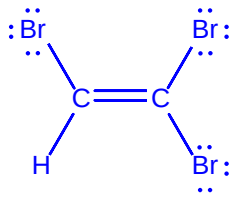
(a) Which peak is the molecular ion? *[1 mark]*

m/z 262

(b) What is the molecular formula for Unknown A? *[2 marks]*

C_2HBr_3

(c) Draw Unknown A. *[2 marks]*



m/z 262 is 79 larger than m/z 183 which is 79 larger than m/z 104 which is 79 larger than m/z 25. That suggests loss of three successive ^{79}Br atoms. This is supported by the shapes of the clusters of peaks:

- *a 1 : 1 ratio between m/z 104 and 106 (fragment contains one Br)*
- *a 1 : 2 : 1 ratio between m/z 183, 185 and 187 (fragment contains two Br)*
- *a 1 : 3 : 3 : 1 ratio between m/z 262, 264, 266 and 268 (fragment contains three Br)*

The remaining mass (25 g/mol) can best be accounted for using two C and one H.

There is only one way to assemble C_2HBr_3.

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2. *...continued*

(d) Explain the cluster of peaks from m/z 262 to m/z 268. Your answer should address exactly what each of the four peaks corresponds to as well as the ratio of the heights of the four peaks.

[5 marks]

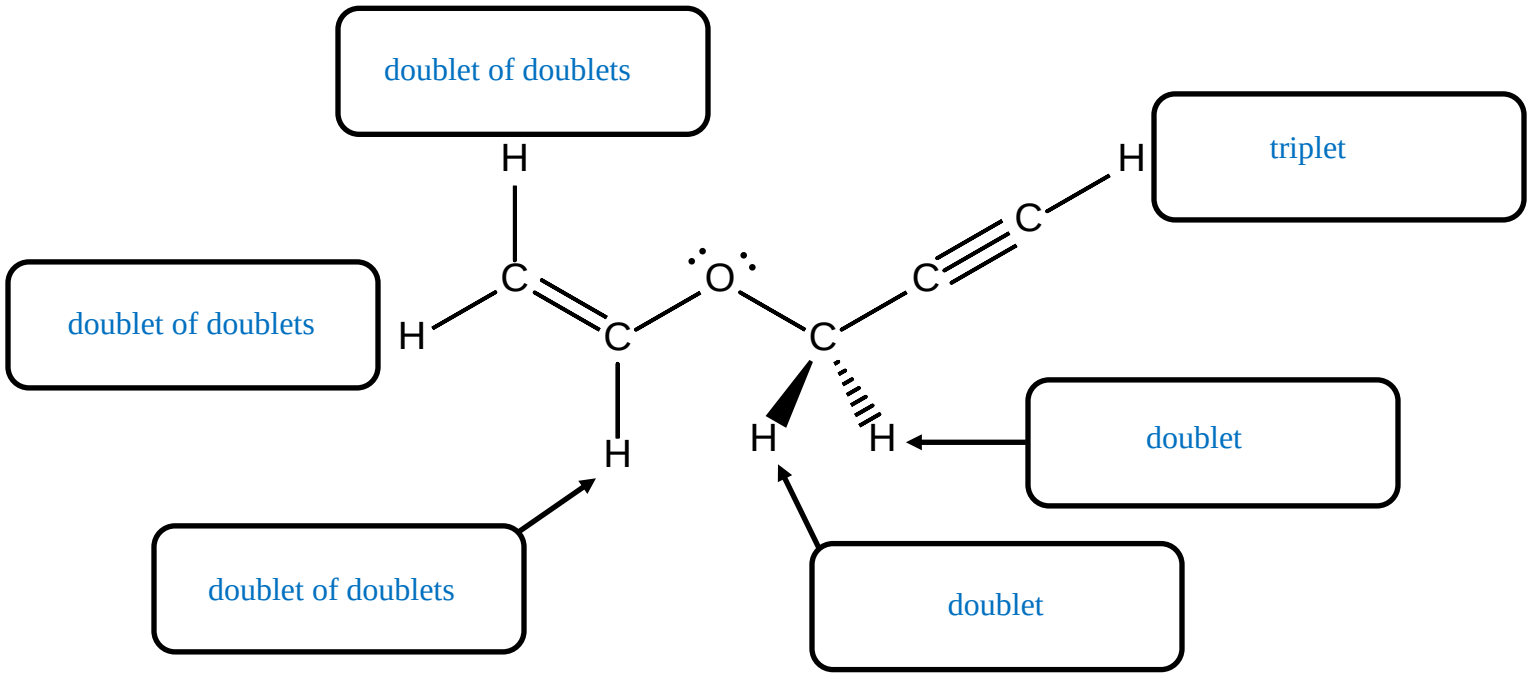
^{79}Br and ^{81}Br exist in approximately a 1 : 1 ratio.

The peaks between m/z 262 and m/z 268 all correspond to the molecular ion for C_2HBr_3.

- m/z 262 is for C_2HBr_3 containing three ^{79}Br (only one possible combination)
- m/z 264 is for C_2HBr_3 containing two ^{79}Br and one ^{81}Br. Because any of the three Br could be the ^{81}Br, this peak is three times as tall as m/z 262.
- m/z 266 is for C_2HBr_3 containing one ^{79}Br and two ^{81}Br. Because any of the three Br could be the ^{79}Br, this peak is three times as tall as m/z 262.
- m/z 268 is for C_2HBr_3 containing three ^{81}Br (only one possible combination therefore same height as m/z 262)

Thus, the cluster of peaks has a 1 : 3 : 3 : 1 height ratio.

3. Consider the molecule below. In the boxes provided, label each proton with the predicted splitting pattern it would exhibit in a ^{1}H NMR spectrum. **[6 marks]**
Assume that any long range coupling has J > 0 Hz.



The two H on the end of the $C = C$ double bond are NOT equivalent. They both couple to each other as well as to the H on the other carbon in the $C = C$ double bond, making all three signals doublet of doublets.

Because there is at least one pi bond (the triple bond) between the H on the end of the alkyne and the CH_2 group, long range coupling is possible. While the triplet and doublet will both be narrow, it is likely that the 4-bond coupling would be observed. The two H of the CH_2 group are shift equivalent so they do not couple to each other.

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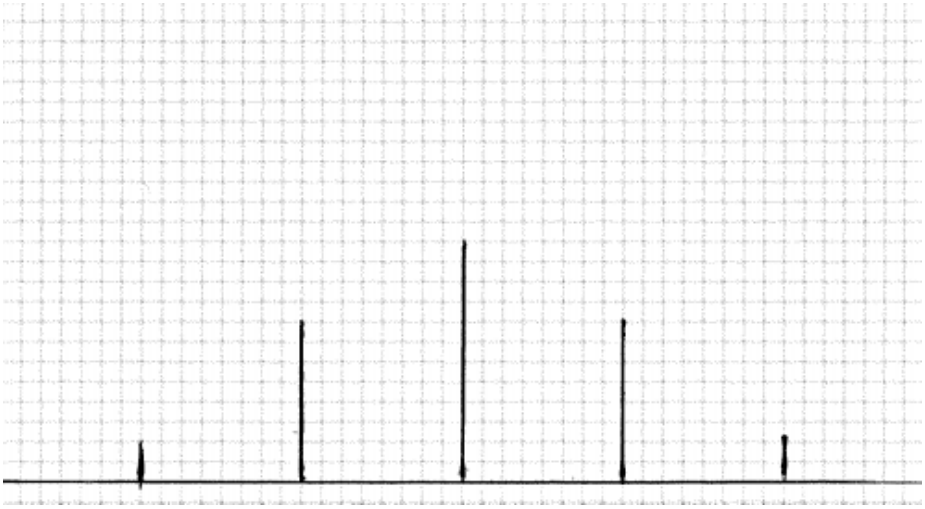
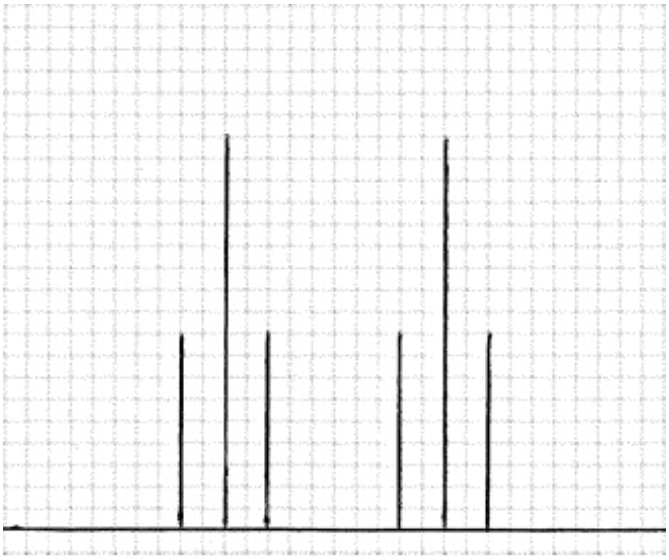
4. **[6 marks]**

(a) Use the graph paper below to draw (to scale) a pentet ($J = 8\ Hz$).
You do not need to draw the tree diagram.
Use 1 square = 1 Hz as your horizontal scale. Line heights must also be to scale. *[2 marks]*



Ratio of lines must be 1 : 4 : 6 : 4 : 1
Distance between adjacent lines must be 8 squares (for a coupling constant of 8 Hz)

(b) Use the graph paper below to draw (to scale) a doublet ($J = 10\ Hz$) of triplets ($J = 2\ Hz$).
You do not need to draw the tree diagram.
Use 1 square = 1 Hz as your horizontal scale. Line heights must also be to scale. *[4 marks]*



Ratio of lines within each triplet must be 1 : 2 : 1
The two triplets must be of equal height
Distance between lines within a triplet must be 2 squares (for a coupling constant of 2 Hz)
Distance between the same line in each triplet must be 10 squares (for a coupling constant of 10 Hz).

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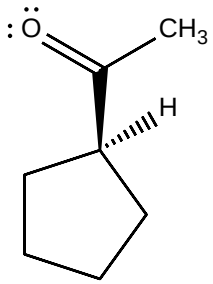
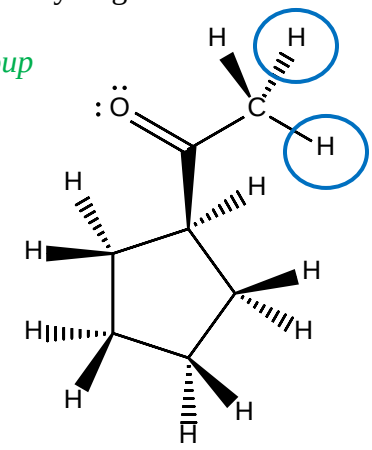
5. Consider the following molecule: **[6 marks]**



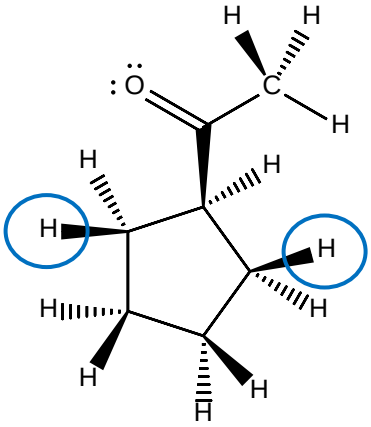
(a) On the picture below, circle two hydrogen atoms which are homotopic: *[2 marks]*

any two of the three H in the CH_3 group



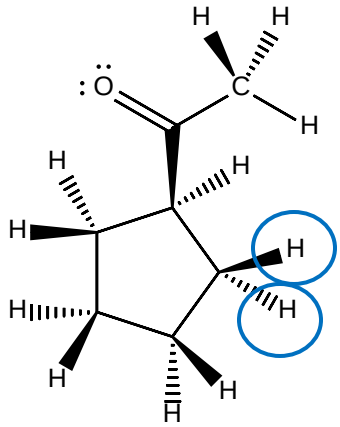
(b) On the picture below, circle two hydrogen atoms which are enantiotopic: *[2 marks]*

any two H attached to equivalent carbon atoms where the H are either both cis or both trans to the ketone



(c) On the picture below, circle two hydrogen atoms which are diastereotopic: *[2 marks]*

any two H attached to equivalent (or the same) carbon atom(s) where one H is cis to the ketone and the other is trans to the ketone



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6. The following page contains spectra for Unknown X ($C_8H_{14}O_4$). **[20 marks]**

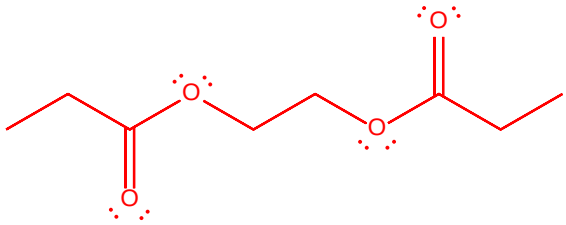
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning.

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. *For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.*

(d) Label any important peaks on the IR.

Unknown X:



General breakdown of marks:
1 mark for correct answer
1 marks for IR peak assignment (C=O)
3 marks for ^{1}H NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
4 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
1 mark for calculating DU
10 marks for logic (this page plus legible rough work on spectra, etc.)

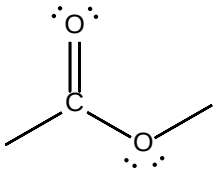
One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(8)+2-14}{2} = \frac{4}{2} = 2$
- Therefore, there is either a triple bond, two double bonds, a double bond and a ring, or two rings.

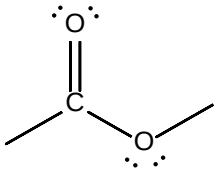
Step 2: Look at IR for relevant peaks

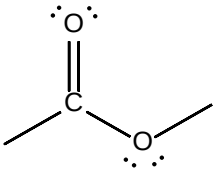
- The large peak at 1743 cm^{-1} strongly suggests a C=O bond. This peak must be due to an ester since that is the only type carbonyl that gives a peak in this region except for anhydride (which would give a second peak above 1800 cm^{-1}) or conjugated acid chloride (which would require a Cl in the molecular formula).
  - There is a peak on the ^{13}C NMR at about 175 ppm. That is consistent with an ester.



Step 3: Recognize symmetry

- The integrals on the ^{1}H NMR are 4 : 4 : 6. That strongly suggests a pair of equivalent CH_2, another pair of equivalent CH_2 and a pair of equivalent CH_3.
- The ^{13}C NMR has four peaks, but the molecular formula has 8C. So, there are only four different environments for eight carbon atoms.
- Both of these points strongly suggest a symmetrical molecule.
- If there are two equivalent carbonyl carbons, that means two esters – which uses up both DU.





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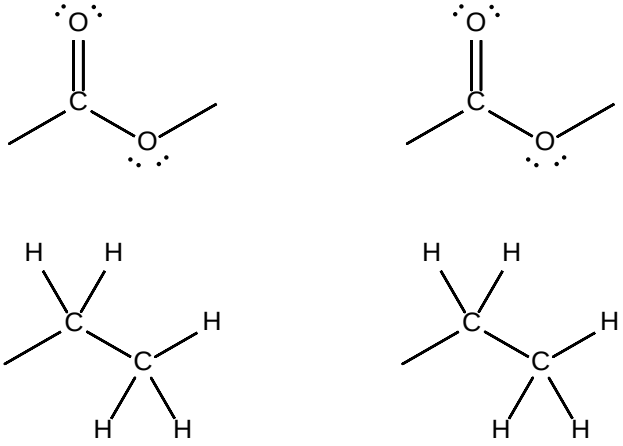
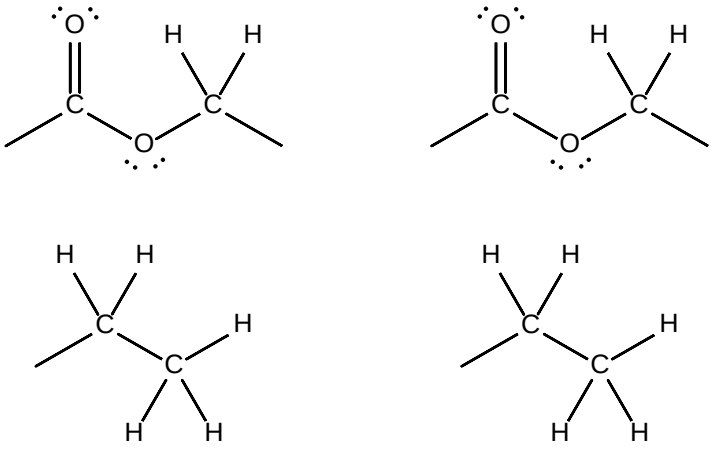
Step 4: Look at ^{1}H NMR to account for remaining atoms

- Calculate integrals! You should get a 2 : 2 : 3 ratio which is doubled because there are 14H in the molecular formula. So, the integrals are 4 : 4 : 6.
- Triplet at ~1.3 ppm integrates to 6H. This strongly suggests two equivalent CH_3 groups, each next to CH_2.
- Quartet at ~2.4 ppm integrates to 4H. This strongly suggests two equivalent CH_2 groups, each next to CH_3.
- Triplet + quartet therefore suggest two equivalent ethyl groups.



- Singlet at ~4.3 ppm integrates to 4H. These must be the remaining H and they must all be shift equivalent. Because the chemical shift is over 4 ppm, it is most likely that these are both CH_2 attached to O.



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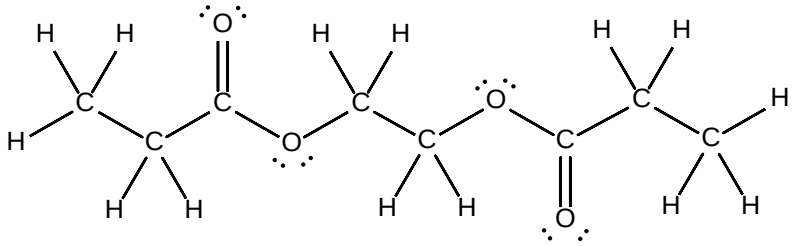
Step 5: Assemble the pieces.

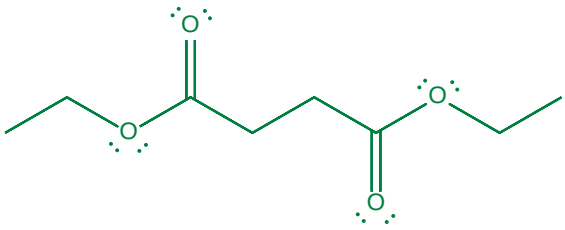
- These pieces consume $C_8H_{14}O_4$, which means that there are no other atoms and all that remains is to assemble the pieces. The ethyl groups cannot be attached to the other CH_2 because, if they did, more coupling would be observed (there would be a triplet, a sextet and another triplet instead of the singlet, quartet and triplet shown on the spectrum). So, the ethyl groups must be attached to the carbonyl carbon atoms – consistent with a chemical shift of ~2.4 ppm for the quartet. This gives:



- The central CH_2 groups are shift equivalent due to symmetry so they do not couple to each other.

Notes and Rants That Everyone Should Read

- If you aren't comfortable calculating integral values from the trails, you should practice. It will make these questions easier.
- CH_2 or CH on the ^{13}C NMR table means on a tetrahedral atom. The C from a CH_2 on the end of a double bond shows up in the "alkene" region (110-150 ppm) on ^{13}C NMR.
- Atoms that are not carbon do not appear on a ^{13}C NMR. I know the data sheet says "alcohol", but we discussed this in class. That means "C attached to O" – like in an alcohol. Also, it does not guarantee an actual alcohol in your molecule; you could have an ether or ester, for example.
- For full marks, it must have been clear that you had good reason to choose this answer and that you had eliminated the alternative below. This is best done by looking at the chemical shifts of the singlet and quartet on the ^1H NMR. The singlet is at ~4.3 ppm; the quartet is at ~2.4 ppm. Therefore, the CH_2 group producing the singlet is attached to O while the CH_2 group producing the quartet is next to a carbonyl carbon.



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$C_8H_{14}O_4$