NAME:______________________ Section:_____ Student Number:_______________

Spring 2017 **Chemistry 2600 Midterm** ____/ 78 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 9 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 7:00pm Mountain Time on Friday, February 10th, 2017. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/78 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: Spring 2017
The University of Lethbridge

Question Breakdown

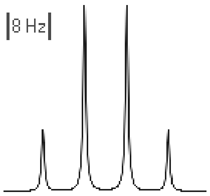
Q1	/ 10
Q2	/ 6
Q3	/ 4
Q4	/ 6
Q5	/ 12
Q6	/ 20
Q7	/ 20

Total	/ 78

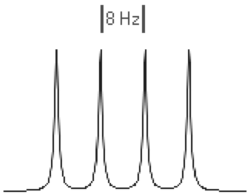
NAME:______________________ Section:_____ Student Number:________________

1. The two signals below both have four lines; however, they communicate different information about the hydrogen atom(s) to which they correspond. **[10 marks]**

Signal A



Signal B



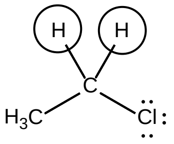
(a) multiplicity: quartet doublet of doublets

coupling constant(s): J = 8 Hz J_{larger} = 16 Hz and $J_{smaller}$ = 8 Hz

If your coupling constants didn't have units, they didn't get marks. Numbers without units are meaningless.

(b) What does Signal A tell you about the hydrogen atom(s) to which it corresponds? Give an example… and circle the hydrogen atom(s) giving that signal.

The hydrogen atom(s) corresponding to Signal A couple to three other hydrogen atoms with the same coupling constant.

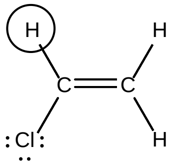


CH_3CH_3 is not a valid example. Equivalent hydrogen atoms don't couple, so the ^1H NMR would just be one singlet.

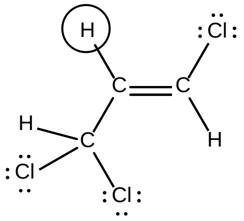
The most common –R groups are CH_3 and CH_2CH_3. So, using –R groups instead of just picking a real molecule did not get full marks (since, in most cases, there would also be coupling to H within the –R group).

(c) What does Signal B tell you about the hydrogen atom(s) to which it corresponds? Give an example… and circle the hydrogen atom(s) giving that signal.

The hydrogen atom(s) corresponding to Signal B couple to two other hydrogen atoms with different coupling constants.



or



While many molecules containing double bonds give doublets of doublets, that's not the only way to get one. That said, two H with a trans relationship across a double bond are the only way you know of to get a coupling constant of 16 Hz.

Coupling between two hydrogen atoms on the same carbon of an alkene is only 0-2 Hz. Signal B does not have any coupling constants that small. So, none of the H not circled would work.

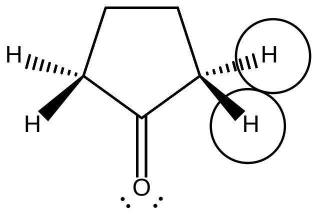
$H_2C{=}CH_2$ is not a valid example. Equivalent hydrogen atoms don't couple, so the ^1H NMR would just be one singlet.

NAME:______________________ Section:_____ Student Number:__________________

2. Below each molecule, write one of the following abbreviations (H, E, D or CD) to indicate the relationship between the circled hydrogen atoms: **[6 marks]**

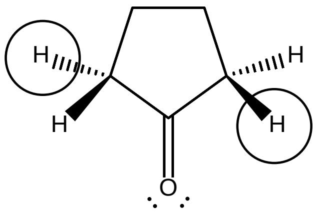
- Homotopic (H)
- Enantiotopic (E)
- Diastereotopic (D)
- Constitutionally different (CD)

(a)



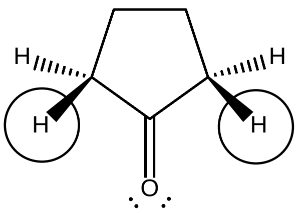
E

(b)



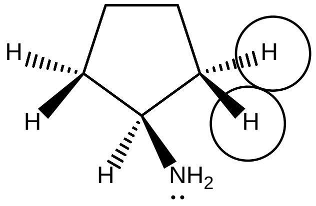
H

(c)



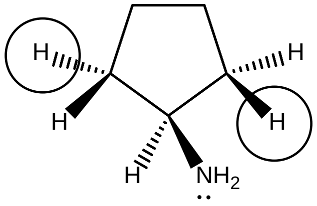
E

(d)



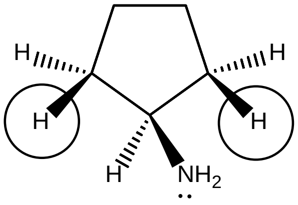
D

(e)



D

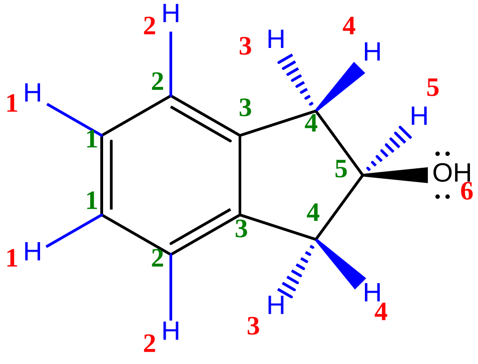
(f)



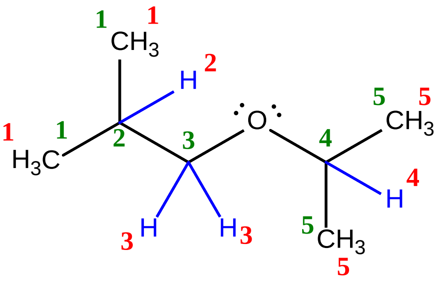
E

3. How many signals would you expect to see on the ^{1}H NMR and ^{13}C NMR spectra for each of the following molecules? *Assume that none of the signals coincidentally overlap.* **[4 marks]**

(a)



(b)

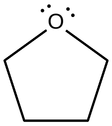


Numbers in red are for hydrogen atoms. Numbers in green are for carbon atoms.

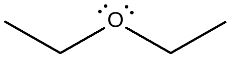
	(a)	(b)
^{1}H NMR	__6__ signals	__5__ signals
^{13}C NMR	__5__ signals	__5__ signals

NAME:____________________________ Section:_____ Student Number:___________________

4. Tetrahydrofuran (THF) and diethyl ether (Et_2O) are commonly used solvents in the organic chemistry lab: **[6 marks]**



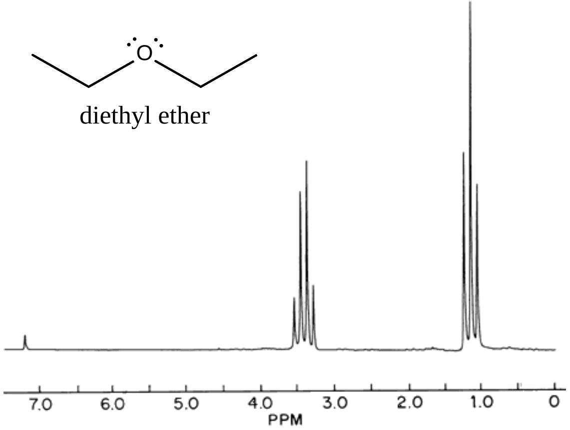
THF

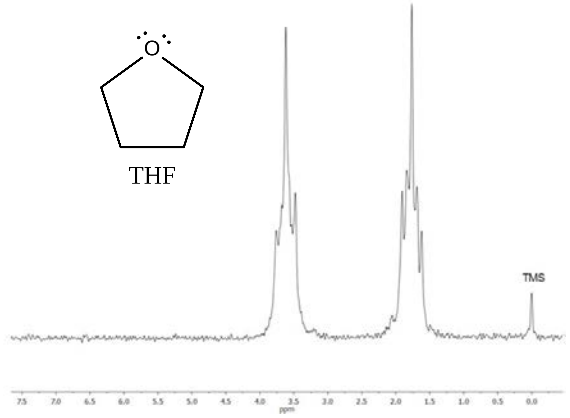


diethyl ether

The ^1H spectra for these two solvents are shown below.

(a) Clearly indicate which spectrum corresponds to which solvent. In the space next to the spectra, explain your reasoning.





Diethyl ether is expected to give a triplet (CH_3 next to CH_2) and a quartet (CH_2 next to CH_3). This spectrum has a triplet and a quartet. The other spectrum does not.

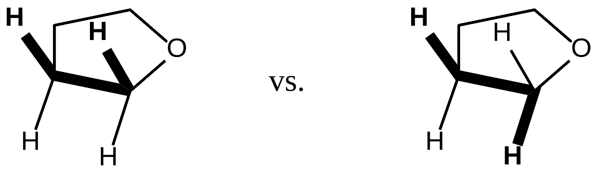
Some people argued that both CH_2 groups in THF will be more deshielded than the CH_3 group in diethyl ether. While this is true (and was given credit), it's not as simple or compelling as looking at the peak shapes.

If you said that THF would give a triplet and a pentet, you lost a mark. Equivalent H do not couple, so there is no way to get a pentet. Besides, the two peaks on the THF NMR are almost identical in shape; they clearly have the same multiplicity.

(b) Explain why the first spectrum has clearly defined peak shapes but the second one does not. Why do we not see clearly defined peak shapes on the second spectrum?

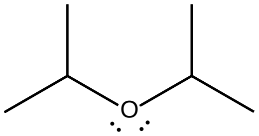
In diethyl ether, all the bonds can rotate freely. Thus, all coupling constants are based on average dihedral angles.

THF is a ring, so free rotation about the C-C or C-O bonds in the ring is not possible. As such, the dihedral angles between C-H bonds on neighbouring carbon atoms are not all the same. Since coupling constants are based on bond angles, we get different coupling constants between H that have a *cis* relationship and between H that have a *trans* relationship:

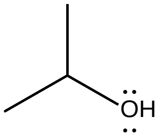


5. *I am listing many reasonable answers. You needed two (using different types of spectroscopy).*

(a)



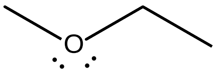
vs.



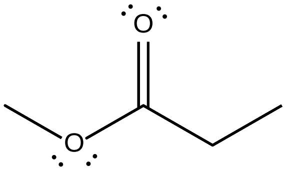
IR	no O-H stretch	O-H stretch at 3200-3500 cm^{-1}
^{1}H NMR	2 signals (doublet and septet)	3 signals (doublet, septet, broad singlet)
	No broad singlet for OH	OH gives a broad singlet that disappears with D_2O shake
MS	Molecular ion is m/z 102	Molecular ion is m/z 60

The ^{13}C NMR for these two molecules are expected to be <u>very</u> similar. Both will have two signals, one in the CH_3 range and one in the "C attached to O" range.

(b)

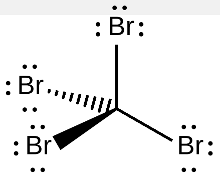


vs.

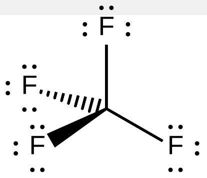


IR	no C=O stretch	C=O stretch at about 1730-1750 cm^{-1}
^{13}C NMR	3 signals	4 signals
	No signals downfield of 100 ppm	C=O signal at about 160-180 ppm
^{1}H NMR	Quartet is at about 3.5 ppm Singlet is at about 3.3 ppm	Quartet is at about 2.2 ppm Singlet is at about 3.7 ppm
MS	Molecular ion is m/z 60	Molecular ion is m/z 88

(c)



vs.



^{13}C NMR	Br is less electronegative than F, so the signal for CBr_4 will be upfield of that for CF_4.	F is more electronegative than Br, so the signal for CF_4 will be downfield of that for CBr_4.
	Signal is a singlet.	Signal will be a pentet due to coupling with four ^{19}F atoms.
MS	Molecular ion is m/z 328	Molecular ion is m/z 88
	Br exists as a 1 : 1 mixture of ^{79}Br and ^{81}Br, so we see a 1 : 4 : 6 : 4 : 1 ratio of $[M]^+$: $[M+2]^+$: $[M+4]^+$: $[M+6]^+$: $[M+8]^+$	^{19}F is the only naturally occurring isotope of F, so there will be no signals at $[M+2]^+$, $[M+4]^+$, etc.

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6. The following **two** pages contain spectra for Unknown X. **[20 marks]**

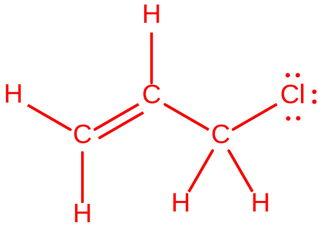
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your logic (including how you determined the molecular formula).

(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 and Mass Spectrum.

Unknown X:



General breakdown of marks:
1 mark for correct answer
2 marks for MS peak assignments
2 marks for IR peak assignments
4 marks for ^{1}H NMR assignments (correct for correct answer;
"reasonable" for incorrect answers)
3 marks for ^{13}C NMR assignments (correct for correct answer;
"reasonable" for incorrect answers)
8 marks for logic (this page plus legible rough work on spectra, etc.); 4 marks for how to get to C_3H_5Cl

One Way to Arrive at the Answer

Step 1: Work out the Molecular Formula

- Molecular ion appears to be m/z 76 (with an $[M+2]^+$ peak about one third as high)
- $[M]^+$: $[M+2]^+$ appears to be 3 : 1 therefore there is probably one Cl (this is backed up by the presence of a tall peak at m/z 41 (76 – 35 = 41; 78 – 37 = 41)
- ^{13}C NMR shows three signals, so there are at least three C
- ^{1}H NMR has integrals adding up to 5, so there are at least five H
- C_3H_5Cl = 76 g/mol (for ^{35}Cl)

Step 2: Calculate Unsaturation Index (Degrees of Unsaturation)

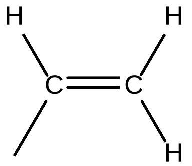
- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(3)+2-1-5}{2} = \frac{2}{2} = 1$
- Therefore, there is either a double bond or a ring in this molecule

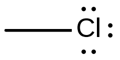
Step 3: Look for Presence/Absence of Alkene

- IR shows C=C at about 1650 cm^{-1} and has C-H stretch above 3000 cm^{-1}
- ^{13}C NMR has two signals in the C=C region, one at ~120 ppm and one at ~135 ppm
- ^{1}H NMR has three signals in the vinyl region (5-6 ppm), each integrating to 1H
- Therefore, there is certainly a C=C double bond in this molecule (and it has 3 H attached).

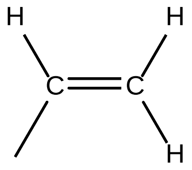
Step 4: Put Together the Pieces

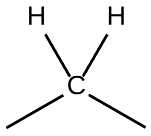
- So far, we have two pieces:

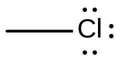




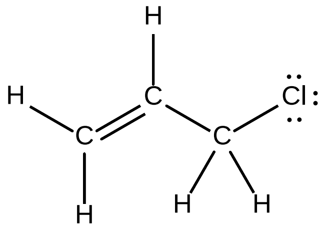
- The remaining atoms are CH_2, so there ought to also be a CH_2 group (confirmed by doublet integrating to 2H on ^{1}H NMR).
- That gives three pieces in total:







- There is only one way to assemble them:



Notes and Rants That Everyone Should Read

- Follow the instructions! You were given a box on each NMR in which to draw the molecule and label it. Flipping pages back and forth and trying to guess whether you meant that a C was #1 or an H was #1 is **very** difficult and makes it take longer for you to get your test back.
- If you're not given a molecular formula but you are given a molar mass (or mass spectrum with molecular ion), start by finding the molecular formula. It will make your life much easier since you know you can rule out functional groups containing atoms (or degrees of unsaturation) your molecule doesn't have. Your ^{13}C NMR gives you a minimum number of carbon atoms, and your ^{1}H NMR gives you a minimum number of hydrogen atoms (by adding the integrations; also, your total number of hydrogen atoms must be a multiple of the sum of the integrations).
- While we don't typically care about C-H peaks between 2900-3000 cm^{-1} on an IR (tetrahedral C), C-H peaks above 3000 cm^{-1} carry important information about the presence of either an alkene (3000-3100 cm^{-1}) or alkyne (near 3300 cm^{-1}). Similarly, a C-H peak at around 2800 cm^{-1} could suggest an aldehyde – though, admittedly, there are better ways to look for an aldehyde.
- Even if you can't measure an exact coupling constant on ^{1}H NMR, look at how widely spaced the lines are. The bigger the distance between lines, the bigger the coupling constant. This can be used to assign, for example, which H is *cis* to another H vs. which H is *trans* to it.
- A sextet has six lines in the pattern 1 : 5 : 10 : 10 : 5 : 1. There was no sextet on this ^{1}H NMR. There was a doublet of doublets of triplets – but you couldn't tell that until you got the answer. "Multiplet" is the term for "peak that's too messy to figure out the coupling".
- Benzene is not the only ring that exists!!! Less than 4 degrees of unsaturation or less than 6 carbon atoms does not mean "no ring"!!! A ring is just one degree of unsaturation. See question 4 for a ring that is not benzene. I am *so* tempted to put a cyclic compound on your final...

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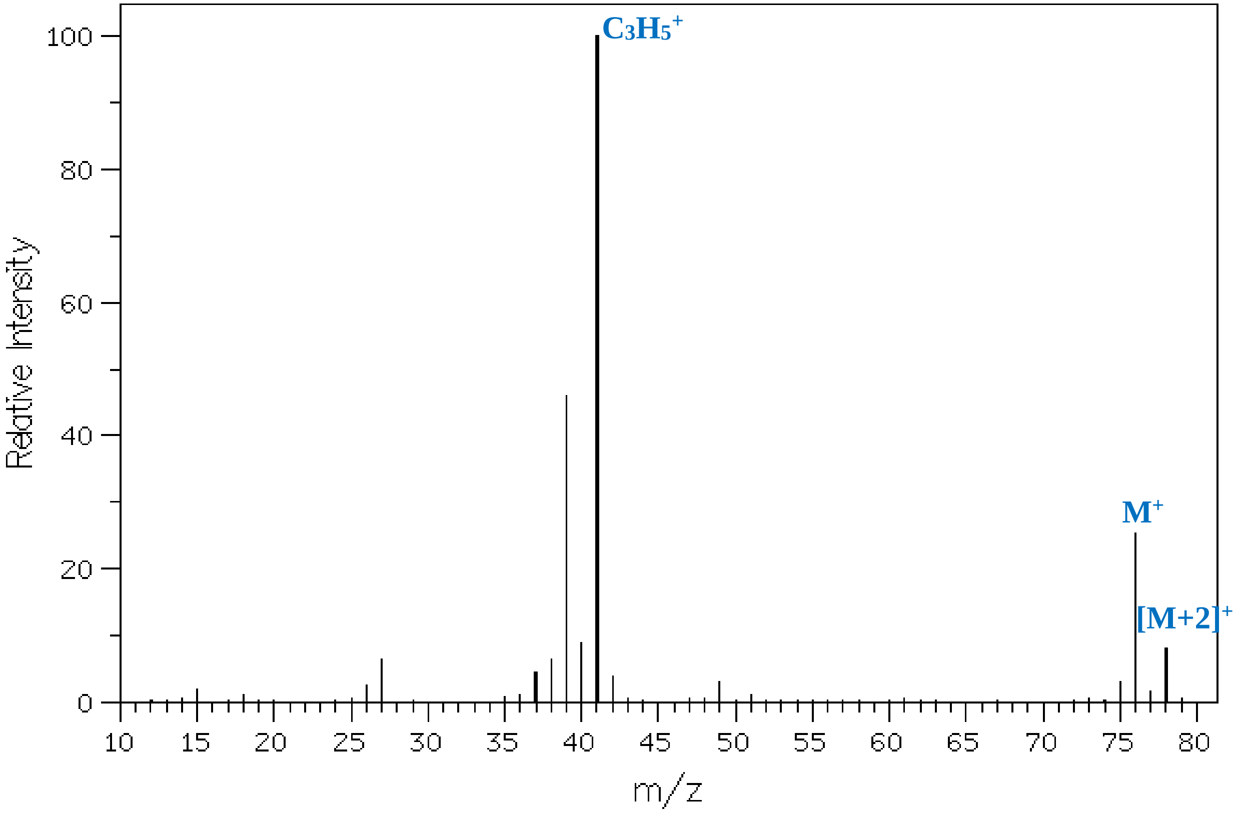
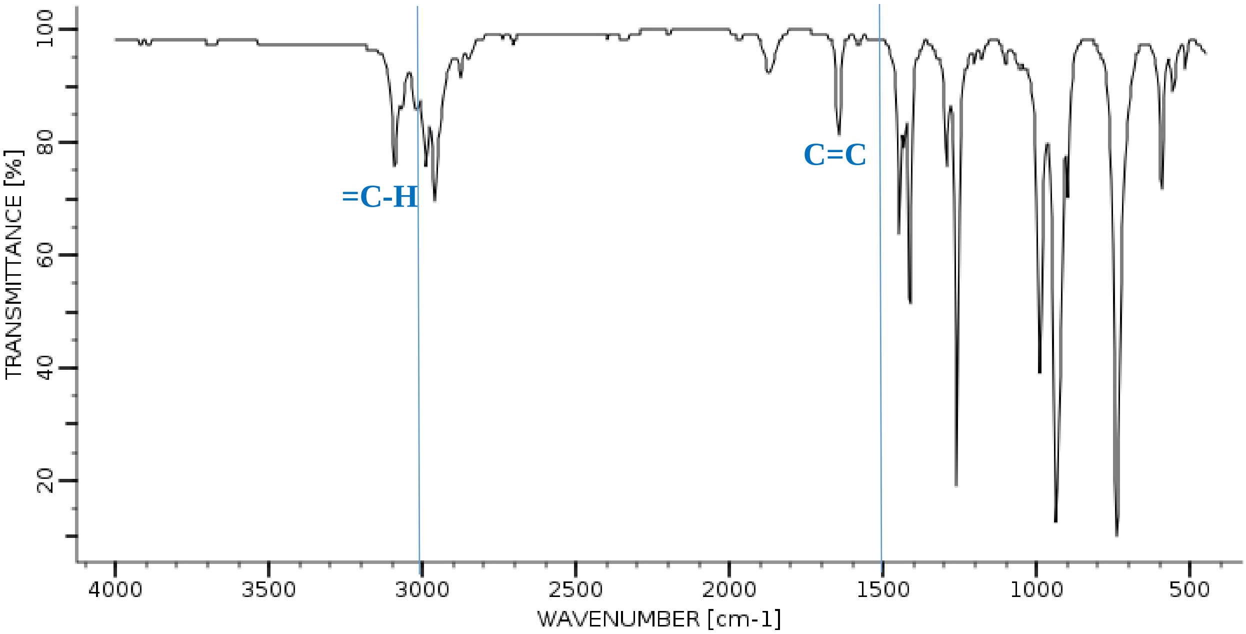
Mass Spectrum



IR



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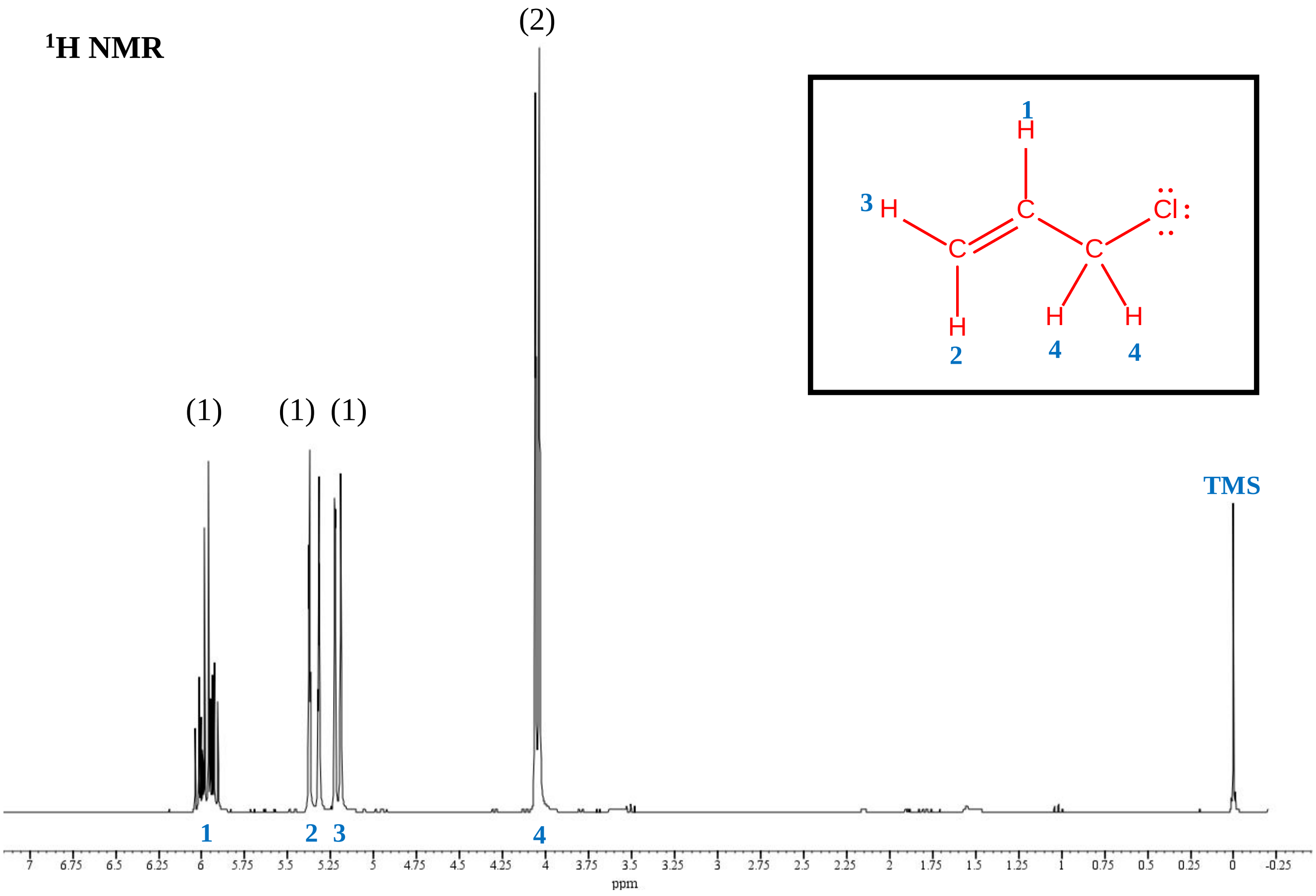
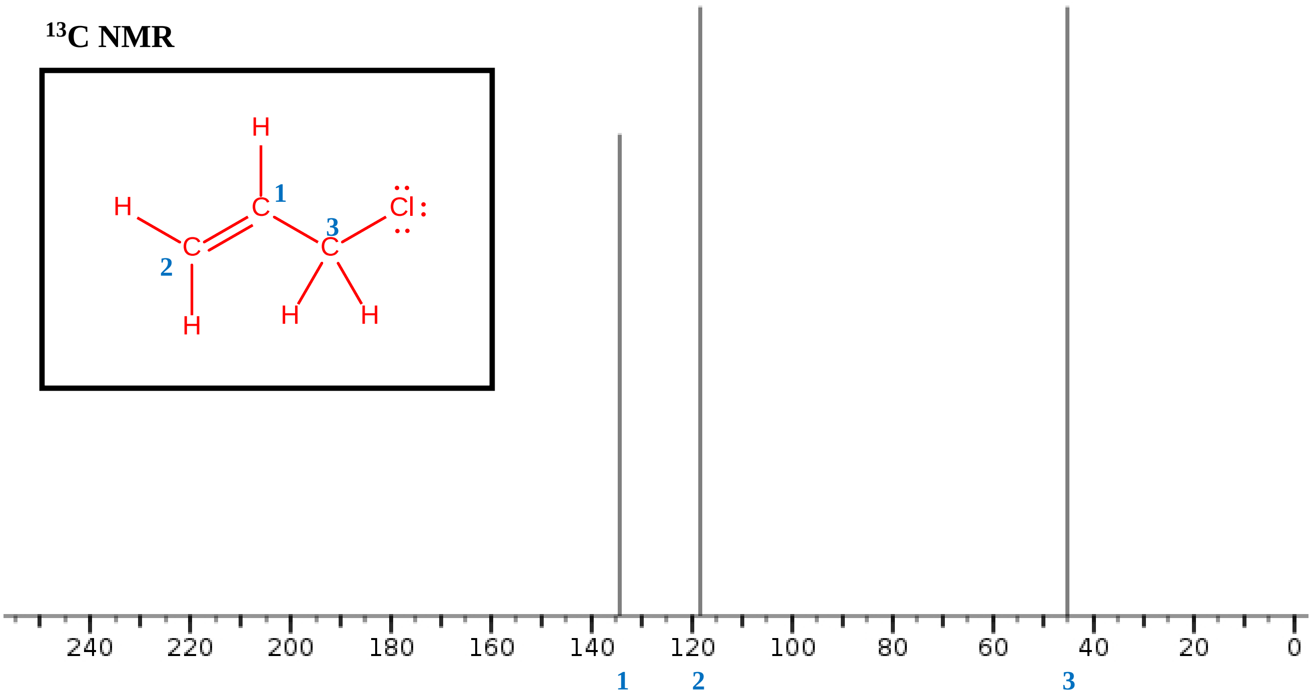
^{1}H NMR



^{13}C NMR



NAME:____________________________ Section:_____ Student Number:___________________

7. The following page contains NMR spectra for Unknown Y ($C_6H_{10}O_3$). **[20 marks]**

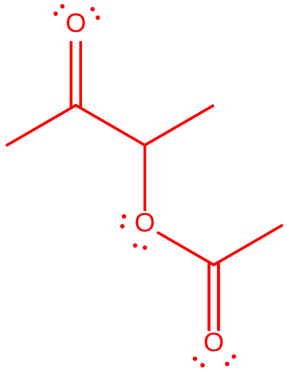
(a) Identify Unknown Y based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your logic.

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown Y 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.*

General breakdown of marks:
1 mark for correct answer
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)
12 marks for logic (this page plus legible rough work on spectra, etc.)

Unknown Y:



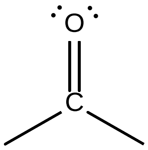
One Way to Arrive at the Answer

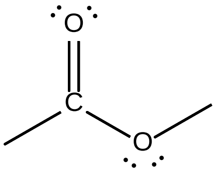
Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(6)+2-10}{2} = \frac{4}{2} = 2$
- Therefore, there is either a triple bond, two double bonds, a double bond and a ring, or two rings in this molecule

Step 2: Look at ^{13}C NMR for C=C, C≡C or C=O peaks

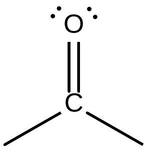
- The two peaks above 160 ppm are most likely C=O signals; this accounts for both degrees of unsaturation.
    - Signal at 205 ppm is either ketone or aldehyde. No signal for aldehyde on ^{1}H NMR (between 9-10 ppm), so C=O is ketone.
    - Signal at 170 ppm is either carboxylic acid or ester (since no N in molecule). No signal for carboxylic acid on ^{1}H NMR (broad singlet above 10 ppm), so C=O is ester.

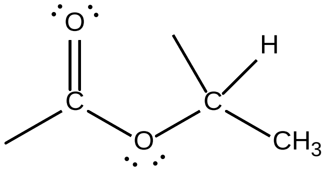




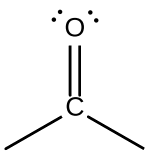
Step 3: Look at ^{1}H NMR to account for remaining atoms (C_4H_{10})

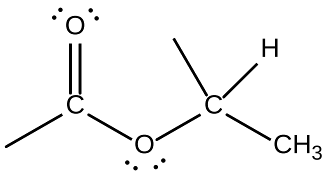
- Doublet at 1.4 ppm integrates to 3H; quartet at 5.1 ppm integrates to 1H. No other coupling is observed. This must be a CH_3CH group. 5.1 ppm is very far downfield (usually vinyl H are found here, but there are no degrees of unsaturation left). CH must be attached to an oxygen atom. CH attached to O of ester is ~4.8 ppm, so this is not too far off.

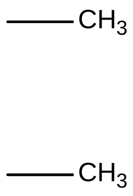




- Remaining two peaks are singlets each integrating to 3H at 2.14 ppm and 2.17 ppm. That must be two methyl groups attached to carbon atoms with no H. (i.e. not to the CH)



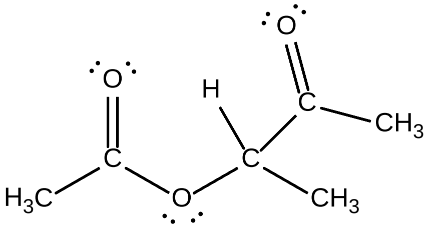




- This uses up all of the atoms.

Step 4: Assemble the pieces.

- There is only one way to assemble the pieces if neither –CH_3 can be attached to CH:



- This also works well for the chemical shifts of the two methyl singlets since CH_3 next to a carbonyl typically appear in the 2-2.5 ppm range.

Notes and Rants That Everyone Should Read

- You CANNOT definitively assign the two CH_3 singlets on the ^{1}H NMR. They are only 0.03 ppm apart! I don't care that the data sheet says 2.0 ppm for one type and 2.2 ppm for the other type. It's not accurate enough to be able to distinguish peaks that are 0.03 ppm apart.
- Similarly, you CANNOT definitively assign the three CH_3 peaks on the ^{13}C NMR. The one not next to a carbonyl is *probably* farthest upfield – but even that's subject to the conformation of the molecule.
- Several people thought that "ester" referred to C-O-C (which is actually an ether). You have to know your functional groups! Especially if you're going to rely on reading tables rather than having done enough practice problems to "just know" that all almost peaks over 160 ppm on a ^{13}C NMR are some sort of carbonyl.
- 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.
- O-H protons do not couple on ^{1}H NMR. If a peak is a quartet/doublet/multiplet/etc, it's not OH.
- If you have a C=C double bond, you need TWO peaks in the C=C region (110-150 ppm) on your ^{13}C NMR unless your double bond is symmetrical, making the two carbon atoms homotopic. Having a heteroatom (O, Cl, etc.) attached to an alkene carbon might shift it slightly farther downfield (*maybe* up to 160 ppm – or 170 ppm if there were two heteroatoms on the same carbon) – but nothing will pull it upfield to 75 ppm or as far downfield as 205 ppm!)
- If you have a peak in the ketone/aldehyde range on ^{13}C NMR, look for an aldehyde H (narrow peak at 9-10 ppm) on the ^{1}H NMR. If present, you have aldehyde. If absent, you have ketone.

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- If you have a peak in the carboxylic acid/ester/amide range on ^{13}C NMR, look for a carboxylic acid H (broad singlet >10 ppm) on the ^{1}H NMR. If present, you have carboxylic acid. If absent, you have ester or amide. Molecular formula and/or IR can tell you which.
- Being attached to an oxygen atom is much more deshielding than being next to a C=O group. OCH_3 is always downfield of 3 ppm on ^{1}H NMR. CH_3 next to C=O (and nothing else deshielding) will usually be closer to 2 ppm.

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$C_6H_{10}O_3$