

NAME: _____ Section: _____ Student Number: _____

Fall 2019

Chemistry 2600 Midterm

_____/ 65 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 8 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.
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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 Tuesday, October 8th, 2019. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/65 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 2019

The University of Lethbridge

Question Breakdown

Q1	/ 12
Q2	/ 6
Q3	/ 8
Q4	/ 19
Q5	/ 20

Total	/ 65
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1. *I am listing many reasonable answers. You needed two (using different types of spectroscopy).*

(a)



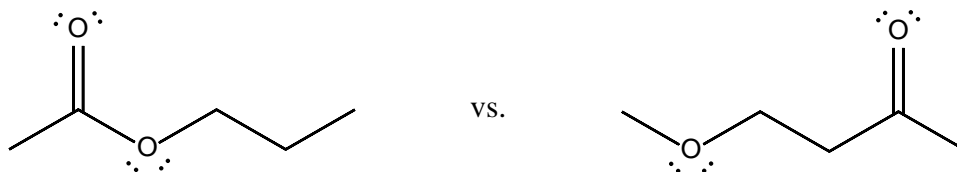
¹H NMR The most deshielded peak is a quartet at ~3.4 ppm (for CH₂O). The most deshielded peak is a quartet at ~1.3 ppm (for CH₂).

¹³C NMR The most deshielded peak (for CH₂O) should appear between 60 and 80 ppm. The most deshielded peak (for CH₂) should appear between 25 and 45 ppm.

MS Molecular ion is m/z 74. Molecular ion is m/z 58.

Because the two CH₂ groups in the middle of butane are shift equivalent, they do not couple to each other. So, both molecules give a triplet and quartet with integral ratios of 3 : 2.

(b)



¹H NMR Splitting patterns and integrations:

<ul style="list-style-type: none"> • Singlet integrating to 3H • Triplet integrating to 2H • Sextet integrating to 2H • Triplet integrating to 3H 	<ul style="list-style-type: none"> • Singlet integrating to 3H • Triplet integrating to 2H • Triplet integrating to 2H • Singlet integrating to 3H
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<p>One peak downfield of 3ppm:</p> <ul style="list-style-type: none"> • Triplet (2H) at ~4.1 ppm 	<p>Two peaks downfield of 3ppm:</p> <ul style="list-style-type: none"> • Singlet (3H) at ~3.3 ppm • Triplet (2H) at ~3.4 ppm
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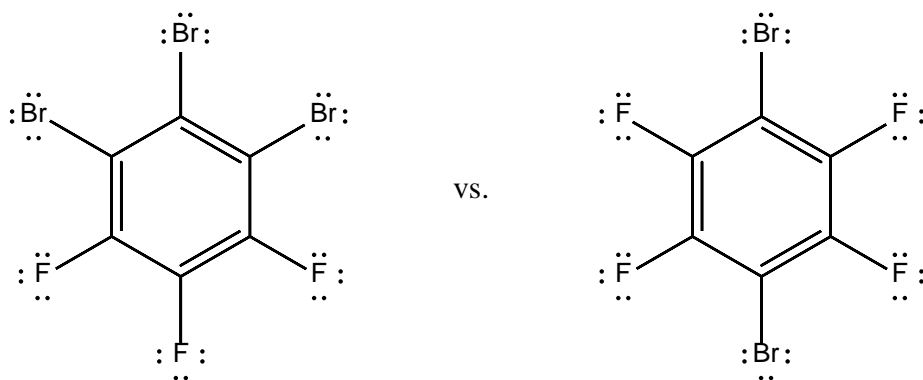
¹³C NMR Carbonyl C for ester is expected to appear between 155 and 175 ppm, so if the carbonyl C appears below 175 ppm, it is this isomer. Carbonyl C for ketone is expected to appear between 175 and 220 ppm, so if the carbonyl C appears above 175 ppm, it is this isomer.

IR An unconjugated ester gives a C=O stretch between 1735 and 1750 cm⁻¹. An unconjugated ketone gives a C=O stretch between 1705 and 1725 cm⁻¹.

Several students listed overly broad ranges for the C=O stretches on IR. These C=O groups are not conjugated (not part of a larger pi system), so only the dark bars on the data table apply to them. (The light bars are for conjugated C=O groups.)

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(c)



¹³C NMR 4 peaks

2 peaks

MS Molecular ion is m/z 366.

Molecular ion is m/z 306.

M^+ : $[M + 2]^+$: $[M + 4]^+$: $[M + 6]^+$ is
1: 3: 3: 1 (because there are three Br)

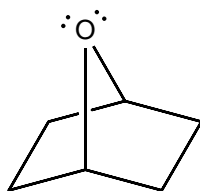
M^+ : $[M + 2]^+$: $[M + 4]^+$ is 1: 2: 1
(because there are two Br)

When calculating molecular ion values, remember to use the mass of the lightest isotope of each element – NOT the average atomic mass listed on the periodic table – for Cl and Br.

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2. Consider the following molecule:

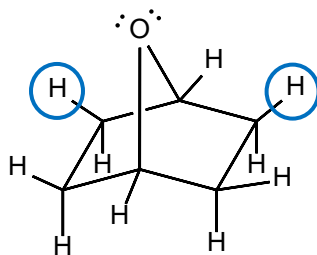
[6 marks]



*A representative correct answer is shown for each part of this question.
There are many acceptable combinations for each.*

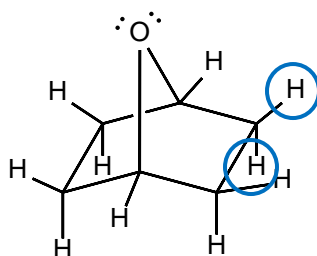
(a) On the picture below, circle two hydrogen atoms which are enantiotopic:

[2 marks]



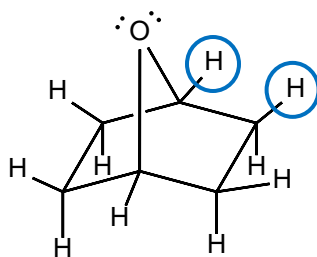
(b) On the picture below, circle two hydrogen atoms which are diastereotopic:

[2 marks]



(c) On the picture below, circle two hydrogen atoms which are constitutionally different:

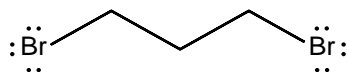
[2 marks]



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3. Consider the following molecule:

[8 marks]



- (a) If you were to analyze this molecule by mass spectrometry, what would you expect to see **in the molecular ion region**? Your answer should address both the value(s) at which you would see peaks and the ratio of those peaks. [4 marks]
You do not need to explain your answer.

Because there are two bromine atoms, $M^+ : [M + 2]^+ : [M + 4]^+$ is 1: 2: 1

Those peaks are found at m/z 200, 202 and 204

Many students answered this question by sketching a picture showing the three peaks with the middle one twice as tall and labeling the peaks as m/z 200, 202 and 204. That was, by far, the clearest way to answer this question.

- (b) Identify two fragments you would also expect to see on the mass spectrum. For each, identify **both** the value for the peak **and** the chemical formula for the fragment (or draw it). [4 marks]
You do not need to explain your answer.

Remember that each fragment needs to be made by a piece breaking off the molecule. So, while there are two bromine atoms in this molecule, you will not see a fragment for Br_2 (for example). Common good answers included:

m/z 121 for $[^{79}BrCH_2CH_2CH_2]^+$

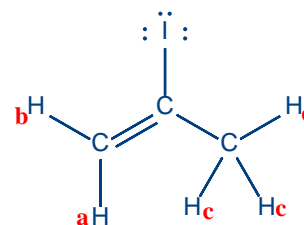
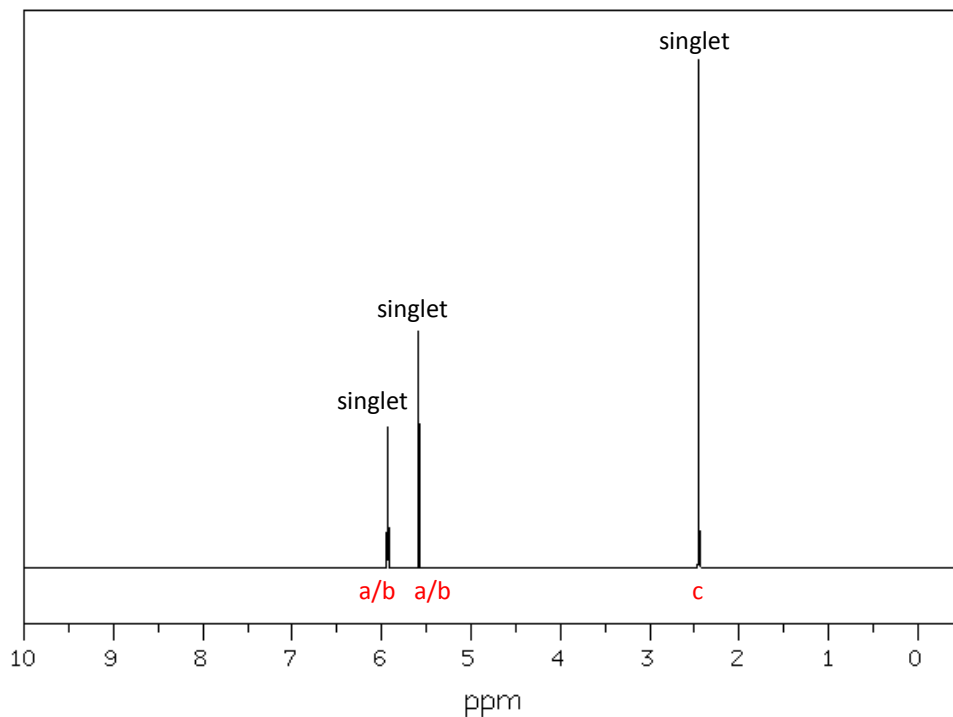
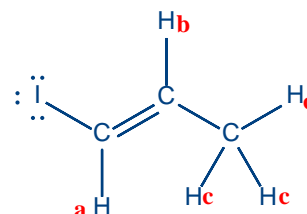
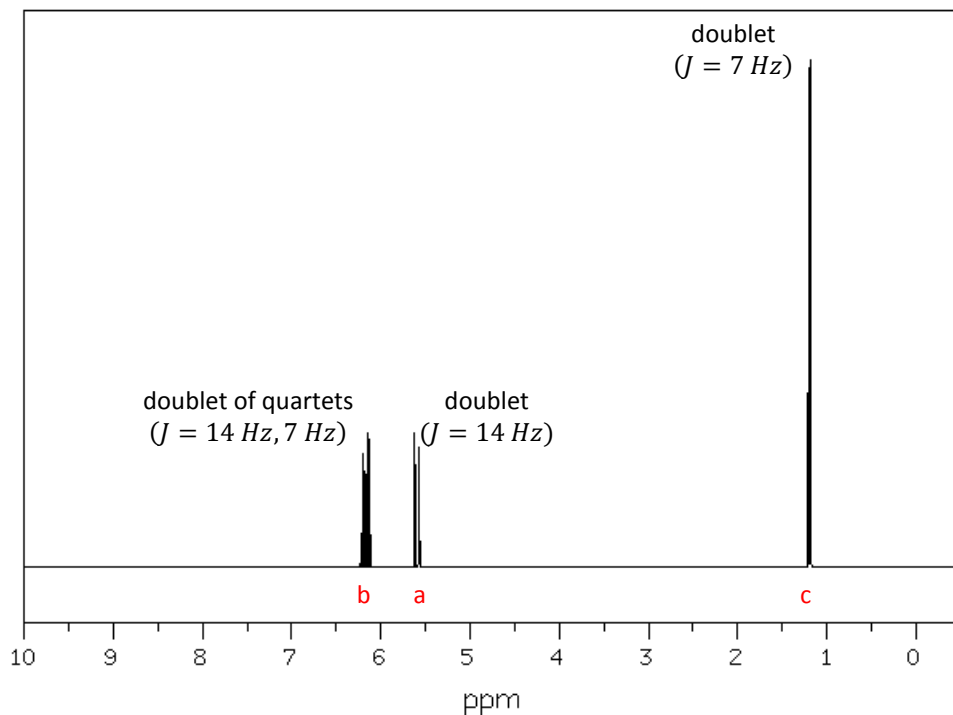
m/z 42 for $[CH_2CH_2CH_2]^+$

m/z 107 for $[^{79}BrCH_2CH_2]^+$

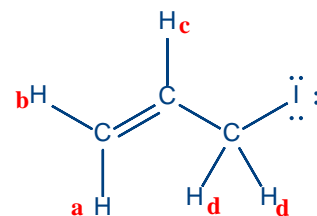
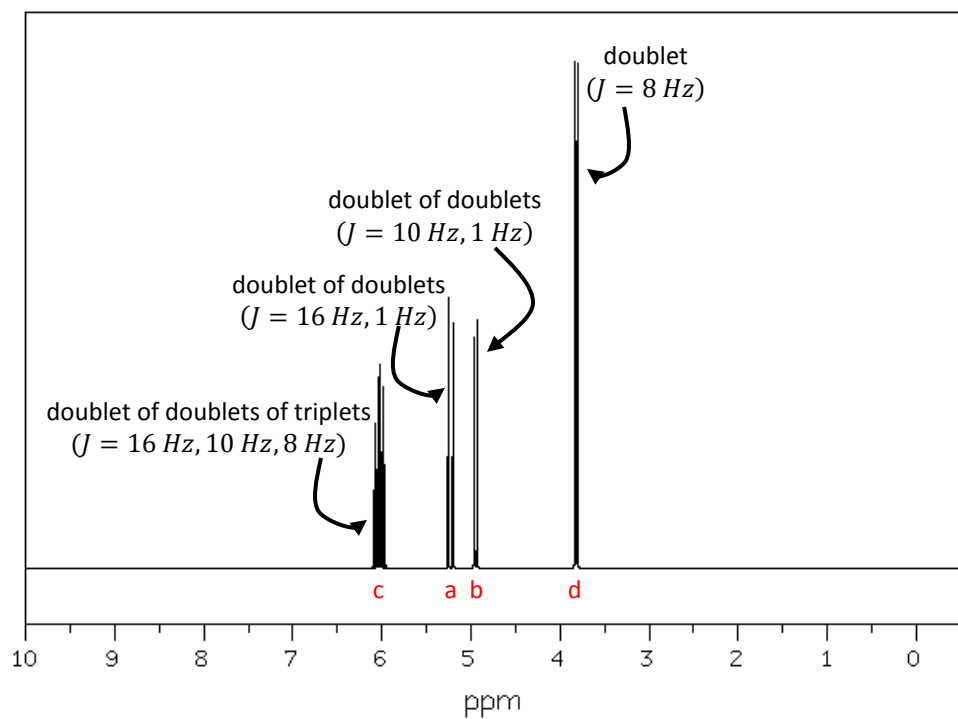
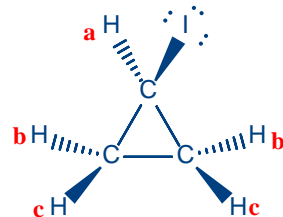
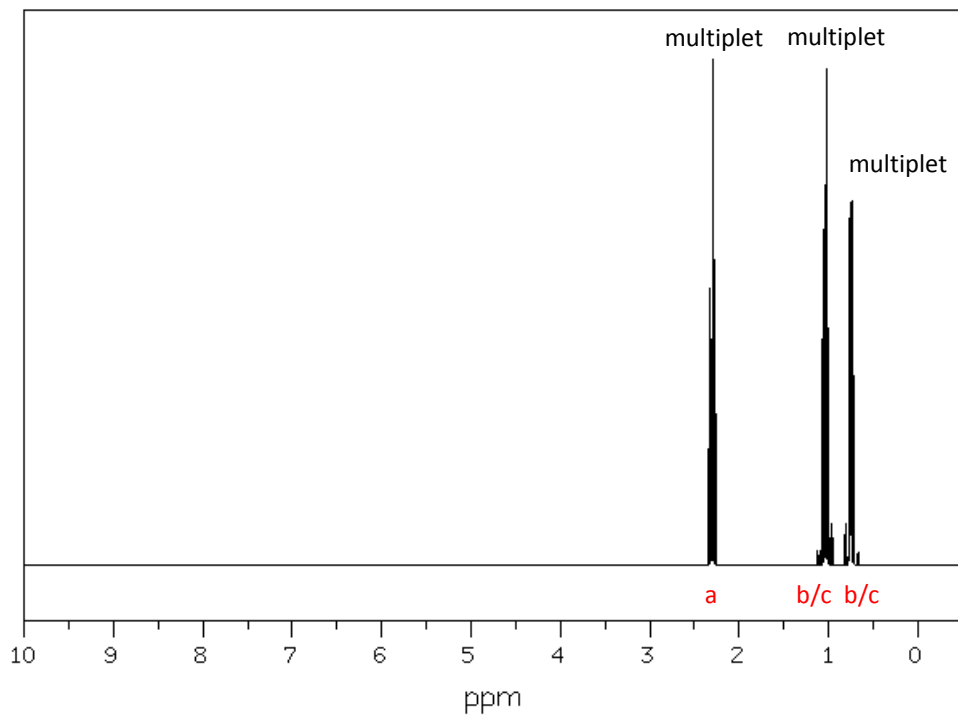
m/z 93 for $[^{79}BrCH_2]^+$

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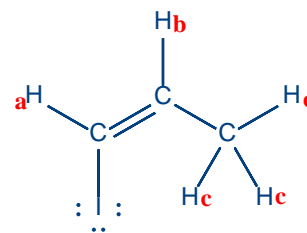
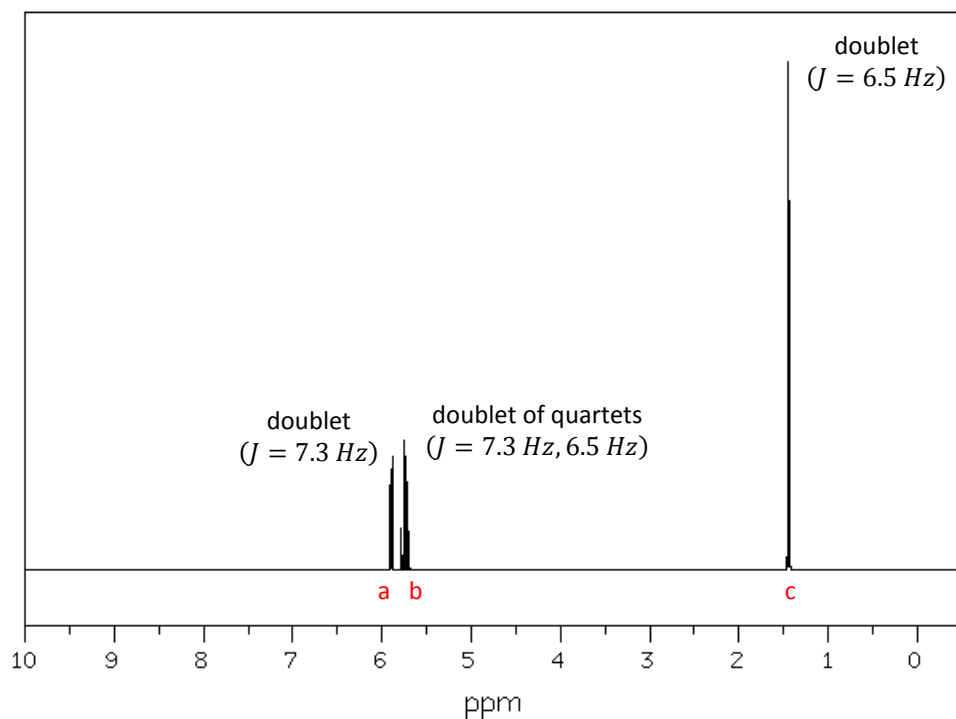
4. Including stereoisomers, five isomers are possible for C_3H_5I . 1H NMR spectra for these five isomers are shown on the next three pages. Multiplicity and coupling constants (where applicable) are listed above each peak; integration is listed below. Next to each spectrum, draw the isomer to which it corresponds. Label each hydrogen (or set of shift equivalent hydrogens) with a unique number or letter. Use these labels to identify the 1H NMR peak corresponding to each hydrogen. In cases where it is not possible to know which of two hydrogen atoms made each of two peaks, label both peaks with both options. **[19 marks]**



4. ...continued...

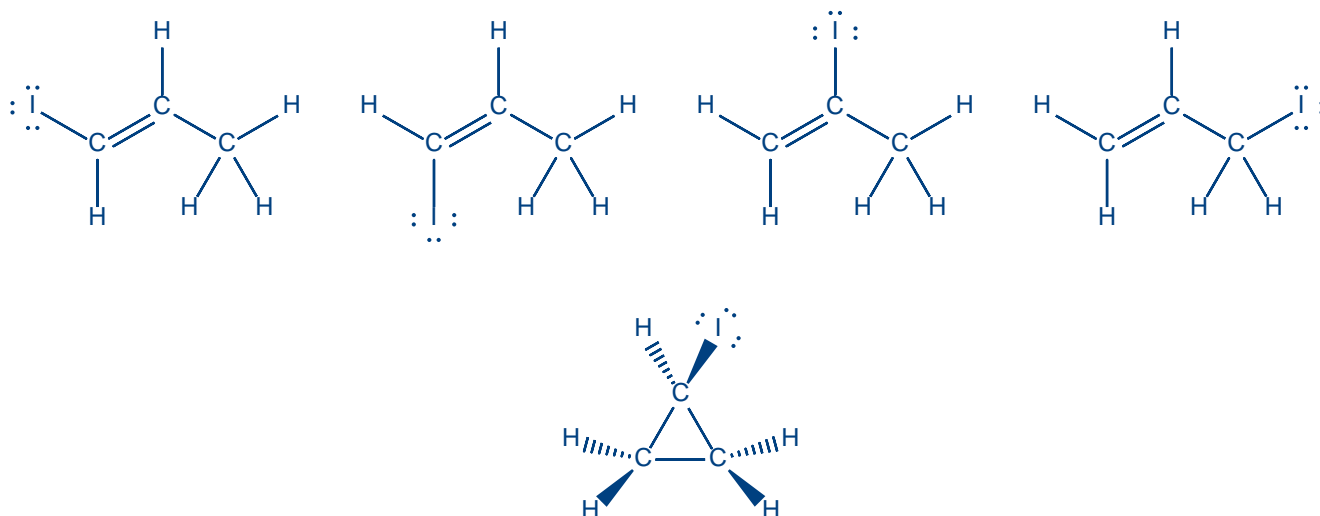


4. ...continued



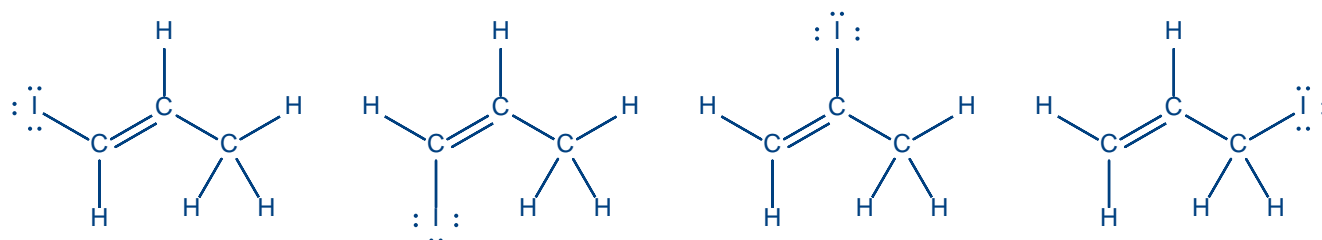
In my opinion, the easiest way to answer this question was to start by drawing the five isomers of C₃H₅I then to look for distinguishing characteristics of each isomer (number of expected peaks, chemical shift of expected peaks, multiplicity of expected peaks, etc.) that would allow you to match it to a spectrum.

Step 1: Draw the five isomers of C₃H₅I

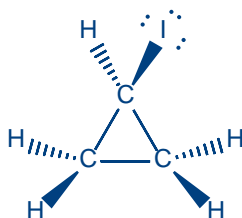


Step 2: Match spectra to isomers**Third Spectrum**

Four of the isomers are alkenes and are expected to produce ^1H NMR spectra with peaks in the vinyl region (5-6 ppm for unconjugated alkenes):



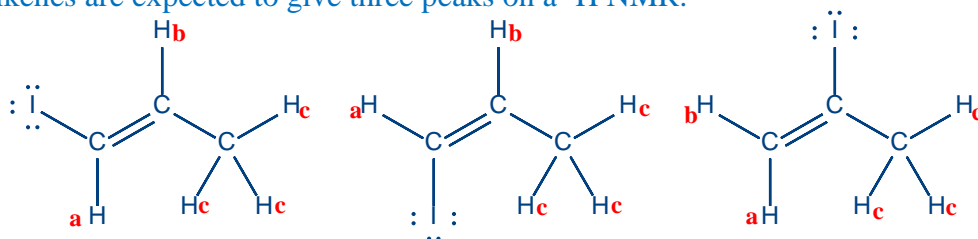
One does not:



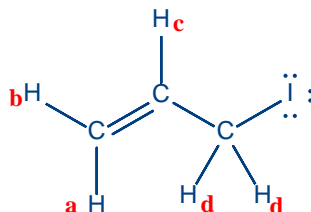
Of the five spectra, only one has no peaks above 5 ppm. So, the third spectrum must correspond to iodocyclopropane. The H attached to the same C as the I should give the peak at ~2.2 ppm. The other two peaks will correspond to the other four hydrogen atoms. Note that the two hydrogen atoms *cis* to I will give one peak and the two hydrogen atoms *trans* to I will give the other. (*Many students suggested that the H cis to I would be more deshielded than those trans to it. That turns out not to be the case, likely due to the length of the C-I bond.*)

Fourth Spectrum

Three of the alkenes are expected to give three peaks on a ^1H NMR.



One is expected to give four peaks:

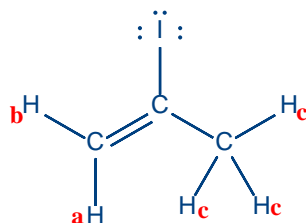


Of the remaining spectra, only one has four peaks. So, the fourth spectrum must correspond to 3-iodopropene. The doublet integrating to 2H at ~3.8ppm corresponds to H_d . The doublet of doublet of triplets must correspond to H_c . The remaining peaks are both doublets of doublets, suggesting that long range coupling between H_d and H_a/H_b is not observed (consistent with the H_d peak being a doublet). One peak has coupling constants of 16 Hz and 1 Hz; the other has coupling constants of 10 Hz and 1 Hz. As such, H_a and H_b must couple to each other with a coupling constant of 1 Hz. The other coupling constant for each peak will represent the coupling constant of that hydrogen to H_c . The larger coupling constant should be for the hydrogen *trans* to H_c .

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Second Spectrum

The second spectrum has three peaks, all of which are singlet. Of the remaining three alkenes, only one can reasonably produce that spectrum:

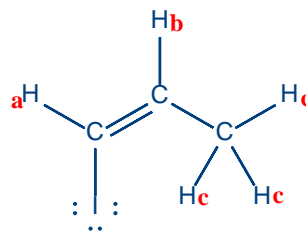
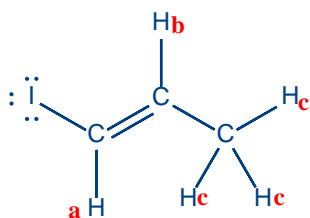


So, the second spectrum must correspond to 2-iodopropene. H_a and H_b are expected to experience 2-bond coupling, but the coupling constant for geminal vinyl coupling is typically very small so it must just not be visible on this spectrum. Similarly, long-range coupling between H_c and H_a/H_b is expected but could have a very small coupling constant and not be visible on the spectrum.

The singlet at 2.5 ppm integrating to 3H corresponds to H_c . The other two peaks correspond to H_a and H_b ; it is not obvious which is which.

First and Fifth Spectra

That leaves *trans*-1-iodopropene and *cis*-1-iodopropene



Both are expected to give three peaks:

- A peak at ~1.6 ppm integrating to 3H that is either a doublet (if no long-range coupling observed) or a doublet of doublets (if long-range coupling observed). This corresponds to H_c .
- A doublet of triplets integrating to 1H in the 5-6 ppm region. This corresponds to H_b .
- A doublet (or doublet of quartets) integrating to 1H in the 5-6 ppm region. This corresponds to H_a .

The key difference between the two spectra will be the coupling constant between H_a and H_b . When those two hydrogen atoms are *trans* to each other, the coupling constant is large (~12-18 Hz). When those two hydrogen atoms are *cis* to each other, the coupling constant is smaller (~6-12 Hz).

Therefore, the first spectrum (with a coupling constant of 14 Hz between H_a and H_b) must correspond to *trans*-1-iodopropene while the fifth spectrum (with a coupling constant of 7 Hz between H_a and H_b) must correspond to *cis*-1-iodopropene.

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5. The following page contains spectra for Unknown X ($C_8H_{10}O$). [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.

General breakdown of marks:

1 mark for correct answer

1 marks for IR peak assignment

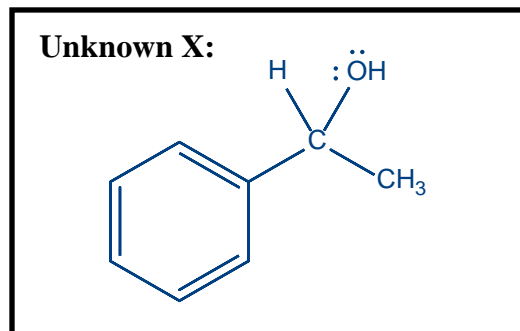
4 marks for 1H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)

4 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)

1 mark for calculating DU

1 mark for calculating integrals

8 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)

$$DU = \frac{2C + 2 + N - X - H}{2} = \frac{2(8) + 2 - 10}{2} = \frac{8}{2} = 4$$

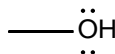
- Each degree of unsaturation corresponds to either a pi bond (double bond = 1 DU; triple bond = 2 DU) or a ring.

Step 2: Calculate the integrals on the 1H NMR

- From left to right, you should get 5 : 1 : 1 : 3.

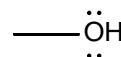
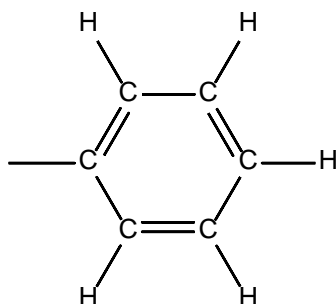
Step 3: Look at IR for relevant peaks

- The large broad peak at 3325 cm^{-1} strongly suggests an O-H bond.
 - There is a peak on the 1H NMR at ~ 3.2 ppm that exchanges with D_2O . That is also consistent with an alcohol.



Step 4: Given that there $DU \geq 4$, look for aromatic peaks on 1H NMR and ^{13}C NMR

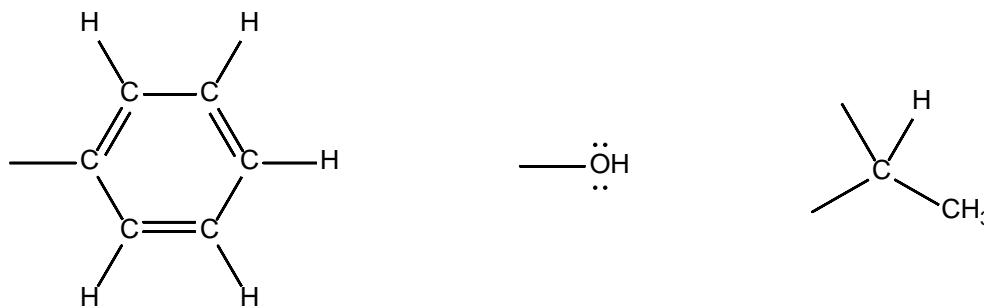
- There is a large peak at ~ 7.4 ppm (or possibly a large one and a small one) integrating to 5H.
- There are four peaks between 120 and 150 ppm on the ^{13}C NMR spectrum.
- These two pieces of information suggest a monosubstituted benzene ring.



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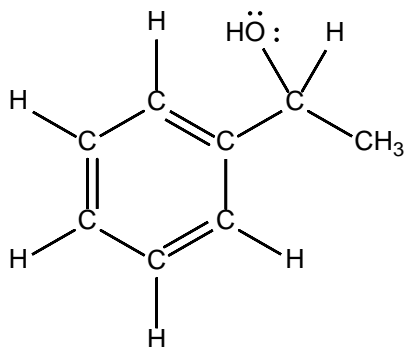
Step 5: Consider the remaining peaks on the ^1H NMR spectrum

- Two C and four H remain of the molecular formula. The remaining peaks on the ^1H NMR are as follows:
 - Quartet integrating to 1H at ~ 4.8 ppm
 - Doublet integrating to 3H at ~ 1.5 ppm
- A quartet integrating to 1H and doublet integrating to 3H almost certainly corresponds to a CH attached to a CH_3



Step 6: Assemble the pieces.

- There is only one way to assemble these three pieces:

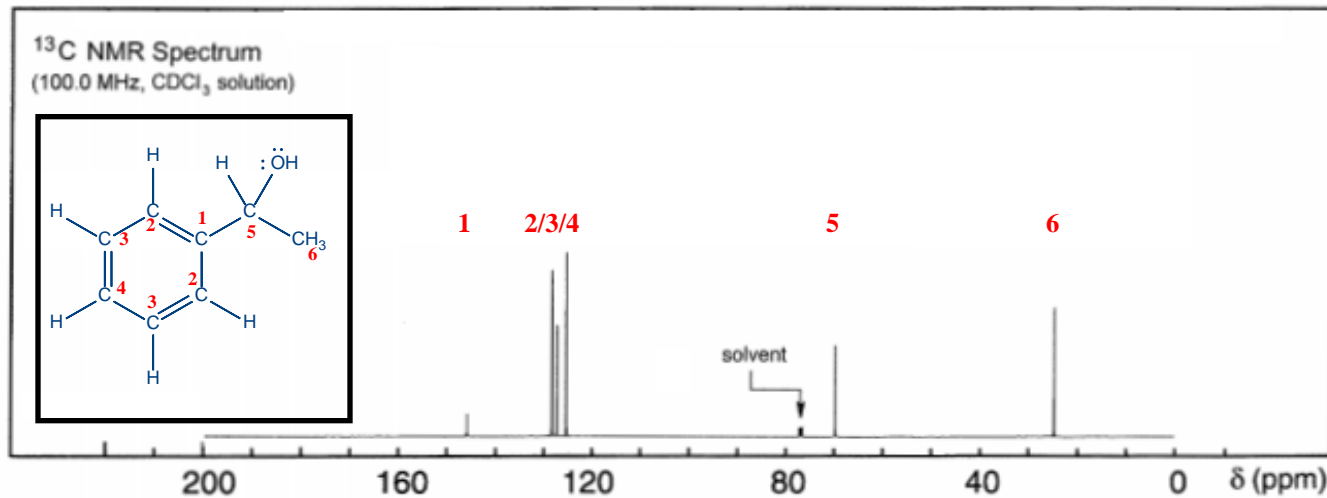
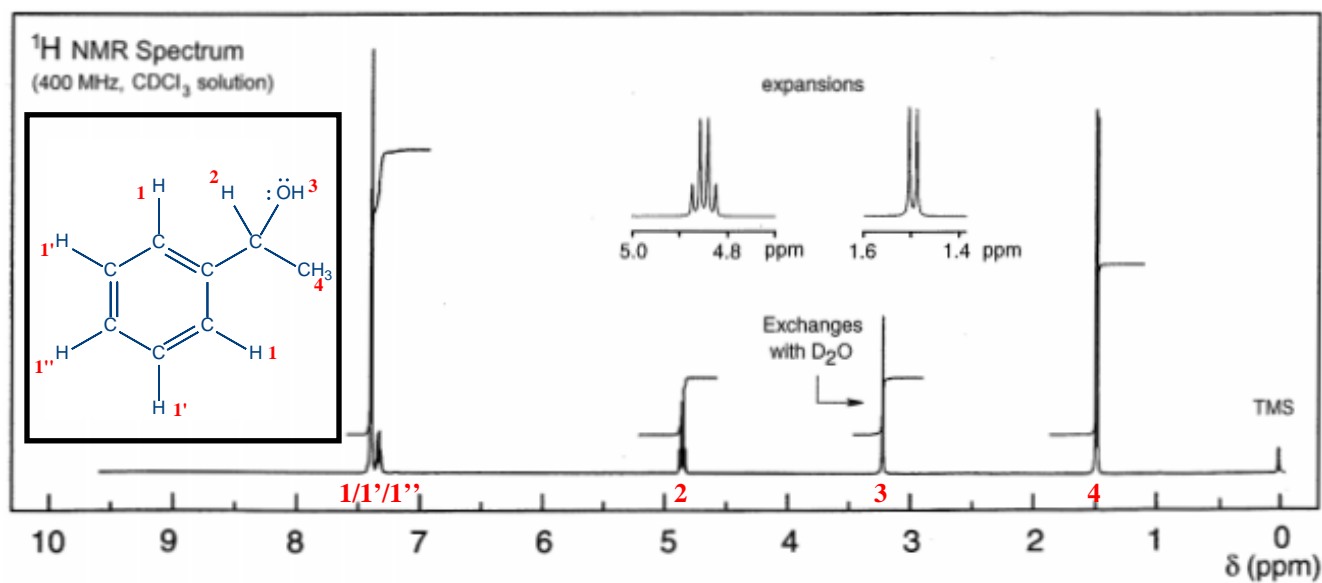
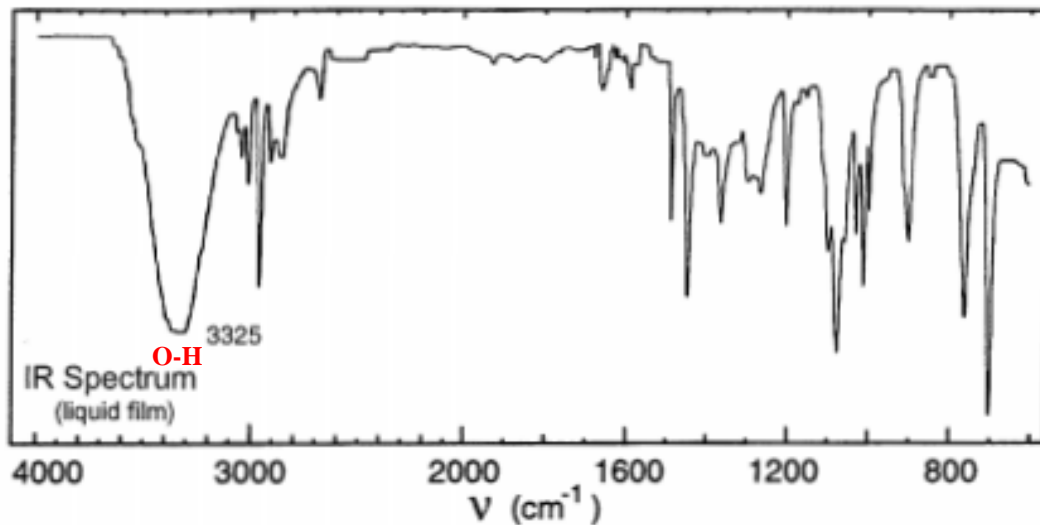


Step 7: Check your answer against the spectra and assign the peaks.

- The IR shows An O-H stretch at 3325 cm^{-1} . The peak is entirely over 3000 cm^{-1} , consistent with an alcohol (rather than a carboxylic acid; also, there is no $\text{C}=\text{O}$ peak on the IR or ^{13}C NMR)
- The peaks on the ^{13}C NMR are consistent with the six carbon environments of this molecule.
 - A peak at ~ 146 ppm for the quaternary carbon of the benzene ring
 - Three peaks at $120\text{-}130$ ppm for the remaining five carbons of the benzene ring (symmetry means that we only expect three peaks)
 - A peak at ~ 70 ppm for the carbon attached to the oxygen atom
 - A peak at ~ 25 ppm for the carbon of the methyl group
- The peaks on the ^1H NMR are consistent with the six hydrogen environments of this molecule:
 - Peaks at $7.4\text{-}7.5$ ppm correspond to the aromatic hydrogen atoms (integration of 5H). Coincidental overlap of chemical shifts means that we don't see much coupling.
 - The quartet integrating to 1H at ~ 4.8 ppm corresponds to the CH attached to an oxygen atom, a benzene ring and a methyl group.
 - The peak at ~ 3.2 ppm that integrates to 1H and exchanges with D_2O corresponds to the OH
 - The doublet integrating to 3H at ~ 1.5 ppm corresponds to the CH_3 attached to CH

5. ...continued

C₈H₁₀O



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CHEM 1000 Standard Periodic Table

1																	18																														
1.0079 H 1												13	14	15	16	17	4.0026 He 2																														
2												B	C	N	O	F	Ne																														
6.941 Li 3	9.0122 Be 4												10.811 B 5	12.011 C 6	14.0067 N 7	15.9994 O 8	18.9984 F 9	20.1797 Ne 10																													
22.9898 Na 11	24.3050 Mg 12	3	4	5	6	7	8	9	10	11	12	26.9815 Al 13	28.0855 Si 14	30.9738 P 15	32.066 S 16	35.4527 Cl 17	39.948 Ar 18																														
39.0983 K 19	40.078 Ca 20	44.9559 Sc 21	47.88 Ti 22	50.9415 V 23	51.9961 Cr 24	54.9380 Mn 25	55.847 Fe 26	58.9332 Co 27	58.693 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.9216 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36																														
85.4678 Rb 37	87.62 Sr 38	88.9059 Y 39	91.224 Zr 40	92.9064 Nb 41	95.94 Mo 42	(98) Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.411 Cd 48	114.82 In 49	118.710 Sn 50	121.757 Sb 51	127.60 Te 52	126.905 I 53	131.29 Xe 54																														
132.905 Cs 55	137.327 Ba 56	La-Lu	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.19 Pb 82	208.980 Bi 83	(210) Po 84	(210) At 85	(222) Rn 86																														
(223) Fr 87	226.025 Ra 88	Ac-Lr	(265) Rf 104	(268) Db 105	(271) Sg 106	(270) Bh 107	(277) Hs 108	(276) Mt 109	(281) Ds 110	(280) Rg 111	(285) Cn 112	(284) Nh 113	(289) Fl 114	(288) Mc 115	(293) Lv 116	(294) Ts 117	(294) Og 118																														
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center;">138.906 La 57</td> <td style="text-align: center;">140.115 Ce 58</td> <td style="text-align: center;">140.908 Pr 59</td> <td style="text-align: center;">144.24 Nd 60</td> <td style="text-align: center;">(145) Pm 61</td> <td style="text-align: center;">150.36 Sm 62</td> <td style="text-align: center;">151.965 Eu 63</td> <td style="text-align: center;">157.25 Gd 64</td> <td style="text-align: center;">158.925 Tb 65</td> <td style="text-align: center;">162.50 Dy 66</td> <td style="text-align: center;">164.930 Ho 67</td> <td style="text-align: center;">167.26 Er 68</td> <td style="text-align: center;">168.934 Tm 69</td> <td style="text-align: center;">173.04 Yb 70</td> <td style="text-align: center;">174.967 Lu 71</td> </tr> <tr> <td style="text-align: center;">227.028 Ac 89</td> <td style="text-align: center;">232.038 Th 90</td> <td style="text-align: center;">231.036 Pa 91</td> <td style="text-align: center;">238.029 U 92</td> <td style="text-align: center;">237.048 Np 93</td> <td style="text-align: center;">(240) Pu 94</td> <td style="text-align: center;">(243) Am 95</td> <td style="text-align: center;">(247) Cm 96</td> <td style="text-align: center;">(247) Bk 97</td> <td style="text-align: center;">(251) Cf 98</td> <td style="text-align: center;">(252) Es 99</td> <td style="text-align: center;">(257) Fm 100</td> <td style="text-align: center;">(258) Md 101</td> <td style="text-align: center;">(259) No 102</td> <td style="text-align: center;">(262) Lr 103</td> </tr> </table>																		138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71	227.028 Ac 89	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(240) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(262) Lr 103
138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71																																	
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Developed by Prof. R. T. Boeré (updated 2016)