

Chm 222
Section 1
Problems, Set Two: Spectroscopic Analysis

Spring 2012
Mr Linck
Version 1.2

NOTE: Problems with a zero following a number, 58.0., are NOT part of problem 58. They will be assigned separately. Assignment of 58 means doing 58. If I want you to do 58.0., it will be assigned as 58.0. Clearly, 58.0.1. thru 58.0.5. are part of 58.0. Likewise, if problem 65 is assigned, it means doing 65.1. and 65.2.

57. Review your notes from the last lecture. Organize into major topics and sub-topics.

57.0.1. A compound has “molecular” peaks in the mass spectrum at 135 and 137 of about equal intensity. What can you say about this compound?

57.0.2. A compound has “molecular” peaks in the mass spectrum at (mass, (intensity)) 76 (25.3); 77 (0.9); 78 (8.0); and 79 (0.3). What can you say about this compound?

57.0.3. For the compound in 57.0.2., use the ^{13}C percentage to estimate the number of carbon atoms.

57.0.4. Here are some “fudged” data to make the analysis easy. A compound has mass spectrum peaks at 92 (70.0) and 93 (5.5). How many carbons are in the material?

57.0.5. Here is the real data for the compound in the last problem. The peaks and intensities are: 91 (100); 92 (77.7), and 93 (5.5). Figure out why and how I “fudged” the data and be sure you see that it was “legal”. HINT: Think about the number of carbons likely in that peak at 91 and the consequences for the peak at 100.

58.0. The frequency at which a peak occurs in the IR spectrum caused by a bond stretch is governed by the equation:

$$\nu = (1/2\pi) \sqrt{(k/\mu)}$$

where k is the force constant, a measure of the bond strength, and μ is the reduced mass, equal to $m_1m_2/(m_1+m_2)$.

58.0.1. Why do C-H, O-H, and N-H bond stretches occur at higher ν than C-C, O-C, and N-C?

58.0.2. Why do C=C bond stretches occur at higher ν than C-C?

58.0.3. Where would you expect C=O stretches to occur relative to C-O stretches?

58.0.4. Where would you expect the stretches of triple bonded C/C bonds to occur relative to double bonded C/C?

58.0.5. Where would you expect C=S stretches to occur relative to C=O stretches?

58. You have two compounds of formula C_6H_{12} . Compound **1** has peaks in the IR at 3016, 2861-2961, 1658 cm^{-1} and a bunch of stuff in the region below 1500 cm^{-1} . Compound **2** has peaks at 2853-2928 cm^{-1} and a bunch of stuff below 1500 cm^{-1} . Which is cyclohexane? Why do you reach this conclusion?

59.0. If the value of ν for a E-X stretch is close (in energy) to that for a E-Y stretch (where E is some element and X and Y can be the same element), they usually “couple” to give, for instance, a symmetrical stretch (X and Y both moving away from the E at the same time) and an asymmetrical stretch (X moving toward the E as Y moves away, and the reverse), each with a slightly different ν . Compounds containing an $-NH_2$ group have two peaks near 3300-3400 cm^{-1} . Why?

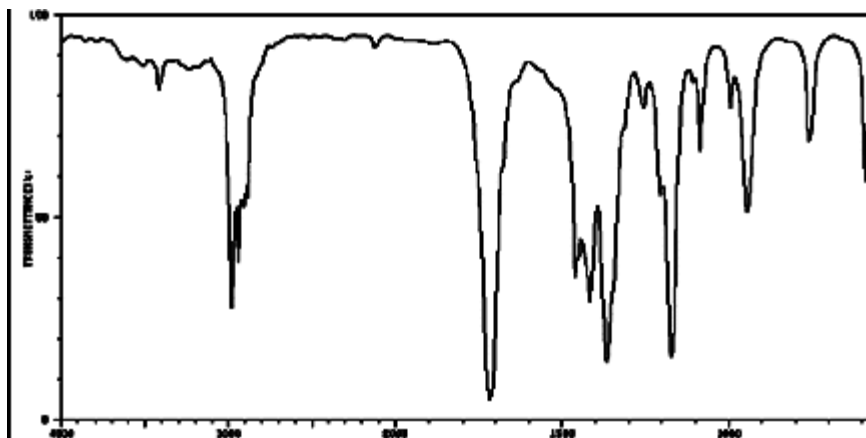
59. What can you say about the following compounds given their IR spectra in the functional group region (all reported in units of cm^{-1}).

- A 3410 sharp, 2900-3000, 2150 sharp
- B 3400 broad, 2900-3020
- C 2850-3000, 2710, 1725

60.0.1. A student treats 3-hexanol with PCC (a Cr(VI) compound, which we will use extensively later in the semester, that is an oxidizing agent) to try to form 3-hexanone. What should she look for in the IR to verify that reaction occurred?

60.0.2. A sample of propanone is treated with CH_3MgCl and then H^+ in water. How would you detect that reaction occurred?

60. What can you say about the compound whose IR is given in figure 3? The numbers on the scale are (from left to right) 4000, 3000, 2000, 1500, 1000.

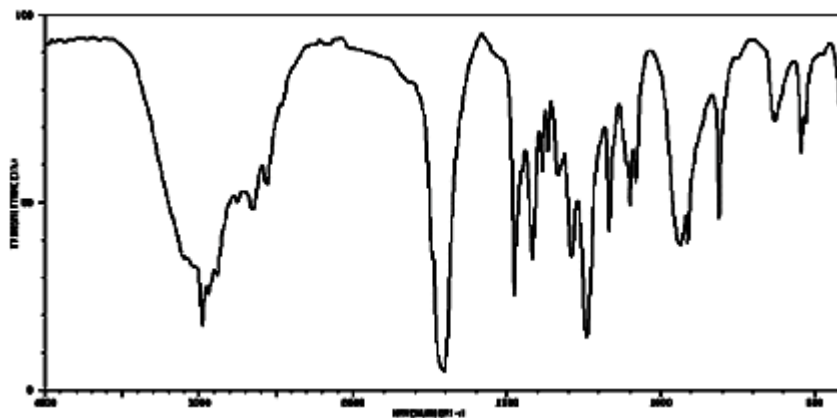


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61.0.1. 2-Butene reacts with O_3 to form two moles of ethanal (as we will see later). What would you look for in the IR to detect this reaction?

61.0.2. 2-Butene reacts with H_2 in the presence of Pt metal to yield butane. What would you look for in the IR to detect this reaction?

61. What can you say about the compound whose IR is given in 4? The scale on the bottom is the same as in problem 60., with the addition of a scale marker at 500.

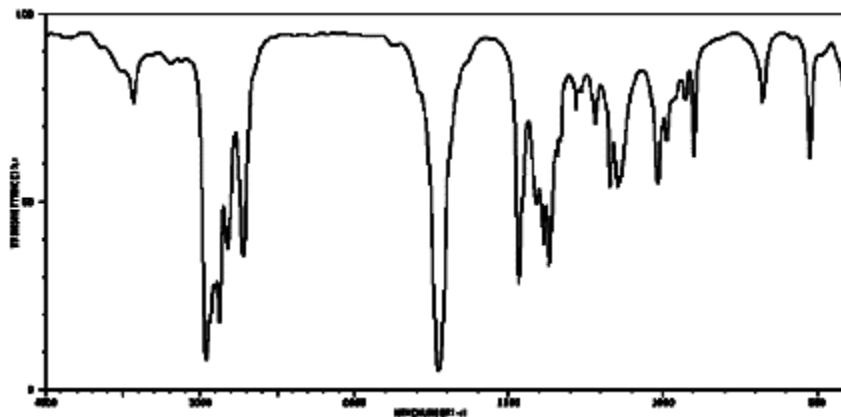


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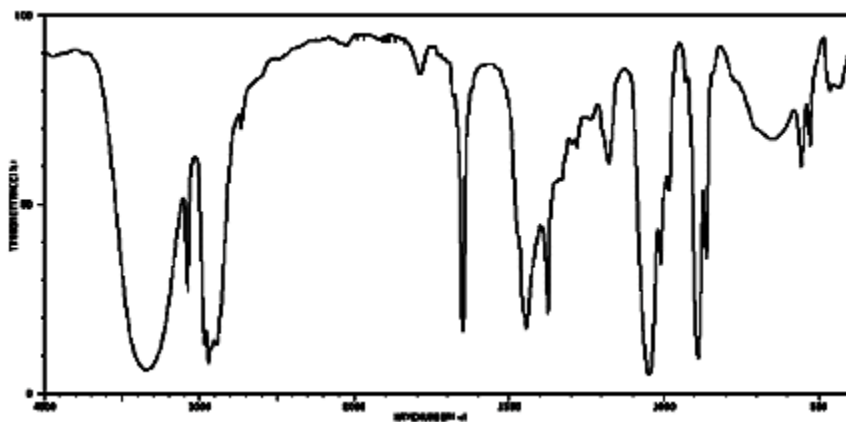
62. What can you say about the following compounds given their IR spectra in the functional group region (all reported in units of cm^{-1}).

- A 3450-3600, broad with some sharp peaks on top of it in the 2950-3000 region, 1723 sharp
- B 3450-3600, broad with some sharp peaks on top of it in the 2950-3000 region, 1700 sharp, 1650 sharp
- C broad peak centered at 3350, 3080 sharp, 1650, sharp.

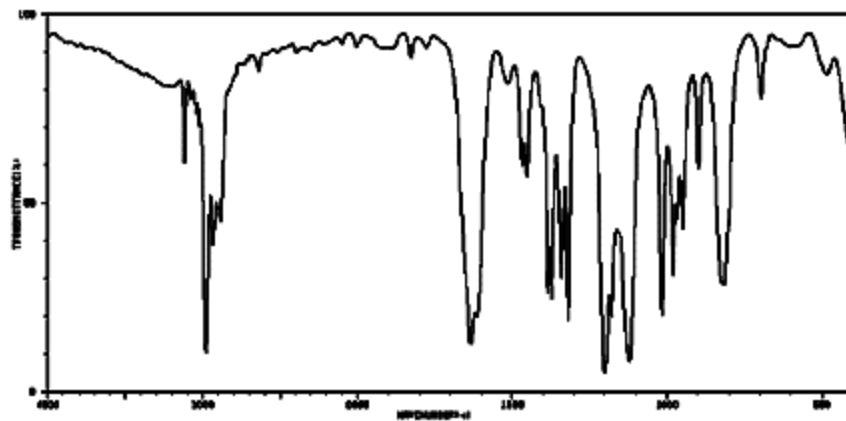
63. Figures 5-7 give three IR spectra, all of compounds of the formula $C_5H_{10}O$. Find a structure that is consistent with each spectrum. Scale as in problem 61.



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64.0.1. Use epwa to show what happens when BH_4^- reacts with 2-propanone.

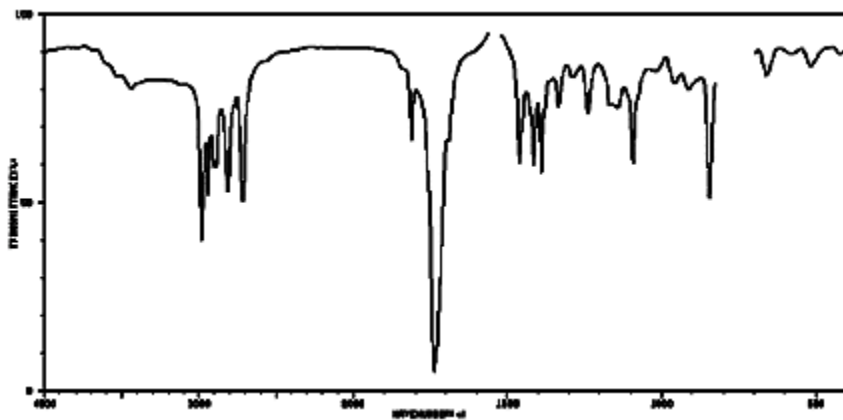
64.0.2. Use epwa to show what happens when the product of exercise 64.0.1. reacts with H_3O^+ .

64.0.3. Use epwa to show what happens when OH^- reacts with 2-propanone.

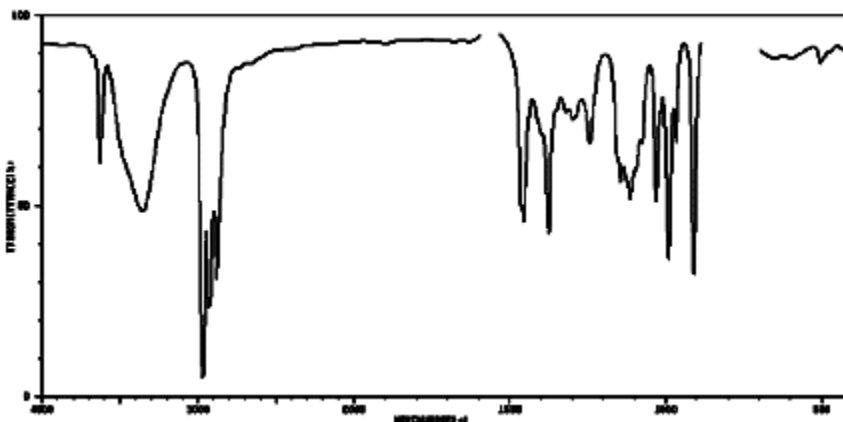
64.0.4. Use epwa to show what happens when the product of exercise 64.0.3. reacts with H_3O^+ .

64.0.5. How do the reactions in the first two parts of this exercise compare with those in the last two? HINT: An answer “Are the same” is useful as is an answer that explains some differences.

64. Propanal, whose IR spectrum is given in figure 8 reacts with a reagent to produce a compound whose spectrum is given in figure 9. What can you say happened in the reaction?



8



9

65.1. Make a summary of the positions, intensities, and broadness of peaks caused by various X-H stretches in the region between 3000 and 3600 cm^{-1} .

65.2. Make a summary of the positions, intensities, and broadness of peaks caused by various stretches in the region between 1500 and 1800 cm^{-1} .

66.0. The force constants for the C-H and the H-H bonds are about the same. Yet the C-H bond stretch occurs at a much higher wave number than does the C-C stretch, which is buried in the garbage below 1500 cm^{-1} . Why?

66. Two isomers of $\text{C}_4\text{H}_6\text{O}$, **A** and **B**, are both symmetric. Isomer **A** has IR peaks at 3090 and 1620 cm^{-1} , whereas isomer **B** has peaks at <3000 and 1780 cm^{-1} . Neither material absorbs in the 3300-3700 cm^{-1} region. Propose structures for the two isomers.

67.0.1. You would (if you are wise) never use IR to tell the difference between a compound containing a C-Cl bond and one containing a C-Br bond. Why not?

67.0.2. If you were pressed on the issue, what would you say the difference between the two would be?

67.1. Without looking at any tables, at what energy (units of wave number) do carbonyl compounds absorb in the IR?

67.2. Without looking at any tables, at what energy (units of wave number) do alcohol compounds absorb in the IR?

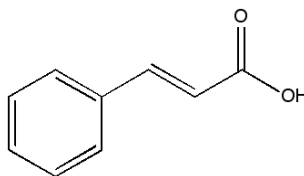
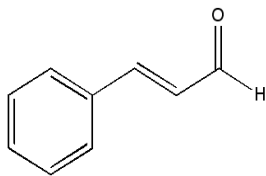
67.3. Without looking at any tables, at what energy (units of wave number) do alkene compounds absorb in the IR? HINT: If you can't answer the last three questions you are not studying correctly in this course.

68.0. How could you use IR to distinguish between butanone and buta-2-en-1-ol?

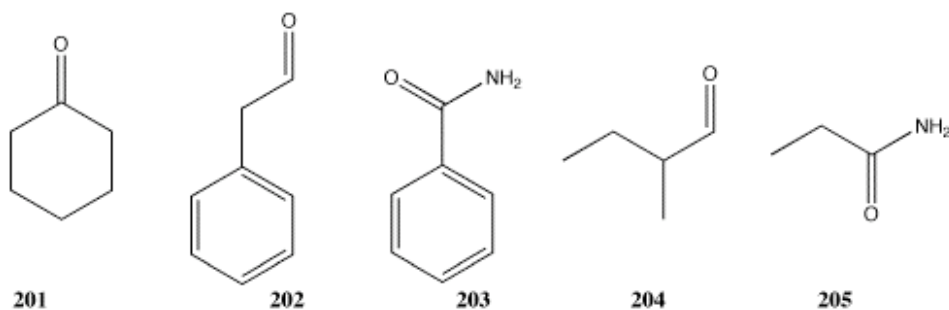
68.1. Why is the C triple bond C stretch absent in the IR of a symmetrical alkyne?

68.2. Why is the C triple bond C stretch weak in the IR of an asymmetrical alkyne?

69. How would you distinguish between these two compounds using IR?



69.0. Here are three IR spectra, **A**, **B**, and **C**. Assign each to one of the following compounds:



A < 3000 including 2700; 1722 cm^{-1}

B Broad peak with two maxima 3200-3400, < 3000, broad peak 1620-1680 cm^{-1} .

C < 3000, 1703 cm^{-1} .

70.0. How could you use IR to tell when the reaction between 2-hexene and H_2 (to form hexane) was complete?

70.1. Find a table in your text that lists examples of compounds with methyl, methylene ($-\text{CH}_2-$), and methine ((CH) hydrogen atoms. What do you learn about the relative chemical shift of methine versus methylene versus methyl hydrogen atoms when other groups around the carbon are roughly the same?

70.2. What do you learn about the position of a $\text{CH}_3\text{C}(\text{O})\text{R}$ signal? [When I see a $\delta 2.1$ signal I hear “ding, (pause), ding, (pause) ding”.]

70.3. What do you learn about a CH_3-C signal compared to a CH_3-O signal?

70.4. What do you learn about a $-\text{CH}-\text{C}$ signal compared to a $-\text{CH}-\text{Cl}$ signal?

70.5. What do you learn about a $\text{CH}_3-\text{C}-\text{Cl}$ signal compared to a $-\text{CH}-\text{Cl}$ signal?

70.6 On the next exam, I am absolutely positive that several students will see an nmr spectrum with a peak at 4.0 δ . They will say “H of an OH.” What would you say?

71.1. Examine a table in your text and learn where the signals for ROH, $\text{C}=\text{CH}$, benzenoid (or aromatic)-H, aldehydic-H, and $\text{RC}(\text{O})\text{OH}$ signals are.

71.2. True or false? If I told you that there is a signal in the ^1H nmr at 4.0, you would be justified in saying “This molecule contains an ROH group.” Give your reasoning.

72. Which of the following hydrogen nuclei would you expect to have a signal at higher field (near TMS) and which at lower field (near CHCl_3).

- a. R_2BCH_3 b. CH_2F_2 c. $\text{CCl}_3\text{CHClCCl}_3$ d. $\text{N}(\text{CH}_3)_4^+$

73. Which member of each pair would you expect to have the most downfield signal?

- a. CH_3Cl or C_2H_6
b. CCl_3CH_3 or CF_3CH_3
c. CH_3R or CH_2ClR
d. $\text{RC}(\text{O})\text{CH}_3$ or RCH_3

HINT: R is a non-electronegative/non-electropositive group.

73.0.1. What is the δ of a CH_3 group next to a benzene ring? of a CH_2 group? of a CH group?

73.0.2. Might a CH_2 group between a benzene ring and a $-\text{CH}_2\text{Cl}$ group appear deshielded?

74.0. We use mass spectroscopy only slightly in this course. The key to our usage involves the molecular radical ion which is the molecule with an electron knocked out. It is an ion, a cation to be precise, because of the loss of that electron. It is a radical because it has an odd number of electrons. Since the mass of the electron is small compared to that of nuclei, the mass of the molecular radical ion is essentially the same as that of the unionized material from which it arose. You should be able to handle problems such as the following.

74.0.1. Octane would have a molecular ion peak at what mass number?

74.0.2. Why do compounds with an odd number of N have an odd mass number for the molecular ion when the mass of N is 14. HINT: Think about what an $-\text{NH}_2$ group replaces in a hydrocarbon to make an amine.

74.0.3. For Br, there are two common isotopes, ^{79}Br and ^{81}Br . These occur in nearly equal quantities in nature. What would the mass of the molecular ions be for ethyl bromide and what are their relative intensities? These peaks are usually called the M and M+2 peaks. HINT: Look at the grammar of the question, especially the use of plurality.

74.0.4. The common isotopes of Cl are ^{35}Cl and ^{37}Cl ; the former is three times as abundant as the latter. What would the molecular ions be for 3-chlorohexane and what are their relative intensities?

74.0.5. Compounds of carbon with lots of carbon atoms often show a small peak one unit in mass higher than the molecular ion peak due to the 1.1% of carbon that is ^{13}C . If you

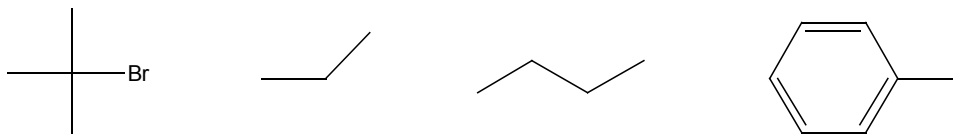
have a compound containing five carbons (each of which has a 1.1% chance of being a ^{13}C , what will be the relative height of the M+1 peak relative to the M peak.

74.0.6. A compound has molecular ion peaks (judged to be so because there is nothing at a higher mass number) of 136 and 138 of about equal intensity. Make an intelligent guess as to the identity of the compound.

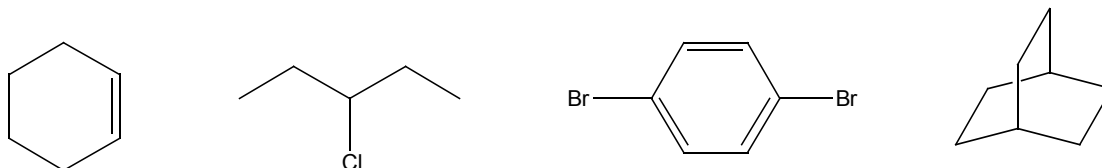
74.0.7. A molecule is isolated from a biological sample. It has the following IR: a broad peak between 3200 and 3600 cm^{-1} and two peaks in the region between 1600 and 1700 cm^{-1} . What functional groups are in the molecule?

74.0.8. Same molecule as in exercise 74.0.7. The mass spectrum shows a M+1 peak with relative intensity of 3.9 and a M peak of intensity 27.2. How many carbons are (likely) in the molecule?

74. Are all the hydrogen atoms in the same environment in each of the following?
HINT: Make sure that you consider “free” rotation.



75. How many ^1H nmr signals will we see for each of the following compounds? HINT: if you have heard of it, ignore spin-spin coupling.



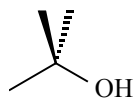
76. Review your notes from the last lecture. Summarize the points of discussion. How are they interconnected?

76.0. Predict the approximate position of the signal(s) in the ^1H nmr spectrum for 2-butenal and for methylbutyrate.

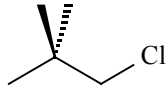
77. Predict the approximate position of the signal(s) in the ^1H nmr spectrum for compounds **1** to **8**. Use the δ scale. (If you want to be reasonably accurate, use a table in your text or the nice tables at

<http://www.chem.wisc.edu/areas/reich/handouts/nmr-h/hdata.htm>.)

Give integrations. **You should neglect spin-spin coupling in this problem.**



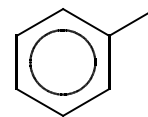
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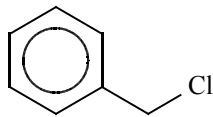
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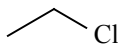
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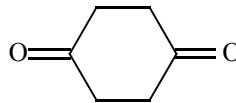
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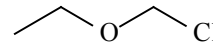
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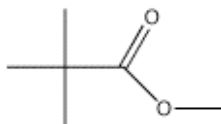


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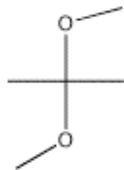


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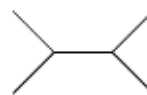
77.0.1. How would you distinguish between **744** and **745** using ^1H nmr (ignoring spin-spin coupling):



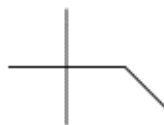
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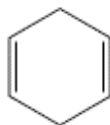
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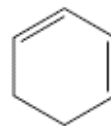
746



747



748



749

77.0.2. How would you distinguish between **746** and **747** using ^1H nmr (ignoring spin-spin coupling):

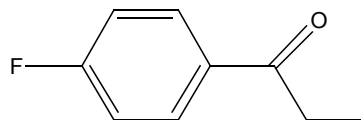
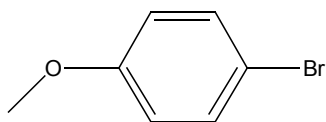
77.0.3. How would you distinguish between **748** and **749** using ^1H nmr (ignoring spin-spin coupling):

78. Predict the approximate positions of the signals present in the ^1H nmr spectrum of $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$.

79.0.1. A compound of formula $\text{C}_2\text{H}_6\text{O}$ has only one peak in the nmr spectrum. Give a structural formula for this compound?

79.0.2. A compound of formula $\text{C}_3\text{H}_6\text{Cl}_2$ has only one peak in the nmr spectrum. Give a structural formula for this compound?

79. For each of the following find the number of ^1H signals and determine their relative areas:



80.0. How many different chemical shifts would you expect in 1-chloro-3-fluoropropane? Which signal is due to which hydrogen atoms? What are the relative areas?

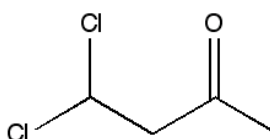
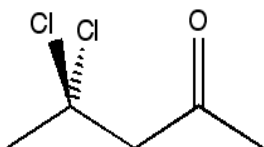
80. A compound of formula $\text{C}_4\text{H}_9\text{Br}$ has three ^1H nmr signals, one at about 1.0δ (Area 3), a second at 2.0δ (0.5) and a third at 3.3δ (1). What is the compound? HINT: If you have heard of spin-spin splitting, ignore it for this problem.

81.0.1. A compound with the formula $\text{C}_7\text{H}_{16}\text{O}$ has two ^1H nmr signals. What is the compound? If you have heard of spin-spin coupling, ignore it.

81.0.2. A compound with the formula $\text{C}_5\text{H}_{12}\text{O}$ has ^1H nmr signals at 3.2δ (20) and 1.2δ (59). What is the compound?

81.0.3. A compound with the formula $\text{C}_9\text{H}_{10}\text{O}_2$ has ^1H nmr signals at 7.4δ (108), 5.2δ (45) and 2.2δ (66). What is the compound?

81. Predict the ^1H nmr spectrum (with integration) for the following compounds.



82.0.1. Bromomethyl-methyl ether has an ^1H nmr spectrum with signals at 5.7δ (Area 2) and 3.2δ (3). Assign the peaks to hydrogen atoms in the structure.

82.0.2. 1-Bromo-2-methylpropane has an ^1H nmr spectrum with signals (ignoring spin-spin coupling) at 1.05δ (6), 1.98δ (1) and 3.3δ (2). Assign the peaks to hydrogen atoms in the structure.

82. A compound of formula $\text{C}_7\text{H}_{14}\text{O}$ has the following ^1H nmr spectrum (with integration): 1.0δ (Area 18) 2.1δ (6), and 2.3δ (4). What is the compound?

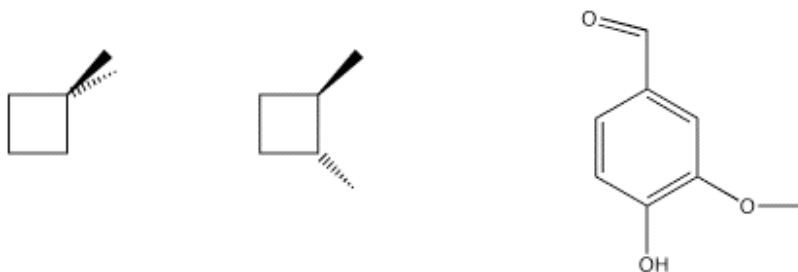
83. A compound of formula $\text{C}_9\text{H}_{13}\text{N}$ has the following ^1H nmr spectrum (with integration): 2.25δ (Area 3) 3.4δ (1), and 7.3δ (2.5). What is the compound?

84. Predict the approximate positions of the signals present in the ^1H nmr spectrum of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$.

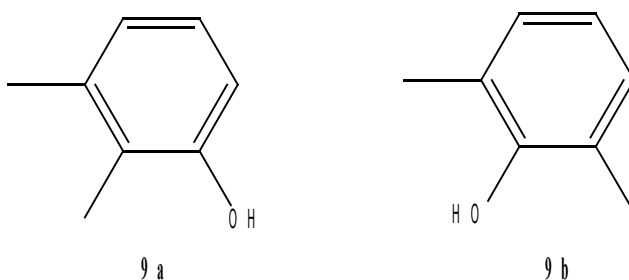
85. How would you use chemical shift and integration to distinguish between HCCCH_2OH and $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{H}$?

86. A compound with the formula $\text{C}_6\text{H}_3\text{Cl}_2(\text{NO}_2)$ has an ^1H nmr spectrum (with integration): 7.63δ (Area 1) 8.09δ (1), and 8.36δ (1). What structures are **not** possible? HINT: This question is ignoring spin-spin coupling. Also, the formula implies that the compound contains an $-\text{NO}_2$ group and not some other combination of N and O.

87.0. How many ^1H nmr signals in the following? HINT: If you think about the ring as being planar (it isn't, but that works, as we will see), and consider hybridization for four-coordinate carbons, you will the first two molecules have a top and a bottom side.



87. Using chemical shift and integration data only, how would you distinguish between **9a** and **9b**?



88.1. In ^1H nmr, where does the H atom in $\text{R}-\text{C}(\text{O})\text{OH}$ absorb? HINT: "R" is some unspecified C,H group.

88.2. In ^1H nmr, where does the H atom in $\text{CH}_3-\text{C}(\text{O})-\text{R}$ absorb?

88.3. In ^1H nmr, where do the H atoms in benzene-R absorb?

88.4. In ^1H nmr, where does the H atom in $\text{CF}_3\text{C}(\text{O})\text{H}$ absorb?

88.5. As they say in Searcy, Arkansas, which is right down the road from Beebe, "There ain't no more bells in ^1H spectroscopy."

88.0.1. A CH₃ group has one H atom on the neighboring carbon atom. How is the CH₃ group split?

88.0.2. A CH group has one H atom on the neighboring carbon atom. How is the CH group split?

88.0.3. A CH₃ group has two H atoms on the neighboring carbon atom. How is the CH₃ group split?

88.0.4. A CH₂ group has three H atoms on the neighboring carbon atom. How is the CH₂ group split?

88.0.5. A CH group has two neighboring equivalent CH₃ groups. How is the CH group split?

89. A compound of formula C₄H₈O has three ¹H nmr signals: 1.06δ (triplet J=7.6, Area 3) 2.14δ (s, 3), and 2.45δ (q, J=7.6, 2). What is the compound?

89.0.1. A compound of formula C₄H₈Br₂ has two ¹H nmr signals: 1.97δ (s, 6) and 3.89δ (s, 2). What is the compound?

89.0.2. A compound of formula C₈H₉Br has ¹H nmr signals: 2.01δ (d, 3), 5.14δ (q, 1) and 7.35δ (broad s, maybe g, 5). What is the compound?

90. A compound of the formula C₅H₁₀O₂ has four ¹H nmr signals: 1.14δ (t, J=7.7, 3), 1.26δ (t, J=7.2, 3), 2.32δ (q, J=7.7, 2), and 4.13δ (q, J=7.2, 2), What is the compound?

90.0. A compound of the formula C₇H₁₄O has ¹H nmr signals: 1.06δ (s, 6), 2.15δ (s, 2), and 2.33δ (s, 1.4), What is the compound?

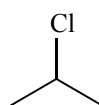
91. A compound of the formula C₅H₁₀O₂ has two ¹H nmr signals: 1.14δ (s, 9), 11.49δ (broad singlet, exchangeable, 1), What is the compound?

91.0. A compound of the formula C₇H₁₄O has ¹H nmr signals: 0.9δ (t, 3), 1.1δ (d, 6), 1.6δ (sextet, 2), 2.42δ (t, 2), and 2.6δ (heptet, 1), What is the compound?

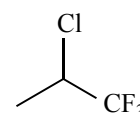
92. A compound of the formula C₅H₁₀O₂ has four ¹H nmr signals: 0.99δ (d, 6), 2.12δ (m, 1), 2.23δ (d, 2), and 11.9δ (broad singlet, exchangeable, 1), What is the compound?

93.1. Predict the spin splitting of the hydrogen atom(s) indicated.

- CH₃ in **6**.
- CH₂ in **6**.
- H on C2 of **10**.



10



11

- d. H on C2 of **11**. Be careful; F has a spin of 1/2.
e. CH₃ of **11**.

93.2. What would be the splitting pattern of the underlined hydrogen atom in CH₃CH₂CH₂Br?

93.3. What would be the splitting pattern of the underlined hydrogen atom in (CH₃)₂CHSH?

94. How would you use ¹H nmr to distinguish between the following compounds? Remember that integration is relative only, so it cannot be used absolutely.

94.1. 2,3-dimethylbutane and 2,2-dimethylbutane.

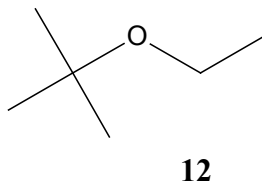
94.2. diethylether and ethyl-methyl ether

94.3. 3,6-dimethyl-1,4-cyclohexadiene and 1,3-dimethyl-1,4-cyclohexadiene

94.4. methylethanol (isopropanol) and propanol

94.5. 1,2,3-trichloropropane and 1,1,1-trichloropropane

94.6. 2,2-dimethylbutane and **12**.



94.0.1. A compound of formula C₄H₈Br₂ has IR, 2850-3000 cm⁻¹ and a ¹H nmr of 1.87δ (s, 9.1), 3.86δ (s, 3.0). What is it?

94.0.2. A compound of formula C₉H₁₈O has IR, 1710 cm⁻¹ and a ¹H nmr of 1.2δ. What is it?

94.0.3. A compound of formula C₂H₄Cl₂ has IR, 2850-3000 cm⁻¹ and a ¹H nmr of 2.1δ (d), 5.9δ (q). What is it?

94.0.4. A compound of formula C₃H₆Br₂ has IR, 2850-3000 cm⁻¹ and a ¹H nmr of 2.4δ (quintet), 3.5δ (t). What is it?

94.0.5. A compound of formula C₅H₁₀O₂ has IR, 1740 cm⁻¹ and a ¹H nmr of 1.15δ (t, 3), 1.25δ (t, 3), 2.3δ (q, 2), and 4.32δ (q, 2). What is it?

94.0.6. A compound of formula $C_6H_{14}O$ has IR, 2850-3000 cm^{-1} and a broad band at 3200 cm^{-1} . It has a 1H nmr of 0.8 δ (t, 6), 1.0 δ (s, 3), 1.5 δ (q, 4), and 1.6 δ (s, 1). What is it?

94.0.7. A compound of formula $C_6H_{14}O$ has nothing of interest in the IR. The 1H nmr has peaks at 1.1 δ (d, 30) and 3.6 δ (heptet, 5). What is it?

95. A compound of formula $C_8H_{12}O$ has a IR with prominent peaks at 1685 cm^{-1} (broad and strong), 1625 cm^{-1} (sharp), 3105 cm^{-1} , and 2950-3000 cm^{-1} . The 1H nmr has a doublets at 6.7 and 5.85 δ , both with integrations of 1, triplets at 1.87 and 2.47 δ , both with integrations of 2, and a singlet at 1.16 δ with an integration of 6. Identify the compound.

95.0.1. Predict the decoupled ^{13}C of ethanal.

95.0.2. Predict the decoupled ^{13}C of 3-butene-2-one.

95.0.3. Predict the decoupled ^{13}C of 2-butanol.

95.0.4. Predict the position and splitting of the ^{13}C peaks in 2-butanol with off resonance decoupling.

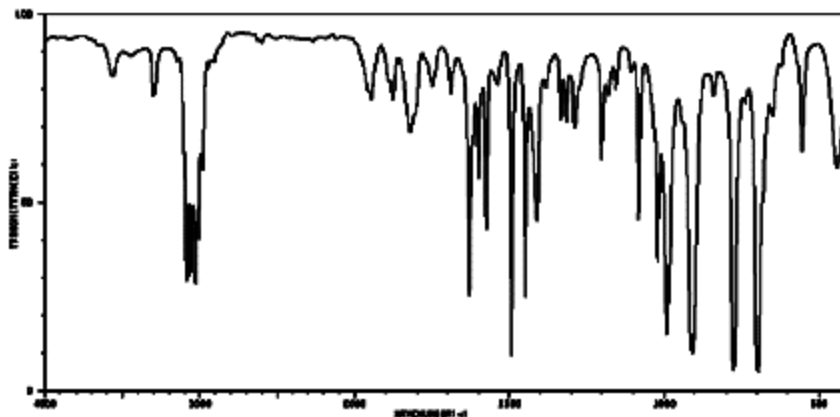
96. A compound of the formula C_4H_8O has four ^{13}C nmr signals: 7.87 δ (q), 29.43 δ (q), 36.87 δ (t), and 209.28 δ (s) where the values in parenthesis are the off-resonance decoupled splittings. What is the compound?

96.0. A compound of the formula C_6H_{12} has ^{13}C nmr signals: 17 δ , 25 δ , and 138 δ . What is the compound?

97. A compound of the formula C_7H_7Br has seven decoupled ^{13}C nmr signals: 21.05 δ , 122.31 δ , 127.65 δ , 128.48 δ , 129.70 δ , 132.06 δ , and 140.07 δ . What is the compound?

98. A compound has five ^{13}C peaks: 11.97 δ , (q), 25.90 δ , (t), 132.10 δ , (d), 160.24 δ , (d) and 194.09 δ (s) [splitting patterns from off-resonance decoupling] and five 1H nmr peaks: 1.13 δ (t, 3), 2.38 δ (quintet, 2), 6.12 δ (d of d, 1), 6.942 δ (d of t, 1), and 9.52 δ (d, 1). What is the compound?

99. A compound has the following IR:



The ^1H nmr has peaks at 5.225, 5.737, 6.692, and between 7.1 and 7.5 δ . The first two are doublets with an integration of 1, the third is a doublet of doublets with an integration of 1, and the last is a mess (sometimes called garbage) with an integration of 5. The ^{13}C has 6 peaks at 113.7, 126.2, 127.8, 128.5, 137.0, and 137.6 δ . What is the compound?

100. A compound with formula $\text{C}_4\text{H}_8\text{O}_2$ has a ^1H nmr with a broad singlet at 12.2 δ , a heptet at 2.6 δ , and a doublet at 1.21 δ . What is the compound?

101.0. A compound of formula $\text{C}_3\text{H}_6\text{O}$ has IR, 1730 cm^{-1} and a ^1H nmr of 1.11 δ (t), 2.46 δ (g) and 9.79 δ (t). What is it?

101. A compound of formula $\text{C}_5\text{H}_8\text{O}_2$ has a ^1H nmr with a triplet at 1.1 δ , a singlet at 2.32 δ , and a quartet at 2.78 δ . The relative integrations are 3, 3, and 2, respectively. What is the compound?

102. A compound of the empirical formula $\text{C}_4\text{H}_8\text{O}$ has three ^1H nmr signals: 1.06 δ (d, 6); 2.39 δ (garbage, 1), and 9.57 δ (d,1). What is the compound?

103. Predict the spin-spin splitting pattern (i.e., triplet at 1.5 δ , etc) for 1,1,2-tribromoethane.

103.0. Formula $\text{C}_4\text{H}_8\text{O}_2$; IR 1730 cm^{-1} . The ^1H nmr has peaks at 2.1 δ (s, 31), 3.4 δ (s, 30), and 3.9 δ (s,18.8). What is the compound?

104. A compound with the empirical formula $\text{C}_4\text{H}_8\text{O}_2$ has an ^1H nmr spectrum as follows:
 triplet at 1.27 δ , integration 1.0
 singlet at 2.03 δ , integration 1.05
 quartet at 4.11 δ , integration 0.68.

What is the compound?

105.0.1. A compound of formula $\text{C}_8\text{H}_{14}\text{O}_2$ has IR, 1718 cm^{-1} and a ^1H nmr of 1.4 δ (t, 3), 4.4 δ (d, 6) and peaks at 7.4, 7.6, and 8.2 δ (a mess, with a total area of 5). What is it?

105.0.2. A compound of formula C_9H_{12} has IR, 2850-3150 cm^{-1} and a 1H nmr of 1.25 δ (d, 6), 2.95 δ (heptet, 1) and 7.3 δ (g, 5). What is it?

105. A compound with formula C_4H_8O has four ^{13}C peaks: 37.11 δ , (t), 61.61 δ , (t), 117.21 δ (t), and 135.02 δ (d) [splitting patterns from off-resonance decoupling] and six 1H nmr peaks: 2.318 δ (g, 2), 2.76 δ (broad, exchanges, 1), 3.65 δ (t, 2), 5.10 δ (d of d, 1), 5.13 δ (d of d, 1), and 5.82 δ (g, 1). What is the compound?

106. A compound with the formula $C_9H_{13}N$ has an 1H nmr spectrum as follows: 2.25 δ (s, 6), 3.43 δ , (s, 2), 7.32 δ , (g, 5). What is the compound?

107. A compound with formula $C_7H_{14}O$ has six ^{13}C peaks: 13.81 δ , 17.24 δ , 18.23 δ , 40.80 δ , 42.26 δ and 214.77 δ [decoupled] and five 1H nmr peaks: 0.96 δ (t, 3), 1.09 δ (d, 6), 1.59 δ (sextet, 2), 2.42 δ (t, 2), and 2.61 δ (heptet, 1). What is the compound?

108. A compound with formula C_5H_9N has four ^{13}C peaks: 21.79 δ (q), 25.98 δ , (d), 26.13 δ (t), and 118.89 δ (s) [off-resonance decoupled] and three 1H nmr peaks: 1.07 δ (d, 6), 2.02 δ (nonet, 1), and 2.23 δ (d, 2). What is the compound?

109. A compound with formula $C_6NO_2ClH_4$ has an 1H nmr with two peaks, a doublet at 7.4 δ and another doublet at 8.2 δ . What is the compound?

110.1. Make a list of the steps you would take to determine the identity of a compound given the 1H nmr spectrum of the compound.

110.2. Concerning problem 110.1., could you change the order of attack? How?

111.1. How would you use IR to distinguish between cyclohexane and *trans*-2-hexene.

111.2. How would you use 1H nmr to distinguish between cyclohexane and *trans*-2-hexene.

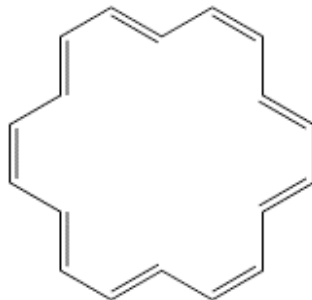
111.3. How would you use ^{13}C nmr to distinguish between cyclohexane and *trans*-2-hexene.

112. Find a structure for a C_9 compound whose 1H nmr has two singlets.

113. The proton nmr of CHD_2I consists of a five line pattern with intensities 1:2:3:2:1. HINT: D has a spin of 1. Justify this splitting of the proton spectrum.

114.0.1. The 1H nmr of N,N-dimethylformamide has signals at 2.9 δ , 3.0 δ , and 8.0 δ . Explain.

114.0.2. The compound, 18-annulene, shown below, has 1H nmr signals at 8.9 δ (s, 12) and -1.8 δ (s, 9). Explain. HINT: That really is a minus sign!



114. A compound with formula $C_6H_{14}O$ has four ^{13}C peaks: 17.7 δ , 26.4 δ , 38.9 δ , and 73.0 δ and four 1H nmr peaks: 0.90 δ (d, 6), 1.10 δ (s, 6), 1.25 δ (broad, disappears upon treatment with D_2O (s, 1), and 1.3 (heptet, 1). What is the compound?

115.0.1. Construct a Newman projection of 3-methyl-2-chlorobutane looking down the C_2-C_3 bond.

115.0.2. Why does this compound show five ^{13}C signals?

115. The proton nmr spectrum of 2,2,3,3-tetrachlorobutane is a function of temperature. At room temperature, it exhibits a single peak. At low temperatures, a pair of peaks, rather closely spaced, are found. Explain.

115.0.0.1. Give the zigzag line structure, and indicate the hybridization at each carbon atom, for pent-3-ene-2-one.

115.0.0.2. Sketch or describe the highest occupied molecular orbital (HOMO) on the molecule of question 115.0.0.1.

115.0.0.3. Are there any other electron pairs in the molecule of question 115.0.0.1. that are relatively loosely held? Is so, how would you describe (for instance, σ electrons between C_1 and C_2) those electrons?

115.0.0.4. At what site (or sites) might a nucleophile such as H^- attack the molecule of question 115.0.0.1.?

115.0.0.2.1. If we look at a benzene ring which lies in the x,y plane, what hybridization is used by a carbon atom in that molecule?

115.0.0.2.2. Be specific in stating what orbitals are used in making those hybrid orbitals?

115.0.0.2.3. What orbital(s) is(are) not used for the hybrid orbitals?

115.0.0.2.4. Is a pi bond stronger or weaker than a sigma bond? Explain briefly.

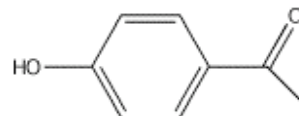
115.0.0.3.1. Make a drawing of the most stable form of 1-chloropropane?

115.0.0.3.2. Make a drawing of a less stable form of 1-chloropropane that could be isolated at low temperatures. HINT: I do NOT want a diagram of a material on the “top of an energy mountain.”

115.0.0.4. Use epwa to illustrate the following reactions.

115.0.0.4.1. BH_4^- reacts with pentanal, followed by treatment with H^+ .

115.0.0.4.2. A mole of ethyl Grignard with a mole of:



115.0.0.4.3. A mixture of these two chemicals,



followed by H^+ .

115.0.0.5. Give the product of each of the following acid/base reactions. HINT: It is possible that you will predict “no reaction,” which might be indicated by “NR”.

115.0.0.5.1. $\text{OH}^- + \text{HF}$

115.0.0.5.2. $\text{OH}^- + \text{NH}_3$

115.0.0.5.3. $\text{H}_2\text{O} + \text{HS}^-$

115.0.0.5.4. H_3PO_4 (which has a pK_a of 2.1) + $\text{CH}_3\text{C}(\text{O})\text{O}^-$ (whose conjugate acid has a pK_a of 4.8).

115.0.0.6. How would you make 2-methyl-3-pentanol from compounds containing 3 carbon atoms (or fewer)? Use epwa to explain your reasoning.

115.0.0.7. A compound of formula $\text{C}_4\text{H}_{10}\text{O}$ has an IR with peaks between $2800\text{-}3000\text{ cm}^{-1}$ and no other interesting peaks above 1500 cm^{-1} . The ^1H nmr has four peaks: 3.34δ (t, 2), 3.33δ (s, 3), 1.59δ (sextet, 2), and 0.93δ (t, 3). What is the compound? HINT: For partial credit you must given your reasoning.

115.0.0.8. A compound has a M^+ of 121, an IR as given in the drawing, a ^{13}C nmr with peaks at 151δ , 129δ , 117δ , 113δ , and 40.5δ , and a ^1H nmr with peaks at 2.89δ (s, 1.7) and 6.6 to 7.4δ (g, or m, 1.4). What is the compound? HINT: For partial credit you must given reasoning.

