

HINTS AND ANSWERS TO CHM 222, SECTION I, EXERCISES

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The exercises in this course are designed to give you the ability to do organic chemistry. Reading my answers to questions is a passive way to obtain organic chemistry knowledge; therefore I do not provide you with that option. The hints (mainly) and answers in this document are designed to help you do the exercises on your own, or with help from your fellow students. In addition, I often offer study guides to help you assimilate the material. You may ask me about any problem in CHREM or office hours if you remain baffled.

1. PRELIMINARIES

1.2. O, S, and Se all have 6 valence electrons.

1.4. O^- and F are isoelectronic.

1.5. Valence shell isoelectronic in this case means the same number of electrons around the central atom. So NH_2^- and OH^- are valence shell isoelectronic.

2.0 CH_3 is isoelectronic with fluoride. Among other things, this means that in a Lewis structure you can replace a methyl group with a fluorine.

2. There are several possible answers for the last.

3.1. Use periodic position.

3.2. An electronic pull on one end of a molecule dies in effectiveness with distance.

3.3. Use periodic position.

3.4. Use geometry

3.6. Are the geometries the same?

5.0. In HN_3 the terminal N is -1 and the central N is +1.

5.1. Carbon "always" has 4 bonds, N three, O two, F, one.

5.2. OH^- is isoelectronic is FH and both have one bond. NH_4^+ is isoelectronic with CH_4 and each have four bonds.

6.2. The sulfur atom is attached to two carbons and double bonded to an oxygen.

Date: Last revised: 27/xii/11.

7. In the second the geometry about each carbon is trigonal, so all angles are 120° and the molecule is planar.

7.0. In the third case the double bonds could go where they are or could be permuted one step clockwise. Actually they are in both positions: the Lewis structure breaks down and we have to use resonance (to which we will return ultimately).

8.5. You could start by putting the six carbons in a chain and putting a double bonded oxygen in a position to make a ketone. Be careful to note that an oxygen on carbon two is the same compound as one with an oxygen on carbon five. Then build branched chains and put oxygen in various positions.

9.1 It is always useful to use the index of a book.

9.3. Since you are drawing an alkene, you need no letters in your structure, only lines.

10.4. Questions like these are giving you the bonding characteristics. The two (CH_3CH_2) groups are both attached to the adjacent "CH".

11.0. There is an alkene, an ether, an alcohol, an amide, and a benzene ring. Don't be fooled into calling the amide a carbonyl and an amine. There are next to each other and because of that have special properties that deserve a separate name.

12.0. You need to find the electrons least tightly held. First are lone pairs; then double/triple bonds; finally single bonds. In the third exercise ambiguity can be removed if you are wary of where the positive charge "ends up" after a little epwa, on oxygen (not so hot) or carbon (better).

13.1. When judging overlap, you may move the orbitals closer together (depending on how big you drew them in the first place) to see if there is net constructive (or destructive) interaction.

14.1. The resultant orbitals point in the positive and negative z direction.

14.2. Which p orbital you use determines the direction the hybrid points.

14.3. This problem is sneaky. Along the line $y=x$ the functions overlap constructively. Along the line $y=-x$ destructively. What is the net effect?

15.1. You will have to determine a coordinate system to answer this problem.

17.2. Since this atom is sp hybridized, it is using an sp hybrid to form a σ bond to a hydrogen and the other sp hybrid to form a σ bond to the carbon. That leaves two p orbitals left which are forming two π bonds to the neighboring carbon.

18.0.2. With those defined axes, the sp^2 hybrids use the s, the p_x , and the p_y orbitals, so the π bond is formed from overlap of the two p_z orbitals.

18.1. Which atom has the highest I.E., C or O? An orbital is more like the atomic orbital it is closest to in energy.

18.2. Conservation of orbital is a useful concept. If you use a lot of an atomic orbital in one mo, you have little left for the other.

19.1. sp^3

19.2. The hybrids do not point at the atoms to which you wish to bond the carbon atom.

19.3. Less stable than expected.

21.2. An sp^2 carbon will form three σ and one π bond.

22. To do a π only problem, simply remove any orbitals used in σ bonding from the problem. It makes the mo diagram very simple.

23.0.2. A sp hybrid is 50% s and 50% p, so equal amounts.

23.0.3. Since s is more stable than p, an orbital that is 50% s (sp) is more stable than an orbital that is only 33% s (sp^2).

24.0.2. You start with a pair of electrons in the π bonding orbital, then one to the π^* level. So now you have one bonding and one antibonding electron: net, no π bond.

25. The fourth exercise. The longest chain, from upper right to lower left, is six carbon atoms, so it is a hexane. There are substituents (in this case methyl groups) on the 3 and 5 positions numbering from the upper right. But if I number from the lower left, they are at the 2 and 4 positions: better. 2,4-dimethylhexane.

26. Last compound. The order of precedence (google "IUPAC nomenclature of organic chemistry") is ketone over alcohol, to it is a heptane, a heptanone, a 3-heptanone, a 5-hydroxy-3-heptanone.

30. The carbon level is the number of bonds that a carbon atom has to more electronegative atoms. So in the first compound, all c.l. are 0. In the second, the carbon attached to the OH is c.l. 1.

30.0.2. 1, 1, 1, 1, 2.

30.0.4. You need an electron rich site. Double bond, O, O, triple bond.

30.0.5. You need an electron poor site. C attached to Cl, C attached to O, C attached to N (or the H of the N), positively charged carbon atom.

31.5. Hydride is a nucleophile, so it would attack the positive C attached to the oxygen in butanal. An epwa from the hydride to a dotted line between the hydride and the carbon forms the new bond. This demands (because C now has five bonds) that the double bond be moved to a lone pair position on the oxygen, ogeda. The result is a negatively charged oxygen, which, when H^+ is added gives an alcohol.

35.0.1. Newman projections require a specified C-C bond, unless there is only one.

35.0.2. Same as for ethane but one H replaced with a -CH₃.

40. There are no isomers as only rotation about a σ bond converts the forms into each other. There are two unique conformers, gauche and anti. The conformer with the compound at the top of the potential energy surface does not live long enough to be considered a conformer.

41. We have

$$K = \frac{11}{89}$$

which is the definition for an equilibrium constant for products (gauche) over reactants. Now the free energy change under standard conditions is related to the equilibrium constant by

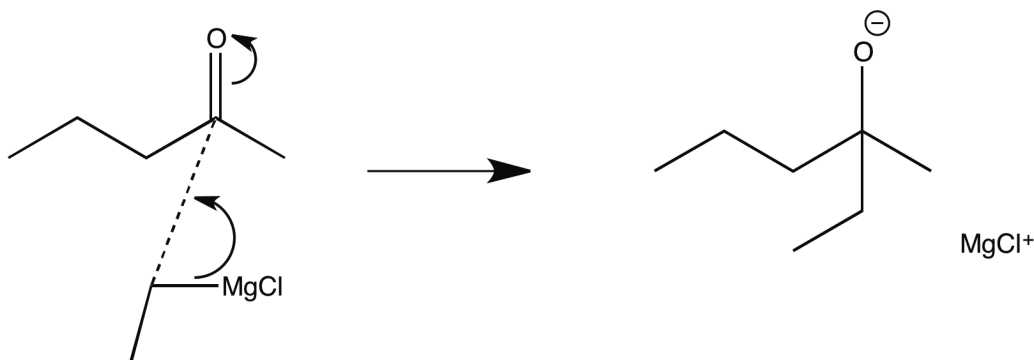
$$\Delta G^o = -RT \ln K$$

42. Br₂ is to the right in the periodic table and hence electrophilic. A double bond is somewhat electron rich (the electrons are more loosely held than those in a normal, σ , bond. Hence we get an epwa from the double bond to a Br and an ogeda from that Br to the other. Then attack of the Br⁻ on the positively charged carbon. Write it out.

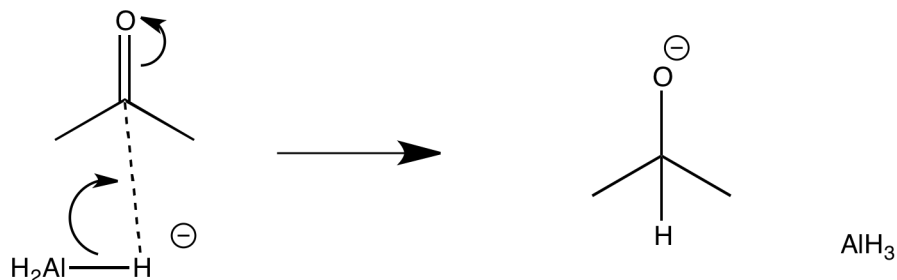
44.0.3. Epwa the double bond of the oxygen to form a bond to H⁺ and the carbonyl carbon becomes positive.

45. Reactions of H⁺ are usually fast compared to other reactions. Mixing BH₄⁻ with H⁺ causes hydride to react with a proton to form H₂, fast; and therefore, no reaction with the organic compound.

46. Is there a positively polarized site in **2**? If so, there must also be a negatively polarized one (as the molecule is neutral). So you could have the positively polarized Mg attack the negative site on **2** – the oxygen atom – or the negatively polarized carbon – the one adjacent to the magnesium atom – attack the positively polarized site on **2** – the carbonyl carbon. The former occurs without net effect. The latter leads to the reaction of interest. If you epwa the electrons between the carbon and the magnesium to the carbonyl carbon, and then ogeda the C=O to the oxygen, you have the first step in the mechanism:



49.1. Do you see the similarity between this mechanism and the one in exercise 46?



49.2. Which atom is more electropositive, B or Al? What does that do to the hydride attached to each?

53.1. In water is there a positive site? What happens if the C^- of the Grignard reacts with it? Use epwa.

53.2. In CO_2 is there a positive site? What happens if the C^- of the Grignard reacts with it? Use epwa.

54. "How would you synthesize?" That question will come up again and again. "Synthesize" usually means making a new bond. Look at the target molecule and figure out where the new bond is relative to the starting material. Then ask yourself "What ways do I know to make that kind of bond?" At the moment, very few ways to do anything. As we go along, many more. So find a way to organize the reactions in your head. From bromoethane we insert a magnesium into the C-Br bond simply by mixing the two reagents together (under dry conditions).

55. The only kinds of bonds that we know how to make within organic molecules are C-C and C-H. Both require using a ketone or aldehyde. So in **5** I would expect we are making the C-C bond right below the C-OH bond. We do that with a Grignard or an alkyl Li reagent, then add H^+ to protonate the negative oxygen.

56.0.1. Looks to me as if we are making a new C-H bond.

56.0.2. Looks to me as if we are making a new C-C bond.

56. You need to draw the molecule. When I do so I see a need a bond between the C that used to be the carbonyl of acetone and an ethyl group.

2. SPECTROSCOPIC ANALYSIS

58.0.1. There are only two variables in the equation for the frequency, the strength of the bond and the mass of the atoms. The common feature looks to me to be the mass.

58.0.2. And if there ever was a change in bond strength, here it is.

58. The first has characteristics of an alkene (3016 cm^{-1} and 1658 cm^{-1} ; the latter does not.

59. A peak at 3410 cm^{-1} (sharp) and 2150 cm^{-1} (sharp and weak) is characteristic of an alkyne. The broad peak at 3400 cm^{-1} suggests an OH, and the peak at 1725 suggests a C=O, which, with the peak at 2710 cm^{-1} may be an aldehyde.

60.0.1. What is the difference in IR between an alcohol and a ketone?

61.0.1. The alkene peaks at about 1600 cm^{-1} and about 3100 cm^{-1} will disappear to be replaced by a peak at about 1700 cm^{-1} .

61. There is an OH peak clearly. Also a carbonyl which suggests, if you believe in Occam's razor, a carboxylic acid group.

62. **C** has an OH and an alkene with at least one hydrogen.

63. For structure **7**. With an oxygen in the molecule I might look for an OH. But I do not see any sign of that in **7**. Or it could be a carbonyl compound; again no sign of that. That leaves an ether.

64. HINT: The broad peak centered near 3400 cm^{-1} is less intense than normal.

66. **A** is clearly an alkene with the C-H of 3090 cm^{-1} and the C=C of 1620 cm^{-1} . The O atom in the molecule must therefore be an ether oxygen in the middle of the molecule with an alkene on each side in order to have symmetry.

67.3. My memory is not good and requires reminders often. Writing down an answer often if one way to train your mind.

69.0. **A** has a carbonyl, but that doesn't help much. No peak above 3000 cm^{-1} eliminates **202** and **203**. The amide, **205** is eliminated because of the lack of the broad signal(s) due to the NH_2 group. Between **201** and **204**, the former is a ketone and would not have the 2700 cm^{-1} peak.

B is the amide. **C** is either **201** or **204** because of the lack of a double bond and the lack of NH stretches. Which is not easy. The 2700 cm^{-1} peak that we used in fixing **A** could be there and was overlooked. So "don't bet the ranch" on this one.

70. Although some texts suggest actual numbers to reflect a shift of the nmr signal of a proton from its normal position, I feel that clutters my brain unnecessarily. For instance, it is said that a methylene group (normally at about 1.2δ) is shifted by 2.5δ if it is next to an OH, but is shifted by 3δ if it is next to an ester oxygen atom. I think you can do nmr by just knowing that a methylene group is shifted by about $2-3\delta$ by an oxygen (or a Cl or a Br).

71.2. Have I baited you into this trap enough times? You **cannot** use the position of a signal to ascertain the presence of an OH group. That is one reason we have IR.

72. Part d. Because it is positively charged, it is deshielded. Far from TMS.

74.0.1. 114.

74.0.2. An NH_2 group (mass 16) replaces a hydrogen atom (mass 1). Net increase in mass is odd. Compare this to a CH_3 group (mass 15) replacing a hydrogen atom for a net increase in mass of 12.

74.0.3. There would be two molecular ions of mass 108 and 110 of nearly equal intensity.

74.0.4. There would be two molecular ion peaks of mass 120 and 122 of ratio 3:1.

74.0.5. Five times 0.011 or 0.055.

74.0.6. Contains a single bromine atom.

74.0.7. Looks like it has an OH and maybe a couple of alkene groups.

74.0.8. The M+1 peak has intensity that is $\frac{3.9}{27.2}$ of the M peak. Divide this by .011 to find there are 13 carbon atoms in the molecule.

74. Yes, no, no, no.

75. 3, 3, 1, 2. In the last, there is the bridgehead proton (where three bonds to other C occur) and the external hydrogens.

76. For methylbutyrate, the methyl is deshielded by the O to around 4δ . The other end of the chain is essentially unaffected by the functional group, hence that methyl occurs at about 1δ . The methylene group next to the carbonyl is at $2.1\delta +$ the 0.2δ difference between methylene and methyl, or 2.3δ , and the methylene group at position 3 will be between 2.3δ and 1.0δ , say 1.3δ for a guess.

77. For **2**, one signal with area of 9 at about 1.0δ and a second signal of area 2 at about 3.4δ .

For **7**, one signal at about 2.4δ .

77.0.3. In **748**, there are only two kinds of hydrogens, one an alkene ($4-5\delta$) and the other around 2.3δ . (close to an alkene). They have equal areas. In **749**, there are two kinds of alkene hydrogens and one alkyl hydrogen of areas 1:1:2.

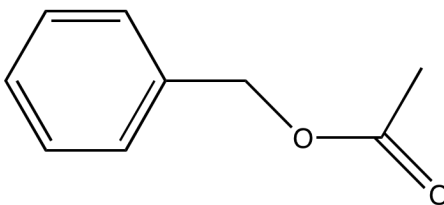
79. For the first, there is the methyl group, then the two hydrogens ortho to the methoxy group, then the two hydrogens ortho to the bromine atom. (ortho is the position in the benzene ring next to the substituent).

80. Fixing the areas so that the smallest is 1, I get 6:1:2. The total is 9, which is consistent with the formula, so I am on the right track. The six are likely two methyl groups because of the chemical shift and the area. This suggests a $(\text{CH}_3)_2\text{C}-$ group. They must be a long way from the Br. The signal at 3.3δ is next to the Br, and is a pair of H's, so that suggests a $-\text{CH}_2\text{Br}$ group. I am missing only one H, so the compound is $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$.

81.0.1. $\text{ihd} = 0$. There must be a lot of hydrogens in the same environments – the molecule must be symmetrical. I looked at some ether possibilities, but that didn't work because of the odd number of carbon atoms. An alcohol suggests itself. In fact, how about 1,1-diethylpropanol.

81.0.2. Here is our first case with "real" data. **You have to approximate areas.** $\text{ihd} = 0$ and areas suggesting 1:3 hydrogen environments, or, if you want the total area to equal the number of hydrogen atoms, 3:9. The three have a δ value that suggests they are next to an O. The nine are further away. How about tert-butyl methyl ether?

81.0.3. $\text{ihd}=5$ means most likely a benzene rings is present. That is supported by the signal at 7.4δ with an area of 108. I am going to guess only one substituent on the benzene, so that area implies one H has an area of 21, which means the other environments are of 2 and 3, for a total of 10 H, which is what the formula says. OK! The rest of the ihd (over 4 for the benzene) says a double bond, so I suspect a C=O. The 2.2δ signal (with area of 3) is a methyl group next to the carbonyl (2.1δ , close enough, ding, ding, ding), and the 5.2δ is then a methylene between the deshielding benzene ring and a deshielding oxygen. I think the compound is:



82. 4,4-Dimethyl-2-pentanone

83. $\text{ihd} = 4$ suggests a benzene ring. The 7.3δ signal supports. If I assume a monosubstituted benzene, then I need to double the areas to get an area of 5 for the 7.3δ signal. So the other environments are 6 and 2. All the other environments are deshielded, so next to the benzene ring or the N. How about dimethylbenzylamine?

87. In one word: symmetry.

89. A classic case of everything falling into place when you listen to a few bells. Firstly, $\text{ihd} = 1$. Secondly, 2.1δ unsplit with an area of 3: ding, ding, ding. CH_3 next to a carbonyl. Then a splitting into a triple and a quartet – ding, ding – with areas 3 and 2, respectively, an ethyl group. The chemical shift of the CH_2 group (2.4δ) suggests it also is next to the carbonyl. So the compound is easily found to be butanone.

89.0.1. $\text{ihd}=?$ No splitting, so all H are greater than three bonds away from each other. Area of 6 suggests? Area of 2 deshielded to 3.9δ ?

89.0.2. $\text{ihd}?$ 7.3δ signal with area of 5? The rest of the molecule has a quartet and a double splitting each other with the quartet – the single H – strongly deshielded.

90. An exercise where you take advantage of coupling constants. The 1.14δ signal and the 2.32δ signal split each other – suggesting an ethyl group – and the 1.26δ and 4.13δ signal split each other – suggesting a second, non-equivalent, ethyl group. The second ethyl group has its CH_2 strongly deshielded – next to an O? And, ding ding ding, the first next to a carbonyl?

91. $\text{ihd}=1$. First problem with an exchangeable hydrogen – usually means an OH or an NH. It comes on and off rapidly, so that if you put your sample in deuterated solvent, the signal from this H disappears as it is replaced with a D. Also, 1.14δ with an area of 9: DING. tertiary butyl group.

95.0.1. There is the methyl carbon and the carbonyl carbon. The former has a signal probably near 20δ , the latter is in the $190\text{--}220\delta$ region.

95.0.4. There four carbon environments in 2-butanol. One, that bonded to the OH, is strongly deshielded, 70δ , and will be a doublet because of the H on that carbon. The two methyl groups at the two ends of the chains will both be quartets, the one in the "4" position will be less deshielded, 10δ , whereas the other will be slightly deshielded, 20δ . The CH_2 group will be a triplet and will be slightly deshielded, 30δ .

96. The 209δ signal says carbonyl of aldehyde or ketone. That it is a singlet means there are no hydrogens on the carbon, so it must be a ketone. The splitting of the other signals imply two methyl groups and a methylene. 2-butanone.

96.0. $\text{ihd} = 1$, so an alkene or ring. Only three kinds of C, symmetrical. One of the ^{13}C positions suggests an alkene (138δ). So cis or trans 3-hexene.

97. $\text{ihd} = 4$, benzene. Also 6 different aromatic peaks and one non-aromatic carbon. So CH_3 and Br on the ring, either in ortho or meta positions, but not para (for then there are only four kinds of C in the ring).

99. IR says, remarkably, that ALL the C-H bonds are sp^2 . Also the peaks in the $1600\text{--}1700\text{ cm}^{-1}$ region and the little peaks in the 1800cm^{-1} region suggest a benzene. This is supported by the integration of 5 for the signals between 7.1 and 7.5δ . Use ^{13}C data to determine nature of other carbons. H integration suggest three separate single proton environments splitting each other in a certain fashion.

103.0. $\text{ihd} = ?$ What does IR tell you? Any support for that in ^1H ? Check the shielding or lack thereof.

104. $\text{ihd} = ?$ Singlet at 2.03δ . Triplet and quartet with 3/2 ratio. Deshielded methylene.

107. $\text{ihd} = ?$ ^{13}C data, especially 214δ . The heptet must have the 1.09δ two methyls as a neighbor. The 1.59δ sextet must be between a CH_3 and a CH_2 .

113. The possible spin states for the 2 deuterium atoms are: total of -2: (-1,-1), one way total of -1: (-1,0), two ways total of 0: (0,0), and two other ways total of 1: (1,0), and one other way total of 2: two ways.

114.0.2. Think about ring current and how that affects the position of a signal.

115. Think about how low temperature can freeze out conformers.