Chem 331, Spring 2006

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Name Key

PLEASE ALSO WRITE YOUR NAME ON THE TOP OF THE BACK OF YOUR EXAM

Please check off which recitation section you are registered for:

_____ Monday, 2:10 p.m.

_____ Monday, 4:10 p.m.

_____ Tuesday, 9:00 a.m.

_____ Tuesday, 11 a.m.

MIDTERM 4
3 April, 2006

Problem (max score)	Score
I (27)	
II (12)	
III (16)	
IV (20)	
V (16)	
VI (9)	
Total (102)	

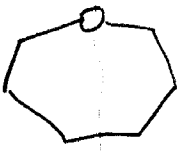
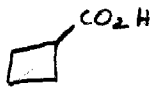
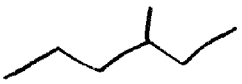
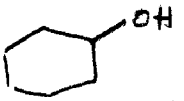
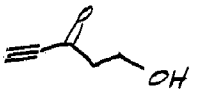
I. Suppose you take a mass spectrum of a sample that results in a molecular ion M^+ of mass 100.

(a) 9 points. Write down three molecular formulae (e.g., H_2O, CCl_4) that correspond to this mass. You may use the elements C, H, N, O, S.

C_7H_{16} $C_6H_{12}O$ $C_5H_8O_2$ C_5H_8S etc

Note $O = 16\ g/mol = CH_4$

(b) 12 points. Write down two molecular structures that correspond to each of these formulae (i.e., a total of six structures).

 4	 3	 4
 7	 4	 5

(c) 6 points. In the boxes above, indicate the number of unsaturations for each molecule.

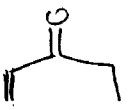
There are many possible answers on this page.
Parts b and c are graded based on your answers for (a).

II. (a) 6 points. Propose a structure below that is consistent with a mass of 86 and a strong, sharp band in the infrared spectrum at 1715 cm^{-1}.

C=O

86 with 10 = $C_5H_{10}O$ (70 + 16)

Again, many possible answers



(b) 6 points. Assume your answer in (a) is correct, but that you want to check it by looking back at the mass spectrum. Propose the mass (m/z) of one prominent fragment (besides the molecular ion) that you would expect to see.

Here, a good choice is α-cleavage $\overset{+}{C}\equiv O$ 86-29=67

III. A particular compound has been examined by ~~Mass Spectrometry~~ and IR. The mass spec shows the formula is C_4H_6. The IR spectrum shows no significant IR bands above 3000 cm^{-1}.

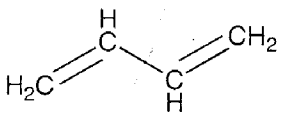
No $=C-H$ or $\equiv C-H$ or OH

(a) 5 points. Three possible structures for this formula are shown below. Circle the correct one.

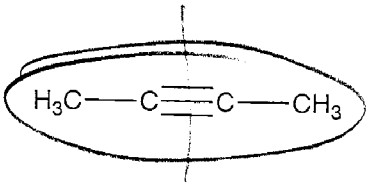
(b) 5 points. Briefly explain your reasoning.

only middle structure does not have $=C\overset{H}{}$ or $\equiv C-H$, which would give bands over 3000 cm^{-1}

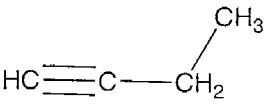
(c) 6 points. In the small boxes below each structure, indictate the number of ^{13}C NMR signals that would be observed for each compound.



2



2



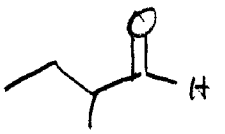
4

Need a chiral center

IV. A compound is optically active (rotates plane polarized light). Its high resolution mass spectrum provides a formula of $C_5H_{10}O$. Its IR spectrum has a large, sharp peak at 1730 cm^{-1}

C=O

(a) 8 points. Propose a structure consistent with these data.



only plausible answer

(b) 2 points. How many ^{13}C signals does this molecule give?

5

A different compound that is NOT optically active also has a formula of $C_5H_{10}O$. It has a large, broad IR band at about 3300 cm^{-1} but no IR peaks between 3000 cm^{-1} and 3200 cm^{-1}. It has a mass spec peak at its molecular ion (M^+ = 86) and another prominent peak at M^+ = 68.

No chiral center

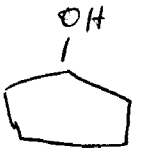
(c) 8 points. Propose a structure consistent with these data.

OH

OH

(M-18)

NO



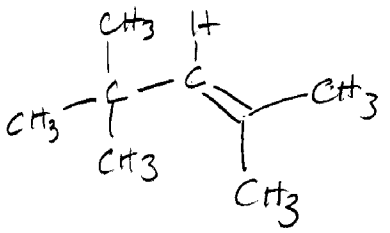
(d) 2 points. How many ^{13}C signals does this molecule give?

3

V. 8 points each. Propose structures consistent with these data:

C_8H_{16}

^{1}H NMR: δ 5.2 ppm (1H, singlet), 1.7 ppm (3H, singlet), 1.65 ppm (3H, singlet), 1.1 ppm (9H, singlet)
^{13}C NMR: δ 135 ppm, 130 ppm, 32 ppm, 31 ppm, 26 ppm, 19 ppm



$C_3H_6Br_2$

^{1}H NMR δ 3.6 ppm (4H, triplet), 2.3 ppm (2H, quintet)
^{13}C NMR: two signals, both under 100 ppm
IR: No peaks above 3000 cm^{-1}

VI. 9 points. Assign the ^{13}C spectral signals to the correct atoms in the molecule shown below. Show your assignments by writing the letter(s) of the carbons near the peak. Note that there are 6 signals and 8 carbon atoms.

This spectrum was obtained under conditions where the CH and CH_3 peaks are upside down, which should help you assign which peaks go with which carbon atoms. If you don't think you have quite enough information, you may write "a or b" (or whatever) and if one signal corresponds to more than one carbon, indicate that by writing "a and b" (or whatever).