Name _____ Test 3 (4/29)
CHEM 0203 (Organic II) Spring 2011

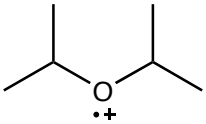
1. A molecular fragment that has an m/z of 57 was observed in a mass spectrum. The relative intensities of the peaks at m/z 57 and m/z 58 are 47.6 and 1.6 respectively. (8 pts.) Is the formula of the fragment $C_4H_9^+$ or $C_3H_5O^+$? Explain your choice.

1. _____

2. _____

3. _____

2. (16 pts) The structure of a molecular ion generated in a mass spectrometer is drawn below. (a) Draw and label the mechanisms for the likely homo- and heterolytic cleavage reactions, and (b) determine the m/z for the detectable fragments.



4. _____

5. _____

6. _____

7. _____

8. _____

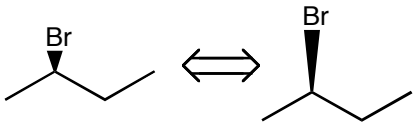
9. _____

10. _____

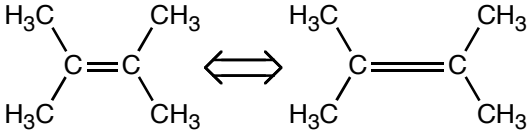
3. (8 pts.) The molar mass of 2-bromobutane is 137.02 g/mol. Nevertheless, the mass spectrum does not contain a peak with an m/z = 137. The mass spectrum does, however, contain two peaks of nearly equal intensity near 137, the m/z of these peaks are 136 and 138. Explain this observation.

4. (3 pts. each) Which of the following vibrational modes would be IR active,

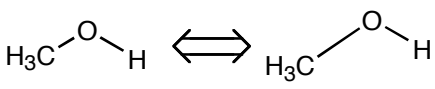
a.



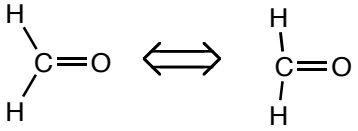
b.



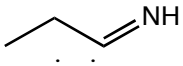
c.



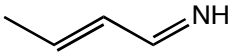
d.



5. (10 pts.) The stretching frequency for a typical imine can be seen in the range of 1690–1640 cm^{-1}. However, conjugated imines have stretching frequencies (wave numbers) that are a bit lower.



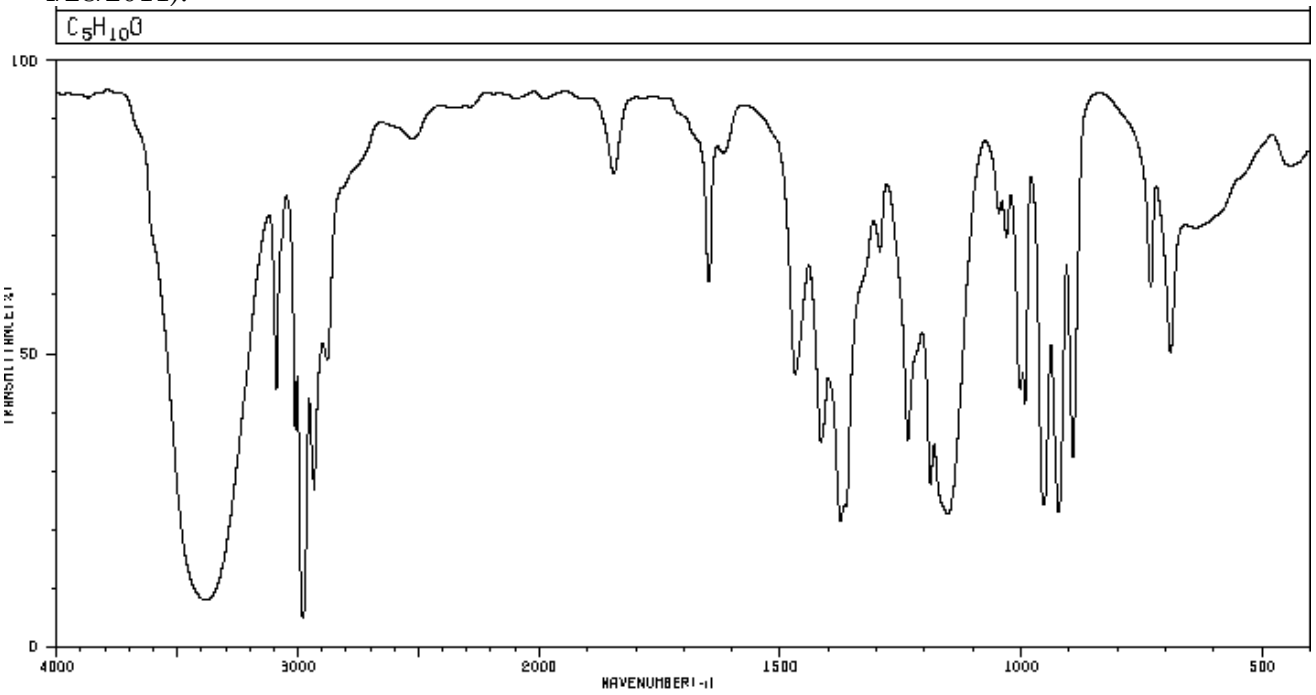
imine



conjugated imine

Explain why the stretching frequency for a conjugated imine would be lower.

6. (10 pts) In IR spectrum for a molecule with the formula $C_5H_{10}O$ is pictured below. (Data downloaded from http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng on 4/28/2011).

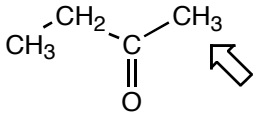


3390	7	2632	84	1375	20	1031	68	690	49		
3380	7	2522	84	1364	23	1002	42	439	79		
3089	42	1645	77	1293	64	992	39				
3011	35	1649	60	1236	34	952	29				
2979	4	1618	81	1188	26	922	21				
2933	26	1469	44	1153	21	893	31				
2879	47	1416	39	1047	70	731	68				

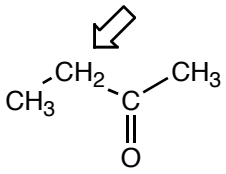
Identify as many structural features of the molecule as you can. Remember to indicate which peak in the IR spectrum is being used as evidence for the structural feature. Remember to be as specific as possible.

7. (3 pts. each) Determine the multiplicity (singlet, doublet, etc.) of the peaks associated with the indicated protons.

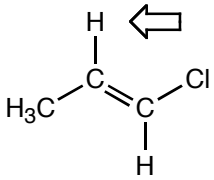
a.



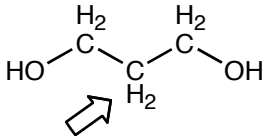
b.



c.

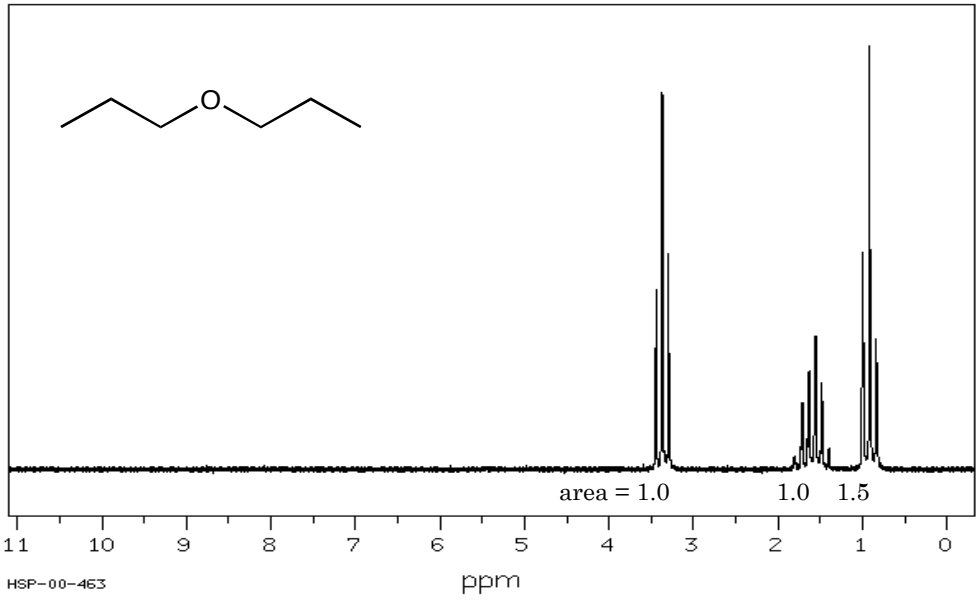


d.

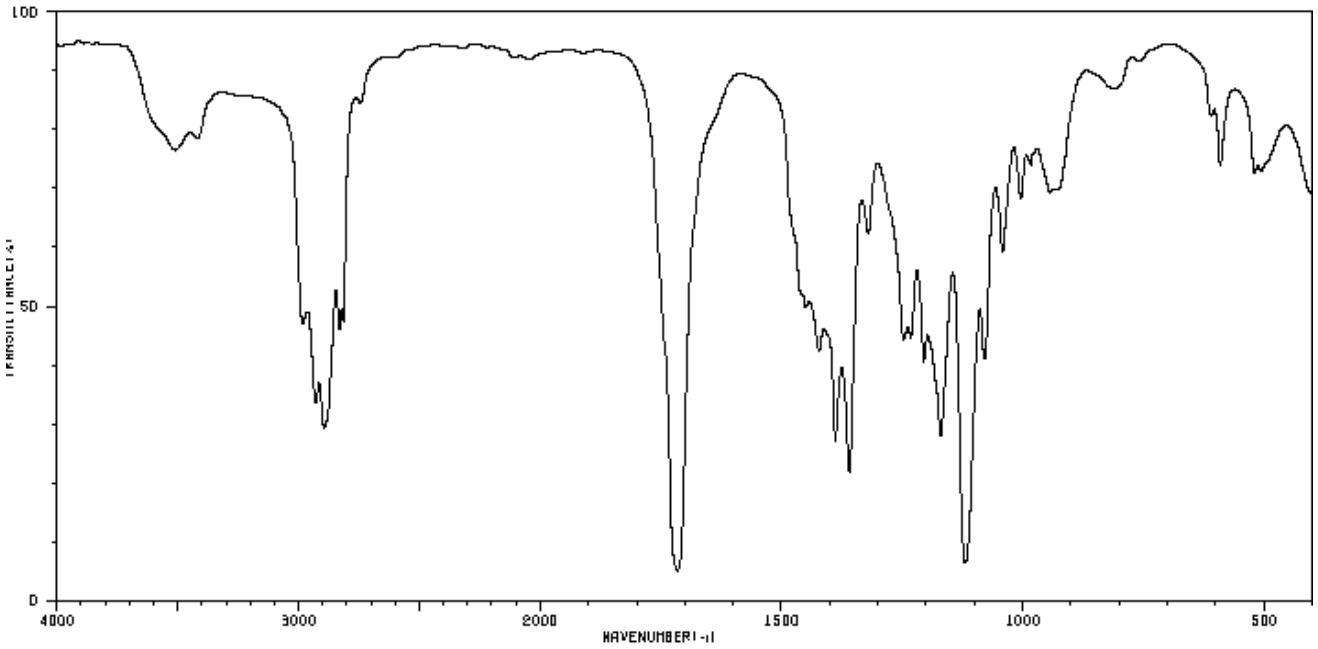


8. (10 pts) What does the chemical shift of a peak in the NMR spectrum of a molecule tell us about the protons associated with the peak. In other words, if a given peak is farther to the left that another, what does that suggest about the protons associated with the peak further to the left? Explain your response.

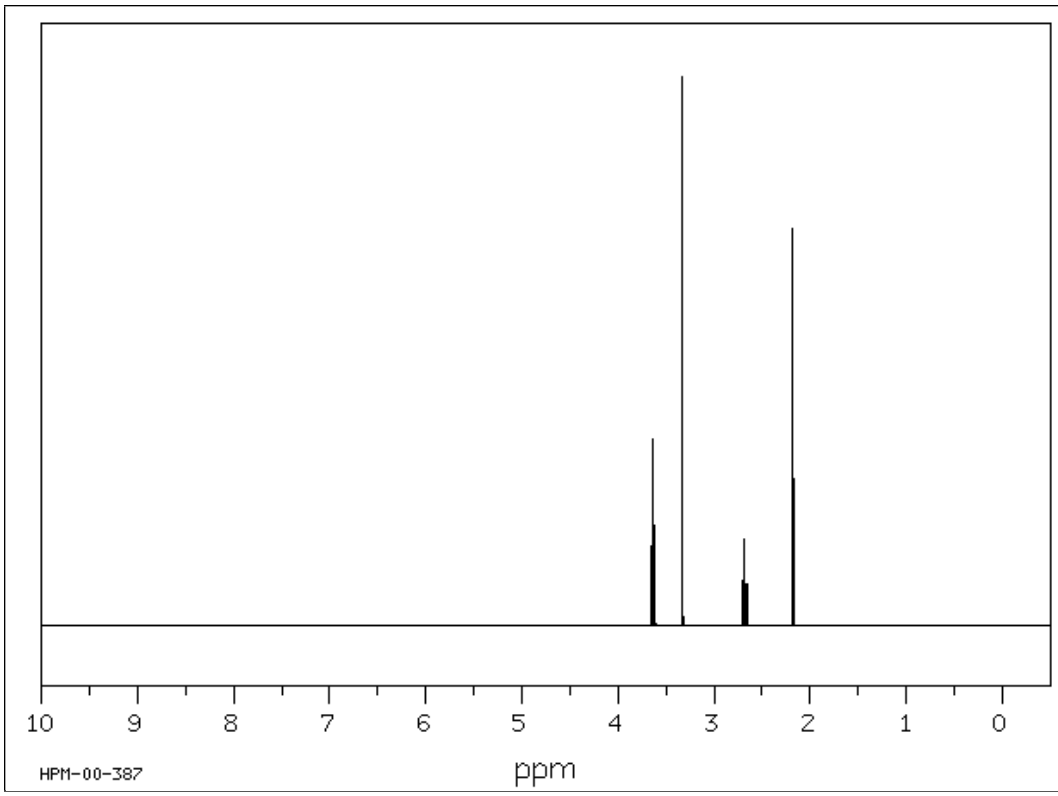
9. (10 pts) Assign the peaks in the following ^{1}H NMR to the structure drawn on the spectrum.



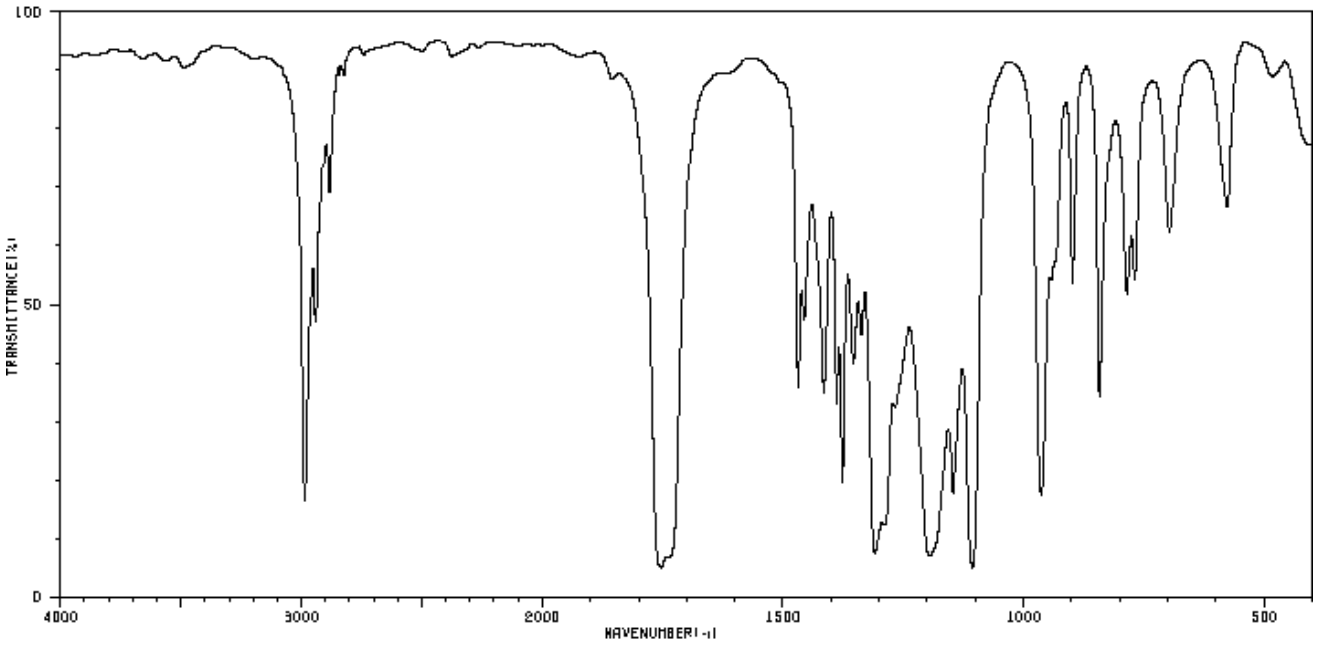
10. (10 pts.) Determine the structure of **one** of the molecules on the following pages. **Clearly indicate which page should be graded.**



3607	74	1716	4	1206	38	944	66	620	70	$C_5H_{10}O_2$	
2983	44	1422	41	1170	26	935	66	511	70		
2929	32	1389	26	1119	6	927	66	505	70		
2895	28	1360	21	1079	39	816	84				
2830	44	1320	60	1042	57	810	84				
2814	46	1247	42	1004	66	591	70				
2743	81	1232	49	984	70	584	77				

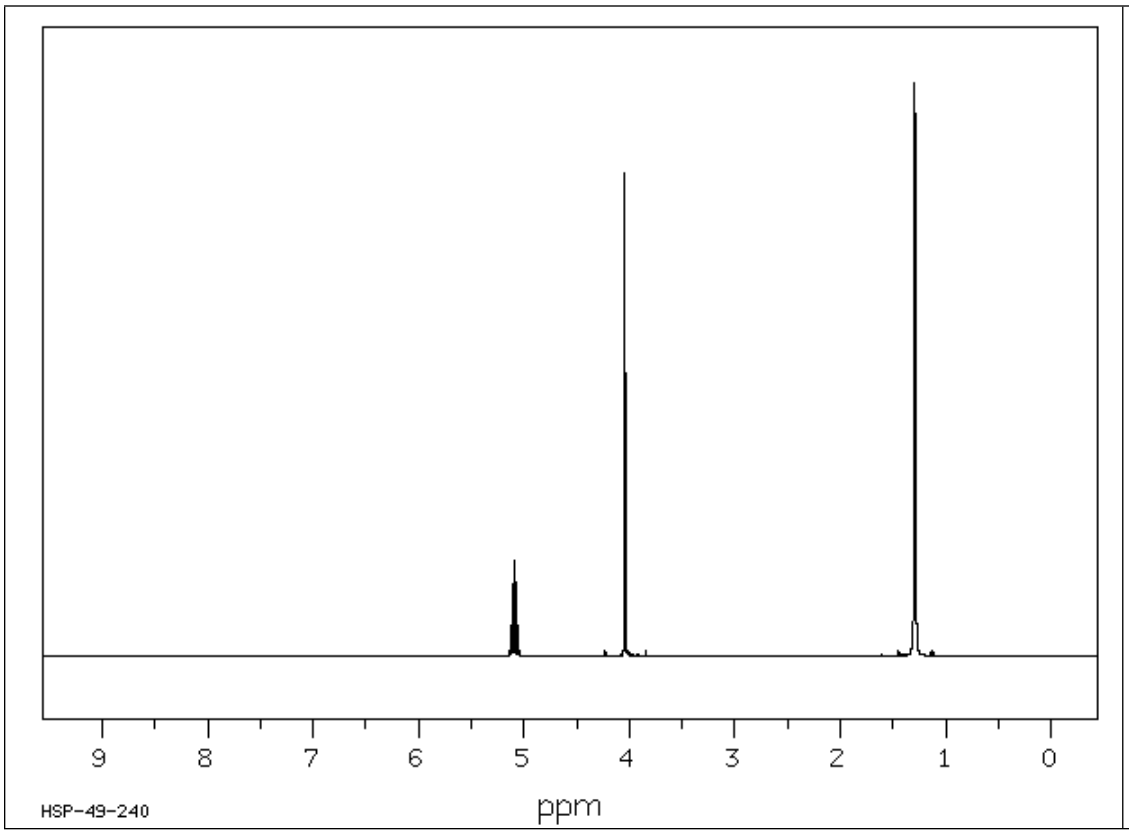


ppm	height
3.660	157
3.640	326
3.620	170
3.332	1000
2.706	116
2.686	218
2.666	106
2.184	737



The peak list for this IR spectrum was not correct. You should be able to estimate the positions of the important peaks, if you are having difficulty estimating their positions, please ask for help.

$C_5H_9ClO_2$



ppm	height
5.123	52
5.108	127
5.092	166
5.076	129
5.060	53
4.040	842
1.297	1000
1.281	946