Chem 342 Organic Chem II

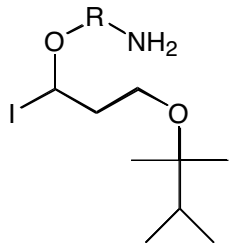
Midterm Exam 01
08 February 2002

NAME_____**KEY**_____

QUOTE OF THE DAY

It is disconcerting to reflect on the number of students we have flunked in chemistry for not knowing what we later found to be untrue.

-- Robert L. Weber, Science With a Smile (1992)



A 1-I-1-ORN-flying-propyl-people-ether

Please read through each problem carefully. Enter your answers in the spaces provided.

Problem 1	16 pts	_____
Problem 2	8 pts	_____
Problem 3	8 pts	_____
Problem 4	9 pts	_____
Problem 5	18 pts	_____
Problem 6	20 pts	_____
Problem 7	20 pts	_____
given	1 pts	**1**
TOTAL	100 pts	_____

A note about drawing structures: you should make your drawings as clear as possible to understand. Stereochemistry should be indicated unambiguously using conventional drawing techniques (eg. bold wedges and dashes).

The most common mistake on an exam is not reading the question carefully. I suggest you go through the exam and answer the questions that come easily. Then go back and tackle the more challenging problems. Finally, check any work you have done, but remember, your first instinct is usually correct.

If you need scrap paper or more room, use the back of the test pages.

1. Indicate whether the following statements are True or False. (16 points)

T Infrared Spectroscopy can give us information about functional groups.

F Molecules will fragment in the Mass Spectrometer to give only the most stable fragment.

F A kinetically controlled reaction gives the most stable product because the reaction is reversible.

T Conjugation lowers the energy of a molecule because the electrons are more delocalized.

F The energy required to flip a nuclear spin state aligned with a magnetic field lies in the microwave region of the electromagnetic spectrum.

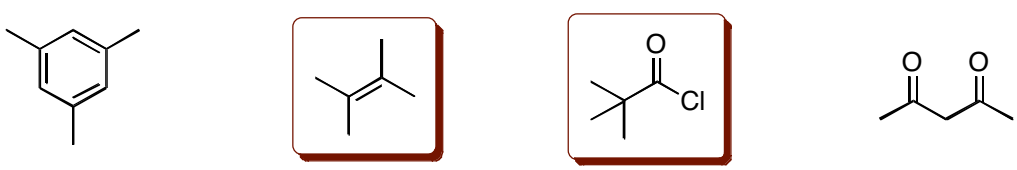
T A proton signal in the NMR will be split into three peaks if it has two neighboring protons.

F Two proton resonances that are coupled to one another will each be split with different coupling constants.

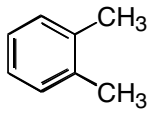
T In a Diels-Alder cycloaddition reaction, all new bonds are formed in a single step.

2. Circle all the following molecules that have conjugated pi-systems. (8 points)

3. Circle all the following molecules that would show only a single peak in the ^{1}H NMR. (8 points)

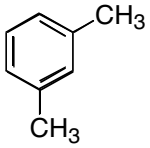


4. The three compounds shown below, ortho-, meta-, and para-xylene have very different ^{13}C NMR spectra. Match the structures with the correct spectra by placing the letter of the compound in the appropriate box. (9 points)



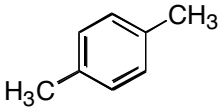
ortho-xylene

A



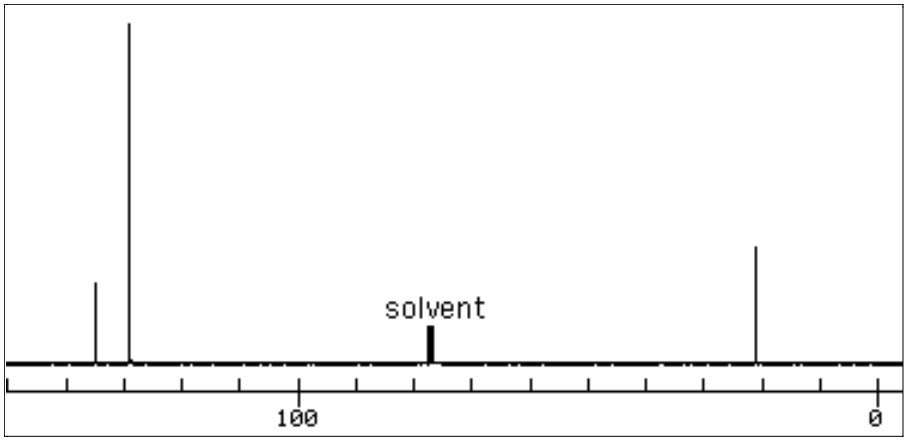
meta-xylene

B

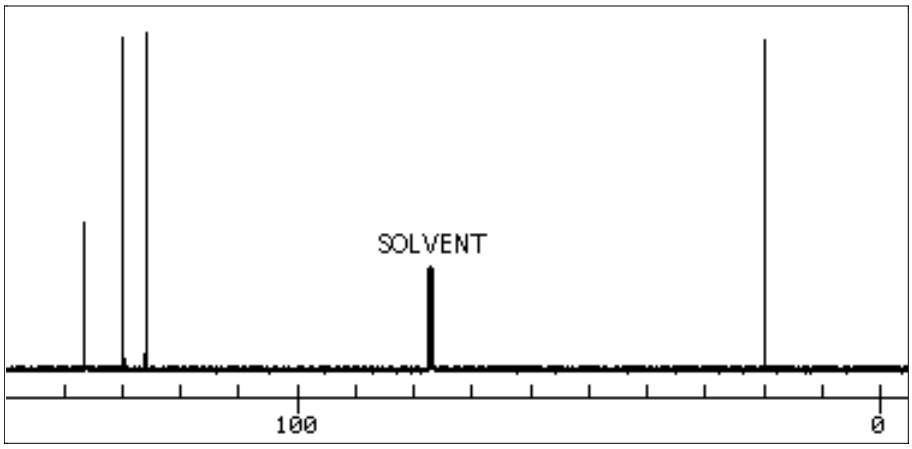


para-xylene

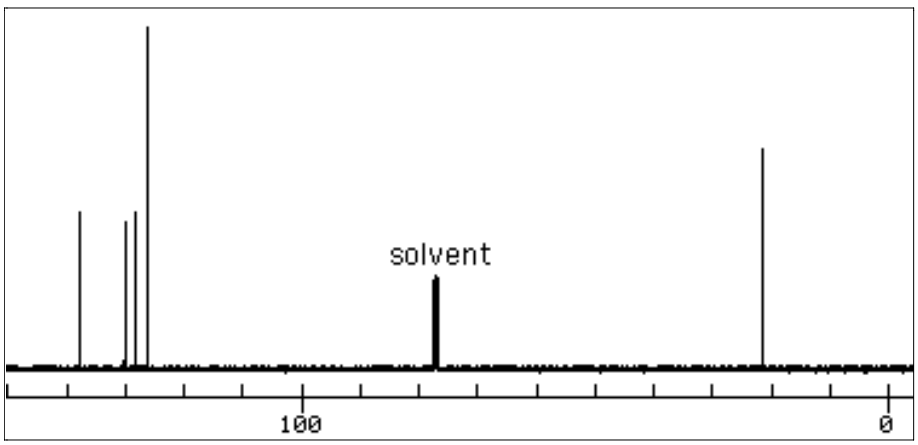
C



C

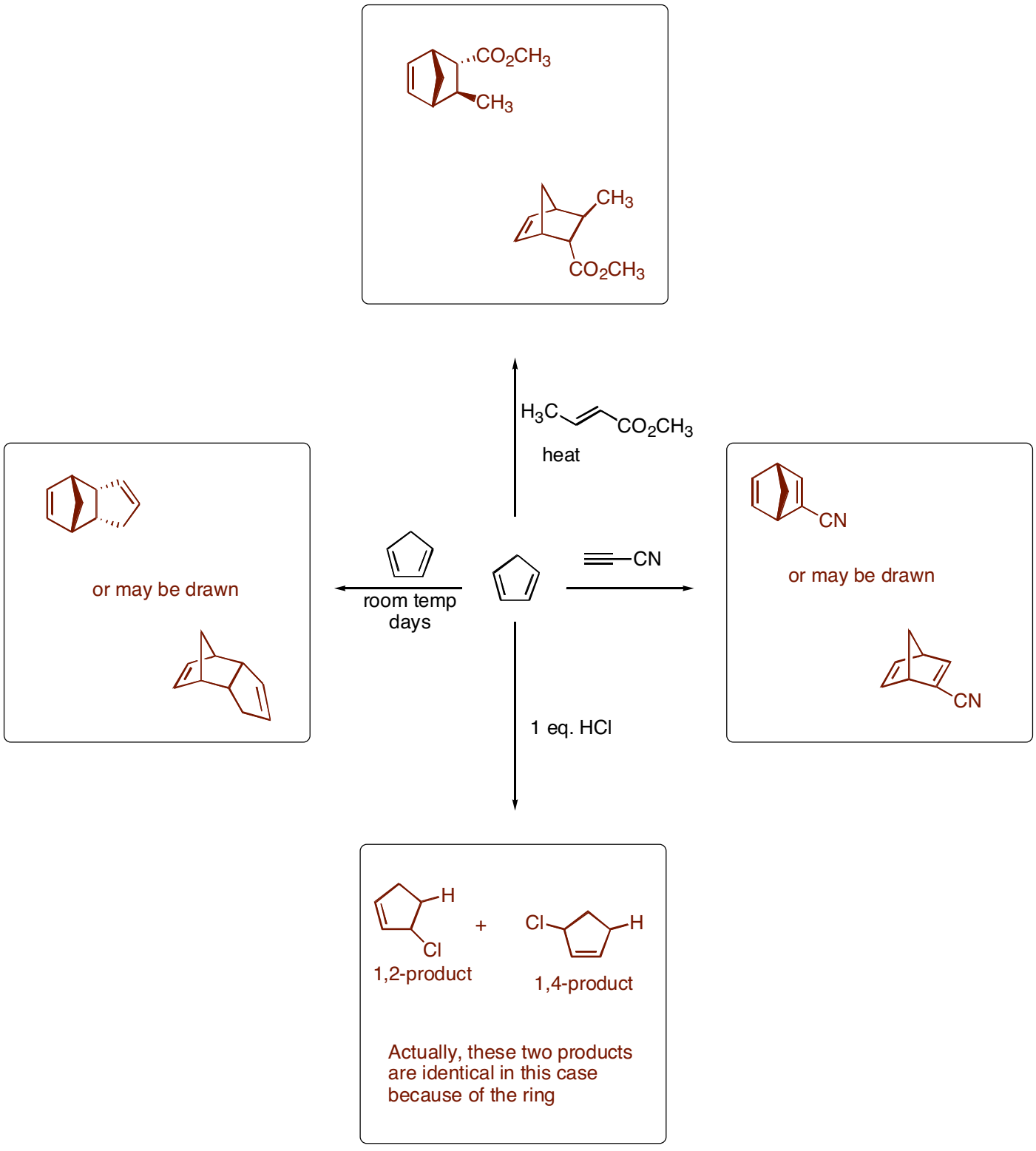


A



B

5. Draw the product or products of the following reactions. Show any stereochemistry clearly where appropriate. (18 points)



6. Answer the following questions about an unknown molecule with a molecular formula of C_9H_{12}. The ^1H NMR, ^{13}C NMR mass spectrum for this unknown compound are shown on the following page. (20 points)

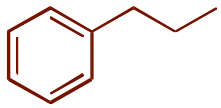
How many degrees of unsaturation does the molecule possess?

4

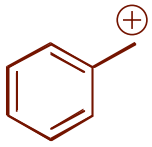
What type of functional group do the proton resonances between 7.0 and 8.0 ppm represent?

AROMATIC
or BENZENE

What is the structure of the unknown molecule?

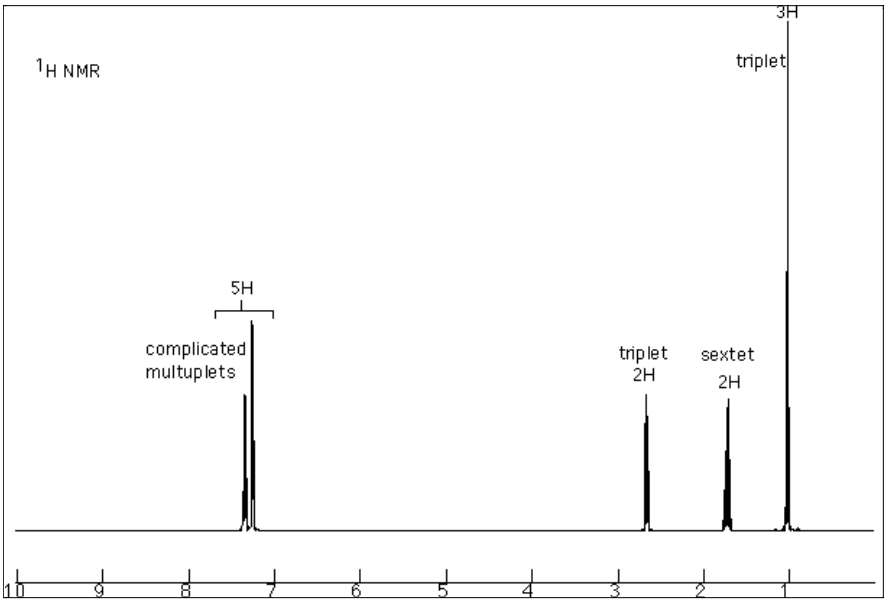


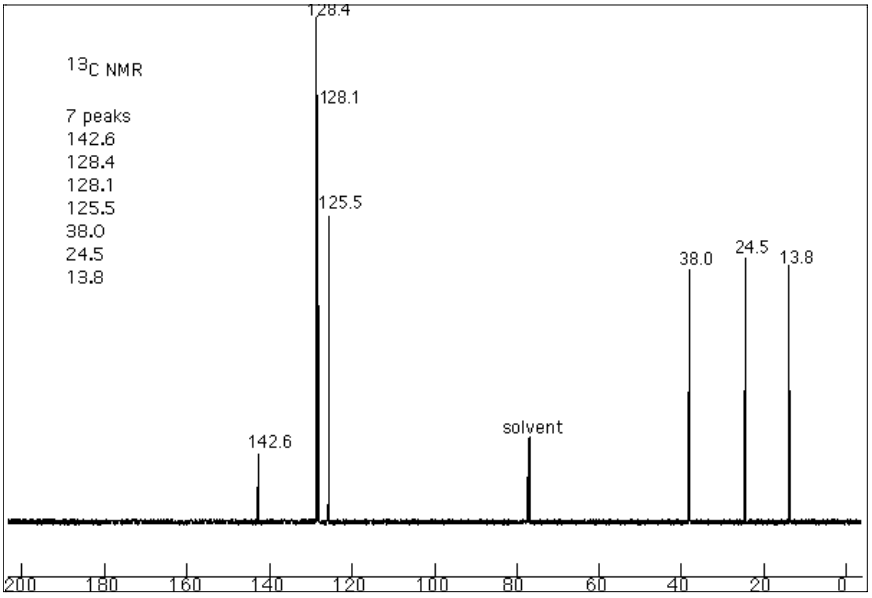
In the Mass Spectrum, what does the peak at m/z 91 correspond to (draw a structure)?

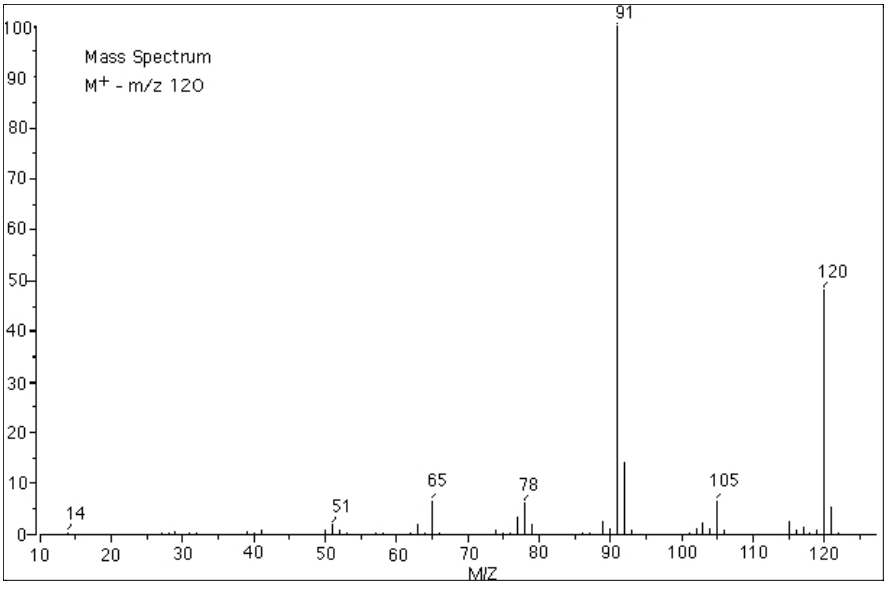


Briefly explain why the MS peak at m/z 91 is the base peak.

The molecule will fragment to put the positive charge on the benzylic carbon (the carbon adjacent to the benzene ring) because this allows for resonance stabilization.


1H NMR
3H
triplet
5H
complicated
multuplets
triplet
2H
sextet
2H
10
9
8
7
6
5
4
3
2
1


13C NMR
7 peaks
142.6
128.4
128.1
125.5
38.0
24.5
13.8
128.4
128.1
125.5
38.0
24.5
13.8
142.6
solvent
200
180
160
140
120
100
80
60
40
20
0


Mass Spectrum
M+ - m/z 120
91
120
65
78
105
51
14
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
110
120
M/Z

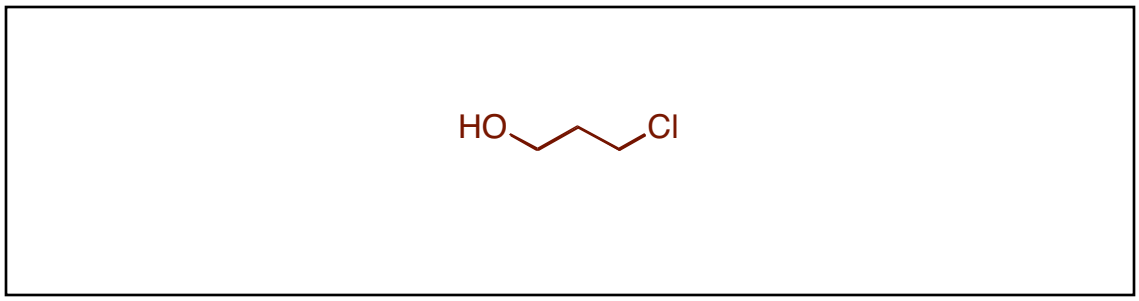
7. Answer the following questions about an unknown molecule with a molecular formula of C_3H_7ClO. A strong and broad IR absorbance is observed centered at 3500 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra for this unknown compound are shown on the following page. (20 points)

How many degrees of unsaturation does the molecule possess? **0**

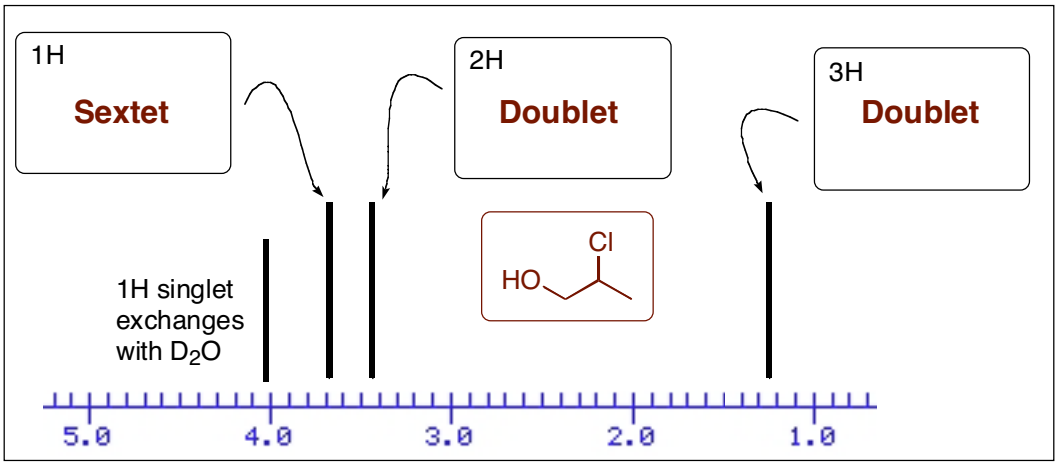
What functional group does the proton resonance at 3.8 ppm correspond to?

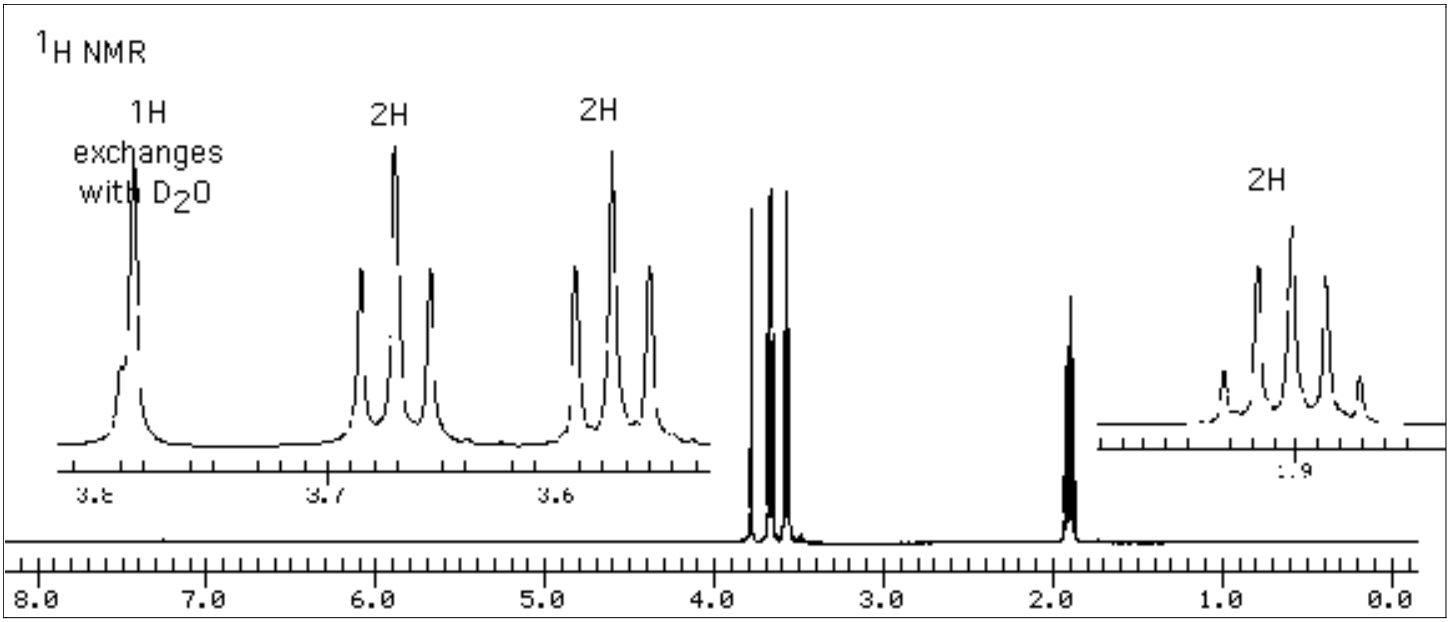
Alcohol (O-H)

What is the structure of the unknown molecule?



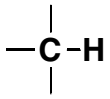
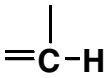
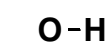
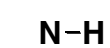
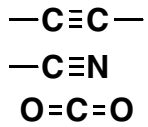
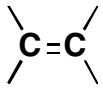
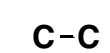
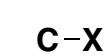
If the chlorine were moved to the middle carbon, indicate on the example spectrum below what you would expect the splitting patterns to be (eg. singlet, doublet, triplet, quartet, etc.)



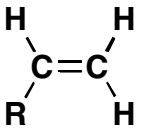
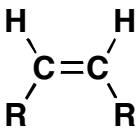
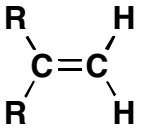
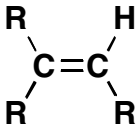
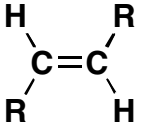

1H NMR
1H
exchanges
with D2O
2H
2H
2H
3.8
3.7
3.6
1.9
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


13C NMR
solvent
200
100
0

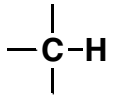
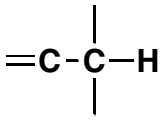
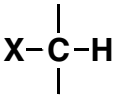
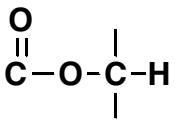
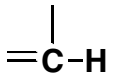
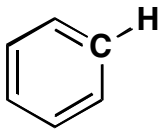
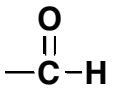
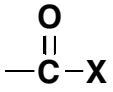
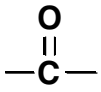
Infrared Stretching Absorptions

Functional Group	Wavenumber Range (cm^{-1})	Absorption Strength	notes
	2850-2960	medium-strong	below 3000
	3020-3100	medium	above 3000
	3300	strong	above 3000
	3400-3650	broad-strong	
	3300-3500	medium	#H's = #peaks
	2100-2260	medium	
	1680-1750	strong	
	1640-1750	medium	
	800-1300	medium	
	1050-1150	medium	
	<1000	strong	

Alkene out of plane bending

	910 and 990	strong		700	strong
	890	strong		815	strong
	970	strong			

Typical NMR Chemical Shifts

Functional Group	Type	^{1}H Chemical Shift (ppm)	^{1}H Chemical Shift (ppm)
	Alkane	0.7 -1.8	10 - 60
	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
	next to halogen or alcohol	2.5 - 4.0	20 - 85
	next to oxygen of an ester	4.0 - 5.0	50 - 85
	vinylic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
	aldehyde	9.7 - 10.0	190 - 220
	alcohol	varies widely will exchange with D_2O	N/A
	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
	carbonyl of ketone or aldehyde	N/A	190 - 220