Chem 342 Organic Chem II

Final Exam

07 May 2002

NAME _____ **KEY** _____

Hey! Be an electron? I'd rather be a proton.

Really!

I'm *Positive*!

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

Problem 1	12 pts	_____
Problem 2	6 pts	_____
Problem 3	20 pts	_____
Problem 4	10 pts	_____
Problem 5	24 pts	_____
Problem 6	15 pts	_____
Problem 7	30 pts	_____
Problem 8	21 pts	_____
Problem 9	16 pts	_____
Problem 10	20 pts	_____
Problem 11	25 pts	_____
given	1 pt	**1**
TOTAL		_____

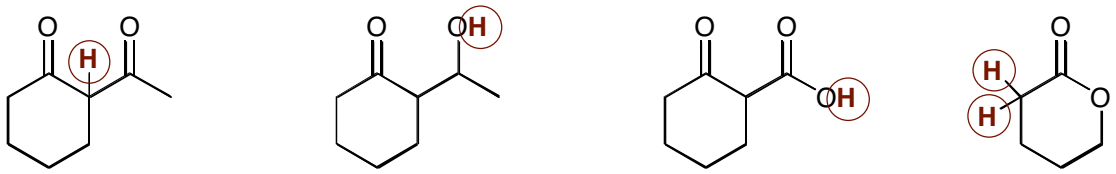
RELAX! Don't get Overwhelmed. Think about what you know.

Try to answer the questions you know and can do quickly first. Then go back and tackle the problems you find more challenging.

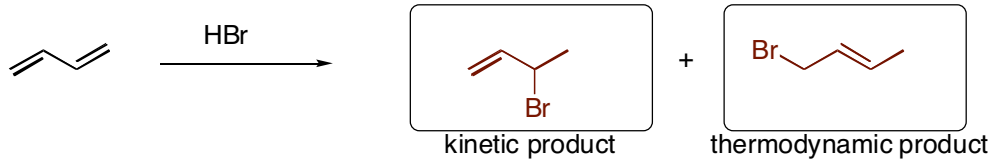
In the multiple step reaction sequences, look at what kind of reaction takes place in the second step to give you clues on what functional group you need to have after the first step.

In synthesis problems, try to work the synthesis forwards AND backwards.

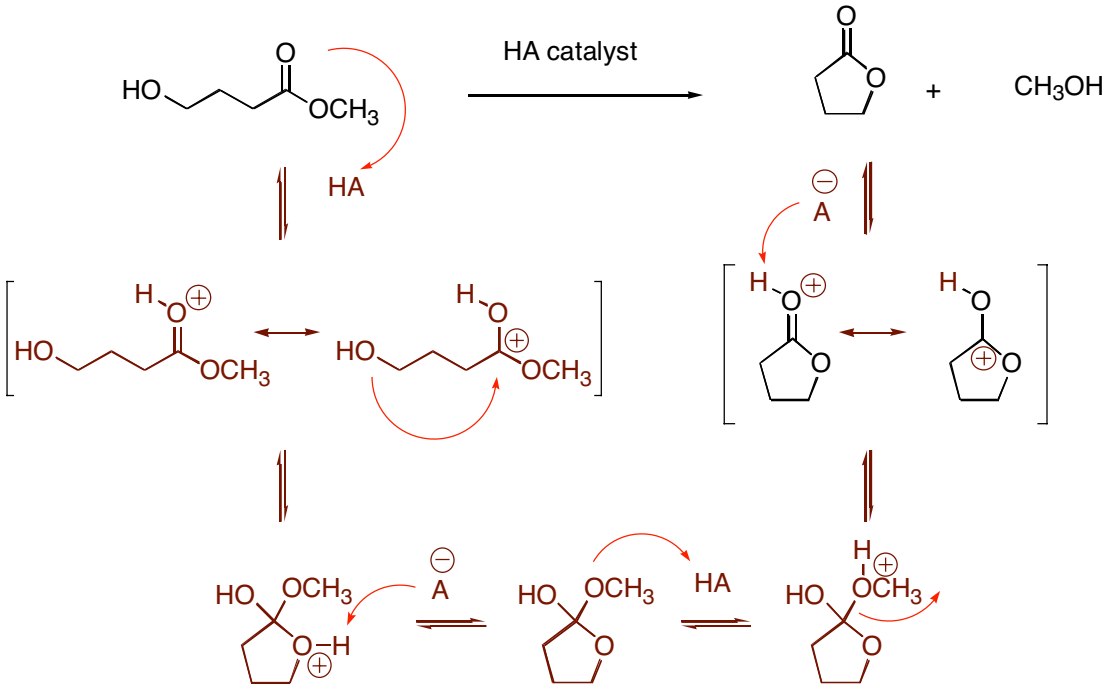
1. Identify the most acidic hydrogens in the following molecules. (12 pts)



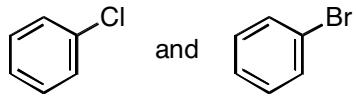
2. The addition of 1 equivalent of HBr to 1,3-butadiene results in two products. The major product changes if the reaction is carried out at low temperature (kinetic) or high temperature (thermodynamic). Write the structure of these products. (6 pts)

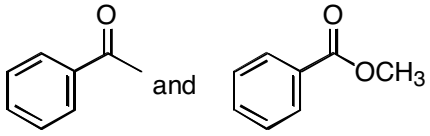


3. When methyl 4-hydroxybutanoate is treated with an acid catalyst a transesterification takes place to yield a lactone. The mechanism is identical to a Fischer esterification except methanol is the leaving group instead of water. Write out the complete mechanism showing all intermediates and arrows indicating electron flow. (20 pts)



4. Describe how you would distinguish between the following molecules using NMR, IR, or Mass Spectrometry. (eg. What technique and what would you observe as the difference) (10 pts)

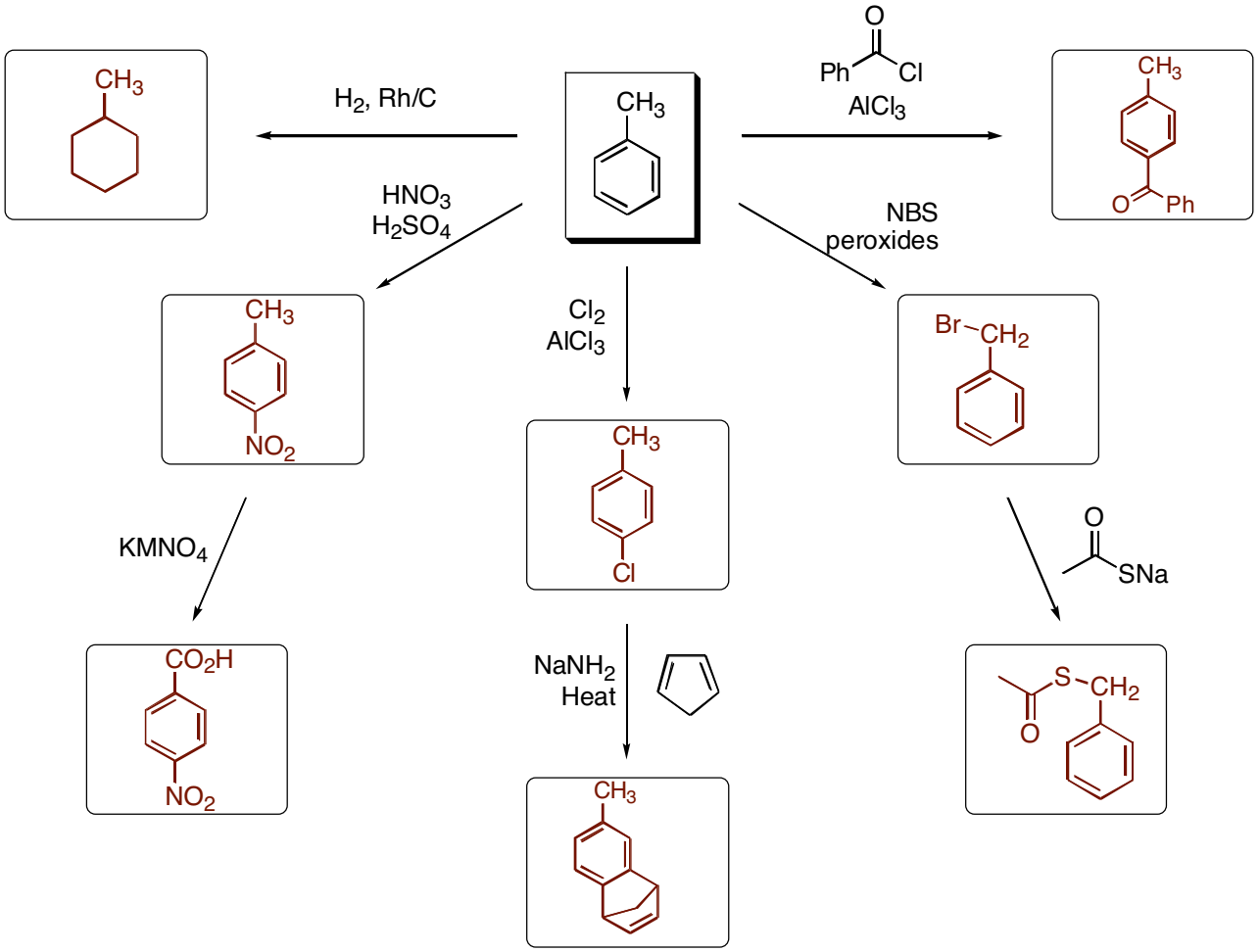
a)  and

b)  and

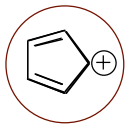
a) Chlorobenzene and Bromobenze can be most easily distinguished by Mass Spectrometry. The mass would be different and the isotope ratios would be very revealing. They would be difficult to distinguish by NMR.

b) NMR would be the way to go. The chemical shift in the proton NMR for the ester CH_3 and the ketone CH_3 would be different (3.5 ppm vs 2.0 ppm). Carbon NMR would be the best way to tell them apart - Ketone 200 ppm, ester 175 ppm.

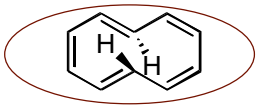
5. Provide the major product for the reactions below. For ortho-para directors you need only show the para product. (24 pts)



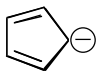
6. Which of the following molecules are **NOT** aromatic. Briefly explain why. (15 pts)

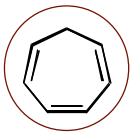


only 4 pi-electrons



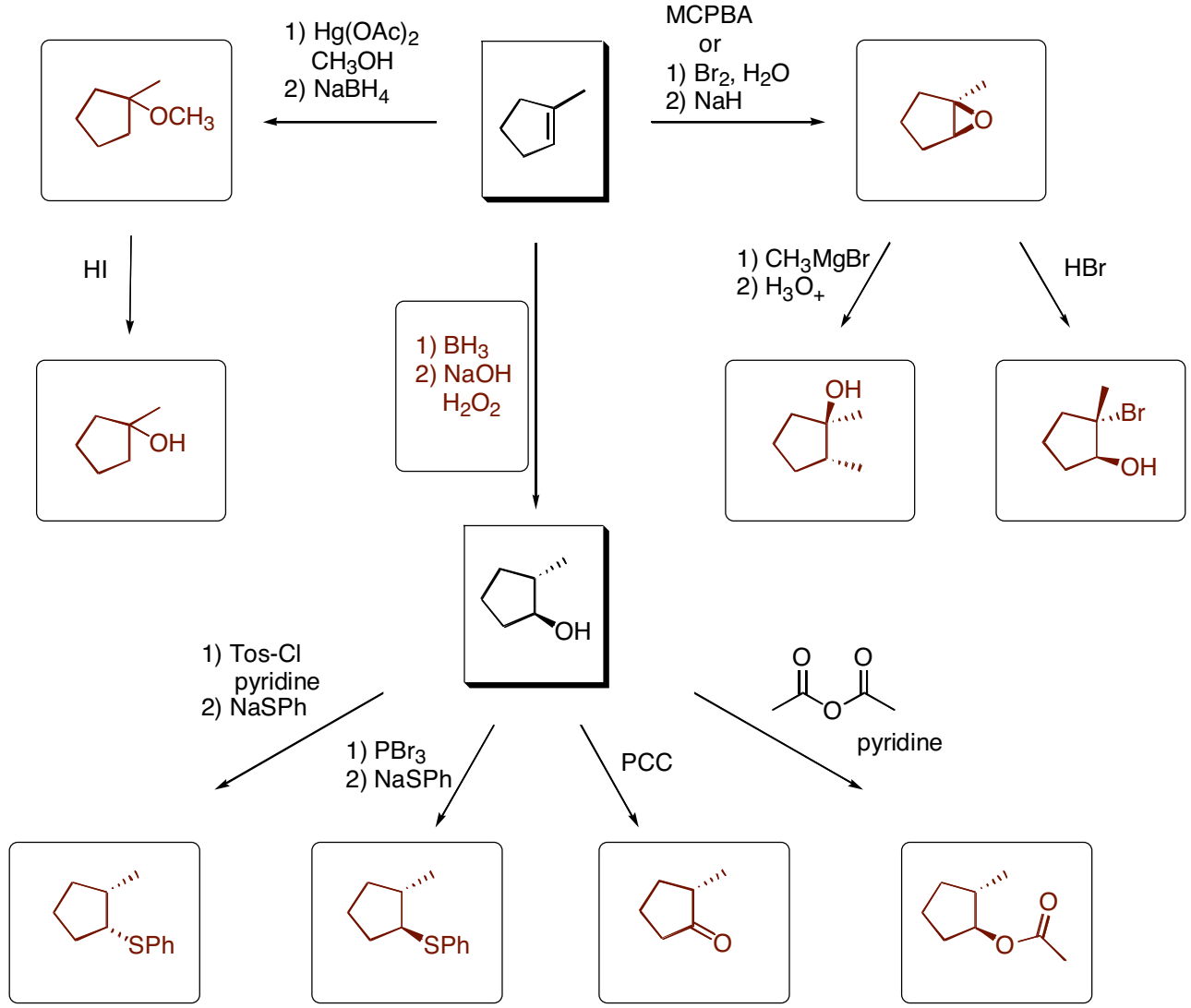
not planar



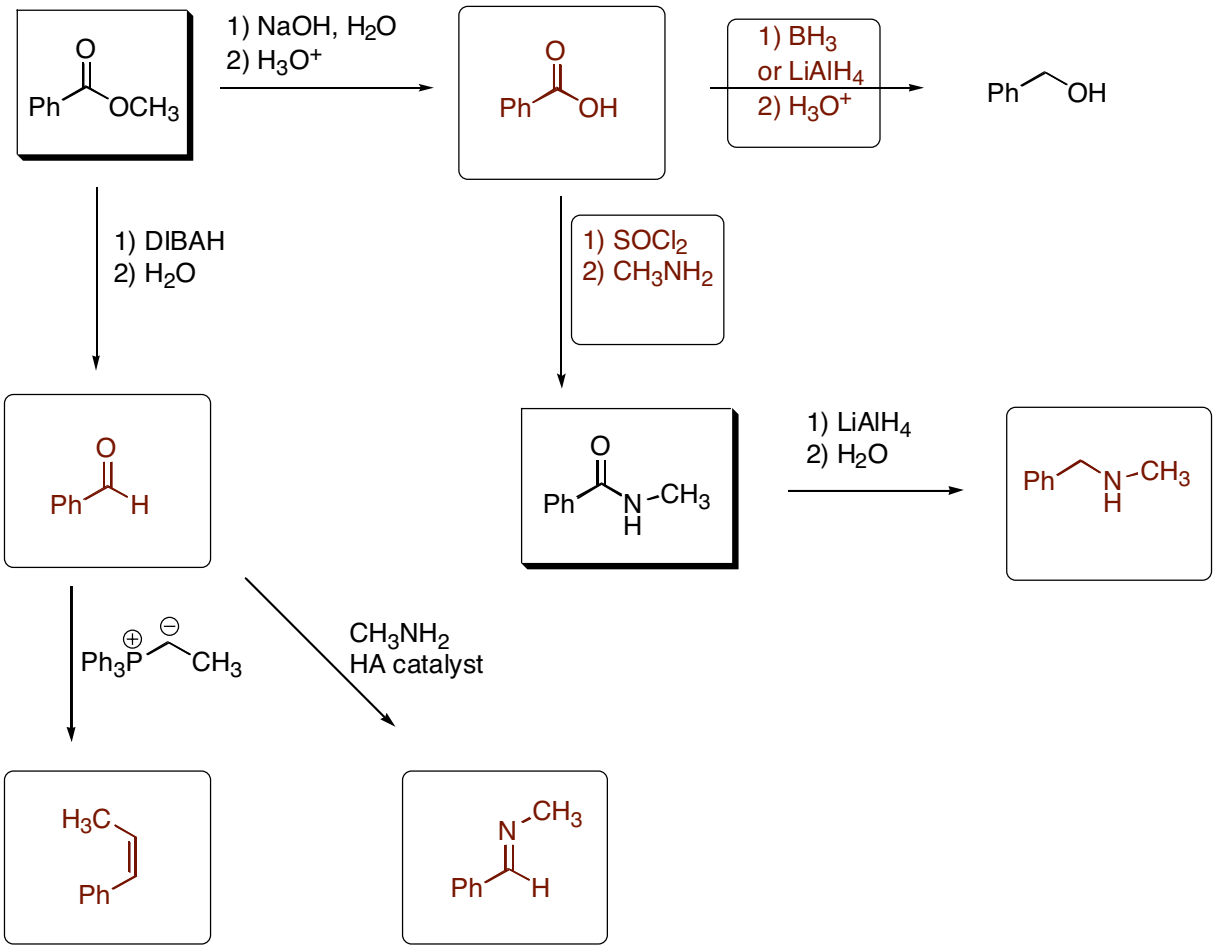


not fully conjugated

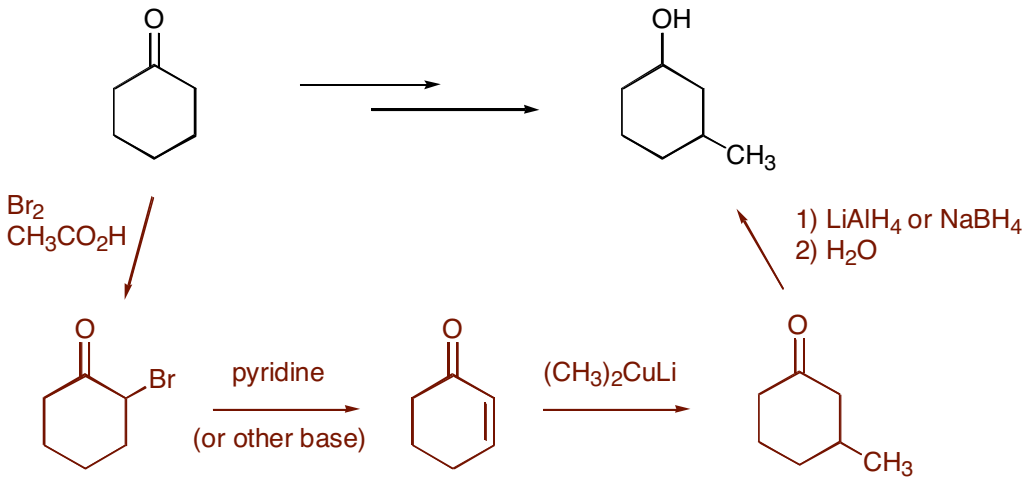
7. Provide the missing major products or reagents for the following. (30 pts)



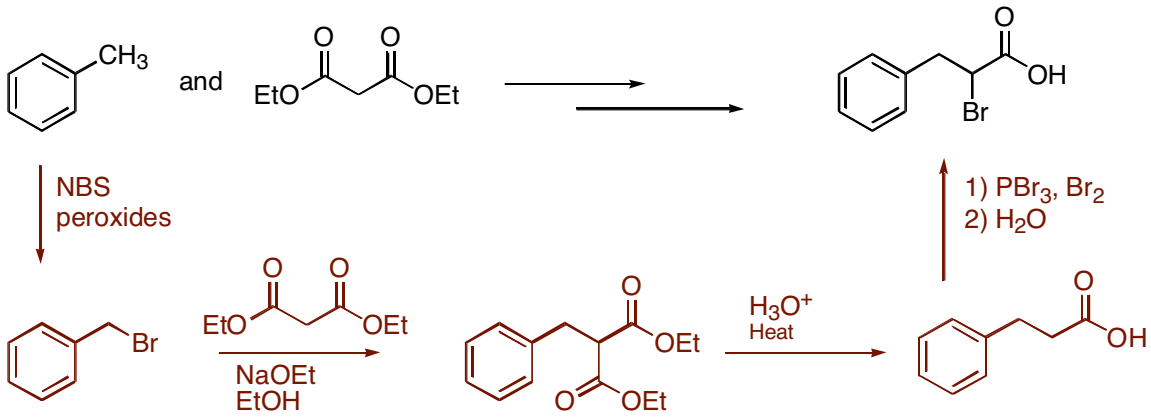
8. Provide the missing major products or reagents for the following. (21 pts)



9. Show how you would synthesize 3-methylcyclohexanol from cyclohexanone. Hint: This can be done in 4 steps. (5 counting an H_2O workup step) (16 pts)



10. Show how you would synthesize the following bromoacid starting from toluene and diethylmalonate. Hint: This can be done in 5 steps counting a hydrolysis and uses a Hell-Volhard-Zelinskii reaction. (20 pts)



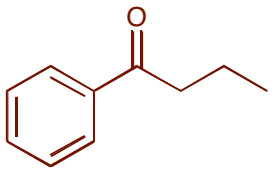
11. Answer the following questions about an unknown molecule with a molecular formula of $C_{10}H_{12}O$. The IR spectra shows a strong absorbance at 1680 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, and mass spectrum for this unknown are shown on the following page. (25 points)

How many degrees of unsaturation does the molecule possess? **5**

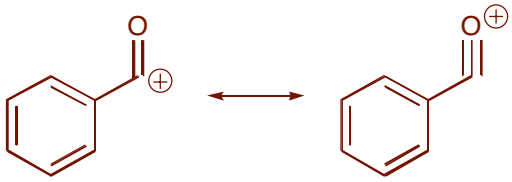
What type of functional group does the carbon resonance at 200 ppm represent?

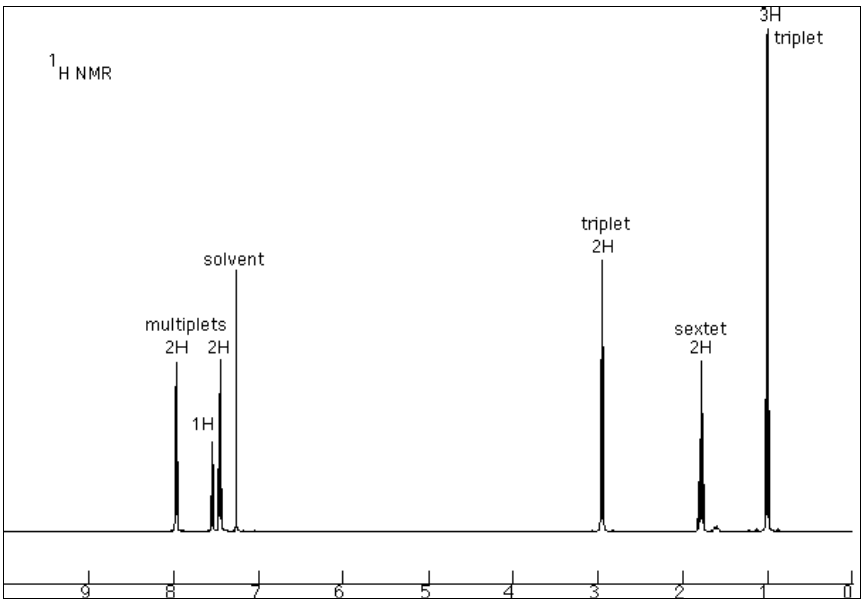
Ketone

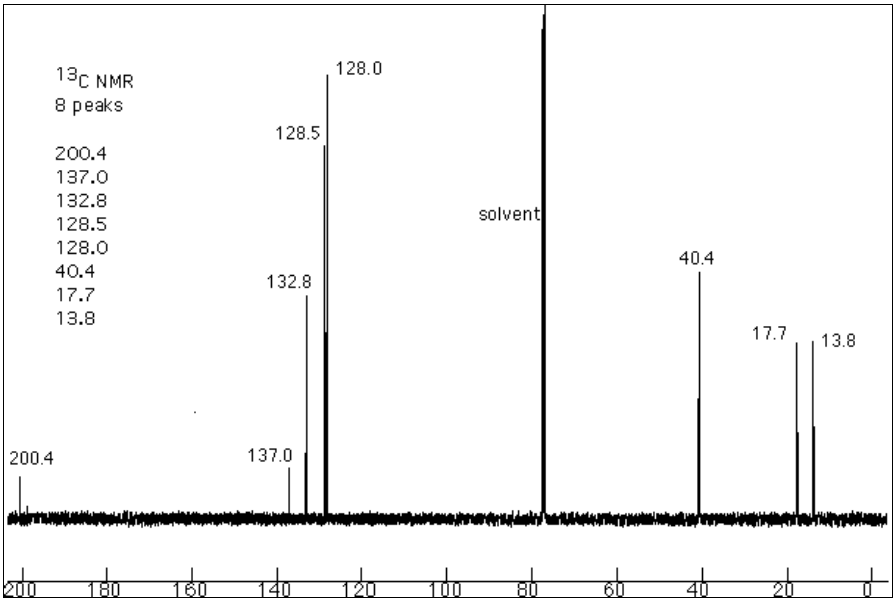
What is the structure of the unknown molecule?

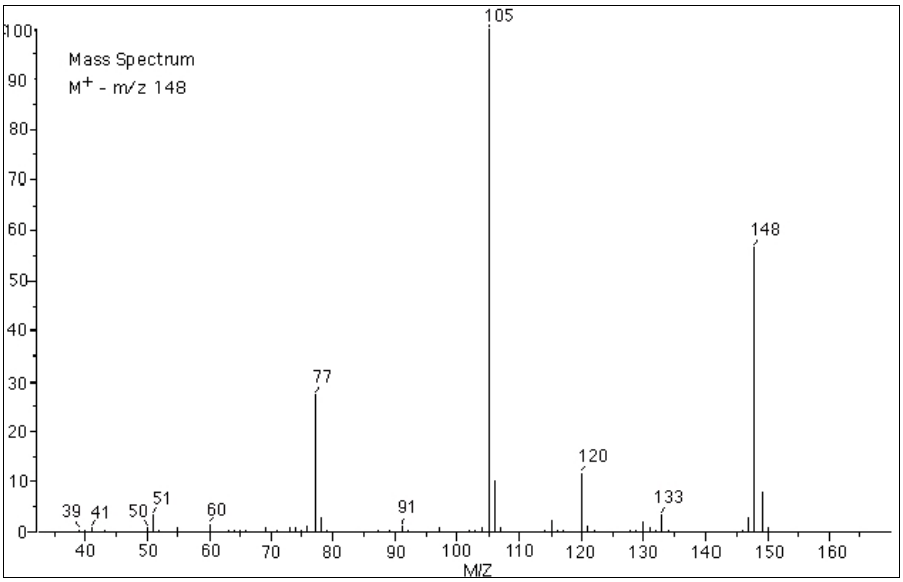


In the Mass Spectrum, what does the base peak correspond to (draw a structure)?

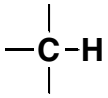
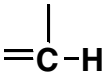
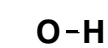
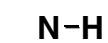
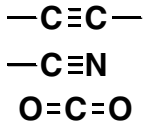
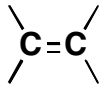
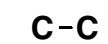
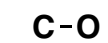
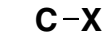



1H NMR
3H
triplet
triplet
2H
solvent
multiplets
2H
2H
1H
sextet
2H
9
8
7
6
5
4
3
2
1
0

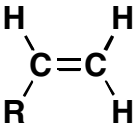
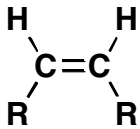
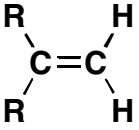
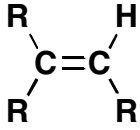
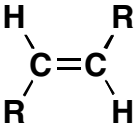

13C NMR
8 peaks
200.4
137.0
132.8
128.5
128.0
40.4
17.7
13.8
128.0
128.5
solvent
40.4
132.8
17.7
13.8
200.4
137.0
200
180
160
140
120
100
80
60
40
20
0


Mass Spectrum
M+ - m/z 148
105
148
77
120
133
39
41
50
51
60
91
100
90
80
70
60
50
40
30
20
10
0
40
50
60
70
80
90
100
110
120
130
140
150
160
M/Z

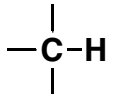
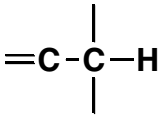
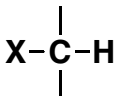
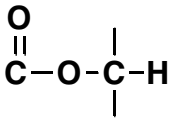
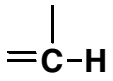
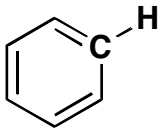
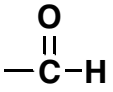
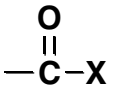
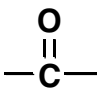
Infrared Stretching Absorptions

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)	^{13}C 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