Organic 211 Test # 4 December 5, 2019

Name:_____

Directions: The exam is worth 106 points but scored out of 100.

1) a) Give a possible molecular formula for a molecule that weighs 215 g/mole and contains a bromine. Show your work. (4 pts.)

215 − 80 = 135

135/13 = 10.xx

10 × 12 = 120 weight of carbon

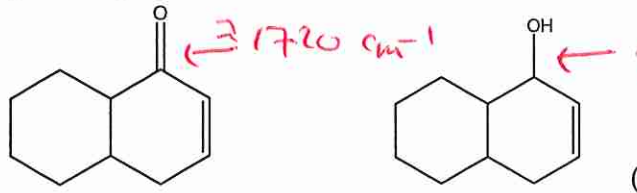
135 − 120 = 15 weight of hydrogen

$C_{10}H_{15}Br$

b) What is the intensity of the M+2 peak relative to the M+ peak for your molecule in part a. (3 pts.) equal heights

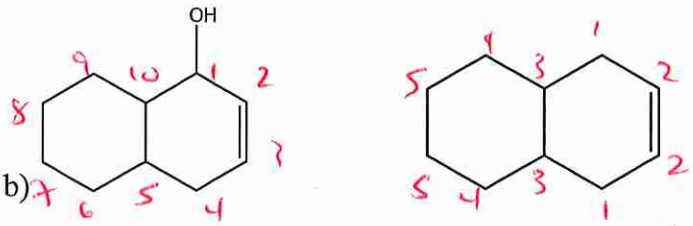
Br exists as two isotopes so M+2 = M+ in intensity.

2) Using the method requested, explain how you would identify which molecule you have. (3 pts. each)

a) 

← 1720 cm⁻¹ ← ≈ 3200 cm⁻¹ (IR)

look at 1720 or near. if no peak look at 3200 cm⁻¹!

b) 

(¹³C NMR)

10 types of carbon

5 types of carbon

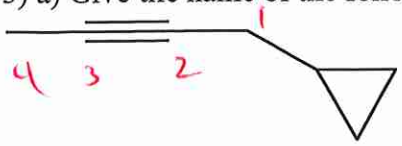
in proton decoupled

c) 

A B (¹H NMR)

what peak is farthest downfield? For A, a singlet at 3.8 δ. for B, a quartet at 3.8 δ.

3) a) Give the name of the following molecule. (3 pts.)

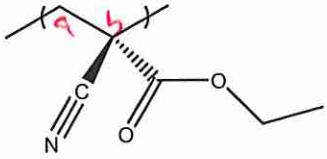


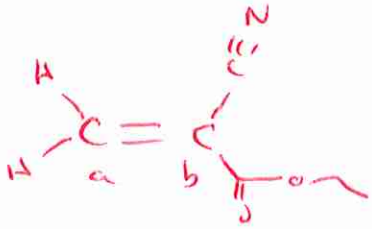
I named it as 1-cyclopropylbut-2-yne

Chemdraw named it as but-2-yn-1-yl cyclopropane

b) Give the structure for the following molecule.
(S)-but-3-yn-2-ol (3 pts.)

4) Super Glue sticks because of its ready conversion to the vinyl polymer below. What is the monomer for Super Glue? (4 pts.)





10.15

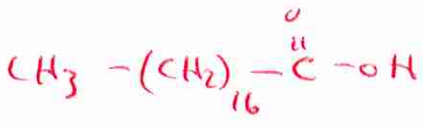
5) Oleic acid and stearic acid are naturally occurring compounds, which can be isolated from various fats and oils. In the laboratory, each can be prepared by hydrogenation of a compound known as stearolic acid which has the formula below. Oleic acid is obtained by hydrogenation of stearolic acid over Lindlar palladium. Stearic acid is obtained by hydrogenation over platinum. Elaidic acid is formed by sodium-ammonia reduction of stearolic acid. (3 pts. each)

9.22

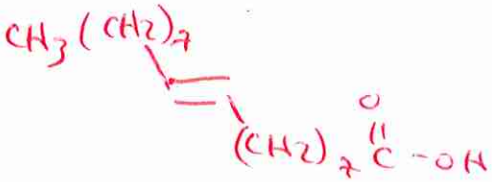
Stearolic acid

a) What is the structure of oleic acid?

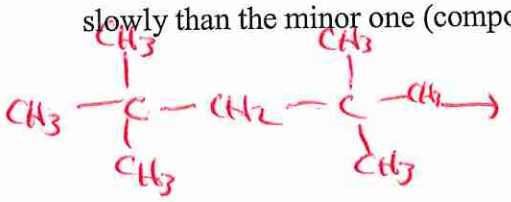
b) What is the structure of stearic acid?



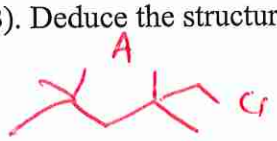
c) What is the structure of elaidic acid?



6) Photochemical chlorination of $(CH_3)_3CCH_2C(CH_3)_3$ gave a mixture of two monochlorides in a 4:1 ratio. The structures of these two products were assigned on the basis of their SN_1 hydrolysis rates in aqueous ethanol. The major product (compound A) underwent hydrolysis much more slowly than the minor one (compound B). Deduce the structures of compounds A and B. (4 pts)



A



80%

B

20%

10.24 hydrolysis = SN_1

∴ 2° >> 1°

eq H_2O

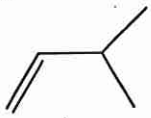
7) Calculate the reactivities of the hydrogens for the molecule in # 6. SHOW YOUR WORK! (4 pts.)

A $\frac{80}{18} = 4.44$ $\frac{4.44}{4.44} = 1$

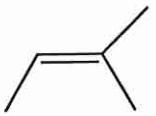
B $\frac{20}{2} = 10$ $\frac{10}{4.44} = 2.25$

8) Electrophilic addition of HBr to Compound A below gives a mixture of two constitutional isomers C and D. Only D is formed, however, when Compound B below reacts with HBr in the presence of peroxides. Identify C and D and explain your reasoning. (4 pts.)

10.12



Compound A



Compound B

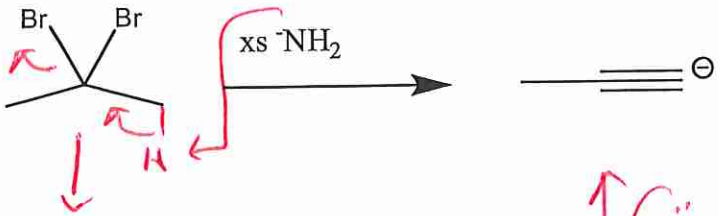
carbocation rearrangement

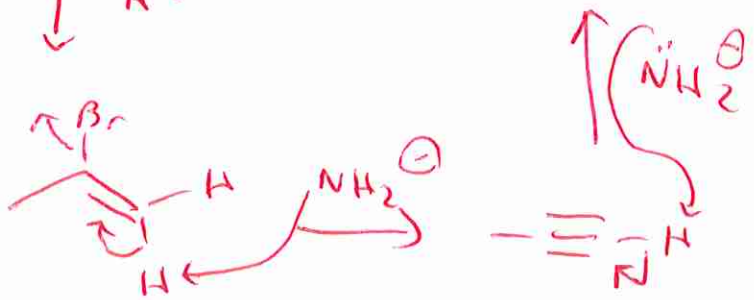
HBr, peroxides

≠ D

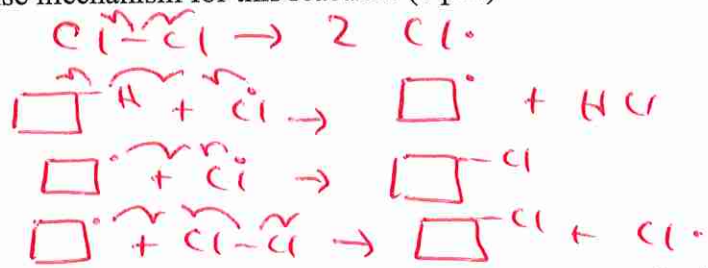
radicals do not rearrange and add in anti-Markovnikov fashion

9) Mechanism: Show the arrows and intermediates for the alkyne reaction below. (6 pts.)





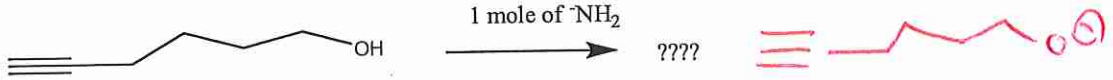
10) Cyclobutyl chloride has been prepared by the free radical chlorination of cyclobutane. Write a stepwise mechanism for this reaction. (6 pts.) 10.33

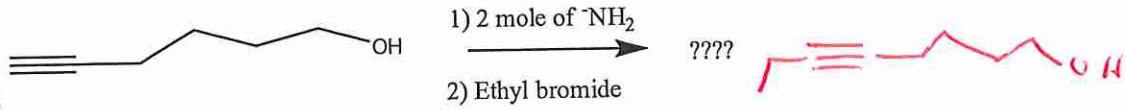


or

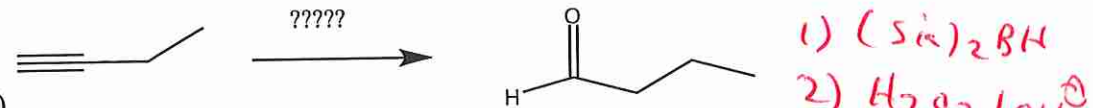
11) Reactions: Give the missing reactant, reagent or product for the following reactions. It is only required to draw the Organic piece and not everything that is generated (e.g. for a radical reaction with chlorine, + HCl can be left off). Show stereochemistry if important. Indicate if no reaction is possible. Assume monohalogenation. Draw all of the possible products. Assume a water quench. (3 pts. each)

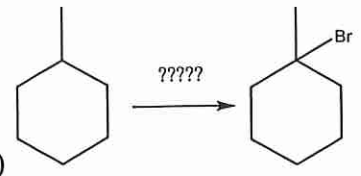
a) 

b) 

c) 

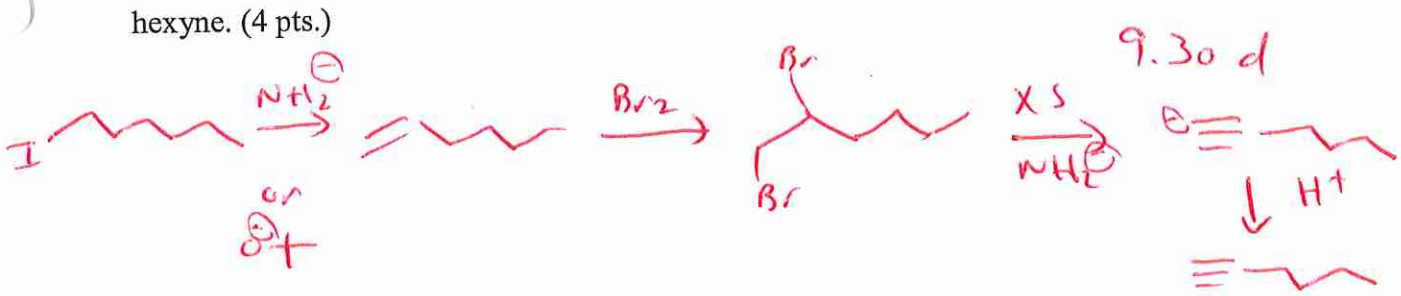
d) 

e) 

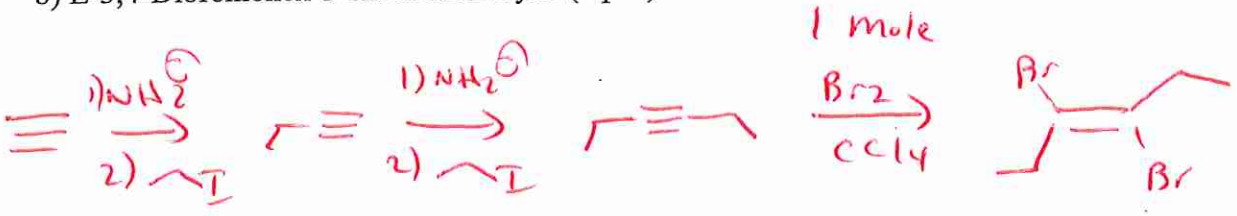
f) 

g) 

12) a) Show by writing appropriate chemical equations how 1-iodohexane can be converted to 1-hexyne. (4 pts.)



b) E-3,4-Dibromohex-3-ene from Ethyne (4 pts.)



13) Give something you will remember about Organic 1. (3 pts.)

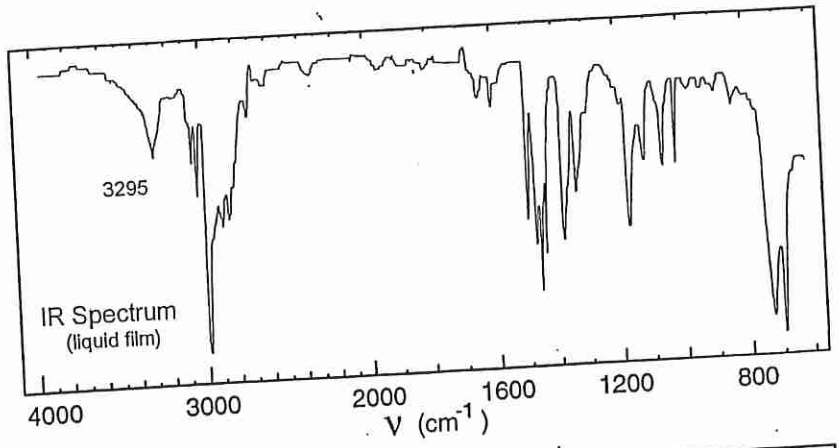
How fun it was! :)

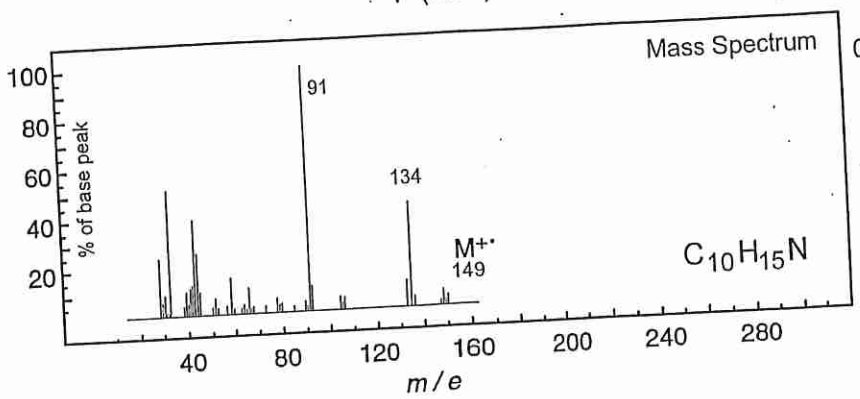
14) For the following three spectral sheets , give a structure that will give the spectra. (5 pts. each)

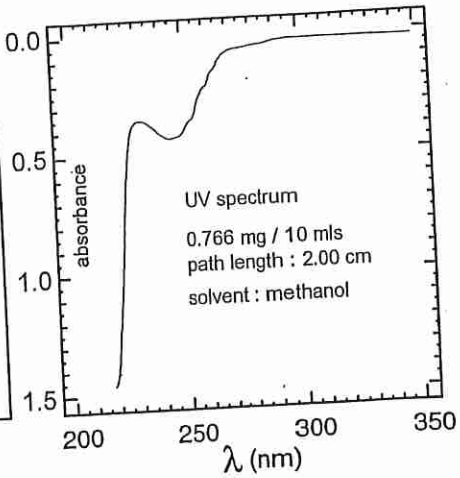
a)

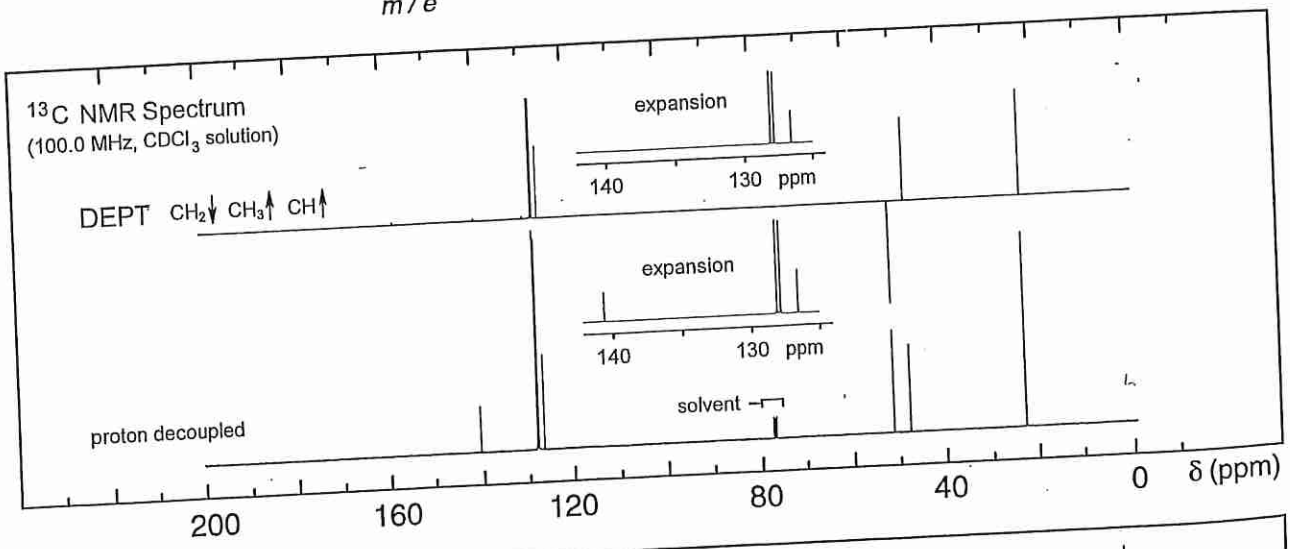
b)

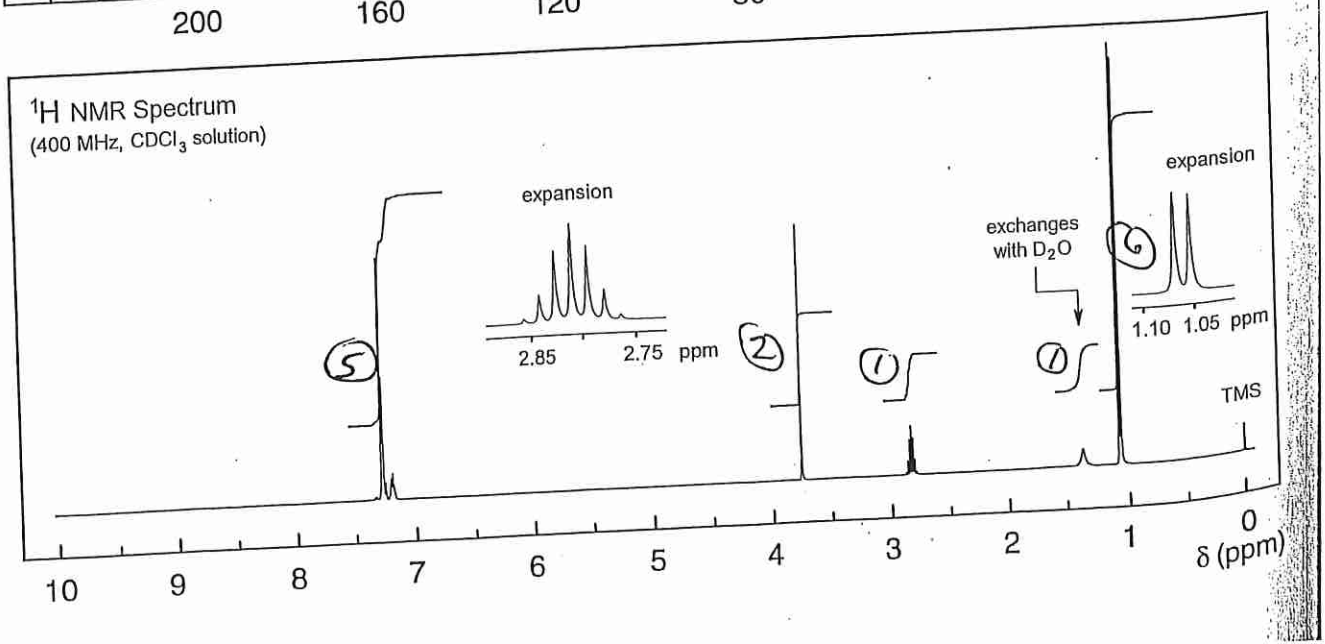
c)

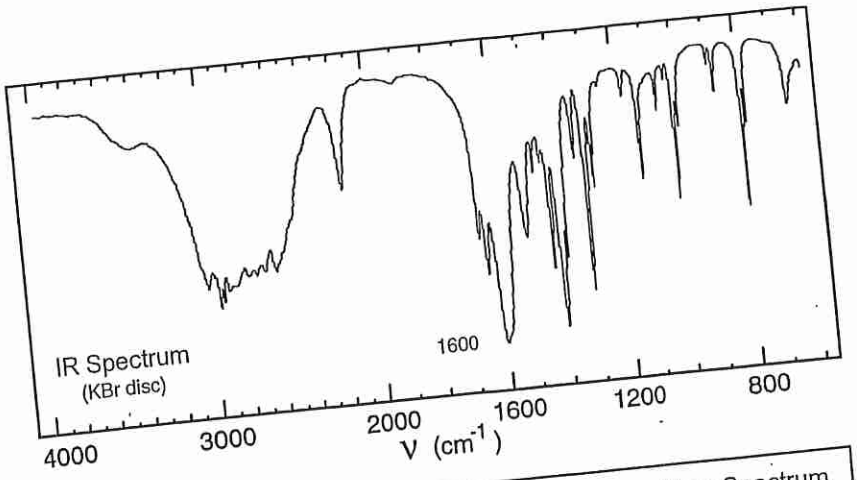

3295
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

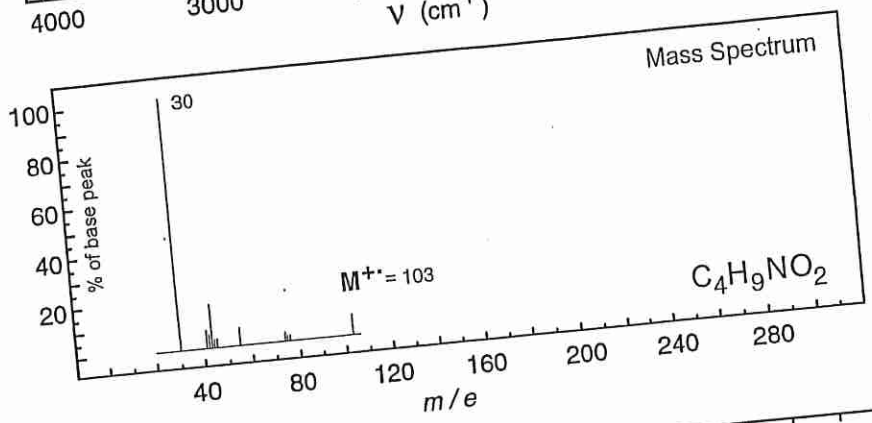

Mass Spectrum
100
80
60
40
20
% of base peak
91
134
M+·
149
C10H15N
40
80
120
160
200
240
280
m/e


0.0
0.5
1.0
1.5
absorbance
UV spectrum
0.766 mg / 10 mls
path length : 2.00 cm
solvent : methanol
200
250
300
350
λ (nm)

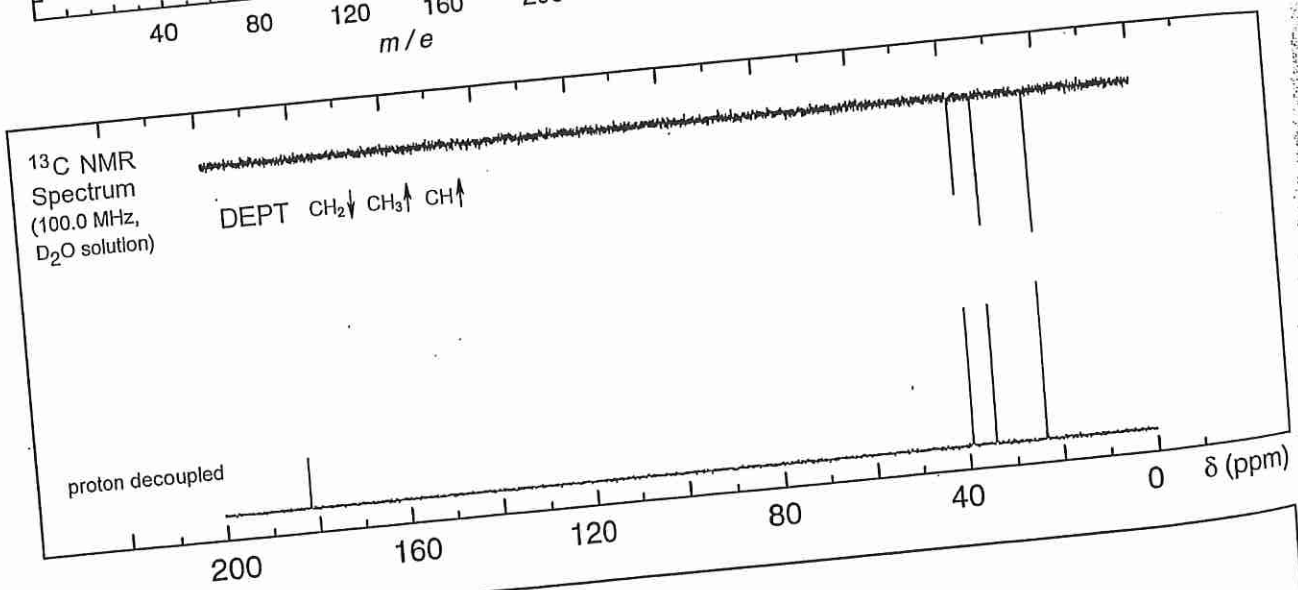

13C NMR Spectrum
(100.0 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
140
130 ppm
expansion
140
130 ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

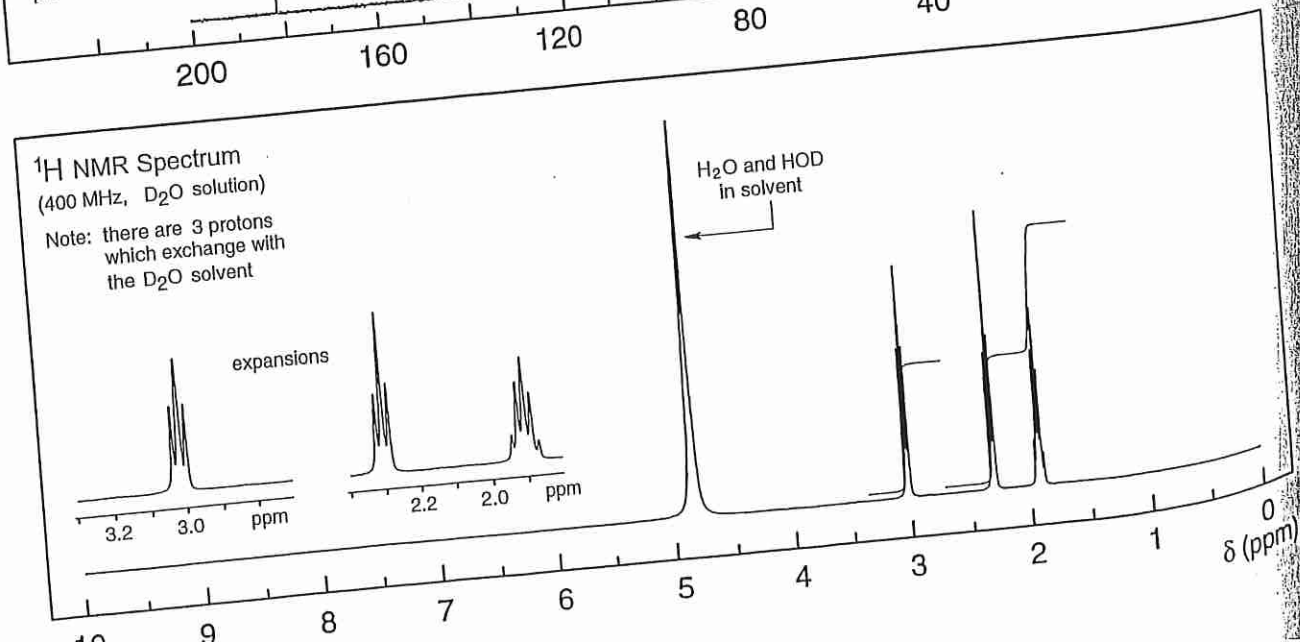

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
2.85
2.75 ppm
5
2
1
1
exchanges
with D2O
expansion
1.10
1.05 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

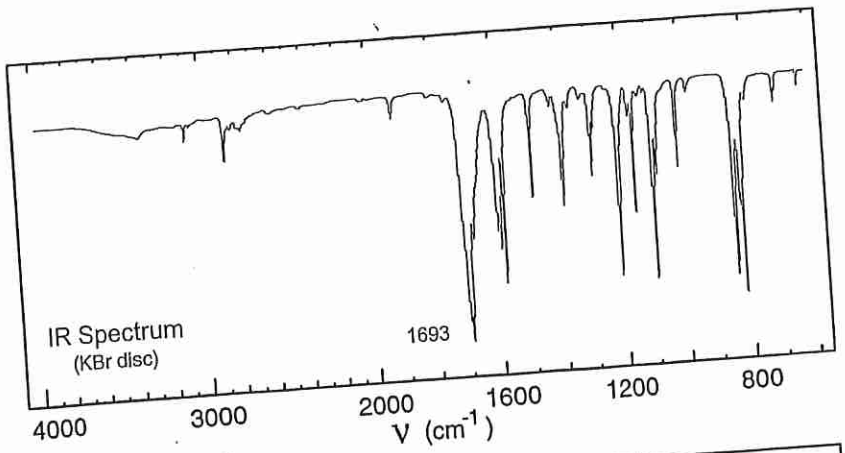


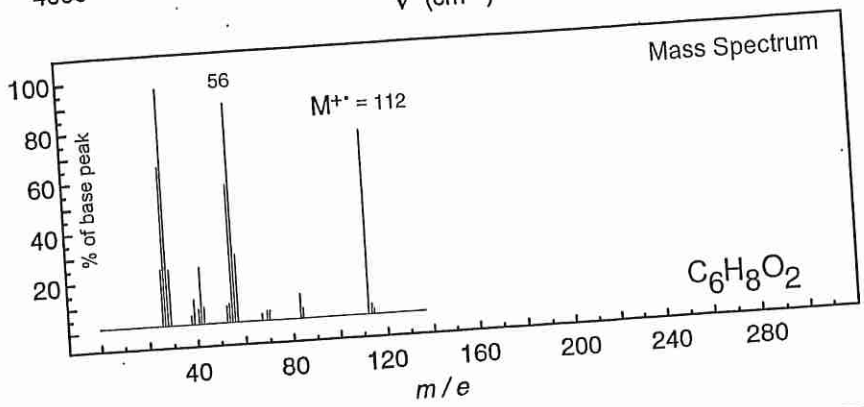


No significant UV absorption above 220 nm

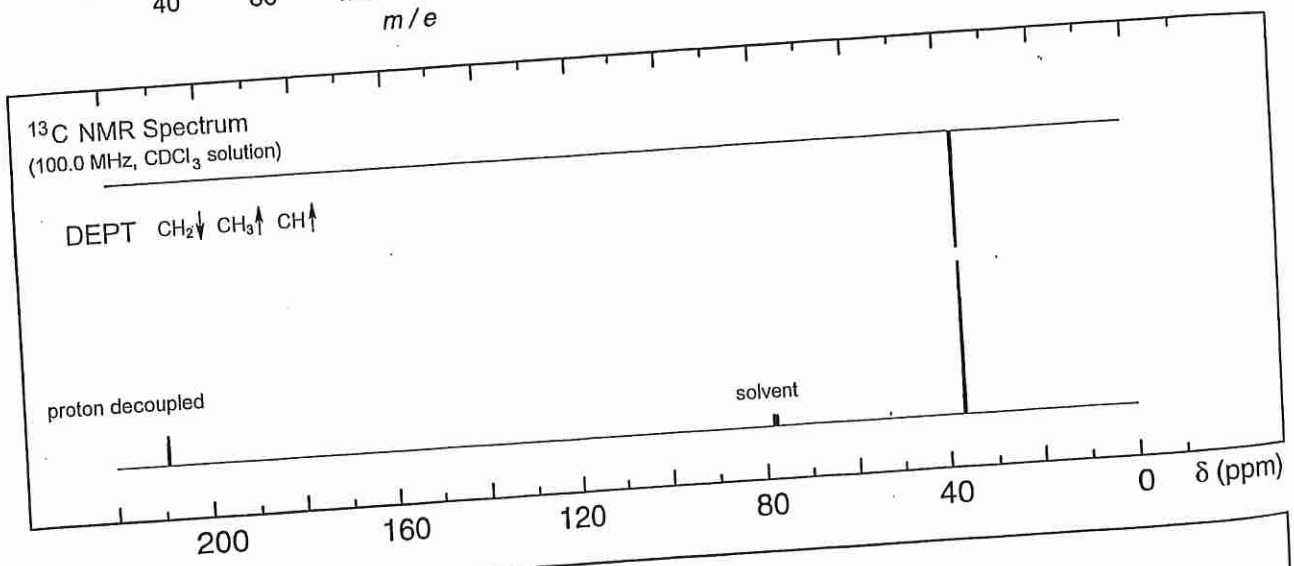








No significant UV absorption above 220 nm



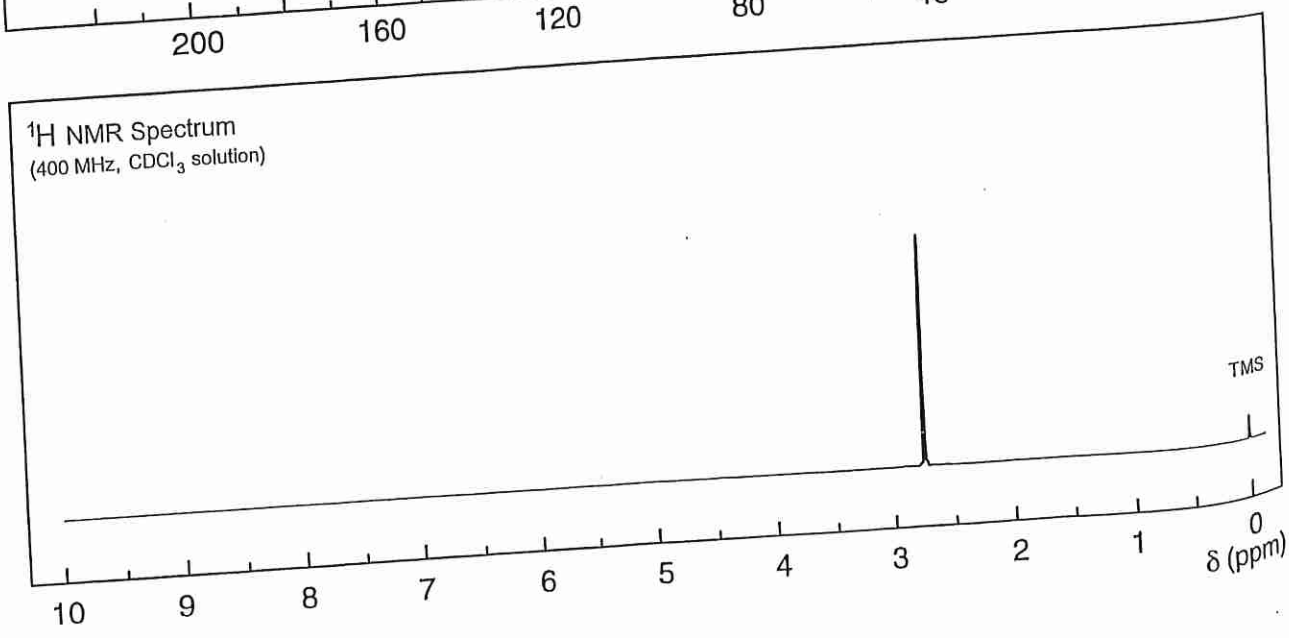


TABLE 13.1 Approximate Proton Chemical Shifts

TYPE OF PROTON	CHEMICAL SHIFT, DELTA, PPM
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.5
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RC(=O)CH_3$	2.1–2.6
Aldehyde, $RC(=O)H$	9.5–9.6
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RC(=O)OH$	10–13[a]
Phenolic, $ArOH$	4.5–7.7[a]
Amino $R{-}NH_2$	1.0–5.0[a]

[a]The chemical shifts of these groups vary in different solvents and with temperature and concentration.

TABLE 13.2 Approximate Carbon-13 Chemical Shifts

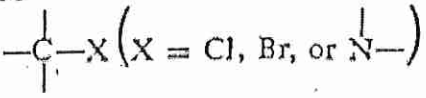
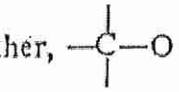
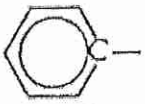
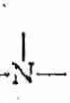
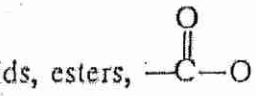
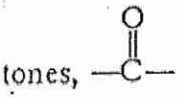
TYPE OF CARBON	CHEMICAL SHIFT, DELTA, PP
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, 	10–65
Alcohol or ether, 	50–90
Alkyne,	60–90
Alkene,	100–170
Aryl, 	100–170
Nitriles, 	120–130
Amides, 	150–180
Carboxylic acids, esters, 	160–185
Aldehydes, ketones, 	185–215

TABLE 13.3 Characteristic Infrared Absorptions of Functional Groups

GROUP		FREQUENCY RANGE cm^{-1}	INTENSITY[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $-CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $-C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
$R-CH=CH_2$ (out-of-plane C—H bendings)		985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$ (out-of-plane C—H bendings)		880–900	(s)
cis-RCH=CHR (out-of-plane C—H bendings)		675–730	(s)
trans-RCH=CHR (out-of-plane C—H bendings)		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o-Disubstituted		735–770	(s)
m-Disubstituted		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–840	(very s)
E. Alcohols, Phenols, Carboxylic Acids			
OH (alcohols, phenols, dilute solns)		3590–3650	(sharp, v)
OH (alcohols, phenols, hydrogen bonded)		3200–3550	(broad, s)
OH (carboxylic acids, hydrogen bonded)		2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O stretch		1630–1780	(s)
aldehydes		1690–1740	(s)
ketones		1680–1750	(s)
esters		1735–1750	(s)
carboxylic acids		1710–1780	(s)
amides		1630–1690	(s)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

[a]Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.