Chemistry 344: Spectroscopy Problem Set 3

Name (print): ______________________________ **(Not for credit)**

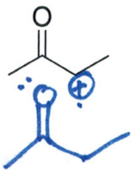
TA Name (print): ______________________________

I. For each of the following molecules, draw the most likely molecular ions **(always a radical cation)** that you would expect to be formed in an EI-MS experiment. For each case, calculate the *m/z* value for the molecular ion of the most abundant isotopomer and second most abundant isotopomer. % are approximate ...

$m/z = 72$

$m/z = 73$ (5%)

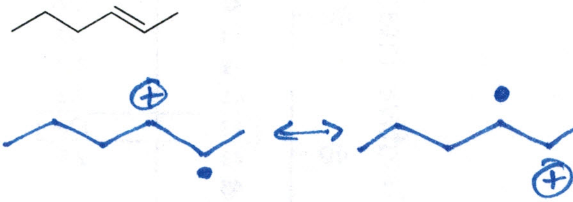
A.



$m/z = 84$

$m/z = 85$ (7%)

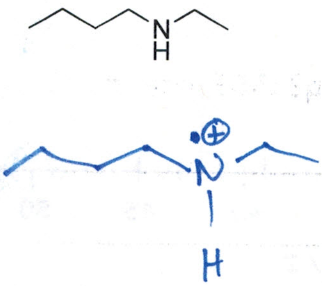
B.



$m/z = 101$

$m/z = 102$ (7%)

C.

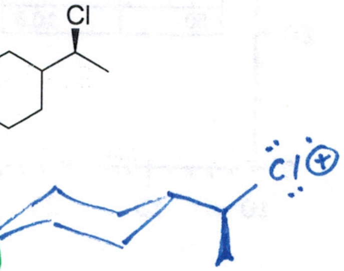


$m/z = 146$

$m/z = 147$ (9%)

$m/z = 148$ (24%)

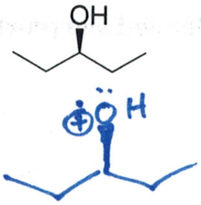
D.



$m/z = 88$

$m/z = 89$ (6%)

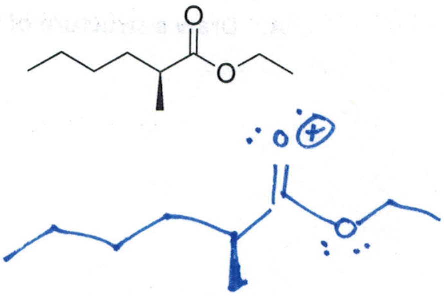
E.



$m/z = 158$

$m/z = 159$ (10%)

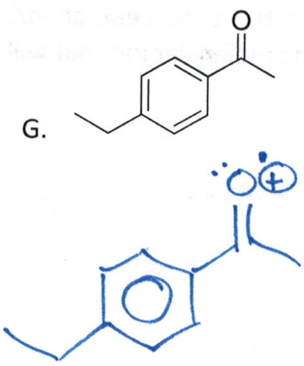
F.



$m/z = 148$

$m/z = 149$ (11%)

G.

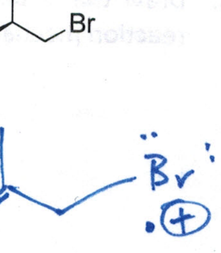


$m/z = 136$

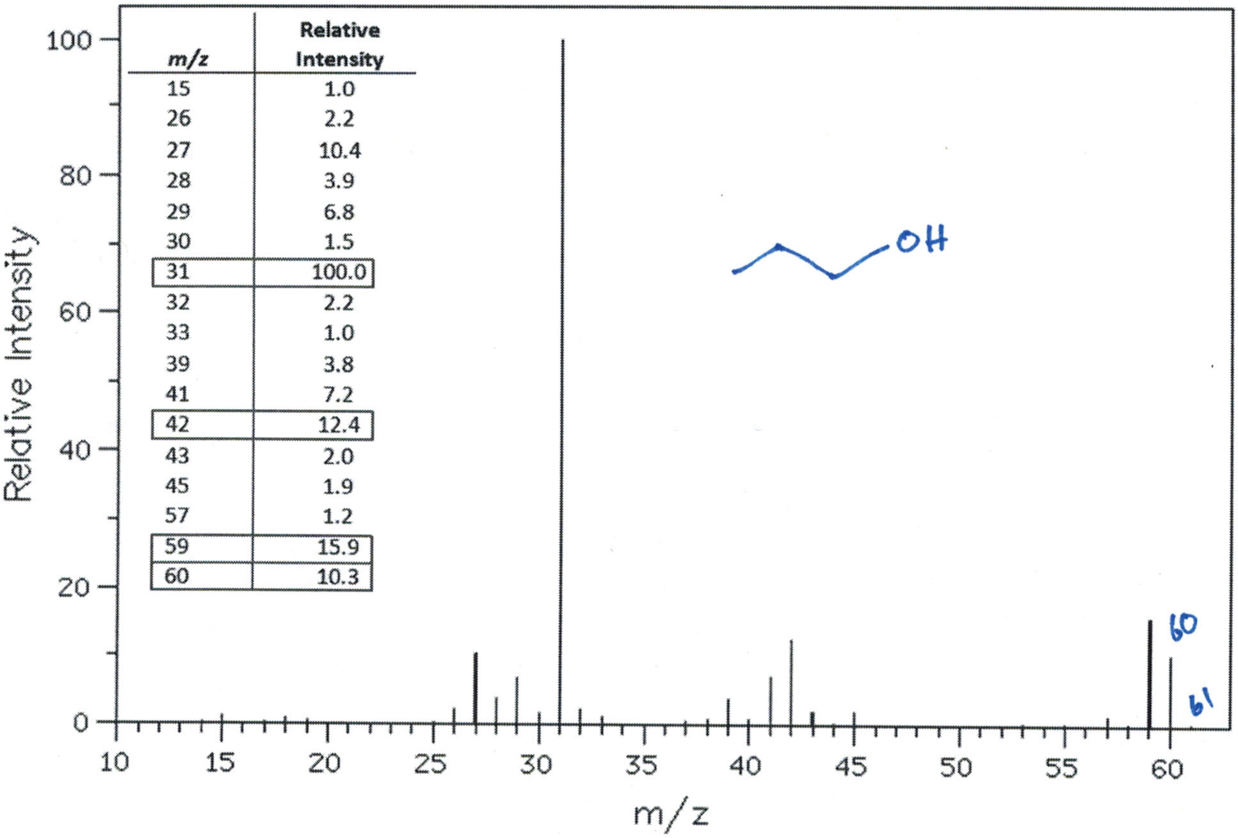
$m/z = 137$ (5%)

$m/z = 138$ (49%)

H.



II. Using the mass spectrum of 1-propanol shown below, answer the questions that follow about its fragmentation. Remember that you are not expected to interpret all signals in a mass spectrum.



m/z	Relative Intensity
15	1.0
26	2.2
27	10.4
28	3.9
29	6.8
30	1.5
31	100.0
32	2.2
33	1.0
39	3.8
41	7.2
42	12.4
43	2.0
45	1.9
57	1.2
59	15.9
60	10.3

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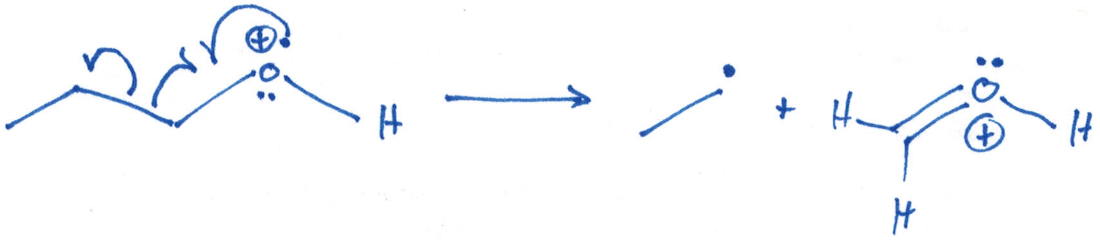
A. Draw a structure of the most likely molecular ion formed and provide its *m/z* value.

$m/z = 60$

$m/z = 61$ (3%)

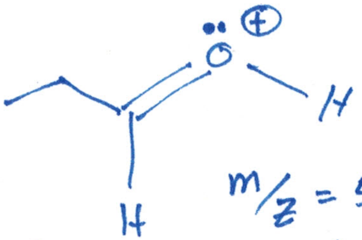
B. Draw the structure of the ion responsible for the base peak at *m/z* = 31. Provide a reaction mechanism of the fragmentation of the molecular ion that will lead to that ion.



$m/z = 31$

$m/z = 32$ (less than 2%)

C. Likewise, draw a likely structure for the ion that produces the next most intense signals at $m/z = 59$ and 42.



$m/z = 59$

(loss of H• from $m/z = 60$)

$m/z = 42$

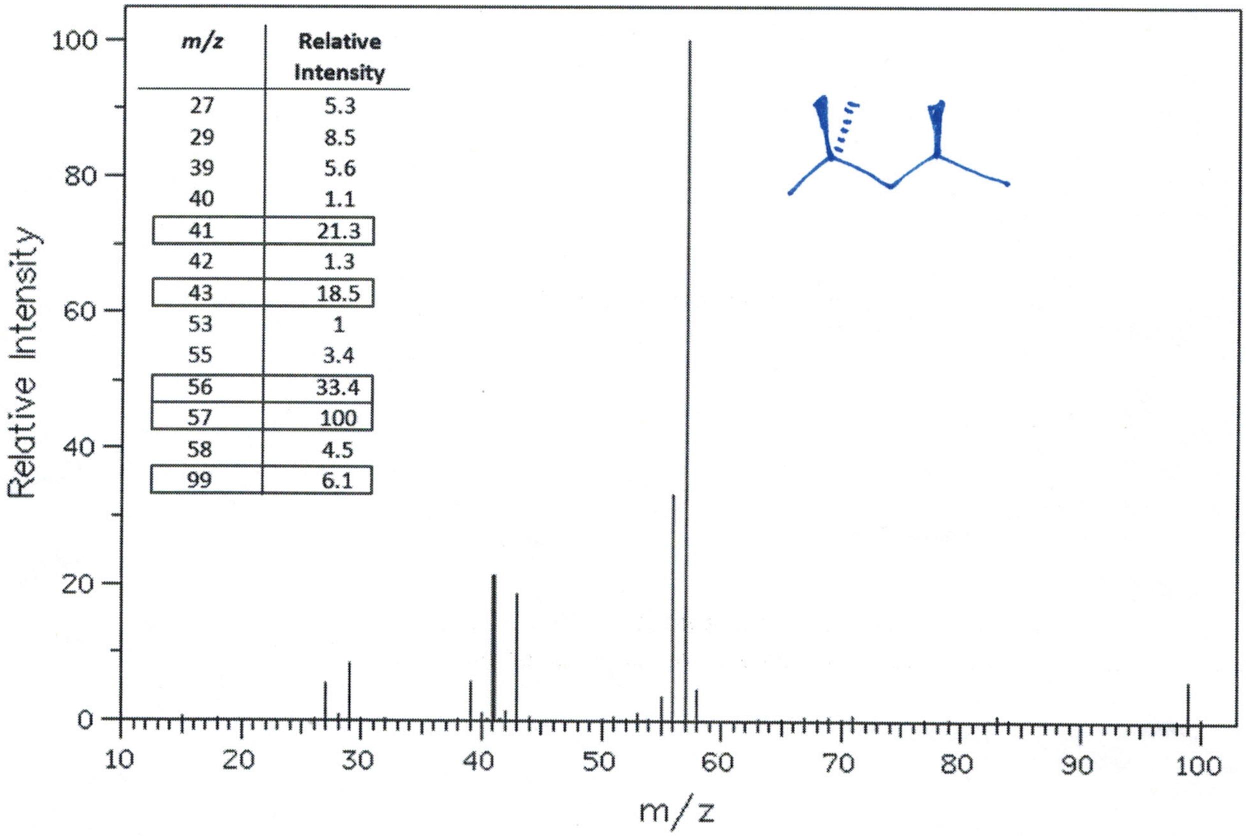
(loss of H_2O from $m/z = 60$)

D. Why does the peak at $m/z = 15$ have such a low relative intensity?

$\oplus CH_3$ is not a highly stable ion.

$m/z = 15$

III. Using the mass spectrum of 2,2,4-trimethylpentane shown below, answer the questions that follow about its fragmentation. Remember that you are not expected to interpret all signals in a mass spectrum.



m/z	Relative Intensity
27	5.3
29	8.5
39	5.6
40	1.1
41	21.3
42	1.3
43	18.5
53	1
55	3.4
56	33.4
57	100
58	4.5
99	6.1

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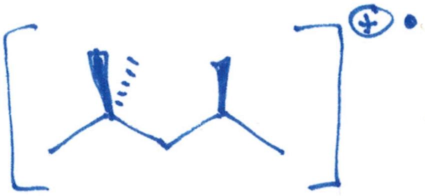
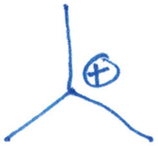
A. In this case, the molecular ion is of such a low intensity it is not detected. Draw the molecular ion of 2,2,4-trimethylpentane and determine its m/z value.



$m/z = 114$

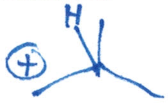
so unstable it doesn't appear in the mass spectrum.

B. Draw a likely structure for the ion that produces the base peak signal at $m/z = 57$.



$m/z = 57$

or less likely



$m/z = 58$ (5%)

C. Draw a fragmentation mechanism that could produce the ion responsible for the signal at $m/z = 56$ from the base peak ion?

$m/z = 56$

$m/z = 57$ (5%)

D. Draw likely structures for the ions that produces the signals at m/z = 43 and 41.

$m/z = 43$

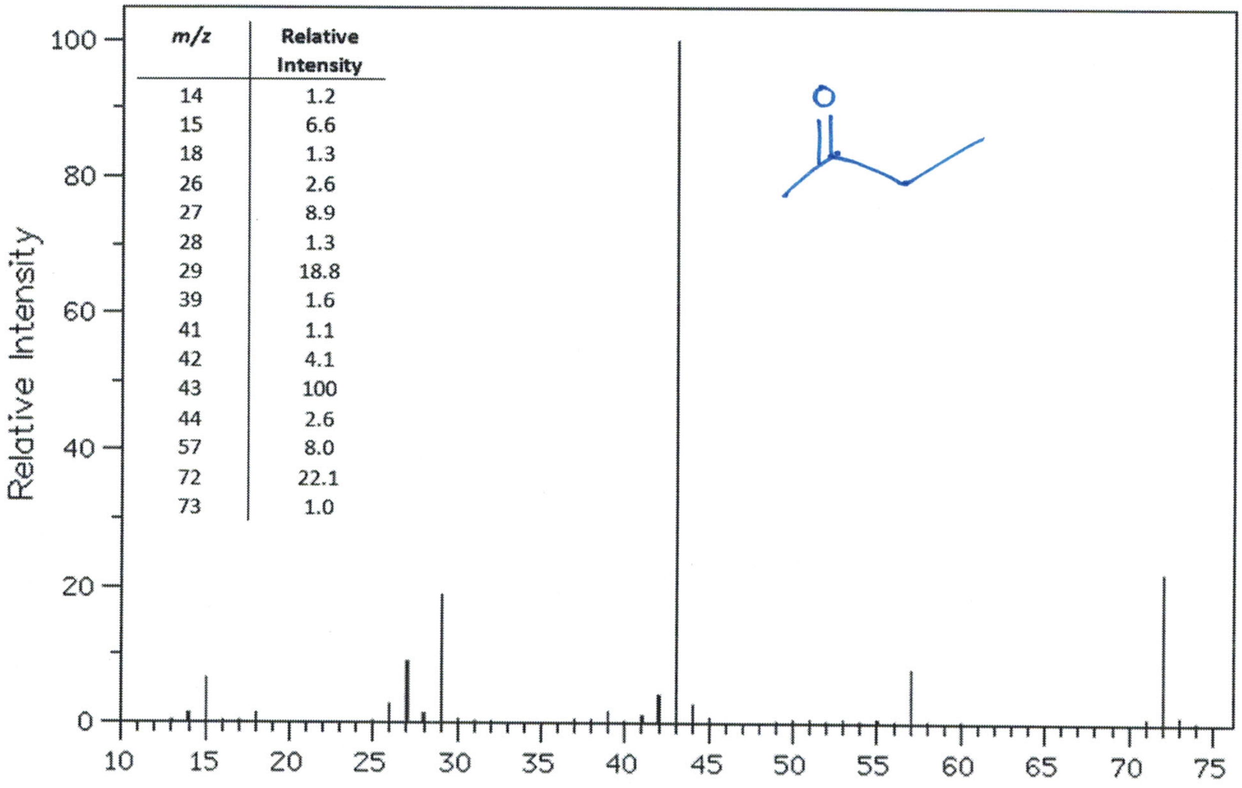
allyl cation (awesome!)

$m/z = 41$

$m/z = 44$ (3%)

$m/z = 42$ (3%)

IV. Using the mass spectrum of 2-butanone shown below, answer the questions that follow about its fragmentation.



m/z	Relative Intensity
14	1.2
15	6.6
18	1.3
26	2.6
27	8.9
28	1.3
29	18.8
39	1.6
41	1.1
42	4.1
43	100
44	2.6
57	8.0
72	22.1
73	1.0

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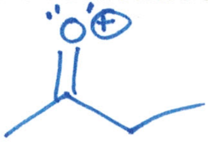
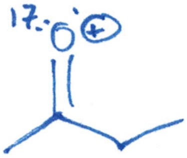
A. Draw a structure of the most likely molecular ion formed and provide its *m/z* value.



$m/z = 72$

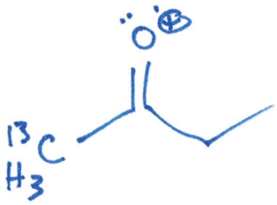
$m/z = 73$ (5%)



$m/z = 73$

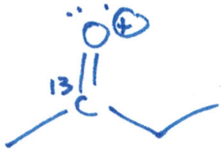
0.37 %

B. Why is there a small peak at *m/z* = 73?



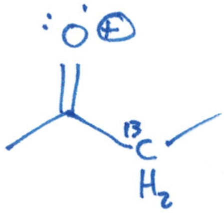
$m/z = 73$

1.1 %



$m/z = 73$

1.1 %



$m/z = 73$

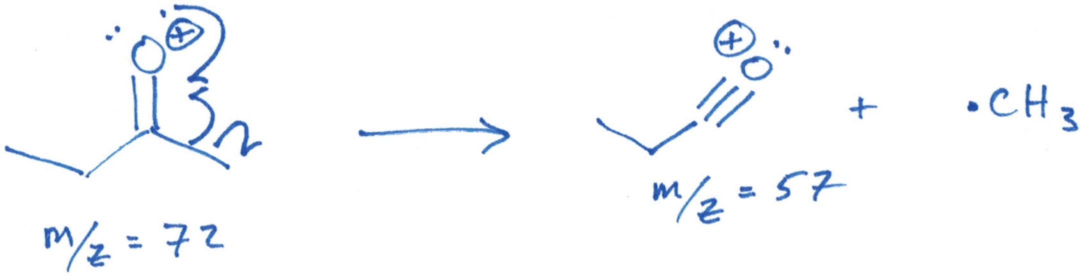
1.1 %

$m/z = 73$

1.1 %

$1.1 + 1.1 + 1.1 + 1.1 + 0.37 = 4.77 \doteq 5\%$

C. The dominant decomposition pathways for the molecular ion of an aliphatic ketone such as 2-butanone is by α-cleavage. Draw a fragmentation mechanism for both viable α-cleavage pathways and determine the *m/z* value for each product.

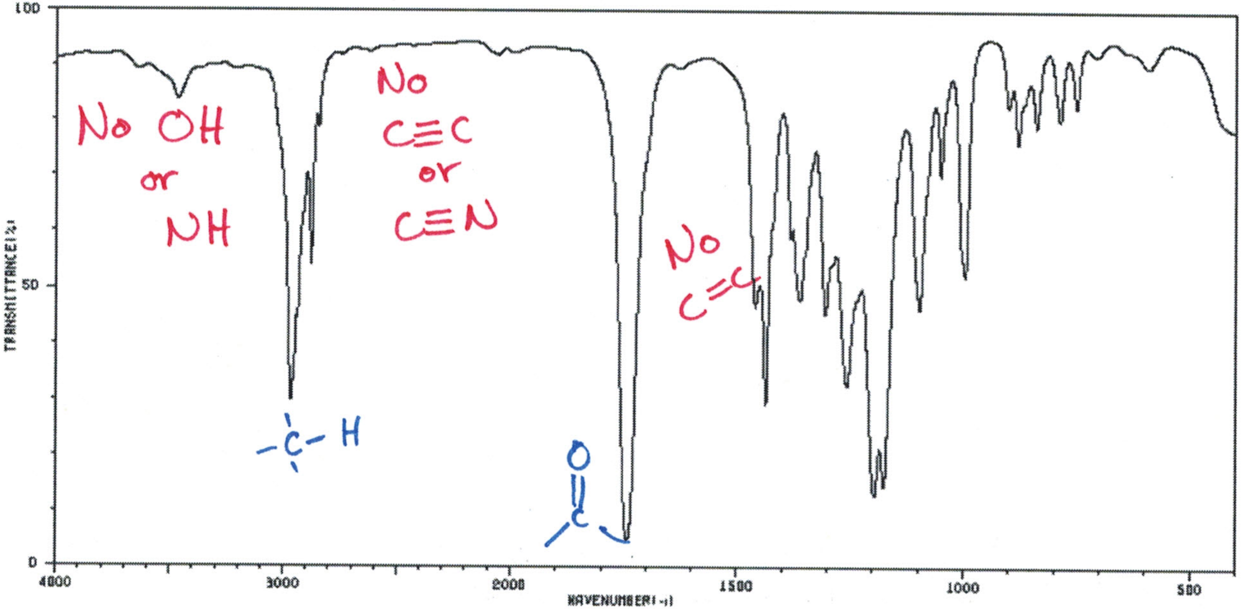


D. The fragmentation of the products in part ~~B~~ C is responsible for the strong peaks at *m/z* = 29 and *m/z* = 15. Draw a fragmentation mechanism for this process and explain why it is so favorable?

These reactions occur despite the formatio of fairly high energy cations, because they produce a VERY stable small gas molecule carbon monoxide.

V. The IR, ^{1}H-NMR, ^{13}C-NMR, and MS spectra below correspond to the product of a reaction between butyryl chloride and methanol. Analyze each of the spectra, assign signals to structural features or fragments of the molecule, and answer the questions below.

A. What functional groups can you identify as being present or absent in the product of the reaction based upon the IR below?



3466	81	1460	49	1177	13	840	77
2967	28	1437	28	1097	44	768	77
2940	43	1382	57	1051	88	752	79
2879	62	1362	46	997	60	694	86
2846	77	1306	43	902	79		
1742	4	1258	31	881	72		
1460	44	1198	12	869	79		

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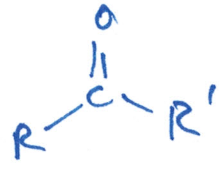
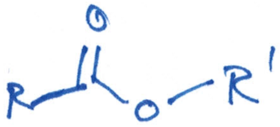
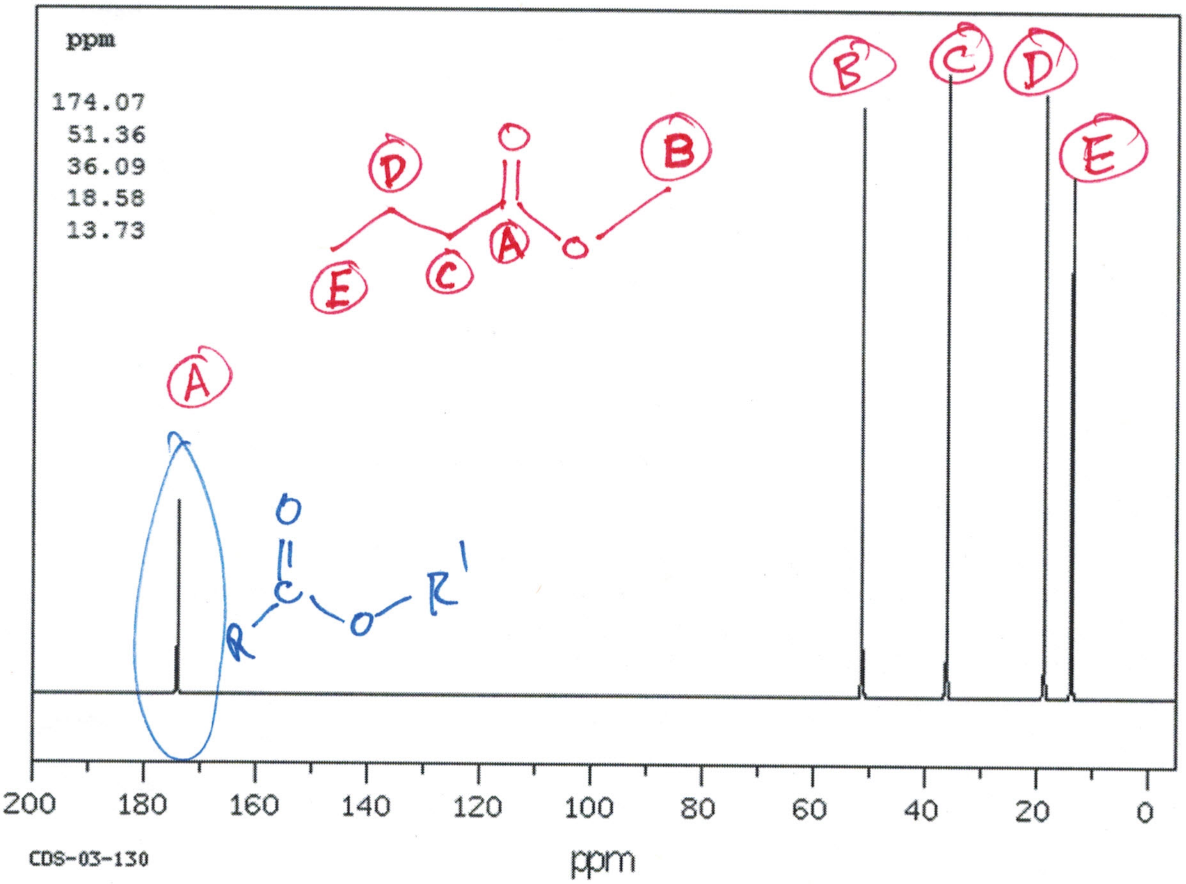
1742 cm^{-1} is likely a  $R-C(=O)-R'$ of some sort, most likely an ester  $R-C(=O)-O-R'$

B. Is your IR analysis and prediction of likely functional groups consistent with the ^{13}C-NMR spectrum below? Assign the signal at δ 174 to a likely carbon atom in the product molecule. Once you are certain of the structure by ^{1}H-NMR, it may be a good idea to return to this spectrum and assign the other ^{13}C-NMR signals to their corresponding carbon atoms.

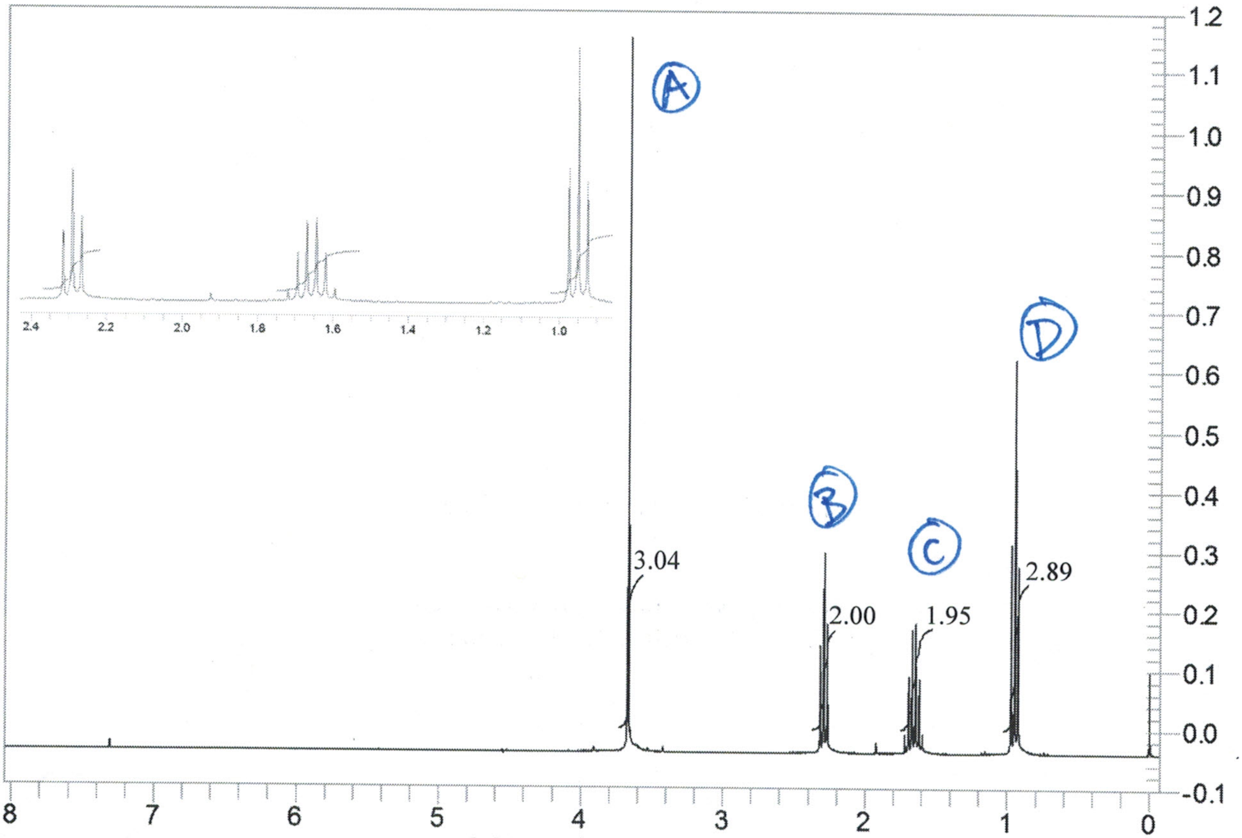


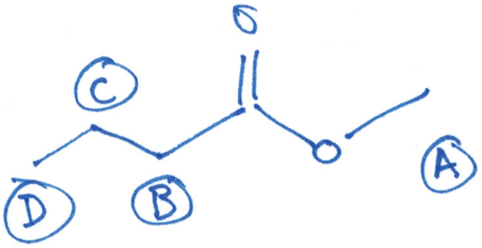
SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)

^{13}C-NMR also shows a carbonyl compound. Most likely it is an ester.

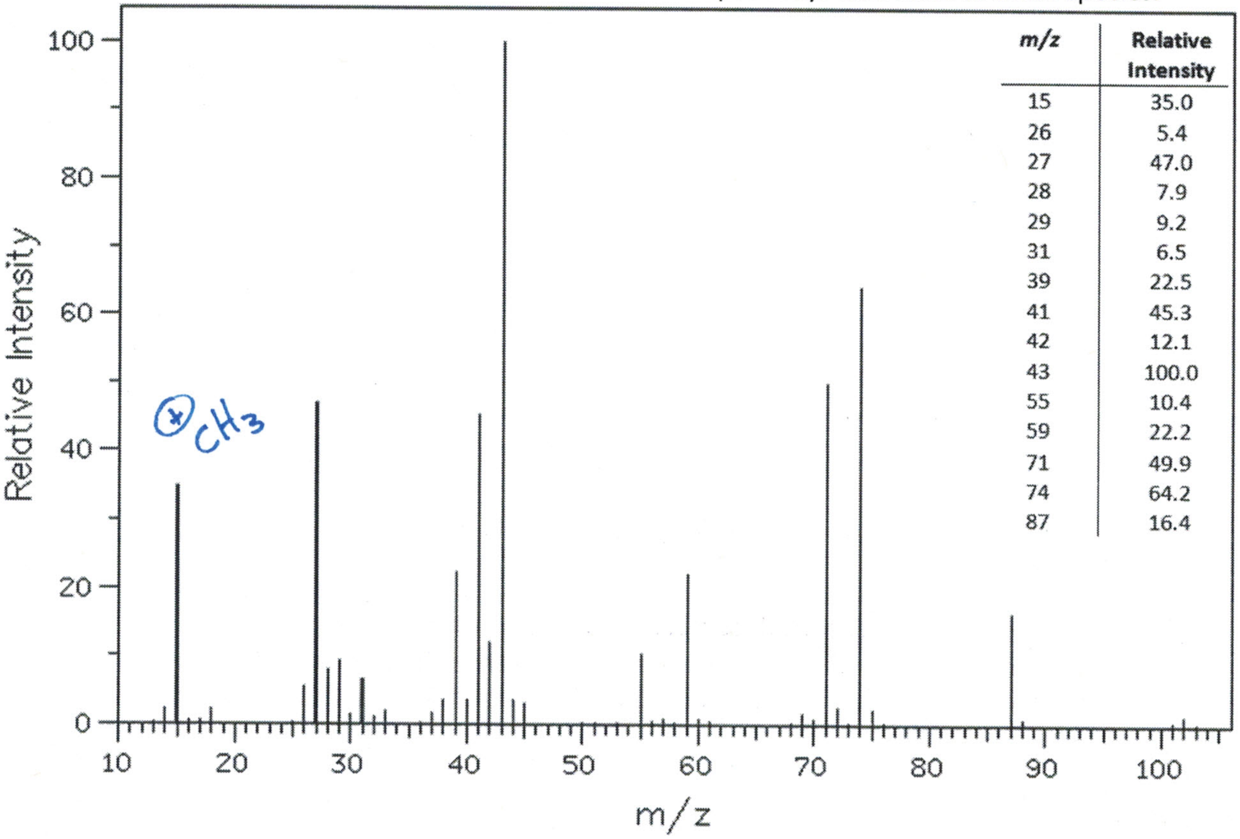
C. Use the ^{1}H-NMR spectrum below to conclusively determine the structure of the product molecule. Assign each of the ^{1}H-NMR signals to its corresponding H-atom.

300 MHz ^{1}H NMR
In CDCl3



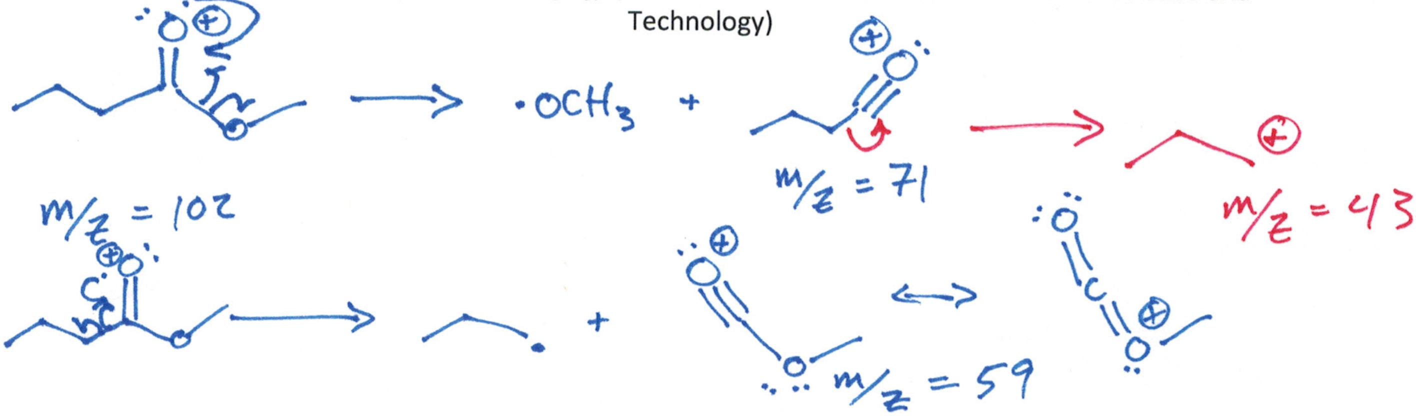


D. The mass spectrum of the product molecule contains intense signals at *m/z* = 71, 59, and 43 all of which can arise from the α-cleaveage of the most likely molecular ion, draw a reaction mechanism for the reaction pathways that leads to these species.

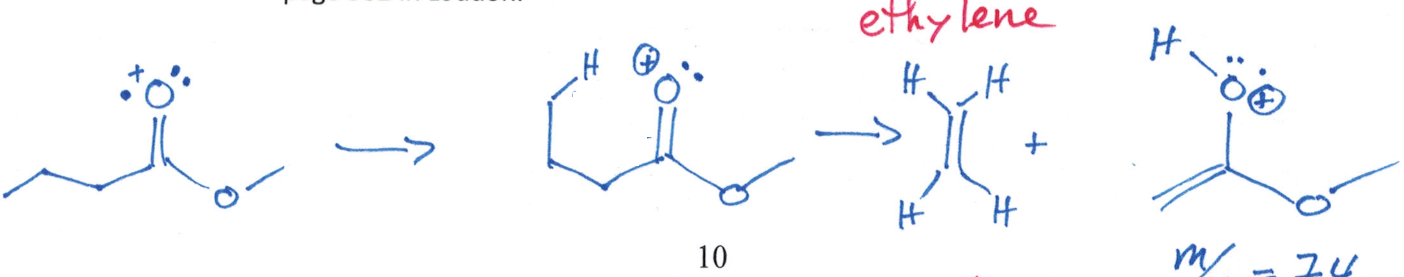


m/z	Relative Intensity
15	35.0
26	5.4
27	47.0
28	7.9
29	9.2
31	6.5
39	22.5
41	45.3
42	12.1
43	100.0
55	10.4
59	22.2
71	49.9
74	64.2
87	16.4

SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)



E. The McLafferty Rearrangement of the molecular ion leads to an ion responsible for the peak at *m/z* = 74, for an extra challenge and extra fun, draw this fragmentation. See page 902 in Loudon.

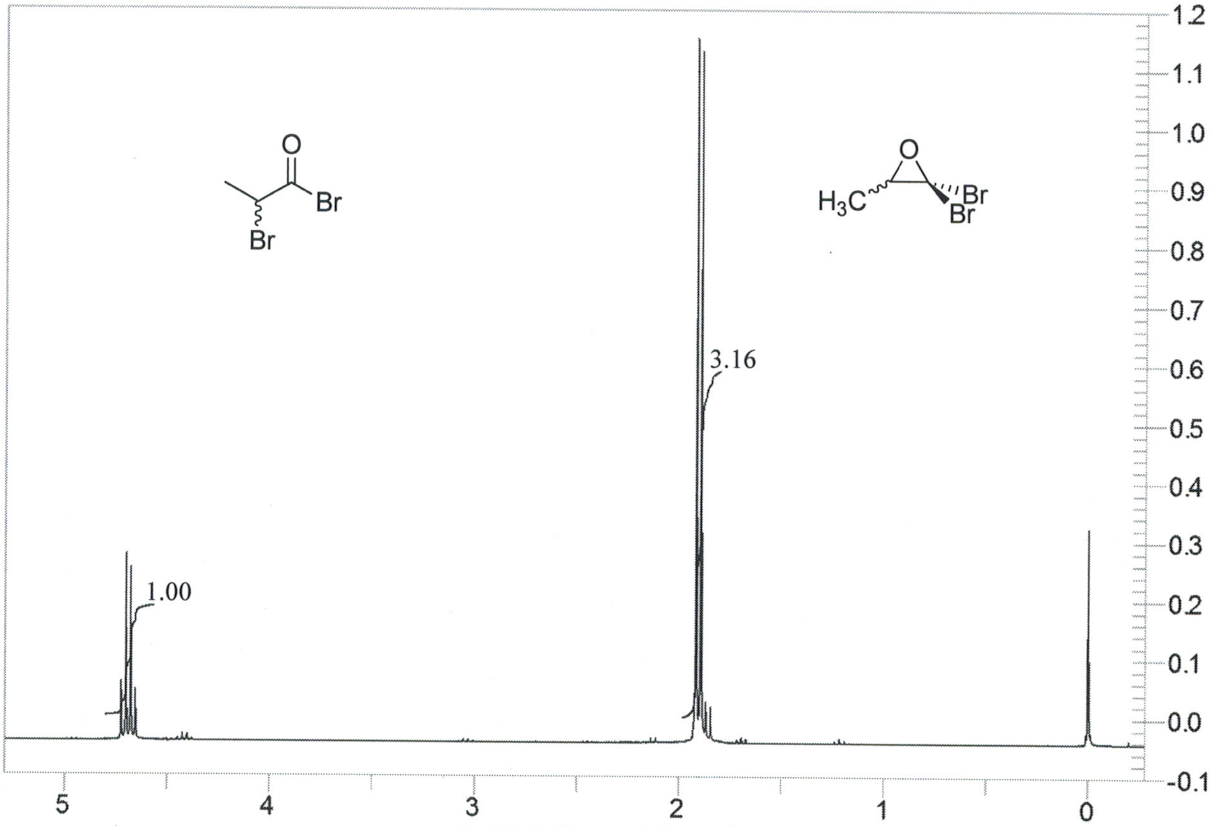


Very common in carbonyls with long enough chains

VI. In spectroscopy problem set 1, a few students came up with two plausible answers for the ^{1}H-NMR spectrum of $C_3H_4OBr_2$. One was the correct answer and the other is a molecule that has only been reported in all of the chemistry literature in a single computational/theoretical work. Both of the two proposed molecules are shown on the NMR below.

300 MHz ^{1}H NMR

In CDCl3



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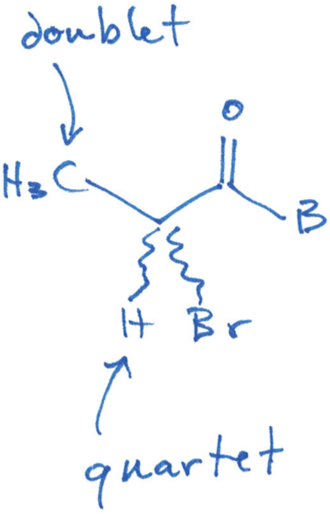
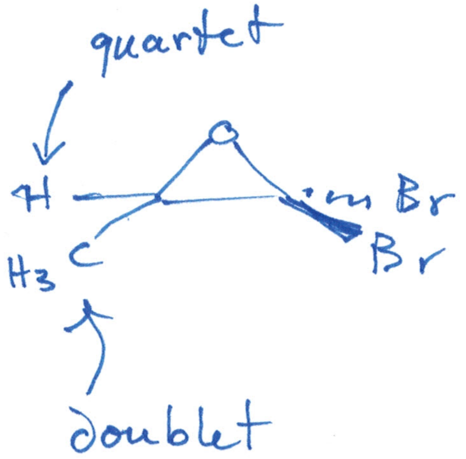
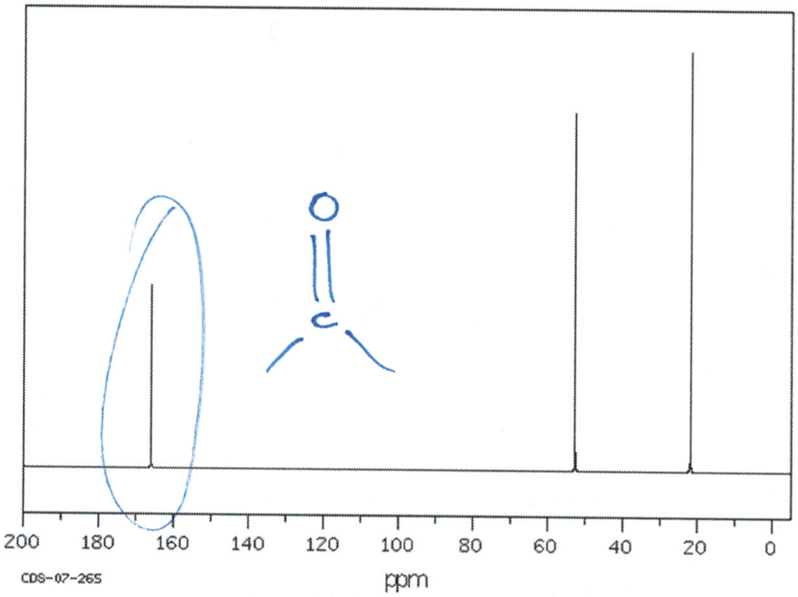
A. Confirm that each of the molecules would have the appropriate coupling to produce the splitting pattern on the ^{1}H-NMR spectrum.





B. The identity of the correct $C_3H_4OBr_2$ species can be confirmed in several independent ways. Explain how the evidence presented below can confirm the identity of the correct molecular structure.

i. ^{13}C-NMR



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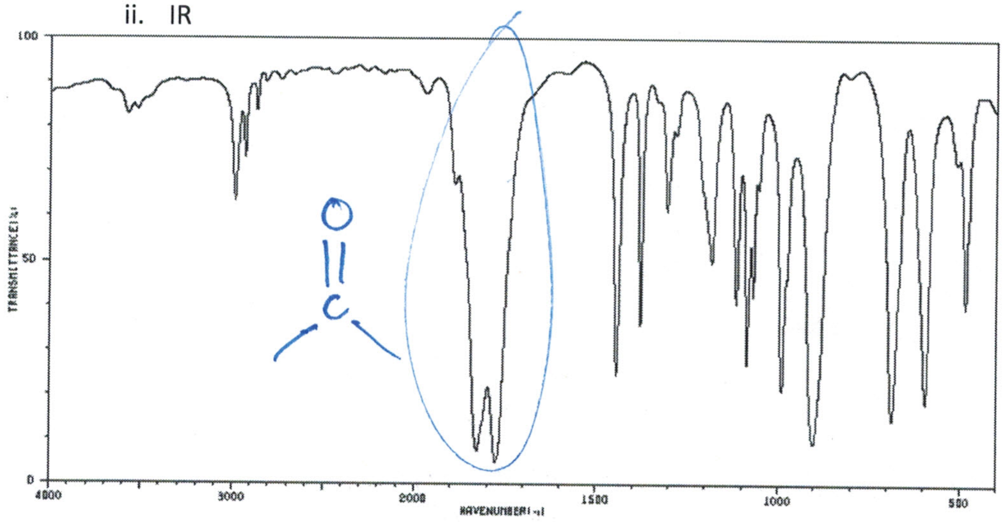
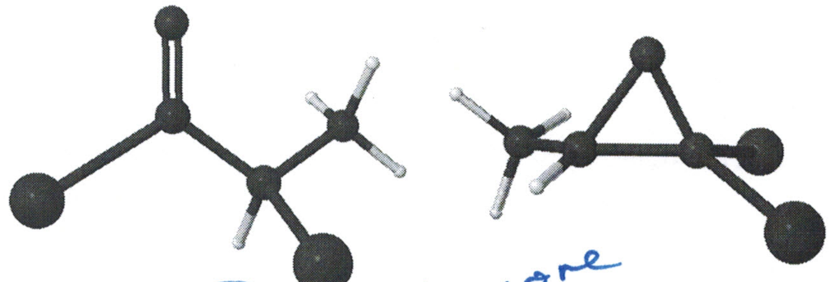
ii. IR



SDBSWeb : http://sdbs.riodb.aist.go.jp (National Institute of Advanced Industrial Science and Technology)

iii. Computational Molecular Modeling (B3LYP/6-31G(d))

The structure of each possible molecule was optimized and an NMR calculation was performed to determine the approximate chemical shift of the H-atoms in each structure.



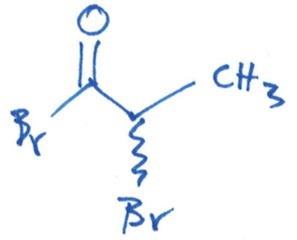
Relative Energy (kcal/mol)	$\boxed{0.0}$	**32.4**
Predicted δ of Methyl H-atoms (ppm)	1.5	1.3
Predicted δ of Methine H-atom (ppm)	4.4	3.0

Much more stable molecule. More likely to have been synthesized.

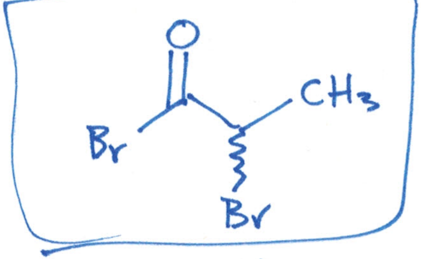
Experimental δ 4.68

δ 1.91

Chemical shifts fit

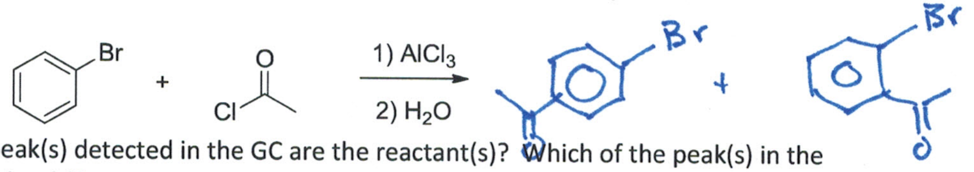


C. Identify the correct structure of $C_3H_4OBr_2$ and justify your answer based upon the evidence available.



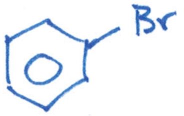
This is the more stable isomer by molecular modeling which makes it likely to be easier to make. Its predicted shifts fit closely to the observed ones. The conclusive assignment comes from the IR and ^{13}C-NMR both of which indicate the presence of a carbonyl.

VII. Use the GC/MS spectrum of the student product obtained from the Friedel-Crafts acylation of bromobenzene (shown on the subsequent page) to answer the following questions. (Loudon p 759) Only signals with intensity greater than 15% relative intensity to the base peak are shown for clarity.



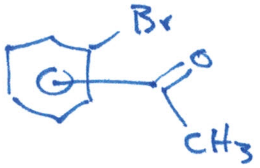
A. Which of the peak(s) detected in the GC are the reactant(s)? Which of the peak(s) in the GC are the product(s)?

Peak # 1



m/z = 156
158 (50%)

Peaks #2, #3



m/z = 198
200 (50%

B. Which of the MS peaks contain bromine atoms? How can you tell?

GC Peak # 1
m/z = 156 + 158

GC Peak # 2
m/z = 200 + 198
183 + 185
155 + 157

They all have the tell-tale doublets of equal height separated by 2 mass units.

C. Identify the species most likely responsible for the following *m/z* signals:
  i. Peak #1 – 158, 156, 77, 51, 50
  ii. Peak #2 – 200, 198, 185, 183, 157, 155, 76
  iii. Peak #3 – 200, 198, 185, 183, 157, 155, 76

D. What is the conversion percentage from reactant to product by GC?

14.73 % starting material

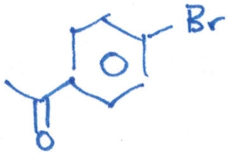
2.50 + 82.77 % products => ~ 85 % conversion

E. What is the ratio of the major to minor isomer by GC?

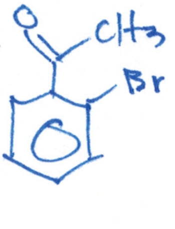
$$\frac{82.77\ \%\ \text{Major}}{2.50\ \%\ \text{Minor}} = 33.1\ \text{Major to Mino}$$

F. Identify the major and minor isomer by the ^{1}H-NMR spectra provided.

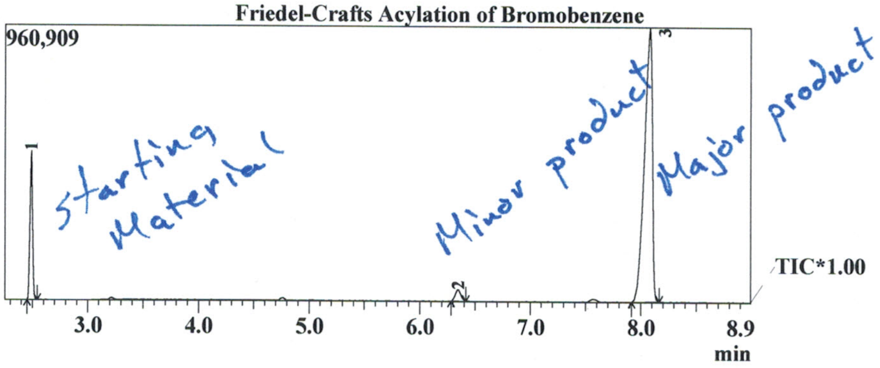
Major



Minor



these are really tough

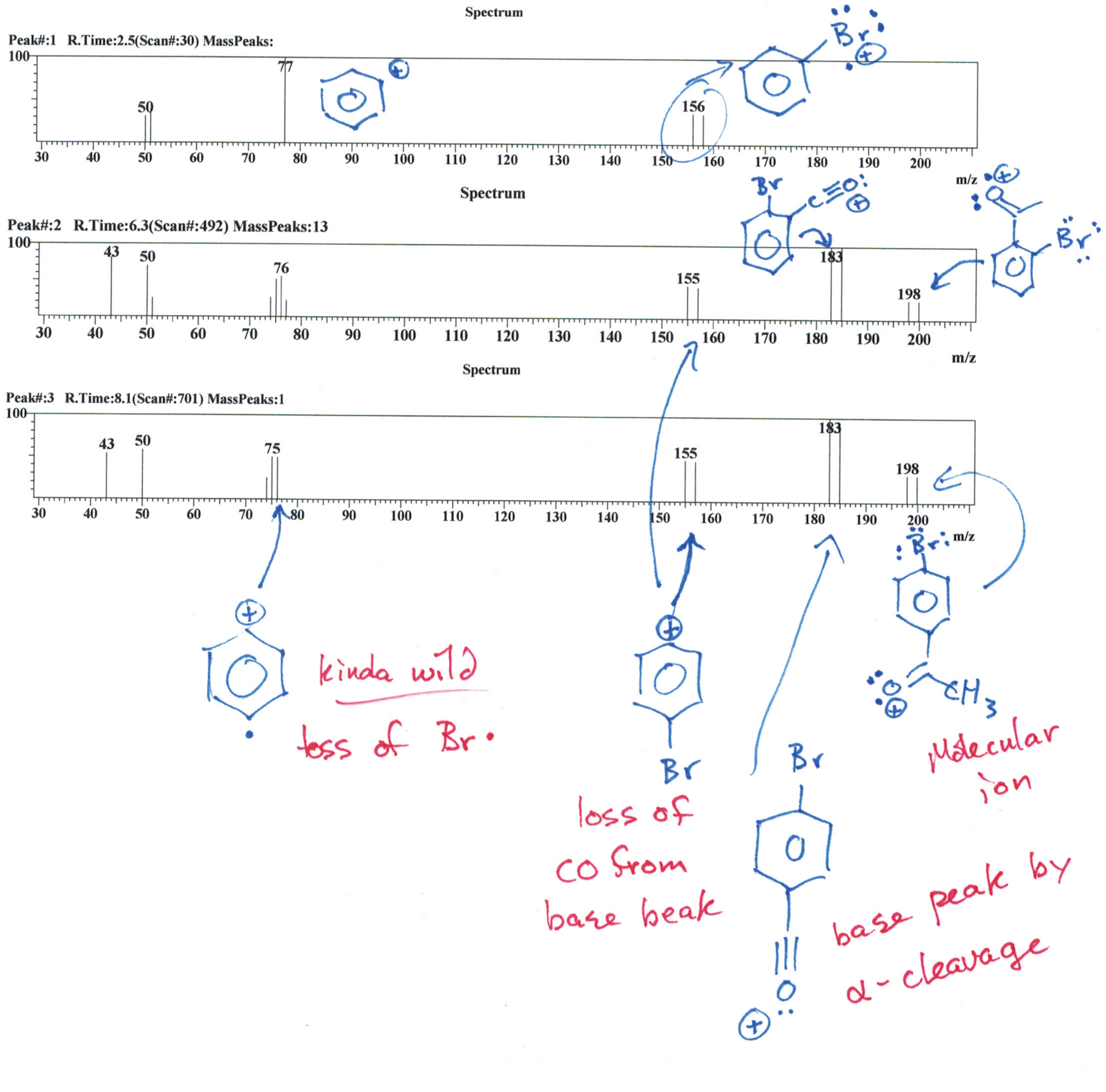


Peak Report TIC

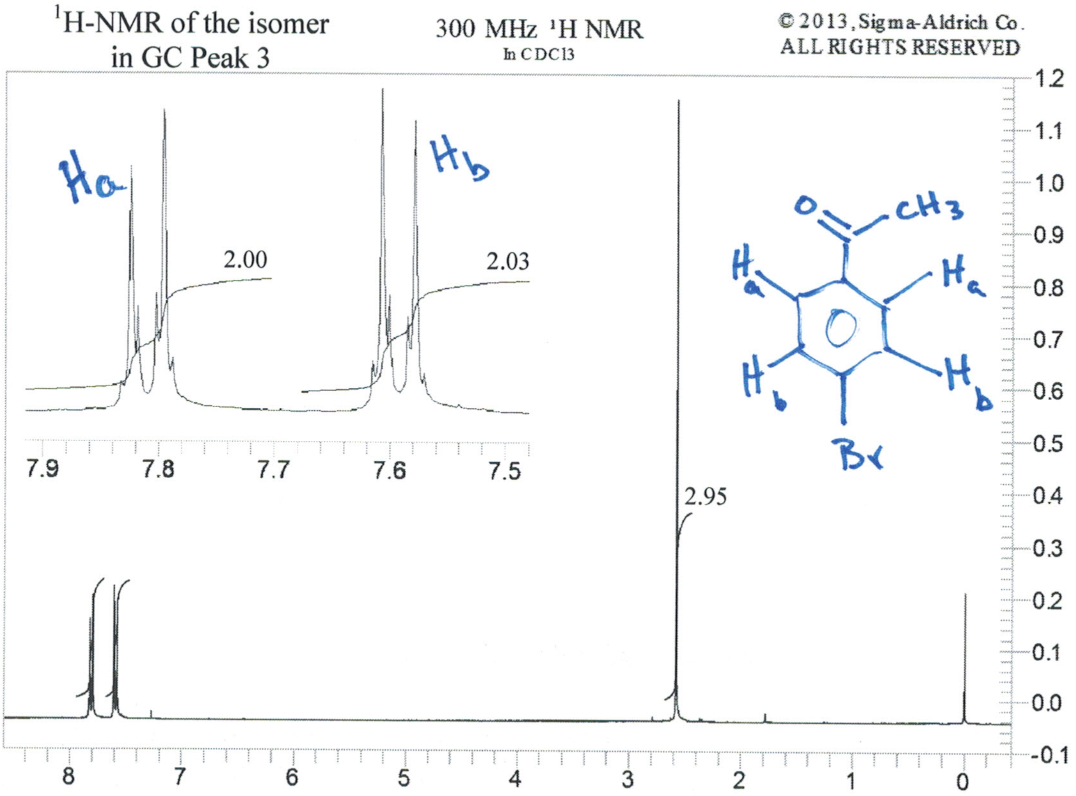
Peak#	R.Time	Area	Area%
1	2.488	842786	14.73
2	6.345	143248	2.50
3	8.081	4736553	82.77
		5722587	100.00

m/z = 51 $C_4H_3^+$

m/z = 50 $C_4H_2^+$



^{1}H-NMR of the isomer in GC Peak 3



^{1}H-NMR of the isomer in GC Peak 2