CHEM 3201A Fall 2020 Midterm Examination I
October 16, 2020
120 minutes, 6 questions.
80 Marks (+ 6 bonus marks)

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Part marks are available so show your work! Marks per question or part thereof are shown in square brackets [#].

Your course textbook, a molecular model kit, ruler and calculator are permitted. ***You are not permitted to have inserted extra paper (sticky notes and flags are permitted) into your textbook. This is considered cheating, as stated in your course prospectus.*** If you have extra paper in your book, speak to the professor or the TA before you begin the exam.

You are allowed to write on this exam sheet and it will be graded, as will your submissions on other paper. It helps us grade faster and more accurately if you write "see exam sheet for question 2" or something similar to help us connect items on the question sheets and your additional pages.

FREE ADVICE: **BEFORE STARTING, LOOK THROUGH THE ENTIRE EXAM AND START WITH YOUR FAVOURITE QUESTION.**

1. A sample has a molecular ion (in EIMS) at m/z 170. Determine the molecular formula based on each restriction below (separately, which mean that c does not include the restrictions from b and so on). *NOTE: No formula should have fewer than 6 hydrogen atoms (only because I said so).*

a) C and H only **[2]**

b) One chlorine **[2]**

c) One sulfur and one oxygen **[2]**

d) Two nitrogens **[2]**

e) If the EIMS shows M and M+2 peak with relative abundances of 22% and 7.3%, respectively, which formula is correct? **[2]**

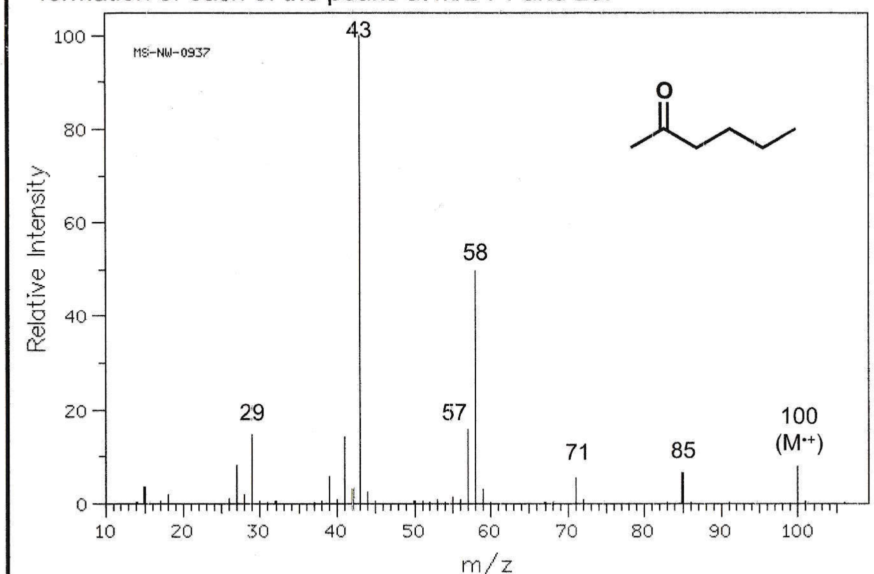
f) Which formula is correct if the EIMS shows the following relative abundances? *m/z* 170, 50.0%; 171, 7.3%; 172, 0.5%. **[2]**

2. Using the molecular formula you generated in question 1d, calculate U. **[4]**

3. a) For the formula you generated in question 1c, calculate the theoretical high-resolution mass of the molecular ion that would be observed in chemical ionization MS. **[4]**

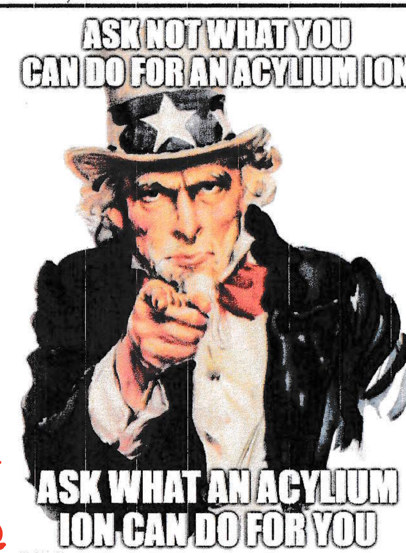
b) Given your answer in 3a, what is the highest mass-to-charge ratio that could be observed and still constitute proof that your formula is correct? **[2]**

4. Below is the EI mass spectrum for 2-hexanone (MW = 100). Provide the structure and a fragmentation mechanism to explain the formation of each of the peaks at *m/z* 85, 58, 57, and 43. **[20**: 5 for each peak (2 for structure, 3 for mechanism)**]**. *BONUS* **[3 each]**: Provide the structure and a fragmentation mechanism to explain the formation of each of the peaks at *m/z* 71 and 29.



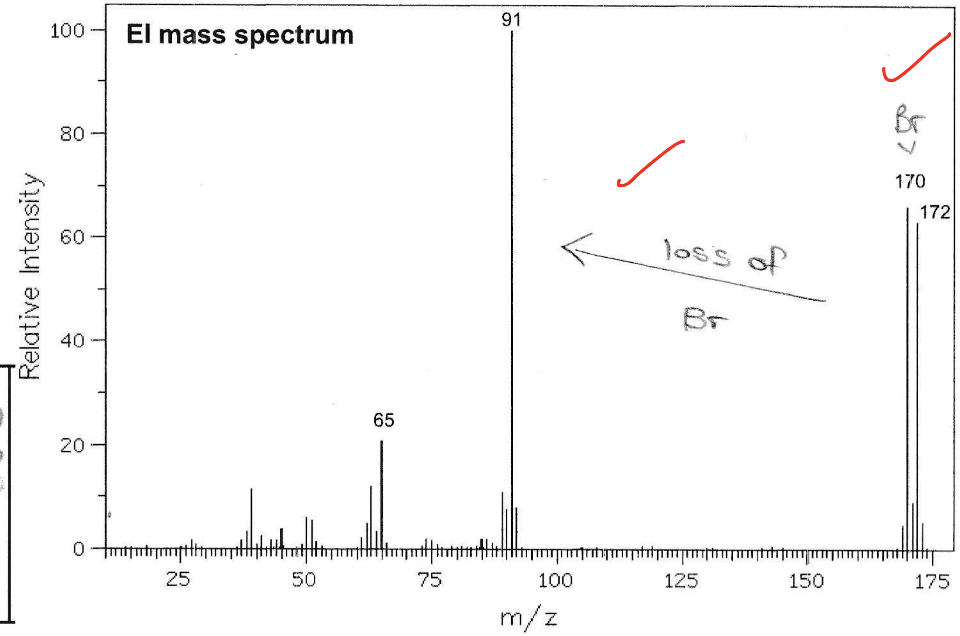
I couldn't get anything to fit in this area. D'oh!

… And then one of the students in the class sent me this:



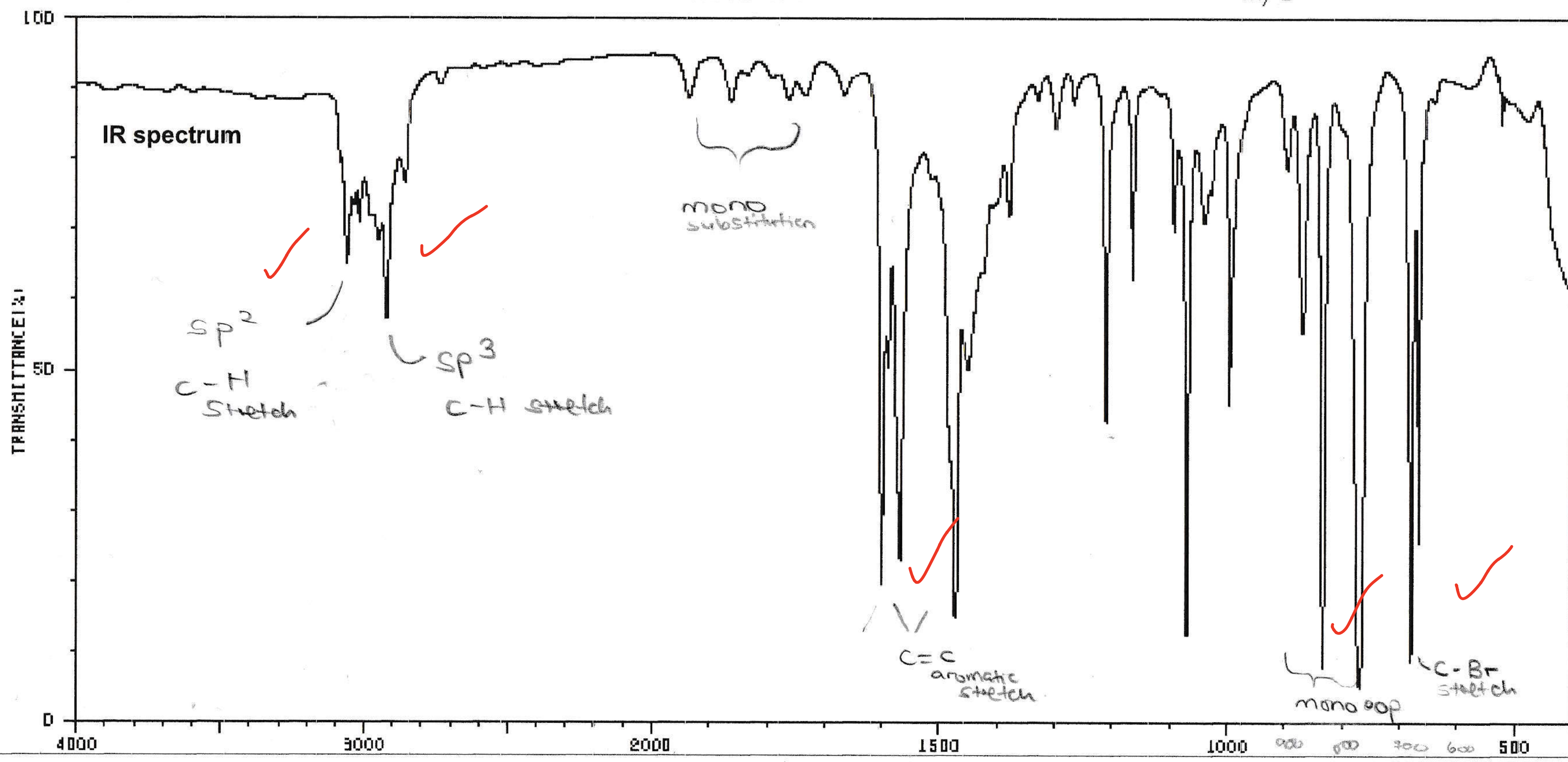
Q1	12
Q2	0
Q3	0
Q4	23
Q5	16
Q6	20
total	71

5. An unknown compound was found in my lab. We analyzed it using EIMS and IR spectroscopy.
a) What is the molecular formula? **[4]**
b) What is the degree of unsaturation? **[2]**
c) What is the structure? Explain your answer. **[12]**



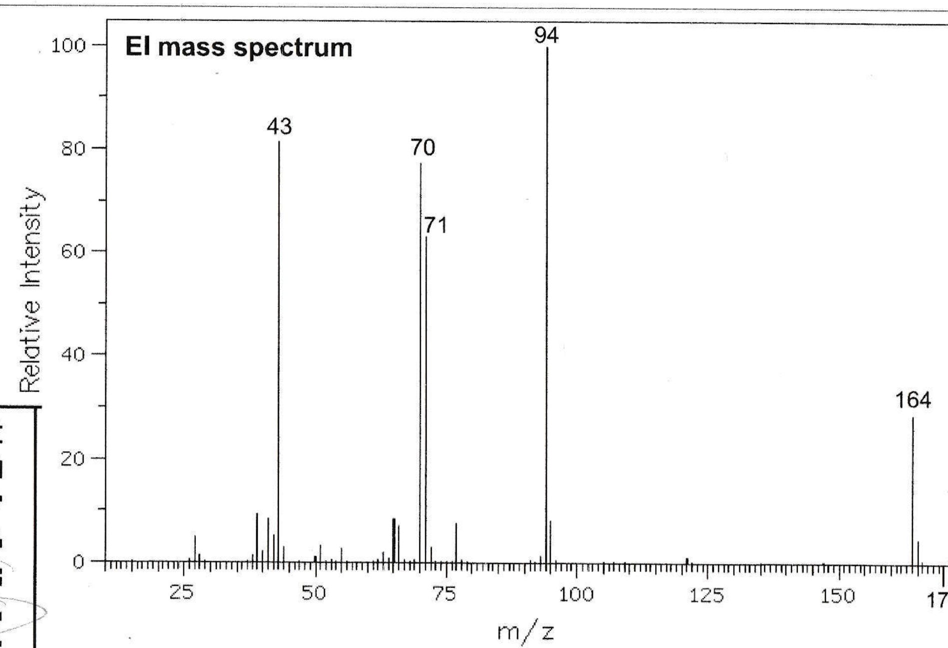
IR peak list: 3 or 4 digits = peaks in cm^{-1}; 2 digits = % transmittance

3061	62	1762	84	1473	14	1166	60	869	53
3035	70	1734	86	1452	47	1093	68	834	7
3017	88	1667	86	1380	88	1071	12	770	4
2961	66	1601	18	1330	84	1040	68	681	8
2923	55	1590	49	1299	81	1029	72	667	24
2858	74	1569	21	1268	84	996	45	522	61
1862	84	1482	36	1212	41	896	77	477	81



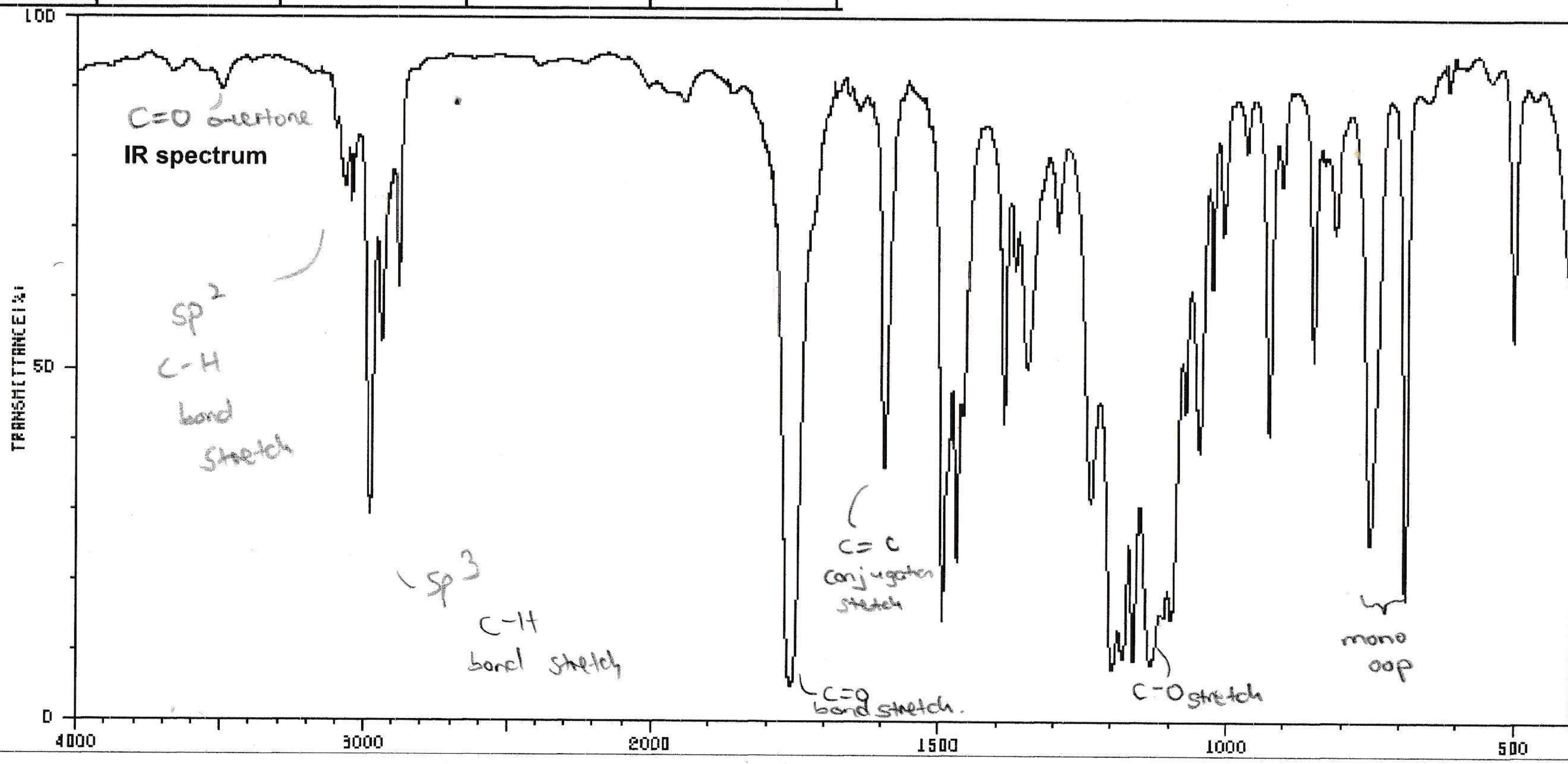
6. Another unknown compound was found in my lab. We analyzed it using combustion analysis, EIMS and IR spectroscopy. Combustion analysis gave the following data: C, 73.14%; H, 7.38%; N, ~0%.

a) What is the molecular formula? **[6]**
b) What is the degree of unsaturation? **[2]**
c) What is the structure? Explain your answer. **[12]** Note that there are two possible structures that will be accepted as correct because they cannot be readily distinguished using that data provided.



IR peak list: 3 or 4 digits = peaks in cm^{-1}; 2 digits = % transmittance

3099	81	1768	4	1348	49	1097	19	903	72
3065	72	1595	34	1294	68	1072	42	849	49
3044	70	1495	15	1236	30	1047	36	830	77
3032	77	1470	21	1200	7	1026	58	812	66
2977	28	1459	42	1181	8	1007	66	752	23
2938	52	1388	41	1163	8	965	79	690	16
2879	68	1370	62	1132	7	926	38	601	62



1. (a) $m/z = 170$

$\frac{170}{13} = 13\frac{1}{13}$ ✓

$= C_{13}H_{14}$ ✓ possible 2/2

(b) $m/z = 170$

$\frac{170}{13} = C_{13}H_{14}$

$-3C$, add 1 H ↓ add Cl ✓ 2/2

$C_{10}H_{15}Cl$ ✓ possible

(c) $m/z = 170$

$\frac{170}{13} = C_{13}H_{14}$

$-CH_4$ ↓ add O

$C_{12}H_{10}O$

$-C_2H_8$ ↓ add S ✓

$C_{10}H_2OS$

× doesn't seem feasible

(c) continuation

$170 - 32\ (S) = 138$

now $\frac{138}{13} = 10\frac{8}{13}$

$C_{10}H_8S$ ✓

$-CH_4$ ↓ add O

$C_9H_4SO_x$ not feasible either

$170 - 32\ (S) - 16\ (O) = 122$

$\frac{122}{13} = 9\,5/13$

$C_9H_{14}OS$ ✓ possible 2/2

(d) $m/z = 170$

$\frac{170}{13} = 13\,1/3$

$= C_{13}H_{14}$ ✓

$-C_2H_4$ ↓ add 2 N

$= C_{11}H_{10}N_2$ ✓ possible 2/2

(e) To determine the correct formula

$M \rightarrow 22\% \xrightarrow{\times 50/11} 100\%$

$M+2 \rightarrow 7.3\% \xrightarrow{\times 50/11} 33.181818$

formula is most likely $C_{10}H_{15}Cl$ ✓
(because Cl is commonly known for having 1:3 ✓ ratio when discussing relative abundance

2/2

(f)

m/z		relative abundance		
170	—	50.0	$\xrightarrow{\times 2}$	100.0%
171	—	7.3	$\xrightarrow{\times 2}$	14.6%
172	—	0.5	$\xrightarrow{\times 2}$	1%

Starting with the formula $C_{13}H_{14}$ ✓ 2/2

$M+1 = (13 \times 1.1) + (14 \times 0.015)$

$= 14.51\%$ close to actual value

$M+2 = \frac{(13 \times 1.1)^2}{200}$

$= 1.02245$ close to actual value

So correct formula is $C_{13}H_{14}$ ✓

2. Formula generated in 1(d) — $C_{13}H_{14}$

Formula of saturated molecule ← $C_{13}H_{28}$ ✗

$\therefore U = \frac{28-14}{2}$ ✗

$= 7$

0/4

3 (a) using formula generated in 1(c) which is $C_{13}H_{14}$

Theoretical mass would be

$13(12.0000) + 14(1.00783)$

$= 170.10962$

X 0/4

(b) Another peak that could have been noted is one that had ^{13}C and ^{2}H

X 0/2

This would make the highest mass to charge ratio

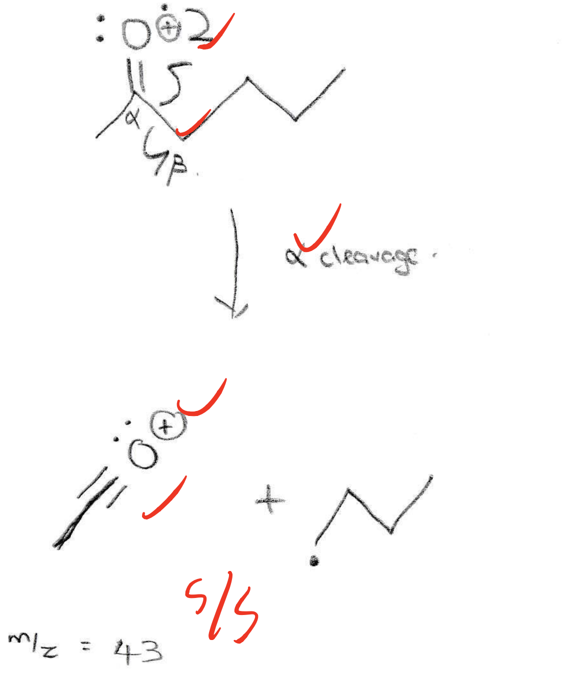
$= 13(13.00336) + 14(2.01410)$

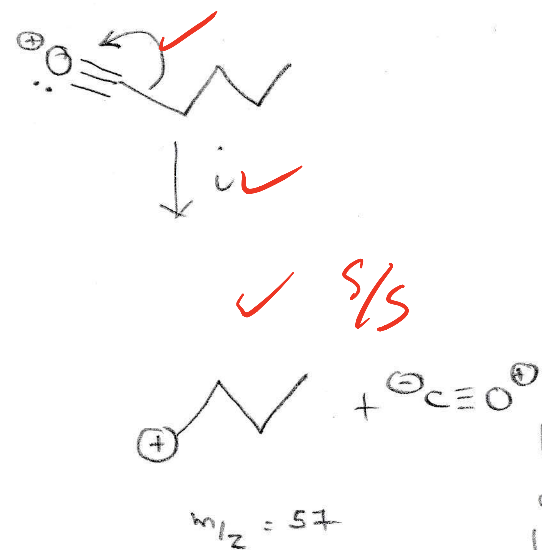
$= 197.24108$

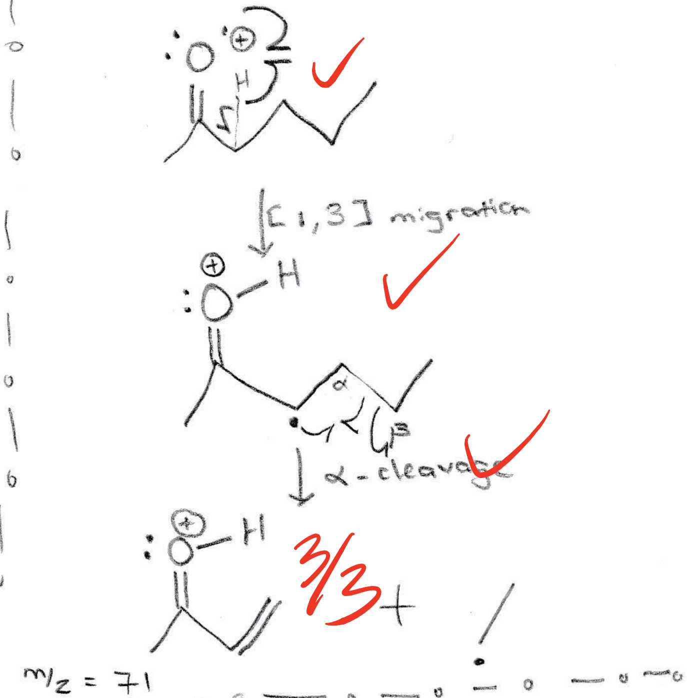
X

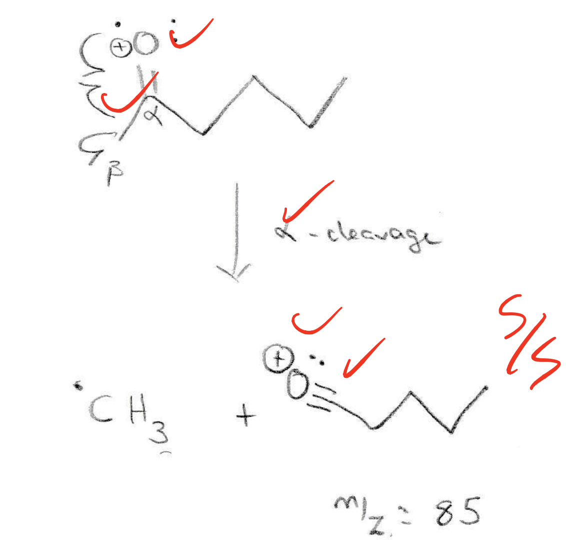
this could have been present on the mass spectrum but would have very low abudance

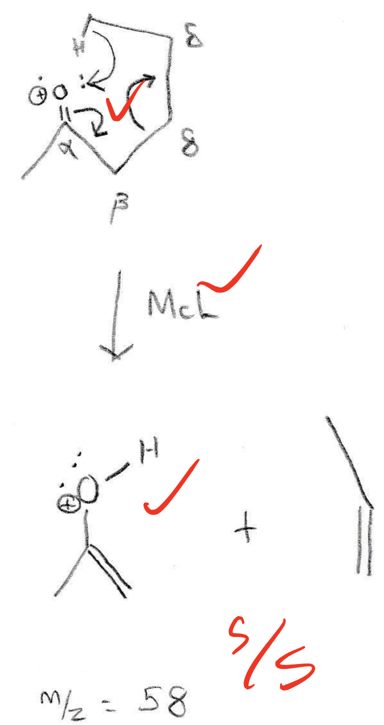
4


α cleavage
m/z = 43
5/5


i
m/z = 57
5/5


[1,3] migration
α-cleavage
m/z = 71
3/3


α-cleavage
$\cdot CH_3$
m/z = 85
5/5


McL
m/z = 58
5/5

5 (a) The relative abudances of the base peaks suggests the presence of a bromide thus.

$\frac{170}{13} = C_{13}H_{14}$

C_6H_7 | Br

C_7H_7Br ✓

4/4

(b) Degrees of Unsaturation

Saturated Formula C_7H_{16}

$C_7H_{15}Br$

$U = \frac{15-7}{2}$

$= \frac{8}{2}$

$= 4$ probably an aromatic ring

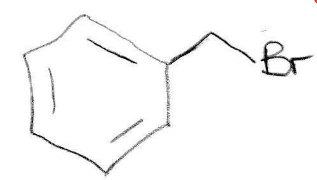
→ Yup

2/2

The IR has been labelled to show how it has a C - Br stretch and a monosubstituted pattern and an aromatic C=C stretch. Thus there is a monosubstituted methyl aromatic bromide.

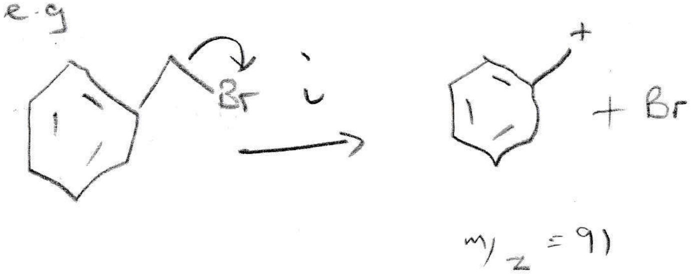
→ actually more consistent w/ meta substitution

10/12



Fragmentation of aromatic compounds often gives a molecular ion peak of 91 and fragmentation of halides results in the loss of the Bromide

e.g



6 (a) (i) Empirical formula.

Percentages dont add to 100% ∴

$\% O = 100 - (73.14 + 7.38)$

Since there was combustion $= 19.48\%$

6/6

hence	per 100g	number of moles	Ratio (divided by $\frac{19.48}{16}$ of O)
C	73.14	$\frac{73.14}{12}$	5.00616 ..
H	7.38	$\frac{7.38}{1}$	6.0616...
O	19.48	$\frac{19.48}{16}$	1

so empirical formula is C_5H_6O

now Molecular mass = 164

$164 = x(C_5H_6O)$

$164 = x(60+6+16)$

$2 = x$

∴ molecular formula is

$C_{10}H_{12}O_2$

(b) Degree of unsaturation

saturated formula: $C_{10}H_{22}$

$C_{10}H_{22}O_2$

2/2

$\therefore u = \frac{22 - 12}{2}$

$= \frac{10}{2}$

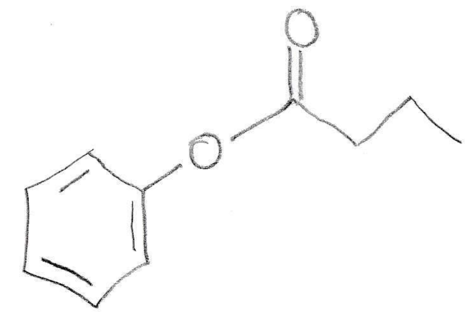
$= 5$ probably there is an aromatic group

(c) The C=O bond stretch is quite high (1768) ~~which~~ means it could be an ester that is conjugated with the single bonded oxygen which would cause it frequency to be higher than usual.

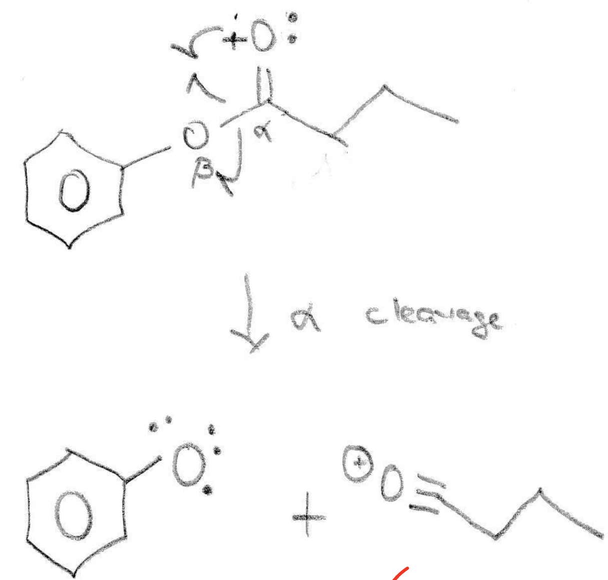
Also the C=C conjugation stretch is probably from the phenyl group as there is evidence of monosubstitution at 690 and 752 cm^{-1}.

hence

12/12



Example of fragmentation



$m/z = 71$ which is one of the prominent peaks

43 also shows loss of $^{\ominus}C\equiv O^{\oplus}$