S343 Midterm Exam
3/3/15

Name Key

AI or Section _____

This exam contains 9 questions on 13 pages. It contains 102 points and will be graded out of 100 points.

1. _____ (12pts)

2. _____(18pts)

3. _____ (10pts)

4. _____(14pts)

5. _____(12pts)

6. _____(10pts)

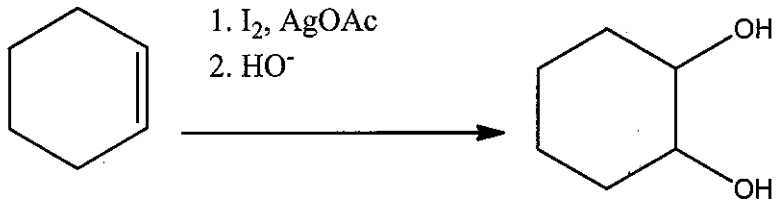
7. _____(6pts)

8. _____(10pts)

9. _____(10pts)

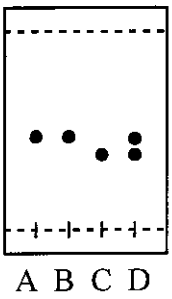
Total:

1. (12 pts) Answer the questions on the next page based on the procedure and data below, similar to the dihydroxylation experiments that you performed.



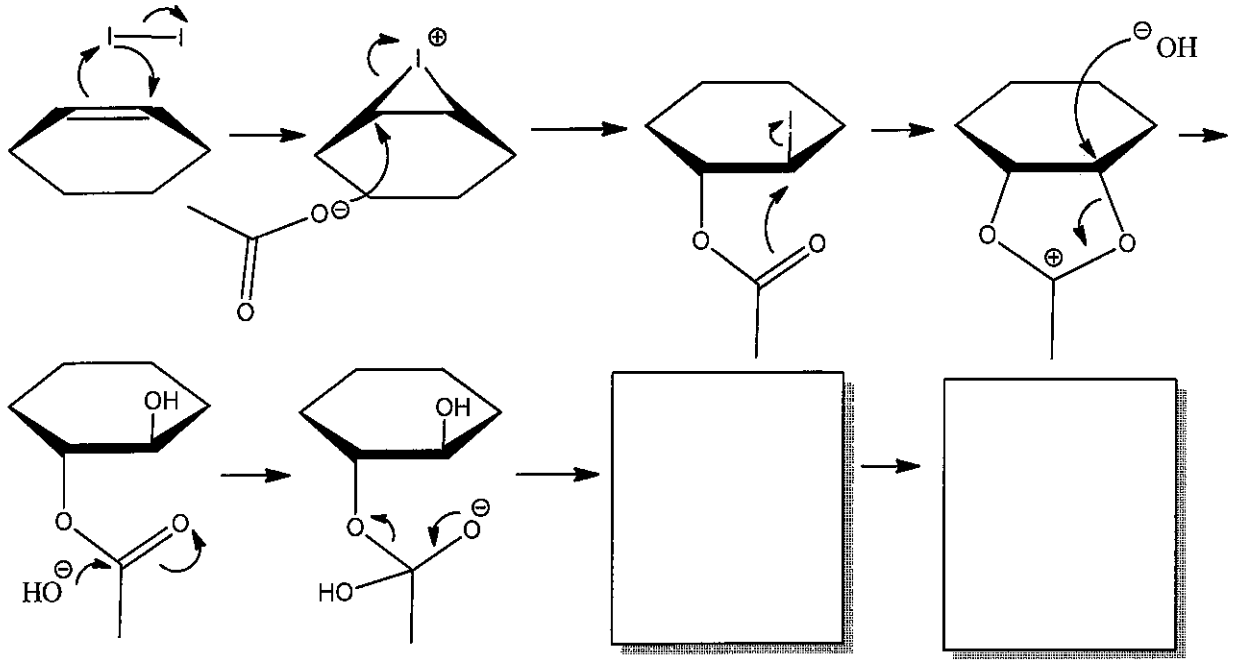
Woodward dihydroxylation: In a small Erlenmeyer flask with a magnetic stirbar, mix 3.0 mL of concentrated acetic acid and 0.15 mL of water. Add 50 μL of cyclohexene. Suspend 0.20 g of silver acetate in the solution, and add 0.135 g of finely powdered iodine in one portion. Heat the reaction gently for 20 minutes until the yellow-green AgI precipitate forms. Cool the reaction flask in ice and add 10 M NaOH quickly dropwise with swirling until the reaction is basic pH. Heat the reaction to boiling for 10 minutes, then cool to room temperature. Obtain a TLC of the unpurified reaction mixture.

TLC Data:



Lane A: Impure reaction mixture
Lane B: meso cyclohexane-1,2-diol
Lane C: racemic trans cyclohexane-1,2-diol
Lane D: mixture of meso and trans diol

A proposed mechanism:



1a. Which product is formed according to the proposed mechanism: cis diol, trans diol, or a mix of cis and trans diols?

(+3) trans diol

1b. Which product is formed according to the data: cis diol, trans diol, or a mix of cis and trans diols?

(+3) cis diol

1c. The crude reaction was investigated by TLC of the crude mixture because it is very difficult to isolate the diol product from the reaction. Explain why it would be difficult to use extraction as a purification technique.

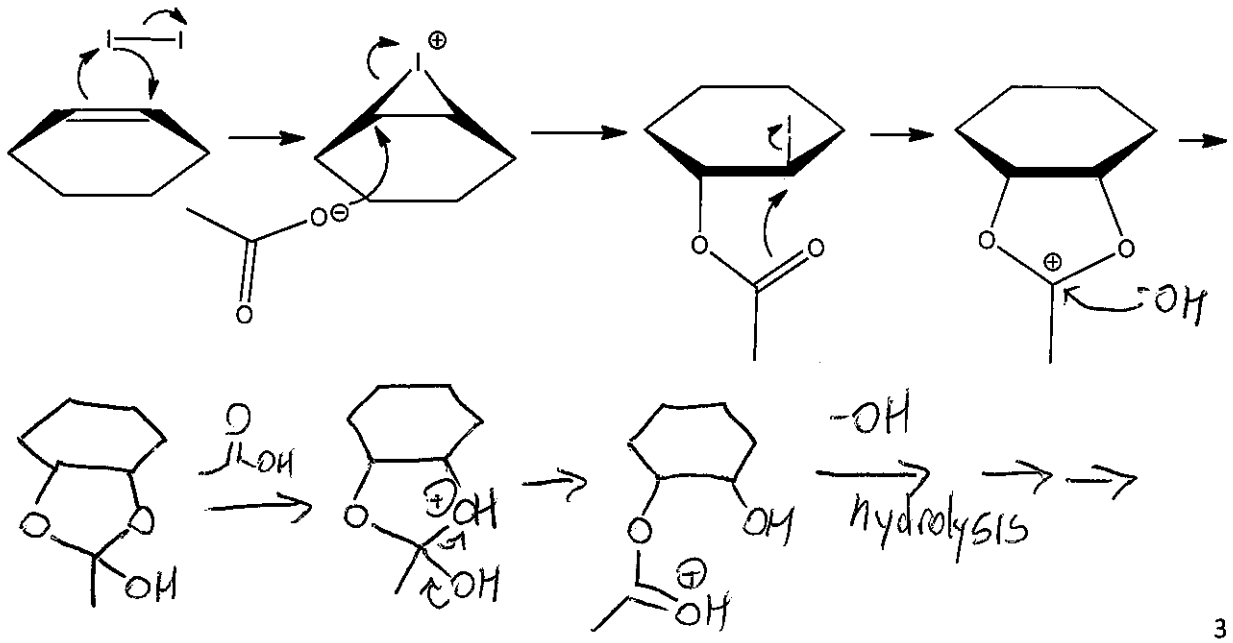
(+3) The diol is water soluble, and so are the major impurities such as acetate and iodide.

1d. Even though the diol is a solid, it would be very difficult to isolate it by recrystallization. Explain,

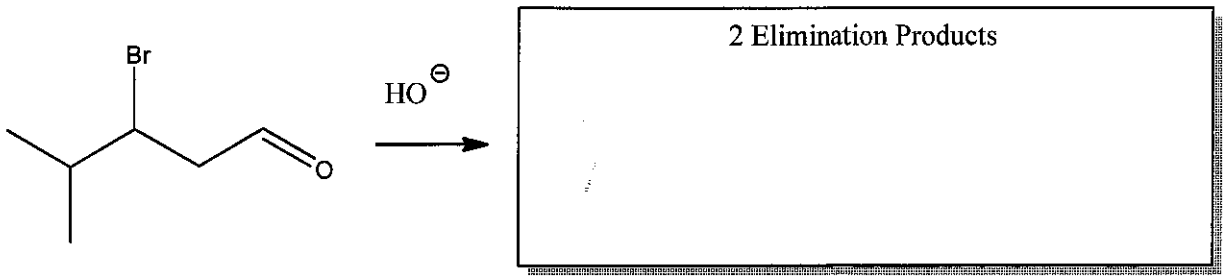
(+3) Recrystallization is only effective in removing relatively small amounts of impurity - this diol has been dissolved in "impurity." (Also accept solubility argument)

1d. The fact that silver iodide precipitates in this reaction suggests that the first three steps of the proposed mechanism is correct. Using the first three steps, propose a mechanism for the Woodward hydrolysis that is consistent with the data.

+2 bonus



2. (18pts) Answer the questions on this page and the next page based on the procedure and data below, similar to the elimination experiment that you performed.



Procedure: Put 20 mL of basic 1-propanol solution in a 50 mL round bottom flask. (There are 3.0 g of KOH per 20 mL of the solution.) Slowly pour 3.0 mL of 3-bromo-4-methylpentanal into the basic solution. Boil the reaction under reflux for one hour in a water bath, monitoring the temperature closely so that it does not exceed 90 °C during the reflux period. Cool the reaction flask, then pour the reaction into 50 mL of water in a separatory funnel. Extract with ether (3 x 20 mL) Combine the ether layers and wash with dilute aqueous acid (20 mL) then water (20mL). Dry the ether layer and evaporate the ether to give a yellow-tinted oil. Dissolve 2 drops of product in 0.5 mL of pentane and obtain GC data. (Pentane has a retention time of 34 seconds under these conditions.) Collect GC and IR data for the product.

GC data:

Peak	Retention time (s)	Peak area (no units)
A	34	900
B	58	99
C	67	1

IR data: 3080 cm^{-1}, 2950 cm^{-1}, 2810 cm^{-1}, 2710 cm^{-1}, 1697 cm^{-1} (strong), 1648 cm^{-1} (medium, sharp)

2a. Refer to the procedure, and explain what it means to

Boil under reflux: A condensor is attached to the roundbottom so that solvent won't evaporate during a long boiling time.

+2

Dry the ether layer

A drying agent, such as Na_2SO_4, is added to remove water

+2

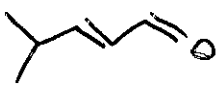
2b. What is the purpose of washing the ether layer with aqueous acid?

(+2) Quench any base from the rxn that got into the ether layer.

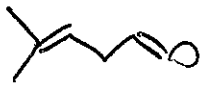
2c. Draw the structures of the two possible elimination products for this reaction.

(+2) 

2d. Use the data to determine the product distribution for the elimination reaction. Show your work and explain your thought process.

(+1) 

major product: 99 %

(+1) 

minor product: 1 %

(+3) * % distribution came from GC peak area

$\frac{\text{Peak B}}{\text{B + C}} = 99\%$ $\frac{\text{Peak C}}{\text{B+C}} = 1\%$

(+3) * Identity came from IR - both show alkene formation, but the carbonyl is conjugated ($1697\ cm^{-1}$)

2e. Use structural principles to explain why the major product formed preferentially.

(+2) The more stable product formed. Even though it is less substituted, it is conjugated, making it form preferentially.

3. (10pts) Fran Chemist has a 10 gram sample of benzoic acid (mp 122 °C, bp 249 °C) that is contaminated with a small amount of pentanoic acid (mp -34 °C, bp 186 °C.)

½ point for each

A. Circle all of the techniques below that would be likely to EFFECTIVELY PURIFY this sample, and put an "X" through all that would be ineffective for purification:

IR Gas Chromatography basic extraction neutral extraction melting point

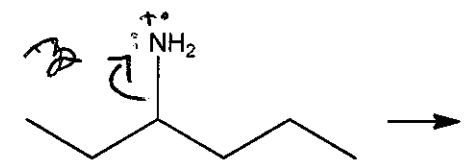
column chromatography Recrystallization Mass Spec TLC distillation

B. Circle all of the techniques below that could be used to DETERMINE THE PURITY of this sample, and put an "X" through all that could not be used to determing product purity:

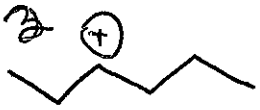
IR Gas Chromatography basic extraction neutral extraction melting point

column chromatography Recrystallization Mass Spec TLC distillation

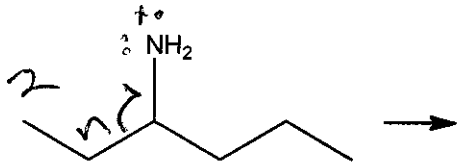
4. (14pts) Provide mechanisms of fragmentation and the structure of the fragments observed in the Mass Spec of 3-aminohexane (m/z = 101.)



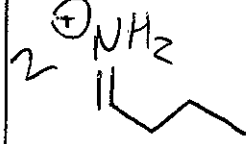
fragment m/z = 85



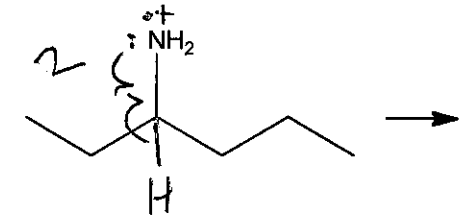
-16



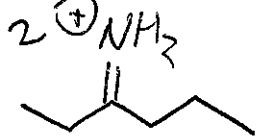
fragment m/z = 72



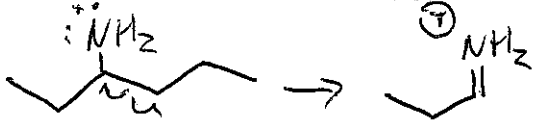
-29



fragment m/z = 100

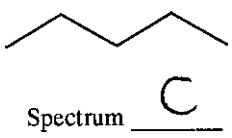


Another major fragment would occur at m/z = 258

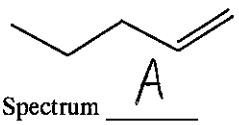


+2 each

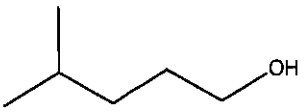
5. (12pts) Under each of the following structures, write the letter of the IR spectra most consistent with the structure.



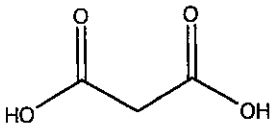
Spectrum C



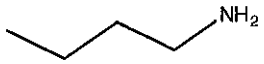
Spectrum A



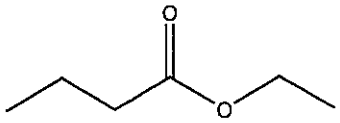
Spectrum D



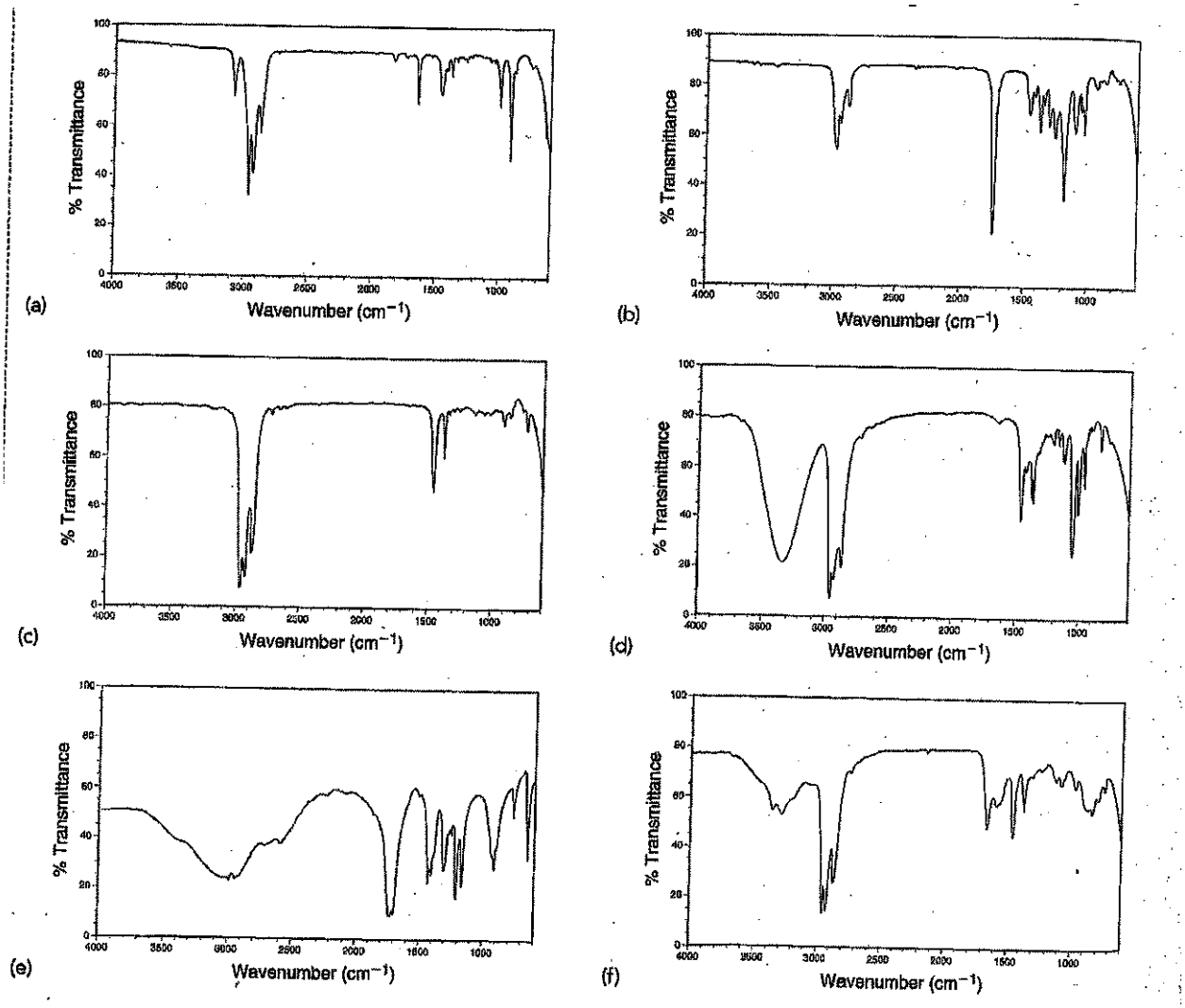
Spectrum E



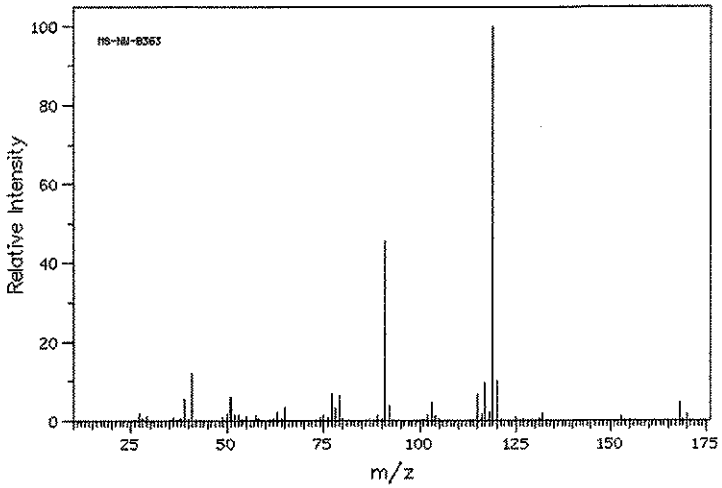
Spectrum F



Spectrum B



6. (10pts) Answer the following questions based on this mass spectrum (M^+ = 168).



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
27.	2.0	55.0	1.1	89.0	1.3	117.0	9.6
29.0	1.0	57.5	1.2	91.0	45.7	118.0	2.1
39.0	5.4	63.0	2.2	92.0	3.7	119.0	100.0
41.0	12.0	65.0	3.2	102.0	1.3	120.0	10.0
50.0	2.0	75.0	1.3	103.0	4.5	132.0	1.8
51.0	5.9	77.0	6.8	104.0	1.0	153.0	1.0
52.0	1.3	78.0	3.3	115.0	6.4	168.0	4.7
53.0	1.2	79.0	6.3	116.0	1.6	170.0	1.5

(+2) A. True, False, or cannot be determined? This compound is likely to contain a halogen atom. Explain.

True - significant $M^+ + 2$ peak

(+2) B. True, False, or cannot be determined? This compound is likely to contain a nitrogen atom. Explain.

False - has even M^+

(+2) C. True, False, or cannot be determined? This compound is likely to contain a benzyl group. Explain.

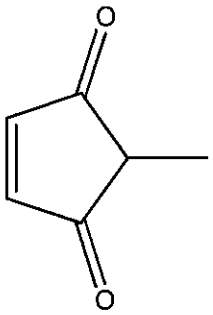
True - major peak at m/z = 91

(+2) D. True, False, or cannot be determined? This compound tends to lose an ethyl fragment. Explain.

False - no peak at m/z = 139 (168 - 29 = 139)

(+2) E. The base peak occurs at m/z = 119.

7. (6pts) Cross out any of the following frequencies which would not be observed in the IR spectrum of this compound.



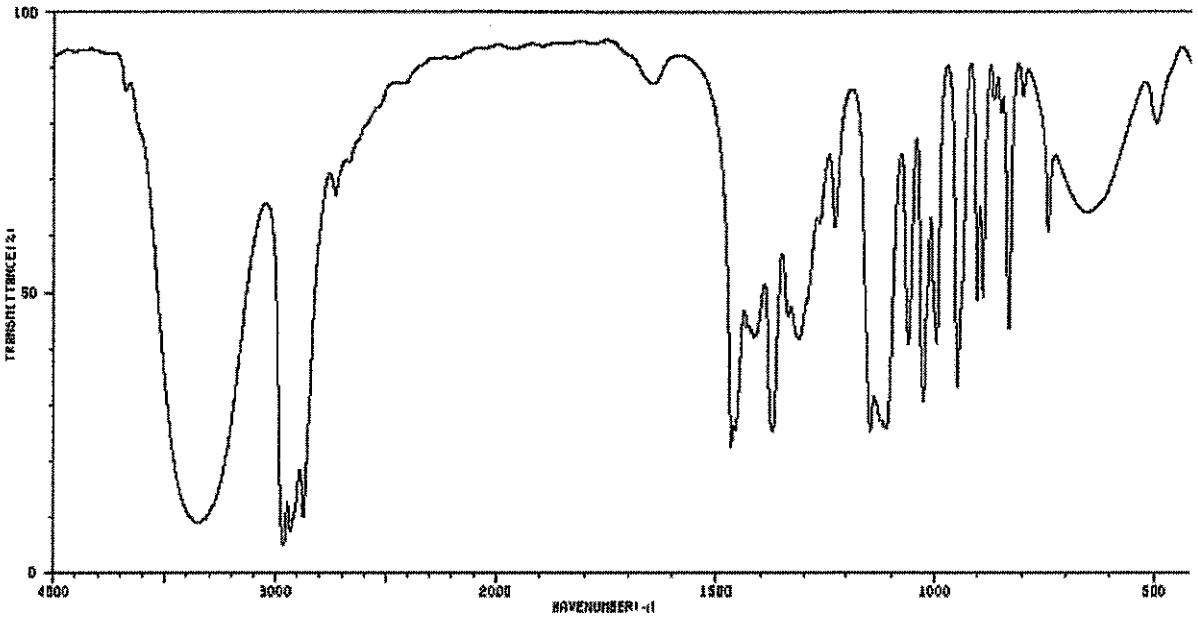
~~3300 cm^{-1}~~ above 3000 cm^{-1} below 3000 cm^{-1}

~~2150 cm^{-1}~~ 1698 cm^{-} ~~1650 cm^{-}~~

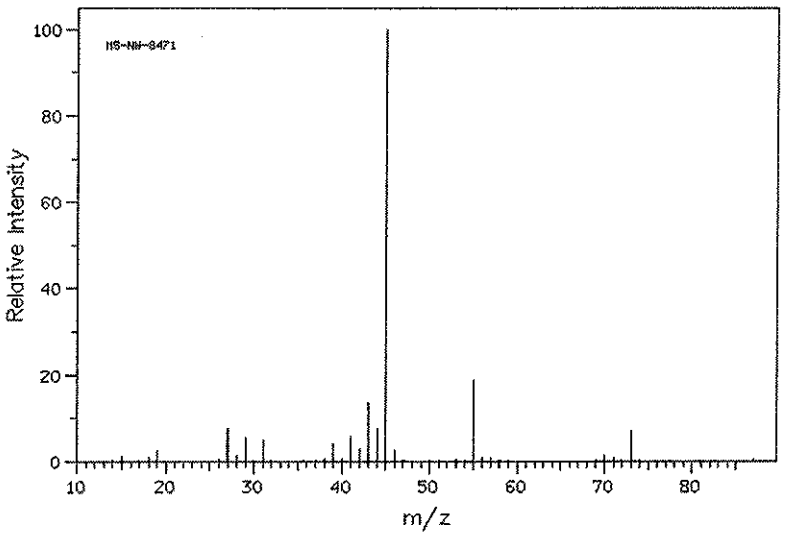
+2 each correct X

(-2 if wrong Frequency X'd out)

8. (10pts) Given the following IR and MS data for this unknown compound, answer the questions on the following page.



3683	81	1644	84	1231	60	948	32	743	68
3359	8	1468	21	1149	24	904	47	655	62
3349	6	1453	24	1124	25	882	47	497	77
2969	4	1416	41	1113	24	866	81		
2938	7	1374	24	1061	39	852	79		
2875	9	1339	44	1027	29	832	42		
2732	64	1314	39	998	39	802	81		



m/z	abundance
15.0	1.4
18.0	1.1
19.0	2.4
27.0	7.6
28.0	1.4
29.0	5.3
31.0	5.0
39.0	4.1
41.0	5.8
42.0	3.0
43.0	13.7
44.0	7.5
45.0	100.0
46.0	2.3
55.0	18.7
70.0	1.4
73.0	7.1
88.0 (M^+)	0.3

Problem 8. Show work for partial credit.

Molecular formula: Rule of 13 $13\overline{)88}^{\,6\text{ r }10} = C_6H_{16}$ ← impossible formula

IR shows at least one oxygen

$C_5H_{12}O$

+2

$C_5H_{12}O$

Key pieces of structure based on IR and MS:

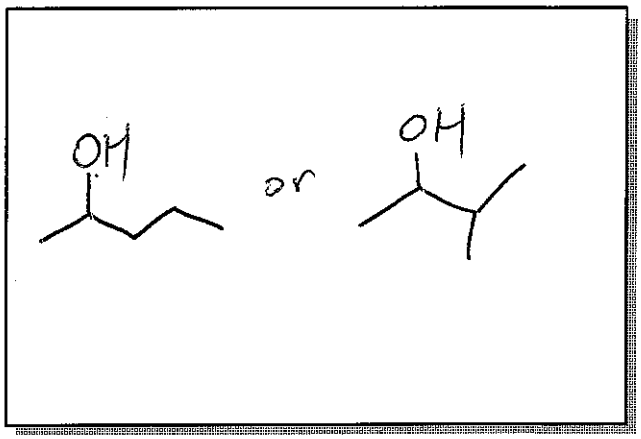
+2 IR: saturated alcohol - only peaks 3300, below 3000 cm^{-1}

+2 MS: very small M^+ - lots of fragmentation

base peak is loss of propyl

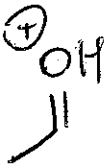
Final Structure:

+2

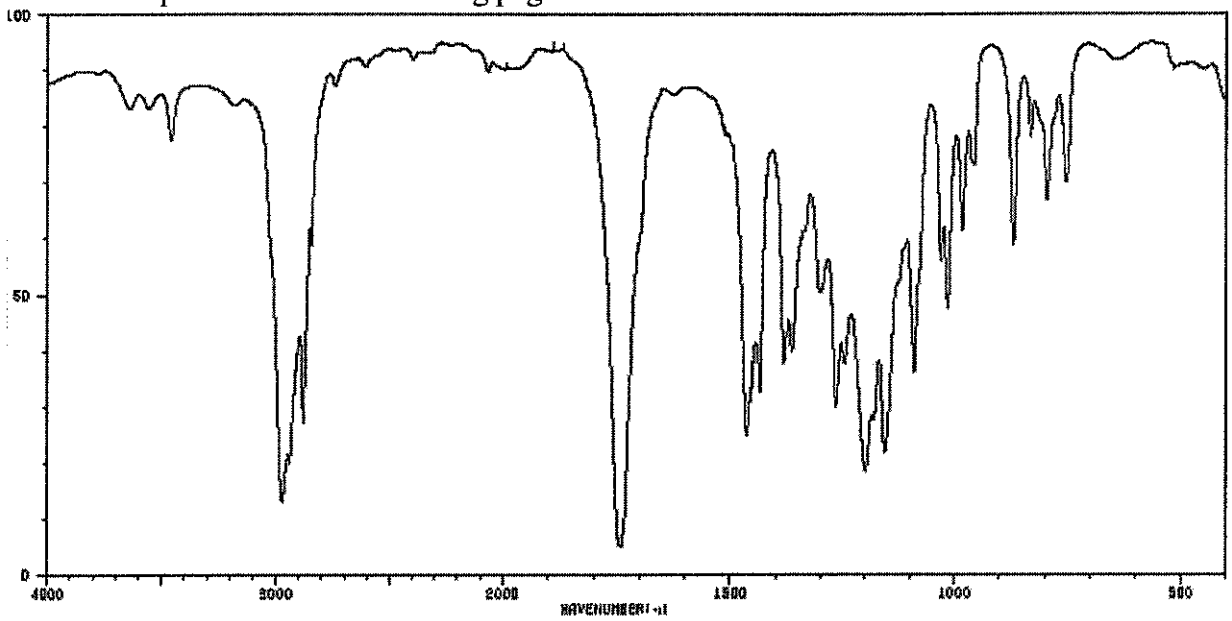


Structure of base peak fragment:

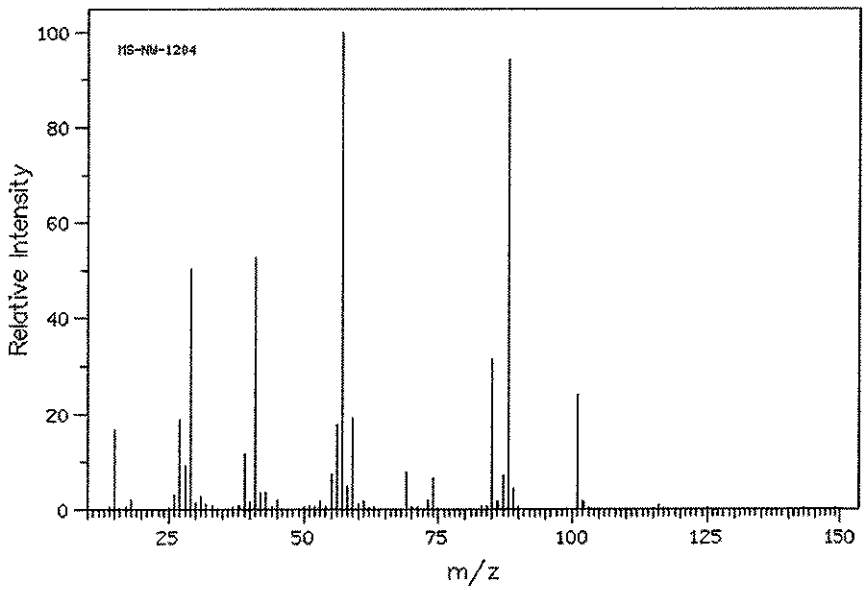
+2



9. (10pts) Given the following IR and MS data for this unknown ester, propose a structure and answer the questions on the following page.



3642	79	2846	67	1383	36	1156	21	884	74
3556	79	2740	84	1377	41	1090	34	798	64
3458	74	2057	66	1365	38	1032	53	755	66
3178	81	1740	4	1304	49	1016	46		
2973	12	1620	81	1265	28	984	58		
2941	16	1464	29	1245	36	956	70		
2880	26	1436	31	1200	17	871	57		



m/z	abundance
15.0	16.5
26.0	2.9
27.0	18.9
28.0	9.2
29.0	50.2
31.0	2.6
39.0	11.6
41.0	52.8
42.0	3.5
43.0	3.6
55.0	7.4
56.0	17.8
57.0	100.0
58.0	4.8
59.0	19.1
69.0	7.9
73.0	1.9
74.0	6.5
85.0	31.4
87.0	7.1
88.0	94.3
89.0	4.4
101.0	24.0
116.0 (M^+)	0.5

Problem 9. Show work for partial credit.

Molecular formula: ester

$13\overline{)116}$ r 12 (8) $C_8H_{20} \rightarrow C_6H_{12}O_2$

$C_6H_{12}O_2$ (+1)

Give the frequency of two observed characteristic IR peaks and what it means about this structure:

(+1) Below $3000 cm^{-1}$ = saturated C-H

(+1) $1740 cm^{-1}$ = ester C=O

What information can you gather from the MS fragment peaks at m/z = 59, 85, and 88?

(+1) $m/z = 59$ is loss of butyl group

$m/z = 85$ is loss of 31 (loss of oxygen atom)

(+1) $m/z = 88$ is McLafferty

Final Structure:

(+2) other saturated esters