

CHEM 302 Exam 1

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June 23, 2008

Honor Pledge:

In Part V of the Winthrop University Student Conduct Code, it is stated that "A fundamental tenet of all institutions of higher learning is academic honesty. ... Misrepresentation of someone else's work as one's own is a most serious offense in any academic setting. ... Academic misconduct includes but is not limited to providing or receiving assistance in a manner not authorized by the professor in the creation of work to be submitted for academic evaluation including papers, projects, and examinations ..."

By my signature below, I pledge that I did not commit academic misconduct (cheat) on this examination.

KEY

Printed Name

Signature

Part 1 _____/20

Part 2 _____/10

Part 3 _____/10

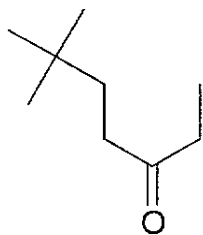
Part 4 _____/15

Part 5 _____/15

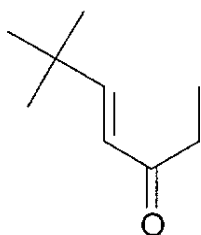
Part 6 _____/30

Total _____/100

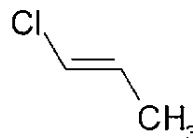
1. Concepts (20 pts)



1



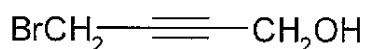
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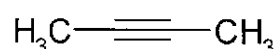
3



4



5

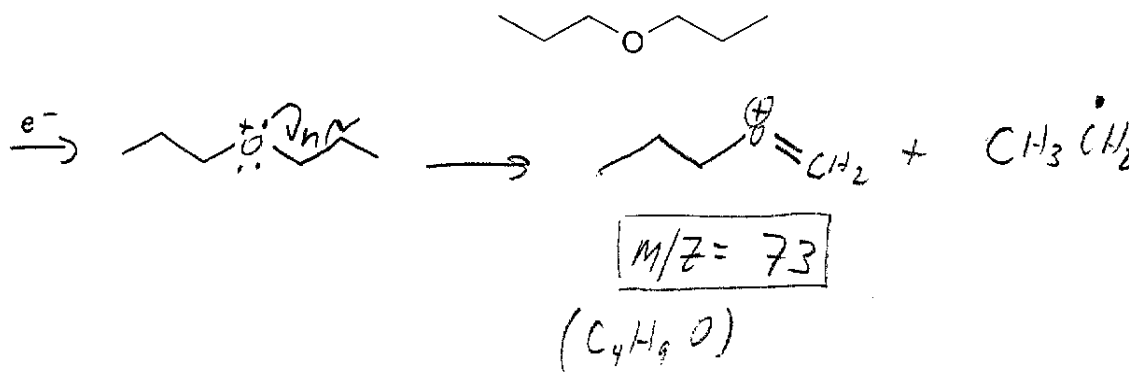


6

- a. How many proton resonances will compound 1 have in its $^1\text{H-NMR}$ spectrum? 5
- b. Which compound will have a proton resonance in its $^1\text{H-NMR}$ spectrum which will likely disappear upon treating the sample with D_2O ? 5
- c. Of compounds 3 and 4, which will have the larger vinyl proton coupling constant? 3
- d. Of compounds 1 and 2, which compound will have the lower carbonyl stretching frequency in its IR spectrum? 2
- e. Of compounds 5 and 6, which compound which will have no alkyne stretching absorption in its IR spectrum? 6
- f. How many absorptions will compound 1 have in its UV spectrum? 2 ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$)
- g. How many carbon resonances will compound 1 have in its $^{13}\text{C-NMR}$ spectrum? 7
- h. How many methyl signals will appear in the $^1\text{H-NMR}$ spectrum of compound 6?
1
- i. Of the compounds above, which one will give an M/M+2 ratio of 1:1 in its mass spectrum?
5
- j. Of compounds 1 and 2, which will have the longer wavelength $\pi \rightarrow \pi^*$ UV absorption?
2

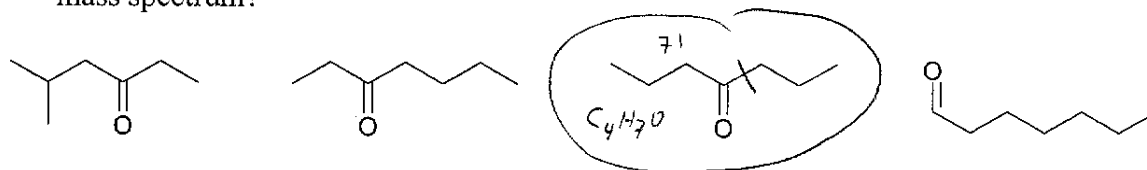
2. Mechanism (10 pts)

When ionized by electron impact at 70 eV, 1-propoxypropane (shown below) can undergo fragmentation by α -cleavage. (a) Draw a complete arrow pushing mechanism to show the α -cleavage. (b) What is the nominal mass of the fragment ion?

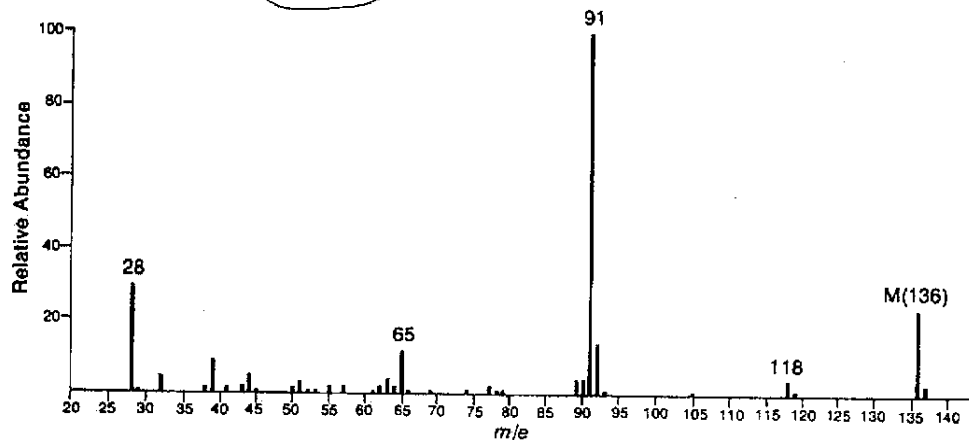
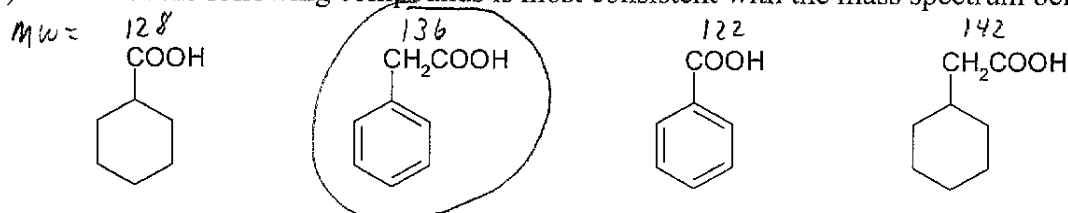


3. Mass Spectrometry (10 pts)

(a) Which of the compounds below will show a significant fragment ion at $m/z = 71$ in its mass spectrum?



(b) Which of the following compounds is most consistent with the mass spectrum below?



4. Infrared Spectroscopy (15 pts)

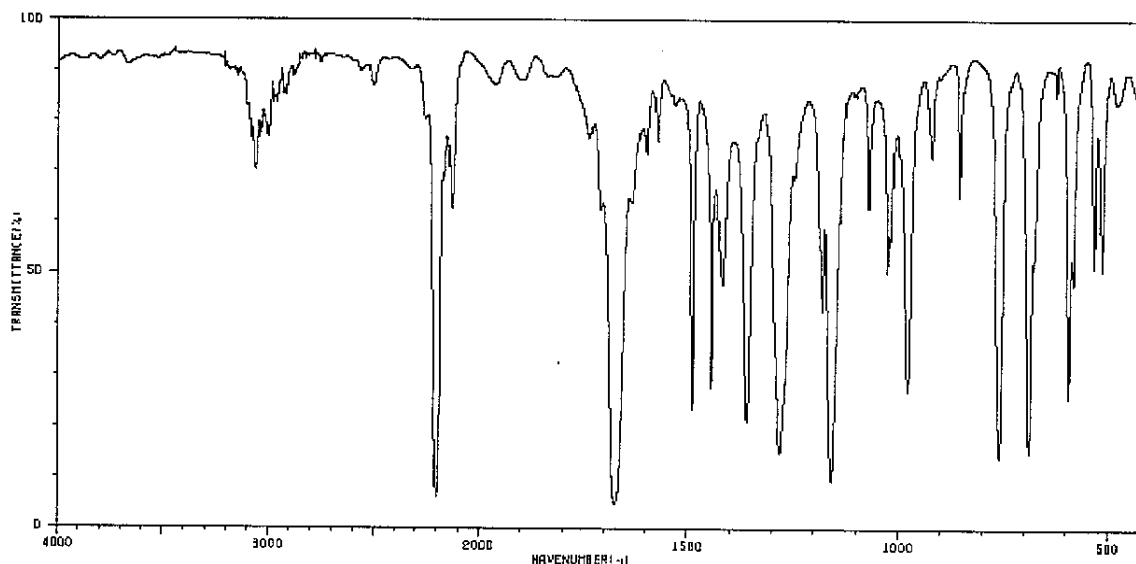
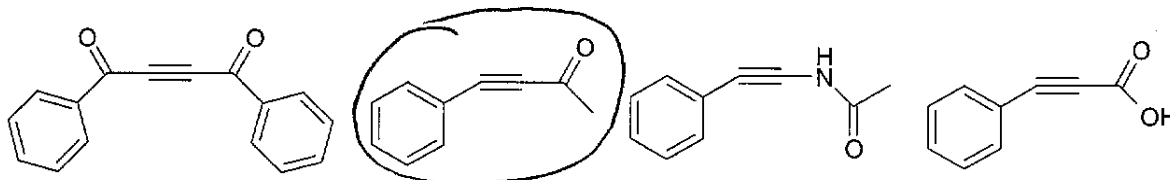
(a) Give the likely functional groups responsible for the following IR stretching absorptions:

i) 2 bands at 2820 cm^{-1} and 2720 cm^{-1} : $\overset{\text{H}}{\text{C-H}}$

ii) A strong, broad absorption at 3400 cm^{-1} : OH


iii) A strong absorption at 1100 cm^{-1} : C-O

(b) Which compound produced the IR spectrum shown below? Explain your reasoning.



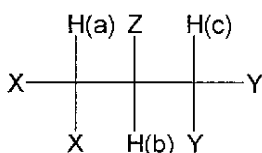
- No N-H, No OH
($\sim 3400\text{ cm}^{-1}$) ($\sim 3300\text{ cm}^{-1}$)

- Symmetrical Alkyne gives NO Alkyne stretch @ $\sim 2250\text{ cm}^{-1}$

\therefore ONLY  CAN FIT SPECTRUM.

5. NMR Spectroscopy (15 pts)

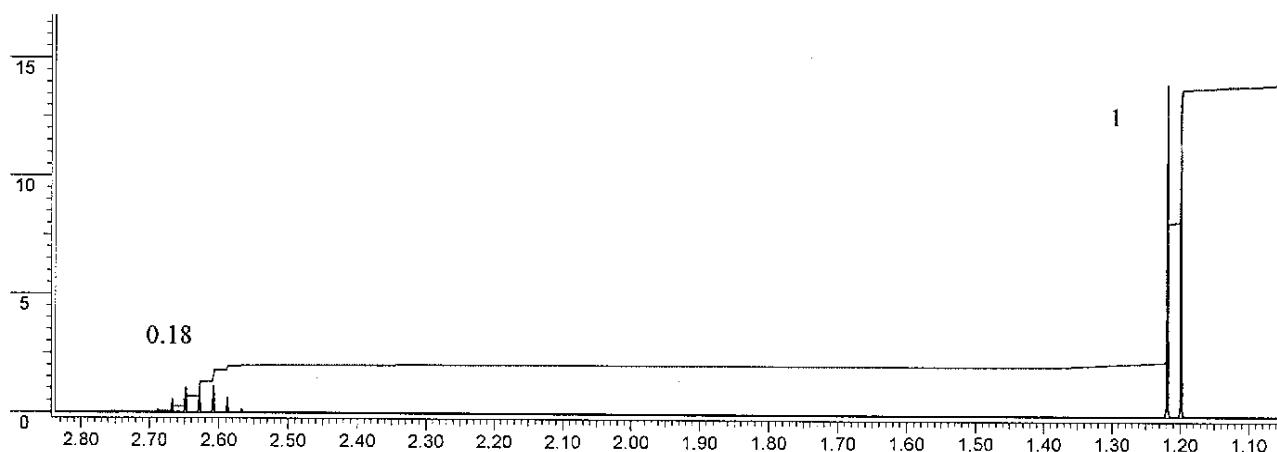
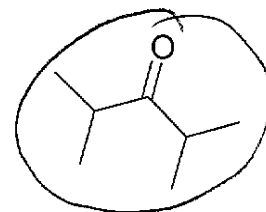
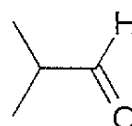
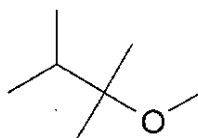
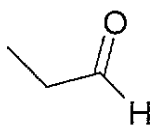
(a) For the hypothetical compound below, predict the multiplicity for H(b) if



(i) $J_{ab} = J_{bc}$ *Triplet*

(ii) $J_{ab} \neq J_{bc}$ *Doublet of Doublets*

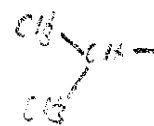
(b) Which compound produced the $^1\text{H-NMR}$ spectrum below? Explain your reasoning.



Note: The resonances shown are the only ones present in this spectrum.

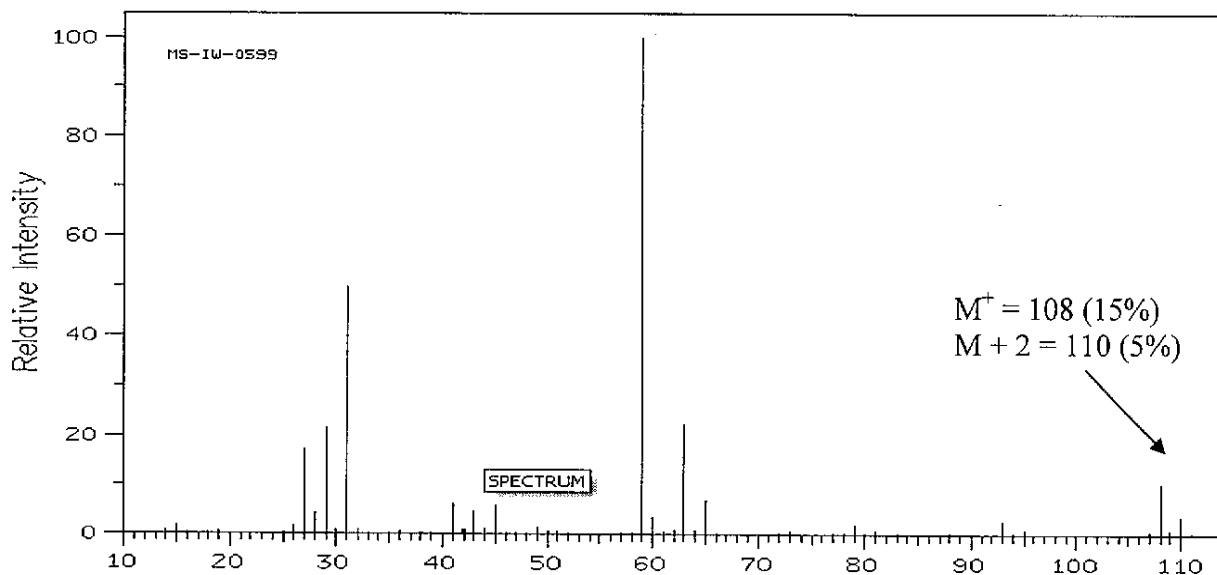
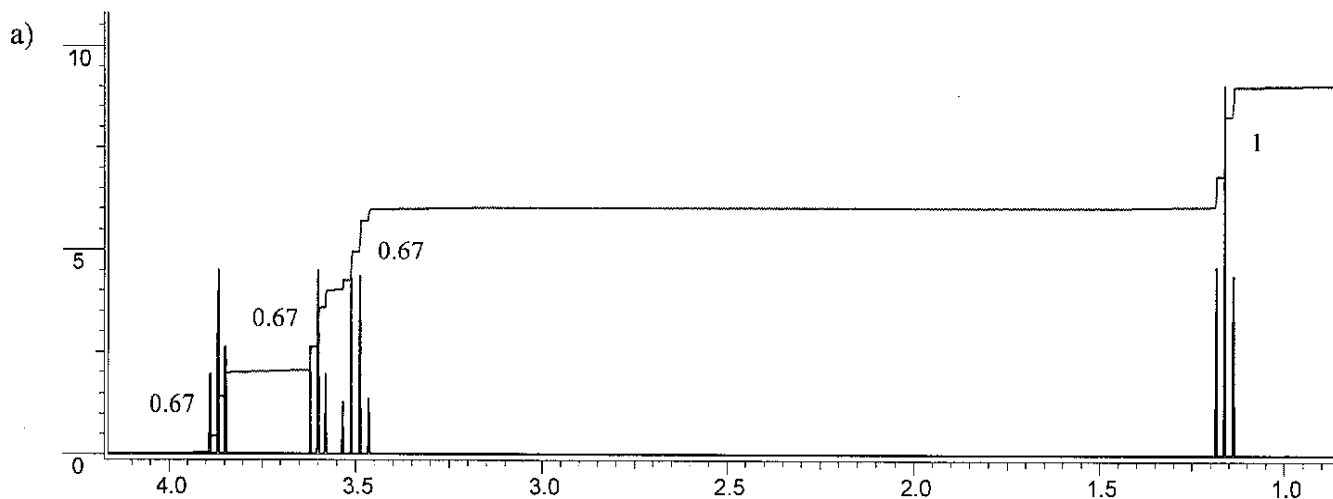
- No ALDEHYDE H (@ ~ 9 ppm)
- No CH_3 SINGLETs
- 1:6 septet: doublet implies

\therefore only CC(C)C(=O)C(C)C FITS SPECTRUM.



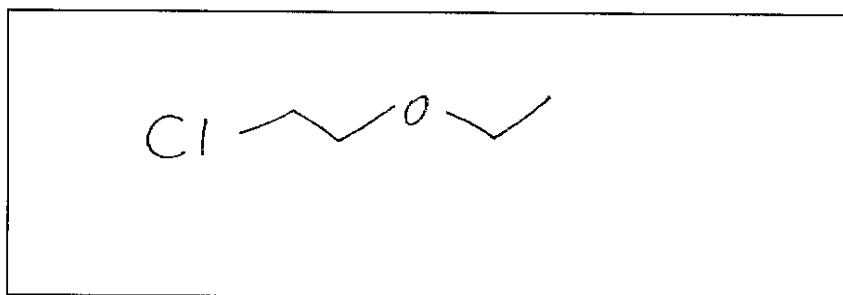
6. Structure Determination (30 pts)

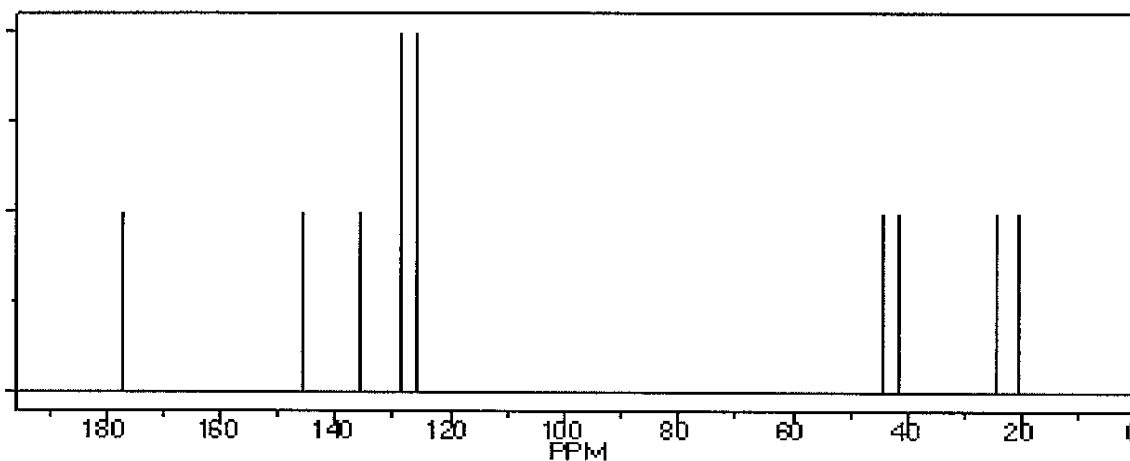
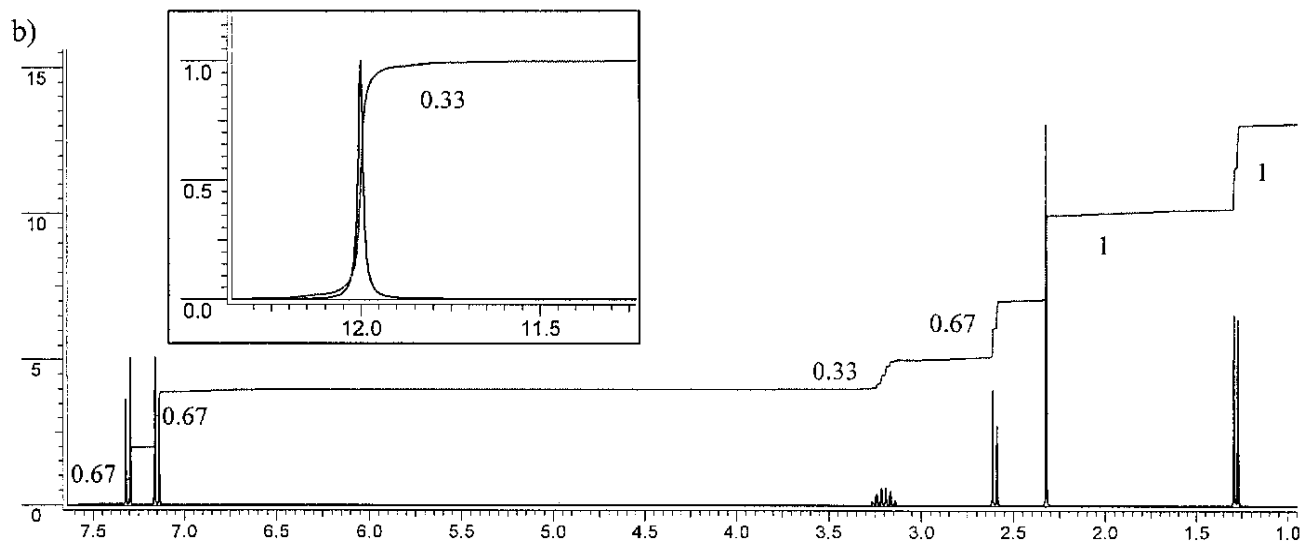
In the boxes provided, draw the structure of the compound that is consistent with each of the following sets of spectra.



IR shows significant absorptions at $2900, 1100\text{ cm}^{-1}$

No HRMS available





The resonance at 12.0 ppm in the proton NMR disappears when the sample is treated with D₂O

IR shows significant absorptions at 3300 (broad), 3100, 2900, 1704, 1600, 1500, 1060 cm⁻¹

HRMS indicates a molecular formula of C₁₁H₁₄O₂

