CH 254, Spring 2008 Name KEY

Exam #1, 22 February 2008 (PRINT CLEARLY PLEASE!)

Question #	Points Possible	Points Received
1	20	
2	8	
3	8	
4	15	
5	9	
6	12	
7	12	
8	16	
Subtotal	100	
Extra Credit	2	
Total	102	

1. (20 points) Multiple Choice. For each question, circle ONE answer. 2 pts each

a. Which of the following statements best explains the information we can gain from mass spectrometry?

1) It allows us to determine the number of protons in a compound.
2) It allows us to determine the kinds of functional groups in a compound.
3) It allows us to determine the molecular weight and mass of some fragments of a compound.
4) It allows us to determine the presence and nature of a carbocation in the compound.
5) It allows us to determine the presence and nature of a free radical in the compound.

b. Which of the following is <u>not</u> true about the M+1 peak?

1) It is one m/z unit higher than the base peak.
2) It is one m/z unit higher than the molecular ion peak.
3) It is one m/z unit higher than the parent ion peak.
4) It occurs because there is more than one naturally occurring isotope of carbon.
5) This means that the number of carbon atoms in a compound can be calculated if the relative abundance of both the M and M+1 peaks is known.

c. The mass spectra of alcohols often fail to exhibit detectable M peaks but instead show relatively large _____ peaks.

1) M+1
2) M+2
3) M-16
4) M-17
5) M-18

d. Which of the following normally occurs in a molecule when a photon of infrared light is absorbed?

1) An electron moves to an orbital of higher potential energy.

2) The vibration energy increases.

3) An electron changes alignment in a magnetic field.

4) The molecule gains an electron.

5) The molecule loses an electron.

e. When a solution of an organic compound absorbs light whose wavelength is 700 nm, the solution appears:

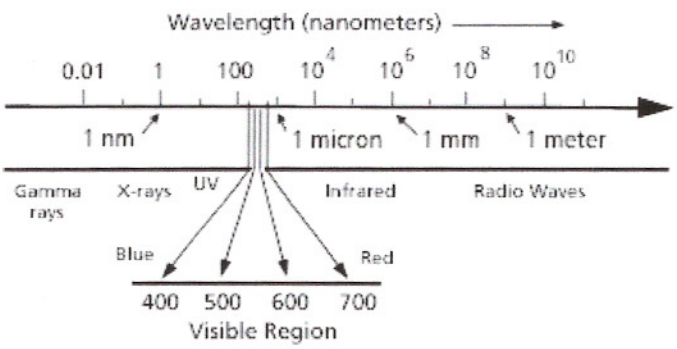
1) yellow

2) green

3) red

4) orange

5) purple



Electromagnetic Spectrum

f. Ethyne (HCCH) does not show IR absorption in the region 2000-2500 cm^{-1} because:

1) C-H stretches occur at lower energy

2) CC stretches occur at about 1640 cm^{-1}

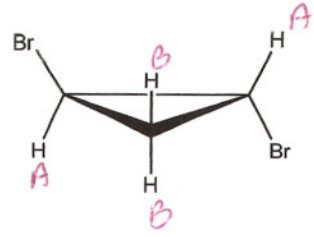
3) There is no change in the dipole moment when the CC bond in ethyne stretches

4) There is a change in the dipole moment when the CC bond in ethyne stretches

g. Absorption of UV-vis energy by a molecule results in:

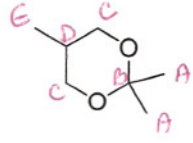
1) vibrational transitions
2) electronic transitions
3) rotational transitions
4) nuclear transitions
5) none of the above

h. How many signals would you expect to see in the ^{1}H NMR spectrum of the following compound?



1) 2
2) 5
3) 1
4) 4
5) 3

i. How many distinct carbon signals are expected in the proton-decoupled ^{13}C NMR spectrum of the following compound?



1) 7
2) 6
3) 5
4) 4
5) 3

j. Aromatic molecules contain _____ π electrons.

1) no
2) 4n+2 (where n is an integer)
3) 4n+2 (where n = 0.5)
4) 4n (where n is an integer)
5) unpaired

2. (8 points) Short answer.

a. Explain why ^{13}C NMR is much less sensitive than ^{1}H NMR.

Because the relative (natural) abundancy of ^{13}C is only 1.1%, while for ^{1}H it is >98%.

b. Why do we not see carbon-carbon splitting in the ^{13}C NMR?

Because of the low natural abundancy of ^{13}C, the chances of two ^{13}C's appearing next to each other in the same molecule are slim to none.

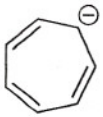
8

3. (6 points) While cleaning a stockroom, a student found a bottle of ethanol labeled "Denatured with Benzene". He decided to determine the concentration of benzene in the ethanol by obtaining the UV spectrum of the liquid in a 2.0 cm cell. There was a particular peak in the spectrum at 260 nm that was attributable to benzene, and the absorbance of this peak was 0.69. In a reference source, the student found that the molar absorptivity of the benzene band in ethanol was 230 $M^{-1}cm^{-1}$. What is the concentration of benzene in the sample? (Show your work.)

$$A = \varepsilon b C$$

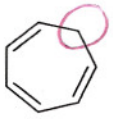
$$C = \frac{A}{\varepsilon b} = \frac{0.69}{(230)(2)} = 0.0015 \text{ M}$$

4. (15 points) Label each of the following as aromatic, nonaromatic, or antiaromatic, and provide a rationale for the label you choose.

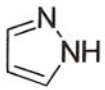


antiaromatic 8 π e's = 4n

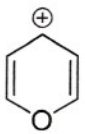
aromatic 10 π e's = 4n+2



nonaromatic sp³ carbon

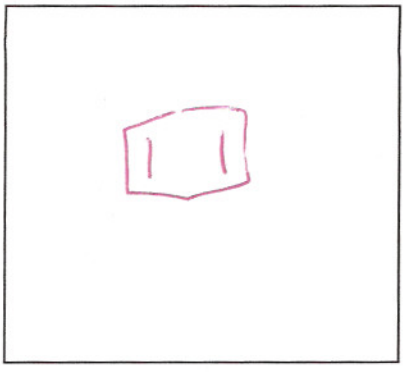


aromatic 6 π e's = 4n+2

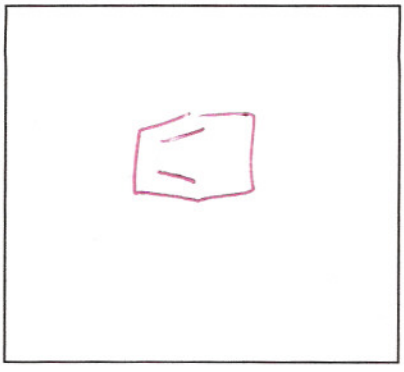


aromatic 6 π e's = 4n+2

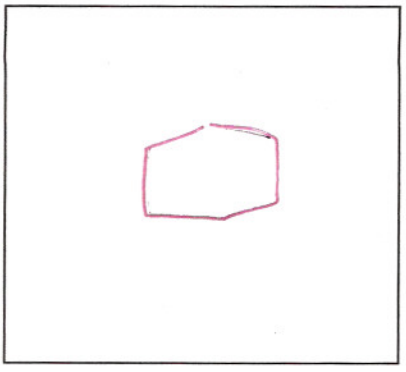
5. (9 points) Compounds E and F are isomers with the formula C_6H_8. Both react with H_2 in the presence of Pt to give compound G, formula C_6H_{12}. G shows a single peak in its ^{13}C NMR spectrum. E has no absorption maximum above 200 nm in its UV-vis spectrum, while F has λ_{max} = 259 nm (ϵ=10,000). What are the structures of E, F, and G? Show your reasoning.



Compound E



Compound F



Compound G

C_6H_8 SODAR = 3

$\downarrow H_2, Pt$

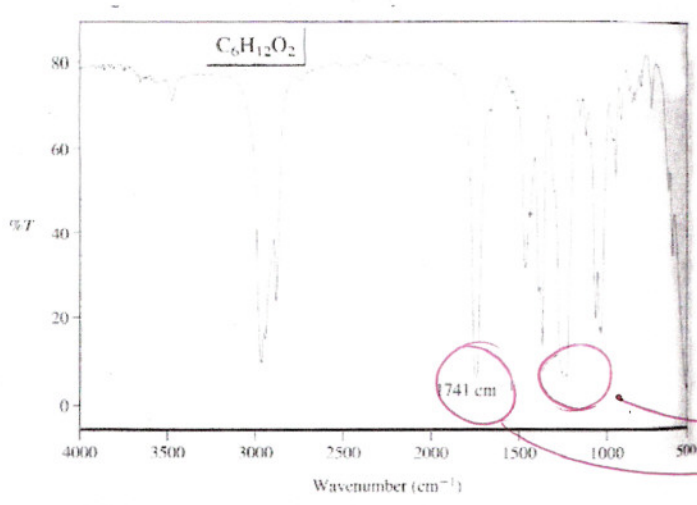
C_6H_{12} SODAR = 1 $\Rightarrow$ 1 ring

Single peak in ^{13}C = all equiv. C's

NO UV = no conjugation

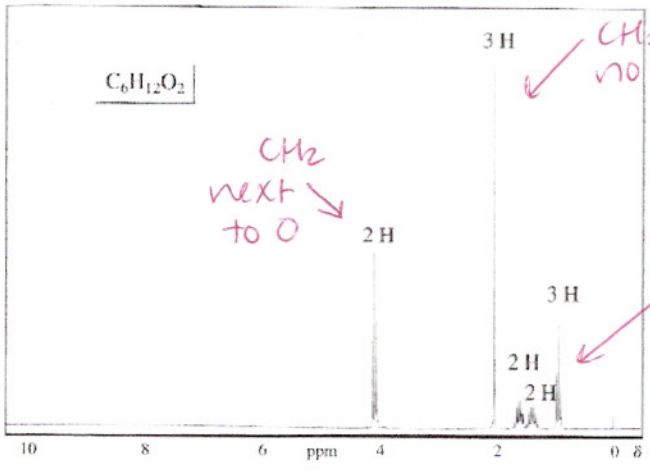
12

6. (10 points) Suggest a reasonable structure for the compound with formula $C_6H_{12}O_2$ that has the following IR, ^1H NMR, and ^{13}C NMR spectra. Be sure to include a SODAR calculation and show your reasoning.



SODAR = 1

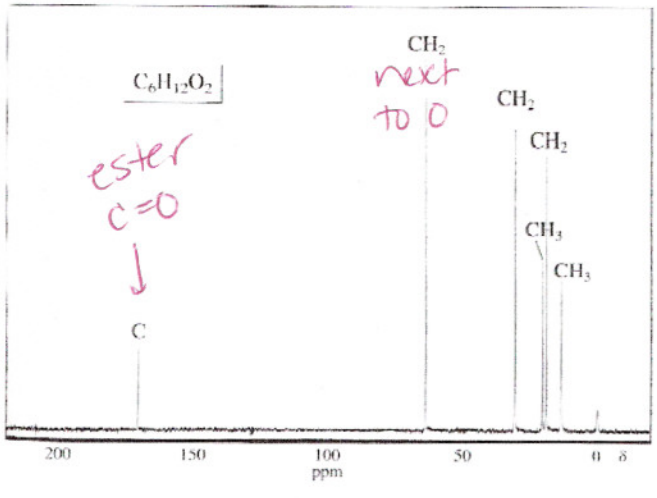
C-O
C=O
ester



CH_3 no neighbors

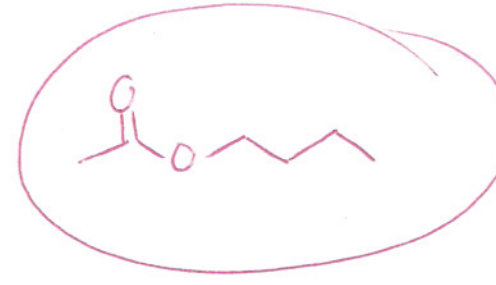
CH_2 next to O

CH_3 2 neighbors



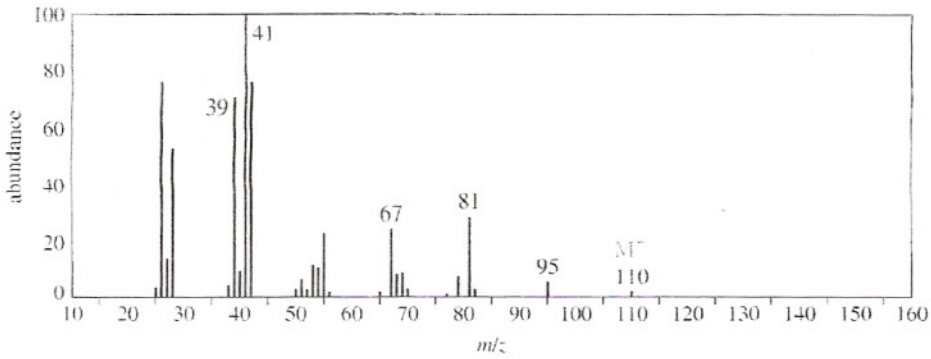
ester C=O

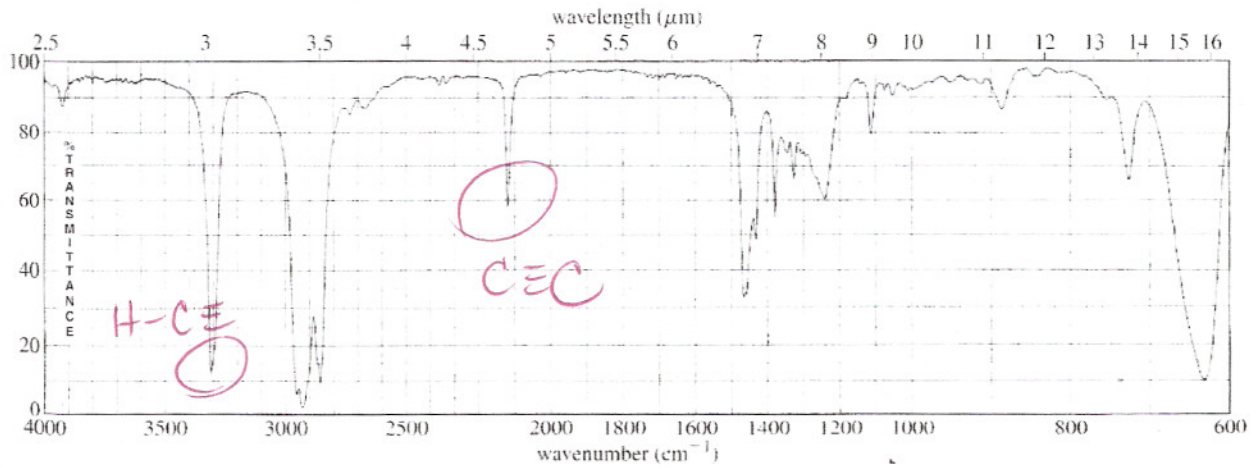
CH_2 next to O



12

7. (16 points) An unknown, foul-smelling hydrocarbon gives the mass spectrum and IR spectrum shown below.





a. The relative abundancies of the M and M+1 peaks are 2 and 0.18. Propose a molecular formula.

$$\#C's = \frac{M+1}{0.011 \times M} = 8$$

C_8 is 96

$MW = 110$

C_8H_{14}

b. What is SODAR for the molecular formula that you proposed?

SODAR = 2

c. Use the IR spectrum to determine any functional groups that may be present.

terminal alkyne

(continued on next page)

d. Propose two possible structures for this compound. What parts of the structure are uncertain?

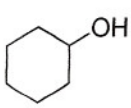
the alkyl part is uncertain.

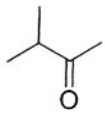
e. If you knew that hydrogenation of the compound gave octane, would the structure still be uncertain? (This is a yes or no question!) What structure would you then propose for the compound?

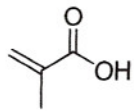
No, it wouldn't be uncertain.

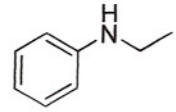
must be 

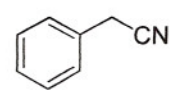
8. (16 points) Four IR spectra are shown, corresponding to four of the following compounds. For each spectrum, determine the structure and indicate how you made your decision.

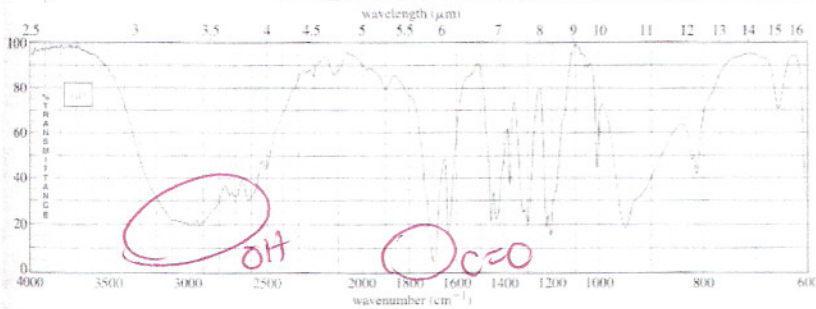




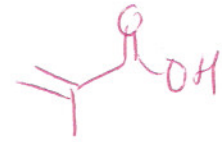


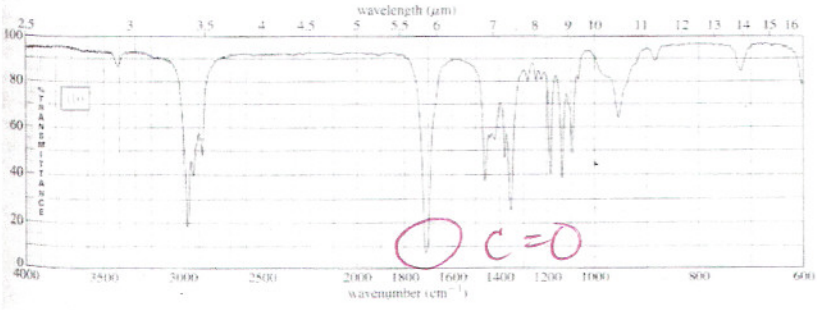


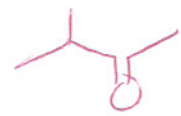


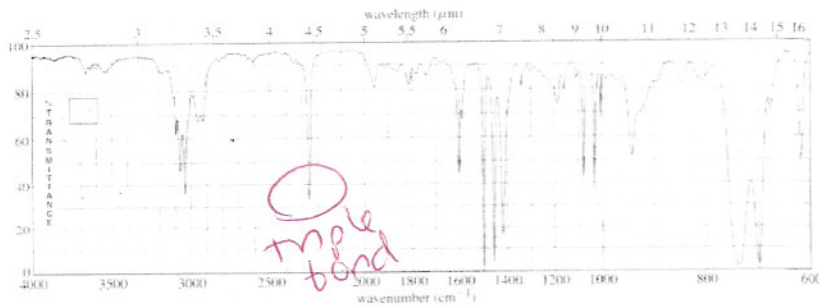


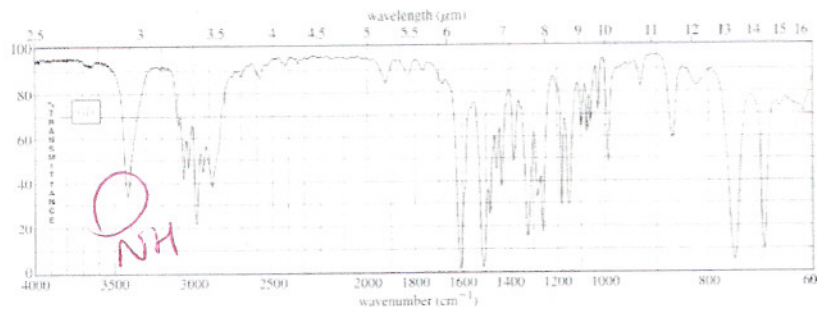
acid

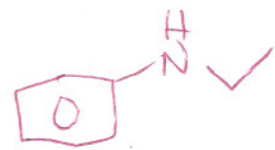












***Extra credit question: What is the general term for trees that lose their leaves in the winter?

deciduous