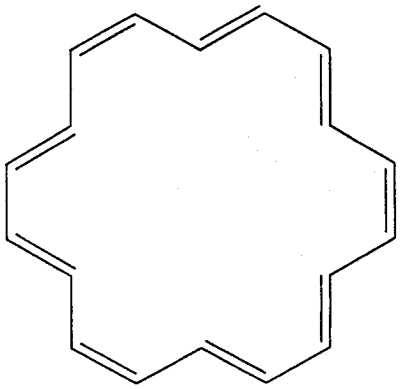
1. (10 pts) The following compound called 18-annulene has an unusual ^{1}H NMR spectrum with protons resonating at 8.9 ppm and –1.8 ppm. Suggest an explanation for this result.



- Huckel/aromatic 3
- ring current 3
- shielding/deshielding 4

+1 for just "shielding"
+1 for just "aromatic"
-2 not explaining how shielded
+2 for assignment + mention of magnetic field

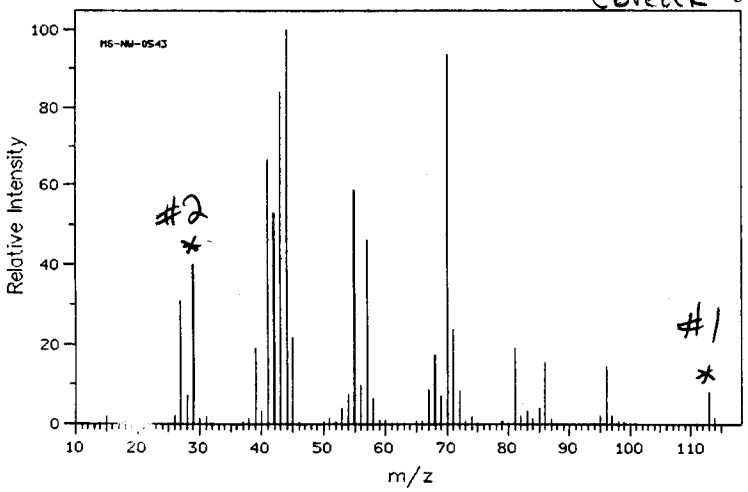
-1 assignment only
-2 for π density

-1 for all right except aromatic
-2 for ring current w/o mag. field

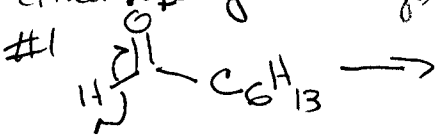
2. (18 pts) The compounds, 5-methyl-3-hexanone, heptyl aldehyde, and 4,4-dimethyl-2-pentanone all have a parent ion of M+=114. Based upon their fragmentation patterns assign the following mass spectra (next page) to the proper member of this family of compounds. Show detailed (curved arrow) mechanisms for the diagnostic fragmentations upon which you are basing your answer. Do not try to assign all of the fragments.

Total 18 pts (6 pts each)
+2 for correct ID of mol
+2 for showing fragmentation (break on either side of carbonyl)
+2 for arrows
$-\frac{1}{2}$ for missing charge
−1 for wrong arrow
$-\frac{1}{2}$ for skipping radical

Spectra for Question 2

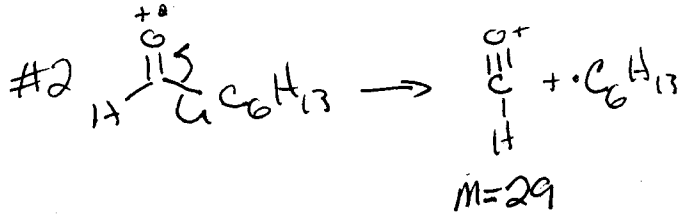


#1

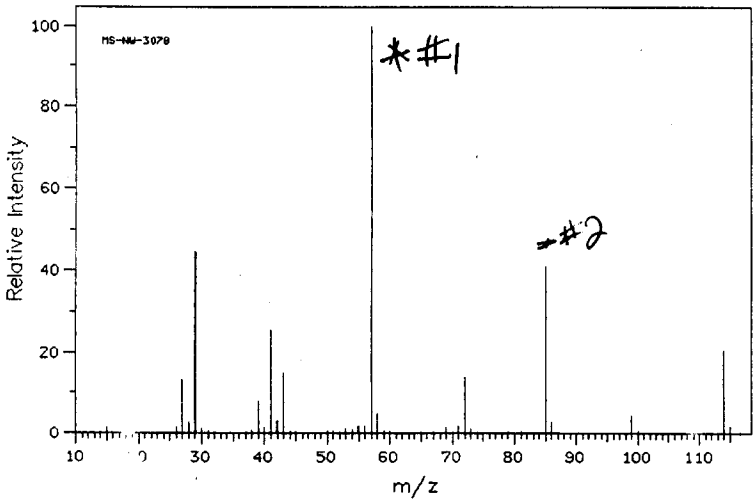


M = 113

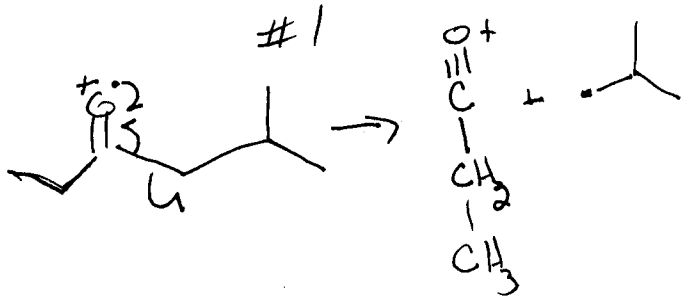
#2



M = 29

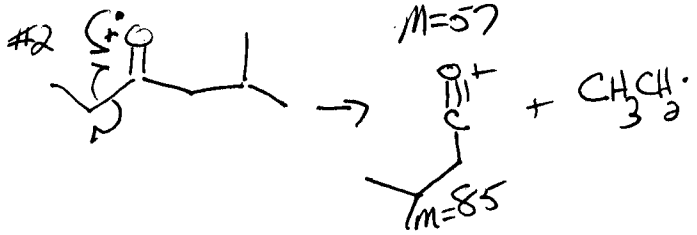


#1

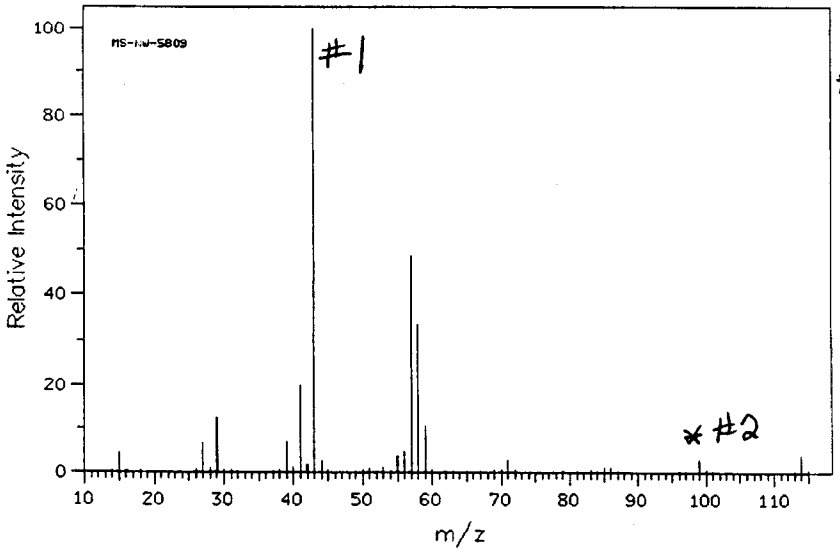


M = 57

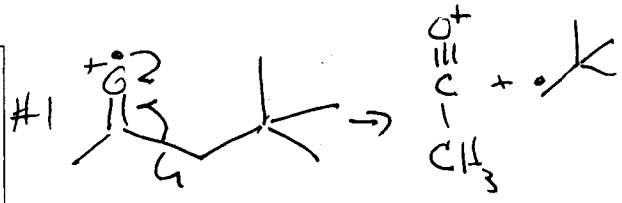
#2



M = 85

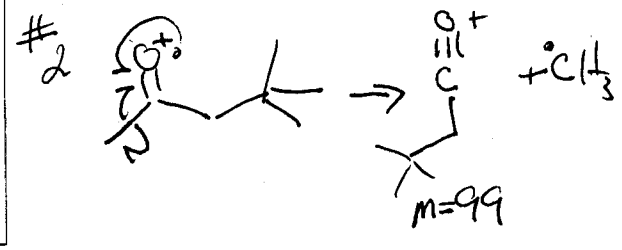


#1



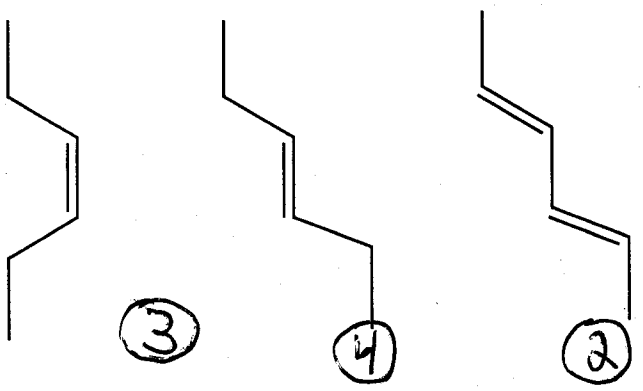
M = 43

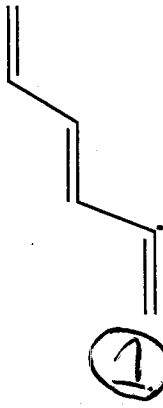
#2



M = 99

3. (16 pts) (a) Rank the following alkenes in terms of their C=C stretching frequencies. Explain your ranking. 1= Lowest wavenumber





1 POINT PER GOOD ORDER
IF JUSTIFIED (4)

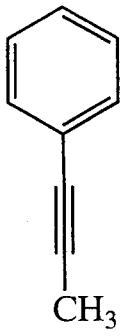
+1 TRANS > CIS

+1 ISOLATED > CONJUGATED

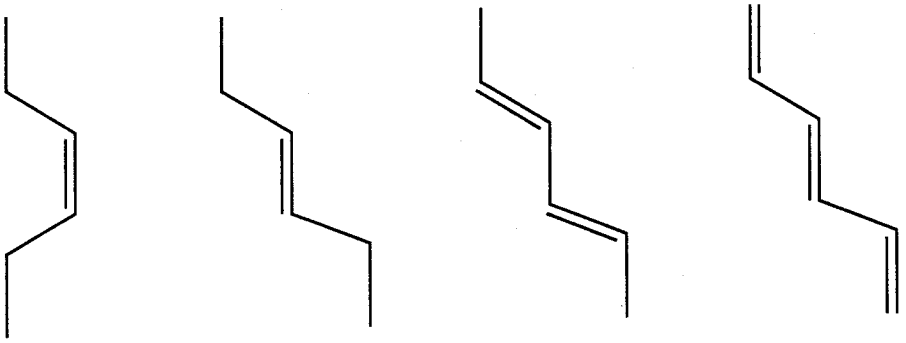
+1 MORE EXTENDED CONJUGATION ON 1 VS 2

+1 GENERAL EXPLANATIONS

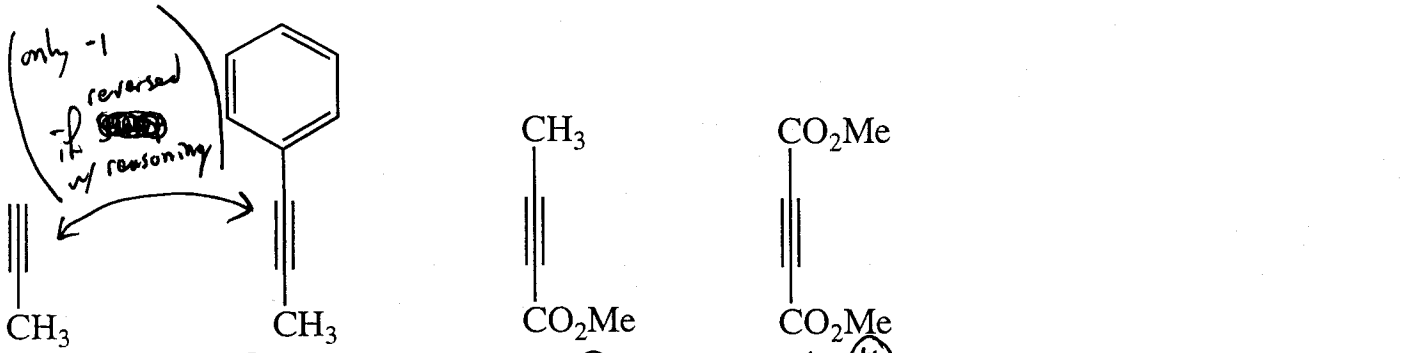
(b) Rank the following acetylenes in terms of the strength (intensity) of their C≡C stretching absorptions in the IR. Explain your ranking. 1= Most absorbing



3. (16 pts) (a) Rank the following alkenes in terms of their C=C stretching frequencies. Explain your ranking. 1= Lowest wavenumber



(b) Rank the following acetylenes in terms of the strength (intensity) of their C≡C stretching absorptions in the IR. Explain your ranking. 1= Most absorbing



3 (+1)

(Some dipole, but not a huge dipole)

2 (+1)

(sp^2 C of Ph is more e⁻ withdrawing than H)

1 (+1)

(large dipole)

4 (+1)

Sym, no dipole (+1)

(OR +1 for mentioning importance of dEWG's)

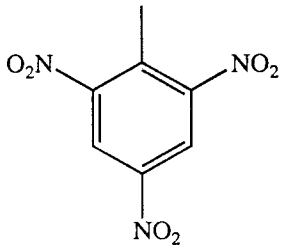
(+1) • Strength of absorption scales with the dipole (degree of polarization) of the C≡C

(+1) • $-CO_2Me$ is the most withdrawing

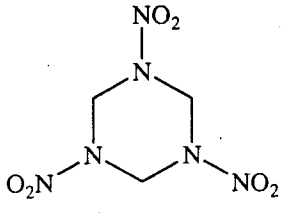
OR

"Some Conjugation" is worth (+1) or resonance

4. (16 pts) Briefly describe the principles used in ion mobility explosive detectors used in airports. Explain the mechanism of detection of explosives such as TNT and RDX. Are the ions of nitro compounds the same types as typical of most organics? Explain.



TNT

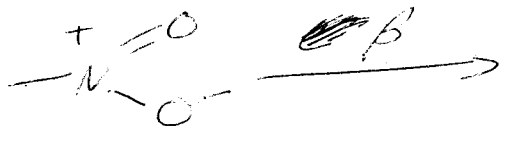


RDX

Negatively charged ions — 4pts
Go against a flow of [redacted] gas
toward positively charged plates — 4pts
Time of [redacted] flight analysis — 4pts

Radioactive — 1pt

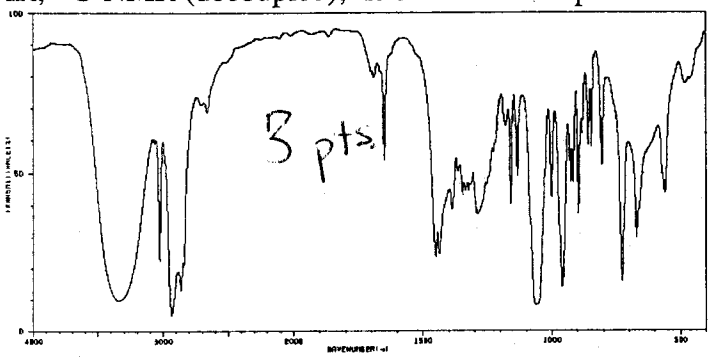
Ionization source — 2pts



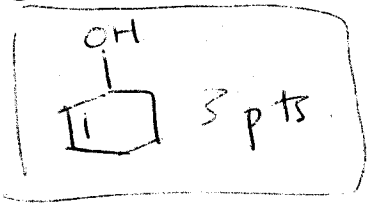
1pt

5. (24 pts) Compound A (F.W.=98.1) when treated with CrO_3:pyridine gives compound B with a F.W.= 96. Provide the structures of A and B and your reasoning for the structural assignment.

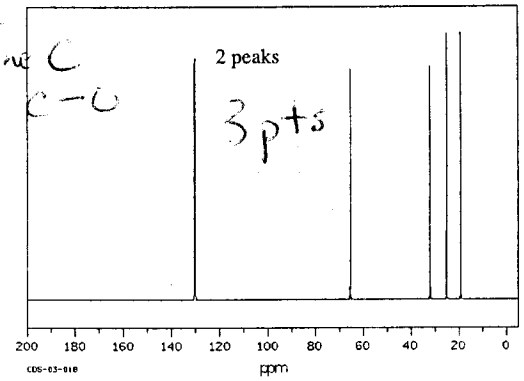
IR, ^{13}C-NMR (decoupled), ^{1}H-NMR of Compound A.

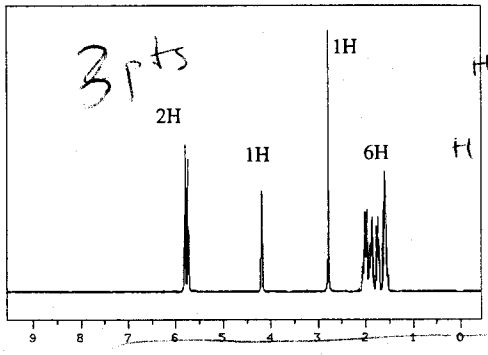


OH ⇒ 1 pt.
C=C ⇒ 1 pt.
C-O or alkene C-H ⇒ 1 pt.



1 pt. 6 C
1 pt. alkene C
1 pt. for C-O

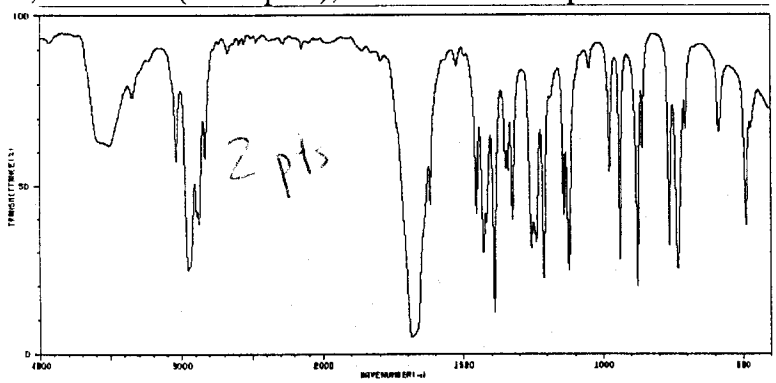




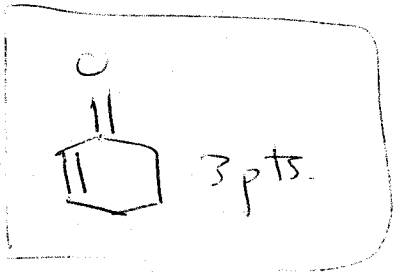
C=C ⇒ 1 pt.
C-O ⇒ 1 pt.
O-H ⇒ 1 pt.

+2 pts. C-O-H ⟶ C=O

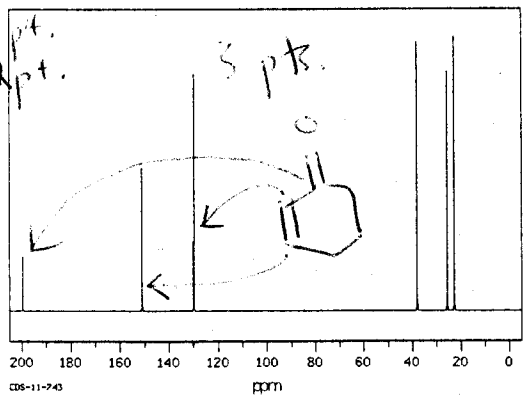
R, ^{13}C-NMR (decoupled), ^{1}H-NMR of Compound B.

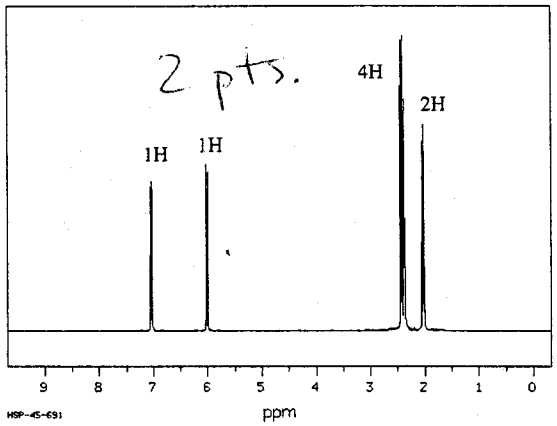


C=O ⇒ 2 pt. (under 1700 cm⁻¹)



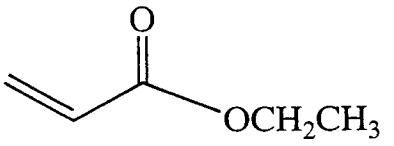
C=O ⇒ 1 pt.
C=C ⇒ 2 pt.

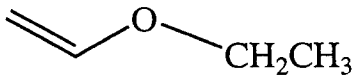


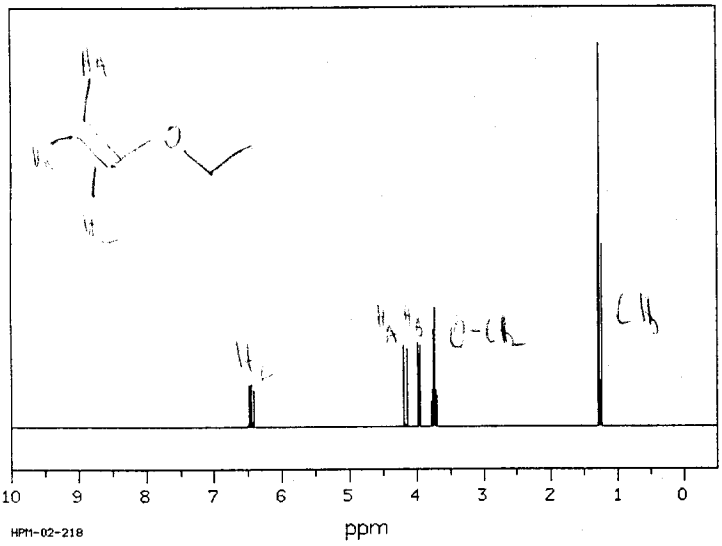


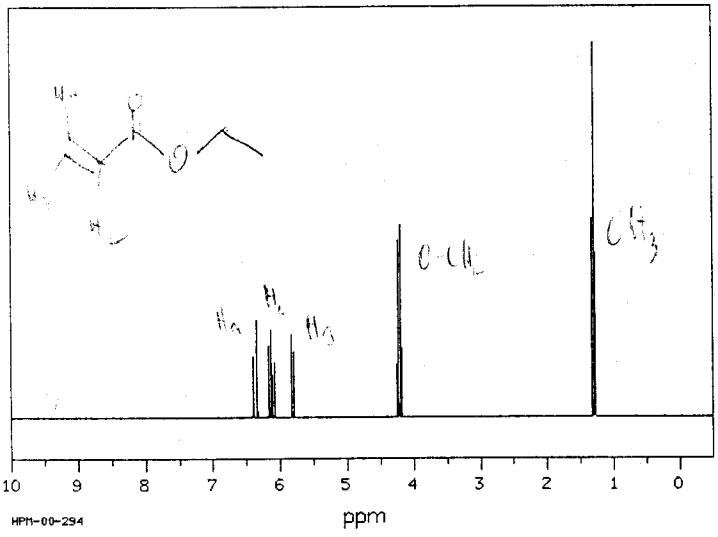
C=C-H ⇒ 1 pt.
diff. ⇒ 1 pt.

6. (16 pts) The following ^{1}H-NMR (taken at 300 mHz) spectra are for the compounds shown. Assign the spectra to the proper compounds and all of the resonances to the specific proton(s). Explain your reasoning.









4 marks proper assignment of spectra to compound

2 marks for explanation of above assignment

5 marks per spectra for proton assignments