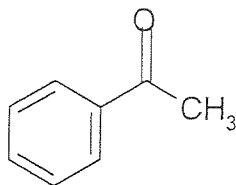


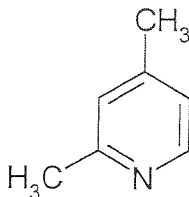
1. (15 pts, 3 each) Give the IUPAC name of the following compounds (except for a – give the common name).

a)



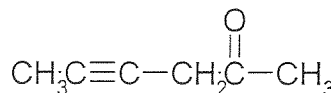
acetophenone

b)



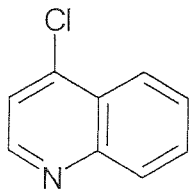
2,4-dimethylpyridine

c)



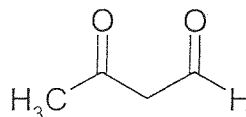
4-hexyn-2-one

d)



4-chloroquinoline

e)



3-oxobutanal

2. (6 pts, 3 each) Classify the following substances as either aromatic or nonaromatic.

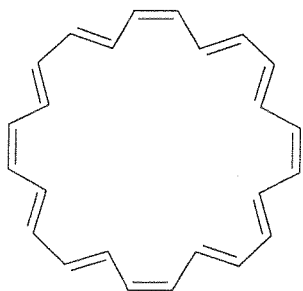
a) (the ring is planar)

b)

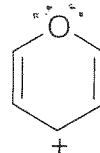
Huckel's Rule

$$4n+2$$

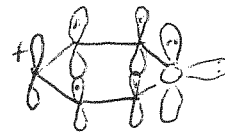
24 π e⁻
doesn't fit
Huckel's Rule



nonaromatic

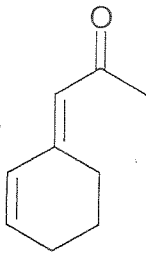


aromatic



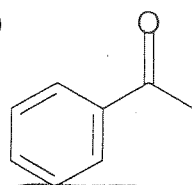
3. (4 pts) Rank the order of expected λ_{max} for the $\pi \rightarrow \pi^*$ transition for these substances in their UV/Vis spectra.

I)



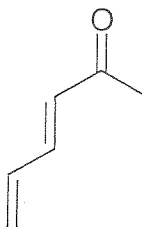
longer λ_{max}
than III
because more
alkyl groups
than III

II)

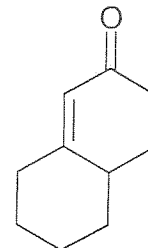


longest λ_{max}
must conjugate!

III)



IV)



shortest λ_{max}
least conjugated

a) longest λ_{max} I > II > III > IV shortest

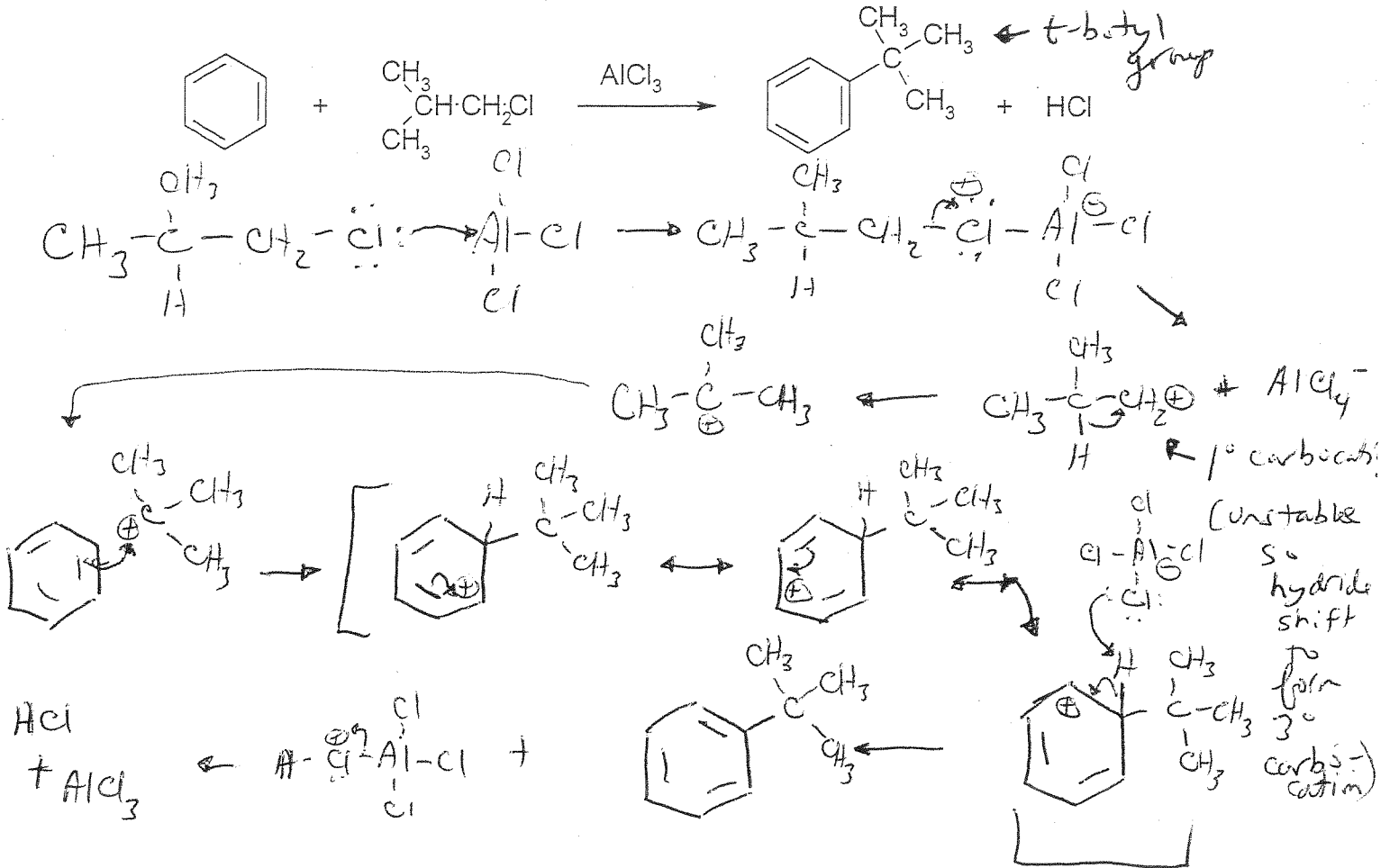
b) longest λ_{max} II > I > III > IV shortest

c) longest λ_{max} II > III > I > IV shortest

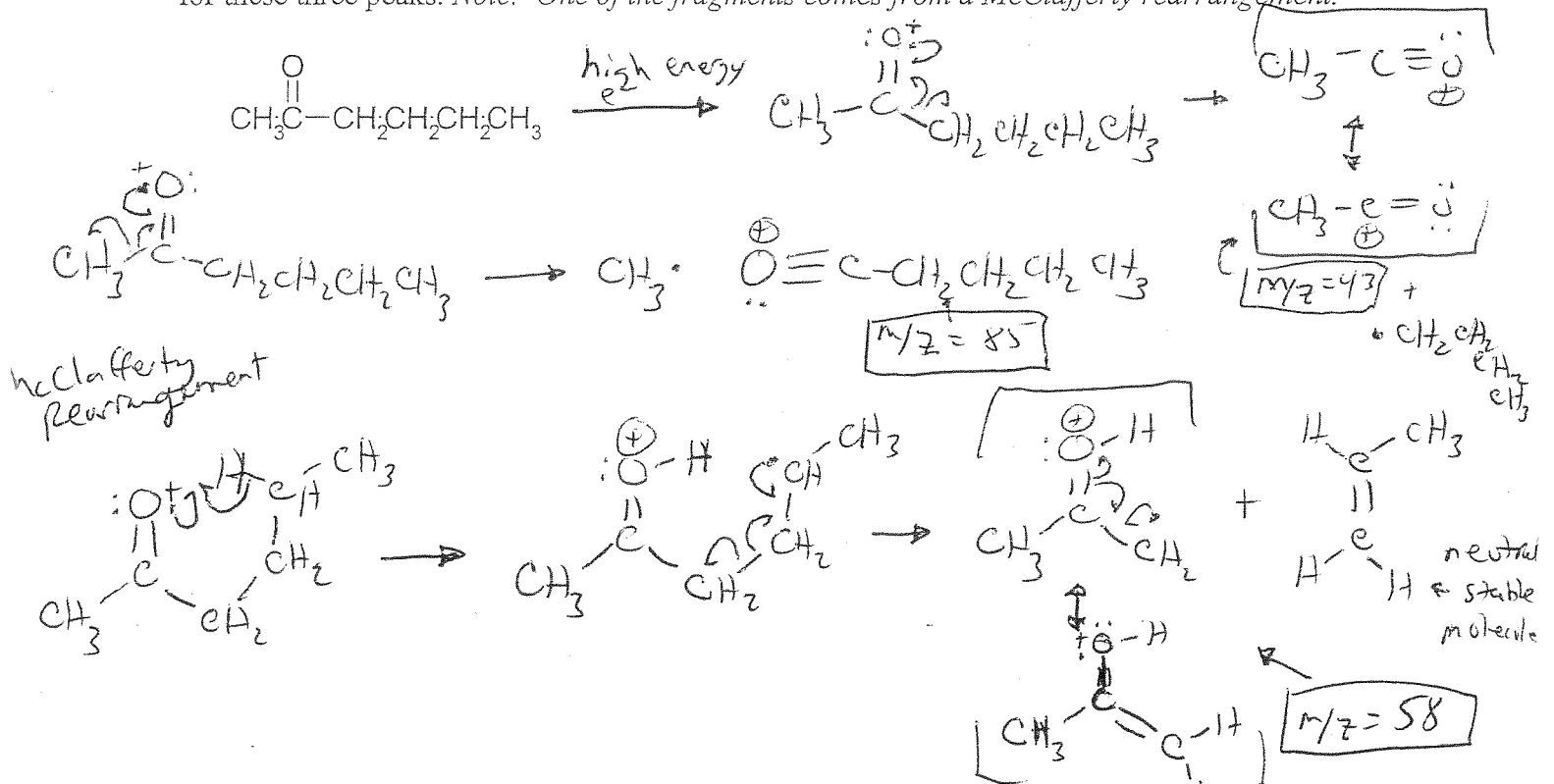
d) longest λ_{max} I > III > II > IV shortest

e) longest λ_{max} II > IV > I > III shortest

4. (9 pts) Draw a step-wise mechanism for the following electrophilic aromatic substitution reaction. Please include the resonance structures of the intermediate in your mechanism.



5. (10 pts) The low resolution mass spectrum of 2-hexanone ($\text{MW} = 100$) shows 3 large peaks, due to fragmentation of the molecular ion, in the spectrum. These peaks have $m/z = 85, 43,$ and 58 . Using curved arrows, show the mechanism and the principle fragments that are the cause for these three peaks. Note: One of the fragments comes from a McLafferty rearrangement.



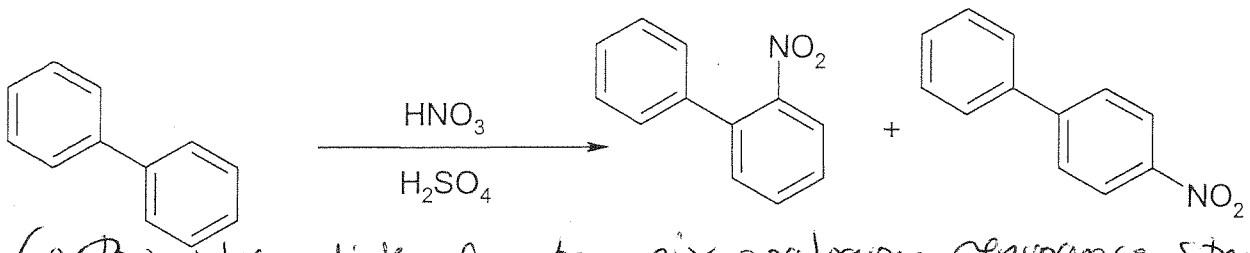
$$E = h\nu \quad c = \lambda\nu$$

HOMO - π } smaller ΔE than ethene
 - π^* LUMO }
 1,3-cyclooctadiene

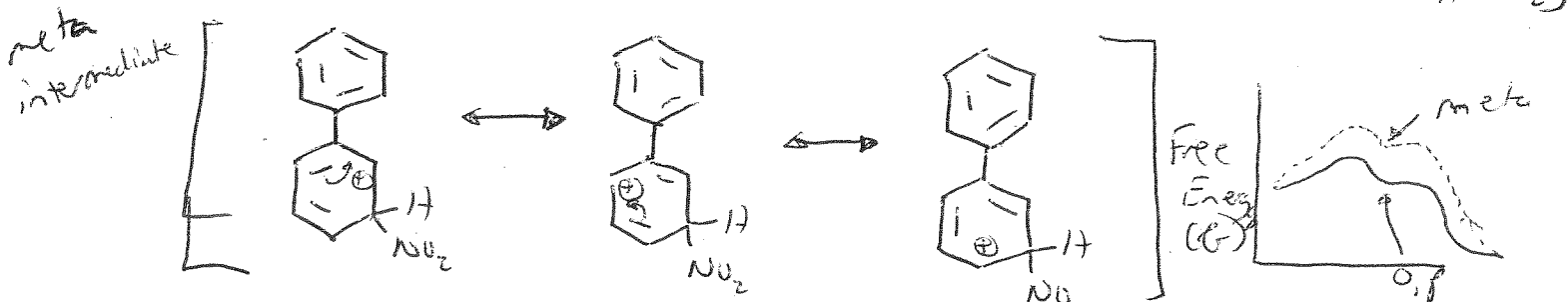
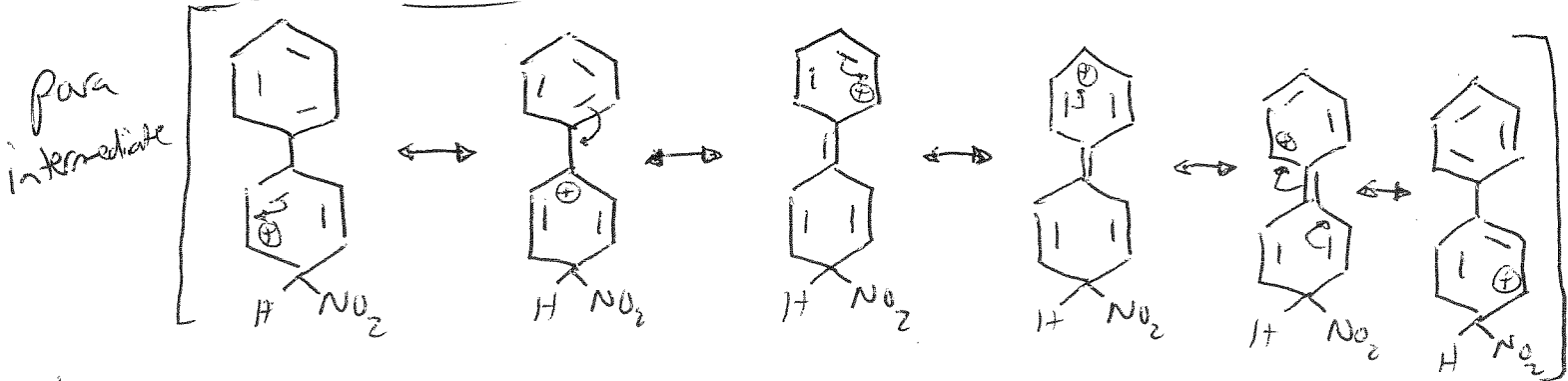
6. (5 pts) The λ_{max} for the $\pi \rightarrow \pi^*$ transition in ethene is 170 nm. Is the HOMO-LUMO energy difference in ethene **greater than** or **less than** that of 1,3-cyclooctadiene, which has a λ_{max} of 230 nm (circle answer)? Briefly explain why you chose your answer.

Ethene's HOMO-LUMO gap is **greater than** cyclooctadiene's HOMO-LUMO gap because 1,3-cyclooctadiene is conjugated while ethene is not. (The more conjugated the molecule, the smaller the HOMO-LUMO gap).
 When a molecule absorbs UV-vis electromagnetic radiation at a longer wavelength this indicates that the HOMO-LUMO energy difference is smaller \rightarrow smaller ΔE than smaller $\nu \rightarrow$ when $\nu \downarrow$ then λ goes up.

7. (9 pts) Explain, using resonance structures of the intermediate in the following nitration reaction, why a phenyl group is an ortho, para director and not a meta director.



(ortho intermediate also has six analogous resonance structures)

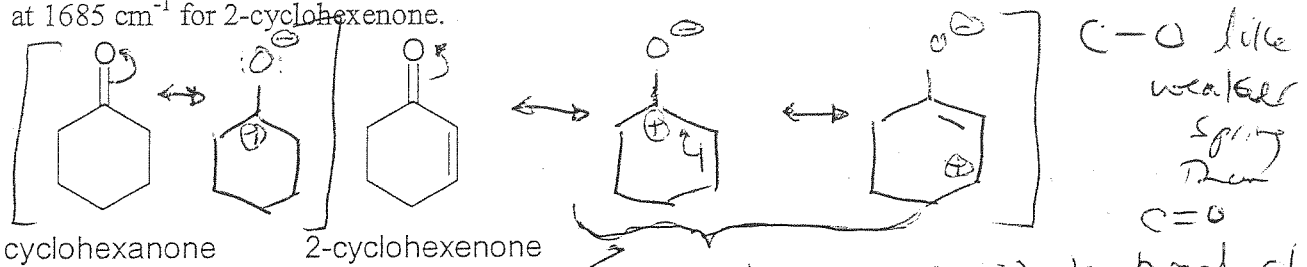


The ortho/para intermediates have 6 resonance structures compared to only 3 for meta. Consequently, the ortho/para path is more readily formed than the meta path because it is more energetically favorable.

8. (1 pt) Assuming that the force constants are the same (same bond strength), which will occur at a **higher IR frequency**, a C-O stretch or a C-Cl stretch? (circle answer)

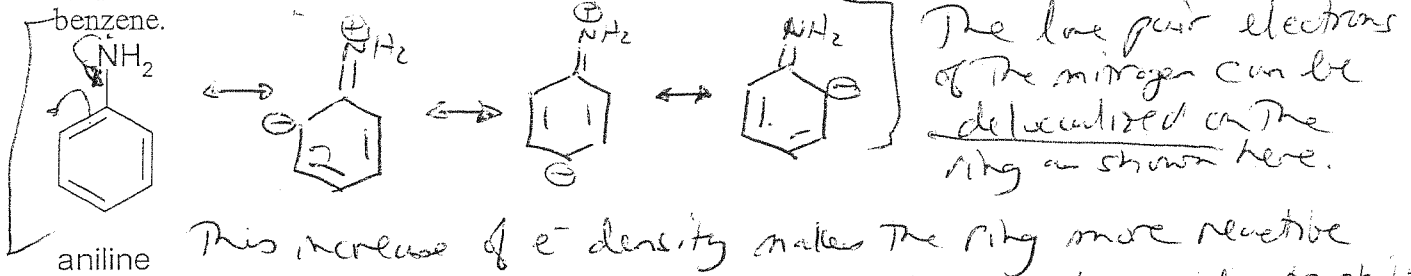
lower mass, higher frequency

9. (5 pts) Explain why a carbonyl absorption shifts to a lower frequency in an α,β unsaturated carbonyl compound – a compound having a carbonyl group bonded directly to a carbon-carbon double bond. For example, the carbonyl absorption occurs at 1720 cm^{-1} for cyclohexanone and at 1685 cm^{-1} for 2-cyclohexenone.



In 2-cyclohexenone the carbonyl group has more single bond character due to two resonance structures w/ a C-O single bond compared to 1 for cyclohexanone. Single bond C-O stretch longer than C=O.

10. (6 pts) Explain why aniline is more reactive in an electrophilic aromatic substitution than



This increase of e^- density makes the ring more reactive + more nucleophilic so it can more easily attack an electrophile in an EAS rxn. In addn, the lone pair also helps stabilize the intermediates.

11. (4 pts) A mass spectrum of an unknown carbon, hydrogen, and oxygen containing compound has a molecular ion peak with a relative intensity of 43.27% (compared to the base peak) and $M + 1$ peak with a relative intensity of 3.81% (also compared to the base peak). How many carbon atoms are in this hydrocarbon. Please show your work.

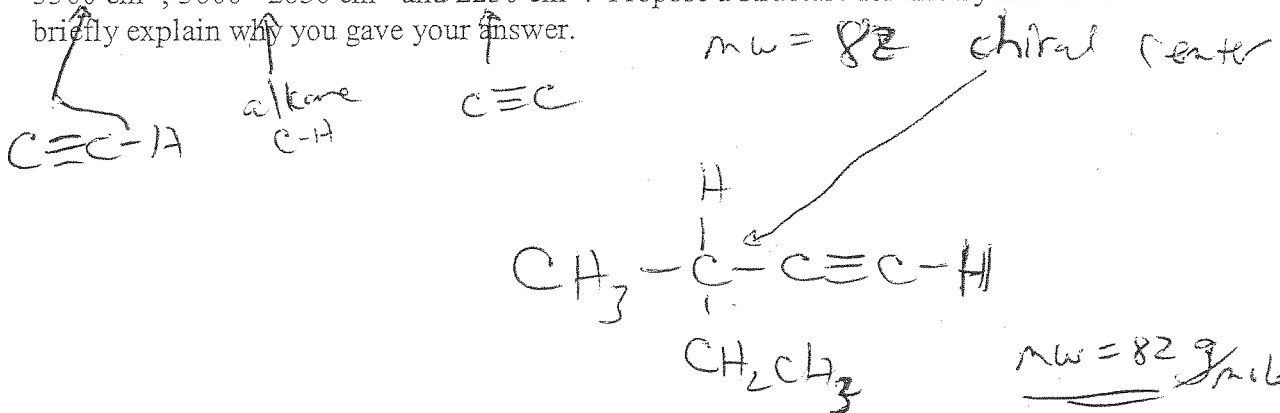
$$\frac{43.27}{3.81} = \frac{100}{x} \quad x = 8.805$$

$$C^{13} = 1.08$$

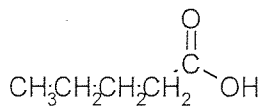
$$1.08 \overline{) 8.805} = 8 \text{ carbons}$$

formed because the \oplus charge can be delocalized onto the nitrogen & make it more stable instead.

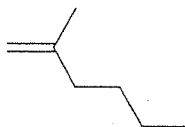
12. (8 pts) A chiral hydrocarbon (contains only C and H atoms and 1 chiral center) exhibits a molecular ion of 82 in its mass spectrum. The IR spectrum of this hydrocarbon shows peaks at 3300 cm^{-1} , $3000 - 2850\text{ cm}^{-1}$ and 2250 cm^{-1} . Propose a structure for this hydrocarbon and briefly explain why you gave your answer.



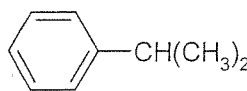
12. (12 pts, 2 each) Match each compound to its IR spectrum. (Write the correct compound letter next to the spectrum number).



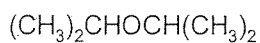
A



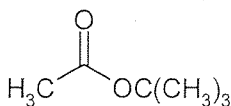
B



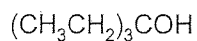
C



D

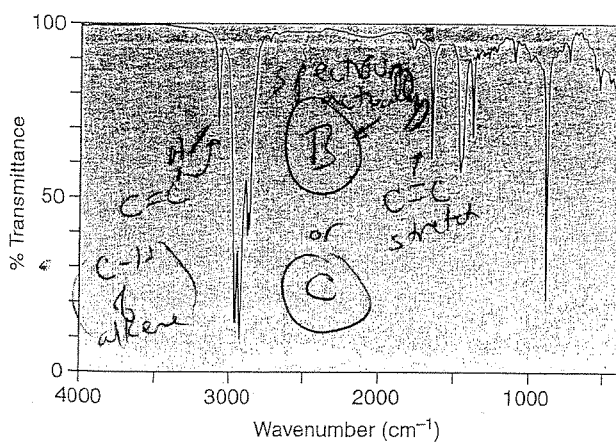


E

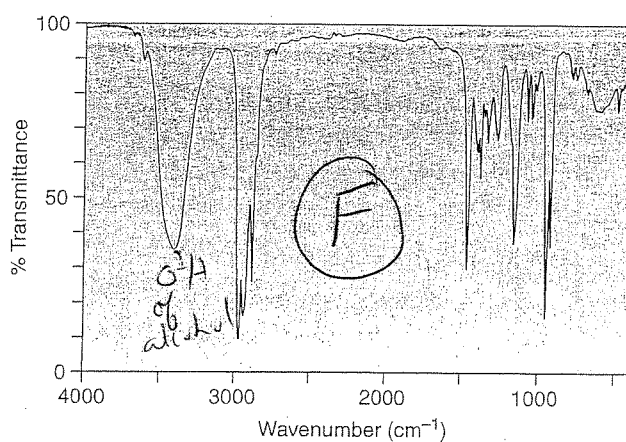


F

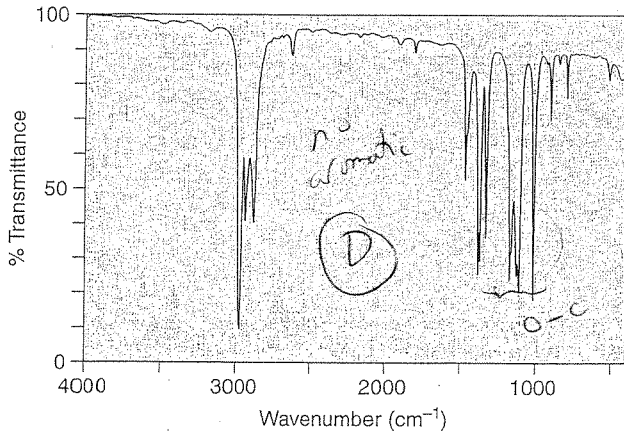
Spectrum [1]



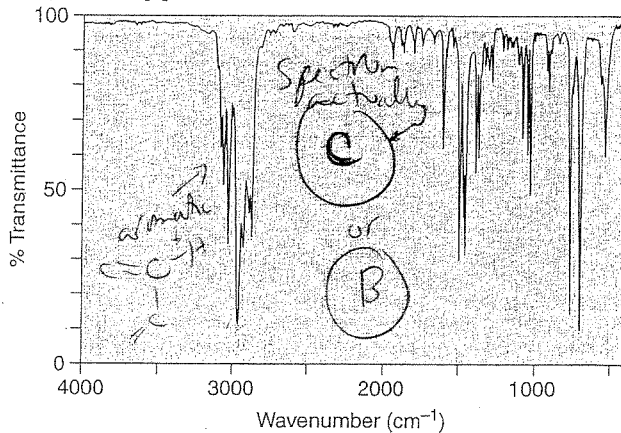
Spectrum [2]



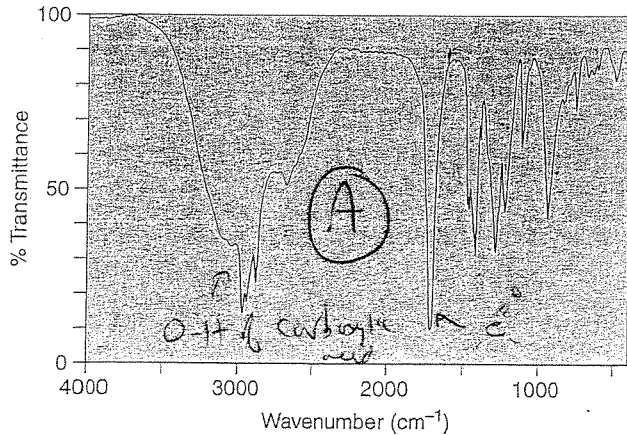
Spectrum [3]



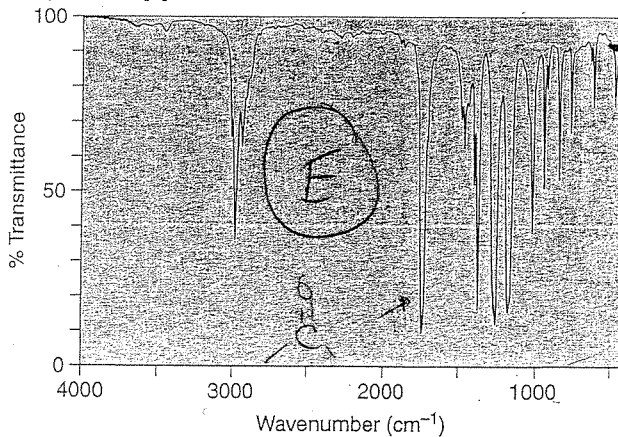
Spectrum [4]



Spectrum [5]

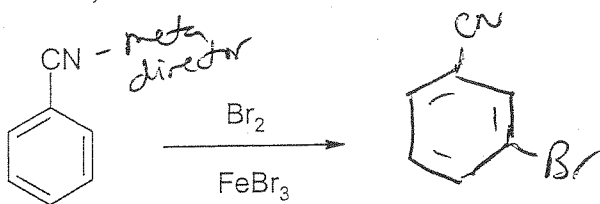


Spectrum [6]



13. (6 pts, 3 each) Give the structures for the **major product** for the following transformations. If no reaction occurs, write **NO RXN**.

a)



b)

