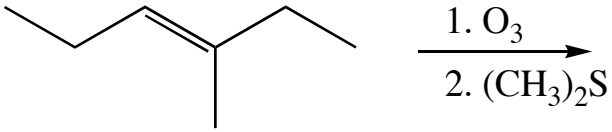
# Chemistry 250B – Final Exam – December 19, 2008

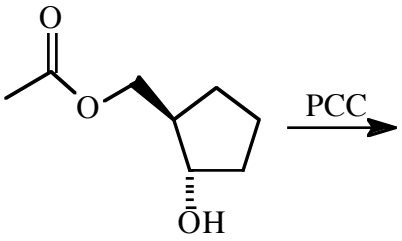
Show non-zero formal charges on all atoms for all structures. There are 11 pages.

1. (42 pts) Complete the following reactions. Show the stereochemistry of the products when appropriate. If more than one significant product is formed, please indicate "major" and "minor" (or I will assume that they are formed in approximately equal amounts). Note: They all react.

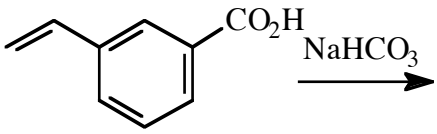
a)



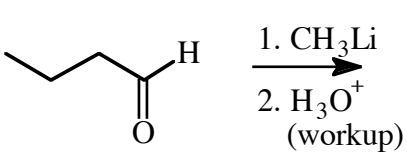

b)



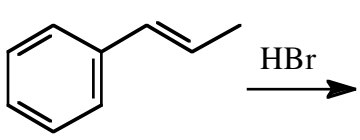

c)



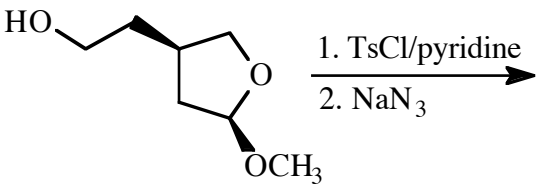

d)



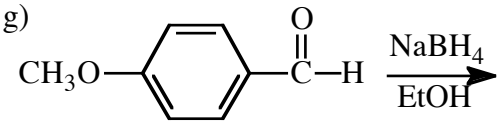

e)



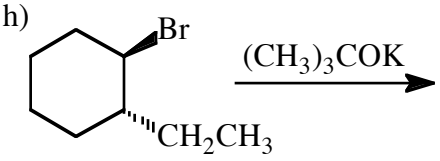

f)



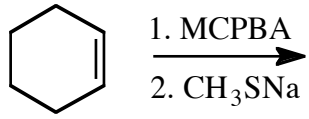

g)



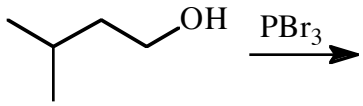
h)


Br
$(CH_3)_3COK$
$CH_2CH_3$

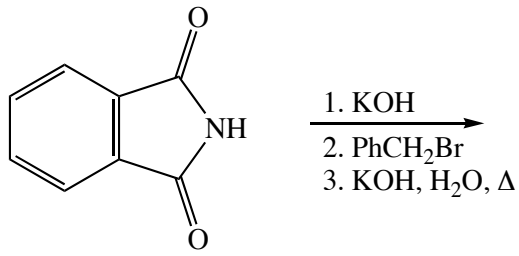
i)


1. MCPBA
2. $CH_3SNa$

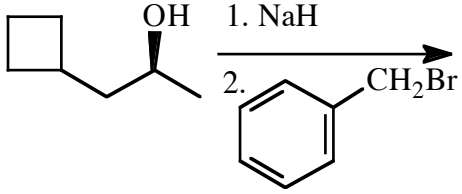
j)


OH
$PBr_3$

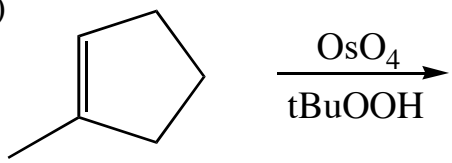
k)


O
NH
O
1. KOH
2. $PhCH_2Br$
3. KOH, $H_2O$, Δ

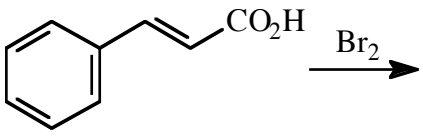
l)


OH
1. NaH
2.
$CH_2Br$

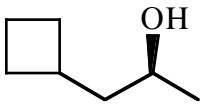
m)

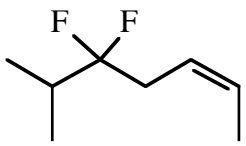

$OsO_4$
tBuOOH

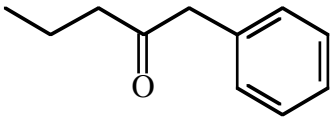
n)

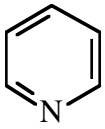

$CO_2H$
$Br_2$

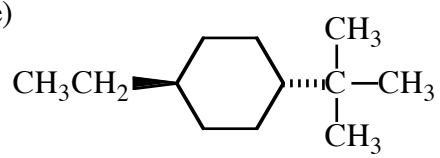
2. (17 pts) Name the following compounds. Be sure to give stereochemical descriptors when necessary.

a) 


b) 


c) 


d) 


e) 


3. (14 pts) Draw structures for the following compounds.

a) Chloroform b) Benzyl vinyl ether c) (*E*)-4-Bromo-3-pentenal

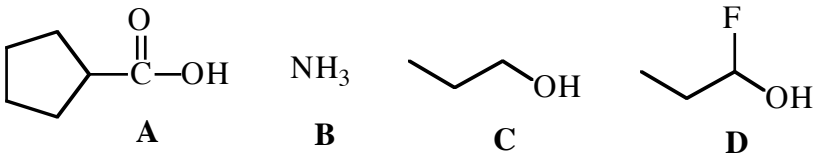
d) Formaldehyde e) TsCl

4. (8 pts) The most stable conformation of 1,2-dimethoxyethane is anti, while the most stable conformation of 1,2-ethanediol is gauche. Draw Newman projections down the C-C bond for the **anti conformation of 1,2-dimethoxyethane** and the **gauche conformer of 1,2-ethanediol**.

b) Explain why the gauche conformer is more stable for the 1,2-ethanediol, but the anti conformer is more stable for the 1,2-dimethoxyethane.

5. (20 pts) Rank the following compounds according to the indicated properties:

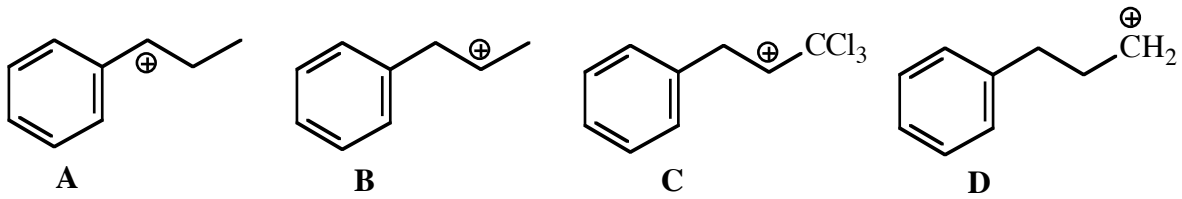
a) acidity




**A** **B** **C** **D**

most acidic _____ > _____ > _____ > _____ least acidic

b) carbocation stability




**A** **B** **C** **D**

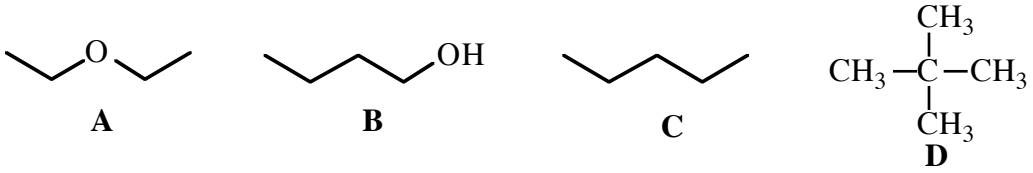
most stable _____ > _____ > _____ > _____ least stable

c) rate of reaction with methyl bromide (in isopropanol as solvent):

$CH_3OH$ **A** $CH_3CH_2Cl$ **B** $CH_3ONa$ **C** $CH_3SNa$ **D**

fastest reaction _____ > _____ > _____ > _____ slowest reaction

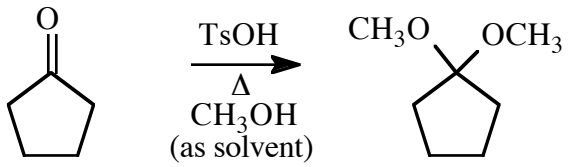
d) boiling point



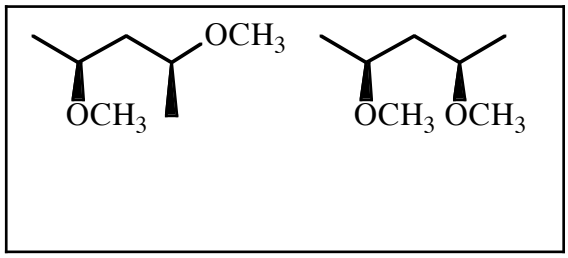

**A** **B** **C** **D**

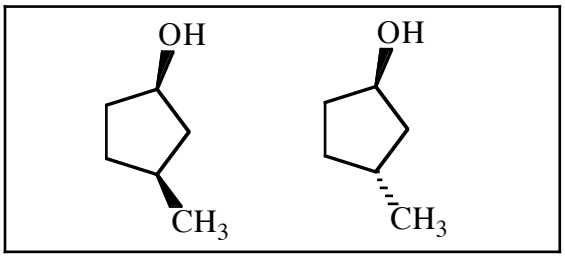
highest bp _____ > _____ > _____ > _____ lowest bp

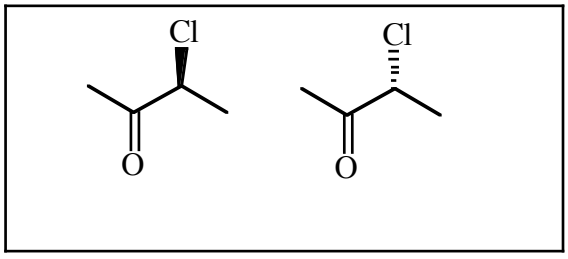
6. (10 pts) Write a detailed mechanism (using curved arrows) for the following reaction:

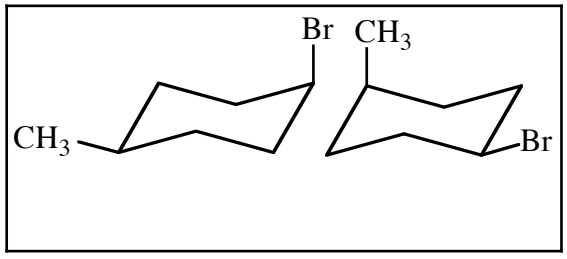



7. (12 pts) Label each of the following pairs of compounds as either: constitutional (structural) isomers, enantiomers, diastereomers, conformers, tautomers, resonance forms, or identical. **Circle all meso compounds. Put an X through any molecules that are NOT optically active.**

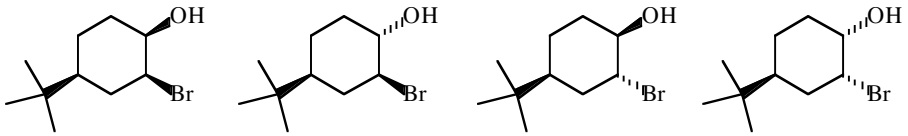


8. (11 pts) When treated with sodium hydroxide in water at room temperature, one of the bromohydrins shown below reacts rapidly to form an epoxide while the others do not.




a) Circle the molecule that reacts to form the epoxide.

b) Draw the two chair conformations of the molecule you circled and identify which one is most stable.

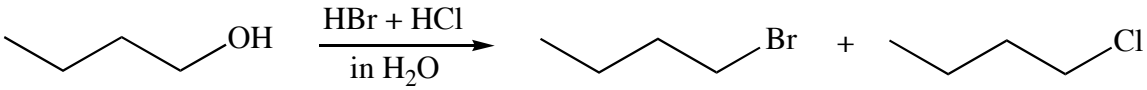
c) Draw a complete mechanism (using curved arrows) for formation of the epoxide. Be sure to clearly show the stereochemistry of the resulting epoxide.

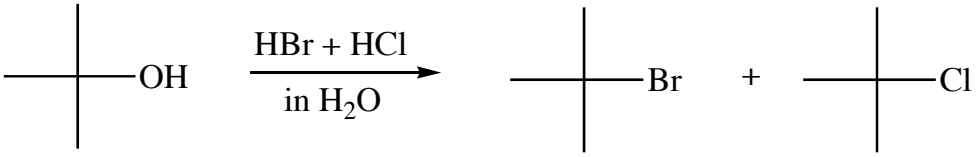
9. (10 pts) When n-butanol or t-butanol is treated with a 1:1 molar mixture of HBr and HCl in water, the corresponding alkyl halides are produced as shown below. One reaction gives about a 50:50 mixture of the two alkyl halides, and one gives about an 80:20 mixture of products.

a) For each reaction, write a detailed mechanism (complete with curved arrows) for formation of the products.

b) Label each reaction as $S_N1$ or $S_N2$.

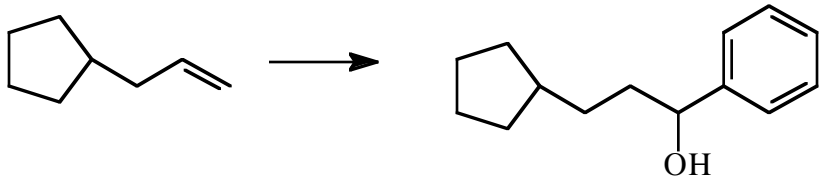
c) Under the appropriate products write 50:50 or 80:20, clearly indicating which product is the major one in the 80:20 reaction. Explain why the one reaction gives a 50:50 mixture and the other an 80:20 mixture.



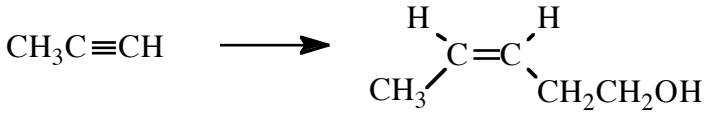



10. (17 pts) List the reagent(s) necessary to accomplish the following transformations. If the transformation requires more than one step, show the major organic product for each step in your transformation.

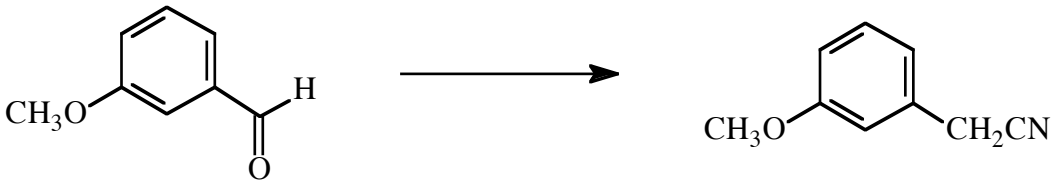
a)



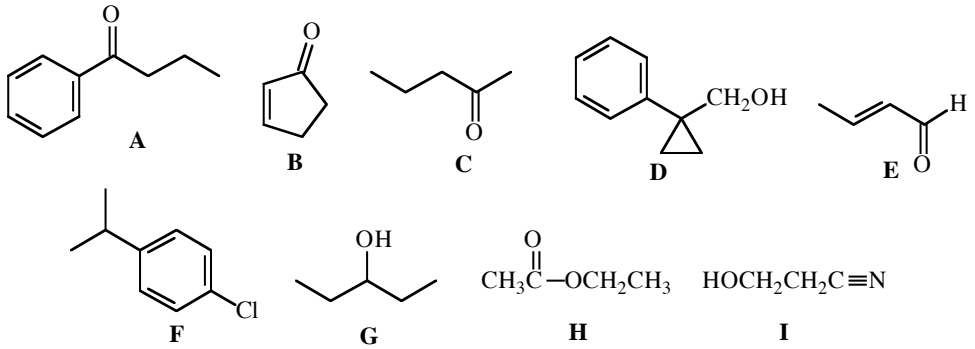

b)

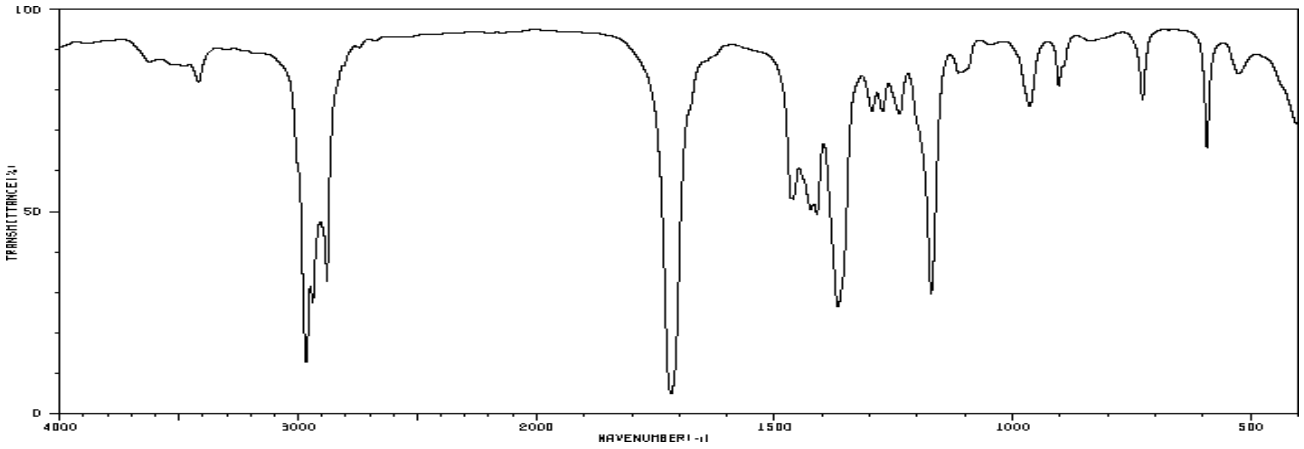


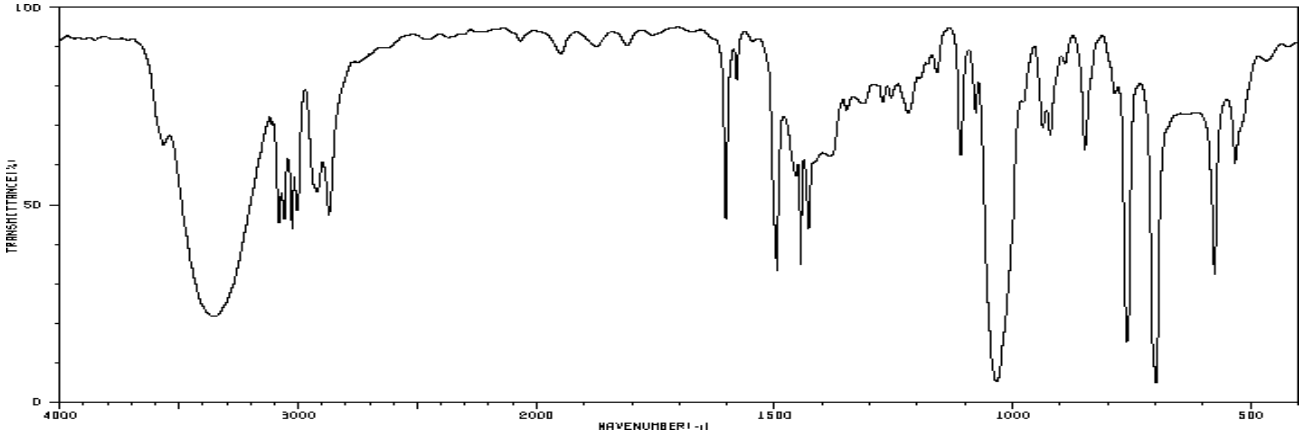

c) R.B.Woodward was one of the most brilliant organic chemists of all time. (He won the Nobel Prize in 1965.) He entered MIT as a 16-year-old freshman in 1933 and four years later was awarded the Ph.D.! While a student there he carried out a syntheis of *estrone*, a female sex hormone. The early stages of Woodward's estrone synthesis required the following conversion. Suggest a reasonable series of steps to carry out this transformation.

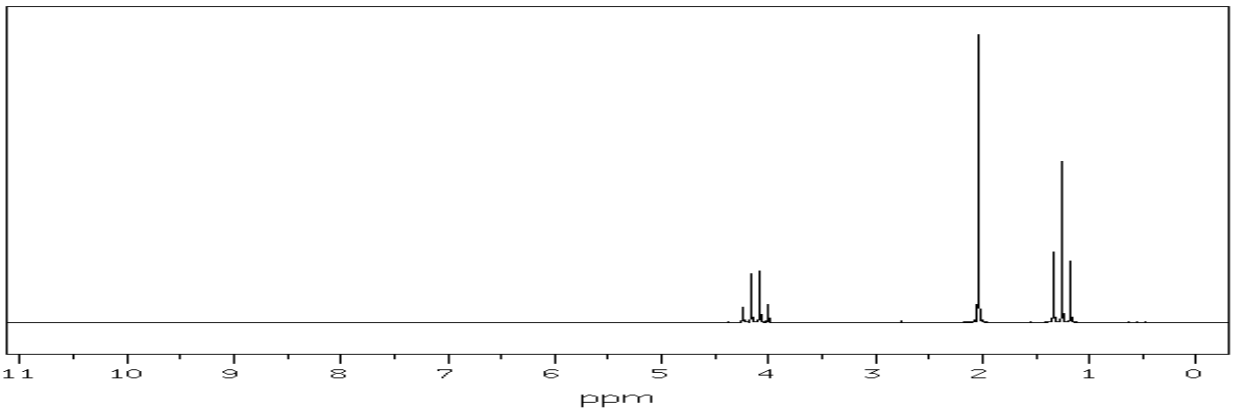


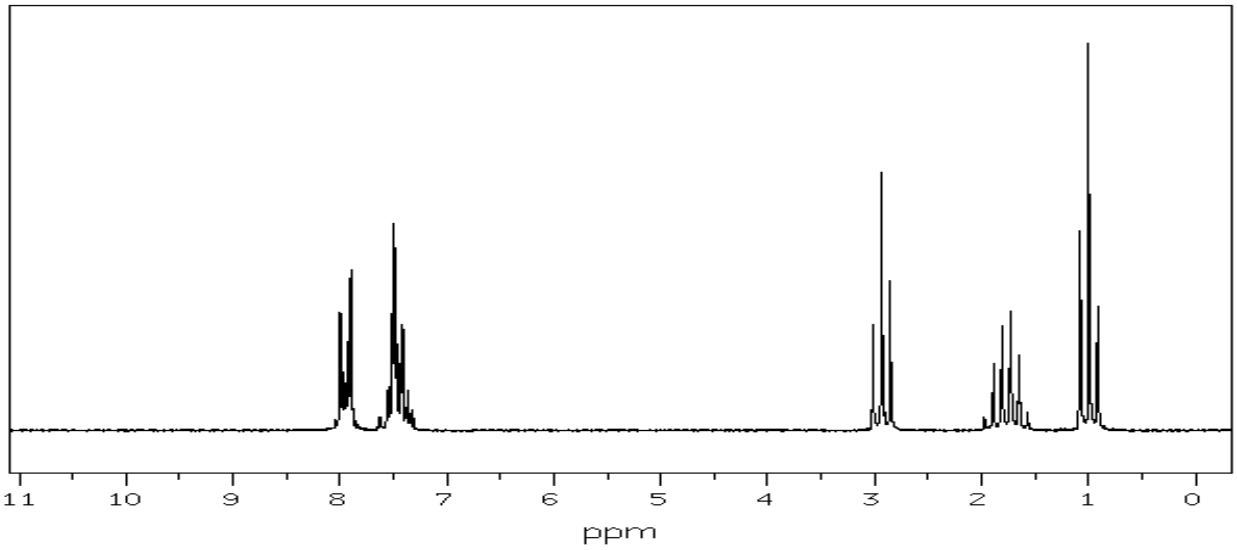
11. (16 pts) Each of the spectra shown below (and on the next page) corresponds to one of the structures A-I. Identify which spectra go to which structures. For full credit you must assign the peaks in the NMR spectra to the protons in the molecule and assign the important IR absorptions to their respective bands.



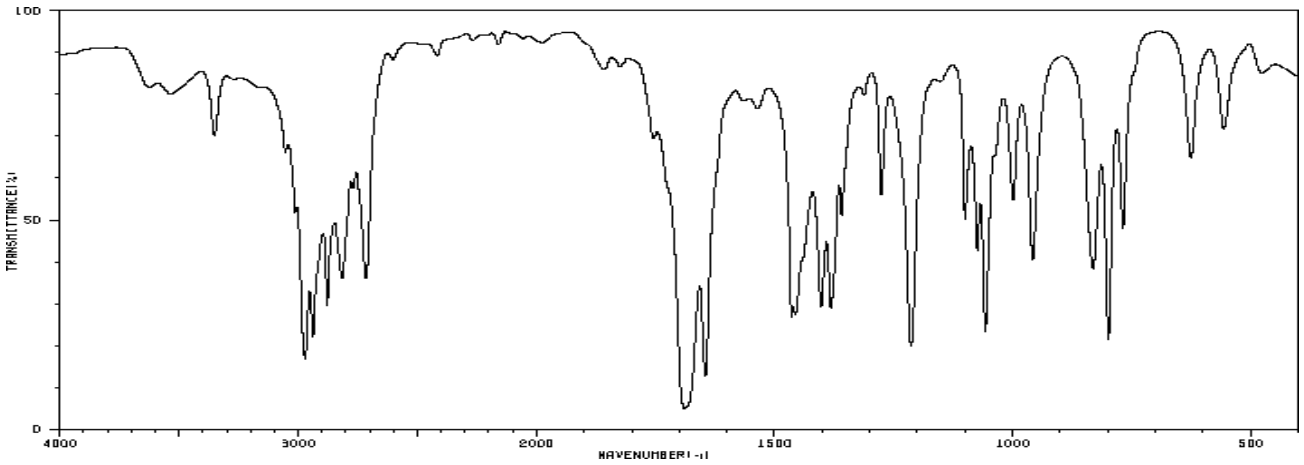



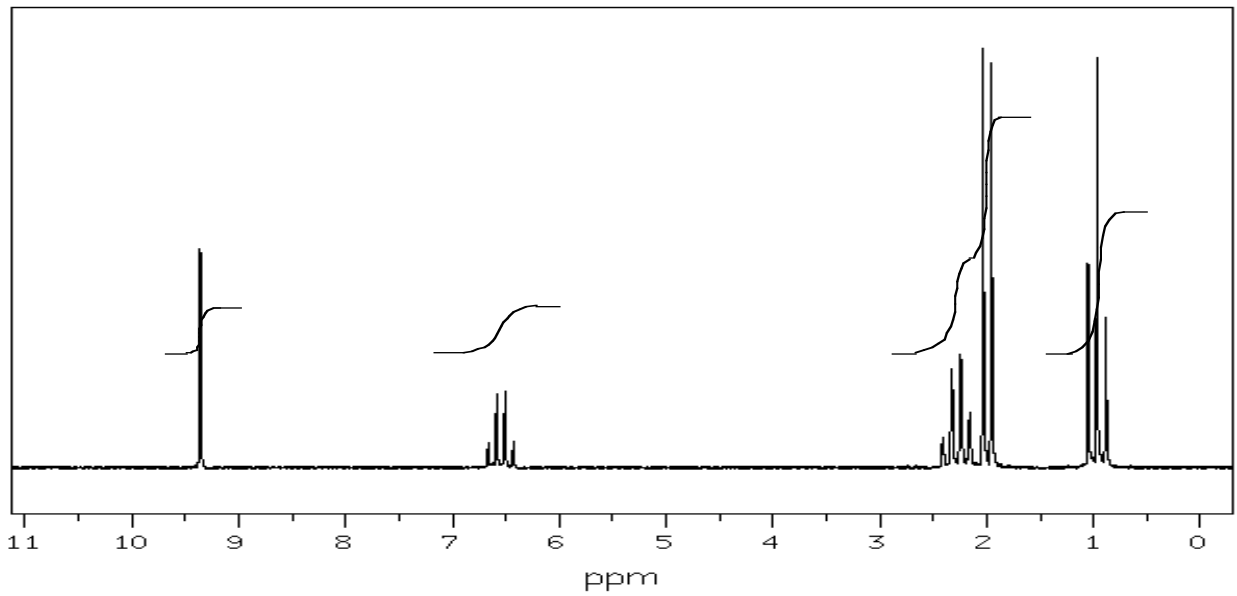





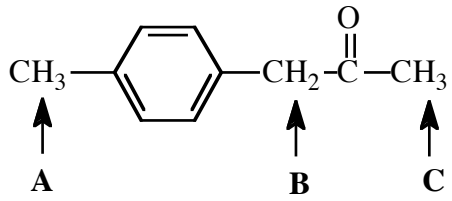

11. (8 pts) Draw the structure of the compound whose H-NMR and IR spectra are shown below. The molecular formula is $C_6H_{10}O$. Assign the peaks in the NMR to the protons in the molecule. Also assign the important IR absorptions.



12. (15 pts) In the molecule shown below there are three positions (**A**, **B**, and **C**) that could potentially be deprotonated by a strong base. Rank the acidity of these three positions and **explain your ranking**. As part of your explanation, draw Lewis structures (show all atoms, lone pairs and formal charges explicitly) for all the important resonance forms of the various conjugate bases.

a)




most acidic > _____ > least acidic

b) Draw the Lewis structure of the three conjugate bases and their important resonance forms below. **Show all lone pairs and formal charges.**

c) Rationalize the relative acidities of these three positions. (That is, explain the ordering you made in part a.)