Chem 2600 Final Exam 2006, April 20th, 9:00 am to 12:00 am

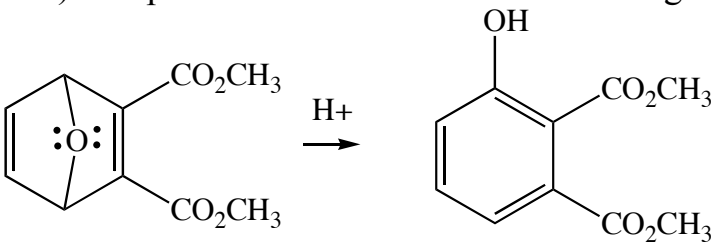
You are permitted the use of a model kit; data sheets of pKas, pi Mos, periodic table and NMR/IR tables are provided by your instructor. No other aids are allowed and no electronic devices are to be present while writing this exam. Sign your name below. Your signature indicates that you agree not to divulge or discuss the contents of this exam in any way until the final marks have been released. 87 marks available.

IN GENERAL, IF YOU USE RESONANCE ARGUMENTS AS PART OF YOUR REASONING, THEN DRAW THE RELEVANT STRUCTURES.

Name:_____ Signature:_____

Question One (4 marks)

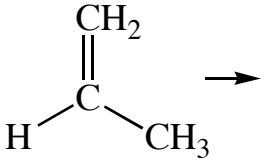
i) Propose a mechanism for the following reaction.

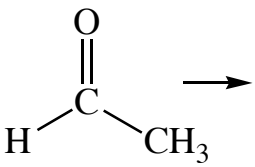


ii) This reaction can be classified as one discussed in the course. It is …?

Question Two (5 marks)

i) Using the two molecules below, and using CH_3Li as the nucleophile, explain why C=O bonds undergo nucleophilic addition but alkenes do not.

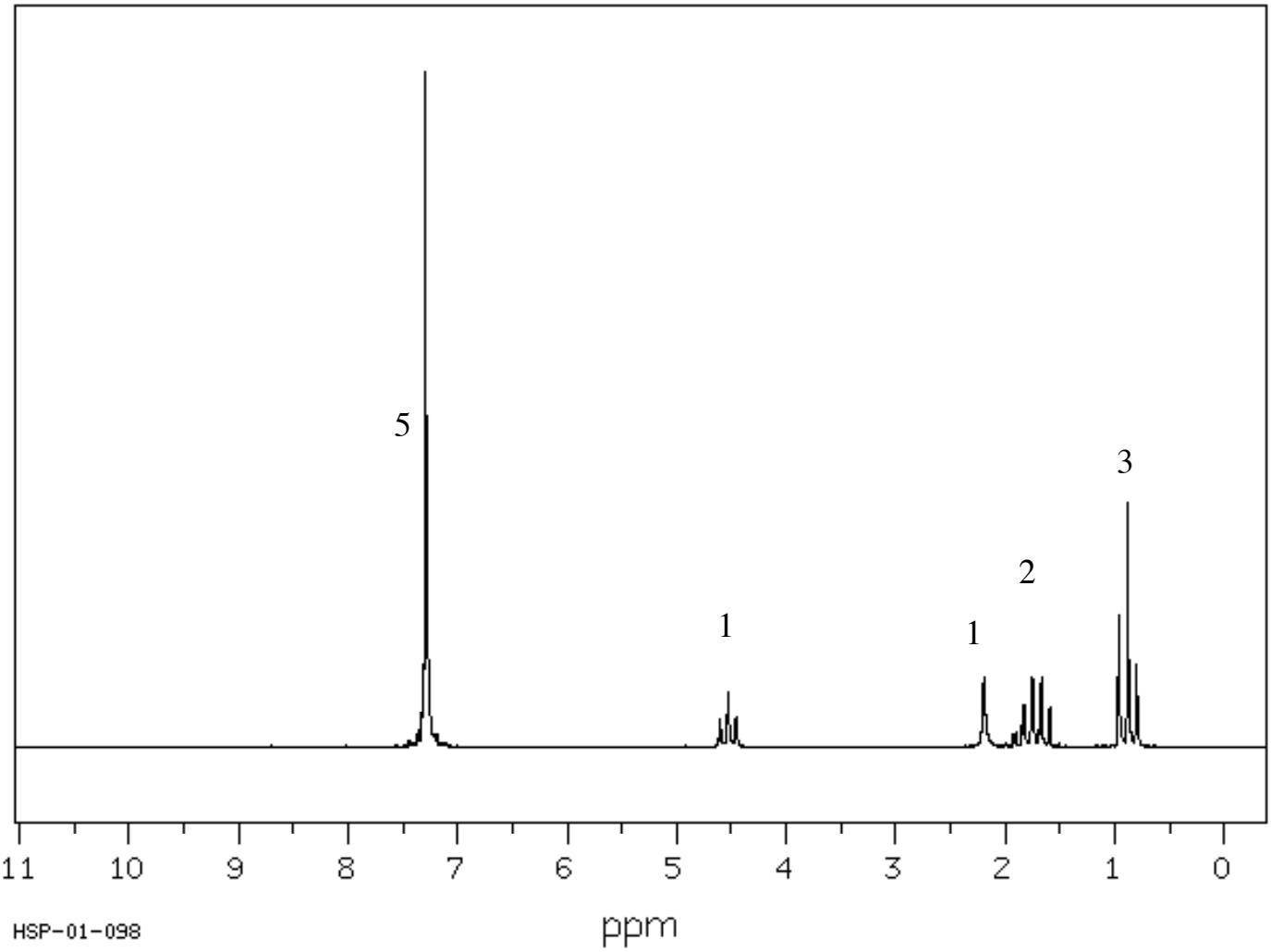


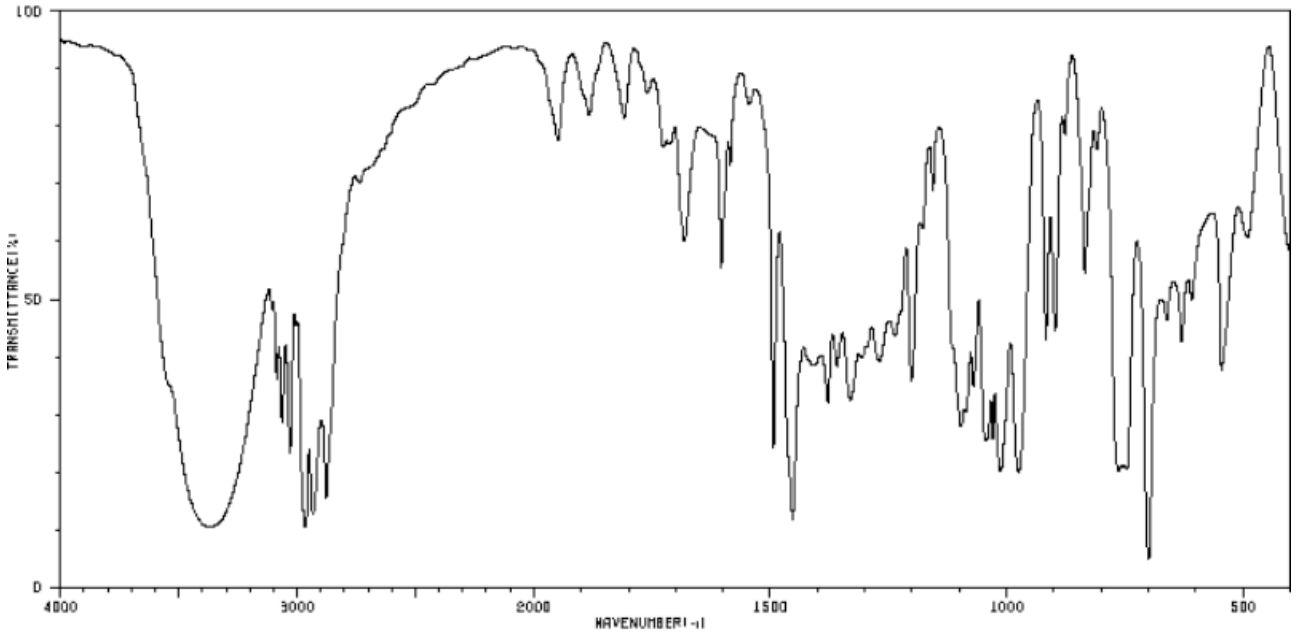


ii) Nothing is absolute: the alkene below does in fact undergo nucleophilic addition with CH_3Li. Give the structure of the intermediate addition product and explain why this reaction takes place.

Question Three (6 marks)

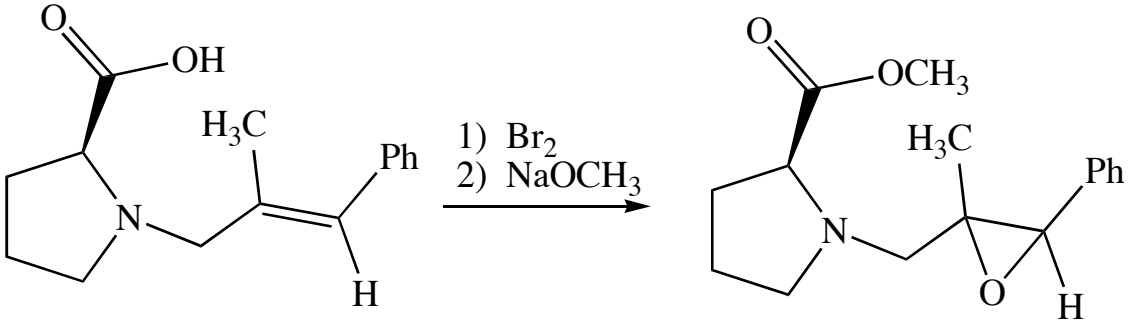
For the following proton NMR and IR spectra, deduce the structure of the compound ($C_9H_{12}O$), assign the peaks in the NMR spectrum and important bands in the IR spectrum.





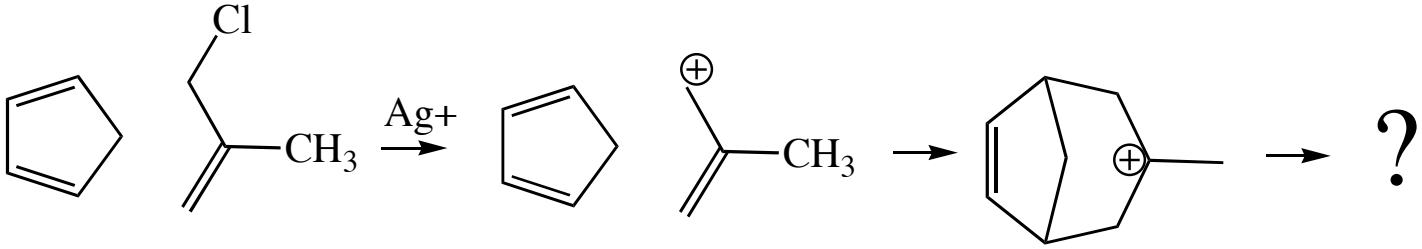
Question Four (5 marks)

Provide a mechanism for the following reaction.



Question Five (6 marks)

i) Add arrows to the following scheme to indicate electron movement.



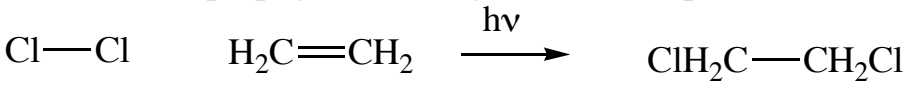
ii) Determine whether the cycloaddition (second step) is an orbital symmetry allowed process.

iii) What is the purpose of the silver ion?

iv) Give the structure of the final product (which has the formula C_9H_{12})?

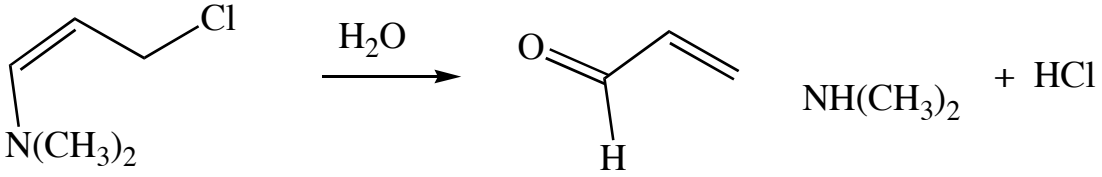
Question Six (6 marks)

We have looked at a mechanism for the electrophillic addition of chlorine to alkenes. Propose a different, radical chain mechanism for the same reaction, identify the steps as initiation and propagation, and give one example of a termination step.



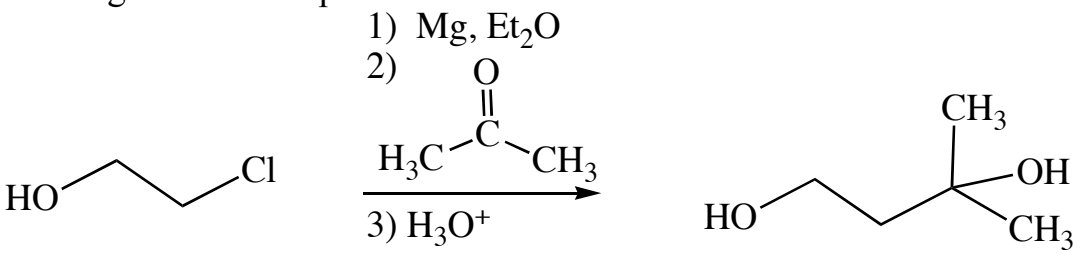
Question Seven (5 marks)

Propose a mechanism for the following process.



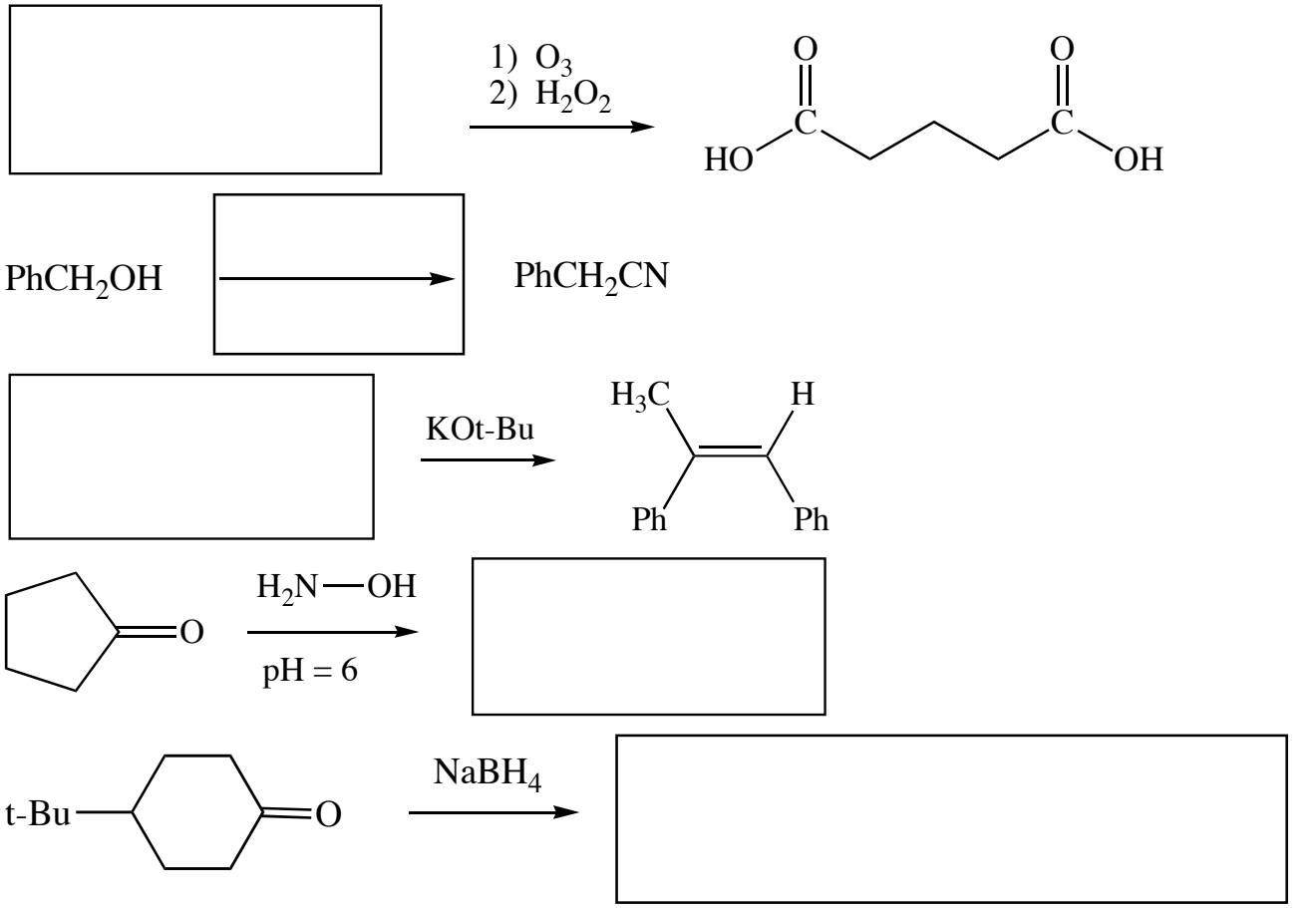
Question Eight (5 marks)

The transformation shown below won't work. Explain the problem and describe a solution showing all of the steps involved.

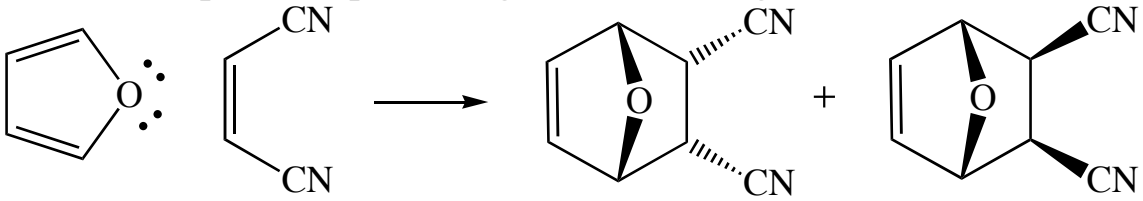


Question Nine (10 marks)

For each of the following reactions, fill in the box with either the reactant, the reagents (if the box is over the arrow), or the product. Stereochemical considerations may be important.



Question Ten (11 marks)
Answer the questions pertaining to the following reaction:



i) Label the adducts as endo and exo.

ii) Which is the kinetic product?

iii) If you wanted to obtain more of the thermodynamic product, what would you do?

iv) What is the driving force for this reaction?

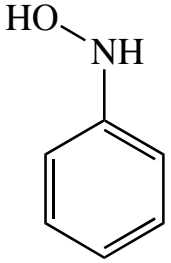
v) If the products are heated, they revert back to the reactants shown. Why?

vi) Is this reaction stereospecific, stereoselective, or both? Explain.

vii) Furan is considered to be an aromatic molecule. What does the fact that this reaction takes place say about its resonance energy compared to that of benzene?

Question Eleven (5 marks)

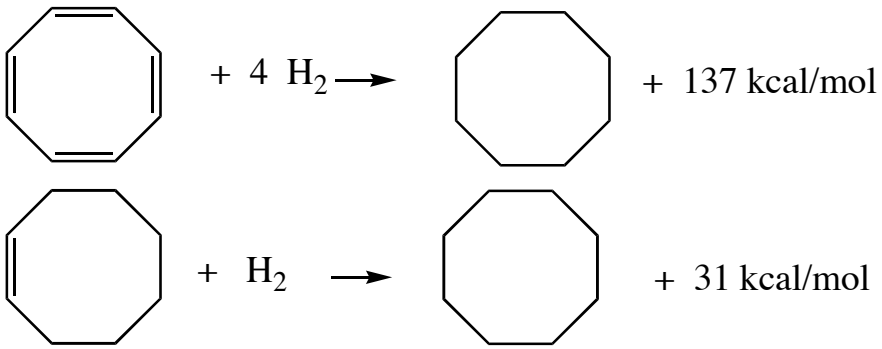
i) Would electrophilic aromatic substitution of the following compound give predominantly meta, or ortho/para products? Explain your reasoning.



ii) Explain how the proton NMR spectrum of the molecule above would tell you whether this substituent is a meta or an ortho/para directing group?

Question Twelve (7 marks)

One of the nice things about Hyperchem is that you can calculate thermodynamic parameters for molecules that don't exist. I used it to calculate the heats of hydrogenation for FLAT cyclooctatetraene and for cyclooctene as given below.



i) What is the resonance energy for FLAT cyclooctatetraene

ii) Draw the pi MO diagram for this molecule. Does it predict flat cyclooctatetraene to be aromatic or antiaromatic?

Question Thirteen: 4 x 3 = 12 marks. I will mark them all and take your best four.

Propose syntheses of the following molecules. As starting materials, you may use benzene and any stable organic reactant of 5 carbons or less. You may use any inorganic or organic reagent you may need, regardless of the number of carbons it may contain, but carbon-containing reagents must be used as a reagent only.