

**Chem 2600 Final Exam 2007, April 21st, 9:00 am to 12:00 am**

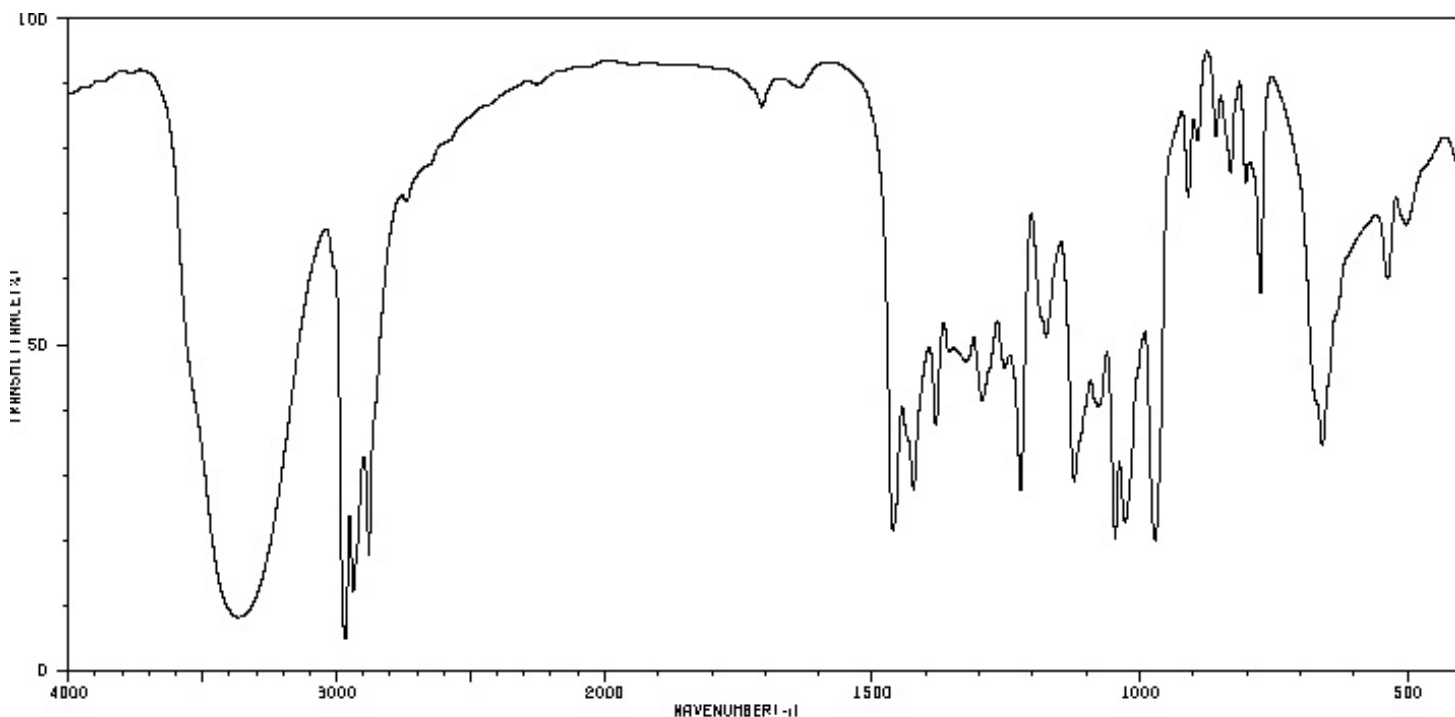
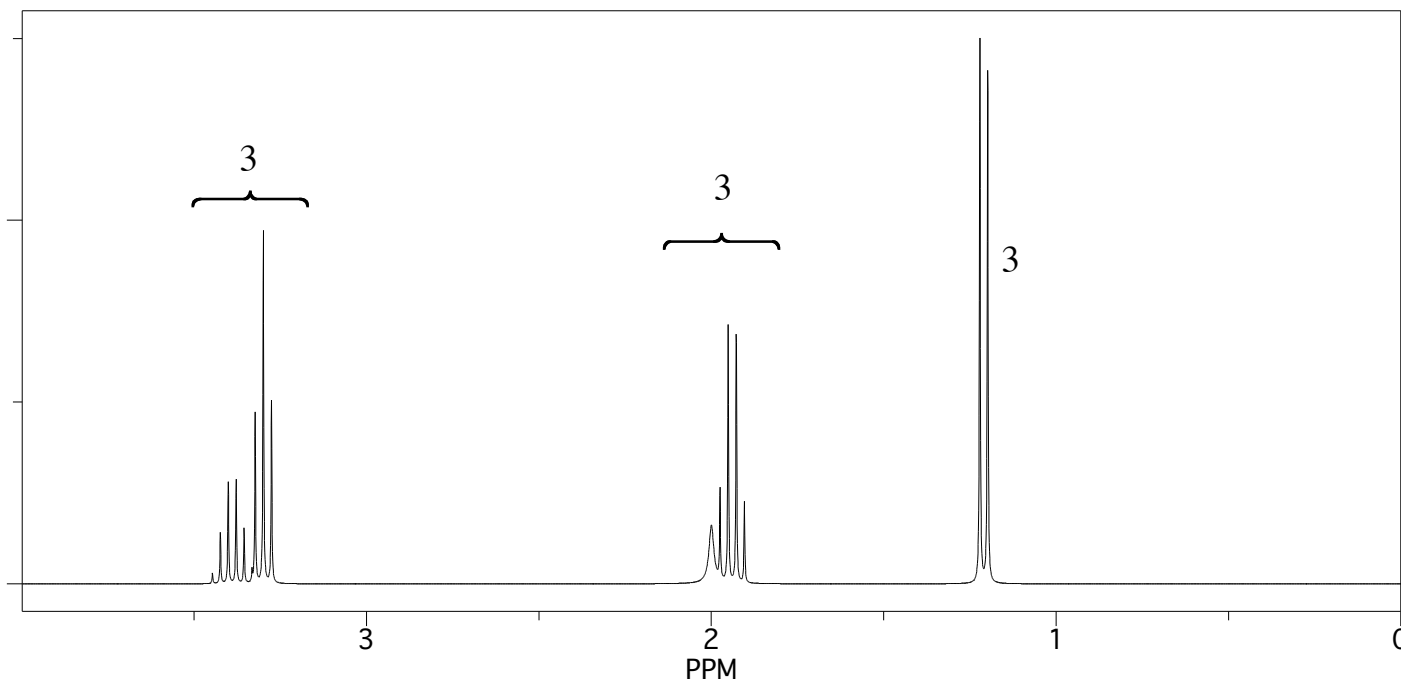
You are permitted the use of a model kit; data sheets of pKas, pi Mos, periodic table and NMR/IR tables are provided by your instructor. No other aids and no scrap paper are allowed. No electronic devices are to be present while writing this exam. Sign your name below. Your signature indicates that you agree not to divulge or discuss the contents of this exam in any way until the final marks have been released. 100 marks available. IN GENERAL, IF YOU USE RESONANCE ARGUMENTS AS PART OF YOUR REASONING, THEN DRAW THE RELEVANT STRUCTURES.

Name: \_\_\_\_\_

Signature: \_\_\_\_\_

**Question One (10 marks)**

Deduce the structure a molecule,  $C_4H_9BrO$ , that gives the following proton and IR spectra. Assign all proton resonances and assign two meaningful IR bands.



### Question Two (ten marks)

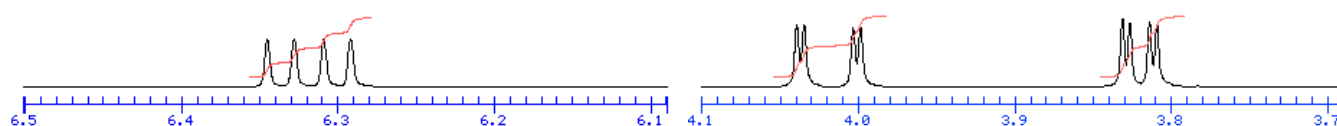
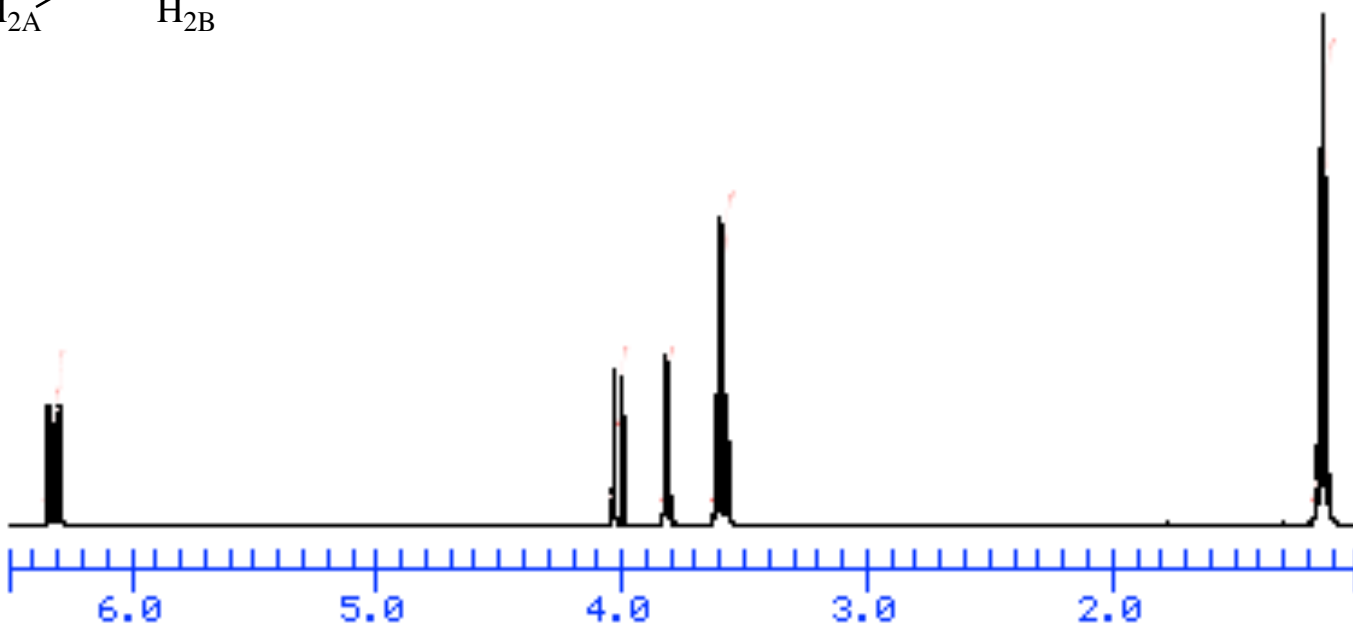
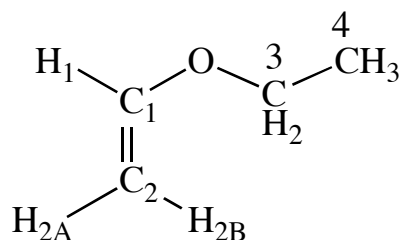
The 400 MHz proton NMR spectrum (with expansions) appears below.

i) using the numbering provided, assign all proton and carbon signals.

ii) from the proton expansions, measure the coupling constants and fill in the following:

$$J_{1-2A} = \text{_____} \quad J_{1-2B} = \text{_____} \quad J_{2A-2B} = \text{_____}$$

iii) The vinyl protons are separated by over two ppm and are outside the normal range for alkenyl protons. A similar anomaly exists in the carbon spectrum. Explain.



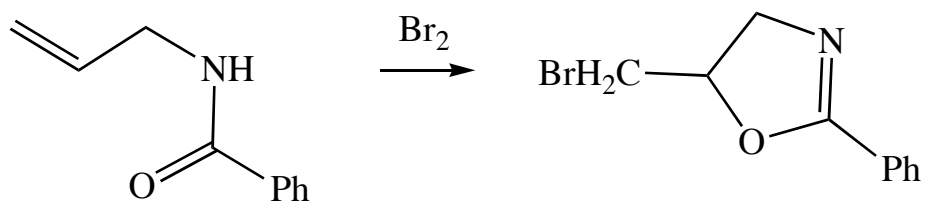
These expansions are to the same scale.

### Question Three (five marks)

Give a single example of a Diels-Alder reaction that exhibits regioselectivity, stereoselectivity and stereospecificity – at the same time – and label the structural features of the product that pertain to each term.

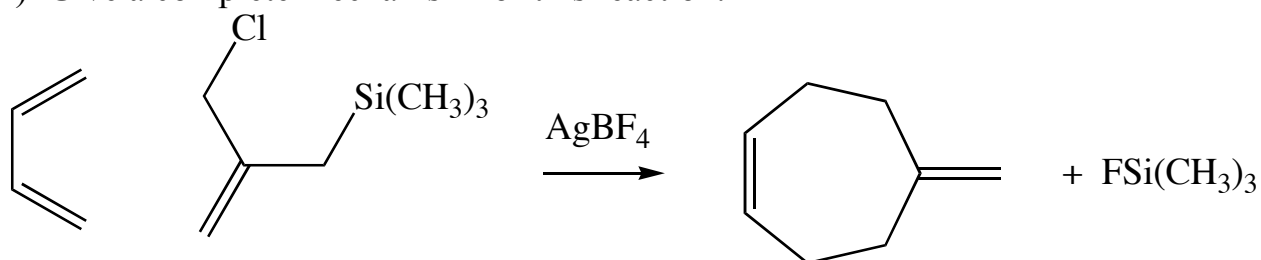
**Question Four (six marks)**

Propose a mechanism for the following process.

**Question Five (five marks)**

The following three step reaction begins with ionization of the allyl chloride followed by an electrocyclic process that is orbital symmetry controlled.

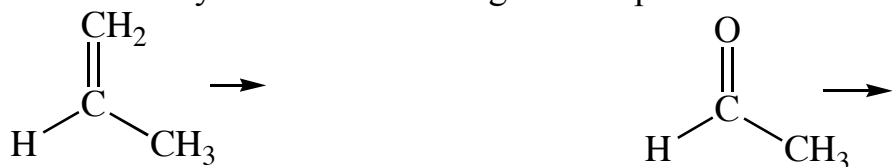
i) Give a complete mechanism for this reaction.



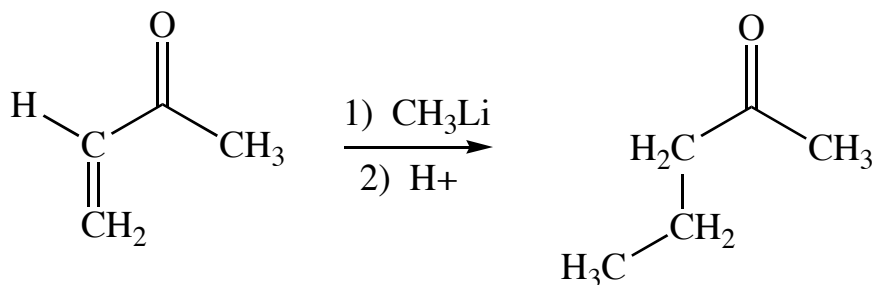
ii) Using one set of molecular orbitals, show that the electrocyclic process is symmetry allowed.

**Question Six (six marks)**

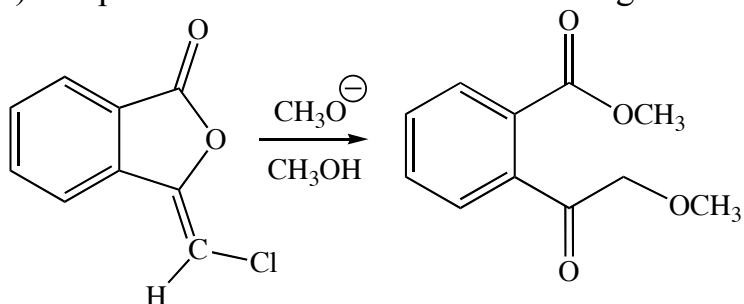
- i) Using the two molecules below, and using  $\text{CH}_3\text{Li}$  (or  $\text{H}_3\text{C}^-$ ) as the nucleophile, explain why  $\text{C}=\text{O}$  bonds undergo nucleophilic addition but alkenes do not.



- ii) Nothing is absolute: the alkene below does in fact undergo nucleophilic addition with  $\text{CH}_3\text{Li}$ . Give the structure of the intermediate addition product and explain why this reaction takes place.

**Question Seven (ten marks)**

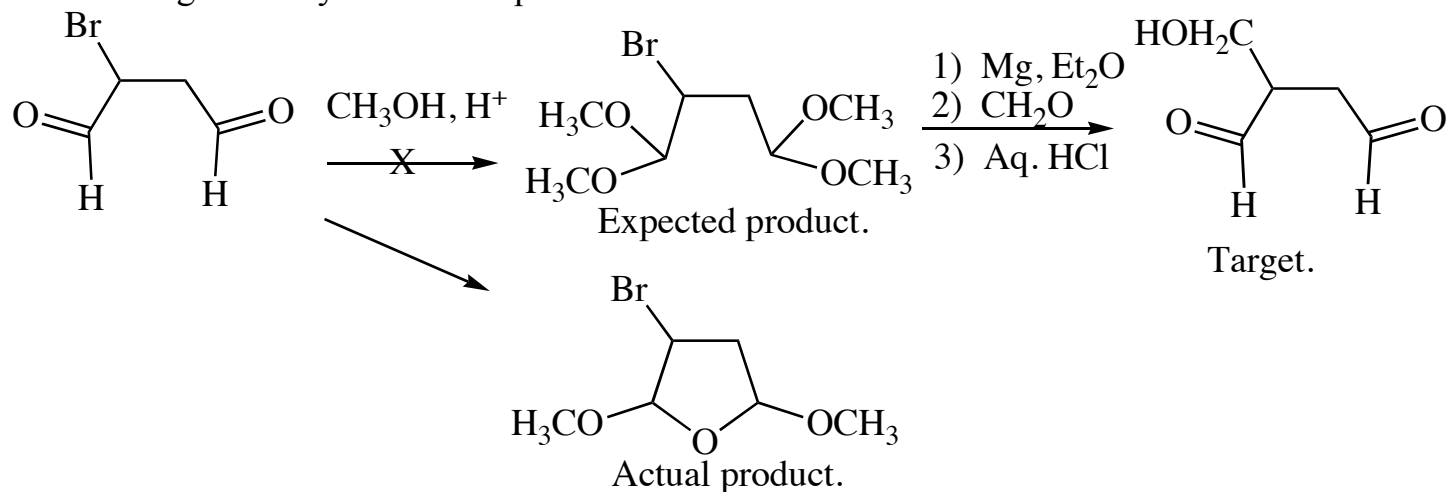
- i) Propose a mechanism for the following reaction.



- ii) This molecule acts as a suicide substrate for some esterase enzymes (enzymes that cleave esters). Explain.

### Question Eight (ten marks)

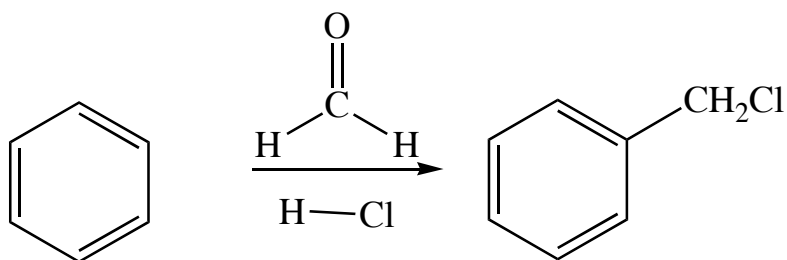
Fred Frosh wishes to prepare the target molecule using the reactions below. He needs to prepare a Grignard reagent from the dialdehyde reactant. To do so, he must first protect the aldehyde functional groups. When Fred attempts to do this, however, instead of getting the expected diacetal he gets the cyclic “actual product” shown.



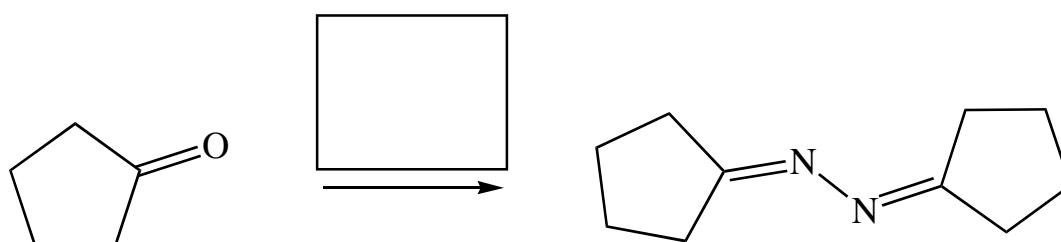
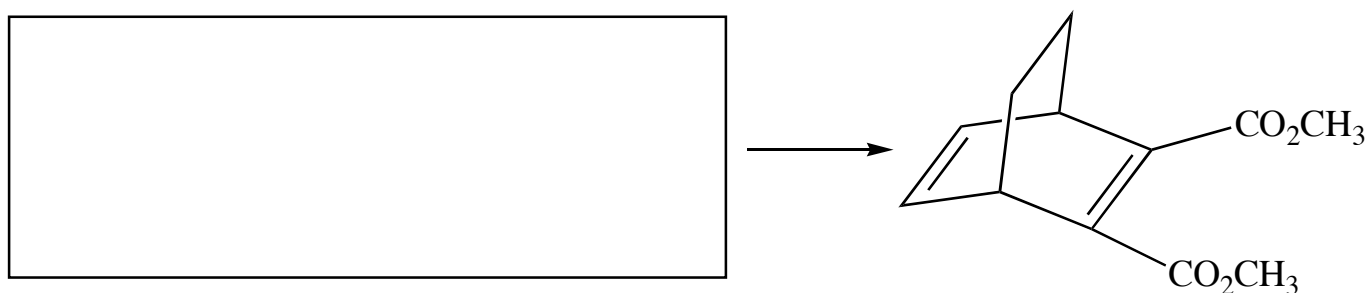
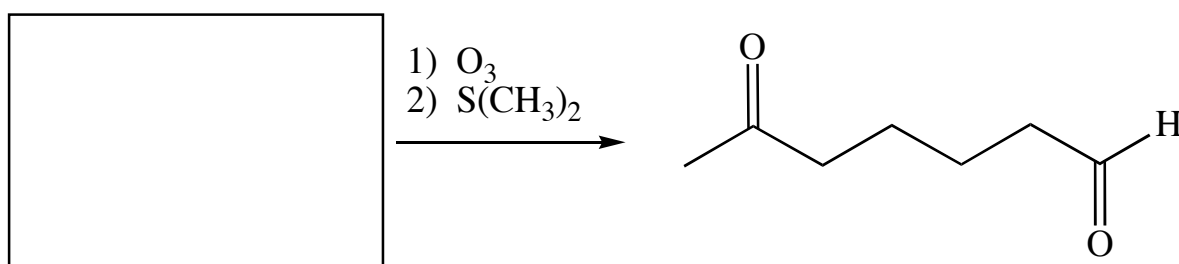
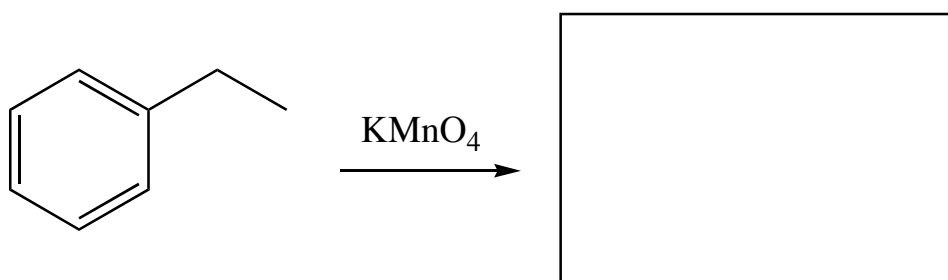
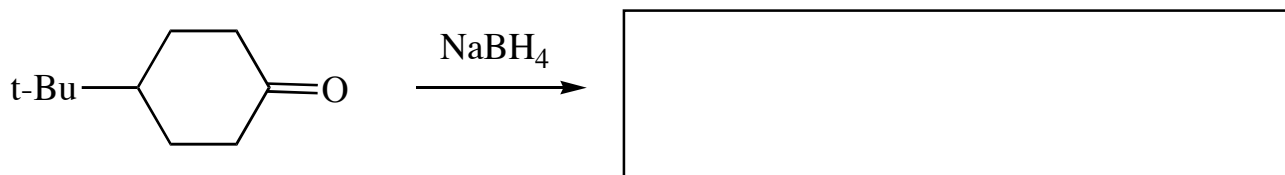
- Why is this protection necessary?
- Why is the cyclic product formed and not the expected product?
- Is Fred toast? What should he do?
- Propose a mechanism for the formation of the cyclic “actual product”.

**Question Nine (five marks)**

Offer a mechanism for the following reaction.

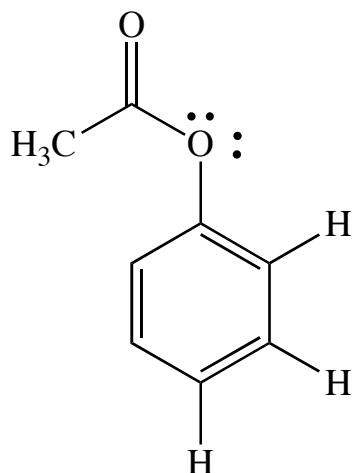
**Question Ten (nine marks)**

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 Eleven (six marks)**

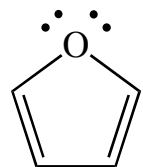
i) Would electrophilic aromatic substitution of the following compound give predominantly meta, or ortho/para products? Explain your reasoning based on the mechanism of electrophilic aromatic substitution.



ii) Explain your reasoning based on the chemical shift effect exhibited by this substituent on the protons of the benzene ring.

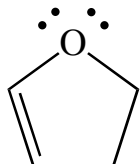
**Question Twelve (nine marks)**

a) Sketch the pi MO diagram for the molecule furan and use it to predict whether furan is aromatic or antiaromatic.



Furan

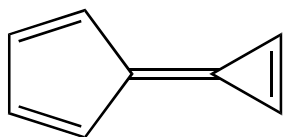
b) The calculated heat of hydrogenation of furan is -51.2 kcal while that of dihydrofuran is -28.6 kcal. Calculate the resonance energy of furan.



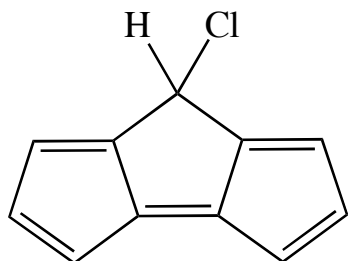
Dihydrofuran

c) Use aromaticity arguments to rationalize why...

i) this molecule has a substantial net molecular dipole



ii) this molecule undergoes SN1 reactions many orders of magnitude faster than expected.



**Question Thirteen: 3 x 3 = nine marks. I will take your best three.**

Propose syntheses of the following molecules. As starting materials, you may use benzene, toluene 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.

