Fall 2017 **Chemistry 2600 Midterm I**

INSTRUCTIONS:

1) Please read over the exam carefully before beginning. This exam consists of 7 questions.
2) You have also been given a Spectral Data Booklet. **Please do not write on theses data sheets!** If you need scrap paper, use the back of the cover page or the back of the last page.
3) You may use a molecular model kit and a ruler. You may not have any papers or other written materials in your model kit.
4) No electronic devices can be present with you during the exam unless authorized by the instructor.
5) If your work is not legible, it will be given a mark of zero.
6) Marks will be deducted for incorrect information added to an otherwise correct answer.
7) You have 2 hours to complete this exam.
8) Most of the marks on the exam are for explaining/showing your work rather than for reaching the correct answer. Explain all of your answers fully. Hint: Figures really are worth a thousand words! If you are using a resonance argument to make a point, you must show the pertinent structures.
9) Marks will be deducted for poorly drawn structures.
10) Although complete sentences are not required (point form is acceptable), marks will be deducted for poor spelling and grammar.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until they have all been marked and returned. I understand that, if I were to break this agreement, I would be choosing to commit academic misconduct, a serious offense which will be punished. The minimum punishment would be a mark of 0% on this exam and the maximum punishment would include expulsion from this university.

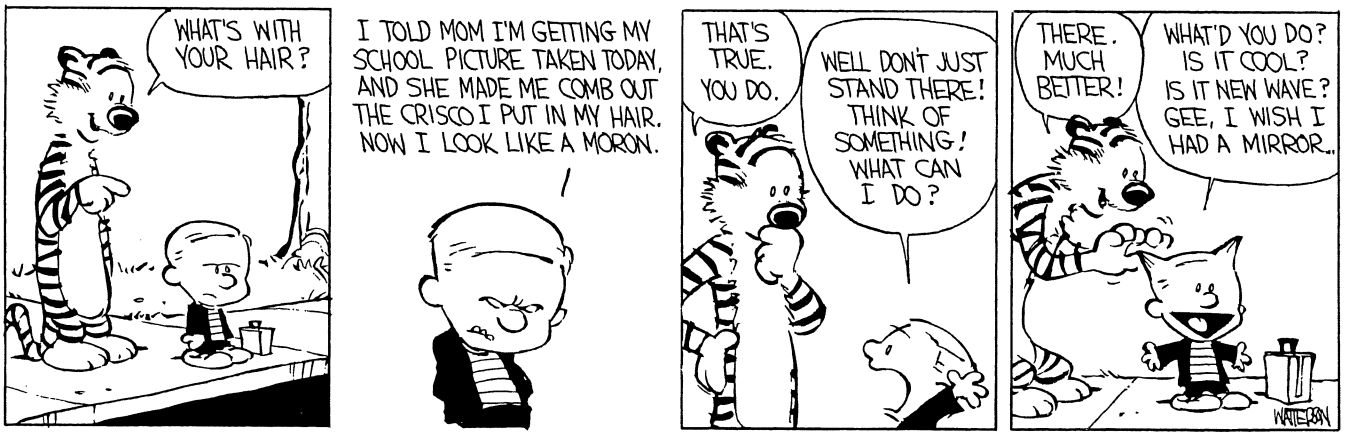
Signature: _____ Date: _____

Course: CHEM 2600 (Organic Chemistry II)
Semester: Fall 2017
The University of Lethbridge

KEY

Question Breakdown

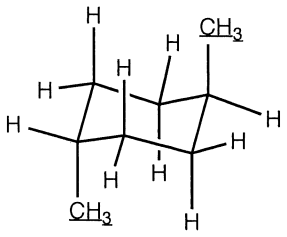
Q1	**/8**
Q2	**/4**
Q3	**/10**
Q4	**/25**
Q5	**/6**
Q6	**/6**
Q7	**/6**
Total	**/65**



Chem 2600 Midterm #1
October, 2017

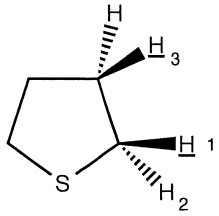
Question One (8 marks)
Referring to the structures below, are the underlined atoms/groups homotopic, enantiotopic, diastereotopic or none of the above? No explanation is required.

a)



CH_3 and CH_3 HOMOTOPIC

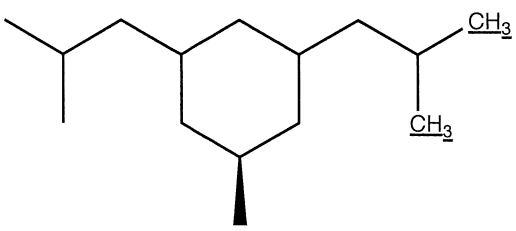
b)



H_1 and H_3 NONE OF THE ABOVE

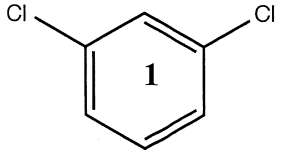
H_1 and H_2 ENANTIOTOPIC

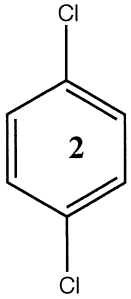
c)

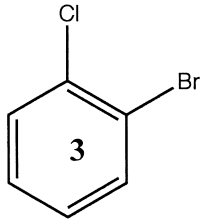


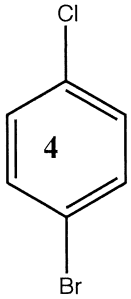
CH_3 and CH_3 DIASTEREOTOPIC

Question Two (4 marks)
How could you distinguish between the following 4 molecules using only ^1H decoupled ^{13}C NMR ($^{13}C\{^1H\}$) and ^{13}C DEPT 135 NMR (CH and CH_3: ↑, CH_2↓, quaternary C not observed)?





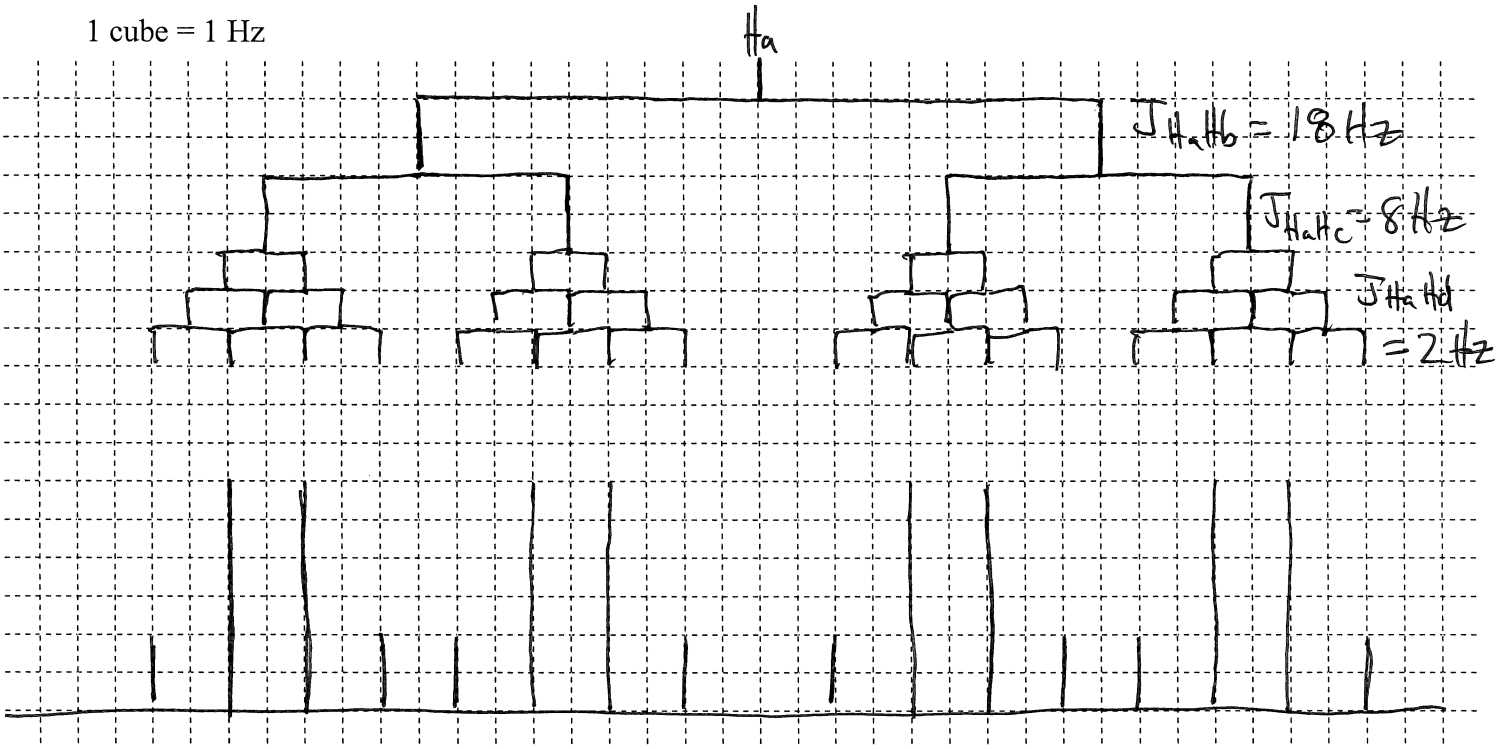




^{13}C NMR	4 peaks	2 peaks	6 peaks	4 peaks
^{13}C DEPT NMR	3 ↑ peaks	1 ↑ peak	4 ↑ peaks	2 ↑ peaks

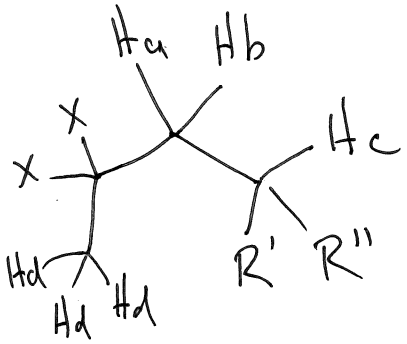
Question Three (10 marks)

(a) Use the grid below and the provided scale to draw and label a ***complete*** tree diagram with accompanying spectrum for a doublet (18 Hz) of doublets (8 Hz) of quartets (2 Hz).



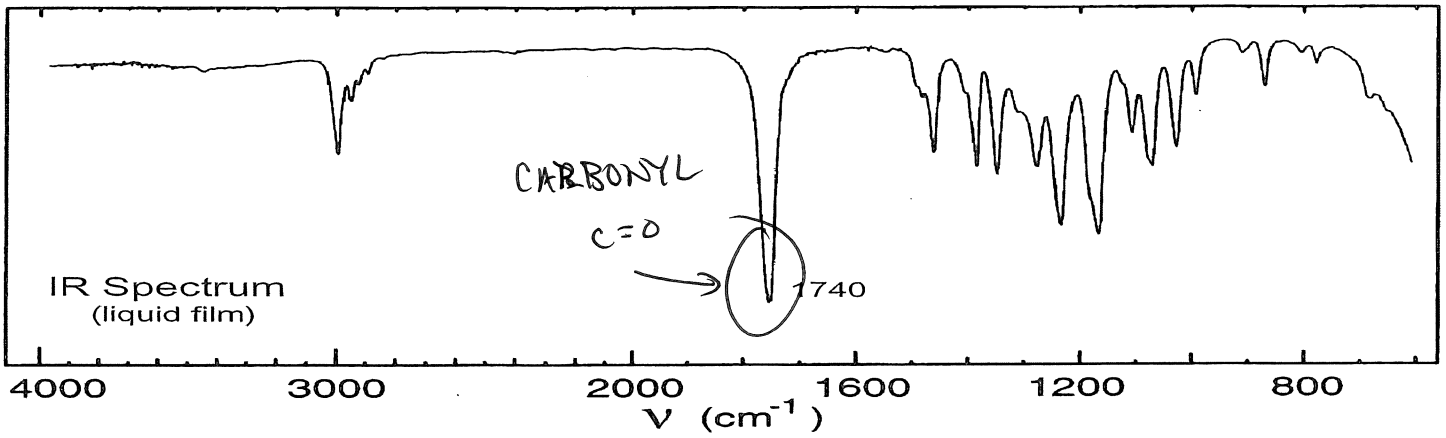
(b) Draw a molecule or part of a molecule containing a proton (Ha) which could give this doublet of doublets of quartets pattern. Make sure that your labels are consistent with those of your tree diagram.

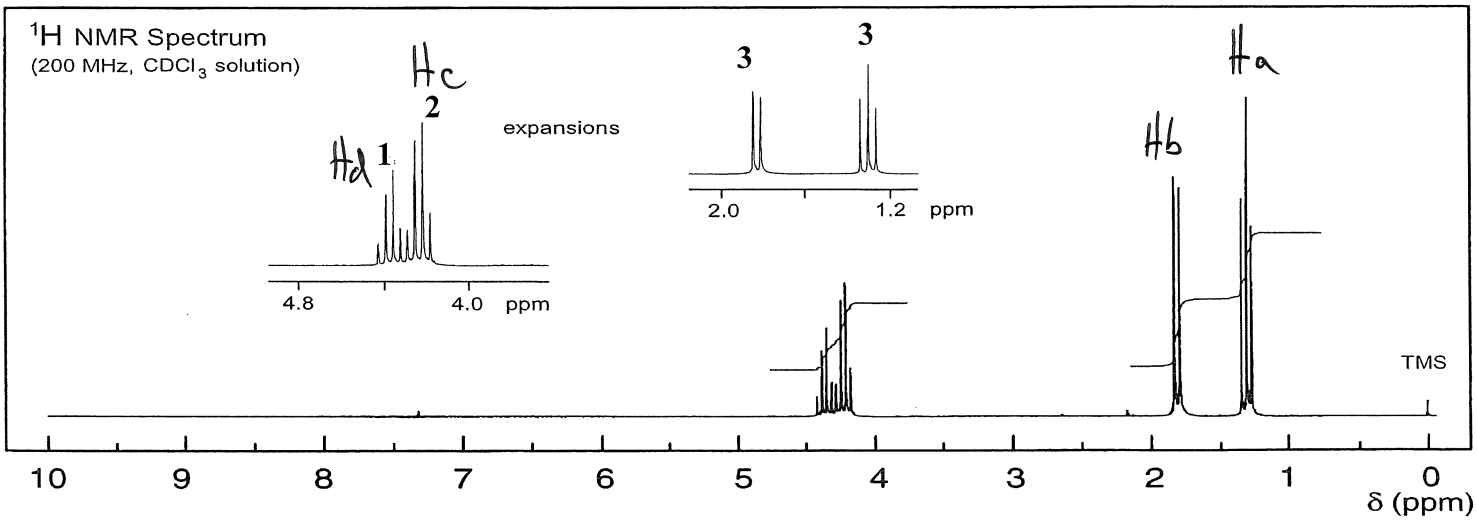
one possibility:

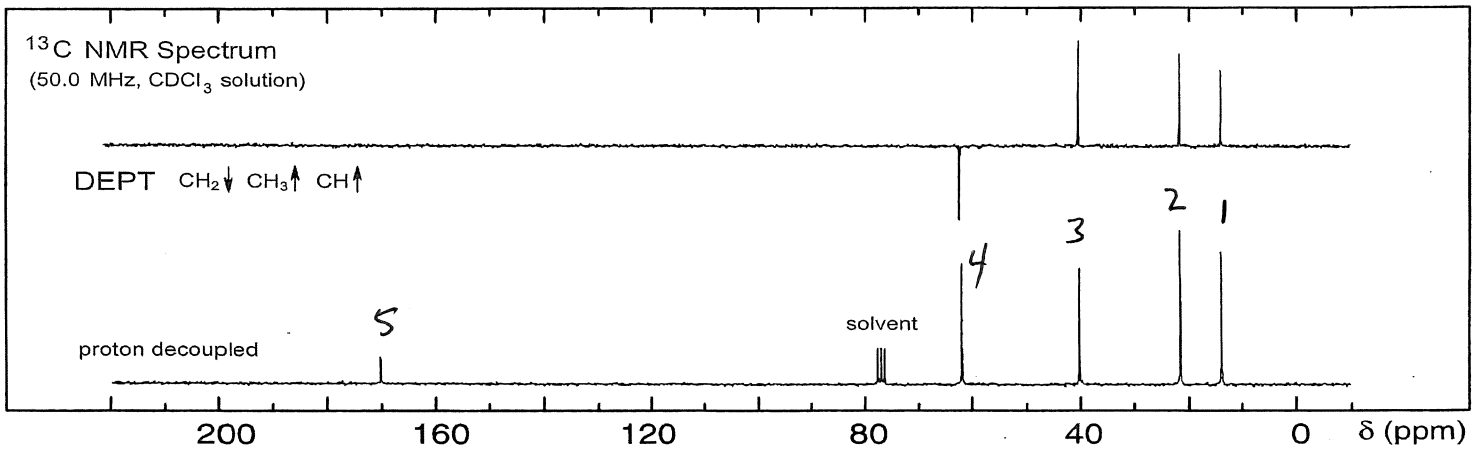


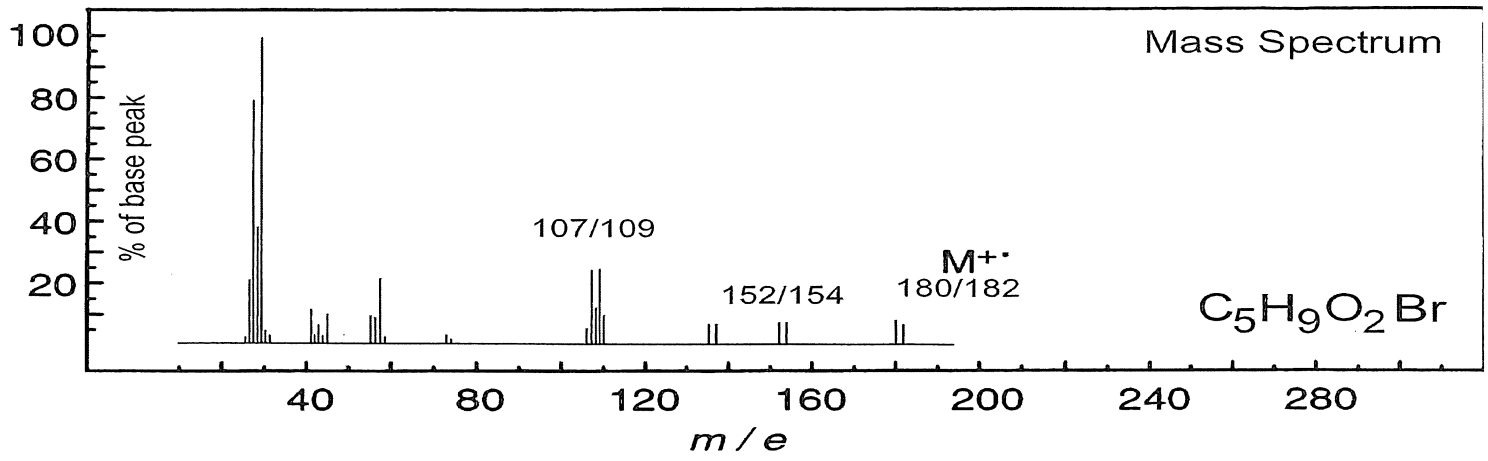
Question Four (25 marks)

- Using the following spectra, deduce the structure of this unknown molecule with a molecular formula of $C_5H_9O_2Br$.
- **Label each peak** on each NMR spectrum (^1H and ^{13}C) as much as is possible and label any important IR bands.
- In the Mass Spectrum, identify and explain the origin of the two peaks at 107/109 amu and 180/182 amu.
- Explain all the logic you used to determine the structure of the unknown molecule.









(question four con't)

$C_5H_9O_2Br$ $\quad DU = 5 - \frac{9}{2} - \frac{1}{2} + 1$

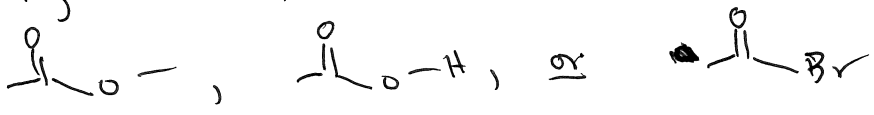
$= 5 - \frac{10}{2} + 1$

$= 5 - 5 + 1$

$= 1$

IR

- In the IR we can clearly see a carbonyl stretch. This is confirmed by the peak @ ~170ppm in the ^{13}C NMR. Because this peak appears @ 170 ppm we can rule out an aldehyde or ketone as these usually appear at 190+ ppm. Our choices would be ester, carboxylic acid, or acid bromide.



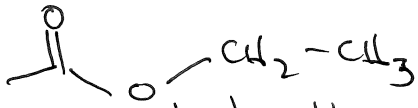
we can rule out the carboxylic acid as there is no peak @ 12-13ppm in the ^1H NMR as well as the -OH stretch in the IR.
Also note that there is no aldehyde peak (9-10 ppm) in the ^1H NMR, definitively ruling out aldehydes.

Thus 

The presence of the carbonyl group also accounts for our degree of unsaturation.

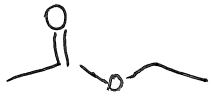
'H NMR • 'H NMR shows 4 distinct peaks, a triplet, a doublet, and 2 quartets.

- A triplet & quartet, which integrate to 3 & 2 respectively, strongly indicate the presence of an ethyl group. $-CH_2-CH_3$. Also, the chemical shift of the $-CH_2-$ group (quartet) is above 4 ppm, strongly suggesting that it is attached to an electronegative group. Oxygen maybe?



this is consistent as the $-CH_3$ group (triplet) is slightly above 1 ppm feeling some effects of the oxygen atom.

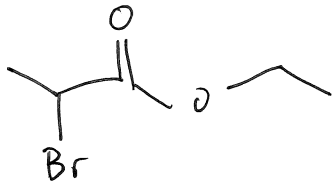
Therefore: most likely have an ester, not acid bromide, with an ethyl group attached to the oxygen atom.



- the remaining 2 peaks are a doublet integrating to 3 and a quartet integrating to 2. this strongly suggests a methyl group attached to a methine group: CH_3-CH-

Because the methine proton is so downfield (~4.4 ppm) it too is feeling some deshielding effects. The carbonyl group could account for this as well as the electronegative Br atom.

Therefore, piecing our molecule together we get:



The CH_3 group (doublet) also is deshielded slightly from the bromine atom & the carbonyl group.

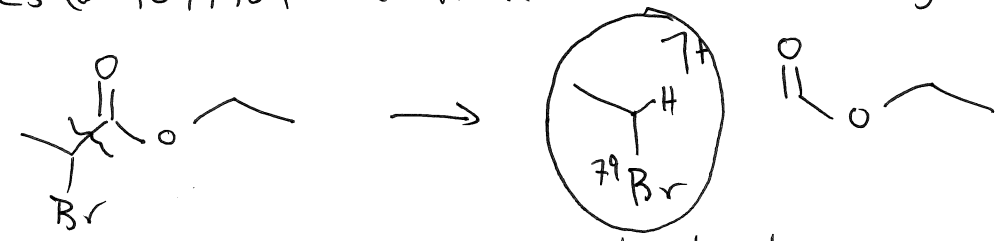
The molecule above is consistent in the coupling & chemical shifts from the 'H NMR.

13 NMR

- The ^{13}C NMR shows 5 distinct peaks which is also consistent in our molecule.
- A peak @ 170 ppm is due to the carbonyl carbon. The other 4 peaks appear between 0–70 ppm, consistent for $-CH_3$, $-CH_2-$, & $-CH$ groups.
- The 2 $-CH_3$ groups appear @ ~13 & 22 ppm. The $-CH$ group appears @ 40 ppm and the $-CH_2-$ group @ ~61 ppm
- This is also consistent in the ^{13}C DEPT NMR. The carbonyl peak should disappear in the ^{13}C DEPT & does. The $-CH_2-$ group points down & the $-CH_3$ groups & $-CH$ group point up.

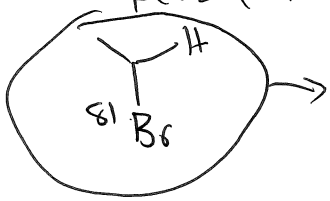
Mass Spec:

- The peaks at 180/182 are due to the molecular ion. The reason there are 2 peaks is from the 2 isotopes of Br. The molecular ion w ^{79}Br gives the peak at 180 amu and the peak @ 182 amu is the molecule with ^{81}Br.
- The peaks @ 107/109 are from the cationic fragment shown below

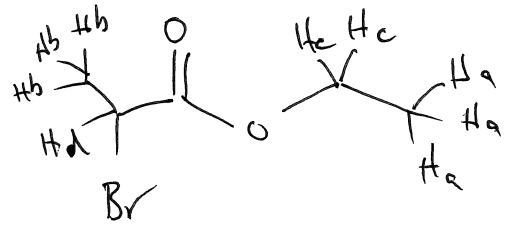


↳ this has a mass of 107 amu

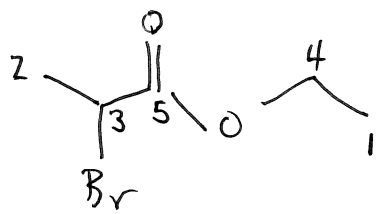
The peak @ 109 is from the same fragment but with the ^{81}Br isotope



→ 109 amu.



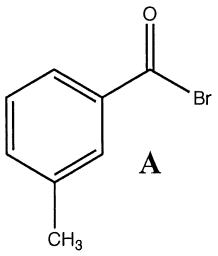
^1H



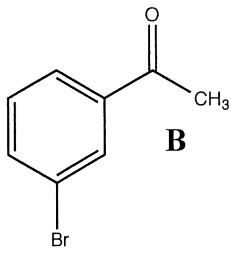
^{13}C

Question Five (6 marks)

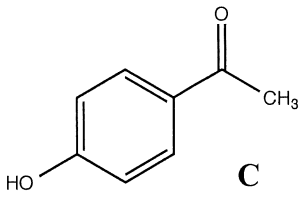
In the boxes provided, label the ^{13}C NMR spectra (**1-6**) with the matching letter of the correct chemical structure (**A-F**). No explanation is required.



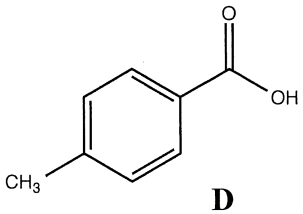
A



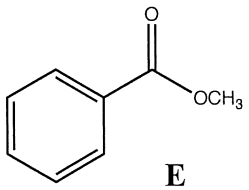
B



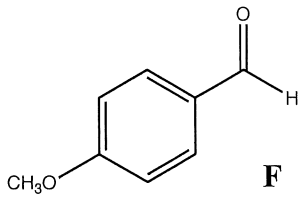
C



D

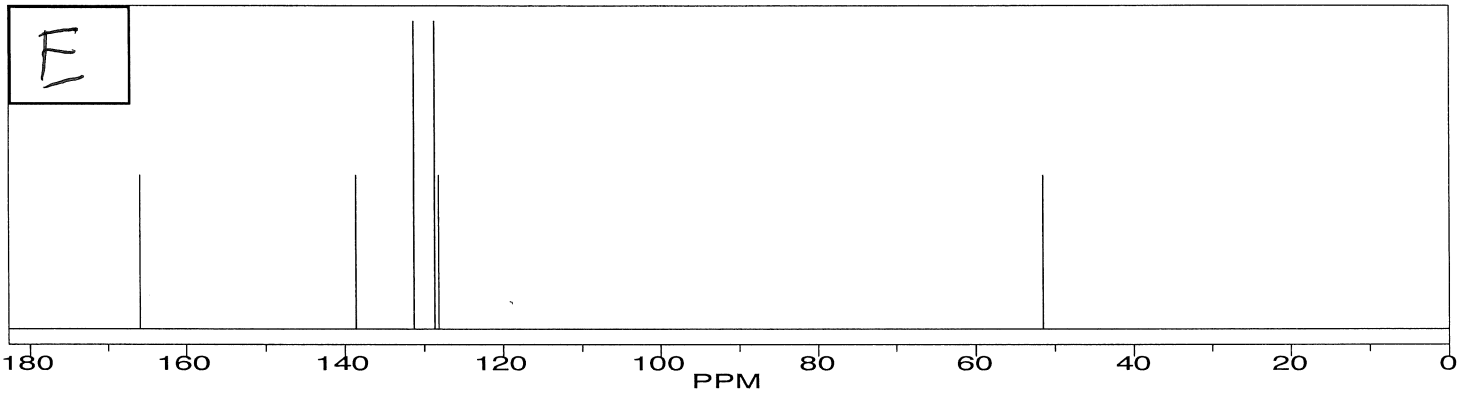


E

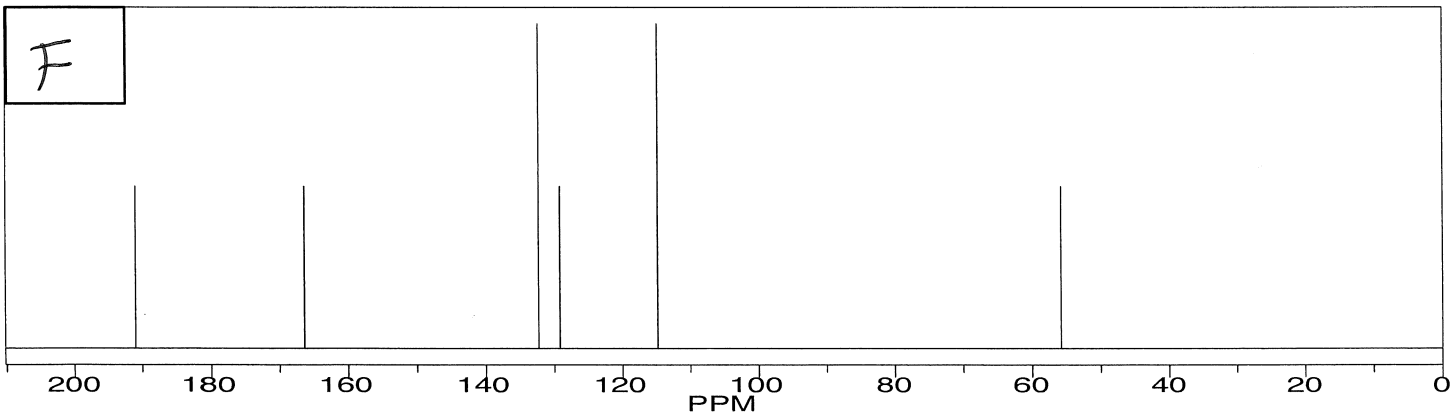


F

spectrum 1:

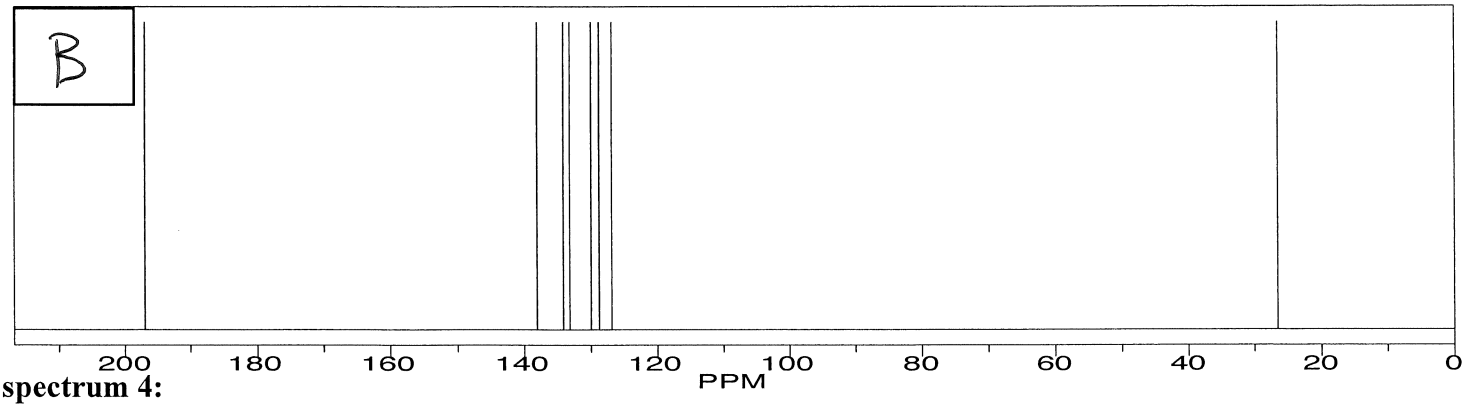


spectrum 2:

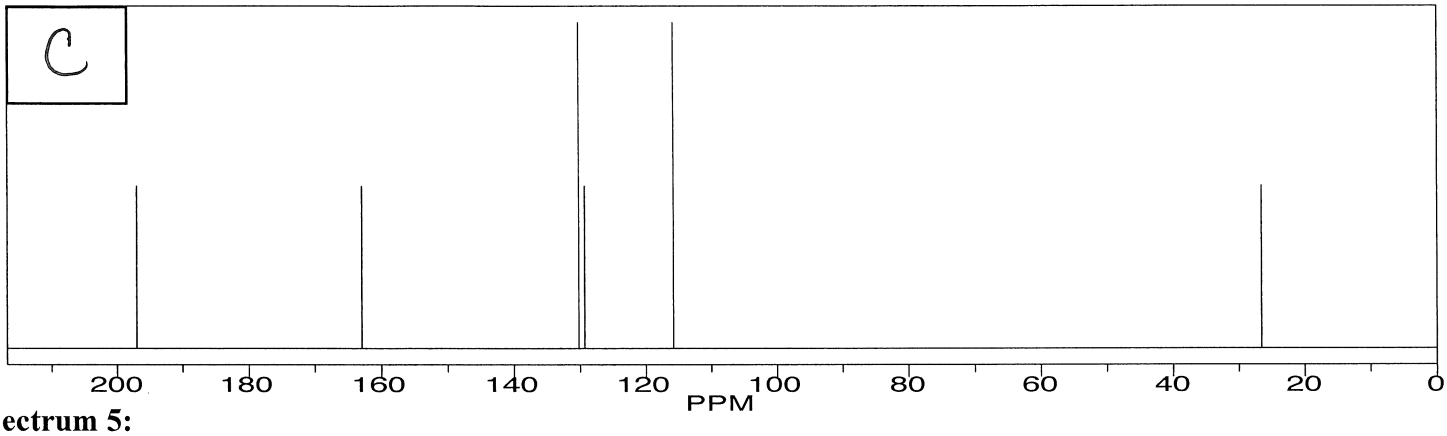


(question five con't)

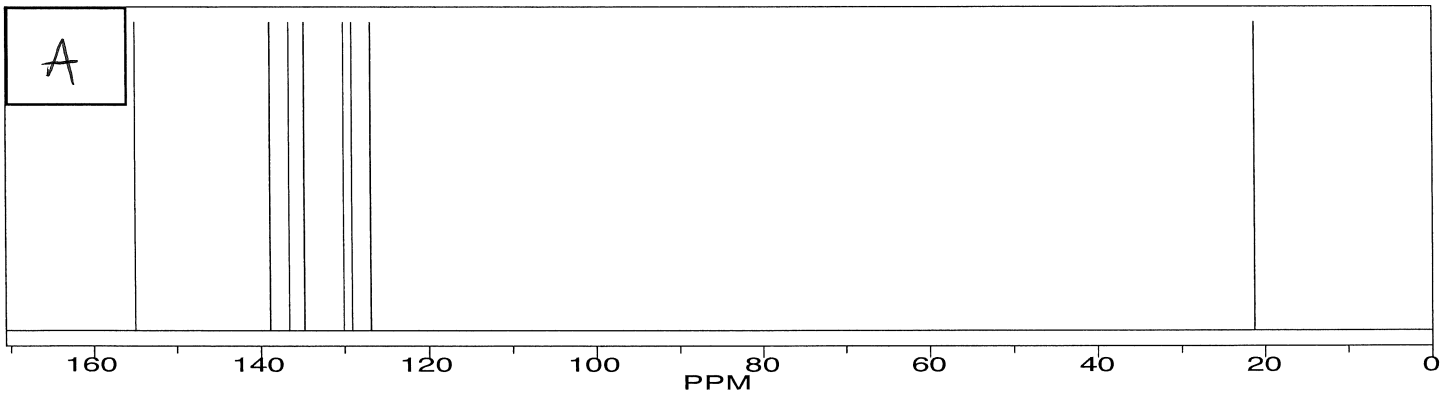
spectrum 3:



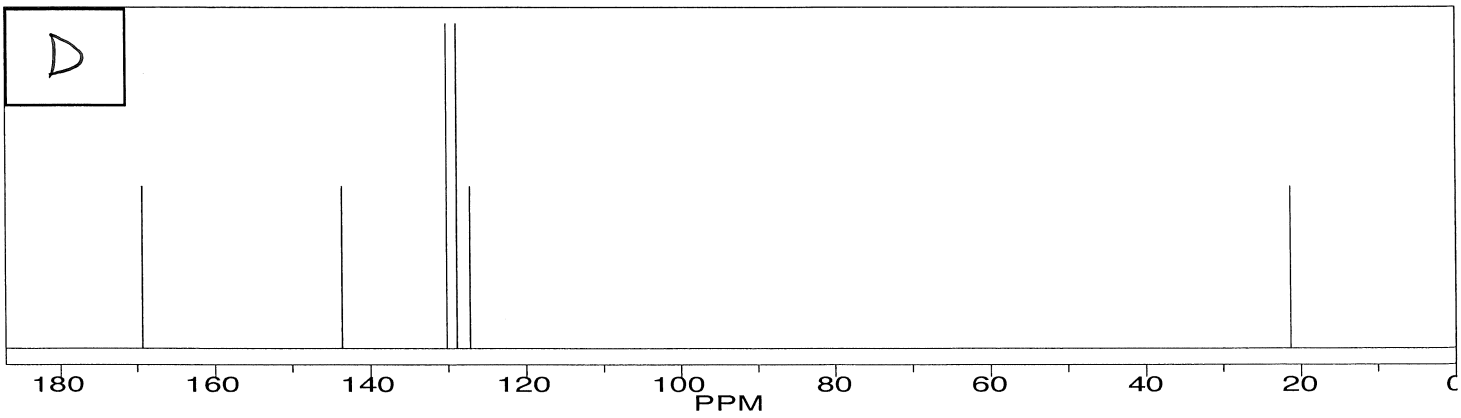
spectrum 4:



spectrum 5:



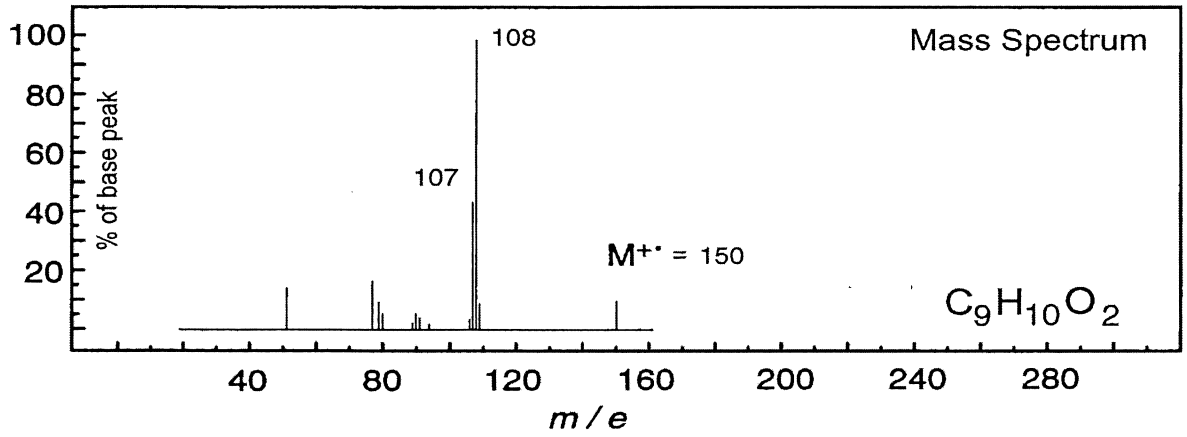
spectrum 6:

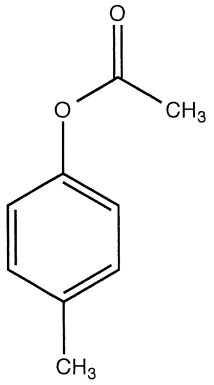


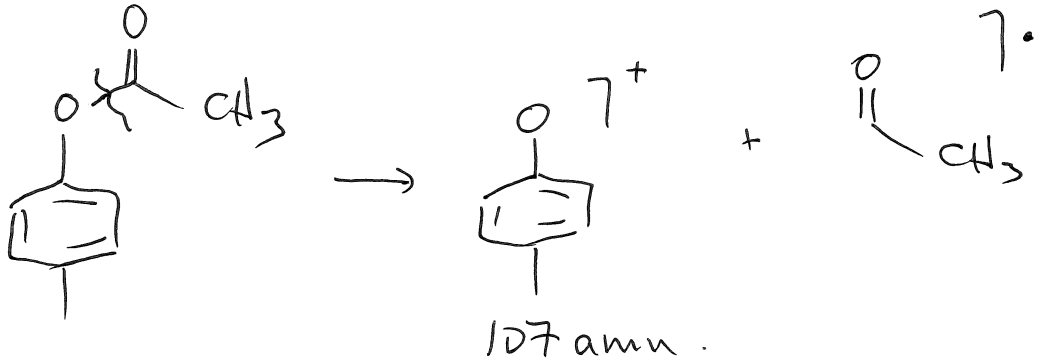
Question Six (6 marks)

Consider the structure of *p*-tolyl acetate and its Mass Spectrum shown below.

- Give the structure of the fragment giving the peak at 107 amu.
- The peak at 108 amu is due to a McLafferty rearrangement. Give the structure of the rearrangement product and show the mechanism of its formation.

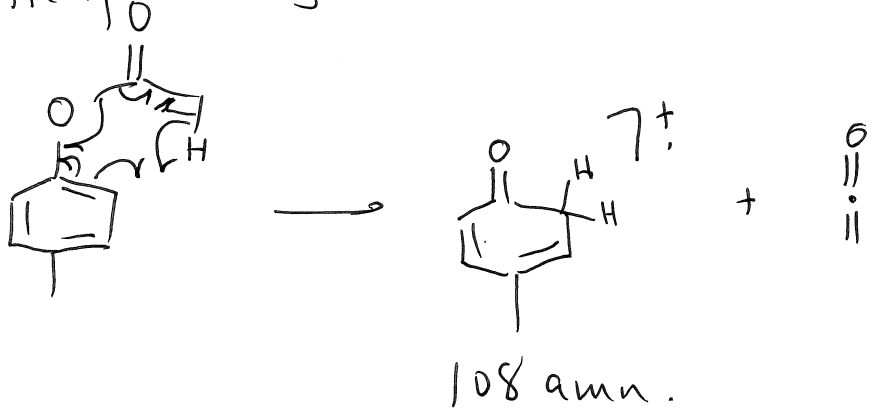






107 amu.

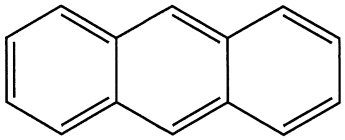
McLafferty rearrangement:



108 amu.

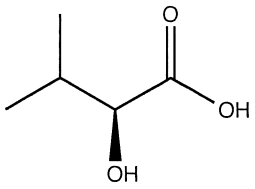
Question Seven (6 marks)
How many ^{1}H signals and how many ^{13}C signals would you expect from each of the following molecules? No explanation is required.

(a)



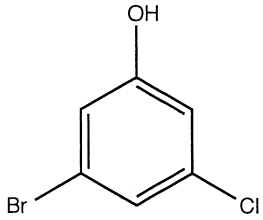
$^{1}H =$ 3 $^{13}C =$ 4

(b)

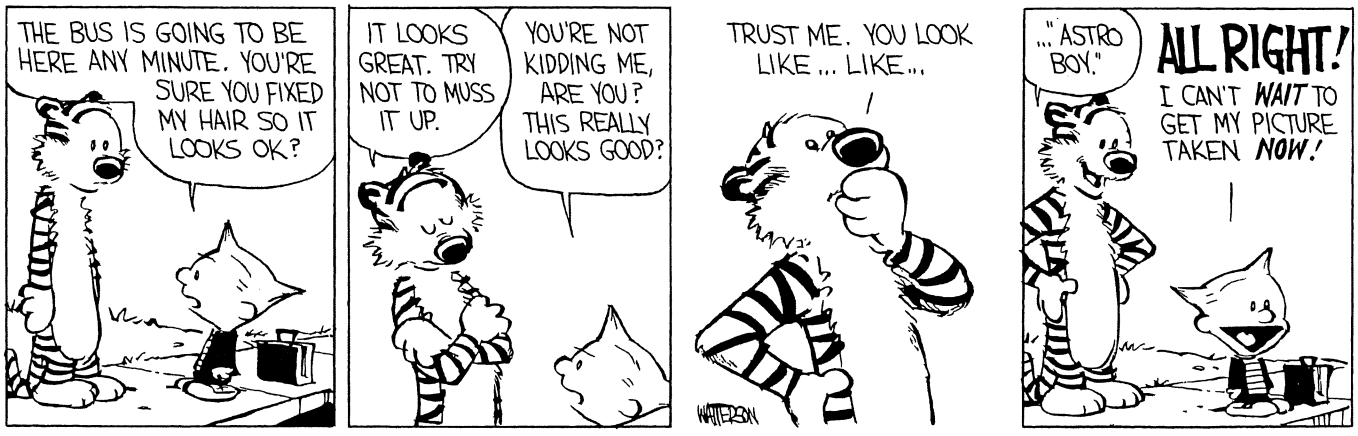


$^{1}H =$ 6 $^{13}C =$ 5

(c)



$^{1}H =$ 4 $^{13}C =$ 6



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Course: CHEM 2600 (Organic Chemistry II)
Semester: Fall 2017
The University of Lethbridge

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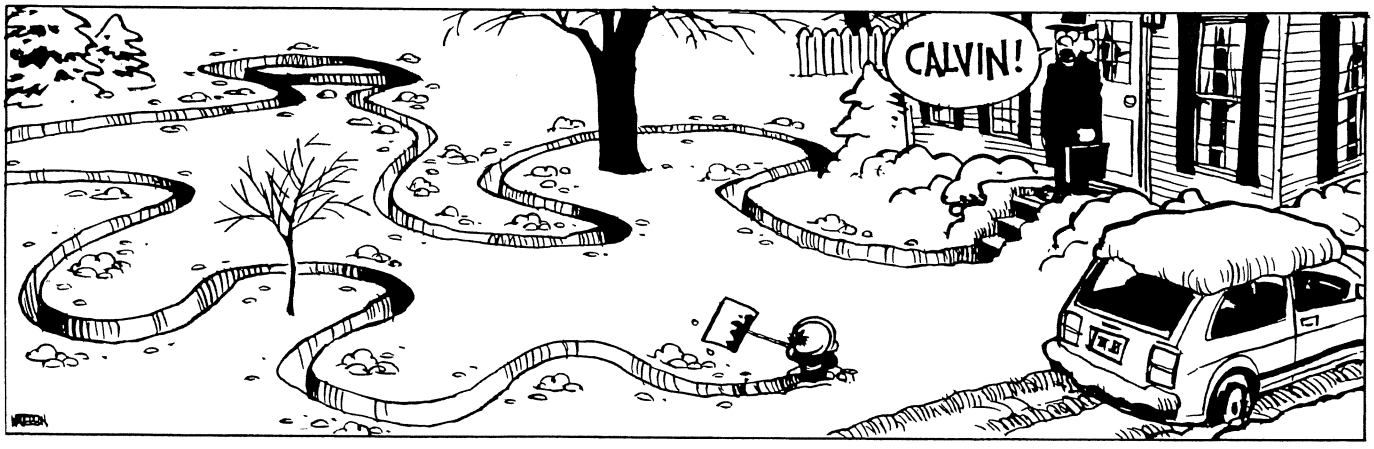
Q6	**/12**
Q7	**/6**
Q8	**/4**
Total	**/50**



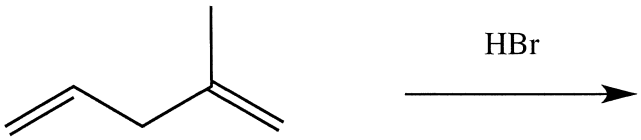
Chem 2600 Midterm #2
November, 2017

Question One (6 marks)
We learnt in class that the addition reaction of alkenes follows Markovnikov's rule.

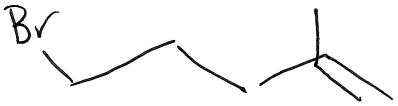
(a) Briefly define Markovnikov's rule.

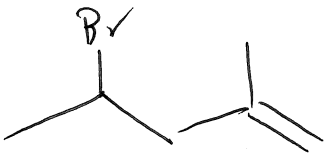
Add^n reactions proceed via the most stable carbocation.

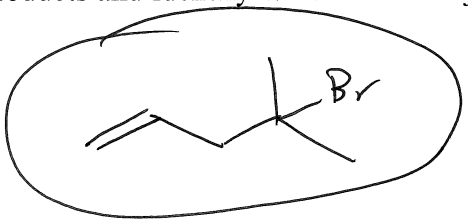
(b) Consider the addition reaction of HBr to the following alkene:



Draw the structure of the 4 different possible products and identify which is the major product. Briefly explain your choice.

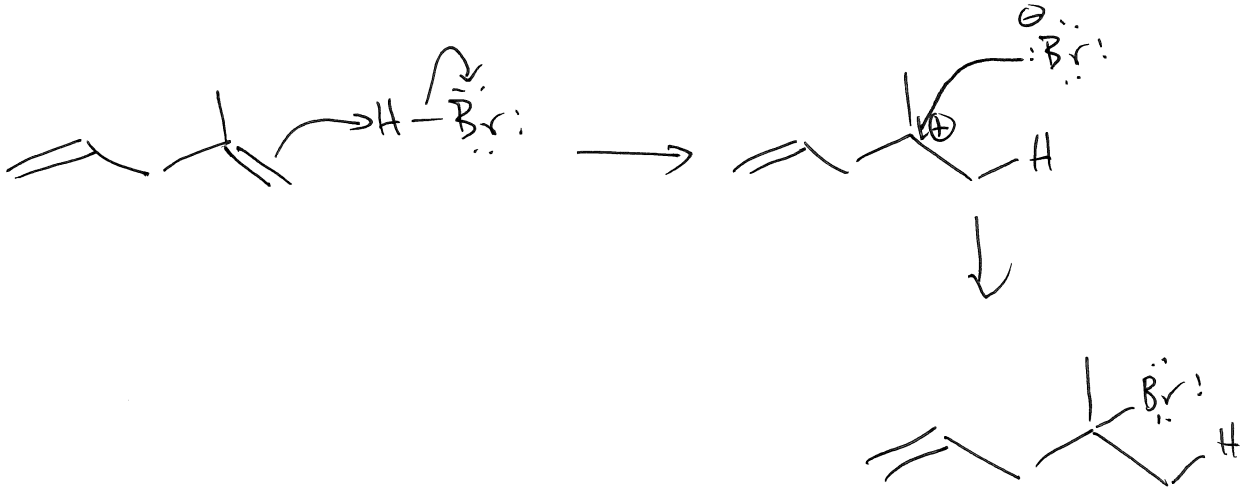






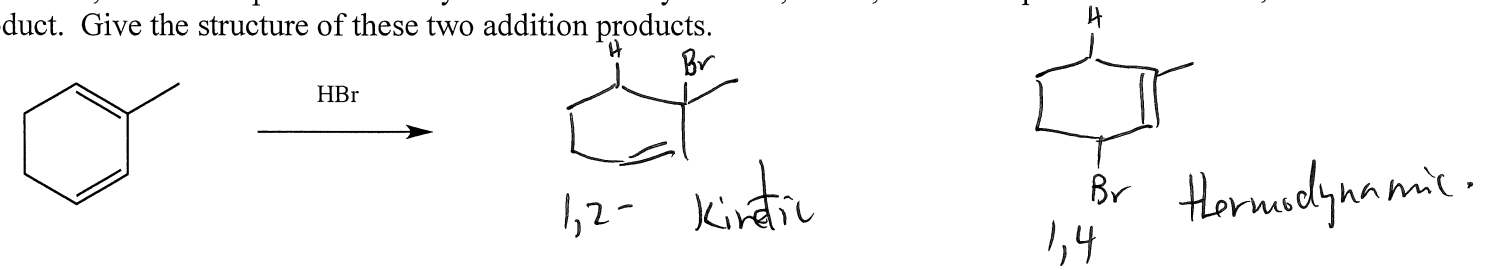
This is the major product b/c it proceeds via a 3° carbocation. Other products proceed via 1° or 2° carbocation.

(c) Draw the mechanism (show the movement of electrons) for the formation of the major product only.



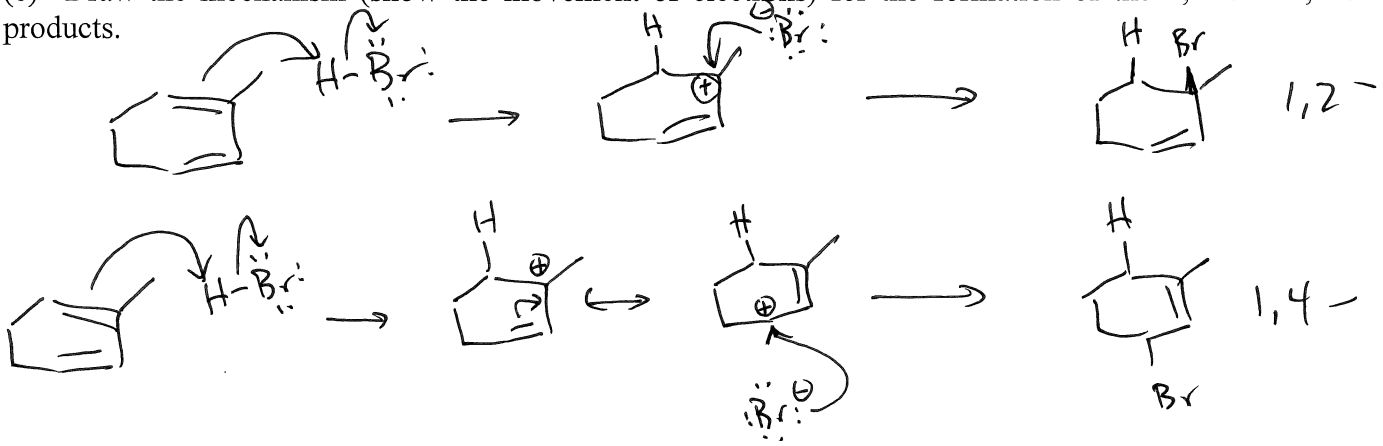
Question Two (6 marks)

(a) In the addition of HBr to the following conjugated diene there are, in principle, several different possible 1,2- and 1,4- addition products. Only two are actually formed; one 1,2-addition product and one 1,4-addition product. Give the structure of these two addition products.



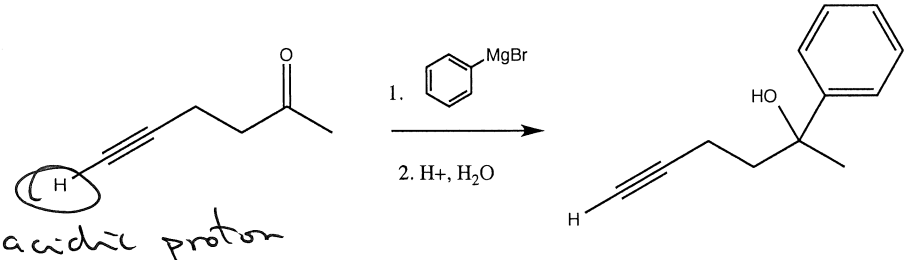
(b) Of the two addition products, identify which is the kinetic product and which is the thermodynamic product.

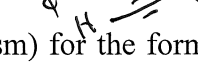
(c) Draw the mechanism (show the movement of electrons) for the formation of the 1,2- and 1,4-addition products.



Question Three (5 marks)

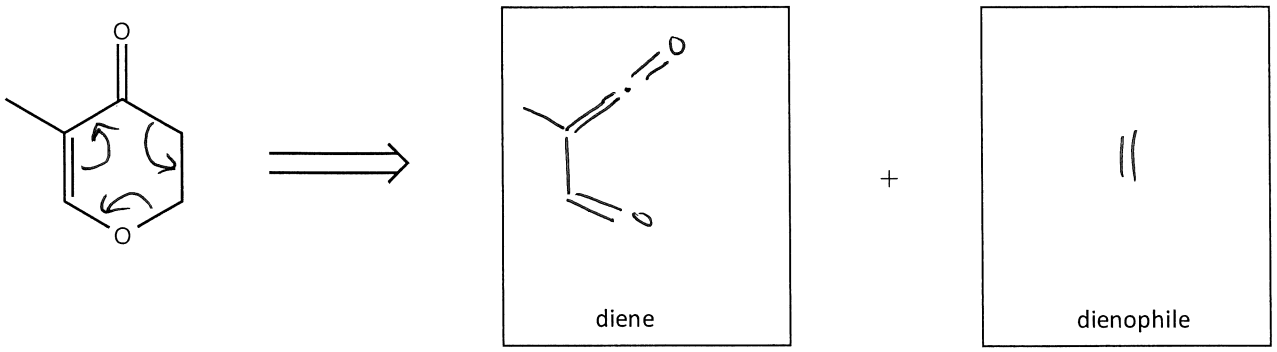
Al Kane proposes to do the following Grignard reaction but it does not work as planned.



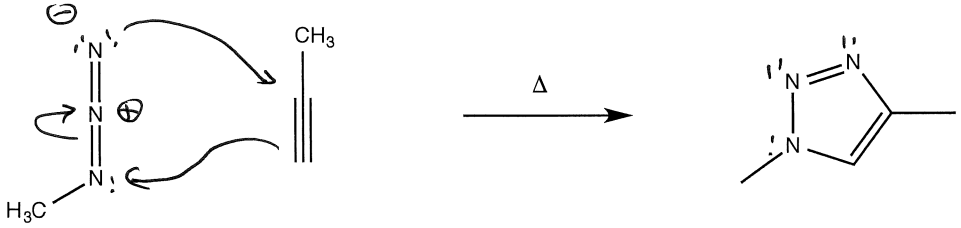
(a) Briefly explain why the reaction does not work as planned. Draw the structure of the product that is actually produced. The rxn does not work bc there is a relatively acid proton present and the Grignard reagent is a strong base which would deprotonate the proton. After adding H⊕ to the soln it would have  &  in soln.

(b) Write the reaction equation (not mechanism) for the formation of the Grignard reagent used by Al Kane. Include an appropriate solvent for the reaction.

Question Four (3 marks)
The following molecule can undergo a retro Diels-Alder reaction to give a diene and a dienophile. Add arrows to show the movement of electrons for the retro Diels-Alder reaction and draw the diene and dienophile in the space provided.

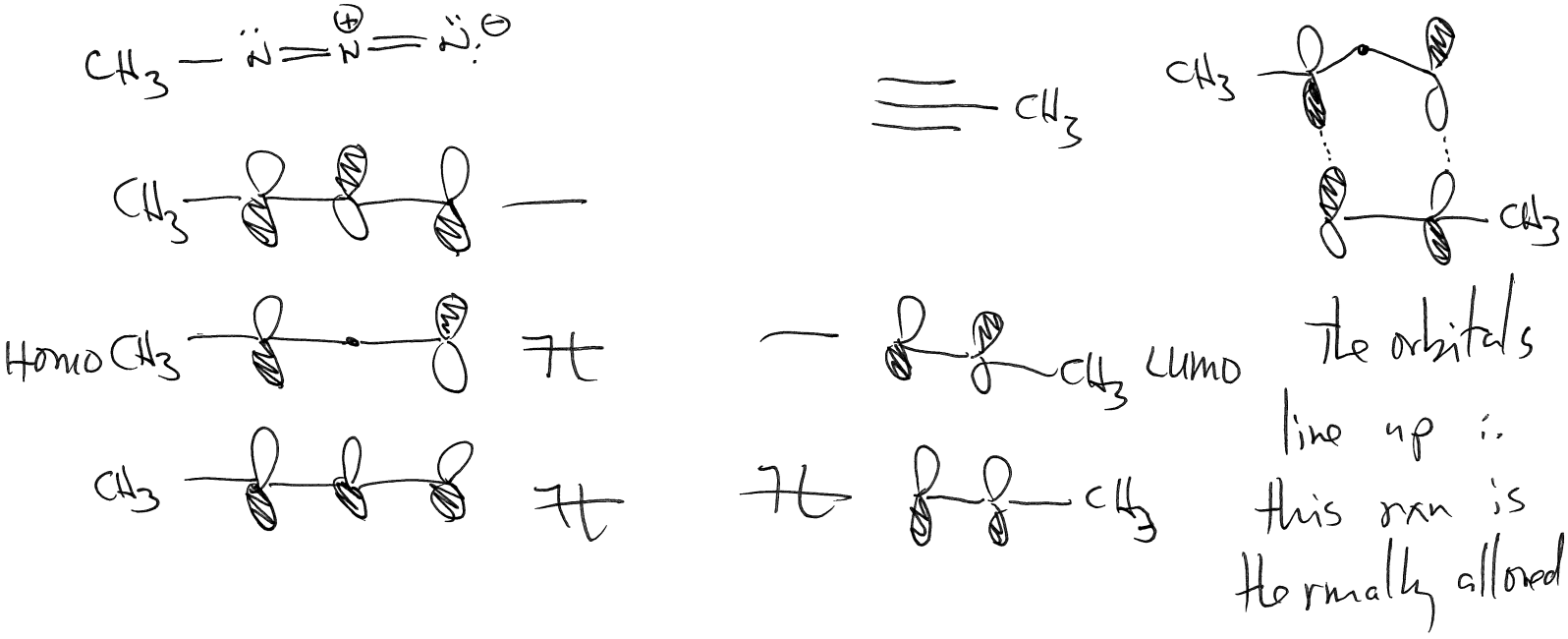


Question Five (8 marks)
Consider the following 1,3-dipolar cycloaddition reaction:



(a) Complete the Lewis structures of the reactants and product by adding any missing electrons and/or charges then add arrows to the reaction to show the movement of electrons.

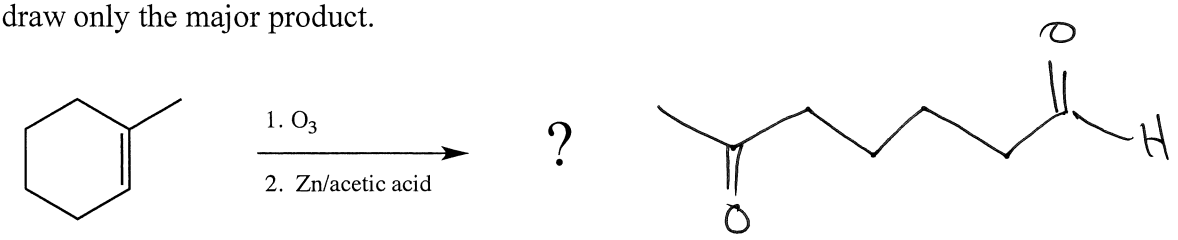
(b) Draw and label the HOMO and LUMO π–orbitals that are involved in this reaction. According to your orbitals, is this reaction thermally allowed or forbidden. Briefly explain.



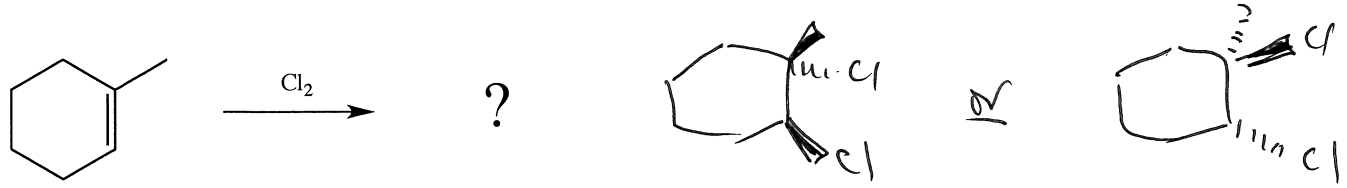
Question Six (12 marks)

For each of the following reactions, fill in the missing reactants, products or reagents. Be sure to include appropriate stereochemistry and/or regiochemistry where necessary. For reactions that give more than one product, draw only the major product.

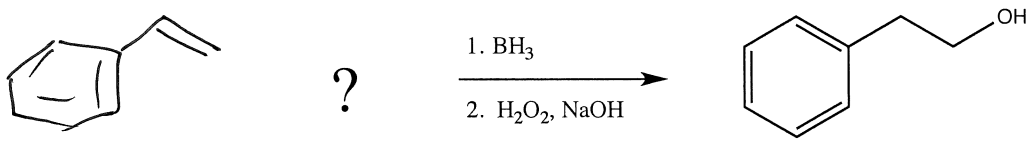
(a)



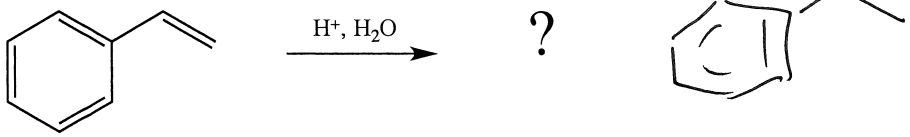
(b)



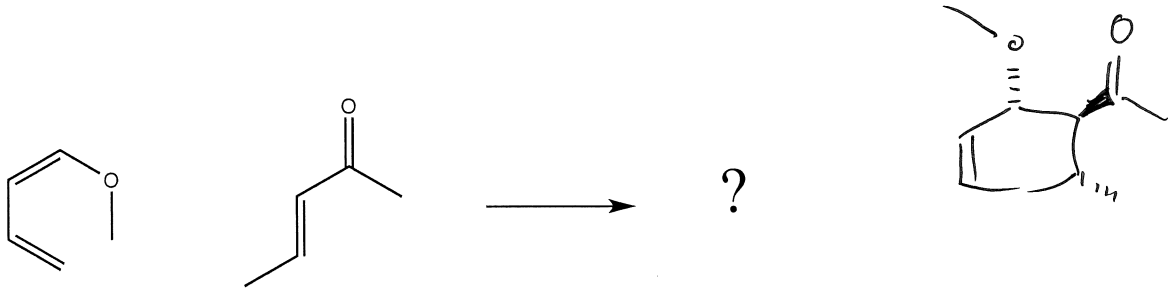
(c)



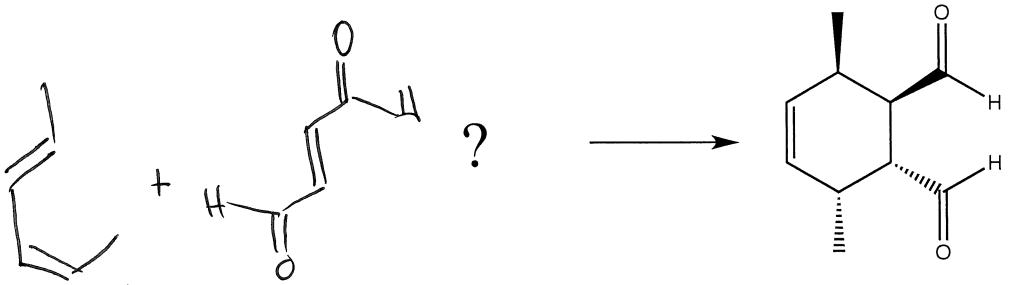
(d)



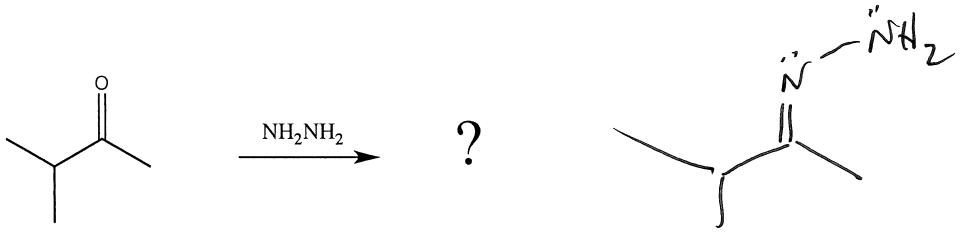
(e)



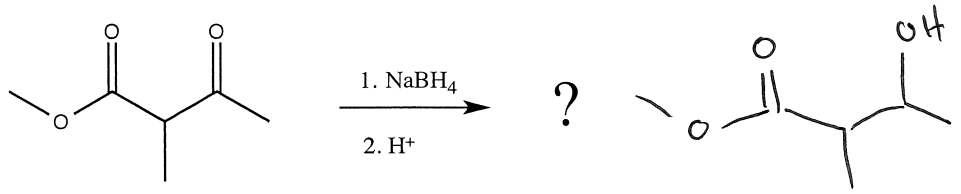
(f)



(g)



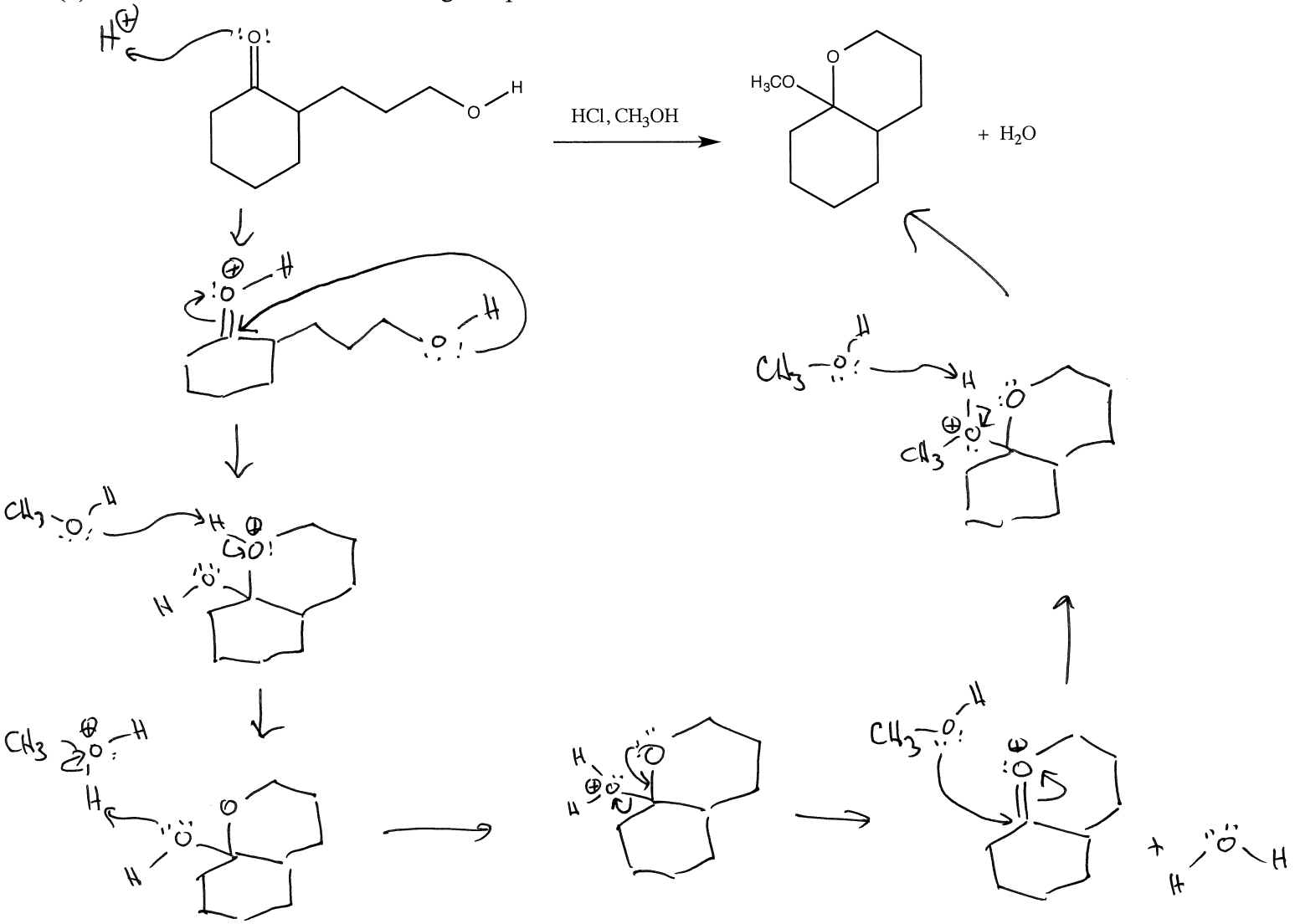
(h)



Question Seven (6 marks)

(a) Propose a reasonable mechanism (show the movement of electrons) for the following transformation. Be mindful of the reaction conditions and of your charges.

(b) What kind of molecule is the organic product?



Question Eight (4 marks)

Propose a synthesis (reaction equations only, no mechanisms) for the following molecule. You may use benzene or any other organic reagent of five carbon atoms or less (carbon atoms attached to the oxygen of esters do not count towards your carbon count), and any inorganic reagents needed.