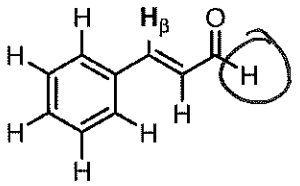
Part I: Short Answer (20 points)

Questions 1-3 refer to the structure below, which has all hydrogens explicitly drawn on it for clarity. The hydrogen β- to the carbonyl is labeled as such, and is referred to by Question 3.



*If circled 2 or more H then no credit

1. (Multiple Choice, 2 points) How many signals do you expect to see in the proton NMR?

a) 3

b) 4

c) 5

d) 6

e) 8

2. (2 points) Circle the hydrogen or hydrogens whose signal would appear the furthest **downfield** in the proton NMR.

3. (Multiple choice, 2 points) What should be the splitting pattern for H_β's signal?

a) singlet

b) doublet

c) triplet

d) quartet

e) pentet

4. NMR spectrometers are often described by a frequency. For example, this is a quote from the UD chemistry website: "The nuclear magnetic resonance (NMR) Laboratory of the Department of Chemistry and Biochemistry houses six state-of-the-art NMR spectrometers with operating frequencies ranging from 400 MHz to 850 MHz."

a) (2 points) What does this frequency refer to? Be specific.

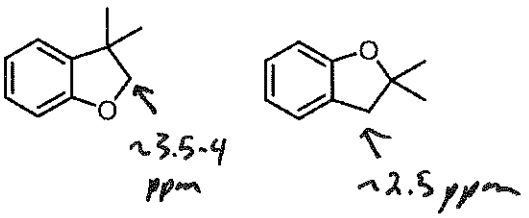
ν of photons that are absorbed by ^1H (protons)

b) (2 points) Which spectrometer would have a stronger magnetic field strength, a 400 MHz spectrometer or an 850 MHz?

c) (2 points) Give one advantage that NMR spectrometers with stronger magnets have over those with weaker magnets.

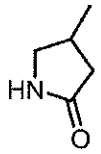
e.g. - greater sensitivity (α vs. β)
- size of $\Delta\delta$ w.r.t. J increases - better resolution
- fewer "2nd order" signals

5. (2 points) Explain how you could use proton NMR to distinguish between the two compounds below. Specifically, what key signal or signals will differ between the two spectra, and how?



6. Nomenclature (6 points)

a) Give a proper IUPAC name for the following compound:

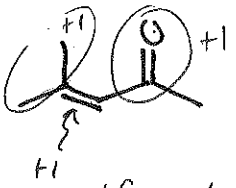


2-aza-4-methylcyclopentanone

1 1 1

+1 +1 +1

b) 4-methyl-3-penten-2-one is a common impurity in acetone. Provide its structure.

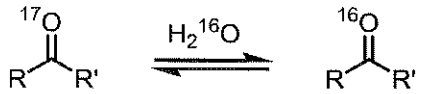


If cyclic: (-1/2)

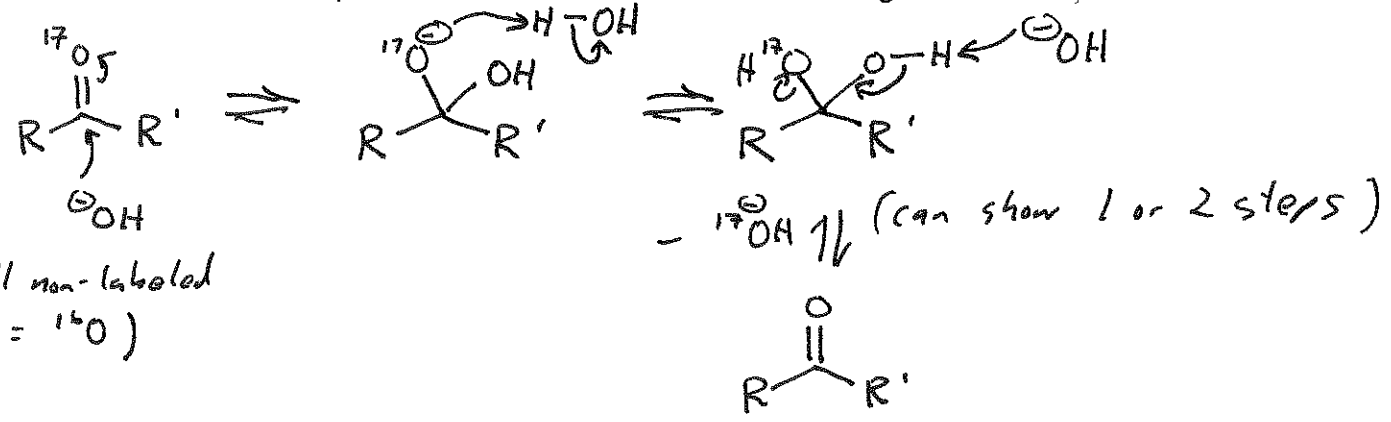
Part II: Mechanisms (25 points)

7. (6 points) Almost all oxygen found in nature is the isotope ^{16}O. The rare ^{17}O isotope can be used as a "label" to gain insight into reaction mechanisms. Whereas ^{16}O nuclei cannot be detected by NMR (spin = 0), ^{17}O can be (spin = 5/2).

The rate of hydrate formation as a function of pH was studied by following the rate of decay of the ^{17}O signal in isotopically-labeled aldehydes and ketones when dissolved in aqueous buffers:



Give a mechanism in aqueous base that accounts for this exchange of ^{17}O for ^{16}O.



(all non-labeled O = ^{16}O)

- ^{17}OH ½ (can show 1 or 2 steps)

2 per step

No lonepairs attacking: (-1/2)

If show correct O's getting protonated/~~attack~~ or attacking/deprotonated

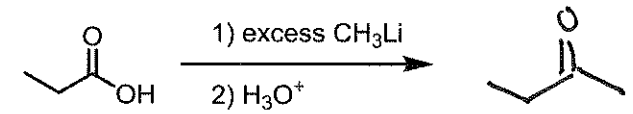
If No deprot. before O attacking, (-1) (+1)

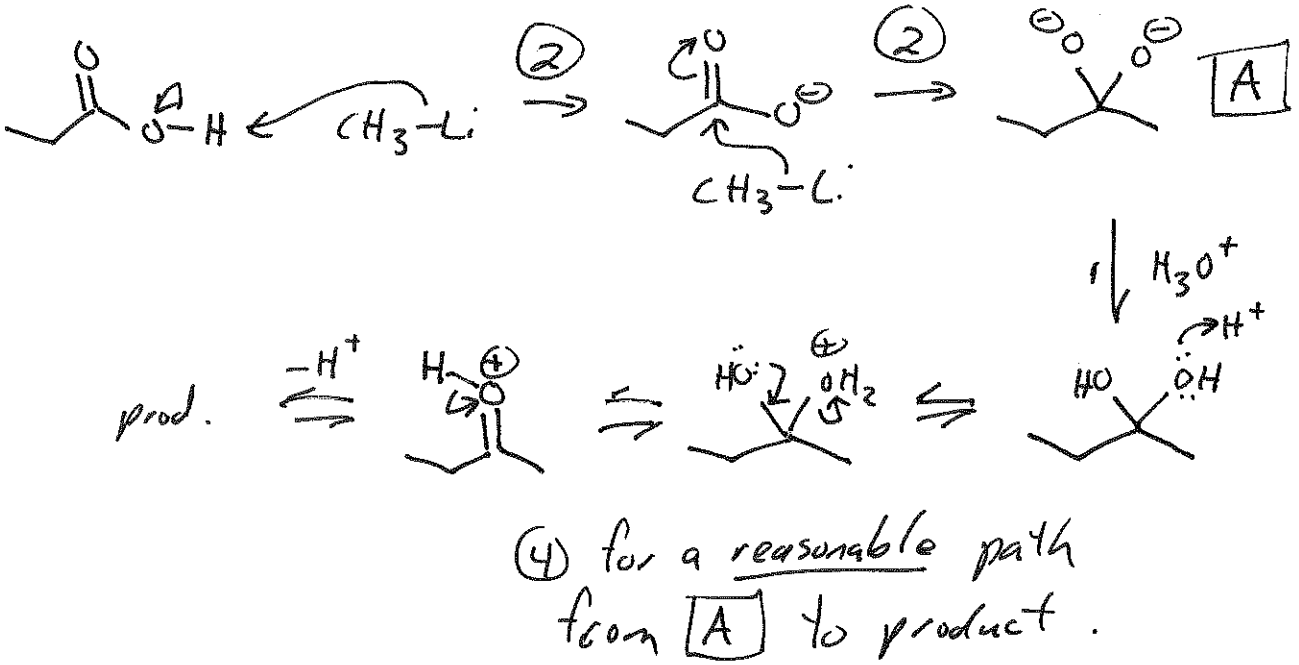
Acidic cond's: (-3) completely.

If show both acidic & basic: (-3)

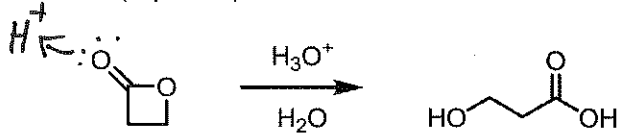
+/2 Total

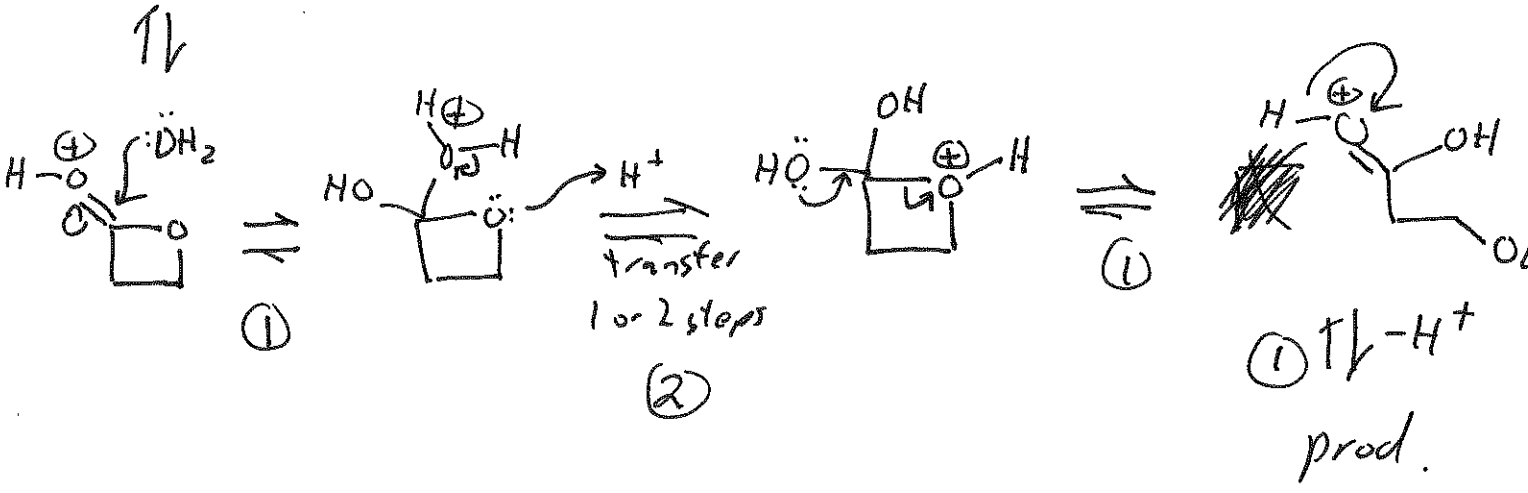
8. (8 points) Give the product of the following reaction, and provide a mechanism accounting for its formation.



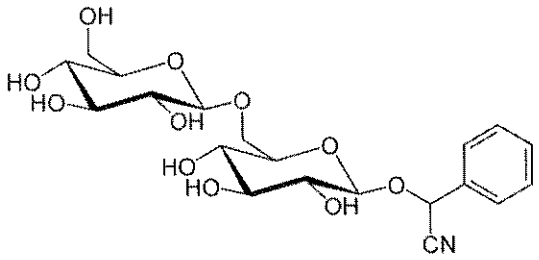


9. (5 points) Provide a mechanism for the following reaction:

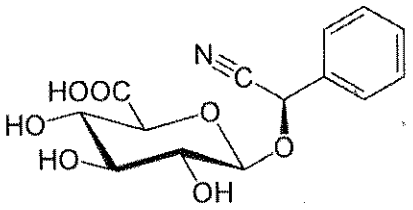




10. (6 points) Amygdalin is a compound found in the pits of peaches and apricots, as well as almonds. It, and a related compound laetrile, have been promoted as cancer cures, but there is no evidence for this and it is considered quackery by the scientific community. In fact, they liberate the poison hydrogen cyanide when ingested.

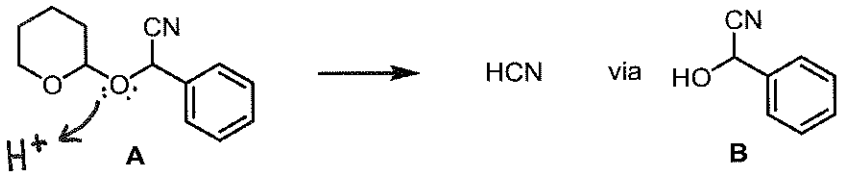


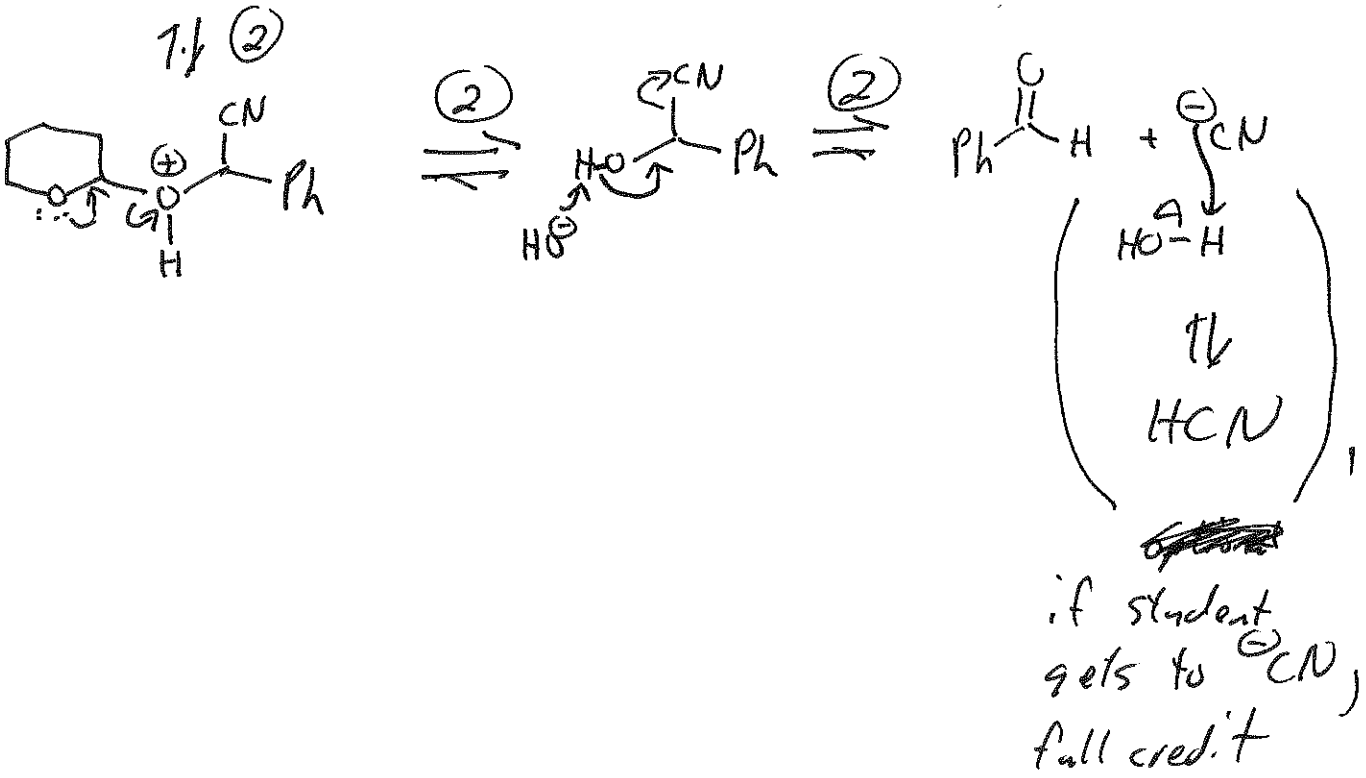
amygdalin



laetrile

Using the simplified structure **A** shown below on the left, give a mechanism that accounts for the formation of HCN in aqueous acid. As a hint, an intermediate **B** in the process is shown below on the right. The actual mechanisms involve enzymes; for your mechanism use aqueous acid to convert **A** to **B**, and then aqueous base to liberate HCN from **B**.

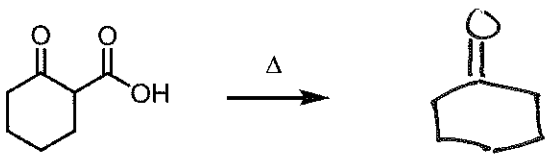




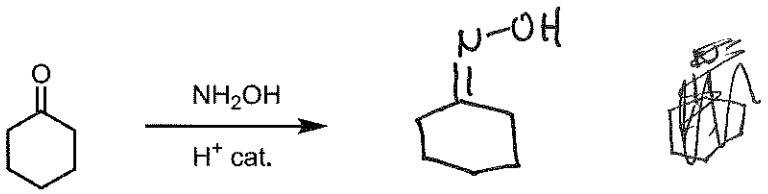
Part III: Reactions (32 points)

11. (24 points) Give the major organic product(s) for the following reactions: 3 each.

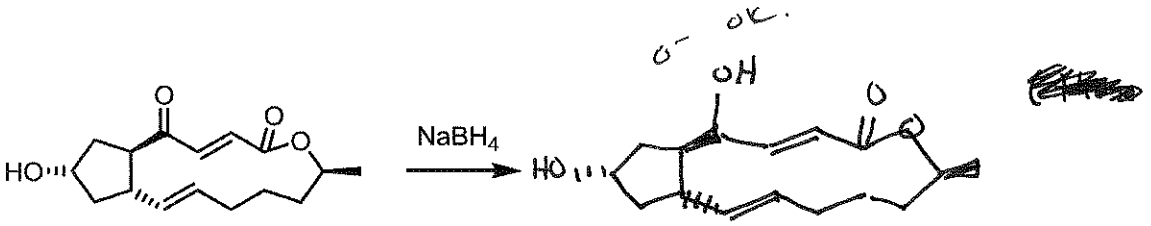
a)



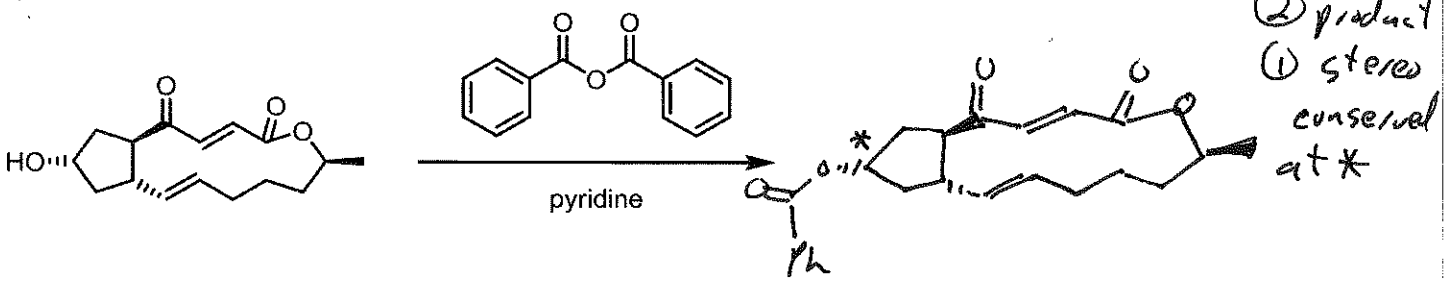
b)



c)

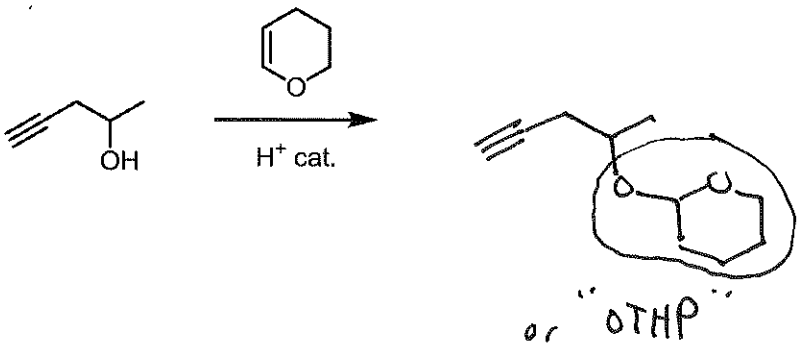


d)

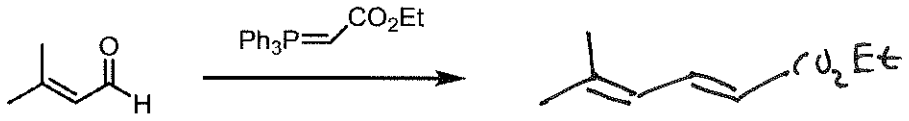


(2) product
(1) stereo conserved at *

e)



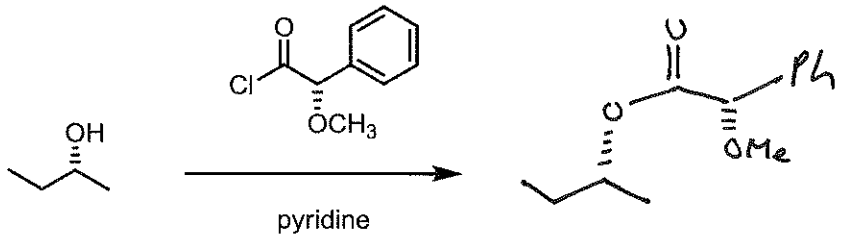
f)



ignore E/Z

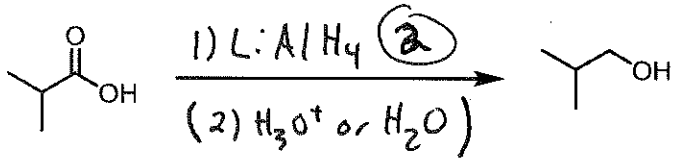
g)

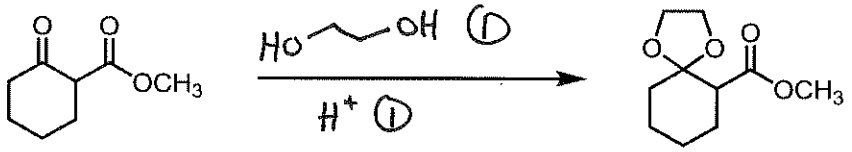
h)

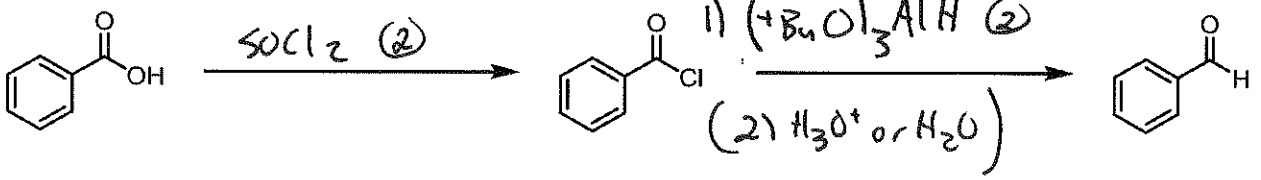


(2) prod
(1) stereo

12. (8 points) Provide reagents that would effect the following transformations.



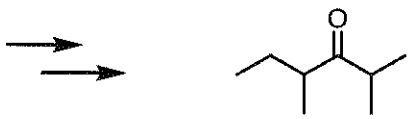




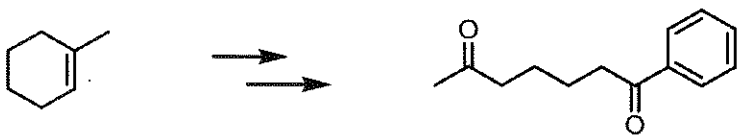
Part IV Multistep Synthesis (8 points)

13. (8 points) Choose **ONE** of the following two synthesis problems, and provide a sequence of reactions that will synthesize the compound on the right from the starting material on the left. Draw out the structures of the intermediate reaction products. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

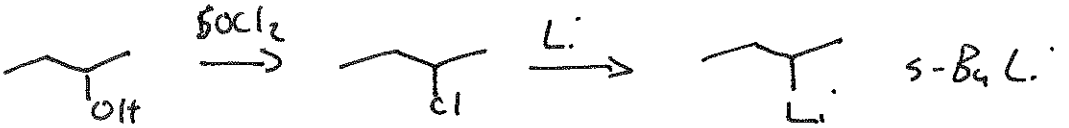
a)

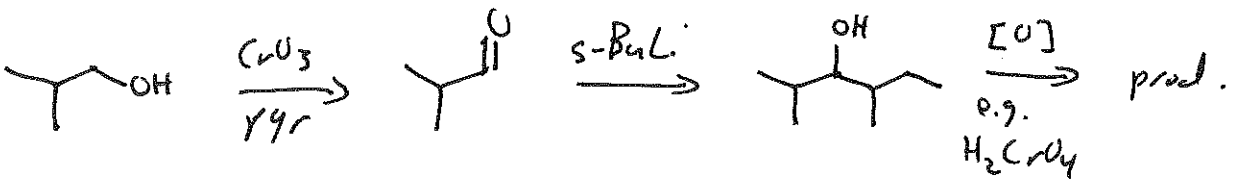
any alcohol with 4 or fewer carbons 

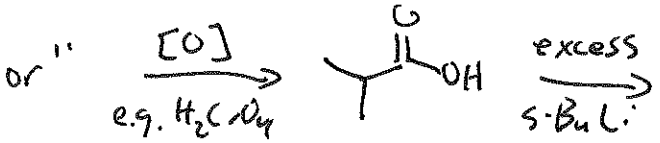
b)



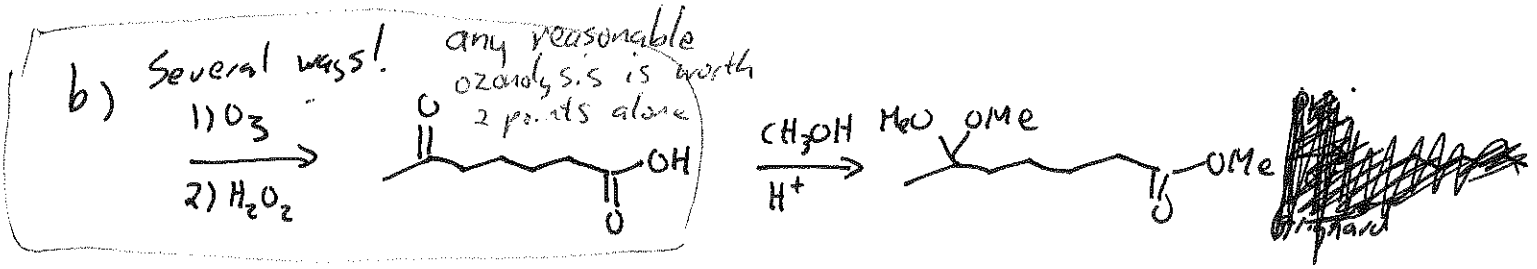
a) several ways! e.g.

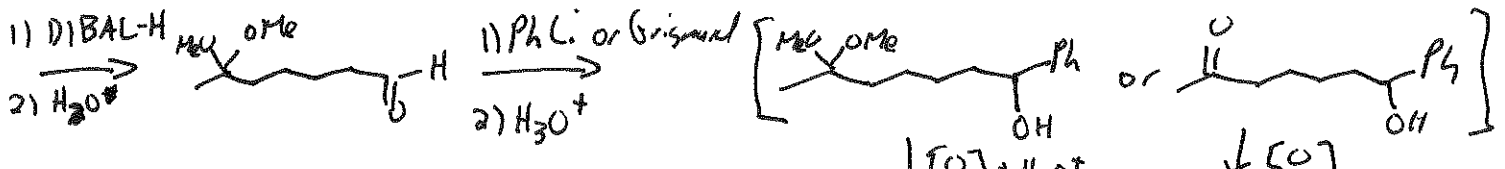




or " 

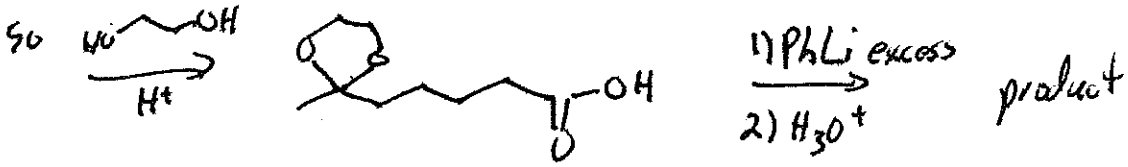
b) Several ways! any reasonable ozonolysis is worth 2 points alone





See over

- I think it should be possible to make acetal w/o ester if control equivalents, esp. if cyclic;

so 

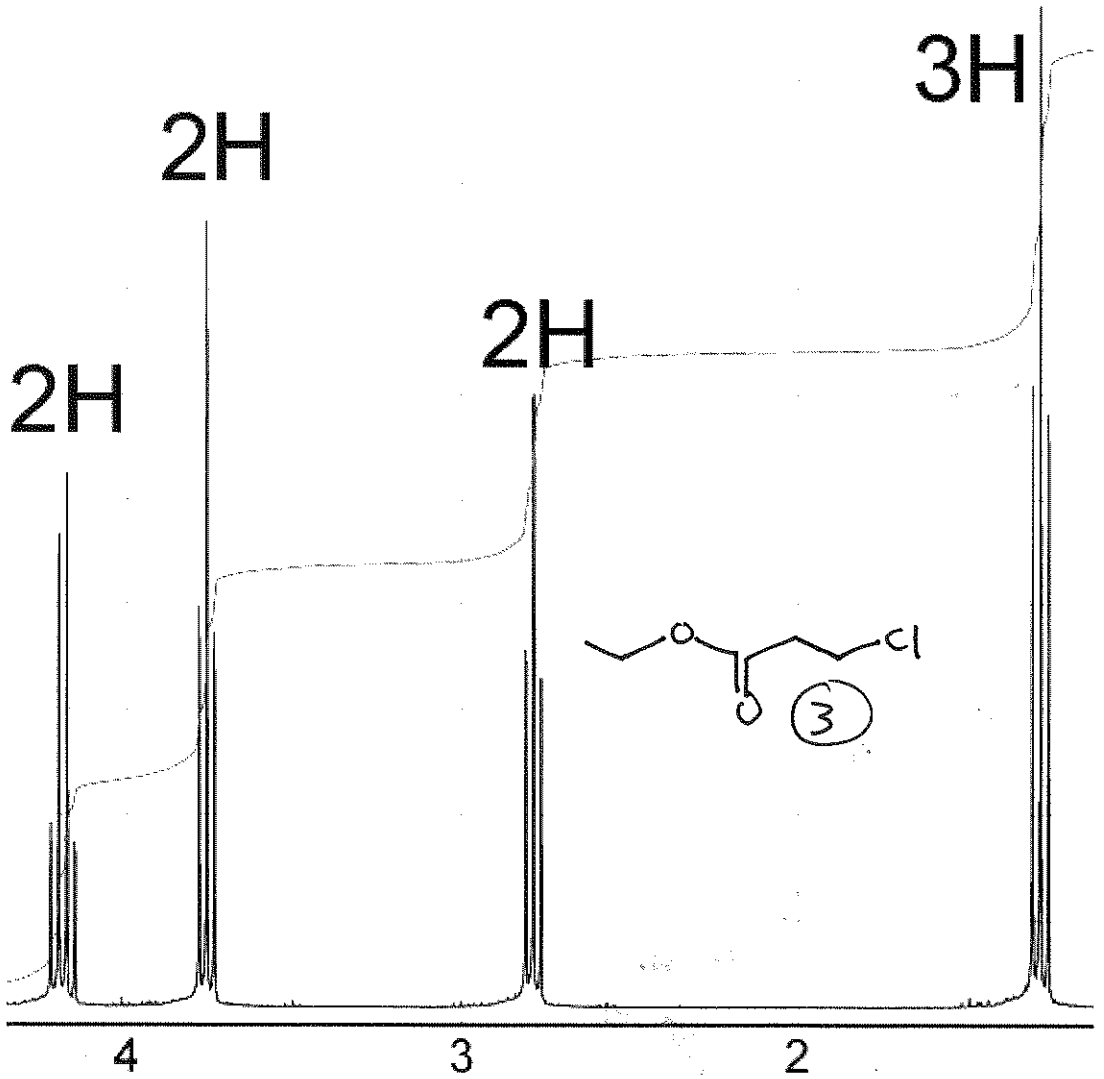
product

is even shorter!.

Part VI: Spectroscopic Analysis of an Unknown Compound (15 points)

14. The ^{1}H and ^{13}C NMR spectra for a compound with the formula $C_5H_9ClO_2$ are shown on the next page, as well as the IR spectrum. An expansion of the ^{1}H spectrum is shown below for clarity. Identify the structure of the compound. Use the ^{1}H NMR data to construct a table (chemical shift, integration, multiplicity, assignment *with the hydrogens giving rise to the signal underlined*) to identify structural fragments, then arrive at the structure. **You are being graded on your analysis**. Any use of the degrees of unsaturation (also called DBE or IHD), IR, or ^{13}C NMR will be considered for extra credit.

In the ^{13}C NMR spectrum on the next page (which is shown above the ^{1}H spectrum), the signals for the unknown compound are marked with an asterisk (*) for clarity. The three lines at ca. 77 ppm are from $CDCl_3$ (the solvent) and can be ignored.



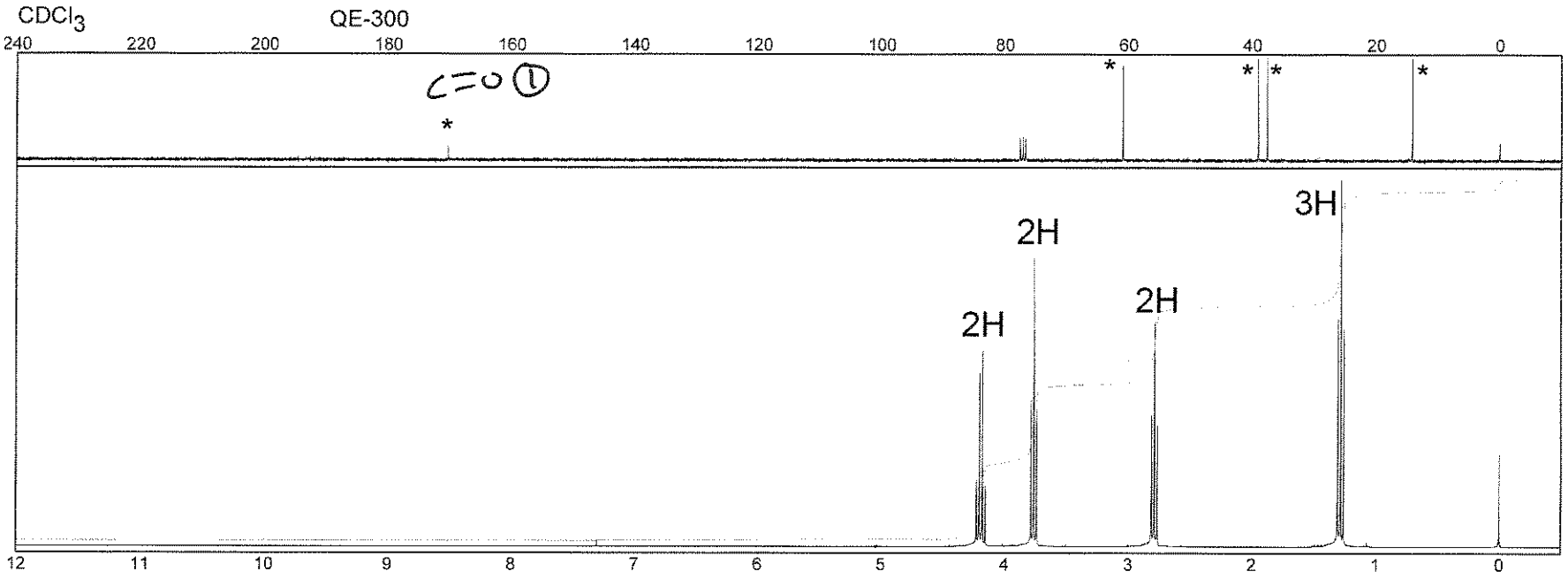
δ	int	mult	assgt
4.2	2H	q	$O\underline{CH_2}CH_3$
3.7	2H	t	$O\underline{CH_2}CH_2$ or $Cl\text{-}\underline{CH_2}CH_2$ (H underlined)
2.8	2H	t	$X\underline{CH_2}CH_2$ (X: C=O?)
1.2	3H	t	$\underline{CH_3}CH_2$

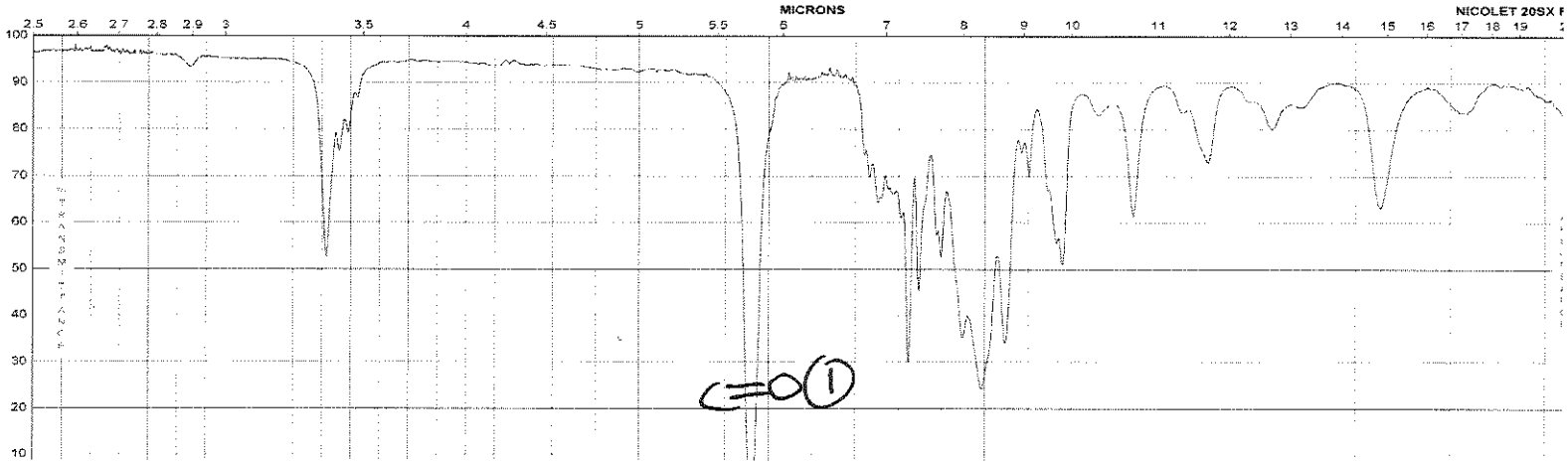
3 points each for δ, int, mult. = (12)

Extra credit: 4 total

1 DBE (1)

5 different C (1)





(extra page for Problem 14 work)