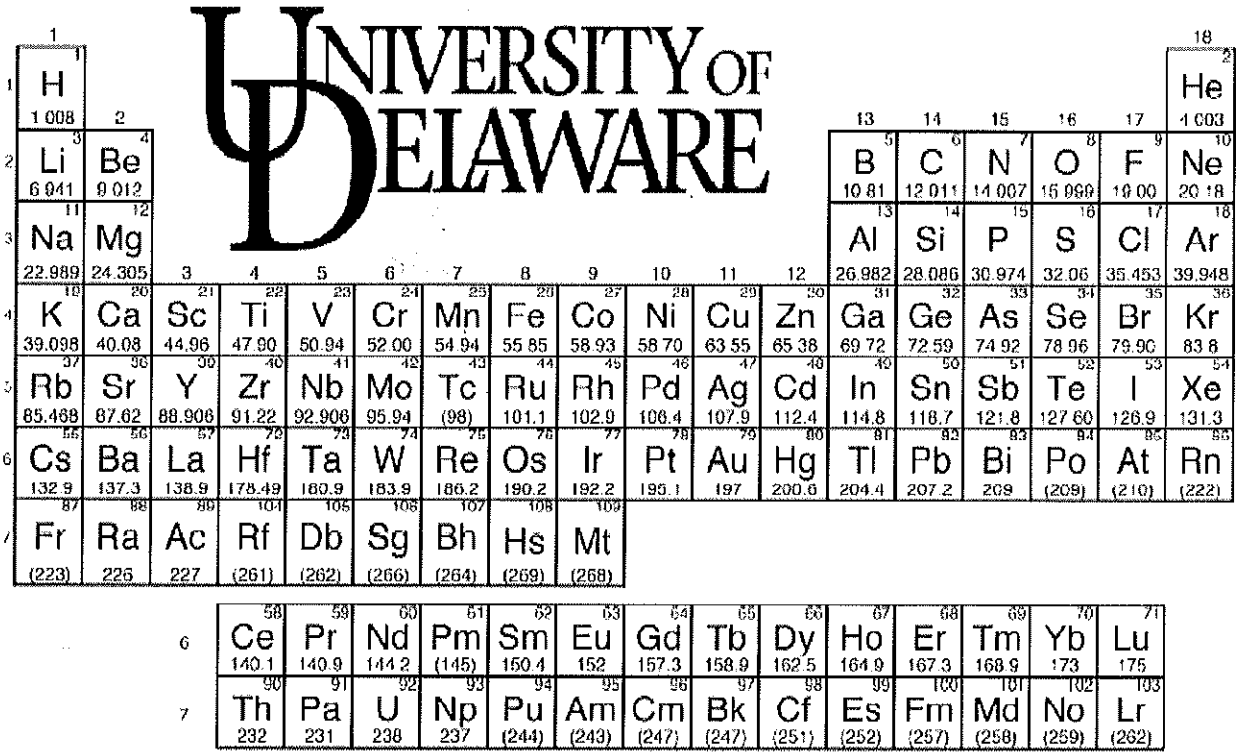
Name: Key S

(Print your name clearly!)

Sametz: CHEM 322 Spring 2012

Organic Chemistry Exam 2

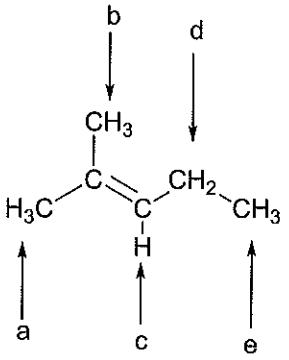
All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



You may raise your hand to ask a question if you are unsure what a question is asking of you.

Part I: Multiple Choice (8 points)

Questions 1-3 refer to the following structure:



1. How many signals do you expect to see in the proton NMR?

a) 3

b) 4

2 c) 5

d) 6

e) 12

2. Which of the indicated protons should appear the furthest **downfield** (i.e. have the highest chemical shift) in the proton NMR?

a) a

3 b) b

c) c

d) d

e) e

3. What should be the splitting pattern of the **e** protons?

a) singlet

3 b) doublet

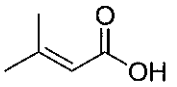
c) triplet

d) quartet

e) nonet

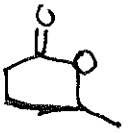
5. Nomenclature (6 points)

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



3-methyl-2-butenoic acid
(or but-2-enoic)
① but__oic acid ① 3-Me
① 2-ene

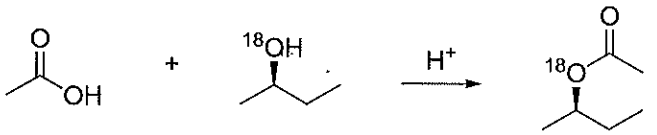
b) Draw the structure of 3-methyl-2-oxacyclopentanone (1) (1)

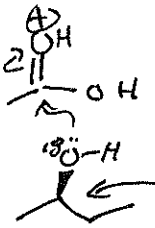


6. (8 points) Almost all oxygen found in nature is the isotope ^{16}O. The rare ^{18}O isotope can be used as a "label" to gain insight into reaction mechanisms.

Explain why the first reaction shown below (Reaction **A)** proceeds with ~~inversion~~ retention of stereochemistry and provides an isotopically-labeled ester, but the second reaction (Reaction **B**) proceeds with inversion and with no ^{18}O incorporation.

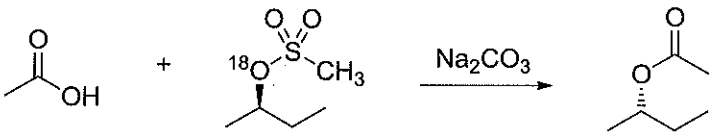
Reaction **A**:

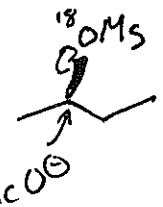




^{18}O forms bond (2) to carbonyl C; this C-O bond (2) remains intact

Reaction **B**:

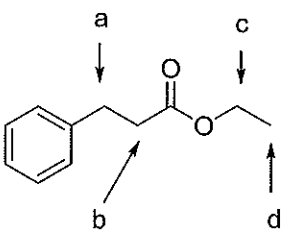




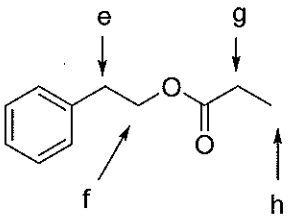
^{18}O is part of leaving group (2); S_N2 proceeds with inversion (2)

Part II: Short Answer

4. (8 points) The spectra for ethyl 3-phenylpropionate (**A**) and phenyethyl propionate (**B**) are shown on the next page. Match each spectrum on the following page with the corresponding compound, and use labels (a, b, c, d) to correlate the protons indicated on the structure with their signals in the NMR. Note: The protons on the benzene ring are not labeled, and you do not have to assign them. The spectrum for 2-chloropropane is shown below to demonstrate correlating protons in the structure to signals in the spectrum.

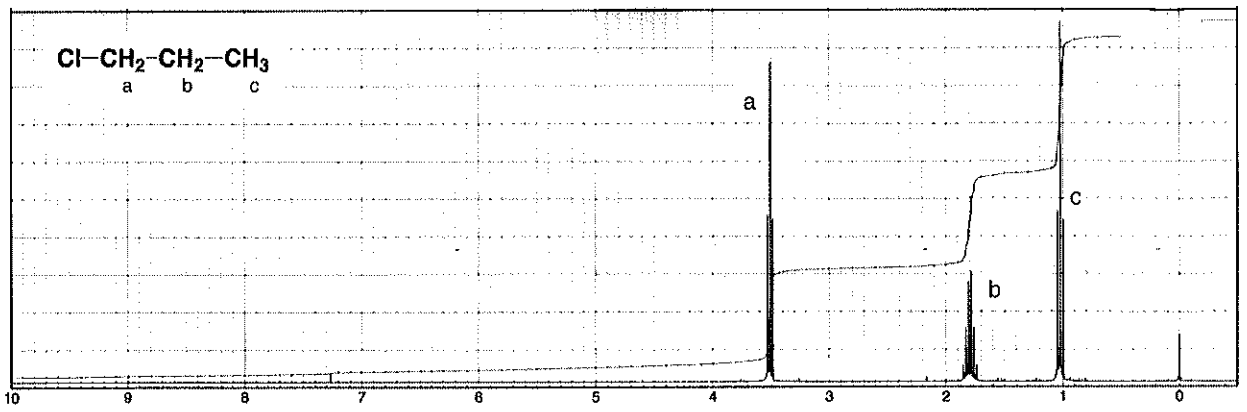


A

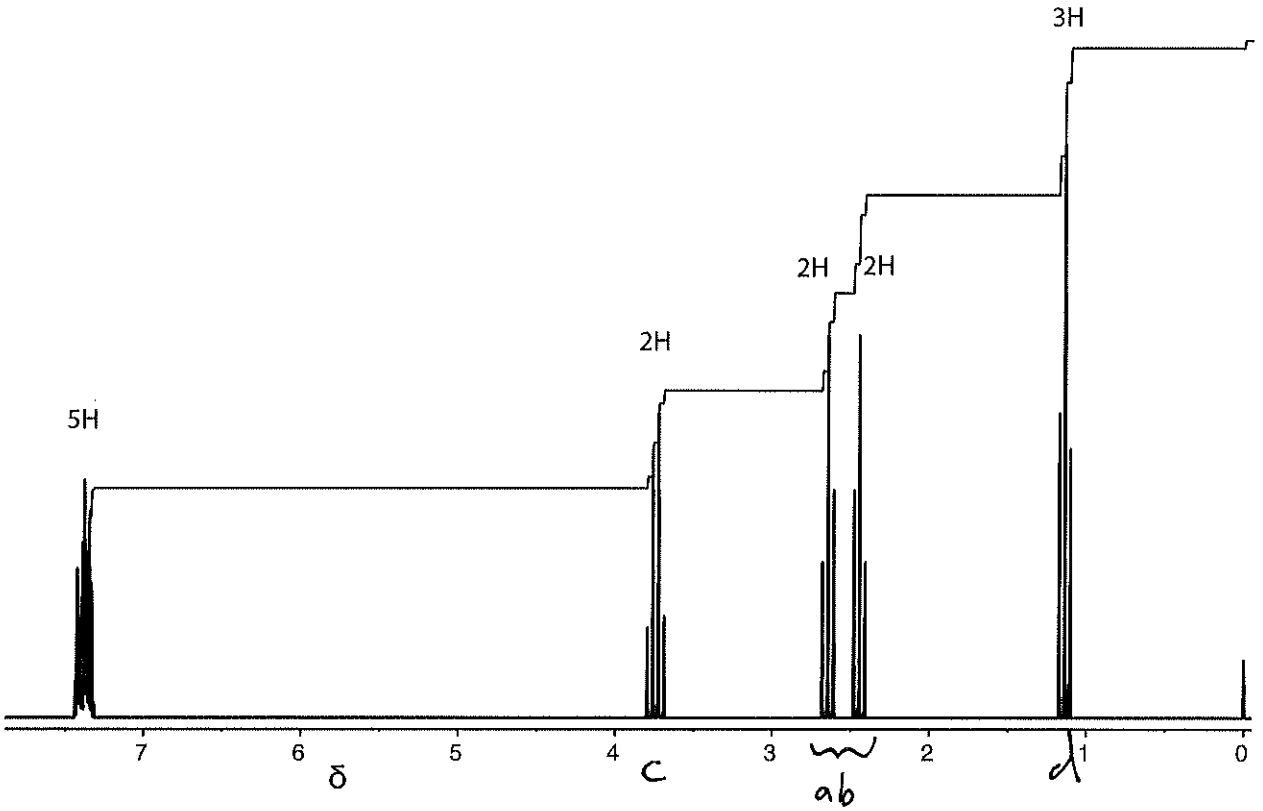


B

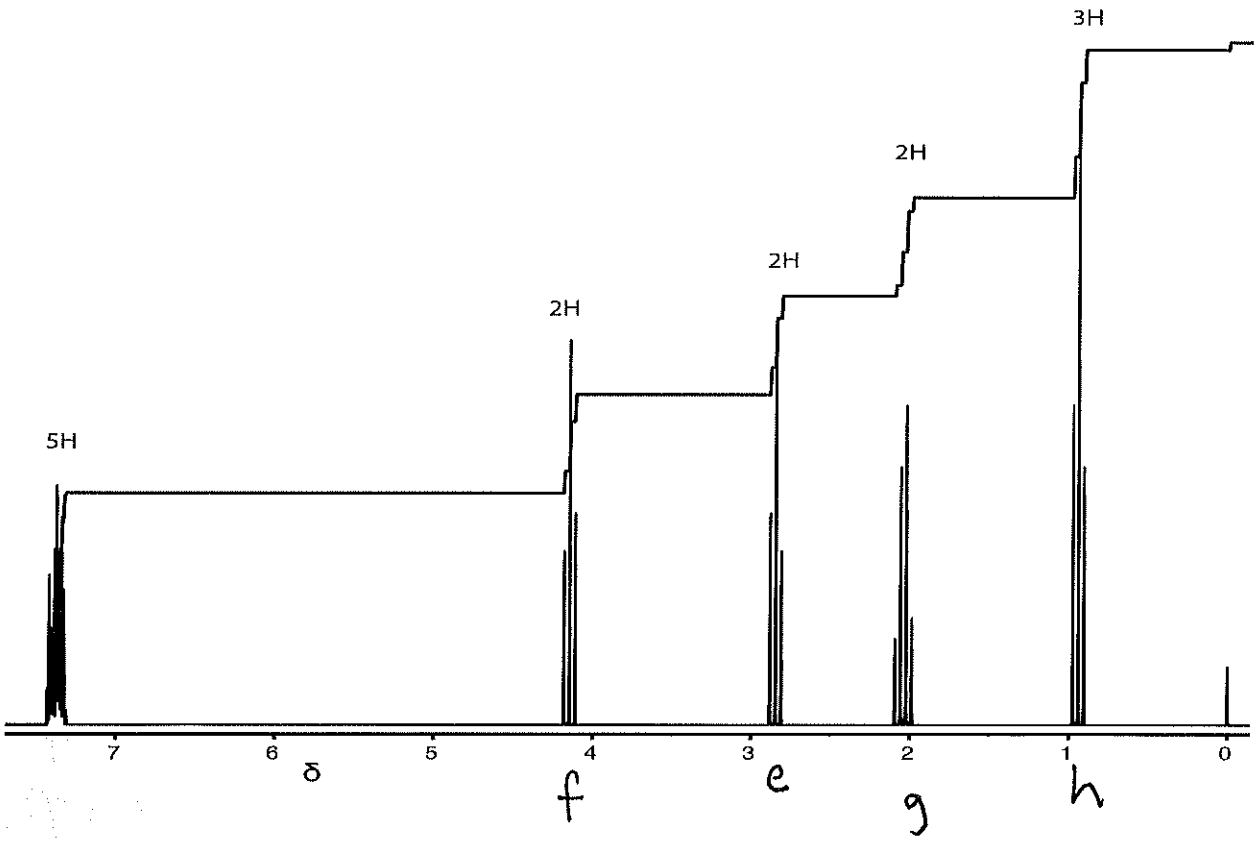
Example:



1 pt. ea.



A

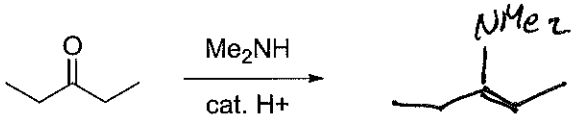


B

Part III: Reactions

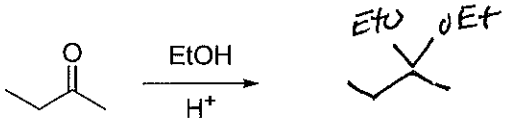
7. (36 points) Give the major organic product(s) for the following reactions:

a)

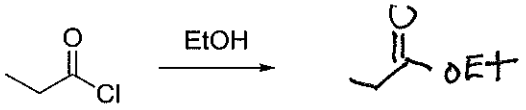


(ignore E/Z both possible; accept either)

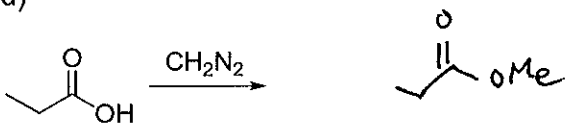
b)



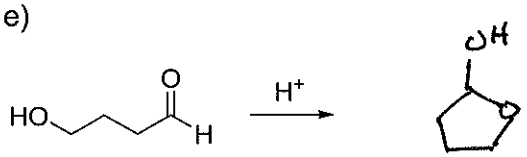
c)



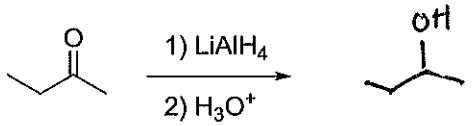
d)



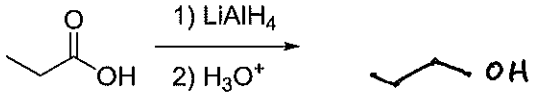
e)



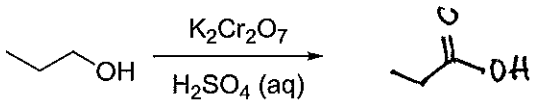
f)



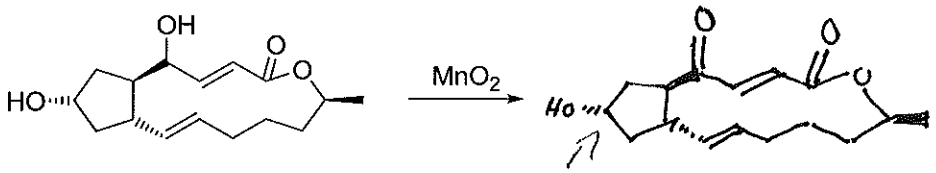
g)



h)



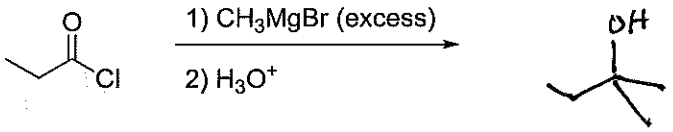
i)



here also 1/3

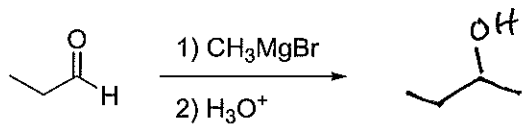
~~wrong~~ one 1/3

j)

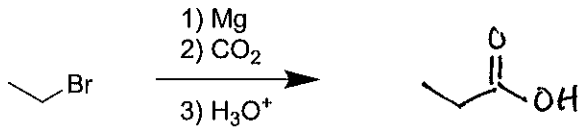


3 each

k)

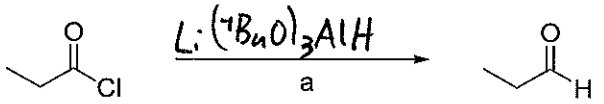


l)

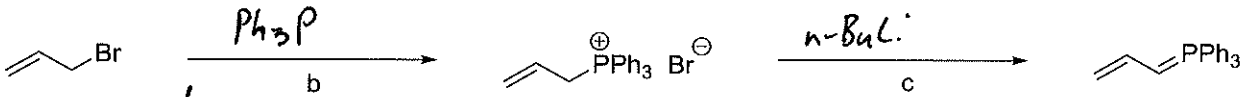


8. (9 points) Provide reagents that would effect the following transformations.

3 each.



(DIBALH = 2.



Mg, Ph_3P = no pt.

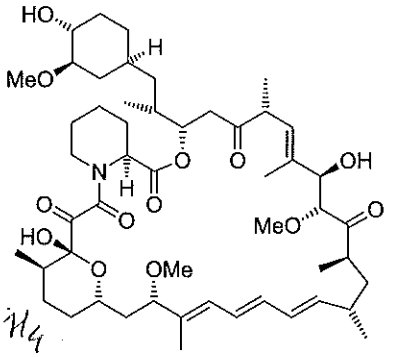
~~LiPPh3~~ = 2 pts

① Mg, ② Ph_3P = 2 pts.

(consider other strong base)

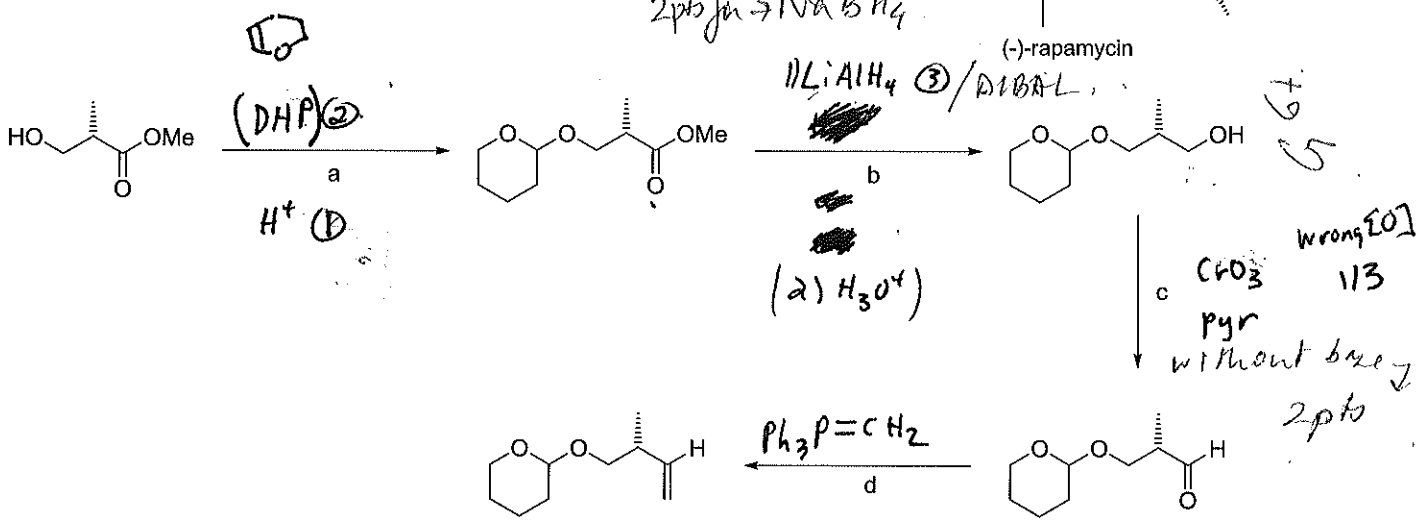
KOH = 2 pts.

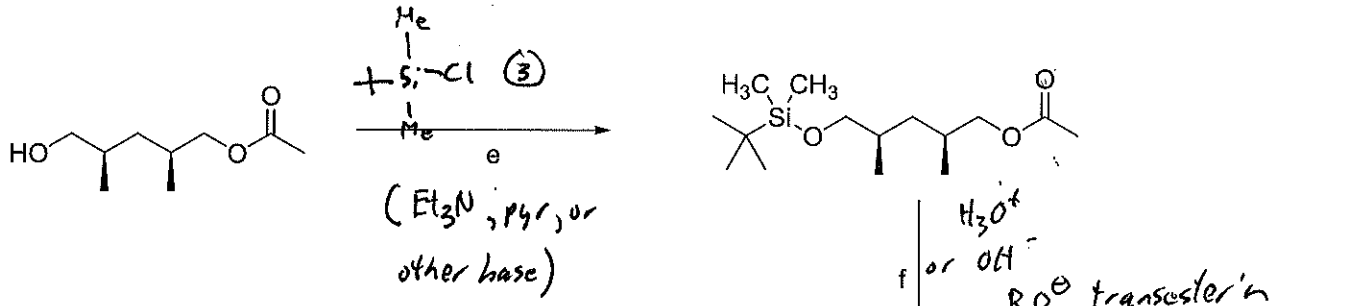
9. (24 points) The transformations shown below are found in (or are very similar to those in) a report in the literature on the synthesis of (-)-rapamycin, an important immuno-suppressant drug used to prevent organ transplant rejection. Provide reagents that would effect these transformations.

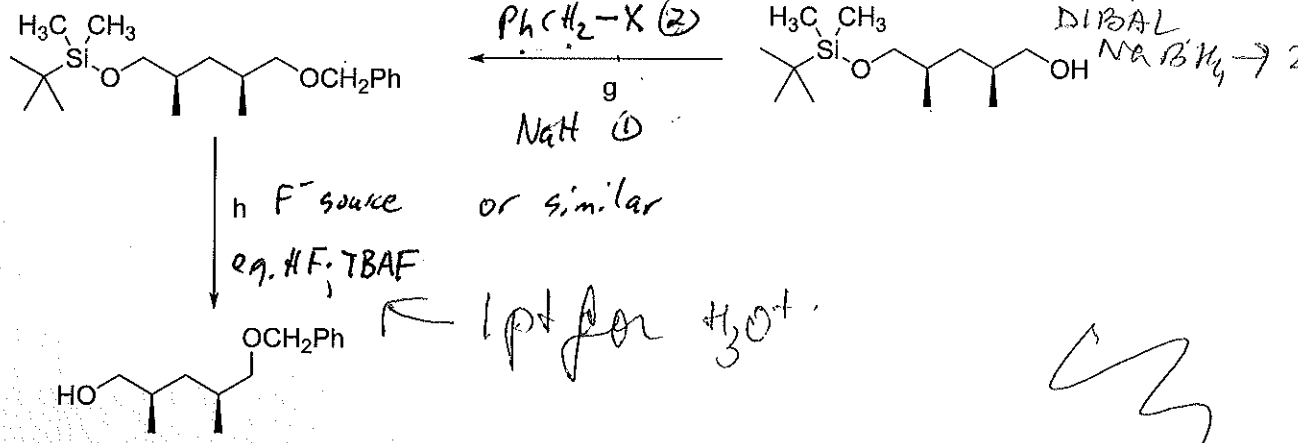


(-)-rapamycin

2pts for $NaBH_4$



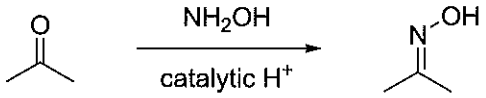




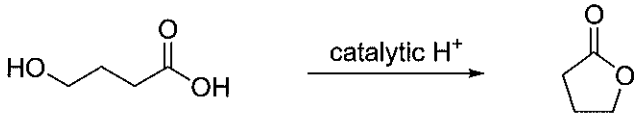
Part IV: Mechanisms

10. (6 points) Choose **ONE** of the following two reactions and give a complete reaction mechanism. It is best if you only show work on one. 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.

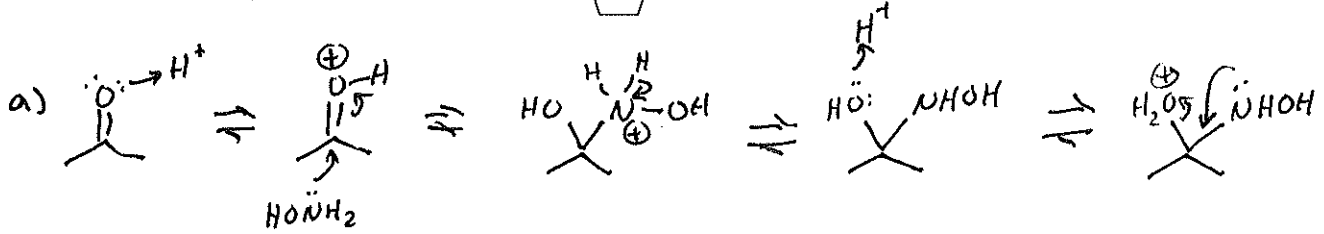
a)



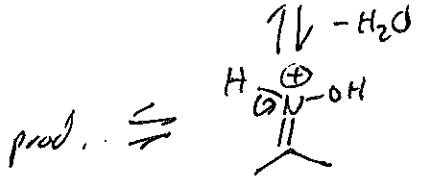
b)



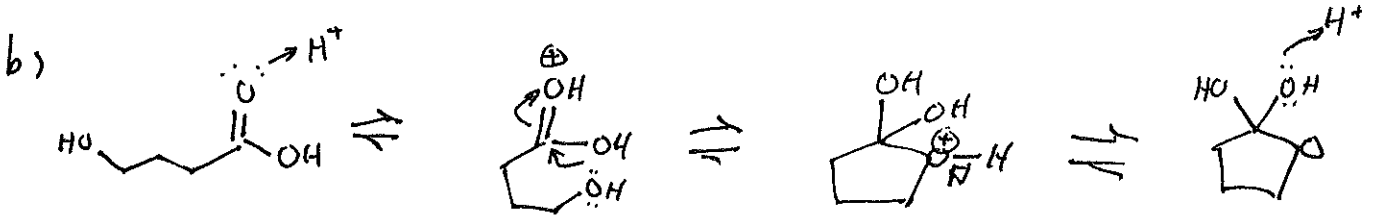
a)



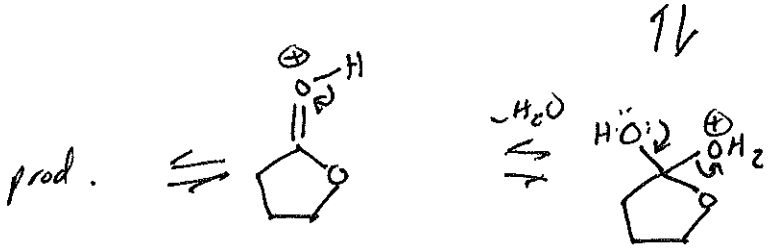
① for step



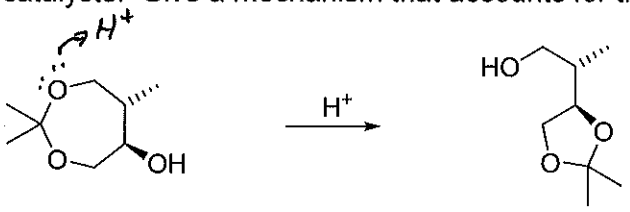
b)

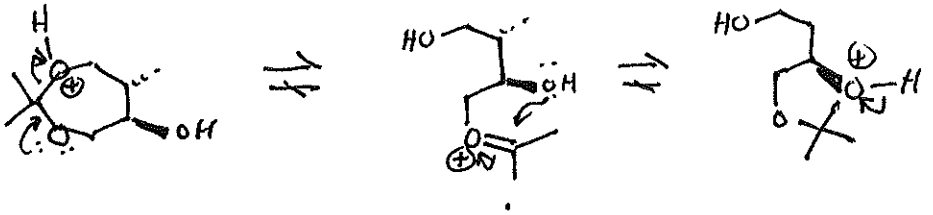


① for step



11. (6 points) It is possible to interconvert acetals using Lewis (e.g. BF_3) or Brønsted (i.e. H^+) catalysts. Give a mechanism that accounts for the following conversion:





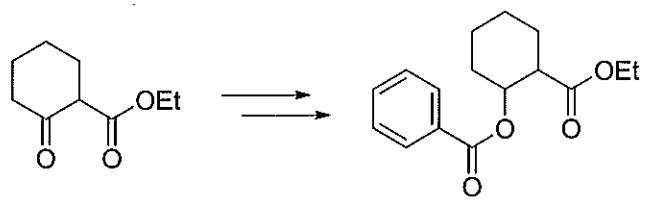
(2) per intermediate

if via  : this would require H_2O. (-1)

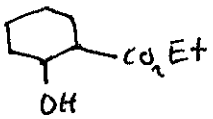
Part V Multistep Synthesis (16 points)

12. (12 points) Multistep synthesis Propose an efficient synthesis for each of the compounds below on the right from the starting material on its left. Please draw the structures of the intermediate reaction products. (Just the product, not the mechanism)

a)



1) $NaBH_4$ (3)
2) H_3O^+

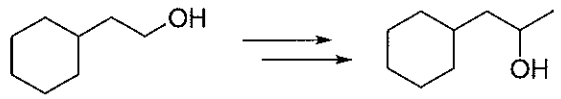


- chloride
- anhydride
- Fischer esterification
- transesterification

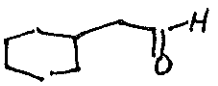
} 3 } 1 — DCC

CO_2Et compatibility

b)



CrO_3
pyr
(3)

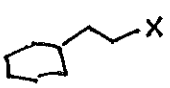


1) CH_3MgBr (or Li) (3)
2) H_3O^+

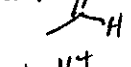
① for wrong [O]

or:

$SOCl_2$
or PBr_3
etc.



1) Mg
2)



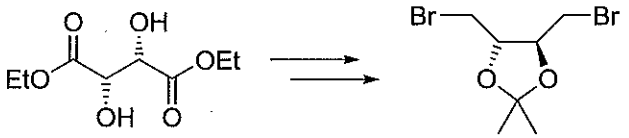
3) H^+

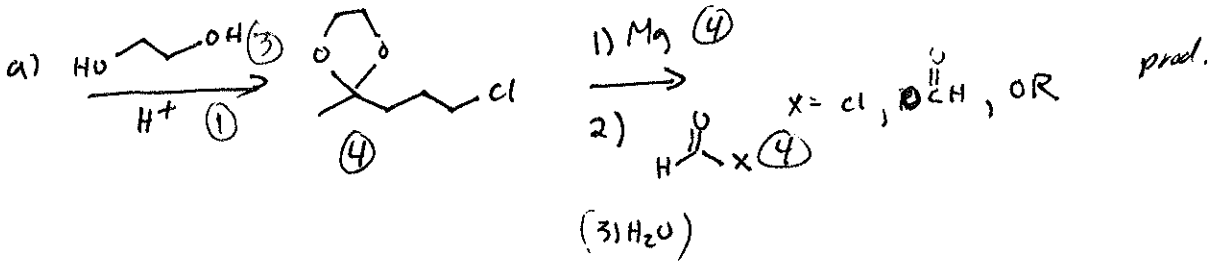
prod.

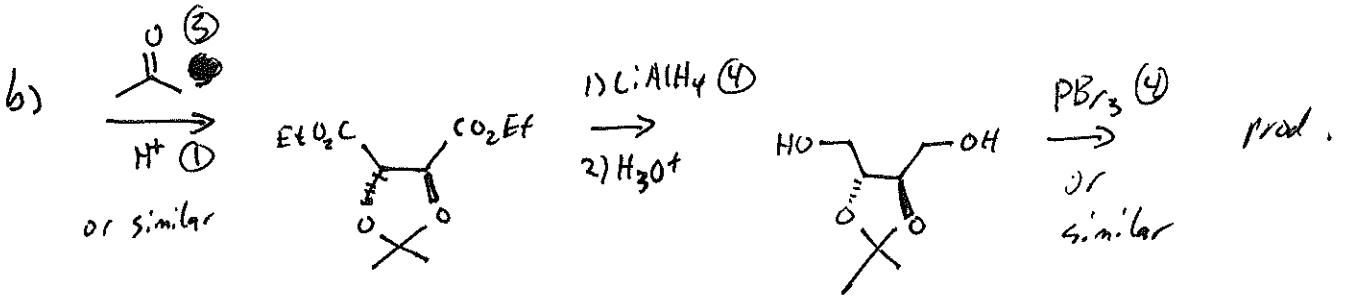
13. (12 points) Choose **ONE** of the following two synthesis problems, and provide a sequence of reactions that will synthesize the compound on the right from the starting material on the left. Draw out the structures of the intermediate reaction products. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

a)

b)



a) 

b) 

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 $C_9H_{16}O_4$ are shown on the next page. An expansion of the ^{1}H spectrum is shown below for clarity. The IR spectrum for this compound shows a strong absorption at around 1740 cm^{-1}. Identify the structure of the compound. Use the ^{1}H NMR data to construct a table (chemical shift, integration, multiplicity, assignment) 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.

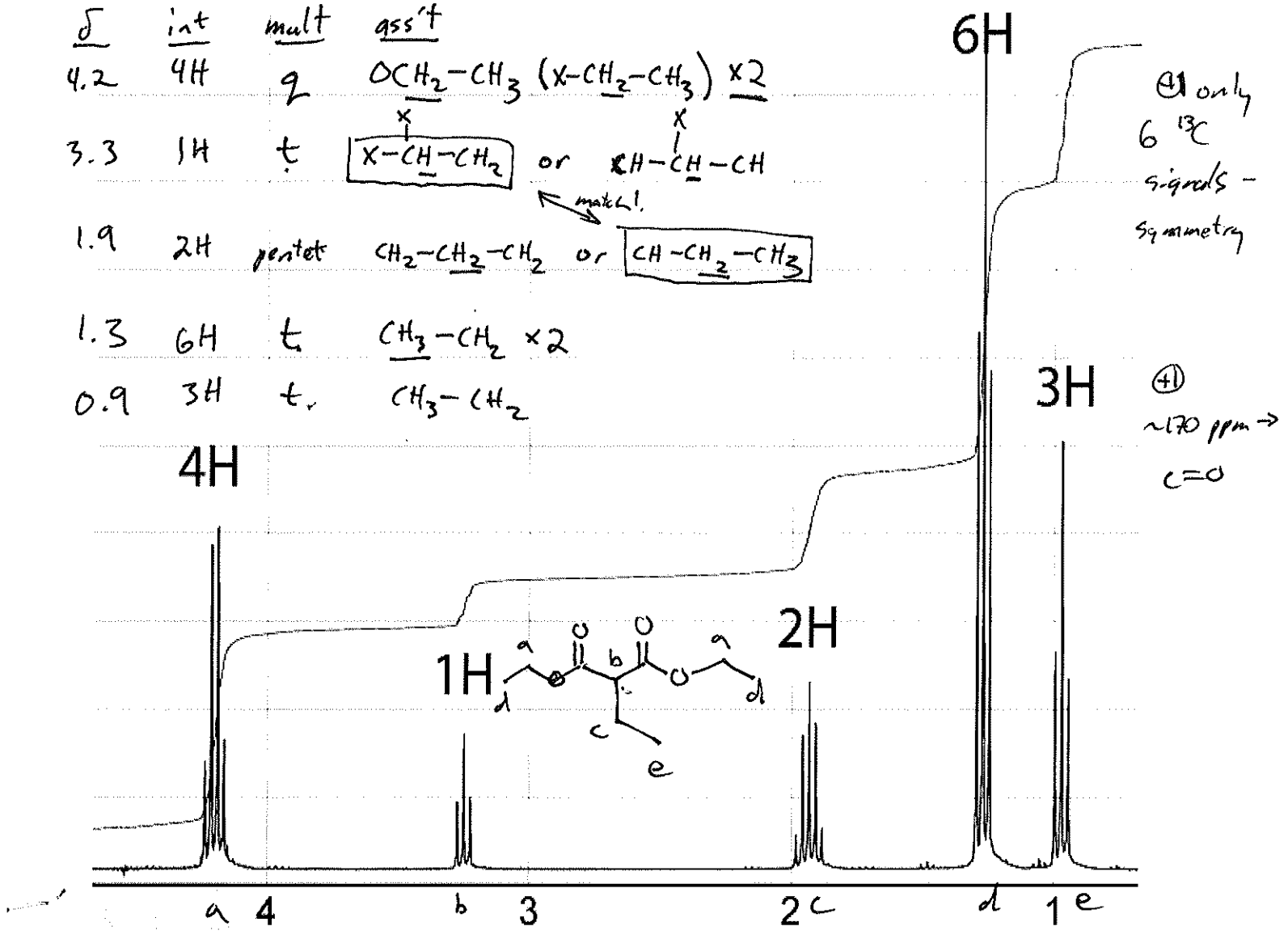
2 DBE (+1)

C=O (+1)

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 labeled "$CDCl_3$" (the solvent) and can be ignored.

δ	int	mult	ass't
4.2	4H	q	OCH_2-CH_3 ($X-CH_2-CH_3$) ×2
3.3	1H	t	$X-CH-CH_2$ or $CH-CH-CH$
1.9	2H	pentet	$CH_2-CH_2-CH_2$ or $CH-CH_2-CH_3$
1.3	6H	t	CH_3-CH_2 ×2
0.9	3H	t	CH_3-CH_2

make!



(+1) only 6 ^{13}C signals - symmetry

(+1) ~170 ppm → C=O

~(+3) per correctly analyzed NMR signal
(+1) if signal ✓ but doesn't match their structure)