EXAMINATION 2
Chemistry 3B

Name: Key
Print first name before second!
Use capital letters!

SID #:_____

Laboratory GSI (if applicable):

_____

Peter Vollhardt
November 4, 2008

Please provide the following information if applicable.

Making up an I Grade _____
(If you are, please indicate the semester during which you took previous Chem 3B:

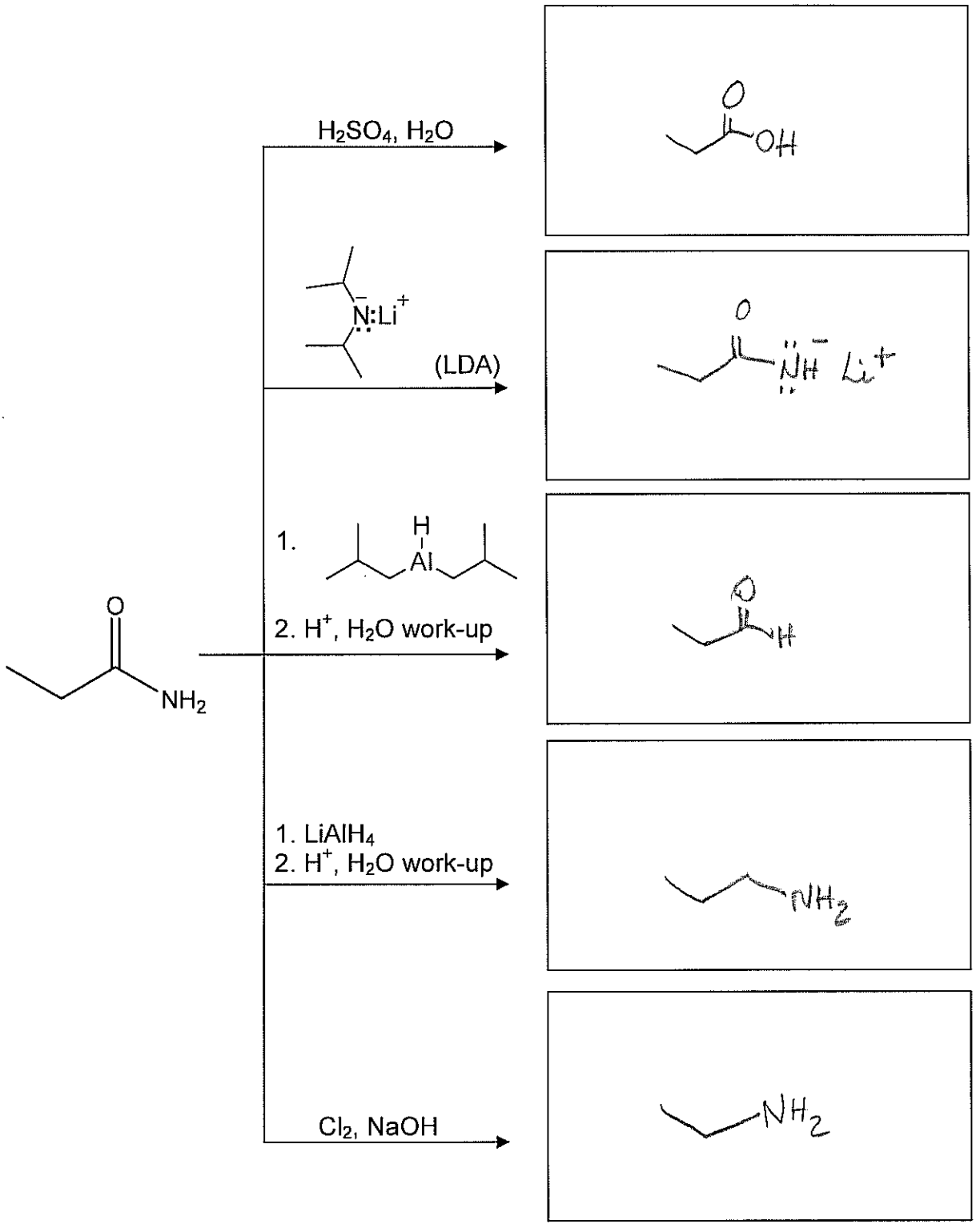
_____ _____
Semester Instructor

Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have **20** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** ***Good Luck***!

DO NOT WRITE IN THIS SPACE

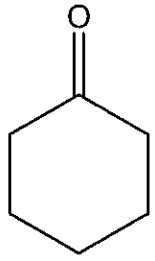
I.	_____	**(25)**
II.	_____	**(50)**
III.	_____	**(50)**
IV.	_____	**(45)**
V.	_____	**(45)**
VI.	_____	**(35)**
Total:	_____	**(250)**

I. [25 Points] Write the organic products of the following reactions of the starting amide.



II. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to follow each step. It is not part of any answer.

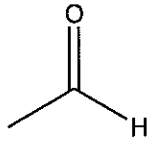
a.



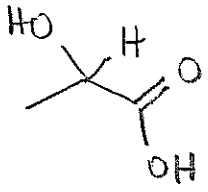
D_2O, NaOD

Mass spectrum of product: *m/z* = 102

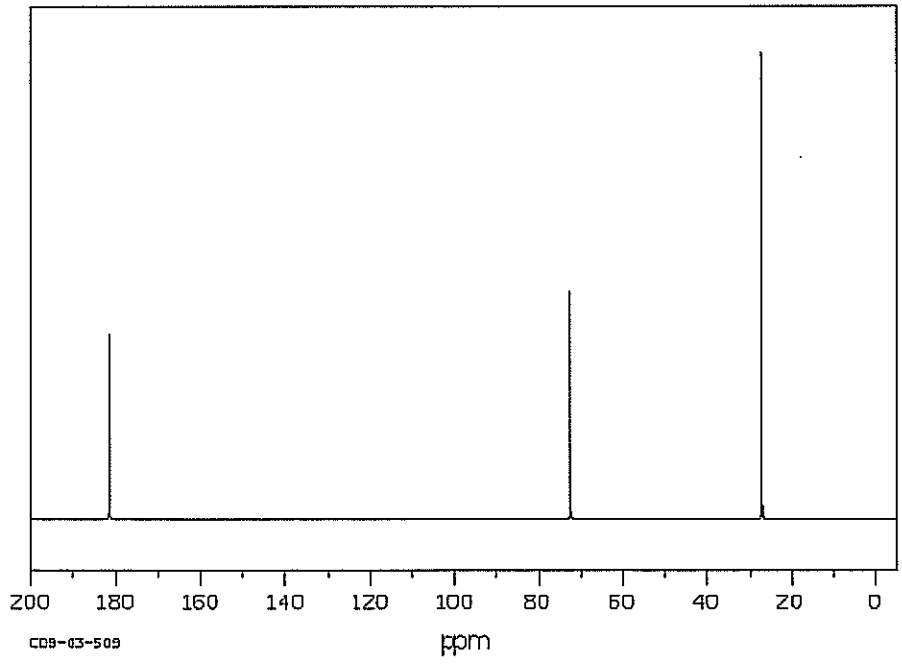
b.



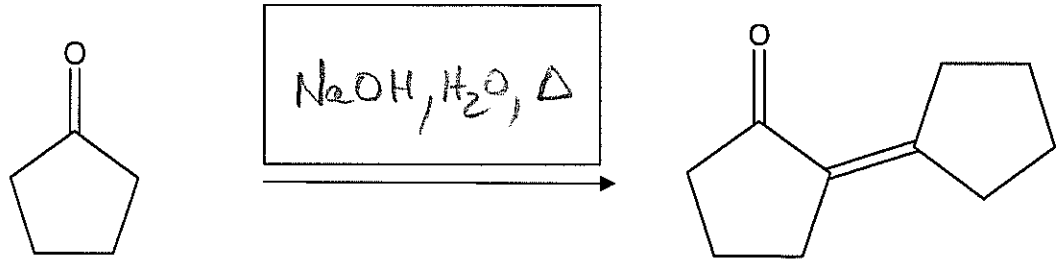
1. HCN
2. H^+, H_2O, Δ



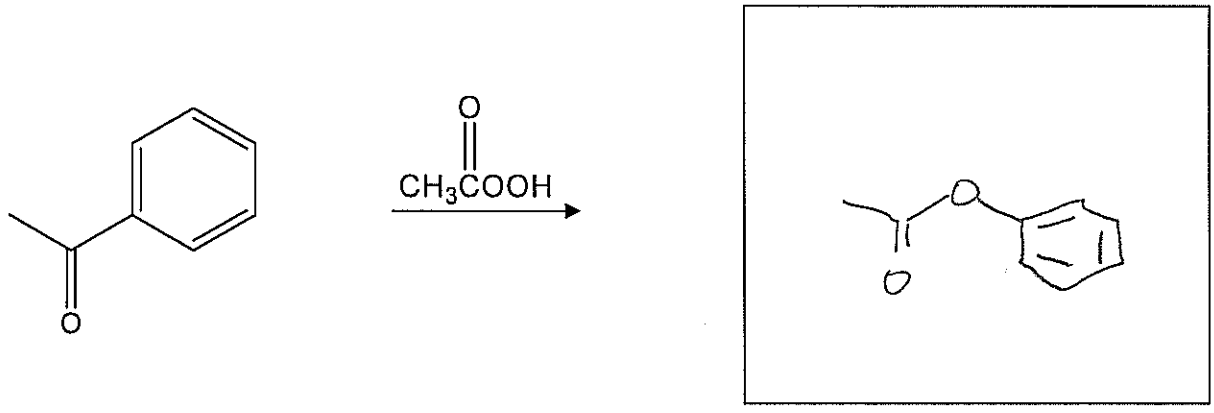
^{13}C Spectrum of product:



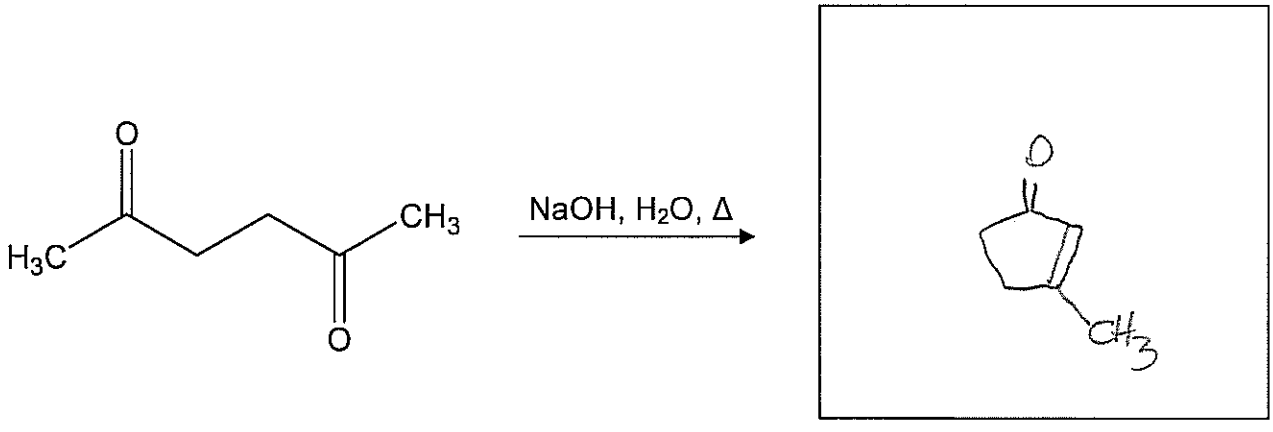
c.



d.

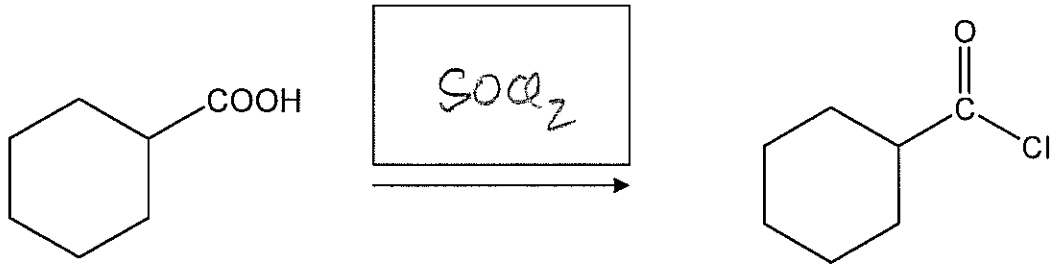


e.

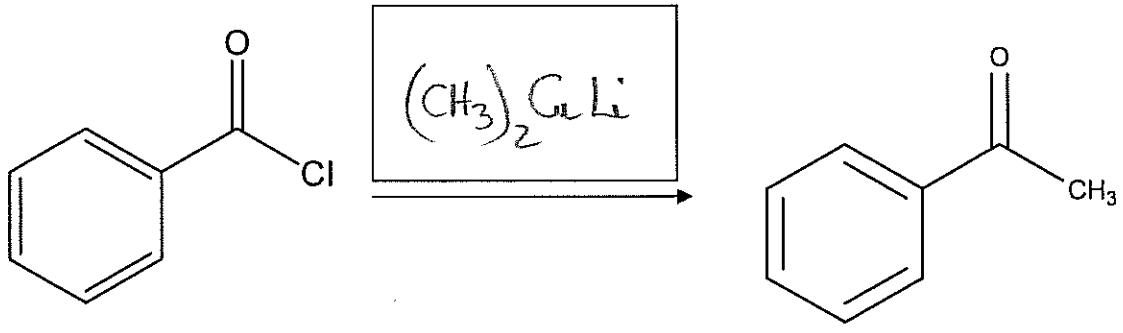


C_6H_8O

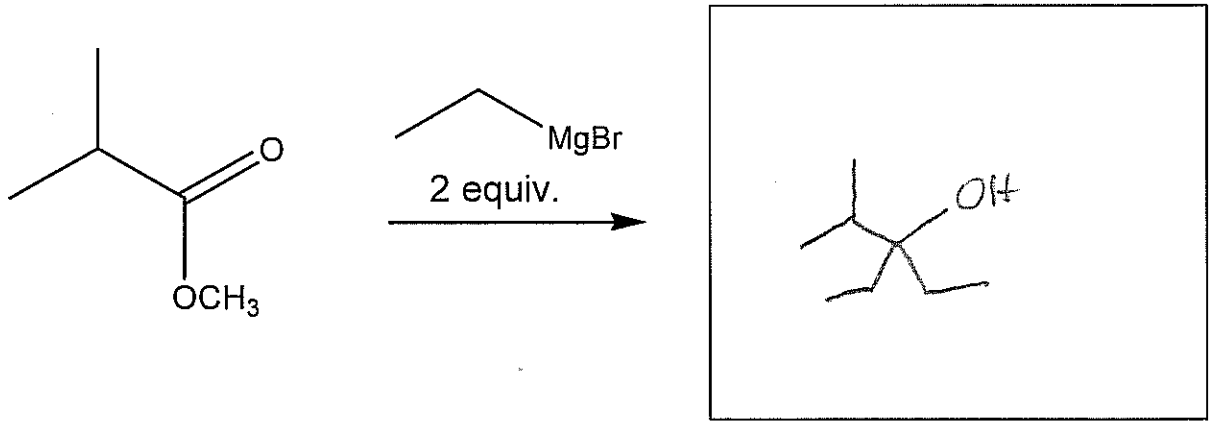
f.



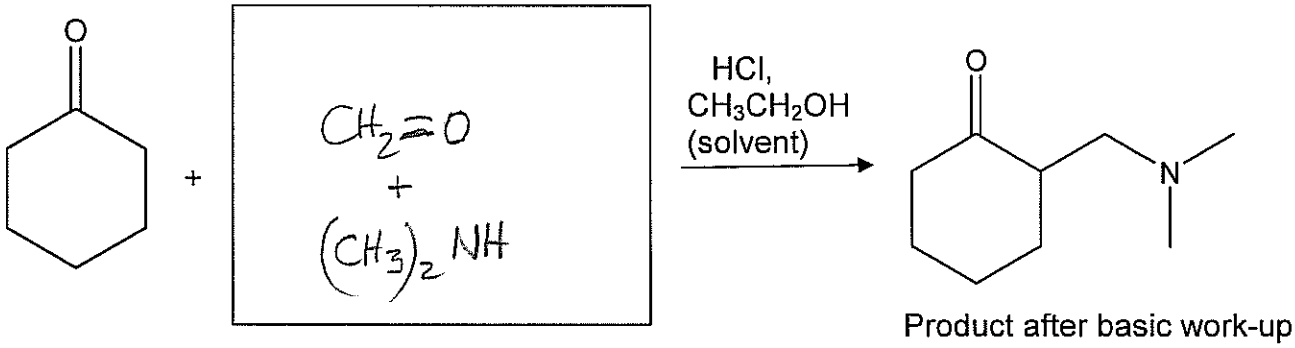
g.



h.



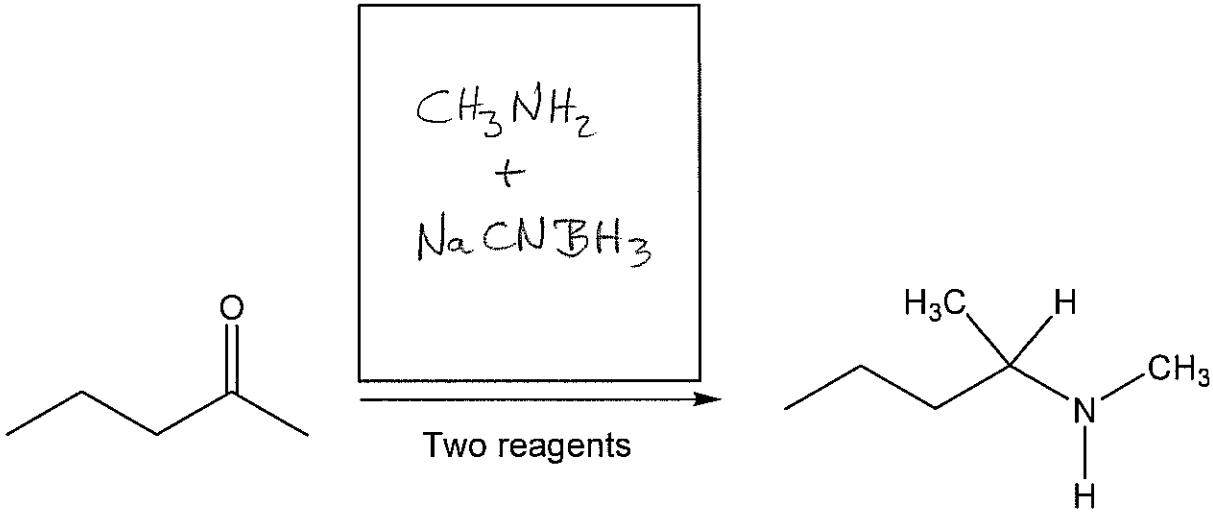
i.



Two additional neutral reagents

Product after basic work-up

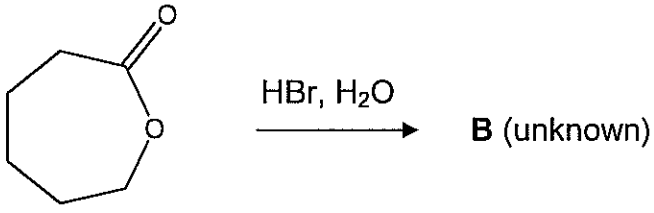
j.



Two reagents

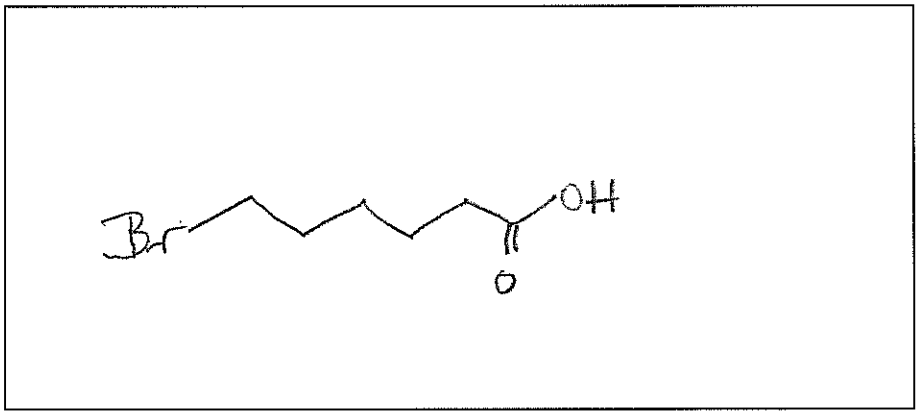
III. [50 Points] In an attempt to hydrolyze lactone **A** with concentrated aqueous HBr, a student obtained compound **B**. The complete spectral data for this product are shown below in the sequence:

1. ^{1}H NMR, 2. ^{13}C NMR, 3. Mass, 4. IR.

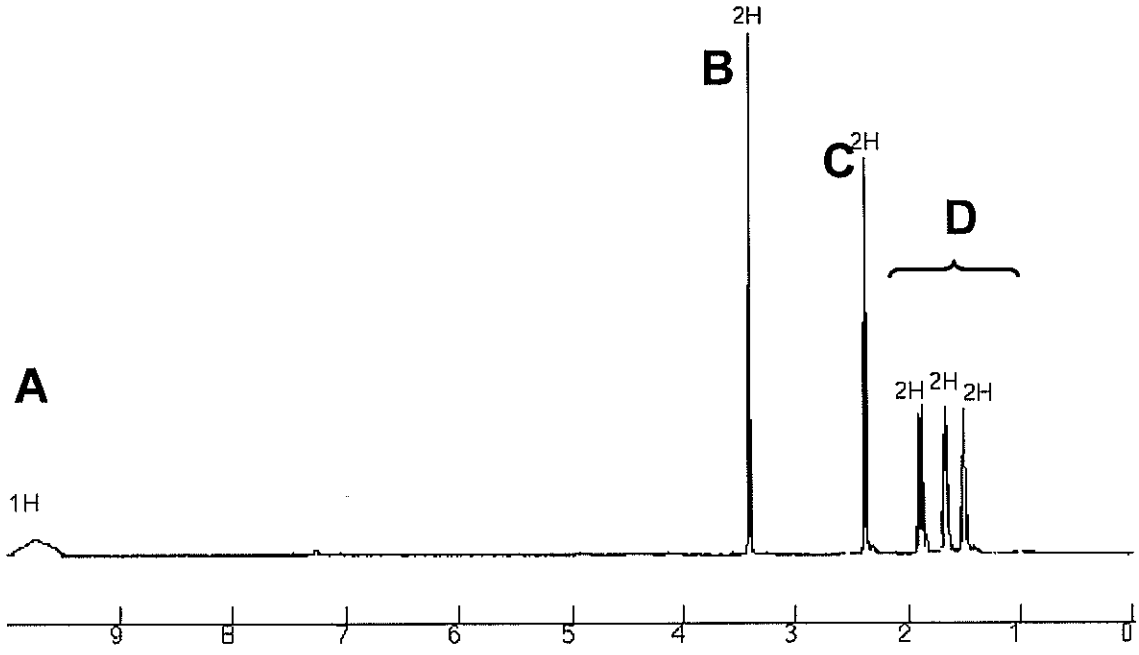


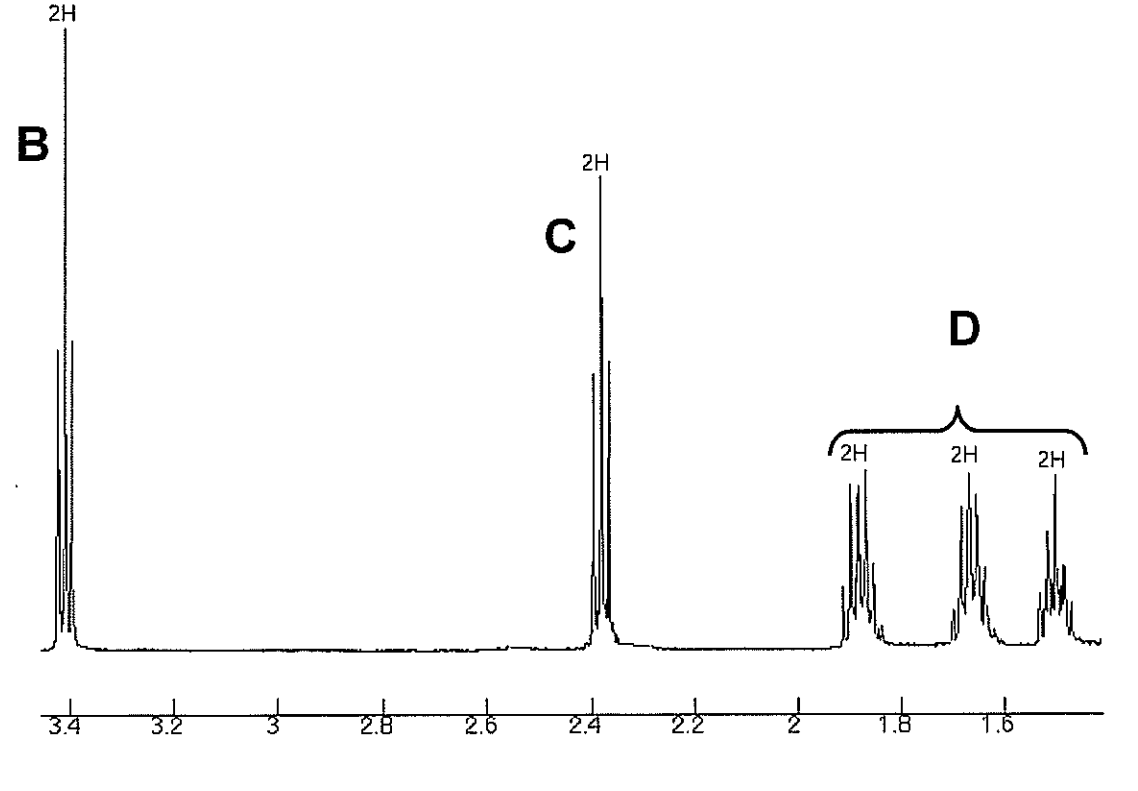
A

a. After consideration of the spectral data, write the structure of the product in the box below.

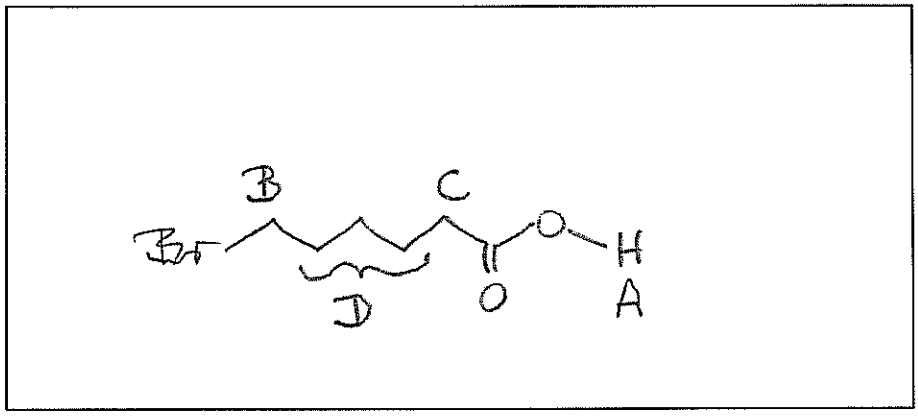


1. ^{1}H NMR spectrum (for expanded section, see bottom spectrum).



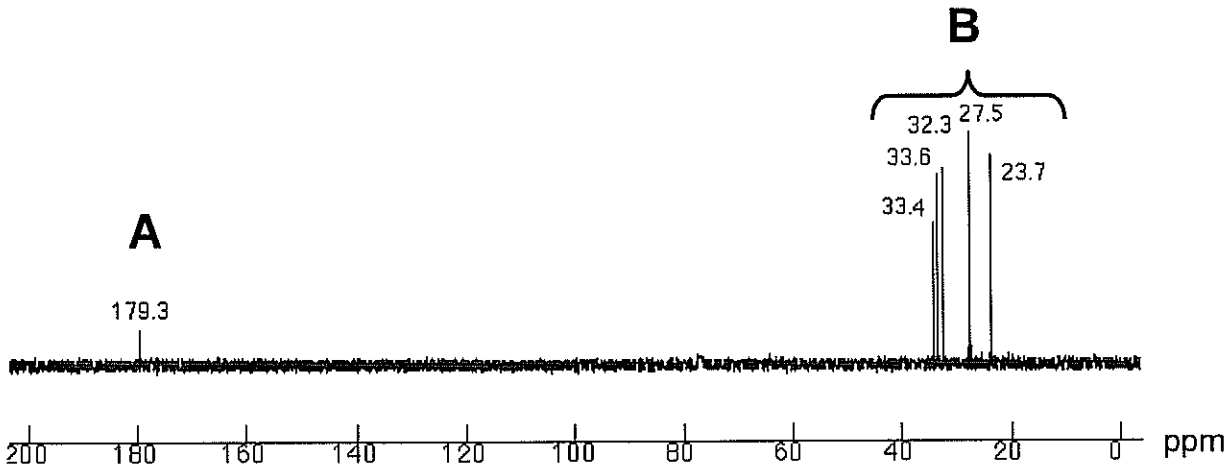


b. Draw again your suggestion for the unknown in the box and label the hydrogens A, B, C, and D giving rise to the corresponding signals in the spectrum. Use the Table below, if necessary.

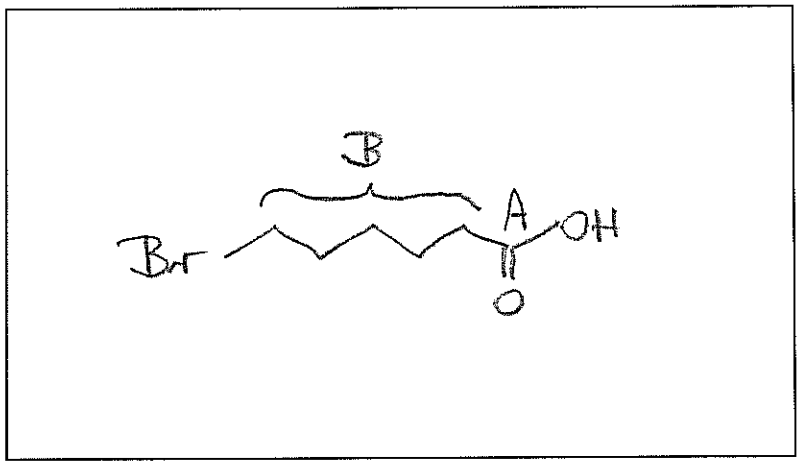


Type of hydrogen[a]	Chemical shift δ in ppm	
Primary alkyl, RCH_3	0.8–1.0	Alkane and alkane-like hydrogens
Secondary alkyl, RCH_2R'	1.2–1.4	
Tertiary alkyl, R_3CH	1.4–1.7	
Allylic (next to a double bond), $R_2C{=}C(CH_3)R'$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $ArCH_2R$	2.2–2.5	
Ketone, $RCCH_3$ (C=O)	2.1–2.6	
Alkyne, $RC{\equiv}CH$	1.7–3.1	
Chloroalkane, RCH_2Cl	3.6–3.8	Hydrogens adjacent to electronegative atoms
Bromoalkane, RCH_2Br	3.4–3.6	
Iodoalkane, RCH_2I	3.1–3.3	
Ether, RCH_2OR'	3.3–3.9	
Alcohol, RCH_2OH	3.3–4.0	
Terminal alkene, $R_2C{=}CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C{=}CHR'$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, RCH (C=O)	9.5–9.9	
Alcoholic hydroxy, ROH	0.5–5.0	(variable)
Thiol, RSH	0.5–5.0	(variable)
Amine, RNH_2	0.5–5.0	(variable)

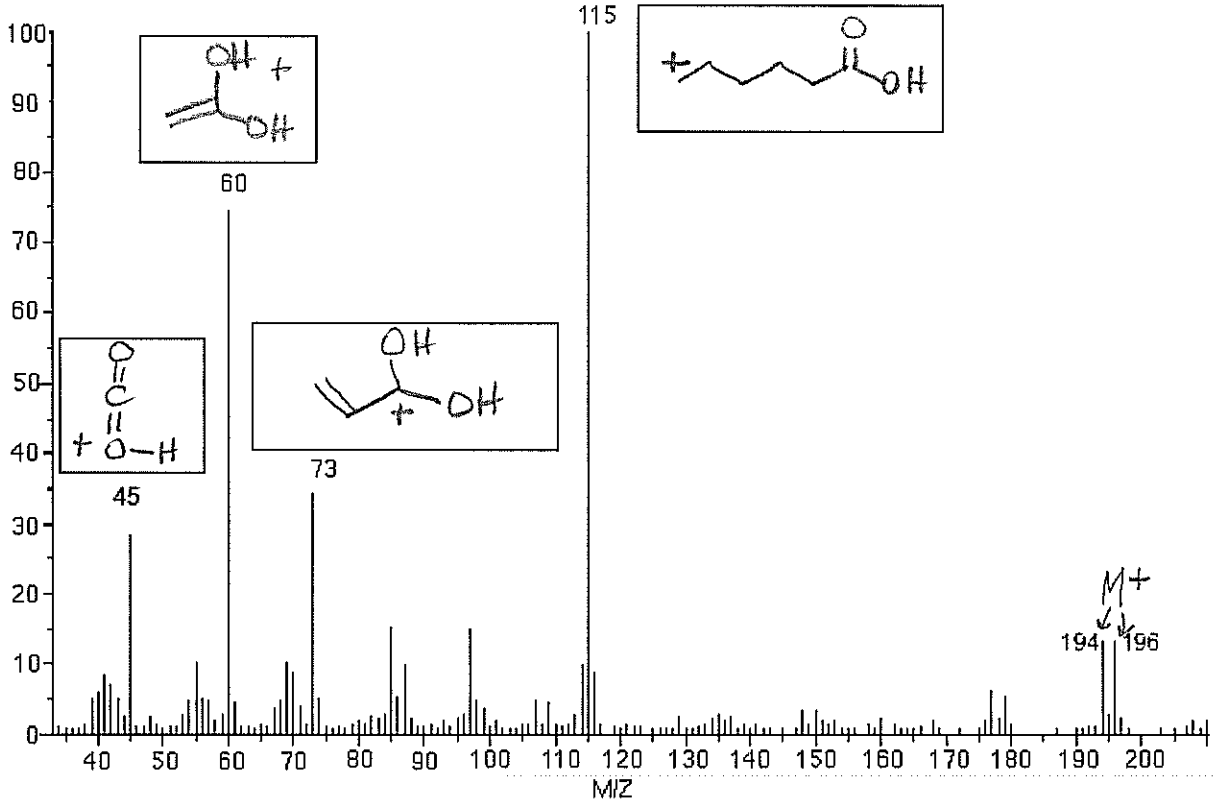
2. ^{13}C NMR spectrum.



Draw again your suggestion for the unknown in the box below and label the types of carbon atoms A and B giving rise to the corresponding signals in the spectrum.



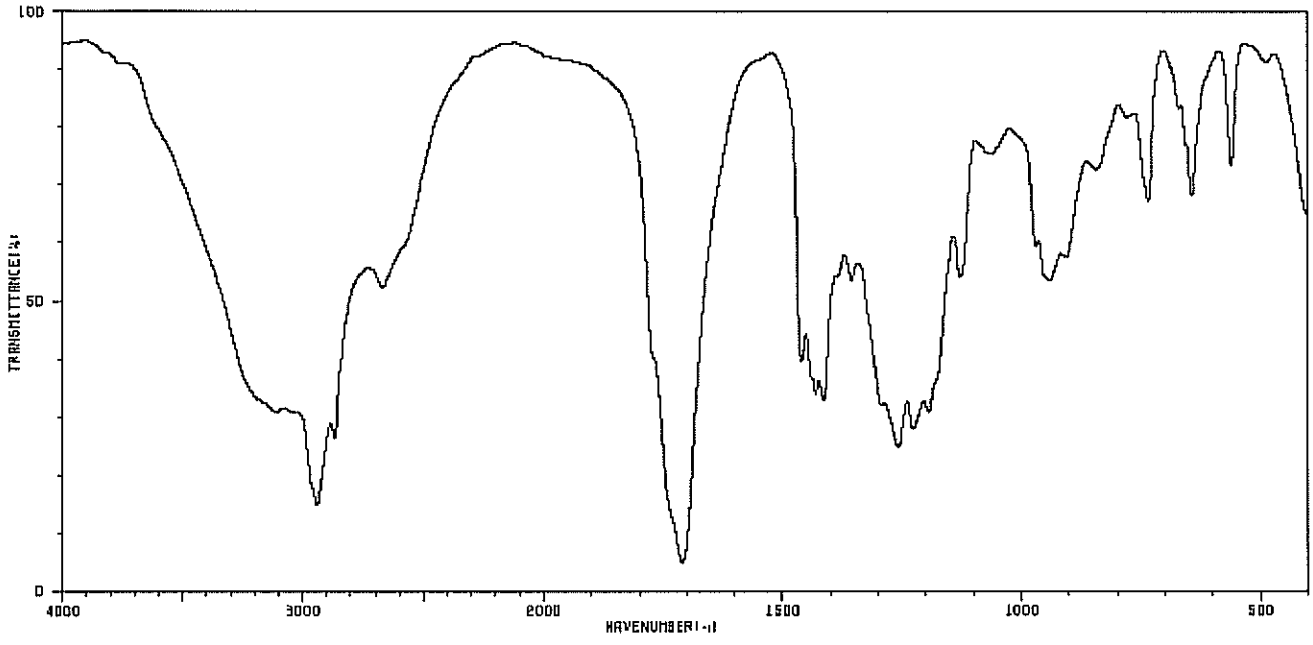
3. Mass spectrum. **Hint**: Atomic weights: C = 12; H = 1; O = 16; Br exists in nature as a 1:1 mixture of Br = 79 and Br = 81.



a. Clearly mark on the spectrum the molecular ion(s) as "M^+".

b. In the boxes above the respective fragment ions, indicate the structure of the fragment.

4. IR spectrum.



Confirm the presence or absence (circle one) of the following bonds. Enter an approximate expected stretching frequency in the box.

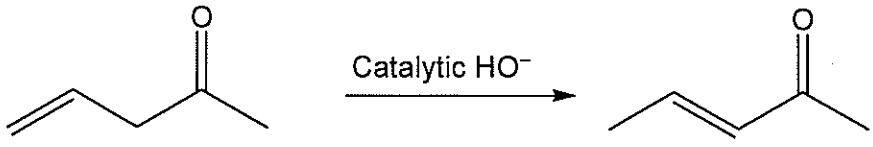
$\tilde{\nu}$ (C_{sp^3}–H) is: (present) absent at ~2950 cm^{-1}

$\tilde{\nu}$ (O–H) is: (present) absent at ~3100 cm^{-1}

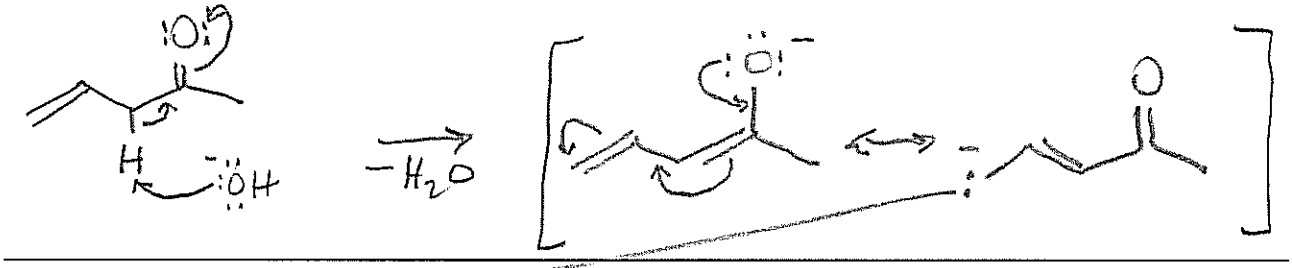
$\tilde{\nu}$ (C=O) is: (present) absent at ~1700 cm^{-1}

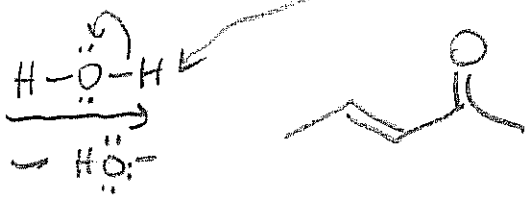
IV. [45 Points] Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have!

a.

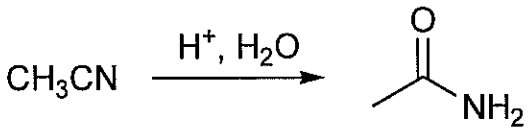


Work from left to right in the following spaces. There is more space than you will need.

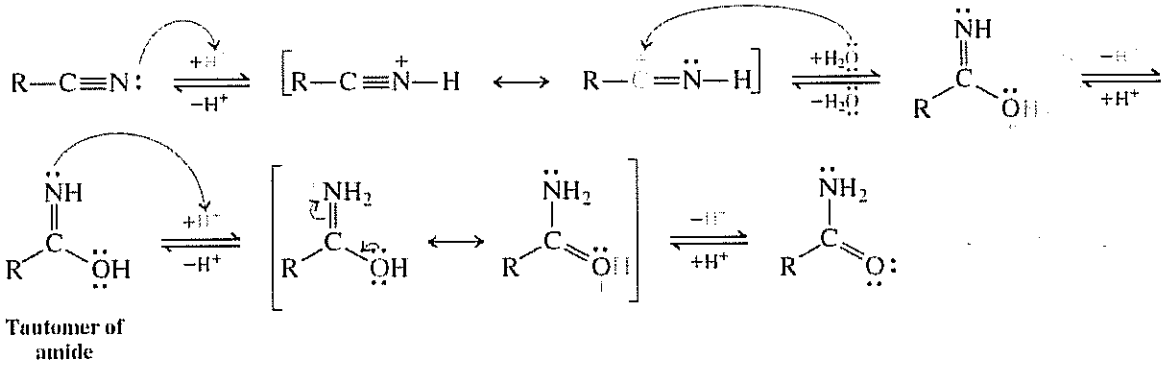




b.

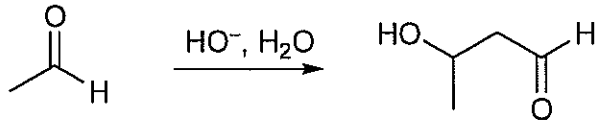


Work from left to right in the following spaces. There is more space than you will need.



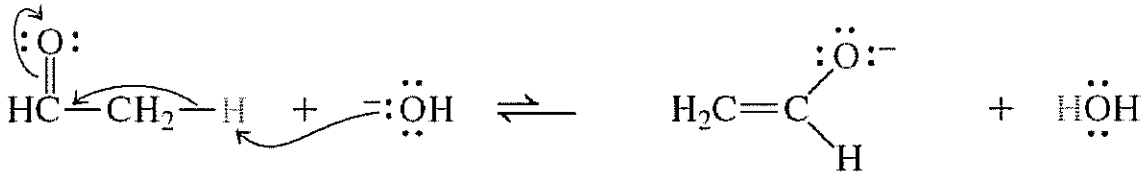
R = CH_3

c.



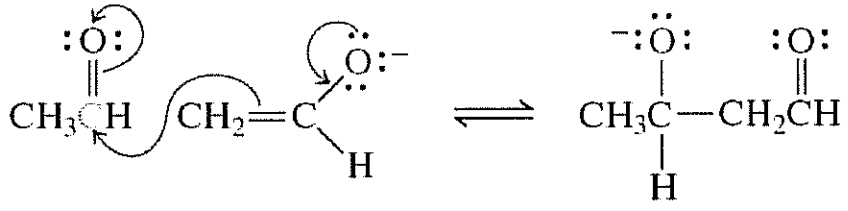
Work from left to right in the following spaces.

STEP 1. Enolate generation

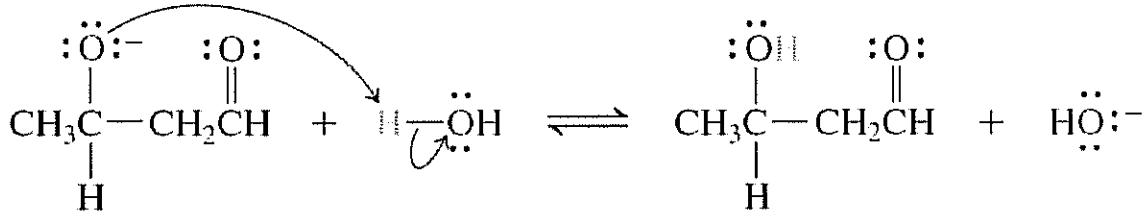


Small equilibrium concentration of enolate

STEP 2. Nucleophilic attack



STEP 3. Protonation

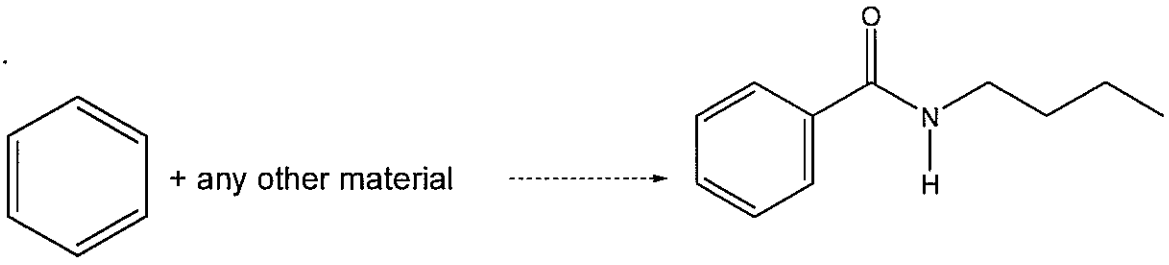


50–60%

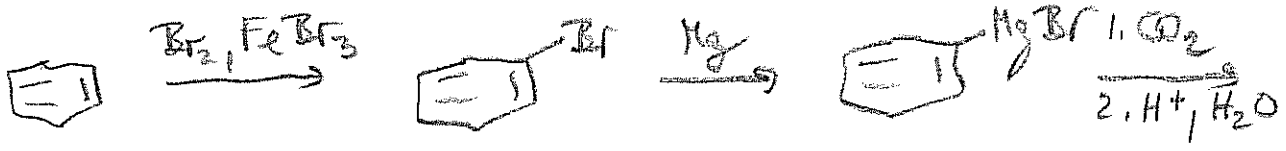
3-Hydroxybutanal (Aldol)

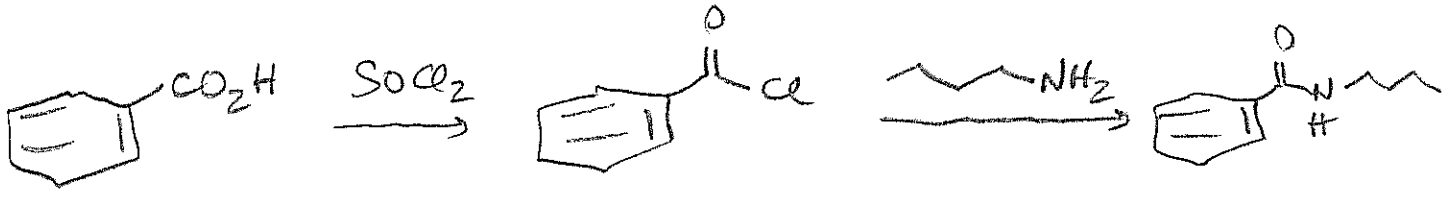
V. [45 Points] Provide a reasonable synthetic route from starting material to product.
Note: Several steps are required, and there may be more than one solution to the problem.
Do not write mechanisms! Write out each step separately, including reagents and products.
You need to apply retrosynthesis!

a.

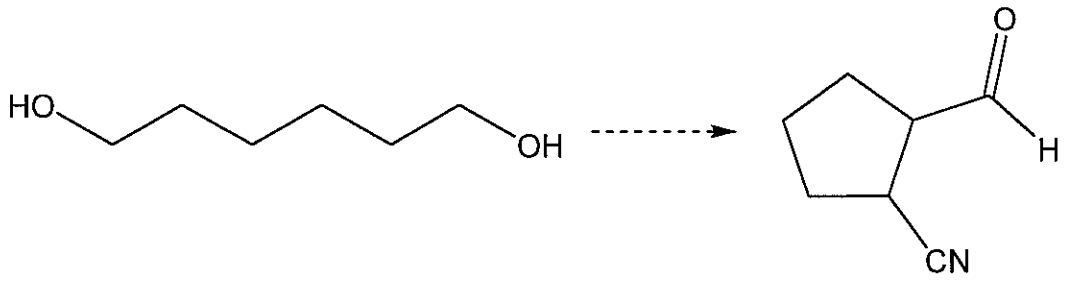


Work from left to right in the following spaces. There is more space than you will need.

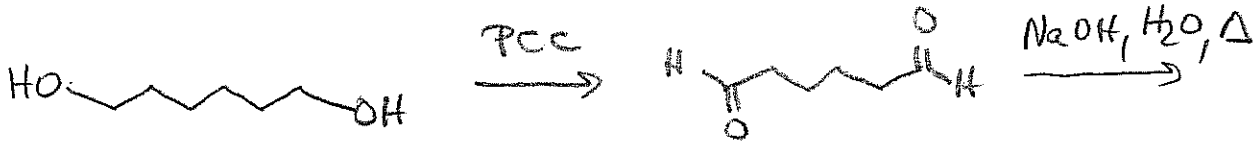


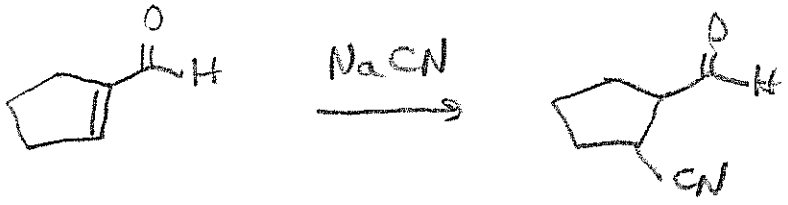


b.

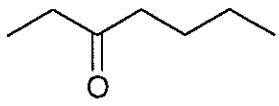


Work from left to right in the following spaces. There is more space than you will need.



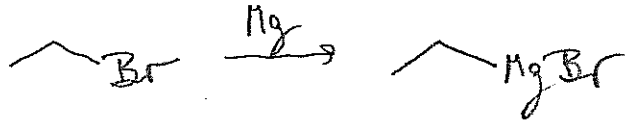


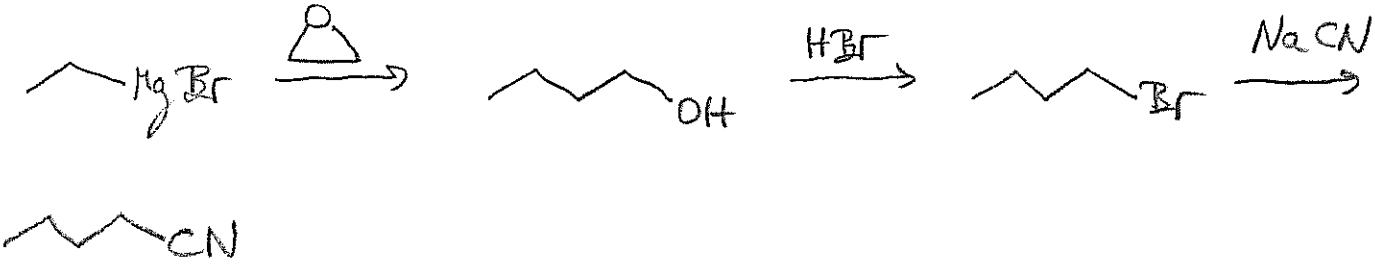
c. Synthesize ketone **A** from starting materials containing one or two carbons only.

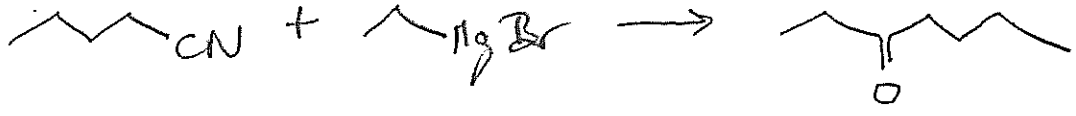


A

Work from left to right in the following spaces. There is more space than you will need.

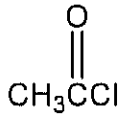
1. 

2. 

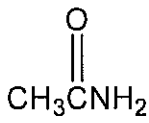
3. 

VI. [35 Points] Place an X mark in the box next to the most accurate statement.

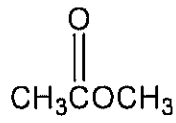
a. The reactivity of **1–4** toward H_2O increases in the order



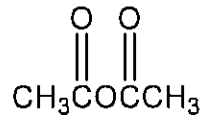
1



2



3



4

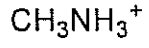
☐ **1, 2, 3, 4**

☐ **4, 3, 2, 1**

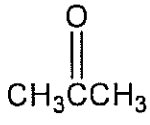
☒ **2, 3, 4, 1**

☐ **3, 2, 1, 4**

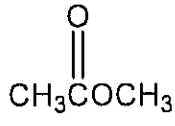
b. The acidity of **1–4** increases in the order



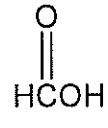
1



2



3



4

☐ **1, 2, 3, 4**

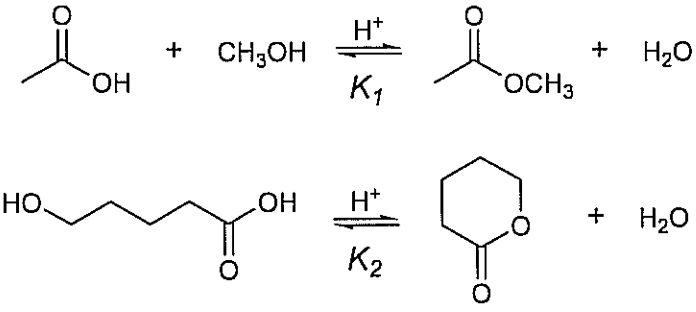
☐ **4, 3, 2, 1**

☐ **2, 3, 4, 1**

☒ **3, 2, 1, 4**

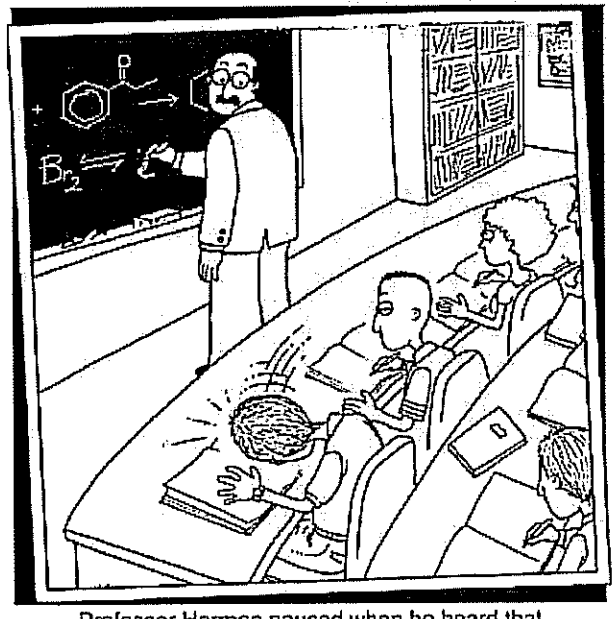
c. Explain the following finding in one sentence. For the equilibria shown below,

$K_1 = \sim 1$, but $K_2 > 1$



Place your answer into the box below.

The entropy is positive for the equilibrium with K_2; entropy is ~0 for K_1



Professor Herman paused when he heard that unmistakable thud – another brain had imploded.

"The End"