Easily Legible Printed Name: _____

CHEM 3331 (100), Fall 2017
Professor Walba
Third Hour Exam
November 28, 2017

scores:

1) 20
2) 20
3) 20
4) 20
5) 20

100

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Signature: Key

Recitation TA Name: _____

Recitation day and time: _____

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear Ziploc bag. Please put all your answers on the test in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

PLEASE read the questions very carefully!

Partial Periodic Table

1A							8A
1 H	2A	3A	4A	5A	6A	7A	2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

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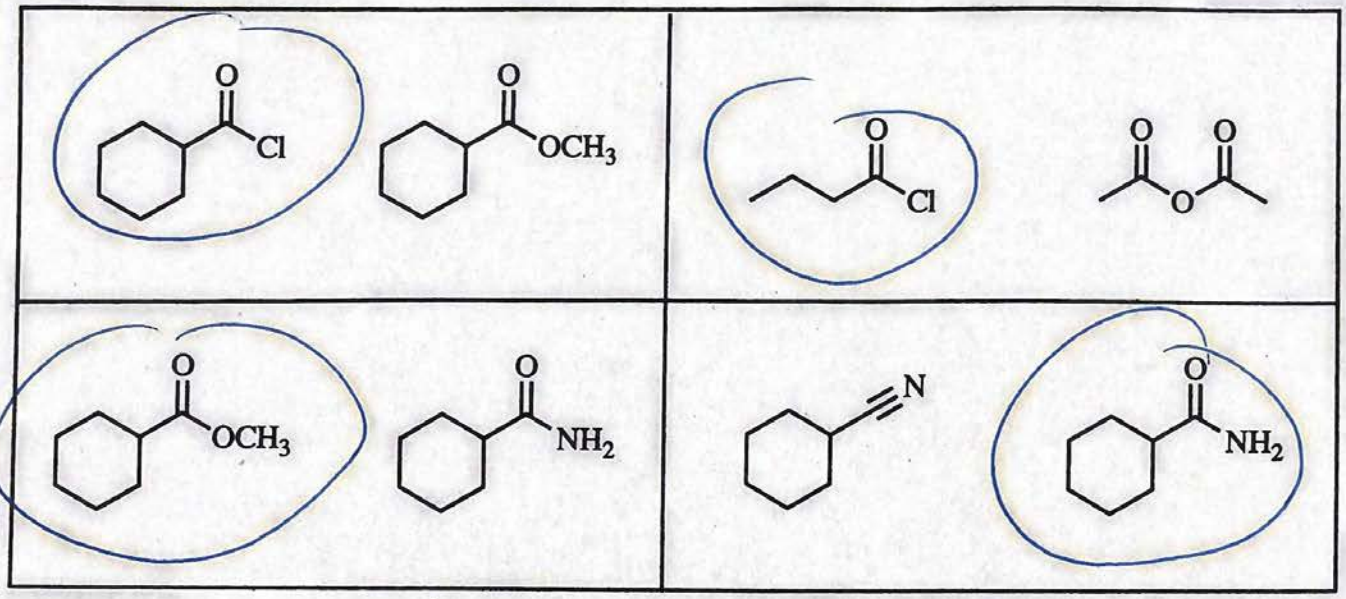
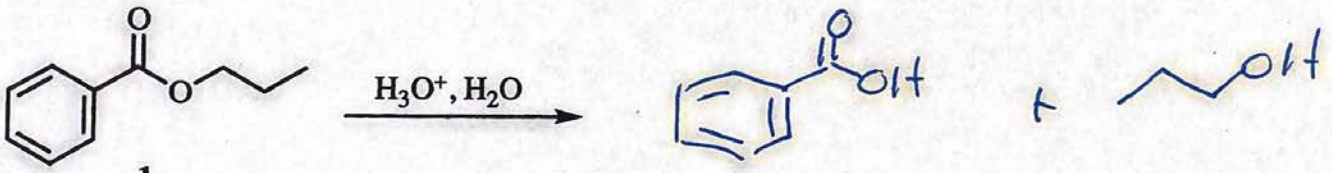
1 (20 pts) a) For each of the following pairs of carbonyl compounds, circle the more reactive compound with respect to hydrolysis to a carboxylic acid using aqueous acid (H_3O^+).



b) Give both organic products of acid catalyzed hydrolysis of n-propyl benzoate (1)



1

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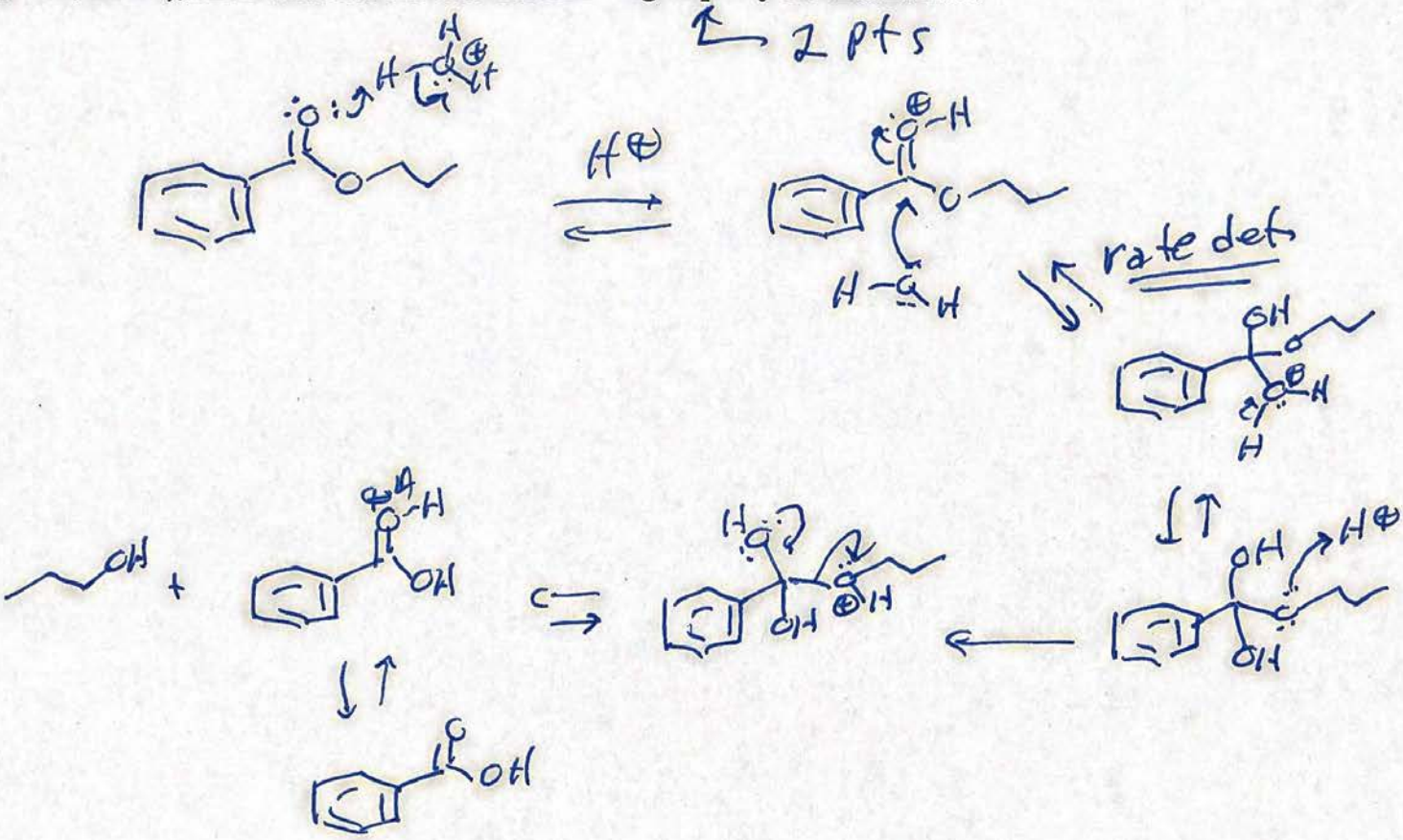
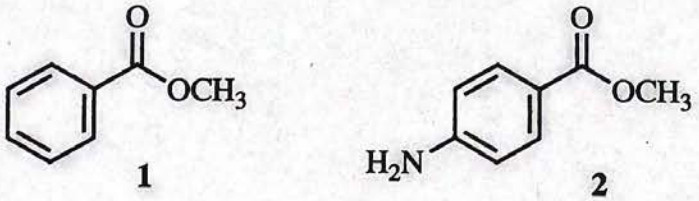
c) Propose an arrow-pushing mechanism for the acid-catalyzed hydrolysis of n-propyl benzoate (the reaction in part b) above), **AND Indicate the rate determining step in your mechanism.**



d) Experimentally, methyl p-aminobenzoate (**2**) undergoes acid catalyzed hydrolysis about 50 times slower than methyl benzoate (**1**). **Briefly** explain why the methyl p-aminobenzoate hydrolyzes more slowly than the methyl benzoate. Note that the acid is catalytic. These are not "strong acid" conditions.



The NH_2 group is electron donating, and stabilizes the ester carbonyl by stabilizing the charge-separated resonance contributor. The more stable carbonyl reacts more slowly

12

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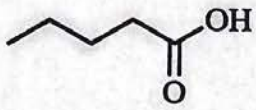
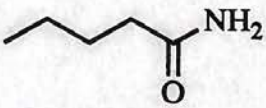
2) (20 pts) Give the **single major product (or two major products, if you think two are formed)** for each of the following reactions, carefully showing stereochemistry using wedges and dashes if appropriate. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting materials are single pure enantiomers unless they are labeled "rac."

a) 

a) $LiAlH_4$, ether

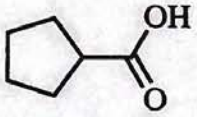
b) H_3O^+ Workup

b) 

a) $LiAlH_4$, ether

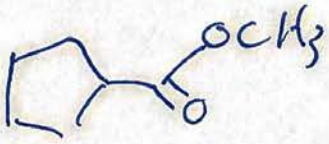
b) H_3O^+ Workup

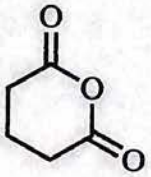
c) Dilute NaOH workup

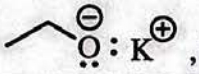
c) 

CH_2N_2

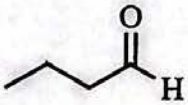
ether



d) 

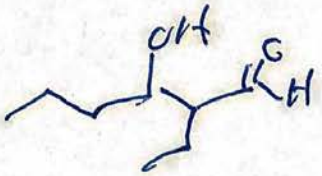
a)  , EtOH

b) H_3O^+ workup

e) 

$NaOH, H_2O$

room temperature



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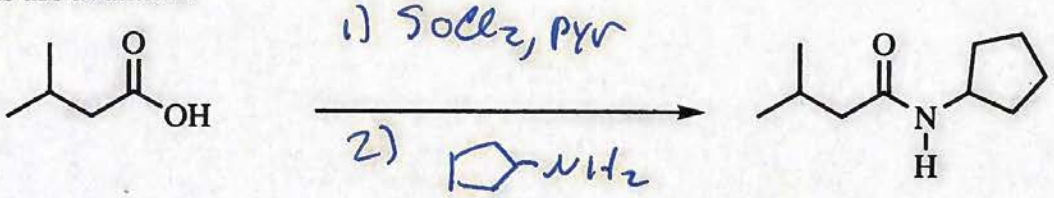
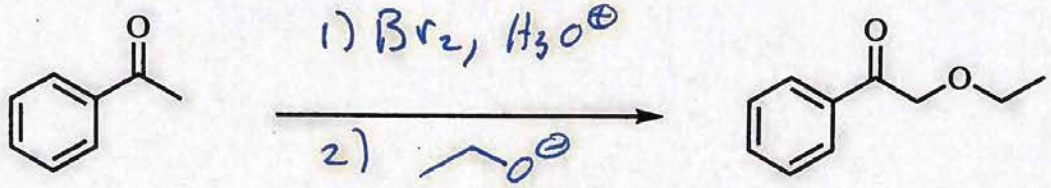
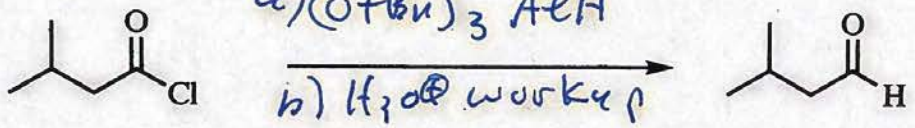
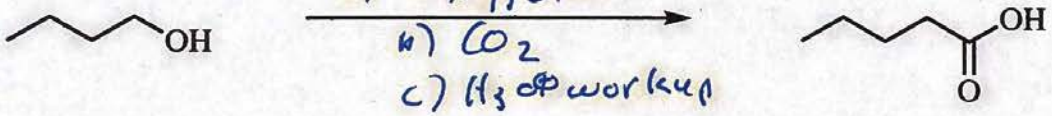
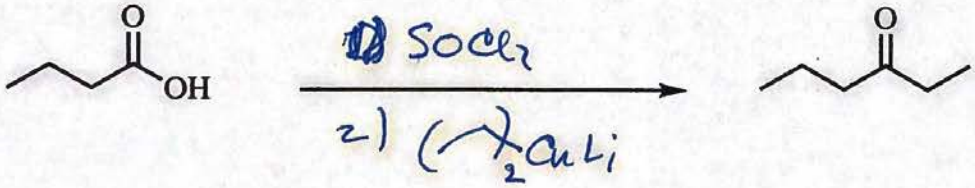
3) (20 pts) Propose reagents for accomplishing each of the following transformations. For reactions involving sequential addition of reagents, label the two parts of the reaction using letters. Your synthesis may require multiple reactions, with isolation of intermediate products, to make the target. Use numbers to indicate individual steps in a multi-step synthesis. Make your synthesis efficient (i.e. the target product should be the major product). Assume chiral starting materials and products are single pure enantiomers unless they are labeled "rac." Assume you can buy any inorganic reagents you might need. Assume simple organometallic reagents are available.

a) 

b) 

c) 

d) 

e) 

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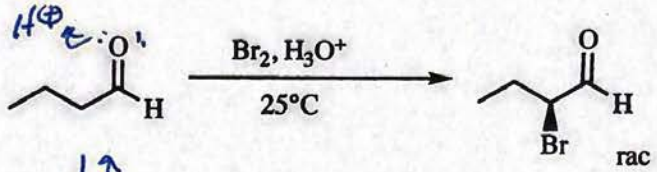
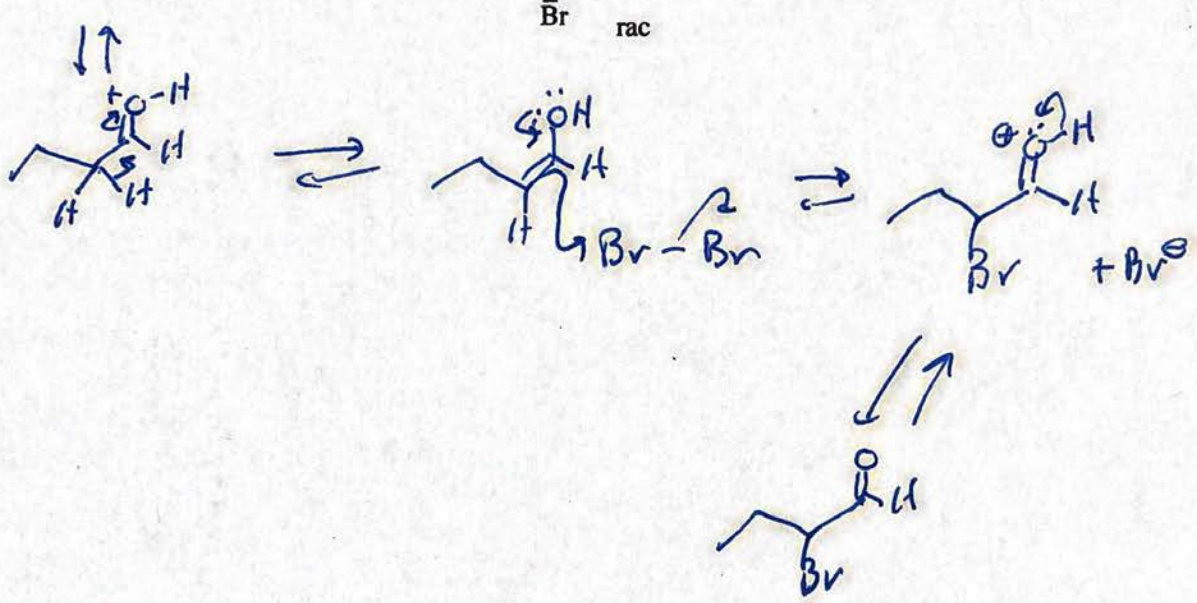
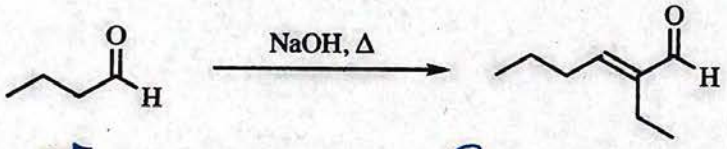
4) (20 pts) Propose an arrow-pushing mechanism for each of the following reactions.

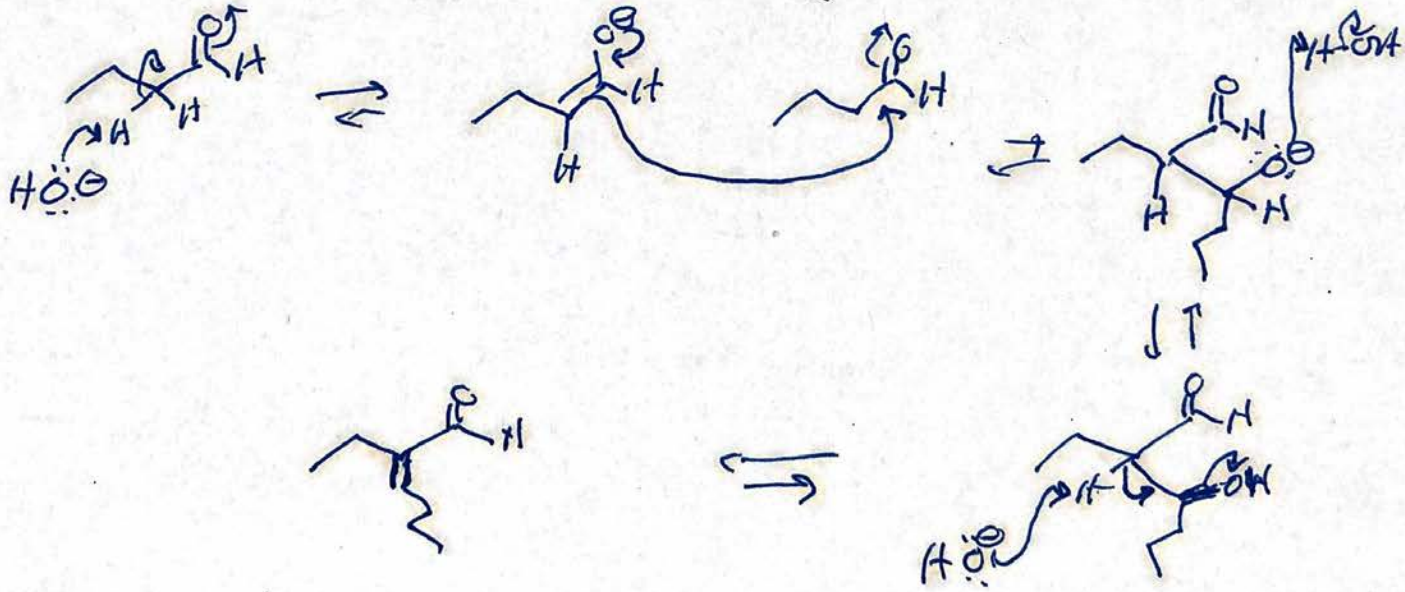
a)





b)





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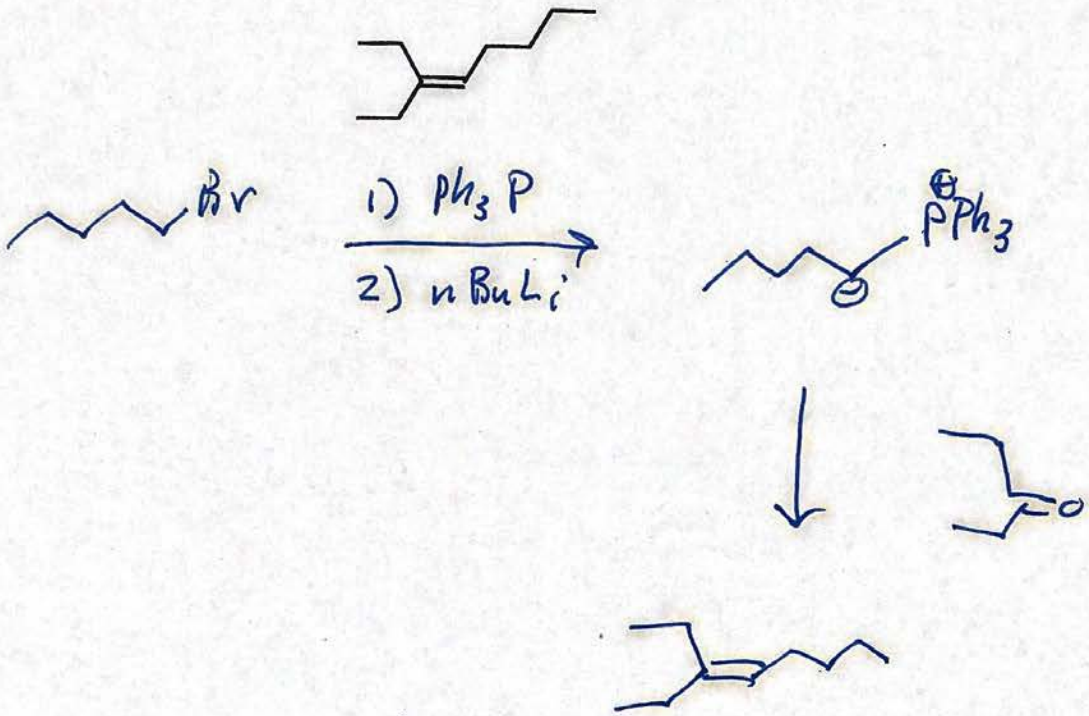
5) (20 pts) Propose a synthesis of each of the following targets using any organic starting materials with **five carbons or less**. You may use any necessary reagents that would typically be available commercially. Try to make your synthesis efficient (i.e. the target should be produced in high yield). More than one step will be required. Each reaction in the sequence leading to an isolated and purified product should be shown. Use letters to indicate sequential addition of reagents in a single reaction. **Do not put multiple reactions over/under one arrow!**

a)



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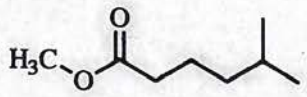
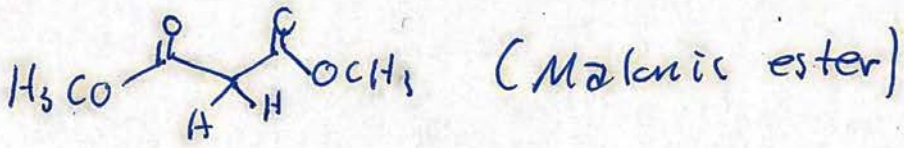
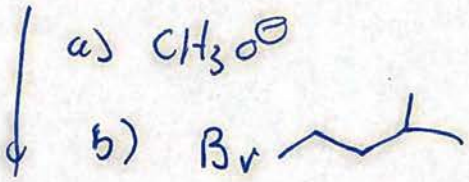
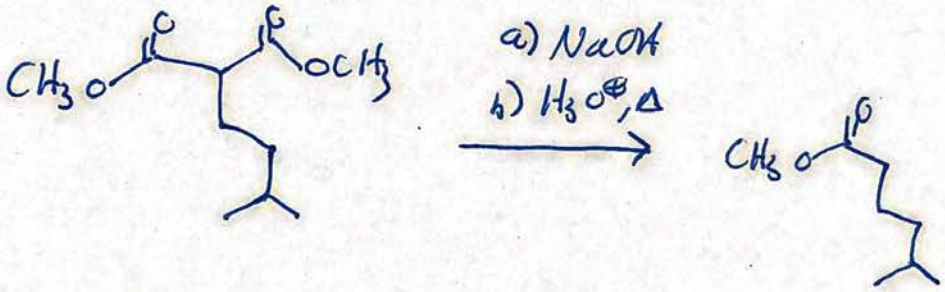
Q5, continued.

b) Note!!! **For this question, you cannot use LDA!**









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