Easily Legible Printed Name:______________________________

CHEM 3371 (100), Spring 2017
Professor Walba
Third Hour Exam
April 18, 2017

scores:

1) 20

2) 20

3) 20

4) 24

5) 16

____
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: Ed Guzman

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	2A	3A	4A	5A	6A	7A	8A
1 H							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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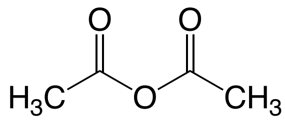
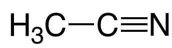
1 (20 pts) a) The relative stability of acid derivatives is a simple but powerful concept for understanding important properties, such as their relative rates of hydrolysis. Arrange the following acid derivatives in order of increasing reactivity towards hydrolysis in aqueous base (H_2O, NaOH) by putting the compound numbers in the boxes below.


1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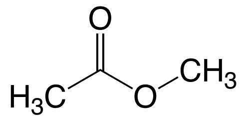
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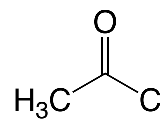
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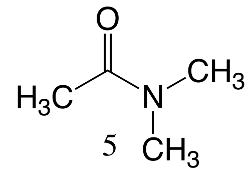
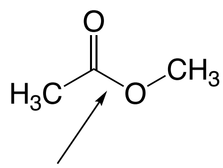
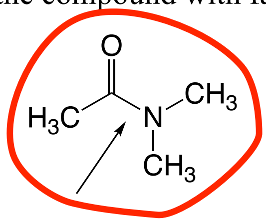

5

2	5	3	1	4

Least reactive — Most reactive

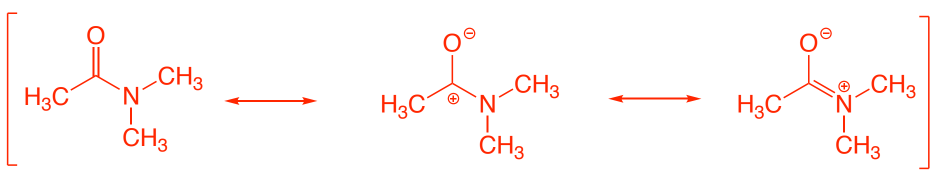
b) For the compounds below, rotation about the bond indicated by the arrows occurs. But, this rotation is much faster for one of the compounds than for the other. Circle the compound with faster rotation about the indicated bond.

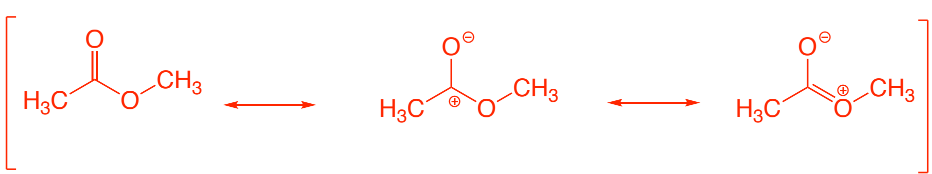




c) Give a short argument to explain your answer in part b) above. Please use resonance structures to augment your written argument.

The stability of a carbonyl compound is related to the ability of a substituent to stabilize the charge separated carbonyl resonance contributor with positive charge of the carbonyl carbon, as indicated by the two center structures below. The simple model is that substituents that stabilizes the carbonyl "cationic" carbon stabilize the structure. For amides and esters, there is a third important resonance contributor putting the positive charge on the amide nitrogen or the ester oxygen. Since nitrogen is less electronegative than oxygen, nitrogen can more easily accommodate positive charge. Thus, the "third" resonance contributor is more important for amides than for esters, and this extra delocalization of charge stabilizes the amide structure relative to the ester. Since the C-N bond has more double bond character that the C-O bond, rotation about the amide C-N bond is much slower than rotation about the ester C-O bond.





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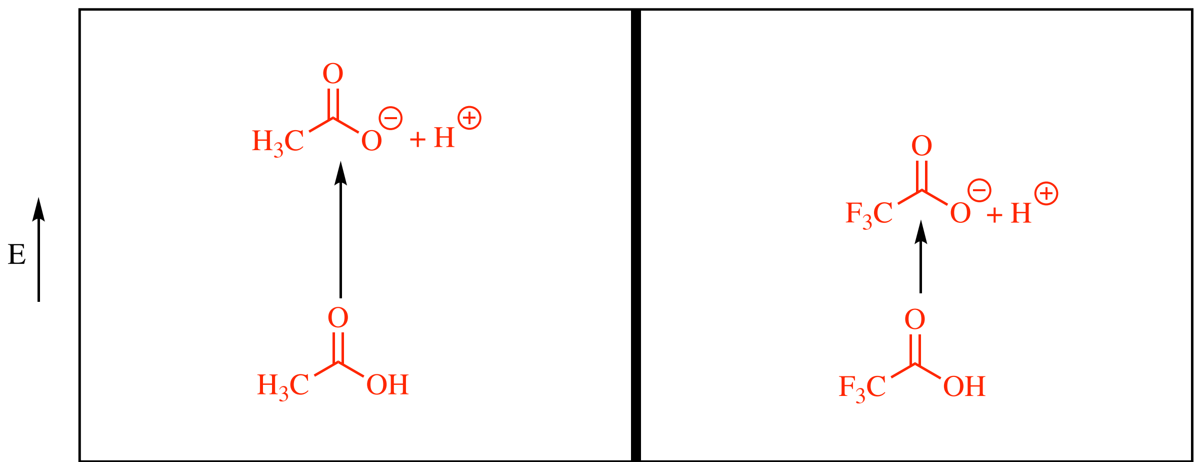
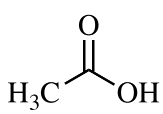
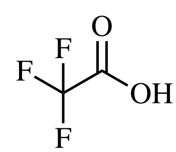
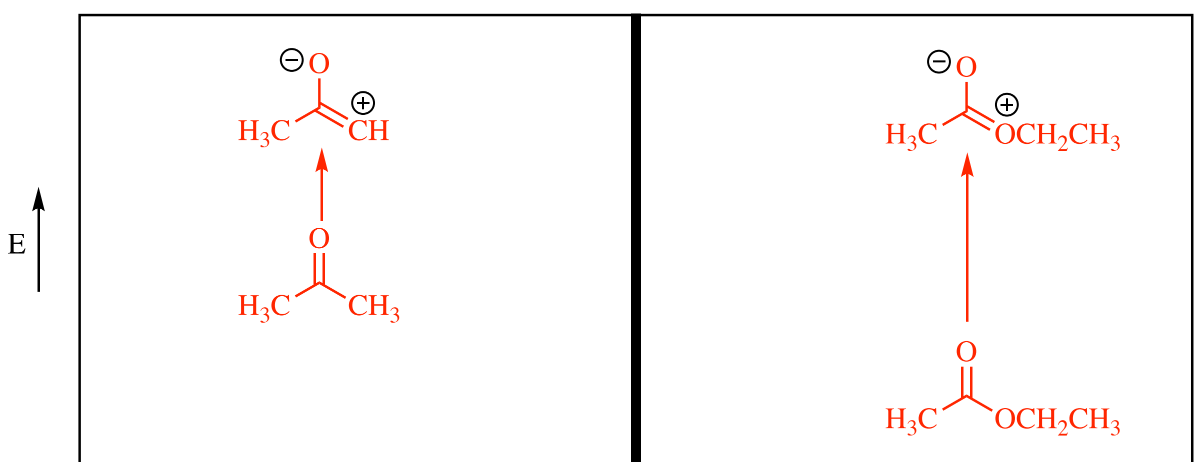
1. – Continued

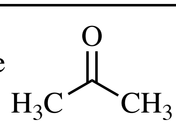
c) For Brønsted acid-base reactions the energy barrier between the acid and conjugate base is typically very small (Brønsted acid-base reactions are very fast). For this reason, energy diagrams describing the relative energies (stabilities) of acid and conjugate base often leave out a transition state, and simply put the two species on the energy diagram one above the other with a vertical arrow, to illustrate their relative energies. Complete energy diagrams for the four acid-base reactions given below. The structures of the acids are given, you need to put the structures of the acids AND conjugate bases on the diagram.

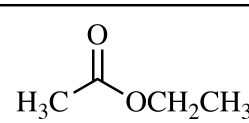


acetic acid 

trifluoroacetic acid 



acetone 

ethyl acetate 

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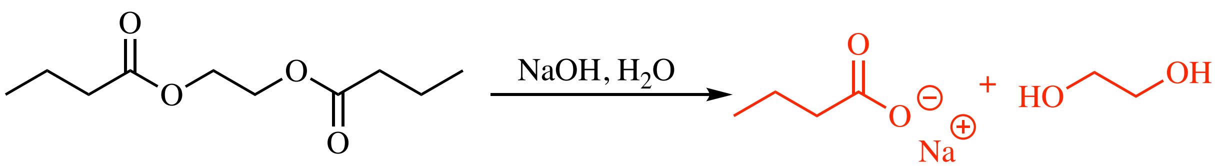
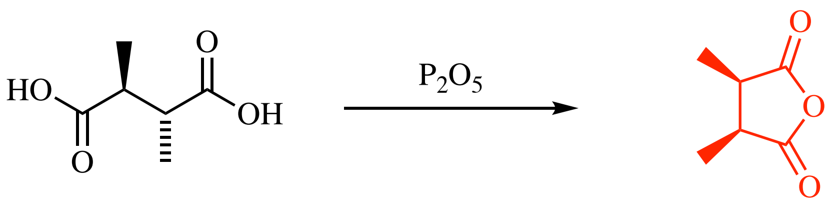
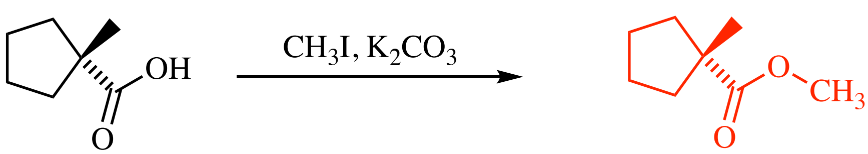
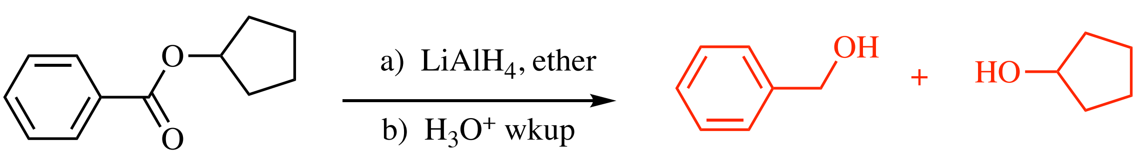
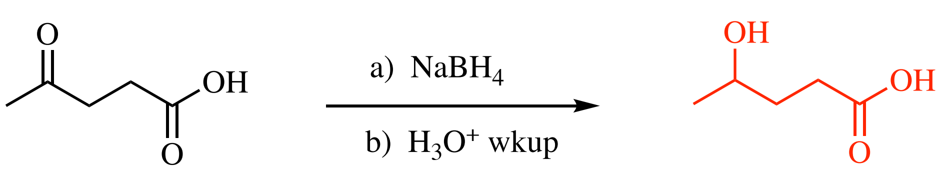
2) (20 pts) Give the **single major product (or two major products, if you think two are formed)** for each of the following reactions, carefully showing stereochemistry using wedges and dashes if appropriate. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting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

a)


b)


c)


d)


e)


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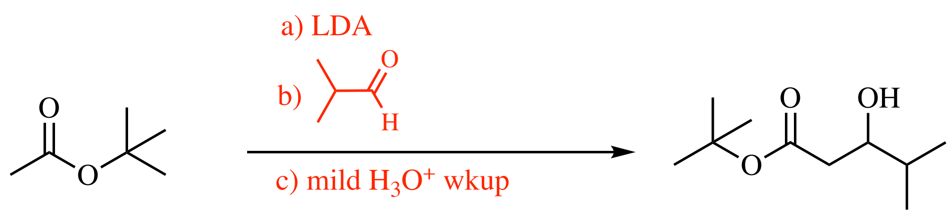
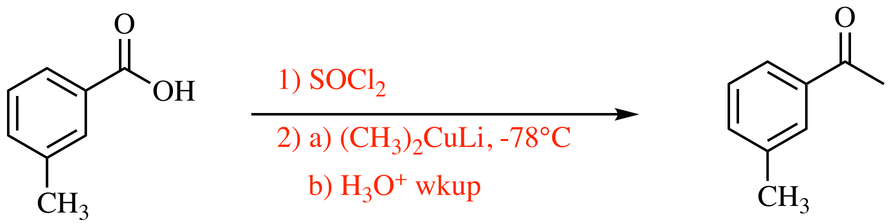
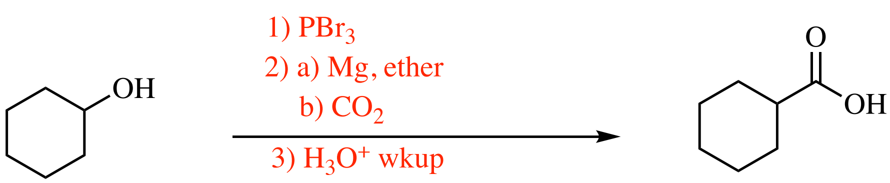
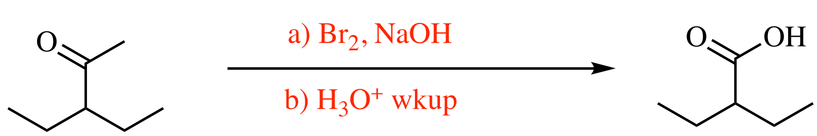
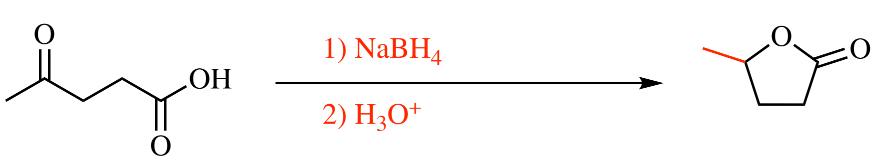
3) (20 pts) Propose reagents for accomplishing each of the following transformations. For reactions involving sequential addition of reagents, label the two parts of the reaction using letters. Your synthesis may require multiple reactions, with isolation of intermediate products, to make the target. 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. If you need an organometallic reagent that's not commercial (assume only alkyllithium reagents are commercial), show how you would make it.

a) 

b) 

c) 

d) 

e) 

red carbon should have been there - chemdraw typo

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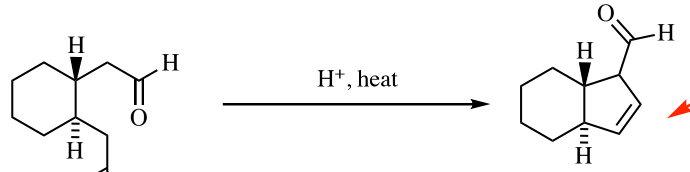
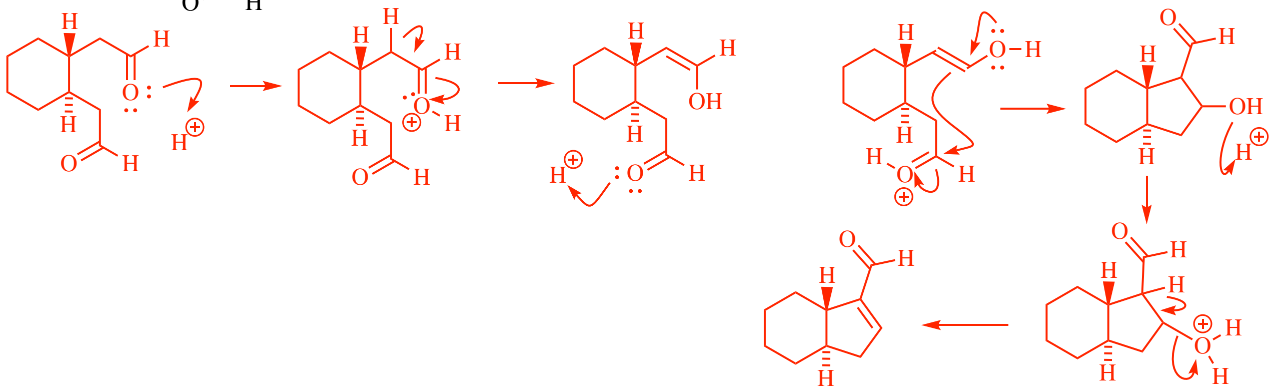
4) (24 pts) Propose an arrow-pushing mechanism for each of the following reactions.

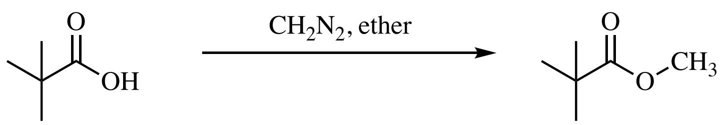
a)

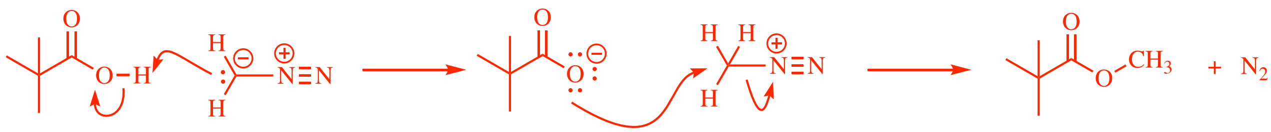


this was another typo.
You get the conjugated DB

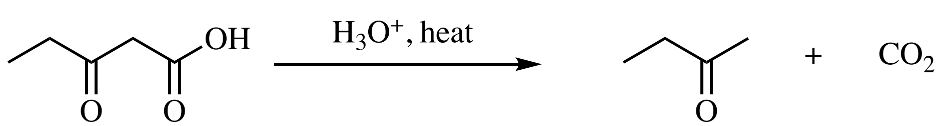


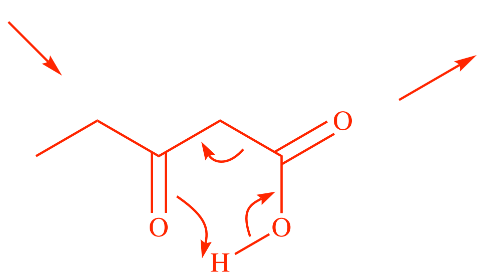
b)





c)





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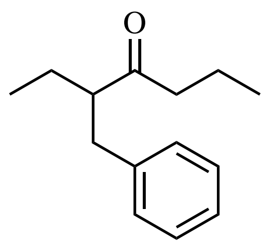
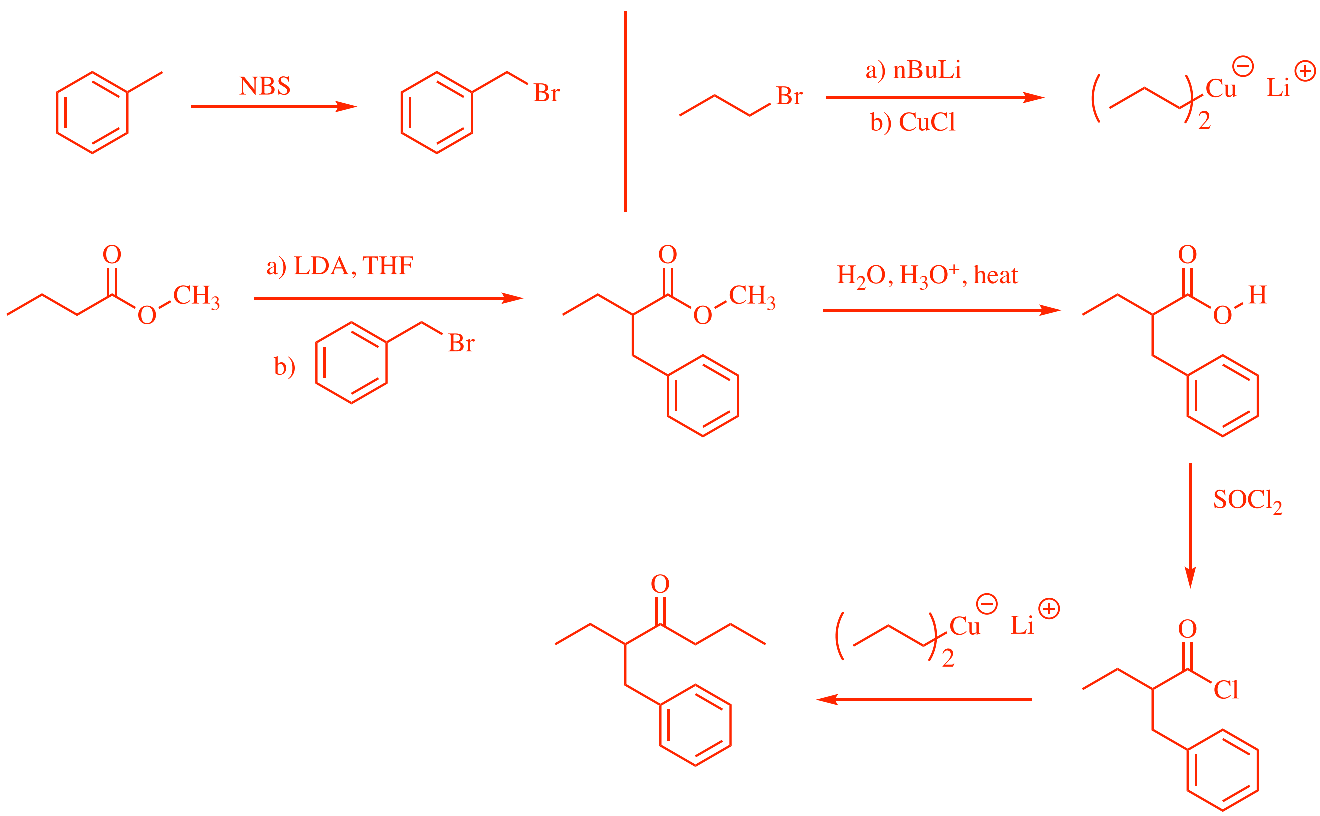
5) (16 pts) Propose a synthesis of the following target using any organic starting materials with **five carbons or less**, benzene, or toluene. You may use any necessary inorganic reagents. Try to make your synthesis efficient (i.e. the target should be produced in high yield). More than one step will be required. Each reaction in the sequence leading to an isolated and purified product should be shown. Please note – according to Loudon **one cannot alkylate a ketone enolate, so don't try it**. Use letters to indicate sequential addition of reagents in a single reaction. **Do not put multiple reactions over/under one arrow!**





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