

CHEM 3371, Spring 2015
Professor Walba
Third Hour Exam
April 14, 2014

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.

Name (printed): Key

Signature: _____

Recitation TA: Patrick Chaffey or Carley Little
(circle your TAs name)

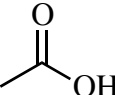
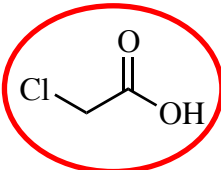
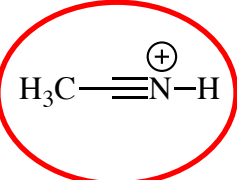
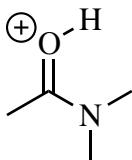
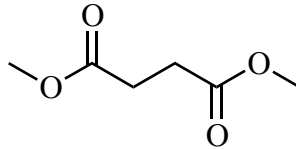
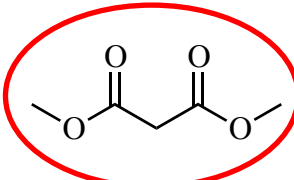
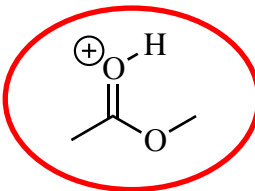
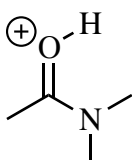
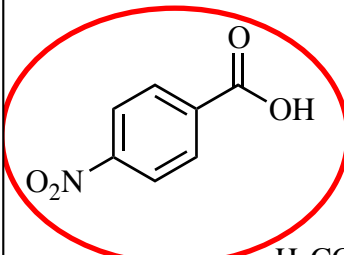
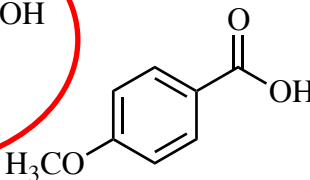
Recitation day and time: _____

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 ziplock bag. Please put all your answers on the test. Use the backs of the pages for scratch.

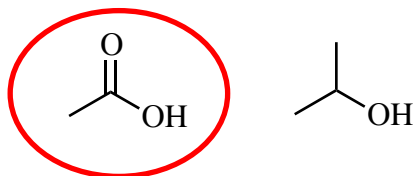
PLEASE read the questions very carefully!

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

1 (20 pts) a) For each of the following pairs of compounds, circle the stronger Brønsted acid.

 	 
 	 
 	<p>Left blank intentionally</p>

b) For the two structures below, circle the compound with the higher boiling point.



c) Referring to question 1b above, give a very short explanation for your answer (must fit in the space below).

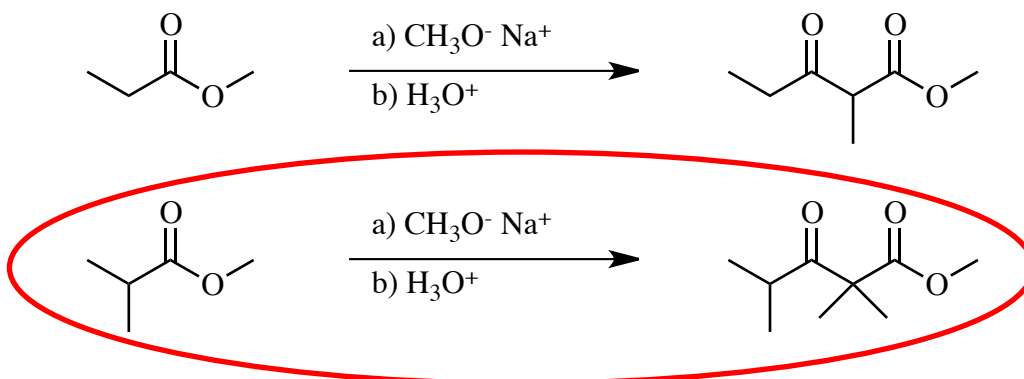
The carboxylic acid forms a hydrogen bonded dimer, which increases the boiling point.

OR

More H-bonding

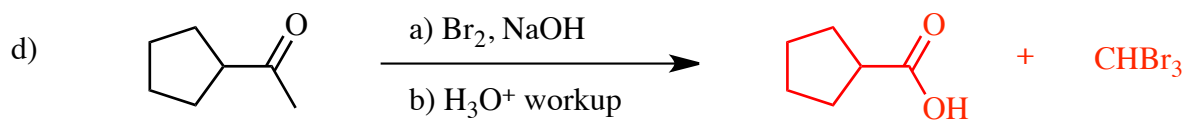
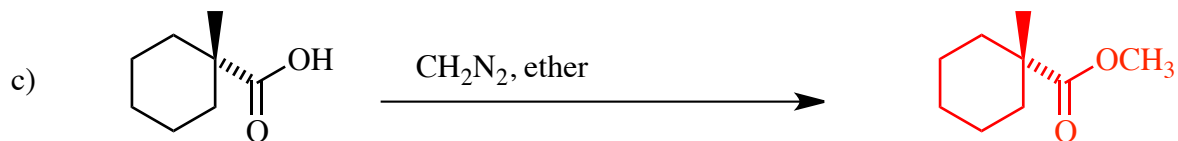
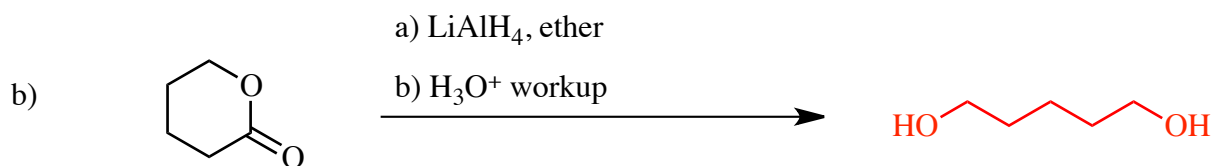
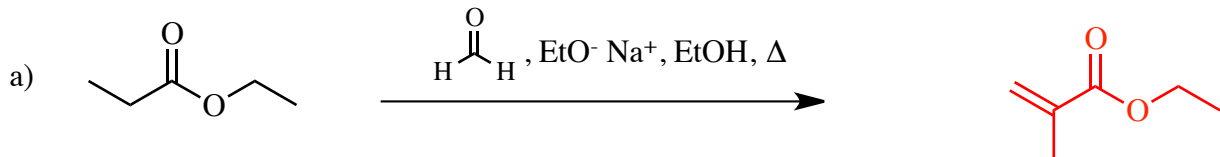
1 – Continued

c) For the following reactions, circle the reaction which does NOT work.

d) Referring to question 1c above, please **briefly** explain why the reaction you circled doesn't work.

The Claisen condensation only works when the product can be deprotonated on the beta carbon of the beta dicarbonyl system to give a stable anion. This drives the equilibrium. If you can't deprotonate between the carbonyls, the product actually goes back to starting materials. [Note – this is a key fact driving the rearrangement in question 4b]

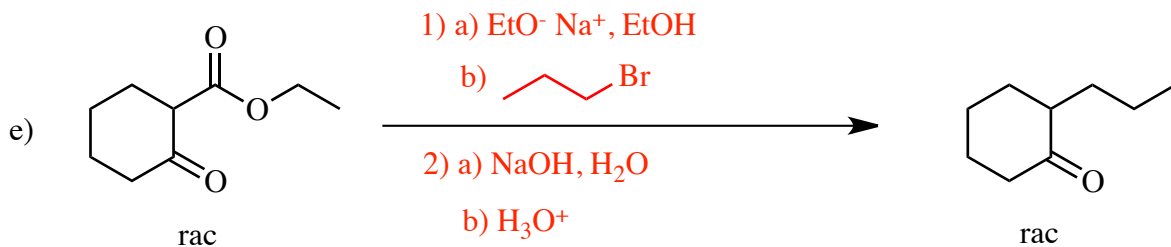
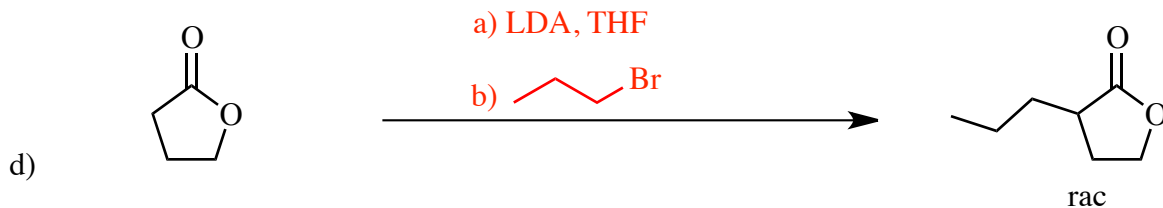
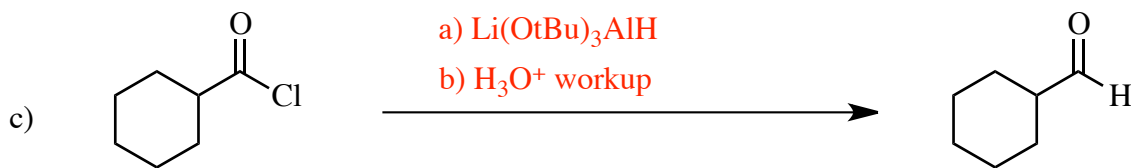
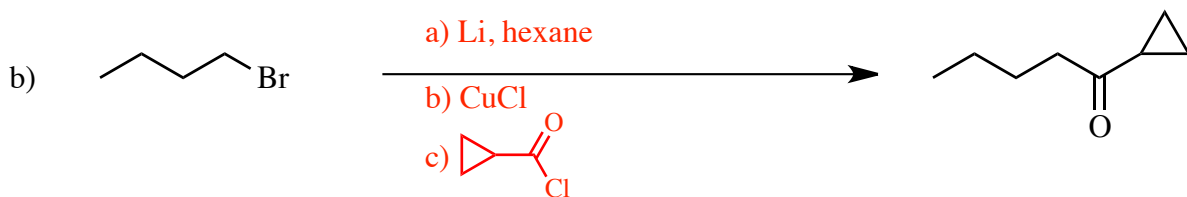
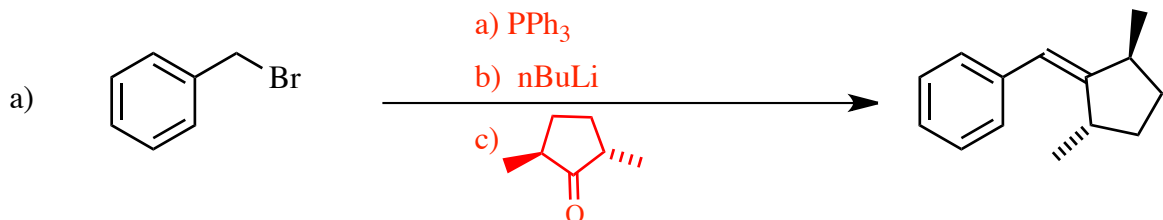
2) (20 pts) Give the single major product of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac."



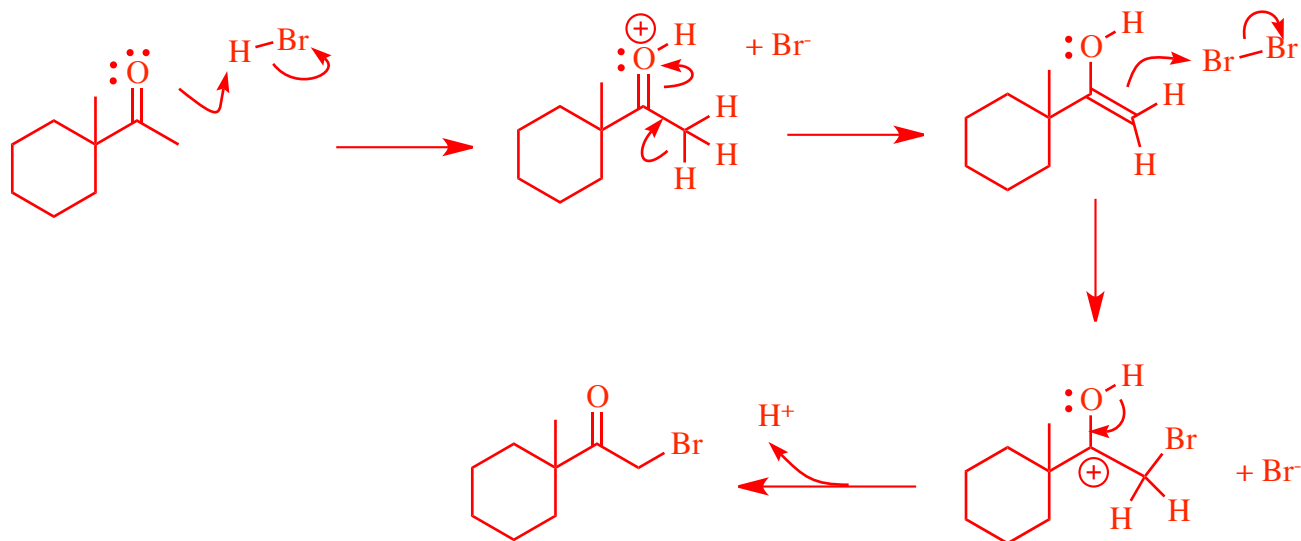
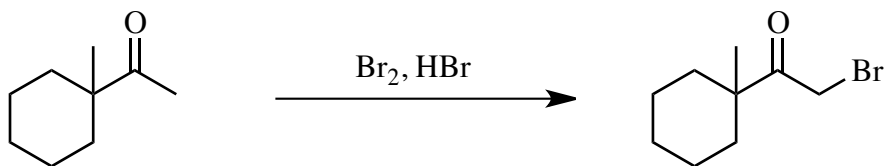
Give two organic products for the reaction in part d



3) (20 pts) Propose reagents for accomplishing each of the following transformations. Make your reactions efficient (i.e. the target product should be the major product). More than one step may be required - try to use the minimum number of steps. Assume chiral starting materials or products are single pure enantiomers unless they are labeled "rac." You may use organometallic reagents without showing how they are synthesized.



4) (20 pts) a) Propose an arrow-pushing mechanism for the following reaction.

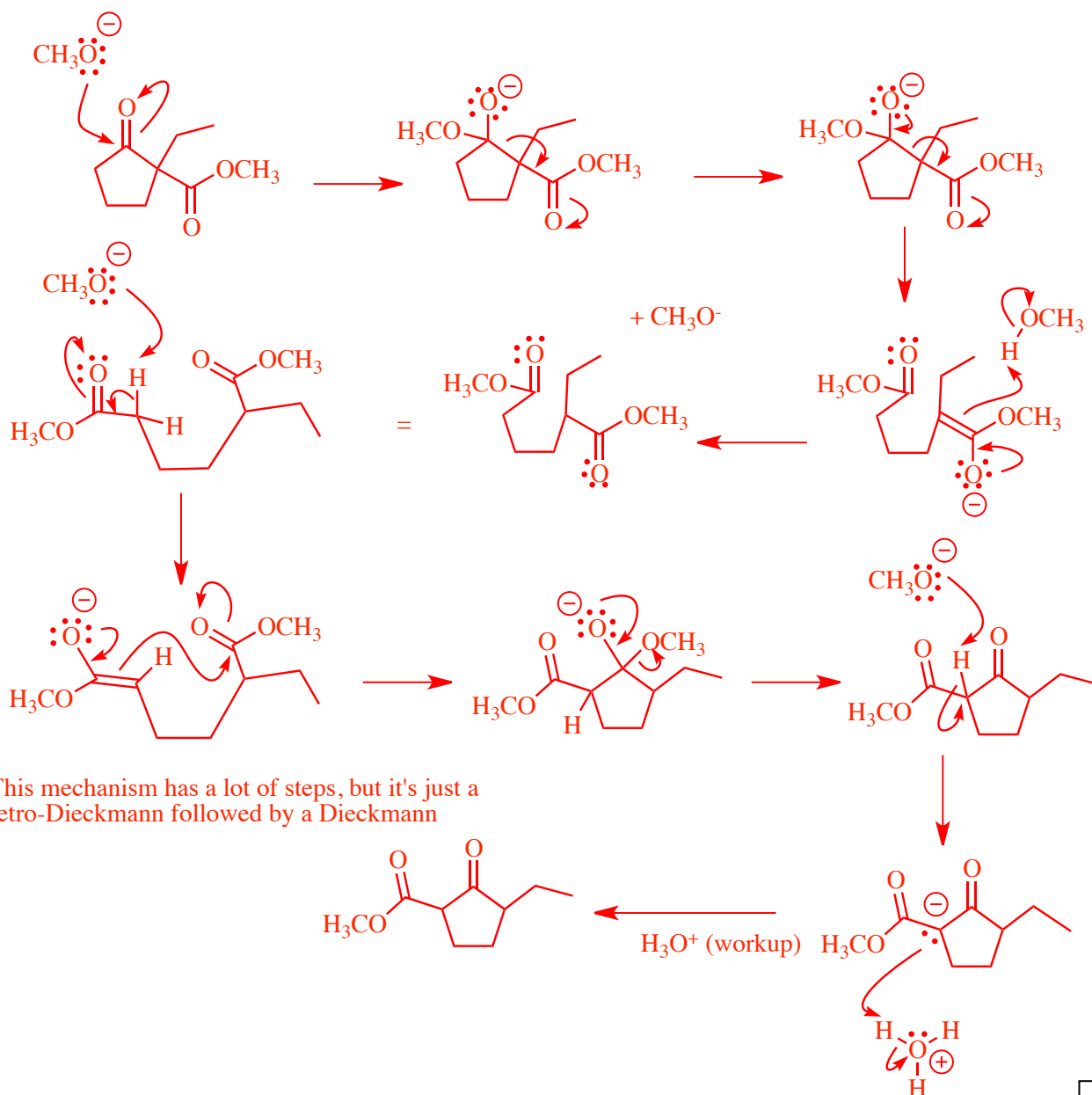
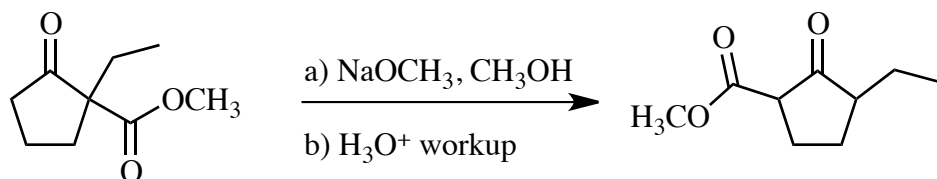


4 - Continued

b) Propose an arrow-pushing mechanism for this seemingly mysterious reaction.

Hint: Dimethylcarbonate ($\text{H}_3\text{CO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$) is not involved in the mechanism.

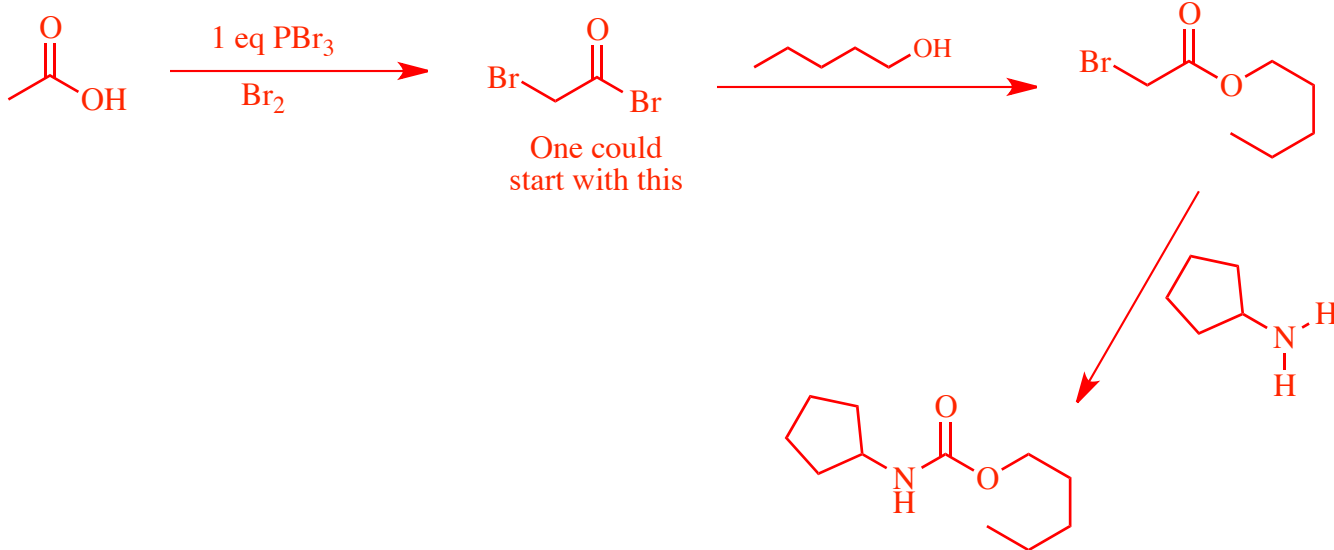
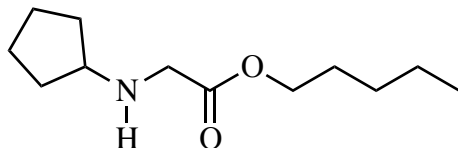
Also, the product is a mixture of isomers, which can be ignored for your answer.



This mechanism has a lot of steps, but it's just a retro-Dieckmann followed by a Dieckmann

5) (20 pts) Propose a synthesis for each of the following targets. Allowed starting materials include benzene, Ph_3P , and/or any other organic molecules containing **five (5) carbons or less**. You may use any necessary inorganic reagents. Try to make your syntheses efficient (i.e. the target should be produced in the highest possible yield). More than one step will be required. Please show all the intermediate **products** in your synthesis (not reactive intermediates involved in the mechanisms, but actual isolated molecules on the path from starting material to product). Please put reagents for reactions involving sequential addition of reagents, over an arrow using letters (a, b, c...) to designate the sequence of addition. Please do **not** put multiple reactions over one arrow. (Continued on next page)

a)



5) – Continued –

b)

