CHEM 3331, Spring 2011
Professor Walba
Second Hour Exam
March 10, 2011

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 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 you answers on the test. Use the backs of the pages for scratch.

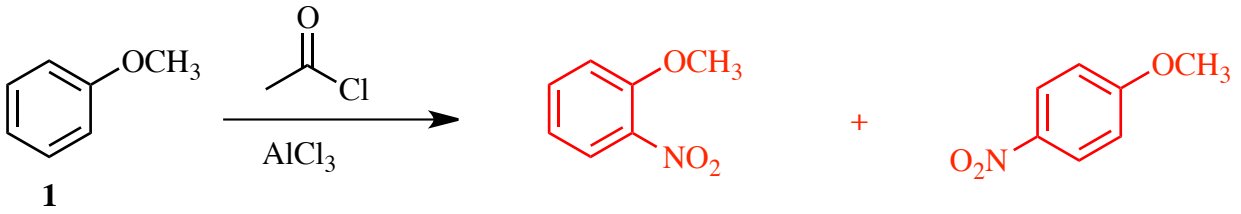
PLEASE read the questions very carefully!

Partial Periodic Table

1A							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	

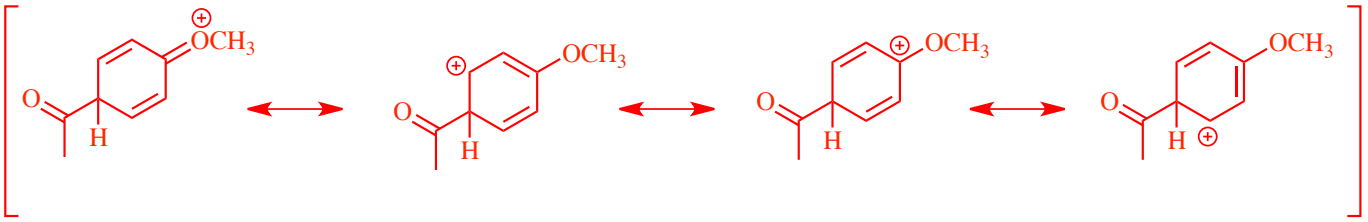
Printed Name:_____

1. (20 pts) a) Anisole (**1**) reacts with acetyl chloride and aluminum trichloride to give **two** major products. Give the structure of the two major products.



1

b) The reactions above involve formation of reactive intermediate cations with molecular formula $C_9H_{12}O_2^+$. For **ONE** of your products (you pick which one), draw **all** of the important resonance contributors to the structure of the cation intermediate.



c) Are the reactions in part 1b FASTER or SLOWER than the acylation of benzene?

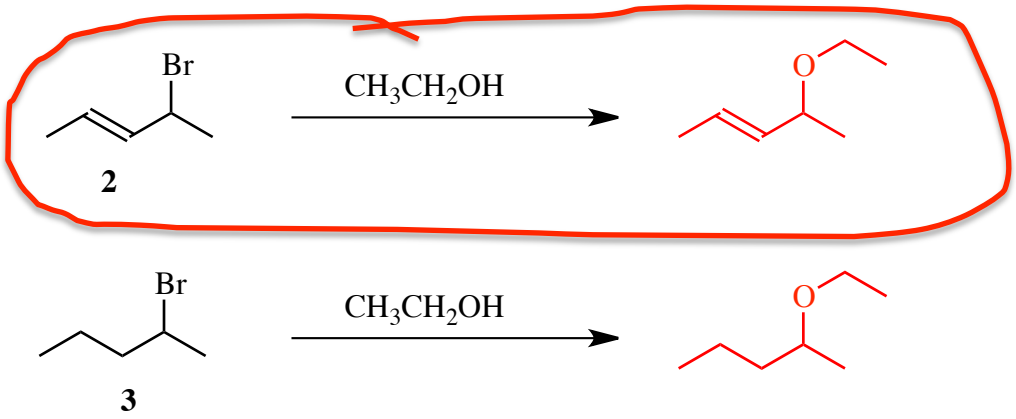
FASTER

Total points for this page: ____

Printed Name:_____

1. –continued-

d) Give the structure of the product obtained when bromide **2** is dissolved in ethanol. Also give the structure of the product obtained when bromide **3** is dissolved in ethanol. For this question (1d), ignore stereochemistry.



d) Give the name of the mechanism of the reactions in part 1d.

S_N1

e) Under the same conditions, one of the reactions in part 1c proceeds to give product much faster than the other. **Circle the faster reaction**.

f) Briefly explain the reasoning behind your solution to part 1d. That is, why is the reaction you circled faster?

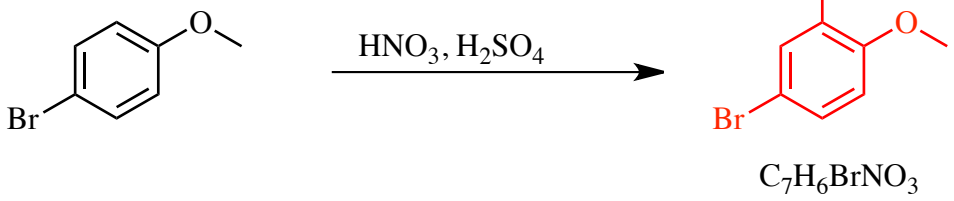
Reaction of 2 involves a secondary allylic cation as the intermediate in an S_N1 reaction, while reaction **3** involves a secondary cation. The allylic cation is more stable, and is formed faster. Since the ionization to the cation is the rate determining step, the product from reaction 2 is formed faster.

Total points for this page: ____

Printed Name:_____

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."

a)

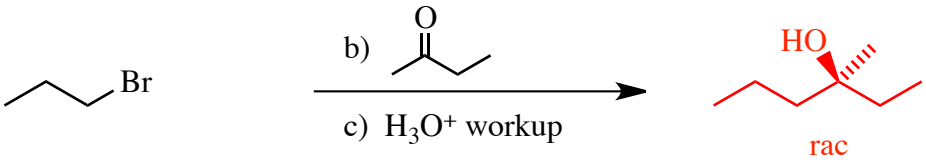


$C_7H_6BrNO_3$

---

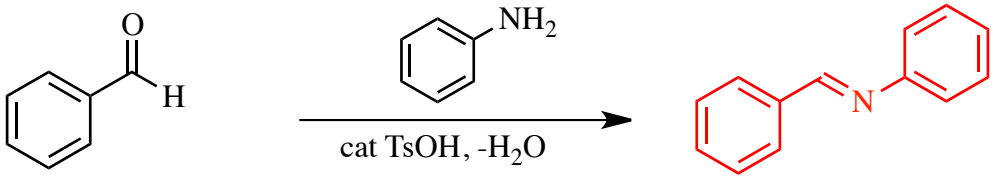
b)

c)

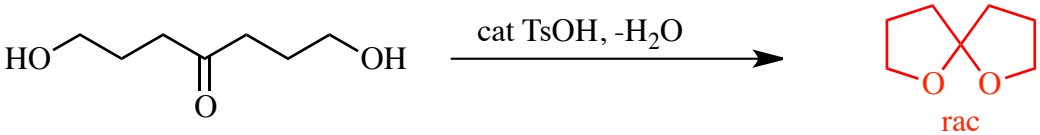


rac

d)



e)



rac

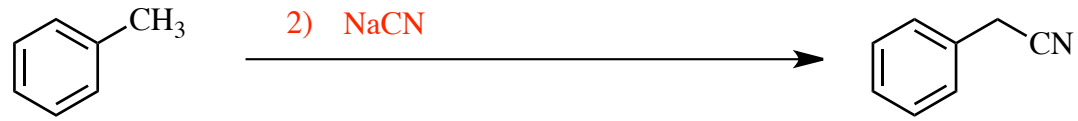
Total points for this page: ____

Printed Name:_____

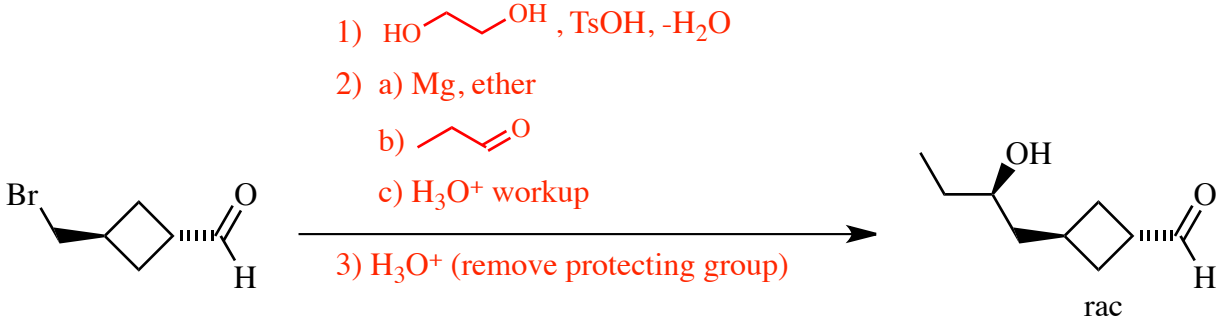
3) (20 pts) Propose reagents for accomplishing the following transformations. NOTE: more than one step may be required! Try to make your synthesis efficient (i.e. the desired product should be the major product, and generally a shorter synthesis is better than a longer one). You must use the starting material given; you may use any other reagents you need.

a)

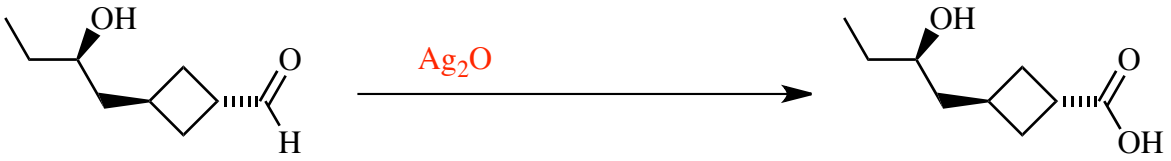
b)



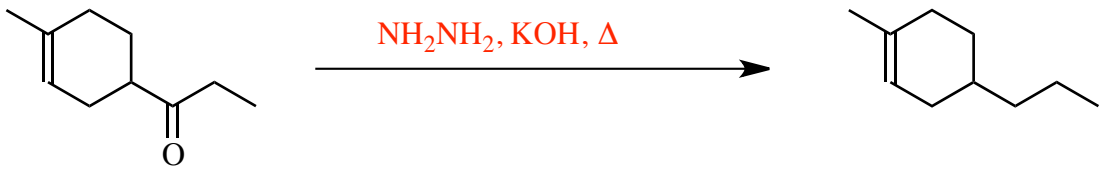
c)



d)



e)

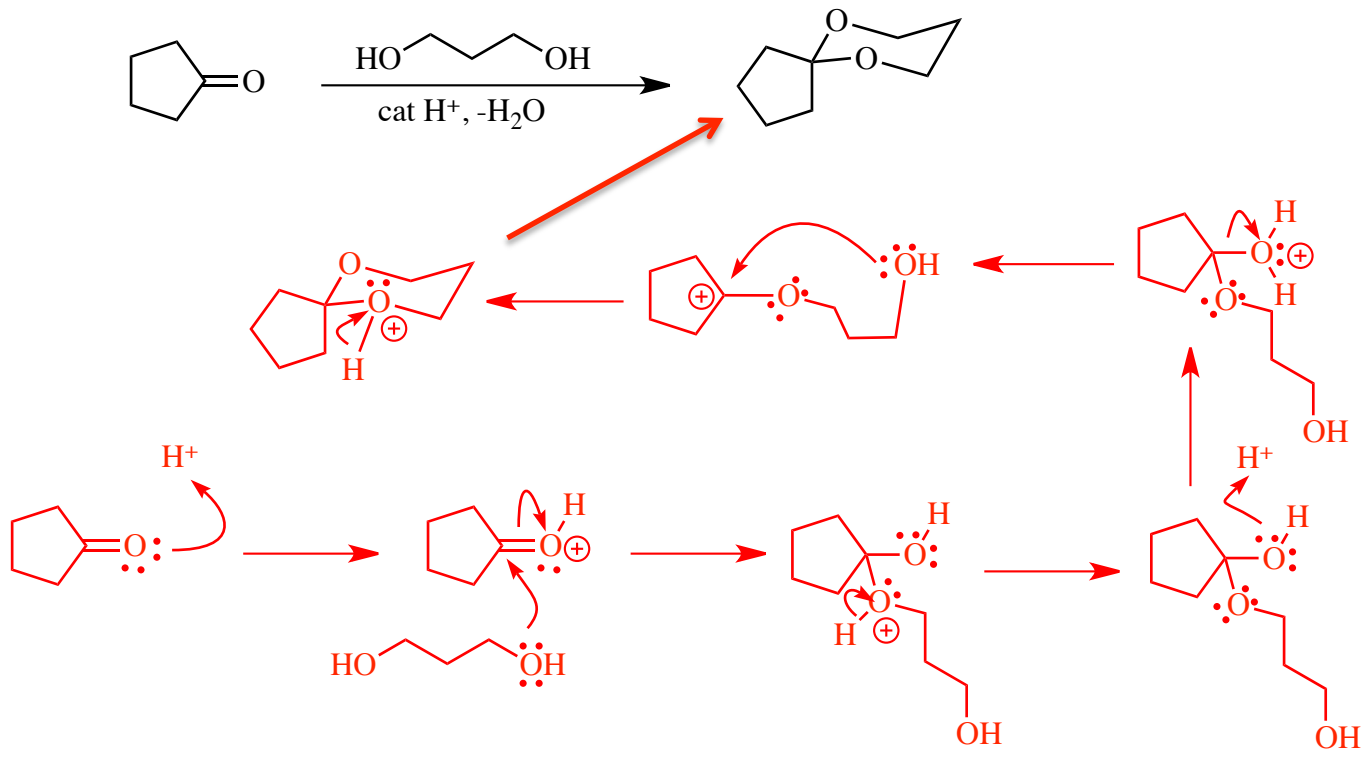


Total points for this page: ____

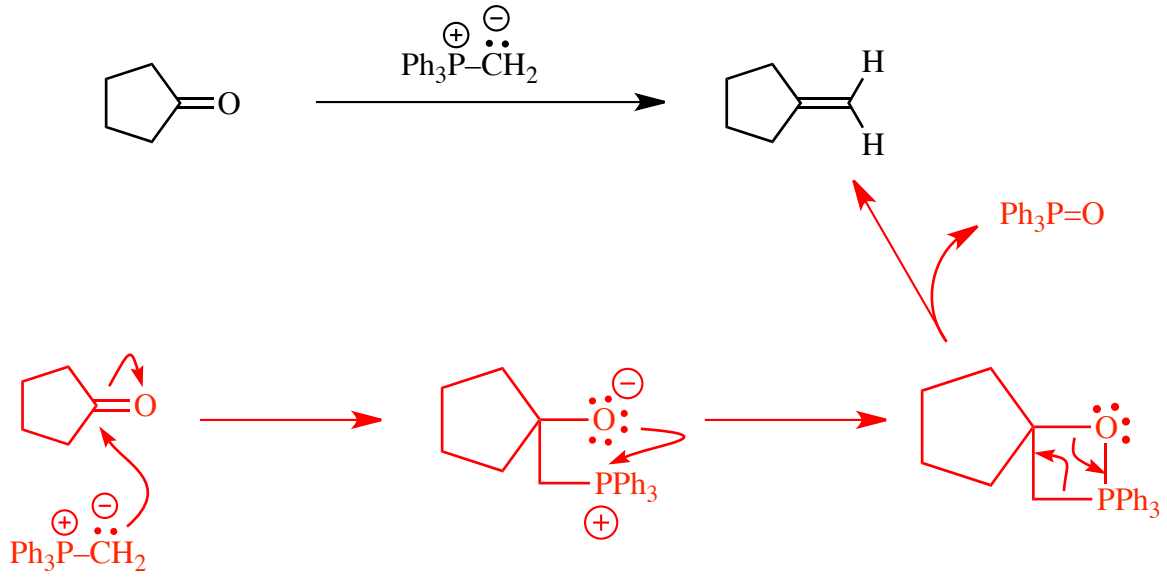
Printed Name:_____

4) (20 pts) Propose arrow-pushing mechanisms for the following transformations.

a)



b)

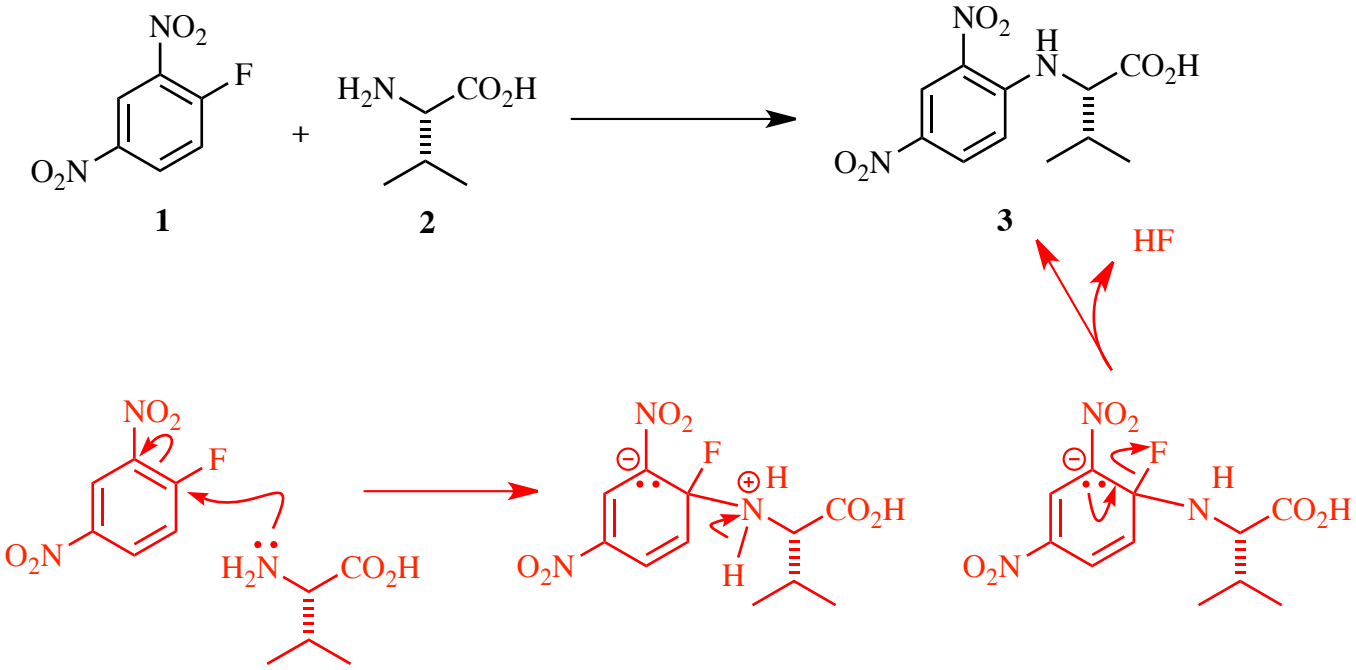


Total points for this page: ____

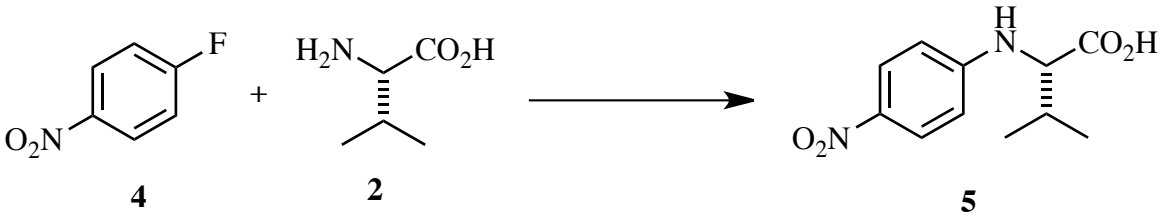
Printed Name:_____

4. –continued-

c) 1-fluoro-2,4-dinitrobenzene (**1**) reacts cleanly with the amino acid valine to give the benzene derivative **3**. Propose an arrow-pushing mechanism for this transformation.



d) p-Nitrofluorobenzene (**4**) reacts with valine to give **5**. Which reaction is faster – 4c or 4d? 4C

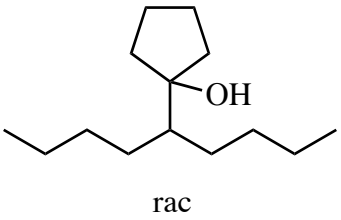


Total points for this page: ____

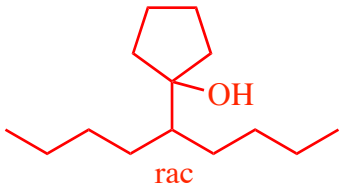
Printed Name:_____

5) (20 pts) Propose a synthesis of each of the following targets. Allowed starting materials include benzene, triphenylphosphine, 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 may be required.

a)



rac



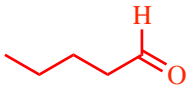
rac

a) Mg, ether

b) 

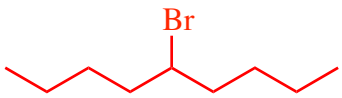
c) H_3O^+ workup

1) a) Mg, ether

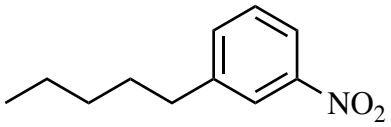
b) 

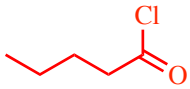
c) H_3O^+ workup

2) PBr_3



b)

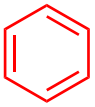


1) 

, $AlCl_3$

2) HNO_3, H_2SO_4

3) NH_2NH_2, KOH, Δ

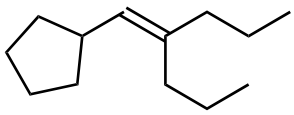


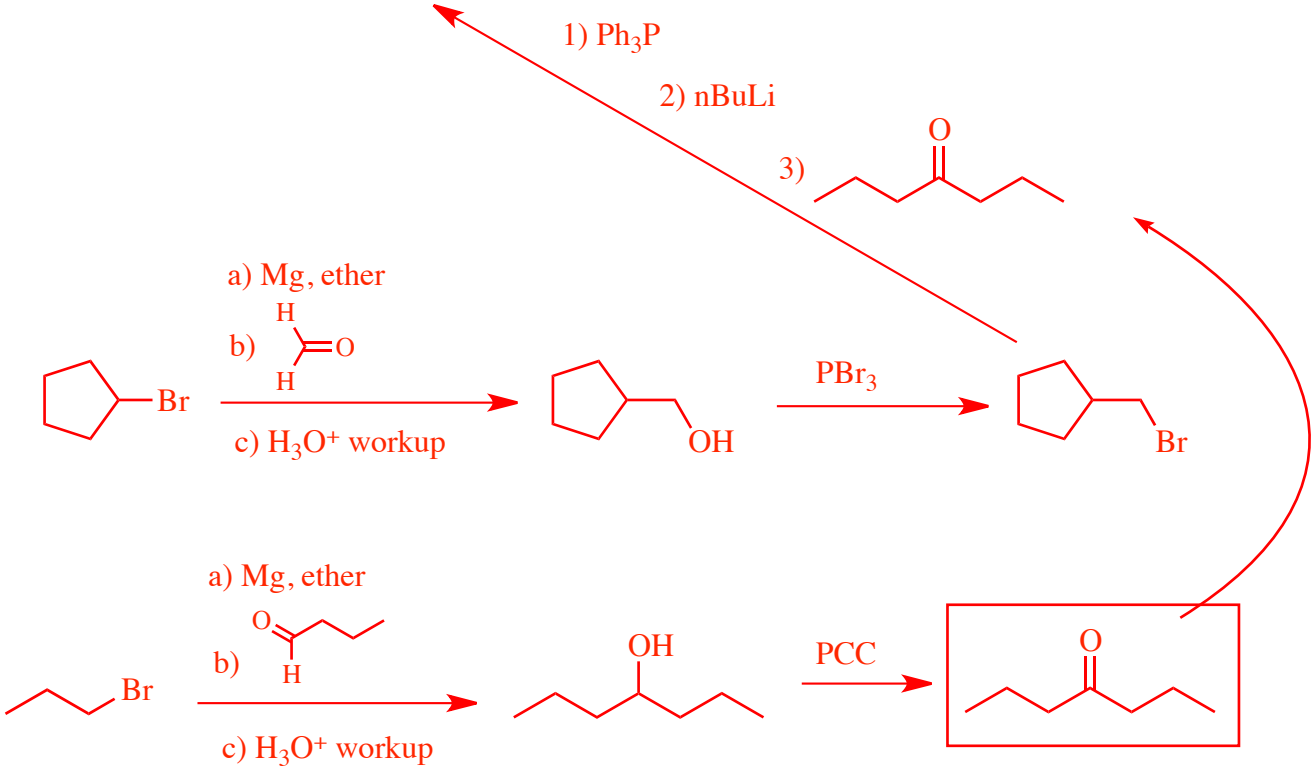
Total points for this page: ____

Printed Name:_____

5) – Continued

c)





Total points for this page: ____