CHEM 3371, Spring 2014
Professor Walba
Second Hour Exam
March 11, 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 Name: Thomas Carey

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	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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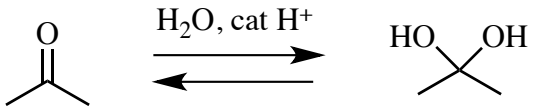
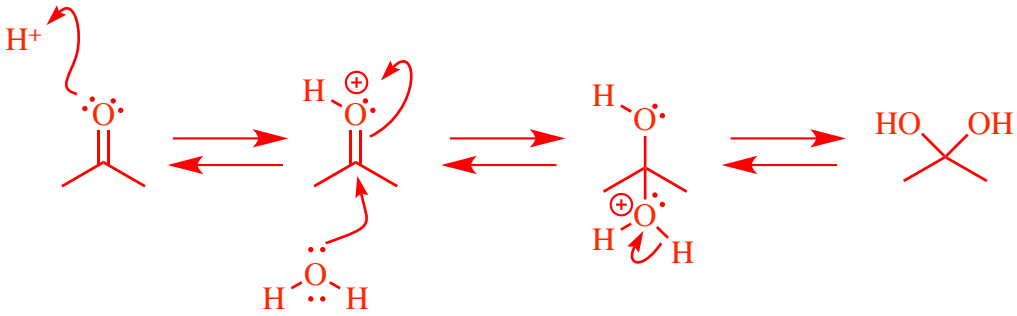
1 (20 pts) a) Acetone (**1**) in water reacts in the presence of a trace of acid to give an equilibrium mixture with acetone hydrate (**2**).



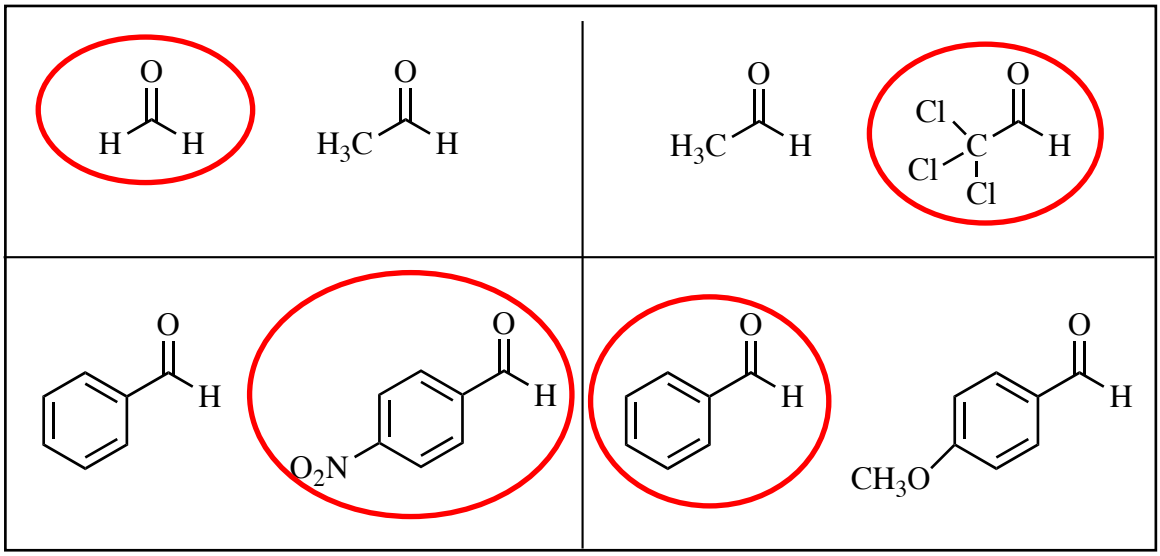
1 **2**

Propose an arrow-pushing mechanism for the transformation of acetone to the hydrate.



b) The reaction given in part a) is very general for ketones and aldehydes, but the equilibrium constant can be drastically different depending upon the structure of the carbonyl compound. The equilibrium constant for hydrate formation is determined by many factors, including e.g. steric strain in the tetrahedral hydrate relative to the trigonal carbonyl compound. However, for most ketones and aldehydes the equilibrium concentration of hydrate is determined mainly by the **stability** of the carbonyl group (a **less stable** carbonyl group gives a **higher concentration** of hydrate). In determining relative stability of the carbonyl groups of two carbonyl compounds, one should examine the important charge-separated resonance contributor to the structure of the carbonyl compound, and using this, determine the relative stability of the two carbonyl groups.

For each of the following pairs of carbonyl compounds, circle the compound that would show the highest concentration of hydrate at equilibrium.



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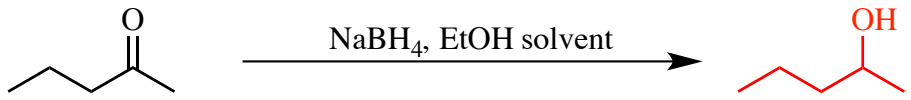
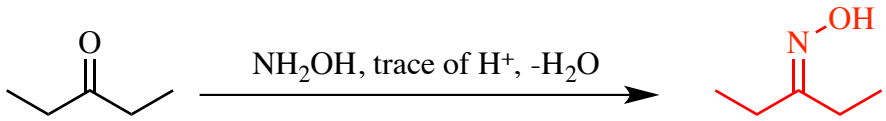
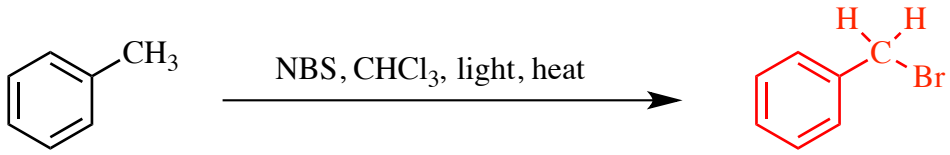
2) (20 pts) Give the single major product of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac."

a) 

b) 

c) 

d) 

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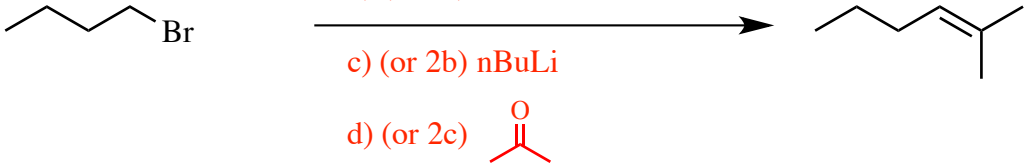
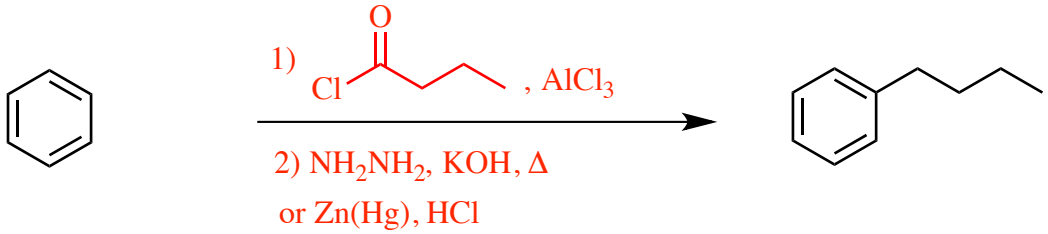
3) (20 pts) Propose reagents for accomplishing each of the following transformations. Make your reactions efficient (i.e. the target product should be the major product). More than one step may be required. Assume chiral starting materials or products are single pure enantiomers unless they are labeled "rac."

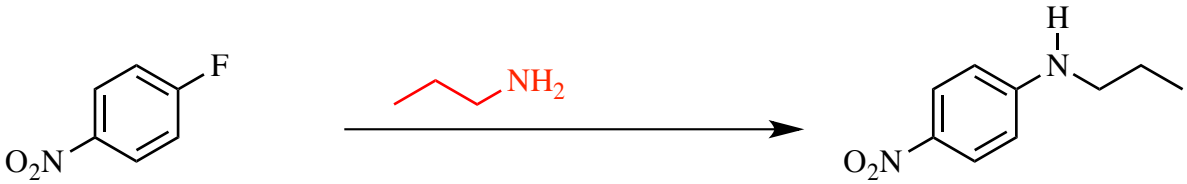
a)



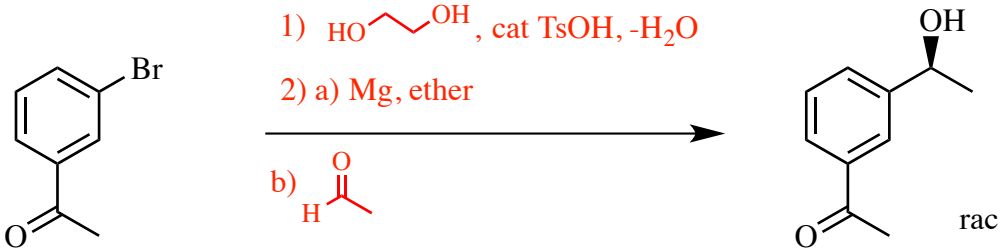
b)



c)



d)



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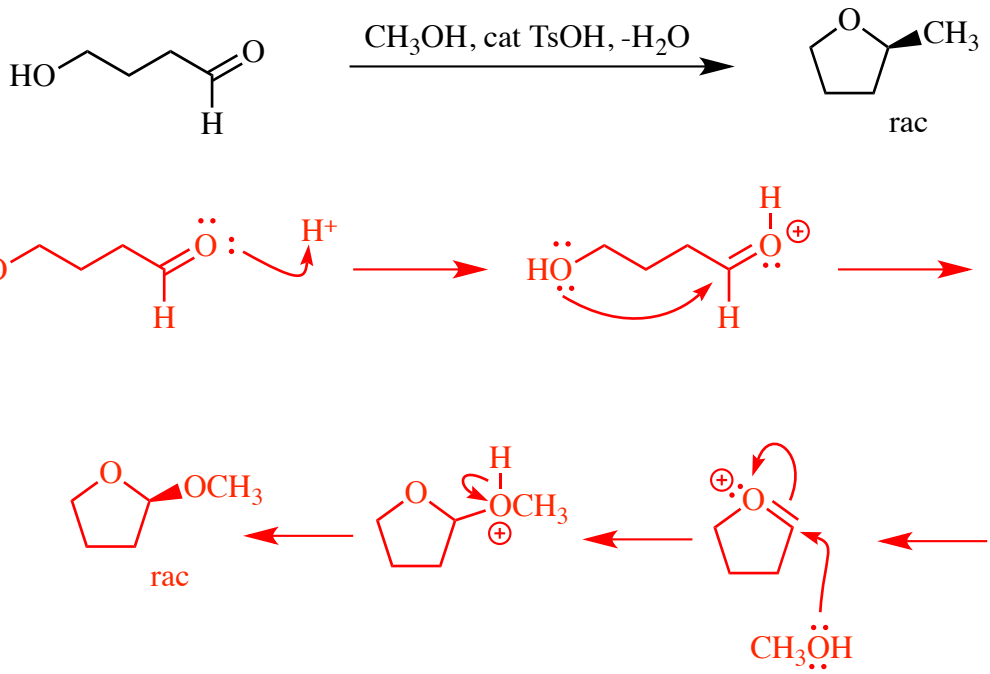
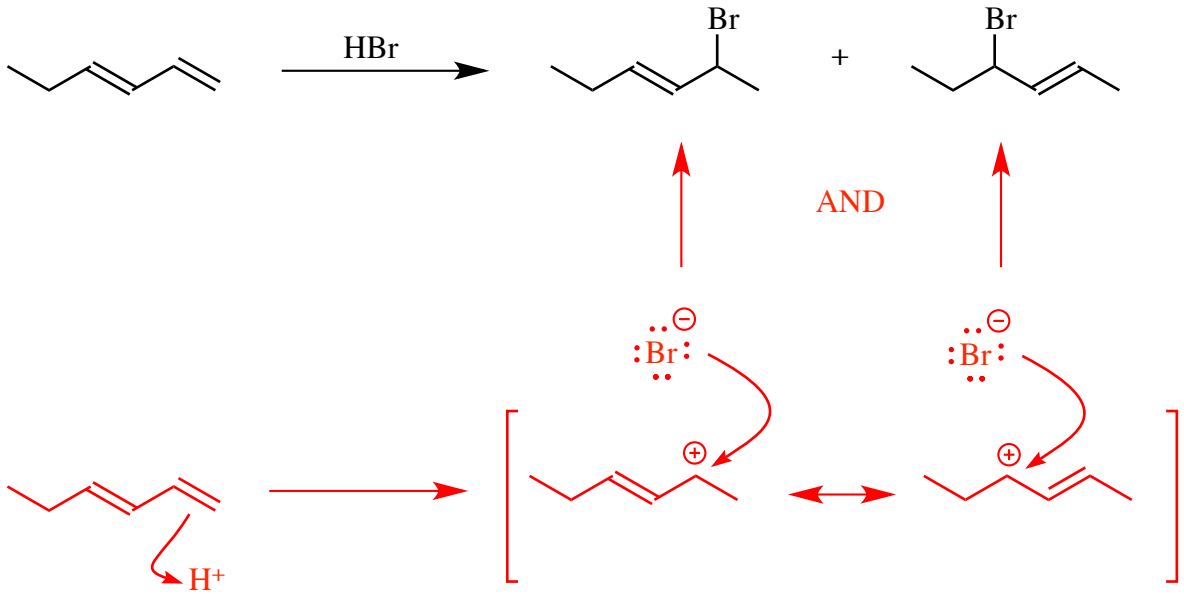
4) (20 pts) Propose an arrow-pushing mechanism for each of the following reactions. (continued on next page)

a)



b)



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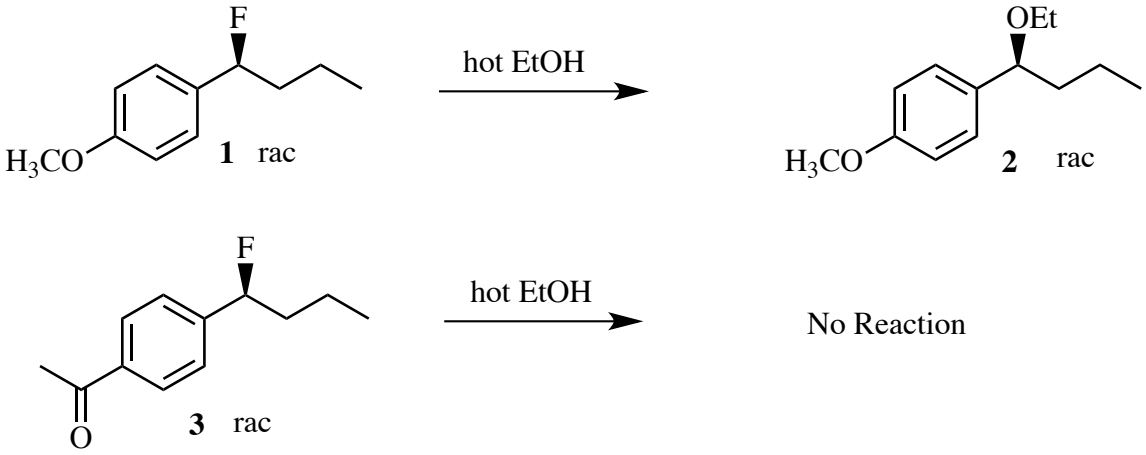
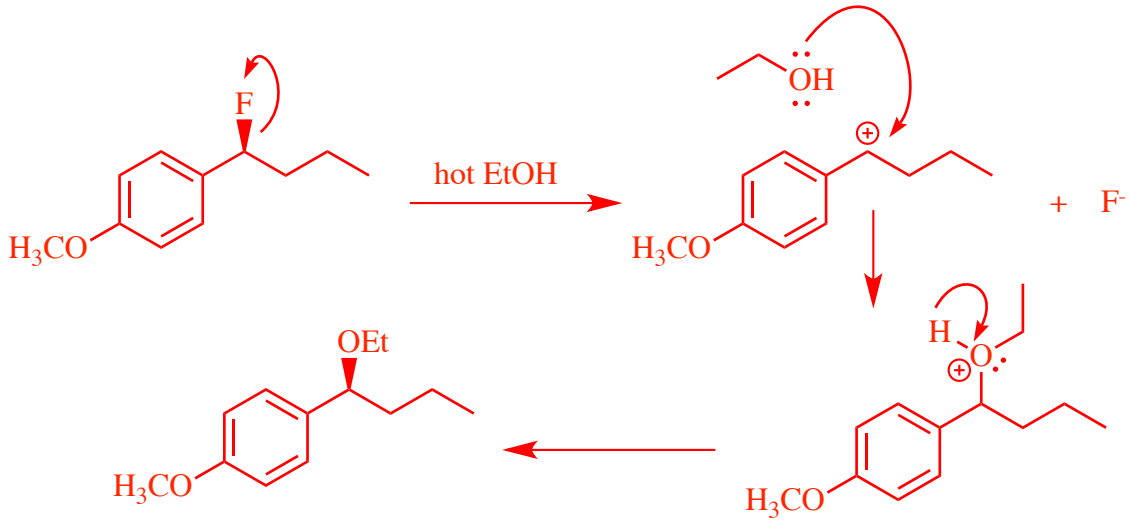
4) – Continued –

A graduate student at CU synthesized the 1-fluoroalkylbenzene **1**. But, when he tried to purify the product by recrystallization from ethanol, compound **1** reacted to give the ether **2**. Luckily, the similar compound **3** was easily recrystallized from ethanol to give pure compound **3** without any reaction.



c) Propose and arrow pushing mechanism for the formation of ether **2** from compound **1**.



d) Propose a **short** explanation for why compound **1** reacts in hot ethanol, and why compound **3** does not react.

The methoxy group para to the fluoroalkyl chain in compound **1** stabilizes the carbocation intermediate in this S_N1 reaction by resonance, leading to the observed solvolysis product. However, the carbonyl group in compound 3 destabilizes the cation, and compound 3 is stable in hot ethanol, and can be recrystallized without undergoing the solvolysis.

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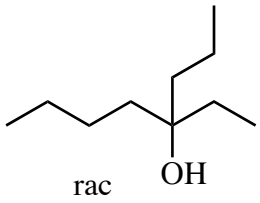
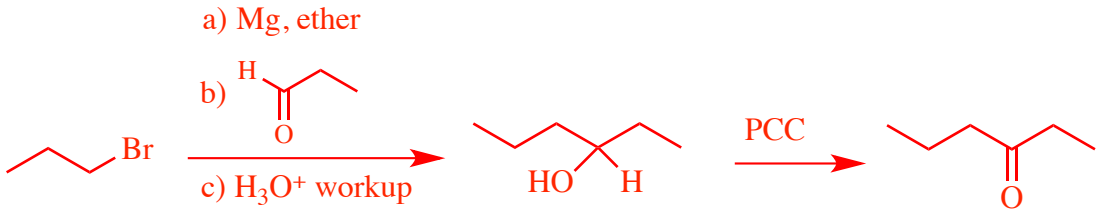
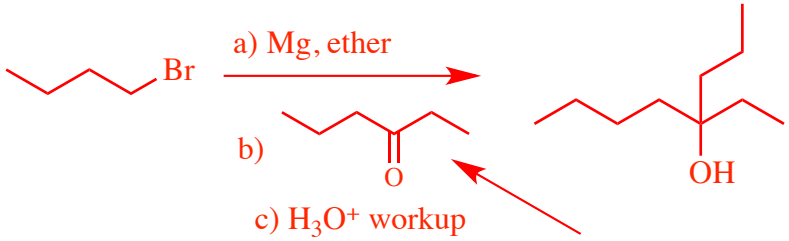
5) (20 pts) Propose a synthesis for each of the following targets. Allowed starting materials include benzene, Ph_3P, and/or any other organic molecules containing **five (5) carbons or less**. You may use any necessary inorganic reagents. Try to make your syntheses efficient (i.e. the target should 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 do not put multiple reactions over one arrow. (Continued on next page)

a)



There is always more than one way to get a target. This is just one full credit answer.





I made this ketone above, so I can use it as a starting material in this reaction

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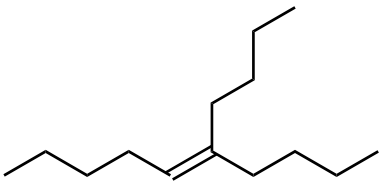
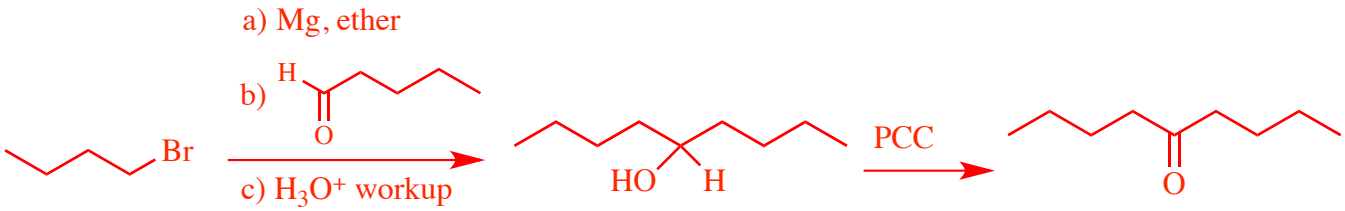
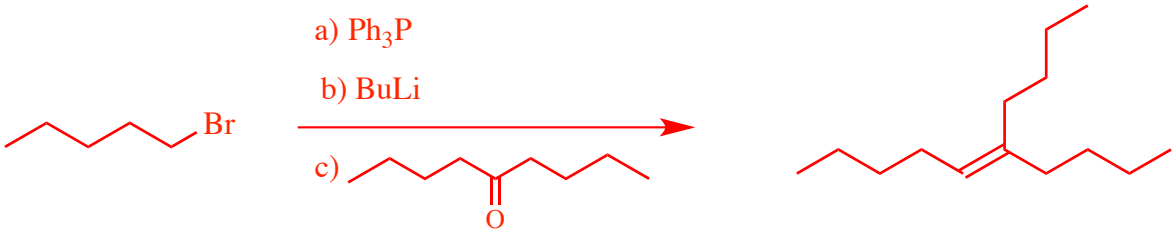
5) – Continued –

b)







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