CHEMISTRY 3331, Spring 2005
Professor Walba
First Hour Exam, February 10

scores:

1) 25

2) 25

3) 25

4) 25

_____
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, models, calculators, scratch paper, or any other paraphernalia will not be allowed during the exam. Please put all your answers on the test. Use the backs of the pages for scratch.

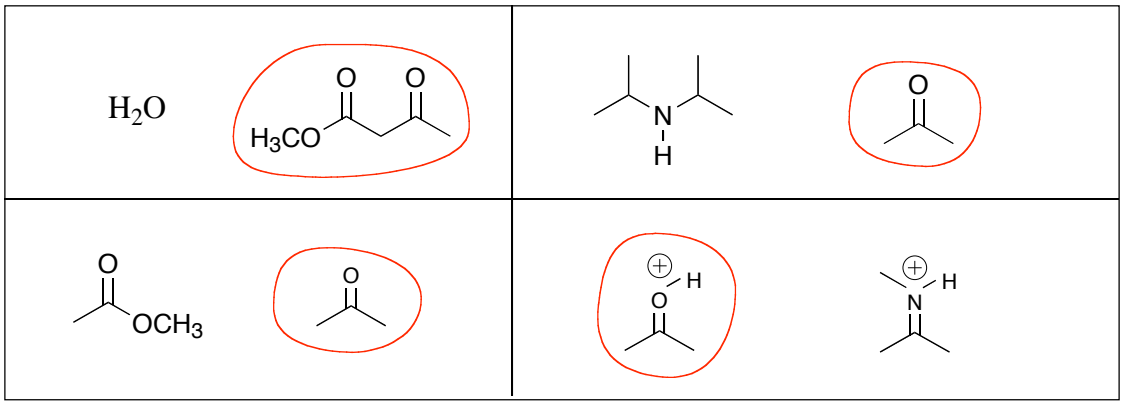
*PLEASE read the questions carefully!*

# Partial Periodic Table

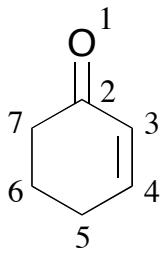
| 1A | 2A | 3A | 4A | 5A | 6A | 7A | 8A |
|---|---|---|---|---|---|---|---|
| 1 H | | | | | | | 2 He |
| 3 Li | 4 Be | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 11 Na | 12 Mg | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| | | | | | | 35 Br | |
| | | | | | | 53 I | |

Name:_____

1) (25 pts) a) Circle the stronger Brønsted acid for each of the following pairs of compounds.

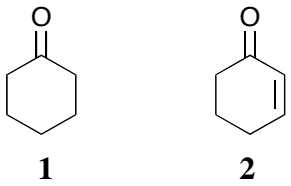



b) Indicate all of the electrophilic atoms in cyclohexenone using the atom numbering shown.




2 and 4

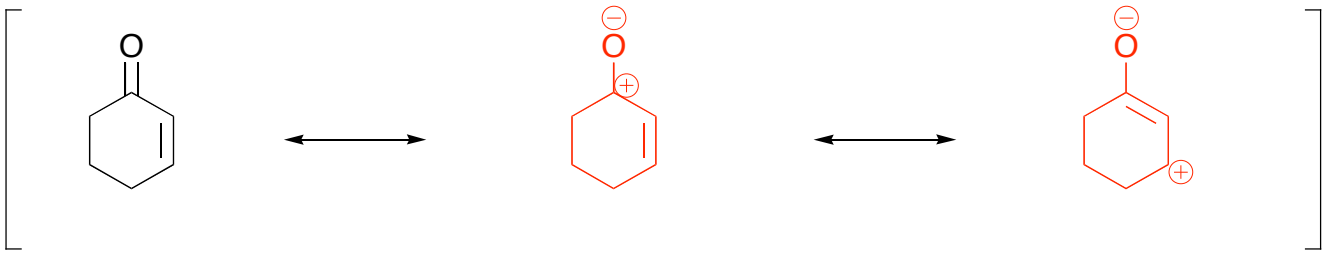
c) Which carbonyl compound is more stable, cyclohexanone (**1**) or cyclohexenone (**2**)?




**1** **2**

2

d) Complete the drawing showing the most important resonance contributors to the structure of cyclohexenone.

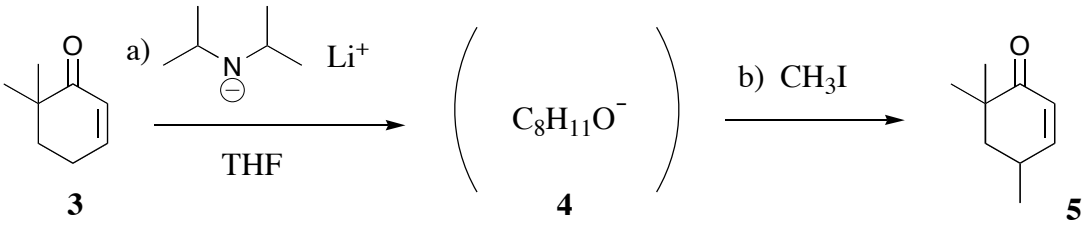


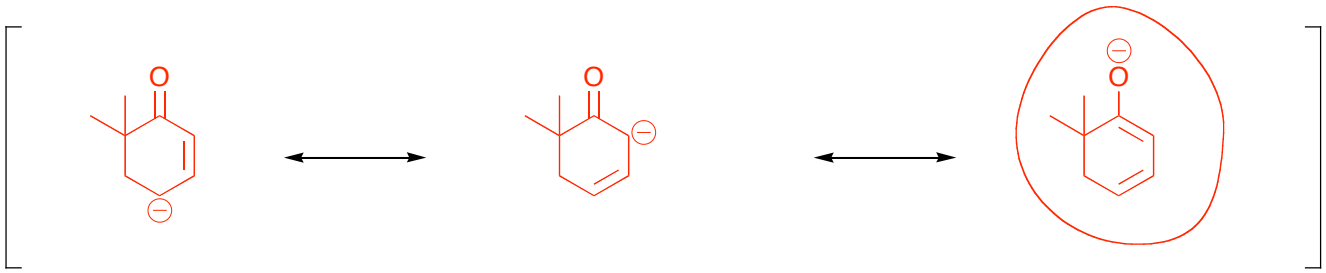
Name:_____

(1) – continued

e) Note – you might consider working this problem last. The dimethylcyclohexenone **3** has no α-hydrogens. But, treatment of compound **3** with LDA gives an anionic intermediate **4**, with molecular formula $C_8H_{11}O^-$. Addition of methyl iodide then gives the alkylated product **5**! Show the three most important resonance contributors to the structure of intermediate **4**, and circle the major contributor.

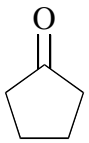
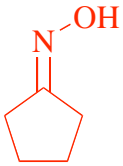
Note: As you can see, there IS an α hydrogen in this molecule – on an sp2 carbon. I was trying to make this question a little easier, and should have put a methyl group there. However, even with the mistake, I think it's pretty clear where the deprotonation must occur from the site of alkylation – my suggestion that there was no α hydrogen is a kind of hint, I guess.

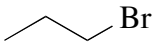
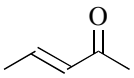
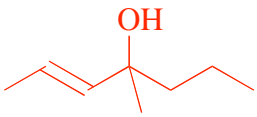


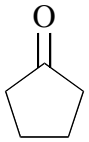
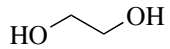
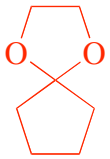



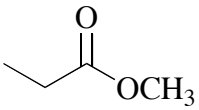
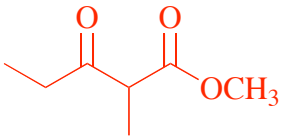
Name:_____

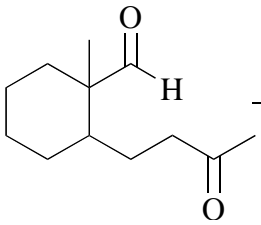
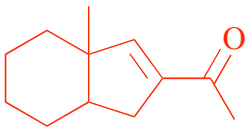
2) (25 pts) Give the single major product of each of the following reactions (ignore stereochemistry for this question).

a)  $NH_2OH$, mild $H_3O^+$ 

b)  a) Mg, ether; b)  ; c) $H_3O^+$ workup 

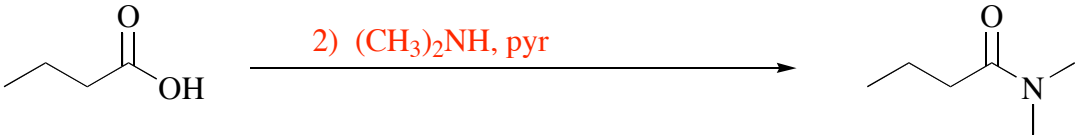
c)   cat. $H_2SO_4$, $-H_2O$ 

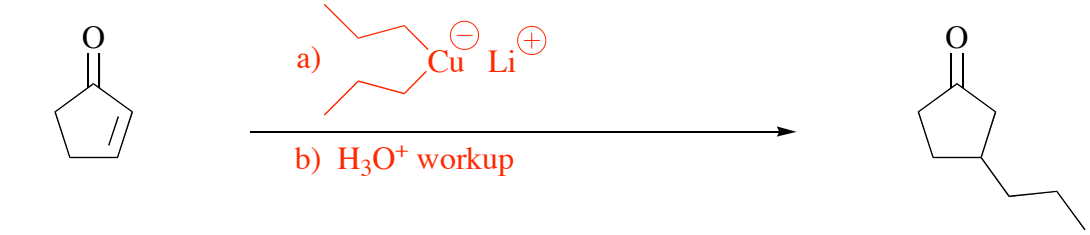
d)  a) $CH_3O^-$, $CH_3OH$; b) $H_3O^+$ workup 

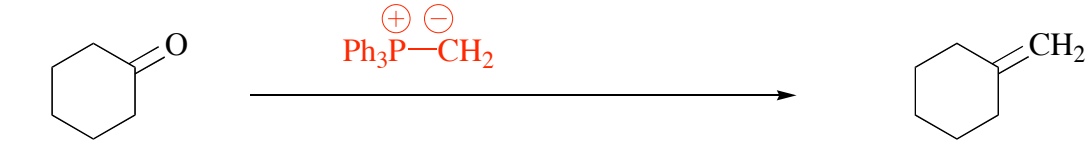
e)  $NaOH$, $H_2O$, $\Delta$ 

Name:_____

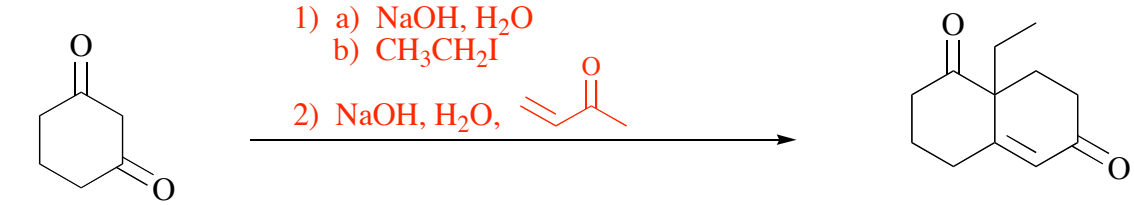
3) (25 pts) Propose reagents for accomplishing the following transformations. NOTE: more than one step may be required! Try to make your synthesis efficient (i.e. the desired product should be the major product, and generally a shorter synthesis is better than a longer one). For this question, you may use any organic or organometallic reagent you need. For example, if you need a Grignard reagent, you can use it without showing how to make it.

a) 


b) 

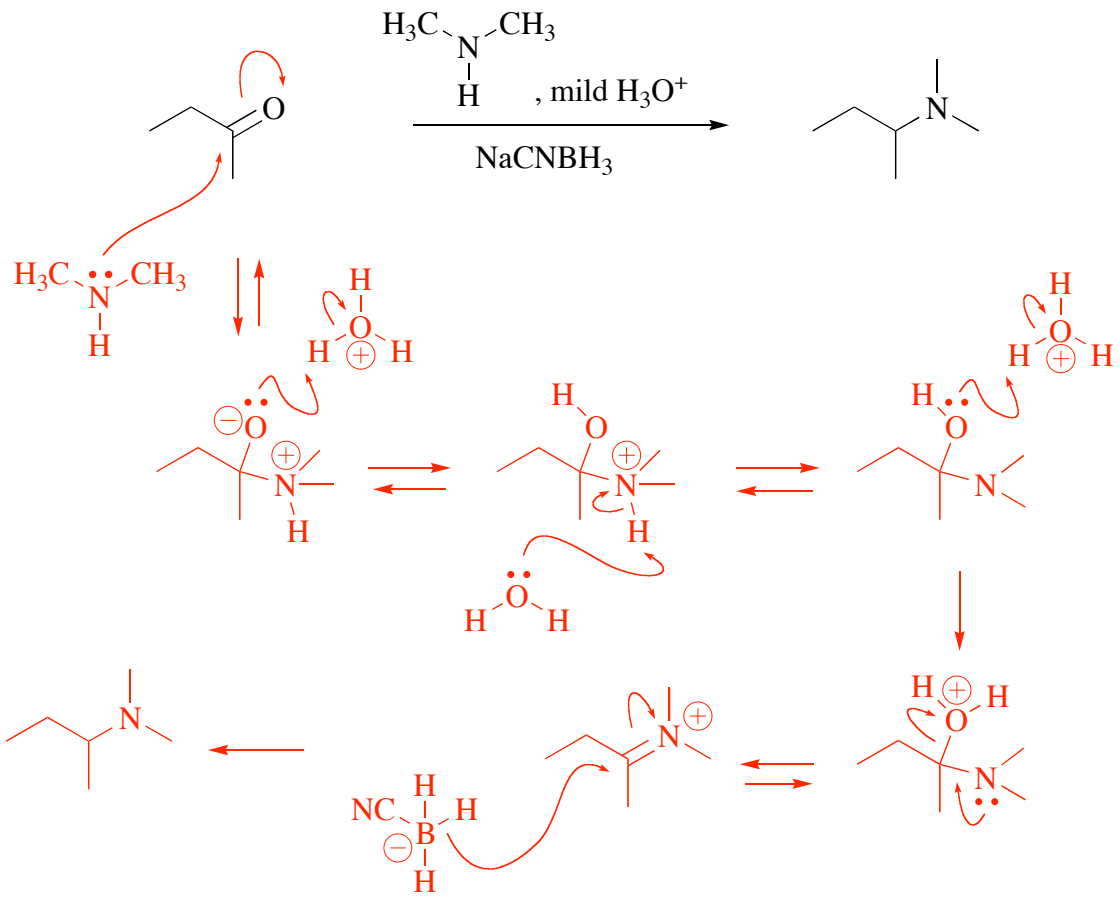

c) 


d) 


e) 

Name:_____

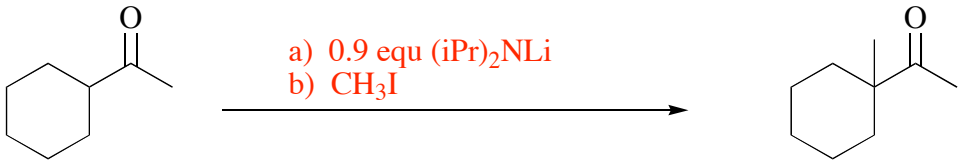
4) (25 pts) a) Propose an arrow-pushing mechanism for the following transformation. Please be sure to show all the intermediates in your mechanism, but do not show transition states. You can use any single valid valence bond structure for your intermediates.



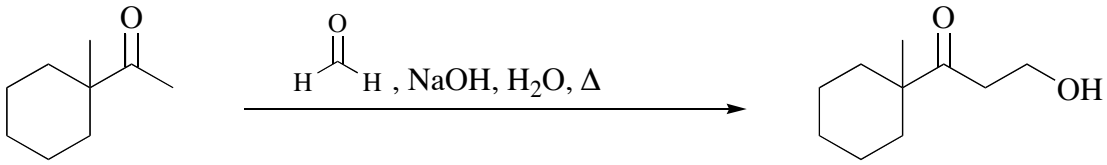
Name:_____

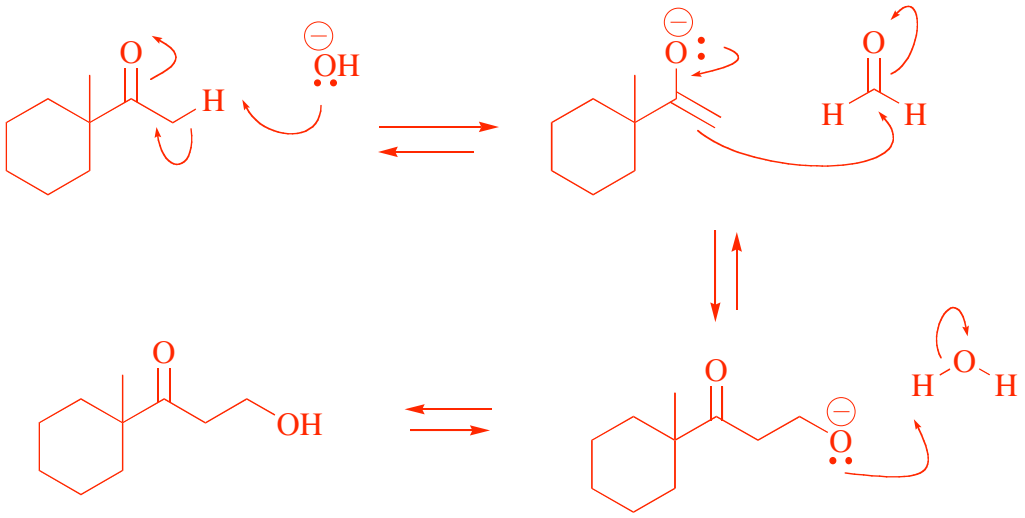
(4) – continued

b) Propose reagents for accomplishing the following transformation.




c) Propose an arrow-pushing mechanism for the following transformation.




I actually meant to put the enone as the product, so you would have had to show the E1Cb mechanism for the elimination of hydroxide. This mistake made the problem easier, but I'm sorry if people were confused by the Δ. (heat).