Chem 112A: Final Exam

December 15th, 2010

Please provide all answers in the spaces provided. You are not allowed to use a calculator for this exam, but you may use molecular model kits. Only cyclohexane rings may be pre-assembled. Including the title page, there should be **10** total questions spread over **9** pages. There is also a **tenth** page that should be blank. You can use this last page for scratch paper if you need it, but please remember to copy your answers into the blanks that are provided for each question.

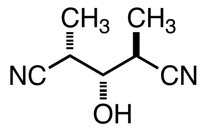
Name: ____

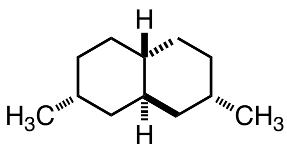
GSI/Section: ____

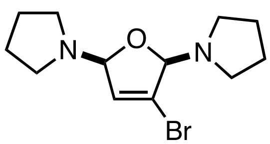
(1)	_____________	(20 points)
(2)	_____________	(8 points)
(3)	_____________	(15 points)
(4)	_____________	(14 points)
(5)	_____________	(13 points)
(6)	_____________	(34 points)
(7)	_____________	(16 points)
(8)	_____________	(32 points)
(9)	_____________	(24 points)
(10)	_____________	(24 points)
TOTAL	_____________	(200 points)

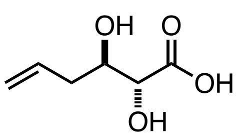
Thanks for a great semester, and have a great winter break!

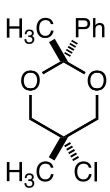
1. Identify all of the stereocenters in the following compounds and label them as "*R*" or "*S*" as appropriate. Also indicate whether the compounds are "*chiral*" or "*achiral*" (20 points).

a. 

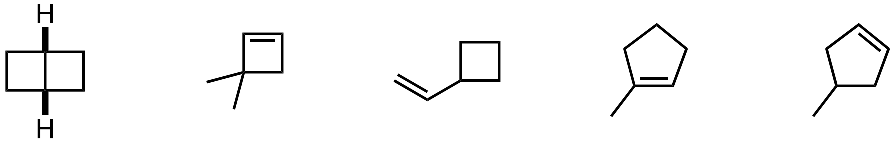
b. 

c. 

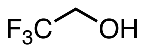
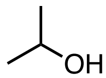
d. 

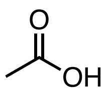
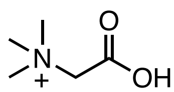
e. 

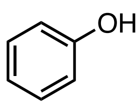
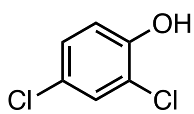
2. Rank the following isomeric compounds in terms of their *relative stability*, using "1" for the most stable and "5" for the least stable (8 points).

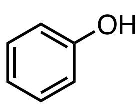
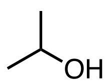


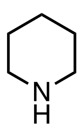
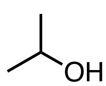
3. For each of the following pairs of compounds, circle the one that is the *most acidic*. Justify your choices using 10 words or less (15 points).

a.  vs. 

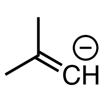
b.  vs. 

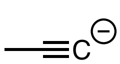
c.  vs. 

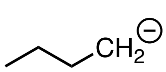
d.  vs. 

e.  vs. 

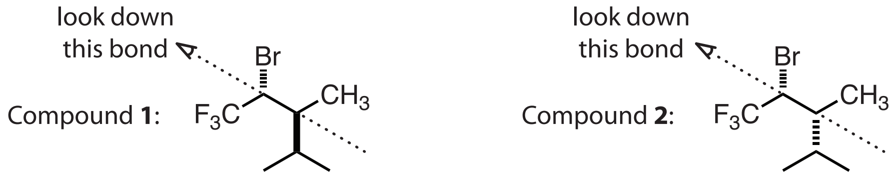
4. Consider the following carbanions to be free ionic species in solution. For each, provide a clear drawing that shows the orbital containing the electron lone pair. Next, indicate the hybridization of the lone pair orbital by specifically labeling it. Finally, indicate which carbanion is the *most basic* and which one is the *least basic* (14 points).

a. 

b. 

c. 

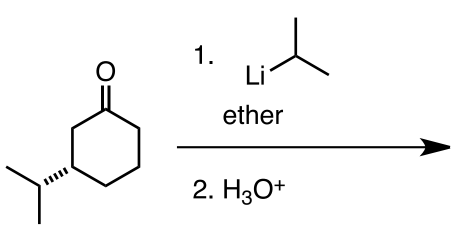
5. Suppose each of the compounds shown below is exposed to LDA in THF to form the corresponding elimination product.



a. For each compound, provide a single clear Newman projection (looking down the indicated bond) that corresponds to the best conformation for the elimination step. Also provide the structures of the alkene products that would result and label them appropriately as (*E*) or (*Z*) (8 points).

b. The elimination reaction rates for these two isomers are very different. Which one would you expect to eliminate faster and why (5 points)?

6. The following reaction sequence provides two possible products:



a. In the space after the reaction arrow, provide a clear structural drawing for each product (4 points).

b. Clearly draw the two possible chair conformations for each of the two structures you provided in (a) and circle the lowest energy chair for each product (note that a total of 4 chair structures should be drawn, 12 points).

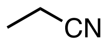
	Chair A	Chair B
First product:		
Second product:		

c. Based on your analysis in part b, which structure would correspond to the *thermodynamic product* of the reaction (5 points)?

d. Is the product ratio likely to be determined by thermodynamic or kinetic control? Explain your reasoning using 10 words or fewer (5 points).

e. Assume that the most thermodynamically stable structure is obtained as the major product *regardless of your answer for d*. Use this information to generate a reaction coordinate diagram that compares the energetics leading to the formation of the two possible products during the first step of the reaction (i.e. before the "2. H_3O^+" step). Clearly label the energy difference on the diagram that is responsible for the observed product ratio *in a manner that is consistent with your answer in part d* (8 points).

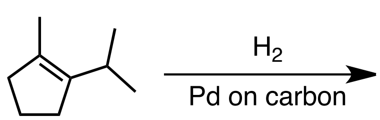
7. For the CN bond of the following nitrile compound, provide (1) a clear spatial drawing of the bonding and lone pair orbitals and (2) an interaction diagram that shows the relative energy levels of the bonding and antibonding orbitals. You do not need to draw out any orbitals for the C-C and C-H bonds (12 points).

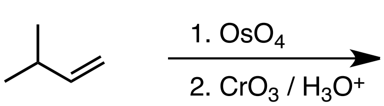
   nitrile for this question: 

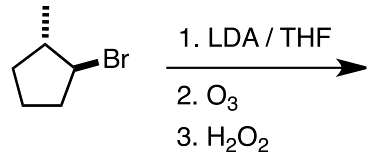
   a. Structural drawing with orbitals: Orbital interaction diagram:

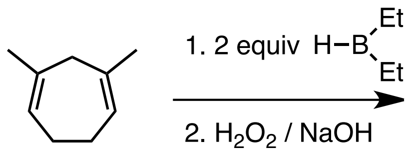
   b. Suppose this nitrile group is exposed to a strong nucleophile, such as methyl lithium. Use your diagrams in part a to determine which atom would be attacked by the nucleophile during the reaction. *Briefly* explain your answer (4 points).

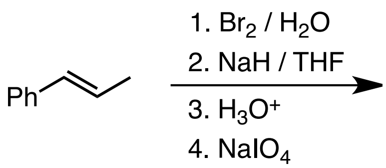
8. Provide the major products for each of the following reactions, including all relevant stereochemistry. Provide both enantiomers for the products that are chiral. You do not need to provide the intermediates for multistep reactions, and you do not need to assign the stereocenters (4 points each).

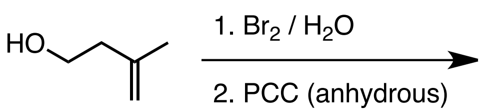
   a. 

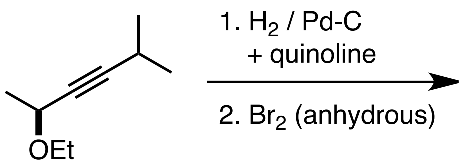
   b. 

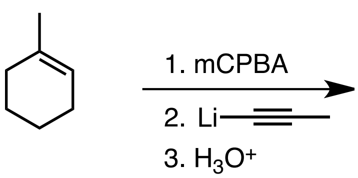
c. 
Br
1. LDA / THF
2. O_3
3. H_2O_2

d. 
1. 2 equiv H–B(Et)(Et)
2. H_2O_2 / NaOH

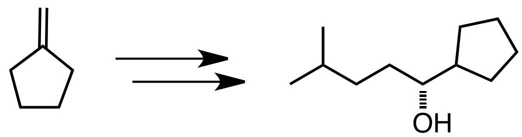
e. 
Ph
1. Br_2 / H_2O
2. NaH / THF
3. H_3O^+
4. $NaIO_4$

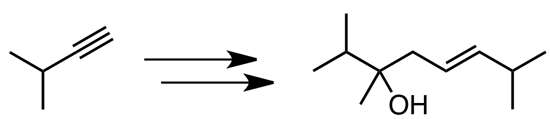
f. 
HO
1. Br_2 / H_2O
2. PCC (anhydrous)

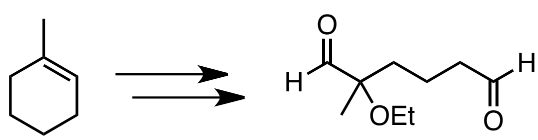
g. 
OEt
1. H_2 / Pd-C
+ quinoline
2. Br_2 (anhydrous)

h. 
1. mCPBA
2. Li
3. H_3O^+

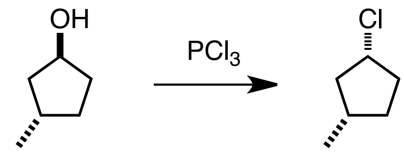
9. Each of the following overall transformations occurs through a series of multiple chemical steps. Link together the reactions you have learned in class to show how each starting compound can be converted into the indicated product. Draw all of the intermediates along the synthetic routes that you propose, and supply all reagents and reaction conditions as appropriate. No "arrow-pushing" mechanisms are required. For the compounds that are chiral, you only need to indicate how the racemic mixture can be made. There can be more than one answer in some cases (8 points each).

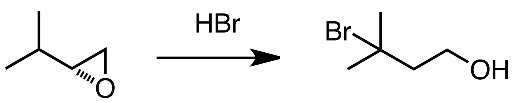
a. 

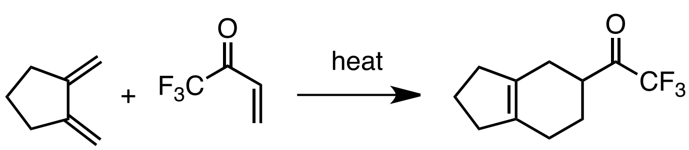
b. 

c. 

10. Provide detailed arrow pushing mechanisms for each of the following reactions (8 points each).

a. 

b. 

c. 

Chem 112A 2013 - don't do this problem

This last page should be blank. You may use it as scratch paper, but be sure to recopy your answers into the exam questions so that we can grade them easily.