Chem 112A: Final Exam

December 14th, 2011

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 **11** total questions spread over **11** pages. There is also a **12th** 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.

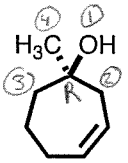
Name: Key

GSI/Section: _____

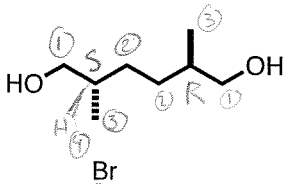
(1)	_____	(20 points)
(2)	_____	(16 points)
(3)	_____	(12 points)
(4)	_____	(6 points)
(5)	_____	(16 points)
(6)	_____	(10 points)
(7)	_____	(24 points)
(8)	_____	(34 points)
(9)	_____	(14 points)
(10)	_____	(24 points)
(11)	_____	(24 points)
TOTAL	_____	(200 points)

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

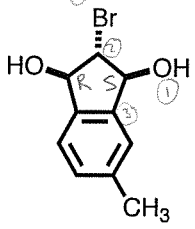
1. Indicate which of the following compounds are "chiral" or "achiral". For all of the chiral compounds, label all of the stereocenters as "*R*" or "*S*", as appropriate. (20 points).

a. 

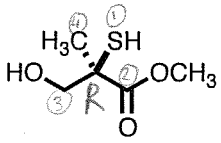
chiral

b. 

achiral (meso)

c. 

chiral

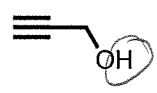
d. 

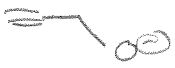
chiral

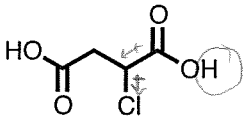
e. 

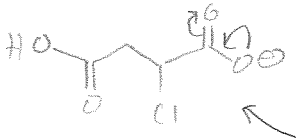
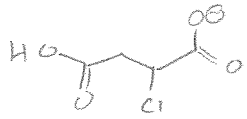
achiral

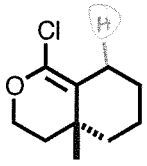
2. For each of the following compounds, circle the most acidic proton. Draw the resulting anion, and justify your choices using 3 words or fewer. Draw any resonance structures contributing to the stability, as appropriate (16 points).

a. 

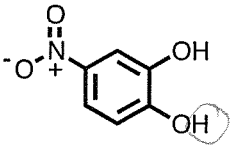

oxygen is electronegative

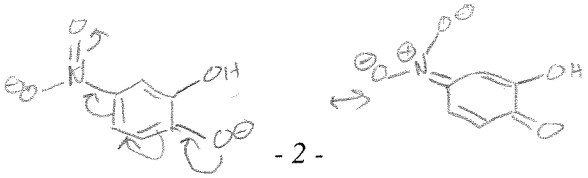
b. 


inductive effect


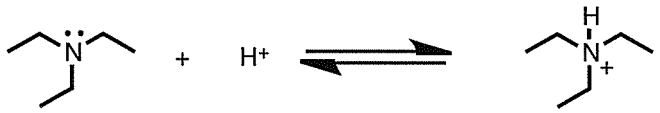
c. 


resonance

d. 

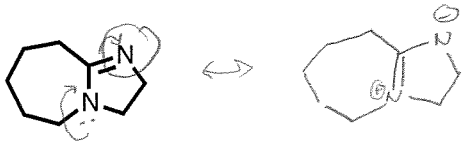

resonance

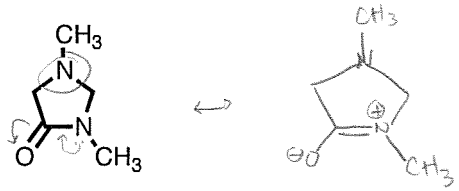
3. Amines are generally basic, as the lone pair on the nitrogen atom can readily pick up a proton to form the "ammonium" species. This is exemplified by triethylamine:

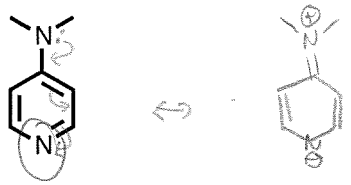


triethylamine triethylammonium ion

The following compounds contain two nitrogen atoms. For each structure, circle the nitrogen atom that would be the *most basic*. Also provide clear resonance structures to support your answers (12 points).

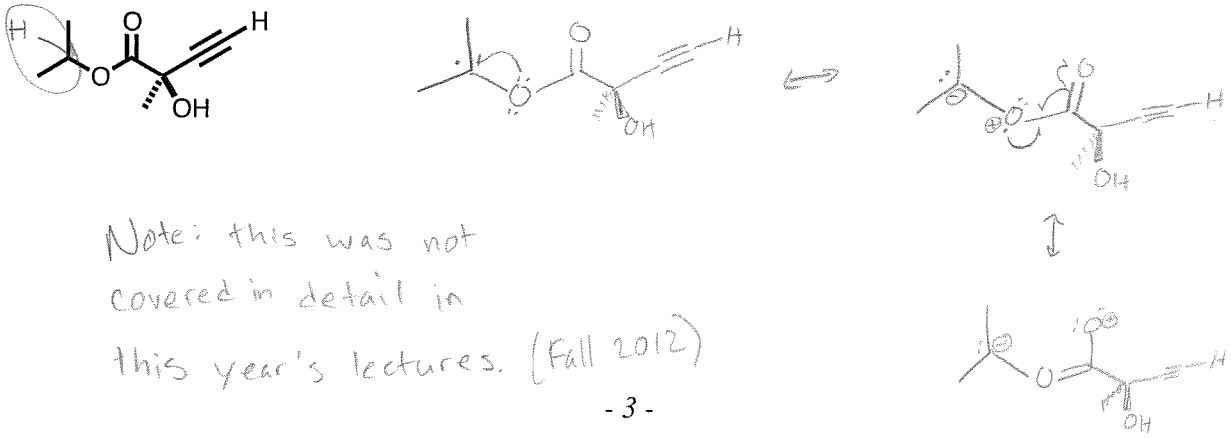
a. 

b. 

c. 

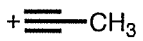
If the nitrogen has a ⊕ in a resonance structure, that makes it less basic.

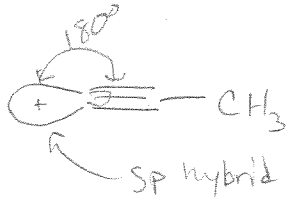
4. For the compound below, determine the weakest CH bond. Also provide the structure that would result when this bond is broken homolytically, and provide all reasonable resonance structures that would be associated with this species (if any) (6 points).



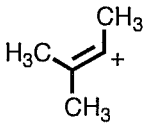
Note: this was not covered in detail in this year's lectures. (Fall 2012)

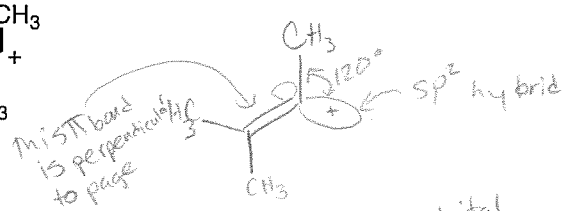
5. Consider the following carbocations to be free ionic species in solution. For each, provide a three-dimensional drawing that clearly shows the empty orbital associated with the positive charge. Next, indicate the hybridization of this orbital. Finally, indicate which of these carbocations would be expected to form the most readily, and which one would be the most difficult to form (16 points).

a. 

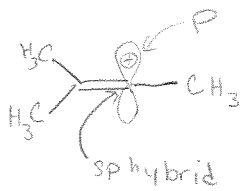


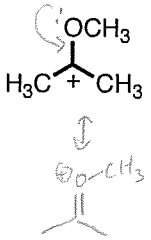
hardest to form

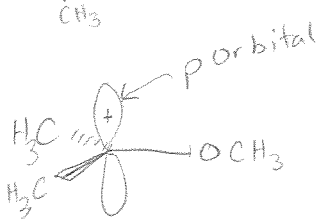
b. 



or

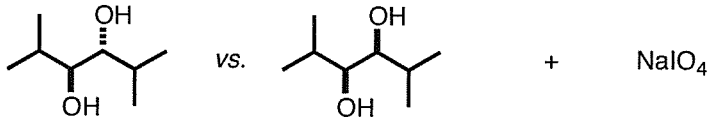


c. 



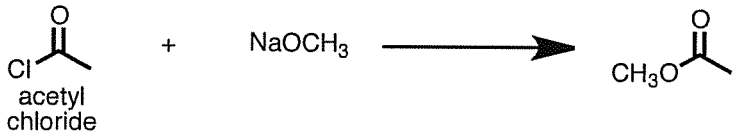
easiest to form

6. When exposed to sodium periodate, the two following compounds form the same expected product(s), but with very different rates. Use Newman projections to determine which one reacts faster. Justify your answer using 10 words or fewer (10 points).



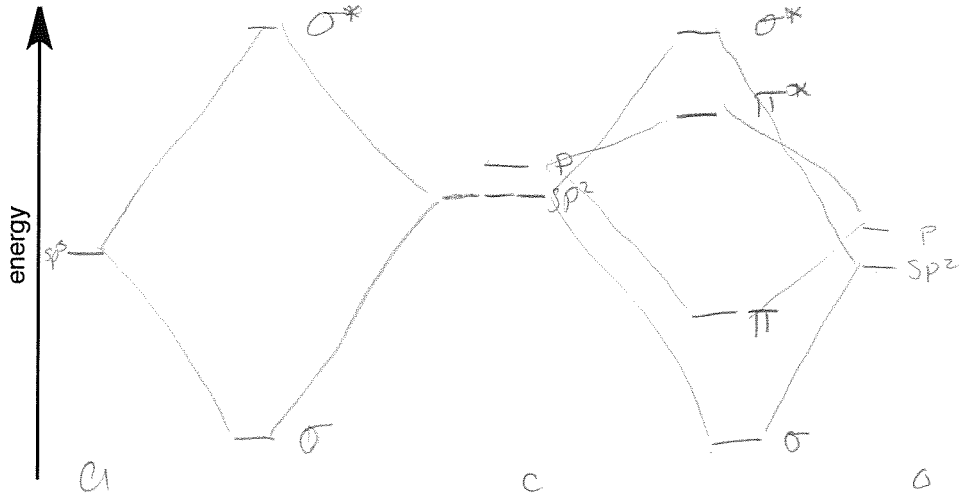
Skip this problem - Not covered in Fall 2012

7. Acid chlorides are highly reactive compounds that participate in a number of organic transformations. As one example, they can react with nucleophiles like sodium methoxide to form esters:



a. For the *acetyl chloride* molecule shown above, construct orbital interaction diagrams for (1) the carbon-chlorine bond, and (2) the carbonyl group *using the same energy scale* (10 points).

acetyl chloride: carbon-chlorine bond carbonyl group



b. Based on the diagram you provided in a, draw clear, three dimensional pictures of the lowest unoccupied molecular orbitals (LUMOs) that are associated with each of these bonds (6 points).

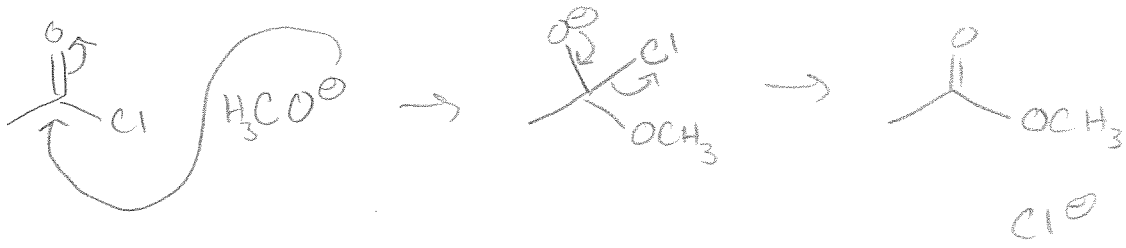
carbon-chlorine bond carbonyl group

LUMO:

c. Using your answers for a and b, determine the *specific orbital* and the *specific atom* that will most likely be attacked by the methoxide anion. Indicate how your diagrams led you to this conclusion using 10 words or fewer (4 points).

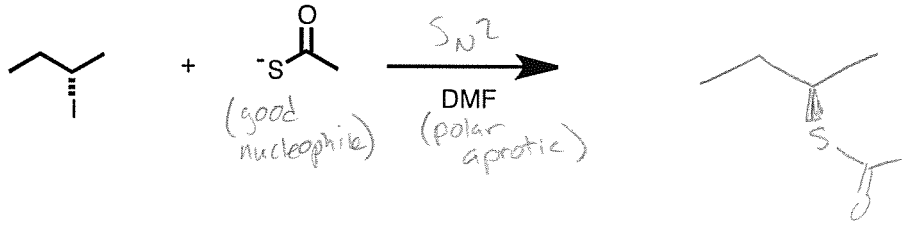
π^*_{CO} is lower energy than σ^*_{CCl}, so the carbon will be attacked at π^*_{CO}

d. Considering your answers to the questions above, provide a detailed arrow-pushing mechanism for the reaction of acetyl chloride with sodium methoxide (4 points).

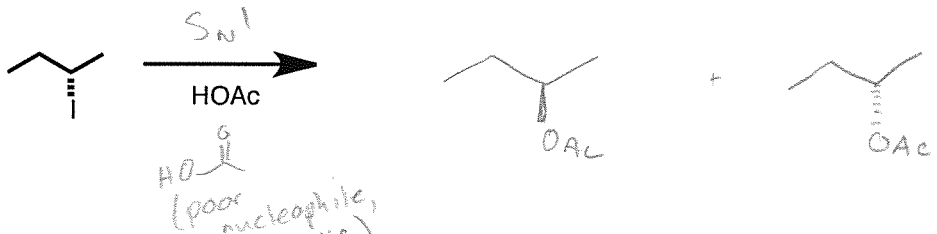


8. Provide the major products for each of the following reactions, including all relevant stereochemistry. Provide both enantiomers for the products that are chiral. You do not need to provide the intermediates for multistep reactions, and you do not need to assign the stereocenters (34 points).

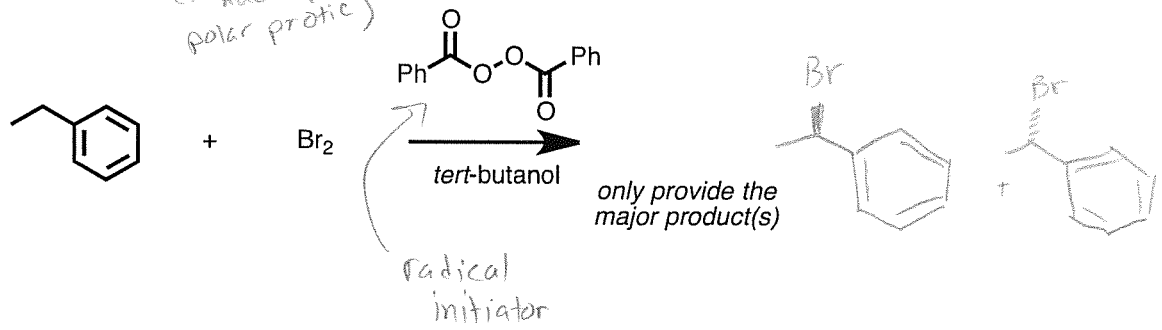
a.

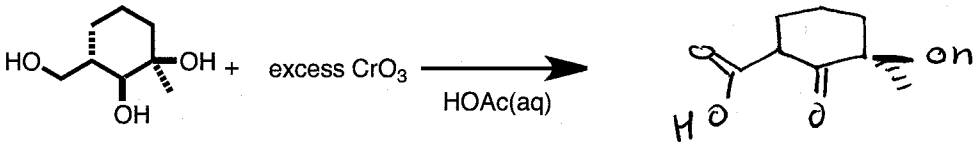


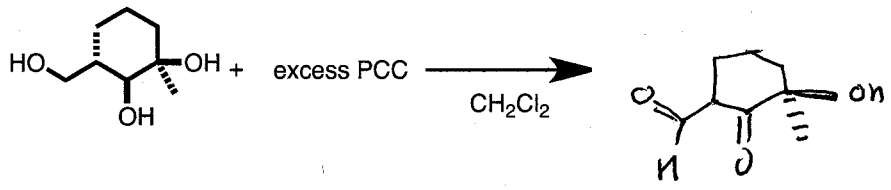
b.

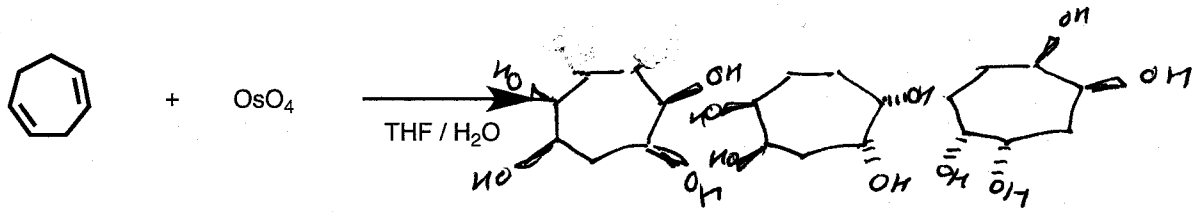


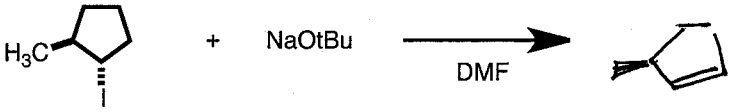
c.

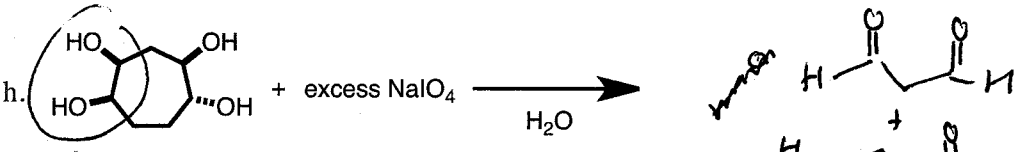


d. 

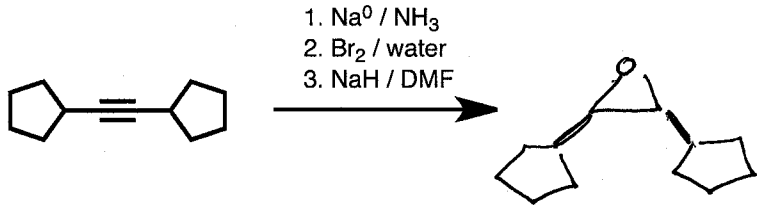
e. 

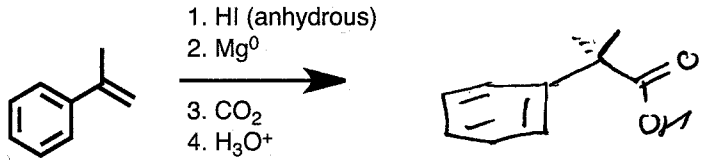
f. 

g. 

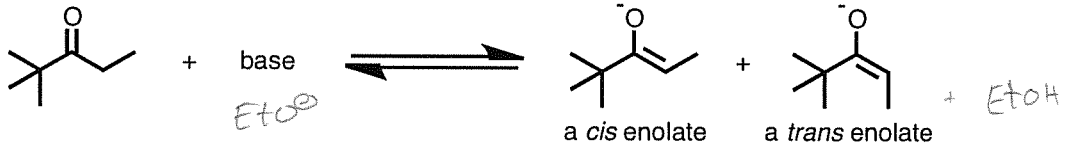
h. 

React first; then transdial once ring has been opened.

i. 

j. 

9. Enolates are among the most useful intermediates in organic chemistry. They are prepared through the removal of acidic protons located next to carbonyl groups using strong bases. In the example shown, two different enolate geometries can be formed.

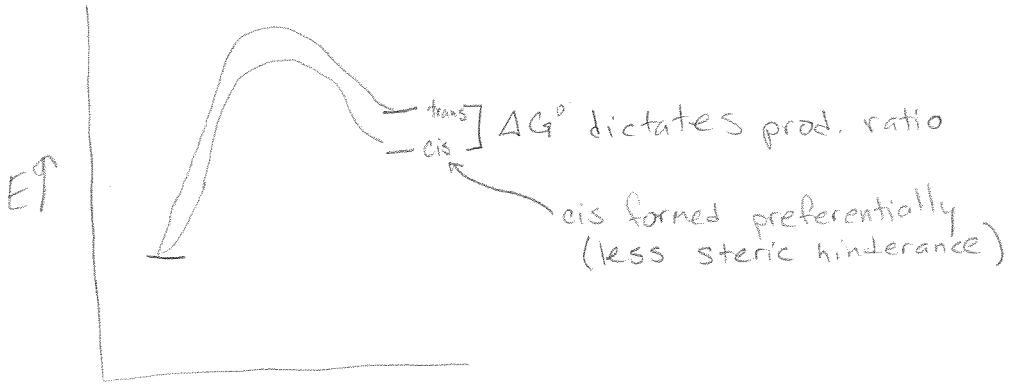


a. Given that the pK_a of the protons next to the carbonyl group is 22, provide an estimate of the equilibrium constant for this reaction when one equivalent of *sodium ethoxide* is used as the base. Show how you arrived at your conclusion (4 points).

pKa of EtOH ≈ 16

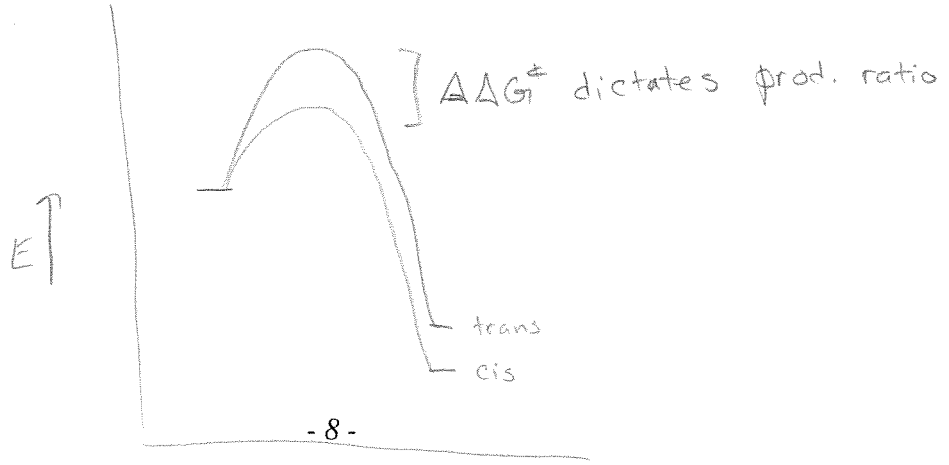
$K_{eq} = 10^{\Delta pKa} = 10^{-6}$ negative exponent – favors starting material

b. In the space below, construct a reaction coordinate diagram for the formation of the two enolate products using sodium ethoxide. Clearly indicate which product would be formed preferentially, and label the energy difference that dictates the product ratio (5 points).



c. When the sodium ethoxide is replaced with LDA and the reaction is conducted at -78 °C, the cis enolate product is formed preferentially. In the space below, construct a reaction coordinate diagram for the formation of the two enolate products using LDA. Clearly indicate the energy difference that dictates the product ratio under these conditions (5 points).

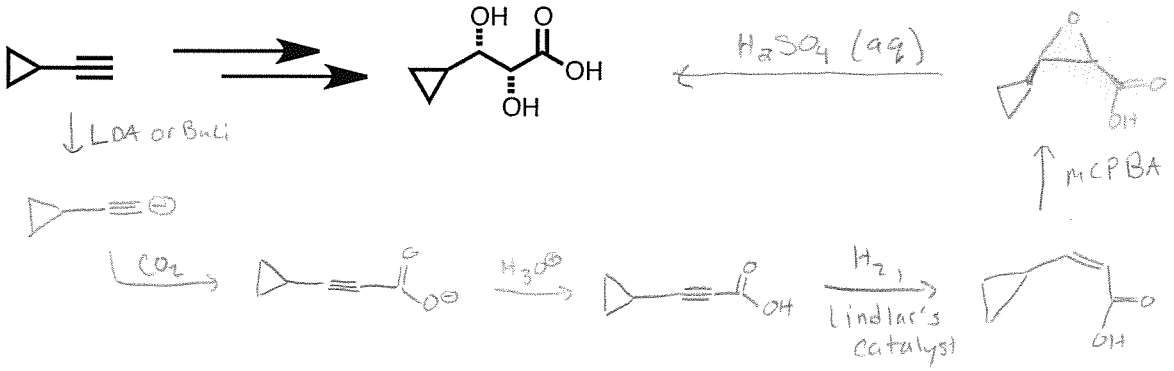
stronger base



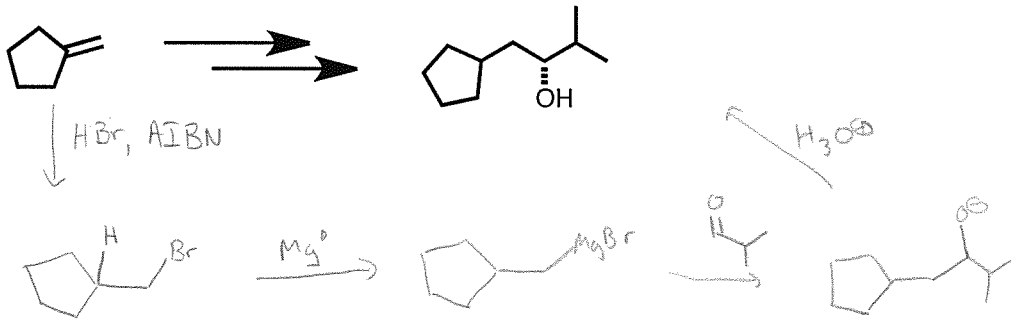
For each of these, there may be other acceptable answers

10. Each of the following transformations occurs through a series of multiple chemical steps. Show how each starting compound can be converted into the indicated product, providing all of the intermediates along the synthetic routes that you propose. Also supply all reagents and reaction conditions as appropriate. For the compounds that are chiral, you only need to indicate how the racemic mixture can be made (24 points).

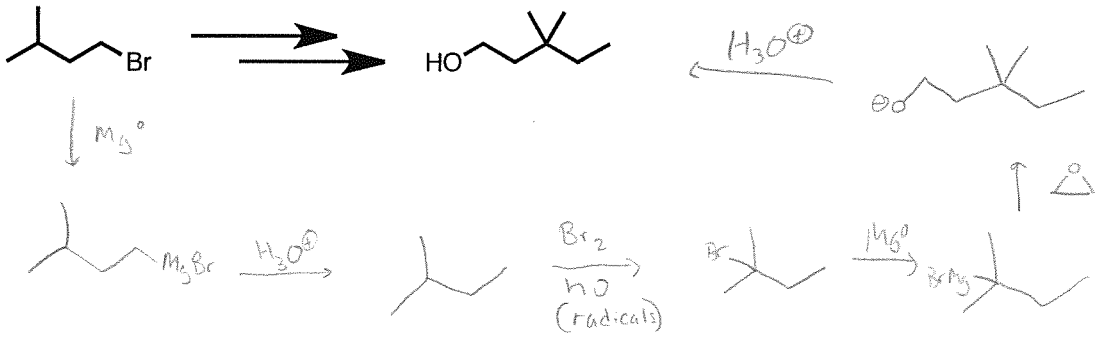
a.



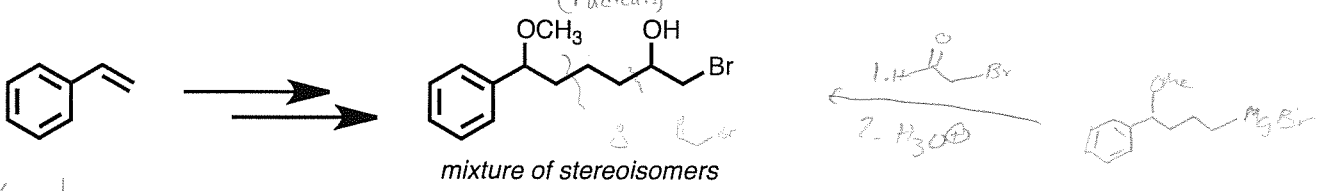
b.



c.

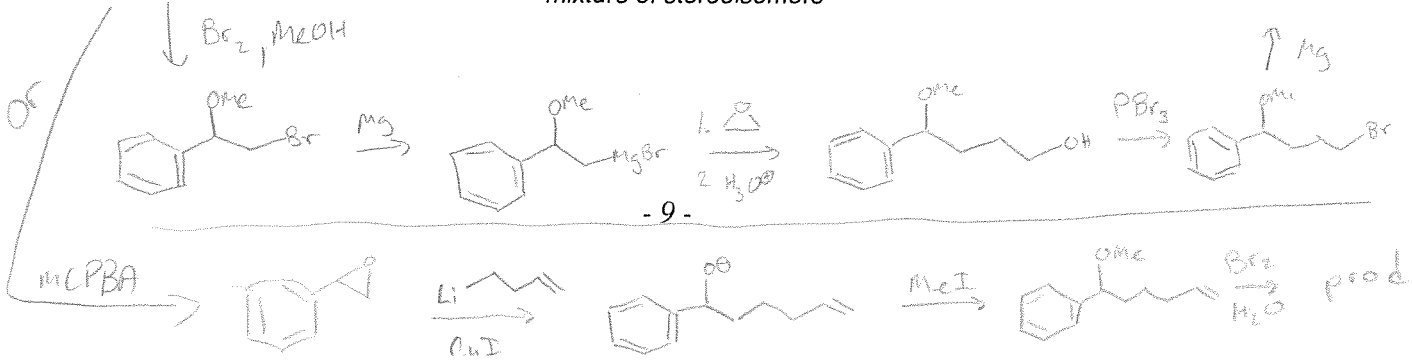


d.



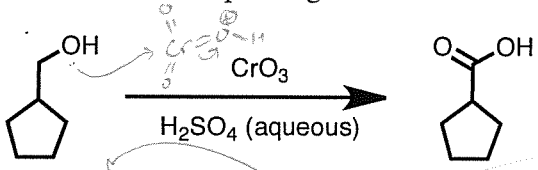
mixture of stereoisomers

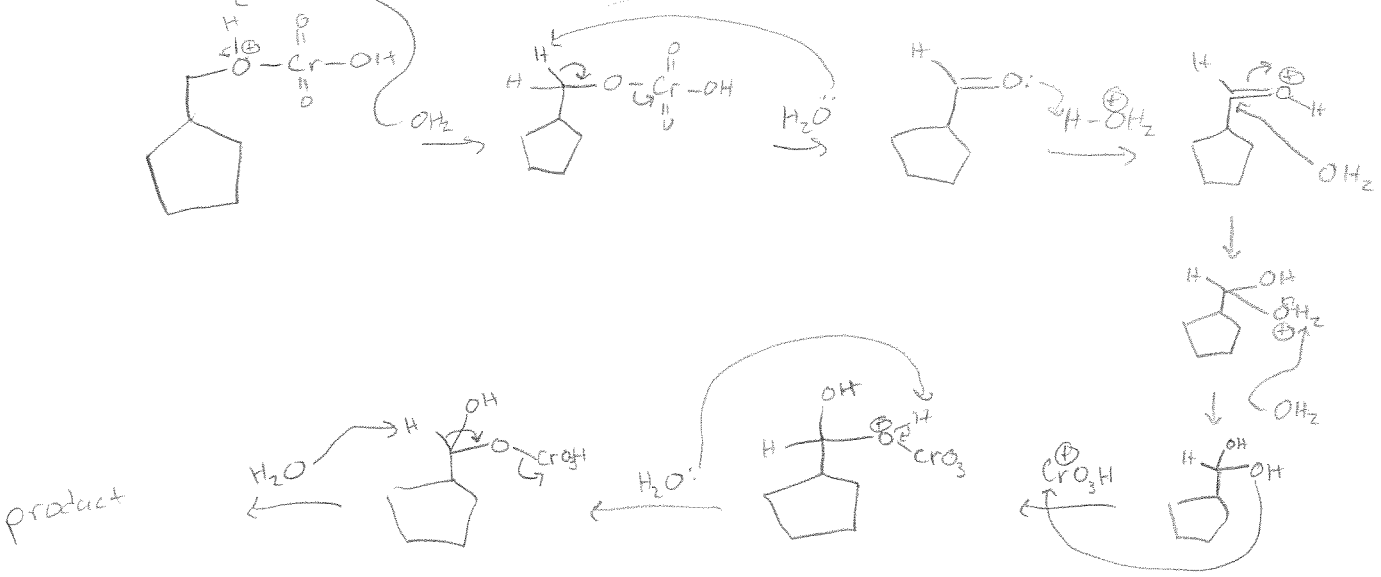
OR



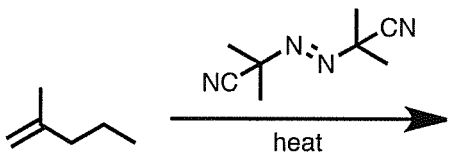
11. Provide detailed arrow pushing mechanisms for each of the following reactions (24 points).

a.



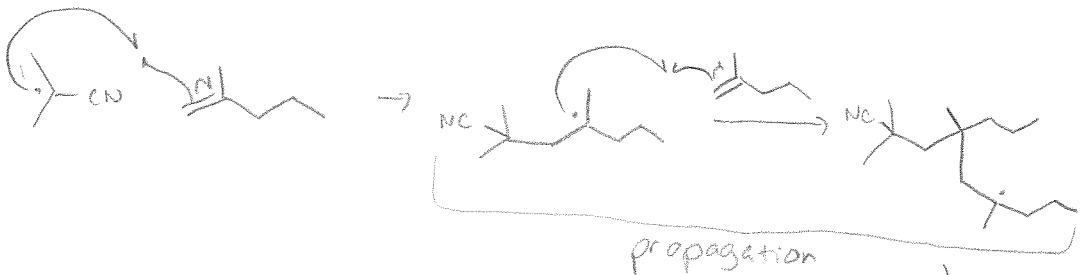


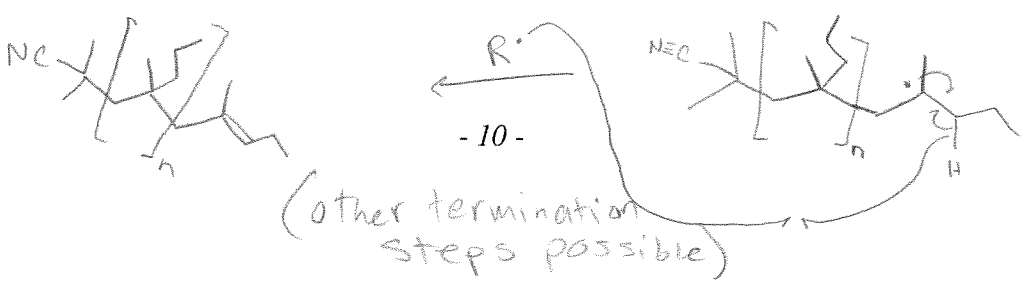
b.



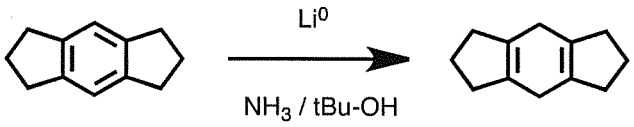
provide the structure of polymer product and label the initiation, propagation, and termination steps of your mechanism

Initiation

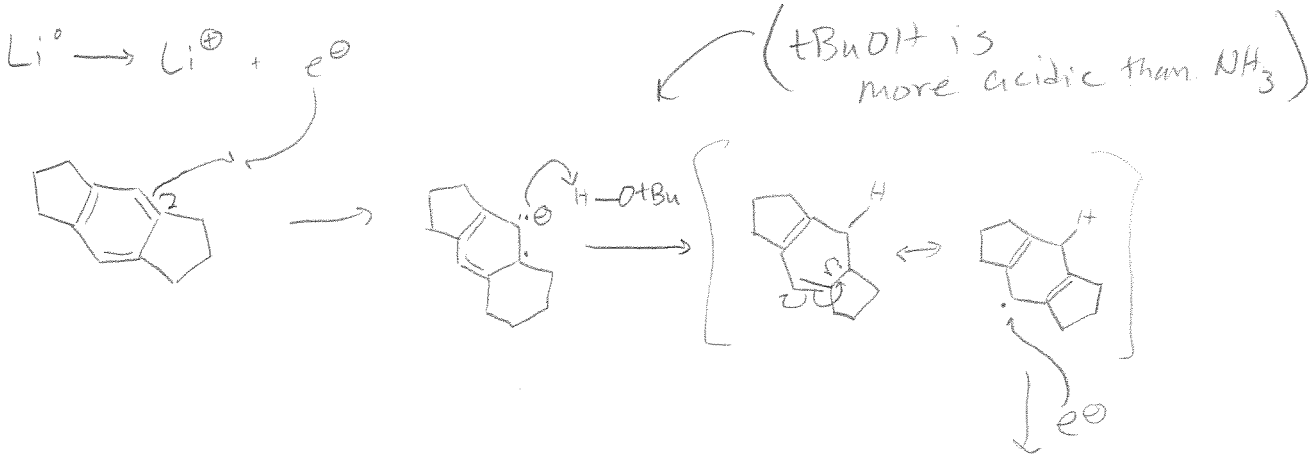




c.

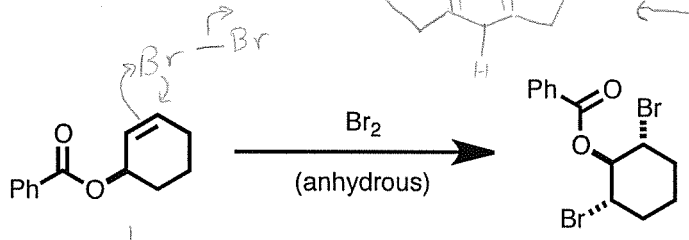


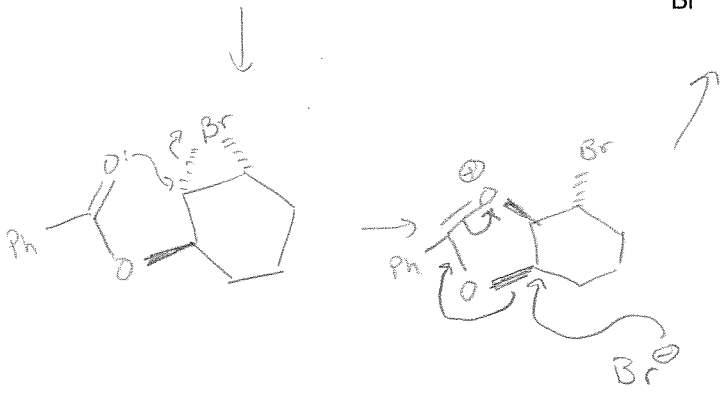
(Note similarity to the reduction of alkynes using Na° in NH_3)



(tBuOH is more acidic than NH_3)

d.





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.