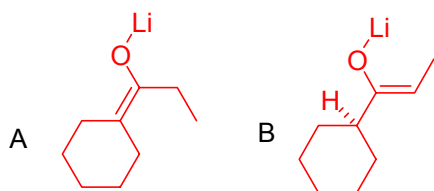
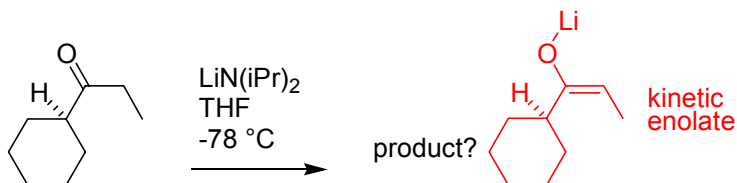


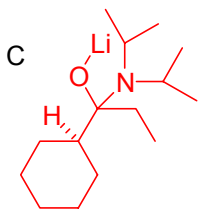
**U. of Kentucky Chemistry 535 Synthetic Organic Chemistry Spring 2007  
Final Exam Closed Notes**

1. Consider the reaction below.

- (15 pts.) Predict the product (the species that predominates in solution after this single step) and draw the transition state that results in the product.
- (15 pts.) Exhaustively consider other products that could be reached via reasonable mechanisms. [various deprotonation pathways and / or 1,2-additions]. Give reasons why these products do not predominate the reaction mixture.

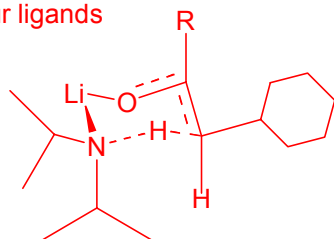


Steric strain makes the pathway to A have a high-energy transition state. The Z-enolate, B, has a higher-energy transition state than does the E-enolate (kinetic enolate) even though the Z-enolate is lower energy. See the low-energy transition state for the formation of the E-enolate.

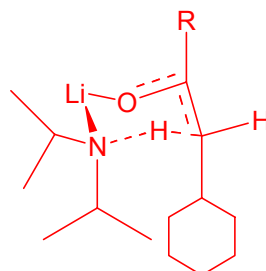


1,2 addition, all diastereomers are impeded by the hindered nucleophile.

These amides are better bases.  
Li has four ligands

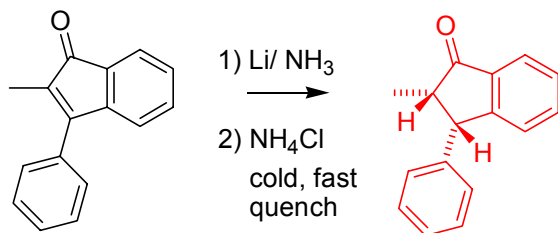


or



bad sterics between chex and iPr

c. (10 pts.) Draw the product below. Show stereochemistry.

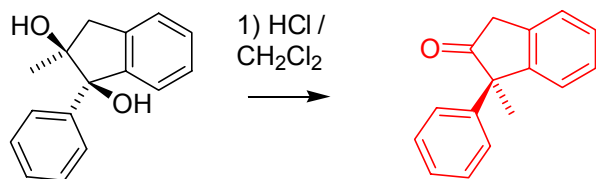


d. (10 pts.) Explain the observed diastereoselection.

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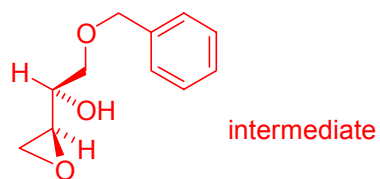
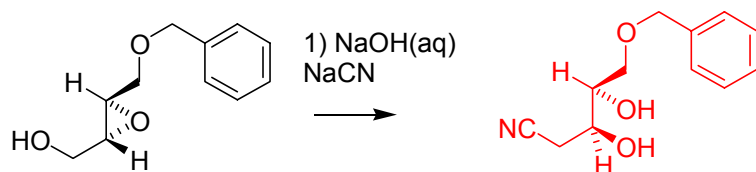
The proton is delivered in an S<sub>N</sub>2 type reaction and is added from the least hindered face of the enolate.

2. (10 pts.) Predict the product. You will have to worry about stereochemistry.

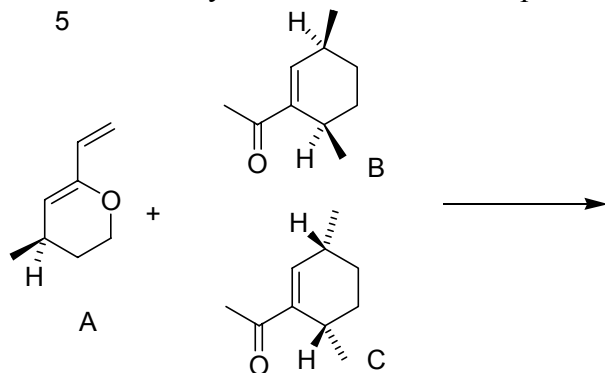


Doubly benzylic OH leaves and methyl migrates from the same face (suprafacially).

3. (10 pts.) Predict the product. You will have to worry about stereochemistry. [Hint: Payne Rearrangement]



4. (10 pts.) One of these reactions runs much faster than the other and gives much greater selectivity among diastereomers. Even though you don't know anything about the reaction you should be able to explain this phenomenon.



a. \_\_\_\_\_

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b. (10 pts.) Pick the fastest reaction and draw the Diels-Alder product.

I recycled this question from the 2006 Spring midterm. Have a look at that key.

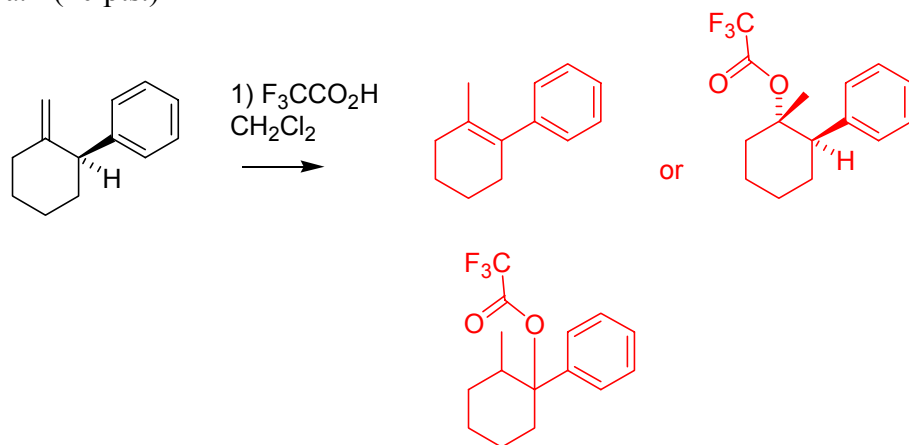
5. (10 pts.) Define what is meant by atom economy and why this is a good thing to try maximize when planning organic synthesis?

(Mass of Product)/ (Mass of Reagents Used to make Product)

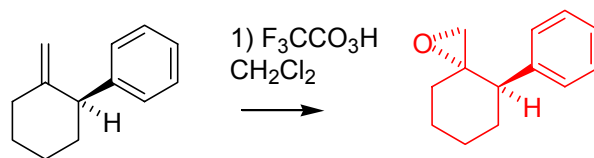
Atom economy maximized means that nothing is wasted. A purist would add items to the list that the chemist might think unfair like silica gel and solvent.

6. Predict the products?

a. (10 pts.)



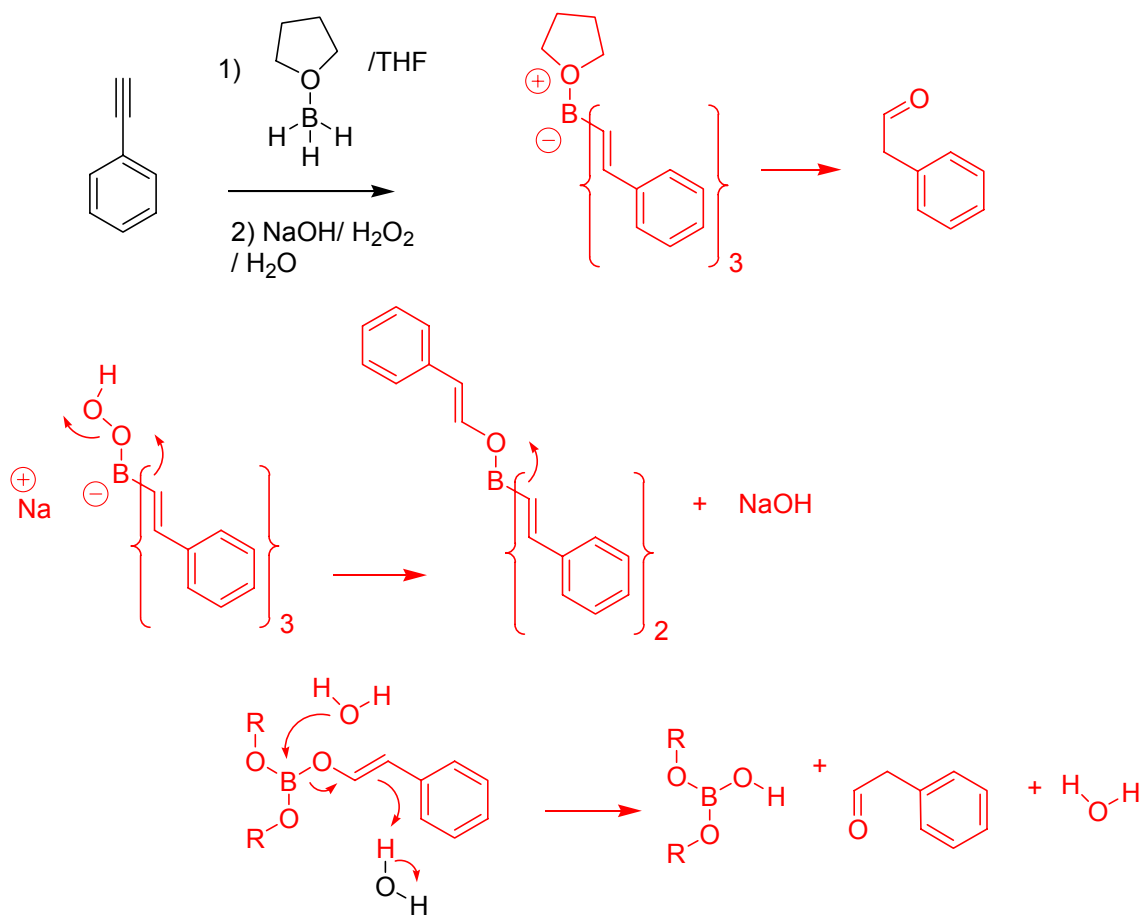
b. (10 pts.)



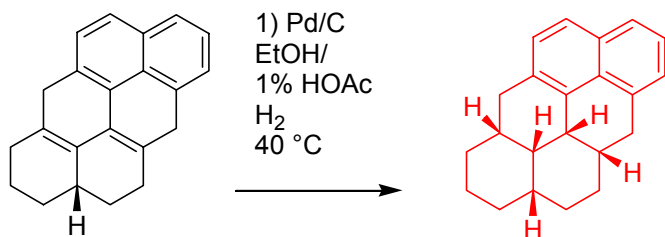
7.

a. (10 pts.) Write out a mechanism for the oxidation of the organoborane synthetic intermediate in the reaction below (step 2). The entire mechanism is not required.

b. (5 pts.) Make sure you draw the product.



8. (10 pts.) Draw the product. Stereochemistry is important.



9. (5 pts.) Define the molecular complexity that arises from remote stereochemistry. What is remote stereochemistry and why is it a problem?
- 

Asymmetric synthesis predicates on being able to use extant stereochemical bias in a molecule to create stereogenicity at a desired locus. For this to happen there needs to be a rate difference and hence an energetic difference, between at least two diastereomeric pathways. This energy difference is inversely dependent, in general, on the distance between the extant stereogenic atom and the desired one.

Remote stereochemistry is a problem when a molecule has stereogenic atoms or chirotopic regions separated by tethers that equalize the energies of the diastereomeric pathways.