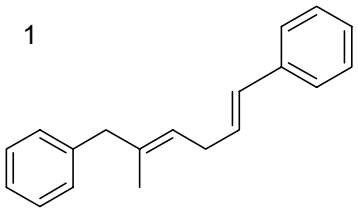
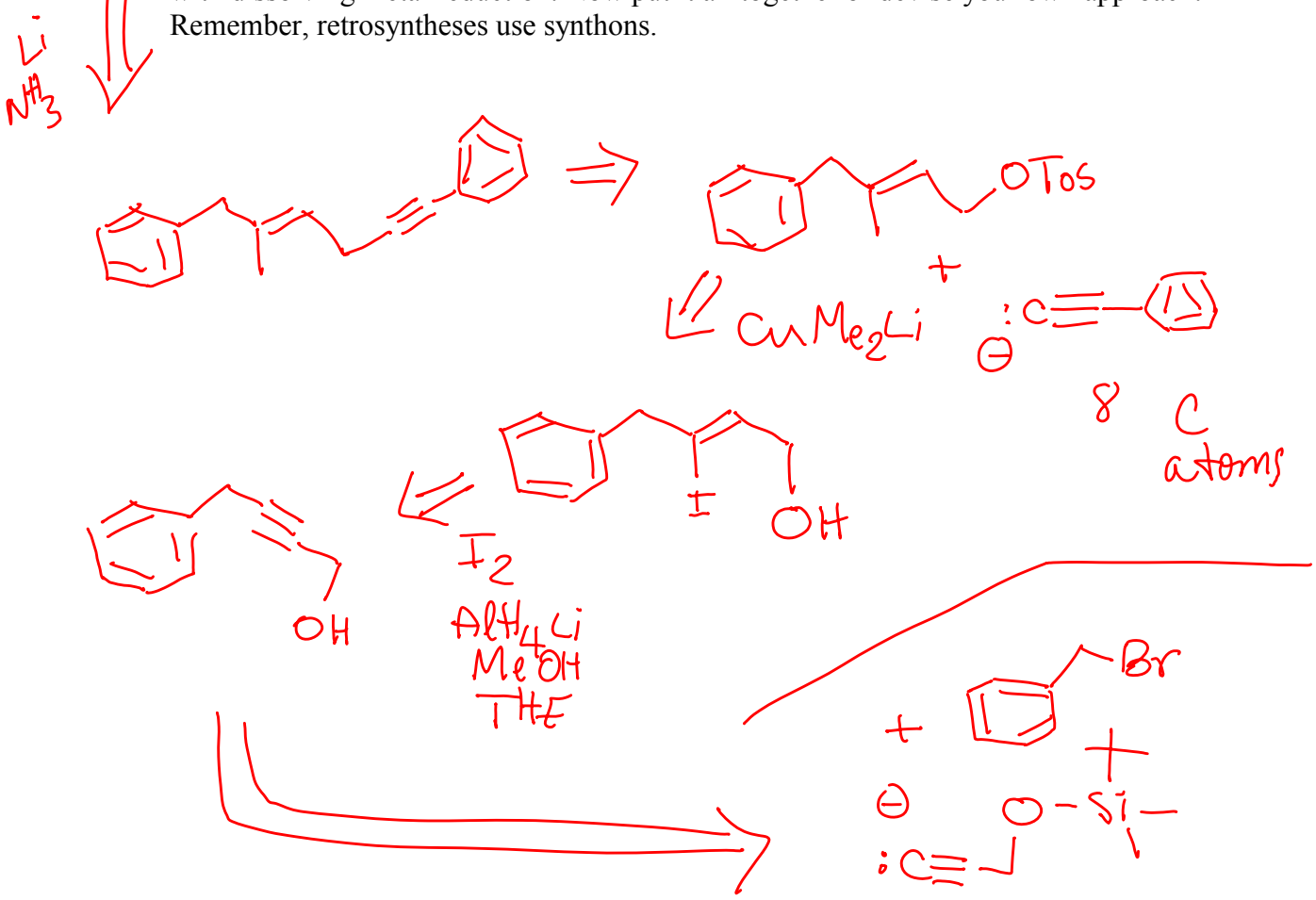
# U. of Kentucky Chemistry 535 Synthetic Organic Chemistry Spring 2007
# Midterm Exam

**1.** (20 pts.) Devise a stereocontrolled, convergent route to the diphenyl diene **1**. Show a retrosynthetic analysis that leaves no doubt for the reader that you can make the molecule. You may start with molecules containing no less than *eight* carbon atoms.

1



**Clues**: E. J. Cory synthesis of cecropia-C18 juvenile hormone, aluminum reduction of propargyl alcohols, C-C bond formation with alkyne anions. trans-selectivity with dissolving metal reduction. Now put it all together or devise your own approach. Remember, retrosyntheses use synthons.

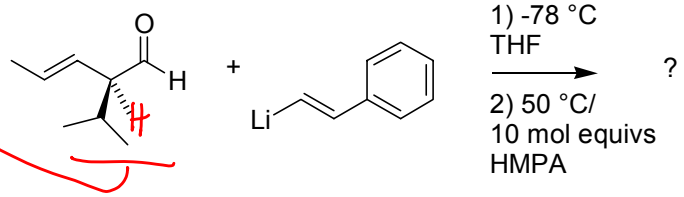


I graded your exams accordingly. I will discuss this in class.

This is the structure I want to draw.

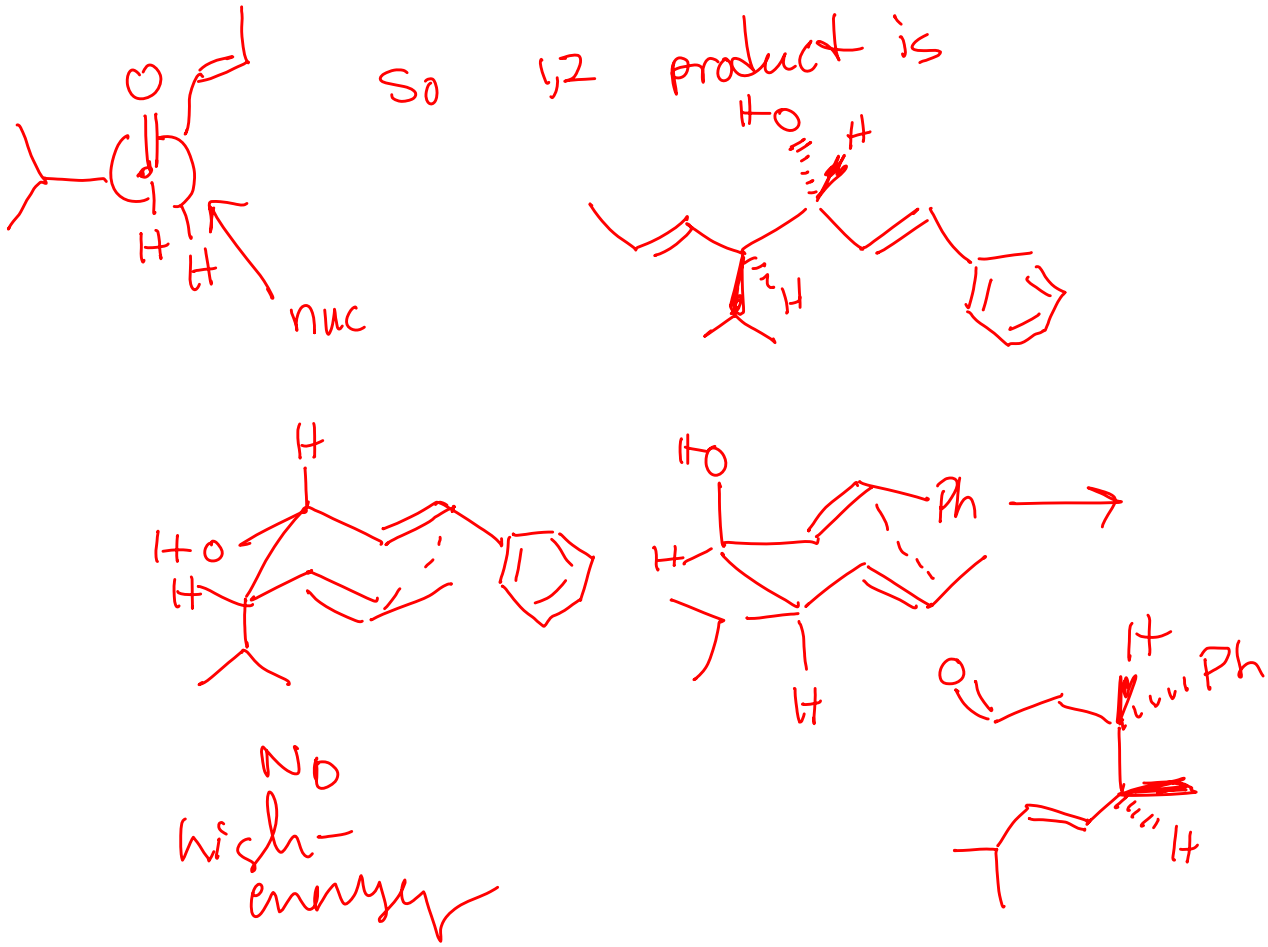


**2.** (20 pts.) The oxy-Cope rearrangement (3,3-sigmatropic rearrangement) is often set up by a 1,2-nucleophilic addition to an b,c-unsaturated aldehyde without isolation of the 1,2-adduct. Predict the enantiospecific oxy-Cope end product in the example below.




**Clues**:

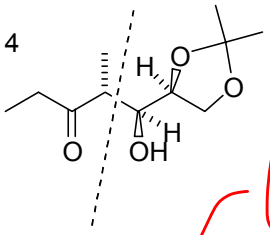
**a.** You will need to work out the stereochemistry of the 1,2-addition product.
**b.** iPr group is the biggest.
**c.** Oxy-Cope has six-membered ring transition state.
**d.** For partial credit figure out the 1,2-addition first using and draw out all transition states. Explain everything.

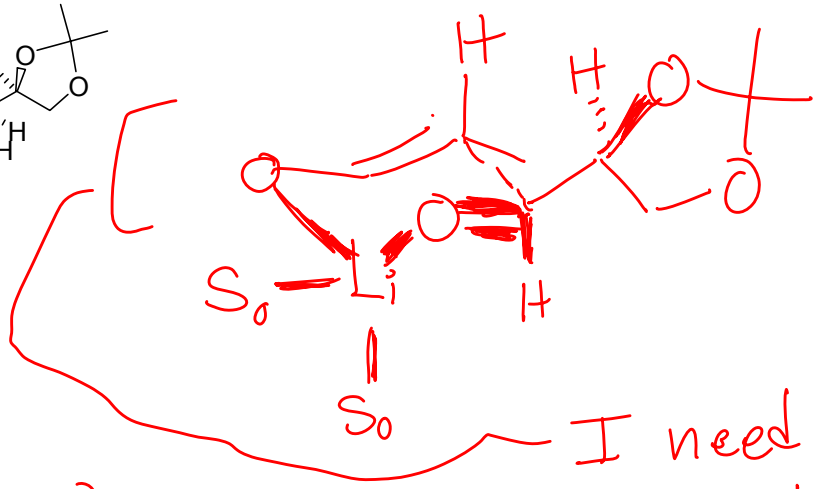


**3.** (10 pts.) Short answer. When choosing a synthetic method why is it best to choose a convergent approach? What is inherently wrong with multi-step linear syntheses?

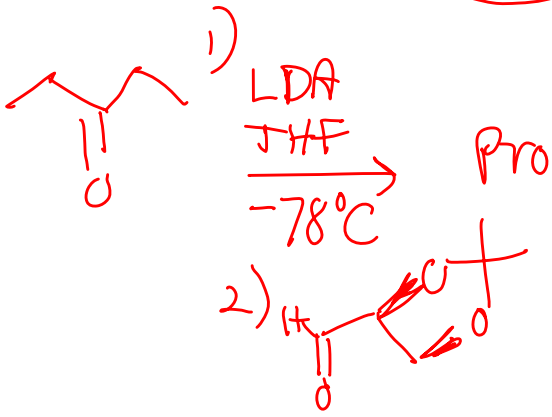
linear synthesis = yield = $(f)^n$ where f = fraction of product and n is number of linear steps. Convergent synthesis decrease n.

**4.** (10 pts.) Construct the bond indicated below. You will have to worry about stereochemistry.



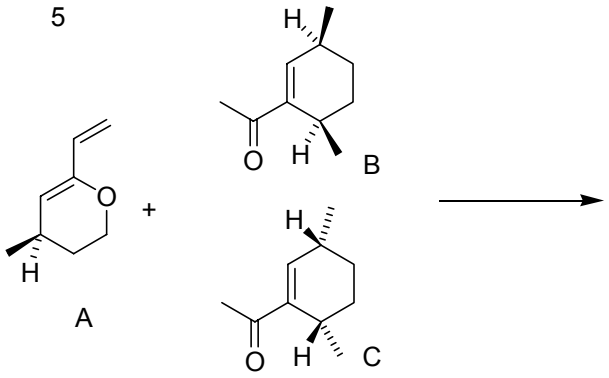

I need the E enolate from kinetic deprotonation with hindered base.




product

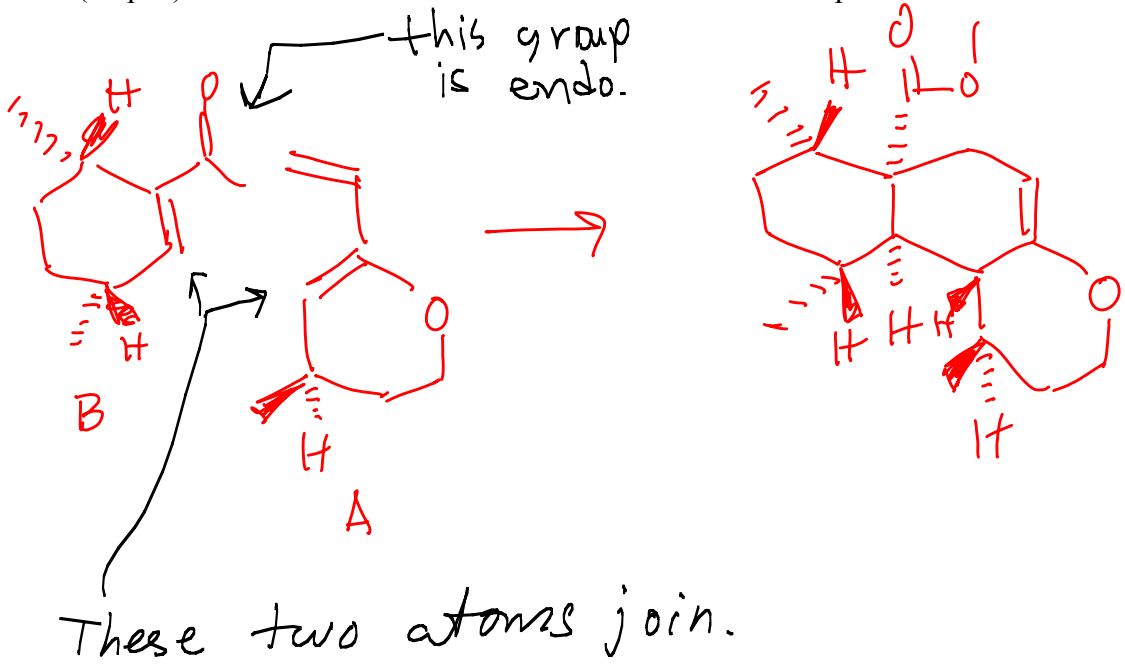
**5.** (10 pts.) One of these reactions runs much faster than the other and gives much greater selectivity among diastereomers. Even though you don't know anything about the reaction you should be able to explain this phenomenon.

5

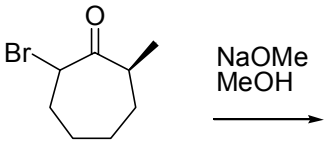



a. The result is a product of double diastereo selectivity. Two reactants have facial selectivity.

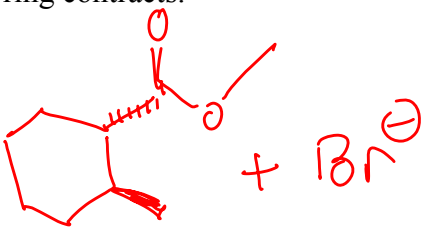
b. (10 pts.) Pick the fastest reaction and draw the Diels-Alder product.

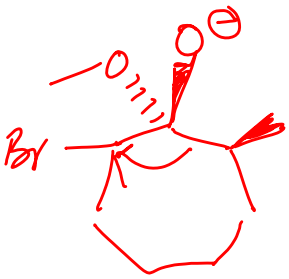


**6.** (10 pts.) Predict the product. The ring contracts.




NaOMe
MeOH




cis + trans equilibriates to trans

**7.** (5 pts.) What is driving the 1,2-addtion reaction in question # 2?

formation of C=O; stronger bond than C.

**8.** (5 pts.) What is driving the reaction in question # 5?

net π → σ conversion

**9.** (5 pts. extra) What is driving the reaction in question # 6?

Δ pka HBr versus R-Ö-H