Chem 634
Professor Fox
Exam 3
May 21, 2004
3 hours

Your Name_____

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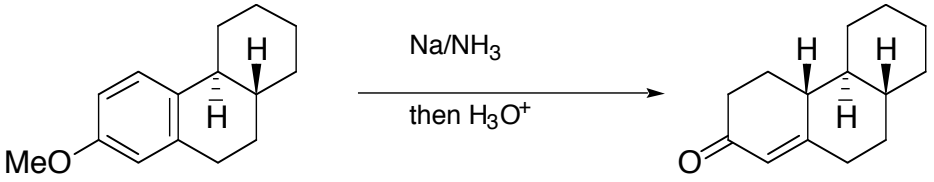
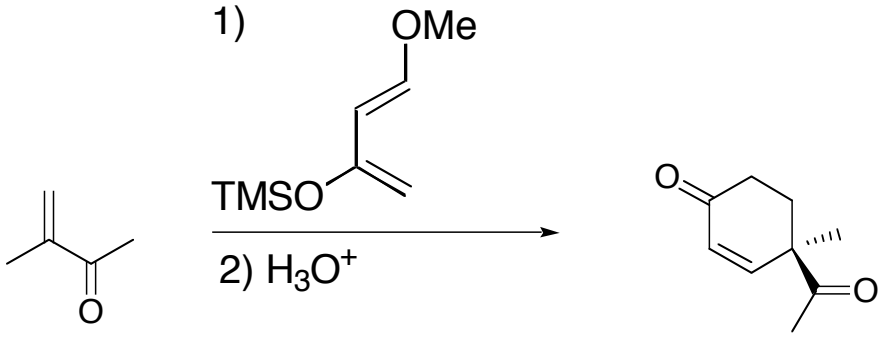
May 21, 2004

1. Provide reagents for the following transformations. Mechanistic details are not required, but be sure to indicate relative stereochemistry where necessary (six parts; 3 pts each). More than one step may be required.

a



b



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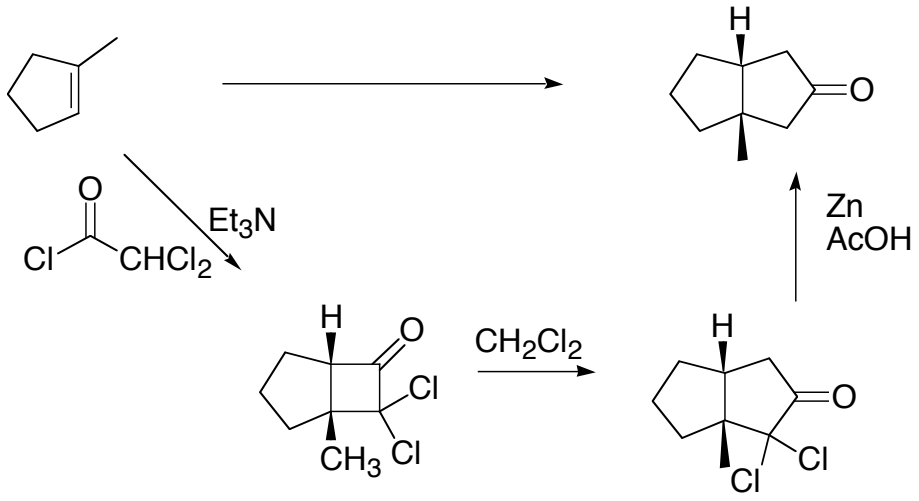
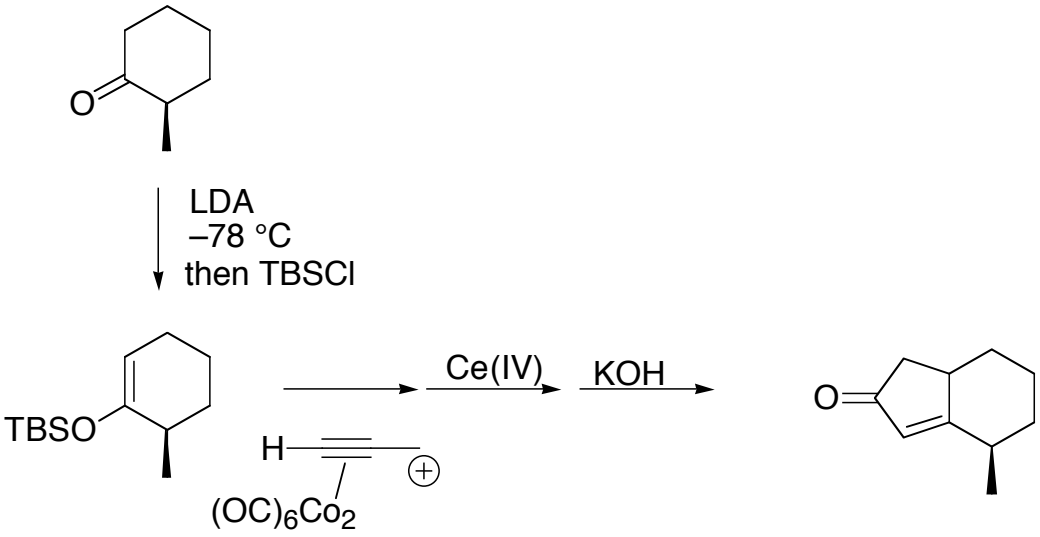
1. (continued)

c



d



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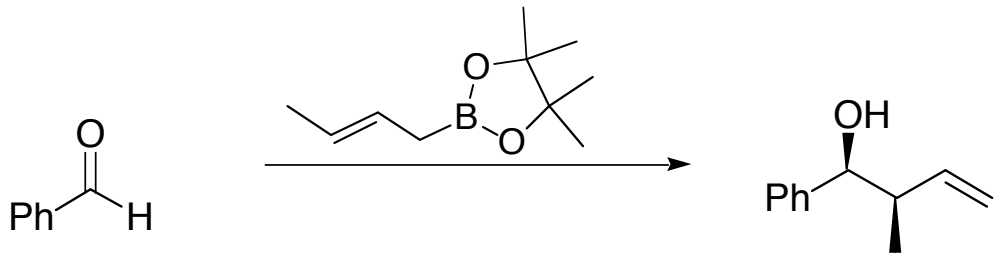
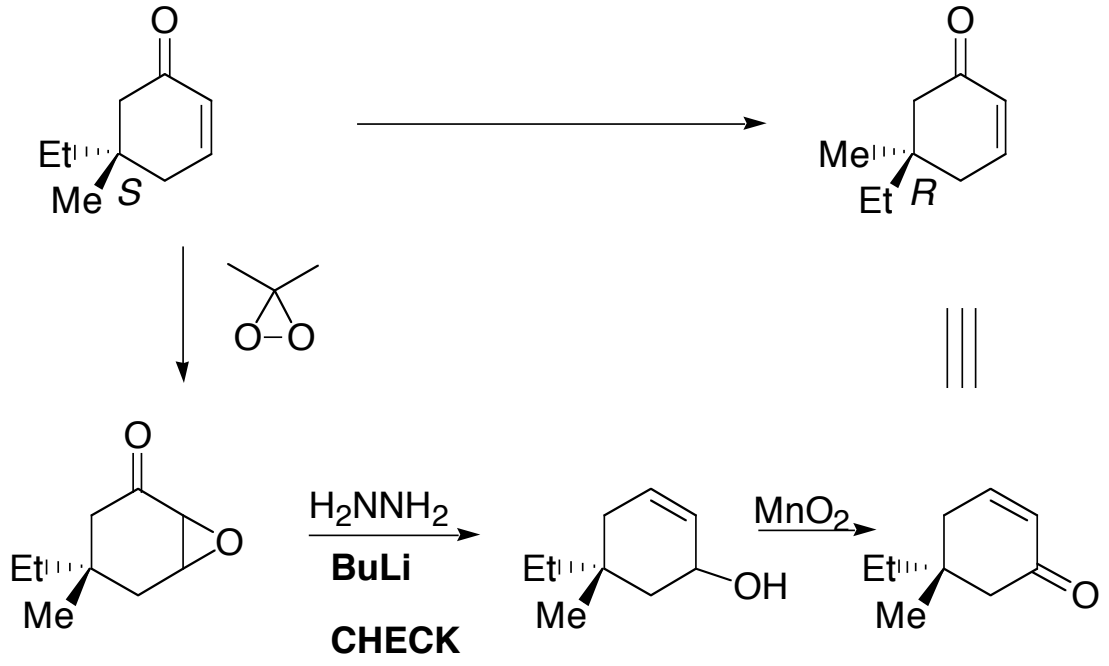
1. (continued)

e



f



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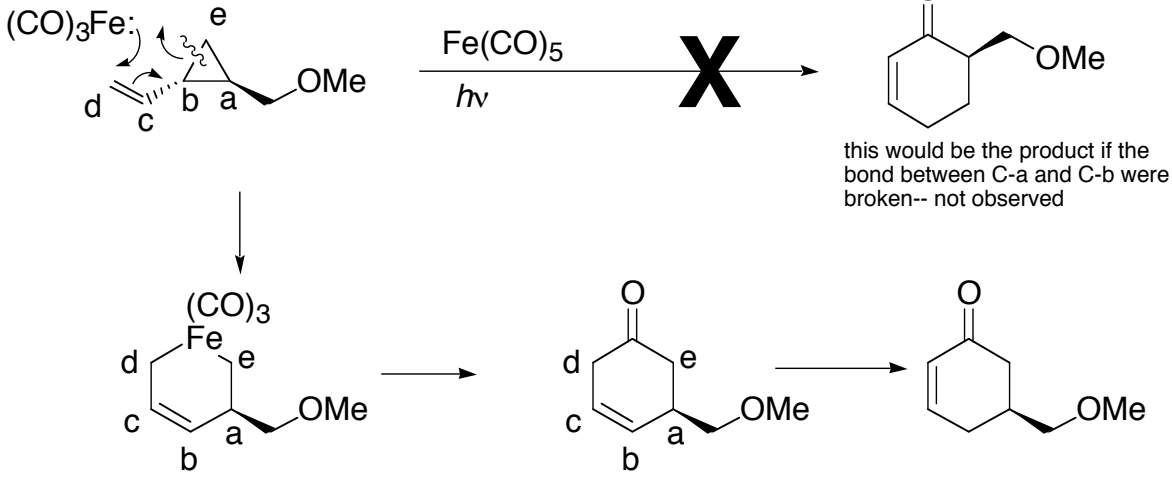
2. Predict if each of the following reactions would proceed as written.
If you feel that the reactionwould proceed, simply write “will proceed as written”.
If you feel that the reaction would not proceed as written, provide a brief but detailed explanation, and indicate the structure of the product(s) that would be formed instead of (or in addition to) the product that is drawn (3 points each).

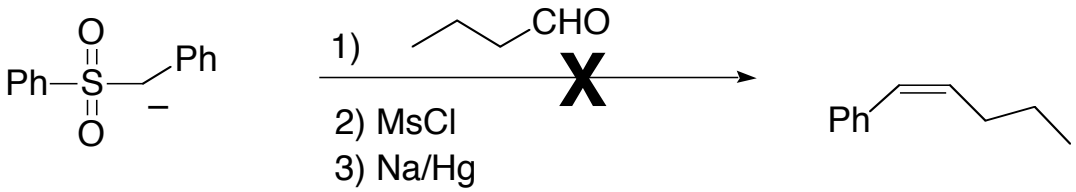
a

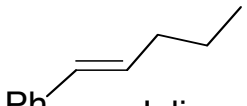


this would be the product if the bond between C-a and C-b were broken-- not observed

the reaction proceeds by inserting into the less substituted side of the cyclopropane. Thus, the bond between C-b and C-e is broken

b

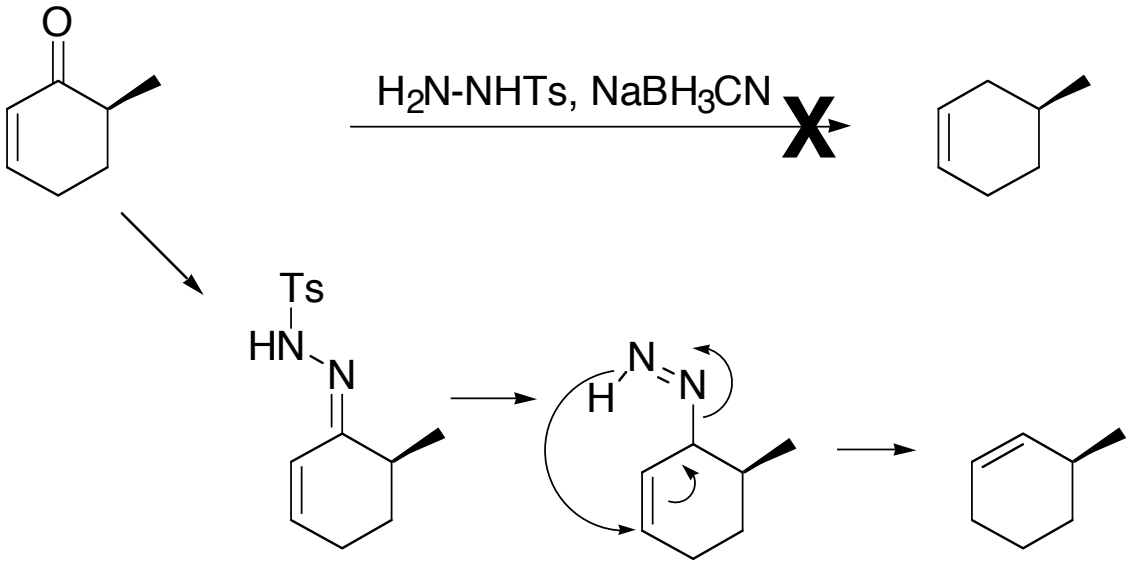




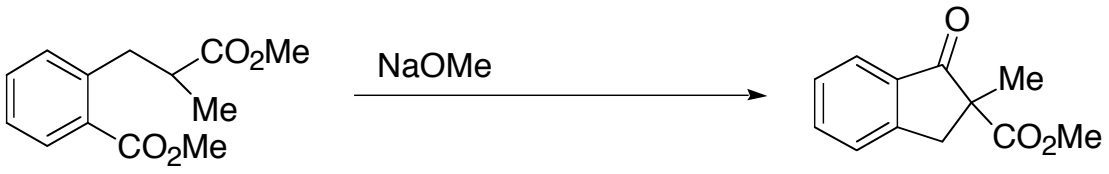
Julia coupling gives the trans alkene

2. (continued).

c

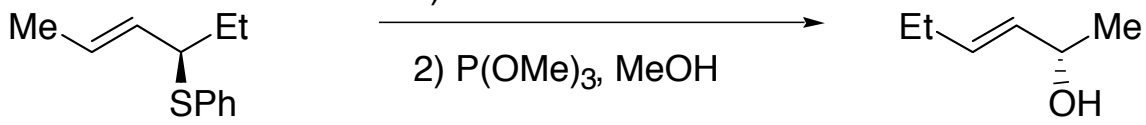


d

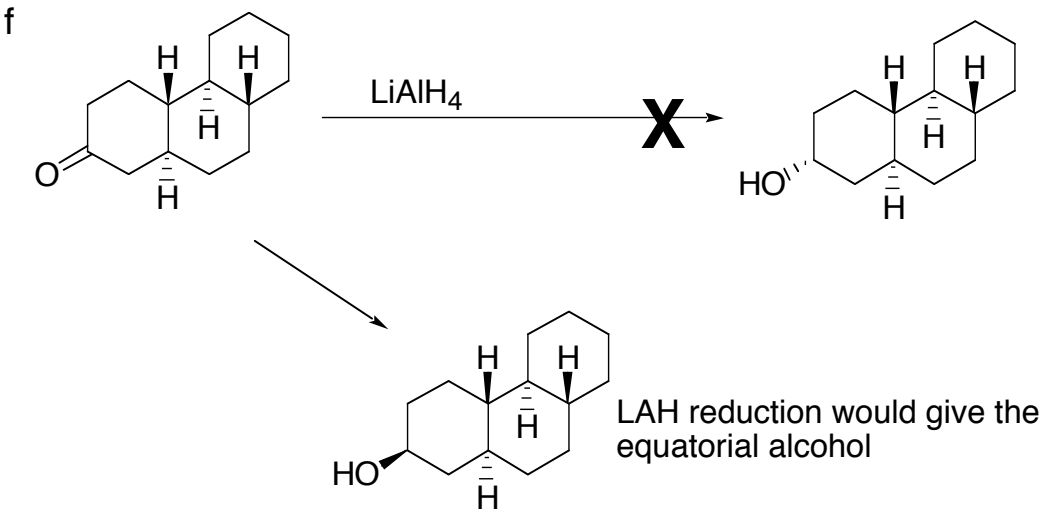


Dieckmann condensation would not proceed because the product is not enolizable

2. (continued).

e 

would proceed as written

f 

LAH reduction would give the equatorial alcohol

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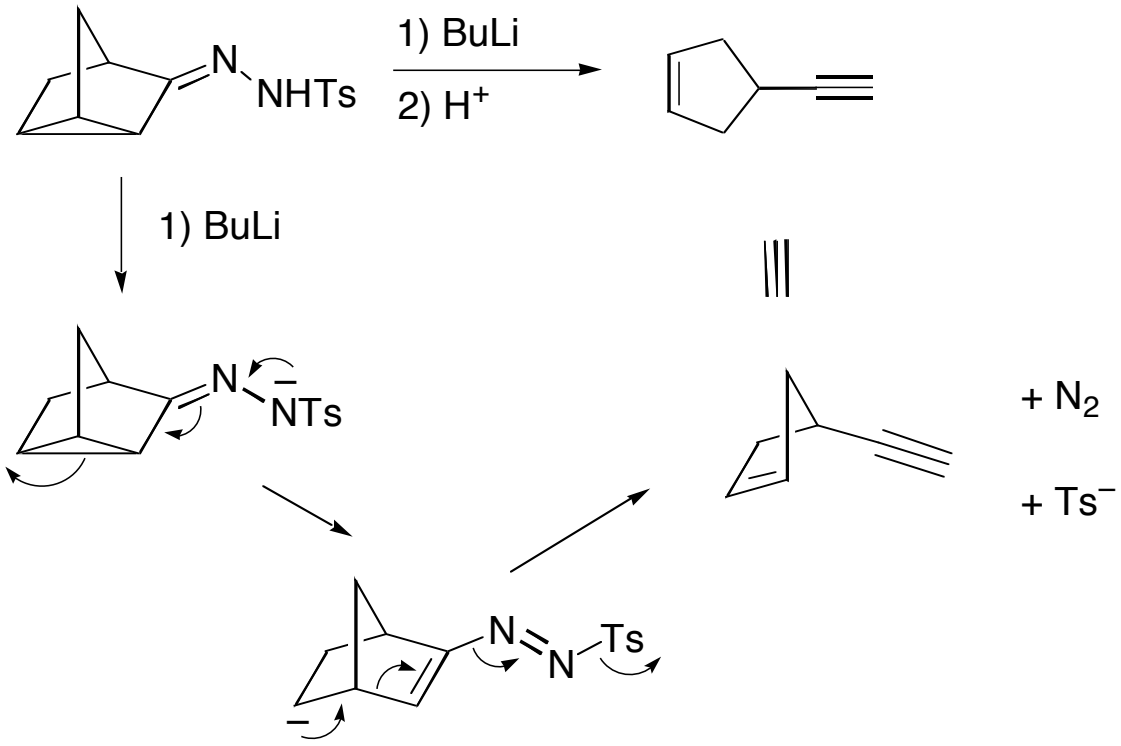
3. Provide a detailed arrow pushing mechanism (15 pts)



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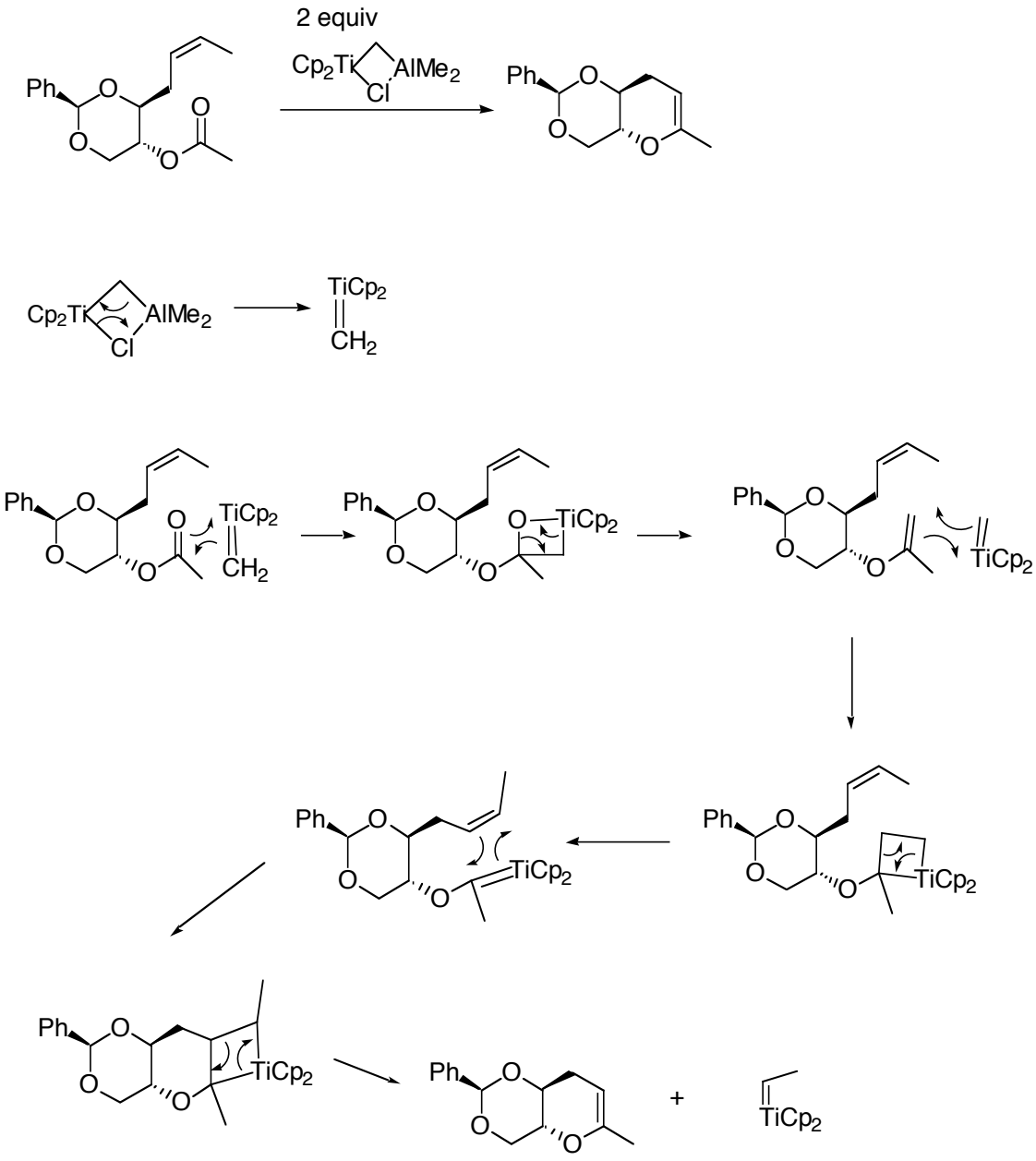
4. Provide a detailed arrow pushing mechanism (15 pts)



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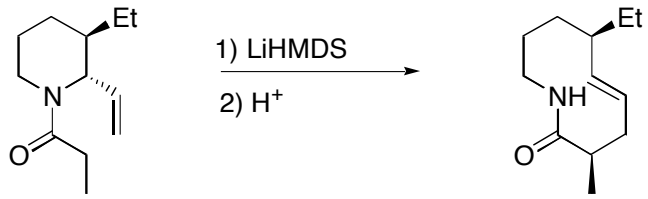
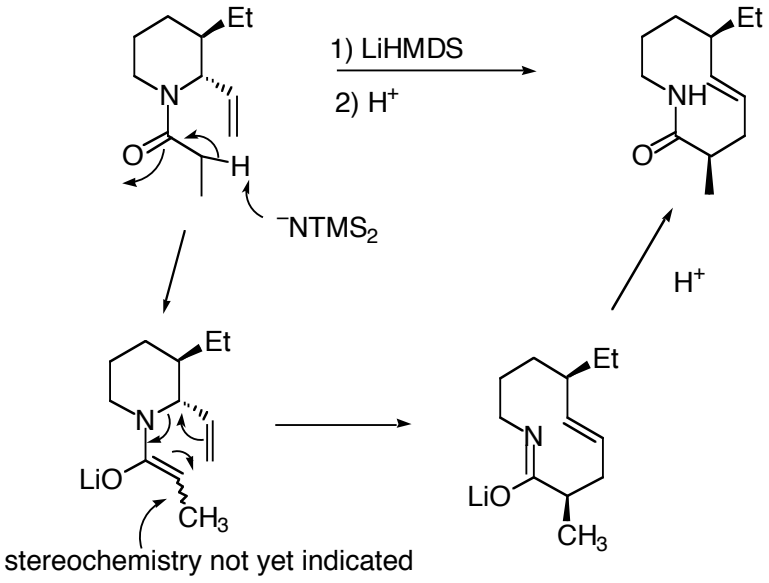
5. Consider the following reaction



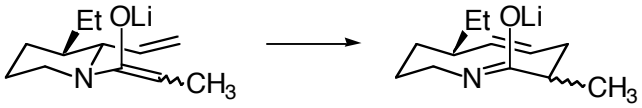
LiHMDS = TMS_2NLi

a) Provide an arrow pushing mechanism (5 pts)
b) Propose a transition state model for the transformation (7 pts)
c) Based on your answer to (b), what does the relative stereochemistry of the product tell you about the stereochemistry of the enolization. In otherwords, do you form the E or Z enolate. Explain your answer (7 pts)

a.

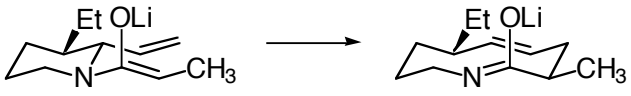


b.



Chair transition state for the Claisen rearrangement in which the ethyl and vinyl groups occupy equatorial positions.

c.



The model above tells us that the enolate stereochemistry is *Z*

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5. Propose a synthesis using any acyclic materials (15 pts)