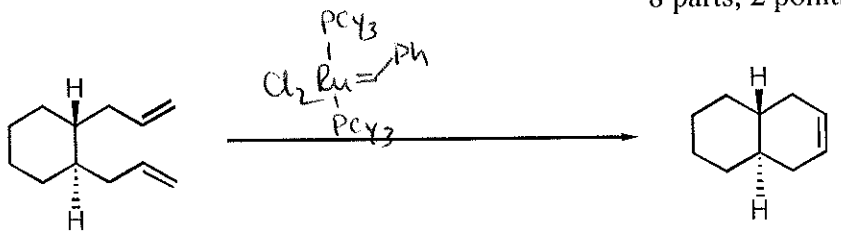
Chem 634
Exam 2
December 16, 2005
3 hours
Prof. Fox

Your Name KEY

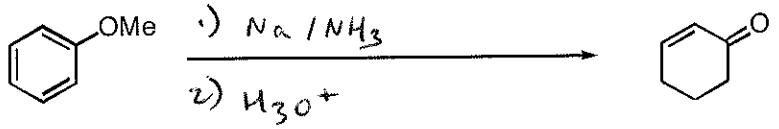
1. Provide reagents for the following transformation. More than one step may be required. Do not write mechanisms.

8 parts, 2 points each

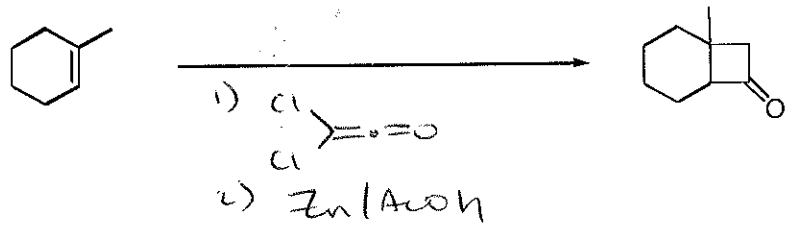
a



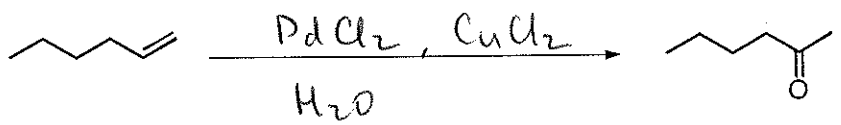
b



c

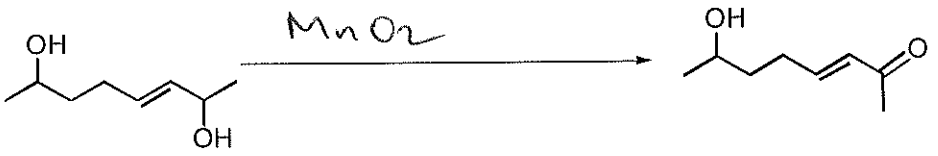


d

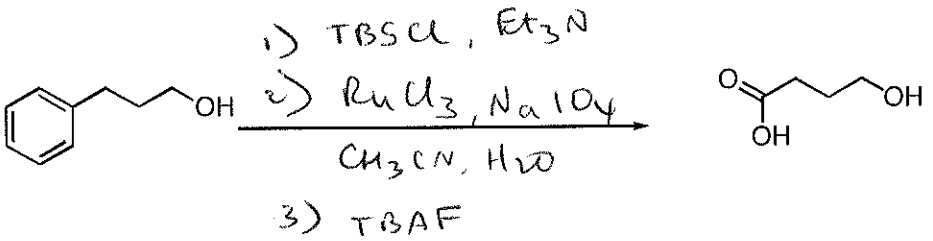


Question 1 continued

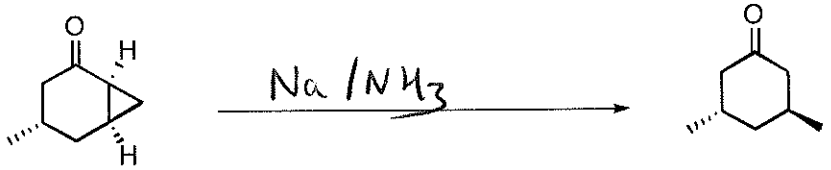
e



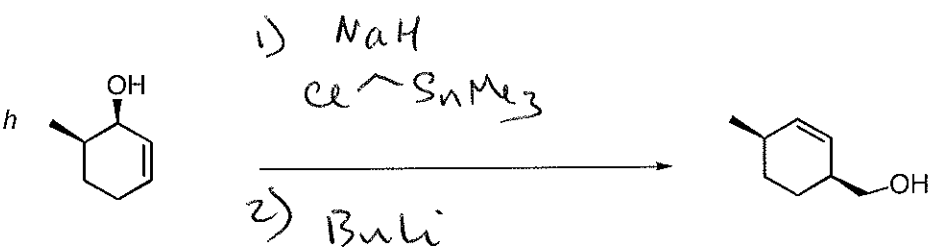
f



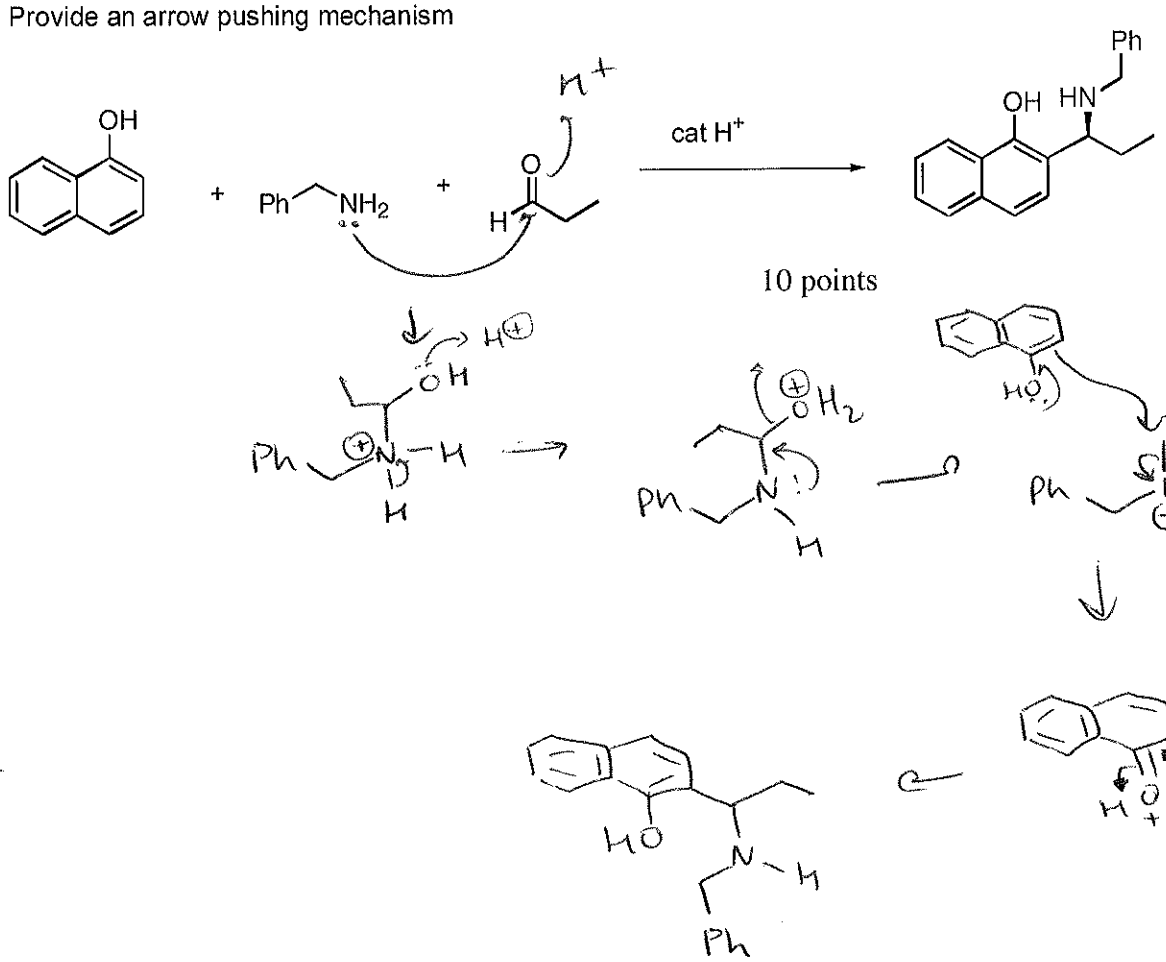
g



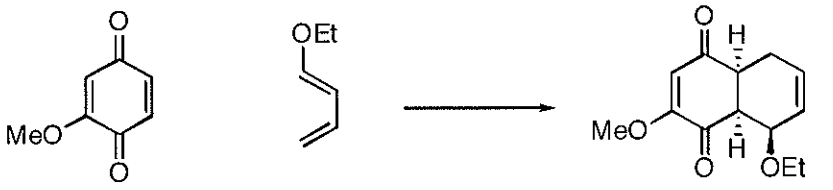
h



2. Provide an arrow pushing mechanism

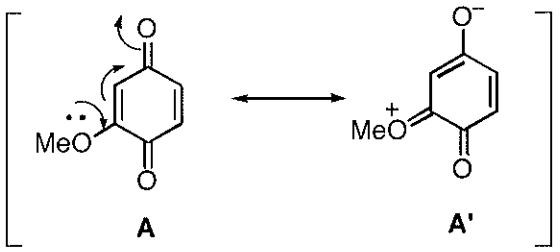


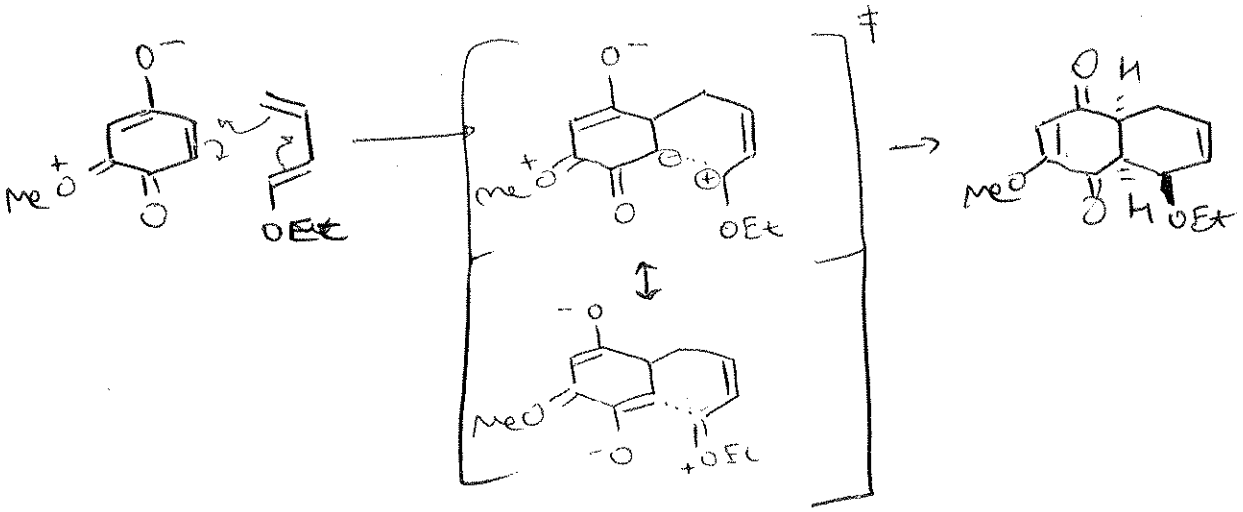
3(a) The reaction of diene **A** with dienophile **B** is regioselective. Explain.



A **B** 6 points

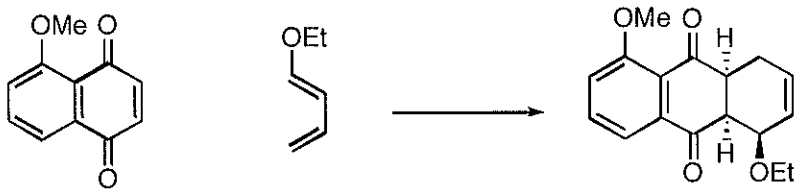
When preparing your answer, consider that the methoxy 'deactivates' the top carbonyl through resonance as shown below. You may assume that the resonance form A' is the dominating factor that guides the regioselectivity.



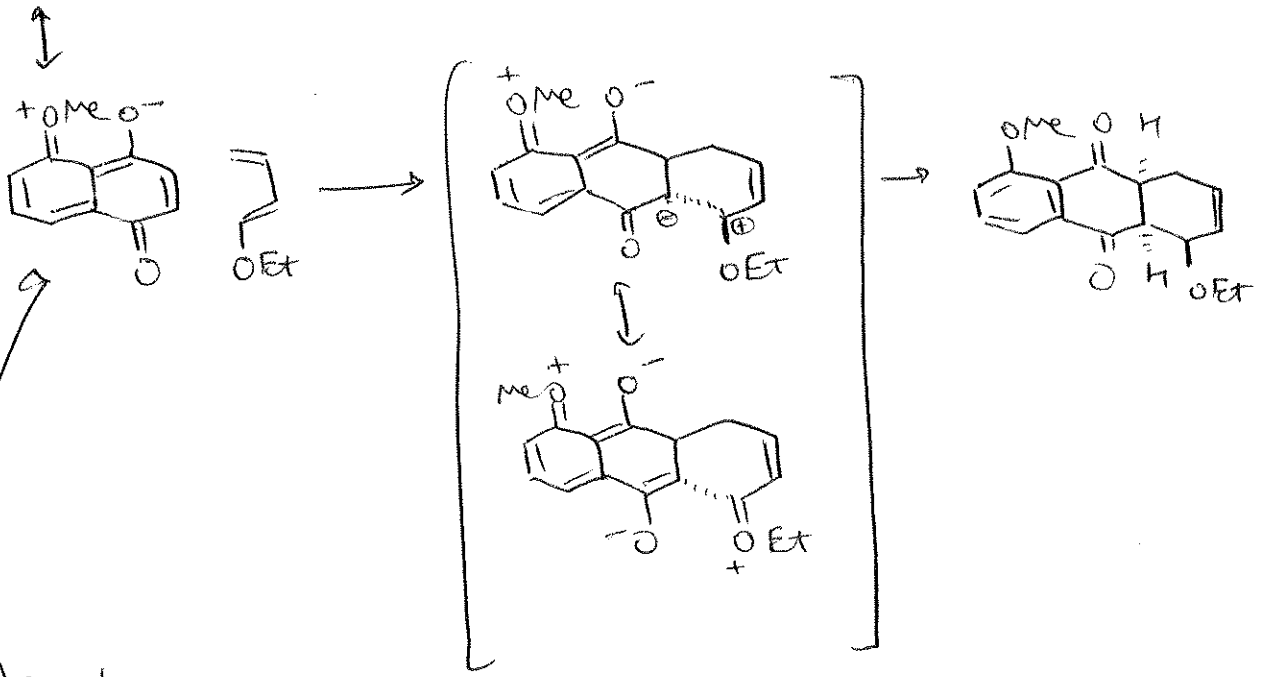


The concerted, asynchronous Transition State has the "flavor" of a stepwise process with buildup of charge. The favored TS places partial positive charge next to the ethoxy, and partial negative charge next to the carbonyl.

3(b) The reaction of diene **C** with dienophile **B** is also regioselective. Explain.

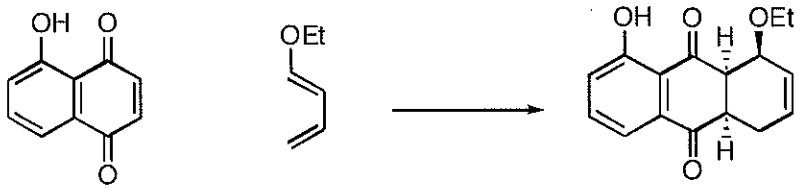


C **B** 6 points



Asynchronous, Concerted TS Dominated by This resonance structure

3(c) The reaction of diene **D** with dienophile **B** displays opposite regioselectivity as compared to **C**. Explain.

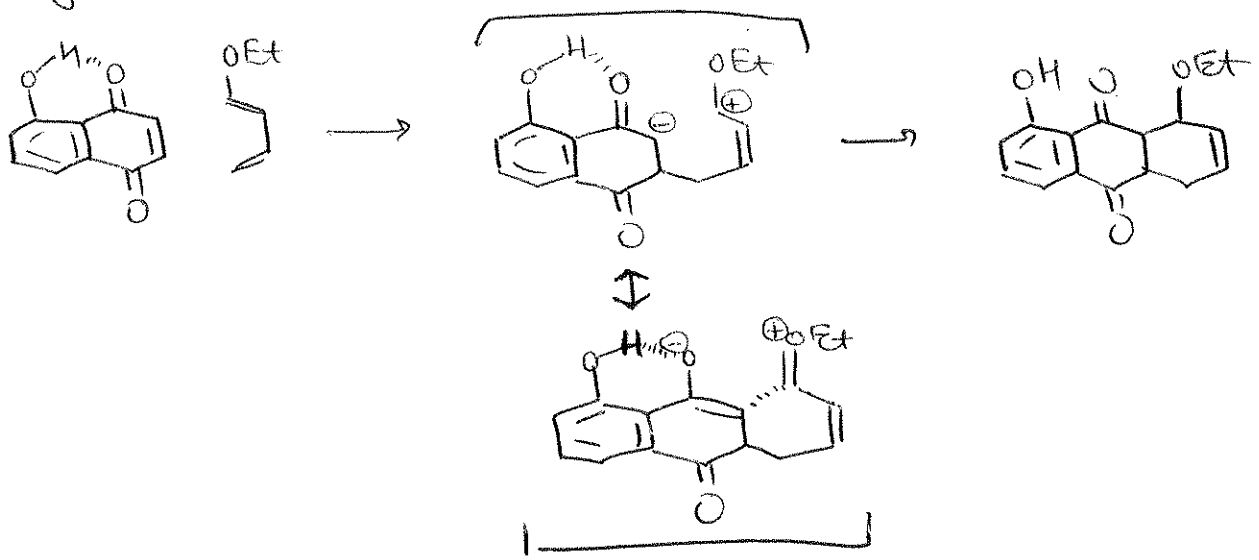


D **B**

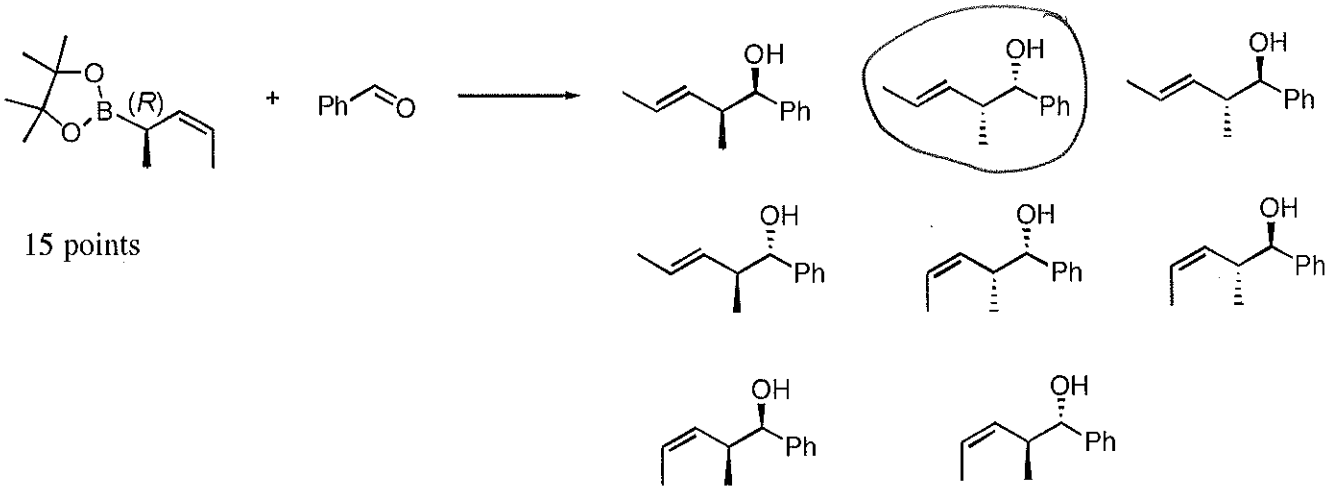
10 points

Hint 1: disregard what you wrote in parts (a) and (b) of this question. It is overwhelmed by another effect.
Hint 2: the phenolic hydrogen of **D** is acidic. Recall the effect that Lewis acids have on Diels Alder reactions

Hydroxyl acts as a "local" Bronsted Acid

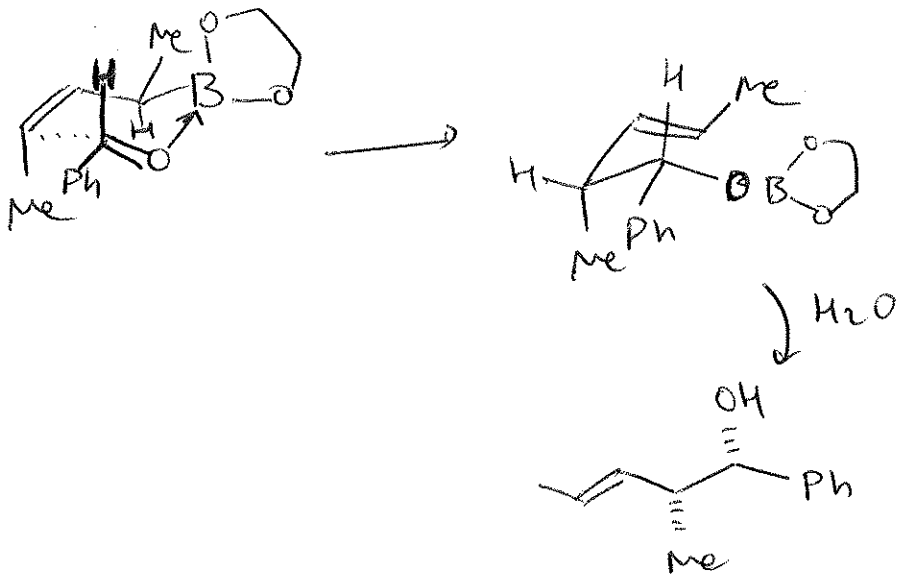


4. Circle the correct product. Explain your choice with a carefully drawn analysis of the transition state.

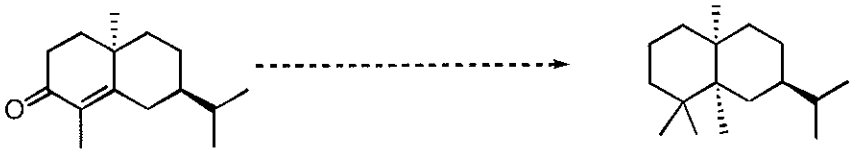


15 points

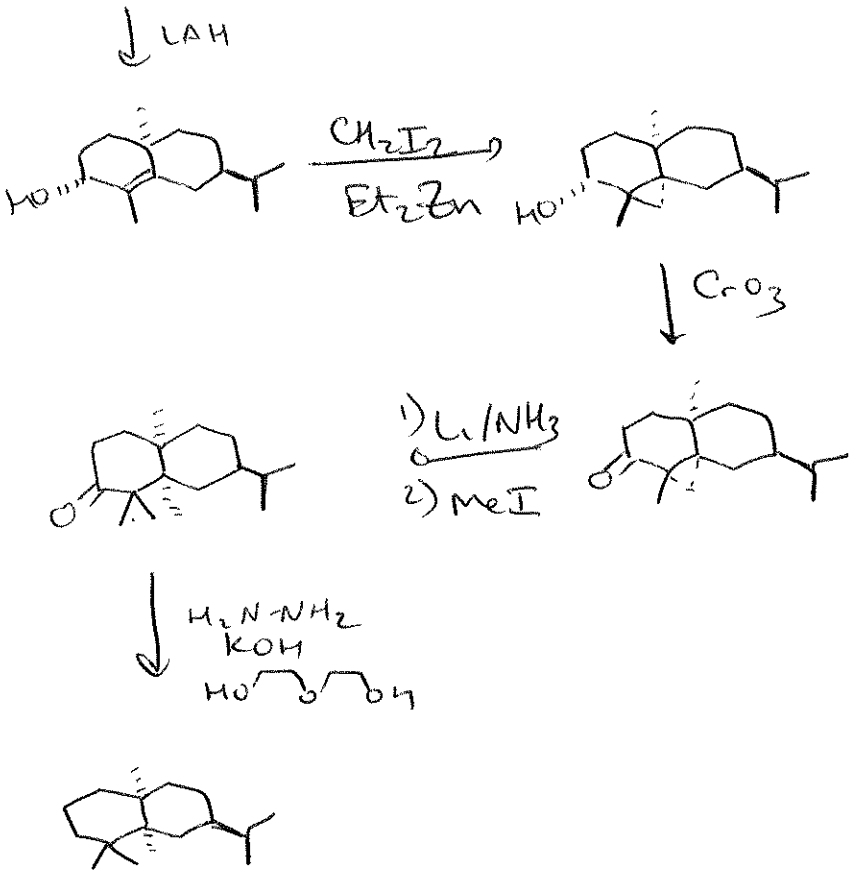
CHAIR TS



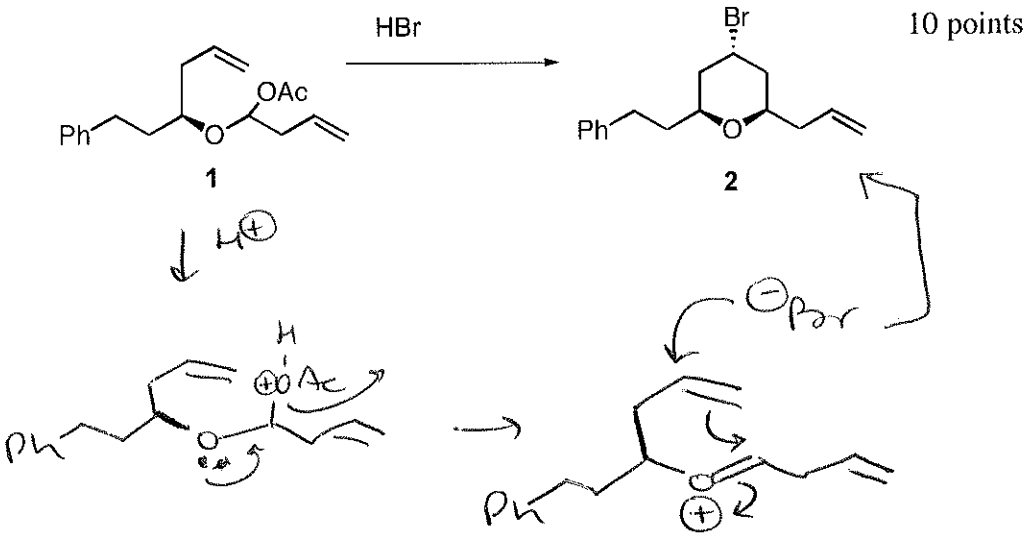
5. Propose a multistep synthesis



15 points



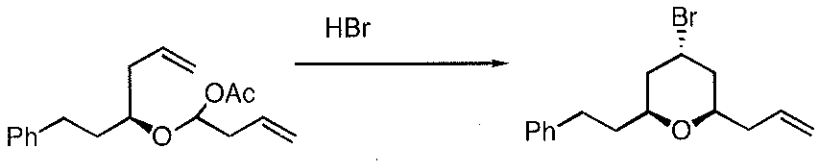
6(a) Propose an arrow pushing mechanism



10 points

6(b) When the reaction in 6(a) is carried out with enantiomerically enriched **1**, the product **2** that is obtained is nearly racemic. Propose an explaination

12 points



1
97% ee

2
4% ee

RATE OF RACEMIZATION VIA Claisen Rearrangement is COMPETITIVE WITH ATTACK OF BROMIDE