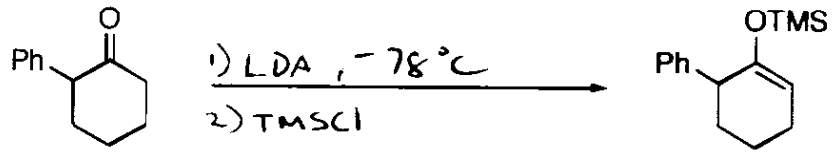
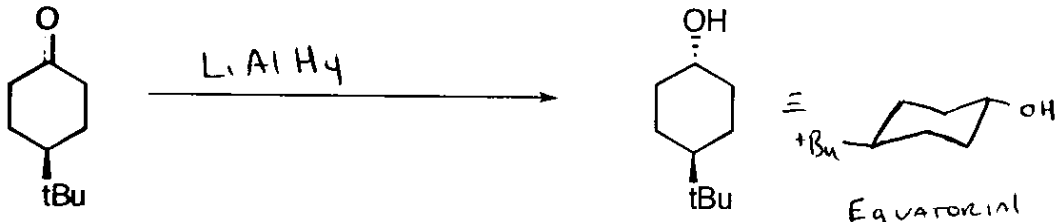
Chem 634 Exam 1 Your Name_____

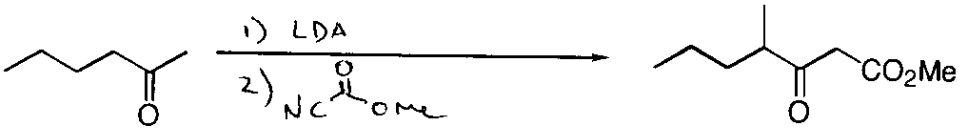
1. Provide reagents for the following transformations. More than one step may be required. Mechanistic details are not needed. (five parts; 3 pts each)

a 

b 

Equatorial Alcohol:

Axial Delivery of $[H^{\ominus}]$

c 

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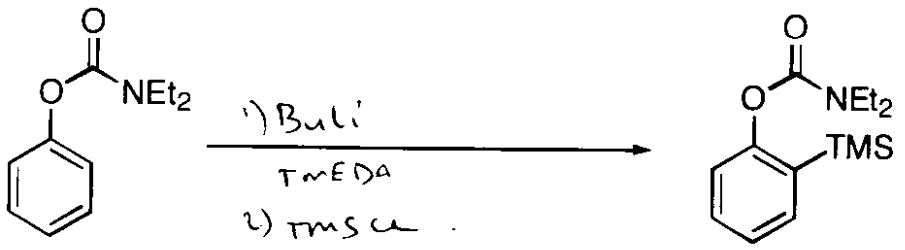
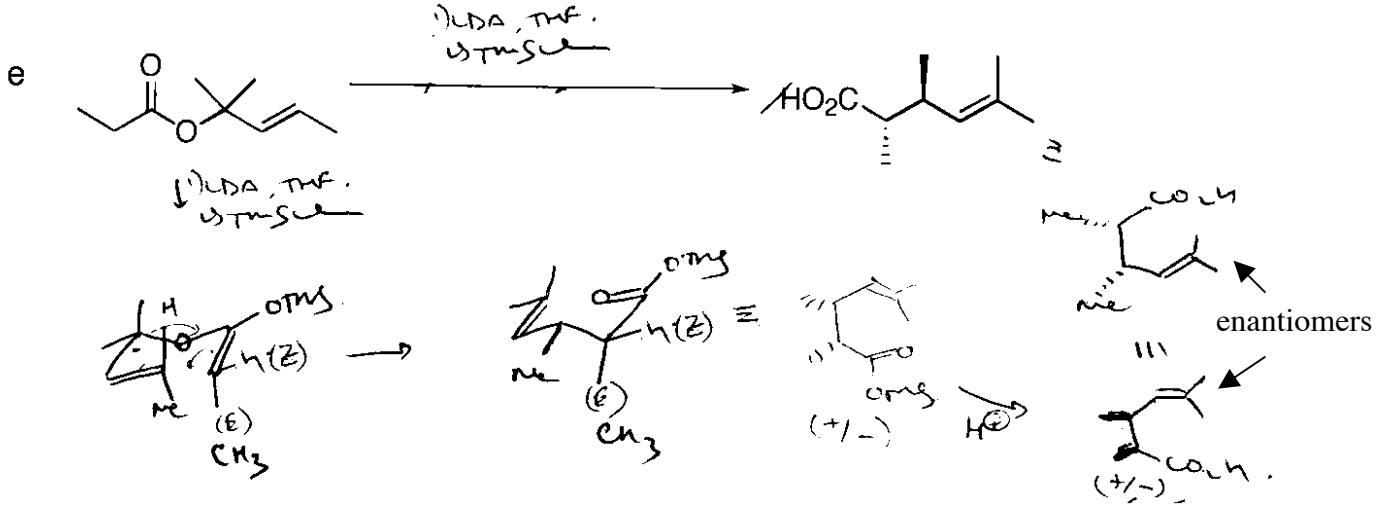
1. (continued)

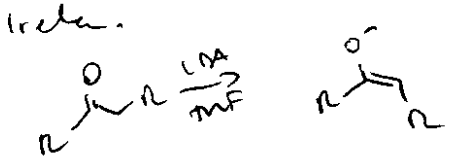
d



The analysis below shows that we need to generate the *E*-enolate. We can do this using Ireland methodology for stereoselective enolate generation

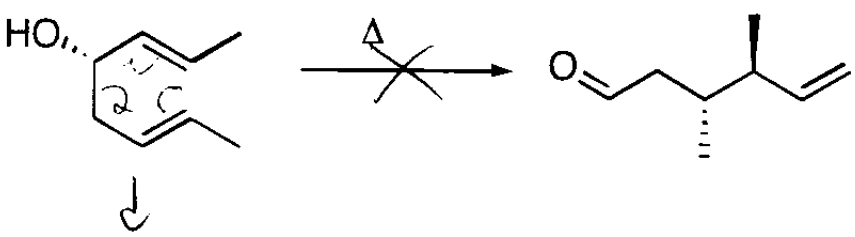
e

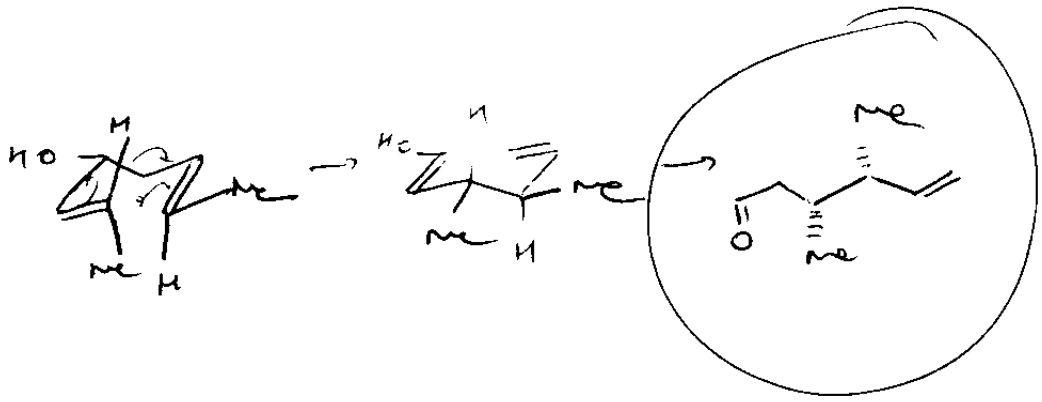




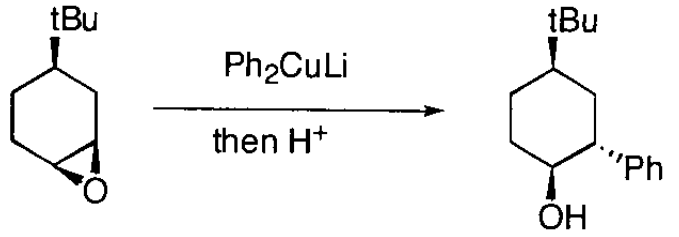
2. Predict if each of the following reactions would proceed as written. If you feel that the reactionwould proceed, simply write "will proceed as written". If you feel that the reaction would not proceed as written, provide a brief but detailed explanation, and indicate the structure of the product(s)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

a



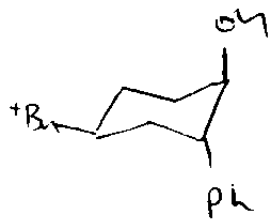


b

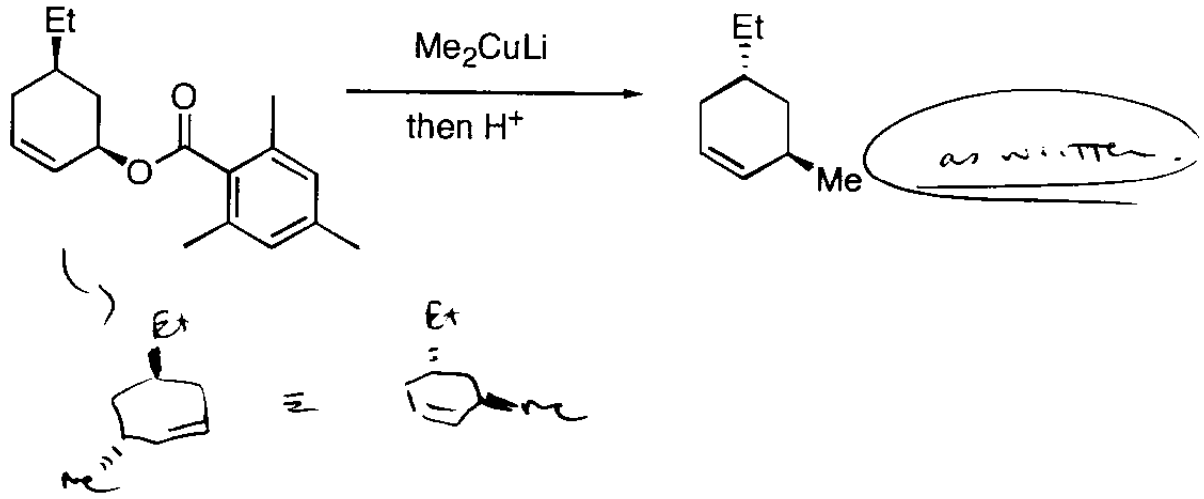


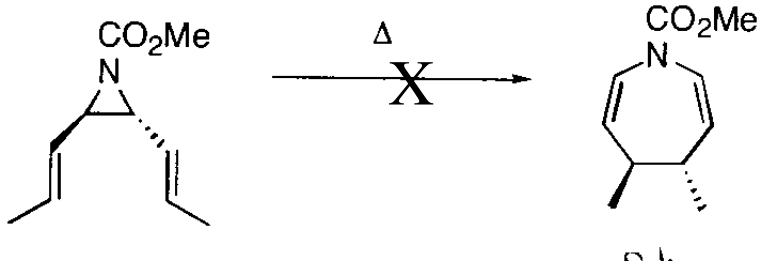
✓

D. axial opening as written



2. (continued).

c 

d 

While cis divinylcyclopropanes undergo rapid and stereospecific Cope rearrangements, the trans divinyl Cyclopropane cannot adopt a chair nor boat TS. Thus, the reaction would not be expected to be Stereospecific, since it can only proceed via a di-radical pathway.

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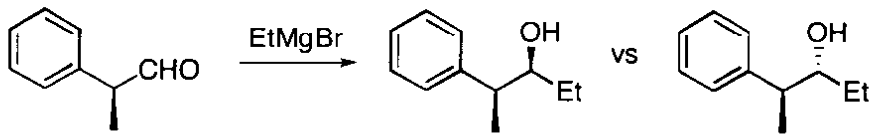
3. Identify the type of selectivity for each reaction.
Circle the correct answer. 2 pts each.

a



chemoselectivity

regioselectivity

diastereoselectivity

enantioselectivity.

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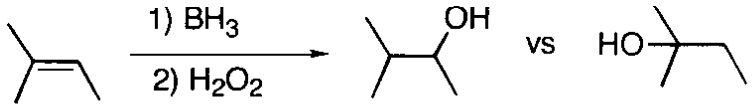
b



chemoselectivity

regioselectivity

diastereoselectivity

enantioselectivity.

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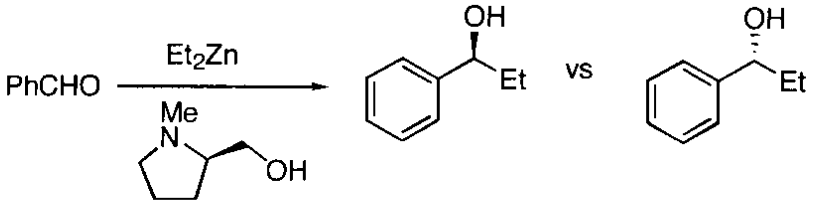
c



chemoselectivity

regioselectivity

diastereoselectivity

enantioselectivity.

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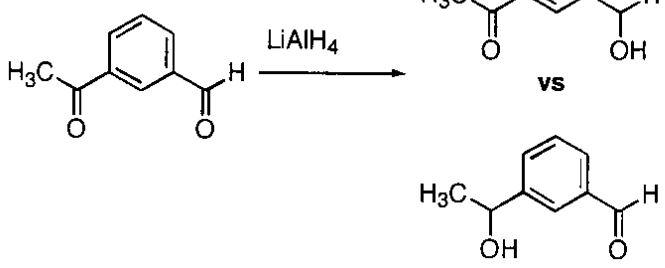
d



chemoselectivity

regioselectivity

diastereoselectivity

enantioselectivity.

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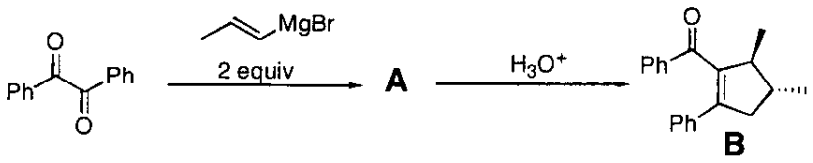
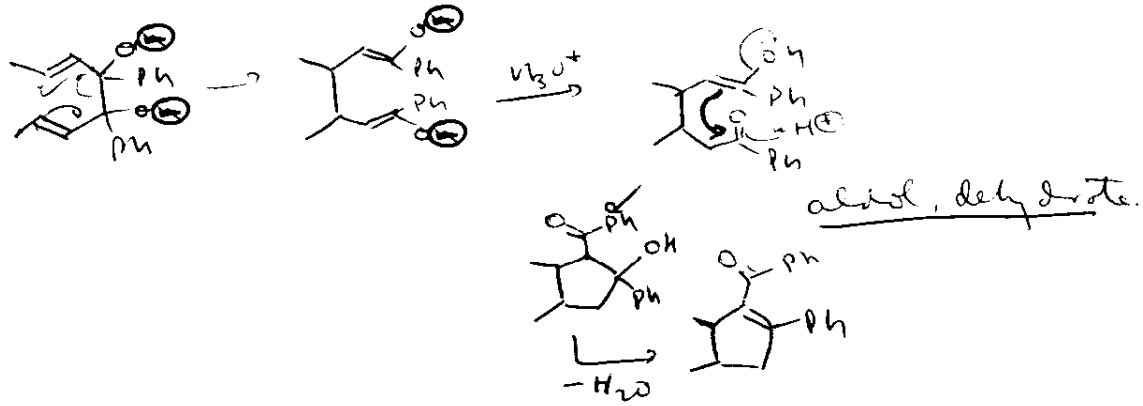
4a. Propose a structure for intermediate **A**. Propose an arrow pushing mechanism for the formation of **A** and **B**. For this part of the problem, it is not necessary to explain the stereochemical aspects of the reaction. Just push the arrows and show how the final product is formed. (9 pts)





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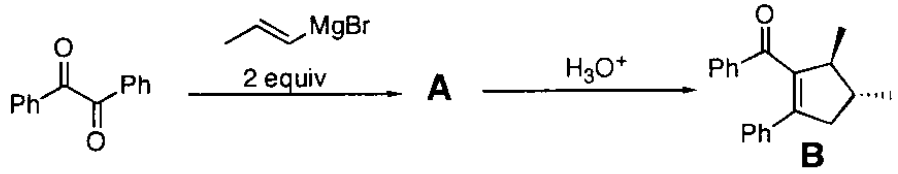
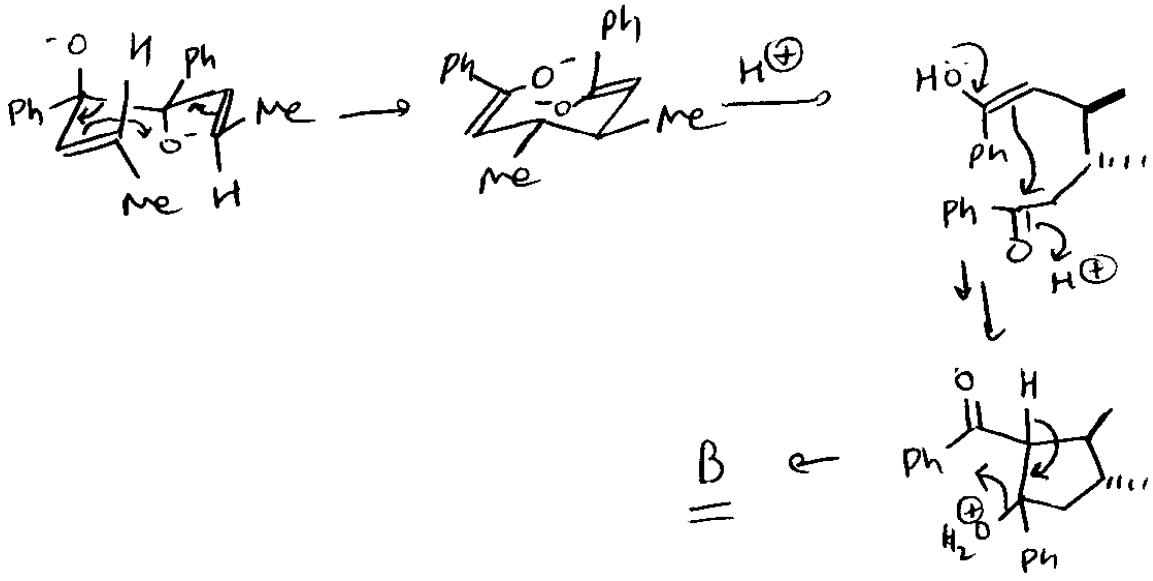
4b. Propose a model that explains the diastereoselectivity of the reaction (6 pts)





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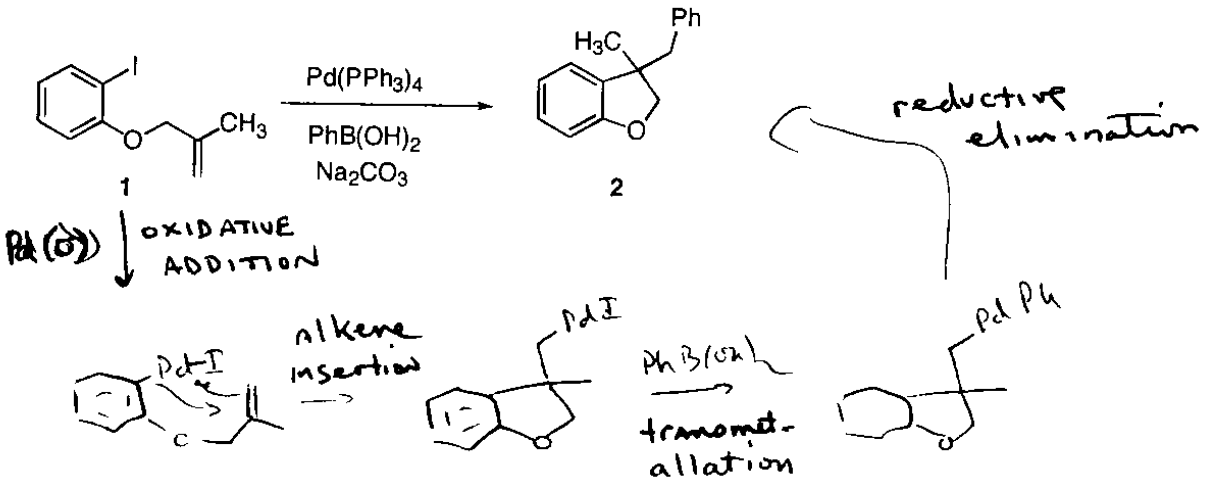
5 (a) Write a detailed mechanism for the reaction below. (8 pts)



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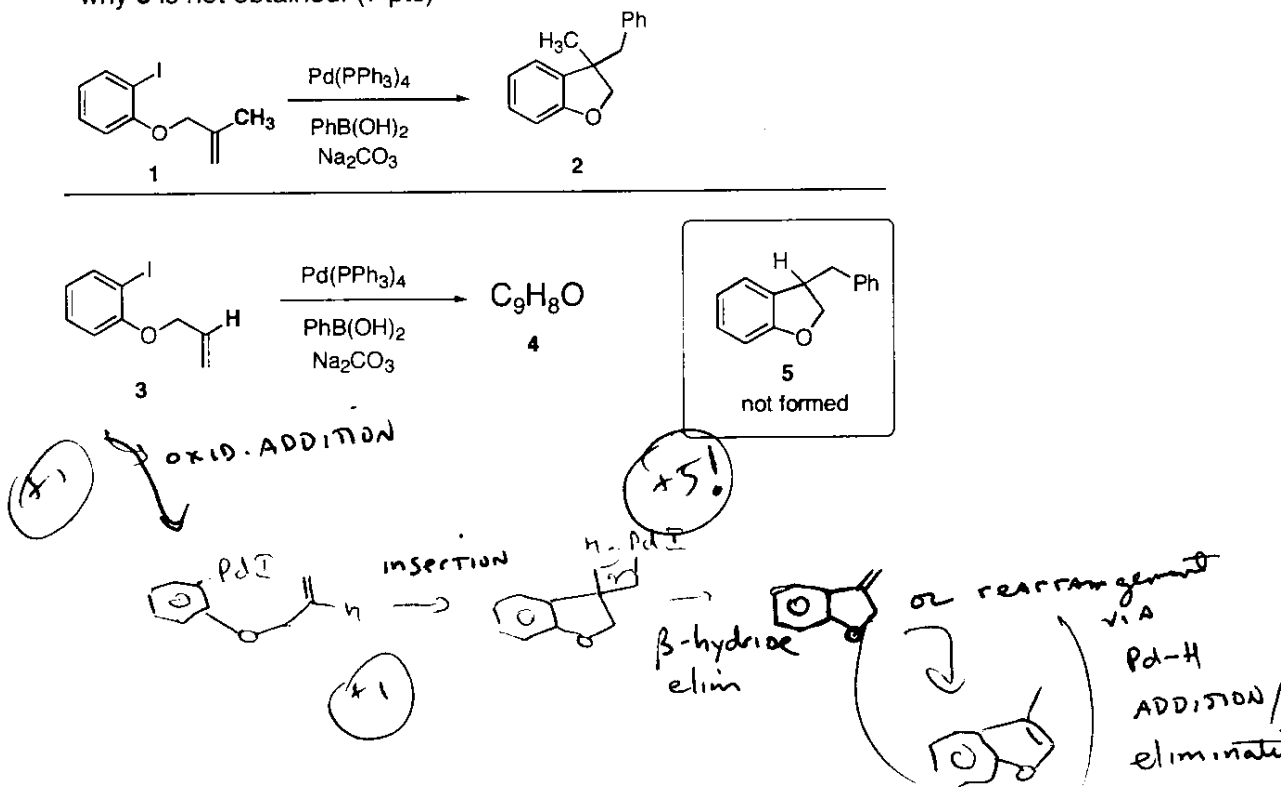
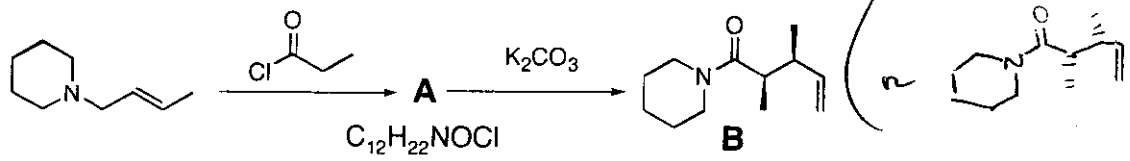
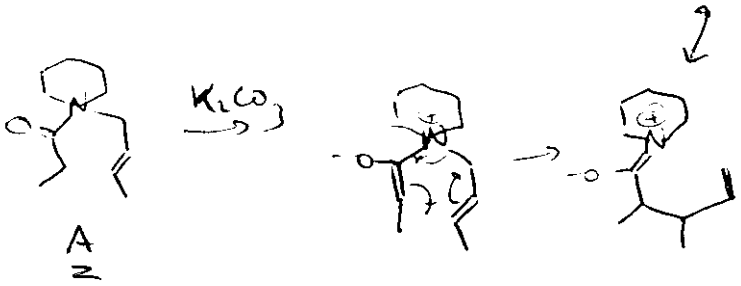
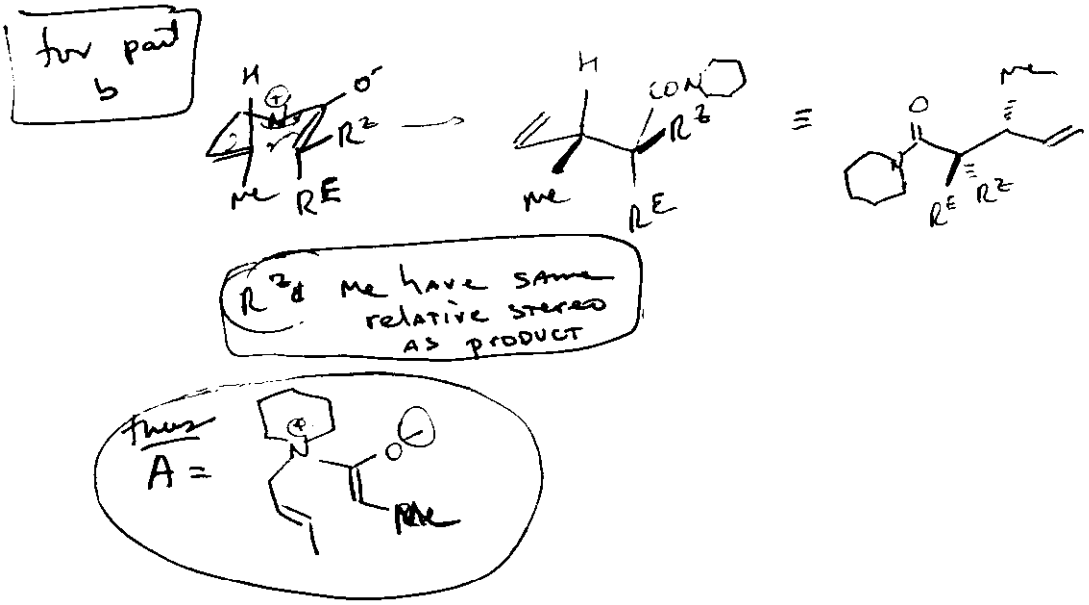
5 (b) Unlike the reaction of **1** to **2**, the reaction of **3** does not give the analogous product **5**. Instead, product **4** is obtained. Write a mechanism for the formation of **4**, and explain why **5** is not obtained. (7 pts)



6 a. Propose a structure for intermediate **A**. Propose an arrow pushing mechanism for the formation of **A** and **B**. For this part of the problem, it is not necessary to explain the stereochemical aspects of the reaction. Just push the arrows and show how the final product is formed. (8 points)







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7. Outline a multistep synthesis using any materials with 6 carbons or less (20 points)