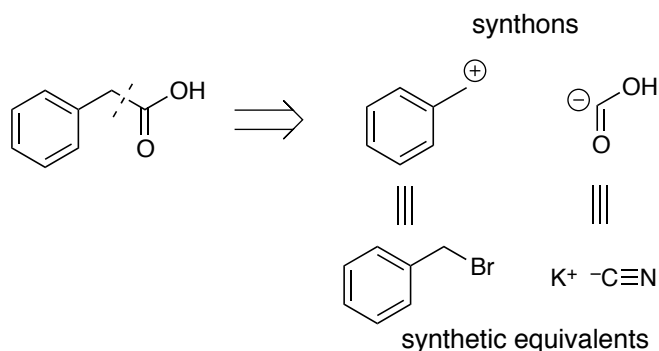


CEM 852 Exam-1 Key

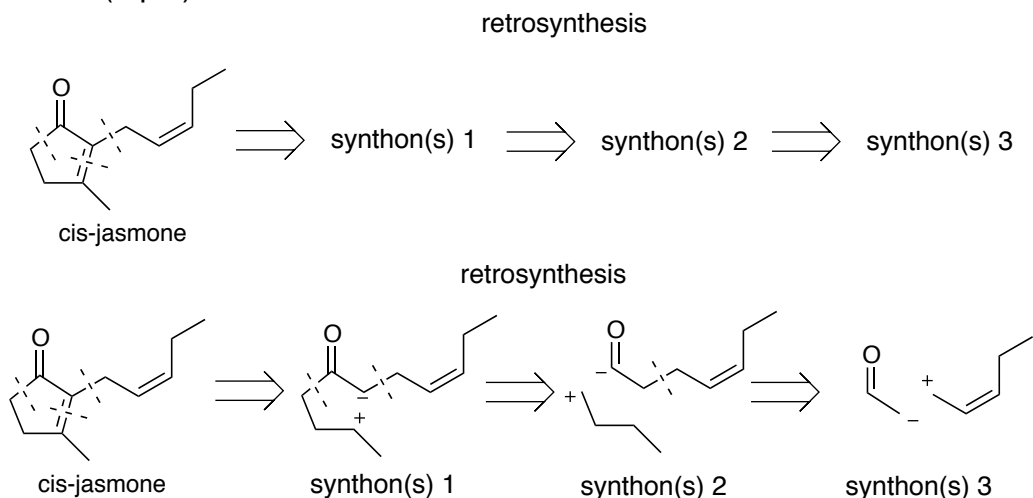
February 20, 2021

This exam consists of 5 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 100. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

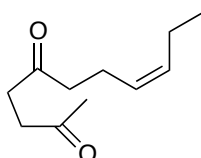
- I. Below is a retrosynthesis of phenyl acetic acid. The disconnection indicated leads to two synthons. The synthetic equivalents for each of those synthons, which would allow one to make the indicated bond in a forward synthesis, are also indicated.



- (a) Devise retrosynthesis of cis-jasmone using the three disconnections indicated, illustrating the synthon(s) your retrosynthesis generates after each subsequent disconnection (3 pts).

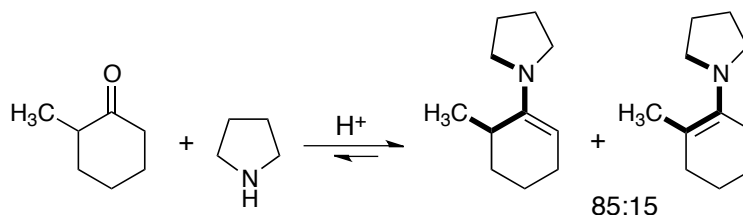


- (b) Illustrate synthetic equivalents for the synthon(s) generated after your first disconnection. (4 pts)

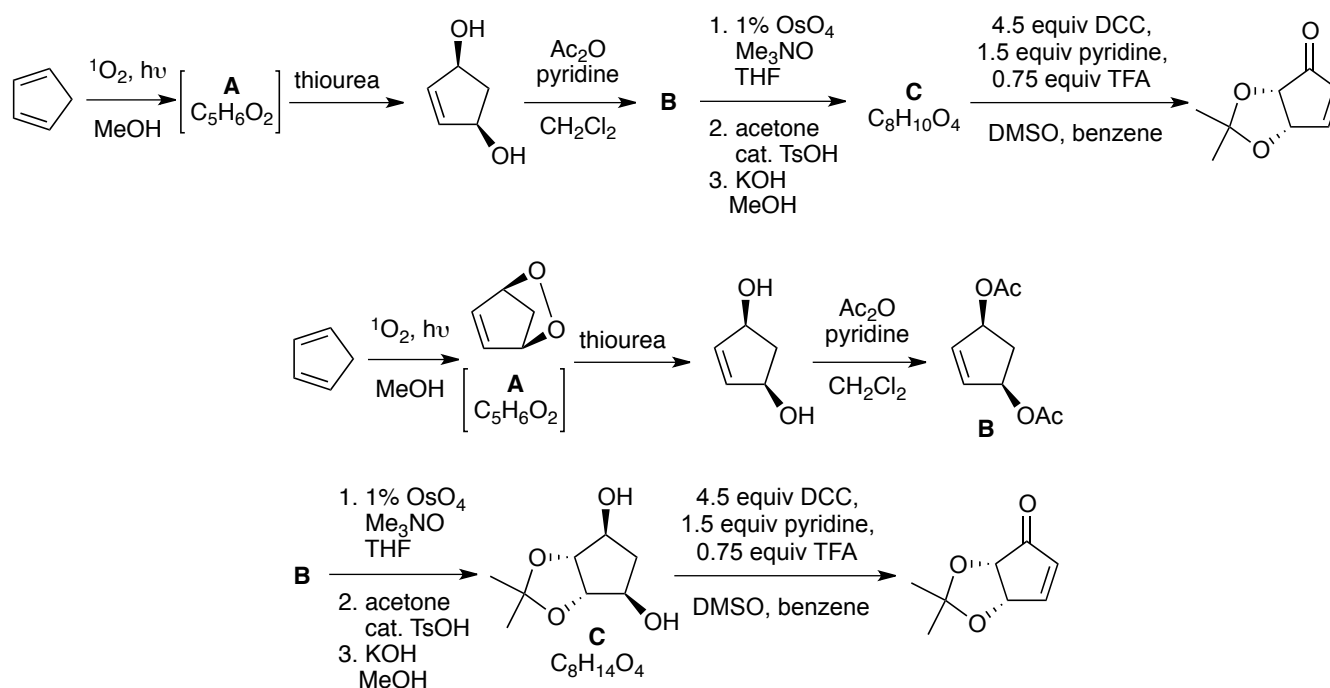


- II. The reaction of methyl cyclohexanone and pyrrolidine generates enamines **A** and **B**. Illustrate how minimization of $A_{(1,3)}$ - vs. $A_{(1,2)}$ -strain explains the observed selectivity (6 pts)

$$\Delta E (A_{1,2}) 3.0 \text{ kcal/mol} < \Delta E (A_{1,3}) 3.9 \text{ kcal/mol}$$

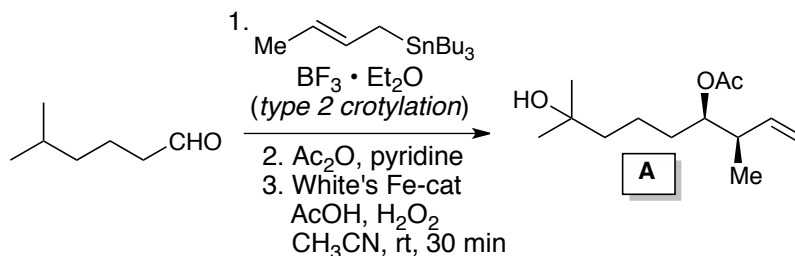


- III. Provide the structures of **A**, **B**, and **C**. (9 pts)

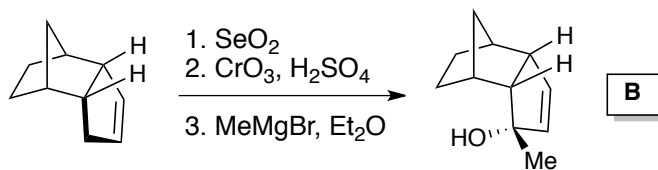


- IV. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (15 pts)

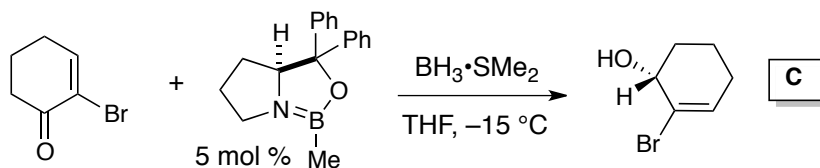
1.



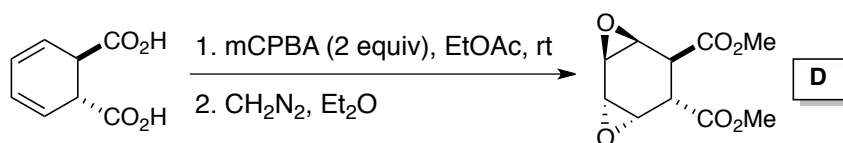
2.



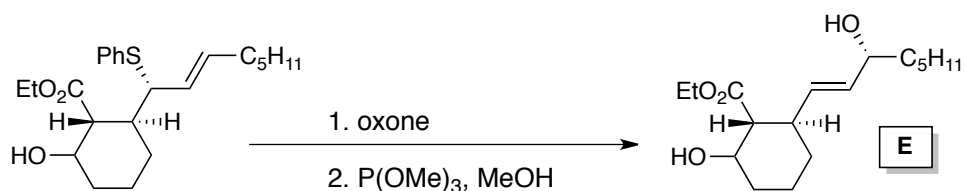
3.



4.

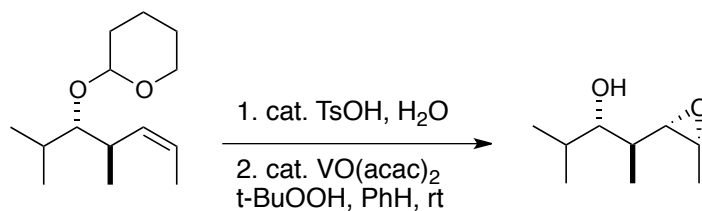


5.

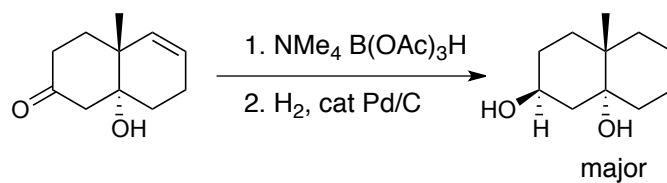


V. Provide conditions that will afford the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (15 pts)

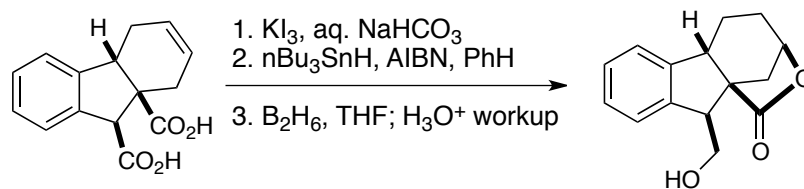
1.



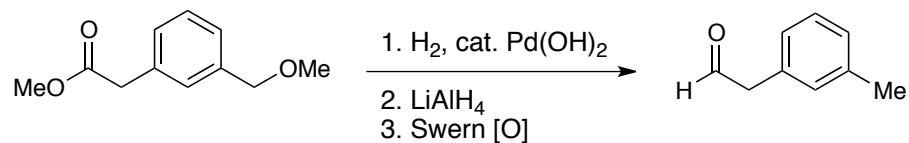
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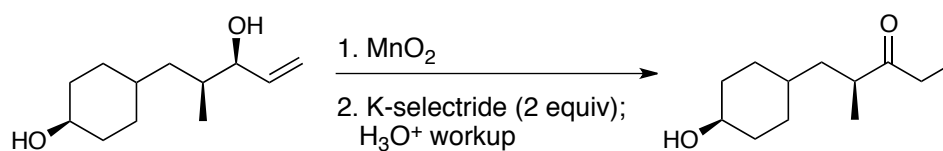
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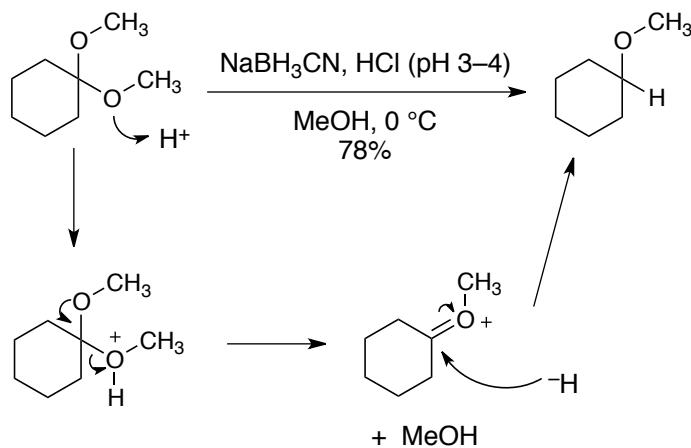
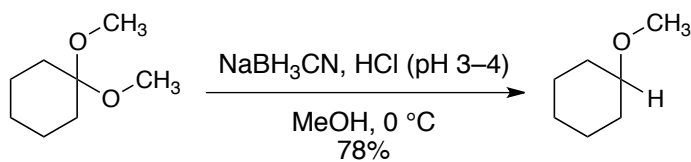
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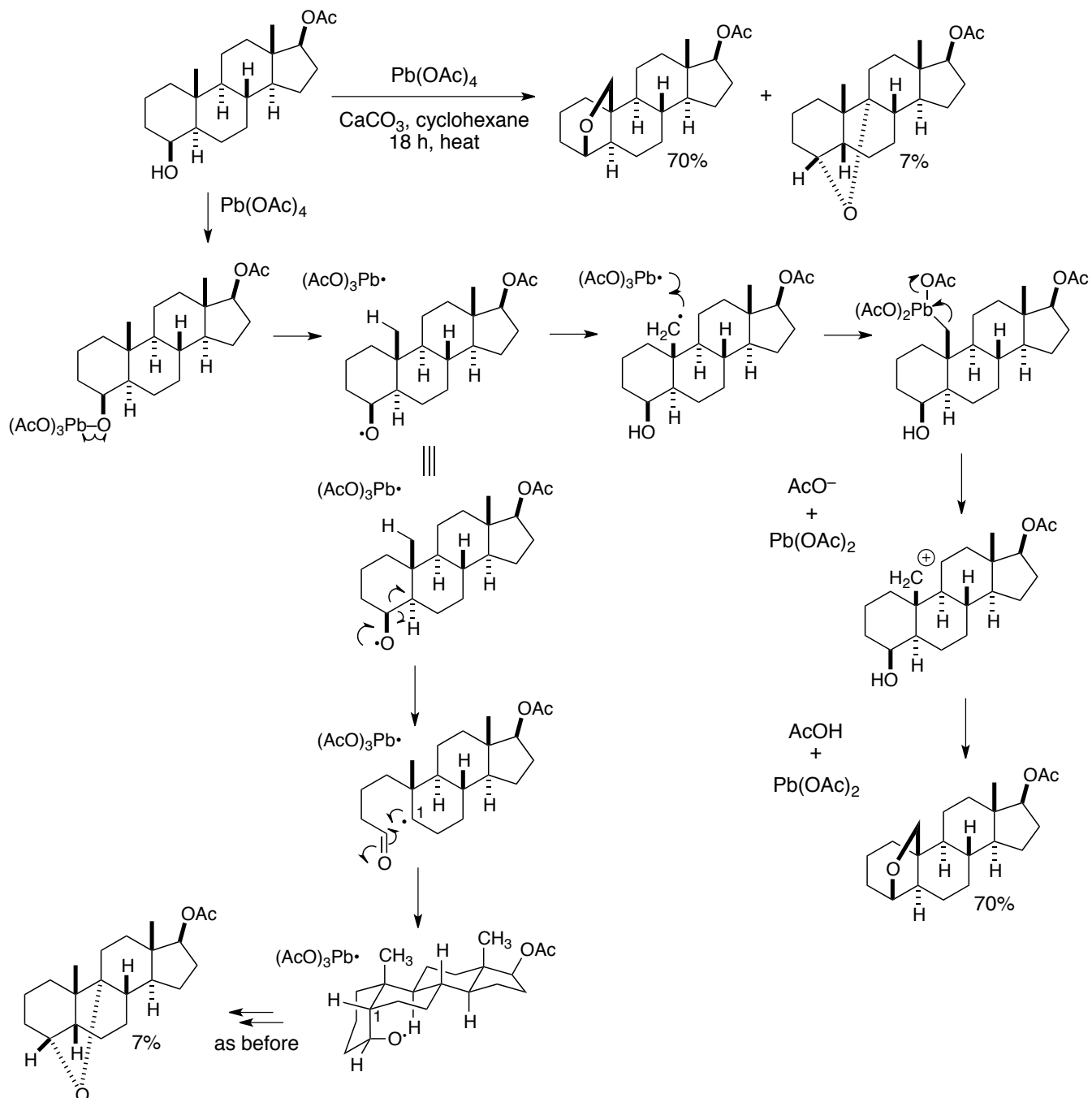
5.



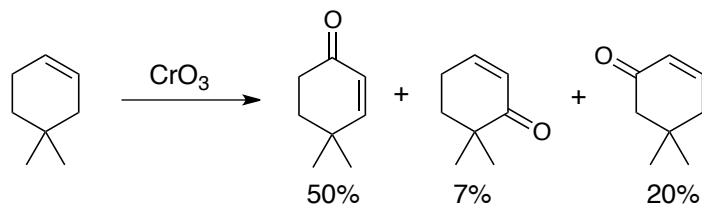
VI. Provide a complete arrow (electron) pushing mechanism for the following transformation.
(8 pts)



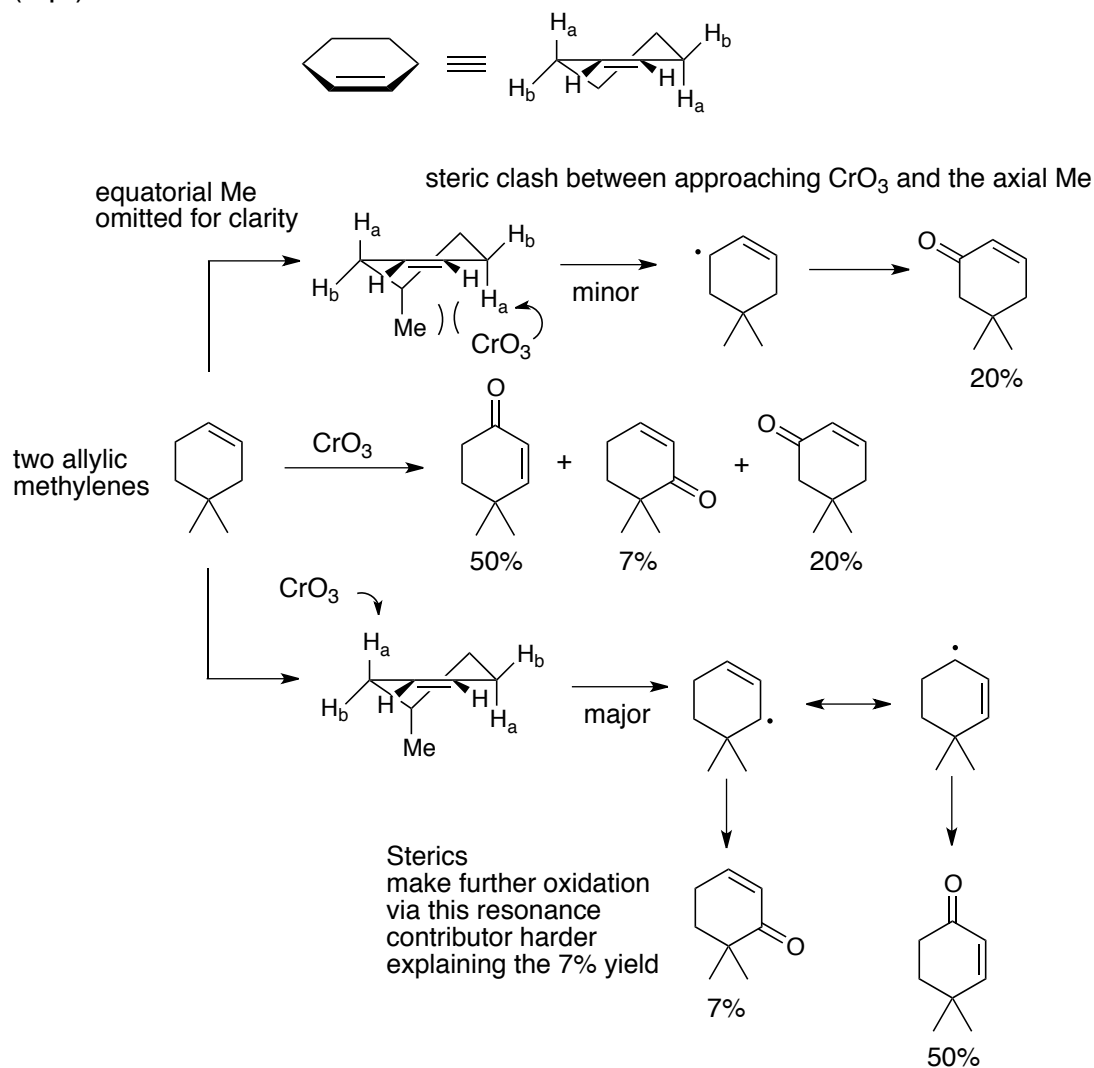
- VII. In class, we saw the Barton oxidation of a remote methyl group shown below. In that lecture, the mechanism explaining formation of the the major (70%) product was illustrated. Though not shown in lecture, a minor product is also formed in 7% yield. Provide a complete arrow (electron) pushing mechanism that explains the formation of that minor product. (8 pts)



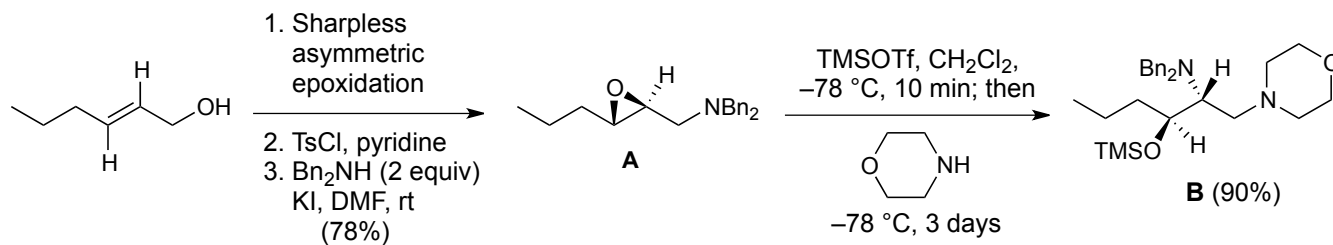
VIII. CrO_3 is capable of doing allylic oxidations. This reaction differs from allylic oxidations with singlet oxygen or selenium dioxide in that CrO_3 allylic oxidations appear to involve the generation of allylic radicals. Thus, CrO_3 allylic oxidations often afford mixtures of products with retention and transposition of the double bond. In the case of cyclohexenes, generation of the allylic radical is thought to involve hydrogen atom abstraction of axially disposed allylic hydrogens. Such an example is shown below:



- (a) Using the information provided above, provide an explanation for the formation of the three products above (8 pts).
- (b) Using conformational analysis, provide an explanation for the observed selectivity. In providing your answer, you may wish to consider the cyclohexene structures illustrated below. (6 pt)

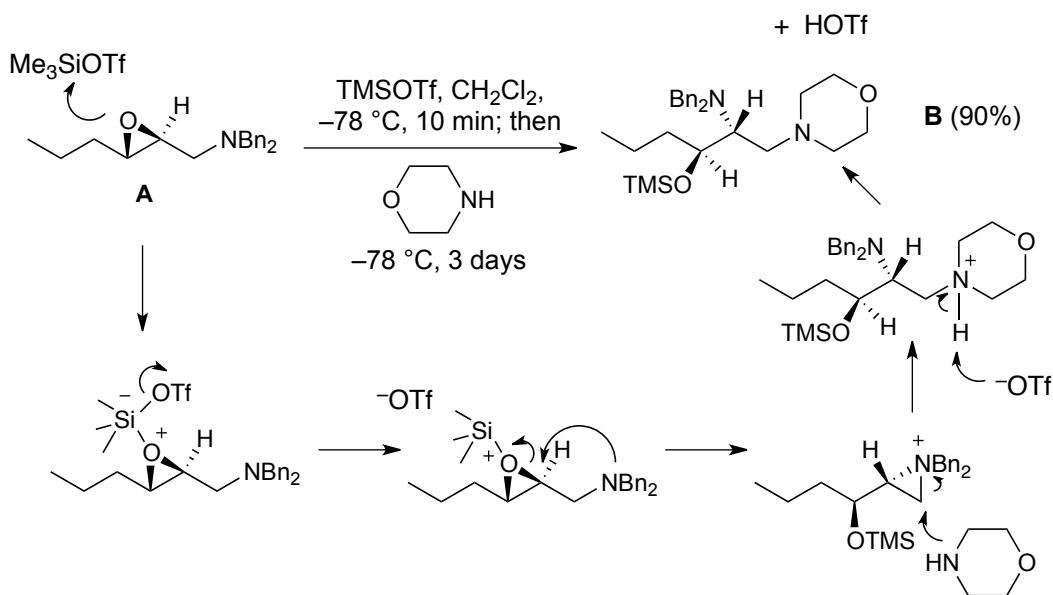


IX. The Scheme below begins with a Sharpless asymmetric epoxidation. The product is then tosylated followed by a nucleophilic displacement with Bn_2NH to give **A**. Treatment of **A** with TMSOTf leads to an aza-Payne rearrangement sequence that affords **B** in 90% yield.

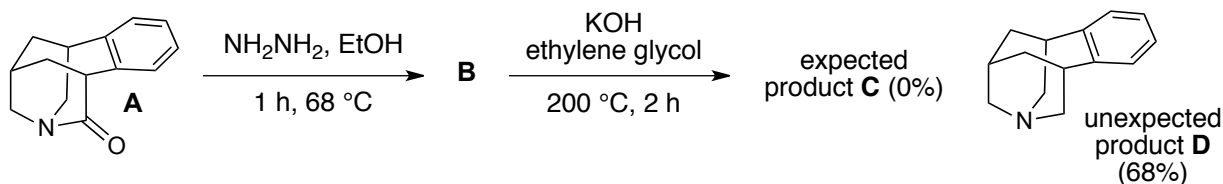


(a) For the desired Sharpless asymmetric epoxidation, what diethyl tartrate (+ or -) was used? (2 pts) **(+)-DET**

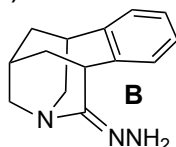
(b) Provide a complete arrow (electron) pushing mechanism for the transformation of **A** to **B**. (8 pts)



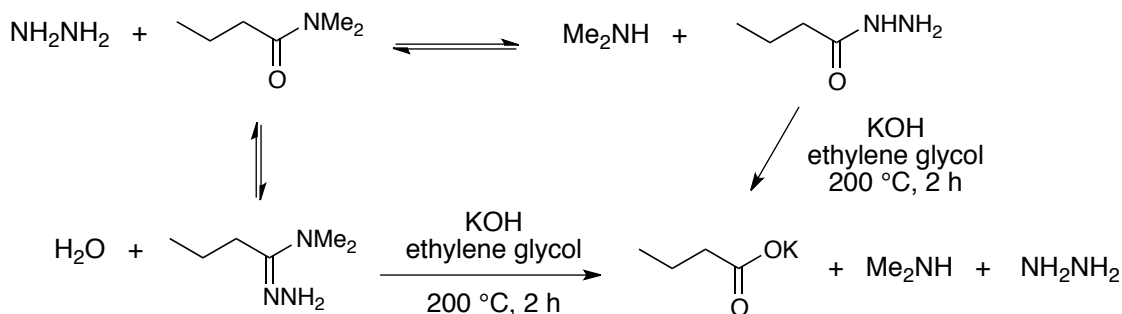
- X. Researchers at Pfizer have investigated the chemistry of the bicyclic amide **A**. Reaction of **A** with hydrazine gave **B**. When **B** was treated with KOH in ethylene glycol at 200 °C the reaction afforded **D** in an apparent Wolff-Kishner-type reduction. The Pfizer chemists were surprised by this result as amides normally do not undergo Wolff-Kishner-type reductions.



- (a) What is the structure of **B**? (2 pts)



- (b) What do amides normal afford when subjected to Wolff-Kishner conditions? (2 pts)



- (c) Provide a hypothesis about the structure of **A** that led to **D** instead of **C**? (2 pts)

Owing the nitrogen being a bridgehead there is no amide resonance. Hence the carbonyl in **A** acts more like a ketone carbonyl rather than an amide carbonyl.

- (d) How might you test this hypothesis? (2 pts) **IR**

Bonus Question: Recently, MSU Today had a story of the career of the David Dickson, the first African-American MSU faculty member. Who was the first African-American faculty member in MSU Chemistry? (2 pts)

- (a) James Hamilton
 (b) Rawle Hollingsworth
 (c) Kevin Walker
 (d) Clifton Wharton