

Advanced Organic Chemistry (CHE 311/511)
First Mid-term Examination
Oct. 7, 2004
Prof. W. P. Malachowski

Name: _____

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics. The exam has a total of seven pages and five questions.

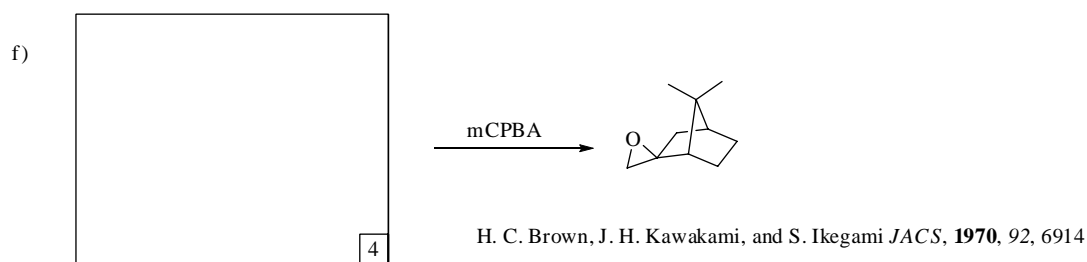
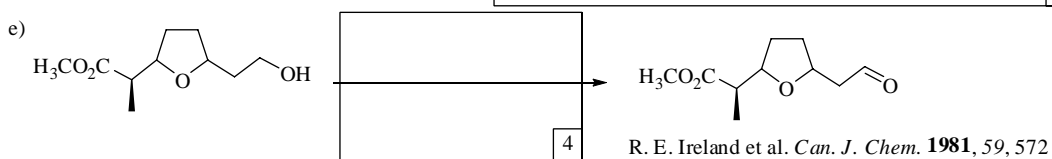
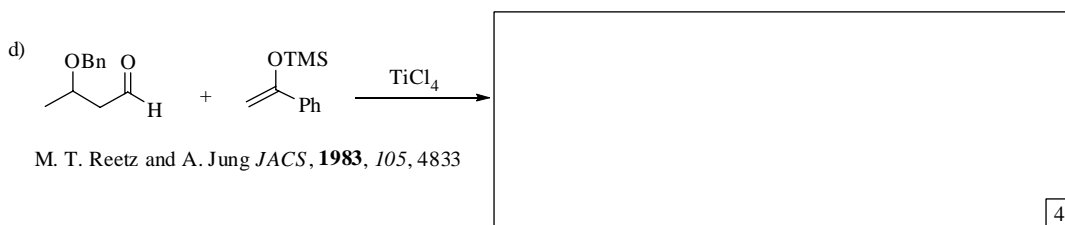
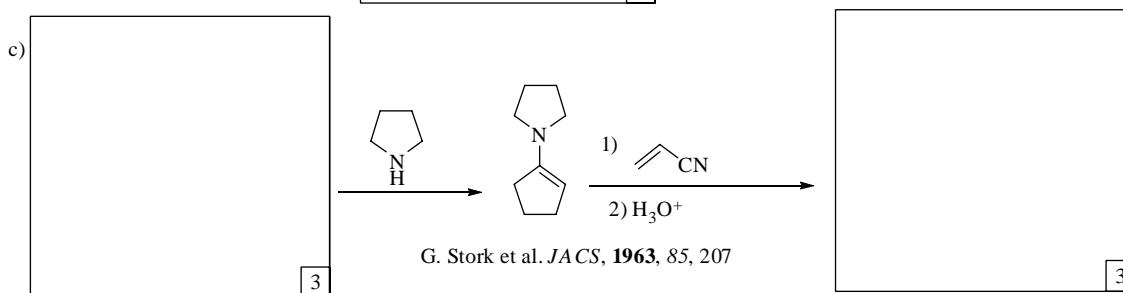
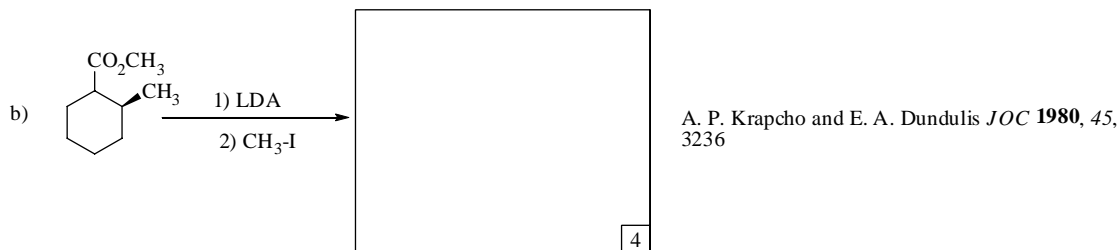
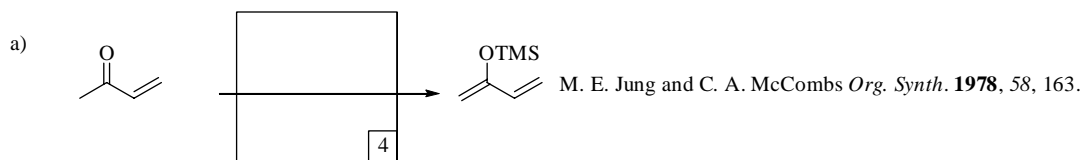
In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include formal charges when appropriate.

You may use models to assist in determining answers. You may use scrap paper to work out problems before entering your final answer on the exam sheets. In addition, feel free to use the back side of the exam sheets for scrap. If necessary, you may enter exam answers on the back side of the exam sheets, however you must clearly indicate which problems are located on the back of the exam pages.

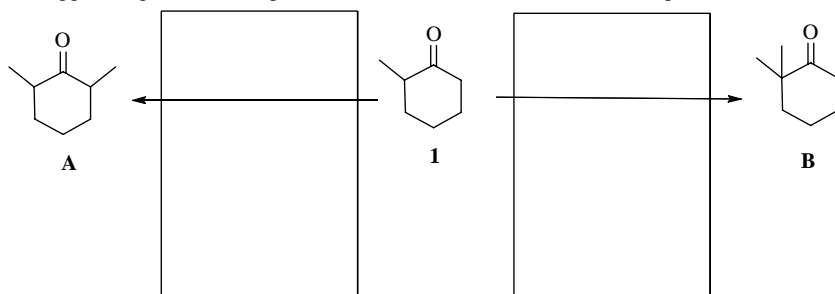
Note that question 6 on page 6 has different requirements of graduate students and undergraduate students. Although the point total for the page is the same, *graduate students must answer both questions*, while *undergraduates only have to answer two*.

Bonus points: You may attempt to answer both parts of question 4 on page 4 and some bonus points may be given for correct answers. Undergraduates may attempt the second synthesis on page 6 and receive bonus points.

1. Provide the necessary information (product, reagent or starting material) to complete the following reactions and answer the associated questions.

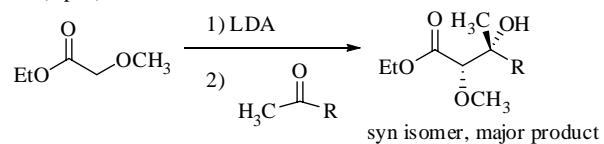


2. a) Suggest reagents to accomplish both transformations shown below. (3 pts. each)



b) Explain your choice of reagents in each case shown in part a. (6 pts.)

3. In the asymmetric synthesis of the deoxyamino sugar of L-callipeltoside A discussed in class (D. A. Evans et al. *Org. Lett.* **2001**, 3, 3133), the researchers reported problems in getting the desired anti stereoselectivity in the reaction shown below. Instead they obtained the syn isomer (shown) as the major product. What was the problem and how did the researchers overcome the problem? (8 pts.)



4. Choose one of the two reactions shown below and answer the following questions.

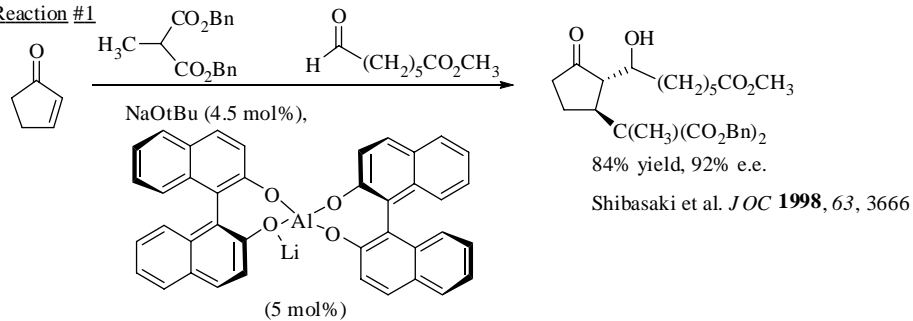
a) Show the reaction mechanism for the steps involving C-C bond formation. You may abbreviate your mechanism to show only the essential atoms and molecules involved in the reaction mechanism.. You do not need to address stereoselectivity issues here. (4 pts.)

b) Name the reaction type. (2 pts.)

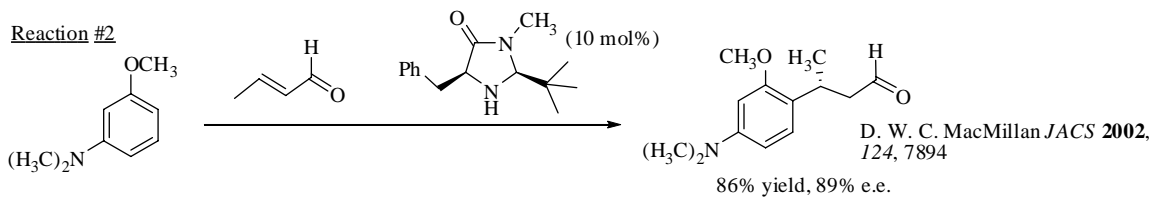
c) What does "e.e." mean? (Both reactions list an e.e. percent after the yield.) (3 pts.)

d) Briefly describe (or use pictures to show) why the reaction affords a stereoselective outcome. (4 pts.)

Reaction #1

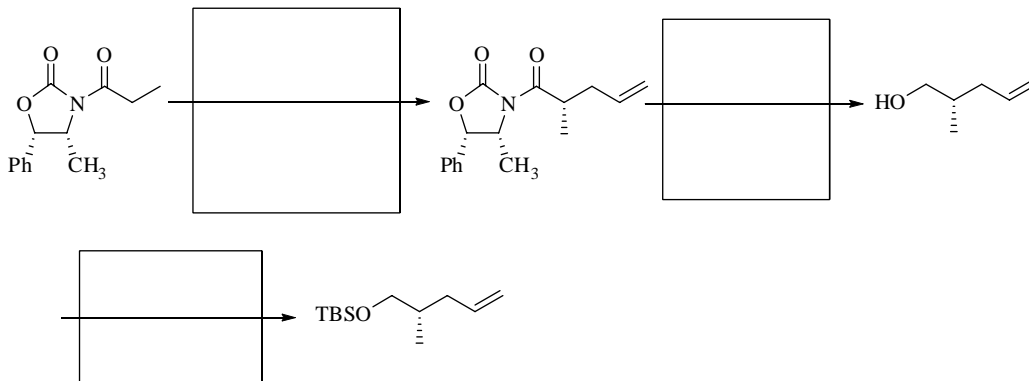


Reaction #2

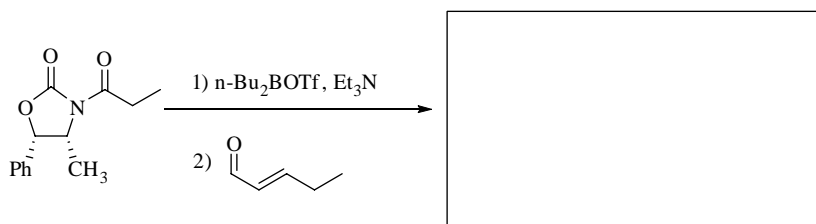


5. In their synthesis of the macrolide antibiotic cytovaricin (*JACS* **1990**, *112*, 7001), David Evans and co-workers performed the following reactions. Answer the associated questions.

a) Fill in the reagents necessary to complete the transformation shown. (4 pts. each)



b) Provide the product of the following reaction also used in the synthesis of cytovaricin. (4 pts.)



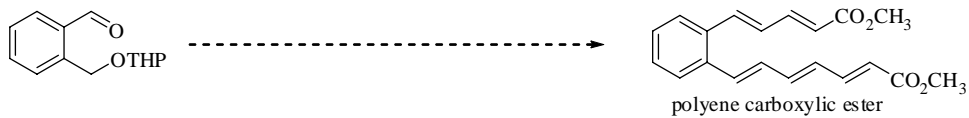
c) What is the usual role of a TBS group shown in the final product of part a? (3 pts.)

d) Choose either the first reaction in part a or the reaction shown in part b and explain with diagrams the stereoselectivity seen in the product. (6 pts.)

6. **Undergraduate students:** Answer one of the two synthesis questions below. (16 pts.)

Graduate students: Answer both synthesis questions. (8 pts. each)

a) The polyene carboxylic ester molecule shown below was recently isolated from *Streptomyces* and reported in the *Journal of Natural Products* (2004, 67, 1631). Devise a synthesis of the molecule from the starting material on the left and any reagent with six or fewer linear carbons. (10 pts.)



b) Create a synthesis of the molecule on the right from the starting material on the left.

