CEM 852 Final Exam

April 29, 2003

This exam consists of 4 pages, please make certain that your exam has all of the necessary pages. Total points possible for this exam are 150. Please write ALL your answers in the answer books. Please write legibly and draw all structures clearly. Good luck.

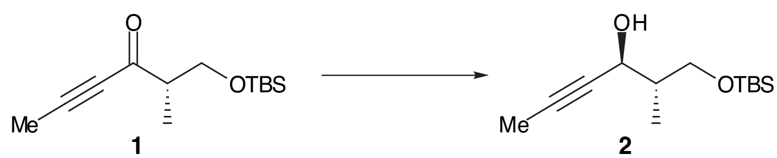
I. Provide the bond energies in kcal/mol for the following: (12 pts)

(a) (C–C)$_\sigma$ (b) (C–C)$_\pi$ (c) C≡C (d) $C_{(sp^3)}$–H (e) O–H (f) N–N

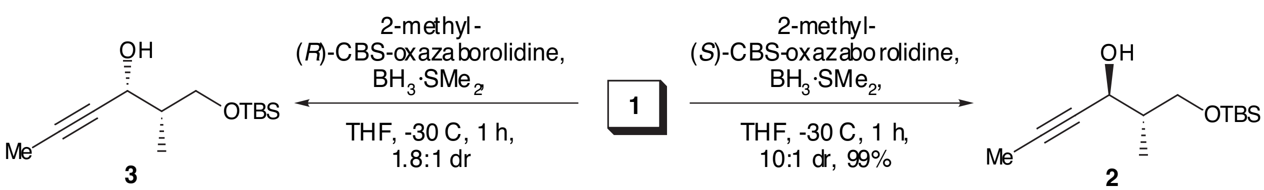
II. Provide definitions of the following terms. Feel free to define these terms through the use of chemical examples. (16 pts)

1. Absolute stereocontrol
2. Relative stereocontrol
3. [2,3]-Wittig rearrangement
4. Oxidative addition

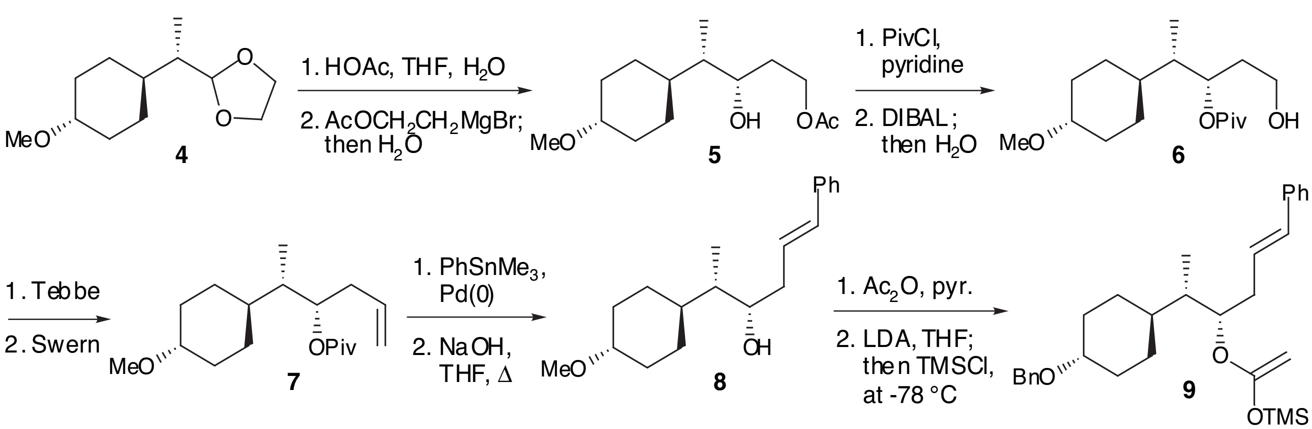
III. (a) In principle using a CBS reduction to perform the stereoselective transformation of **1** to **2** would constitute a waste of time and money. Why? (5 pts)



(b) Despite "principle" in practice (*J. Am. Chem. Soc.* **2001**, *123*, 9449) a 2-methyl (*S*)-CBS-oxazaborolidine, borane reduction was required in order to afforded **2** in a high diastereomeric ratio. In contrast, borane reduction of **1** with 2-methyl (*R*)-CBS-oxazaborolidine gives **3** in low erythro:threo ratios. Explain. (10 pts)

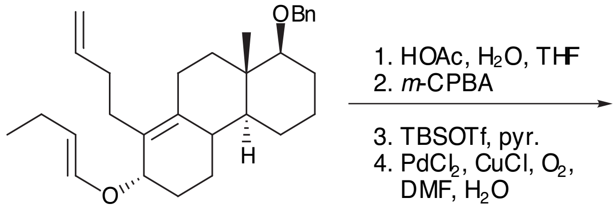


IV. List 6 problems with the Scheme shown below. (12 pts)



V. 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. (30 pts)

1.



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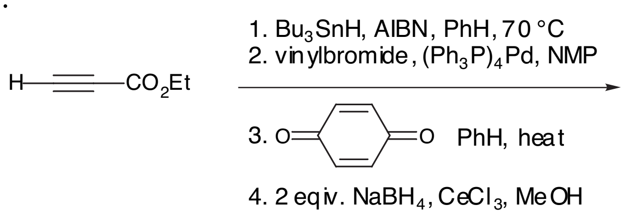

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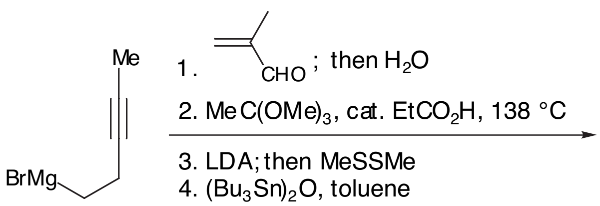

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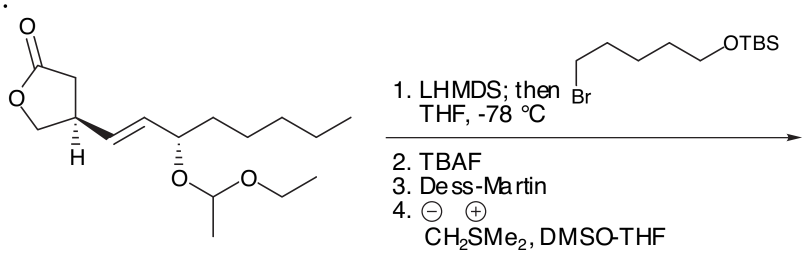

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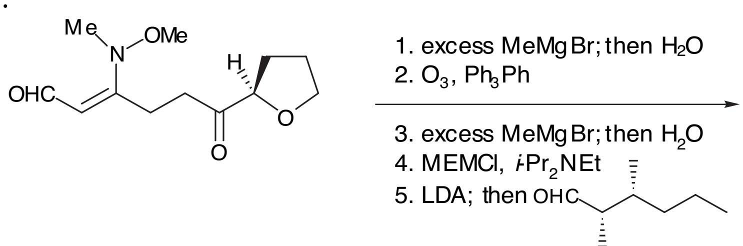
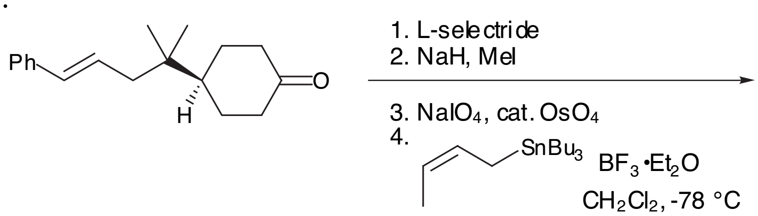


6.

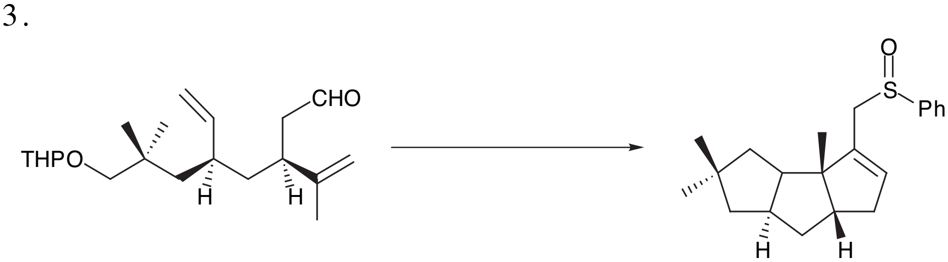


VI. Provide conditions which will effect the transformations outlined below. Most of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (30 pts)

1.

2.

3.



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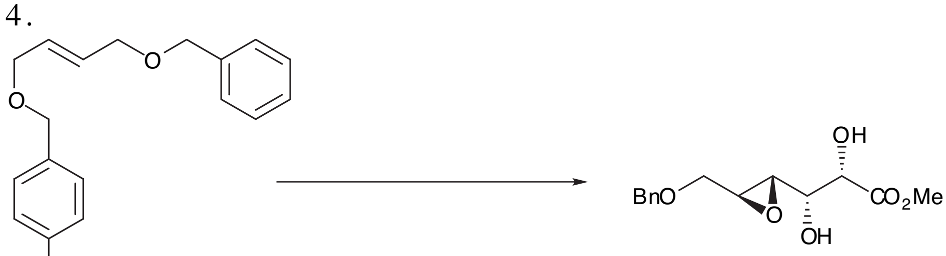
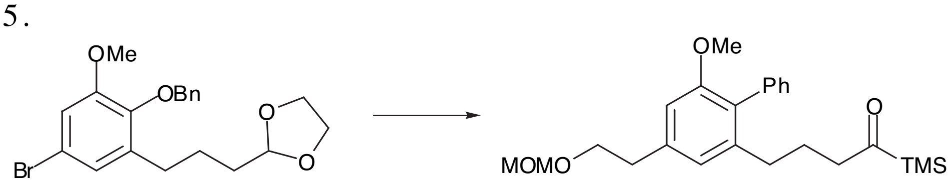
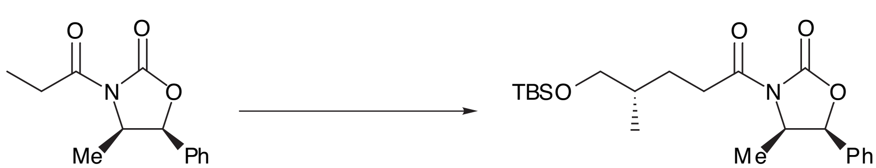


Note: the product is optically active

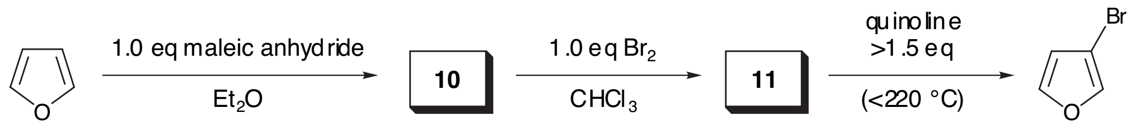
5.



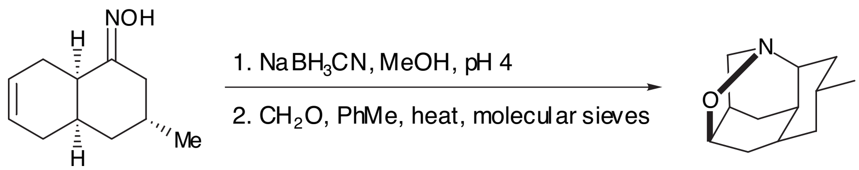
6.



VII. Give a detailed arrow (electron) pushing mechanistic account of the preparation of 3-bromofuran from furan, making sure to identify the structures of intermediate products **10** and **11**. (10 pts)

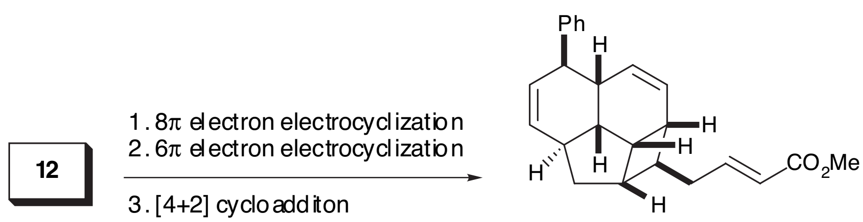


VIII. Give a detailed arrow (electron) pushing mechanistic account of the sequence shown below. (10 pts)



IX. Illustrate the catalytic cycle of any Heck reaction, *describing each step in words* as well showing all pertinent intermediates. Be sure to indicate the oxidation state of palladium throughout the cycle. (10 pts)

X. Justas presented Nicoloau's synthesis of the endiandric acids. Biosynthetically endiandric acid B methyl ester is thought to be prepared from **12** which undergoes a thermally allowed conrotary 8π electron electrocyclization, followed by a thermally allowed disrotary 6π electron electrocyclization, and then an intramolcular Diels-Alder. What is the structure of **12**. (5 pts)



endiandric acid B methyl ester

Bonus Question I: How can a carboxylic acid be reduced to an aldehyde in one-pot? (2 pts)

Bonus Question II: Which chemistry couple drives "his & her" Porsches? (2 pts)

a. Jacqueline K. Barton and Peter B. Dervan (Cal. Tech.)

b. Craig J. Forsyth and Karin Musier-Forsyth (Minnesota)

c. Robert A. Holton and Marie E. Krafft (Florida State)

d. Kendall N. Houk and Joan S. Valentine (UCLA)

e. Suzy Miller and Mitch Smith (East Lansing)