

# CEM 852 Final Exam

May 6, 2015

This exam consists of 7 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 150. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

I. For the following compounds provide their pKa's within 2 pKa units. (5 pts)

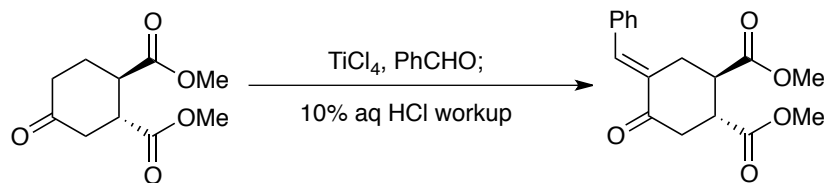
1. acetone
2. diacetylacetone
3. dimethylsulfoxide
4. dimethylsulfone
5. nitromethane

II. Explain, describe, or illustrate each of the following: (15 pts)

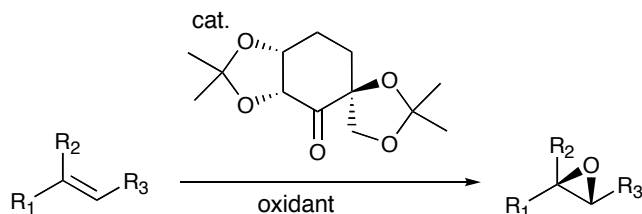
1. 60% ee
2. a lipase hydrolysis
3. a synthon
4. a Felkin-Ahn reduction
5. a mismatched Sharpless epoxidation

III. Provide the name associated with each of the name reactions shown below. (10 pts).

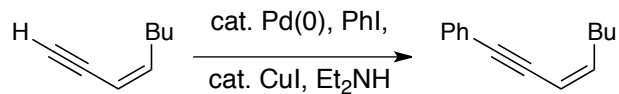
1.



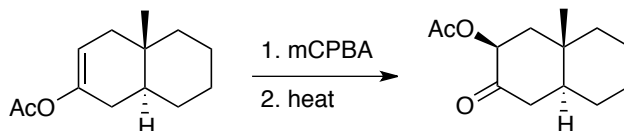
2.



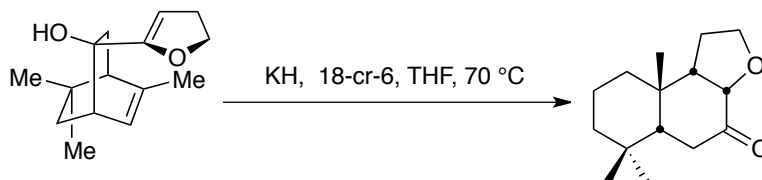
3.



4.

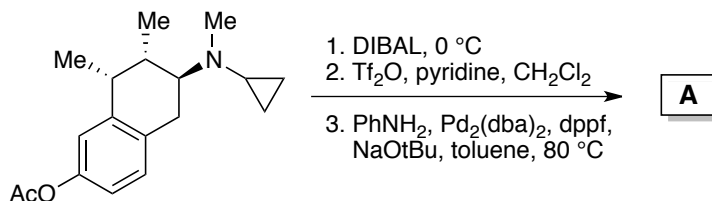


5.

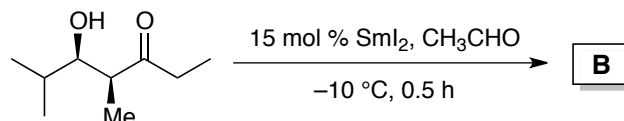


IV. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (30 pts)

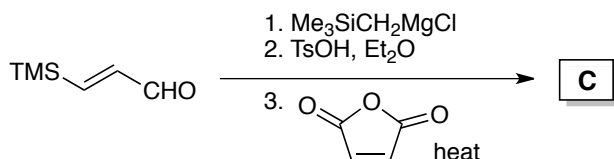
1.



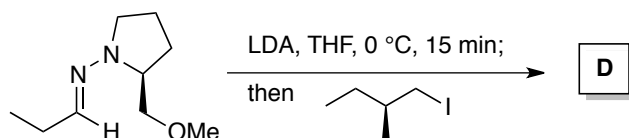
2.



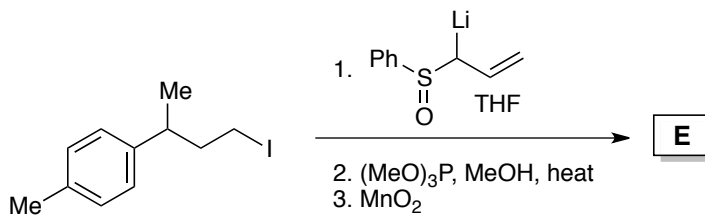
3.



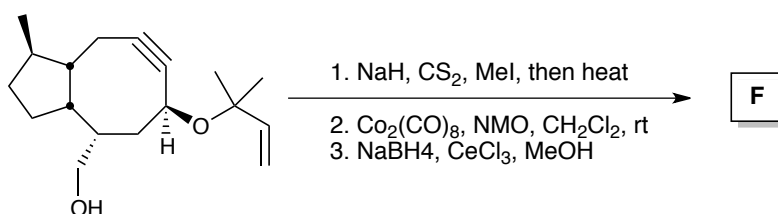
4.



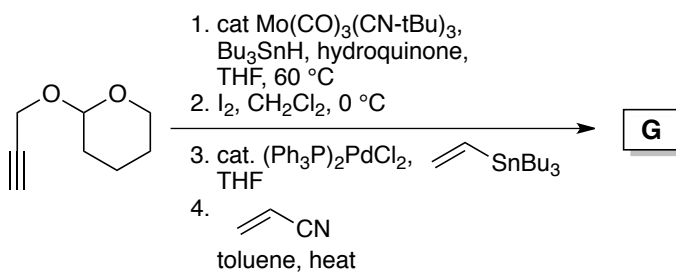
5.



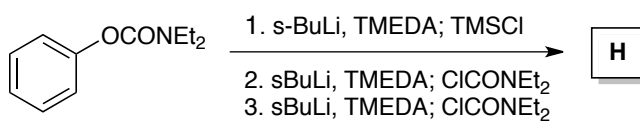
6.



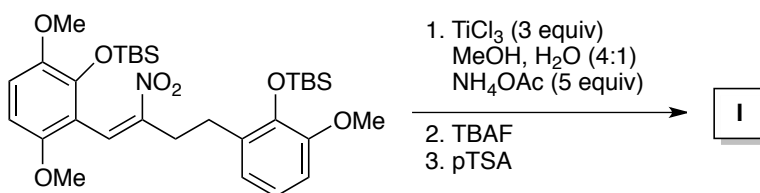
7.



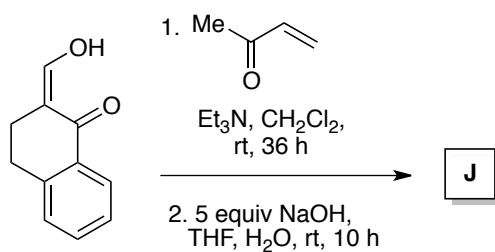
8.



9.



10.



V. Provide conditions that will effect the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (24 pts)

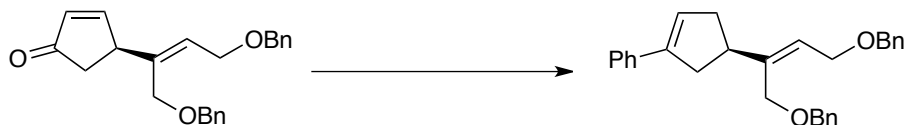
1.



2.



3.



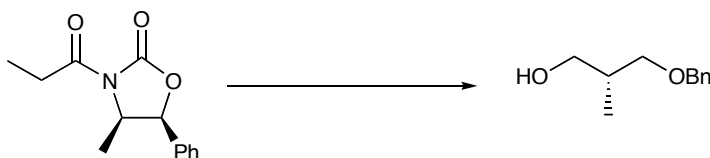
4.



5.



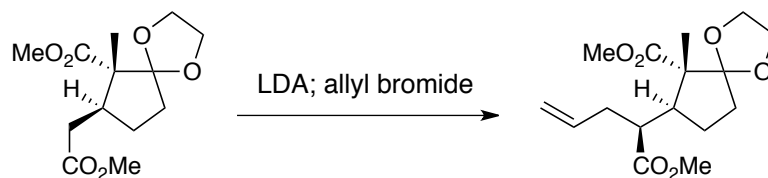
6.



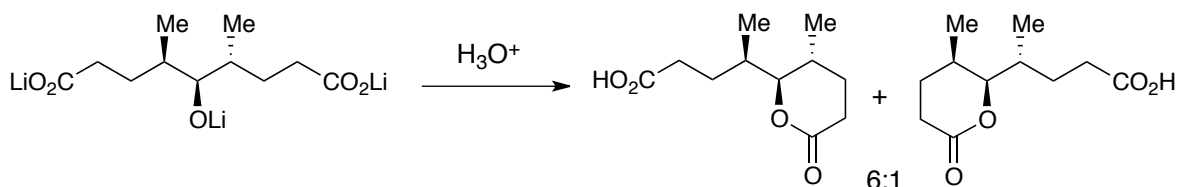
8.



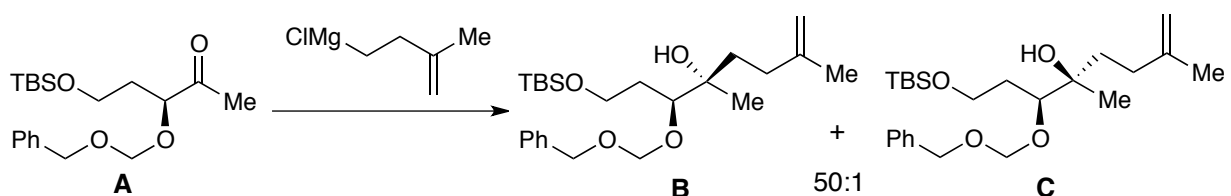
VI. The stereoselectivity of the reaction below arises from the minimization of A(1,3) strain in the transition structure leading to the major product. Illustrate this. (5 pts)



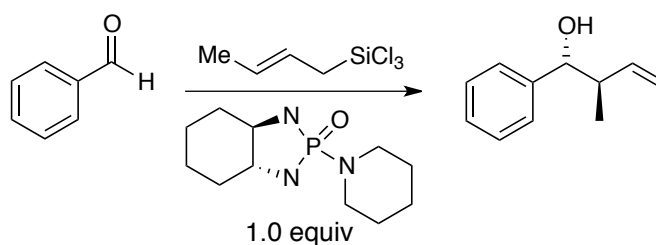
VII. The stereoselectivity of the reaction below arises from the minimization of syn pentane interactions in the transition structure leading to the major product. Illustrate this. (5 pts)



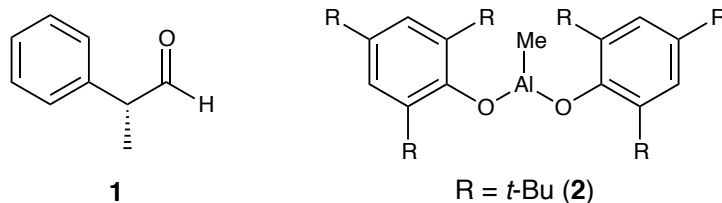
VIII. Explain the stereoselectivity observed for the reaction below (5 pts). Using the same starting ketone (**A**), provide a practical (i.e. selective) synthesis that would afford **C** as the major product (you may use more than one step) (5 pts).



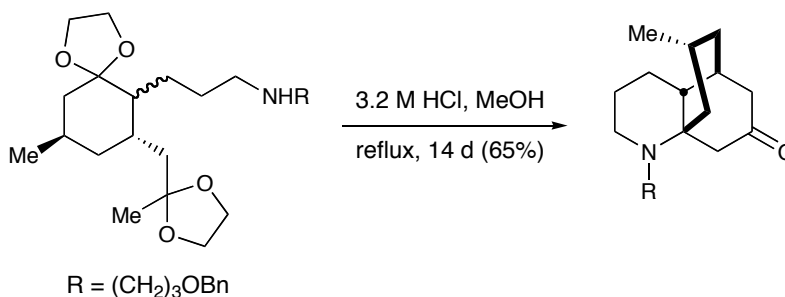
IX. The asymmetric reaction below is thought to proceed through a boat transition structure and exhibits a positive non-linear effect. What is a positive non-linear effect (3 pts)? Offer an explanation for this positive non-linear effect (10 pts). (Note: you do not have to explain the absolute stereochemical outcome.)



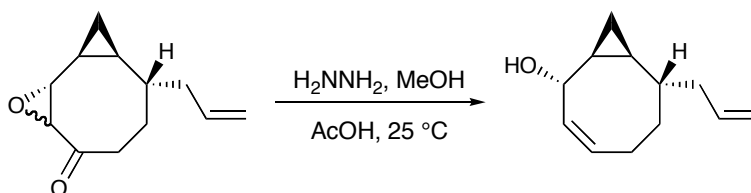
- X. Reaction of aldehyde **1** with EtMgBr at  $-78\text{ }^{\circ}\text{C}$  affords an 81/16 ratio of the Felkin to anti-Felkin products. However if a bis(alkylphenoxy)aluminum salt (e.g. **2**) is added prior to the addition of the EtMgBr the anti-Felkin product predominates by a ratio of 80/20. Explain. (5 pts)



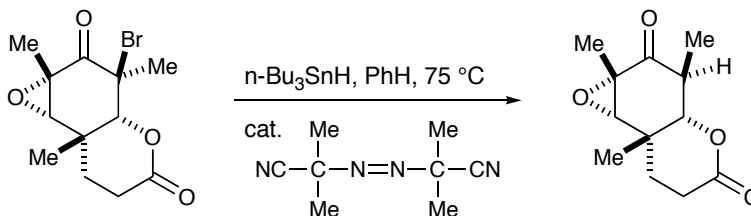
- XI. Give a *detailed* mechanistic account of the following reaction sequence. (10 pts)



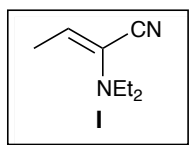
- XII. A variation of the Shapiro reaction is the Wharton rearrangement, an example of which is shown below. Provide a complete arrow (electron) pushing mechanism for the Wharton rearrangement. (10 pts)



- XIII. Give a *detailed* mechanistic account of the following reaction sequence. (5 pts)



IX. Give an example that illustrates how compound I can be viewed as a synthon for C–C–CO<sub>2</sub>H (3 pts)



**Bonus Question:** During the synthesis presentations we mentioned Columbia's Gilbert Stork. Here is a question about another Columbia chemist. After earning a degree in chemistry from Atlanta University, he moved to New York and began post-graduate work at Columbia University. Soon though he also began to pursue his other passion, jazz. As leader of the first great jazz big band, his ability to spot talent was legendary. Indeed he hired many future jazz greats including an up and coming trumpet player named Louis Armstrong. Who was he?

- a. Fletcher Henderson
- b. Earl Hines
- c. Johnny St. Cyr
- d. Kid Ory
- e. Kid Rock