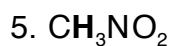
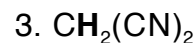
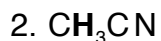
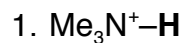


CEM 852 Final Exam

May 7, 2004

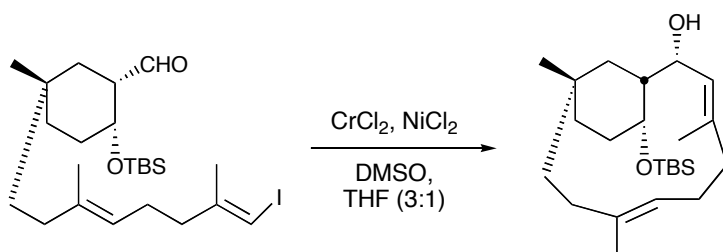
This exam consists of 5 pages. Please write ALL your answers in the answer books. Please write legibly and draw all structures clearly. Good luck.

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

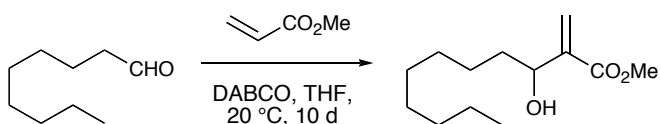


II. Provide the names of the following "name" reactions. (10 pts)

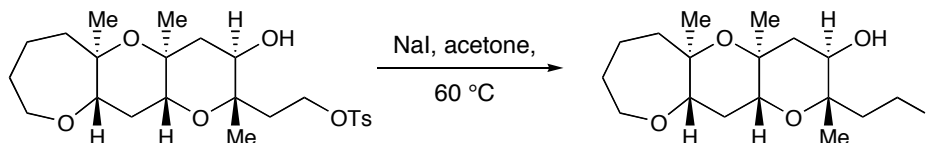
1.



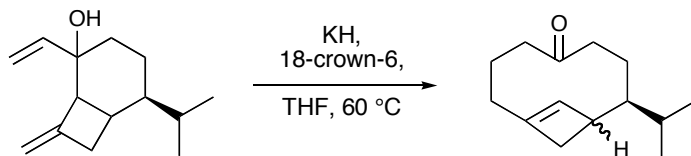
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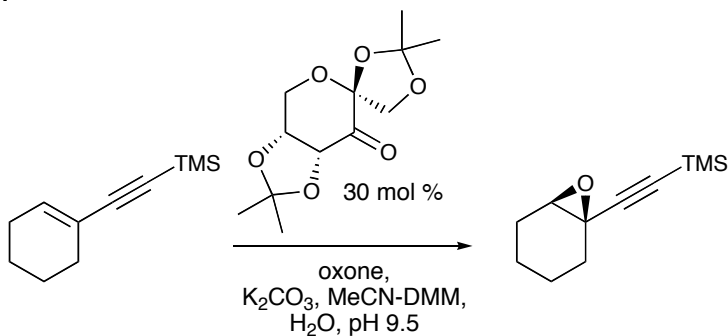
3.



4.

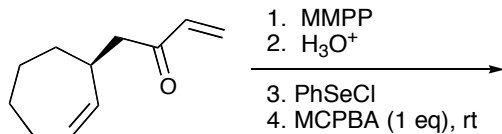


5.

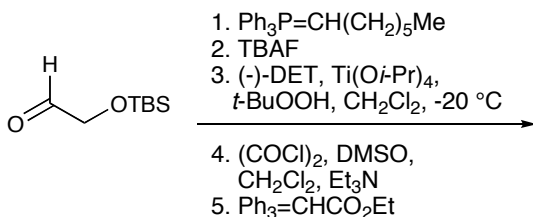


III. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, indicate the major and minor species. (35 pts)

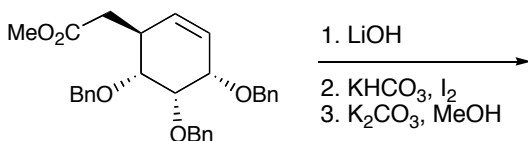
1.



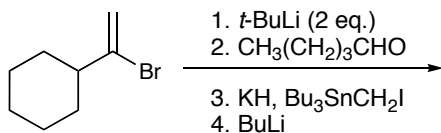
2.



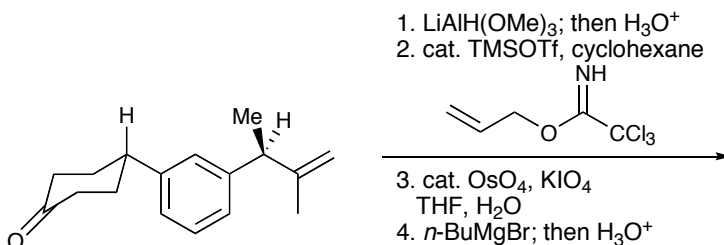
3.



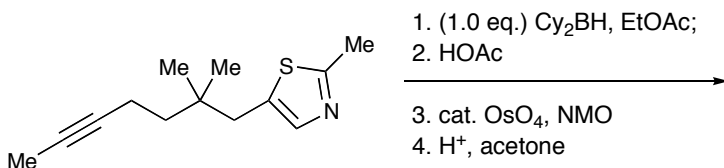
4.



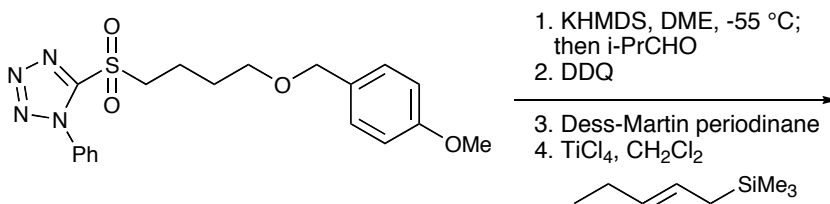
5.



6.

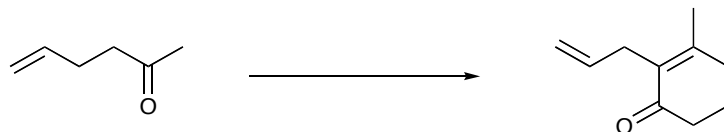


7.

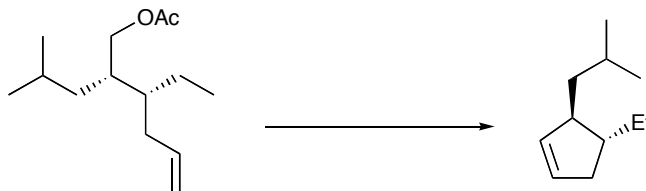


IV. Provide the reagents necessary to convert the starting material to the product. Most of these transformations will require more than one step. Be sure to consider the product's relative or absolute stereochemistry. To maximize your chances at partial credit, it is recommended that you show all intermediate compounds. (35 pts)

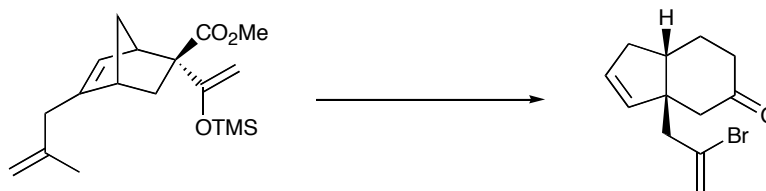
1.



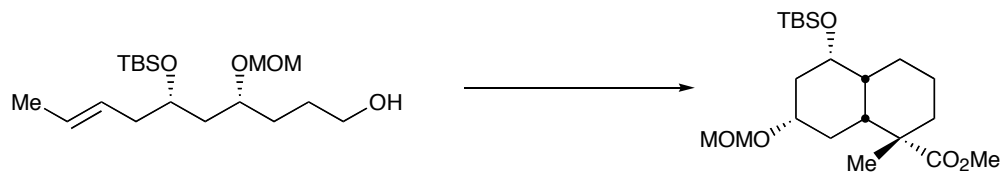
2.



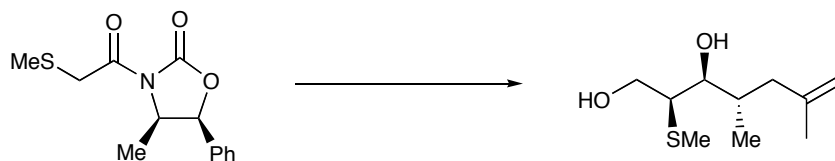
3.



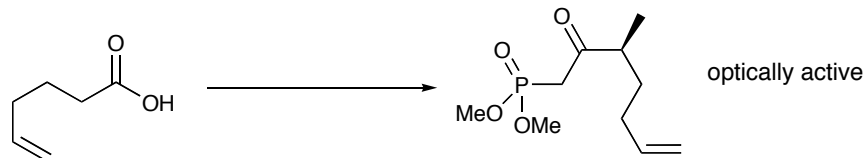
4.



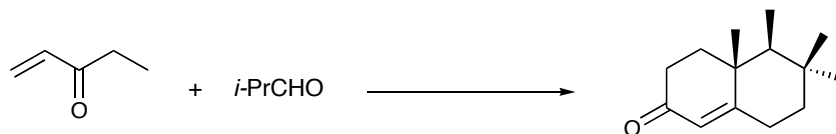
5.



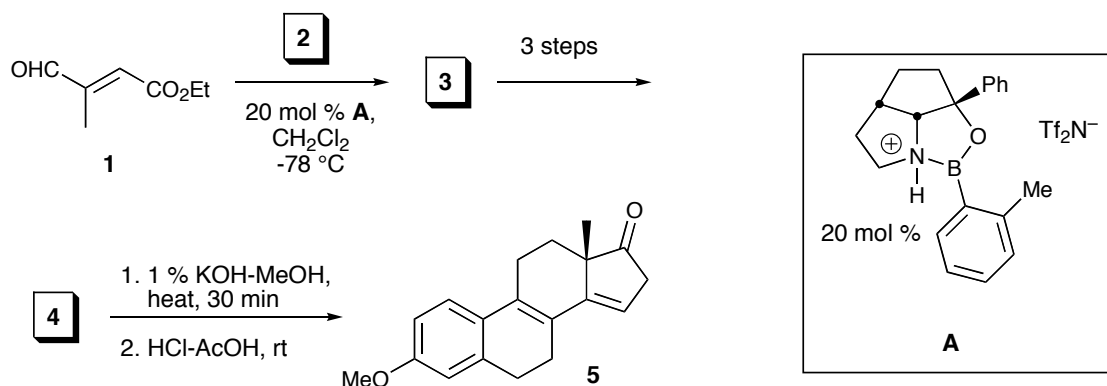
6.



7.

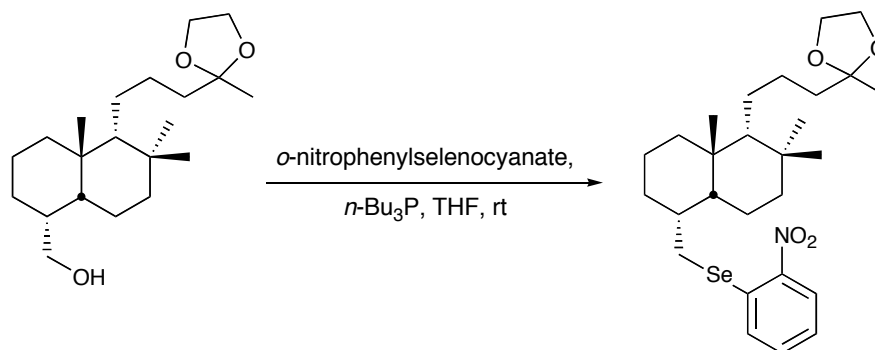


V. Torgov's diene (**5**) is an intermediate in Corey's recent synthesis of estrone. In preparing **5**, Corey carried out an asymmetric Diels-Alder between **1** and **2** to give **3**. **3** was then converted in three steps to **4**. Base catalyzed aldol condensation of **4** followed by reaction with HCl-AcOH to migrate the olefins into conjugation with the aryl ring afforded **5**. Provide the structures for **2** – **4** as well as **the three steps** required to convert **3** into **4**. (15 pts)

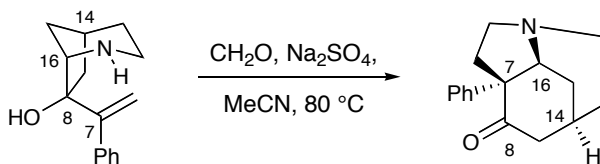


VI. Provide complete arrow (electron) pushing mechanisms for the reactions shown below.

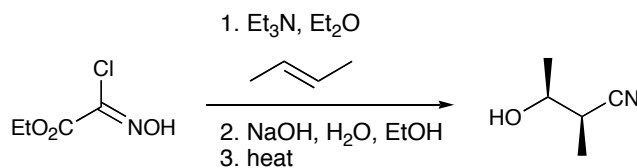
1. (10 pts)



2. (10 pts)

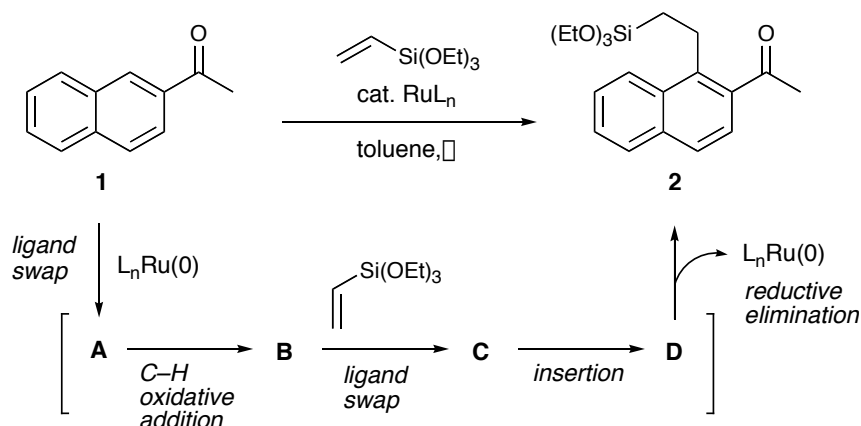


3. (10 pts)



VII. In CEM 252 we teach students that reactions between esters and Grignard reagents typically don't stop at the ketone, but go on to afford the bis-addition product. However, if an ester is aged with TMSCl prior to introduction of the Grignard reagent, one can prepare the corresponding ketone in high yields. Explain. (8 pts)

VIII. Ru-mediated C–H activation / olefin insertion can be viewed as the equivalent of a reductive Heck reaction. An example of this reaction and the steps of its catalytic process are described below. Provide the structures of **A** – **D**. (12 pts)



Bonus Question: Sir Edward Elgar's choral masterpiece "The Dream of Gerontius" was first heard on October 3, 1900 in Birmingham, England. In October 2000, the Woking Choral Society joined with other choirs, the London Philharmonic Orchestra, and one of Britain's foremost bass-baritone soloists who also happened to be trained as a chemist for a special centenary performance of Elgar's oratorio in the Royal Albert Hall, London. Who sang bass?

- John Cotterill
- Arthur Davies
- Waverley S. Maidenhead
- John Shirley-Quirke
- Barry White