CEM 852 Final Exam

May 4, 2016

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.

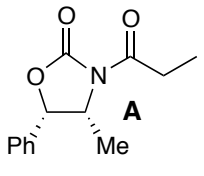
I. For the following compounds provide the pKa's of the hydrogen in **bold** within 2 pKa units. (10 pts)

1. $C\mathbf{H}_2(NO_2)_2$
2. $C_6H_5O\mathbf{H}$
3. $C\mathbf{H}_2(CN)_2$
4. $(CH_3)_3C–CO–C\mathbf{H}_3$
5. $N\mathbf{H}_3$
6. $C_6H_5C\mathbf{H}_3$
7. $C\mathbf{H}_3CN$
8. $C\mathbf{H}_3CO_2C_2H_5$
9. $CH_3O\mathbf{H}$
10. $HC{\equiv}C\mathbf{H}$

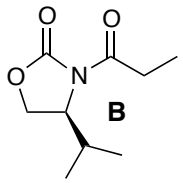
II. Explain, describe, or illustrate each of the following: (15 pts)

1. kinetic resolution
2. a syn-pentane interaction
3. double diastereodifferentiation
4. organocatalysis
5. an outersphere mechanism (as coined by Noyori)

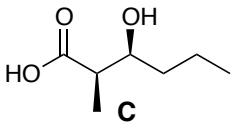
III. Which Evans' oxazolidinone should one use to form **C** in high enantiomeric excess? Explain your choice by illustrating a Zimmerman-Traxler transition structure that employs the oxazolidinone of your choosing. (6 pts)



A



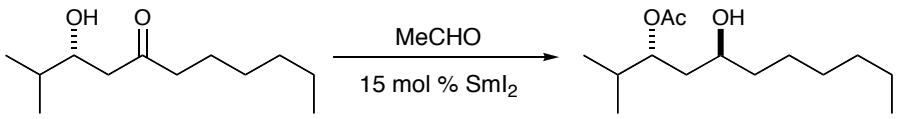
B



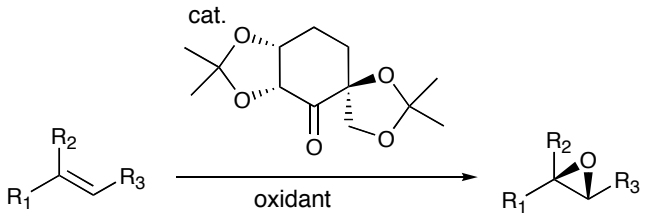
C

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

1.



2.



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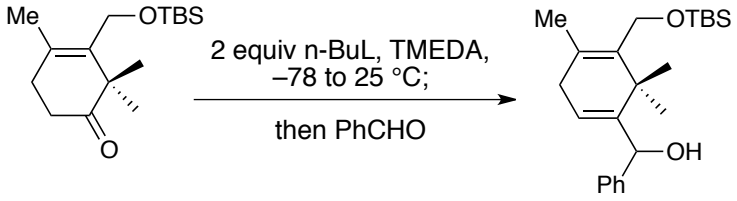

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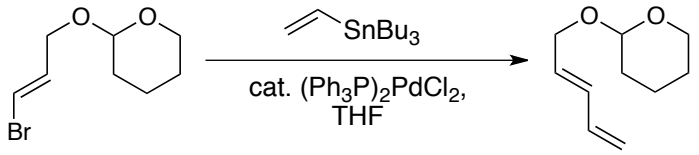
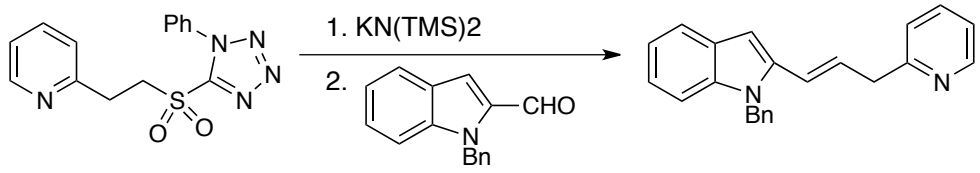
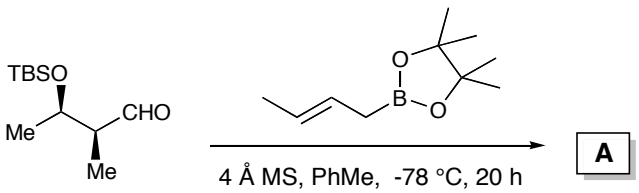


5.

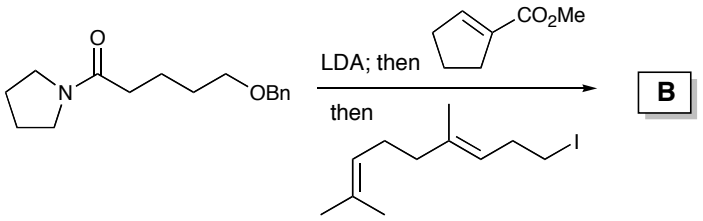


V. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (40 pts)

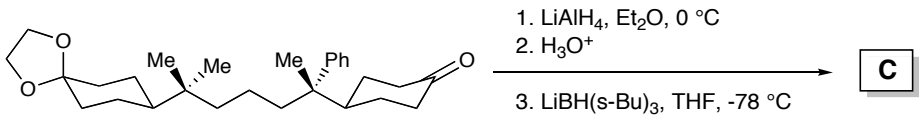
1.



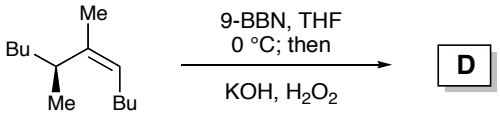
2.


O
N
OBn
LDA; then
then
CO2Me
I
B

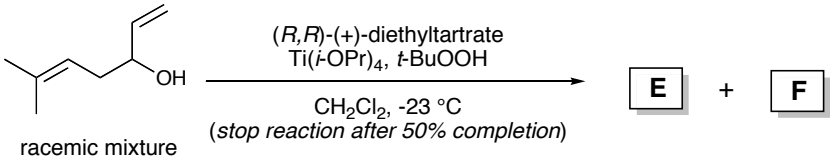
3.


O
O
Me
Me
Me
Ph
O
1. LiAlH4, Et2O, 0 °C
2. H3O+
3. LiBH(s-Bu)3, THF, -78 °C
C

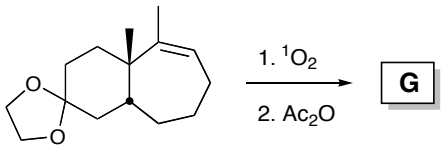
4.


Me
Bu
Me
Bu
9-BBN, THF
0 °C; then
KOH, H2O2
D

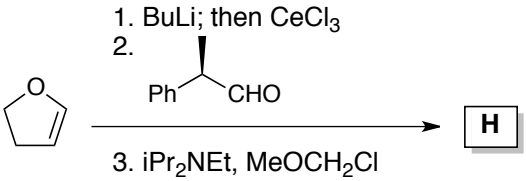
5.


OH
racemic mixture
(R,R)-(+)-diethyltartrate
Ti(i-OPr)4, t-BuOOH
CH2Cl2, -23 °C
(stop reaction after 50% completion)
E
+
F

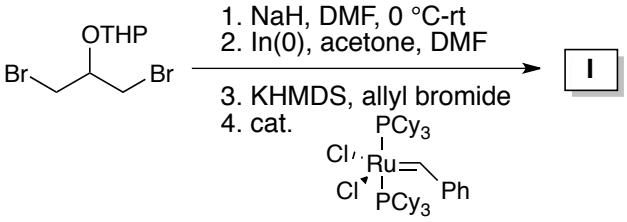
6.


O
O
1. 1O2
2. Ac2O
G

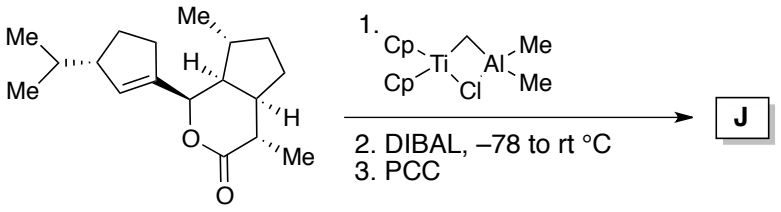
7.


O
1. BuLi; then CeCl3
2.
Ph
CHO
3. iPr2NEt, MeOCH2Cl
H

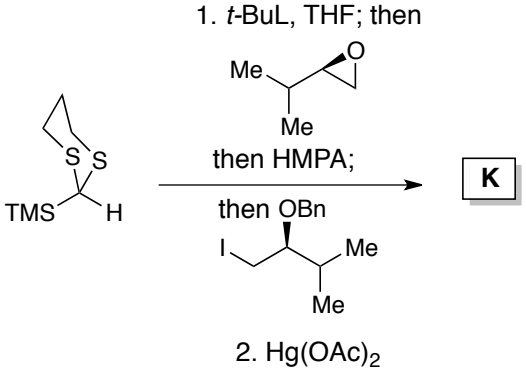
8.


OTHP
Br
Br
1. NaH, DMF, 0 °C-rt
2. In(0), acetone, DMF
3. KHMDS, allyl bromide
4. cat.
PCy3
Cl
Ru
Cl
PCy3
Ph
I

9.



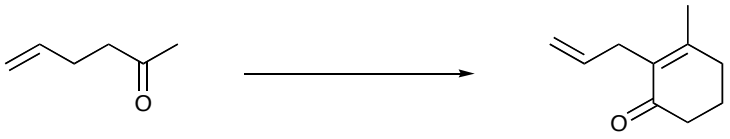
10.



VI. 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. (20 pts)

1.

2.

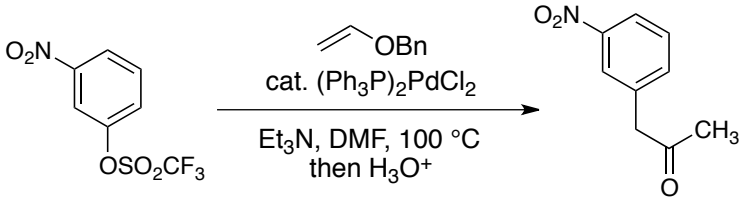


3.

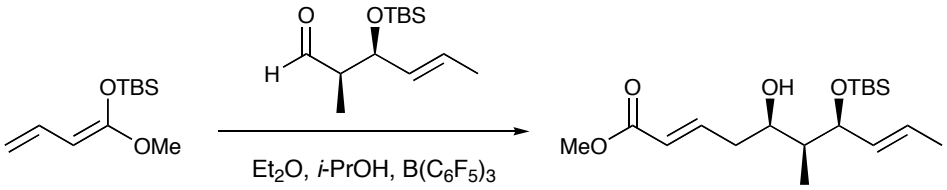
4.

5.

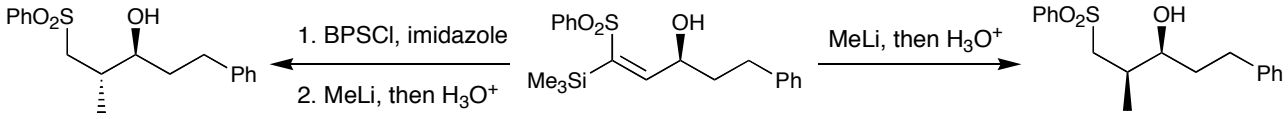
VII. Illustrate the catalytic cycle for the reaction below. (6 pts)



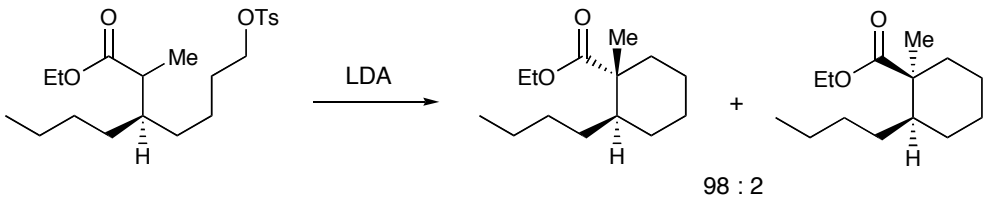
VIII. An example of the vinylogous Mukaiyama Aldol is shown below. Provide an explanation for the observed stereochemical outcome of that reaction. (6 pts)



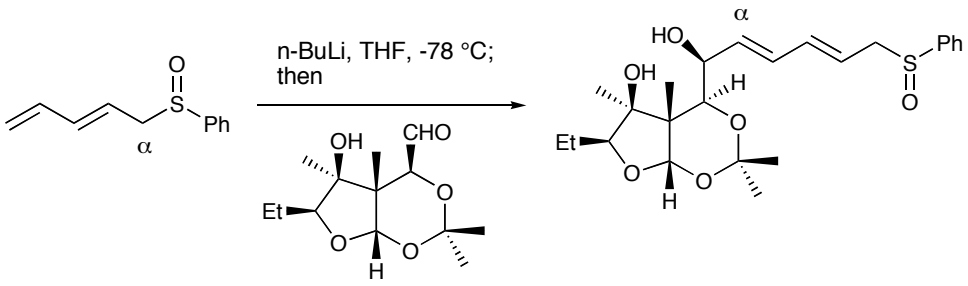
IX. When the alcohol shown below reacts with MeLi the (*R*)-isomer is formed. When that same alcohol is protected as a tert-butyldiphenylsilyl ether the reaction with MeLi affords the (*S*)-isomer. Using Felkin-Ahn**–like** models explain these observations. (6 pts)



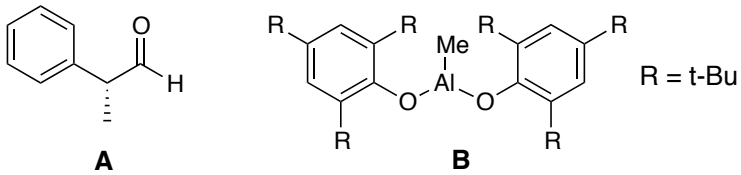
X. For the reaction shown below explain the stereochemical outcome. (6 pts)



XI. In the reaction shown below, the deprotonated ✔carbon of the sulfoxide reacts with the aldehyde, before 2,3-sigmatropic rearrangements leads to the final product. Give a *detailed* mechanistic account of that reaction sequence. (10 pts)

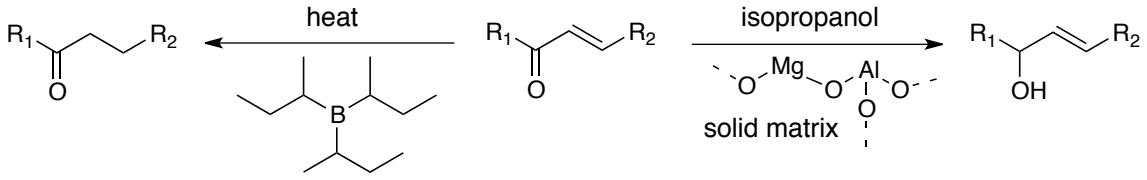


XII. Reaction of aldehyde **A** with EtMgBr at –78 °C affords an 81/16 ratio of the Cram to anit-Cram products. However if a bis(alkylphenoxy)aluminum salt (e.g. **B**) is added prior to the addition of the EtMgBr the anti-Cram product predominates by a ratio of 80/20. Explain (5 pts)

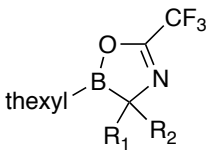


A **B**

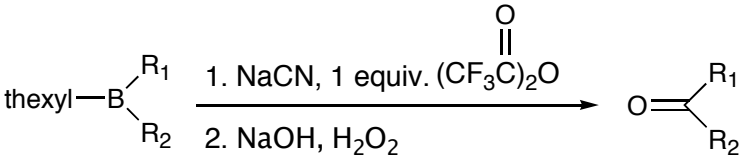
XIII. Provide a mechanistic rational for two complementary regiochemical hydride reductions shown below (Hint: Think about the origin of the hydride). (10 pts)



XIV. In class we saw how reacting the appropriate trialkylborane with carbon monoxide could afford ketones. Toxicity and handling issues with CO inspired development of the Pelter modification to the CO reaction (shown below). Step one of this reaction sequence involves the generation of a heterocyclic boron containing species. Provide a complete arrow (electron) pushing mechanism for the Pelter modification. (Hint: compound **C** is the product of step 1). (10 pts)



C



Bonus Question: (2 pts) It appears the US Presidential election will pit Donald Trump vs. Hillary Clinton. Thus the US may see its first female President or it's first President to have been inducted into the World Wrestling Entertainment Hall of Fame, we will once again not see a chemist as President. History though has occasionally seen chemists rise to high political office, albeit not without the occasional controversy. Which chemist/political figure had the dubious distinction of being thrown out of a chemistry exam for cheating.

a. Former Vice Prime Minister of Romania, Elena Ceausescu

b. Princess of Thailand, HRH Princess Chulabhorn

c. Former Massachusetts State Assemblyman, William S. Clark

d. Former Prime Minister of the United Kingdom, Margaret Thatcher

e. Fictional President in the 1973 film Escape from the Planet of the Apes, Matthew Williams