CEM 852 Final Exam

May 3, 2017

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.

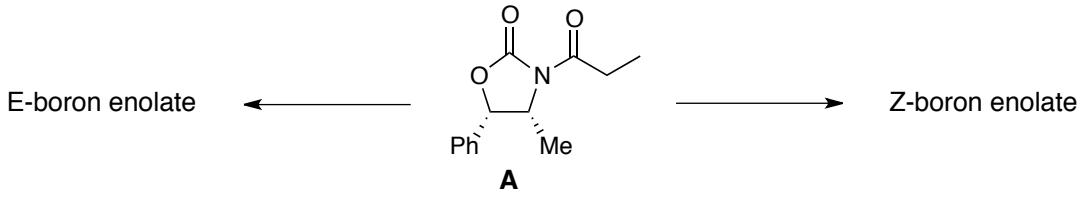
I. Provide the pKa's of the most acidic proton on following solvents within 2 pKa units. (10 pts)

1. acetic acid
2. acetone
3. acetonitrile
4. *t*-butanol
5. diisopropylamine
6. DMSO
7. ethanol
8. ethyl acetate
9. toluene
10. water

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

1. the Bürgi-Dunitz angle
2. the Felkin-Ahn model
3. matched/mismatched diastereoselectivity
4. the Sharpless epoxidation mnemoninc
5. a Zimmerman-Traxler transitions state

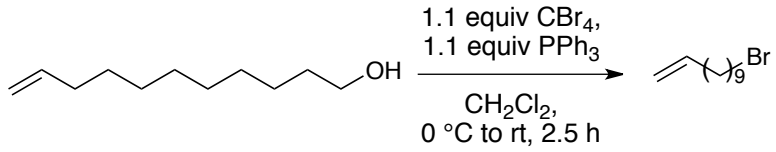
III. Provide conditions to convert Evans' oxazolidinone A into its *E*- and *Z*-boron enolates. Be sure to draw the *E*- and *Z*-boron enolates. (8 pts)



A

IV. Provide the name associated with each of the name reactions shown below. (15 pts).

1.



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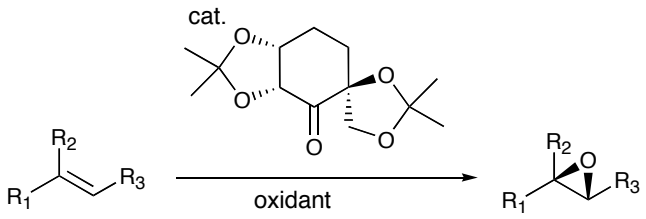

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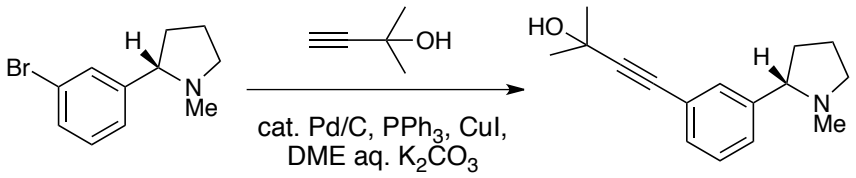

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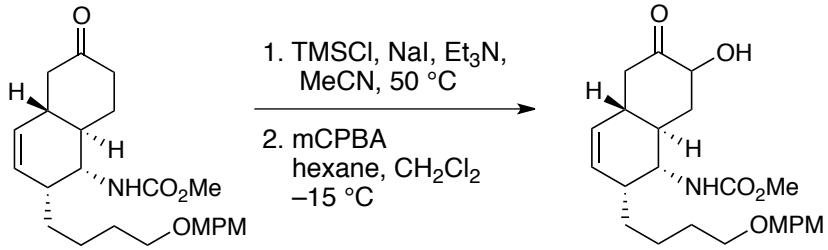

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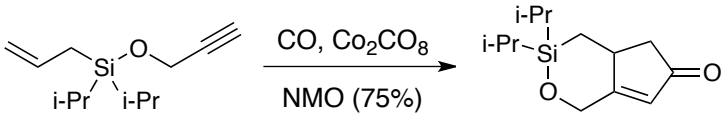
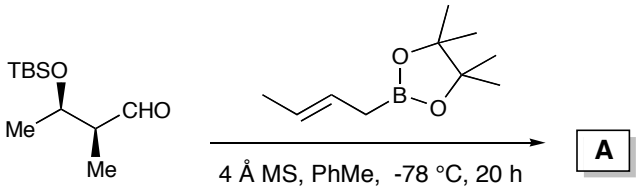
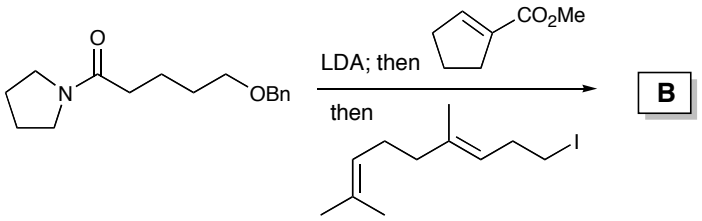


V. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (40 pts)

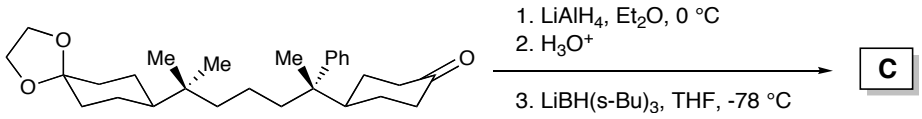
1.


TBSO
Me
CHO
Me
O
B
O
4 Å MS, PhMe, -78 °C, 20 h
A

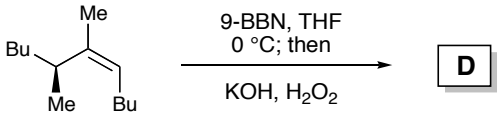
2.


O
N
OBn
LDA; then
CO2Me
then
I
B

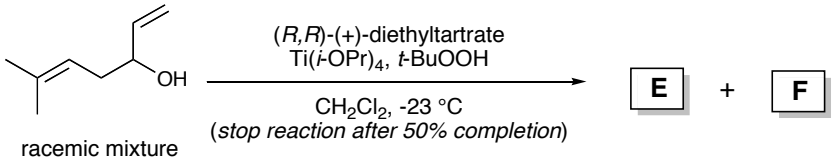
3.


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

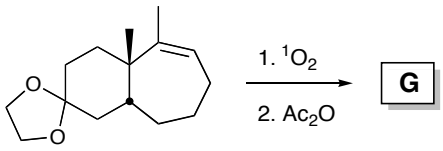
4.


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

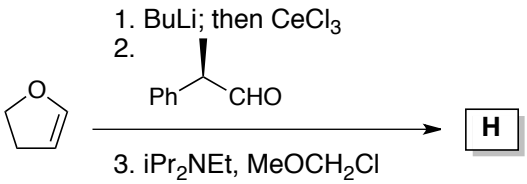
5.


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

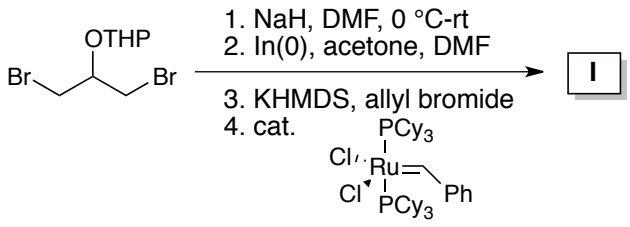
6.


O
O
1. 1O2
2. Ac2O
G

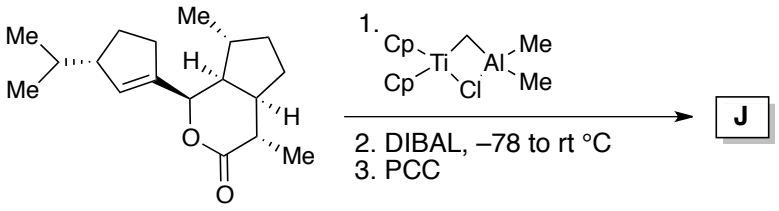
7.


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

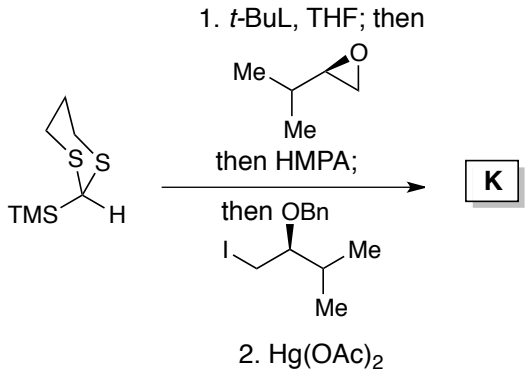
8.



9.



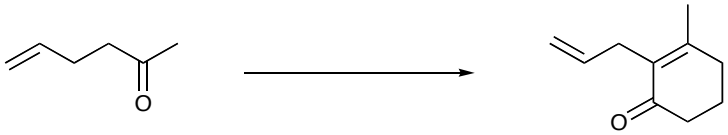
10.



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.

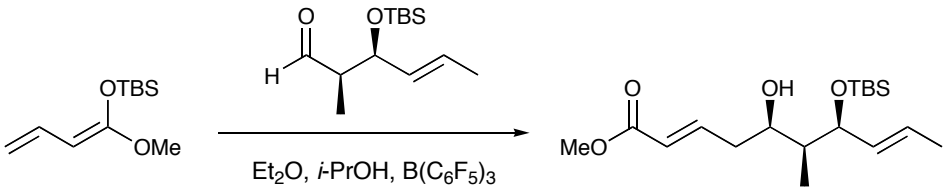


3.

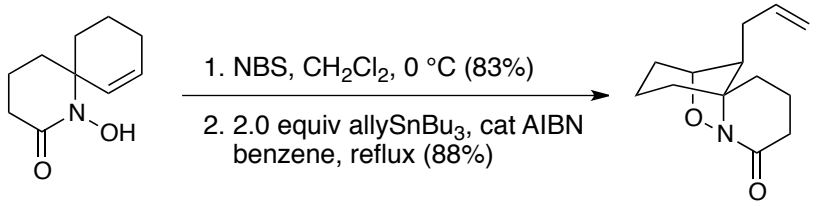
4.

5.

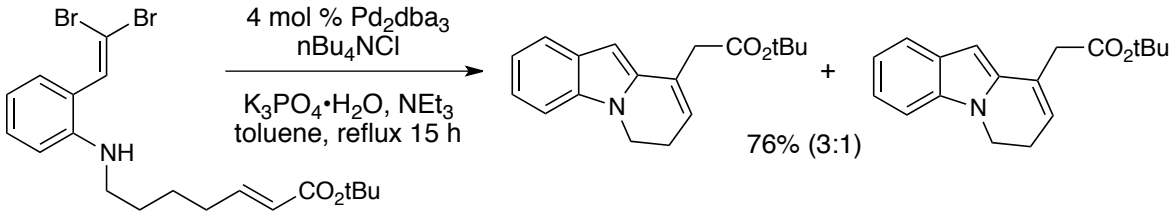
VIII. An example of the vinylogous Mukaiyama Aldol is shown below. Provide an explanation for the observed stereochemical outcome of that reaction. (6 pts)



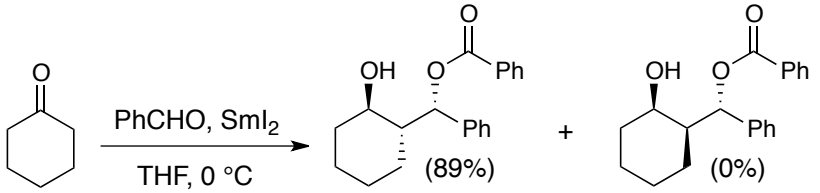
X. Provide a detailed arrow pushing mechanism for the reaction sequence below. For the first step, you may simply consider NBS as a source of "Br+". For the second step be sure your mechanism expains the role of AIBN and how the reaction propogates. (10 pts)



XI. For the reaction shown below, illustrate the catalytic cycle indicating all Pd bearing intermediates. (12 pts)

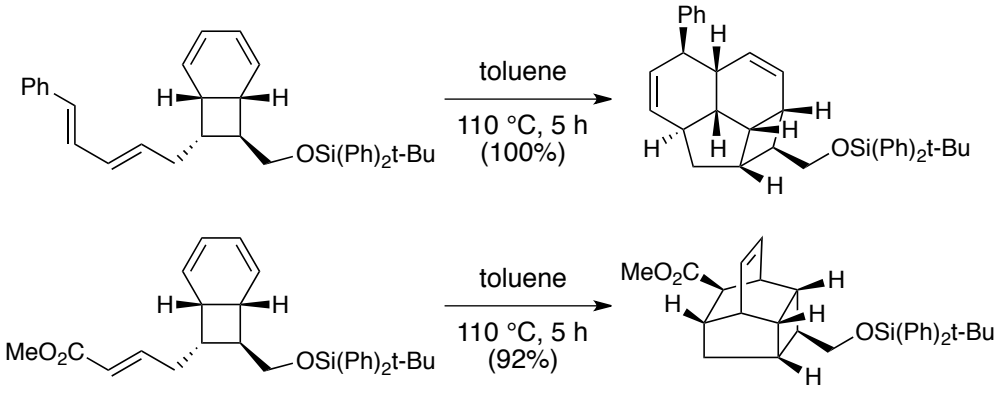


XII. Reaction of cyclohexanone, benzaldehyde, and samarium iodide exclusively affords the 1,2-syn-1,3-anti-product and none of the 1,2-anti-1,3-anti-product is observed.



The reaction is thought to proceed via a Sm mediated aldol, followed by an Evans-Tischenko reaction. Curiously, by adjusting the stoichiometry and stopping the reaction at low conversion, the 1,2-anti-aldol product predominates. Owing to this they suggest that this is an example of Le Chatelier's principle, with the relative rates of Evans-Tischenko reaction driving the equilibrium. Provide arrow pushing mechanisms for the Evans-Tischenko reaction on both the syn and anti aldolates. Why would one be favored over the other? (Hint: think about cyclohexaone reductions.) (12 pts)

XIII. Provide detailed arrow pushing mechanisms for two complementary reactions shown below. (10 pts)



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