CEM 852 Final Exam

May 5, 2011

This exam consists of 8 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 mnemonics for the following chemical processes: (10 pts)

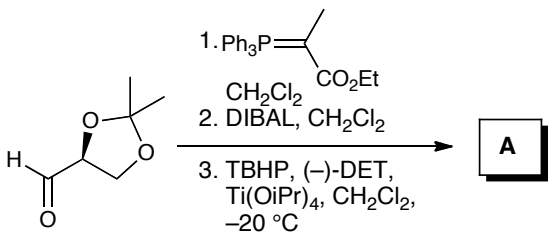
1. Sharpless asymmetric epoxidation
2. Sharpless asymmetric dihydroxylation
3. CBS reductions
4. Yeast reduction
5. Nucleophilic addition to a carbonyl with an α-asymmetric center

II. Explain, describe, or illustrate each of the following chemical processes: (10 pts)

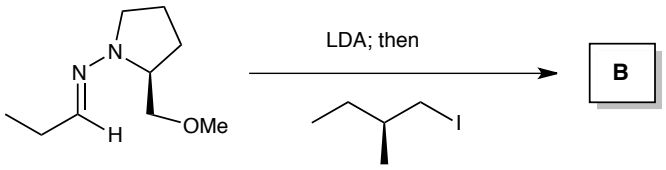
1. A Lipase mediated kinetic resolution
2. chiral amplification / non-linear effects
3. enantiotopic protons
4. oxidative addition
5. reductive elimination

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

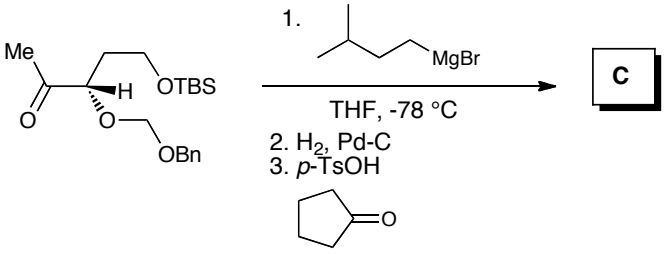
1.



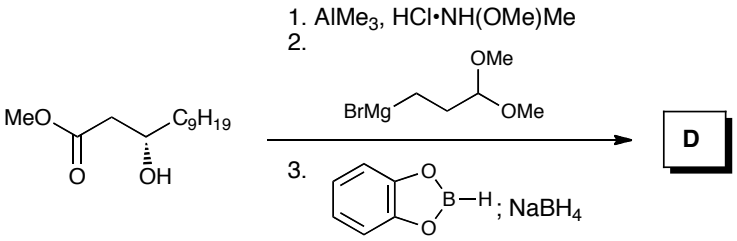
2.


LDA; then
OMe
I
B

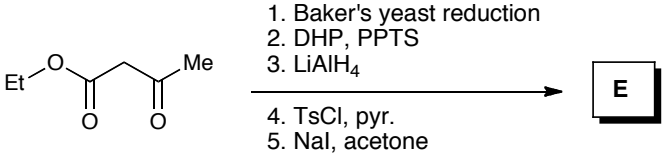
3.


Me
OTBS
OBn
1.
MgBr
THF, -78 °C
2. H2, Pd-C
3. p-TsOH
O
C

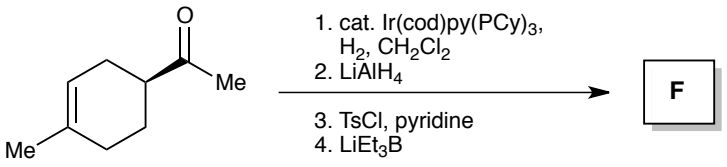
4.


1. AlMe3, HCl•NH(OMe)Me
2.
OMe
BrMg
OMe
MeO
C9H19
OH
3.
B—H; NaBH4
D

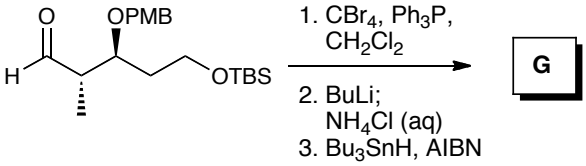
5.


1. Baker's yeast reduction
2. DHP, PPTS
3. LiAlH4
Et
Me
4. TsCl, pyr.
5. NaI, acetone
E

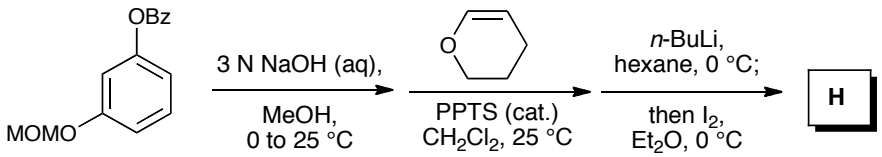
6.


1. cat. Ir(cod)py(PCy)3,
H2, CH2Cl2
2. LiAlH4
Me
Me
3. TsCl, pyridine
4. LiEt3B
F

7.


O
OPMB
H
OTBS
1. CBr4, Ph3P,
CH2Cl2
2. BuLi;
NH4Cl (aq)
3. Bu3SnH, AIBN
G

8.



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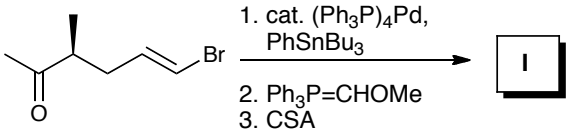
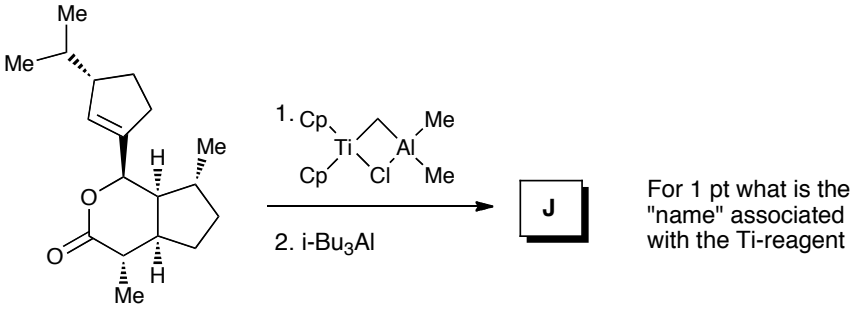
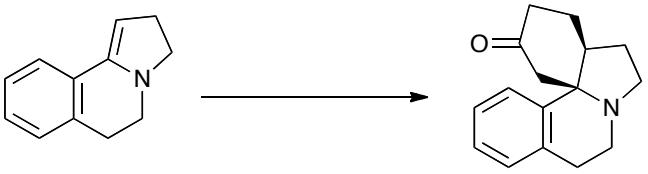


10.



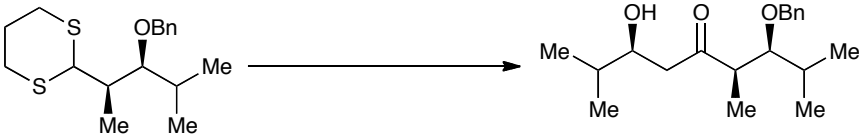
IV. Provide conditions that will effect the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (30 pts)

1.

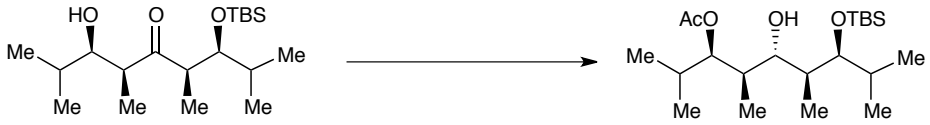


2.

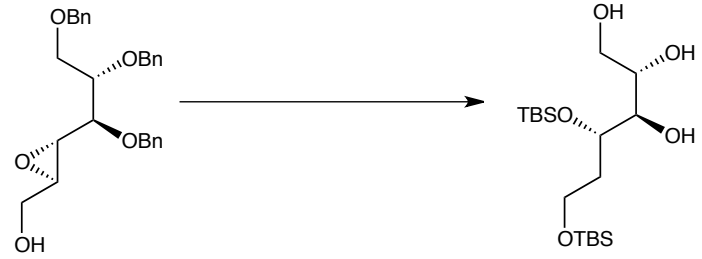
3.



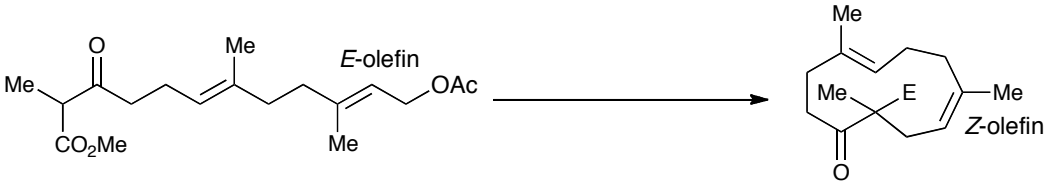
4.



5.



6.



E = CO_2Me

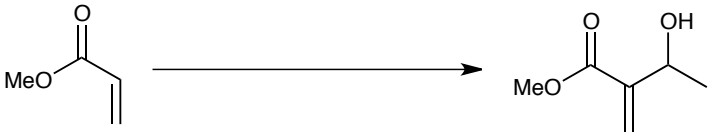
7.

single enantiomer

8.

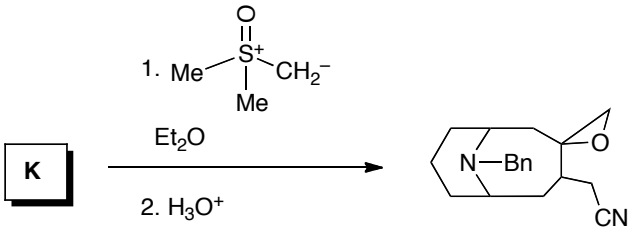
9.

10.

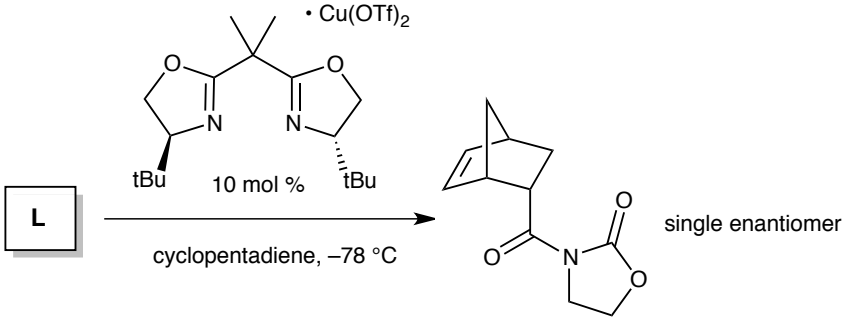


V. Provide the starting substrate for the reactions outlined below. (18 pts)

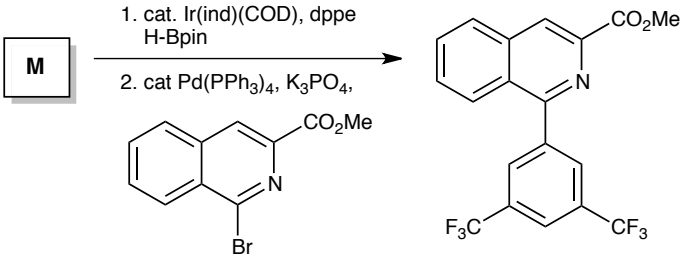
1.



2.



3.



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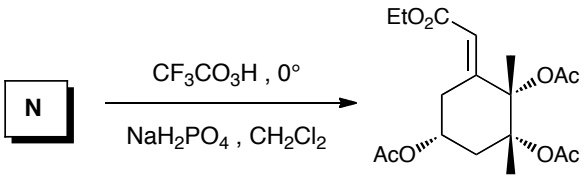
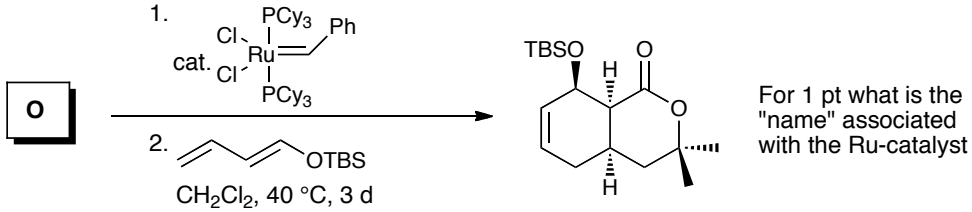
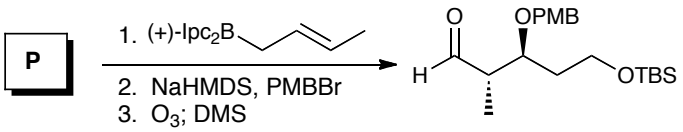


5.

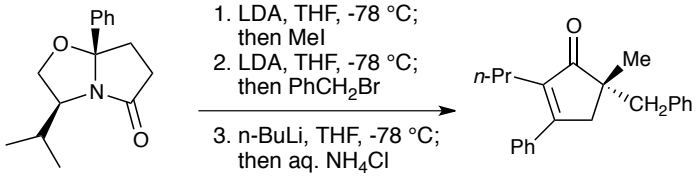


For 1 pt what is the "name" associated with the Ru-catalyst

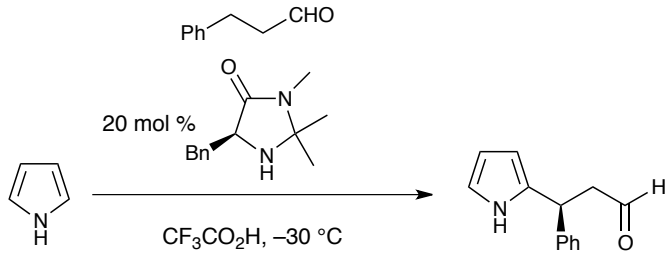
6.



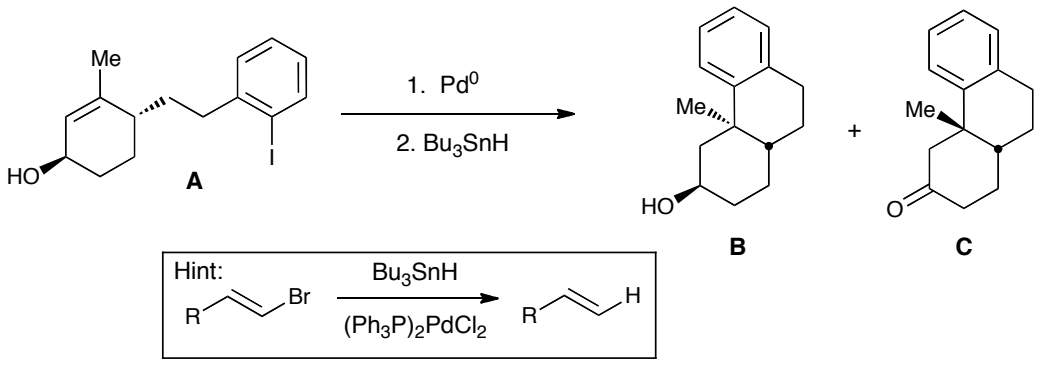
VI. Provide a complete arrow (electron) pushing mechanisms for the following transformation. (5 pts)



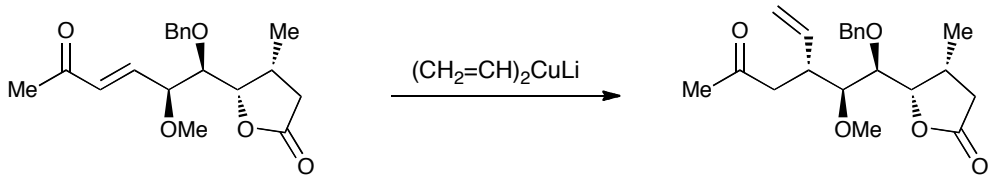
VII. Provide a complete arrow (electron) pushing mechanisms for the following transformation. You do not have to explain the absolute stereochemistry but you should account for the catalytic nature of the reaction. (8 pts).



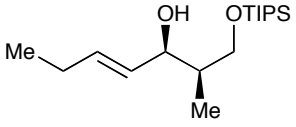
VIII. Applying Heck reaction conditions in the presence of tributytin hydride to **A** affords **B** and **C** in approximately 1:1 ratio. Provide a mechanistic explanation of the stereoselective formation of these two products. (8 pts)



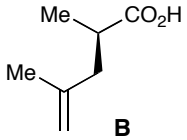
IX. Organocuprates often add to trans-enones with excellent stereocontrol, but such selectivity is often lacking with cis-enones. Predict the major product of the reaction below and through the use of Newman projects explain the stereochemical outcome of the reaction as well as the poor stereoselectivity observed for cis enones. (8 pts)



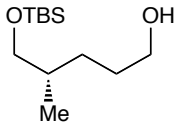
X. The following compounds can be made using Evan's chiral auxiliaries. How? You don't need to show a preparation of either the auxiliary or the electrophile, but please show all other steps in detail. (9 pts)



A

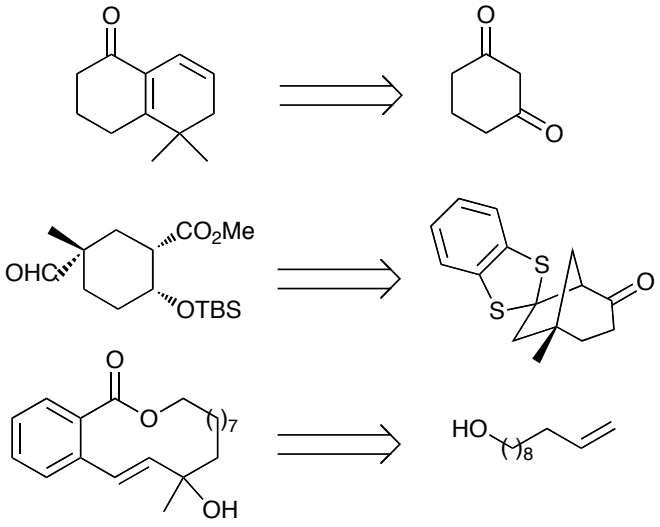


B



C

XI. Provide a synthesis of ONE of the compounds shown below, beginning with the indicated starting material (12 pts).



Bonus Question: Last Fall, Heck, Suzuki, and Negishi were awarded the Nobel Prize in Chemistry for the development of the reactions that bear their names. Nearly 100 years before, Victor Grignard and won the Nobel for his work on the reaction that bears his name. He shared the award with fellow Frenchman Paul Sabatier, who was a pioneer in the invention of catalytic hydrogenations. Perhaps a reflection of the Franco centric nature of that year's award, Grignard felt obliged to make a stink and protested that there should have been two awards for 1912, one to Sabatier and Sabatier's assistant, Abbe Jean-Baptiste Senderens and a second to Grignard and Grignard's old advisor. Who was Grignard's advisor?

a. Phillippe Barbier

b. Yves Chauvin

c. Henri Kagan

d. Henri Moissan

e. Henri Richard