# CEM 852 Final Exam

**May 5, 2009**

This exam consists of 5 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 100. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

**I.** Describe the differences between type I, type II, and type III crotylations (5 pts)

**II**. Arrange compounds 1-5 according to their propensity to alkylate enolates at C over O. (5 pts).

| $CH_3Br$ | $CH_3Cl$ | $(CH_3O)_2SO_2$ | $CH_3I$ | $(CH_3)_3O^+ BF_4^-$ |
|---|---|---|---|---|
| **1** | **2** | **3** | **4** | **5** |

C-alkylation ——— > ——— > ——— > ——— > ——— O-alkylation

**III**. Provide examples of each of the name reactions shown below. (5 pts).

1. Nozaki-Hyama-Kishi (NHK) coupling

2. Mukaiyama aldol

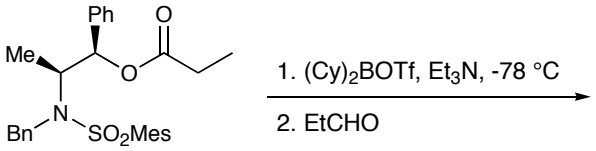
3. Brook rearrangement

4. Paterno-Büchi reaction

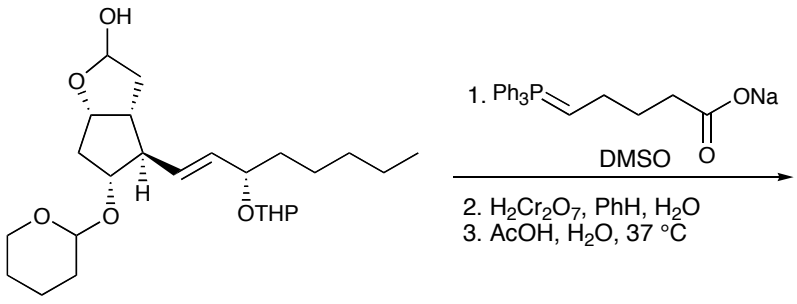
5. Robinson annulation

**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.



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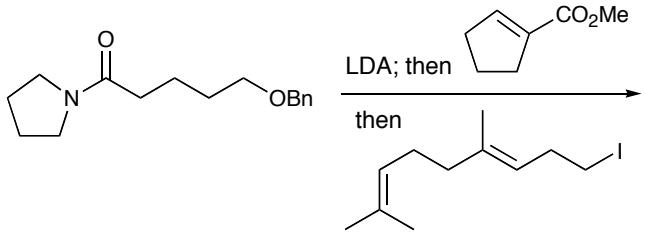
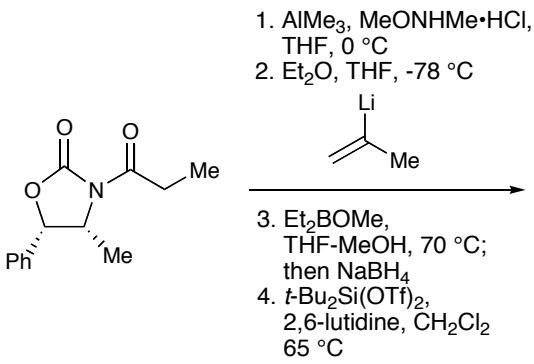
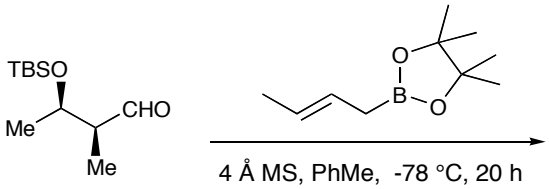

O
N
OBn
LDA; then
CO2Me
then
I

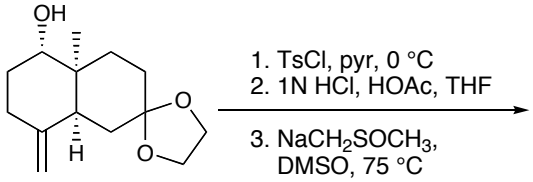
4.


1. AlMe3, MeONHMe•HCl,
THF, 0 °C
2. Et2O, THF, -78 °C
Li
Me
O
O
O
N
Me
Ph
Me
3. Et2BOMe,
THF-MeOH, 70 °C;
then NaBH4
4. t-Bu2Si(OTf)2,
2,6-lutidine, CH2Cl2
65 °C

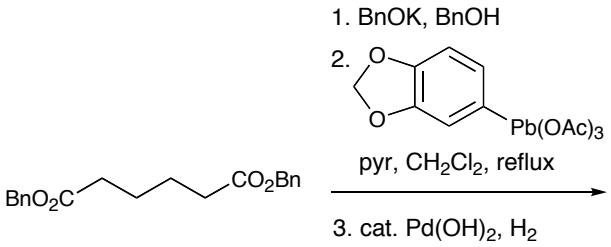
5.


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

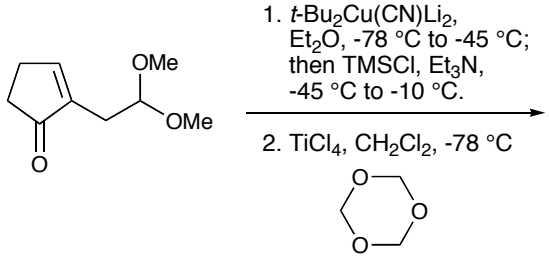
6.


OH
H
O
O
1. TsCl, pyr, 0 °C
2. 1N HCl, HOAc, THF
3. NaCH2SOCH3,
DMSO, 75 °C

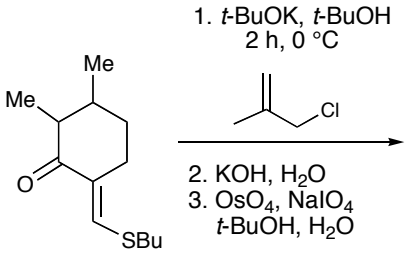
7.


1. BnOK, BnOH
2.
O
O
Pb(OAc)3
pyr, CH2Cl2, reflux
BnO2C
CO2Bn
3. cat. Pd(OH)2, H2

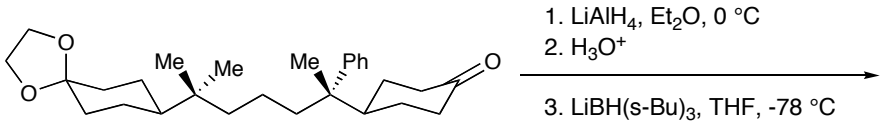
8.


OMe
OMe
O
1. t-Bu2Cu(CN)Li2,
Et2O, -78 °C to -45 °C;
then TMSCl, Et3N,
-45 °C to -10 °C.
2. TiCl4, CH2Cl2, -78 °C
O
O
O

9.

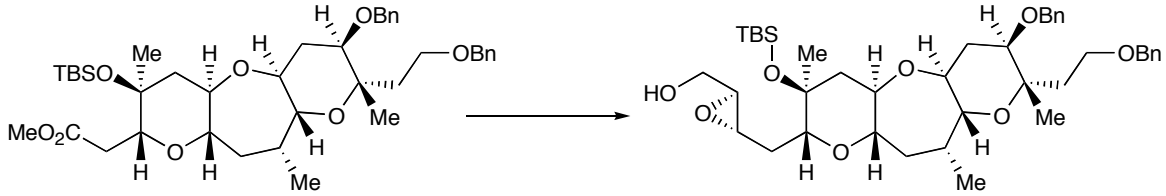



10.




**V.** Provide conditions which will effect the transformations outlined below. Many of these conversions will require more than one reaction, but none should require more than four. Show all intermediate compounds. (18 pts)

1.

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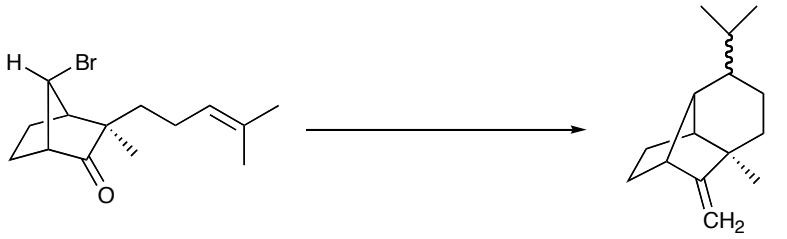


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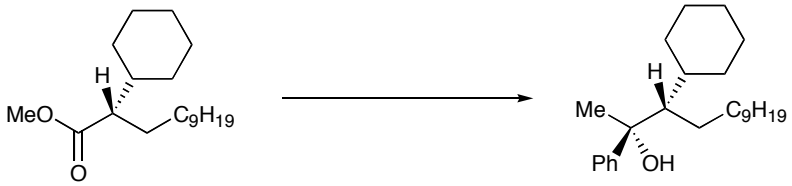
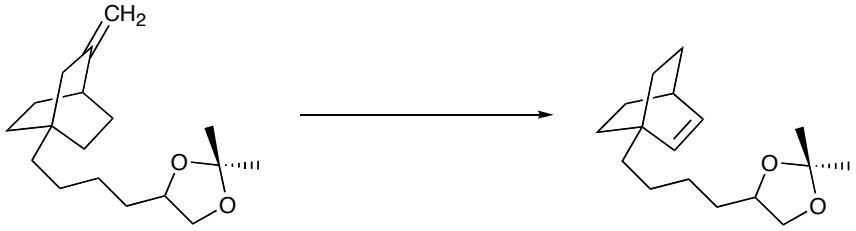
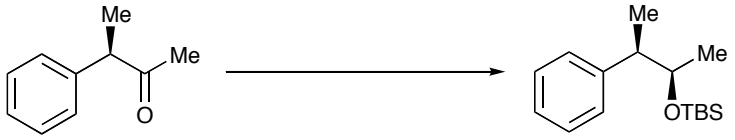



4.



5.

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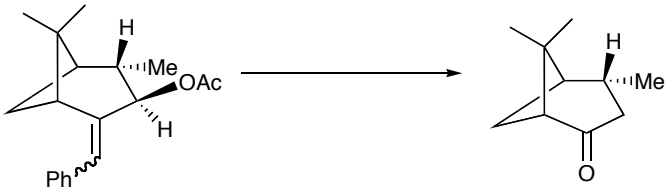
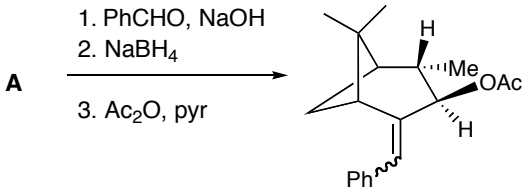
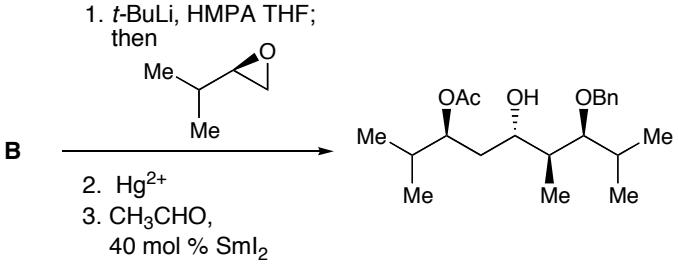



**VI.** Provide the starting substrate for each transformation shown below. (15 pts)

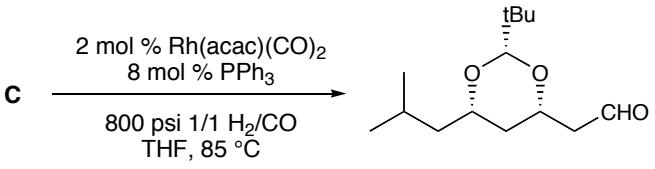
1.



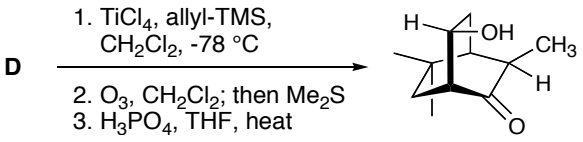

2.



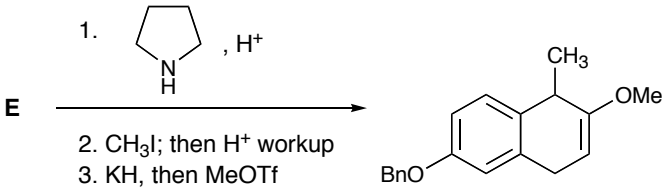

3.



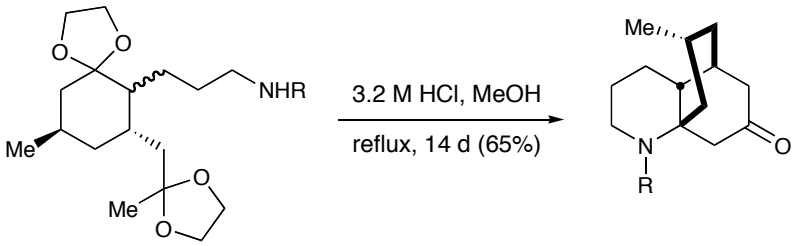

4.




5.



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




R = $(CH_2)_3OBn$

**VIII**. As shown below, changing the "R" group on ketone **F** can impact the stereocontrol observed upon the addition of PhMgBr. Furthermore changing the counter ion of the nucleophile from the *relatively* hard MgBr to the *relatively* soft Li also impacts the stereoselectivity of the addition. Based on your knowledge to the Felkin-Ahn model explain these results. (12 pts)


**F** **G** **H**

| R | nucleophile | **G:H** |
|---|---|---|
| Me | PhMgBr | 22:78 |
| Me | PhLi | 50:50 |
| $CH_2OSi(i\text{-}Pr)_3$ | PhMgBr | >1:99 |
| $CH_2OMe$ | PhMgBr | 84:16 |

**Bonus Question**: During last week's organic seminar, Professor Karabatsos described how his love for baseball helped him get an offer from MSU. Many chemists are die-hard baseball fans, including Steve Knight, who, as a graduate student member of the Overman group, finished the total synthesis of strychnine. Among Steve's other claims to fame is that during the summer before starting his Ph.D. studies he attended a game at every ballpark in the major leagues. What is Steve's favorite team? (2 pts)

**a.** Boston Red Sox

**b.** Chicago Cubs

**c.** Los Angeles Dodgers

**d.** New York Yankees

**e.** Durham Bulls