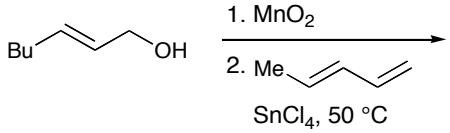
CEM 852 Final Exam

May 1, 1997

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 150. In answering your questions, please write legibly and draw all structures clearly. Good luck.

I. (60 pts) 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.

1.



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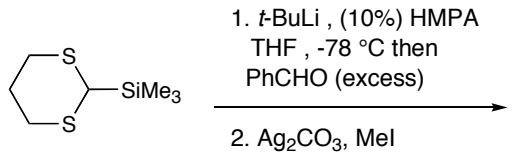

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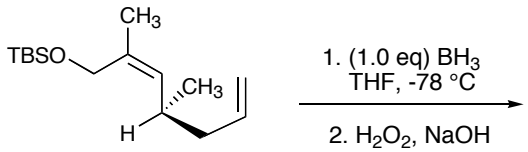

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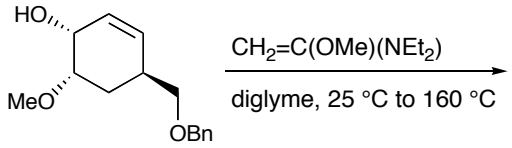

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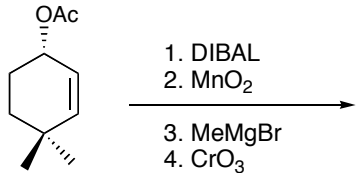

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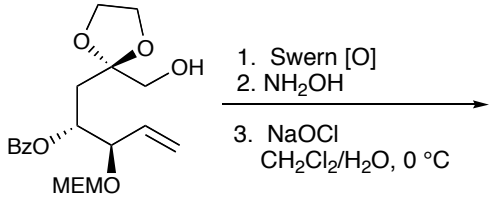

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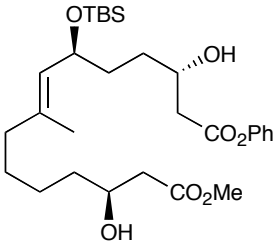
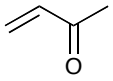
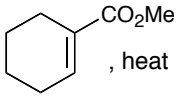
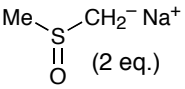


1. DMSO, NaCl
2. 2,4,6-trichloro-benzoyl chloride DMAP, Et_3N, THF
3. $VO(acac)_3$

8.

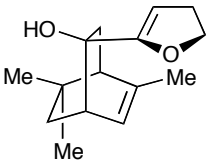


1. TMSCl, Et_3N, DMF
2. 

, heat
3. 

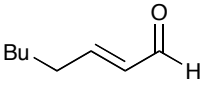
(2 eq.)
4. H_3O^+
5. Al(Hg)

9.



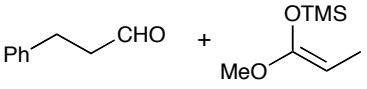
1. KH, 18-cr-6, 70 °C
2. PhSeCl, THF 0 °C
3. $NaIO_4$, $NaHCO_3$, MeOH

10.



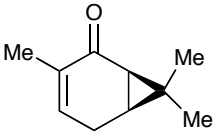
1. LDA, THF -78 °C; then MeI
2. $PhCH_2CH_2MgBr$
3. H_3O^+

11.



1. $TiCl_4$, -10 °C, Et_2O
2. 2N HCl, 0 °C
3. LAH
4. acetone, *p*-TSA

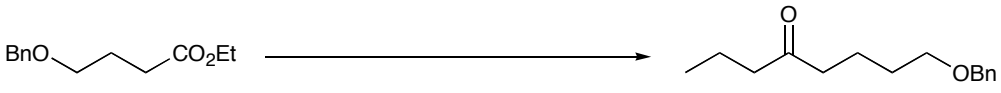
12.



1. NaOH, H_2O_2, MeOH
2. NH_2NH_2

II. (40 pts) Provide conditions which will effect the transformations outlined below. Most of these conversions will require more than one reaction, so be sure to show all intermediate compounds.

1.



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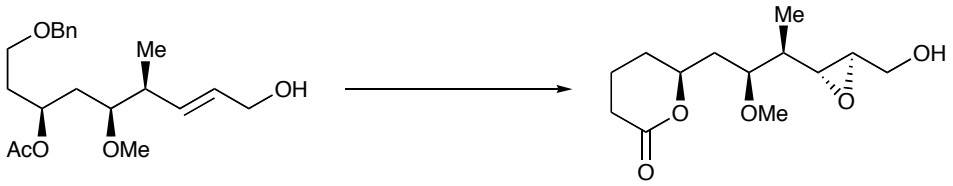

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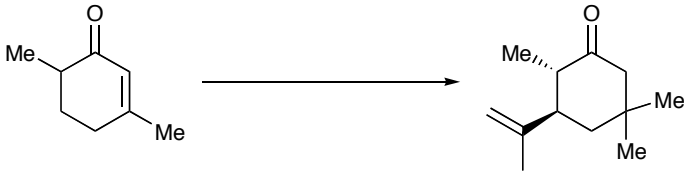

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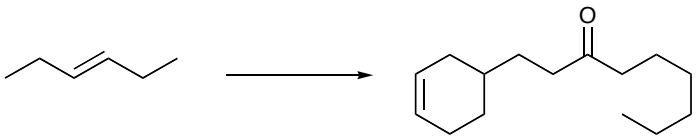
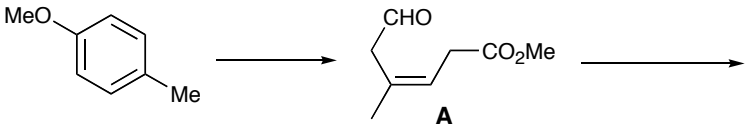
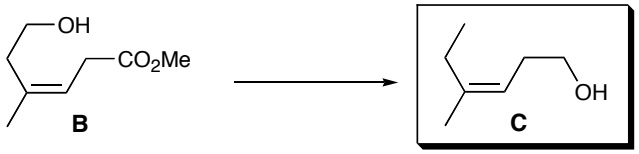


5.

6.





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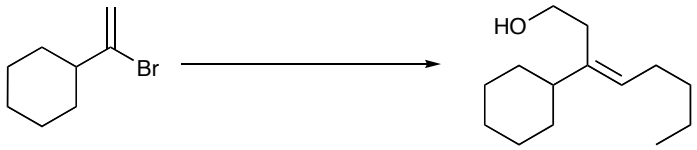

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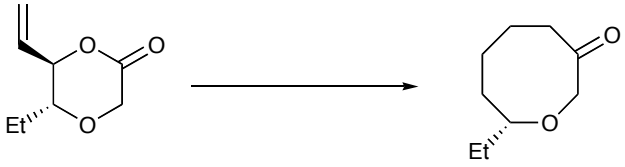
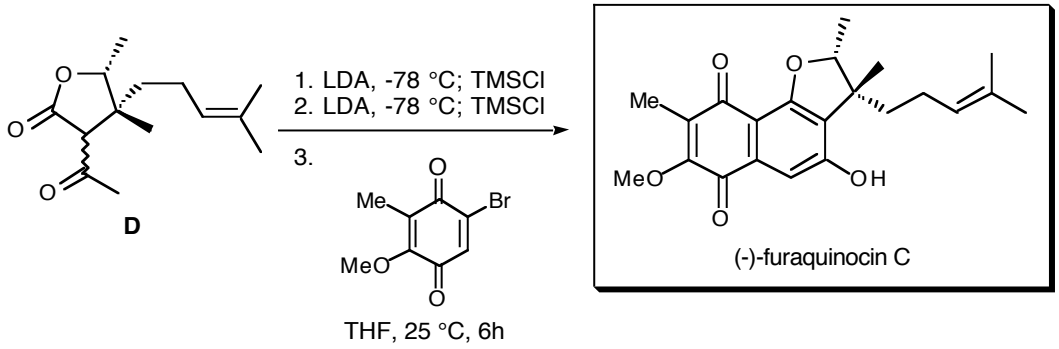
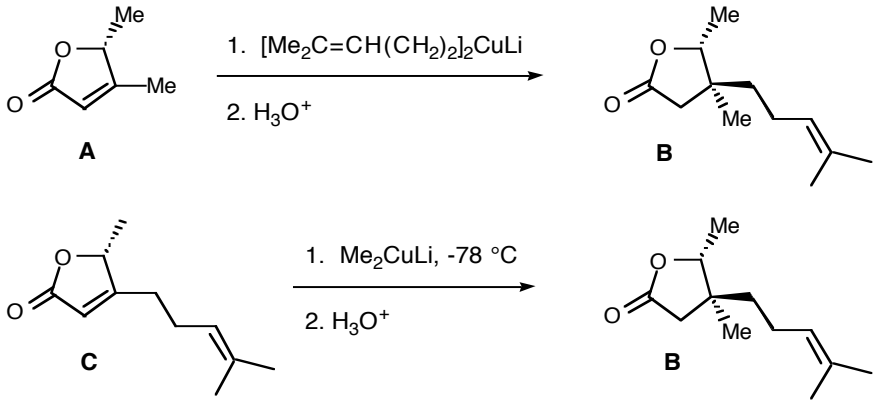


III. (20 pts) High levels of chirality transfer is found in reactions of (*Z*)-pentenylboronates with aldehydes. In contrast, additions of the isomeric (*E*)-pentenylboronates to aldehydes give a mixture of stereoisomeric products. Explain these observations in mechanistic terms. Be sure to show the key transition structures and point out any interactions which account for the stereochemical outcome of these reactions.

IV. (30 pts) A very short an efficient synthesis of (-)-furaqinocin C was published in late 1995. The last step in this synthesis was the coupling of **D** and the bromoquinone. The key step in this sequence is the Diels-Alder cycloaddition between the bromoquinone and the diene derived from **D**. (a) Provide a detailed mechanistic account of the entire sequence and (b) give a brief written explanation of the observed regiochemistry of the Diels-Alder step.



An interesting observation was made during this synthetic study. As expected when the long chain cuprate was added to unsaturated lactone **A** the cuprate added *anti* to the □-methyl group. Unexpectedly, when the dimethyl cuprate was added to unsaturated lactone **C** the major product was again **B**, with the cuprate adding *syn* to the □-methyl, (c) why?.


Me
O
O
Me
1. [Me2C=CH(CH2)2]2CuLi
2. H3O+
Me
O
O
Me

A **B**

O
O
1. Me2CuLi, -78 °C
2. H3O+
Me
O
O
Me

C **B**