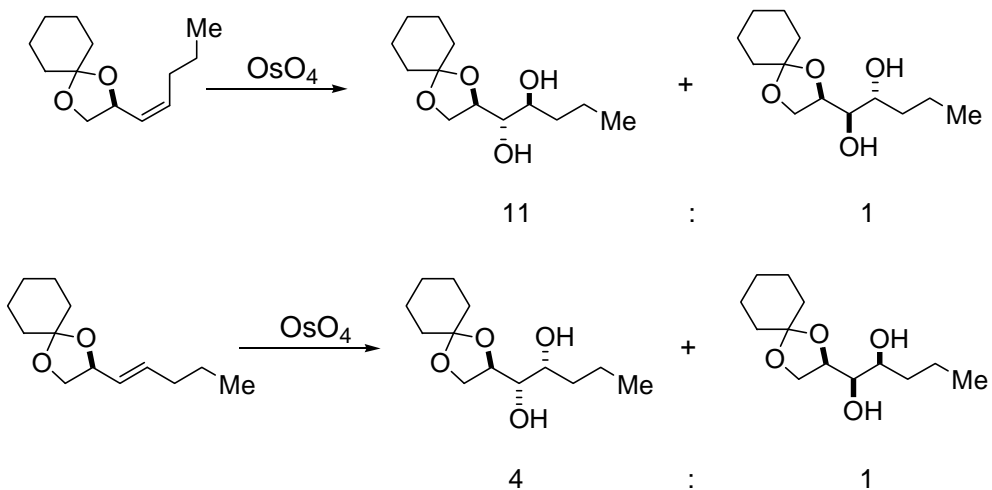


Problem Set No. 10 (16.7.2012)

1. Explain why the stoichiometric osmylation of the *cis*-olefin shown is more diastereoselective than osmylation of the *trans*-isomer.



2. a) Write the complete formula of the chiral ligand in AD-mix- $\alpha$  for the Sharpless dihydroxylation!

b) The asymmetric dihydroxylation of (*E*)-1-phenylpropene with AD-mix- $\alpha$  provides one product in high enantiomeric excess. Which enantiomer predominates? What is the oxidizing species in the Sharpless dihydroxylation?

3. a) Ethyl 4-pentenoate reacts with AD-mix- $\beta$  at the 4,5-double bond to give a compound which smoothly cyclizes to give a  $\gamma$ -lactone. Draw the structure of the major enantiomer of this product and protect the free hydroxyl group with a *tert*-butyldimethylsilyl group!

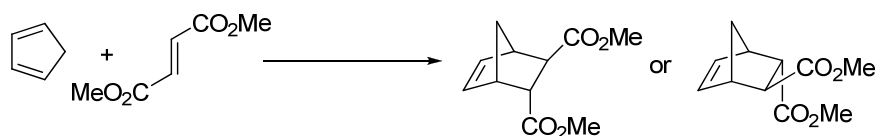
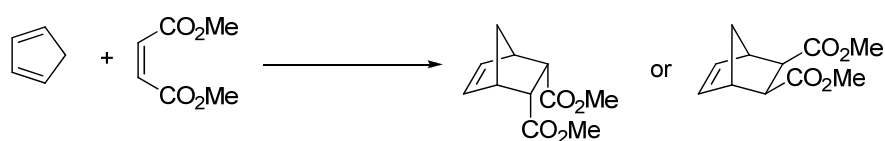
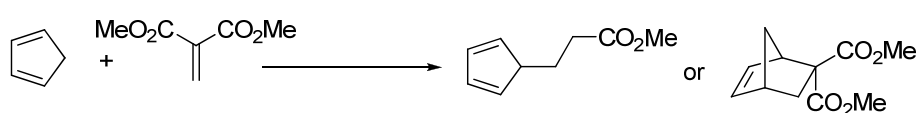
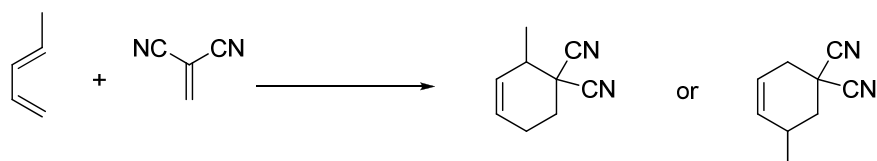
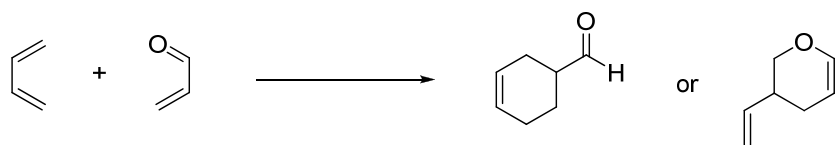
b) Deprotonation of the protected  $\gamma$ -lactone by LDA and treatment of the resulting lithium enolate with benzyl iodide will provide an alkylation product! Which major isomer do you expect?

4. a) What is 9-BBN and how is it prepared?

b) The hydroboration with 9-BBN of 7,7-dimethylnorbornene followed by oxidative work-up gives a high selectivity for the *endo*-alcohol! Explain this result!

c) The hydroboration/oxidation of (*R*)-3-methylcyclohexene with diborane provides four isomeric alcohols! With 9-BBN the reaction is slightly more selective giving only three products (*cis*-2-methylcyclohexanol is not formed). Explain these results!

5. The selectivity terms chemoselectivity, periselectivity, regioselectivity, diastereoselectivity and enantioselectivity can be assigned to the following (hypothetic) reactions giving two products! Please write the correct selectivity term to the appropriate equation!



6. 8-Phenylmenthol (enantiomer as given in the course) should be transferred into the corresponding ester of *trans*-2-butenoate! Suggest appropriate conditions for the ester formation! This product will react in the presence of  $\text{AlCl}_3$  with 1,3-butadiene with good selectivity. Draw the major isomer of this Diels-Alder reaction!

7. Draw the Evans auxiliary derived from L-valine and connect it to *trans*-2-butenate! This amide should react with cyclopentadiene in the presence of two equivalents of Et<sub>2</sub>AlCl. Draw the transition state of this Diels-Alder reaction and the major product!

8. In the presence of Cu(OTf)<sub>2</sub> and SbF<sub>5</sub> bisoxazoline ligand **A** catalyzes the Diels-Alder reaction of dienophile **B** with 1,3-butadiene. Draw the transition state of this reaction and the major product! If the oxazolidinone ring of **B** also bears a stereogenic center which of the two possibilities will be the matched case?

