Problem set 13
Chem 131/231 a

1. Make a model of cis- and trans-fused bicyclo[3.3.0]octane. Can you "feel" the strain? If you have access to the software, carry out a molecular mechanics calculation on each to determine the difference in strain energy. If you don't have the software, challenge yourself to look in the literature to find the accepted value. You should easily be able to think of several places to look.

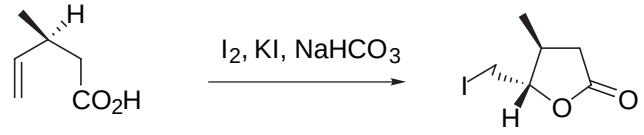
2. Make a model of the CBS catalyst. Convince yourself of the role of the methyl group appended to boron and the role of the endo-Ph substituent. Examine each of the modes of complexation between the carbonyl's two sets of lone pair electrons and the boron of the B-Me unit. Convince yourself that there are eight possibilities! Convince yourself that one of the eight ought to be of significantly lower energy. Which one is it?

3. Look at the transition state for hydride transfer from the activated form of the catalyst that is illustrated in Clayden, et.al. Using the molecular model you've constructed, do you think their formulation of a chair transition state is accurate? What alternative[s] is[are] possible?

4. Re. The PG chemistry we've been discussing in class: Use either the text's model [look at Bruckner's model, too] or one with which you feel more comfortable [perhaps your own slight variation of the textbooks?], to predict the stereoselectivity of the reduction at the pro-C_{15} carbon of the PG precursor enone.

5. Is the rationale for enantioselectivity a ground state argument? Is it based upon kinetic control? Is it based upon the relative energies of the diastereomeric transition states? Is it a thermodynamic argument? That is, is the product distribution determined by the thermodynamic stability of the products? For each of these queries, explain your thoughts.

6. Use the Houk model (pp. 895-ff of Clayden et.al.) to rationalize the stereochemical course of the following iodolactonization reaction.



7. Look again at
http://icg.harvard.edu/~chem117/files/L15/Lecture_15.pdf