1. Write the missing reactants, reagents, or products in the boxes. Make sure to indicate all stereochemistry as appropriate.

- **HOCl**
  - 1. BH$_3$ / THF
  - 2. NaOH, H$_2$O$_2$

- **3-phenyl-1-propene**
  - 1. BH$_3$ / THF
  - 2. NaOH, H$_2$O$_2$

- **Br$_2$**
  - CH$_2$Cl$_2$

- **5-methyl-1-hexene**
  - 1. Hg(OAc)$_2$ / H$_2$O
  - 2. NaBH$_4$

- **3-phenyl-1-propene**
  - 1. O$_3$
  - 2. Me$_2$S

- **3-phenyl-1-propene**
  - 1. O$_3$
  - 2. H$_2$O$_2$

- **C$_5$H$_{10}$O**
  - OH

- **C$_5$H$_{10}$O**
  - OH

1
2. Write the missing reactants, reagents, or products in the boxes. Make sure to indicate stereochemistry as appropriate.

- 1-methylcyclopentene
  1. Hg(OAc)$_2$/H$_2$O
  2. NaBH$_4$
  \[\text{OH}\]

- 3,3-dimethyl-1-pentene
  1.BH$_3$/THF
  2. NaOH, H$_2$O$_2$

- an alkene
  1. Hg(OAc)$_2$/H$_2$O
  2. NaBH$_4$
  \[\text{HOCl}\]

- an alkene
  KMnO$_4$
  \[\text{H}_2\text{O}\]

- HBr, peroxides
  (free-radical chain reaction)

- 1-methylcyclopentene
  \[\text{H}_2\text{SO}_4\]
  \[\text{H}_2\text{O}\]

- \[\text{H} \text{Br}, \text{peroxides}\]
3. Explain the following observations: Treatment of 4-methylcyclopentene with OsO$_4$ and H$_2$O$_2$ gives two diastereomeric meso compounds, while treatment of 4-methylcyclohexene with OsO$_4$ and H$_2$O$_2$ gives two diastereomeric racemic compounds.

b. The cyclic amine 1-chloro-2,2-dimethylaziridine can be resolved into enantiomers, but the acyclic amine chloroisopropylmethylamine (and other acyclic amines bearing three different substituents on nitrogen) cannot.

![1-chloro-2,2-dimethylaziridine](image)

![chloroisopropylmethylamine](image)

c. Treatment of styrene (Ph-CH=CH$_2$) with osmium tetroxide gives racemic 1-phenylethane-1,2-diol (Ph-CHOH-CH$_2$OH), but treatment of styrene with osmium tetroxide in the presence of a ligand (a compound that binds to a metal) derived from dihydroquinine gives optically active 1-phenylethane-1,2-diol.

![dihydroquinine](image)
4. The A value of a methyl group is 1.7 Kcal/mol, and that of the hydroxy group is ca. 0.7 Kcal/mol.

a. Make a drawing that best depicts the most stable conformation of cis-4-methylcyclohexanol.

b. Make a drawing that best depicts the most stable conformation of trans-4-methylcyclohexanol.

c. Make a drawing that best depicts the less stable chair conformation of cis-4-methylcyclohexanol.

d. Calculate the percentages of the two conformers of cis-4-methylcyclohexanol present at 298 K. (Note that R = 0.001987 Kcal / mol K.) Show your work.

e. In nonpolar solvents, cis-1,3-cyclohexanediol favors a chair conformation in which the two hydroxy groups are axial. Draw this conformation and provide an explanation for this interesting observation.
Problems 5-7 involve perhydroanthracenes.

5. Perhydroanthracene can be formed by the hydrogenation of anthracene.

![Chemical structure of anthracene and perhydroanthracene](image)

There are 5 diastereomers of perhydroanthracene, which are shown below.

![Diastereomers of perhydroanthracene](image)

The following six molecular models correspond to the stable conformers of these five diastereomers. Note: one of these diastereomers can adopt two different conformations, both of which are shown. Use PyMOL to view and rotate the models. The models are available at the website on the "Perhydroanthracenes" page, which is linked to the "Conformational and Stereochemical Models" page.

Model A. What diastereomer does this model correspond to? _______
Model B. What diastereomer does this model correspond to? _______
Model C. What diastereomer does this model correspond to? _______
Model D. What diastereomer does this model correspond to? _______
Model E. What diastereomer does this model correspond to? _______
Model F. What diastereomer does this model correspond to? _______

In which of these models are all of the cyclohexane rings in chair conformations? _____________________
In which of these models is at least one of the cyclohexane rings in a boat (twist-boat) conformation? ________________
6. As we have discussed in class, it's important to be able to make conformationally realistic drawings of structures containing cyclohexane rings. Draw the carbon skeletons of models A-F. Do not draw the hydrogens or the C-H bonds; just draw the C-C bonds.

A.  

B.  

C.  

D.  

E.  

F.
7. Which diastereomer is unstrained? ________

How many 1,3-diaxial interactions are present in the ct diastereomer? ________ Estimate how much higher in energy (enthalpy) it is than the unstrained one. ________

How many 1,3-diaxial interactions are present in the cac diastereomer? ________ Estimate how much higher in energy (enthalpy) it is than the unstrained one. ________

Estimate how much higher in energy (enthalpy) the tat diastereomer is than the unstrained one. ________

Explain why the two conformers of the remaining diastereomer are of roughly comparable energy. Hint: They are both very strained, but in different ways.______________________________________________________
__________________________________________________________________________________________
__________________________________________________________________________________________
__________________________________________________________________________________________

Two of the five diastereomers can be resolved into enantiomers. Which are they? __________ (Hint: all conformers of each diastereomer can interconvert rapidly.)
8.

a. Make conformationally realistic drawings of the tat, tsc, and cat stereoisomers of perhydrophenanthrene. Note that all rings are in the chair conformation.

(Hint - begin by drawing the middle ring, and then draw the left- and right-hand rings.)

b. How many 1,3-diaxial interactions are present in each diastereomer: ____ (tat); ____ (tsc); ____ (cat).

c. Estimate the relative energies (enthalpies) of the three diastereomers.

________________ (tat); ________________ (tsc); ________________ (cat).

d. Briefly show how you came up with these enthalpies.