Chem 220a

Problem Set 4

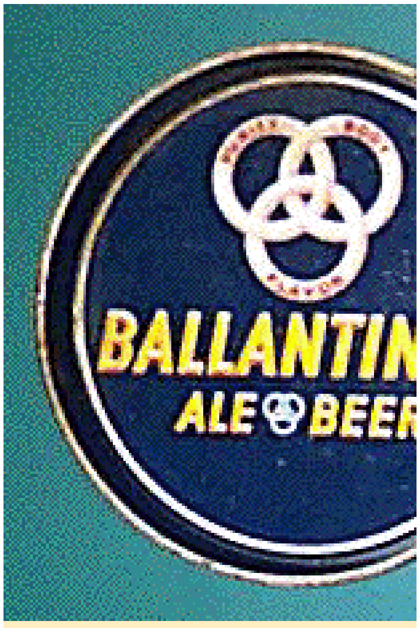
Chapter 5

Due: Monday, October 8, 2001

The Borremean Rings

Versions of this symbol date to the time of the Vikings. In the 15th century, it was apparently the symbol of a tripartite alliance of the Milanese families Visconti, Sforza and Borromeo via intermarriage. Break any (wedding?) ring and the others separate, hence the alliance is broken. The rings form a chiral object (left) that are not superimposable on their mirror image. A set of Borremean rings has been used as the logo for a certain refreshment that extols purity, body, and flavor. Is the sense of chirality of the two sets of Borremean rings the same or different? For some other examples, click here.

1) Read the stereoisomers module in the StudyAids and do the exercises. There is no need to record answers on your homework. Don't forget the Chirality of Shells (Powerpoint).



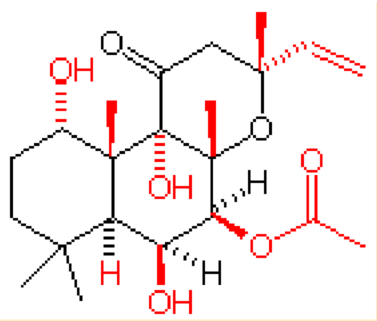
2) The naturally-occurring compound forskolin (**1**), $C_{22}H_{34}O_7$, is the stereoisomer shown.

a) Locate and name five different functional groups in **1**.

b) How many stereogenic centers are present in **1**?

c) Label each stereogenic center with the correct R/S configuration.

d) How many stereoisomers of **1** are possible, including **1**? Explain.



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e) The three rings of **1** are all in chair conformations that are incapable of flipping to their respective, alternate chair conformations. Why? [Review 3-16B in your text. Making a model of trans-decalin as suggested will be of great help.]

f) Given the information provided in 2e, assign equatorial or axial positions to each of the substituents designated in red. [Hint: In trans-decalin, the methine (tertiary) hydrogens are always axial.]

3) An optically-active compound **A** ($C_{10}H_{16}$, $[\alpha]_D = +124^o$) reacts with H_2 in the presence of a catalyst to provide compounds **B** and **C**. [Note: Hydrogen adds to double bonds under these conditions. Thus, ethylene is converted into ethane.] Both **B** and **C** show no optical rotation, even when the solutions are diluted, both compounds have the formula $C_{10}H_{20}$, and both compounds are 1,4-disubstituted cyclohexanes. Compound **B** has an energy difference of 3.8 kcal/mol between its two chair conformations.

a) With the aid of Table 3-5, determine the structures of **B** and **C**. Show your reasoning.

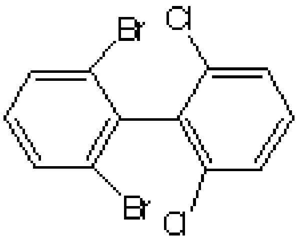
b) What is the energy difference between the two chair conformations of **C**? Show work.

c) Can the structure of **A** be determined from the information provided? If so, draw its structure, independent of which enantiomer it is. If not, draw structures that may fit the data.

d) A sample of **A** is isolated from mandarin oranges and it is found to have $[\alpha]_D = +62^o$. How much of the l-enantiomer is present in the sample? Show work.

4) Which of the following structures are capable of resolution at room temperature? Explain and illustrate.

a)



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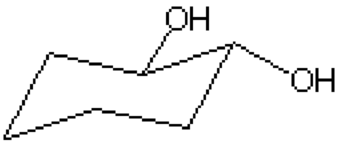
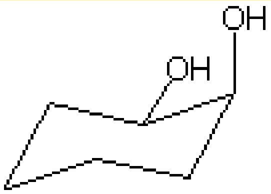
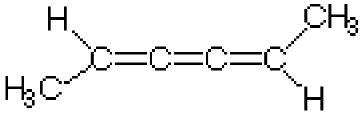


c)



d)



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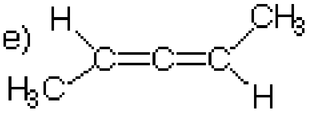
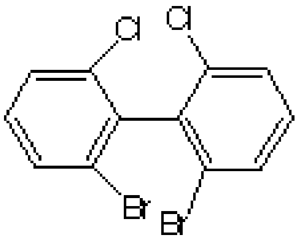
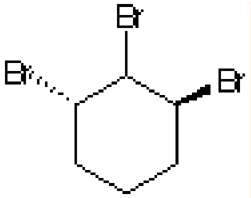


f)



5) The 1,2,3-tribromocyclohexane **1** is optically active yet there is no stereochemistry assigned to the C_2-substituent. Explain and illustrate.



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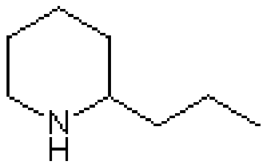
6) In 1886, Albert Ladenburg, synthesized the Socratic poison, coniine [2-propylpiperidine (**1**)], in racemic form. He resolved the racemate into its enantiomers using the reverse of the technique employed by Pasteur ~25 years earlier.

a) What did Ladenburg do?

b) Was he able to predict which enantiomer he would isolate in his very first experiment? Elaborate.

c) The enantiomer of coniine present in hemlock (*Conium maculatum L.*, *Umbelliferae*) is (S)-(-)-coniine, $[\alpha]_D = -18^o$. Draw the (S)-enantiomer of coniine.

d) Assume that Ladenburg obtained a sample of coniine on his first resolution that had $[\alpha]_D = +16^o$. What should he have concluded about his resolving agent? How much of each enantiomer would have been in his sample?



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Albert Ladenburg (1842-1911)