Chem 220a

Problem Set 4

Chapter 5

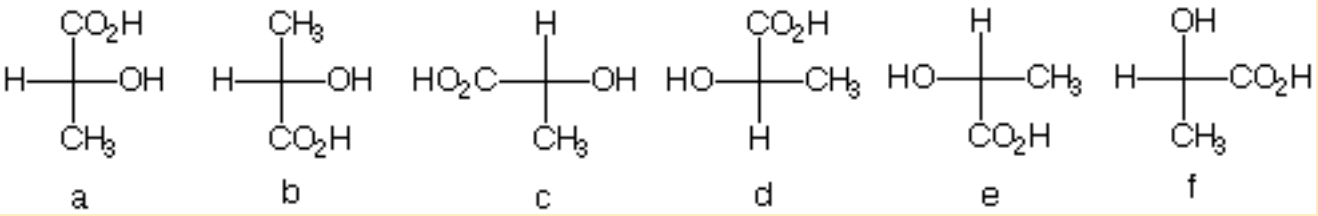
Due: Monday, October 7, 2001

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).

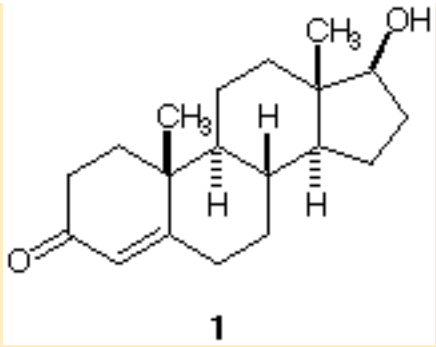
2. There are twelve possible Fischer projections for a given enantiomer of lactic acid. Why? (S)-(+)-Lactic acid, the cause of cramping after vigorous physical exercise, was isolated from human muscle by Berzelius. Which of the following Fischer projections represent (S)-(+)-lactic acid?



3. a) How many stereoisomers of testosterone (**1**; $[\alpha]_D = +109^o$) are possible? Explain.

b) What is the R/S designation for each of the chiral centers?

c) If the hydroxyl group of **1** were of the opposite configuration, would the compound still be optically active? Would it be expected to have the same melting point?



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4. (S)-α-Phellandrene ($[\alpha]_D = +86^o$) is a monoterpene with the characteristic fragrance of dill. Monoterpenes, which are C_{10} compounds, are dimers of two branched C_5 compounds (structure **1**). (S)-α-Phellandrene reacts with 2 moles of hydrogen gas in the presence of Pd to give two cyclohexanes **A** and **B**, both of which have the formula $C_{10}H_{20}$ and both of which are optically inactive. Compound **A** has an energy difference of 0.4 kcal/mol between its two chair conformations while compound **B** has a value of 3.8 kcal/mol for the same equilibrium. Explain the loss of optical activity, the energy differences, and identify the structures **A** and **B**.

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5. (R)-α-Phellandrene has been reported to have a specific optical rotation of -217^o. This observation suggest that the sample of the enantiomer used in problem 4 above is contaminated. Assume that the contaminant is the (R)-enantiomer. What percentage of each enantiomer is present in the sample of problem 4? Show work.

6. A partially racemized compound ($[\alpha]_D = 48^o$) is analyzed by chromatography using a chiral support and it is shown to be a 2:3 mixture. Why is this technique possible? What are the rotations of the pure enantiomers? Which one is the minor isomer? What is the ee?

7. Free radical chlorination of (R)-1-chloro-2-methylbutane leads to how many constitutionally isomeric dichloro compounds? What are their structures? Which ones, if any, form diastereomers? Which ones are optically active? Which ones are optically inactive?