Chem 220a

Problem Set 4

Chapter 5

Due: Monday, October 2, 2005

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.

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).

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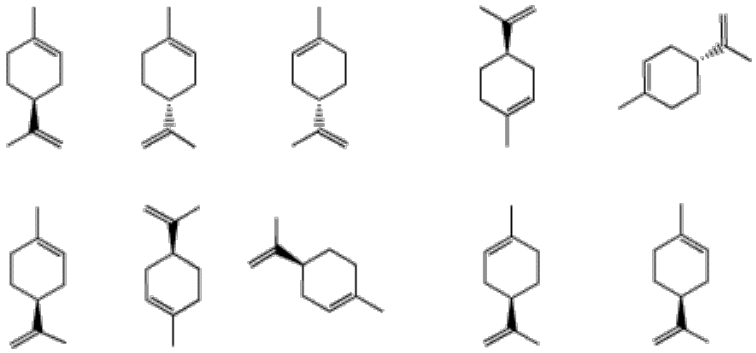
1. When (R)-1-chloro-2-methylpentane is subjected to free radical chlorination, eight dichloro compounds are possible.

a) Draw them and name them with the appropriate R,S-descriptors.

b) Two of the dichlorides are optically inactive. Which ones are they? Explain and illustrate.

2. Terpenes are naturally occurring compounds that are comprised of multiples of the C_5 unit isoprene (it looks like 2-methylbutane). Limonene is a monoterpene that occurs as both enantiomers in nature. The (*R*)-enantiomer has an orange, citrus-like aroma while the (*S*)-enantiomer has a harsher, lemony fragrance.



a) Of the limonenes shown on the right, identify the R and S enantiomers.

b) (R)-Limonene (d-limonene) is reported to have a rotation of $[\alpha]_D$ 123.8°. Its enantiomer is reported as $[\alpha]_D$ 101.3°. Assume that the enantiomer with the lower rotation is contaminated with the other enantiomer, calculate the percent of (+)- and (-)-enantiomers in the sample.

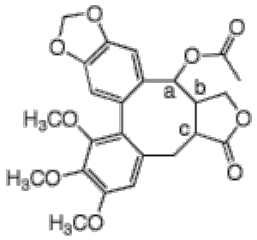
c) When compounds containing double bonds are treated with H_2 in the presence of a noble metal catalyst, hydrogen is added to the double bond. In the case of (R)- and (S)-limonene, compounds **A** and **B** are formed, both with the formula $C_{10}H_{20}$. Are **A** and **B** formed in the same ratio?

d) The energy difference between the chair conformations of **A** is greater than the energy difference of the chair conformations in **B**. What are the structures of **A** and **B**? What are the energy differences? Explain and illustrate the equilibria involved. Show work. [Use values posted on the Bulletinboard.]

3. Steganacin (**1**), an optically-active, naturally-occurring lignan lactone, is active against certain cancer cell lines. Steganacin has three asymmetric carbons labeled a, b, and c, all of the (*R*)-configuration.

a) Draw steganacin with its absolute stereochemistry.

b) One might argue that there are eight possible stereoisomers of **1**. There are, in fact, sixteen because **1** has the property of atropisomerism. Draw the two possible stereostructures for **1**. Why do they not interconvert?



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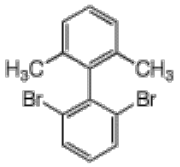
4. a) 1,2-Dibromoethane is optically inactive yet it has a dipole moment . Explain and illustrate.
b) meso-Tartaric acid exists in three staggered conformations, none of which has a plane of symmetry. Yet the compound is optically-inactive. Explain and illustrate.

5. a) Which of the compounds on the right are, in principle, capable of resolution? Explain and illustrate.

b) Why is no stereochemistry shown for the middle bromine in structure 5?



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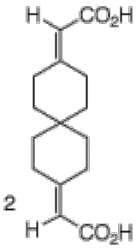

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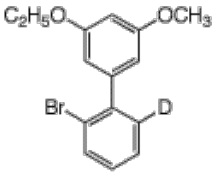

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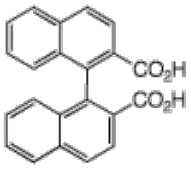

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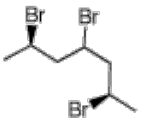

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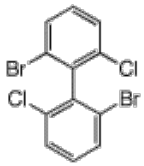

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6. A mixture of enantiomers contains 1-1/2 times more of one and shows $[\alpha]_D$ -25.0^{o}. What are the rotations of the pure enantiomers? Which one is in excess?