Chem 220 - Organic Chemistry

Problem Set 4, Solution Set

Chapter 5, Stereochemistry

Due: Monday, October 4, 2010

The Borremean Rings

Versions of this symbol date to the time of the Vikings. In the 15th century, it was 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 is not superimposable on its 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 discourses on chirality, see:

Potpourri

The Figure 8 Knot

Gentlemen's Neckties

Molecular Knots

Snails and Crabs

Snails, Snakes and
Darwin (html) 1 2
(pdf) 1 2

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). Do left-handed whelks have a better survival rate than their mirror image brethren? Click here.

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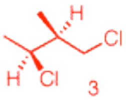
1. When (*R*)-1-chloro-2-methylbutane undergoes free radical chlorination, five dichloro constitutional isomers are formed. What are these structures? Draw them. Be explicit as to diastereomers, enantiomers, racemates, etc.
The five constitutional isomers (different atom connectivity) are: 2, (3, 4), 5, 6 and 7. Still optically active: 2 (R), 3 (2S, 3S), 4 (2S, 3R) and 5 (R). Notice in 3 and 4, which are diastereomers, the (R, S)-configuration has changed at C_2 *from the monochloro compound although the asymmetric center has not been altered. This is a change in group priority. #6 is racemic because abstraction of the tertiary hydrogen in the first propagation step creates a planar radical. In the second propagation step, chlorination occurs with equal facility on either face of the planar radical. #7 is achiral; two identical groups, -*CH_2Cl*, in the molecule.*

2



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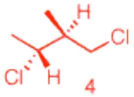

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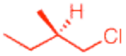

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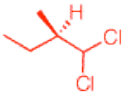

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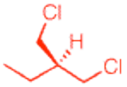
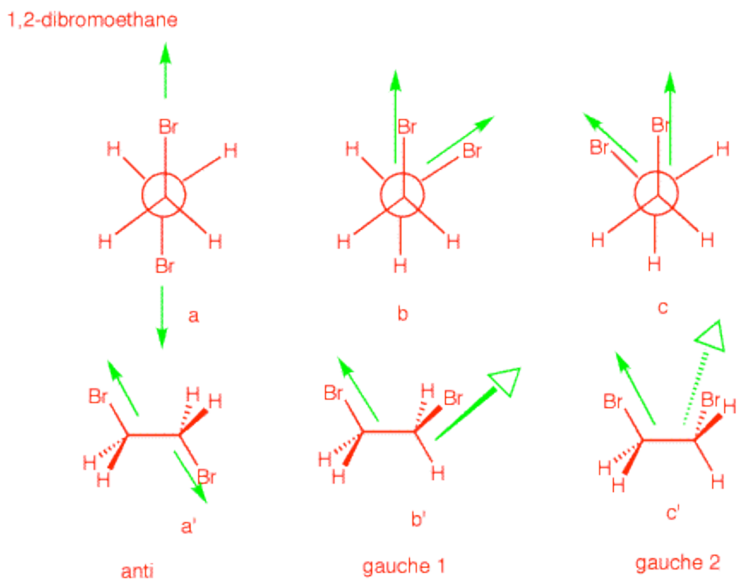


7

2. A 4:1 mixture of enantiomers has $[\alpha]_D = +120^{o}$. What is the rotation of the levorotatory enantiomer? The dextrorotatory enantiomer? Show work. *Because the net rotation is positive, the major enantiomer must be dextrorotatory; the minor one, levorotatory. A 4:1 mixture is 80% dextro-, 20% levo. Thus, +120 = 0.80x(+rot.) + 0.20x(-rot.); +120 = 0.60x(+rot.); +rot. = 120/0.60 =* $+200^{o}$ *for the dextrorotatory enantiomer;* -200^{o} *for the levorotatory enantiomer.*

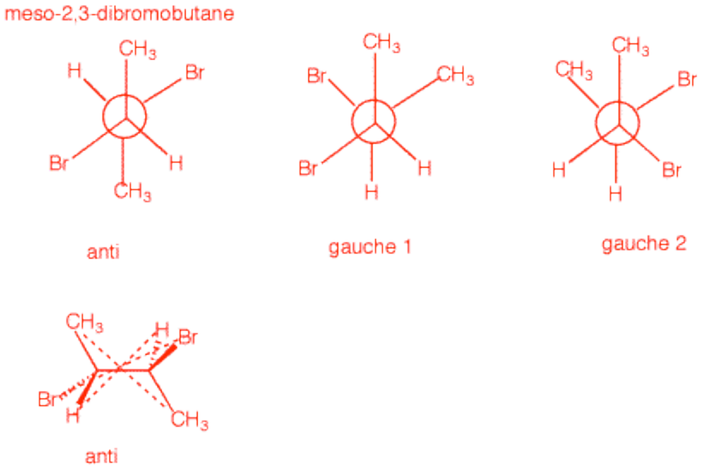
3. a) 1,2-Dibromoethane is optically inactive yet it has a dipole moment. Explain and illustrate. [Hint: Draw the staggered conformations and assess optical activity and dipole moment for each.]
Optical activity is an algebraically

Optical activity is an algebraically additive property; dipole moments are cumulative in nature. The three staggered conformations of 1,2-dibromobutane are shown on the right in both Newman projections and sawhorse views. The anti conformation has no net dipole. The bond dipoles cancel. [Only the green C-Br bond dipoles are shown.] The two gauche conformations have net dipoles. The vector sum of the bond dipoles gives the molecular dipole. As to optical activity, the anti conformation is achiral [center of symmetry]. The gauche conformations are chiral and form a racemate. No net optical activity.

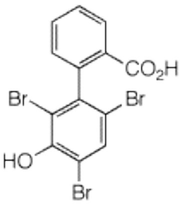


b) meso-2,3-Dibromobutane exists in three staggered conformations, none of which has a plane of symmetry. Yet the compound is optically-inactive. Indeed, the only conformation that has a plane of symmetry is quite unstable. Explain and illustrate.

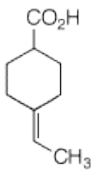
Gauche 1 and 2 form a racemic pair (external comparison). The anti conformation has a center of symmetry at the center of the C_2-C_3 bond (internal comparison). The eclipsed conformation of the meso compound in which all groups are paired is unstable. The eclipsed conformation is used as a test of whether or not there is a plane of symmetry in the the molecule.



4. Which of the following compounds are, in principle, capable of resolution? Explain and illustrate. [For 3-D Jmol views of these structures click here.: a, b, c, d, e, f.]



a



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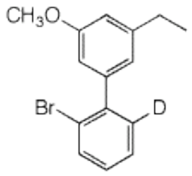

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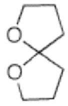

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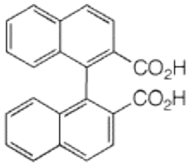

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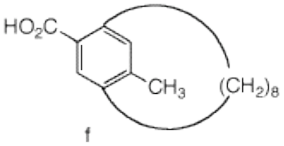


f

5a) This biphenyl is not planar owing to the three large groups (Br, Br, CO_2H) at the ortho positions that inhibit planarity. The two rings are orthogonal to one another thereby producing two non-superimposable mirror images.

b) This compound can be resolved. Imagine that the CO_2H group is above the plane of the molecule. Draw its mirror image. They are not superimposable. The double bond and the 6-membered ring are an extension of the cumulated double bonds in the resolvable 1,3-disubstituted allenes.

c) Not resolvable. Free rotation about the biphenyl bond is too rapid for resolution. No different from ortho-bromobiphenyl.

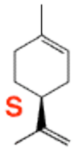
d) Resolvable. Similar to trans-cyclooctene. Not superimposable on its mirror image. This compound is not planar but tetrahedral at the carbon bearing the two oxygens.

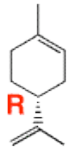
e) Resolvable. Same as 5a.

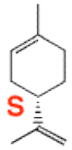
f) Eight CH_2 groups in a row are just enough to span the aromatic ring. Neither the CO_2H nor the methyl group can pass through the large ring to effect racemization. Cf.; trans-cyclooctene. The compound is resolvable.

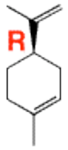
5. Terpenes are naturally occurring compounds that are comprised of multiples of the C_5 unit isoprene (it looks like 2-methylbutane). Limonene is a monoterpene that occurs as both enantiomers in nature. The (*R*)-enantiomer has an orange, citrus-like aroma while the (*S*)-enantiomer has a harsher, lemony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

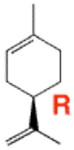
a) Of the limonenes shown, identify the R and S enantiomers.











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. *d-Limonene is* +123.8°, by definition*; l-limonene is* -101.3°. *Let* n_d *= mole fraction of d-limonene and* n_l *the mole fraction of l-limonene. Then* $n_l = 1 - n_d$ *and* $[\alpha]_d = -[\alpha]_l$

Now, $[\alpha]_{obs} = n_d([\alpha]_d) + (1-n_d)([\alpha]_l)$

and $[\alpha]_{obs} = n_d([\alpha]_d) + (1-n_d)(-[\alpha]_d)$

gives $[\alpha]_{obs} = ([\alpha]_d)(2n_d - 1)$ [Note: $2n_d - 1$ = ee = op]

rearranging $(([\alpha]_{obs}/[\alpha]_d) + 1)/2 = n_d$

and $n_d = ((101.3/123.8) + 1)/2 = 0.91$ = 9.1% d-limonene and 90.9% l-limonene.

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*)-limonene, two compounds, **A** and **B** (both $C_{10}H_{20}$), are formed. Are they necessarily formed in equal amounts? Explain. *No. The two compounds are cis- and trans-1-isopropyl-4-methylcyclohexane. Both are achiral.*
Is the ratio **A/B** different when (*S*)-limonene is used? Explain. *No, the ratio is the same. It is the mirror image procedure.*

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? Go here for data. *See below. Incidently, at 27°C,* ***A*** *has* $K_{eq} = 610$; ***B*** *has* $K_{eq} = 1.6$.