Chem 225b - Comprehensive Organic Chemistry

Problem Set 3

Chapter 4

Due: Monday, February 11, 2008

The Baeyer Laboratory, Munich, 1893

(This photograph is in the hallway across from 110 SCL)

- Adolf von Baeyer (1835-1917); Nobel Prize 1905. (center, seated with derby), who was a student of Kekulé, succeeded Liebig at Munich. In the photograph (second row; third from right) is Henry Lord Wheeler (1867-1914); Yale Faculty 1896-1911. As was the custom in the 19th century, many Americans, such as Wheeler, would do advanced study in chemistry in Europe. Karl, is the laboratory assistant. (The only person wearing an apron and no tie; upper left.)

  In 1885, as an addendum to a paper on acetylenic compounds, Baeyer proposed that cyclopentane was the least strained of the cycloalkanes. While he accepted the idea that the carbon atoms in cycloalkanes were tetrahedral, he treated the cycloalkanes as though they were flat. He argued that there is only one cyclohexane carboxylic acid, not two (axial and equatorial) as was predicted by a chair cyclohexane.

- Equatorial is frequently misspelled.
- A Projection of Melvin Newman (Son of Yale: 1929, BS; 1932, PhD)

Reading and Enrichment Assignments:

a. Work through How to Draw Cyclohexanes (PowerPoint)

b. Visit the Conformation Module in the Study Aids for cycloalkanes

c. Cultural Enrichment: The Evolution of Formulas and Structure in Organic Chemistry During the 19th Century (PowerPoint).

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1. Compound **A**, a 1,4-disubstituted cyclohexane, contains 22.08% chlorine.

    a) Determine the formula of **A** and the formula of the remaining substituent in **A** from the information in the lead sentence.

The difference in conformational energy for the two chair conformations of **A** is 1.68 kcal/mol.

    b) Using the data in Table 4-3, page 145, determine the structure of **A**. Illustrate and explain.

    c) Estimate the conformational (lower limit) if the substituent had been attached differently (only one other way). Illustrate and explain.

    d) What is the conformational energy difference for the stereoisomer of **A**, ---namely **A'**. Explain and illustrate. Show the chair comformations of **A** and **A'** with the appropriate equilibrium arrows to illustrate the major and minor conformations. Label each conformation with its energy.

2. Explain why cyclohexane is the least strained cycloalkane based upon heats of formation.

3. Check out the structure of limonene on Wikipedia (don't worry about the issue of (+)-limonene or (*R*)-enantiomer.) While the 2-D structure is truthful, the 3-D version contains only "truthiness" (Wikipedia this!). What would be a better

presentation? Your 2-D version of your 3-D revision must be able to be superimposed on the original 2-D version of limonene.

4. Hydrogenation of limonene produces cycloalkanes **A** and **B**, both $C_{10}H_{20}$. Compound **A** has the lower heat of formation.

a) Draw the conformational equilibrium for each of these compounds.

b) Determine the energy difference for each equilibrium and designate the more stable conformation in each equilibrium.

c) Draw the most stable arrangement of the larger substituent when it is in the equatorial position.

5. *cis*-Decalin is ~2.6 kcal/mol less stable than *trans*-decalin (pg. 150) where a gauche butane interaction is worth 0.85 kcal/mol (one-half the value of CH_3 in Table 4-3). [Hint: If you focus on axial substituents, you will probably get too large an answer. Think about the real source of the interactions.]

a) Explain and illustrate.

b) What is cis-decalin capable of doing that the trans-decalin cannot do?

Consider the structure of cholic acid (pg. 154). It contains both a cis- and trans-decalin.

a) Redraw the structure on pg. 154 and label them.

b) Why is the cis-decalin not capable of conformational inversion? (Make a stripped down version of the A-B-C ring system with your models to help yourself.)

c) Label all the methyls, hydroxyls and hydrogens attached to 6-membered rings in the picture as equatorial or axial.

d) Draw cholic acid as a 3D-structure (vide supra, pg. 154). Use the letter "R" for the carboxylic acid side chain.

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