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 <u>Conformation Module</u> in the Study Aids for cycloalkanes

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

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1. Using the <u>heats of formation tables</u>, explain the difference in the heats of formation of cis- and trans-1,4-dimethylcyclohexane. What are the heats of combustion of these stereoisomers? Show work. Draw a diagram of the heats of formation and combustion for these stereoisomers relative to the standard state. Put your values on the chart.
2. Compound **A** (MW=142.19), a 1,4-disubstituted cyclohexane, has the following composition: C, 67.57%; H, 9.92%. The difference in conformational energy for the two chair conformations of **A** is 0.3 kcal/mol. Using the data in Table 4-3, page 142, determine the structure of **A**. Illustrate and explain. 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.
3. There are seven dimethyl cyclohexanes. Draw them as an equilibrium of both their chair conformations. Calculate the energy between the chair conformations for the seven equilibria.
4. *cis*-Decalin is ~2.6 kcal/mol less stable than *trans*-decalin (pg. 146) where a gauche butane interaction is worth 0.85 kcal/mol (one-half the value of CH_3 in Table 4-3).

a) Explain and illustrate.

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

5. Consider the structure of cholic acid (pg. 150). It contains both a cis- and trans-decalin.

a) Redraw the structure on pg. 150 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. 150). Use the letter "R" for the carboxylic acid side chain.

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