Chem 220a - Organic Chemistry

Problem Set 2

Chapter 3

Due: Monday, September 20, 2004

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 custonm 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. The Conformation Module in the Study Aids will give you a good overview of the subject of conformation. Work your way through it.

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

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1. Redraw (line angle formula) and name (IUPAC) the hydrocarbon in this problem. For a dynamic view click here. For a static view click here.

2. There are four principle conformations of n-pentane (relative energies) resulting from rotation about the two interior C-C bonds: anti-anti (0 kcal/mol); anti-gauche (0.9 kcal/mol); gauche-gauche (1.8 kcal/mol); and gauche-gauche (syn-pentane, 3.8 kcal/mol). Draw each of these conformations of pentane and rationalize the energies of the first three of these. Why is the syn-pentane conformation the least stable? Given the above data, determine the energy of each of the chair conformations of cis-1,3-dimethylcyclohexane and the energy difference between the two conformations. [Molecular models will be a big help.]

3. There are four different 1,2,4-trimethylcyclohexane isomers (exclusive of mirror images). Draw each one in its more and less stable conformation. Determine the energy of each conformation and the difference in energy for the four pairs.

4. Four disubstituted cyclohexanes (MW=140; C = 85.7%, H = 14.3%) each have two chair conformations of equal energy. What are their structures? Explain and illustrate. [Correct version of this problem posted Friday, 9/17, 11:00 AM].

5. Given the molar heat of combustion of cyclohexane at 25°C in Table 3-5 of the text and the heat of combustion at the same temperature of graphite and hydrogen given here and here,

a) Determine the heat of formation of cyclohexane. Illustrate and calculate.

b) How does your answer compare with the answer given here?

c) Since Table 3-5 shows that cyclohexane is strain free, determine the heat of formation of an unstrained methylene (-CH_2-) group. Illustrate and calculate.

d) Compare your answer with the normal alkanes butane through octane shown here.

6. Determine the energy of the staggered and eclipsed conformations of 2,3-dimethylbutane using Newman projections. Show work. What is the difference in the heat of formation of the isomers n-hexane and 2,3-dimethylbutane? Use this Table. What is the difference in the heat of combustion of these two isomers? Illustrate.