Comprehensive Organic Chemistry - Chem 225b

Problem Set 2

Chapters 2 & 3

Due: Monday, January 30, 2006

The Conformation Module in the Study Aids will give you a good overview of the subject of conformation. Work your way through ethane, propane, and butane.

The alkane module in ORGO will be of assistance in solving some of these problems.

The Heats of Reaction module (StudyAids/thermochemistry) will of assistance.

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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. Calculate the energy of the three staggered and three eclipsed conformations of 2,3-dimethylbutane about the C_2-C_3 bond.

3. The free radical chain chlorination of 2-methylbutane leads to four monochloro constitutional (structural) isomers. Using the values for the relative reactivity of primary (methyl), secondary (methylene) and tertiary (methine) hydrogens --- 1:4:5, respectively ---, calculate the expected percentage of each isomer. Draw their structures and name them.

4. Consider the free radical bromination of neopentane (2,2-dimethylpropane).

a) Illustrate the initiation and propagation steps.

b) Provide the enthalpies of the propagation steps and the heat of the overall reaction. BDEs are here.

c) Why was the enthalpy of the initiation step ignored?

d) Draw a reaction coordinate diagram (energy vs. reaction coordinate) for this process. Label the enthalpies and activation energies. Which of the two activation

energies is lower. [Does your diagram comply with the Hammond Postulate?]

e) Determine the heat of formation of gaseous 1-bromo-2,2-dimethylpropane (neopentyl bromide) using heats of formation located here.

5. There is a regular increment in the heats of combustion and the heats of formation in the gas phase of the straight chain alkanes. Look here.

a) Determine these two increments. Show work.

b) Show how these increments agree with the combustion of a methylene group, -CH_2-.

c) Complete the Table for C_{11} - C_{19} odd.