Organic Chemistry - CHEM 331A

Problem Set #2

Due 10/11/2000

1. Using only chair conformations, make and draw molecular models for all of the 1,4–dibromocyclohexanes. Clearly indicate which are related as conformational isomers and which are related as configurational isomers. Designate the configurational isomers as *cis* or *trans*. **Explain** which isomers equilibrate rapidly with each other (interconvert).

2. The addition of HBr to 2–methylpropene can, in principle, give either 1–bromo–2–methylpropane or 2-bromo-2-methylpropane. In practice, only the latter is formed. Show mechanisms for the formation of each of these alkyl bromides, using curved arrows to indicate the movement of electron pairs. Also, construct reaction energy diagrams that describe the energy of the system as a function of the progress of the formation of each alkyl bromide. Use these reaction coordinate diagrams to **explain** why 2-bromo-2-methylpropane is the only product.

3. The cyano group (–CN) can be hydrolyzed to a carboxylic acid group (–CO_2H). During this complex process, the steric size increases relative to that of the original cyano group. Any steric interaction of the cyano group with the rest of the molecule would tend to slow down its hydrolysis. Draw the most stable conformation for *cis*– and for *trans*–4–t–butyl–1–cyanocyclohexane and, on the basis of the above information, predict which isomer would hydrolyze most rapidly. Construct a reaction energy diagram that illustrates your analysis.

4. The addition of Br_2 to cis 4-t-butyl-5-methylcyclohexene yields predominantly one stereoisomeric compound.
   a. What is the general reaction that is occuring?
   b. What is the specific reaction for the given starting material and what are the possible products?
   c. Which product is the major product?
   d. Using the mechanism of the reaction and an energy diagram, explain your answers.