DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA

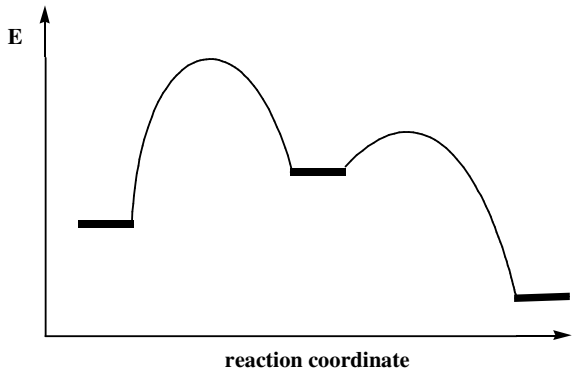
CHEMISTRY 241, Fall 2007

ORGANIC CHEMISTRY WORKSHOP

Problem Set III.

1. The heat of combustion of *cis*-1,2-dimethylcyclopropane is larger than that of the *trans* isomer. Which isomer is more stable? Use drawings to explain this difference in stability.

2. Consider the following reaction-energy diagram.



   a) Label the reactants and the products.
   b) Label the activation energies for the first and the second step.
   c) Label the transition states.
   d) Is this reaction exothermic or endothermic? Label the ΔH^0 of this reaction.
   e) Which of the steps is the *rate-determining step*?

3. Compounds **A** and **B** can react at a certain temperature to give compound **C**, the *rate-controlled (kinetic)* product. At a higher temperature they give **D**, they may react differently to form a *thermodynamically-controlled* product. Use an enthalpy diagram to explain this behavior and indicate the relative temperatures needed.

4. It is widely known that only a few radical halogenation reactions are used in practice due to their low selectivity. Chlorination reactions of certain higher alkanes, however, can be used for laboratory preparations. Examples are the preparation of *neopentyl chloride from neopentane* and *cyclopentyl chloride from cyclopentane*. What structural feature of these molecules makes this possible?

5. For each compound shown below, predict the major product of free-radical bromination and give the IUPAC name of the products. (Hint: Please note that bromination is highly selective and only the most stable radical will be formed.)

   a) cyclooctane
   b) methylcyclohexane
   c) 3-methyloctane
   d) propylbenzene
   e) 1,2-dimethylcyclopentene
   f) decalin (decahydro-napthalene)

6. The light-catalyzed reaction of cyclopentene with a low concentration of bromine gives exclusively 3-bromocyclopentene. Propose a mechanism to explain this preference of substitution.

7. When CH_3Br reacts with NaCN, the major product is CH_3CN, but some CH_3NC is formed as well. Write the Lewis structure for both products and explain this finding.