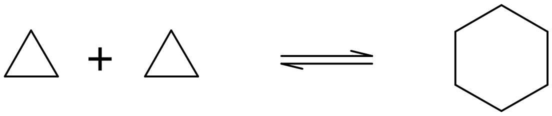
Chem 201, 2009
HW #5, due Th, Nov 5, 12 PM

ANSWERS

1. A. Using the heat of formation data in your book, estimate ΔH_{rxn} for the following reaction:

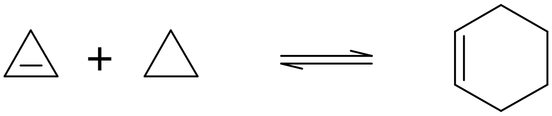


The book gives heats of formation <u>*per methylene*</u> *group. The values for cyclopropane and cyclohexane are +17.8 and -16.9 kJ/mol, respectively. The heat of reaction would be the difference in these values (-16.9 – 17.8) multiplied by 6, or* ***-208 kJ/mol****. The reaction is* ***very exothermic.***

B. Bond energies suggest this reaction should be thermoneutral, so how do you account for your answer in part A?

The energy that is released in this reaction is due to ***angle strain in the reactants****. Strain destabilizes a molecule.*

C. Bond energies suggest the following reaction should also be thermoneutral, but $\Delta H_{rxn} \approx$ -334 kJ/mol. How do you account for this? (Make sure you compare this value to the one from part A as part of your answer.)



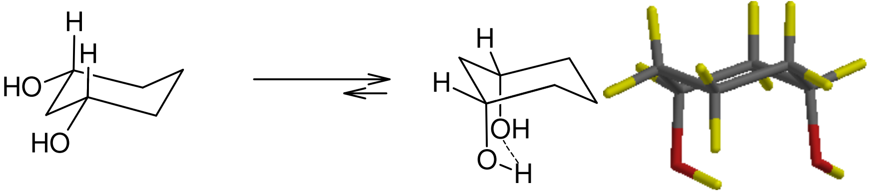
The reactants are destabilized by angle strain. The product is destabilized by angle strain too, but the bond angles in the reactants deviate from their ideal values (109^o and 120^o) to a much greater extent.

The reaction is analogous to, but ***much more exothermic*** *than, the reaction shown in part A. This suggests that* ***cyclopropene is much more strained than cyclopropane****. Again, this is expected since two of the bond angles in cyclopropene (~60^o) deviate from their ideal angles (120^o) to a greater extent than the bond angles in cyclopropane (60^o vs. 109^o)*

2. To explain the following phenomena, you need to invoke the interatomic forces discussed in chapter 8.3.

   A. The diaxial conformation of *cis*-1,3-cyclohexanediol is more stable than the diequatorial conformation. Why? Provide a drawing that supports your answer.

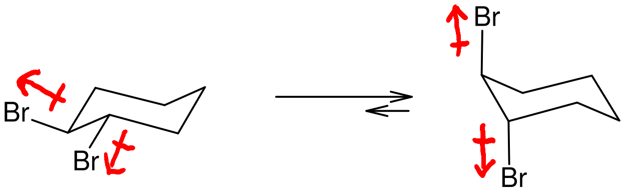
   The diaxial conformation is stabilized by an intramolecular hydrogen bond.



   B. The diaxial conformation of *trans*-1,2-dibromocyclohexane is more stable than the diequatorial conformation. Why? Again, a drawing might be useful.

   We are used to thinking about steric repulsion, but it turns out that this plays only a modest role here because the C-Br bond is very long so each Br is relatively far from the other atoms that might create steric repulsion with it.

   On the other hand, there is a bond dipole associated with each C-Br bond. This dipole is significant because, even though the partial charges are small, they are separated by a large distance. The diequatorial conformation aligns the dipoles in similar directions, putting the negative end of one dipole near the negative end of the other, and is destabilized. The diaxial conformation aligns the dipoles in opposite directions and is stabilized. As a general rule, in the absence of other competing effects, ***conformations with smaller dipole moments are preferred****.*

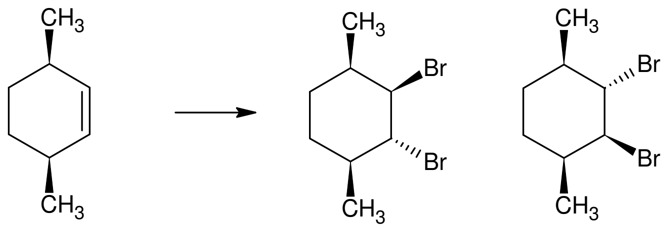


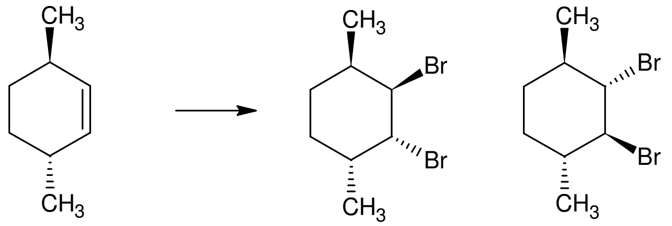
3. An optically active mixture of *trans*- and *cis*-3,6-dimethylcyclohexene is treated with Br_2 in CCl_4.

   A. Which cyclohexene is responsible for the optical activity? Arbitrarily choose one enantiomer of this cyclohexene for part B.

   The trans isomer is chiral. The cis isomer is achiral. The trans isomer is optically active.

B. Draw all of the product(s) that will be obtained from each cyclohexene (no conformations needed, just planar structures with stereochemical symbols).





C. Will the product mixture be optically active? Explain.

Yes. The achiral cis isomer gives a racemate (see above). The optically active trans isomer gives a mixture of optically active diastereomers.

5. The preferred geometry of 12-crown-4 is shown below from two points-of-view along with a space-filling model (size is reduced 25% to make it fit on page). The OCCO dihedral angles are 83° if you would like to build a plastic model. What notable feature of the usual drawing of 12-crown-4 (Loudon, p. 351) actually is missing in the model?

   *To figure out what structural feature is "notable", you must pay attention to what properties of 12-crown-4 are "notable". The relevant "notable" property is the ability of this crown ether to bind cations. The drawings on p. 351 and adjoining pages all suggest that cation-binding occurs when the cation sits inside a **cavity surrounded by oxygens**. The drawings of crown ethers on p. 351 do not show cations, but they still position the oxygen atoms in a way that suggests the availability of such a cavity. However, as the model shows, **no such cavity exists.** Not only does the molecule prefer a more compact shape (when cations are unavailable), it also prefers to orient the C-O-C groups so their dipoles do not point directly at one another (see problem #2B for another example of dipole-dipole interactions).*