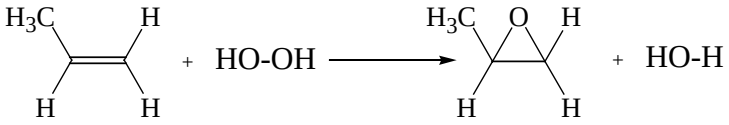
**Chemistry 891G** **CORE COURSE** **Fall 2002**

## QUIZ #1 (100 points)

**Answer all questions as completely as you can. Clearly show your work and reasoning.**

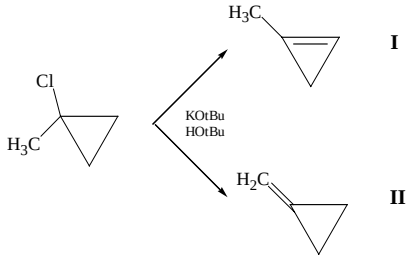
1. Epoxidation is a typical reaction of alkenes. Use the bond energies given below to estimate the exothermicity of a hypothetical catalytic epoxidation of an alkene by hydrogen peroxide. (50 pts)




ΔE(C-C) = 85 kcal/mol, ΔE(C-O) = 87 kcal/mol, ΔE(C=C pi) = 65 kcal/mol, ΔE(O-O) = 51 kcal/mol, ΔE(O-H) = 119 kcal/mol, ΔE(C-H) = 98 kcal/mol, three-ring strain = 27.6 kcal/mol.

ΔH(reaction) = -enthalpy of product bonds made + enthalpy of reactant bonds broken
so, consider the NET bonds formed and broken, to get
= {–2(C-O) – (O-H)} + (C=C + O-O + O-H} (three bonds made, three bonds broken) + strain
= -2(87) - (119) + 27.6 + 65 + 51 +119 + 27.6 {strain is + on products side, anti-enthalpic)
= -30 kcal/mol, a substantially exothermic reaction, despite three ring formation

2. Use the Benson equivalent data to estimate the difference in energy between products **I** and **II.** (35 pts). Product **II** is isolated from the reaction. Does this fit the pseudothermodynamic model (briefly explain using a diagram that shows the relative energies of **I** and **II**)? (15 pts)




| | | | |
|---|---|---|---|
| C(H)3(Cd) | -10.1 | C(H)2(C)2 | -5.0 |
| C(H)2(Cd)2 | -4.3 | C(H)2(C)(Cd) | -4.8 |
| C(H)(C)3 | -1.9 | Cd(C)(C) | 10.3 |
| Cd(H)(H) | 6.3 | Cd(C)(H) | 8.6 |
| Cyclobutane strain | 27.6 | Cyclopropane strain | 26.2 |
| Cyclopropane with internal alkene | 53.7 | Cyclopropane fused to $sp^2$ carbon | 40.9 |

ΔH(**I**) = C(H)3(Cd) + C(H)2(Cd)2 + Cd(C)(C) + Cd(C)(H) + {cyclopropane strain with internal alkene)
= -10.1 + (-4.3) + 10.3 + 8.6 + 53.7 (only one strain correction per ring)
= +58.2 kcal/mol

ΔH(**II**) = 2C(H)2(C)(Cd) + Cd(C)(C) + Cd(H)(H) + {cyclopropane fused to $sp^2$ carbon)
= 2(-4.8) + 10.3 + 6.3 + 40.9
= +47.9 kcal/mol

**II** is thermodyamically preferred (less positive enthalpy of formation). Since it is isolated from the reaction and is most stable, it is likely that it is formed first (though not a sure thing), so this fits the pseudothermodynamic model. Note that the *most* substituted alkene is *not* the most stable in this particular case (due to ring strain!).