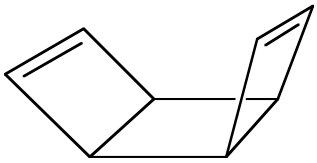
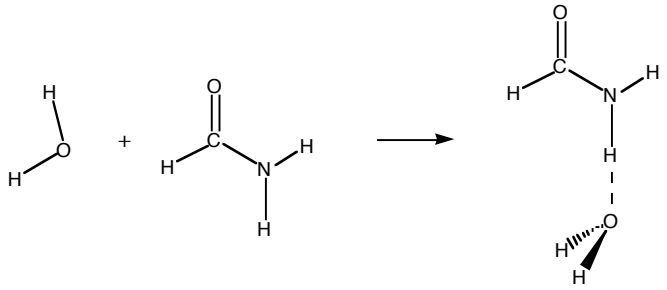
Project IV
Chemistry 5021/8021, Computational Chemistry, Spring, 2005
Assigned: April 15, 2005. Due: May 1, 2005

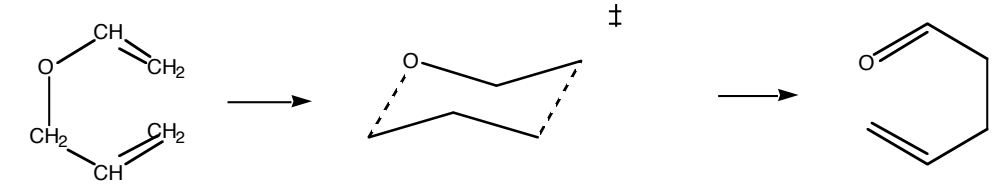
1 Use the concept of through space and through bond interactions to construct an "interaction diagram" between the two p orbitals and the two relevant s orbitals for the following compound. First, identify two key symmetry elements in this compound. Then, construct the "fragment" orbitals due resulting from through space interactions. Arrange these orbitals in order of relative energies, and label them with the proper symmetry according to the two symmetry operations. Finally, construct the final key molecular orbitals through bond interactions. Draw a qualitative picture of the HOMO for the compound. Hint, you may use gaussview to display the MOs from HF/STO-3G or semiempirical AM1 calculations.



2 Using HF/3-21G//HF/3-21G, HF/6-31G*//HF/6-31G*, HF/6-311G*//HF/6-311G*, and MP2/aug-cc-pVDZ//HF/6-311G* to calculate the interaction (hydrogen-bonding) energy for the following complex. Make sure that the complex have a **Cs symmetry**. Tabulate total energies in a.u. upto 5 decimal digits, and interaction energies in kcal/mol upto one decimal point. Are these results consistent with the variational principle?



3 Locate the reactant state (allyl vinyl ether) and transition state structures for the Cope rearrangement using HF/3-21G method. Calculate $\Delta E^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ at 298 K.



Ally viny ether TS product