THEORETICAL STUDY OF MECHANISM AND STEREOSELECTIVITY OF THE RING OPENING OF FORMYLOXIRANE

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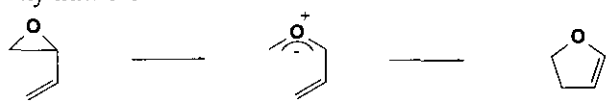
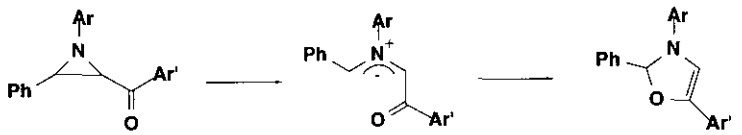
Abstract - The stereochemistry and reaction mechanism of the thermal ring opening of formyloxirane and subsequent cyclization were studied by using the *ab initio molecular orbital calculations. Stationary points along lowest energy pathways,* including the unstable carbonyl ylide intermediate were located.

Dedicated to Professor E. C. Taylor on the occasion of his seventieth birthday.

1,3-Dipoles have played an important role in the synthesis of heterocyclic systems.[1] The ring opening of oxiranes or aziridines yields carbonyl ylides or azomethine ylides, which are commonly trapped with olefins (1,3-dipolar cycloaddition) to form 5-membered rings.[2] Electrocyclic ring-closure is possible if the 1,3-dipole has an unsaturated substituent. Cyclizations of vinyl substituted systems have been reported by many authors.[3]



Padwa[4] and Baldwin[5] reported cyclizations of formyl substituted azomethine ylides formed by the ring opening of aziridines.



Vinyl and formyl groups in these examples are required to be oriented as shown above to accomplish the cyclization.

Because of our interest in stereochemistry in the direction of ring opening in electrocyclic processes (torquoselectivity),[6] we have undertaken *ab initio* molecular orbital calculations on the torquoselectivity of the ring opening of the formyloxirane, and the mechanism of subsequent cyclization. Since the intermediate ylide is so unstable compared to both reactant and product, there is also a possibility that ring opening of oxirane and cyclization occur in concert *via* a single transition state for a 1,3-sigmatropic shift. All calculations were carried out with GAUSSIAN 90 and 92.[7] Geometries of the

stationary points were fully optimized at MP2/6-31G* level of theory and were characterized by vibrational analysis.

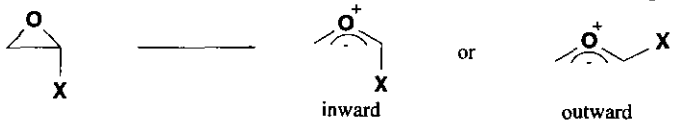
Schaefer *et al.* reported a high level study on the conrotatory ring opening of parent oxirane including the isomerization of the product carbonyl ylides.[8] The results obtained with HF theory are compared to various correlation levels in Table 1. At the MP2/6-31G* level, the ring opening barrier and the energy of the ylide are both about 10 kcal/mol too high.

Table 1. Energetics[kcal/mol] for the electrocyclic C-C bond breaking of parent oxirane

Theoretical level	Conrotatory TS	Carbonyl ylide
HF/ 6-31G*	90.3	70.9
HF/DZP[a]	85.9	67.3
MP2/6-31G*	66.0	50.6
DZP TCSCF[a]	46.5	38.3
DZP 2R CISD+Q[a]	52.6	39.6

a. ref.8

We have studied the electrocyclic ring-opening of a variety of substituted systems.[9] Substituents on the oxirane ring may rotate either inward or outward upon conrotatory opening.



inward outward

The formyl group, which is strong electron-withdrawing, has been reported to show inward torquoselectivity during the thermal ring opening of cyclobutene.[10] Indeed, the same torquoselectivity is found with oxirane. Figure 1 summarizes the potential energy diagram for the reactions of formyloxirane. As is seen, inward rotation was found to be preferred by 2.8 kcal/mol to outward rotation.

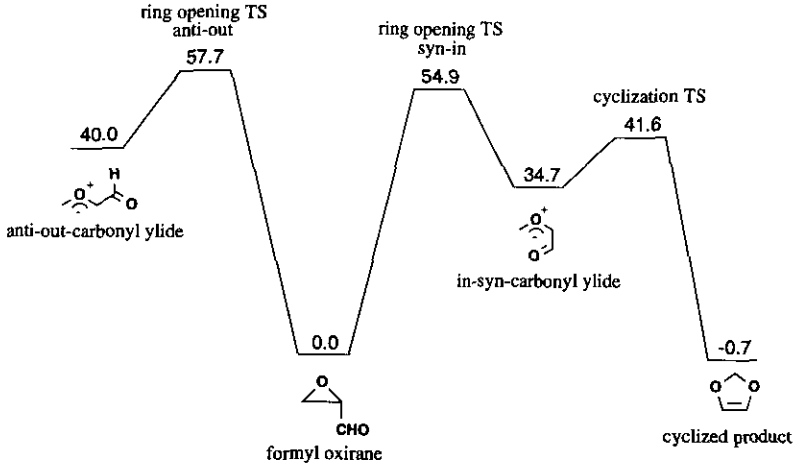


Figure 1. Schematic potential energy diagram of the reactions of formyloxyrane with MP2/6-31G* calculations. Energies are in kcal/mol.

Figure 2 shows the transition structure for inward rotation of the formyl group. For each species, two conformations are possible, with the carbonyl oxygen syn or anti to the ring. Only the more stable isomers are shown (syn for inward, and anti for outward). The product ylide shown is 5.3 kcal/mol more stable than the *trans* ylide.

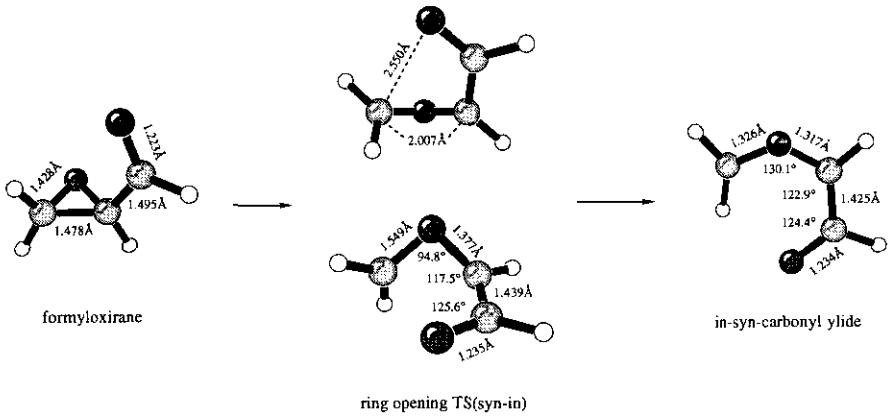


Figure 2. *Pictures of transition structures for ring open(inward-syn) of* formyloxirane(MP2/6-31G*).

Table 1 shows the effect of basis set and electron correlation on the activation and reaction energies for the parent system. Formation of the carbonyl ylide is endothermic by 35~40 kcal/mol at MP2/6-31G* level. Table 1 suggests that inclusion of more correlation energy would lower the formyloxirane ring opening activation energy by an additional 10 kcal/mol. The formyl group lowers the activation energy by 11 kcal/mol and stabilizes the carbonyl ylide by 16 kcal/mol.

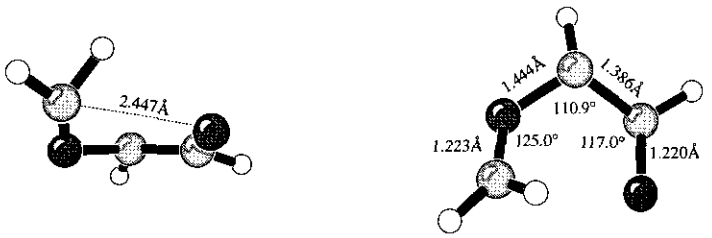


Figure 3. Structure of cyclization transition state from formyl carbonyl ylide (MP2/6-31G*).

The conrotatory cyclization of the ylide has an activation energy of 6.9 kcal/mol. The cyclization transition state structure is shown in Figure 3. The forming C-O bond (2.447 Å) is longer than those in other usual pericyclic reactions, which indicates the transition state is relatively early, because of the

large exothermicity of the reaction (35.4 kcal/mol). Comparison with the isoelectronic transition state of the cyclopentenyl anion ring opening[11] shows that they have very similar geometries.
For formyloxirane, the lowest energy pathway to the cyclized product is through inward rotation of the formyl group upon ring opening, followed by cyclization. No transition state for the direct reaction could be located.

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