

# Molecular Orbital Theory of Alkylideneoxirane-Cyclopropanone Rearrangements

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Received March 22, 1983

Ab initio Hartree-Fock geometry optimizations are performed on cyclopropanone, allene oxide, oxyallyl, and two other  $C_3H_4O$  structures. Basis set and correlation effects on the electronic structure and relative stabilities of the  $C_3H_4O$  structures are calculated. Proposed mechanisms for the allene oxide to cyclopropanone rearrangement are discussed. The oxyallyl intermediate is lower in energy than the intermediate proposed in a bond angle distortion mechanism. The results are interpreted in terms of qualitative molecular orbital concepts, which retain their validity in view of the ab initio results.

## Introduction

The isomerization reaction of alkylideneoxiranes to form cyclopropanones has stimulated several recent investigations of the mechanism of this reaction.<sup>1</sup> Several experimental and theoretical studies suggest that the reaction proceeds through an oxyallyl intermediate.<sup>2</sup> For cyclopropanone and allene oxide, an alternative mechanism<sup>3</sup> hypothesizes the distortion of bond angles to obtain bent intermediates. The relative stabilities of the  $C_3H_4O$  isomers are evaluated ab initio with Gaussian 80.<sup>4</sup> The results are interpreted in terms of qualitative molecular orbital concepts.

The electronic structures (Figure 1) of cyclopropanone (CYONE) and oxyallyl (OXYAL) have been studied computationally by various means.<sup>5</sup> Earlier suggestions of the importance of OXYAL led to studies of the relative stabilities of OXYAL and CYONE with extended Hückel theory.<sup>2b</sup> Although the analysis of the molecular orbitals from these works remains valid in view of the present calculations, to make a choice between the reaction paths necessitates a more exact calculation. Several previous calculations are summarized in Table I. The disagreement between the computational results and the experimental estimate of approximately 40 kcal/mol<sup>1a</sup> for the energy difference between CYONE and OXYAL led Zandler et al. to propose a reaction pathway via the intermediates of Figure 2. CNDO/2 and INDO calculations indicated this pathway has a lower barrier than the OXYAL pathway, where OXYAL is defined to be planar and to have  $C_3-C_2-C_4$  and  $C-C_2-O$  bond angles of  $120^\circ$ . Ab initio calculations are made here to test the two alternatives.

## Results

Preliminary geometry optimizations were carried out at the Hartree-Fock STO-3G level.<sup>6</sup> Each structure was optimized subject to certain constraints. The fixed bond lengths and bond angles are given with the optimized geometrical parameters in Table II.  $C_{2v}$  symmetry was imposed for CYONE and OXYAL; elsewhere  $C_s$  symmetry was imposed. For OXYAL, the angle of each  $CH_2$  plane with the  $C-C-C$  plane was chosen to be  $90^\circ$ . This structure will be called perpendicular OXYAL. Since these calculations are only intended to give a rough idea of the energy separation of the isomers, the geometrical parameters obtained for the  $90^\circ$  configuration are retained for the planar form of OXYAL. For the ALBEND (structure 2 of Figure 2) calculations, the structure with the exocyclic  $CH_2$  hydrogens in the plane of the ring is optimized. The angle  $\alpha$  is fixed at  $120^\circ$  for OXYAL in accordance with

Table I. Previous Calculations: Total Energy (OXYAL) - Total Energy (CYONE)

| method          | energy barrier, kcal/mol | ref  |
|-----------------|--------------------------|------|
| extended Hückel | -23                      | 2b   |
| INDO            | 232                      | 5b-d |
| MINDO           | 78                       | 5a   |
| ab initio       | 83                       | 5c   |
| MINDO           | 66                       | 5e   |
| ab initio       | 49                       | 5f   |

Table II. Hartree-Fock STO-3G Geometry Optimization

| CYONE                                    |  |
|--|--|
| $D(C-H) = 1.080$ Å fixed                 | $D(C-O) = 1.207$ Å,<br>$\theta(C_3-C_2-C_4) = 66.8^\circ$                              |
| $\theta(C_2-C-H) = 120^\circ$ fixed      | $D(C_2-C_3) = 1.470$ Å   |
| ALOX                                     |  |
| $D(C-H) = 1.080$ Å fixed                 | $D(C_2-O) = 1.370$ Å,<br>$\theta(C_2-O-C_1) = 63.1^\circ$                              |
| $\theta(C_2-C-H) = 120^\circ$ fixed      | $D(C_2-C_3) = 1.467$ Å,<br>$\theta(O-C_2-C_1) = 143.2^\circ$<br>$D(C_2-C_1) = 1.301$ Å |
| perpendicular OXYAL                      |  |
| $D(C-H) = 1.080$ Å fixed                 | $D(C_2-O) = 1.235$ Å   |
| $\theta(C_2-C_3-H) = 120^\circ$ fixed    | $D(C_2-C_3) = 1.449$ Å   |
| $\theta(O-C_2-C_3) = 120^\circ$ fixed    |  |
| CYBEND                                   |  |
| $\theta(C_3-C_2-C_4) = 66.8^\circ$ fixed |  |
| $D(C-H) = 1.080$ Å fixed                 |  |
| $\theta(C_2-C-H) = 120^\circ$ fixed      |  |
| $\alpha = 90^\circ$ fixed                | $D(C-O) = 1.288$ Å,<br>$D(C_1-C_3) = 1.594$ Å,<br>$D(C_2-C_4) = 1.462$ Å               |
| $\alpha = 80^\circ$ fixed                | $D(C-O) = 1.351$ Å,<br>$D(C_2-C_3) = 1.547$ Å,<br>$D(C_2-C_4) = 1.390$ Å               |
| $\alpha = 70^\circ$ fixed                | $D(C-O) = 1.369$ Å,<br>$D(C_2-C_3) = 1.590$ Å,<br>$D(C_2-C_4) = 1.388$ Å               |
| ALBEND                                   |  |
| $\theta(O-C_2-C_3) = 63.1^\circ$ fixed   |  |
| $D(C-H) = 1.080$ Å fixed                 |  |
| $\theta(C_2-C-H) = 120^\circ$ fixed      |  |
| $\alpha = 90^\circ$ fixed                | $D(C_2-O) = 1.376$ Å,<br>$D(C_3-C_2) = 1.542$ Å,<br>$D(C_2-C_4) = 1.365$ Å             |
| $\alpha = 80^\circ$ fixed                | $D(C_2-O) = 1.380$ Å,<br>$D(C_3-C_2) = 1.556$ Å,<br>$D(C_2-C_4) = 1.413$ Å             |
| $\alpha = 70^\circ$ fixed                | $D(C_2-O) = 1.379$ Å,<br>$D(C_3-C_2) = 1.574$ Å,<br>$D(C_2-C_4) = 1.495$ Å             |

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previous works. The initial choices of  $\alpha$  for ALBEND and CYBEND were taken from the potential energy surface

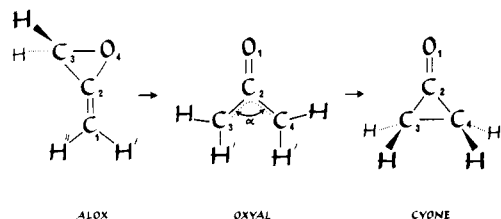


Figure 1.

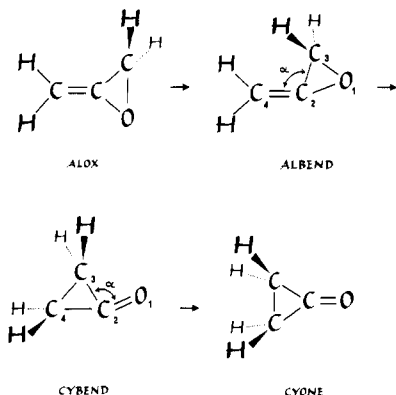


Figure 2.

diagram of Zandler et al.<sup>3</sup> Some searching with respect to  $\alpha$  was done until ALBEND and CYBEND were reasonably close in energy (within a few kcal/mol), but with bond angles about the central carbon not too different from each other. The choices of  $\alpha = 70^\circ$  for ALBEND and  $\alpha = 70^\circ$  for CYBEND were found to be reasonably close in energy and these structures are therefore employed in making an estimate of the barrier along the suggested path.

Relative energies are given in Table III. Some of the correlation corrections are important in stabilizing OXYAL. Since a ring carbon-carbon bond is being stretched to about 2.5 Å in forming OXYAL, it is reasonable to ask how correlation might affect the calculated stability of OXYAL. In the perpendicular form of OXYAL, the occupied  $8a_1$  molecular orbital has major contributions from the  $p_x$  and  $p_z$  orbitals of the carbon atoms A and B (see Figure 3) in the combination:

$$\psi_{8a_1} = (c_1A p_x + c_2A p_z) + (-c_1B p_x + c_2B p_z) \cong \phi_A + \phi_B \quad (1)$$

(1) (a) Camp, R. L.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 7349. (b) Crandall, J. K.; Machleder, W. H. *J. Heterocycl. Chem.* **1969**, *6*, 777. (c) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723. (d) Chan, T. H.; Ong, B. S.; Mychajlowskij, W. *Tetrahedron Lett.* **1976**, 3253. (e) Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994.

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(3) Zandler, M. E.; Choc, C. E.; Johnson, C. K. *J. Am. Chem. Soc.* **1974**, *96*, 3317.

(4) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. Gaussian 80, Quantum Chemistry Program Exchange No. 406, Indiana University.

(5) (a) Bodor, N.; Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1970**, *92*, 3854. (b) Olsen, J. F.; Kang, S.; Burnelle, L. *J. Mol. Struct.* **1971**, *9*, 305. (c) Liberles, A.; Greenberg, A.; Lesk, A. *J. Am. Chem. Soc.* **1972**, *94*, 8685. (d) Liberles, A.; Kang, S.; Burnelle, L. *J. Org. Chem.* **1973**, *38*, 1922. (e) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H., *J. Am. Chem. Soc.* **1975**, *97*, 1302. (f) Schaad, L. J.; Hess, B. A.; Zahradnik, R. *J. Org. Chem.* **1981**, *46*, 1909.

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Table III. Relative Energies (in kcal/mol) of  $C_3H_4O$  Structures Optimized with STO-3G Basis

|  | Hartree-Fock | MBPT(2) | MBPT(3) |
|--|--------------|---------|---------|
| CYONE                                  | 0.0          | 0.0     | 0.0     |
| ALOX                                   | -1.6         | 3.8     | 1.0     |
| OXYAL                                  | 124.7        | 75.9    | 63.1    |
| (perpendicular)                        |              |         |         |
| OXYAL (Planar)                         | 109.1        | 73.4    | 70.4    |
| CYBEND ( $\alpha = 90^\circ$ )         | 118.3        | 103.2   | 101.1   |
| ( $\alpha = 80^\circ$ )                | 188.1        | 197.3   | 193.4   |
| ( $\alpha = 70^\circ$ )                | 168.2        | 182.1   | 178.8   |
| ALBEND ( $\alpha = 90^\circ$ )         | 97.9         | 83.7    | 81.5    |
| ( $\alpha = 80^\circ$ )                | 138.0        | 114.0   | 114.7   |
| ( $\alpha = 70^\circ$ )                | 183.4        | 154.1   | 159.9   |
| twisted ALBEND ( $\alpha = 70^\circ$ ) | 168.8        | 182.5   | 179.3   |

The doubly occupied  $8a_1$  orbital gives the following two electron configurations in terms of atomic orbitals,

$$(8a_1)^2: \psi_{8a_1}(1) \psi_{8a_1}(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \cong [\phi_A(1)\phi_A(2) + \phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2) + \phi_B(1)\phi_B(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (2)$$

where the last terms of the right hand side show the separation of the two-electron wavefunction into a product of orbital and spin functions. In doubly excited configuration  $(8a_1)^2 \rightarrow (5b_2^*)^2$  where

$$\psi_{5b_2^*} \cong \phi_A - \phi_B \quad (3)$$

the same expansion in terms of atomic orbitals gives

$$(5b_2^*)^2: \psi_{5b_2^*}(1) \psi_{5b_2^*}(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \cong [\phi_A(1)\phi_A(2) - \phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2) + \phi_B(1)\phi_B(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (4)$$

For the linear combination of the reference determinant minus the doubly excited configuration, the overall result is

$$(8a_1)^2 - (5b_2^*)^2 = \frac{1}{2} [\psi_{8a_1}(1) \psi_{8a_1}(2) - \psi_{5b_2^*}(1) \psi_{5b_2^*}(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = [\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (5)$$

that is, a valence bond description of a diradical singlet. (The plus combination of these two configurations is higher in energy because the cancellation of the diradical component leaves only the ionic terms.) In the limit where the doubly excited configuration becomes as important as the reference configuration, the system becomes a diradical. Similar arguments apply for the planar form of OXYAL, but the orbitals involved this time are part of the  $\pi$  system. In the Hartree-Fock wave function, the  $\pi$  orbital  $2b_1$  is doubly occupied. (See Figure 4.) This orbital contains the bonding combination of the  $p_y$  orbitals of carbon atoms A and B. The unoccupied orbital  $1a_2^*$  contains the antisymmetric combination of the same orbitals. A linear combination of the reference configuration minus the double excitation  $(1b_1)^2 \rightarrow (1a_2^*)^2$  will give the same kind of valence bond descriptor of the  $\pi$  diradical as was obtained for the stretched  $\sigma$  bond of the perpendicular form of OXYAL. Such doubly excited contributions to the configuration interaction wavefunction are included in the first order many-body perturbation theory (MBPT) corrections to the Hartree-Fock wave function.<sup>7</sup> These corrections are also known as Moller-Plesset theory corrections, since partitioning schemes other than that of Moller and Plesset have been employed.<sup>11</sup> The size con-

(7) Bartlett, R. J.; *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

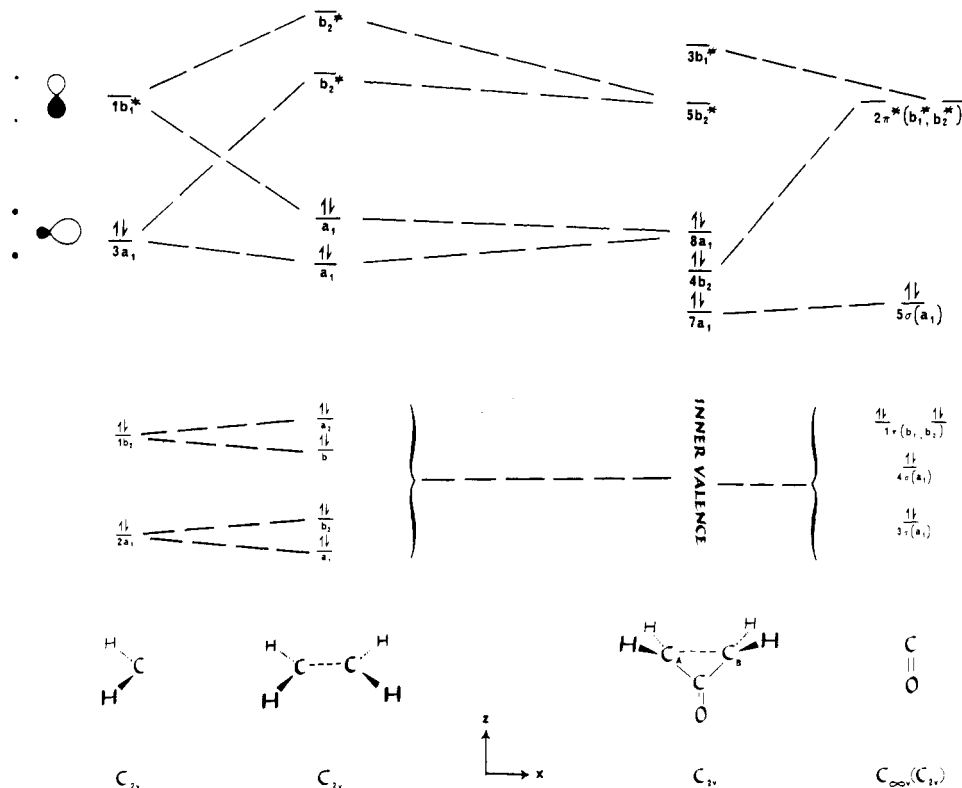


Figure 3.

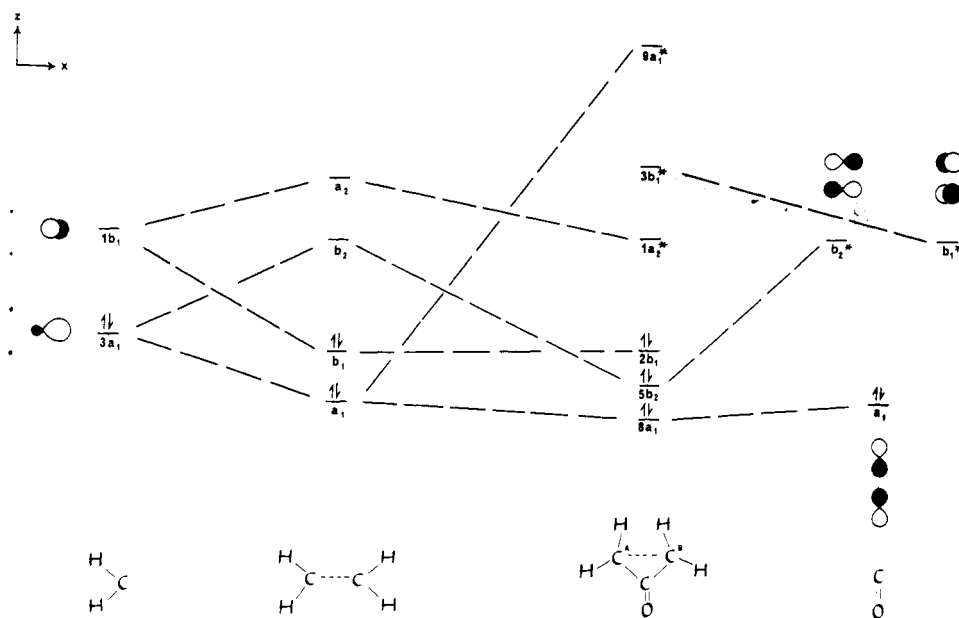


Figure 4.

sistent contributions to the total energy from the first order MBPT wavefunction are given by the second and third order MBPT diagrams. (For a review of the many-body theory approach to electron correlation see ref 7.) These perturbative total energy expressions will give a balanced treatment of correlation for the various isomers.

On examining the STO-3G calculations, especially after permitting the correlation corrections to properly describe diradical character, planar OXYAL appears to be the most stable of the intermediates. On the basis of this evidence alone, it seems that the path with the bent intermediates is not as favorable as the path through OXYAL. The transition-state energy for the OXYAL path is still too large compared with the experimental estimate of about 40 kcal/mol for the activation barrier. Calculations of a

more precise type are required for such an estimate, and therefore 4-31G<sup>8</sup> (valence double  $\zeta$ ) and 6-31G\*<sup>9</sup> (valence double  $\zeta$  plus polarization functions on non-hydrogen atoms) basis sets are employed. These calculations also help to establish whether the sizeable correlation contribution to the stabilization of OXYAL with the STO-3G basis is a genuine manifestation of diradical character or merely an artifact of an incomplete basis. Valence double zeta basis sets have been employed successfully in the calculation, to within a few kcal/mol, of Hartree-Fock energy differences. In combination with MBPT corrections ap-

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Table IV. Hartree-Fock 4-31G Geometry Optimizations

| CYONE  |  |                                     |
|--|--|-------------------------------------|
| $D(C_2-O) = 1.195 \text{ \AA}$ ,             | $\theta(C_3-C_2-C_4) = 70.9^\circ$     |                                     |
| $D(C_2-C_3) = 1.445 \text{ \AA}$ ,           | $\theta(H-C_3-C_2) = 121.5^\circ$      |                                     |
| $D(C-H) = 1.070 \text{ \AA}$                 |  |                                     |
| ALOX   |  |                                     |
| $D(C_2-O) = 1.389 \text{ \AA}$ ,             | $D(C_3-H) = 1.069 \text{ \AA}$ ,       | $\theta(O-C_2-C_1) = 139.1^\circ$   |
| $D(C_2-C_3) = 1.432 \text{ \AA}$ ,           | $D(C_1-H) = 1.070 \text{ \AA}$         | $\theta(H-C_3-C_2) = 120.2^\circ$   |
| $D(C_2-C_1) = 1.299 \text{ \AA}$             | $\theta(O-C_2-C_2) = 64.4 \text{ \AA}$ | $\theta(H-C_1-C_2) = 120.9^\circ$   |
| perpendicular OXYAL                          |  |                                     |
| $D(C-O) = 1.224 \text{ \AA}$ ,               | $\theta(H-C_3-C_2) = 120.4^\circ$      |                                     |
| $D(C_2-C_3) = 1.416 \text{ \AA}$ ,           |  |                                     |
| $D(C-H) = 1.070 \text{ \AA}$                 |  |                                     |
| planar OXYAL                                 |  |                                     |
| $D(C-O) = 1.284 \text{ \AA}$ ,               | $\theta(H-C_3-C_2) = 120.7^\circ$      |                                     |
| $D(C_2-C_3) = 1.392 \text{ \AA}$ ,           |  |                                     |
| $D(C-H) = 1.071 \text{ \AA}$                 |  |                                     |
| (these lengths were constrained to be equal) |  |                                     |
| CYBEND                                       |  |                                     |
| $D(C_2-O) = 1.363 \text{ \AA}$ ,             | $D(C_2-C_4) = 1.392 \text{ \AA}$       | $D(C-H) = 1.080 \text{ \AA}$ fixed  |
| $D(C_2-C_3) = 1.633 \text{ \AA}$ ,           |  | $\theta(C_2-C-H) = 120^\circ$ fixed |
|  |  | $\alpha = 70^\circ$ fixed           |
| ALBEND                                       |  |                                     |
| $D(C_2-O) = 1.376 \text{ \AA}$ ,             | $D(C_2-C_4) = 1.511 \text{ \AA}$       | $D(C-H) = 1.080 \text{ \AA}$ fixed  |
| $D(C_3-C_2) = 1.598 \text{ \AA}$             |  | $\theta(C_2-C-H) = 120^\circ$ fixed |
|  |  | $\alpha = 70^\circ$ fixed           |

Table V. Relative Energies (in kcal/mol) of  $C_3H_4O$  Structures Optimized with 4-31G Basis

|                                | Hartree-Fock<br>4-31G | MBPT(2)<br>4-31G | MBPT(3)<br>4-31G | Hartree-Fock<br>6-31G* | MBPT(2)<br>6-31G* |
|--------------------------------|-----------------------|------------------|------------------|------------------------|-------------------|
| CYONE                          | 0.0                   | 0.0              | 0.0              | 0.0                    | 0.0               |
| ALOX                           | 7.0                   | 8.2              | 6.1              | 4.6                    | 4.4               |
| OXYAL (perpendicular)          | 68.1                  | 42.5             | 43.4             | 71.5                   | 48.7              |
| OXYAL (planar)                 | 42.0                  | 38.8             | 39.0             | 48.6                   | 45.2              |
| CYBEND ( $\alpha = 70^\circ$ ) | 176.4                 | 174.5            | 172.2            |                        |                   |
| ALBEND ( $\alpha = 70^\circ$ ) | 180.2                 | 148.6            | 157.5            |                        |                   |

appropriate for the consideration of OXYAL, similar accuracy with respect to basis set improvements can be expected. Polarization basis set augmentations serve as a final test of the convergence of the relative energies with respect to basis set improvements.

The geometries are optimized at the Hartree-Fock 4-31G level. The MBPT calculations and the calculations with the 6-31G\* basis set are done at these geometries. No constraints on the bond lengths and bond angles are imposed in the 4-31G\* geometry optimizations on OXYAL, CYONE, or ALOX. Only point group symmetry is imposed on the geometries. In addition, there are separate geometry optimizations for the perpendicular and the planar forms of OXYAL. (See Table IV.) The ALBEND and CYBEND calculations have constraints similar to those imposed in the STO-3G calculations. The optimized geometries, obtained with the analytical gradients minimization procedure of Gaussian 80, are in good agreement with previously reported 4-31G results.<sup>5f</sup> The improved basis set results, given in Table V, lower the energy of OXYAL relative to CYONE even at the Hartree-Fock level. (Compare with the results from ref 5f.) The relative energy of the planar form of OXYAL has been reduced to a value that is close to the experimental estimate. Correlation corrections lower the barrier slightly for planar OXYAL, but the corrections for perpendicular OXYAL remain substantial. The ALBEND and CYBEND forms are still much higher in energy than the OXYAL forms. The relative smallness of the third order corrections compared to the second order corrections indicates good convergence of the MBPT expansion and implies that the Hartree-Fock configuration remains dominant in the

correct wave function. The diradical nature of planar OXYAL is not large enough to make the correlation corrections important in the calculation of the barrier. For perpendicular OXYAL, the diradical character is not large enough to affect the convergence of the perturbation expansion, but diradical character is important enough to affect the relative energy by a significant amount. An approximate criterion of diradical character is the smallness of the difference between the energies of the unoccupied and occupied orbitals that describe the bond stretching process.<sup>10</sup> For planar OXYAL the orbital energy difference  $\epsilon_{1a_2^*} - \epsilon_{2b_1}$  is 7.0 eV for the 4-31G basis and is 5.8 eV for the STO-3G basis. These numbers indicate less diradical character for the larger basis and imply that the large correlation corrections in stabilizing planar OXYAL for the STO-3G basis are artifacts of a basis that is not flexible enough to describe the diffuse  $\pi$  character of the  $1b_1$  orbital. For perpendicular OXYAL, there is a similar, though less pronounced basis set trend. The orbital energy difference  $\epsilon_{5b_2^*} - \epsilon_{8a_1}$  for 4-31G is 8.1 eV and is 7.7 eV for STO-3G. Corrections from the addition of polarization functions are small. The approximate additivity of the polarization basis set corrections and the correlation corrections to the relative energies of the isomers is tested in Table VI.<sup>12</sup> The correlation corrections with the 6-31G\* basis set are terminated at second order

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Table VI. Relative Energies (in kcal/mol) of C<sub>3</sub>H<sub>4</sub>O Structures

|                       | total energy expression | exact calculation | approximation of additivity of polarization and correlation corrections |
|-----------------------|-------------------------|-------------------|---|
| CYONE                 | MP2 6-31G*              | 0.0               | 0.0   |
|                       | MP3 6-31G*              | 0.0               | 0.0   |
| ALOX                  | MP2 6-31G*              | 4.4               | 5.8   |
|                       | MP3 6-31G*              |                   | 3.7   |
| OXYAL (perpendicular) | MP2 6-31G*              | 48.7              | 45.9  |
|                       | MP3 6-31G*              |                   | 46.8  |
| OXYAL (planar)        | MP2 6-31G*              | 45.2              | 45.4  |
|                       | MP3 6-31G*              |                   | 45.6  |

due to the present limitations of Gaussian 80.

Unrestricted Hartree-Fock (UHF) calculations also give correct descriptions of diradicals, but the perturbative calculations are preferable whenever they are convergent. In general, UHF calculations produce different orbitals for different spins and have a lower total energy than restricted Hartree-Fock (RHF) for certain regions of the potential energy surface, especially where diradical character is dominant. The energy lowering appears suddenly as a bond is stretched; for some regions of the potential energy surface where diradical character is small, no energy lowering at all is obtained. The UHF description of diradical character is in some sense discontinuous. Therefore, the continuous description of diradical character afforded by the MBPT corrections to the RHF wavefunction is employed here. (For a thorough description of the conditions under which UHF total energies are lower than RHF total energies, as well as a discussion of the properties of the UHF method, see ref 10.) UHF descriptions of diradicals also suffer from spin contamination.

When UHF calculations are performed at the RHF 4-31G optimized geometry, no different orbitals for different spin behavior are obtained. The UHF calculation is re-

duced to the special case of an ordinary RHF wavefunction. This result and the behavior of the MBPT corrections imply that, at this geometry, correlation corrections due to the formation of a diradical are not qualitatively important. This observation does not in itself imply that there is no stable geometry corresponding to a wavefunction that does contain strong correlation effects. With this rubric in mind, it is possible to state that at this geometry, the closed shell formulation is qualitatively correct.

To summarize the calculations, single  $\zeta$  calculations with correlation corrections that describe the diradical parts of the potential energy surface give a reasonable qualitative treatment of the relative stabilities of the isomers of C<sub>3</sub>H<sub>4</sub>O, but double  $\zeta$  calculations in combination with the same correlation corrections give a good numerical approximation of the relative energy of the OXYAL intermediate. The single  $\zeta$  calculations exaggerate the importance of correlation corrections because of the inability of the basis to describe the weak interactions between the carbon atoms A and B of Figure 3 and Figure 4. The OXYAL intermediate is found to be above CYONE and ALOX by an amount that is close to experimental estimates for the barrier of a similar system.

Mulliken population analysis information, obtained from RHF calculations is given in Table VII. The atomic charges corroborate the approximate picture of OXYAL as an allyl cation plus an oxygen anion. Most of the trends in going from CYONE to OXYAL and then to ALOX are independent of basis sets. Some results require detailed discussion. The C<sub>3</sub>-C<sub>4</sub> overlap population declines from

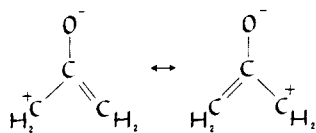


Figure 5.

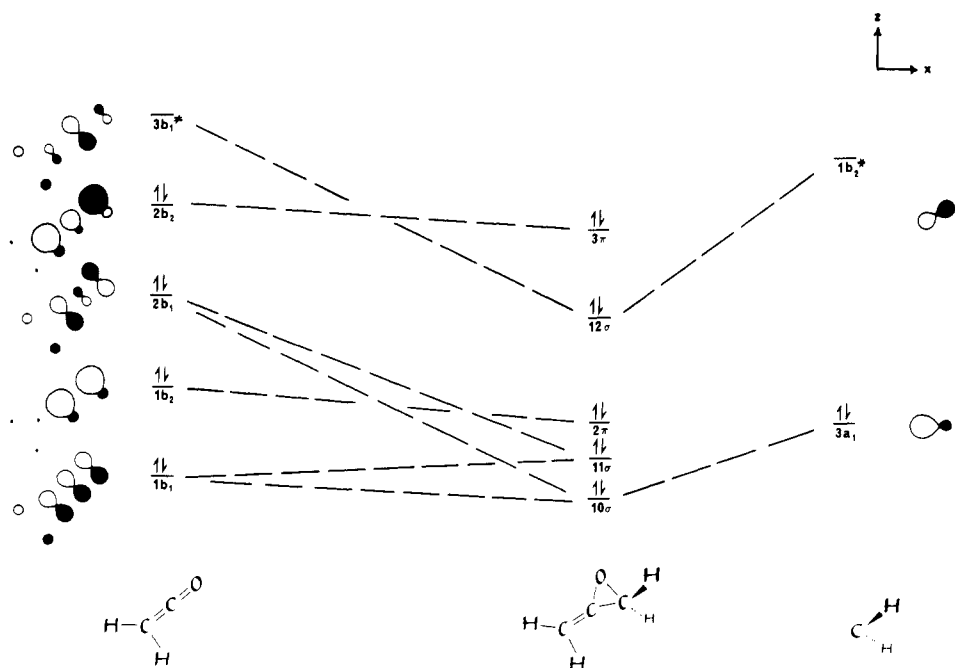


Figure 6.

Table VII. Mulliken Population Analysis

| C <sub>3</sub> H <sub>4</sub> O | atom           | charge | atoms                          | overlap population |
|---------------------------------|----------------|--------|--------------------------------|--------------------|
| CYONE                           |                |        |                                |                    |
| STO-3G                          | O <sub>1</sub> | -0.19  | C <sub>2</sub> -O <sub>1</sub> | 0.44               |
|                                 | C <sub>2</sub> | 0.22   | C <sub>2</sub> -C <sub>3</sub> | 0.32               |
|                                 | C <sub>3</sub> | -0.18  | C <sub>3</sub> -C <sub>4</sub> | 0.19               |
|                                 | H              | 0.08   | C <sub>3</sub> -H              | 0.39               |
| 4-31G                           | O <sub>1</sub> | -0.51  | C <sub>2</sub> -O <sub>1</sub> | 0.44               |
|                                 | C <sub>2</sub> | 0.44   | C <sub>2</sub> -C <sub>3</sub> | 0.17               |
|                                 | C <sub>3</sub> | -0.41  | C <sub>3</sub> -C <sub>4</sub> | 0.01               |
|                                 | H              | 0.22   | C <sub>3</sub> -H              | 0.38               |
| 6-31G*                          | O <sub>1</sub> | -0.47  | C <sub>2</sub> -O <sub>1</sub> | 0.57               |
|                                 | C <sub>2</sub> | 0.55   | C <sub>2</sub> -C <sub>3</sub> | 0.28               |
|                                 | C <sub>3</sub> | -0.49  | C <sub>3</sub> -C <sub>4</sub> | 0.09               |
|                                 | H              | 0.22   | C <sub>3</sub> -H              | 0.38               |
| OXYAL, planar                   |                |        |                                |                    |
| STO-3G                          | O <sub>1</sub> | -0.41  | C <sub>2</sub> -O <sub>1</sub> | 0.39               |
|                                 | C <sub>2</sub> | 0.13   | C <sub>2</sub> -C <sub>3</sub> | 0.42               |
|                                 | C <sub>3</sub> | -0.04  | C <sub>3</sub> -C <sub>4</sub> | -0.03              |
|                                 | H              | 0.10   | C <sub>3</sub> -H              | 0.39               |
| 4-31G                           | H'             | 0.08   | C <sub>3</sub> -H'             | 0.38               |
|                                 | O <sub>1</sub> | -0.81  | C <sub>2</sub> -O <sub>1</sub> | 0.46               |
|                                 | C <sub>2</sub> | 0.34   | C <sub>2</sub> -C <sub>3</sub> | 0.29               |
|                                 | C <sub>3</sub> | -0.22  | C <sub>3</sub> -C <sub>4</sub> | -0.11              |
| 6-31G*                          | H              | 0.25   | C <sub>3</sub> -H              | 0.37               |
|                                 | H'             | 0.20   | C <sub>3</sub> -H'             | 0.34               |
|                                 | O <sub>1</sub> | -0.80  | C <sub>2</sub> -O <sub>1</sub> | 0.52               |
|                                 | C <sub>2</sub> | 0.47   | C <sub>2</sub> -C <sub>3</sub> | 0.40               |
| ALOX                            | C <sub>3</sub> | -0.31  | C <sub>3</sub> -C <sub>4</sub> | -0.08              |
|                                 | H              | 0.26   | C <sub>3</sub> -H              | 0.37               |
|                                 | H'             | 0.21   | C <sub>3</sub> -H'             | 0.34               |
|                                 | O <sub>4</sub> | -0.21  | C <sub>2</sub> -O <sub>4</sub> | 0.23               |
| STO-3G                          | C <sub>2</sub> | 0.11   | C <sub>2</sub> -C <sub>1</sub> | 0.60               |
|                                 | C <sub>1</sub> | -0.17  | C <sub>2</sub> -C <sub>3</sub> | 0.30               |
|                                 | C <sub>3</sub> | -0.07  | C <sub>3</sub> -O <sub>4</sub> | 0.17               |
|                                 | H              | 0.09   | C <sub>1</sub> -H'             | 0.39               |
| 4-31G                           | H'             | 0.08   | C <sub>1</sub> -H''            | 0.39               |
|                                 | H''            | 0.08   | C <sub>3</sub> -H              | 0.39               |
|                                 | O <sub>4</sub> | -0.63  | C <sub>2</sub> -O <sub>4</sub> | 0.02               |
|                                 | C <sub>2</sub> | 0.30   | C <sub>2</sub> -C <sub>1</sub> | 0.65               |
| 6-31G*                          | C <sub>1</sub> | -0.42  | C <sub>2</sub> -C <sub>3</sub> | 0.18               |
|                                 | C <sub>3</sub> | -0.07  | C <sub>3</sub> -O <sub>4</sub> | 0.09               |
|                                 | H              | 0.22   | C <sub>1</sub> -H'             | 0.38               |
|                                 | H'             | 0.20   | C <sub>1</sub> -H''            | 0.39               |
| OXYAL, perpendicular            | H''            | 0.18   | C <sub>3</sub> -H              | 0.39               |
|                                 | O <sub>4</sub> | -0.59  | C <sub>2</sub> -O <sub>4</sub> | 0.17               |
|                                 | C <sub>2</sub> | 0.46   | C <sub>2</sub> -C <sub>1</sub> | 0.68               |
|                                 | C <sub>1</sub> | -0.54  | C <sub>2</sub> -C <sub>3</sub> | 0.34               |
| STO-3G                          | C <sub>3</sub> | -0.15  | C <sub>3</sub> -O <sub>4</sub> | 0.14               |
|                                 | H              | 0.21   | C <sub>1</sub> -H'             | 0.38               |
|                                 | H'             | 0.20   | C <sub>1</sub> -H''            | 0.39               |
|                                 | H''            | 0.20   | C <sub>3</sub> -H              | 0.38               |
| 4-31G                           | O <sub>1</sub> | -0.21  | C <sub>2</sub> -O <sub>1</sub> | 0.42               |
|                                 | C <sub>2</sub> | 0.17   | C <sub>2</sub> -C <sub>3</sub> | 0.39               |
|                                 | C <sub>3</sub> | -0.13  | C <sub>3</sub> -C <sub>4</sub> | 0.00               |
|                                 | H              | 0.08   | C <sub>3</sub> -H              | 0.39               |
| 6-31G*                          | O <sub>1</sub> | -0.50  | C <sub>2</sub> -O <sub>1</sub> | 0.38               |
|                                 | C <sub>2</sub> | 0.32   | C <sub>2</sub> -C <sub>3</sub> | 0.36               |
|                                 | C <sub>3</sub> | -0.35  | C <sub>3</sub> -C <sub>4</sub> | -0.03              |
|                                 | H              | 0.22   | C <sub>3</sub> -H              | 0.38               |
| ALOX                            | O <sub>1</sub> | -0.50  | C <sub>2</sub> -O <sub>1</sub> | 0.51               |
|                                 | C <sub>2</sub> | 0.50   | C <sub>2</sub> -C <sub>3</sub> | 0.40               |
|                                 | C <sub>3</sub> | -0.47  | C <sub>3</sub> -C <sub>4</sub> | 0.00               |
|                                 | H              | 0.23   | C <sub>3</sub> -H              | 0.38               |

cyclopropanone to oxyallyl and is actually negative for oxyallyl in the 4-31G basis. This serves as another confirmation of the portrayal of oxyallyl as an oxygen anion plus an allyl cation, or the equivalent valence bond description (see Figure 5). The C<sub>4</sub>-C<sub>3</sub> overlap population

for cyclopropanone depends heavily on the basis set and is only 0.01 for the 4-31G basis. The second result worthy of special mention is the increase in C-O overlap population in going from CYONE to OXYAL, even though the C-O distance has increased. The  $\pi$  overlap population decreases by 0.15 electron. The principal part of the compensating  $\sigma$  increase is the 0.11-electron increase in the overlap population between the C<sub>2</sub> outer p<sub>y</sub> atomic orbital and the O outer p<sub>y</sub> atomic orbital. The basis dependence of this result reveals a detailed balancing between decreased  $\pi$  overlap and increased  $\sigma$  overlap. Finally, in ALOX, the overlap populations for the O-C<sub>2</sub> and O-C<sub>3</sub> bonds are quite low. The C<sub>3</sub>-C<sub>2</sub> overlap population is the largest of the ring bond overlap populations.

### Discussion

It is now possible to examine under what circumstances the CYONE-like molecules may be destabilized and the OXYAL-like intermediates may be stabilized. Electronegative substituents on the CH<sub>2</sub> groups where one of the hydrogens has been removed will cause the CYONE-like molecule to be less stable. The molecular orbital diagram in Figure 3 shows that the weak coupling of the 3a<sub>1</sub> and the 1b<sub>1</sub> CH<sub>2</sub> orbitals in the formation of H<sub>2</sub>C-CH<sub>2</sub> gives rise to two a<sub>1</sub> and two b<sub>2</sub>\* orbitals. The b<sub>2</sub>\* orbitals become important in mixing with the LUMO of CO to form the 5b<sub>2</sub>\* unoccupied orbital of CYONE. Since the 5b<sub>2</sub>\* orbital becomes important in the correlation description of perpendicular OXYAL, the more the 5b<sub>2</sub>\* is stabilized the more CYONE will be destabilized. This can be achieved by reducing the overlap of the 3a<sub>1</sub> CH<sub>2</sub> orbitals by substituting an electronegative group for one of the hydrogens. F- and MeO-substituting CYONE were found to follow this trend in a MINDO and INDO study.<sup>5d</sup>

In addition to considering the destabilization of CYONE, the stabilization of OXYAL can also be considered with molecular orbital arguments. (See Figure 4.)  $\pi$ -donating substituents will increase the overlap between the 1b<sub>1</sub> orbitals of the CH<sub>2</sub> fragments, will stabilize the OXYAL 2b<sub>1</sub>  $\pi$ -bonding orbital, and will destabilize the 1a<sub>2</sub>\* antibonding  $\pi$  orbital. As the separation between the 1a<sub>2</sub>\* orbital and the 2b<sub>1</sub> orbital increases, the importance of the doubly excited configuration will decrease, the amount of diradical character will be diminished, and the  $\pi$  bonding between the carbon atoms A and B will increase.

For the case of ALOX, Figure 6 shows how the upper valence molecular orbitals of methylene and ketene interact to form ALOX molecular orbitals. Of principal importance in stabilizing ALOX is the interaction of the 1b<sub>1</sub> orbital of methylene with the unoccupied 3b<sub>1</sub>\* of ketene. As the methylene pivots around the central carbon to form twisted OXYAL, the resulting molecular orbital will have increasing oxygen lone pair character and decreasing methylene 1b<sub>1</sub> character. The substitution of  $\pi$ -donating groups on the methylene is a possible way of increasing the bonding from this orbital interaction.

The qualitative molecular orbital analysis retains its validity in describing the chemistry of this isomerization reaction. The ab initio calculations introduce quantitatively improved molecular orbital descriptions, as well as introducing the dominant correlation effects.

**Acknowledgment.** Support of this research through NSF Grant CHE 7719899 is acknowledged. Jean Evans prepared the figures.

**Registry No.** Cyclopropanone, 5009-27-8; allene oxide, 40079-14-9; oxyallyl, 17440-65-2.