

Table III. Chromatographic and UV Spectrophotometric Characteristics Used for Analysis of Electrolysis Products<sup>a</sup>

	R <sub>f</sub> (TLC)	HPLC retention time, min	λ <sub>max</sub> (UV), nm
4-pyridine- carboxaldehyde	0.62	7.1	256, 283 <sup>b</sup>
meso-pinacol	0.02	7.6	251
dl-pinacol	0.06	8.6	
4-pyridinecarbinol	0.28	5.3	253

<sup>a</sup> See the Experimental Section for the conditions used.

<sup>b</sup> Corresponding absorption bands; molar absorptivities are a function of pH (cf. ref 12).

expected electrolysis product subjected to an identical treatment as the sample, but without electrolysis. Typical recoveries were 80-90%. In alkaline solutions the extent of chemical decomposition of the aldehyde during the period of the electrolysis was determined by using a control solution.

**Analysis for Products.** The sample solution, after dilution, was subjected to analysis by UV spectrophotometry (Table III). Subsequently, the standard and sample solutions were filtered through polycarbonate membrane filters (Nucleopore Corp., 0.2 μm, stock no. 100406) and analyzed by high-pressure LC. The eluant for high-pressure LC was composed of 80% (by volume) of 0.02 M sodium phosphate buffer (pH 6.9) and 20% methanol-water mixture (60/40 v/v). A flow rate of 2.0 mL min<sup>-1</sup> was used, and the column pressure was in the range of 2000-2500 lb

in.<sup>-2</sup> Sample solutions were delivered to the injection valve by using a Precision Sampling Corp. 100-μL syringe (catalogue no. 100025). The column was equilibrated with eluant for at least 1 h prior to use. Under the conditions of the analysis, the response of the detector was linear for 4-pyridinecarbinol and meso-4,4-dipyridyl-1,2-ethanediol for amounts of solute between 0.1 and 4.0 μg. Product concentrations in the sample solutions were calculated by comparing peak heights for the sample solutions with those of the appropriate standards. Retention times for both dimers (Table III), the aldehyde, and the carbinol agreed with those found in the analysis of the electrolysis products within ±0.1 min.

Prior to investigation by TLC, the sample solution was extracted with chloroform. Water was removed from the organic extract with sodium sulfate. The solvent was removed by using a stream of nitrogen, and the residue was chromatographed in a closed container which had been preequilibrated with solvent. The chromatograms were eluted for a distance of 5 cm by using ethyl acetate as the solvent. Quenching of fluorescence of the TLC plate by the sample components in ultraviolet light was used for detection. R<sub>f</sub> values (Table III) agreed with those for the corresponding electrolysis products within ±0.01.

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**Registry No.** 1, 872-85-5; 4-pyridinecarbinol, 586-95-8; meso-pinacol, 4972-49-0; dl-pinacol, 5486-06-6.

## Ab Initio Self-Consistent-Field Study of Favorskii Rearrangement Intermediates

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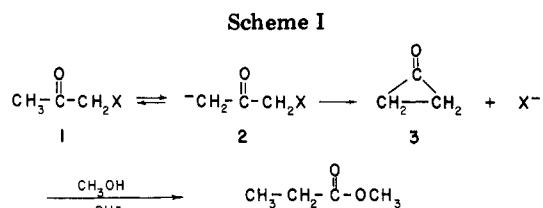
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Single-configuration SCF calculations using Pople's 4-31G basis were carried out on cyclopropanone and on oxyallyl. C<sub>2v</sub> symmetry was assumed for both, but, otherwise, the geometries were optimized completely. Oxyallyl is computed to close disrotatorily to cyclopropanone with no energy barrier and is thus excluded as a possible intermediate in the Favorskii rearrangement.

One of the most intensely studied mechanisms in organic chemistry has been that of the Favorskii rearrangement.<sup>1</sup> Mechanisms have been proposed involving virtually every reactive intermediate known to organic chemists. A number of these were eliminated, first by McPhee<sup>2</sup> and then by Loftfield,<sup>3,4</sup> whose work indicated that a symmetrical intermediate, most likely a cyclopropanone, was present. This gained further support when Turro<sup>5</sup> found that tetramethylcyclopropanone rearranged in basic methanol solution to give methyl 2,2,3-trimethylbutanoate. There is now general agreement that the mechanism is as shown in Scheme I.



More recent studies, in particular the extensive work of Bordwell,<sup>6</sup> have concentrated on the second step of the mechanism, i.e., conversion of the carbanion 2 to cyclo-

(1) For a recent review see: Chenier, P. J. *J. Chem. Educ.* 1978, 55, 286.

(2) McPhee, W. D.; Klingsberg, E. *J. Am. Chem. Soc.* 1944, 66, 1132.

(3) Loftfield, R. B. *J. Am. Chem. Soc.* 1950, 72, 632; 1951, 73, 4707.

(4) Loftfield, R. B.; Schaad, L. *J. Am. Chem. Soc.* 1954, 76, 35.

(5) Turro, N. J.; Hammond, W. B. *J. Am. Chem. Soc.* 1965, 87, 3258.

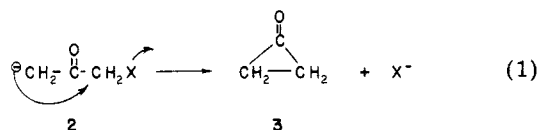
(6) (a) Bordwell, F. G.; Frame, R. R.; Scamehorn, R. G.; Strong, J. G.; Meyerson, S. *J. Am. Chem. Soc.* 1967, 89, 6704. (b) Bordwell, F. G.; Scamehorn, R. G. *Ibid.* 1968, 90, 6751. (c) Bordwell, F. G.; Scamehorn, R. G.; Springer, W. R. *Ibid.* 1969, 91, 2087. (d) Bordwell, F. G.; Carlson, M. W. *Ibid.* 1970, 92, 3370, 3377. (e) Bordwell, F. G.; Scamehorn, R. G. *Ibid.* 1971, 93, 3410. (f) Bordwell, F. G.; Almy, J. *J. Org. Chem.* 1973, 38, 575; (g) Bordwell, F. G.; Strong, J. G. *Ibid.* 1973, 38, 579.

Table I. Calculated and Experimental Geometry of Cyclopropanone

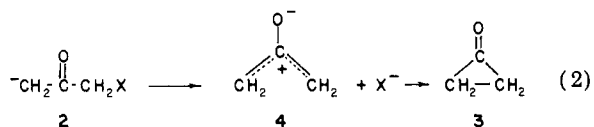
parameter <sup>a</sup>	present work	exptl <sup>b</sup>
C <sub>2</sub> -C <sub>3</sub>	1.561	1.575
C <sub>1</sub> -C <sub>2</sub>	1.459	1.475
C <sub>1</sub> -O	1.198	1.200
C-H	1.073	1.086
<HCH	114.3	114.13
θ <sup>c</sup>	27.0	28.58

<sup>a</sup> Bond distances are given in angstroms and angles in degrees. <sup>b</sup> Reference 8. <sup>c</sup> The angle made by the local C<sub>2</sub> axis of the methylene groups with the C<sub>1</sub>-C<sub>2</sub> or C<sub>1</sub>-C<sub>3</sub> bond.

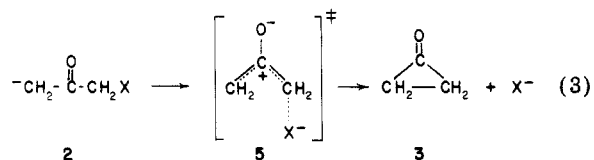
propanone (3). Bordwell<sup>6c</sup> has considered three paths. Path 1 is considered to be an internal S<sub>N</sub>2 displacement,



path 2 is an S<sub>N</sub>1-type reaction producing oxyallyl 4 as a



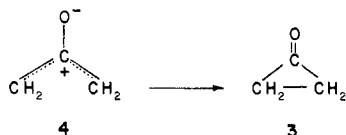
dipolar ion intermediate which subsequently undergoes a disrotatory ring closure to 3, and path 3 is a direct con-



version of 2 to 3 with 5, or something similar to it, representing a transition state. Bordwell has ruled out path 1 on the basis of electronic effects and stereochemical studies. Of the two remaining paths he favors path 2. This choice is based on electronic and stereochemical effects, in particular in substituted cyclohexanones.<sup>6a</sup> However, his experiments do not rule out path 3 (see below). The essential distinction between paths 2 and 3 is that in path 2 the dipolar ion 4 is an intermediate; that is, it is a local minimum in the reaction path. In path 3, 4 may appear, perhaps as a transition state, or it may not, but it is *not* a local minimum.

### Results and Discussion

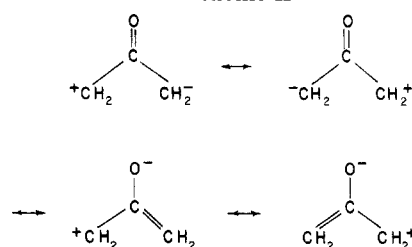
We have undertaken an ab initio calculation of the energy difference between 3 and 4 and of the potential



surface linking these two structures in an attempt to determine whether path 2 or 3 is operative in the Favorskii rearrangement. All calculations were carried out with a single-configuration SCF wave function by using Ditchfield, Hehre, and Pople's 4-31G Gaussian basis together with their recommended molecular scaling factors.<sup>7</sup> These were done by using the POLYATOM program on a DEC 1099 computer. With the assumption of C<sub>2v</sub> symmetry, the

(7) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* 1970, 54, 724.

### Scheme II

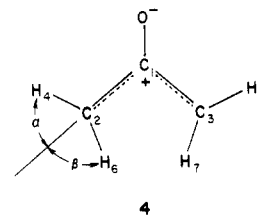
Table II. Mulliken Population Analysis<sup>a</sup> of Cyclopropanone and Oxyallyl

	cyclopropanone (3) <sup>b</sup>	oxyallyl (4)
Gross Atomic Charges		
C <sub>1</sub>	+0.44 (+0.41)	+0.39
C <sub>2</sub>	-0.38 (-0.34)	-0.25
C <sub>3</sub>	-0.38 (-0.34)	-0.25
O	-0.53 (-0.40)	-0.77
H <sub>4</sub>	+0.22 (+0.16)	+0.24
H <sub>6</sub>	+0.22 (+0.16)	+0.21
Overlap Populations		
C <sub>1</sub> -O	+0.92 (+0.89)	+0.98
C <sub>1</sub> -C <sub>2</sub>	+0.30 (+0.61)	+0.57
C <sub>2</sub> -C <sub>3</sub>	-0.10 (+0.48)	-0.29
C <sub>2</sub> -H <sub>4</sub>	+0.75 (+0.76)	+0.73
C <sub>2</sub> -H <sub>6</sub>	+0.75 (+0.76)	+0.72

<sup>a</sup> Mulliken, R. S. *J. Chem. Phys.* 1955, 23, 1833. <sup>b</sup> All values given were obtained from the 4-31G wave functions except those in parentheses which are from a STO-3G wave function.

geometry of cyclopropanone is fixed by the five bond lengths and angles in Table I. Starting with experimental values,<sup>8</sup> we varied these parameters one by one in the order listed to minimize molecular energy. Typically only three or four points were required to obtain the best value of each variable. The parameters are surprisingly independent, and after only two cycles (a total of 37 energy calculations) all bond lengths were optimized to 0.002 Å and angles to 0.1°. The best values are given in Table I. It is seen that there is excellent agreement between calculated and experimental parameters. While there have been several previous ab initio calculations of cyclopropanone,<sup>9</sup> our calculated total energy of -190.437 084 68 hartrees is 0.56 hartree below the best previously reported energy of Liberles, Greenberg, and Lesk.

A similar optimization of the planar dipolar ion 4 with



the assumption of C<sub>2v</sub> symmetry gave C<sub>1</sub>-O = 1.263 Å, C<sub>1</sub>-C<sub>2</sub> = 1.404 Å, C<sub>2</sub>-H<sub>4</sub> = 1.072 Å, C<sub>2</sub>-H<sub>6</sub> = 1.070 Å, ∠ C<sub>2</sub>-C<sub>1</sub>-C<sub>3</sub> = 108.6°, α = 60.2°, β = 57.3°, and an energy of -190.358 860 75 hartrees. On comparison of the geometry of 4 with that of 3, most notable is the lengthening

(8) Pochan, J. M.; Baldwin, J. E.; Flygare, W. H. *J. Am. Chem. Soc.* 1969, 91, 1896.

(9) (a) Liberles, A.; Greenberg, A.; Lesk, A. *J. Am. Chem. Soc.* 1972, 94, 8685. (b) Rohmer, M.; Roos, B. *Ibid.* 1975, 97, 2025. (c) Deakne, C. A.; Allen, L. C.; Laurie, V. W. *Ibid.* 1977, 99, 1343. (d) Martino, P. C.; Shevlin, P. B.; Worley, S. D. *Ibid.* 1977, 99, 8003; (e) Yamabe, S.; Minato, T.; Osamura, Y. *Ibid.* 1979, 101, 4525.

Table III. Calculated Energy Difference between 3 and 4

method	$E_4 - E_3$ , kcal/mol	ref
extended Hückel	-23	15
INDO	220	8
INDO	232	9a
MINDO/2	78	12
MINDO/3	66	13
ab initio <sup>a</sup>	83	9a
present ab initio	49	

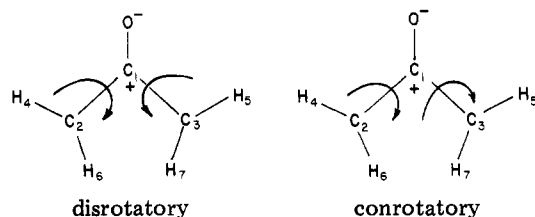
<sup>a</sup> Geometry not optimized.

of the C<sub>1</sub>-O bond and the shortening of the C<sub>1</sub>-C<sub>2</sub> bond, indicative of  $\pi$  delocalization over the four heavy atoms as would be expected from the possible resonance structures of 4 (Scheme II).

A Mulliken population analysis of our wave functions for 3 and 4 is given in Table II. The decrease in negative charge on C<sub>2</sub> and C<sub>3</sub>, the increased negative charge on O, and the increase of the C<sub>1</sub>-C<sub>2</sub> overlap population in going from 3 to 4 are all expected; but the slight increase in C<sub>1</sub>-O overlap population is not easy to reconcile with the increase in this bond length. Interaction between C<sub>2</sub> and C<sub>3</sub> is antibonding in the ion 4, as, even more surprisingly, it is in cyclopropanone itself. This is consistent with the observed cycloaddition of cyclopropanone across the C<sub>2</sub>-C<sub>3</sub> bond to dienes such as furan<sup>10</sup> and with the fact that this bond is "one of the longest carbon-carbon single bonds ever measured spectroscopically".<sup>8</sup> However, these conclusions must be considered tenuous as Mulliken population analyses can be quite basis-set dependent. In fact, such an analysis with an STO-3G rather than a 4-31G basis gives a positive overlap for the C<sub>2</sub>-C<sub>3</sub> bond (Table II). The bond is still the weakest in the molecule, and this is still consistent with cycloaddition across the C<sub>2</sub>-C<sub>3</sub> bond, but the large change from basis to basis suggests caution in interpreting the population analysis.

Table III compares our result for the energy difference between 3 and 4 with those of previous calculations.<sup>11-15</sup> In agreement with all earlier calculations except the extended Hückel,<sup>15</sup> we find 3 to be more stable than 4. However, our 49-kcal/mol difference is the smallest value calculated to date, again excepting the extended Hückel result.

Conversion of 4 to 3 was then examined by rotating the methylene groups of 4 about the C<sub>1</sub>-C<sub>2</sub> and C<sub>1</sub>-C<sub>3</sub> axes in both disrotatory and conrotatory fashions. Results of



these calculations are summarized in Table IV, where  $\gamma$  is the angle of rotation. No additional geometry optimization was carried out at the various values of  $\gamma$ , and all bond distances and angles were those in planar 4. It is

Table IV. Energies of Disrotatory and Conrotatory Ring Closure of 4 to 3

type of rotation	$\gamma$ , deg	energy, hartrees
	0	-190.358 860 75
disrotatory	1	-190.358 862 72
disrotatory	5	-190.358 907 06
conrotatory	5	-190.357 788 25

immediately seen that the disrotatory ring closure is favored over the conrotatory. Furthermore, there is no indication of an energy barrier to disrotatory ring closure since a rotation of even only 1° lowers the energy. Reoptimization of geometry after rotation would, of course, lower the energy still farther. The principal conclusion to be drawn is that 4 is not a minimum on the potential surface. Therefore, it is not an intermediate in the Favorskii rearrangement although it may be a point on the reaction pathway. These results therefore exclude path 2 for the Favorskii mechanism. Path 3 remains possible although details are unknown. All that can be concluded about path 3 is that if 4 lies on path 3, it cannot be an intermediate. It may be a transition state, or it may lie elsewhere on the reaction coordinate. Our finding is compatible with Bordwell's results in that path 3 is not ruled out by his experiments. One can envision an S<sub>N</sub>1-like ionization of 2 which would produce a dipolar ion not as an intermediate but merely as a point along the reaction coordinate. This would still accommodate Bordwell's large negative  $\rho$  (-4.23) found from chloride loss from ArCH<sub>2</sub>-COCH<sub>2</sub>Cl systems.<sup>6c</sup>

In several substituted  $\alpha$ -halocyclohexanones, Bordwell<sup>6a</sup> has ascribed the change in stereochemistry of the Favorskii products on changing methoxide concentration to cyclopropanone intermediates interconverting through a dipolar ion intermediate. But again these stereochemical observations can be explained as well if the dipolar ion is a transition state rather than an intermediate.

Here, as in all calculations on systems of this size, several cautions are in order. First, the 4-31G basis is about as large as is feasible for cyclopropanone, but its energy is probably still a few tenths of a hartree above the Hartree-Fock limit. Second, correlation-energy corrections (again on the order of some tenths of a hartree) to go from the Hartree-Fock limit to the exact energy may well be different for cyclopropanone and oxallyl. Sinanoğlu's treatment of correlation energy based on atomic charge densities,<sup>16</sup> Lie and Clementi's density functional method,<sup>17</sup> and the examples presented by McKelvey and Streitwieser<sup>18</sup> all suggest a larger correlation correction for oxallyl than for cyclopropanone. Third, these exact energies are those of the molecular potential minima. Further corrections, the largest of which are due to zero-point vibrational energies, are required to go to the Gibbs free energies appropriate to constant  $P$  and  $T$  reactions. These last corrections are on the order of hundredths of a hartree. Finally, even if all these corrections were made, the resulting  $\Delta G$ 's would refer to ideal gas reactions. Ion cyclotron resonance experiments<sup>19</sup> have shown striking differences between gas- and solution-phase results for a given series of reactions. Subject to all these strictures our results rule out path 2 for the conversion of 2 to 3 in the Favorskii rearrangement.

Registry No. 3, 5009-27-8; 4, 51747-40-1.

(10) Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* 1973, 2, 663 (1 atomic unit of length = 0.529 177 06 Å, 1 atomic unit of energy = 1 hartree = 627.5092 kcal/mol)

(11) Turro, N. J. *Acc. Chem. Res.* 1969, 2, 25.

(12) Olsen, J. F.; Kang, S.; Burnelle, L. *J. Mol. Struct.* 1971, 9, 305.

(13) Bodor, N.; Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* 1970, 92, 3854.

(14) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, 97, 1302.

(15) Hoffmann, R. *J. Am. Chem. Soc.* 1968, 90, 1475.

(16) Sinanoğlu, O.; Pamuk, H. O. *J. Am. Chem. Soc.* 1973, 95, 5435.

(17) Lie, G. C.; Clementi, E. *J. Chem. Phys.* 1974, 60, 1275.

(18) McKelvey, J. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1977, 99, 7121.

(19) Arnett, E. M. *Acc. Chem. Res.* 1973, 6, 404.