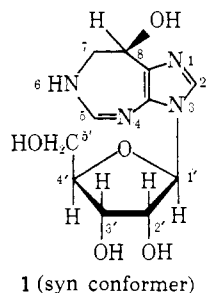


Figure 1.

The unequivocal formulation of the structure as 1



has been accomplished by the X-ray crystallographic study of coformycin itself.<sup>5</sup> The crystals of coformycin were grown from an aqueous solution as colorless thin plates. Lattice constants and intensities were measured by a four-circle X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. Crystal data for coformycin sesquihydrate, C<sub>11</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub>·1.5H<sub>2</sub>O: formula weight = 311.3; orthorhombic;  $a = 11.960$ ,  $b = 23.500$ ,  $c = 4.935$  Å;  $D_x = 1.49$  g cm<sup>-3</sup>,  $Z = 4$ ; absent reflections,  $h00$  when  $h \neq 2n$ ,  $0k0$  when  $k \neq 2n$ ; space group  $P2_12_12$ . Integrated intensities were measured by the  $\omega$ - $2\theta$  scanning method with a scan speed of  $4^\circ 2\theta \text{ min}^{-1}$ . The crystal was about  $0.13 \times 0.025 \times 0.9$  mm in size and no correction was applied for absorption. A total of 1021 independent reflections with  $F > 3\sigma(F)$  were measured. These structure factors were then converted to the normalized structure factors;  $E$  and the phases of 81 reflections with  $E > 1.8$  were determined by the symbolic addition procedure. These phases were then refined and extended to 182 reflections with  $E > 1.49$ . The resulting  $E$  map showed the locations of 17 non-hydrogen atoms. Refinement of the atomic parameters for these 17 atoms was carried out by the least-squares method. Subsequent Fourier and difference Fourier syntheses revealed the whole structure including hydrogen atoms. The  $R$  value at the present stage of the refinement is 0.057 for 1021 reflections. Thus, the

present analysis establishes the structure of coformycin to be 3-( $\beta$ -D-ribofuranosyl)-6,7,8-trihydroimidazo[4,5- $d$ ] [1,3]diazepin-8( $R$ )-ol. The structure resembles that of formycin B in some respects, but the base moiety is modified and links to the sugar moiety through a usual carbon–nitrogen glycosyl bond. Figure 1 illustrates the conformation of the molecule. The conjugated system of the base is interrupted at C(7) and the seven-membered ring takes a puckered form. Thus the ten atoms comprising the base are nearly coplanar except for C(7). The C(7) atom deviates from the plane formed by the remaining nine atoms (they are planar within  $\pm 0.06$  Å) by 0.72 Å in the opposite direction to O(8). The glycosyl torsion angle  $\chi$  [C(2)–N(3)–C(1')–O(1')],  $73^\circ$ , lies in the range of usual anti conformation which is different from that found in either formycin hydrobromide monohydrate<sup>2</sup> or formycin monohydrate.<sup>6</sup> The torsion angles of the furanose ring are  $\tau_0 = -40^\circ$ ,  $\tau_1 = 45^\circ$ ,  $\tau_2 = -33^\circ$ ,  $\tau_3 = 12^\circ$ , and  $\tau_4 = 17^\circ$ , and the conformation of the ring is C(2')-endo-C(1')-exo. Similar conformation has been found in formycin monohydrate.<sup>6</sup> The conformation about the C(4')–C(5') bond is gauche–gauche with  $\phi_{OO} = 74^\circ$  and  $\phi_{OC} = 45^\circ$ , which also differs from that of formycins.<sup>2,6</sup> As a whole, the conformation about the glycosyl bond, furanose ring, and the C(4')–C(5') bond are those which have been most commonly observed in nucleoside and nucleotides.

**Acknowledgment.** We wish to express our cordial thanks to Meiji Seika Kaisha, Ltd., for the supply of natural coformycin, and to Drs. Y. Suhara and S. Shibahara for the helpful discussion.

(6) P. Prusiner, T. Brennan, and M. Sundaralingam, *Biochemistry*, **12**, 1196 (1973).

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## Organic Transition States. II. The Methylenecyclopropane Rearrangement. A Two-Step Diradical Pathway with a Secondary Minimum<sup>1</sup>

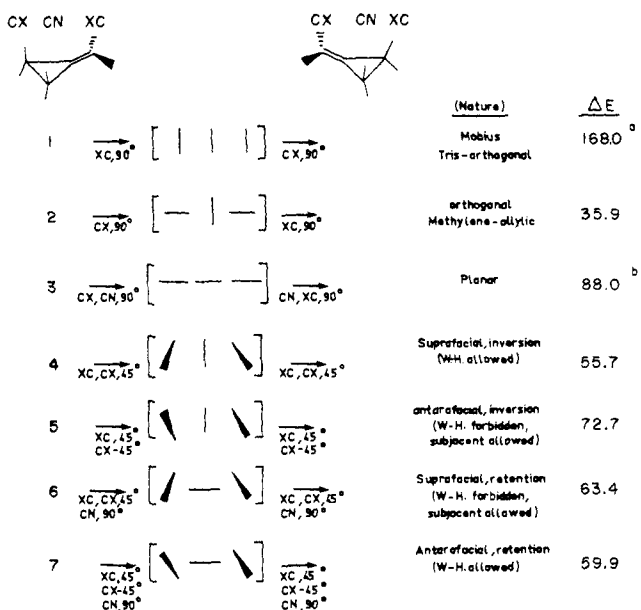
Sir:

Methylenecyclopropane, first as Feist's acid, then as a variety of other derivatives, has been found to undergo facile degenerate rearrangement.<sup>2</sup> This reaction is interesting since in principle appropriate labeling can distinguish between Woodward–Hoffmann allowed,<sup>3</sup> Woodward–Hoffmann forbidden but subjacent al-

(1) Part I: Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem., Suppl.*, **1**, 197 (1971); J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972); Y. Jean, These d'Etat, Université de Paris-Sud, Centre d'Orsay, 1973.

(2) (a) E. F. Ullmann, *J. Amer. Chem. Soc.*, **82**, 505 (1960); (b) W. v. E. Doering and L. Birladeanu, *Tetrahedron*, **29**, 449 (1973); (c) J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971); (d) J. C. Gilbert and D. P. Higley, *Tetrahedron Lett.*, 2075 (1973).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).



**Figure 1.** Ideographs and 4-31G energies (relative to methylenecyclopropane) for the seven possible reaction midpoints. A vertical line represents a  $\text{CH}_2$  group perpendicular to the CCC plane and a horizontal line an inplane  $\text{CH}_2$ . (a)  $D_{3h}$  symmetry; energy is lowered by Jahn-Teller distortion, with ultimate collapse to a  $90^\circ$  twisted methylenecyclopropane, 70.6 kcal/mol above reactant. (b) This value (88 kcal/mol) corresponds to  $D_{3h}$  symmetry where the lowest singlet state is degenerate. Jahn-Teller distortion results in two lower symmetry ( $C_{2v}$ ) forms with energies of 67.5 and 68.5 kcal/mol above the parent hydrocarbon (see W. T. Borden, *Tetrahedron Lett.*, 259 (1967)). D. R. Yarkony and H. F. Schaefer, III (*J. Amer. Chem. Soc.*, submitted for publication) report a much larger energy gain of 47 kcal/mol upon relaxation to a  $C_{2v}$  symmetry, placing it only 4 kcal/mol above their energy for the orthogonal diradical **2**. The reason for the discrepancy is not clear, especially in view of the good agreement between the two theoretical methods on a number of other points. The associated triplet<sup>5,6</sup> is only 17.6 kcal/mol above reactant.

lowed,<sup>4</sup> and two-step pathways involving the elusive trimethylenemethane diradical.<sup>5</sup> We report an extensive *ab initio* study of all, even remotely plausible, transition states for the reaction.<sup>6</sup> Our results implicate a diradical intermediate in thermolysis.

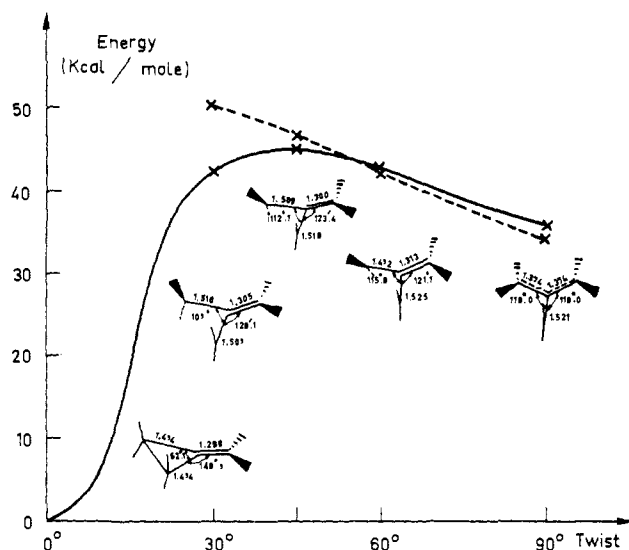
Complete exploration of the energy surface for methylenecyclopropane degenerate rearrangement would require simultaneous variation of 24 degrees of freedom. A less ambitious but enlightening task starts with the computation of energies and molecular geometries of the seven plausible reaction midpoints,<sup>6</sup> followed by a thorough exploration of the potential surface around the lowest. A pathway from reactant to favored midpoint in all probability yields the transition state.

It is convenient to construct an ideograph representing each of the seven possible midpoints (Figure 1). The three methylene groups are labeled CX, CN, and XC corresponding to their roles in the rearrangement: XC changes from exocyclic to cyclic, CX the other way, and CN, the "migrating group," remains in the ring. For the concerted motions (4, 5, 6, 7) the twist angle of the methylene termini has been fixed at  $45^\circ$ .

(4) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

(5) (a) P. S. Dowd, *Accounts Chem. Res.*, **5**, 242 (1972); (b) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971); (c) W. T. Borden and L. Salem, *ibid.*, **95**, 932 (1973).

(6) L. Salem in "Computational Methods for Large Molecules and Localized Solids," F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Press, New York, N. Y., 1972, p 23.



**Figure 2.** Reaction path (4-31G) from reactant to orthogonal diradical. Transition state is 44.7 kcal/mol above methylenecyclopropane. Dotted line shows triplet energies.

The energies of **1** to **7** were calculated using both the closed shell and restricted open shell<sup>7,1</sup> Hartree-Fock Hamiltonians. After  $3 \times 3$  configuration-interaction<sup>8</sup> the best singlet energy given by either of the two was chosen. Midpoint geometries were optimized using the STO-3G minimal basis<sup>9a,10</sup> after which energies were recomputed with the extended 4-31G set.<sup>9b</sup> The results (Figure 1) show the orthogonal methylene-allylic trimethylenemethane diradical **2** to be the most stable of all possible midpoints by almost 20 kcal/mol. The search was pursued by: (a) sampling the potential surface around the orthogonal methylene-allylic diradical **2** (the energy increased for all attempted distortions), (b) running a path from reactant to **2** (with partial optimization<sup>10</sup> along the way). This resulted in a maximum close to the  $45^\circ$  twist structure (Figure 2), which was then considered to be an excellent approximation to the reaction transition state. Full geometric optimization improved the STO-3G energy slightly but not the 4-31G value.<sup>11</sup> The optimized transition state lies 44.7 kcal/mol above starting material compared with the experimental estimate of 40.4 kcal/mol for the rearrangement process in 2-methylmethylenecyclopropane.<sup>12a</sup> The predicted 8.8 kcal/mol depth for the trough between

(7) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).

(8) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(9) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971); calculations were performed using a modified (including Nesbet Hamiltonian and  $3 \times 3$  CI) version of GAUSSIAN 70; W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

(10) Initially certain coordinates (CH bonds and HCH angles) were assigned fixed values, but later, for methylenecyclopropane, the transition state structure and for the diradical intermediate full geometric optimization was performed resulting in a further gain in energy of 1-2 kcal/mol.

(11) This is due to pyramidalization of CN and of the  $45^\circ$  CX group at the STO-3G level. 4-31G level calculations favor arrangements more toward planarity: W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 6377 (1971).

(12) (a) J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963); (b) W. v. E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970). (c) A referee has commented that activation required for rearrangement in parent methylenecyclopropane should be about 43 kcal/mol, as 2.5 kcal/mol is the usual stabilization imparted by a methyl.

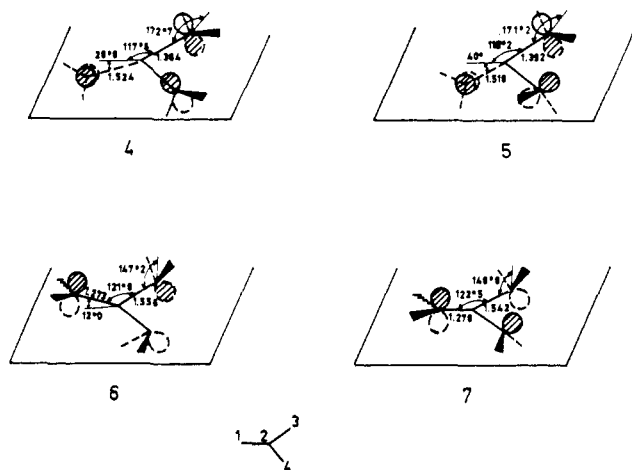


Figure 3. Optimized (STO-3G) geometries for midpoints of orbitally concerted pathways ( $C_1$  is assumed to migrate from  $C_3$  to  $C_4$ ).

transition state and diradical intermediate **2** makes this potential minimum an interesting target for experimental detection.

Why does the reaction shun orbital concert? The optimized geometries<sup>10</sup> shown in Figure 3 provide some insight. The most extraordinary geometry is that of **4**, in which the migrating bond bends *away* from the nearest, suprafacial face of the allylic group. Conservation of favorable in-phase overlap between the  $C_1$  orbital and the  $C_3C_4$  allylic system is sacrificed in favor of restored conjugation involving  $C_3$ ,  $C_2$ , and  $C_4$ , and no profit is to be gained from orbital concert. Another striking structure is **6**.  $C_1$  moves up out of plane, while  $C_3$  and  $C_4$  pyramidalize so as to create large lobes downwards and away. Thus the unfavorable (Woodward–Hoffmann forbidden<sup>3</sup>) interaction between  $C_1$  and the allylic nonbonding orbital is minimized, while adjacent interactions<sup>4</sup> between  $C_1$  and the allylic bonding orbital (largely on  $C_2$ ) are maximized. The high energies of **6** and **7** (agreeing with the experimental exclusion of stereochemical retention<sup>12b</sup>) may be attributed to their resemblance to the planar diradical **3**. Structures **3** and **1** have extremely high energies<sup>13</sup>—the former due to the large ionic character of its wave function,<sup>5c</sup> the latter because both the double bond and the ring bond have been lost without compensation.

It must be commented that our assignment of a favored diradical pathway is not entirely in keeping with all the experimental evidence, namely, that at least 10% of the reaction passes through an achiral array. Whether this is due to differences between parent methylenecyclopropane—on which the calculations were performed—and the substituted forms which have undergone experimental scrutiny or to fundamental limitations in the theoretical model is not clear to us at this time.

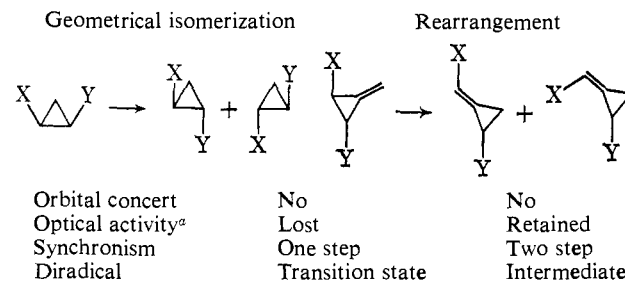
We wish to compare and contrast the geometrical isomerization of cyclopropane<sup>1</sup> and the degenerate methylenecyclopropane rearrangement. Both reactions follow orbitally nonconcerted pathways and yet maintain stereochemical integrity.<sup>14</sup> Here for a trans 1,2-

(13) See also A. S. Kende and R. Greenhouse, quoted in ref 2a, p 507.

(14) (a) For the most recent experimental proof on cyclopropane see: W. v. E. Doering and K. Sachdev, *J. Amer. Chem. Soc.*, in press; (b) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968); (c) W. L. Carter

disubstituted reactant, optical activity is preserved,<sup>2a,12</sup> only two of the four possible products being obtained. Also, one reaction occurs in a single step, as a time-unified event, the other as a two-step process. Finally both reactions proceed *via* a diradical. In the first it is a *transition state*<sup>1,14a</sup> and lies right at the col of the potential surface. Here the diradical **2** is an *intermediate*, lying in a secondary minimum. These results are summarized below (Chart I). The comparison throws light

Chart I



<sup>a</sup> Optical activity is retained if X rotates faster than Y.

on the notion of concert<sup>15,16</sup> and increases our knowledge of diradicals. It appears that quantum mechanics will yield a diradical transition state<sup>8</sup> when there is no source of secondary stabilization and an intermediate in those cases where one of the odd electrons finds such a source.<sup>17</sup> Whereas the thermochemical viewpoint consistently leads to diradicals as secondary intermediates,<sup>18</sup> quantum mechanical calculations offer a varied picture of diradicals on potential energy surfaces.<sup>19</sup>

**Acknowledgment.** The authors thank the French National Research Center for a generous allocation of computer time.

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(15) For a stimulating discussion see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Fortsch.*, **15**, 281 (1970).

(16) J. P. Lowe, *J. Chem. Educ.*, submitted; A. H. Andrist, *J. Org. Chem.*, **38**, 1772 (1973).

(17) See second footnote, p 110 of ref 8, where the possibility was raised that delocalization could stabilize a diradical.

(18) (a) R. G. Bergman in "Free Radicals," Vol. 1, J. Kochi, Ed., Wiley, New York, N. Y., 1973, p 191; (b) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2849 (1973).

(19) Preliminary results from this laboratory suggest that in other thermal reactions of hydrocarbons, diradicals may be resting points on the side of a hill leading to the transition state.

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Received January 26, 1974

## Synthesis and Structure of $\pi$ -Phosphinoacetylene Complexes of Zerovalent Palladium and Platinum

Sir:

Acetylene  $\pi$ -complexes of the type  $[(C_6H_5)_3P]_2ML$  (I) where M = Ni, Pd, or Pt and L is an acetylene ligand, have played a leading role in the development of models