# Location of the Transition Structure for a Concerted Pathway in the Methylenecyclopropane Rearrangement

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Abstract: Ab initio SCF/3-21G, SCF/6-31G*, and MP2/6-31G* calculations suggest a closed-shell $^1A'$ (C_s) transition structure for a concerted mechanism in the degenerate rearrangement of methylenecyclopropane.

The degenerate thermal rearrangement of methylenecyclopropane has been of studied by experimental and theoretical chemists for over two decades.[1-3] Stereochemical investigations of optically active Feist's ester (**1**, X = CO_2CH_3)[4] and *trans*-
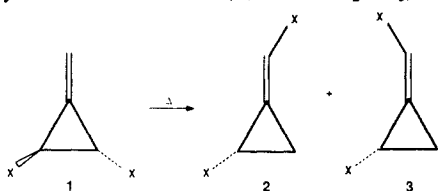
2,3-dimethylmethylenecyclopropane (**1**, X = CH_3)[5,6] show that in both syn and anti products the migrating CHX group has undergone predominantly an inversion of configuration, which leads to optically active rather than racemic **2** and **3**. More recently Baldwin and Chang[7] in a detailed kinetic and stereochemical study of optically active 2-(methoxymethyl)-2,3-dideuterio-1-(dideuteriomethylene)cyclopropane (**4**) concluded that
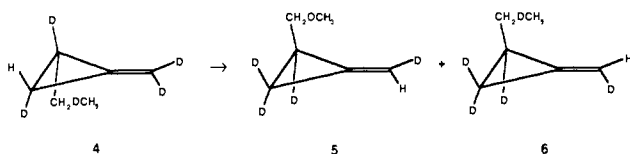
the $CDCH_2OCH_3$ group migrates in a 1,3-shift to form **5** and **6** with no epimerization at the migrating group. Hence, this rearrangement occurs with complete inversion of configuration at the $CDCH_2OCH_3$ carbon.

Therefore, for these systems the major pathway must involve either a chiral intermediate in a nonconcerted reaction or a chiral transition structure in a concerted reaction to account for the observed stereochemistry. Recent theoretical studies[8] have focused on the nonconcerted pathway and suggest that the likely intermediate along this pathway is a singlet diradical (**7**) in which one
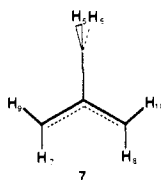
of the methylene groups lies in a plane orthogonal to the plane of all other atoms. The transition structure linking this intermediate and methylenecyclopropane has been reported by Davidson and Borden.[8a]

The concerted pathway has received little attention. Here, we report the transition structure for this pathway. Because reactant and product are equivalent, the migrating CH_2 group in the transition structure of a concerted pathway must be symmetrically arranged between the two carbon atoms with which it is breaking and forming bonds. The migrating carbon therefore must lie on a plane of symmetry of the transition structure. Furthermore,
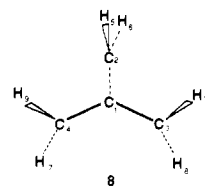
Table I. Optimized Geometry of the $^1A'$ (C_s) Transition Structure **8**

parameter[a]	computation	
	SCF/6-31G*// SCF/6-31G*	MP2/6-31G*// MP2/6-31G*[b]
Bond Distances		
C_1C_2	1.440	1.466
C_1C_3	1.367	1.384
C_2H_5	1.079	1.089
C_2H_6	1.071	1.085
C_3H_8	1.079	1.089
C_3H_{10}	1.073	1.086
Angles		
$\angle C_2C_1C_3$	108.9	114.0
$\angle C_3C_1C_4$	135.3	127.2
$\angle C_1C_2H_5$	126.5	125.8
$\angle C_1C_2H_6$	116.6	116.0
$\angle H_5C_2H_6$	116.9	118.2
$\angle C_1C_3H_8$	123.5	122.6
$\angle C_1C_3H_{10}$	119.2	119.4
$\angle H_8C_3H_{10}$	117.2	117.7
$\angle H_7C_4C_1C_2$	137.7	142.0
α^c	31.8	23.8
energy	−154.7606	−155.3228

[a] Bond distances in angstroms, angles in degrees, and energies in au. [b] Complete MP2 with full-core. [c] α is the angle between the C_1C_2 bond and the $C_1C_3C_4$ plane.

to explain the observed stereochemistry, the transition structure for the concerted process must be chiral when appropriately substituted. We were able to locate such a transition structure (**8**) on the $^1A'$ potential surface by imposing C_s symmetry in closed-shell SCF/3-21G calculations using GAUSSIAN 82.[9] The single imaginary frequency of **8** showed it to be a transition structure.

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(3) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981.

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Table II. Total Energies (au) and Relative Energies (kcal/mol, in Parentheses) of Three C_4H_6 Species

species	calculation		
	CI-SDQ/STO-3G[a]	SCF/3-21G[b]	MP2/6-31G*//SCF/3-21G[b]
$^1A_1$ methylenecyclopropane (C_{2v})	-153.293	-154.019	-155.395
$^3A_2'$ trimethylenemethane (D_{3h})	-153.247 (28.9)	-154.039 (-12.9)	-155.343 (32.9)
$^1B_1$ trimethylenemethane (C_{2v})	-153.223 (43.9)	-154.010 (5.6)	-155.316 (49.4)

[a] Reference 8a. [b] RHF and RMP2 calculations were done for the first species and UHF and UMP2 for the second and third. The frozen-core approximation was used in the MP2 calculations.
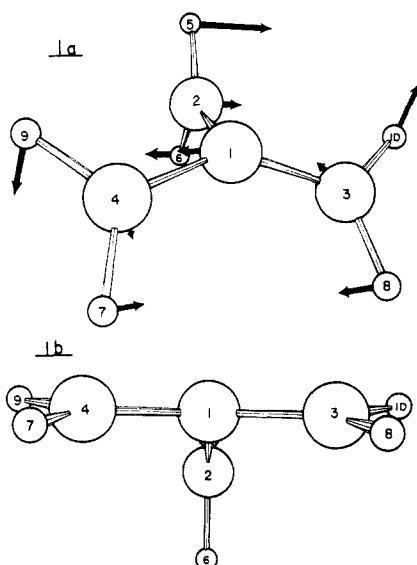

Figure 1. ORTEP views of the SCF/6-31G* transition structure **8**. **1a** shows motion (not mass-weighted) in the normal mode with a negative force constant.

Table III. Structure of the $^1B_1$ Diradical (**7**)

geometric param in optimized structure[a]	calculation	
	UHF/3-21G	MCSCF/STO-3G[b]
C_1C_2	1.493	1.508
C_1C_3	1.392	1.405
$\angle C_3C_1C_4$	120.5	121.0
$\angle C_1C_2H_5$	120.4	121.0

[a] Bond lengths in angstroms; angles in degrees. [b] Reference 8a.

We then carried out more elaborate SCF/6-31G* and MP2/6-31G* geometry optimizations on transition structure **8**, and the results are summarized in Table I. Vibrational analysis of the SCF/6-31G* structure again gave a single imaginary frequency, thus confirming that the stationary point **8** is a transition structure. ORTEP drawings showing two perspectives of **8** in the SCF/6-31G* calculation are given in Figure 1 where it is clear that structure **8** is quite different from the diradical intermediate **7** (although both have a plane of symmetry perpendicular to the $C_4C_1C_3$ plane). The central carbon atom in **8**, but not in **7**, is pyramidalized, presumably to maximize carbon–carbon σ bonding during the course of the reaction. Also, the two equivalent CH_2 groups in **8** are significantly twisted out of the plane of carbon atoms 1, 3, and 4 in a disrotatory fashion. One direction of the normal mode with imaginary frequency is shown in Figure 1a. Carbon atom 2 is forming a bond to carbon 3, and groups $C_2H_5H_6$ and $C_3H_8H_{10}$ are moving in a disrotatory way to become perpendicular to the emerging $C_1C_2C_3$ ring. The $C_4H_7H_9$ group is rotating into the ring plane to become the *exo*-methylene as the C_1C_4 bond is shortening. Motion along the normal mode in the opposite direction forms the $C_1C_2C_4$ ring with $C_3H_8H_{10}$ as the *exo*-methylene group.

Comparison of the MP2/6-31G* energy of **8** with that of the analogous MP2/6-31G* full-core calculation for methylenecyclopropane ($E = -155.4106$ au)[10] predicts an activation energy of 55 kcal/mol for the concerted pathway. This is in reasonable agreement with the enthalpy of activation (40.4 kcal/mol) reported

by Chesick[11] for the rearrangement of 2-methylmethylenecyclopropane.

Although the complete reaction path has not been followed from transition structure **8** down to energy minima, the geometry of **8**, the nature of motion in its normal mode with a negative force constant, and the fact that substituents would give chirality in **8** all make it appear that **8** is the transition structure for a concerted degenerate rearrangement of methylenecyclopropane.

We have not repeated Davidson and Borden's search for the transition structure leading to **7**; but in addition to the $^1A'$ transition structure **8**, we also computed the structure of **7** ($=^1B_1$ trimethylenemethane), planar triplet trimethylenemethane (**9**),

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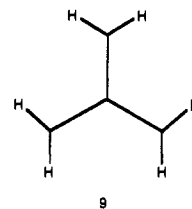
and the $^1A_1$ ground-state methylenecyclopropane with the 3-21G basis in order to be sure all are distinct stationary points on the 3-21G surface. Since all were found to be stationary points, eigenvalues of the respective force constant matrices were computed. Structures **7**, **9**, and **1** (X = H) had no negative eigenvalues and therefore correspond to minimum energy structures. As mentioned above **8** is a transition structure. These open-shell calculations done with GAUSSIAN 82 use the formulation of Pople and Nesbet[12] and hence do not give proper eigenfunctions of S^2, nevertheless as Table II shows these three structures do lie in the same energy order in an MP2/6-31G* calculation at the SCF/3-21G geometries as found by Davidson and Borden[8a] in their CI-SDQ/STO-3G calculations. Table III shows that even our SCF/3-21G-optimized structure of **7** is similar to Davidson and Borden's MCSCF/STO-3G structure.

(10) Staley, S. W., private communication.

(11) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.
(12) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.