Structural isomerization of cyclopropane: a new mechanism through propylidene

Holger F. Bettinger,[a] Jonathan C. Rienstra-Kiracofe,[a] Brian C. Hoffman,[a] Henry F. Schaefer III,[a] John E. Baldwin[b] and Paul v. R. Schleyer*[a]

[a] *Center for Computational Quantum Chemistry, The University of Georgia, 1004 Cedar Street, Athens, GA, 30602-2556, USA. E-mail: schleyer@paul.chem.uga.edu*
[b] *The Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100, USA.*

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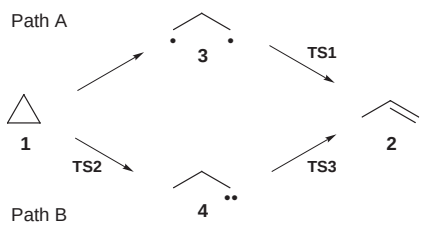
***Ab initio* coupled cluster methods indicate that the isomerization of cyclopropane to propene (E_a = 64–66 kcal mol^{-1} experimentally) might involve two different mechanisms: the barrier for the newly proposed pathway through propylidene is only slightly higher ($\Delta E^{\ddagger}$ = 66.6 kcal mol^{-1}) than that of the traditional trimethylene route ($\Delta E^{\ddagger}$ = 64.2 kcal mol^{-1}).**

Even though cyclopropane (**1**) and propene (**2**) have comparable thermodynamic stabilities (8 kcal mol^{-1} in favor of **2**),[1] a remarkably high activation energy of approximately 65 kcal mol^{-1} hampers their interconversion.[2–9] Both concerted and stepwise mechanisms have been considered for this isomerization.[3,5,10–14] The stepwise pathway (A in Scheme 1) involving trimethylene (**3**) has generally been favored since Benson[11] presented arguments against a concerted reaction: his estimated barrier for such a process was significantly higher than the activation energy determined experimentally.[5] However, the most recent computational study purported to have located a transition state 'connected to cyclopropane and propylene without an intermediate.'[14] We examine another path (B in Scheme 1) involving carbene **4** as an intermediate which apparently has not been considered for the parent rearrangement, although carbene pathways have been implicated in more elaborate systems.[15]

The singlet biradical **3** is assumed to be involved in the geometrical and the 'optical' (*i.e.* enantiomeric) isomerization of appropriately labeled cyclopropanes,[16–30] but has only been observed recently *via* femtosecond laser spectroscopy. The extremely rapid ring closure to **1** limits the lifetime of **3** to 120 fs.[29]

Although the [1,2]-H shift *via* **TS1** is the rate determining step in the **1** → **2** isomerization *via* **3**, the **3** to **2** rearrangement has not been studied as comprehensively as the **1** ⇌ **3** process. A barrier of approximately 5 kcal mol^{-1} was estimated for the **3** → **2** [1,2]-H shift.[13] This was based both on the experimental finding that the structural isomerization of **1** at 480 °C is approximately an order of magnitude slower than the **1** ⇌ **3** process (ΔE_a = 3.7 kcal mol^{-1})[31] and on the theoretical barrier of less than 1 kcal mol^{-1} for the **3** → **1** reaction.[18–20]

Fan *et al.*[13] recently computed pathway A (Scheme 1) at various levels, but found good agreement with the experimental activation energies for the overall **1** → **2** reaction (64–66 kcal mol^{-1})[2–9] only at UB3LYP/6-31G**//UMP2/6-31G** (66.1 kcal mol^{-1}). However, the **3** → **2** barrier *via* **TS1** was 9.5 kcal mol^{-1}, indicating that the computed energy of the trimethylene intermediate might be somewhat too low. Doubleday obtained a zero point corrected barrier of 6.9 kcal mol^{-1} for the **3** → **2** [1,2]-H shift reaction at MR-CISD//CASSCF(4,4).[22] Dubnikova and Lifshitz[14] reported a transition structure at UB3LYP/cc-pVDZ which is very similar to Doubleday's TS1 for the **3** → **2** reaction; however, their intrinsic reaction coordinate (IRC) computation was not able to locate intermediate **3** and was said to connect **TS1** to **1** and **2** directly.[14] This result is the only evidence in favor of a concerted process, but may be an artifact due to the inadequacy of density functional methods for closed shell biradicals.



Scheme 1 Ring opening of cyclopropane (**1**) *via* trimethylene (**3**) (Path A) or propylidene (**4**) (Path B) to propene (**2**).

We now propose a new possibility. Our *ab initio* data† suggest a carbene mechanism (path B in Scheme 1) involving propylidene (**4**) to be competitive energetically to the traditional trimethylene (**1** → **3** → **2**) pathway A.

A transition state (**TS2**, 66.6 kcal mol^{-1} above **1**) for the endothermic ring opening of **1** leads directly to propylidene (**4**, Fig. 1). The carbene obtained from this reaction is in conformation **4a** (66.5 kcal mol^{-1}), where the divalent carbon center is stabilized by the adjacent C2–C3 bond through hyperconjugation and by interaction with the methyl CH bond (analogous stabilizations have been reported for related carbocations).[34,35] Isomer **4b**, oriented in a conformation favoring CH hyperconjugation, is slightly lower in energy (1.5 kcal mol^{-1}). The [1,2]-H shifts in acyclic alkylcarbenes are well known to be very facile.[36–38] Indeed, only an very small barrier (0.07 kcal mol^{-1} *via* **TS3**), which disappears after the CCSD/DZP ZPVE correction, is predicted for the **4b** → **2** rearrangement.

In addition to **TS1**, Doubleday obtained a structure very similar to **TS2** previously at the CASSCF(4,4) level.[22] However, his intrinsic reaction coordinate (IRC) computation at CASSCF(4,4) with a modified 6-31G* basis set indicated that his **TS2**-like transition structure connects **3** and **4**. In contrast to Doubleday's report, our CASSCF(4,4)/TZ2P IRC clearly shows that **TS2** is not connected to **3** but rather joins **1** to **4a**

Table 1 Relative energies, zero-point corrected relative energies (in parentheses), and zero-point vibrational energies of C_3H_6 stationary points.

Species	CCSD/DZP	CCSD/TZ2P	CCSD(T)/TZ2P[a]	ZPVE[b]/ kcal mol^{-1}
1	0	0	0	52.1
2	−7.2 (−8.7)	−8.4 (−9.9)	−9.2 (−10.7)	50.6
4a	70.9 (68.2)	69.8 (67.1)	69.2 (66.5)	49.4
4b	69.3 (65.6)	68.8 (65.1)	68.7 (65.0)	48.4
TS1	79.7 (73.9)	78.6 (72.8)	70.0 (64.2)	46.3
TS2	72.0 (68.9)	71.1 (68.0)	69.7 (66.6)	49.0
TS3	70.9 (66.3)	69.7 (65.1)	68.8 (64.2)	47.5

[a] Single point energies employing the CCSD/TZ2P geometries. [b] Computed at the CCSD/DZP level; not scaled. The imaginary vibrational frequency of transition structures is ignored.

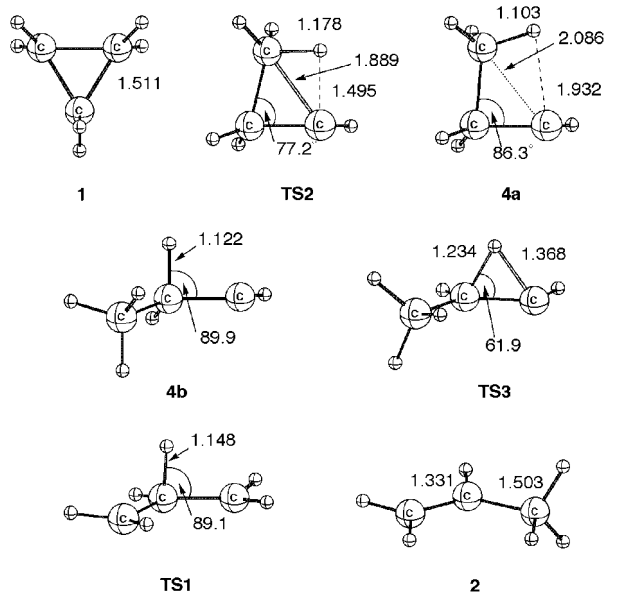


Fig. 1 Geometries of C_3H_6 stationary points optimized at the CCSD/TZ2P level of theory. All distances are in Å, all angles in degrees.

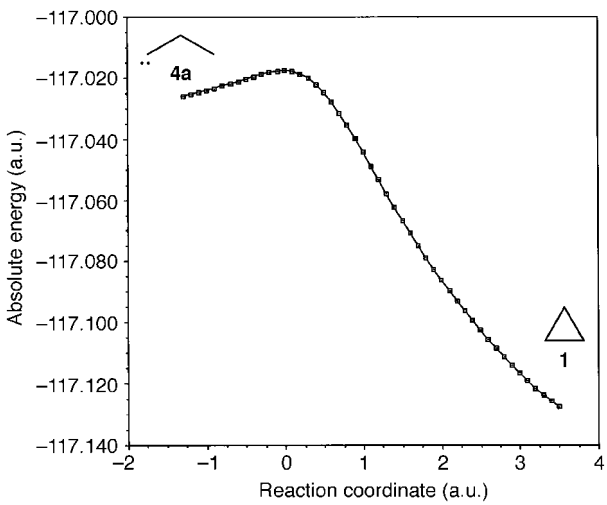


Fig. 2 The intrinsic reaction coordinate for the propylidene (**4a**) to cyclopropane (**1**) reaction *via* **TS2**.

(Fig. 2). The dominating initial mode along the path towards **1** is the migration of the H atom approximately in the ring plane. This motion is accompanied by a shortening of the C1–C3 distance and a decrease of the C1–C2–C3 angle leading ultimately to **1**.

We restricted our investigation to the highest point along path A, *i.e.* the transition structure (**TS1**) for the [1,2]-H shift from **3** to **2**. The analyses of the CCSD wave function (small T_1 diagnostic value of less than 0.02) as well as that of CISD (the Hartree–Fock configuration has a coefficient of 0.93) indicate that **TS1** should be computed reliably using coupled cluster methods. We find that **TS1** is 64.2 kcal mol^{-1} above **1**, and therefore 2.4 kcal mol^{-1} lower in energy than **TS2**. This difference is significantly smaller than that reported by Doubleday [5.5 kcal mol^{-1} in favor of **TS1**] at the MRCI/VTZ(2d,p)//CASSCF(4,4)/VTZ(2d,p) level. Our more extensive computations suggest that the carbene mechanism for the rearrangement of **1** to **2** has a zero-point corrected barrier of 66.6 kcal mol^{-1} which agrees with the barrier deduced experimentally (64–66 kcal mol^{-1}).[2–9] Hence, the carbene pathway might compete energetically with the trimethylene mechanism (64.2 kcal mol^{-1}). As experimental data have been discussed traditionally in terms of the latter mechanism,[5,11] additional investigations of the rearrangement of appropriately labeled cyclopropanes to propenes are desirable.

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Notes and references

† This study employed double-ζ and triple-ζ basis sets augmented with one [DZP, α_p(H) = 0.75, α_d(C) = 0.75] or two [TZ2P, α_p(H) = 1.5 and 0.375, α_d(C) = 1.5 and 0.375] sets of polarization functions. Single point energy computations at the CCSD(T)/TZ2P level employed the CCSD/TZ2P geometries.[32] In addition the geometry of **TS2** was optimized with the complete active space SCF method and the TZ2P basis set [CASSCF(4,4)/TZ2P] (ref. 33). Harmonic vibrational frequencies were computed *via* finite differences of analytic gradients at CCSD/DZP, and, for **TS2**, *via* analytic second derivatives at CASSCF/TZ2P.

1 J. B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, 1977.
2 M. Trautz and K. Winkler, *J. Prakt. Chem.*, 1922, **104**, 53.
3 T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 1934, **56**, 399.
4 H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. R. Soc. London, Ser. A*, 1953, **217**, 563.
5 B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, 1958, **28**, 504.
6 E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 1960, **82**, 5996.
7 W. E. Falconer, T. F. Hunter and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 609.
8 H. Furue and P. D. Pacey, *Can. J. Chem.*, 1982, **60**, 916.
9 U. Hohm and K. Kerl, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 1414.
10 N. B. Slater, *Proc. R. Soc. London Ser. A*, 1953, **218**, 224.
11 S. W. Benson, *J. Chem. Phys.*, 1961, **34**, 521.
12 K. Jug, *Theor. Chim. Acta*, 1976, **42**, 303.
13 K.-N. Fan, Z.-H. Li, W.-N. Wang, H.-H. Huang and W. Huang, *Chem. Phys. Lett.*, 1997, **277**, 257.
14 F. Dubnikova and A. Lifshitz, *J. Phys. Chem. A*, 1998, **102**, 3299.
15 S. F. Sellers, T. C. Klebach, F. Hollowood, M. Jones and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1982, **104**, 5492.
16 R. Hoffmann, *J. Am. Chem. Soc.*, 1968, **90**, 1475.
17 J. A. Horsely, Y. Jean, C. Moser, L. Salem, R. M. Stevens and J. S. Wright, *J. Am. Chem. Soc.*, 1972, **94**, 279.
18 Y. Yamaguchi, H. F. Schaefer and J. E. Baldwin, *Chem. Phys. Lett.*, 1991, **185**, 143.
19 S. J. Getty, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 2085.
20 J. E. Baldwin, Y. Yamaguchi and H. F. Schaefer, *J. Phys. Chem.*, 1994, **98**, 7513.
21 D. A. Hrovat, S. Fang, W. T. Borden and B. K. Carpenter, *J. Am. Chem. Soc.*, 1997, **119**, 5253.
22 C. Doubleday, *J. Phys. Chem.*, 1996, **100**, 3520.
23 C. Doubleday, K. Bolton and W. L. Hase, *J. Am. Chem. Soc.*, 1997, **119**, 5251.
24 C. Doubleday, K. Bolton and W. L. Hase, *J. Phys. Chem. A*, 1998, **102**, 3648.
25 A. Skancke, D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, 1998, **120**, 7079.
26 W. R. Roth, T. Wasser and M. Boenke, *Liebigs Ann./Rec.*, 1997, 1323.
27 F. Tian, S. B. Lewis, M. D. Bartberger, W. R. Dolbier and W. T. Borden, *J. Am. Chem. Soc.*, 1998, **120**, 6187.
28 E. M. Goldfield, *Faraday Discuss. Chem. Soc.*, 1998, **110**, 185.
29 S. Pedersen, J. L. Herek and A. H. Zewail, *Science*, 1994, **266**, 1359.
30 J. E. Baldwin, in *The Chemistry of the Cyclopropyl Group*, ed. Z. Rappoport, Wiley, New York, 1995, vol. 2, ch. 9.
31 E. V. Waage and B. S. Rabinovitch, *J. Phys. Chem.*, 1972, **76**, 1695.
32 ACES II is a program product of the Quantum Theory Project, University of Florida, J. F. Stanton *et al.* Integral packages included are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. R. Taylor); ABACUS (T. U. Helgaker, H. J. A. Jensen, P. Jørgensen, J. Olsen and P. R. Taylor).
33 GAUSSIAN 94, Revision C.3, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA, 1995.
34 J. W. M. Carneiro, P. v. R. Schleyer, W. Koch and K. Raghavachari, *J. Am. Chem. Soc.*, 1990, **12**, 4064.
35 P. Buzek, P. v. R. Schleyer, S. Sieber, W. Koch, J. W. Carneiro, H. Vancik and E. D. Sunko, *J. Chem. Soc., Chem. Commun.*, 1991, 671.
36 H. F. Schaefer, *Acc. Chem. Res.*, 1979, **12**, 288.
37 J. D. Evanseck and K. N. Houk, *J. Phys. Chem.*, 1990, **94**, 5518.
38 D. A. Modarelli and M. S. Platz, *J. Am. Chem. Soc.*, 1993, **115**, 470.

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