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Evidence for Concert in the Thermal Unimolecular Vinylcyclopropane to Cyclopentene Sigmatropic 1,3-Shift

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Abstract: Gas phase pyrolysis of *cis*-2,3-dideuterio-*trans*-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane at 290 °C gives *trans,trans*-3,4,5-trideuterio-1-*tert*-butylcyclopentene as the major 1,3-shift product with greater than 90% stereospecificity in an orbital symmetry "allowed" suprafacial-inversion sense after correction for the geometric isomerization of starting material and the other materials present. The isotopic substitution at the critical sites of rearrangement eliminates steric or electronic influences of substituents on a biradical pathway as a source of the suprafacial-inversion stereochemistry observed with more highly substituted derivatives. The stereochemical results coupled with a normal deuterium kinetic isotope effect ($k^H/2k^D = 1.14$ at 311.6 °C) at the *exo*-methylene carbon are best interpreted in terms of a concerted pathway for rearrangement. A less likely alternative is a stereospecific disrotatory ring opening to a biradical followed by rate-determining closure to a five-membered ring. Accompanying the rearrangement is geometric isomerization of starting material resulting from C-1−C-2 bond fission which favors either the single methylene rotation or a double rotation by a factor of 10 over single rotation at the vinyl-bearing carbon.

Vinylcyclopropane undergoes a gas phase, first-order allylic rearrangement to cyclopentene[1a] with log k (s^{-1}) = 13.5 − 49700/2.3RT.[1b] Numerous studies reveal that geometric isomerization of starting material occurs roughly 20 times faster than allylic rearrangement.[2] The mechanism of the geometric isomerization is generally attributed to reversible formation of a biradical in which rotation around non-allylic bonds occurs faster than ring closure. Because of the orbital overlap in the allylic moiety, it is generally recognized that both *transoid* and *cisoid* species are possible and the only fate of the former is reclosure to a vinylcyclopropane. The *cisoid* species may also be responsible for geometric isomerization, and it may be involved in the allylic rearrangement (Scheme 1). Alternatively, a concerted sigmatropic 1,3-shift might be envisioned for the ring expansion.

While the mechanism of the rearrangement is the focus of this paper, it should be recognized that more than two decades ago Willcott provided evidence for geometric isomerization being a near-random process kinetically. That is, there was a 2:1 ratio of *trans* to *cis-syn*-2,3-dideuteriovinylcyclopropane formed from *cis-anti*-2,3-dideuteriovinylcyclopropane even at short reaction times.[2c] These data can be interpreted in terms of a randomly rotating biradical ($k_1 = k_2 = k_{12}$) or exclusive single rotation around each stereocenter, with rotation around the methylene being twice as fast as rotation around the vinyl-bearing carbon ($k_2 = 2k_1$), or combinations of these possibilities (Scheme 2). Exclusive double rotation between carbons 1 and 2 (k_{12}) is not permitted by the data. It is important to recognize that C-2−C-3 bond fission is disfavored by ca. 12 kcal/mol


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(1) (a) Overberger, C. G.; Borchert, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 4896. Neureiter, N. P. *J. Org. Chem.* **1959**, *24*, 2044. (b) Wellington, C. A. *J. Phys. Chem.* **1962**, *66*, 1761.
(2) (a) Marshall, D. C.; Frey, H. M. *J. Chem. Soc.* **1962**, 3981. (b) Willcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 273. (c) Willcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1969**, *91*, 4310. The vinyl group of the compounds described in Scheme 2 was also substituted with deuterium which was omitted for purposes of clarity. (d) Doering, W. von E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168. (e) For a review see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1980; pp 81−87.
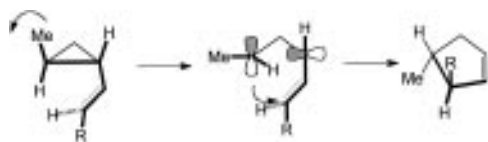
Scheme 1
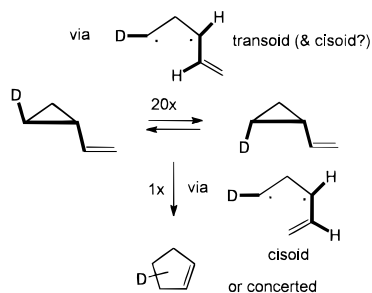
Scheme 2
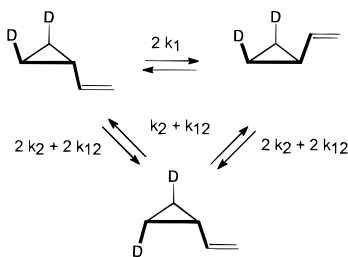
Scheme 3

relative to C-1−C-2 bond fission due to the development of allylic radical resonance energy by the latter cleavage.

Previous efforts to determine the stereochemistry of the vinylcyclopropane to cyclopentene rearrangement[3,4] demonstrated dominant (ca. 55−70%) suprafacial-inversion stereochemistry in this sigmatropic 1,3-shift, but all of these except for those described in two recent papers[4] have utilized methyl substitution at the migrating carbon to reveal the pathway (Scheme 3).

There is concern that steric effects in the *trans*-2-methyl compounds (the only geometric isomer studied)[3] may be responsible for the stereoselectivity by forcing outward rotation of the *trans*-methyl group as the C-1−C-2 bond breaks which might present the back side of the migrating carbon to the end of the allylic moiety for a least motion closure. This prompted examination of the pyrolysis of *cis*-2,3-dideuterio-*trans*-(1′-*tert*-butyl-2′-(*Z*)-deuteriovinyl)cyclopropane, **1D3**. The choice of a *tert*-butyl-substituted material has been justified previously.[3b] It reduces the ratio of geometric isomerization of starting vinylcyclopropane to allylic rearrangement presumably by destabilizing transition states leading to a *transoid* allyl moiety which cannot give the allylic rearrangement but can only be responsible for geometric isomerization in the starting material. Our early work which was communicated previously[4a] revealed that roughly 70% suprafacial-inversion stereospecificity was observed, but more extensive work detailed below suggests still higher stereospecificity. Since our initial paper, Baldwin has communicated work on the parent vinylcyclopropane system which indicates lower stereospecificity.[4b]

(3) (a) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705. (b) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717. (c) Baldwin, J. E.; Gahtlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273. (d) Baldwin, J. E.; Bonacorsi, J., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 10651.

(4) (a) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432. This is a preliminary paper describing some of the results in the current paper. (b) Baldwin, J. E.; Villarica, K. A.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 10845.
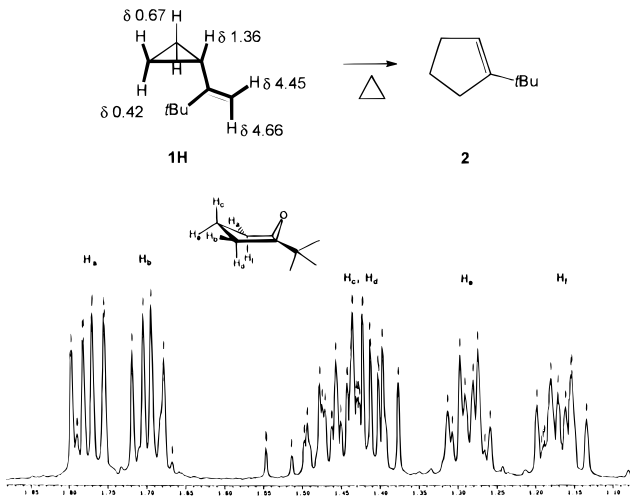
Scheme 4
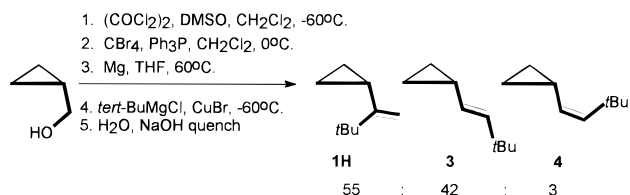
Scheme 5

Figure 1. ^{1}H NMR spectrum (500 MHz) of the methylene protons H_a−H_f of 1-*tert*-butyl-6-oxabicyclo[3.1.0]hexane in benzene solvent.

Results

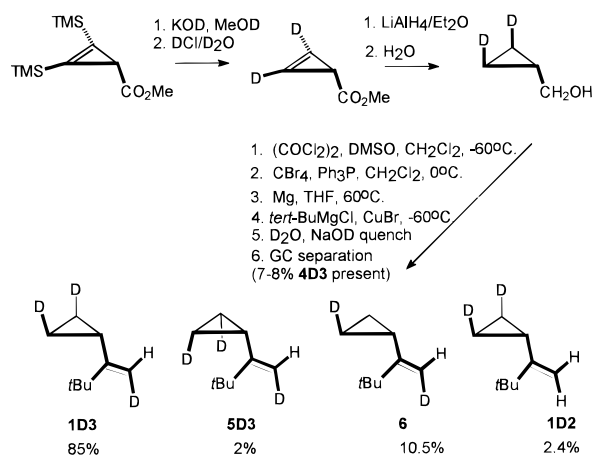**Preparation and Pyrolysis of (1′-*tert*-Butylvinyl)cyclopropane, 1H.** All-protio vinylcyclopropane, **1H**, was synthesized from cyclopropylcarbinol by oxidation to cyclopropanecarboxaldehyde, Wittig-like dibromomethylenation, carbenoid rearrangement to ethynylcyclopropane by treatment with magnesium in tetrahydrofuran, and then reaction with *tert*-butylmagnesium cuprate with aqueous workup (Scheme 4).

The synthetic sequence gives a 55:42:3 mixture of **1H**, (*trans*-2′-*tert*-butylvinyl)cyclopropane, **3**, and apparently its *cis* isomer, **4**, respectively. Separation was accomplished by preparative GC on dibutyl tetrachlorophthalate after thoroughly cleaning the injector and detector and alternating injections of the olefin mixture and diisopropylamine. The (*cis*-2′-*tert*-butylvinyl)-cyclopropane isomer, **4,** could not be separated from the desired (1′-*tert*-butylvinyl)cyclopropane, **1H**, but subsequent experiments revealed that it did not undergo the 1,3-shift under the reaction conditions; however, it did undergo geometric isomerization, a point that will be discussed below. The extent of contamination of **1** by **4** was typically 7−8% in the experiments described below. Fortunately, the presence of **4** provides an internal reference for both the 1,3-shift of **1** and its geometric isomerization.

As expected by analogy to all other vinylcyclopropane thermolyses, pyrolysis of **1H** at 290 °C gives 1-*tert*-butylcyclopentene, **2**, which has been synthesized previously (Scheme 5).[5] For purposes of examining the deuterium distribution in **2** when derived from deuterated **1**, **2** was converted to the epoxide where it was found that all ring protons were separately visible in its ^{1}H NMR spectrum when taken in benzene-d_6. Further, all the coupling constants were different between the ring protons. The proton assignments are consistent with previous

(5) (a) Brown, H. C.; Lynch, G. J.; Hammar, W. J.; Liu, L. C. *J. Org. Chem.* **1979**, *44*, 1910. (b) Buechler, J. D. *ibid.* **1973**, *38*, 904.

Scheme 6

Figure 2. Proton magnetic resonance spectrum from 0.3 to 0.7 ppm of the cyclopropane mixture from 290 °C pyrolysis for 5 h of **1D3** (85%) + **5D3** (2%) + **6** (10.5%) + **1D2** (2.4%).

Figure 3. $^1H\{^2H\}$ NMR spectra (500 MHz) of the methylene protons of the epoxide of **4D3** obtained from a 5.0 h pyrolysis of **1D3** at 290 °C.

work,[6ab] molecular mechanics calculations,[6c] and coupling constants expected on the basis of a boat conformation[7] (Figure 1).

Preparation of *cis*-2,3-Dideuterio-*trans*-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane. Stereospecifically labeled trideuteriovinylcyclopropane **1D3** was prepared from bis(trimethylsilyl)acetylene and methyl diazoacetate followed by hydrolysis in D_2O, lithium aluminum hydride reduction of the dideuteriocyclopropene ester at −78 °C, gradual warming to 0 °C, and quenching with water which gives (*cis*-2,3-dideuterio-*trans*-cyclopropyl)carbinol.[8] Treatment of this material as described above for the protio compound with the exception of a D_2O workup of the cuprate addition furnished **1D3** (Scheme 6). After separation to remove **3D3**, the 300 MHz ^1H NMR spectrum of the product revealed that 85% was **1D3**, 2% was *cis*-2,3-dideuterio-*cis*-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane, **5D3**, 10.5% was *trans*-2-deuterio-*trans*-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane, **6**, and 2.4% was *cis*-2,3-dideuterio-*trans*-(1′-*tert*-butylvinyl)cyclopropane, **1D2**; in addition, roughly 7% of the sample appeared to be *cis*-2,3-dideuterio-1-(1′-deuterio-*cis*-2′-*tert*-butylvinyl)cyclopropane, **4D3**, from the fact that the proton NMR spectrum had an additional doublet at 0.27 ppm, a singlet at 1.18 ppm, and a singlet at 5.25 in the appropriate ratio.

Pyrolysis of *cis*-2,3-Dideuterio-*trans*-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane. Geometric Isomerization. Vinylcyclopropane **1D3** (as the mixture described above) undergoes geometric isomerization at 290.0 °C as evidenced by an increase in the relative area of the 0.65 ppm region. Using the integrated ratios of the 0.65 and 0.39 ppm region and assuming a 1:1 ratio of protons at equilibrium, the first-order, one-way rate constant $k_{geo} = 1.43(0.04) \times 10^{-5}$ s^{-1} could be determined from data at $t = 0$, 5.000 h, 8.000 h, and infinity. However, analysis of this geometric isomerization is more complicated (see below). Further, capillary GC analyses allowed determination of the first-order, irreversible rate constant for the 1,3-shift: $k_{[1,3]} = 2.34(0.17) \times 10^{-6}$ s^{-1} in the same pyrolyses. Thus,

(6) (a) Lafferty, W. J. *J. Mol. Spectrosc.* **1970**, *36*, 84. (b) Steyn, R.; Sable, H. Z. *Tetrahedron* **1971**, *27*, 4429. (c) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2. MMX is a force field similar to MM2 with updates from the current literature; it uses charge−charge rather than dipole−dipole interactions for the electrostatics. PCMODEL is a program containing the MMX force field and is distributed by Serena Software, P.O. Box 3072, Bloomington, IN 47402 (K. E. Gilbert, President).

(7) Haasnoot, C. A. G.; deLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

(8) Vidal, M.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1972**, 678. Domnin, I. N. Dumon, K.; Vincens, M.; Vidal, M. *Izv. Akad. Nauk SSSR* **1985**, *7*, 1593, 1598. We thank Professor John E. Baldwin for suggesting these procedures.
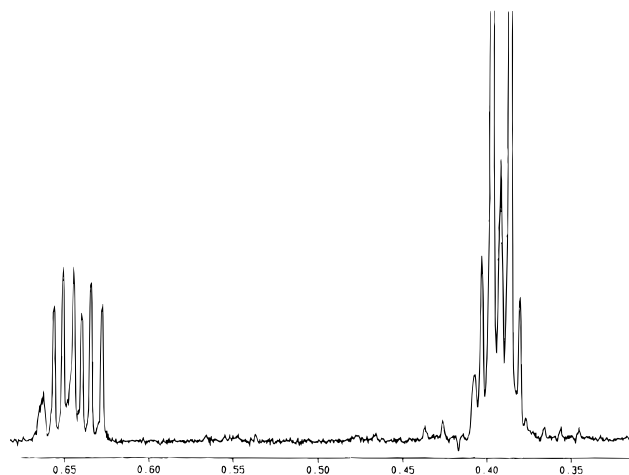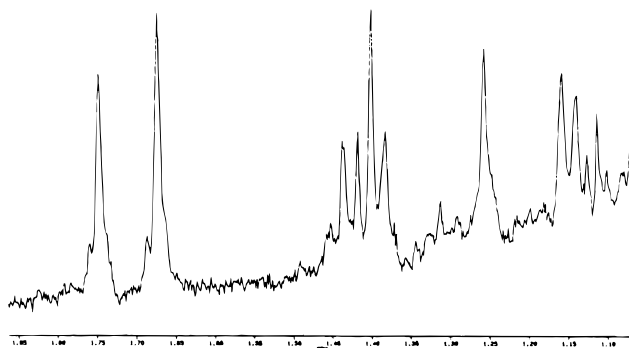
geometric isomerization would appear to be roughly 6 times faster than the 1,3-shift in this reaction; however, a kinetic modeling study revealed (see the Discussion) that the geometric isomerization is in fact 10 times faster than the 1,3-shift.

Examination of the 500 MHz deuterium-decoupled cyclopropane C-2 and C-3 ring proton resonance signals from 0.3 to 0.7 ppm of material recovered from the 5.00 h pyrolysis at 290 °C (Figure 2) reveals that conversion of **1D3** to a mixture of geometric isomers proceeds to almost the extent of 50%; i.e., the 0.65 ppm proton area is ca. 1/3 that of the 0.39 ppm proton area. Further, the 0.65 ppm signals indicate that the geometric isomerization gives a mixture of diastereomers which favors the *trans*-2,3-dideuterio isomer over the *cis*-2,3-dideuterio-*cis*-1-vinyl material by a factor of 4.

Thus, the pattern[2c] consists of a doublet of doublets (8 and 6 Hz) for the one proton of the *trans*-2,3-diprotio material and an 8 Hz doublet for the two protons of the *cis*-2,3-dideuterio-*cis*-1-vinyl compound. The fact that all six of these peaks are nearly equal in intensity requires a 4:1 ratio of the former to the latter. Interestingly, from the spectrum of the cyclopropanes recovered from the pyrolysis for 5 h, it is clear that complete equilibration of the ring deuterium isomers of (*cis*-2′-*tert*-butylvinyl)cyclopropane, **4D3**, occurred since the signals at 0.27 ppm (H's *cis* to vinyl) and 0.71 ppm (H's *trans* to vinyl) are nearly equal in intensity and consist of a random mixture of the two diastereomers; i.e., the relative areas of the major doublet and the doublet of doublets are 1:1 in each of the proton signals.

Stereochemistry of the Vinylcyclopropane Rearrangement. In order to examine the stereochemistry of the rearrangement, the cyclopentene product from the 5.0 h pyrolysis
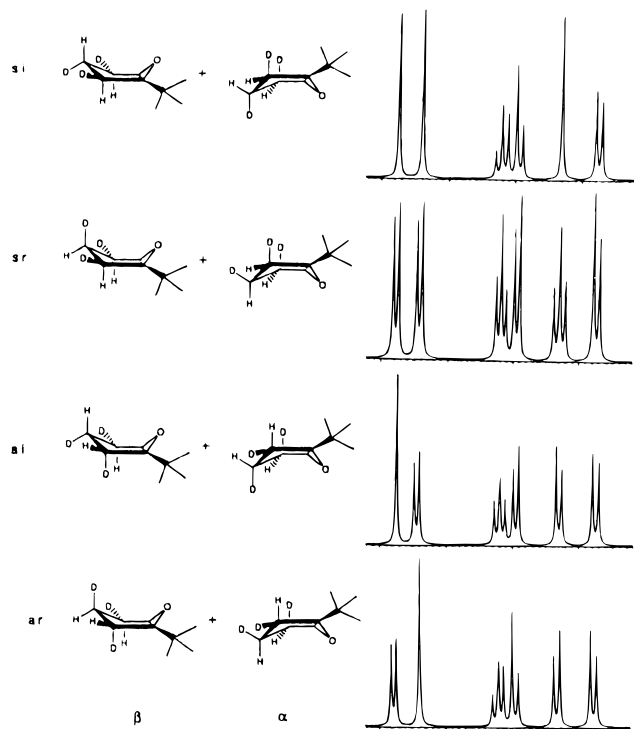
Figure 4. Simulation of the 500 MHz ^{1}H{^{2}H} NMR spectra of each of the pairs of diastereomers of the epoxide of **4D3** derived by the si, sr, ar, and ai modes of the 1,3-shift from **1D3** using the chemical shifts and coupling constants which reproduce the spectrum of Figure 1.

of **1D3** at 290 °C was epoxidized and then purified by GC. The unlocked deuterium-decoupled 500 MHz ^{1}H NMR spectrum above 1.80 ppm consisted of three singlets (full width at half-height 4 Hz) (Figure 3) and of two doublets and a triplet ($J =$ 9 Hz) which correspond to those expected for the suprafacial-inversion pathway.

Using the assigned chemical shifts and coupling constants for the pair of racemic epoxides which would result from each of the four stereochemical pathways si, sr, ar, and ai for reaction of achiral trideuterio compound **1D3**, the four simulated spectra of Figure 4 are obtained. The presence of the three singlets in the actual spectrum is uniquely consistent with the dominant presence of the deuterium isomer expected via the suprafacial-inversion reaction.

For comparison, a sample of **1D3** was pyrolyzed for 5.5 half-lives of geometric isomerization—59% conversion to **2**, and the ^{1}H NMR spectrum is that expected for randomized stereochemistry (Figure 5).

The presence of (nonzero) *cis, vicinal* couplings in the mixture causes the superimposition of 8 Hz doublets at both the *endo*-C-2 and *endo*-C-4 chemical shifts and an 8 Hz doublet and triplet at the *exo*-C-3 chemical shifts upon the singlets observed at low pyrolysis time. There is a 0.007 ppm upfield isotope shift of the *exo*-C-2 and *exo*-C-4 singlets which is probably due to a *gauche* interaction with the *endo*-C-3 deuterium.

It is not possible to calculate the stereospecificity in the 1,3-shift to high accuracy, but it appears to be greater than 70% before correction for incomplete deuteration and loss of stereo-integrity of starting material. Indeed, the analysis in the Discussion suggests nearly complete stereospecificity in the suprafacial-inversion sense.

Secondary Deuterium Kinetic Isotope Effects (DKIE) at the Terminal Methylene of 1. The stereospecificity of the 1,3-shift prompted examination of the secondary deuterium kinetic isotope effect at the terminal methylene position. Previous work by Squicciarini[3b] revealed a substantial normal secondary

deuterium kinetic isotope effect at the terminal methylene position of *trans*-2-methyl- and *trans*-2-methyl-(1′-*tert*-butylvinyl)cyclopropane in their rearrangements to the respective cyclopentenes ($k^H/2k^D = 1.17$ and 1.13, respectively, at 280 °C). Further, Chickos and later Baldwin found a correspondingly large DKIE at the terminal methylene of vinylcyclopropane itself in its sigmatropic 1,3-shift.[9] In the current system, the DKIE at the terminal methylene of (1′-*tert*-butylvinyl)cyclopropane **1XD2** was found to be 1.14(0.02) for two deuteriums at 311.6 °C.

Discussion

Geometric Isomerization of 1D3. In order to determine the stereospecificity of the vinylcyclopropane rearrangement of **1D3**, the direction and extent of loss of stereointegrity of starting material must be known. To review the facts, starting **1D3** is contaminated by ca. 2 mol % of the corresponding *cis*-2,3-dideuterio-*trans*-1-vinyl material **5D3** and by ca. 10 mol % of what appears to be *trans*-2-deuterio-1-(1′-*tert*-butyl-2′-(Z)-deuteriovinyl)cyclopropane, **6**. The latter determination follows from the observation of a 5% proton signal at 0.66 ppm for which there should be a corresponding 10% proton signal enmeshed in the 0.40 ppm proton signal for **1D3**. Table 1 shows a breakdown of the contribution of each material at various extents of pyrolysis. To model the relative proton signal intensities of both the 0.65 and 0.39 ppm signals and the relative amounts of **5D3** and the *trans*-2,3-dideuterio-1-(2′-deuteriovinyl) isomer **7D3** at the indicated pyrolysis times, rate constants for the three-way interconversion of the D$_3$ isomers **1**, **5**, and **7** must be as indicated in Scheme 7 (in units of 10^{-5} s^{-1}; all ±20% assuming that each undergoes the 1,3-shift equally fast and all by unimolecular processes).

The analysis of the recovered vinylcyclopropanes from pyrolysis of **1D3** makes it clear that single rotation of the vinyl-bearing carbon is distinctly slower, by a factor of 10, than either single rotation at C-2 or C-3 or double rotation presumably after breaking the C-1—C-2 or C-1—C-3 bond. This stands in contrast to the observations in the parent case where all rotations appear equally likely.[2c] The size of the *tert*-butyl substituent on the vinyl appears responsible for the difference. Unfortunately it is not possible to dissect the rate constants $k^{1 \rightarrow 7}$ and $k^{5 \rightarrow 7}$ into single and double rotation components, but the fact that these isomerizations occur with the rate constants indicated provides an important correction to the extent of stereospecificity observed in the 1,3-shift.

Stereochemistry of the 1,3-Shift in 1D3. Regardless of the exact value of the extent of suprafacial-inversion stereochemistry in the pyrolysis of **1D3**, it is clear that the 55—70% suprafacial-inversion stereochemistry observed with 2-*trans*-alkyl-substituted vinylcyclopropanes is not a result of steric effects. Furthermore, the stereospecificity is higher with the minimally perturbed system **1D3**. Simulation of the kinetic scheme for interconversion of the trideuterio isomers and irreversible formation of a different cyclopentene isomer from each using the rate constants described above and that determined directly from GC for the 1,3-shift revealed that only 79% of the product in the 5.0 h pyrolysis is formed from **1D3** while 16.4% of the product is formed from **7D3** and 4.6% of the product should arise from **5D3**. Since suprafacial-inversion, si, is the major stereopathway, the pyrolysis of **7D3** should give equal parts of the suprafacial-retention (**2sr**) and antarafacial-retention (**2ar**) products *expected from* **1D3** (Scheme 8); further, the suprafacial-

(9) Chickos, J. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8−13, 1984; American Chemical Society: Washington, DC, 1984; ORGN 228. Baldwin, J. E. Villarica, K. A. *Tetrahedron Lett.* **1994**, 7905.

Table 1. Analysis of the Upfield Proton Region in Recovered Vinylcyclopropane from Pyrolysis of **1D3** at 290.0 °C

	mole fractions			rel area	mole fractions						rel area
time (h)	7D3 (1)[a]	5D3 (2)[a]	6D2 (1)[a]	(δ 0.65)	1D3 (2)[a]	7D3 (1)[a]	6D2 (2)[a]				(δ 0.39)
0.0[b]	0	0.0205	0.105	0.07[c]	0.875	0	0.105				0.93[c]
¹H NMR:[d]	0	0.205 +	0.0525 =	0.073	0.875 +	0 +	0.105			=	0.98
5.00	0.265[e]	0.065[e]	0.105	0.25[c]	0.557[e]	0.265[e]	0.105				0.75[c]
¹H NMR:[d]	0.132[f] +	0.065[f] +	0.065[g] =	0.26	0.557 +	0.1325 +	0.085[g]			=	0.774
8.00	0.334[e]	0.095[e]	0.105	0.31[c]	0.483[e]	0.334[e]	0.105				0.69[c]
¹H NMR:[d]	0.167[f] +	0.095[f] +	0.07[g] =	0.332	0.483 +	0.167 +	0.08[g]			=	0.73

[a] The number in parentheses indicates the number of hydrogens in the signal. [b] At $t = 0$, the ratio **1:7:5:6** is 0.875:0:0.02:0.105, and **1** is a 85:2.4 mixture of **1D3** and **1D2**. [c] Relative ¹H NMR area. [d] Contribution of mole fractions to the ¹H NMR signal with summation below the relative ¹H NMR signal. [e] Relative mole fractions calculated using $k^{1 \rightarrow 7} = k^{5 \rightarrow 7} = 2.4 \times 10^{-5}$ s⁻¹, $k^{7 \rightarrow 1} = k^{7 \rightarrow 5} = 1.2 \times 10^{-5}$ s⁻¹, and $k^{1 \rightarrow 5} = k^{5 \rightarrow 1} = 2.4 \times 10^{-6}$ s⁻¹. [f] The ratio **7:5** from the 0.65 ppm signal is 4 after 5.00 h of pyrolysis and 3.8 after 8.00 h of pyrolysis. [g] Estimated with the rate constants of footnote [e].
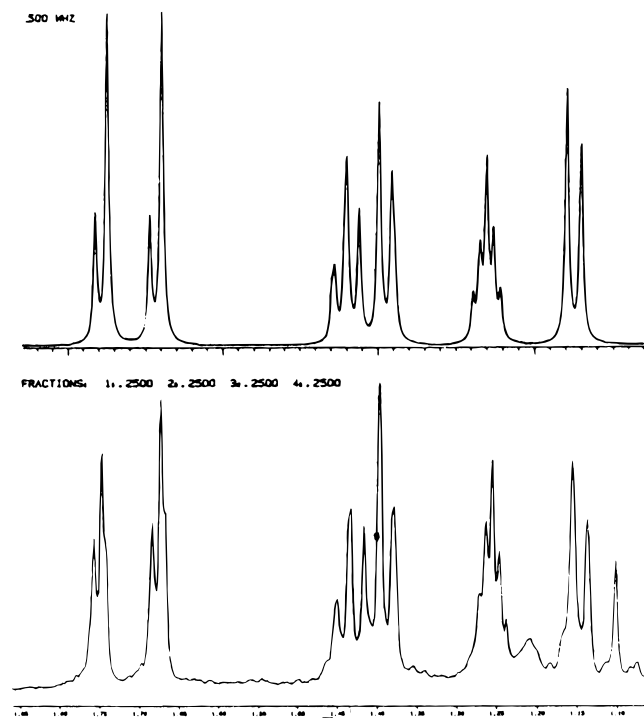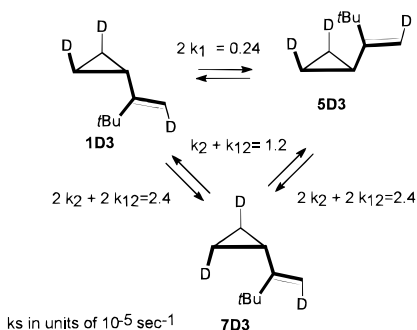

Figure 5. Simulated (top) and experimental (bottom) ¹H{²H} NMR spectra (500 MHz) of the methylene protons of the epoxide of **4D3** obtained from a 59% conversion pyrolysis of **1D3** at 290 °C. The simulated spectrum is of a 1:1:1:1 mixture of si, sr, ar, and ai product-derived epoxides, respectively.

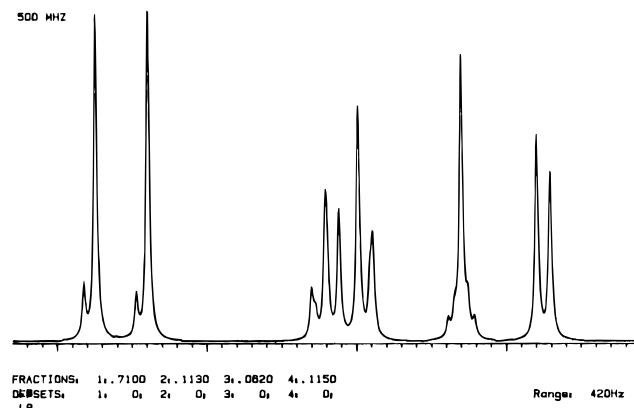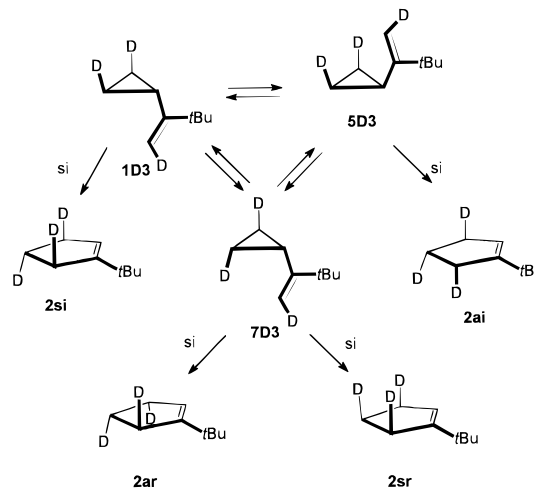**Scheme 7**

Scheme 8

Figure 6. Simulation of the spectrum of Figure 3 by assuming a 71:11.3:6.2:11.5 ratio of si, sr, ar, and ai products.

by assuming only 71% suprafacial-inversion product which implies about 90% stereospecificity.

Provided in Figure 7 is the upfield epoxide region from the cyclopentene product from the 8 h pyrolysis of **1D3**. Also included is a simulated spectrum summing the contributions of the four isomers assuming a 60:13:13:13 ratio of si, sr, ar, and ai product-derived epoxides. Again the fit is remarkably good which further confirms high stereospecificity in the reaction.

The high stereospecificity in the rearrangement suggested by the simulations is remarkable even before correction for the 10% cyclopentene product derived from the dideuterio contaminant **6**. If the si pathway were utilized by this material and there was but a small kinetic isotope effect, which is expected at these high temperatures, **6** should give equal amounts of cyclopentenes **8** and **9**, which would give C-4 diprotio and C-3 diprotio

inversion product from **5D3** is the antarafacial-inversion product (**2ai**) *expected from* **1D3** (Scheme 8).

Addition of the four cyclopentene epoxide spectra of Figure 4 in the ratio described above assuming only suprafacial-inversion stereochemistry for all vinylcyclopropane diastereomers gives a spectrum which generally resembles that from the 5.0 h pyrolysis (Figure 6). A somewhat better fit is provided
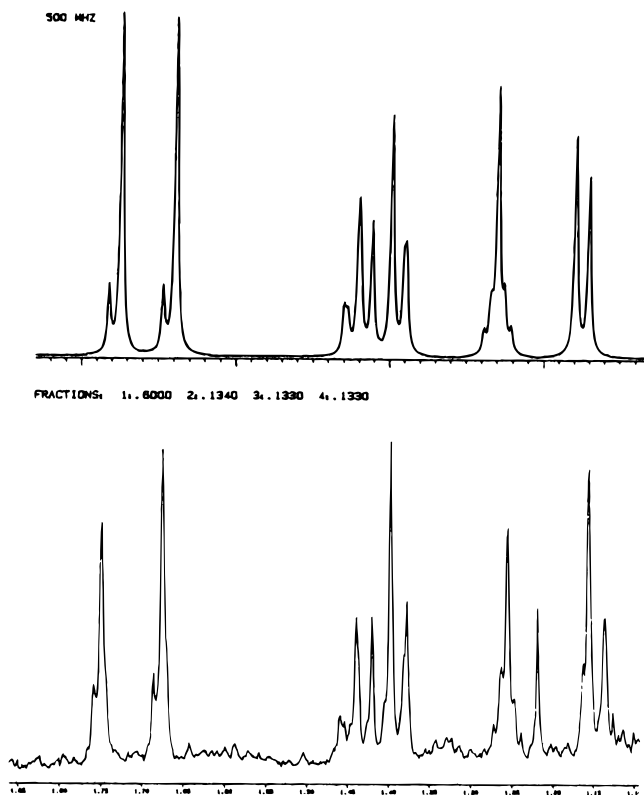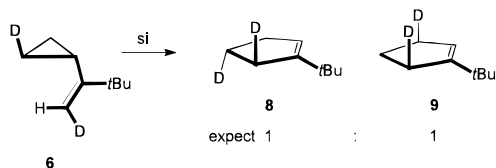
Figure 7. Simulated (top) and experimental (bottom) $^1H\{^2H\}$ NMR spectra (500 MHz) of the methylene protons of the epoxide of **4D3** obtained from an 8.0 h pyrolysis of **1D3** at 290 °C. The simulated spectrum is of a 60:13:13:13 mixture of si, sr, ar, and ai product-derived epoxides, respectively.

Scheme 9

cyclopentene epoxides, respectively, each one of which is a pair of diastereomers (Scheme 9).

The C-4 diprotio epoxide results from C-1—C-2 fission (cleavage to the methylene bearing deuterium) in **6**. The C-4 diprotio epoxide should give a superimposed doublet (J_{gem} = 13 Hz) and doublet of doublets (J_{gem} = 13 Hz, J_{vic} = 9.7 Hz) roughly 5 Hz downfield (due to no isotope effect) from the 1.75 ppm resonance and a similar pattern roughly 5 Hz downfield from the 1.15 ppm resonance, each contributing roughly 10% of the size of the peaks predicted for the si product alone; also resulting from C-1—C-2 fission is an epoxide which should give a 7.6 Hz doublet under the 1.67 ppm resonance signal, and its intensity should be 5% of the main peak. The C-3 diprotio epoxide should give a 7.8 Hz doublet under the 1.75 and 1.67 ppm resonances, contributing 5% of the main peak; in addition a doublet of doublets (J = 9.7 and 9.2 Hz), probably a triplet, should be superimposed on the 1.15 ppm resonance, and it should contribute 5% of the main peak. These additional resonances have the effect of making the simulated spectra more like that observed rather than less by broadening the signals at the bottom. Exact quantification is ultimately foiled by the signal to noise ratio in the spectra. However, 90% stereospecificity in a suprafacial-inversion sense for the vinylcyclopropane rearrangement would appear to be a conservative estimate.

Mechanistic Possibilities. Demonstration of dominant su-

prafacial-inversion stereochemistry is consistent with concert in the rearrangement with a competing, entropically more favorable, biradical pathway(s) which also results in loss of stereochemistry of the starting material. The rearrangement stereospecificity is also consistent with disrotatory ring opening with inward rotation of the vinyl group to produce a biradical which undergoes least motion closure faster than bond rotation. The other biradical(s) resulting from outward rotation of the vinyl group or random rotations about both bonds might be responsible for the loss of stereointegrity of the starting material. The stereospecific formation of a biradical and subsequent rapid closure may not be unlike pathways attributed to dynamical effects by Carpenter[10] although the origin of the disrotatory ring opening stereomode is not obvious. This suggestion runs contrary to the expectation of conrotatory opening based on the through-bond orbital interaction in a π-cyclopropane transition state or intermediate first suggested by Hoffmann.[11]

Kinetic Isotope Effects. The observation of a substantial *normal* deuterium kinetic isotope effect at the terminal methylene carbon in the rearrangement of vinylcyclopropane itself,[9] of 2-methylvinylcyclopropanes,[3b] and of (1′-*tert*-butyl-2′,2′-dideuteriovinyl)cyclopropane, **1XD2**, which is most reasonably attributed to a rotational isotope effect,[12] is consistent with concert. Alternatively, the DKIE may result from formation of a biradical like that described above whose ring closure to cyclopentene is rate determining. Rate-determining formation of a biradical, even the one which must be generated stereospecifically as described above, should result in a very small normal DKIE at the terminal methylene (ca. 1.03) at the temperatures of the reaction.[13] In the concerted reaction, bond formation to the terminal methylene cannot proceed to a significant extent, or a normal DKIE should have been observed. Perhaps it is not unexpected that extensive bond formation does not occur in this reaction given that the activation energy is comparable to the bond dissociation energy of the ring bond being ruptured.

Comparison to Previous Results. The current results represent the first determination, albeit incomplete, of the stereochemistry of the vinylcyclopropane rearrangement without substitution at the migrating carbon and the migration terminus. And, remarkably, it demonstrates that the orbital symmetry controlled suprafacial-inversion pathway is utilized in a steric unbiased case. In more recent work, Baldwin showed that the parent vinylcyclopropane system with deuteriums at C-2, C-3, and C-β also reveals a preference for the suprafacial-inversion pathway; however, the preference is only 40% total relative to all other pathways. Since the temperature is only 10 °C higher, it is not clear what the difference is between the parent and the *tert*-butyl case studied here.

Conclusion. A stereospecific 1,3-shift of carbon is observed in a thermal vinylcyclopropane rearrangement which has deuterium as a stereochemical marker at both the migrating carbon and migration terminus. This structural isomerization occurs slower than geometric isomerization which occurs mostly

(10) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695. Carpenter, B. K. *Acc. Chem. Res.* **1992**, *25*, 520. Some concern might be expressed about the experimental basis of the hypothesized dynamical effect in the case of the rearrangement of the bicyclo[2.1.1]-hexene system. While no temperature dependence of the stereospecificity is observed in phenyl-substituted cases, implying that dynamical effects are involved, the parent system shows normal temperature dependent stereospecificity.

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by methylene single rotation or by C-1—C-2 double rotation. The stereosense of the 1,3-shift is that predicted for a concerted reaction by the Woodward—Hoffmann rules. A large (at these high temperatures) secondary deuterium kinetic isotope effect at the *exo*-methylene group suggests its rotation in the rate-determining transition state for the 1,3-shift. The overall reaction can best be characterized as a competition between an entropically demanding concerted 1,3-shift and a geometric isomerization *via* biradicals or concerted double rotation. A nonconcerted path would require stereospecific disrotatory opening with inward rotation of the vinyl group followed by rapid bond formation, events which currently have no precedent. However, it may be that the two radical sites may be coupled in an orbital symmetry conserved sense and may be more stable than the transition state for ring opening and that for ring closure. Whether or not calculations will reveal this is not yet clear.

Experimental Section

¹H and ¹³C NMR spectra were recorded either on a Bruker AM-500 or a Varian XL-300 spectrometer. ²H NMR spectra were obtained on a Nicolet NT-360 spectrometer operating at 55 MHz. Deuterium-decoupled ¹H NMR experiments were performed using the AM-500 both at Indiana and at Vanderbilt. ¹H—¹H NOE difference spectroscopy experiments were performed on degassed samples in deuteriochloroform using the XL-300 instrument. IR spectra were obtained on a Perkin-Elmer 298 or a Mattson Instruments Galaxy 4020 Fourier transform spectrophotometer. Mass spectra were obtained on a Kratos MS-80 spectrometer or on a Hewlett-Packard 5980 GC/MS system with a Model 5971 mass sensitive detector. Preparative GC was performed using a Varian Model 90-P or a Varian 4700 gas chromatograph with thermal conductivity detection. Capillary gas chromatography was performed using a Varian 3700 gas chromatograph equipped with flame ionization detection; the columns used were coated with DB-5 (50 m × 0.25 mm) or with Supelcowax-10 (60 m × 0.25 mm). Peak area ratios were determined by Varian 4240 or Hewlett-Packard 3390A reporting integrators; the FID sensitivity factors were assumed to be unity for isomers. Dry tetrahydrofuran was obtained by distillation under nitrogen from sodium—benzophenone ketyl. All reactions were carried out under an inert atmosphere of nitrogen.

1-(1′-*tert*-**Butylvinyl)cyclopropane, 1H.** To a stirred solution of triphenylphosphine (16.8 g, 64 mmol) in 35 mL of methylene chloride at 0 °C was added 10.6 g (32 mmol) of carbon tetrabromide in 20 mL of methylene chloride. To the resulting yellow-brown suspension was added over a period of 5 min 1.1 g (16 mmol) of cyclopropanecar-boxaldehyde in 10 mL of methylene chloride. After 5 min of stirring, the mixture was poured into 200 mL of pentane. Filtration, followed by reworking the precipitate by two more cycles of methylene chloride dissolution and pentane precipitation, gave a filtrate which was concentrated by rotary evaporation and distilled bulb to bulb (90 °C, 1 Torr) to give 2.3 g of (dibromovinyl)cyclopropane (11 mmol, 70% yield). ¹H NMR (300 MHz, CDCl₃): δ 5.78 (d, *J* = 1 Hz); 1.64 (m, 1H); 0.87 (m, 2H); 0.55 (m, 2H). FTIR (CDCl₃): 3050, 2950, 1600 cm⁻¹. MS (EI, *m/e*): 226.

A 1.1 g (4.4 mmol) sample of (dibromovinyl)cyclopropane in 10 mL of tetrahydrofuran was added dropwise to a refluxing mixture of magnesium turnings (0.14 g, 5.8 mmol) in 3 mL of tetrahydrofuran which had been previously treated with a small crystal of iodine and heated to reflux until the brown color was discharged. After 30 min at reflux the flask was fitted for distillation, and cyclopropylacetylene was collected along with tetrahydrofuran. Copper(I) bromide (0.726 g, 5.1 mmol) was placed in a flame-dried flask equipped with a stir bar and placed under vacuum (1 Torr) for 1 h. Under nitrogen, 15 mL of dry tetrahydrofuran was added, and then the mixture was cooled to −60 °C and 5.0 mL of *tert*-butylmagnesium chloride (2.0 M in tetrahydrofuran, 10 mmol) was added dropwise with stirring so that the temperature did not rise above −55 °C. The mixture was then stirred at −60 °C for 1 h, after which the cyclopropylacetylene/tetrahydrofuran solution was added dropwise. The mixture was warmed to 0 °C and stirred for 20 min. The reaction was then quenched by dropwise addition of 10% aqueous sodium hydroxide (4.4 mL). Care

was taken during the addition so that the temperature did not rise above 5 °C. The resulting mixture was poured into a solution made by dissolving 0.5 g of sodium cyanide in 50 mL of saturated aqueous ammonium chloride. After 15 min of stirring, the mixture was extracted with pentane (100 mL) and the organic layer was washed with water (2 × 200 mL). The aqueous phases were extracted once with pentane (100 mL), and the organic phases were combined, dried over magnesium sulfate, and filtered. Slow distillation of the pentane through an 18 cm Vigreux column provided a residue of 0.45 g (82% yield) of three products in a 55:3:42 ratio. Preparative GC (10 DBTCP on Chromosorb P, 10 ft × 1/4 in. column) allowed separation of the latter two from the first peak to give 150 μL (0.8 mmol, 10% yield from dibromide) of 1-(1′-*tert*-butylvinyl)cyclopropane. ¹H NMR (300 MHz, CDCl₃): δ 4.66 (d, *J* = 1 Hz, 1H); 4.45 (d, *J* = 1 Hz, 1H); 1.36 (m, 1H); 1.14 (s, 9H); 0.67 (m, 2H); 0.42 (m, 2H). The product is contaminated with a small amount of what appears to be 1-(*cis*-2′-*tert*-butylvinyl)cyclopropane since the first GC peak is almost certainly 1-(*trans*-2′-*tert*-butylvinyl)cyclopropane from its ¹H NMR (300 MHz, CDCl₃): δ 5.55 (d, *J* = 15 Hz, 1H); 4.83 (d,d, *J* = 15, 8 Hz, 1H); 1.30 (m, 1H); 1.0 (s, 9H); 0.66 (m, 2H); 0.3 (m, 2H). This latter material was not further characterized. ¹H—¹H NOE difference results for **1H**: Irradiation of 1.14 ppm (*tert*-butyl protons) resulted in a 17% enhancement at 4.66 ppm and 0.5% enhancement at 4.45 ppm. Irradiation of the multiplet at 1.36 ppm (cyclopropyl methine proton) resulted in a 7% enhancement of the 0.67 ppm resonance and 0.1% enhancement of the 0.42 ppm resonance. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 159.7; 102.0; 31.2; 29.7; 12.9; 7.2. FTIR (CDCl₃): 3050, 2950, 1650, 1380 cm⁻¹. MS (EI, *m/e*): 124.

1-(1′-*tert*-**Butyl-2′-(Z)-deuteriovinyl)-*trans*-2,*trans*-3-dideuteriocy-clopropane, 1D3.** Trideuterio(*tert*-butylvinyl)cyclopropane **1D3** was prepared from methyl bis(trimethylsilyl)cycloprop-2-enecarboxylate[14,15] (8.7 g, 36 mmol) which was added dropwise over 5 min to 40 mL of 10% potassium deuteroxide in methanol-*O*-*d*₁ at 0 °C with stirring. The mixture turned yellow upon addition. After 4 h of stirring at room temperature, the mixture was cooled to 0 °C, and 10% deuterium chloride in deuterium oxide was added until the mixture was neutral to pH paper. At pH 7 the yellow color of the mixture changed to dark green. Methanol was removed by careful rotary evaporation. The resulting aqueous mixture was extracted with diethyl ether (3 × 50 mL portions). The organic phase was washed with water (20 mL), dried with magnesium sulfate, and filtered. The solution was added dropwise to a stirred solution of lithium aluminum hydride in diethyl ether (1 M, 190 mL, 190 mmol) at −78 °C. The mixture was warmed to 0 °C over 3/4 h, and quenched with water (5 mL), 15% aqueous sodium hydroxide solution (5 mL), and then water (15 mL) again. Filtration of the precipitated salts, drying of the filtrate with magnesium sulfate, filtration of the drying agent, and distillation of the solvent through an 18 cm Vigreux column gave a residue which was subjected to short-path distillation (100−140 °C) to give 0.6 g (25% yield) of *cis*-2,3-dideuteriocyclopropane-*trans*-1-methanol. ¹H NMR (300 MHz, CDCl₃): δ 3.43 (d, *J* = 8 Hz, 2H); 2.35 (s, 1H); 1.09 (m, 1H), 0.18 (d, *J* = 5 Hz, 2H).

Collected samples of this alcohol were oxidized to the corresponding aldehyde under Swern conditions: To a mechanically-stirred solution of oxalyl chloride (2.8 g, 22 mmol) in methylene choride (20 mL) at −60 °C under a nitrogen atmosphere was added dropwise anhydrous dimethyl sulfoxide (2.4 g, 30 mmol) in methylene chloride (5 mL). After stirring for 10 min, *cis*-2,3-dideuteriocyclopropane-*trans*-1-carbinol (2.0 g, 27 mmol) in methylene chloride was added over 5 min, and stirring was continued for another 10 min. Triethylamine (12 mL) was added dropwise, and then the cooling bath was removed and 1 M aqueous hydrochloric acid (100 mL) was added. The aqueous phase was extracted with methylene chloride (30 mL), and the combined organic phases were washed with water (40 mL), 10% aqueous sodium carbonate solution (15 mL), water (10 mL), and saturated brine (10

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mL). This solution was dried over magnesium sulfate, filtered, and concentrated by distillation of the solvent through an 18 cm Vigreux column, and the residue was subjected to short-path distillation to give 1.0 g of *cis*-2,3-dideuterio-*trans*-cyclopropanecarboxaldehyde (50% yield based on starting alcohol). ^{1}H NMR (300 MHz in CDCl₃): δ 8.89 (d, *J* = 4 Hz, 1H); 1.84 (m, 1H); 1.09 (s, 0.20H); 1.08 (d, *J* = 7 Hz, 2H).

The aldehyde was immediately converted to the corresponding acetylene, and treated with *tert*-butylmagnesium cuprate as described above for the synthesis of **1H**; however, the vinylcopper intermediate was quenched with 10% sodium deuteroxide in deuterium oxide. GC purification gave 200 μL of **1D3** (10% yield from the dibromide). ^{1}H NMR (300 MHz, CDCl₃): δ 4.66 (d, *J* = 1 Hz, 0.024H) (**1D2**); 4.43 (s, 1H); 1.35 (m, 1H); 1.14 (s, 9H); 0.66 (m, 0.14H) (30% **5D3**, 70% **6**); 0.39 (d, *J* = 5 Hz, 2H) plus a downfield shoulder from **6**. ^{2}H NMR (55 MHz, CDCl₃) δ 4.66 (br s, 1D); 0.61 (br s, 2D). FTIR (CDCl₃): 3100, 2967, 2875, 2871, 2361, 2357, 1606, 1362, 912 cm⁻¹. MS (EI, *m/e*):127.

Also present in this sample was ca. 7% of what appears to be *cis*-2,3-dideuterio-1-(1′-deuterio-*cis*-2′-*tert*-butylvinyl)cyclopropane since a doublet appeared at 0.27 ppm and a singlet at 5.26 ppm in addition to what appears to be a *tert*-butyl singlet at 1.18 ppm—all in the appropriate ratios.

1-*tert*-Butyl-6-oxabicyclo[3.1.0]hexane. To a magnetically stirred slurry of *m*-chloroperbenzoic acid (0.8 g, 10 mmol) in methylene chloride (50 mL) under a nitrogen atmosphere was added dropwise 1-*tert*-butylcyclopentene[4] (1.2 g, 10 mmol) with cooling. The mixture was stirred at room temperature for 28 h; then it was filtered and washed with 5% aqueous sodium bicarbonate solution (2 × 15 mL), water (10 mL), and saturated brine (5 mL). After drying with magnesium sulfate, filtration, and concentration under aspirator vacuum, the residue was distilled (BP 75−90 °C, 25 Torr) to give 1.0 g of epoxide which was further purified by preparative GC (OV-101, 20% on Chromosorb P, 12 ft × 1/4 in. column). ^{1}H NMR (500 MHz, benzene-d₆): δ 3.07 (s, 1H); 1.77 (dd, *J* = 13.6, 7.8 Hz, 1H); 1.68 (dd, *J* = 12.6, 7.5 Hz, 1H); 1.44 (ddddd, *J* = 11.6, 9.7, 9.2, 7.8, 7.5 Hz, 1H); 1.39 (ddd, *J* = 12.6, 9.7, 8.4 Hz, 1H); 1.29 (ddd, *J* = 11.6, 9.2, 8.4, 1H); 1.17 (ddd, *J* = 13.6, 9.2, 9.2, 1H); 0.91 (s, 9H) (see figure in the Results for methylene proton region). IR (neat): 3050, 2950, 1370, 1250 cm⁻¹. MS (EI, *m/e*): 140.

(1′-*tert*-Butyl-2′,2′-dideuteriovinyl)cyclopropane, 1XD2. (1′-*tert*-Butyl-2′,2′-dideuteriovinyl)cyclopropane, **1XD2**, was prepared from *tert*-butyl cyclopropyl ketone[16] (0.8 g, 6.4 mmol) in 2 mL of dimethyl sulfoxide-d₆ which was added dropwise to a stirred solution of (dideuteriomethylene)triphenylphosphorane (8.9 mmol, prepared according to literature procedures[17]) in 20 mL of dimethyl sulfoxide-d₆ under a nitrogen atmosphere. After 5 h of stirring, the reaction mixture was poured into water (75 mL), and extracted with pentane (2 × 75 mL). The combined organic phases were washed with water (2 × 10 mL), dried over magnesium sulfate, filtered, and concentrated by solvent removal through a 18 cm Vigreux column. The residue (0.7 g, 5.2

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mmol, 85% yield) was purified by GC. ^{1}H NMR (300 MHz, CDCl₃): δ 4.65 (s, 0.04H); 4.45 (s, 0.04H); 1.36 (m, 1H); 1.14 (s, 9H); 0.67 (m, 2H); 0.42 (m, 2H).

Pyrolyses. Most of the pyrolyses were carried out in a 2 L Pyrex bulb immersed in a mechanically stirred bath of molten potassium nitrate/sodium nitrite (10:7 v/v). The majority of heat was supplied to the bath by a 500 W Vycor immersion resistance heater connected to a variable transformer; fine temperature control was provided by a 125 W knife blade heater controlled by a Bayley Model 76-8 precision temperature controller with a temperature feedback probe immersed in the bath. The temperature of the bath was monitored with an electronic digital thermometer equipped with a platinum resistance probe. The precision of the thermometer was ±0.1 °C, and the observed temperature variation of the bath during pyrolysis runs was no more than ±0.1 °C.

The bulb was connected to a vacuum line that kept the pressure at <10⁻³ Torr. Samples could be transferred into and out of the bulb with high efficiency. The bulb was conditioned by transferring in 1 mL of dichlorodimethylsilane. The silane was kept in the bulb at 280 °C for 15 min and transferred out. After identical treatment with diisopropylamine, the bulb was evacuated for 3 h. Cyclohexene (0.25 mL) was then used similarly to further condition the bulb overnight. A system of high-vacuum valves was used to ensure that no air was allowed to enter the bulb at any time after conditioning.

Samples were purified by preparative GC prior to pyrolysis. They were degassed by two freeze−pump−thaw cycles, and then distilled into the pyrolysis bulb.

For rate studies of rearrangements of (1′-*tert*-butylvinyl)cyclopropanes, 1.2 μL samples were pyrolyzed; after recovery and dilution with 0.5 mL of pentane, capillary GC analysis was performed. For studies of the rate of geometric isomerization of **1D3**, 5 μL samples were pyrolyzed; after recovery, dilution with 0.5 mL of deuteriochloroform gave a solution suitable for ^{1}H NMR and capillary GC analysis. For stereochemical studies of the rearrangement of **1D3**, 30−70 μL samples were pyrolyzed for varying times; the recovered pyrolysate was diluted with methylene chloride and the percent conversion to cyclopentene product determined by capillary GC. This solution was then treated with *m*-CPBA, and the residue after workup and concentration was subjected to preparative GC. The separated [3.1.0] compound was then diluted with benzene-d₆ (0.5 mL) and analyzed by capillary GC and ^{1}H{^{2}H} NMR to determine the purity and to analyze the stereochemistry of the product. A sample of unpyrolyzed **1** was subjected to similar epoxidation, and no [3.1.0] product was observed by capillary GC or by ^{1}H NMR, demonstrating that cyclopentene is formed exclusively by thermal rearrangement.