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Stereochemistry of the Thermal Isomerization of Vinylcyclopropane to Cyclopentene

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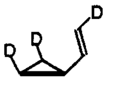
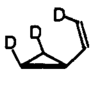
The stereochemistry of the thermal isomerization of vinylcyclopropane to cyclopentene[1] has long been recognized as a mechanistic key for this simplest known [1,3] carbon sigmatropic pericyclic reaction,[2,3] yet experiments to determine reaction stereochemistry—the relative importance of the four stereochemical modes potentially available for the process—have not been reported. Such experiments have appeared most daunting since deuterium-labeled vinylcyclopropanes are known to suffer thermal stereomutations much faster than they isomerize to labeled cyclopentenes.[4] To get past this awkward circumstance, one would need to prepare suitably labeled vinylcyclopropanes, heat them to cause both stereomutations and structural isomerizations, analyze recovered starting material and product mixtures at such short reaction times that substantial stereochemical integrity remained in the vinylcyclopropanes, and calculate the relative rate constants for the *si*, *ar*, *sr*, and *ai* paths characterized by *s*uprafacial or *a*ntarafacial allylic participation and *r*etention or *i*nversion at the migrating carbon atom. This project has now been accomplished. Vinylcyclopropane-*2,3,2′-d*$_3$ isomers *syn-E* and *syn-Z* were prepared[5] and heated in the gas phase at 300 °C. The overall structural isomerizations were followed by capillary GC; the rate constant for isomerizations to cyclopentenes was found to be 3.4×10^{-6} s^{-1}.[6]

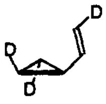


syn-E

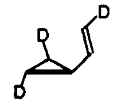


syn-Z

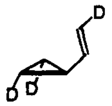
Vinylcyclopropanes recovered from product mixtures were analyzed by ^{1}H NMR to determine the extent of equilibration of *exo*-C(2,3)−H with *endo*-C(2,3)−H absorption intensities associated with (*SS-E* + *RR-E*) = *rac-E* and *anti-E* (or the corresponding Z isomers).[4,7] Rate constants for stereomutations of starting materials, $k_i(syn\text{-}E) = 1.7 \times 10^{-4}$ s^{-1} and $k_i(syn\text{-}Z) = 2.1 \times 10^{-4}$ s^{-1}, were based on ^{1}H NMR spectroscopic analyses of GC-purified vinylcyclopropanes recovered from thermal reaction mixtures (five time, absorption intensity ratio values for each starting material).



SS-E



RR-E



anti-E

Table 1. Absorption Frequencies and Spin−Spin Coupling Constants for the Three Isomers of Cyclopentene−*3,4,5*−*d*$_3$ at Room Temperature

isomer	ν of C(4)−H (Hz at 500 MHz)[a]	C(4)−H vicinal *J* values (Hz)
cc	2.58	9.37, 9.37
rac	0.00	9.41, 5.58
tt	−2.72	5.79, 5.79

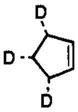
[a] Relative to ν(*rac*) = 0, in CD$_2$Cl$_2$.

Table 2. Cyclopentene-*3,4,5*-*d*$_3$ Isomers from Thermal Gas Phase Reactions of *syn-E* and *syn-Z* at 300 °C

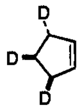
time (min)	all (%)	all (calcd)[a]	*cc* (rel %)	*rac* (rel %)	*tt* (rel %)
61 (*E*)[b]	1.3	1.2	16	60	24
102 (*E*)	2.0	2.1	18	56	26
130 (*E*)	2.7	2.6	18	56	26
48 (*Z*)	1.0	1.0	23	41	36
88 (*Z*)	1.8	1.8	25	42	35

[a] From $k = 3.4 \times 10^{-6}$ s^{-1}. [b] From *syn-E* as starting material.

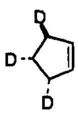
The three cyclopentene-*3,4,5*-*d*$_3$ isomers *cc*, (*SS* + *RR*) = *rac*, and *tt* were quantified through high-resolution ^{1}H{^{2}H} NMR spectroscopy, taking advantage of the expected stereochemically sensitive isotope-induced differences in chemical shift for the C(4)−H absorptions in each. The parameters giving the best fit to the 12 C(4)−H NMR transitions seen for the three isomers are summarized in Table 1 and are consistent with previous data.[8,9] The cyclopentene-*d*$_3$ isomers in product mixtures are recorded in Table 2.



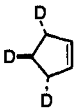
cc



SS



RR



tt

Starting from *syn-E*, the time-dependent fractional concentrations of vinylcyclopropanes are given by [*syn-E*] = exp(−*kt*)(1 + 3 exp(−$k_i t$))/4, [*rac-E*] = exp(−*kt*)(1 − exp(−$k_i t$)/2, and [*anti-E*] = exp(−*kt*)(1 − exp(−$k_i t$))/4. With these and analogous expressions for the *Z* isomers, one may calculate the average concentration of each isomer over a given reaction time (Table 3).[10]

The relative magnitudes of the rate constants for the four paths for the vinylcyclopropane to cyclopentene isomerization (k_{si},

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(1) Vogel, E.; Palm, R.; Ott, K. H., unpublished. See: Vogel, E. *Angew. Chem.* **1960**, *72*, 4−26, note 162. Overberger, C. G.; Borchert, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 1007−1008.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971; pp 120−122.

(3) Reaction stereochemical results for some substituted geometrically unconstrained vinylcyclopropanes have been reported: Doering, W. von E.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512−5520. Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705−6706. Gajewski, J. J.; Warner, J. M. *J. Am. Chem. Soc.* **1970**, *106*, 802−803. Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717−6728. Baldwin, J. E.; Ghatlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273−6274. Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432−7433. Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 10621−10627.

(4) Willcott, M. R.; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723−724; **1969**, *91*, 4310−4311. Cargle, V. H. Ph.D. Dissertation, University of Houston, TX, 1969. Willcott, M. R.; Cargle, V., unpublished results, cited in Willcott, M. R.; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25−98.

(5) Baldwin, J. E.; Villarica, K. A. *J. Org. Chem.* submitted for publication.

(6) Followed over several half-lives, the isomerizations exhibit a diastereotopically distinct k_H/k_D effect; the *Z* isomers rearrange somewhat faster than the *E* isomers.

(7) The relationship between k_i for approach to equilibrium and conventional stereomutation rate constants is $k_i = 4(k_2 + k_{12}) \cong 2(k_1 + k_2 + k_{12} + k_{23})$; [*rac-E*] is always 2[*anti-E*].[4]

(8) Anet, F. A. L.; Leyendecker, F. *J. Am. Chem. Soc.* **1973**, *95*, 156−159.

(9) Details of the NMR spectroscopic work, including temperature-dependent studies, will be published separately.

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Table 3. Calculated Average Concentrations of Vinylcyclopropane-d_3 Isomers over Short Reaction Time Intervals at 300 °C

time (min)	*syn-E* or -*Z*	*rac-E* or -*Z*	*anti-E* or -*Z*
61 (*E*)[a]	80.4	12.6	6.3
102 (*E*)	71.0	18.6	9.3
130 (*E*)	65.8	22.0	11.0
48 (*Z*)	80.9	12.4	6.2
88 (*Z*)	69.8	19.6	9.8

[a] From *syn-E* starting material.

k_{ar}, k_{sr}, k_{ai}) follow from the relevant linear equations, such as eqs 1−3.

$$k_{ar}[syn\text{-}E] + (k_{si} + k_{ai})[rac\text{-}E]/2 + k_{sr}[anti\text{-}E] = [cc] \quad (1)$$

$$(k_{si} + k_{sr})[syn\text{-}E] + [rac\text{-}E]/2 + (k_{ar} + k_{ai})[anti\text{-}E] = [rac] \quad (2)$$

$$k_{ai}[syn\text{-}E] + (k_{sr} + k_{ar})[rac\text{-}E]/2 + k_{si}[anti\text{-}E] = [tt] \quad (3)$$

All vinylcyclopropane concentration terms on the left of eqs 1−3 are averages over a reaction time (Table 3); the relative product concentrations on the right are those observed at that time (Table 2), and $(k_{si} + k_{ar} + k_{sr} + k_{ai}) = 1$. From each product mixture from *anti-E*, one may measure $(k_{si} + k_{sr})$, k_{ar}, and k_{ai}, while each derived from *syn-Z* gives k_{sr}, k_{si}, and $(k_{ar} + k_{ai})$. These experimental relative rate constants are summarized in Table 4.

Table 4. Experimental Relative Rate Constants for the Four Stereochemically Distinct Paths for the Isomerizations of Vinylcyclopropane-*2,3,2′*-d_3 to Cyclopentene-*3,4,5*-d_3 at 300 °C

starting isomer	time (min)	k_{si}	k_{sr}	k_{ar}	k_{ai}
syn-E	61	0.64		0.13	0.24
	102	0.61		0.14	0.27
	130	0.62		0.13	0.27
syn-Z	48	0.40	0.22	0.38	
	88	0.42	0.25	0.37	

The five kinetic runs give quite consistent information: all four paths are kinetically competitive; the relative magnitudes of the rate constants (in percentage terms, ±2−3%) are k_{si} = 40%, k_{sr} = 23%, k_{ar} = 13%, and k_{ai} = 24%. Thus there is no significant kinetic preference for the orbital symmetry-allowed k_{si} and k_{ar} paths, there in no "energy of concert" in evidence, and diradical-mediated paths seem mechanistically essential.

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(10) The average of $f(t)$ on $(0,t)$ is $\int_0^t f(t)\mathrm{d}t/t$.