Suprafacial and Antarafacial Paths for the Thermal Vinylcyclopropane-to-Cyclopentene Rearrangement of 1-Ethenylbicyclo[4.1.0]heptane to Bicyclo[4.3.0]non-1(9)-ene

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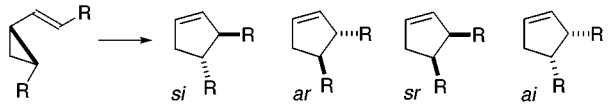
The gas phase thermal rearrangement of 1-ethenylbicyclo[4.1.0]heptane at 338 °C gives the expected vinylcyclopropane-to-cyclopentene product, bicyclo[4.3.0]non-1(9)-ene. The analogous rearrangement of 1-(2′-(*E*)-*d*-ethenyl)bicyclo[4.1.0]heptane takes place with the allylic moiety being utilized in both suprafacial and antarafacial stereochemical ways, for both endo and exo isomers of 8-*d*-bicyclo-[4.3.0]non-1(9)-ene are formed. The product ratio, defined by deuterium NMR in the presence of Ag(fod) and Yb(fod)$_3$ shift reagents, corresponds to (79 ± 2)% suprafacial (*sr* + *si*) and (21 ± 2)% antarafacial (*ar* + *ai*) reaction stereochemistry.

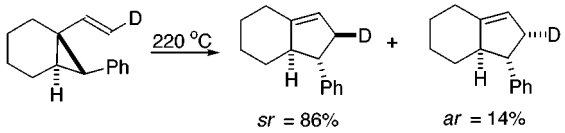
Introduction

The stereochemical aspects of vinylcyclopropane-to-cyclopentene isomerizations[1] gained theoretical prominence in the wake of Woodward−Hoffmann understandings of sigmatropic rearrangements.[2,3] The conversion, a [1,3] sigmatropic carbon shift, was recognized to be "allowed" when occurring through suprafacial, inversion (*si*) or antarafacial, retention (*ar*) paths and "forbidden" when taking place with *sr* or *ai* stereochemistry. Product isomers corresponding to *sr* or *ai* paths "cannot be formed in a symmetry-allowed process." Yet the thermochemical characteristics of the reaction made it seem that a two-step, nonconcerted path for the conversion of vinylcyclopropane to cyclopentene was not "thermodynamically unreasonable."[3]



Determining reaction stereochemistry for vinylcyclopropane-to-cyclopentene isomerizations proved difficult, for stereochemically well-defined starting materials typically showed thermal stereomutations[4] faster than they provided [1,3] sigmatropic shift products, and determinations of rate constants for conversions of specific stereoisomers of a vinylcyclopropane system to specific stereoisomers of cyclopentene products presented nontrivial methodological challenges. But, in time, the stereochemical facts became available and they revealed, for a variety of monocyclic, geometrically unconstrained vinylcyclopropanes substituted with cyano, deuterium, methyl, or phenyl stereochemical markers, that the isomerization takes place through all four paths. All four stereochemical options are kinetically competitive. Of particular interest to the present work, the *ar* and *ai* paths together range in relative importance from 13 to 37% of the four paths in the eight cases most thoroughly investigated.[5−14] Suprafacial utilization of the allylic moiety is always preferred, but the antarafacial alternative is always in evidence as a substantial contributor.

In an effort to test whether extensive rotation about C3−C4 in a hypothetical (2*Z*)-pentene-1,5-diyl system is required for access to antarafacial rearrangement products, deuterium- and phenyl-substituted 1-ethenylbicyclo-[4.1.0]heptanes were prepared and isomerized to the corresponding bicyclo[4.3.0]non-1(9)-enes.[15] The major product isolated corresponded to migration with retention. Both *sr* and *ar* stereochemical paths contributed to the overall isomerization. Starting with the (*E*)-deuterium-labeled ethenyl group as shown, the balance was 86% *sr*, 14% *ar*; the substrate with a (*Z*)-deuterium-labeled ethenyl group gave 84% *sr* and 16% *ar* products.[15]



These stereochemical results imply that an antarafacial outcome when migration proceeds with retention

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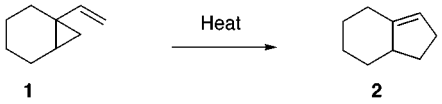
does not require C2−C3−C4−C5 dihedral angle changes of more than 180° in a hypothetical 3,4-tetramethylene-bridged 2-pentene-1,5-diyl species; rather, the conformational flexibility required to present the migrating carbon with the initially less accessible face of the allylic component takes place through planar or nearly planar geometries of the five carbons of the 2-pentene-1,5-diyl structure, with C1−C5 in close proximity.

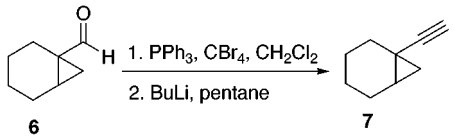
The present study was undertaken to extend these results by progressing to a system that retained the tetramethylene tether to restrict conformation possibilities and yet did not favor any stereochemical outcome based on product stability differences. The reaction selected for study, the isomerization of 1-ethenylbicyclo-[4.1.0]heptane (**1**) to bicyclo[4.3.0]non-1(9)-ene (**2**), satisfies these requirements.



Results

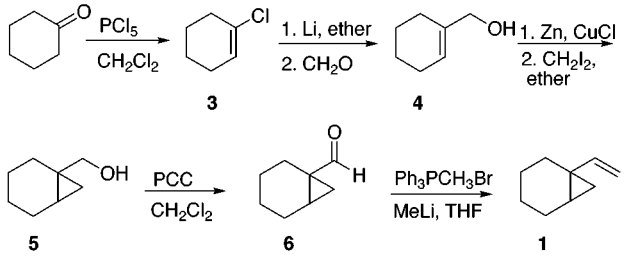
Syntheses. The unlabeled substrate **1** was prepared according to the sequence of reactions outlined in Scheme 1. Cyclohexanone and PCl_5 afford 1-chlorocyclohexene (**3**);[16] the corresponding organolithium compound[17] and formaldehyde give 1-hydroxymethylcyclohexene (**4**).[18] A Simmons−Smith cyclopropanation reaction leads to 1-hydroxymethylbicyclo[4.1.0]heptane (**5**).[19−21] Oxidation of this alcohol[22] gives an aldehyde (**6**) that may be converted through a Wittig reaction[23] to 1-ethenylbicyclo-[4.1.0]heptane (**1**).[24]

Aldehyde **6** served as well as synthetic intermediate for 1-ethynylbicyclo[4.1.0]heptane. The aldehyde was reacted with triphenylphosphine and CBr_4 following Corey and Fuchs[25] to give 1-(2′,2′-dibromoethenyl)bicyclo-[4.1.0]heptane, which was dehydrobrominated with butyllithium to provide alkyne **7**.

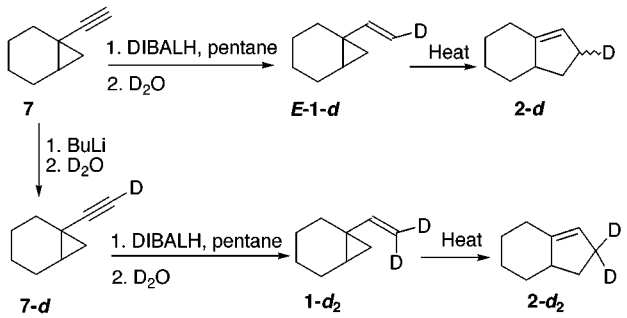


The deuterium-labeled versions of vinylcyclopropane **1** required, 1-(2′-(*E*)-*d*-ethenyl)bicyclo[4.1.0]heptane (***E*-1-*d***) and 1-(2′,2′-d_2-ethenyl)bicyclo[4.1.0]heptane (**1-*d*$_2$**), were made from alkyne **7** through the reactions summarized in Scheme 2. Reduction of the triple bond with DIBALH in pentane, followed by treatment of the reaction mixture with D_2O, gave the (*E*)-deuterio-labeled

Scheme 1



Scheme 2



product ***E*-1-*d*** with very high stereoselectivity, as judged by NMR spectral criteria. The same two-step reaction sequence, starting with 1-(*d*-ethynyl)bicyclo[4.1.0]heptane (**7-*d***), provided **1-*d*$_2$**.

The gas-phase thermal reactions of **1**, **1-*d*$_2$**, and ***E*-1-*d*** were run using a well-conditioned 300-mL kinetic bulb;[26] 6 h at 338 °C was sufficient to achieve a 79% conversion of **1** to the vinylcyclopropane−cyclopentene rearrangement product **2** (70%; 89% yield) and several minor products (9%). The bicyclic olefin **2**, a known compound,[27] was identified through proton and carbon-13 NMR spectroscopy.

The isomerization of **1-*d*$_2$** to **2-*d*$_2$** provided material needed to test NMR methods for measuring integrated absorption intensities for exo and endo deuteriums at C8. The two diastereotopic deuteriums in **2-*d*$_2$**, awkwardly enough, happened to have the same chemical shift: they appeared in a ^{2}H NMR spectrum as a single observable resonance! In the presence of Ag(fod) and Yb(fod)$_3$ shift reagents, however, the resonances were well resolved.[28,29]

The combination shift reagent Ag(fod) and Yb(fod)$_3$ complexes with the most sterically accessible face of an olefin, causing NMR resonance absorptions for allylic protons to shift downfield, with those on the most sterically accessible face of the olefin experiencing the more pronounced shifts.[28,29] On the basis of this precedence, the more downfield resonance observed in the deuterium NMR spectrum of **2-*d*$_2$** was assigned to the exo deuterium at C8, for the exo face of bicyclo[4.3.0]non-1(9)-ene was judged to be the more accessible.

Isomerization of ***E*-1-*d*** for 6 h at 338 °C gave both ***endo*-2-*d*** and ***exo*-2-*d*.** The integrated intensities of the two absorptions in the deuterium NMR spectrum of GC purified product, recorded in the presence of Ag(fod) and Yb(fod)$_3$ shift reagents, showed the more downfield signal (from the ***exo*-2-*d*** isomer) to be the weaker (Figure 1):

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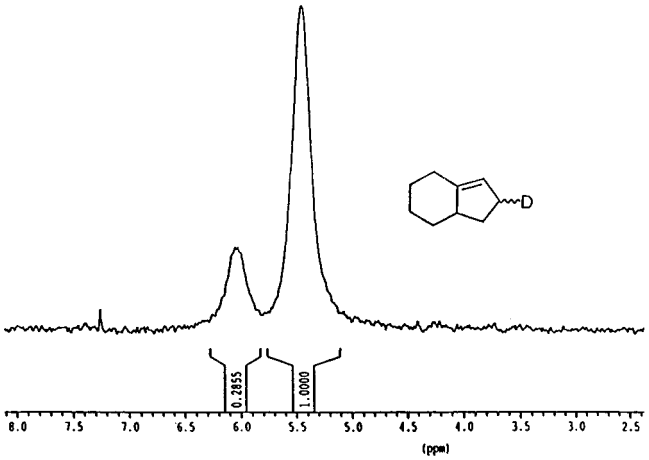
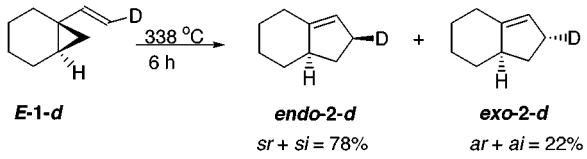


Figure 1. Deuterium NMR spectrum recorded in the presence of Ag(fod) and Yb(fod)$_3$ shift reagents of ***endo*-2-*d*** and ***exo*-2-*d*** obtained through thermal isomerization of ***E*-1-*d*** over 6 h at 338 °C.

the vinylcyclopropane-to-cyclopentene rearrangement occurred with 78% (*sr* + *si*) and 22% (*ar* + *ai*) stereochemistry.

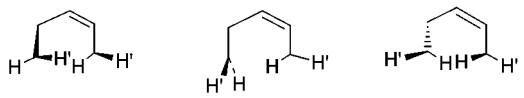


A second isomerization over a 4.5-h period gave a smaller sample of product estimated by ^{2}H NMR in the presence of the mixed shift reagents to be ***endo*-2-*d*** and ***exo*-2-*d*** in 81:19 proportions, an outcome essentially identical to the 78:22 ratio observed for the product mixture from a 6-h reaction, thus providing some assurance that the stereochemical result is reproducible and corresponds to a kinetically controlled product mixture.

Discussion and Conclusions

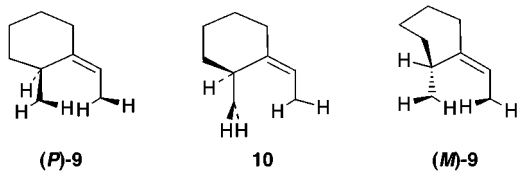
The stereochemical results obtained through the present work may be summarized succinctly: for the isomerization of vinylcyclopropane **1** to the corresponding cyclopentene product **2** at 338 °C, deuterium labeling experiments show that the isomerization modes (*sr* + *si*) and (*ar* + *ai*) take place in (79 ± 2):(21 ± 2) proportions. These stereochemical results may be compared with those reported for the isomerizations of the 7-*exo*-phenyl substituted analogue of **1** at 220 °C: *sr*/*ar* = (85 ± 1):(15 ± 1).[15] The suprafacial to antarafacial balances, with and without contributions from pathways involving inversion at the migrating carbon, are remarkably similar. They also correspond reasonably with the range of observed contributions from antarafacial paths (13−37% of all paths) determined for isomerizations of conformationally less constricted, substituted monocyclic vinylcyclopropanes.[5−14]

The most recent published theoretical models for thermal vinylcyclopropane-to-cyclopentene rearrangements place a C_s-symmetric transition structure (**8**) between and only slightly higher in energy than two enanatiomerically related helical (*Z*)-2-pentene-1,5-diyl transition structures leading to cyclopentene products, one corresponding to suprafacial, the other antarafacial utilization of the allylic moiety (**(*P*)-7** and **(*M*)-7**).[30−32]

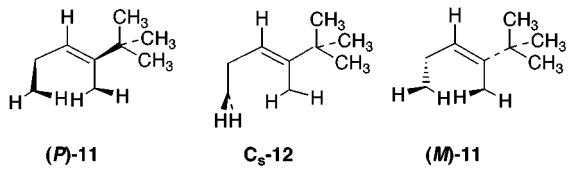


The conformational isomerization by way of ***C*$_s$-8** leaves the choice between inversion or retention stereochemistry unaltered: that option, according to theory,[30,31] is determined earlier in the progress from the ground state to the transition region through conformational flexibilities involving primarily torsions about the C5−C4 axis as the cyclopropyl C−C bond of the starting material lengthens and cleaves.

The present results imply that this configurational freedom remains essentially unimpaired despite the tetramethylene tether for isomerizations that are thermochemically unbiased, for isomerizations free to use inversion as well as retention stereochemical paths. While the respective structures **(*P*)-9** and **(*M*)-9** are no longer enantiomeric, and **10** is no longer of C_s symmetry, access to **(*M*)-9** and thus access to the initially remote face of the allyl π system by way of **10** is apparently not much encumbered by the conformational restraints imposed by the tetramethylene bridge.



These schematic structural representations prompt consideration of other possible influences on conformational flexibility, such as steic effects associated with substituents at C2 of the core (2*Z*)-pentene-1,5-diyl structure. For instance: there is good experimental evidence indicating that vinylcyclopropanes substituted with *tert*-butyl at C1′ of the ethenyl group isomerize to 1-(*tert*-butyl)cyclopentenes with predominant suprafacial, inversion stereochemistry.[33−36] Might the very high preference for suprafacial stereochemistry be associated with passage of the *tert*-butyl group past the C1- and C3-hydrogens in transition structure ***C*$_s$-12**?



That question might be probed computationally. Similar questions could be addressed and answered experi-

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mentally through syntheses and stereochemical studies of suitable vinylcyclopropane systems. The present results for a tetramethylene-tethered reactant stress the conformational flexibility available on paths linking vinylcyclopropane substrate **1** to cyclopentene product **2**; other systems could well provide insights on structural factors that could substantially influence relative preferences among alternative stereochemical outcomes.

Experimental Section

Elemental analyses were done by E & R Microanalytical Laboratory, Corona, NY. The ^{1}H NMR, ^{2}H NMR, and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions.

1-Chlorocyclohexene (3), prepared following the procedure of Brandsma and Verkuijsse,[16] was distilled through a 18-cm Vigreux column and had bp 32−36 °C (12 mm). A small sample was further purified by preparative gas chromatography (17% Carbowax, 45 °C): ^{1}H NMR δ 5.77−5.82 (m, 1 H), 2.25−2.32 (m, 2 H), 2.04−2.12 (m, 2 H), 1.68−1.78 (m, 2 H), 1.53−1.62 (m, 2 H); ^{13}C NMR δ 131.9, 124.5, 33.7, 26.0, 23.7, 21.3.

Cyclohexene-1-methanol (4). A flattened piece of lithium (2.03 g, 275 mmol) containing 0.5−1% sodium was cut directly into a 250-mL three-necked flask containing 60 mL of dry ether.[17] Pieces of glass from 0.5 to 1.5 cm long obtained by breaking cautiously two Pasteur pipets with a hammer were introduced into the flask; it was then fitted with a reflux condenser and mechanical stirrer, and it was flushed with argon. 1-Chlorocyclohexene (11.4 g, 98 mmol) was added and the mixture was stirred slowly at room temperature. After 3 h, the reaction solution was heated to reflux with stirring for an additional 2 h and then cooled to room temperature and stirred for another 9 h. The resultant grayish suspension was transferred to a 250-mL three-necked flask previously flushed with argon. The broken glass pieces were washed with ether (3 × 10 mL), and the ethereal solution was combined with the transferred suspension. Gaseous formaldehyde (from the depolymerization of 4.02 g (123 mmol) of paraformaldehyde in a separate flask at 180−200 °C)[18] was bubbled into the gray mixture at 0 °C; this introduction of paraformaldehyde was repeated to ensure complete reaction of the cyclohexenyllithium. The reaction mixture was allowed to warm to room temperature, stirred for 10 h, and then poured into 300 mL of saturated aqueous NH_4Cl at 0 °C. The two-phase system was stirred vigorously, the ethereal layer was removed, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic material was washed with water (50 mL), dried over $MgSO_4$, filtered, and concentrated. The resultant oil was distilled through an 18-cm Vigreux column to give 4.82 g of cyclohexene-1-methanol (37%) boiling at 84−89 °C (14−16 mm) (lit.[18] bp 84 °C (10 mm)). A small sample was further purified by preparative GC (10% SE-30, 100 °C): ^{1}H NMR δ 5.68 (s, 1 H), 3.98 (s, 2 H), 1.97−2.08 (m, 4 H), 1.54−1.71 (m, 4 H), 1.34 (s, 1 H); ^{13}C NMR δ 137.6, 123.1, 67.7, 25.7, 24.9, 22.6, 22.5; MS *m*/*z* (rel intensity) 112 (34, M^+), 94, (20), 81 (88), 79 (100), 67 (26), 55 (46), 39 (76).

Bicyclo[4.1.0]heptane-1-methanol (5). To a 100-mL three-necked flask were added zinc powder (7.28 g, 111 mmol), copper chloride (1.10 g, 11.2 mmol), and dry ether (50 mL).[19] The flask was fitted with a reflux condenser and flushed with argon, and the reaction mixture was heated to reflux for 1 h. Cyclohexene-1-methanol (4.82 g, 43.0 mmol) and CH_2I_2 (14.9 g, 55.7 mmol, 4.5 mL) were added to the lime green solution. The reaction mixture was heated to reflux for 60 h, and then the gray mixture was cooled to room temperature and filtered. The filtrate was washed with 3 M aqueous NaOH (4 × 30 mL) and water (30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to give 4.29 g (79%) of bicyclo[4.1.0]-heptane-1-methanol[20,21] as a clear oil. A small sample was further purified by preparative GC (10% SE−30, 100 °C): ^{1}H NMR δ 3.28−3.41 (m, 2 H), 1.81−1.94 (m, 2 H), 1.55−1.78 (m, 2 H), 1.15−1.38 (m, 5 H), 0.78−0.88 (m, 1 H), 0.48 (dd, J = 9.3, 4.5 Hz, 1 H), 0.25 (t, J = 5.0 Hz, 1 H); ^{13}C NMR δ 72.7, 26.4, 23.7, 22.0, 21.7, 21.3, 15.7, 15.0; MS *m*/*z* (rel intensity) 126 (2, M^+), 108 (18), 95 (81), 79 (48), 67 (98), 55 (60), 39 (100).

Bicyclo[4.1.0]heptane-1-carboxaldehyde (6). To a 50-mL round-bottomed flask were added PCC[22] (2.57 g, 11.9 mmol), dry CH_2Cl_2 (25 mL), and bicyclo[4.1.0]heptane-1-methanol (1.01 g, 11.9 mmol). The black reaction mixture was stirred for 2 h at room temperature under argon and then diluted with ether (25 mL) and filtered through Florisil. The black tar that remained in the flask was washed with ether (3 × 10 mL), the washings were filtered through Florisil, and the Florisil was washed with ether (100 mL). The combined ethereal material was dried ($MgSO_4$), filtered, and concentrated. Column chromatography (silica gel, hexanes/ethyl acetate 9:1) gave 0.91 g (92%) of aldehyde **6** as a clear oil. A small sample was further purified by preparative GC (10% SE-30, 100 °C): ^{1}H NMR δ 8.64 (s, 1 H), 2.55−2.67 (m, 1 H), 1.82−1.90 (m, 2 H), 1.28−1.61 (m, 6 H), 1.11−1.24 (m, 2 H), 0.91 (dd, J = 7.0, 4.8 Hz, 1 H) (compare ref 21); ^{13}C NMR δ 202.3, 31.3, 22.8, 21.4, 21.2, 20.5, 20.2, 19.0; MS *m*/*z* (rel intensity) 124 (10, M^+), 109 (15), 95 (71), 80 (37), 67 (77), 55 (46), 39 (100).

1-Ethenylbicyclo[4.1.0]heptane (1). To a stirred solution of methyltriphenylphosphonium bromide (5.17 g, 14.5 mmol) in THF (20 mL) under argon was added MeLi (10.4 mL, 14.47 mmol, 1.4 M) at −78 °C.[23] The reaction mixture was warmed to 0 °C and stirred for 1.5 h. The bicyclic aldehyde **6** (1.50 g, 12.0 mmol) in 5 mL of THF was added dropwise to the red solution of Wittig reagent[23] at 0 °C, and the reaction mixture was then warmed to room temperature and stirred for 5 h. It was quenched with water (40 mL); the organic layer was removed, and the aqueous layer was extracted with pentane (3 × 30 mL). The combined organic material was washed with water (15 mL), dried ($MgSO_4$), filtered, and concentrated. Column chromatography (silica gel, pentane) gave 0.96 g (65%) of **1**[24] as a clear oil. A small sample was further purified by preparative GC (15% SE-30, 65 °C): ^{1}H NMR δ 5.48 (dd, J = 17.3, 10.6 Hz, 1 H), 4.90 (dd, J = 17.3, 1.3 Hz, 1 H), 4.84 (dd, J = 10.6, 1.3 Hz, 1 H), 1.85−2.03 (m, 2 H), 1.71−1.81 (m, 1 H), 1.50−1.62 (m, 1 H), 1.11−1.48 (m, 4 H), 0.91−1.02 (m, 1 H), 0.67 (dd, J = 9.3, 4.4 Hz, 1 H), 0.52 (dd, J = 5.9, 4.4 Hz, 1 H) (compare ref 24); ^{13}C NMR δ 148.1, 108.4, 26.0, 23.8, 21.7, 21.6, 21.0, 20.3, 19.0; MS *m*/*z* (rel intensity) 122 (10, M^+), 107 (16), 93 (34), 79 (100), 67 (31), 53 (22), 39 (47).

1-Ethynylbicyclo[4.1.0]heptane (7). To a 100-mL three-necked flask were added under argon CBr_4 (6.04 g, 18.2 mmol), PPh_3 (9.56 g, 36.4 mmol), and dry CH_2Cl_2 (25 mL) at 0 °C.[25] The orange solution was then stirred for 30 min at 0 °C; the bicyclic aldehyde **6** (1.13 g, 9.11 mmol) in CH_2Cl_2 (10 mL) was added, and the reaction mixture was stirred for an additional 12 h at room temperature. It was then filtered, and the filtrate was concentrated. The concentrate was triturated with pentane, and PPh_3 was removed by filtration. Several repetitions of this process (trituration with pentane, filtration, and concentration) served to remove most of the PPh_3. Column chromatography of the final oily concentrate (silica gel, pentane) gave 1.77 g (69%) of the dibromoolefin intermediate as a clear oil: MS *m*/*z* (rel intensity) 278:280:282 (3:6:3, M^+), 252 (7), 226 (21), 212 (16), 199 (17), 171 (13), 145 (14), 119 (99), 91 (100), 77 (35), 65 (34), 51 (39), 39 (74).

To 2.03 g (7.55 mmol) of the dibromide in 30 mL of dry pentane under argon at −78 °C was added 1.6 M BuLi in hexanes (11.3 mL, 18.1 mmol). The reaction mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and stirred for another 1 h. It was then cooled to 0 °C, and 25 mL of water was added slowly. The organic layer was removed, and the aqueous layer was extracted with pentane (3 × 25 mL). The combined organic material was dried ($MgSO_4$) and filtered, and the filtrate was concentrated to give 0.65 g of 1-ethynylbicyclo[4.1.0]heptane (72%) as a clear oil. A small sample was further purified by preparative GC (15%

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SE-30, 65 °C): ^{1}H NMR δ 1.88−2.06 (m, 3 H), 1.86 (s, 1 H), 1.52−1.63 (m, 1 H), 1.06−1.42 (m, 5 H), 0.99 (dd, J = 9.3, 4.4 Hz, 1 H), 0.54 (dd, J = 6.3, 4.4 Hz, 1 H); ^{13}C NMR δ 92.6 (C), 62.6 (CH), 29.3 (CH_2), 23.0 (CH_2), 20.9 (CH_2), 20.9 (CH), 20.3 (CH_2), 19.9 (CH_2), 9.7 (C); MS *m*/*z* (rel intensity) 120 (25, M^+), 105 (60), 91 (100), 77 (35), 65 (22), 51 (24), 39 (52). Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.88; H, 10.23.

1-(2′,2′-*d*$_2$-Ethenyl)bicyclo[4.1.0]heptane (1-*d*$_2$). A sample of the alkyne **7** (0.20 g, 1.66 mmol) dissolved in dry pentane under argon was cooled to −78 °C, and 1.6 M BuLi in hexanes (1.2 mL, 1.99 mmol) was added. The mixture was warmed to room temperature and stirred for 20 min; it was then cooled to 0 °C, and 2 mL of D_2O (99.9% D) was added slowly with rapid stirring. The reaction mixture was transferred to a separatory funnel and extracted with pentane (3 × 10 mL). A second exchange was then performed; ^{1}H NMR spectroscopy showed the acetylenic proton to be substantially replaced with deuterium. To the labeled acetylene **7-*d*** (1.66 mmol) in 20 mL of dry pentane at 0 °C was added DIBALH (0.59 mL, 0.47 g, 3.32 mmol) in 5 mL of dry pentane through an addition funnel. The reaction mixture was warmed to room temperature and monitored by GC. After 2 h, the reaction flask was cooled to 0 °C, and 5 mL of D_2O was added slowly. The resultant mixture was allowed to warm to room temperature and was stirred rapidly for 3 h, and then a small amount of 10% aqueous HCl was added to dissolve the gelatinous mixture that had formed. The contents of the flask were transferred to a separatory funnel, and the aqueous layer was extracted with pentane (5 × 15 mL). The combined organic material was washed with saturated aqueous $NaHCO_3$ (20 mL), dried ($MgSO_4$), and filtered. Concentration of the filtrate gave 140 mg (68% for the three steps) of **1-*d*$_2$**. A small sample was further purified by preparative GC (15% SE-30, 65 °C): ^{1}H NMR (olefinic region) δ 5.48 (s, 1 H), 4.90 (d, J = 17.3 Hz, 13% of 1 H).

1-(2′-(*E*)-*d*-ethenyl)bicyclo[4.1.0]heptane (*E*-1-*d*). To a sample of the bicyclic alkyne **7** (0.10 g, 0.83 mmol) in 10 mL of dry pentane at 0 °C was added DIBALH (0.30 mL, 0.24 g, 1.67 mmol) in 5 mL of dry pentane through an addition funnel. The reaction mixture was allowed to warm to room temperature and monitored by GC. After 4 h, the flask was cooled to 0 °C and 5 mL of D_2O was added slowly. The mixture was allowed to warm to room temperature and was stirred rapidly for 3 h. A workup as described for **1-*d*$_2$** led to 74 mg (73%) of ***E*-1-*d***. A small sample was further purified by preparative GC: ^{1}H NMR (olefinic region) δ 5.48 (d, J = 17.3 Hz, 1 H), 4.90 (d, J = 17.3 Hz, 1 H).

Gas-Phase Reactions. Thermal reactions of unlabeled and deuterium-labeled 1-ethenylbicyclo[4.1.0]heptanes (100-mL of 5% solutions in pentane) were carried out at 338.1 °C in a 300-mL Pyrex bulb encased in an aluminum block.[26] The bulb was conditioned before use by pyrolyzing 50-mL samples of cyclohexene at 350 °C for 24 h three times. A spherical cavity machined in the block accommodated the flask; the aluminum top hemisphere was halved to allow facile dismantling of the apparatus. Eight cartridge heaters in vertical holes around the block were connected alternately to a Variac and to a Bailey Instruments model 253 precision temperature controller. Temperature measurements were made with a calibrated Hewlett-Packard model 2802A digital thermometer and a platinum resistance temperature probe (Omega Engineering, part no. OSK5045 PR-11-3-100-1/8-6-E). The aluminum block was supported with firebrick and enclosed in a 34-cm × 34-cm × 27-cm plywood box packed with diatomaceous earth.

Prior to each thermal reaction, the bulb was evacuated to less than 2.2×10^{-2} Torr and the stopcock was closed. Samples were injected into the bulb through a septum with a 0.5-mL gastight syringe. After a thermal reaction, the stopcock was opened and the reaction mixture was pumped into a liquid nitrogen cooled U-tube attached to the vacuum line with O-ring seals and threaded connectors (Ace Glass No. 5027-30); this method provided immediate recovery of the sample, whereas longer times would have been required for transfers more sensitive to the vapor pressure of the sample. After appropriate stopcocks on the line were manipulated, the trap was removed and its contents dissolved in pentane. The pentane solution was analyzed directly by analytical GC using a 25-m Ultra 2 column, and recovered starting material and unlabeled or deuterium-labeled bicyclo[4.3.0]non-1(9)-ene products were isolated in pure form by preparative GC (15% SE-30, 65 °C).

Thermal reactions of **1** in base-washed sealed ampules gave irreproducible reaction kinetics and complex product mixtures; a substantial component in these mixtures was found to be bicyclo[4.3.0]non-1(6)-ene,[37] a structure presumably formed through an acid-catalyzed isomerization of the primary thermal product, **2**. Compounds **1**, ***E*-1-*d***, and **1-*d*$_2$**, after careful purification by preparative GC, exhibited reproducible kinetic behavior and gave primarily **2**, **2-*d***, and **2-*d*$_2$**, respectively, when isomerized thermally in the gas phase using the well-conditioned kinetic bulb described above.

Bicyclo[4.3.0]non-1(9)-ene (2). Ethenylbicyclo[4.1.0]-heptane (**1**) was heated in the gas phase for 6 h at 338 °C; the reaction mixture was transferred from the kinetic bulb, analyzed by GC, and found to contain unreacted **1** (21%), bicyclo[4.3.0]non-1(9)-ene (**2**, 70%),[27] and several minor products (9%). The rearrangement product **2** was purified by preparative GC: ^{1}H NMR δ 5.23 (t, J = 2.2 Hz, 1 H), 2.48−2.33 (m, 2 H), 2.29−2.22 (m, 2 H), 2.14−2.05 (m, 1 H), 1.99−1.86 (m, 2 H), 1.80−1.70 (m, 2 H), 1.40−1.27 (m, 2 H), 1.23−1.12 (m, 1 H), 0.94 (quartet d, J = 12.6, 3.3 Hz, 1 H); ^{13}C NMR δ 146.4, 120.1, 45.5, 35.9, 31.1, 30.7, 28.9, 27.3, 26.2; MS *m*/*z* (rel intensity) 122 (43, M^+), 107 (10), 93 (85), 80 (97), 79 (100), 67 (16), 53 (15), 39 (36).

8-*d*$_2$-Bicyclo[4.3.0]non-1(9)-ene (2-*d*$_2$). A gas-phase sample of 1-(2′,2′-d_2-ethenyl)bicyclo[4.1.0]heptane (**1-*d*$_2$**) was heated for 6 h at 338 °C. The reaction mixture contained **1-*d*$_2$** (21%), **2-*d*$_2$** (69%) and several minor products (10%). The deuterium NMR spectrum of the preparative GC purified **2-*d*$_2$** showed only a single resonance, at δ 2.25. In the presence of Ag(fod) (22 mg) and Yb(fod)$_3$ (11 mg),[28,29] **2-*d*$_2$** showed two peaks: ^{2}H NMR δ 4.89 (s, 1 D), 4.23 (s, 1 D). The recovered starting material **1-*d*$_2$** isolated by preparative GC was found to be unchanged according to ^{1}H NMR criteria.

8-*d*-Bicyclo[4.3.0]non-1(9)-ene (2-*d*) from 1-(2′-(*E*)-*d*-ethenyl)bicyclo[4.1.0]heptane (*E*-1-*d*). A sample of ***E*-1-*d*** was heated for 6 h at 338 °C. The reaction mixture contained ***E*-1-*d*** (20%), bicyclo[4.3.0]non-1(9)-ene (**2-*d***, 72%), and several minor products (8%). Product **2-*d*** was purified by preparative GC and examined by deuterium NMR in the presence of Ag(fod) (26 mg) and Yb(fod)$_3$ (13 mg): ^{2}H NMR δ 6.05 (s, 22% of 1 D), 5.43 (s, 78% of 1 D) (Figure 1). The stereochemistry about the vinyl group in recovered ***E*-1-*d*** was unchanged (^{1}H NMR).

A second sample of ***E*-1-*d*** was heated for 4.5 h at 338 °C to give a reaction mixture containing unreacted ***E*-1-*d*** (28%), **2-*d*** (60%), and several minor products (12%). Rearrangement product **2-*d*** was purified by preparative GC: ^{2}H NMR δ (in the presence of Ag(fod) (26 mg) and Yb(fod)$_3$ (13 mg)), two peaks, 6.61 (s, 19% of 1 D) and 5.43 (s, 81% of 1 D). Unreacted ***E*-1-*d*** was isolated by preparative GC and shown to have retained stereochemical integrity at the vinyl C2′ position (^{1}H NMR).

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Supporting Information Available: Copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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