Stereochemistry of the Thermal Isomerization of 1-Ethenyl-7-*exo*-Phenylbicyclo[4.1.0]heptane to 7-Phenylbicyclo[4.3.0]non-1(9)-ene: The Conformational Course of an Antarafacial,Retention Vinylcyclopropane−Cyclopentene Rearrangement

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The thermal vinylcyclopropane−cyclopentene rearrangement of 1-ethenyl-7-*exo*-phenylbicyclo[4.1.0]-heptane at 220 °C gives mostly migration with retention to form 7-*exo*-phenylbicyclo[4.3.0]non-1(9)-ene. 1-(*E*-*d*-Ethenyl)- and 1-(*Z*-*d*-ethenyl)-7-*exo*-phenylbicyclo[4.1.0]heptanes give both 8-exo and 8-endo deuterium-labeled products. The suprafacial,retention and antarafacial,retention paths for this rearrangement are used in 85:15 proportions. The antarafacial process may involve passage through a "semicircular" diradical conformation; it cannot occur through rotation in the opposite sense, passing through an "extended" diradical geometry.

Introduction

Soon after the thermal rearrangement of vinylcyclopropane to cyclopentene was first reported in 1960[1] the stereochemical aspects of such transformations came to theoretical prominence, for orbital symmetry theory postulated a clear correspondence between the four possible stereochemically distinct paths and the dichotomous classifications "concerted" and "nonconcerted".[2] The early attempts to determine reaction stereochemistry for selected vinylcyclopropane rearrangements and to test this application of theory were plagued with difficulties. Thermal stereomutations of vinylcyclopropanes turned out to be much faster than [1,3] sigmatropic carbon shifts giving cyclopentene products![3−5] Competitive isomerizations and kinetic complexities contributed to uncertainties regarding reaction stereochemistry, and these circumstances in turn long hindered a sure resolution of the basic stereochemical and mechanistic issues posed by the rearrangement.[1]

Over time, however, the experimental situation was clarified. For seven stereochemically unconstrained *trans*-2-substituted vinylcyclopropanes, complete stereochemical studies have been completed and reported, and a fairly consistent pattern has emerged.[1,6−14] Such vinylcyclopropanes rearrange through all four stereochemically distinct paths. The suprafacial,inversion (*si*) path is favored, but suprafacial,retention (*sr*), antarafacial,-retention (*ar*), and antarafacial,inversion (*ai*) paths all contribute. The relative importance of suprafacial (*sr* + *si*) and antarafacial (*ar* + *ai*) paths ranges from 63:37 to 87:13.[1,6−14]

For the parent system, the vinylcyclopropane to cyclopentene process, studies with deuterium-labeled analogues showed that the four paths are followed in the proportions *si* = 40%, *ar* = 13%, *sr* = 23%, and *ai* = 24%.[10] The two "allowed" or "concerted" paths, *si* and *ar*, are only slightly favored relative to the "nonallowed" or "nonconcerted" paths, *sr* and *ai*. There is no energy of concert in evidence, and the isomerization appears to proceed through diradical transition structures.[1,10]

How the allylic component may give rise to cyclopentenes indicative of antarafacial paths—a question which was suppressed for some years as the possibility of antarafacial [1,3] carbon migrations was generally discounted—was addressed in the present work. Two plausible alternatives for conformational progress leading antarafacially from a vinylcyclopropane to a cyclopentene product were considered, and an experimentally based choice between them was sought. 1-Ethenyl-7-*exo*-phenylbicyclo[4.1.0]heptane (**1**) was selected as a suitable substrate, and the thermal isomerization giving 7-*exo*-

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(1) For a synopsis of work on this rearrangement, and a listing of review articles, see Baldwin, J. E. *J. Comput. Chem.* **1998**, *19*, 222−231.

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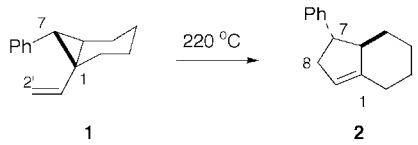
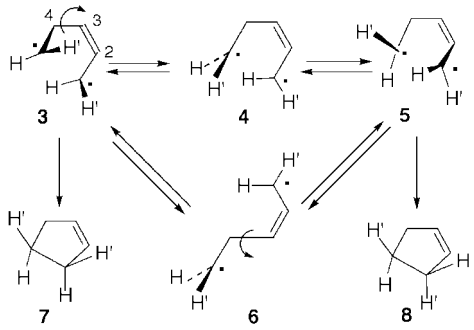
phenylbicyclo[4.3.0]non-1(9)-ene (**2**) was clarified using deuterium-labeled analogues.



1 **2**

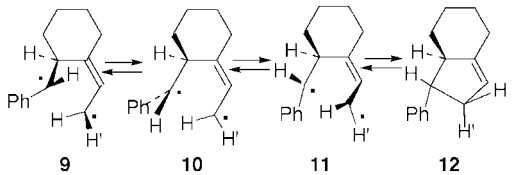
The considerations behind this choice of substrate relate to the conformational choices potentially available to the parent system (Scheme 1). Cleavage of the C1−C2 bond in 1-vinylcyclopropane could provide a helically disposed 2*Z*-pentene-1,5-diyl diradical (**3**) which might proceed through rotation about the C3−C4 bond in either clockwise or counterclockwise senses. From the helical form **3**, rotation about C3−C4 in a clockwise sense would lead to a "semicircular" all-carbons-planar diradical, the C_s-symmetric structure **4**, which could attain through further clockwise rotation a helical geometry **5** enantiomeric (except for distinctions based on possible isotopic substitutions) with diradical **3**. The diradical conformational isomers **3** and **5** could serve as precursors to the transition structures leading to *sr* and *ar* products **7** and **8** (Scheme 1).

Scheme 1

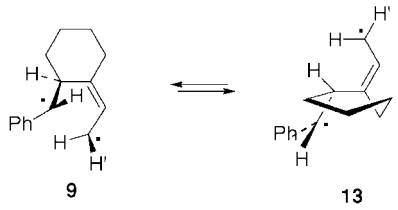


Were the diradical **3** to experience rotation about C3−C4 in a counterclockwise direction, the "extended" all-carbons-planar C_s-symmetric diradical conformation **6** could be reached which, through continued counterclockwise rotation, could arrive at the helical diradical conformation **5**. This path would avoid the possibly energetically costly steric demands present in **4** and yet attain the conformation **5** appropriate for formation of the *ar* product **8**.

So either clockwise or counterclockwise rotations about the C3−C4 bond of diradical **3** could hypothetically lead through different all-carbon-planar conformations to the antarafacial,retention product. For a vinylcyclopropane incorporating a suitable geometry-restricting tether, such as the tetramethylene tether present in **1**, the clockwise route to antarafacial product (**9** → **10** → **11** → **12**) would be unimpeded while the counterclockwise path passing by way of an extended conformation would be inaccessible.



The bridged "extended" 2*Z*-pentene-1,5-diyl diradical **13** just might be reached from **9**, but it surely could not continue through further counterclockwise rotation to give antarafacial product.

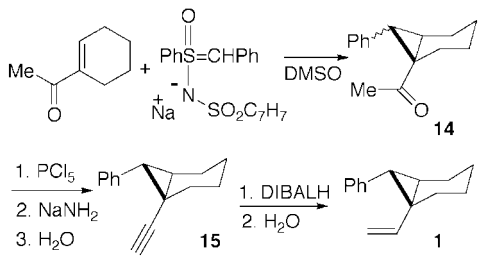


The experimentally testable question, "Is there an antarafacial component in the isomerization of **1** to **2**?", was considered an indicator of whether antarafacial paths require access through and rotational passage beyond "extended" diradical conformations. Were no antarafacial path from **1** to **2** in evidence, the indication would be positive. Were it detected, the indication would be that the more compact "semicircular" diradical conformations in **4** and **10** are not too sterically awkward and may provide a route between enantiomerically related helical forms of 2*Z*-pentene-1,5-diyl diradicals.

Results

Syntheses. The preparation of the unlabeled substrate **1** was done as outlined in Scheme 2. Deprotonation of *S*-benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide with sodium hydride in dimethyl sulfoxide followed by addition of acetylcyclohexene gave a mixture of exo and endo isomers of 1-acetyl-7-phenylbicyclo[4.1.0]heptane (**14**).[15] The mixture was treated with PCl_5 in dry benzene to give a mixture of (1′,1′-dichloroethyl)- and (1′-chloroethenyl)-substituted bicycloheptanes, which were dehydrochlorinated with sodamide in DMSO, followed by an aqueous workup.[16] Under the reaction conditions, epimerization at C7 afforded complete isomerization to the more stable 7-*exo*-phenyl diastereomer of 1-ethynyl-7-phenylbicyclo[4.1.0]heptane (**15**).[17] Hydroalumination of the ethynyl group with diisobutylaluminum hydride (DIBALH), followed by protonolysis,[11,14] gave 1-ethenyl-7-*exo*-phenylbicyclo[4.1.0]heptane (**1**).

Scheme 2



The deuterum-labeled analogues of **1** required for uncovering reaction stereochemistry were prepared from the alkyne **15** (Scheme 3). Treatment of **15** with DIBALH, followed by reaction of the organoaluminum intermediate with D_2O, gave 1-(*E*-*d*-ethenyl)-7-*exo*-phenylbicyclo[4.1.0]-heptane (**1-*E*-*d***). Exchange of the acetylenic hydrogen

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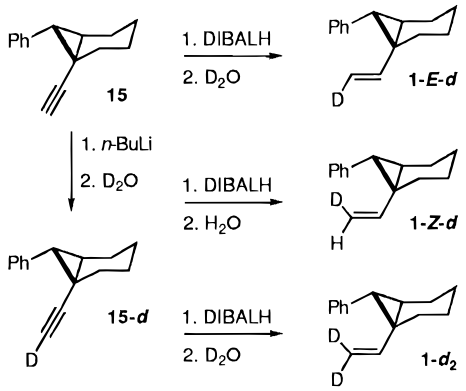
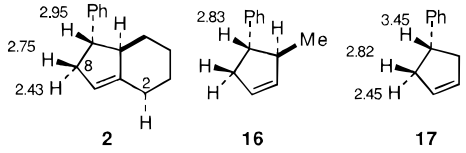
Scheme 3



in **15** with deuterium gave **15-*d***; it was converted with DIBALH, then H_2O, to **1-*Z*-*d***, and with DIBALH, then D_2O, to 1-(2′,2′-d_2-ethenyl)-7-*exo*-phenylbicyclo[4.1.0]-heptane (**1-*d*$_2$**).

Thermal Reactions. The thermal isomerizations of substrates **1**, **1-*E*-*d***, **1-*Z*-*d***, and **1-*d*$_2$** were conducted in carefully prepared sealed ampules in a constant temperature oil bath at 220 °C over 3.5 to 4.0 h. No visible indications of decomposition were apparent; analyses by gas chromatography and mass spectrometry showed one major rearrangement product formed in about 75% yield, along with several minor products. The major product from **1** was assigned structure **2**, based on one- and two-dimensional NMR data.

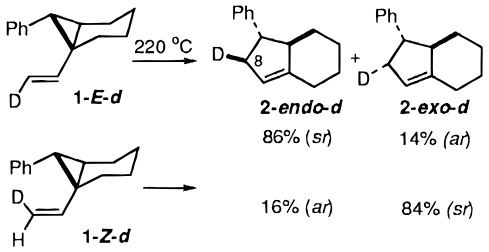
The proton NMR spectrum of **2** showed signals corresponding to five protons at δ 2.95 (q, J = 8.5 Hz, 1 H), 2.66−2.79 (m, 1 H), and 2.38−2.53 (m, 3 H). The ^{1}H NMR spectrum of **2-*d*$_2$** showed three protons in this region, at 2.95 (1 H) and 2.38−2.53 (m, 2 H); the ^{2}H NMR spectrum showed only two singlets, at δ 2.75 and 2.43. The absorptions at δ 2.95 and one contributing to the 2.38−2.53 multiplet were assigned to benzylic C7 and allylic C6 protons, respectively, while the two protons at C8 were characterized by chemical shifts of δ 2.75 and 2.43. The third proton in the δ 2.38−2.53 region was assigned to one of the C2−H resonances, the exo C2−H most perpendicular to the plane of the double bond.



These assignments may be compared with chemical shifts for *trans*-3-methyl-4-phenylcyclopentene (**16**)[9] and 4-phenylcyclopentene (**17**).[14,18] In **16**, the benzylic proton is part of a three-proton multiplet centered at δ 2.83; in the related cis isomer, the benzylic proton appears at δ 3.55 (q, J = 8.3 Hz).[9] For **17**, the benzylic hydrogen is seen at δ 3.45. The chemical shift assignments in **17** have been confirmed through preparations of deuterium-labeled analogues and shift reagent studies of the corresponding epoxides.[14]

The stereochemical assignments for C8 protons were initially based on chemical shift analogies with compounds **16** and **17**. They were confirmed through two-dimensional proton NOSEY spectra, which showed a strong cross-peak for protons at δ 2.95 and 2.75.

Thermal reactions of **1-*E*-*d*** and **1-*Z*-*d*** gave mixtures of **2-*exo*-*d*** and **2-*endo*-*d*** which were quantified by ^{2}H NMR spectroscopy. From **1-*E*-*d*** the product mixture exhibited ^{2}H NMR singlets at δ 2.75 and 2.46 in a 86:14 ratio (86% **2-*endo*-*d*** and 14% **2-*exo*-*d***). Thermal rearrangement of **1-*Z*-*d*** gave a product mixture characterized by ^{2}H NMR singlets at δ 2.74 and 2.45 in a 16:84 intensity ratio (16% **2-*endo*-*d*** and 84% **2-*exo*-*d***). The vinylcyclopropane to cyclopentene rearrangement of **1** to **2** takes place with (85 ± 1)% *sr* and (15 ± 1)% *ar* stereochemistry.



Discussion

If antarafacial paths in vinylcyclopropane rearrangements depend on access to and continued rotation through "extended" all-carbons-planar diradical conformations, no antarafacial products should form from **1**. But deuterium-labeled versions of **1** demonstrate that the antarafacial,retention stereochemical path plays a role. "Extended" diradical conformations which may rotate further are not required for antarafacial allylic participation, and "semicircular" all-carbons-planar diradical conformations such as **4** and **10** may be inferred as significant entities along *ar* reaction paths.

Since these results were presented in preliminary form,[18] two theoretical treatments of the vinylcyclopropane to cyclopentene rearrangement have appeared which bear directly on these conformation issues. Both Davidson and Gajewski[19] and Houk and co-workers[20] have found that a "semicircular" C_s-symmetric diradical transition structure (**4**; "**TS-cs**";[19] "*cis*-(90,0), **4**"[20]) lies between mirror-image related helical conformations of the 2*Z*-pentene-1,5-diyl diradical. The barrier height is estimated to be only 0.2[19] or 0.6[20] kcal/mol above the transition structure for ring-closure (**3** to **7**, or **5** to **8**), so that passage to antarafacial products should be kinetically competitive but less important than suprafacial routes at the thermolysis temperatures employed.

The present experimental results and the most recent theory fit well together. Stereochemical studies and theoretical models both suggest that vinylcyclopropane to cyclopentene rearrangements occur through diradical structures that allow for some conformational flexibility before a transition state region of the potential energy surface is reached. Diradical intermediates in substantial potential energy wells need not be involved,[19,20] but conformationally distinct diradical trajectories between

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a starting material and alternative transition structures appear to be essential aspects of the mechanism.

Experimental Section

Elemental analyses were done by E & R Microanalytical Laboratory, Corona, NY 11368. The high-resolution mass spectrum was secured through the University of Illinois School of Chemical Sciences, Urbana, IL 61801. The ^{1}H NMR and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions. Deuterium NMR spectra at 92 MHz were recorded at the University of Akron, Akron, OH 44325. Other instrumentation and standard procedures used in this work have been detailed elsewhere.[8,9,14]

Benzyl Phenyl Sulfoxide. Benzyl phenyl sulfide (10.0 g, 50.0 mmol) was added to a mixture of $NaIO_4$ (10.69 g, 50.0 mmol) and aqueous methanol (2:1 H_2O:MeOH, 100 mL) at 0 °C.[21] The reaction mixture was warmed to room temperature, stirred for 48 h, and filtered. The filtrate was extracted with CH_2Cl_2 (2 × 50 mL), and the salts were triturated and extracted with CH_2Cl_2 (75 mL); the combined organic extract was dried over $MgSO_4$, filtered, and concentrated. Recrystallization of the crude product from methanol gave benzyl phenyl sulfoxide (7.72 g, 35.7 mmol, 71.4%) as white crystals, mp 122−124.5 °C (lit.[22] mp 122−123 °C).

***S*-Benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide.**[15] To a 100-mL flask were added benzyl phenyl sulfoxide (5.02 g, 23.2 mmol), freshly prepared tosyl azide[23] (6.76 g, 34.3 mmol), 50 mL of anhydrous methanol, and 2 μm Cu power (0.99 g, 15.6 mmol; Allied Chemical). The reaction mixture was heated to reflux for 16 h, cooled, and concentrated by rotary evaporation. Saturated aqueous Na_2EDTA (50 mL) and CH_2Cl_2 (75 mL) were added to the concentrate with stirring, and the mixture was filtered. The salts were washed with additional CH_2Cl_2 (50 mL), and the CH_2Cl_2 solution was extracted with water (2 × 30 mL), dried over Na_2SO_4, filtered, and concentrated to give crude product. Recrystallization from ethanol gave *S*-benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide (3.41 g, 8.84 mmol, 38.1%) as white crystals, 149−151 °C (lit.[15] mp 148−149 °C). ^{1}H NMR δ 2.4 (s, 3 H), 4.8 (q, J = 7.4 Hz, 2 H), 7.0 (d, J = 9.7 Hz, 2 H), 7.25 (m, 6 H), 7.4 (m, 2 H), 7.6 (m, 2 H), 7.9 (d, J = 8.2, 2 H).

1-Acetyl-7-phenylbicyclo[4.1.0]heptanes (14). A 60% dispersion of NaH in mineral oil (1.18 g, 29.4 mmol) under argon was washed with dry pentane (3 × 15 mL). The residual pentane was removed with a stream of argon. Freshly distilled DMSO (80 mL) and *S*-benzyl-*S*-phenyl-*N*-(*p*-tolyl-sulfonyl)-sulfoximide (8.10 g, 21.0 mmol, dried under vacuum over P_2O_5 for 24 h) was added. The mixture was stirred at room temperature until all hydrogen evolution had ceased (2 h), and then 1-acetyl-1-cyclohexene (2.32 g, 19.1 mmol) in 15 mL of dry DMSO was added dropwise. The reaction mixture was stirred for 19 h at room temperature, and then 40 mL of H_2O and 40 mL of ether were added. The organic phase was washed with H_2O (4 × 20 mL), dried over $MgSO_4$, filtered, and concentrated to give a mixture of the bicyclic ketones **14-*endo*** and **14-*exo*** in a 1:4 ratio (analytical GC). Column chromatography (silica gel, hexanes:ethyl acetate, 10:1) gave this mixture of ketones as a clear oil (2.10 g, 9.8 mmol, 51.5%).

1-Acetyl-7-*exo*-phenylbicyclo[4.1.0]heptane (14-*exo*) was purified by preparative gas chromatography (10% SE-30, 125 °C). ^{1}H NMR δ 1.29−1.51 (m, 4 H), 1.78 (s, 3 H), 1.84 (t, J = 6.8 Hz, 1 H), 1.96−2.09 (m, 1 H), 2.12−2.36 (m, 3 H), 2.43 (td, J = 7.0, 1.6 Hz, 1 H), 7.08−7.24 (m, 5 H); ^{13}C NMR δ 20.6, 21.6, 22.3, 22.7, 26.4, 28.0, 38.2, 40.6, 126.3, 128.1, 128.3, 137.2, 206.5; MS *m*/*z* (rel intensity) 214 (21, $M^{+)}$, 199 (15), 171 (31), 129 (55), 115 (23), 91 (58), 43 (100). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.86; H, 8.51.

1-Acetyl-7-*endo*-phenylbicyclo[4.1.0]heptane (14-*endo*) was obtained by preparative gas chromatography (10% SE-30, 125 °C). ^{1}H NMR δ 0.71−0.85 (m, 1 H), 0.85−0.99 (m, 1 H), 1.05−1.26 (m, 2 H), 1.51−1.63 (m, 1 H), 1.82−2.03 (m, 3 H), 2.25 (s, 3 H), 7.18−7.24 (m, 3 H), 7.29−7.36 (m, 2 H); ^{13}C NMR δ 20.1, 20.8, 20.9, 21.0, 25.6, 26.4, 34.1, 34.7, 126.5, 130.7, 136.3, 209.6; MS *m*/*z* (rel intensity) 214 (18, M^+), 199 (21), 171 (33), 129 (74), 115 (31), 91 (81), 43 (100). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.14; H, 8.54.

1-Ethynyl-7-*exo*-phenylbicyclo[4.1.0]heptane (15). To an ice-cooled solution of 2.10 g (9.80 mmol) of ketones was added **14** dissolved in 60 mL of dry benzene slowly with stirring PCl_5 (2.45 g, 11.8 mmol).[16] The reaction mixture was stirred 20 h at room temperature and then poured into ice cold water. The hydrolyzed mixture was extracted with ether (3 × 40 mL); the ethereal solution was washed with aq $NaHCO_3$ (30 mL) and brine (30 mL), dried over $MgSO_4$, filtered, and concentrated to give 3.48 g of a mixture of 1-(1′,1′-dichloroethyl)- and 1-(1′-chloroethenyl)-7-phenylbicyclo[4.1.0]heptanes. The crude mixture of chlorides was dissolved in 50 mL of dry DMSO and placed in a flask equipped with a reflux condenser. As $NaNH_2$ (1.66 g, 38.2 mmol) was added, heat was evolved; the reaction mixture was then stirred at 75 °C for 19 h. It was then cooled to room temperature and treated with 50 mL of ice cold brine; the hydrolyzed mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the organic extract was washed with H_2O (5 × 30 mL), dried over $MgSO_4$, filtered, and concentrated to give 1-ethynyl-7-*exo*-phenylbicyclo[4.1.0]heptane (**15**), a single isomer by GC. Column chromatography (silica gel, pentane) gave the product as a yellow oil (350 mg, 1.8 mmol, 18%). A small sample was further purified by preparative gas chromatography (10% SE-30, 125 °C). ^{1}H NMR δ 1.24−1.48 (m, 4 H), 1.70−1.81 (m, 2 H), 1.82 (s, 1 H), 1.98−2.22 (m, 4 H), 7.16−7.33 (m, 5 H); ^{13}C NMR δ 20.0, 20.4, 21.0, 22.7, 26.9, 30.6, 35.2, 67.5, 89.5, 125.9, 127.7, 127.9, 138.8; MS *m*/*z* (rel intensity) 196 (59, M^+), 195 (37), 168 (55), 167 (100), 165 (54), 153 (71), 141 (29), 128 (36), 115 (56), 91 (52), 77 (29), 51 (25), 39 (30). Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 9.15. Found: C, 92.00; H, 8.45.

1-Ethenyl-7-*exo*-phenylbicyclo[4.1.0]heptane (1). The bicyclic alkyne **15** (350 mg, 1.8 mmol) was dissolved in 35 mL of freshly distilled pentane. Special care was taken to avoid any contamination of the hydrocarbon solvent with ethereal impurities. To the stirring solution was added 3.6 mL (3.6 mmol) of 1.0 M DIBAL in hexanes at room temperature.[11,14] The extent of reduction was monitored by GC, and after 100 min 20 mL of H_2O was added. The hydrolyzed mixture was transferred to a separatory funnel with the aid of additional pentane; the aqueous layer was separated and extracted with pentane (3 × 25 mL). The aluminum salts were extracted with pentane (2 × 25 mL). The combined organic material was dried over $MgSO_4$, filtered, and concentrated to give the crude bicyclic alkene **1**. Column chromatography (silica gel, pentane) gave the product as a clear oil (100 mg, 0.5 mmol, 28%). A small sample of **1** was further purified by preparative gas chromatography (10% SE-30, 100 °C). ^{1}H NMR δ 1.23−1.53 (m, 4 H), 1.62 (td, J = 7.7, 1.5, 1 H), 1.70−1.81 (m, 1 H), 1.87−1.96 (m, 1 H), 1.99−2.18 (m, 3 H), 4.84 (dd, J = 10.6, 1.5, 1 H), 4.97 (dd, J = 17.3, 1.5, 1 H), 5.28 (dd, J = 17.3, 10.6, 1 H), 7.11−7.28 (m, 5 H); ^{13}C NMR δ 21.0, 21.6, 23.3, 24.5, 26.9, 29.5, 35.3, 111.0, 125.6, 127.9, 128.8, 139.6, 143.5; MS *m*/*z* (rel intensity) 198 (23, M^+), 183 (17), 169 (31), 155 (54), 141 (85), 129 (81), 115 (65), 91 (100), 79 (78), 39 (47). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.78; H, 9.21.

1-(*E*-2′-*d*-Ethenyl)-7-*exo*-phenylbicyclo[4.1.0]heptane (*E*-1-*d*). To a sample of the bicyclic alkyne **15** (100 mg, 0.51 mmol) in 10 mL of freshly distilled dry pentane was added with stirring 1.02 mL (1.02 mmol) of 1.0 M DIBALH in hexanes at room temperature. The extent of reduction was monitored by GC, and after 12 h, 3 mL of D_2O was added. The mixture was stirred for 4 h and then transferred to a separatory funnel with the aid of additional pentane. The biphasic mixture was diluted with brine and extracted. The organic layer was separated, dried, filtered, and concentrated to give crude olefin ***E*-1-*d***. Purification by preparative GC on

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a 1-m 20% Carbowax 20M column gave 40 mg (39%) of ***E*-1-*d***. ^{1}H NMR (olefinic region) δ 4.84 (m, 12% of 1 H), 4.97 (d, J = 17.3 Hz, 1 H), 5.23 (d, J = 17.3 Hz, 1 H).

1-(*Z*-2′-*d*-Ethenyl)-7-*exo*-phenylbicyclo[4.1.0]heptane (*Z*-1-*d*). A sample of alkyne **15** (105 mg, 0.54 mmol) dissolved in dry pentane was cooled to −78 °C, and 0.625 mL (1.25 mmol) of 2.0 M *n*-BuLi in pentane was added. The reaction flask was allowed to warm to room temperature, stirred for 1 h, and then cooled to −78 °C. An excess of D_2O was added with stirring. The reaction mixture was transferred to a separatory funnel and extracted with pentane. A second exchange was performed to obtain 99 atom % D (by NMR) 1-(2′-*d*-ethynyl)-7-*exo*-phenylbicyclo[4.1.0]heptane (**15-*d***). Reduction of **15-*d*** with DIBALH followed by quenching the intermediate organoaluminum compound with H_2O gave ***Z*-1-*d***. ^{1}H NMR (olefinic region) δ 4.84 (d, J = 10.6 Hz, 1 H), 5.23 (d, J = 10.6 Hz, 1 H).

1-(2′,2′-d_2-Ethenyl)-7-*exo*-phenylbicyclo[4.1.0]heptane (1-d_2). Reduction of the labeled acetylene **15-*d*** with DIBALH, followed by reacting the organoaluminum intermediate with D_2O, gave **1-d_2**. ^{1}H NMR (olefinic region) δ 4.84 (m 10% of 1 H), 4.97 (m, 15% of 1 H), 5.23 (s, 1 H).

Thermal Isomerizations. The kinetic bulbs used in thermal isomerization reactions were first soaked in concentrated aq HCl for 24 h, rinsed and soaked in concentrated NH_4OH for 24 h, and rinsed at least 20 times with distilled water. The bulbs were then dried in an oven for several weeks prior to use. Reaction bulbs containing samples of **1** or deuterium-labeled analogues purified by preparative GC on a 1-m 20% Carbowax 20M column were sealed under vacuum following two freeze−pump−thaw cycles and were heated in a thermostated oil bath at 220 °C.

A 50-mg sample of **1** in a sealed kinetic bulb was heated at 220 °C for 240 min, removed from the bath, and cooled to room temperature; no visible signs of decomposition were noted. The bulb was cooled to 0 °C, scored, and opened, and the thermolysis reaction mixture was removed with the aid of pentane. Analytical GC showed one major product (73%), several minor products, and some unreacted **1** (2.3%). The major product **2** was isolated by preparative GC on a 1-m 20% Carbowax 20M column at 120 °C. ^{1}H NMR δ 0.98−1.12 (m, 1 H), 1.17−1.31 (m, 2 H), 1.71−1.82 (m, 2 H), 1.89−2.06 (m, 2 H), 2.38−2.53 (m, 3 H), 2.66−2.79 (m, 1 H), 2.95 (q, J = 8.5, 1 H), 5.29 (s, 1 H), 7.15−7.22 (m, 1 H), 7.23−7.33 (m, 4 H); ^{13}C NMR δ 25.8, 26.9, 28.9, 34.7, 40.5, 52.4, 54.0, 119.1, 125.8, 127.4, 128.3, 145.1, 146.6; MS m/z (rel intensity) 198 (90, M^+), 183 (30), 169 (43), 156 (63), 141 (82), 129 (60), 115 (67), 91 (100), 79 (80), 39 (63). Anal. Calcd for $C_{15}H_{18}$: m/z 198.1409; HRMS 198.1400.

Thermal isomerization of **1-d_2** as described above gave **2-d_2**. ^{2}H NMR δ 2.43 (s, 1 D), 2.75 (s, 1 D). Thermal reactions of ***E*-1-*d*** and ***Z*-1-*d*** over reaction times of 210 and 240 min respectively gave **2-*d*** products which were isolated by preparative GC on a 1-m 20% Carbowax 20M column. For the **2-*d*** product mixture from thermal isomerization of ***E*-1-*d***: ^{2}H NMR δ 2.45 (s, 14% of 1 D), 2.75 (s, 86% of 1 D). For **2-*d*** produced through thermolysis of ***Z*-1-*d***: ^{2}H NMR δ 2.45 (s, 84% of 1 D), 2.75 (s, 16% of 1 D).

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Supporting Information Available: Copies of NMR spectra (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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