Thermal Rearrangement of 7-Methylbicyclo[3.2.0]hept-2-ene: An Experimental Probe of the Extent of Orbital Symmetry Control in the [1,3] Sigmatropic Rearrangement

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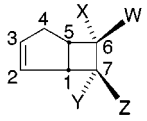
Received December 8, 1999

The gas-phase thermal rearrangement of *exo*-7-methylbicyclo[3.2.0]hept-2-ene yields almost exclusively 5-methylnorbornene products. Inversion (i) of configuration dominates this [1,3] sigmatropic shift although some retention (r) is also observed. Because the [1,3] migration can only occur suprafacially (s) in this geometrically constrained system, the si/sr ratio of 7 observed for the migration of C_7 in *exo*-7-methylbicyclo[3.2.0]hept-2-ene indicates that the orbital symmetry rules are somewhat permissive for the [1,3] sigmatropic migration of carbon.

Introduction

Although it has been 30 years since Berson's seminal study of the [1,3] sigmatropic rearrangement in the bicyclo[3.2.0]hept-2-ene system,[1] the mechanism of this rearrangement has not yet been resolved. At issue is whether the [1,3] sigmatropic rearrangement conforms to the predictive power of the Woodward−Hoffmann rules. In their treatise on orbital symmetry Woodward and Hoffmann state the selection rules for [1,3] sigmatropic carbon shifts which privilege as allowed suprafacial migration with inversion of configuration (si) and antarafacial migration with retention of configuration (ar).[2]

Mechanistic controversy has surrounded [1,3] carbon sigmatropic shifts from the first report by Berson and Nelson that a series of 7-substituted *endo*-6-acetoxybicyclo-[3.2.0]hept-2-ene derivatives (**1**, **2a**, **2b**) undergo rearrangements to the corresponding norbornenes at elevated temperatures. In this geometrically constrained vinylcyclobutane, the only two stereochemical options for the [1,3] carbon shift are si and sr. While a conspicuous stereochemical bias in **1** (si/sr = 19) and **2a** (si/sr = 10) lends credibility to a favored orbital-symmetry-allowed mechanism, the reported activation parameters have been characterized as "only slightly (and perhaps not significantly) below the estimated value for the hypothetical diradical reaction (48−51 kcal.mole)".[3] Hence, most of the theoretical and experimental focus has been on the stereochemical aspects of [1,3] carbon sigmatropic rearrangements.



Compound	W	X	Y	Z
1	H	OAc	H	D
2a	H	OAc	H	CH_3
2b	H	OAc	CH_3	H
3	H	H	H	H
4	D	H	H	D
5a	H	H	H	CH_3
5b	H	H	CH_3	H

The anomalous reversal of stereochemical outcome for the *endo*-methyl epimer **2b** (si/sr = 0.14 or sr/si = 7) has been attributed to a "steric blockade" by the *endo*-methyl overriding orbital symmetry control. Berson has attempted to rationalize the predominance of the orbital-symmetry-forbidden product by invoking a secondary (subjacent) orbital interaction.[3]

A related study of the parent bicyclo[3.2.0]hept-2-ene (**3**) at temperatures greater than 300 °C by Cocks and Frey reveals that direct fragmentation to 1,3-cyclopentadiene and ethylene is competitive with the [1,3] conversion of **3** to norbornene ($k_{1,3}/k_f \approx 1$).[4] As a consequence, the maximum amount of norbornene is observed to be ca. 1%. However, the lack of a stereochemical marker on the migrating carbon (C_7) effectively precludes any conclusions about the extent of orbital symmetry control of the [1,3] shifts.

The parent system, appropriately modified with deuterium labeling to afford a stereochemical marker, has been subsequently reexamined by two independent research groups. Whereas Baldwin observes an si/sr ratio of 3 for **4** at 276 °C,[5] Klärner reports thermal data that yield a si/sr value of 8 at 312 °C.[6] Baldwin and Belfield, using dynamic isotope dilution techniques, also record a $k_{1,3}/k_f$ ratio of 2.[7]

In comparing his results for **4** with those of Berson for **1**, Klärner concludes that "the acetoxy group at C_6 has only a minor effect on the stereochemistry of the [1,3] shift".[6] Yet the *endo*-6-acetoxy system is plagued by numerous side reactions: ester pyrolysis (which gener-

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(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970; pp 119−120.
(3) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406−414.
(4) Cocks, A. T.; Frey, H. M. *J. Chem. Soc. A* **1971**, 2564−2566.
(5) Baldwin, J. E.; Belfield, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 296−7.
(6) Klärner, F.-G.; Drewes, R.; Hasselmann, D. *J. Am. Chem. Soc.* **1988**, *110*, 297−8.
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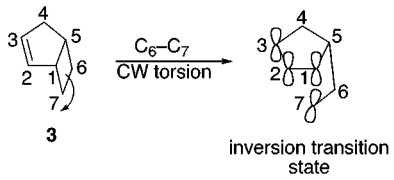
10.1021/jo9918899 CCC: $19.00
Published on Web 08/04/2000

ates acetic acid, a potential catalyst), epimerization at C_6, and Diels–Alder recombination of the fragments.[1] The latter two processes, in particular, can dramatically impact the ratio of norbornene epimers from which the si/sr ratio is derived.

The apparent temperature dependence in the [1,3] shift in the bicyclo[3.2.0]hept-2-ene system, when comparing the different si/sr ratios obtained by Baldwin and Klärner, has led Carpenter to speculate that the enhanced stereoselectivity at higher temperatures (si/sr = 8 at 312 °C versus si/sr = 3 at 276 °C) can be attributed to a greater contribution from a nonstatistical mechanistic pathway (involving either a nonequilibrated diradical intermediate or a concerted process) due to the increased likelihood that the statistical pathway (involving an equilibrated diradical intermediate or a "long-lived", extended-conformation biradical, using Carpenter's terminology) could afford more direct fragmentation (from **3** directly to cyclopentadiene and ethylene rather than via norbornene) at higher temperatures.[8] Direct dynamics calculations using a PM3 model performed by Carpenter on the interconversion of the parent compound **3** to norbornene predict a diradical intermediate as a local minimum on the energy surface. Although the results of the calculation are contrary to experiment[9] in assigning **3** as more thermodynamically stable than norbornene, Carpenter uses the principle of microscopic reversibility to argue that his conclusions are still valid. Torsion in the C_6–C_7 bond (based on [3.2.0] numbering) in **3** dominates the sense of rotation of the migrating carbon, C_7. Calculations suggest that in the transition state C_5–

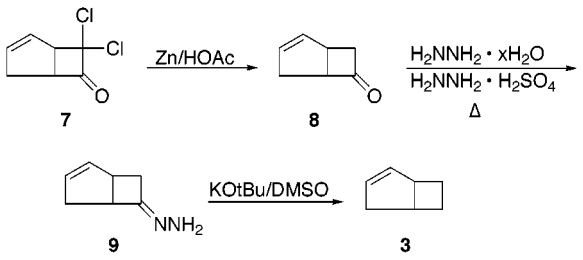


C_6 torsion in combination with clockwise C_6–C_7 rotation maximizes the residual C_1–C_7 bonding. Conservation of angular momentum results in a continuous rotational component of the [1,3] shift that necessarily leads to migration with inversion.

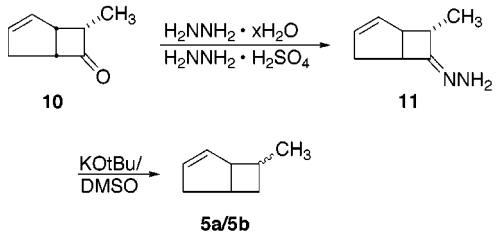
Carpenter has also extended the direct dynamic analysis to *exo*- and *endo*-7-methylbicyclo[3.2.0]hept-2-ene (**5a** and **5b**, respectively). Dynamic modeling of **5a** supports the earlier conclusions derived from the parent **3**. However, a similar internal rotation in **5b** results in a steric effect from the *endo*-methyl that converts the internal rotation into a torsional vibration with a restoring force. This reversal of the initial sense of the internal rotation is used to account for a direct retention trajectory, which is accessible not only to **5b** but also to **5a**.

In summary, Carpenter makes two predictions about the 7-methylbicyclo[3.2.0]hept-2-ene system: (1) a temperature dependence in the [1,3] shift to 5-methylbicyclo-[2.2.1]hept-2-ene (5-methylnorbornene, **6**) that will afford higher si/sr ratios at higher temperatures and (2) a smaller si/sr ratio for **5a** compared to the parent system due to competition between the direct retention and the inversion pathways.[8] Clearly, an experimental study of

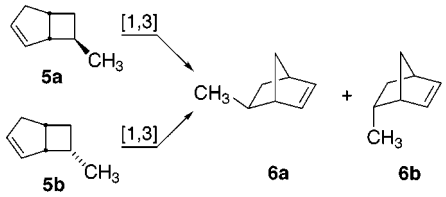
Scheme 1



Scheme 2



compounds **5a** and **5b** would subject these predictions to thorough scrutiny. We have recently completed a thermal investigation of **5a** and **5b** at a temperature of 275 °C and herein report our results. We have also reexamined the thermal behavior of the parent **3** at 275 °C for purposes of direct comparison.



Results

Syntheses. The parent compound **3** was prepared from 7,7-dichlorobicyclo[3.2.0]hept-2-ene (**7**)[10] according to the sequence of reactions outlined in Scheme 1. Reduction of **7** was accomplished by treatment with zinc dust in acetic acid[11] to yield **8**, which was converted to **3** via a two-step cyclobutanone reduction sequence[12] based on low-temperature Wolff–Kishner reduction of the hydrazone derivative of the ketone.

Similarly, a mixture of the 7-methyl epimers **5a** and **5b** was obtained by application of the standard cyclobutanone sequence to *endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one (**10**),[13] as indicated in Scheme 2. Base-catalyzed epimerization occurred at C_7 during the conversion of **10** to **5** to afford **5a**:**5b** in a ca. 2:1 ratio. Separation of the epimers was accomplished via preparative GC, and differentiation and characterization of **5a** and **5b** were based on the shielding of the *endo*-methyl in **5b** observed by NMR spectroscopy, both ^1H and ^{13}C.

The synthesis of **6** was accomplished by conversion of 5-norbornene-2-methanol to its mesylate **12** followed by reduction with Super-Hydride (Scheme 3).[14] The ca. 2:1

(8) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336–6344.
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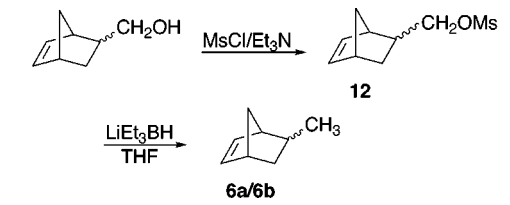
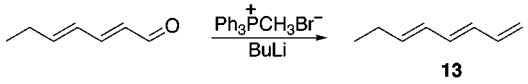
Scheme 3



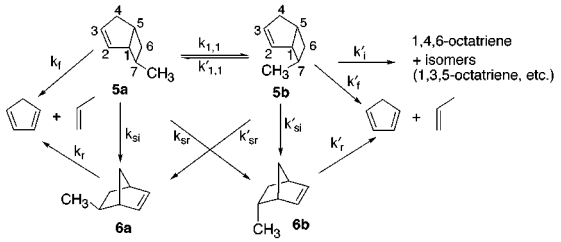
Scheme 4



endo:*exo* ratio of the starting material, as determined by ^{1}H NMR spectroscopy, was maintained in the product composition. In contrast, low-temperature Wolff−Kishner reduction of the hydrazone of 5-norbornene-2-carboxaldehyde afforded, albeit in low yield, **6a** as the major epimer. As in **5b**, the *endo*-methyl in **6b** was obviously shielded, as determined by comparing the ^{1}H and ^{13}C NMR chemical shifts of **6a** and **6b**; independent confirmation of our epimeric assignments was possible due to published ^{13}C NMR data for **6a** and **6b**.[15] A sample of **6** prepared as in Scheme 3 afforded a 28:72 ratio of **6a**:**6b** by ^{1}H NMR integration and a 25:75 ratio of **6a**:**6b** by chiral GC peak area percentage. Unlike **5a** and **5b**, however, the **6a**/**6b** epimeric mixture was not separable by preparative GC nor by using a variety of analytical GC capillary columns. Instead, separation of the diastereomers **6a** and **6b** was fully achieved using a chiral GC column.

Synthesis of 1,3,5-octatriene, a suspected thermal acyclic rearrangement product of **5b**, was achieved in one step via Wittig methylenation of *trans*,*trans*-2,4-heptadienal (Scheme 4). GC co-injection has confirmed that 1,3,5-octatriene or a compound with an identical retention time was indeed formed upon pyrolysis of **5b**.

Thermolysis Reactions. Gas-phase thermal reactions of **5a**, **5b**, and an epimeric mixture of **6a**/**6b** have been performed in a well-conditioned kinetic bulb[16] at 275.0 °C for short pyrolysis times (≤5 h for **5a**, ≤12 h for **5b**, and ≤2 h for the **6a**/**6b** mixture, corresponding to maximum conversions of 24%, 37%, and 75%/96%, respectively). Previous thermal studies of **5a** and **5b** in our laboratory have shown that the interconversion of **5a** and **5b** complicates the kinetic analysis (Figure 1). Pyrolysis of the **6a**/**6b** mixture has been conducted to determine experimental rate constants for the two retro Diels−Alder reactions. All experimental first-order rate constants (or sums of rate constants) are given in Table 1 (k values refer to rate constants for **5a** and **6a**, k' values to those for **5b** and **6b**). Monitoring the disappearance of reactant **5a** or **5b** versus time has resulted in the rate constant for overall decomposition, k_d or k'_d, respectively. Values for $k_{1,1}$ or $k'_{1,1}$ and for $k_{1,3} + k_f$ or $k'_{1,3} + k'_f$, the sum of rate constants for [1,3] sigmatropic shifts and for direct fragmentations, have been obtained from the slopes of linear plots of percentage products versus $1 - e^{-k_d t}$.[4,17]



$k_{1,1}$ = rate of epimerization of **5a** to **5b**.
$k'_{1,1}$ = rate of epimerization of **5b** to **5a**.
$k_{1,3} = k_{si} + k_{sr}$ = rate of [1,3] sigmatropic rearrangement of **5a**.
$k'_{1,3} = k'_{si} + k'_{sr}$ = rate of [1,3] sigmatropic rearrangement of **5b**.
k_f = rate of direct fragmentation from **5a** via [2+2]-cycloreversion breaking C_1–C_7 and C_5-C_6 bonds.
k'_f = rate of direct fragmentation from **5b** via [2+2]-cycloreversion breaking C_1–C_7 and C_5-C_6 bonds.
k_r = rate of retro Diels-Alder Reaction of **6a**.
k'_r = rate of retro Diels-Alder Reaction of **6b**.
k'_i = rate of isomerization of **5b** to acyclic rearrangement products breaking C_1–C_5 and C_6-C_7 bonds.

Figure 1. Kinetic scheme.

Because the epimers **6a** and **6b** were not separable on a 50 m HP methyl silicone capillary column (either by itself or when linked to a variety of other capillary columns of different polarities), a second series of pyrolyses of **5a** and **5b** have been performed to determine si/sr ratios by analysis on a 30 m Chiraldex γ-cyclodextrin TFA column operating at 30 °C. Each of the isomers **5a**, **5b**, **6a**, and **6b** was present as a closely spaced pair of enantiomeric peaks which actually proved useful to our analysis in cases where some peak overlap occurred (see the Experimental Section).

The parent compound **3** has been subjected to thermal rearrangement at 275.0 °C to compare the experimental rate constant for overall decomposition (4.7×10^{-6} s^{-1}) with that derived by calculation (9.2×10^{-6} s^{-1}) using published Arrhenius parameters.[4] On the basis of Carpenter's prediction regarding the anticipated effect of temperature on the [1,3] shift, we also note that the amount of norbornene at short pyrolysis times of 1−4 h at 275.0 °C did not exceed the maximum value of 1% reported by Cocks and Frey at temperatures in excess of 300 °C.

Discussion and Conclusions

The crucial stereochemical issue addressed in this study, the si/sr value for **5a**, is complicated by the fact that the retro Diels−Alder rate constants for **6a** and **6b** (k_r and k'_r, respectively) are not equal. In Figure 1 the observed **6a**:**6b** ratio for **5a** depends not only on k_{si} and k_{sr} but also on k_r and k'_r . The experimental si/sr value for **5a** increases modestly over time due to the fact that **6b** is more reactive than **6a**. We have attempted to factor out this fractionation in two ways: (1) through a graphical extrapolation to time zero by plotting the experimental si/sr values versus time and (2) by an independent determination of an si/sr ratio using rate constants derived through a Runge−Kutta analysis[18] (Table 2). Experimental concentration versus time data have been fit by holding experimentally determined rate constants fixed and permitting only $k_{1,3}$ (including both si and sr components) and k_f to vary. The plot of experimental data (Figure 2) affords a correlation coefficient greater than 0.99 and an intercept of 7.3. The Runge−Kutta calculation yields an si/sr ratio of 6.3. Hence, the average si/sr

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(18) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984; pp 76−81.

Table 1. Experimental Rate Constants ($\times 10^5$ s), 275 °C

	k_d[a] (k'_d)[b]	$k_{1,1}$ ($k'_{1,1}$)	$k_{1,3} + k_f$ ($k'_{1,3} + k'_f$)	k'_i[c]	k_r (k'_r)
5a	1.8 ± 0.2	$(6.3 \pm 0.8) \times 10^{-2}$	1.7 ± 0.4		
5b	1.15 ± 0.05	$(3.9 \pm 0.1) \times 10^{-1}$	$(7.3 \pm 0.6) \times 10^{-1}$	$(6.9 \pm 0.5) \times 10^{-2}$	
6a					$(2.0 \pm 0.1) \times 10$
6b					$(4.7 \pm 0.2) \times 10$

[a] Rate of overall decomposition of **5a**. [b] Rate of overall decomposition of **5b**. [c] Rate of isomerization to acyclic rearrangement products (see the Experimental Section).

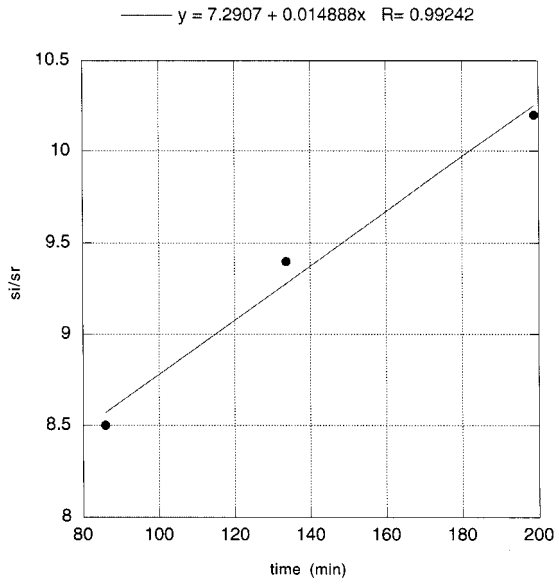

Figure 2. si/sr ratio for **5a** (275 °C).

Table 2. Runge−Kutta Rate Constants ($\times 10^5$ s)

	k_d (k'_d)	k_{si} (k'_{si})	k_{sr} (k'_{sr})	k_f (k'_f)
5a	1.5	1.2	1.9×10^{-1}	9.4×10^{-3}
5b	1.0	4.0×10^{-3}	4.0×10^{-1}	1.2×10^{-1}

ratio of 7 (6.8) for **5a** can be compared with the value of 3 observed by Baldwin for the parent **3** at the same temperature. The stereoselectivity in the [1,3] shift is therefore greater for the *exo*-7-methyl analogue **5a** as compared to the parent **3**.

In the [1,3] rearrangement that **5b** undergoes, **6a** is observed exclusively. On the basis of GC detection limits, it is possible to estimate a minimum sr/si value of 38, but this ignores the fractionation of **6a** and **6b** referred to earlier. (We cannot report an si/sr ratio for **5b** because there is no observable **6b** at the GC detection limits.) The sr/si value derived from Runge −Kutta is ca. 100. While we have no firm numerical sr/si value to report for **5b**, the experimental data indicate that it is a very large number. This result is quite compatible with Carpenter's assertion that only the direct retention pathway would be available to **5b**.

To test Carpenter's prediction about the anticipated temperature dependence of the si/sr ratio, we have pyrolyzed **5a** at temperatures of 250.0 and 300.7 °C, at a series of reaction times as in reactions followed at 275.0 °C. The si/sr value obtained at 300.7 °C by a graphical extrapolation (correlation coefficient 0.998) to time zero (vide supra) was 7.3 (Figure 3). The experimental si/sr ratio of 13.0 at 167.45 min at 250.0 °C was virtually identical to that observed (12.7) at 155.94 min at 300.7 °C. (This high ratio, of course, reflects both the great similarity in reaction stereochemistry at 250.0 and 300.7 °C and the fact that **6b** suffers retro Diels−Alder fragmentation faster than **6a**, thus leading to a higher si/sr ratio.) These observations strongly support the conclusion that there is no substantive temperature dependence in the si/sr ratio for **5a**. According to Carpenter, a temperature-independent mechanistic process almost certainly precludes two competing pathways.

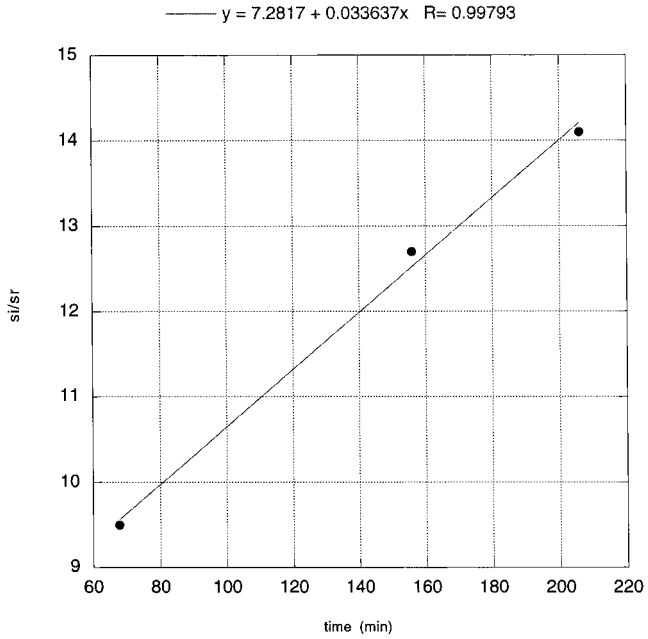

Figure 3. si/sr ratio for **5a** (300.7 °C).

A comparison of $k_{1,3}/k_f$ ratios for **5a** with those of the parent **3** and of 7,7-dimethylbicyclo[3.2.0]hept-2-ene reveals that **5a** is not an intermediate case. Whereas the $k_{1,3}/k_f$ ratio for **5a** as derived from Runge−Kutta analysis is 150, the $k_{1,3}/k_f$ ratio for **3** is 1−2[4,7] and that of 7,7-dimethylbicyclo[3.2.0]hept-2-ene is 0.[19] In the pyrolysis of **5a** at 275.0 °C the maximum concentration of 5-methylnorbornene is 5% compared to a maximum value of 1% norbornene in the pyrolysis of **3** and no observable 5,5-dimethylnorbornene in the thermal rearrangement of 7,7-dimethylbicyclo[3.2.0]hept-2-ene.[19] Unlike the parent system in which direct fragmentation competes with the [1,3] sigmatropic rearrangement, **5a** undergoes virtually no fragmentation (<1% by Runge−Kutta analysis). This observation is inconsistent with expected trends based on relative diradical stability and a hypothetical stepwise process. Even if we adopt Carpenter's notion of a nonstatistical pathway, **5a** should resemble the parent with respect to this component of the rearrangement. The si/sr value of 7 for **5a** does support Carpenter's analysis: there may be some direct retention pathway competing with the inversion pathway. Yet the large $k_{1,3}/k_f$ ratio for **5a** could well mean that the [1,3] shift is concerted. In

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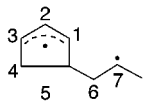
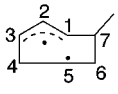
any event, the si/sr ratio of 7 for **5a** indicates that the orbital-symmetry-allowed stereochemistry for the [1,3] sigmatropic migration of carbon is, in this case, dominant but not overwhelmingly so.

In the thermolysis of **5b**, epimerization to **5a** competes with the [1,3] shift. Although the diradical **14a** formed by cleavage of the C_1-C_7 bond can account for epimerization, another possibility is that epimerization of **5b** to **5a** (and to a lesser extent **5a** to **5b**) can occur via C_1-C_5 bond cleavage to form diradical **14b**. Were the latter



14a



14b

interpretation valid, then only a modest amount of rearrangement of **5b** (i.e., direct fragmentation, estimated to be $0.12k_d$ by Runge−Kutta analysis) would be directly attributable to the intermediacy of **14a**. A Benson additivity analysis[20] of the two diradicals places **14b** 0.5 kcal/mol lower in energy than **14a**. We are currently exploring the likelihood that diradical **14b** is a viable intermediate by preparing appropriate optically active precursors.

Experimental Section

Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. NMR spectra were recorded on $CDCl_3$ solutions; definitive ^{13}C NMR assignments were based on a DEPT pulse sequence.

Triethylamine was distilled prior to use from calcium hydride and stored over 5 Å molecular sieves. Chloroform was prepared alcohol-free by washing with concd sulfuric acid followed by successive washes with water; it was distilled from calcium hydride and stored over calcium chloride pellets. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Cyclopentadiene was obtained by "cracking" dicyclopentadiene at 180 °C and stored in the freezer until use. Potassium *tert*-butoxide was sublimed in a sublimation chamber at 190−200 °C at 1−2 Torr.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (**7**) was prepared according to the procedure of Minns[10] from 48 mL (0.50 mol) of dichloroacetyl chloride, 125 mL (1.5 mol) of cyclopentadiene, and 70 mL (0.50 mol) of triethylamine except that chloroform was used as solvent. At the end of the reaction the chloroform was removed by simple distillation. Upon addition of ether, the triethylamine HCl salt was removed via vacuum filtration. The filtrate was dried over $MgSO_4$, concentrated, and distilled at reduced pressure. The first fraction, collected at a boiling range of 55−65 °C at 10 Torr, consisted predominantly of dicyclopentadiene. The second fraction (75−80 °C, 1−2 Torr), identified as primarily 7,7-dichlorobicyclo[3.2.0]-hept-2-en-6-one by GC retention time, weighed 69.6 g (79%).

Bicyclo[3.2.0]hept-2-en-6-one (**8**). A solution of impure dichloroketone **7** (69.6 g, 0.393 mol) in 150 mL of glacial acetic acid was added to a well-stirred suspension of 150 g of zinc dust in 650 mL of glacial acetic acid at a sufficiently rapid rate to induce an exothermic reaction. After the resulting suspension was heated at 50 °C for several hours, the solid residue was filtered through a sintered glass funnel. Due to the pyrophoric nature of the activated zinc, this filtration was completed with extreme caution. Care was taken to keep the solid blanketed by solvent at all times until the residue was washed with chloroform followed by cold water to deactive the elemental zinc. After separation of layers, the aqueous layer was extracted with chloroform. The combined chloroform extracts were washed with water, saturated aqueous $NaHCO_3$, and again water. The chloroform was then dried over $MgSO_4$, filtered, and concentrated to a viscous orange oil. The product was purified by flash column chromatography to yield 26.4 g (62%) of **8**. IR (cm^{-1}): 3040 (m), 1760 (s), 1600 (w), 735 (s), 700 (s). ^1H NMR (ppm): 5.85 (m, 1H), 5.80 (m, 1H), 3.85 (m, 1H), 3.5 (m, 1H), 3.3 (dd, 1H), 2.7 (m, 1H), 2.64 (m, 1H), 2.5 (qq, 1H). ^{13}C NMR (ppm): 212.9 (C═O), 133.0 (CH═), 132.2 (CH═), 62.0 (CH), 54.3 (CH_2), 36.9 (CH), 34.9 (CH_2).

Bicyclo[3.2.0]hept-2-en-6-one hydrazone (**9**). To a 250 mL three-necked flask were added hydrazine sulfate (5.3 g, 41 mmol), hydrazine hydrate (85%, 14.4 mL), and bicyclo[3.2.0]-hept-2-en-6-one (4.3 g, 40 mmol). The reaction was heated at 75 °C for 22 h and then extracted with 3 × 25 mL of ether. The combined ether extracts were dried over $MgSO_4$, filtered, concentrated, and distilled at reduced pressure (90−105 °C, 1−2 Torr) to afford 2.5 g (51%) of **9**. IR (cm^{-1}): 3350 (m), 3190 (m), 3030 (m), 2940 (s), 1675 (m), 1605 (m).

Bicyclo[3.2.0]hept-2-ene (**3**). To a 100 mL three-necked flask was added freshly sublimed potassium *tert*-butoxide (2.6 g, 24 mmol) dissolved in 11 mL of anhydrous DMSO. Over a 6 h period bicyclo[3.2.0]hept-2-en-6-one hydrazone (2.5 g, 20 mmol) was added by gastight syringe. After the resulting solution was stirred under nitrogen overnight, the reaction was quenched with cold water. After addition of pentane and another portion of cold water, the pentane layer was removed and washed six times with water to remove DMSO. The organic layer was dried over $MgSO_4$ and purified by elution through a Waters Sep-Pak silica cartridge. Excess pentane was removed by short-path distillation to yield 1.2 g (63%) of **3**. ^1H NMR (ppm): 5.8 (m, 2H), 3.2 (br s, 1H), 2.9 (p, 1H), 2.5 (dd, 1H), 2.3 (p, 1H), 2.1 (m, 2H), 1.7 (m, 2H). ^{13}C NMR (ppm): 134.2, 130.1, 46.0, 40.8, 35.7, 27.0 (2 overlapping peaks).

***endo*-7-Methylbicyclo[3.2.0]hept-2-en-6-one** (**10**). To a 2 L three-necked flask containing 525 mL of chloroform were added propionyl chloride (75 g, 0.81 mol) and 1,3-cyclopentadiene (225 mL, 1.68 mol). After dropwise addition of triethylamine (120 mL, 0.86 mol) in 150 mL of chloroform, the reaction was allowed to proceed for 24 h. Excess chloroform was removed via distillation. Upon addition of ether, the organic layer was filtered, dried with $MgSO_4$, and concentrated. Purification by reduced pressure distillation (40−60 °C, 5−10 Torr) followed by flash column chromatography on a silica gel column (pure hexane to 80:20 hexane/ethyl acetate) afforded 60.4 g (61%) of **10**. IR (cm^{-1}): 3040 (s), 1770 (s), 1600 (m), 700 (m). ^1H NMR (ppm): 6.0 (m, 2H), 3.9 (m, 3H), 2.8 (m, 2H), 1.2 (d, 3H). ^{13}C NMR (ppm): 215.9 (C═O), 134.5 (CH═), 129.5 (CH═), 59.6 (CH), 59.0 (CH), 42.6 (CH), 33.9 (CH_2), 8.9 (CH_3).

7-Methylbicyclo[3.2.0]hept-2-en-6-one Hydrazone (**11**). To a 250 mL three-necked flask were added hydrazine sulfate (7.8 g, 60 mmol), hydrazine hydrate (85%, 17 mL), and *endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one (6.4 g, 52 mmol). The reaction was heated at 75 °C for 22 h. Workup as for **9** produced 4.2 g (60%) of **11**. IR (cm^{-1}): 3350 (m), 3190 (m), 3030 (m), 2925 (s), 1680 (s), 1605 (m). ^1H NMR (ppm): 5.8 (m, 2H), 4.8 (br s, 2H), 3.5 (m, 3H), 2.6 (m, 2H), 1.2 and 1.05 (d, 3H), major and minor isomers, respectively. ^{13}C NMR, major isomer (ppm): 161.0 (C═N), 134.4 (CH═), 129.4 (CH═), 44.8 (CH), 44.5 (CH), 44.3 (CH), 37.2 (CH_2), 12.0 (CH_3). ^{13}C NMR, minor isomer (ppm): 159.4 (C═N), 133.3 (CH═), 129.3 (CH═), 45.5 (CH), 45.0 (CH), 43.9 (CH), 33.5 (CH_2), 11.6 (CH_3).

7-Methylbicyclo[3.2.0]hept-2-ene (**5**). To a 100 mL three-necked flask was added freshly sublimed potassium *tert*-butoxide (5.2 g, 48 mmol) dissolved in 25 mL of anhydrous DMSO. Over a 6 h period 7-methylbicyclo[3.2.0]hept-2-en-6-one hydrazone (4.4 g, 32 mmol) was added by gastight syringe. After the resulting solution was stirred under nitrogen overnight, workup as for **3** resulted in 2.5 g (72%) of **5**. IR (cm^{-1}): 3050 (s), 1605 (m), 700 (m). The **5a**:**5b** ratio was 69:31 by GC analysis and 67:33 by ^1H NMR integration. The epimers **5a** and **5b** were separated via preparative GC on a 1/4 in. × 8 ft DC-710 column at 80 °C. ^1H NMR, **5a** (ppm): 5.8 (m, 1H), 5.7 (m, 1H), 2.9 (p, 1H), 2.8 (m, 1H), 2.5 (qq, 1H), 2.1 (m, 1H), 2.0 (m, 1H), 1.8 (m, 1H), 1.7 (m, 1H), 1.2(d, 3H). ^{13}C NMR, **5a** (ppm): 133.8 (CH═), 130.1 (CH═), 53.4 (CH), 40.4 (CH_2), 36.0

(20) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 272−284.

(CH), 34.5 (CH_2), 32.2 (CH), 22.3 (CH_3). ^{1}H NMR, **5b** (ppm): 5.8 (m, 1H), 5.7 (dq, 1H), 3.25 (br s, 1H), 2.65 (sextet, 2H), 2.4 (qq, 1H), 2.25 (ddd, 1H), 2.05 (dq, 1H), 1.2 (m, 1H), 0.85 (d, 3H). ^{13}C NMR, **5b** (ppm): 132.1 (CH═), 131.1 (CH═), 50.5 (CH), 40.2 (CH_2), 35.4 (CH_2), 33.0 (CH), 32.4 (CH), 16.6 (CH_3). MS (*m*/*z*): 108 (5%), 66 (100%). Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found (**5a**): C, 89.12; H, 10.95. Found (**5b**): C, 89.27; H, 10.97.

5-Norbornene-2-methanol Mesylate (12). To 350 mL of methylene chloride in a 500 mL two-necked flask under nitrogen atmosphere were added 5-norbornene-2-methanol (9.9 g, 0.080 mol) and triethylamine (18 mL, 0.13 mol). After the solution was cooled to −10 °C, methanesulfonyl chloride (7.5 mL, 0.097 mol) was added dropwise via syringe over 5−10 min. After being stirred for an additional 30 min, the reaction mixture was washed with ice−water, cold aqueous HCl (10%), saturated aqueous $NaHCO_3$, and saturated aqueous NaCl. The organic layer was dried over $MgSO_4$, filtered, concentrated, and distilled at reduced pressure (90−105 °C, 1−2 Torr) to yield 9.7 g (60%) of **12**. ^{1}H NMR (ppm): 6.1 (dd, 1H), 5.9 (dd, 1H), 2.7 (br s, 1H), 2.6 (br s, 1H), 2.1 (m, 1H), 1.85 (2 × dd, 1H), 1.55 (s, 1H), 1.35 (m, 1H), 1.3 (m, 1H), 1.2 (2 × s, 1H), 1.05 and 0.75 (2 × d, 3H), 0.4 (2 × dd, 1H). ^{13}C NMR (ppm): 137.9 (CH═), 131.5 (CH═), 73.1 (CH_2), 44.6 (CH_2), 43.1 (CH), 41.9 (CH), 38.0 (CH_2), 37.0 (CH_3), 29.1 (CH).

5-Methyl-2-norbornene (**6**). To a 200 mL three-necked flask under nitrogen atmosphere containing 5-norbornene-2-methanol mesylate (8.0 g, 40 mmol) dissolved in 40 mL of dry THF was added 80 mL of 1.0 M Super-Hydride in THF solution via gastight syringe. After being refluxed for 4 h at 60 °C, the reaction mixture was cooled in an ice bath. Excess Super-Hydride was quenched by dropwise addition of ice−water, and the organoboranes were oxidized by dropwise sequential addition of 3 M aqueous NaOH and cold 30% H_2O_2. The treated reaction mixture was then refluxed at 100 °C for 1.5 h; after cooling, water was added. The mixture was then extracted successively with hexane; the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated via short-path distillation to yield 2.5 g (57%) of **6**. The **6a**:**6b** ratio was determined to be 25:75 by GC analysis (Chiraldex γ-cyclodextrin TFA column) and 28:72 by ^{1}H NMR integration. ^{1}H NMR (ppm): 6.1 (2 × dd, 1H), 5.9 (2 × dd, 1H), 2.75 (2 × br s, 1H), 2.4−2.6 (2 × br s, 1H), 1.85 (2 × dd, 1H), 1.3 (m, 4H), 1.05 and 0.75 (d, 3H) for **6a** and **6b**, respectively. ^{13}C NMR, **6a** (ppm): 137.0 (CH═), 136.0 (CH═), 48.2 (CH), 44.7 (CH_2), 42.2 (CH), 34.4 (CH_2), 32.5 (CH), 21.5 (CH_3). ^{13}C NMR, **6b** (ppm): 136.9 (CH═), 132.4 (CH═), 50.1 (CH_2), 47.2 (CH), 43.1 (CH), 33.8 (CH_2), 32.5 (CH), 19.3 (CH_3). MS (*m*/*z*): 108 (10%), 66 (100%). Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.87; H, 11.07.

An alternative synthesis of **6** used 5-norbornene-2-carboxaldehyde as starting material. The hydrazone of 5-norbornene-2-carboxaldehyde was prepared as for **9** to yield 2.2 g (37%) of hydrazone from 5-norbornene-2-carboxaldehyde (5.1 g, 42 mmol). The hydrazone (2.2 g, 16 mmol) was subsequently added by syringe to a solution of potassium *tert*-butoxide (2.2 g, 20 mmol) dissolved in 11 mL of anhydrous DMSO, as per the standard Wolff−Kishner reduction of **3**. The yield of **6** was 0.2 g (12%). By ^{1}H NMR integration, the **6a**:**6b** ratio was determined to be 64:36.

***trans,trans*-1,3,5-Octatriene** (**13**). To a 50 mL three-necked flask under nitrogen atmosphere were added methyltriphenylphosphonium bromide (98%, 8.7 g, 24 mmol) dissolved in 75 mL of anhydrous ether and 1.6 M butyllithium in hexane (15 mL). After the resultant solution was stirred for 2 h at room temperature, *trans,trans*-2,4-heptadienal (90%, 2.5 g, 20 mmol) was added via syringe. After the solution was refluxed overnight at 50 °C, the reaction was quenched by addition of aqueous 5% HCl. Upon addition of 300 mL of ether, the solid was removed by filtration, and the filtrate was washed with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated by short-path distillation to afford 0.5 g (22%) of **13**. ^{1}H NMR (ppm): 6.35 (dt, 1H), 6.2−6.0 (m, 3H), 5.75 (dt, 1H), 5.15 (d, 1H), 5.1 (d, 1H), 2.1 (p, 2H), 1.1 (t, 3H). ^{13}C NMR (ppm): 137.5 (CH═), 137.2 (CH═), 133.6 (CH═), 131.0 (CH═), 129.2 (CH═), 116.2 (CH_2═), 25.8 (CH_2), 13.5 (CH_3).

Gas-Phase Reactions. Prior to this study the pyrolysis bulb was treated sequentially with 70% perchloric acid, distilled water, concentrated ammonium hydroxide, diammonium EDTA, and distilled water. The bulb was then oven-dried. After assembly of the pyrolysis system, three successive treatments of 25 μL of chlorotrimethylsilane each were made. The bulb was deemed free of acid when an injected sample of methylenecyclohexane that was pyrolyzed for 4−6 h exhibited less than 1% rearrangement to 1-methylcyclohexene. The bulb was further conditioned by pyrolysis of 5−10 samples of cyclohexene.

Thermal reactions of all hydrocarbons were carried out at 275.0 °C (with temperature control to ±0.1 °C provided by a Bayley Precision Temperature Controller, model 124) in a 100 mL Pyrex bulb immersed in a molten salt bath (composed of a eutectic mixture of $NaNO_2$ and KNO_3). Temperatures were measured with an Omega DP11 thermocouple with a digital readout to ±0.1 °C. Run times were measured to ±0.01 min with a Precision Solid State Time-it. Pyrolysis samples of 5−8 μL were injected into the pyrolysis system using vacuum line transfer techniques by manipulation of a series of all-Teflon stopcocks. Nitrogen gas (ca. 80 Torr) was added to the system as a bath gas. Between three and five GC injections were made on each pyrolysis sample (1 μL of sample withdrawn with a 1 μL gastight Hamilton syringe and diluted 1:40 with pentane) and the numerical data averaged.

Thermolysis samples were analyzed on an HP 5890A GC equipped with an HP cross-linked methyl silicone column (50 m × 0.2 mm i.d. × 0.10 μm film thickness) operating at an initial temperature of 60 °C held for 1 min followed by a temperature ramp of 1.5 °C/min to a maximum temperature of 100 °C. Retention times (min) were as follows: propene (4.25), cyclopentadiene (4.58), **6a**/**6b** (6.99), **5a** (7.30), **5b** (7.71), the internal standard ethylcyclohexane (8.06), five minor acyclic rearrangement products (8.59−9.27), including *trans*,*trans*-1,3,5-octatriene at 9.16 min, in the pyrolysis of **5b**.

To determine the si/sr ratio of **5a**, additional short duration pyrolyses were conducted. These pyrolysis samples were diluted 1:100 with pentane and analyzed on a Chiraldex γ-cyclodextrin trifluoroacetyl G-TA column (30 m × 0.25 mm i.d. × 0.10 μm film thickness) with an initial temperature of 30 °C and a temperature ramp of 0.1 °C/min. Retention times (min) were as follows: **6b** (3.91, 3.98), **6a** (4.20, 4.37), **5a** (4.33, 4.65), **5b** (4.65, 4.95).

A thermolysis sample of **5b** was also analyzed on the HP GCD system using an HP-5 (cross-linked 5% phenyl methyl silicone) capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) at an initial temperature of 60 °C and a temperature ramp of 2 °C/min to verify molecular weights for all major thermal species (**5a**, **5b**, **6a**, and **6b**) and to identify the five minor acyclic rearrangement products observed in the thermolysis of **5b**. Because one of the five was only evident at long pyrolysis times, we obtained mass spectra on four of the five. Of these four, three exhibited a base peak at *m*/*z* 91 (M − 15), indicating loss of a methyl unit, whereas the component coincident with *trans*,*trans*-1,3,5-octatriene had a base peak of *m*/*z* 79 (M − 29), suggesting loss of an ethyl fragment. We have made no further attempt to characterize the three other components because in composite these acyclic rearrangement products constitute less than 6% of the total product distribution in **5b**, as can be seen from the relative magnitude of k'_i in Table 1.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Franklin & Marshall College Hackman Scholars Program for financial support of this work. We are grateful to Prof. Joseph J. Gajewski of Indiana University for providing us with a Simplex/Runge-Kutta software program and to Prof.

John E. Baldwin of Syracuse University for performing a critical reading of the manuscript.

Supporting Information Available: Copies of first-order kinetic rate plots and NMR spectra for **5a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9918899