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Theory and Mechanism of the Allylidenecyclopropane to Methylenecyclopentene Thermal Isomerization

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Abstract: The thermally induced rearrangement of 7-(*trans*-butenylidene)bicyclo[4,1,0]heptane gives 8-methylbicyclo-[5,3,0]undeca-1(2),9-diene with stereospecificity that is opposite that predicted by conservation of orbital symmetry. Further, when optically active starting material is thermolyzed, the product is racemic, but recovered starting material is unchanged. Identical results were obtained upon thermolysis of 6-(*trans*-butenylidene)bicyclo[3.1.0]hexane and of 2-oxo-7-(*trans*-butenylidene)bicyclo[4,1,0]heptane. These results require that the reaction proceeds through one or more achiral species, that at least one of them is planar, that they never return to starting material, and that there is a stereospecific pathway from the intermediate(s) to product. 6-Electron−6-orbital CASSCF calculations with a 6-31G* basis set reveal that the lowest energy singlet intermediates on the parent C_6H_8 energy surface are the achiral *cisoid* and *transoid* orthogonal 2-(1′-allyl)allyl biradicals. The *cisoid* form undergoes conrotatory closure to the methylenecyclopentene product via a transition state that is 2.8 kcal/mol lower in energy than the disrotatory transition state. The conrotatory transition state is consistent with the observed stereospecificity. The highest energy transition state is that from starting allylidenecyclopropane to an orthogonal 2-methylene-*transoid*-1,3-pentadienyl singlet species which then forms the *transoid* orthogonal bisallyl singlet biradical which undergoes bond rotation via a planar *transoid* vinyltrimethylenemethane transition state as well as slower closure to 2-vinylmethylenecyclopropane. Reopening of the latter material to a *cisoid* orthogonal bisallyl singlet biradical then provides the pathway for the stereospecific conrotatory closure to 3-methylenecyclopentene. Besides the cyclopropanes and methylenecyclopentene, the lowest energy species on the entire energy surface is the planar *transoid* vinyltrimethylenemethane triplet. The orthogonal bisallyl singlets are 8 kcal/mol higher in energy than the planar triplet at this level of theory.

Pyrolysis of allylidenecyclopropane, **1**, at 170−200 °C, results in the formation of 2-vinylmethylenecyclopropane, **2**, which rearranges very rapidly to 3- methylenecyclopentene, **3**, via first-order processes.[2] In the case of the 2,2-dimethyl derivatives, both *syn* and *anti* materials **1a** and **1b**, respectively, give the same 2:1 mixture of 3-isopropylidenecyclopentene and 4,4-dimethyl-3-methylenecyclopentene, **3a** and **3b**, respectively.[3] Further, at 100 °C 2-vinylisopropylidenecyclopropane, **2a**, is a steady state intermediate in the reaction along with small amounts of 3,3-dimethyl-2-vinylmethylenecyclopropane, **2b** (Scheme 1).[2]

The formation of **3** is not unexpected since it is the most stable of the isomers **1**−**3**, but it is remarkable that isomers of **2** interconvert rapidly but do not revert to isomers of **1** which are more stable than isomers of **2**. This is also true in the case

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[†] Indiana University.

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[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1995.

(1) Deceased Feb 13, 1993.

(2) Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749.

(3) Kende, A. S.; Riecke, E. E. *J. Am. Chem. Soc.* **1972**, *94*, 1397.

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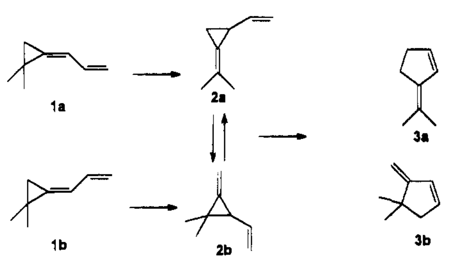
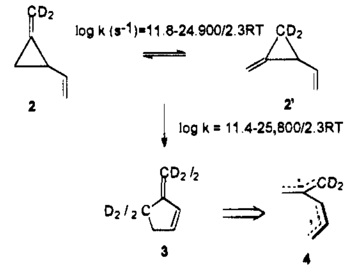
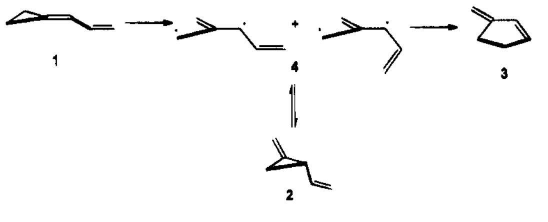
Scheme 1



Scheme 2



Scheme 3



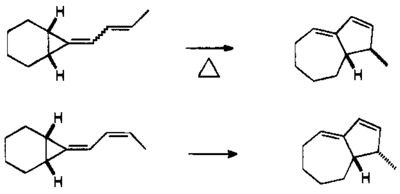
of the desmethyl derivatives of **2b**, namely, **2**.[4] Thus, there must be a kinetic barrier to re-formation of **1** from **2** that is higher than that to give **3**.[3]

A related observation was made by Gilbert in a particularly relevant paper where *exo*-methylene-deuterated 2-vinylmethylenecyclopropane, **2**, equilibrated with the 3-deuterio isomer **2′** approximately 10 times faster than formation of methylenecyclopentene (Scheme 2).[5] Of additional importance is the observation that the deuterium is equally distributed between the *exo*-methylene carbon atom and the allylic methylene ring carbon atom of **3** even at low conversions. Therefore, an orthogonal 2-(1′-allyl)allyl diradical, **4**, is most likely involved.

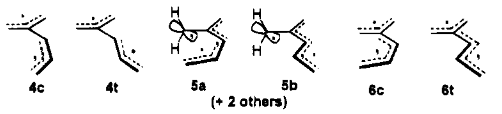
Another remarkable aspect of the overall transformation of **1** to **3** is the fact that the reaction does not proceed directly via an orbital symmetry controlled $2\sigma s + 2\pi s + 2\pi s$ pathway without an intermediate. Two such concerted pathways can be envisioned, giving rise to different stereochemical possibilities for product depending on whether the migrating cyclopropyl carbon undergoes retention or inversion. However, in these acyclic systems, neither pathway is utilized since **2** is, in fact, the intermediate. To put to rest questions of concert, stereochemical studies by Roth with *trans*- and *cis*-2,3-dimethyl-*trans*-butenylidenecyclopropane revealed that the major thermal product in both reactions is *trans*-4,5-dimethyl-3-ethylidenecyclopentene although some *cis* material is also formed.[6] This stereoselectivity and lack of stereospecificity rule out concert in a direct **1** to **3** rearrangement.

All of the previous observations are consistent with a pathway involving ring opening of the allylidenecyclopropane to an orthogonal 2-(1′-allyl)allyl species, **4** (Scheme 3). This requires cyclopropane ring opening with rotation about three bonds; the remaining cyclopropane bonds and the *exo*-methylene π bond. This species could be responsible for the degenerate rearrangements of **2** and, when formed with a *cisoid* allyl group, could give **3**. Re-formation of **1** from **4** would require rotation of the allyl radical back into the plane of the other allyl radical, and this apparently is more difficult than the other pathways. Indeed, as indicated previously, no study of 2-vinylmethylenecyclopropane thermal rearrangements has reported the formation of allylidenecyclopropane.

Scheme 4



Scheme 5



Of importance in connection with the results of this work is the fact that the **1** to **3** rearrangement has been developed as a synthetic method to convert allylidenecyclopropanes fused to a ring into methylenecyclopentenes fused to a ring expanded by one carbon (Scheme 4).[7]

Like the previous observations, the *syn* or *anti* isomers at the allylidene group in unsymmetrical cases give the same mixture of cyclopentene products. However, in an aspect not addressed by the Roth study, the reaction of a *trans*-butenylidenecyclopropane reveals stereospecificity in the formation of the cyclopentene such that the *trans*-methyl group becomes *exo* in the product (and a *cis*-methyl becomes *endo*).[7] This element of stereospecificity, which increases the utility of the synthetic methodology, presents a mechanistic problem as to its origin and, indeed, as to the nature of the energy surface responsible for all of the interconversions. This question is particularly relevant since *the overall stereochemistry observed is the opposite of that predicted for an orbital symmetry controlled direct thermal isomerization of **1** to **3**.*

A concern that can be answered experimentally is whether or not achiral intermediates and transition states are involved. Resolution of this issue is described below in the affirmative. This finding then provoked the question as to the origin of the stereospecificity and the relative energies of the various vinyltrimethylenemethanes and the transition states connecting them. Also at issue are the relative energies of the singlet and triplet states of not only the two isomers of **4**, namely, **4c** and **4t**, but of the four possible 2-methylene-1,3-pentadienyl isomers **5** and of the two possible planar species **6c** and **6t** (Scheme 5).

The current problem therefore takes on the additional concern of the effect of extending the conjugation in trimethylenemethane which itself is a planar ground state triplet having the perpendicular 2-methyleneallyl (orthogonal trimethylenemethane) singlet 14.5 kcal/mol higher in energy.[8] The question then is how conjugation affects the singlet–triplet gap in this non-

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[4] Billups, W. E.; Leavell, K. H.; Lewis, E. S.; Vanderpoll, S. *J. Am. Chem. Soc.* **1973**, *95*, 8096.

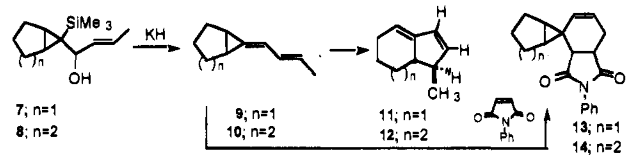
[5] Gilbert, J. C.; Higley, D. P. *Tetrahedron Lett.* **1973**, 2075.

[6] Roth, W. R.; Schmidt, Th. *Tetrahedron Lett.* **1971**, 3639.

[7] Shook, C. A.; Romberger, M. L.; Jung, S.-H.; Xiao, M.; Sherbine, J. P.; Zhang, B.; Lin, F.-T.; Cohen, T. *J. Am. Chem. Soc.* **1993**, *115*, 10754.

[8] Feller, D.; Tananaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967. This MCSCF calculation with an STO-3G basis set was repeated with a 6-31G* basis set to give the singlet–triplet gap cited.

Scheme 6



Kekule molecular system.[9] Thus, the stationary points, both minima and maxima, on this energy surface were pursued with the HONDO program.[10]

Results

Synthesis and Pyrolysis of Optically Active Butenylidenecyclopropanes. Optically active 7-(*trans*-butenylidene)bicyclo-[4,1,0]heptane,[7] **10**, was prepared from β-silyl alcohol precursor **8**,[7] by a previously established route. Resolution of the alcohol **8** was accomplished by destructive asymmetric epoxidation[11] to give material with 45% ee (three passes were necessary) as determined by NMR using the chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]-europium(III), Eu(hfc)$_3$, on the *N*-phenylmaleimide adduct **14** of **10**. Optically active hydrocarbon **10** was subjected to pyrolysis at 180 °C (16 h) and at 190 °C (24 h). The ratio of starting material to product in the two experiments was 68:32 and 32:68, respectively. The ee of recovered starting material was within experimental error of that before pyrolysis. However, the product **12** was >99% racemic as determined by examination of the HC-9 proton (δ ~6.75 and ~6.58) of racemic product with 1 equiv of AgFOD ((6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octadionato)silver) and 70 mol % Eu(hfc)$_3$ (Scheme 6).[12] A similar experiment was performed with identical results upon pyrolysis of hydrocarbon **9**.

The allyl alcohol **16** was prepared from **15**[7] by reductive lithiation with lithium 4,4′-di-*tert*-butylbiphenylide (LDBB)[13] and treatment of the resulting lithiosilane with crotonaldehyde. The kinetic resolution of **16** proceeded in a fashion similar to that of **7** and **8**. Peterson elimination provided nonracemic ketone **17**, the ee of which was assessed by determining that of its Diels–Alder adduct **19** with *N*-phenylmaleimide. Heating **17** in refluxing diglyme again produced racemic ring-expanded product **18** and nonracemic **17** of the same ee as the starting material (Scheme 7). This experiment is important because the result requires that at least one of the achiral intermediates or transition states be planar.

Theory. All calculations were carried out with the HONDO program using a 6-31G* basis set and a complete active space (CAS) multiconfiguration wave function. This wave function included all arrangements of the six electrons among six optimized molecular orbitals involved in bond making and breaking. This is the simplest wave function that can change continuously between all points of interest on the potential energy surface. The HONDO program has analytic gradients for a wave function of this form and is able to directly search for minima and transition states.

Scheme 7

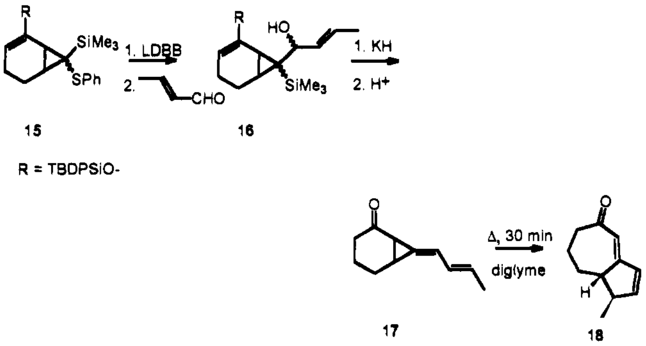


Table 1. Energies of Various C_6H_8 Singlet Minima by 6-Electron–6-orbital CASSCF

C_6H_8 isomer	E (hartrees)	E_{rel} (kcal/mol)
1c, *cisoid* allylidene-C_3	−231.844 017	0.0
1t, *transoid* allylidene-C_3	−231.847 326	−2.08
2c, *cisoid* vinylmethylene-C_3	−231.840 185	2.41
2t, *transoid* vinylmethylene-C_3	−231.841 179	1.78
3, 3-methylenecyclopentene	−231.901 198	−35.88
4c, *cisoid* orthogonal bisallyl	−231.811 179	20.61
4t, *transoid* orthogonal bisallyl	−231.811 072	20.67
5a, 2-orthogonal CH_2-S-*syn*-pentadienyl	−231.797 253	29.34
5b, 2-orthogonal CH_2-W-pentadienyl	−231.803 315	25.54
5c, 2-orthogonal CH_2-U-pentadienyl	−231.792 730	32.18
5d, 2-orthogonal CH_2-S-*anti*-pentadienyl	−231.799 891	27.69

Table 2. Transition states (ts) for Interconversion of the Minima of Table 1 Using the Same Theoretical Level (for E_{rel} Reference See Table 1)

C_6H_8 transition state	E (hartrees)	E_{rel} (kcal/mol)
6c, *cisoid* planar (ts rotation of **4c**)	−231.799 732	27.79
6t, *transoid* planar (ts rotation of **4t**)	−231.805 786	23.99
1t–5b (ts of lowest E from **1**)	−231.791 705	32.83
5a–4c	−231.795 127	30.68
5b–4t	−231.800 785	27.13
4t–2t	−231.800 794	27.12
4c–2c	−231.801 252	26.84
4c–3con	−231.798 109	28.81
4c–3dis	−231.793 622	31.62
5a–3 (avoids **4** and **2**)	−231.791 064	33.23

The stationary points on the relevant C_6H_8 singlet energy surface include the stable species allylidenecyclopropane, **1**, both *transoid* and *cisoid*, 2-vinylmethylenecyclopropane, **2** (although all minima in this subspace with a 6-fold barrier are roughly comparable in energy), and 3-methylenecyclopentene, **3**. Other minima include the four orthogonal 2-methylene-1,3-pentadienyls **5a–d** and the *transoid* and *cisoid* orthogonal 2-(1′-allyl)-allyl species, **4t** and **4c** (Table 1).

The transition states interconnecting the singlet species are given in Table 2 and include the planar forms **6c** and **6t**, which are responsible for rotation about the C-2–C-1′ bonds of **4c** and **4t**, respectively. The lowest energy pathway between allylidenecyclopropane and the orthogonal 2-methylenepentadienyl species **5b** is **1t–5b**. The orthogonal singlet **5b** gives orthogonal 2-(1′-allyl)allyl species **4t** via a lower energy transition state, **5b–4t**, which in turn gives the isomers of **2** via transition state **4t–2t**. The various rotomers of **2** can undergo allylic degenerate rearrangements via the transition states **4t–2t** and **4c–2c** to give the two isomers of singlet **4**, but it is only the *cisoid* isomer **4c** that can give 3-methylenecyclopentene, **3**, directly. The lowest energy path to methylenecyclopentene from **4c** is via **4c–3con**, which was found by using

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(9) For a summary see: Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

(10) Dupuis, M.; Marquez. A.; Chin, S. HONDO 8.4 from CHEM-Station IBM Corp., Kingston, NY 1993.

(11) Martin, V. S.; Woodard, S. S. Kutsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. Gao, Y., Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(12) Krasutsky, P. A.; Yurchenko, A. G.; Rodionov, V. N.; Jones, M., Jr. *Tetrahedron Lett.* **1982**, *23*, 3719. For a review of the use of the chiral shift reagent Eu(hfc)$_3$, see: Sullivan, G. R. *Top. Stereochem.* **1978**, *10*, 287.

(13) Freeman, P.; Hutchinson, L. *J. Org. Chem.* **1980**, *45*, 1924.

Table 3. Energies and Relative Energies of Triplet and Singlet Stationary Points of Biradicals **4**−**6** (E_{rel} Is Referenced to Planar Triplet)

species	E(t) (hartrees)	$E(\mathrm{t})_{\mathrm{rel}}{}^{a}$ (kcal/mol)	$E(\mathrm{s})_{\mathrm{rel}}{}^{a}$ (kcal/mol)
6t, planar *transoid*	−231.824 841	0.0 (MIN)	11.96 (TS)
6c, planar *cisoid*	−231.816 696	5.11	15.76 (TS)
5b, 2-methylenepentadienyl (W)	−231.803 315	13.51	12.69
4c, orthogonal bis-*cisoid*	−231.811 840	8.13	8.57 (MIN)
4t, orthogonal bis-*transoid*	−231.812 392	7.81	8.64 (MIN)

[a] Intermediates (MIN) and maxima (TS) are designated where determined.

a conrotatory path from **4c** to **3**. This pathway is the stereomode required by the experimental observations.

The results of the calculation on the triplet states of the various diradicals is summarized in Table 3, which also includes the singlet energy for each species for comparison.

Discussion

Stereochemical Findings. The stereochemical findings reported here for pyrolysis of **9** and **10**, namely, formation of racemic product with unchanged recovered starting material, along with the previously reported stereospecificity,[7] require a pathway which proceeds via (an) achiral intermediate(s) that do not revert to starting allylidenecyclopropane but form the bond in the cyclopentene ring via a stereospecific pathway. Further, from the formation of racemic product upon pyrolysis of **17**, at least one of the achiral intermediate(s) or transition state(s) must be planar. These requirements are satisfied by the orthogonal biradicals **4**, which not only undergo bond rotation via the planar species **6** but, in the case of **4c**, undergo conrotatory closure to **3**. It is important to recognize that the cyclopropane ring opening in fused systems like **7** can generate an allyl radical within the expanded ring in which both termini have only the *cisoid* configuration. It is only in this system that the stereospecific conrotatory closure to **3** is revealed. It was our concern that these hypotheses, particularly the stereomode of formation of the cyclopentene product, be examined by high levels of theory, pursuing both the singlet and triplet energy surfaces.

Calculations. The need for the 6-electron−6-orbital CASSCF approach can be illustrated by the calculations of the energy of the 2-(1′-allyl)allyl biradical **4**. Restricted Hartree−Fock gives a singlet energy that is much too high because the wave function actually involves two configurations with nearly equal coefficients. A ROHF or UHF calculation for the triplet state gives a lower energy. Broken symmetry UHF calculations for a "singlet state" specified by forcing $M_s = 0$ actually gives a 50:50 mixture of the singlet state and the $M_s = 0$ component of the triplet state with still lower energy. But a simple two-configuration calculation gives a pure singlet state with even lower energy. The 6-electron−6-orbital CASSCF calculation finally provides pure singlet and triplet states with the triplet slightly below the singlet. Thus, only a CASSCF calculation has a chance to correctly describe the relative energy of the singlet and triplet states in the sequence of all of the closed shell and biradical intermediates of interest here. For consistency, the 6-electron−6-orbital CASSCF calculation method was used for both the singlet and triplet states at all points on the potential energy surface.

Singlet Energy Surface. The singlet surface obtained with a 6-electron−6-orbital CASSCF calculation using the 6-31G* basis set in the HONDO program with geometric optimization at this level provides information on the question of spiroconjugation in orthogonal bisallyl singlets and on the stereochemical results of the thermal interconversions of **1**, **2**, and **3**. Of the singlet intermediates, the two orthogonal bisallyl species **4c** and **4t** are roughly the same in energy, indicating little through-space conjugation that might be related to spiroconjugation,[14] and these species are the lowest energy singlet biradicals on the energy surface. The four orthogonal 2-methylenepentadienyls **5** have very different energies which appears to reflect nonbonded interactions. Thus, the "W" form **5b** is only 4.9 kcal/mol higher than the isomers of **4** while the "U" form **5c** is 11.5 kcal/mol higher than the isomers of **4**. The two "sickle" forms, namely, **5a** and **5d**, are roughly 7 and 9 kcal/mol, respectively, higher in energy than the isomers of **4**. Given the large difference in energy, it is reasonable that only **5b** is formed directly from **1**. The calculated structures of the three relevant singlet intermediates and **5a** are given in Figure 1.

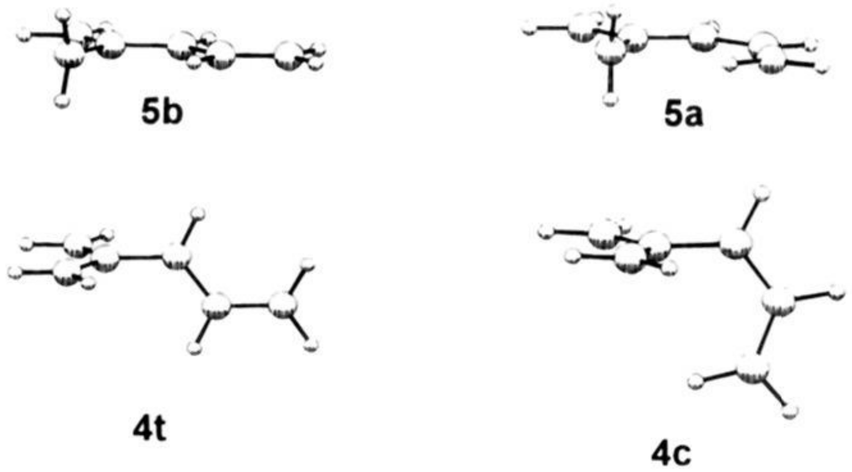

Figure 1. Structures of singlet intermediates calculated by 6-electron−6-orbital CASSCF at the 6-31G* level. E_{rel} (kcal/mol): **4c**, 20.61; **4t**, 20.67; **5b**, 25.54; **5a**, 29.34.

With some effort the transition states for the interconversion of the minima were obtained (Table 2). The lowest energy pathway from either **1c** or **1t** is that to **5b** via structure **1−5b**, then **5b** gives the orthogonal bisallyl species **4t** via transition state **5b−4t**, and in turn, **4t** is converted to **2** via transition state **4t−2**. Since the opening of **1** leads to a *transoid* allylic species attached to C-2 of the allyl derived from the three-membered ring, there is little likelihood of formation of the bis-*cisoid* bisallyl species **4c** without formation of 2-vinylmethylenecyclopropane, **2**. Ring opening of **2** can lead to **4c** in addition to re-forming **4t**, and it is closure of **4c** which leads to the 3-methylenecyclopentene product, **3**. The lowest energy transition state to **3** is from the *cisoid* singlet **4c**, namely, **4c−3con**, via a conrotatory pathway, and this pathway is only 2.0 kcal/mol higher in energy than reclosure back to **2**. Thus, the ratio of rate constants for methylene interchange in vinylmethylenecyclopropane and formation of methylenecyclopentene is approximately reproduced by the calculation, and the Cohen observation of stereochemistry of formation of the methylenecyclopentene is also reproduced at this level of theory. Finally, the conrotatory pathway for five-membered ring closure is 2.8 kcal/mol lower in energy than the next lowest energy transition state, namely, **4c−3dis**, which was discovered by assuming disrotation in the closure. This higher energy transition state appears to uncouple the terminal methylene C-5 from C-4 and C-3, without significant bonding to C-6. The calculated reaction sequence is given in Figure 2.

It is important to note that on the singlet energy surface the depth of the potential well represented by the 2-(1′-allyl)allyl species **4** is roughly 8 kcal/mol relative to the transition state for ring closure to 3-methylenecyclopentene, **3**. Thus, the

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[14] Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. Hoffmann, R.; Imamura, A.; Zeiss, G. D. *Ibid.* 5215.

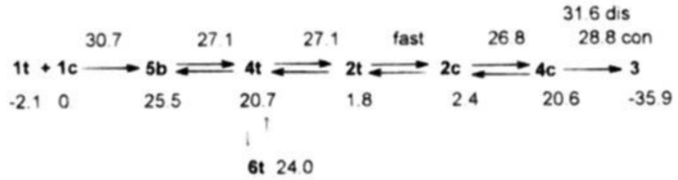

Figure 2. Calculated singlet energy surface, energies in kcal/mol. **1t,c** are *transoid* and *cisoid* allylidenecyclopropane; **5b** is orthogonal 2-methylene-*transoid*-1,3-pentadienyl; **4t,c** are *trans*- and *cis*-2-(1′-allyl)allyl; **2t,c** are *transoid* and *cisoid* 2-vinylmethylenecyclopropane; **6t** is planar 2-methylene-*transoid*-1,3-pentadienyl (planar vinyltrimethylenemethane), a transition state; **3** is 3-methylenecyclopentene.

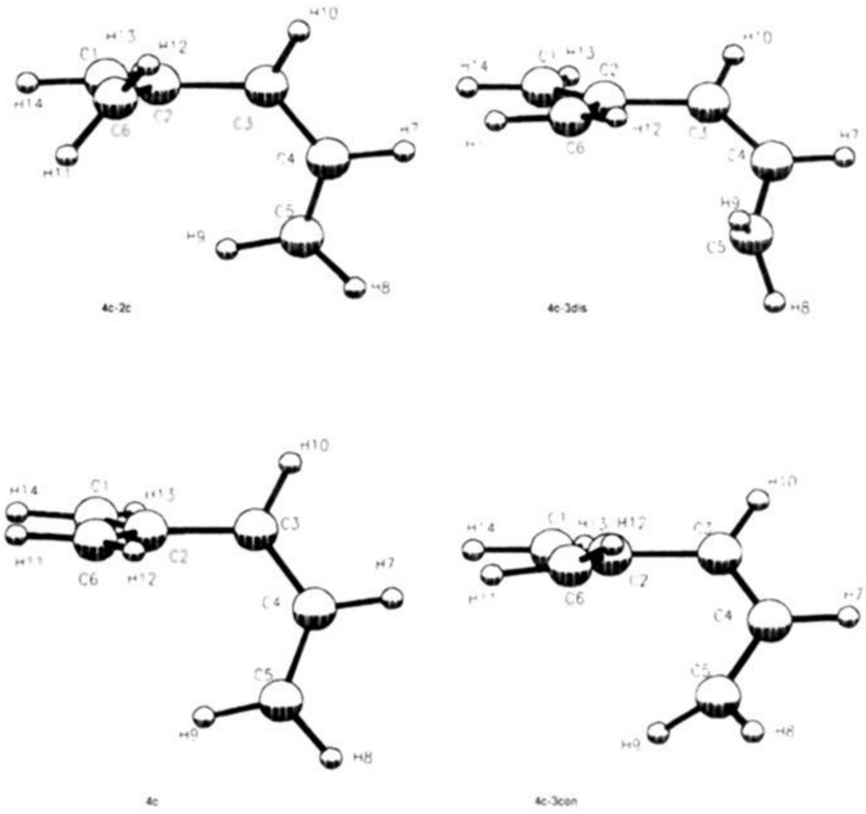

Figure 3. Structures of stationary points on the cisoid 2-(1′-allyl)allyl singlet energy surface. For **4c** (Cs), $r(2-3) = 1.49$ Å; $r(3-6) = 2.48$ Å; $r(5-6) = 3.71$ Å; $\angle(6-2-3-4) = 91.7°$. For **4c−2c**, $r(3-6) =$ 2.39 Å; $r(3-4) = 1.405$ Å; $r(4-5) = 1.37$ Å; $\angle(11-6-2-3) = -121.4°$; $\angle(12-6-2-3) = 40.8°$; $\angle(6-2-3-4) = 102.3°$. For **4c−3con**, $r(2-3) = 1.48$ Å; $r(3-6) = 2.44$ Å; $r(3-4) = 1.35$ Å; $r(4-5) = 1.47$ Å; $r(5-6) = 2.72$ Å; $\angle(11-6-2-3) = -173.5°$; $\angle(12-6-2-3) = 25.0°$; $\angle(6-2-3-4) = 46.3°$; $\angle(3-4-5-8) = -156.2°$; $\angle(3-4-5-9) = 43.4°$. For **4c−3dis**, $r(2-3) = 1.48$ Å; $r(3-6) = 2.50$ Å; $r(3-4) = 1.34$ Å; $r(4-5) = 1.47$ Å; $r(5-6) = 3.07$ Å; $\angle(11-6-2-3) = -174.9°$; $\angle(12-6-2-3) = 11.3°$; $\angle(6-2-3-4) = 40.8°$; $\angle(3-4-5-8) = 127.4°$; $\angle(3-4-5-9) = -76.6°$.

transition state is substantially different in structure and bonding from the biradical intermediate so that there is a distinction between conrotation and disrotation. Another important feature of the energy surface is the relatively low energy (24 kcal/mol) of the *transoid* planar vinyltrimethylenemethane singlet **6t** which is a transition state on this energy surface. It is only this species which can be responsible for racemization of the system prior to formation of product from ketone **17**. The structures and some important distances and dihedrals are given in Figure 3.

In summary, the calculations therefore are consistent not only with the observations that 2-vinylmethylenecyclopropane does not revert to allylidenecyclopropane and that the 2-vinylmethylenecyclopropanes interconvert faster than undergoing ring expansion but also with the fact that the ring expansion occurs with specific rotations to account for the stereochemistry observed by Cohen previously.[7] The stereomode for methylenecyclopentene formation from the *cisoid* biradical **4** would appear to be determined by favorable orbital overlap and steric factors in the transition state despite the fact that there appears to be no orbital overlap between the two allyls in the intermediate **4c**. However, it is not unreasonable to expect that, to whatever extent the transition state represents a species higher in energy than an intermediate which has no specific overlap requirements, transition state geometry controls the stereomode of closure and, by microscopic reversibility, the stereomode for ring opening of the closure product. In the present case this is 3-methylenecyclopentene. Likewise, in the observed conrotatory-bevel ring opening of 1,2-dimethylenecyclobutane and 1,3-dimethylenecyclopentane,[15] the transition states may also be reflecting the same orbital overlap requirements as calculated here for closure of the 2-(1′-allyl)allyl species.

The fact that the conrotatory stereochemistry for closure of the 2-(1′-allyl)allyl species **4** was not observed in acyclic cases is probably due to the loss of stereochemistry at C-1 and C-3 in the 2(1′-allyl)allyl intermediates due to equilibration of *cisoid* and *transoid* substituted allyl head groups. This results from the interconversion of these two allylic sites in isomers of **2** via **4**. However, with a ring spanning these two positions, only *cisoid* allyl species are accessible at the temperatures of the reaction, and these reveal, uniquely, the stereomode for closure. Thus, the constraints imposed by the fused systems studied here provide previously unavailable mechanistic insights. It must be recognized that the fact that **1c** and **1t** can both give the same product is not necessarily due to the preferred transition state for the initial ring opening to intermediate **5** but because of the formation of **2** which reversibly opens to both orthogonal bisallyl species **4c** and **4t**, and it is **4c** which rearranges to 3-methylenecyclopentene, **3**.

Finally, it should be noted that the geometry optimizations were unconstrained and little evidence was found for extensive pyramidalization at any of the carbons unlike the calculation reported by Hess on the trimethylenemethane singlet,[16] although some slight pyramidalization at C-2 of **4c** might occur (note that the C-6−C-2−C-3−C-4 dihedral is 91.7° and not 90.0°). Indeed, the portion of the energy surface calculated here that involves methylenecyclopropane rearrangements is not unlike that calculated previously using a 4-orbital−4-electron MCSCF calculation with an STO-3G basis set and more recently with a 6-31G* basis set.[8]

Triplet Energy Surface. The lowest energy triplet is the planar *transoid* species **6t**, but its *cisoid* isomer is higher in energy by 5.11 kcal/mol. It would appear that nonbonded interactions destabilize the *cisoid* form. Of importance is the fact that the lowest energy singlet is **4c**, the orthogonal *cisoid* bisallyl species, and it is 8.57 kcal/mol higher in energy than the lowest energy triplet **6t**. Not unexpectedly, the orthogonal bisallyl triplets and singlets are nearly the same in energy and are only slightly (3 kcal/mol) lower than the *transoid* planar singlet. The ordering of various geometries of the two spin states is generally like that of the parent trimethylenemethane (TMM) species where the planar triplet is 14.5 kcal/mol lower in energy than the perpendicular singlet at this calculational level.[10] Thus, the Ochinnikov−Borden−Davidson rule is obeyed in a TMM system with extended conjugation. However, the attenuation of the energy gap between the lowest triplet and singlet of this extended system relative to the parent should be noted.

Which Energy Surface, Singlet or Triplet, Is Utilized in the Thermal Rearrangements? The thermal interconversions of **1**, **2**, and **3** and their derivatives provide no clue regarding which energy surface might be involved. However, if triplets are involved, intersystem crossing must occur twice somewhere along the reaction path in order to give stable products. Ultimately, the question can be reduced to that of the relative

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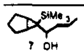
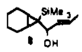
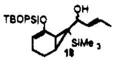
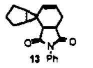
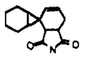
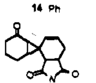
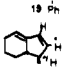
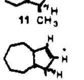
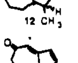
(15) Gajewski, J. J.; Shih, C. N. *J. Am. Chem. Soc.* **1972**, *94*, 1675; Gajewski, J. J. *Ibid.* **1975**, *97*, 3457; Gajewski, J. J.; Salazar, J. *Ibid.* **1979**, *101*, 2739, 2740.

(16) Hess; et al. *J. Am. Chem. Soc.* **1988**, *110*, 5315.

Table 4. Data Obtained from Experiments with Chiral Shift Reagent

substrate	*conc.*[a]	Eu(hfc)3	*% ee*	*peaks*	*chemical shift*
 7	0.07 M	15%	40%	TMS group	δ 0.75 and 0.58
 8	0.10 M	10%	45%	TMS group	δ 0.44 and 0.37
 16	0.07 M	15%	26%	TMS group	δ 0.51 and 0.39
 13	0.25 M	130%	41%[b] 40%[c]	aromatic H	δ 8.71 and 8.53
 14	0.04 M	45%	44%[b] 43%[c]	vinyl H's	δ 6.83 and 6.74 δ 6.58 and 6.49
 19	0.04 M	110%	27%[b] 27%[c]	Me group	δ 2.86 and 2.65
 11	0.05 M[d]	100%	<2%	HC-2	δ 6.53 and 6.42
 12	0.04 M[d]	70%	<1%	HC-9	δ 6.75 and 6.58
 18	0.05 M	65%	<2%	HC-2	δ 12.65 and 12.53

[a] Concentration of substrate at optimum resolution. [b] Enantiomeric excess of substrate before thermal rearrangement. [c] Enantiomeric excess of substrate after partial rearrangement. [d] Sample solution also contains 1 eq. of AgFOD

rates of intersystem crossing and bond formation within singlet biradical species which are, no doubt, the initially formed intermediates in these thermolyses.

Judging by the observations with methylenecyclopropane where roughly 90% of the reaction proceeds via orthogonal trimethylenemethane species despite the fact that the planar triplet is much more stable than orthogonal species, singlet to triplet interconversions are slow relative to bond formation within the singlet species generated by initial bond homolysis. In addition, the potential barriers for reaction calculated for the singlet species, particularly those of **4**, are small enough (8 kcal/mol) to suggest rate constants on the order of 10^{8-9} s^{-1} at the temperatures of the reactions assuming a preexponential term of $10^{12.5}$ s^{-1}. On the other hand, while intersystem crossing from singlet to triplet presumably has no activation energy, it is spin forbidden and is generally assumed to be on the order of 10^{5-7} s^{-1} in strongly interacting biradical systems,[17] so reactions on the singlet surface probably dominate the thermal chemistry.

Experimental Section

General Procedure for the Determination of Enantiomeric Purity. The ^{1}H NMR spectrum of a solution of substrate in $CDCl_3$ (0.5 mL) was recorded before a solution of tris[3-[(heptafluoropropyl)-hydroxymethylene]-(+)-camphorato]europium (Eu(hfc)$_3$) (1 equiv/mL) in $CDCl_3$ was added to the NMR sample in 0.05−0.10 mL increments, and the spectrum was recorded after each increment. In the cases of **11** and **12**, 1 equiv of AgFOD was also added to the solutions. When the optimum enantiomeric shift difference was realized, the percent ee was determined by integration of the resolved peaks. The results reported are the averages of several repeated runs. The results are compiled in Table 4; the asterisks in the last three entries indicate the positions of the protons whose peaks were monitored.

Kinetic Resolution of 7. To a solution of Ti(O-*i*-Pr)$_4$ (1.02 g, 1.07 mL, 3.58 mmol) in CH_2Cl_2 (14 mL) was added a solution of L-(+)-diethyl tartrate (DET) (0.887 g, 4.30 mmol) in CH_2Cl_2 (5 mL) at −23 °C. After 20 min, a solution of racemic **7** (0.802 g, 3.58 mmol) in CH_2Cl_2 (5 mL) was added slowly. After an additional 1.5 h, *tert*-butyl hydroperoxide (TBHP) (0.39 mL, 5.5 M, 2.1 mmol) was added, and the solution was stirred for 18 h. The flask was then removed from the cooling bath, and ether (6 mL) and brine (2 mL) were added. After the reaction mixture had been stirred for 1 h, the white precipitate was removed by filtration through a pad of Celite with ether. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The resulting oil was subjected to flash column chromatography (SiO_2, 7% ethyl acetate−hexanes, $R_f = 0.29$) to afford 0.46 g (52%) of the nonracemic allylic alcohol (~21% ee). This product was subjected twice more to the same procedure to afford the alcohol with 40% ee.

Kinetic Resolution of 8. The procedure was the same as that for the resolution of **7**, but the scale was about twice as great. The crude oily product was subjected to flash column chromatography (SiO_2, 5% ethyl acetate−hexanes, $R_f = 0.27$) to afford 48% of the nonracemic allylic alcohol (~18% ee). This product was subjected twice more to the same procedure to afford the alcohol with 45% ee.

7-(2-*trans*-Butenylidene)bicyclo[4.1.0]heptane (10). A solution of partially resolved **8** (0.142 g, 0.598 mmol) in THF (12 mL) was stirred at ambient temperature as KH powder (0.0698 g, 1.74 mmol) was added all at once. The resultant mixture was stirred for 10 h prior to being poured into a separatory funnel containing brine overlaid with ether. The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo*, and the resulting oil passed through a small pad of silica with hexanes to give 0.824 g (93%) of the diene: IR (neat) 3003 (m), 2976 (s), 2930 (s), 2855 (s), 1448 (s), 1174 (m), 943 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.32 (d, $J = 10.5$ Hz, 1 H, CC*H*), 6.18 (dd, $J_{trans} = 14.8$, $J = 10.5$ Hz, 1 H, CH_3CHCH), 5.77 (dq, $J_{trans} = 14.8$, $J = 6.75$ Hz, 1 H, CH_3CH), 1.77 (d, $J = 6.75$ Hz, 3 H, CH_3), 1.70−1.00 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 135.5, 130.7, 126.7, 117.9, 23.2, 22.6, 21.4, 21.3, 18.3, 12.8, 12.7; exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1252.

7-*exo*-Methylbicyclo[4.3.0]nona-1,8-diene (11). A solution of **9** (0.0273 g, 0.203 mmol), prepared[7] from partially resolved **7**, in benzene (2 mL) was heated at 180 °C for 18 h in a sealed tube.[7] The contents of the tube were transferred to a flask and carefully (bath temperature 0−5 °C) concentrated *in vacuo*. Chromatography (pentane, $R_f = 0.60$) afforded 0.0251 g (92%) of **11**: IR (neat) 3040 (w), 2924 (s), 2855 (m), 1455 (m), 1057 (w), 822 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.11 (dd, $J = 5.46$, 2.04 Hz, 1 H, HC-9), 5.83 (dd, $J = 5.46$, 1.39 Hz, 1 H, HC-8), 5.38 (m, 1 H, HC-2), 2.32−2.45 (m, 1 H, CH_3CH), 2.00−2.25 (m, 3 H, including HC-6), 1.84−1.92 (m, 2 H), 1.42−1.60 (m, 1 H), 1.18−1.35 (m, 1 H), 1.13 (d, $J = 6.92$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 141.0, 131.4, 125.8, 114.9, 48.9, 45.5, 27.1, 25.1, 23.0, 19.1; exact mass calcd for $C_{10}H_{14}$ 134.1096, found 134.1079.

8-*exo*-Methylbicyclo[5.3.0]deca-1,9-diene (12). A solution of allylidenecyclopropane **10** (0.0824 g, 0.557 mmol) in benzene (2 mL) and a trace of radical inhibitor (3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide) were prepared for a sealed tube thermolysis reaction by the standard procedure.[7] The tube was then placed into a thermostated oil bath (220 °C). After 24 h, the heat source was removed and the contents of the tube were transferred to a flask and concentrated prior to chromatography. Passing the resulting oil in hexanes through a small pad of silica yielded 0.075 g (91%) of the titled diene: IR (neat) 3050 (m), 2953 (s), 2919 (s), 2849 (s), 1445 (s), 835 (s), 818 (m), 743 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.95 (dd, $J_{cis} = 5.45$, $J = 1.95$ Hz, 1 H, HC-10). 5.78 (dd, $J_{cis} = 5.45$, $J = 2.05$ Hz, 1 H, HC-9), 5.67 (m, 1 H, HC-2), 2,45 (m, 1 H, CH_3CH), 2.17−2.28 (m, 2 H, includes HC-7), 1.97−2.15 (m, 2 H), 1.72−1.83 (m, 2 H), 1.40−1.62 (m, 1 H), 1.18−1.38 (m, 2 H), 1.07 (d, $J = 6.99$ Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 154.3, 140.2, 132.9, 120.8, 51.5, 48.7, 33.9, 32.1, 29.5, 29.2, 20.5; exact mass calcd for $C_{11}H_{16}$ 148.1252, found 148.1223.

Diels−Alder Adduct 13 of *N*-Phenylmaleimide and 9. A solution of **9** (0.0299 g, 0.223 mmol) and *N*-phenylmaleimide (0.0425 g, 0.245 mmol) in benzene (2 mL) was heated at 70 °C for 23 h. The contents of the cooled sealed tube were transferred to a flask, concentrated, and subjected to chromatography (13% ethyl acetate−hexanes, $R_f = 0.18$) to yield 0.0591 g (86%) of **13**: IR (CCl_4) 2930 (m), 1715 (s), 1651 (w), 1633 (w), 1539 (w), 1375 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19−7.45 (m, 5 H, phenyl H), 5.93 (dd, $J = 8.84$, 3.69 Hz, 1 H), 5.64 (dd, $J = 8.84$, 2.51 Hz, 1 H), 3.19 (dd, $J = 8.44$, 6.39 Hz, 1 H), 2.59−2.65 (m, 1 H), 2.41 (d, $J = 8.58$ Hz, 1 H), 2.16−2.20 (m, 1 H), 1.13−2.04 (m, 10 H, including a doublet at δ 1.49, $J = 7.47$ Hz, 3 H, CH_3); ^{1}C NMR ($CDCl_3$) δ 177.5, 176.8, 136.3, 132.0, 128.9, 128.4, 127.3, 126.6,

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[17] See: *Biradicals*; Borden, W. T., Ed.; John Wiley & Sons: New York, 1982.

50.3, 46.6, 31.4, 31.0, 27.8, 26.9, 25.7, 25.5, 24.0, 16.7; exact mass calcd for $C_{20}H_{21}O_2N$ 307.1573, found 307.1620.

Diels–Alder Adduct 14 of *N*-Phenylmaleimide and 10. A solution of **10** (racemic or scalemic) (0.0400 g, 0.270 mmol) and *N*-phenylmaleimide (0.0515 g, 0.297 mmol) in benzene (2 mL) was heated at 80 °C for 18.5 h. The contents of the cooled sealed tube were transferred to a flask, concentrated, and subjected to chromatography (13% ethyl acetate–hexane, $R_f = 0.18$) to yield 0.0604 g (70%) of **14**: IR (CCl_4) 2932 (m), 2853 (w), 1703 (s), 1496 (w), 1385 (m), 1198 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–7.46 (m, 5 H, phenyl H), 6.02 (dd, J = 8.92, 3.72 Hz, 1 H), 5.75 (dd, J = 8.92, 2.61 Hz, 1 H), 3.25 (dd, J = 8.53, 6.39 Hz, 1 H), 2.53–2.58 (m, 1 H), 2.37 (d, J = 8.64 Hz, 1 H), 1.57–1.80 (m, 3 H), 1.52 (d, J = 7.51 Hz, 3 H), 1.00–1.44 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 177.6, 176.9, 136.3, 132.1, 129.0, 128.4, 127.8, 126.6, 51.9, 47.1, 32.1, 27.3, 21.8, 21.6, 20.3, 19.8, 18.8, 16.9, 16.5; exact mass calcd for $C_{21}H_{23}O_2N$ 321.1729, found 321.1715.

Kinetic Resolution of 16. To a solution of Ti(O-*i*-Pr)$_4$ (1.21 g, 1.27 mL, 4.26 mmol) in CH_2Cl_2 (20 mL) was added a solution of L-(+)-DET (1.05 g, 5.11 mmol) in CH_2Cl_2 (6 mL) at −23 °C. After 30 min, a solution of racemic **16**[7] (2.09 g, 4.26 mmol) in CH_2Cl_2 (6 mL) was added slowly. After an additional 30 min, *tert*-butyl hydroperoxide (TBHP) (0.465 mL, 5.5 M, 2.56 mmol) was added, and the solution was stirred for 18 h. The flask was then removed from the cooling bath, and ether (6 mL) and brine (2 mL) were added. After the reaction mixture had been stirred for 1 h, the white precipitate was removed by filtration through a pad of Celite using an ether wash. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The resulting oil was subjected to flash column chromatography (silica gel, 3% ethyl acetate–hexanes, $R_f = 0.23$) to afford 1.09 g (52%) of the nonracemic allylic alcohol (∼8% ee). This product was subjected to the same procedure twice to eventually afford the alcohol with 26% ee.

Nonracemic 2-Oxo-7-(2-*trans*-butenylidene)bicyclo[4.1.0]heptane (17). A solution of the partially resolved **16** (0.373 g, 0.761 mmol) in THF (8 mL) was treated with KH (0.0914 g, 2.28 mmol) for 16 h at ambient temperature. The reaction mixture was added to an excess of water which was extracted with ether. The combined organic layers were dried ($MgSO_4$), concentrated and subjected to chromatography (8% ethyl acetate–hexanes) to yield 0.107 g (87%) of nonracemic **17**. Its ee was assessed by determining that of its Diels–Alder adduct **19** (see below).

Diels–Alder Adduct 19 of *N*-Phenylmaleimide and 17. A solution of **17** (0.0100 g, 0.0620 mmol) and *N*-phenylmaleimide (0.0110 g, 0.0620 mmol) in benzene (2 mL) was heated at 70 °C for 24 h. The contents of the cooled sealed tube were transferred to a flask, concentrated, and subjected to chromatography (35% ethyl acetate–hexanes, $R_f = 0.14$) to yield 0.0158 g (76%) of the Diels–Alder adduct of **17**: IR (CCl_4) 2928 (s), 1770 (s), 1709 (m), 1375 (m), 1167 (w); ^1H NMR ($CDCl_3$) δ 7.32–7.46 (m, 3 H, phenyl H), 7.17–7.20 (m, 2 H, phenyl H), 6.07 (dd, J = 9.06, 3.27 Hz, 1 H, vinyl H), 6.01 (dd, J = 9.06, 1.90 Hz, 1 H, vinyl H), 3.31 (br t, J = 7.66 Hz, 1 H), 2.70–2.75 (m, 1 H), 2.47–2.52 (m, 2 H), 2.12–2.33 (m, 2 H), 1.73–2.07 (m, 5 H), 1.46 (d, J = 7.36 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 207.2, 176.1, 175.9, 139.8, 131.6, 129.0, 128.6, 126.4, 124.9, 51.6, 46.1, 38.5, 34.2, 33.2, 31.8, 26.6, 24.8, 17.7, 16.4; exact mass calcd for $C_{21}H_{21}O_3N$ 335.1522, found 335.1476.

Partial Rearrangement of Nonracemic Allylidenecyclopropane 17. A solution of allylidenecyclopropane **17** and a trace of radical inhibitor in diglyme was heated at reflux for 30 min, producing a 1:1 mixture of **17** and **18** as determined by NMR analysis. The cooled reaction mixture was diluted with pentane and repeatedly washed with water. Solvent removal from the dried ($MgSO_4$) organic layer and separation by chromatography afforded **17** (10% ethyl acetate–hexanes) and **18** (20% ethyl acetate–hexanes).

Note Added in Proof. The calculations reported herein are not inconsistent with the relative singlet and triplet energies of various geometries of vinyl-TMM reported recently by Roth (Roth, W. R.; Winzer, M.; Korrell, M.; Wildt, H. *Liebigs Ann. Chem.* **1995**, 897) in conformationally restricted systems. Correction must be made for the strain relief in Roth's pyrolysis of 2,6-dimethylenebicyclo[3.1.0]hexane and for an extra *syn*-butene-like interaction in the formation of a planar triplet from 2-methylenespiro[2.4]hept-4-ene. However, the 2.8 kcal/mol barrier to closure of the presumed orthogonal singlet from the latter hydrocarbon is too small by 3.4 kcal/mol relative to the current calculation.

Acknowledgment. We thank the National Institutes of Health (T.C.), the National Science Foundation (E.R.D.), and the Department of Energy (J.J.G.) for support of this work.

Supporting Information Available: Tables giving the Cartesian coordinates of all structures reported in Tables 1–3 (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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