

# Ab Initio Study of 1,4-Pentadienyl Electrocyclic Reactions

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The thermochemistry and transition states of the electrocyclic ring closures of the resonance-stabilized 1,4-pentadienyl radical to cyclopenten-3-yl, cyclobut-2-enylmethyl, and 2-vinylcyclopropyl are investigated at Hartree–Fock and coupled-cluster levels of theory. The CCSD(T)//QCISD/cc-pVDZ calculations predict activation barriers of 130, 169, and 236 kJ/mol, respectively, and  $\Delta H$  values of –60, 115, and 155 kJ/mol. Experimental evidence for the appearance of vinylcyclopropyl following photolytic generation of pentadienyl is more likely the result of a distinct electrocyclic reaction than quenching of a two-step mechanism for formation of cyclopentenyl. Higher energy pathways for formation of polycyclic structures are also briefly examined.

## 1. Introduction

The 1,4-pentadienyl radical (**1**) is an archetypal delocalized system, combining the resonance stabilization of allyl with the conformational degrees of freedom of the polyenes. Numerous theoretical and experimental studies have been directed at the structures, formation enthalpies, and conformational dynamics of pentadienyl and its derivatives,<sup>1–16</sup> including several studies focusing on their activity as intermediates in the action of lipoxigenases.<sup>9,17,18</sup> Despite a resonance stabilization energy for pentadienyl of 60–80 kJ/mol,<sup>2,8</sup> electrocyclic formation of the less-studied cyclopenten-3-yl radical (**2**) from the (*E,E*)-pentadienyl chain **1a** is exothermic by about 48 kJ/mol.<sup>13,19</sup> The resulting radical **2** is similarly stabilized by a three-electron, three-carbon  $\pi$  system; Benson and co-

workers calculated the resonance stabilization of cyclopenten-3-yl to be 53 kJ/mol.<sup>4</sup> The mechanism for this cyclization reaction has consequently been a candidate for computational and experimental investigation for over a decade. Other single-step electrocyclic reactions of **1** to form monocyclic radicals will yield cyclobut-2-enylmethyl (**3**) or 2-vinylcyclopropyl (**4**).

Egger and Benson carried out isomerizations of pentadiene to assess the stabilization energy of the daughter radical and observed a small percentage of cyclic byproduct from which they estimated an activation barrier for **1** to **2** of about 100 kJ/mol.<sup>2</sup> This is perhaps the earliest experimental study of the electrocyclic reactions of pentadienyl and remains one of few. In 1981, Walton and co-workers reported the ESR spectra of the *E,E* and *E,Z* conformers of **1**.<sup>7</sup> In the course of that work, they investigated several mechanisms for generating the pentadienyl radicals, including the ring opening of **3**. Fox et al. performed the earliest computational study of the cyclization of **1c** to **2**, an AM1 semiempirical analysis that formed part of a larger investigation of triphenylmethyl radicals.<sup>10</sup> They predicted activation energies of 113 kJ/mol for a conrotatory ring-closing mechanism and 159 kJ/mol for disrotatory, with a reaction enthalpy of –72 kJ/mol. Following this, De Maré, Deslauriers, and Collin used restricted open-shell Hartree–Fock (ROHF) wave functions and a 3-21G\* basis set as part of a combined experimental and computational study of cyclopentenyl isomerizations.<sup>11,12</sup> They predicted a reaction enthalpy of –79 kJ/mol for the cyclization and also examined barriers to conformational isomerizations in **1** and **4**. In their experimental study of pentadienyl, they found that photolysis products of 3-methylpentadiene in solution included cyclopentadiene as a major product, presumably formed by the elimination of H atom from cyclopentenyl. Surprisingly, carrying out the photolysis in the presence of DI led to the formation of vinylcyclopropene, suggesting that the vinylcyclopropyl radical **4** could be an intermediate to formation of **2** from pentadienyl. Accompanying calculations predicted that the formation of **4** from **1a** is endothermic by 107 kJ/mol, energy that could be drawn from the excess energy of photolysis. Yamamoto, Ohno, and Eguchi chose the **1c** → **2** ring-

(1) Snyder, L. C.; Amos, T. *J. Chem. Phys.* **1965**, *42*, 3670–3683.

(2) Egger, K. W.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 241–246.

(3) Sando, K. M.; Harriman, J. E. *J. Chem. Phys.* **1967**, *47*, 180–185.

(4) Furuyama, S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1970**, *2*, 93–99.

(5) Hinchliffe, A.; Cobb, J. C. *J. Mol. Struct.* **1974**, *23*, 273–279.

(6) Lehr, R. E.; Wilson, J. M.; Harder, J. W.; Cohenour, P. T. *J. Am. Chem. Soc.* **1976**, *114*, 4867–4875.

(7) Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633–641.

(8) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3131–3136.

(9) Bascetta, E.; Gunstone, F. D.; Scrimgeour, C. M.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, *110*, 110–112.

(10) Fox, M. A.; Gaillard, E.; Chen, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 7088–7094.

(11) Maré, G. R. D.; Deslauriers, H.; Collin, G. J. *Res. Chem. Intermed.* **1990**, *14*, 133–159.

(12) Maré, G. R. D.; Collin, G. J. *J. Mol. Struct.* **1991**, *233*, 231–245.

(13) Clark, K. B.; Culshaw, P. N.; Griller, D.; Lossing, F. P.; Simões, J. A. M.; Walton, J. C. *J. Org. Chem.* **1991**, *56*, 5535–5539.

(14) Fort, R. C.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1992**, *58*, 211–216.

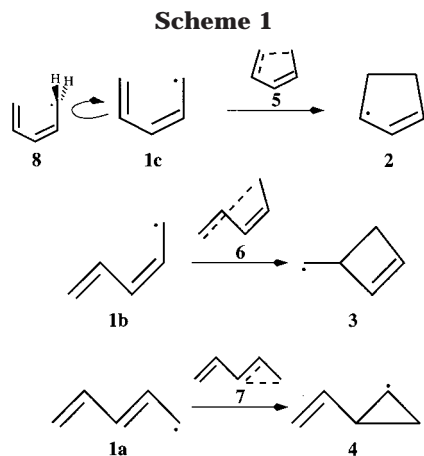
(15) Karadakov, P. B.; Gerralt, J.; Raos, G.; Cooper, D. L.; Raimondi, M. *J. Am. Chem. Soc.* **1994**, *116*, 2075–2084.

(16) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Org. Chem.* **1996**, *61*, 9264–9271.

(17) DeGroot, J. J. J. M. C.; Veldink, G. A.; Vliegththa, J. F. G.; Boldingh, J. *Biochim. Biophys. Acta* **1975**, *377*, 71–79.

(18) Nelson, M. J.; Seitz, S. P.; Cowling, R. A. *Biochemistry* **1990**, *29*, 6897–6903.

(19) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.



closing reaction as an analogue in a more recent investigation of dienoyl radicals, predicting the reaction enthalpy to be  $-45$  kJ/mol and the barrier to be 162 kJ/mol at the UHF/6-31G\* level.<sup>16</sup>

Fort and co-workers have carried out the highest-level study on pentadienyl reported to date, a series of QCISD/6-31G\* calculations on the conformations and intervening transition states.<sup>14</sup> They found the (*E,Z*) and (*Z,Z*) conformers to lie 9 and 23 kJ/mol higher, respectively, than the (*E,E*). The activation barriers lay roughly 43 kJ/mol above the (*E,E*) energy.

Our *ab initio* studies of similar radicals, including  $C_4H_5$ ,<sup>20,21</sup>  $C_3H_3O$ ,<sup>22</sup> and the OCNO isoelectronic series,<sup>23</sup> reveal that relative energies among structural isomers are sometimes quite poorly predicted by a variety of methods, including unrestricted and restricted Hartree–Fock. Most striking among these findings was the range of predicted relative energies for cyclobuten-3-yl relative to 2-butyne-1-yl, from 12 kJ/mol to over 80 kJ/mol, even among post-SCF techniques. Previous computational studies of the pentadienyl electrocyclic reactions have been exclusively at semiempirical or SCF levels of theory, and have primarily focused on the thermochemistry of the  $1 \rightarrow 2$  or  $1 \rightarrow 4$  schemes. Transition state properties have so far been limited to those described by Fox et al.’s semiempirical work. We present here a systematic, *ab initio* study of the electrocyclic reactions of pentadienyl that form **2–4**, including optimization of the respective transition states **5–7**, and a related torsional transition state **8**, with evidence for convergence of the methods used. A cruder examination of the electrocyclic pathways to the affiliated polycyclic structures **9–12** from **1** is also presented.

## 2. Methods

This work is part of a broader study of the global  $C_5H_7$  potential energy surface. Structural isomers of  $C_5H_7$  were initially selected by considering single hydrogen abstractions from the 25 closed-shell  $C_5H_8$  isomers. Surveys of the optimized geometries and energies of the  $C_5H_7$  isomers were carried out at the ROHF and UHF levels using Dunning’s correlation consistent, double- $\zeta$  cc-pVDZ basis set<sup>24</sup> (105 contracted functions). These surveys excluded radical carbenes, anticipating

that they would have particularly high energies, but did include monocyclic and polycyclic species.

The structural isomers associated with the pentadienyl electrocyclic reactions were then re-optimized at the QCISD level, effectively a truncated coupled-cluster (CC) method that incorporates the contributions of singly and doubly excited molecular orbital configurations to the correlation energy.<sup>25</sup> In our previous studies, the UHF level has been found to predict relative energies typically to within 40 kJ/mol of experimental values. In contrast, QCISD has routinely predicted relative energies of structural isomers to within 10 kJ/mol of experimental values, even when spin contamination was substantial,<sup>21</sup> and we have shown that methods immune to spin contamination converge toward the QCISD values when expanded to include contributions to the dynamical correlation energy.<sup>23</sup> Symmetry was not constrained in any of the initial geometry optimizations, but **1a** and **2** converge to  $C_{2v}$  symmetry; **1b**, **10**, and **12** converge to  $C_s$  symmetry, and **1c** converges to  $C_2$  symmetry.

The schemes for formation of the monocycles were assumed to proceed from the most similar conformer of pentadienyl: **1a** for formation of **4**, **1b** for formation of **3**, and **1c** for formation of **2**. The STQN methods of Schlegel and co-workers,<sup>26,27</sup> were used when possible to identify transition states, but these often identified other saddle points on the surface. Conformational changes occur in **1** by torsion about any C–C bond, including torsions that connect two equivalent conformers, such as the  $180^\circ$  rotation of the terminal methene group in **1c** that occurs via transition state **8**. The transition states for these motions lie lower in energy than those for the electrocyclic bond formation, and are sometimes sufficiently similar in geometry that they may be located during the electrocyclic transition state search. The default semiempirical estimates of the second derivatives along methene torsion and bond formation coordinates were also generally too poor to correctly identify the number of coordinates with negative curvature. Numerical evaluations of these were enforced almost without exception during the transition state searches at all levels of theory.

The stationary-point geometries optimized at the QCISD/cc-pVDZ level were used for single-point energy calculations at the CCSD(T)/cc-pVDZ to test convergence of the coupled cluster expansion. Basis set convergence was tested by single-point QCISD/cc-pVTZ calculations at six of those geometries. The CCSD(T) level incorporates an estimated contribution to the wave functions from triply substituted configurations and the cc-pVTZ basis set (248 contracted functions) adds f-orbital functionality to the carbon atomic orbitals.

Vibrational analyses were carried out at the QCISD/cc-pVDZ-optimized geometries for **1a,c**, **2**, **5**, and **8** to predict standard entropies and zero-point vibrational energy corrections and to verify the correct curvature of the surface in the case of transition states. These time-consuming QCISD calculations yield zero-point corrections that differ by less than 2 kJ/mol from the corresponding ROHF corrections and by 2–5 kJ/mol from the UHF values. Higher energy structures such as **4** and **7** were also found to be susceptible to sporadic convergence errors in the SCF wave function during the numerical QCISD vibrational analysis when using default stepsizes. We therefore rely uniformly on the ROHF zero-point corrections in the tabulated values, which imposes a likely additional error of some 2 kJ/mol. Molecular point group symmetry was enforced in vibrational and single-point calculations for any structure that had optimized to a symmetric form.

Spin contamination remains a concern, but our experience has been that relative energies are better predicted by CI and coupled cluster methods built on a single UHF reference than by multireference calculations of similar computational demands. The highest values of  $\langle S^2 \rangle$  in the UHF reference

(20) Parker, C. L.; Cooksy, A. L. *J. Phys. Chem.* **1998**, *102*, 6186–6190.

(21) Parker, C. L.; Cooksy, A. L. *J. Phys. Chem. A* **1999**, *103*, 2160–2169.

(22) Cooksy, A. L. *J. Phys. Chem.* **1998**, *102*, 5092–5099.

(23) Cooksy, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 4003–4013.

(24) T. H. Dunning, *J. J. Chem. Phys.* **1989**, *90*, 1007–1023.

(25) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

(26) Peng, C.; Schlegel, H. B. *Isr. J. Chem.* **1993**, *33*, 449–454.

(27) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49–56.

**Table 1.** CCSD(T)//QCISD/cc-pVDZ Relative Energies (kJ/mol) and UHF  $\langle S^2 \rangle$  Values of Stationary Point Geometries<sup>a</sup>

	$\Delta E$	$\langle S^2 \rangle$		$\Delta E$	$\langle S^2 \rangle$
<b>1a</b> ( <i>E,E</i> -1,4-pentadienyl)	37	1.20	<b>6</b> ( <b>1b</b> $\rightarrow$ <b>3</b> ts)	214	1.13
<b>1b</b> ( <i>E,Z</i> -1,4-pentadienyl)	46	1.22	<b>7</b> ( <b>1a</b> $\rightarrow$ <b>4</b> ts)	273	1.46
<b>1c</b> ( <i>Z,Z</i> -1,4-pentadienyl)	60	1.22	<b>8</b> ( <b>1c</b> CH <sub>2</sub> torsion ts)	132	0.78
<b>2</b> (cyclopenten-3-yl)	0	0.96	<b>9</b> (bicyclo[2.1.0]pent-2-yl)	187	0.77
<b>3</b> (cyclobut-2-enylmethyl)	161	0.83	<b>10</b> (bicyclo[2.1.0]pent-5-yl)	211	0.76
<b>4</b> (2-vinylcyclopropyl)	191	0.82	<b>11</b> (bicyclo[1.1.0]but-2-ylmethyl)	230	0.77
<b>5</b> ( <b>1c</b> $\rightarrow$ <b>2</b> ts)	190	1.26	<b>12</b> (bicyclo[1.1.1]pent-2-yl)	253	0.76

<sup>a</sup> Energies include ROHF/cc-pVDZ zero-point corrections.

functions are roughly 1.3 for **1** and **5** and 1.46 for **7** at the QCISD-optimized geometry; values for all other cases are 1.1 or below. Although we carried out geometry optimizations of **1a** and **2** using multiconfiguration SCF up to a (7,7) active space, limited multireference CI (MRCI), and restricted open-shell CISD (ROCISD),<sup>28</sup> the known relative energy of these two isomers could not be accurately predicted with the available resources. Even an MRCI calculation incorporating all single and double substitutions into the virtual orbitals from a (5,5) reference wave function overestimated that energy by 30 kJ/mol. The selected active spaces included all occupied orbitals nominally participating in the electrocyclic rearrangement, and those virtual orbitals that yielded the lowest variational MCSCF energy at the QCISD-optimized geometry.

Spin contamination can invalidate both the geometries and relative energies predicted by UHF-based methods. Bally, Hrovat, and Borden have established in a series of studies that UHF optimizations of the polyenyl radicals significantly underestimate the alternation in bond lengths along the carbon chain, so the geometries and the associated spin localization (used to predict experimentally measured hyperfine constants) are incorrectly modeled.<sup>29,30</sup> A tendency toward greater spin contamination in the conjugated systems also overemphasizes the stabilizing influence of spin polarization in the reaction endpoints relative to the transition states, and causes UHF to often overestimate reaction barrier heights.<sup>30</sup> However, these deficiencies are generally reduced by a reasonably large CI or CC expansion of the wave function. The excellent convergence of relative energies with respect to level of CC substitutions in the present results implies that the principal effects of spin contamination have been eliminated. Despite their concerns over spin contamination, Borden et al. found that UHF-based CCSD predictions of the polyenyl properties give excellent agreement with the available experimental data, often better than ROHF-based wave functions requiring the same computational resources. Wong and Radom also concluded that QCISD methods could accurately predict the geometries and energetics of alkene-radical reactions,<sup>31</sup> and recent studies of homolytic reactions concur that CCSD(T) provides adequate protection against spin contamination in evaluating transition states.<sup>32,33</sup>

We conclude, therefore, that it remains more important to adequately model the dynamical electron correlation (from CI substitutions involving the lower energy valence orbitals) in these molecules than the nondynamical correlation (which is the strength of the multireference methods).

For comparison to earlier work, AM1 calculations were carried out near the geometry for the transition state **5**. The AM1, UHF, and UHF-reference calculations, including QCISD and CCSD(T), relied on the Gaussian 98 suite of programs.<sup>34</sup> The ROHF and ROHF-based multireference calculations were carried out with Gamess.<sup>35</sup> These programs were executed on a variety of SGI, Compaq, and Intel Linux workstations.

(28) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Handy, N. C.; H. F. Schaefer, I. *Phys. Scr.* **1980**, *21*, 312–322.

(29) Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460–10464.

(30) Bally, T.; Hrovat, D. A.; Borden, W. T. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3363–3371.

(31) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 8582–8588.

(32) Li, X. Z.; Paldus, J. *Int. J. Quantum Chem.* **2000**, *77*, 281–290.

(33) Yuan, H.; Cremer, D. *Chem. Phys. Lett.* **2000**, *324*, 389–402.

**Table 2.** Comparison of Reaction Energies (kJ/mol)<sup>a</sup>

reaction	UHF	ROHF	CCSD(T)	previous
<b>2</b> $\rightarrow$ <b>1a</b>	$\Delta H$ 1	32	37	44 (14) <sup>b</sup> , 48 (6) <sup>c</sup> , 54 <sup>d</sup> , 50 <sup>e</sup>
<b>1a</b> $\rightarrow$ <b>1b</b>	$\Delta H$ 10	8	9	7, <sup>d</sup> 9 <sup>f</sup>
	$E_a$			42 <sup>f</sup>
<b>1b</b> $\rightarrow$ <b>1c</b>	$\Delta H$ 19	14	14	18 <sup>d</sup>
	$E_a$			33 <sup>f</sup>
<b>1c</b> $\rightarrow$ <b>2</b>	$\Delta H$ -30	-55	-60	-45, <sup>d</sup> -72 <sup>g</sup>
	$E_a$ 159	171	130	113, <sup>g</sup> 100, <sup>h</sup> 162 <sup>i</sup>
<b>1b</b> $\rightarrow$ <b>3</b>	$\Delta H$ 167	95	115	
	$E_a$ 218	210	169	
<b>1a</b> $\rightarrow$ <b>4</b>	$\Delta H$ 200	124	155	107 <sup>e</sup>
	$E_a$ 256	284	236	
<b>1a</b> CH <sub>2</sub> torsion	$E_a$			86 <sup>f</sup>
<b>1c</b> CH <sub>2</sub> torsion	$E_a$ 104	35	72	
<b>3</b> $\rightarrow$ <b>9</b>	$\Delta H$ 35	35	27	
	$E_a$ 84			
<b>2</b> $\rightarrow$ <b>10</b>	$\Delta H$ 243	196	211	
	$E_a$ 277			
<b>4</b> $\rightarrow$ <b>11</b>	$\Delta H$ 54	57	39	
	$E_a$ 101			
<b>3</b> $\rightarrow$ <b>12</b>	$\Delta H$ 118	114	92	
	$E_a$ 192			

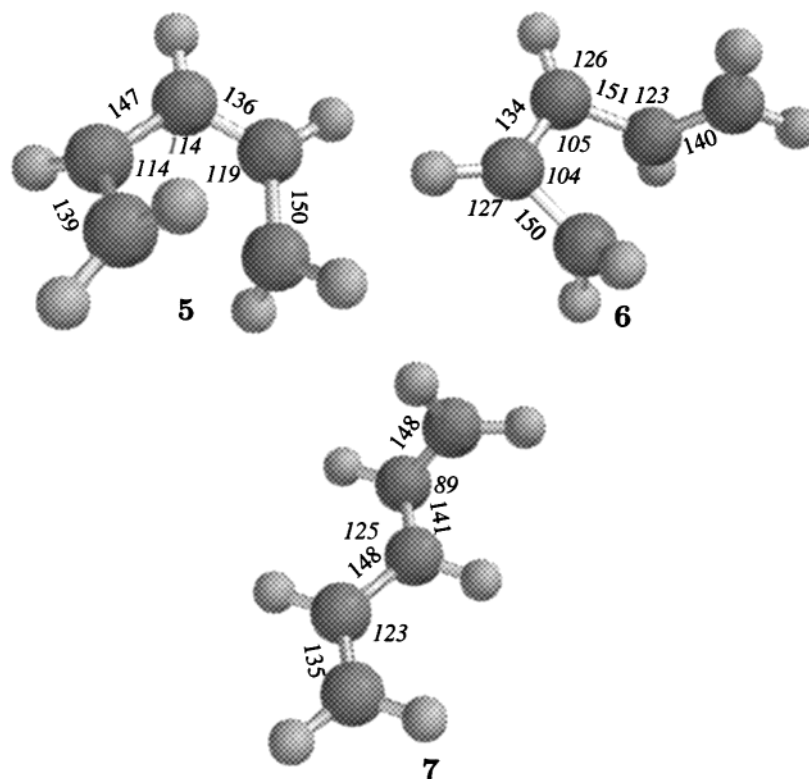
<sup>a</sup> cc-pVDZ basis set; CCSD(T) at QCISD optimized geometries; UHF zero-point corrections included for UHF; ROHF zero-point corrections included for ROHF and CCSD(T). <sup>b</sup> Reference 19; expt. <sup>c</sup> Reference 13; expt. <sup>d</sup> Reference 11; ROHF/3-21G\*. <sup>e</sup> Reference 12; ROHF/3-21G\*. <sup>f</sup> Reference 14; QCISD/6-31G(d). <sup>g</sup> Reference 10; AM1. <sup>h</sup> Reference 2; empirical. <sup>i</sup> Reference 16; UHF/6-31G\*.

### 3. Results and Discussion

**3.1. General Results.** The structural isomer surveys at both restricted and unrestricted Hartree–Fock levels agree that cyclopenten-3-yl (**2**) is the most stable C<sub>5</sub>H<sub>7</sub> isomer and that the only other structural isomers lying within 80 kJ/mol of **2** are pentadienyl (**1**), cyclopenten-4-yl, and 1,3-butadien-2-ylmethyl. However, the surveys differ significantly as to the relative energies of these species. A comparison of relative energies and  $\langle S^2 \rangle$  values among structures involved in the pentadienyl electrocyclic reactions is presented in Table 1, and Table 2 presents reaction  $\Delta H$  and  $E_a$  values, including those from previous experimental and computational work where

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(35) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. J.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.



**Figure 1.** QCISD/cc-pVDZ-optimized transition-state geometries. Bond lengths are given in pm and CCC angles (in italics) in degrees; all CH bond lengths are 110 pm to within 0.5 pm, and unmarked CCH bond angles are between  $116^\circ$  and  $124^\circ$ .

available. The CCSD(T) relative energy of 37 kJ/mol for **1a** relative to **2** is well within the 14 kJ/mol error of an older 44 kJ/mol experimental value,<sup>19</sup> but too low given a revised value of 48(6) kJ/mol determined by Walton and co-workers in 1991.<sup>13</sup> This 10 kJ/mol disparity between CCSD(T) and experimental relative energies is comparable to those seen in the  $C_4H_5$  isomers,<sup>21</sup> and 10 kJ/mol is our estimated accuracy in these results (although we may expect better accuracy in relative conformational energies). Although ROHF values of 50 and 54 kJ/mol have been previously reported for this energy difference, these were for a relatively small basis, 3-21G\* (59 contracted functions). We find that the ROHF value worsens, dropping to 32 kJ/mol, with expansion to the cc-pVDZ basis.

The discrepancies of 30–40 kJ/mol between UHF and CCSD(T) relative energies seen in Table 2 are typical of those seen in earlier work;<sup>21,23</sup> the largest here are 40–50 kJ/mol. The ROHF values are generally in better agreement with CCSD(T); the largest discrepancies are the set of activation energies, 41–48 kJ/mol lower at the CCSD(T) level than at ROHF for the electrocyclic reactions and 37 kJ/mol higher for the methene torsion. Our ROHF and CCSD(T) values for the electrocyclic reaction enthalpies differ in most cases by less than 20 kJ/mol.

The effect of incrementing the level of theory to CCSD(T) from QCISD changes the  $\Delta H$  values by less than 3 kJ/mol and the  $E_a$  values by less than 7 kJ/mol. The only previous QCISD calculations on these systems, using the slightly smaller 6-31G(d) basis set (89 contracted functions), predicted the relative energy of **1c** relative to **1a** to be 23 kJ/mol, identical to our value at the QCISD and CCSD(T) levels. As further evidence that the basis set is well-converged, extension from double- $\zeta$  to triple- $\zeta$  shifts each relative energy by less than 3 kJ/mol. Because

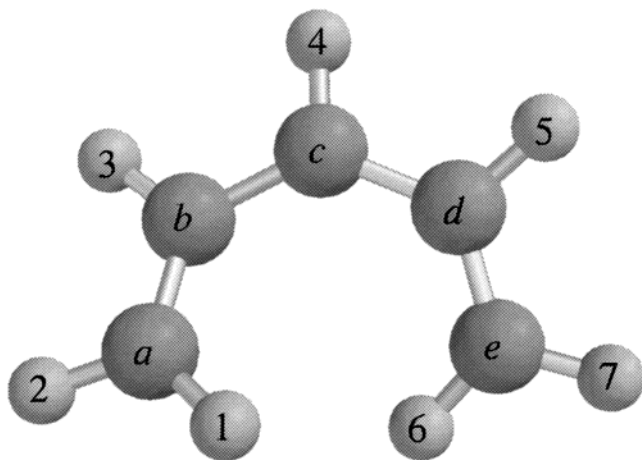
Dunning's correlation-consistent basis sets are specifically designed to converge asymptotically to the complete-basis limit, this is an especially strong indication that little is to be gained by further expansion of the basis set.

The methene group torsion in **1c** was found to have a barrier of 72 kJ/mol. This is somewhat lower than the 86 kJ/mol methene torsion barrier found for **1a** by Fort et al., presumably because this motion in **1c** alleviates some of that repulsion between the endocyclic methene hydrogens that causes the *Z,Z* conformer to be nonplanar in the first place.

Zero-point corrections to the  $\Delta H$  values run as large as 15 kJ/mol in this set, because vibrational motions in **2** are considerably constrained relative to the single bond torsions available in the other species. While the ring atoms are even more constrained in the vinylcyclopropyl radical, the torsion about the C–C bond linking the vinyl and cyclopropyl groups does not disrupt any  $\pi$ -electron conjugation, as in the case of the pentadienyls. Consequently, structure **4** has a zero-point energy roughly equal to that of the chains.

**3.2. Pentadienyl  $\rightarrow$  Cyclopentenyl (**1c**  $\rightarrow$  **2**).** The *Z,Z* conformer of pentadienyl **1c** can be obtained from the more stable *E,E* conformer **1a** by two sequential hindered torsions about partial double bonds, with the *E,Z* conformer **1b** as an intermediate. The barriers for both of these torsions were predicted by Fort et al. to lie between 42 and 43 kJ/mol relative to **1a**.<sup>14</sup>

The transition state for the cyclization of **1c** to **2** was found at activation energies ranging from 130 kJ/mol to 171 kJ/mol, with the CCSD(T) value of 130 kJ/mol our best estimate. The earlier calculations of this energy by semiempirical<sup>10</sup> and UHF<sup>16</sup> methods agree to within about 30 kJ/mol with this result.



**Figure 2.** Atom labels for **1c** used to define geometric parameters.

The pentadienyl cyclization was of only peripheral interest in these previous studies, and transition state geometries were not reported. Figure 1 shows the QCISD/cc-pVDZ optimized geometry for **5**, and Table 3 lists three of the relevant parameters in the transition: the  $C_a - C_e$  separation  $r_{ae}$  and the methene torsion angles  $\phi_a$  and  $\phi_e$ , which have been averaged over the CCCH dihedral angles as follows:

$$\phi_a = (\phi_{eab1} + \phi_{eab2} \pm \pi)/2 \quad (1)$$

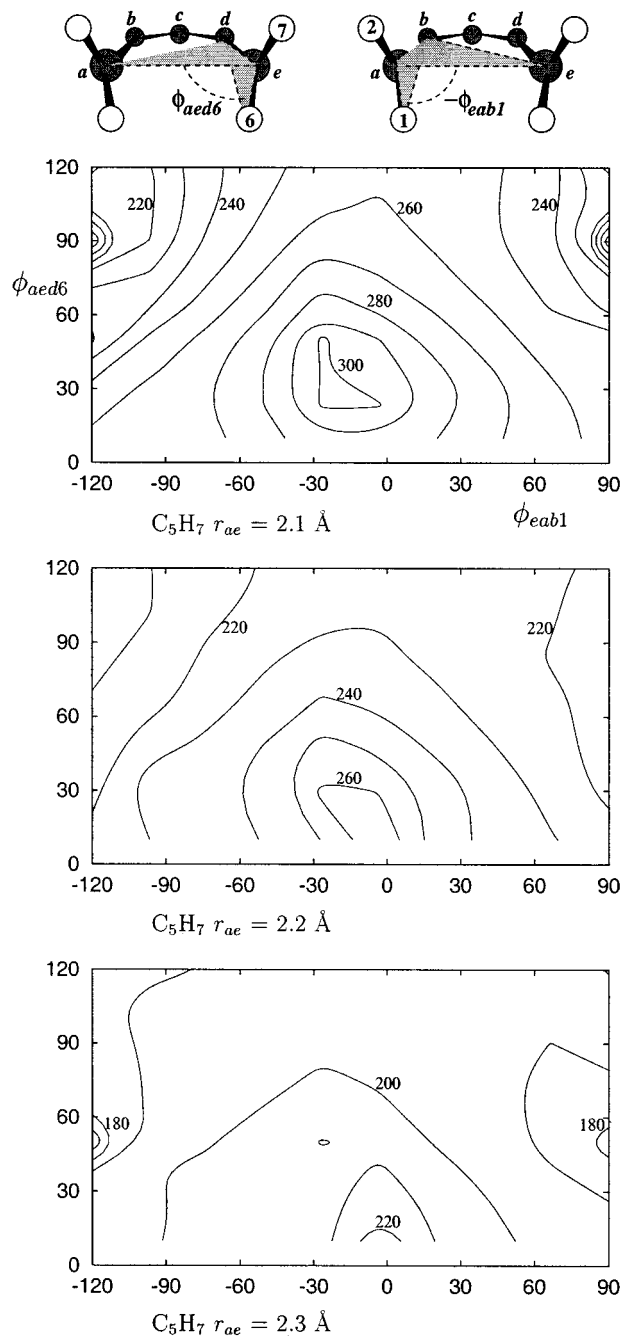
$$\phi_e = (\phi_{aed6} + \phi_{aed7} \pm \pi)/2 \quad (2)$$

with the atoms labeled according to Figure 2 and using the minus sign when either  $\phi_{eab1}$  or  $\phi_{aed6}$  are less than zero. By these definitions,  $\phi_{a,e} = 0$  corresponds to the methene group lying parallel to the CCC plane,  $\phi_{a,e} = \pi/2$  implies the methene rotated perpendicular to the CCC plane, and  $\phi_a$  and  $\phi_e$  have the same sign for conrotatory motion, opposite signs for disrotatory. By measuring the CCCH dihedrals across the  $r_{ae}$  bond (e.g., using  $\phi_{eab1}$  rather than  $\phi_{abc1}$ ), these  $\phi$  values more closely reflect the orientation of the methenes relative to each other, rather than relative to the local carbon atom plane.

The CCCC dihedral angles are predicted to be  $31^\circ$  and  $2^\circ$ . Transition state geometries at the HF levels are qualitatively similar to the QCISD geometry; the ROHF value of  $r_{ae}$  is  $0.14 \text{ \AA}$  smaller and the methene torsion angles differ by  $10^\circ$  or less. In all cases, only a single transition state is found, having one nearly perpendicular methene, and the other methene leaning at a roughly  $25^\circ$  slant.

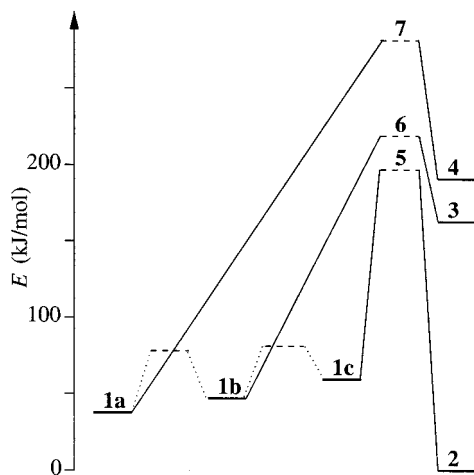
The experimental study by Lehr et al. on substituted pentadienyls found that fewer than 13% of the products had the stereochemistry of the disrotatory mechanism.<sup>6</sup> Lehr et al. noted that a disrotatory pathway is predicted using Woodward and Hoffman rules guided by the HOMO molecular orbital symmetry, but that this reasoning conflicts with other predictive methods in the case of the analogous cyclization of allyl radical to cyclopropyl. They concluded that steric factors are likely to play a dominant role in favoring the conrotatory path in the pentadienyl ring-closing.<sup>6</sup>

Fox et al. reported an AM1 activation barrier some  $45 \text{ kJ/mol}$  higher for the disrotatory mechanism than for the conrotatory.<sup>10</sup> We carried out a cursory three-dimensional



**Figure 3.** Contour plots of AM1 potential energy surfaces near the transition state **5**. The contour spacing is  $10 \text{ kJ/mol}$ . In each plot, the origin corresponds approximately to coplanar methene groups. Motion to the upper left from the origin corresponds to the conrotatory path; motion to the upper right corresponds to disrotatory.

search of the AM1 potential energy surface in the area of the transition state, fixing the parameters  $\phi_{eab1}$ ,  $\phi_{aed6}$ , and  $r_{ae}$  and optimizing all other parameters. Results from this mapping are shown at three bond lengths in Figure 3, each plot based on between 115 and 135 partial optimizations. The map illustrates that the transition state along the path from **1c** to **2**, at roughly  $r_{ae} = 2.2 \text{ \AA}$ , occurs *after* one of the methenes has found a perpendicular orientation ( $\phi_{eab1} \approx 90^\circ$ ) to be most stable. Once either methene becomes perpendicular to the carbon chain, the association of the geometry with either conrotatory or disrotatory motion is lost, and that appears to be the case



**Figure 4.** Reaction diagrams for the electrocyclic reactions of **1** based on CCSD(T)//QCISD/cc-pVDZ energies.

**Table 3.** Comparison of Transition State Geometries for **1c**→**2**

	C <sub>5</sub> H <sub>7</sub>		C <sub>13</sub> H <sub>19</sub> conrotatory	C <sub>13</sub> H <sub>19</sub> disrotatory
	QCISD	AM1	AM1	AM1
<i>r</i> <sub>ae</sub> (Å)	2.277	2.199	2.158	2.214
<i>φ</i> <sub>a</sub> (deg)	87	88	80	-78
<i>φ</i> <sub>e</sub> (deg)	65	69	70	69

for the AM1 transition state as well as those found by ab initio methods. Although not as rigorously mapped, the QCISD reaction surface near the transition state is qualitatively no different.

The investigation of Lehr et al. was carried out using 1,1'-dicyclohexenylmethyl (C<sub>13</sub>H<sub>19</sub>), which ties the two carbons at each end of the chain to a six-membered ring and completely quenches the CH<sub>2</sub> torsion through **8**. In the case of pentadienyl, molecules that can climb the 130 kJ/mol barrier to form the transition state **5** have more than enough energy to overcome the 72 kJ/mol barrier to CH<sub>2</sub> torsion in the *Z,Z* conformer prior to cyclization, and indeed this two-step process is the lowest energy pathway to the "disrotatory" product in the unsubstituted pentadienyl. With that interconversion quenched in 1,1'-dicyclohexenylmethyl, we find that there are now two transition states on the AM1 surface, with the barrier for disrotatory ring-closure 12 kJ/mol higher than for conrotatory. As shown in Table 3, the transition state geometries deviate from the C<sub>5</sub>H<sub>7</sub> transition state by a tilt of the perpendicular methene roughly 10° in either direction, and by a *r*<sub>ae</sub> bond length shifted lower for the conrotatory mechanism and higher for the disrotatory. These findings are consistent with a weak perturbation by the cyclohexene substitutions away from a single transition state shared by both rotatory paths in the unsubstituted pentadienyl.

### 3.3. Pentadienyl → Cyclobutenylmethyl (**1b** → **3**).

Of the three electrocyclic reactions shown in Scheme 1, only the first is exothermic. Formation of the cyclobutenylmethyl radical **3** is predicted to be endothermic by 115 kJ/mol, but the barrier is found to be 169 kJ/mol, only 40 kJ/mol higher than the barrier for the **1c** → **2** reaction.

The only previous mention of this reaction appears to be for the reverse process; cyclobutenylmethyl radical was employed by Davies et al. as a precursor to pentadienyl.<sup>7</sup> In fact, this monocyte has the lowest return activation

**Table 4.** Proton Hyperfine Constants (Gauss)

<b>1a</b>		<b>1b</b>		<b>3</b>	
QCISD	expt <sup>a</sup>	QCISD	expt	QCISD	expt
-14.1	11.6	-15.6	14.4	-25.1	21.0
-11.8	10.4	-12.2	10.1	-24.8	21.0
-11.8	10.4	-11.4	9.7	6.7	9.9
-11.0	9.6	-10.5	9.2	-5.4	9.9
-11.0	9.6	-9.8	8.5	5.1	2.6
3.8	3.3	4.0	3.6	-5.1	1.1
3.8	3.3	3.4	3.1	-1.9	0.5

<sup>a</sup> Reference 7. The sign is not determined in typical experimental measurements.

barrier, 54 kJ/mol, of the reactions in Scheme 1. The QCISD transition state **5**, shown in Figure 1, is even less likely to discriminate between conrotatory and disrotatory pathways than **4**. The *r*<sub>ad</sub> separation is 2.08 Å at this geometry, and the torsion angles (evaluated as in Table 3) are 86° and 80°. The CCCC dihedral angle within the cyclobutyl structure is 3°, and the torsion angle of the methene out of this structure is 114°.

Walton et al. obtained proton hyperfine constants from the ESR spectra of **1a**, **1b**, and **3**, which are compared to our predicted values in Table 4. Predictive accuracy for these values is one arena in which QCISD has been found to perform fairly well compared to other methods.<sup>36</sup>

**3.4. Pentadienyl → Vinylcyclopropyl (**1a** → **4**).** Indirect observation of this reaction by De Maré, Deslauriers, and Collin provides persuasive experimental evidence that, in addition to the one-step cyclization **1c** → **2**, a second pathway for formation of **2** via the vinylcyclopropyl intermediate **4** also exists.<sup>11</sup> We also note the recent finding by Radosevich and Wiest that the hexatriene radical cation, with a π system isoelectronic to pentadienyl, undergoes ring closure by means of a bicyclic intermediate, incorporating a cyclopropyl ring.<sup>37</sup> Nonetheless, a similar mechanism for pentadienyl is problematic for two reasons.

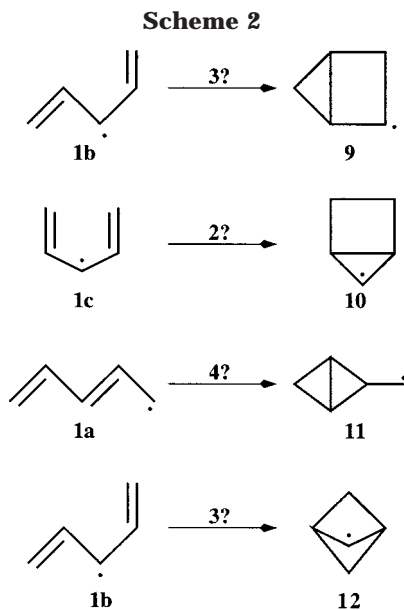
The first step of this pathway, formation of **4** by bonding atoms C<sub>a</sub> and C<sub>c</sub>, can be traced from **1a** through the transition state **7**, but with an activation barrier which we find to lie nearly 100 kJ/mol higher than for the one-step cyclization discussed above. The transition state for this process, drawn in Figure 1, is characterized by a separation of 2.02 Å along the bond formation coordinate and average dihedrals *φ*<sub>a</sub> and *φ*<sub>c</sub> of 83° and -61°, respectively. The carbon chain attached to the incipient cyclopropyl ring is nearly flat, with a CCCC dihedral angle of less than 1°, and is at a dihedral of 121° to the carbons in the ring.

Subsequent steps in this mechanism must break the C<sub>a</sub>-C<sub>c</sub> bond and fuse the C<sub>a</sub>-C<sub>e</sub> bond. We conclude, following fruitless transition-state searches at the UHF and ROHF levels, that this process cannot take place in concerted fashion because the methene hydrogens are simply too constrained in the cyclopropyl group to permit the formation of the C<sub>a</sub>-C<sub>e</sub> bond prior to complete disruption of the C<sub>a</sub>-C<sub>c</sub> bond. Such disruption returns the molecule to one of the conformers of **1**, rather than continuing forward toward **2**.

This is not a consideration in the hexatrienyl cation ring closure, because the three-membered ring in that

(36) Cooksy, A. L.; Tao, F.-M.; Klemperer, W.; Thaddeus, P. *J. Phys. Chem.* **1995**, *99*, 11095-11100.

(37) Radosevich, A. T.; Wiest, O. *J. Org. Chem.* **2001**, *66*, 5808-5813.



instance undergoes cleavage of the bond analogous to our  $C_b-C_c$  bond, leading to a second, monocyclic intermediate.<sup>37</sup> While it is feasible to break the  $C_b-C_c$  bond in **4**, this forms a radical carbene that lies over 350 kJ/mol above **2** at the ROHF and QCISD levels and is hence an entirely improbable intermediate in this reaction.

The rearrangement of vinylcyclopropene to cyclopentene, which has recently been predicted by multireference calculations to proceed via a single-step process,<sup>38,39</sup> is another tempting analogue to the hypothetical second step in a  $1a \rightarrow 2 \rightarrow 4$  mechanism. The vinylcyclopropene rearrangement differs, however, in that complete cleavage of either of two equivalent C–C bonds in the cyclopropyl group forms a high-energy 1-pentene-3,5-diyl biradical intermediate. The concerted mechanism, in which the transition state is essentially a highly strained chain, competes very favorably for formation of the five-membered ring in this case, despite an activation barrier of nearly 200 kJ/mol. The analogous bond cleavage in **4** instead returns the molecule to a much more stable structure **1**, and direct conversion of **4** to **2** therefore appears unlikely.

**3.5. Pathways to Polycyclics.** If vinylcyclopropyl is not an intermediate in the formation of **2** from **1**, it may appear at early times as one of the few products formed by unimolecular reactions of **1**, in the absence of bond cleavage or hydrogen shift reactions. Aside from **2**, **3**, and **4**, possible structures for these molecules include the polycyclic isomers shown in Scheme 2: bicyclo[2.1.0]pent-2-yl (**9**), bicyclo[2.1.0]pent-5-yl (**10**), bicyclo[1.1.1]pent-2-yl (**11**), and bicyclo[1.1.0]but-2-ylmethyl (**12**). (A final monocyclic form, 1,2-dimethenecycloprop-3-yl radical, formed by establishing a bond between the b and d carbons of pentadienyl, reverts spontaneously to pentadienyl at the Hartree–Fock level.)

The most stable of these bicyclo radicals is **9**, which may be formed in a pathway analogous to the stepwise mechanism found for hexatrienyl cation.<sup>37</sup> Davies et al. report the formation of the cyclopenten-4-yl radical from

bicyclo[2.1.0]pentane and *tert*-butoxyl radical, and propose that this transformation occurs via the intermediate **9**.

Searches were not carried out for transition states of the concerted formation of these radicals from pentadienyl. Reaction enthalpies and UHF barriers are listed in Table 2 for the second step of a mechanism in which the bicyclic radical is formed from pentadienyl through an intermediate of the most similar monocycle. In every case the reaction is endothermic, though by as little as 27 kJ/mol in the case of  $3 \rightarrow 9$ . The barriers are nonetheless at least 80 kJ/mol at the UHF level. The predicted barriers for the reverse reactions are under 50 kJ/mol except for  $12 \rightarrow 3$ , which has a UHF barrier of 74 kJ/mol. This suggests that the two-step mechanisms are likely to compete favorably with concerted formation of these radicals from the chain.

### Conclusions

As summarized in Figure 4, the three electrocyclic reactions  $1c \rightarrow 2$ ,  $1b \rightarrow 3$ , and  $1a \rightarrow 4$  follow predictable trends: the initial conformer energy climbs by roughly 11 kJ/mol from **1a** to **1b** to **1c**, while the activation barrier drops steadily from 236 kJ/mol to 169 kJ/mol to 130 kJ/mol. These results appear to be within about 5 kJ/mol of convergence with respect to basis set and level of CI.

The predicted relative energy of **4** (191 kJ/mol) is nearly equal to the energy of the transition state **5** (190 kJ/mol), and the cyclization of **1c** to **2** going through the intermediate **4** is therefore not predicted to be competitive with the direct cyclization from **1c** to **2**. The activation barrier between **1a** and **4** is calculated to lie about 100 kJ/mol higher than **5**.

It remains unclear why evidence for **4**, whether acting as an intermediate or not, should be found in the photolysis of methylpentadiene, when no trace of **3** or the lower energy bicyclic forms **9** and **10** is reported. Formation of the polycyclics is hindered by their comparatively low entropy, predicted for **9** at the ROHF level to be 26.5 J/(mol·K) below **1a** while **4** and **3** have entropies only 7–10 J/(mol·K) below **1a**. At the high effective temperature in photolysis, this may be a determining factor. The lack of **3** is less easily explained, because it is not only more stable than **4**, but has a lower energy transition state relative to the relevant pentadienyl conformer **1b**. Quenched **4** may be manifest at early times simply because it is the cycle formed directly from the *E,E* conformer **1a** of pentadienyl, the most stable. The four-membered ring **3**, although kinetically and thermodynamically more favorable than **4**, is formed from the less abundant *E,Z* conformer.

This is a tentative explanation at best. The predicted activation barriers for the conformational interconversions of **1** are roughly 40 kJ/mol,<sup>14</sup> much lower than the barriers to cyclization. The one-step ring closure of **1c** to **2** in any case remains the lowest energy of the cyclization pathways, and, with a return activation barrier of about 190 kJ/mol, is essentially an irreversible step after relaxation.

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(38) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543–10544.

(39) Nendel, M.; Sperling, D.; Wiest, O.; Houk, K. N. *J. Org. Chem.* **2000**, *65*, 3259–3258.

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**Supporting Information Available:** Transition-state optimization strategy, AM1, UHF, ROHF, QCISD, and CCSD-

(T) geometries, absolute energies, zero-point energies, and  $\langle S^2 \rangle$  values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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