

## Cyclohept-1-en-3-yne

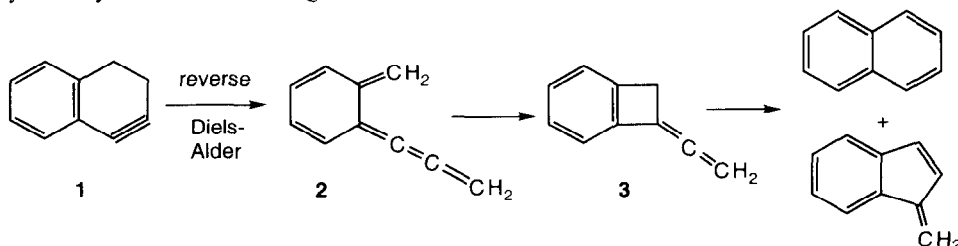
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Received 2 July 1999; revised 13 October 1999; accepted 14 October 1999

**Abstract:** Cyclohept-1-en-3-yne rearranges thermally to toluene via cycloheptatriene, and to a mixture of 1- and 2-vinylcyclopentadiene via an intermediate allene, 1-ethenylidencyclo-2-pentene. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Allenes, Enynes, Radical reactions, Rearrangements

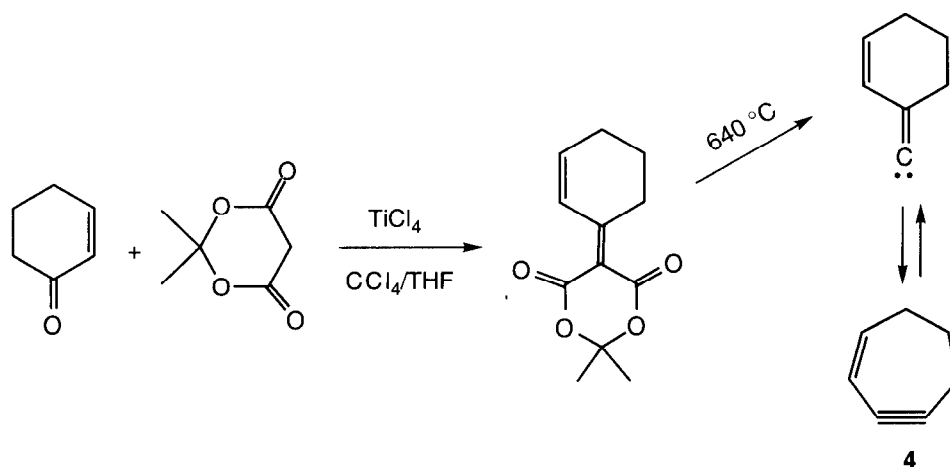
In an attempt to construct a molecular system in which a strained acetylene would mimic a 1,2-dicarbene, we generated benzocyclohex-1-en-3-yne (**1**) and studied its thermal decomposition.<sup>1</sup> The two major products were naphthalene and benzofulvene, and critical intermediates were thought to be the cumulene **2** and the allene **3**. The cyclic acetylene **1** had apparently avoided carbene-like behavior in favor of a relatively low-energy electrocyclic decyclization reaction to give **2**.



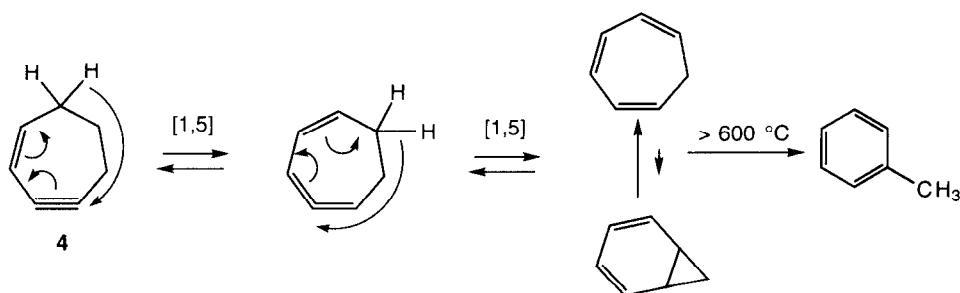
We saw the escape route from **1** to **2** as a fatal flaw in our attempt to coax the acetylene into dicarbene-like behavior,<sup>1</sup> and, naturally, sought to change the ring size from the inauspicious six to something else. Here we describe the thermal chemistry of such an intermediate, cyclohept-1-en-3-yne (**4**).

As in the earlier work<sup>1</sup> we generated our enyne through a vinylidene, which was itself formed in the thermal decomposition of a Meldrum's ester derivative.

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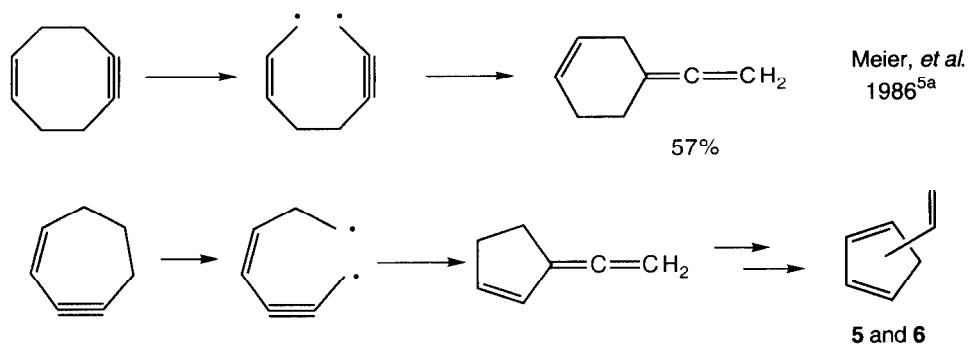


Neither the vinylidene nor the cyclic enyne **4** was isolated. Instead, we found a mixture of toluene (31%) and 1- and 2-vinylcyclopentadiene (**5** and **6**, 13% and 24% respectively). Toluene seemed likely to be the result of the pyrolysis of cyclohepta-1,3,5-triene, and a control experiment showed that cyclohepta-1,3,5-triene did, indeed, rearrange to toluene under our reaction conditions, doubtless through the small amount of norcaradiene present at equilibrium.<sup>2</sup> Cyclohepta-1,3,5-triene could be formed from **4** by two sequential [1,5] shifts of hydrogen.<sup>3</sup>

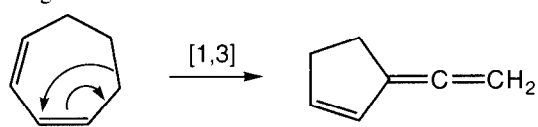


Formation of the vinylcyclopentadienes shows that a ring contraction from seven to five had taken place. This ring contraction was exactly what we had hoped to avoid in changing ring size, and shows that a change from a six to a seven-membered ring is unlikely to induce the acetylene-as-dicarbene behavior we sought. A similar ring contraction had been uncovered by Chapman, Regitz, and their coworkers some time ago when they detected the apparent rearrangement of cyclopentyne to ethynylidenecyclopropane.<sup>4</sup>

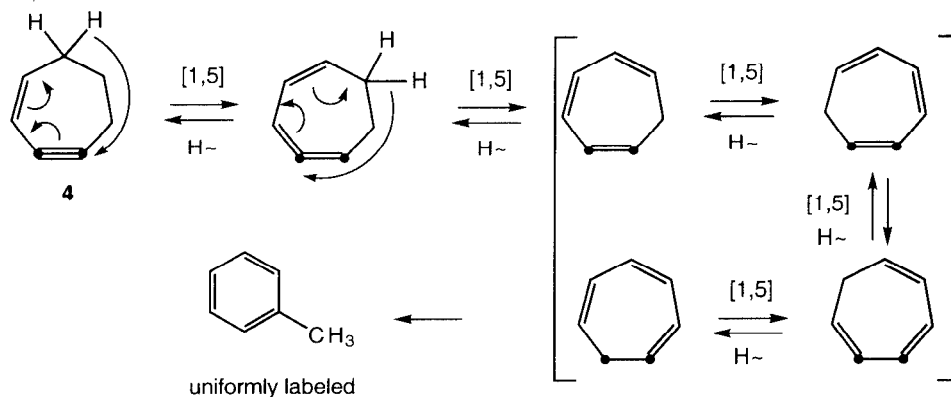
How does the ring contraction work? In the cyclohexyne studied previously<sup>1</sup> we assumed a direct electrocyclic reaction from **1** to **2**. But other, stepwise, possibilities existed and had been suggested earlier in related cases.<sup>5</sup>



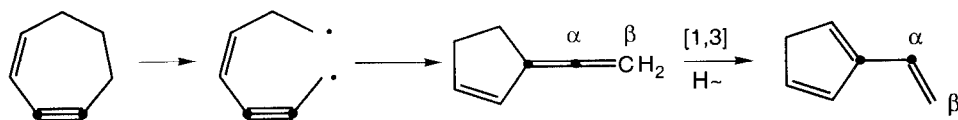
One could also imagine a concerted version of the sequences shown above in which a [1,3] shift of carbon generates the allenes directly. Ordinarily such [1,3] shifts are quite difficult,<sup>6</sup> but not necessarily in the case of alkynes, in which both orbital alignment and strain factors combine to lower activation barriers.<sup>7</sup>



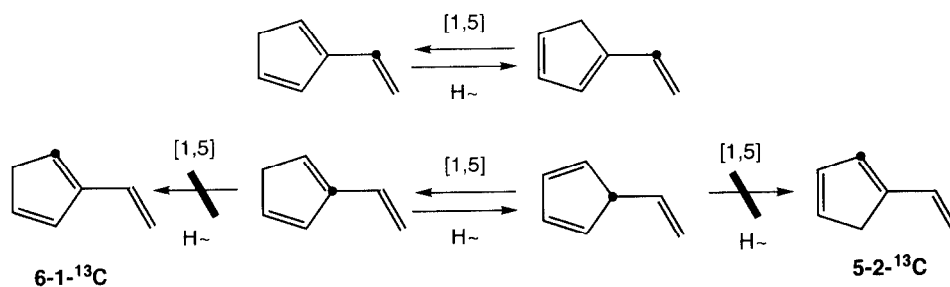
A labeling experiment is consistent with the mechanisms outlined above. We start with <sup>13</sup>C-labelled Meldrum's acid,<sup>1</sup> and thus generate **4** with a label in each of the acetylenic carbons. Our mechanism predicts the initial formation of cyclohepta-1,3,5-triene labeled in both the 1- and 2-positions, but [1,5] shifts of hydrogen will rapidly move the label to all carbons. The ultimate product toluene should therefore also be labeled in all positions, which is the result we observe.



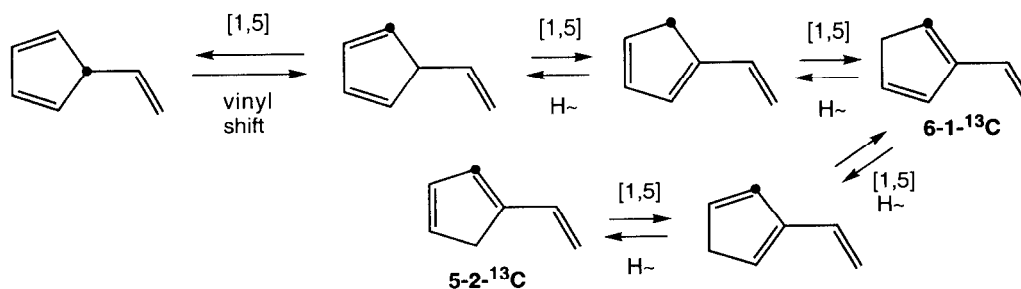
Rather different predictions emerge for the pair of vinylcyclopentadienes. In the initial ring-contracted compound (be the mechanism either stepwise or concerted), the labels appear in the  $\alpha$ -position and in the proximate ring carbon. A [1,3] shift of hydrogen introduces a vinyl group and creates the cyclopentadiene ring.



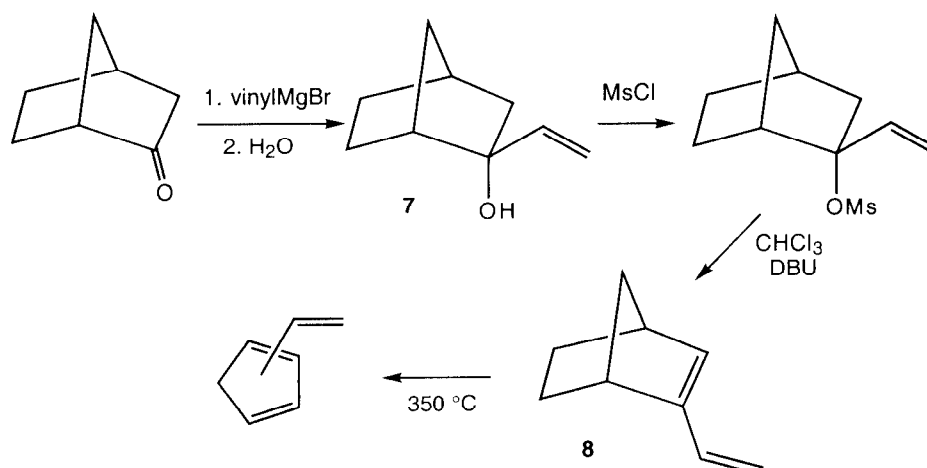
Now a series of rapid [1,5] shifts of hydrogen will surely ensue to generate the equilibrium mixture of labeled 1- and 2-vinylcyclopentadiene (5-vinylcyclopentadiene does not make up an important component of the mixture at equilibrium<sup>8</sup>). If the label is in the  $\alpha$ -position, it will always remain there. In fact, 50% of the label is found in that  $\alpha$ -position. The label can never appear in the  $\beta$ -position, and it is not found there. If the label is in the ring, at the position to which the vinyl group is attached, an equilibrium mixture of vinylcyclopentadienes is also produced. But this sequence of shifts can form neither 1-vinylcyclopentadiene labeled in the 2-position (**5-2-<sup>13</sup>C**) nor 2-vinylcyclopentadiene labeled in the 1-position (**6-1-<sup>13</sup>C**). It is also not possible to form 1- or 2-vinylcyclopentadiene labeled in the 5-position.



Yet these compounds are formed. The vinylcyclopentadienes we isolate are labeled 50% in the  $\alpha$ -position, 0% in the  $\beta$ -position, and the rings are labeled equally in *all* positions. Clearly, something more than [1,5] shifts of hydrogen is occurring. Were a [1,5] vinyl shift, so far unknown in simple vinylcyclopentadienes, to occur, the observed labeling pattern becomes possible. For example, here is a pathway to **5-2-<sup>13</sup>C** and **6-1-<sup>13</sup>C** starting from an intermediate 5-vinylcyclopentadiene labeled in the 5-position.

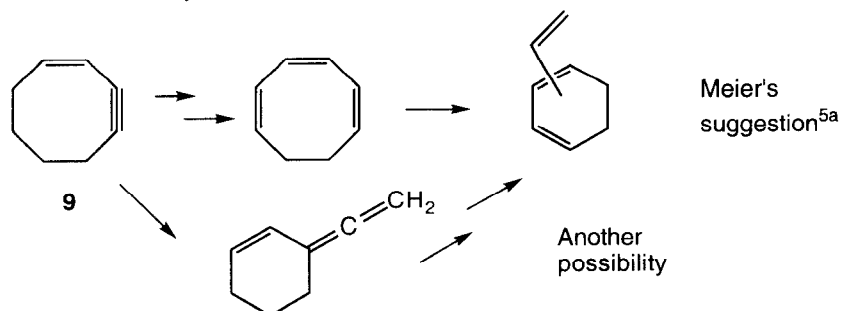


The analysis of our vinylcyclopentadienes was done by  $^{13}\text{C}$  NMR spectroscopy anchored by assignments made for authentic 1- and 2-vinylcyclopentadiene. Our authentic mixture of vinylcyclopentadienes was made by pyrolysis of 2-vinylbicyclo[2.2.1]hepta-2-ene at  $350\text{ }^\circ\text{C}$ . The full synthesis is shown below:

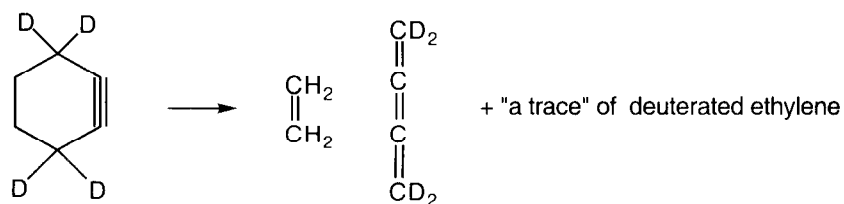


Vinyl shifts in cyclopentadienes are apparently unexplored in the parent system, but are known in a variety of substituted molecules.<sup>9</sup>

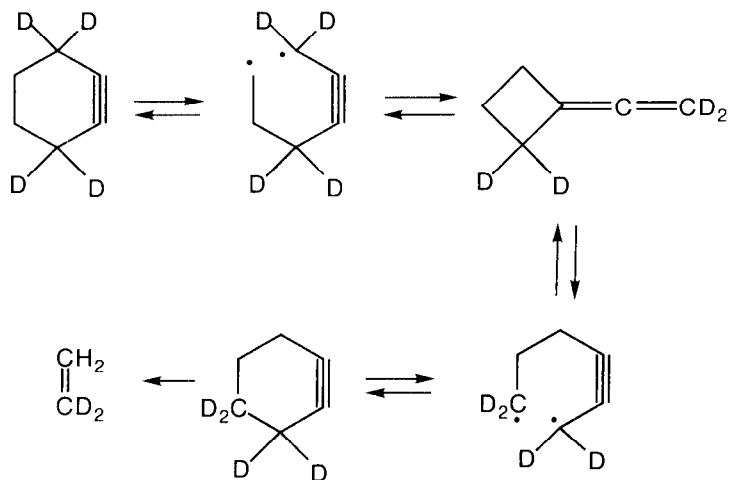
Reaction sequences such as the one suggested for the conversion of **4** into the vinylcyclopentadienes may be rather general. For example, Meier, *et al.* studied the thermal chemistry of cyclooct-1-en-3-yne (**9**) and found, *inter alia*, vinylcyclohexadienes.<sup>4a</sup> They suggested a mechanism that centered upon conversion of **9** into 1,3,5-cyclooctatriene, which was known to rearrange to vinylcyclohexadienes. However, a mechanism related to the one we suggest for the smaller system would do as well.



Our results may even bear on other reactions of cyclic acetylenes. For example, Tseng, McKee, and Shevlin found a trace of deuterated ethylene in the thermal decomposition of deuterated cyclohexyne **8**.<sup>10</sup>



Of course, one mustn't make too much of "a trace," but a stepwise or concerted reversible ring contraction sequence would serve to scramble deuterium into an appropriate position to explain that otherwise mysterious trace.



### Experimental Section

**General.** Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich or as specified) and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with JEOL GSX-270, GE QE-300, and Varian Unity Inova 500 spectrometers. GC/MS analyses were carried out on a Hewlett-Packard 5890/5971 gas chromatograph equipped with a mass selective detector on a 0.25 mm I.D., 0.25 mm film thickness, 30 m HP-1701 capillary column. HPLC separations were carried out on Rainin Dynamax SD-200 instrument. Precise masses were measured on a KRATOS MS 50 RFA high-resolution mass spectrometer. Temperatures were measured with a thermocouple or a thermometer and are uncorrected.

**2,2-Dimethyl-5-(1'-cyclohex-2'-enylidene)-1,3-dioxane-4,6-dione.** A solution of 4.4 mL  $\text{TiCl}_4$  (40 mmol) in 10 mL  $\text{CCl}_4$  was added dropwise to 80 mL dry THF at 0 °C. A yellow precipitate formed. A solution of 1.92 g 2-cyclohexen-1-one (20 mmol) and 2.9 g Meldrum's acid (20 mmol) in 10 mL dry THF and 3 mL

methylene chloride (used to dissolve the reactants completely) was added slowly to the yellow precipitate and was followed by 6.4 mL pyridine (79 mmol) in 10 mL dry THF. The flask was then rinsed with an additional 5 mL of dry THF. The ice bath surrounding the vessel was allowed to warm to room temperature and the reaction to stir for 16 h, after which time the mixture became brownish orange-red and contained some suspended solid. The solid dissolved upon addition of dilute NaCl solution (125 mL of a 4:1 water and saturated NaCl solution) and 200 mL ether, and the aqueous layer was separated. The organic layer was washed with 125 mL of a dilute NaCl solution, 75 mL of a saturated NaCl solution, 125 mL of saturated NaHCO<sub>3</sub>, and twice more with a total of 220 mL dilute NaCl solution. The solution was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solution was concentrated on a rotary evaporator to yield a viscous, yellow liquid. After the solution stood for several days, crystals formed spontaneously. The residual liquid was removed with three successive rinses of 2–5 mL ice-cold ether to yield 977 mg (4.40 mmol) of off-white, translucent, spear-shaped crystals, mp 66–68 °C (22%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.60 (dt, *J*<sub>d</sub> = 10.3 Hz, *J*<sub>t</sub> = 2.2 Hz, 1H), 6.80 (dt, *J*<sub>d</sub> = 10.3 Hz, *J*<sub>t</sub> = 4.5 Hz, 1H), 3.09 (d, *J* = 7.0 Hz, 1H), 3.07 (d, *J* = 6.0 Hz, 1H), 2.33 (m, 2H), 1.80 (tt, *J* = 6.0, 7.0 Hz, 2H), 1.69 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 167.31, 161.72, 161.18, 149.74, 126.87, 110.99, 103.44, 29.59, 27.12, 26.12, 21.76. HRMS calculated for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub> 222.0891, observed: 222.0869.

**2,2-Dimethyl-5-<sup>13</sup>C-5-(1'-cyclohex-2'-enylidene)-1,3-dioxane-4,6-dione.**

This compound was synthesized in a similar fashion as was the unlabeled compound in a yield of 26%.

**Pyrolysis of 2,2-Dimethyl-5-(1'-cyclohex-3'-enylidene)-1,3-dioxane-4,6-dione.** This compound (145 mg, 0.65 mmol) was pyrolyzed as described earlier<sup>1</sup> at ca. 600 °C to give products as a yellow oil. GC-MS and NMR analysis of the products revealed toluene (0.20 mmol, 31%), 1-vinylcyclopentadiene **5** (0.16 mmol, 13%) and 2-vinylcyclopentadiene **6** (0.09 mmol, 24%) as the major products.

**Pyrolysis of 2,2-Dimethyl-5-<sup>13</sup>C-5-(1'-cyclohex-3'-enylidene)-1,3-dioxane-4,6-dione.** The <sup>13</sup>C content of the products was measured by comparing the corresponding signal intensities to those from the products of the experiment using unlabelled material. Thus, the toluene was found uniformly labelled, while **5** and **6** were labelled unequally (see text).

**Synthesis of 2-Vinylbicyclo[2.2.1]hept-2-ene **8**:** 2-Hydroxy-2-vinylbicyclo[2.2.1]-heptane **7** (1.4 g), 1.5 mL pyridine, and 20 mL CHCl<sub>3</sub> were placed in a round-bottom flask. After cooling to 0 °C, 1.5 mL mesyl chloride was added with stirring. The mixture was allowed to warm to room temperature and stirred for 2 days and filtered. The filtrate was concentrated and DBU (1.5 mL) was added. Following 10 h reflux, the products were distilled into a cold bath trap under reduced pressure. Pentane (20 mL) was added to the distillate, which was subsequently washed with 2 x 10 mL portions of water. After removal of solvent by careful fractional distillation, 0.8 g of **8** as colorless liquid was obtained.<sup>11</sup>

<sup>1</sup>H (500 MHz, CDCl<sub>3</sub>): δ 6.35 (dd, *J* = 10.6, 17.5 Hz, 1H), 5.91 (d, *J* = 3.1 Hz, 1H), 5.22 (dd, *J* = 1.7, 17.5

Hz, 1H), 5.01 (dd,  $J=1.7, 10.6$  Hz, 1H), 3.20 (br s, 1H), 2.91 (br s, 1H), 1.9 (m, 1H), 1.78–1.74 (m, 1H), 1.70–1.66 (m, 1H), 1.43–1.42 (m, 1H), 1.20–1.12 (m, 1H), 1.05–1.01 (m, 1H).  $^{13}\text{C}$  (125.6 MHz)  $\delta$ : 134.22, 132.27, 112.59, 47.85, 43.04, 41.25, 27.66, 25.0. The quaternary vinylic carbon was not observed.

**Synthesis of 1- and 2-vinylcyclopentadienes 5 and 6:** A sample of 400 mg **8** was passed through a small tubular oven maintained at 350 °C and packed with glass wool. The flow rate was controlled by cooling the **8** so that the evaporation took place over 1 h. As soon as the vacuum was removed, the products were dissolved in 5 mL of pentane. The pentane layer was washed twice with 1 mL of 5%  $\text{Na}_2\text{CO}_3$  (aq) and subsequently dried over  $\text{Na}_2\text{SO}_4$ . After the pentane was removed by distillation, about 0.2 g of yellow oil remained which contained vinylcyclopentadienes **5** and **6** along with some residual pentane. A combination of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY, and  $^1\text{H}$ - $^{13}\text{C}$  COSY give a partial assignment for the NMR signals of **5** and **6**. Compound **6**:  $^1\text{H}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.14 (br s, 2H, H5), 5.05 (d,  $J=10.5$  Hz, 1H, H2'), 5.36 (d,  $J=17.5$  Hz, 1H, H2'), 6.44 (s, 1H, H1), 6.51 (m, 1H), 6.34 (m, 1H), 6.67 (m, 1H, H-1').  $^{13}\text{C}$  (125.6 MHz)  $\delta$  39.39 (C-5), 112.07 (C-2'), 131.84 (C-1), 132.26 (C-3 or C-4), 132.82 (C-1'), 133.13 (C-4 or C-3), 147.0 (C-2). Compound **5**:  $^1\text{H}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.10 (br s, 2H, H5), 5.18 (d,  $J=10.5$  Hz, 1H, H2'), 5.50 (d,  $J=17.5$  Hz, 1H, H2'), 6.81 (d,  $J=5.2$  Hz, 1H), 6.67 (m, 1H, H1'), 6.31 (d, 1H), 6.50 (m, 1H).  $^{13}\text{C}$  (125.6 MHz)  $\delta$  41.76 (C-5), 114.07 (C-2'), 130.2 (CH), 130.53 (CH), 132.14 (C-1'), 134.24 (CH), 147.0 (C-1).

**Acknowledgements.** We thank the National Science Foundation (grant CHE-9702823), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Dr. Wei Wang for valuable assistance in obtaining NMR spectra.

#### References and Notes:

1. Lu, P. J.; Pan, W.; Jones, M. Jr. *J. Am. Chem. Soc.* **1998**, *120*, 8315.
2. Warner, P. M.; Lu, S.-L. *J. Am. Chem. Soc.* **1973**, *95*, 5099.
3. ter Borg, A. P.; Kloosterziel, H.; van Meurs, N. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 717. ter Borg, A. P.; Razenberg, E.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1230.
4. Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.
5. (a) Meier, H.; Hanold, N.; Molz, T.; Bissinger, H. J.; Kolshorn, H.; Zountsas, J. *Tetrahedron*, **1986**, *42*, 1711. (b) Meier, H.; Schmitt, M. *Tetrahedron Lett.* **1989**, *30*, 5873.
6. Lewis, D. R.; Cochran, J. C.; Hossenloop, J. M.; Niller, D. M.; Sweeny, T. E. *J. Phys. Chem.* **1981**, *85*, 1787.
7. Jensen, F. *J. Am. Chem. Soc.* **1995**, *117*, 7487.
8. Brinker, U. H.; Fleischhaver, I. *Chem. Ber.* **1986**, *119*, 1244.
9. Jones, M. Jr. *J. Org. Chem.* **1968**, *33*, 2538. Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292. Semmelhack, M. F.; Weller, H. N.; Clardy, J. *J. Org. Chem.* **1978**, *43*, 3791.
10. Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474.
11. Imae, H.; Matsuno, M.; Yasudo, M. CAN: 81:151648.