Registry No. I, 83463-72-3; II, 82336-38-7; III, 83463-75-6; IV, 83463-78-9.

Supplementary Material Available: Structure factor tables for $(Ph_4P)_2[(CS_4)_2MoS]\cdot DMF$ and for $(Ph_4P)_2[(CS_4)Mo_2S_4(CS)_4]\cdot{}^1/_2DMF$ (40 pages). Ordering information is given on any current masthead page.

Photochemistry of a Triplet Biradical. Cyclization, Cleavage, and Hydrogen Shift in 2-Isopropylidenecyclopentane-1,3-diyl

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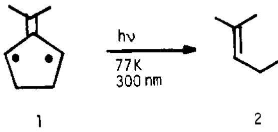
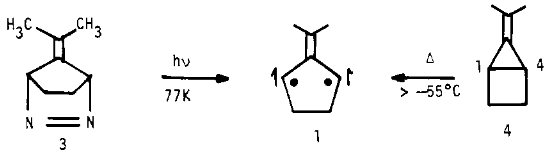
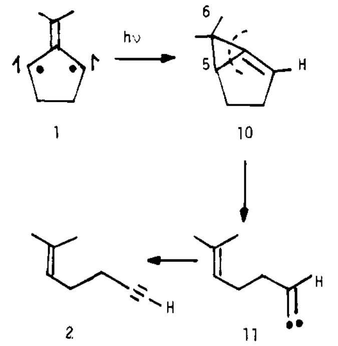
The literature of photochemistry provides few descriptive examples of the excited-state behavior of non-Kekulé molecules.[3] The present study of 2-isopropylidenecyclopentane-1,3-diyl (**1**) has uncovered a remarkable light-induced rearrangement to 2-methylhept-2-en-6-yne (**2**).

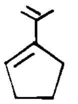




Biradical **1** in its triplet ground state[4,5] is generated by photodeazetation of the diazene **3** in glassy matrices at 77 K,[4] and its electron paramagnetic resonance (EPR) signal persists under these conditions for at least 1 h after irradiation is terminated. Melting the matrix produces high yields of dimers of **1**.[4,6,7] In the present experiments, the course of the photolysis of **1** at wavelengths appropriate to the absorption maxima between 299 and 322 nm[8] in glassy preparations at 77 K was monitored either by determining the relative yields of monomeric and dimeric[9] products obtained upon melting the matrix or by following the decline of the EPR signal intensity. In a typical run (diethyl ether–methylcyclopentane glass, 120 min of irradiation with Rayonet "3000 Å" lamps of a sample of **1** that had been prepared by photolysis of **3** with "3500 Å" lamps), an absolute yield of 44% of monomeric products was obtained, which consisted of 93% enyne **2**, identified by isolation and spectroscopic comparison[10] with an independently synthesized authentic sample,[11] and 0.5–1% each of minor products, of which we have identified three resulting from formal disproportionation (1-isopropylcyclopentene, isopropylidenecyclopentane, and 6,6-dimethylfulvene) and two from hydrogen shift (**5** and **6**). Compound **5** also is a product of the pyrolyses of **3** and **2**,[12] but it is noteworthy that the acyclic trienes **7**–**9** which are prominent bond cleavage products of the latter reactions, did not constitute more than 0.1% of the present photolysis mixtures.

Scheme I





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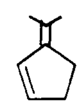

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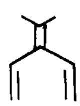

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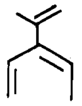

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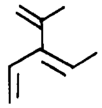

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The most reasonable *formal* mechanism for the deep-seated rearrangement leading to the enyne **2** involves photochemical ring closure of biradical **1** to the bicyclo[3.1.0]hex-1-ene **10** (Scheme I) followed by a vinylidene cycloreversion to give **11**, which then undergoes hydrogen shift. Whether the intermediates **10** and **11** are ground- or excited-state species is not yet clear. For example, the carbene rearrangement **11** → **2** is an amply precedented thermal reaction at ordinary or elevated temperatures,[13] but if the activation barrier of 8.6 kcal/mol calculated.[14a,b] for the parent vinylidene → acetylene reaction applies here, the process should be immeasurably slow at 77 K. Either the barrier is lower,[14c] the shift is facilitated by quantum mechanical tunneling, or the overall reaction **10** → **2** occurs without relaxation to the ground vibronic state of **11**. Similarly, the vinylidene cycloreversion step **10** → **11** is a well-known photochemical reaction of methylenecyclopropane,[15] but until recently[12] has had no thermal precedent. Thus, cleavage of **10** may occur before relaxation to the ground state. Alternatively, ground-state bicyclohexene **10** might be formed and

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[1] National Research Service Awardee (Fellowship F32-GM 07997) of the National Institute of General Medical Sciences, 1980–1982.

[2] National Science Foundation Science Faculty Development Awardee, 1981–1982.

[3] For a study of the photochemistry of a 1,8-naphthoquinodimethane, see: Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629.

[4] (a) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544. (b) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

[5] Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725.

[6] Berson, J. A.; Duncan, C. D.; O'Connell, G. C.; Platz, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 2358.

[7] (a) Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 6743; (b) **1980**, *102*, 2358.

[8] Turro, N. J.; Mirbach, M. J.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653.

[9] Most of the dimeric product was apparently identical with the dimer mixture obtained when **4** or **3** is thermally decomposed in fluid media. However, under certain conditions, a new set of dimers constituted as much as 40% of the dimeric products. The formation of these "abnormal" dimers was favored by media of high viscosity.

[10] Cf.: (a) Sato, K.; Inoue, S.; Ota, S. *J. Org. Chem.* **1970**, *35*, 565. (b) Chuit, C.; Cahiez, G.; Normant, J.; Villieras, J. *Tetrahedron* **1976**, *32*, 1675.

[11] By the method given in the following: Kobayashi, S.; Mukaiyama, T. *Chem. Lett.* **1974**, 705.

[12] Mazur, M. R.; Potter, S. E.; Pinhas, A. R.; Berson, J. A. *J. Am. Chem. Soc.*, following paper in this issue.

[13] (a) Hartzler, H. D. In "Carbenes"; Moss, R. A.; Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 2. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (c) Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Chapter 5.

[14] (a) Dykstra, C. E.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1978**, *100*, 1378. (b) Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288. (c) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469. Harding calculates a barrier of only 5.0 kcal/mol.

[15] (a) Brinton, R. K. *J. Phys. Chem.* **1968**, *72*, 321. (b) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606. (c) Gilbert, J. C.; Butler, J. R. *Ibid.* **1970**, *92*, 7493. (d) Gilbert, J. C.; Luo, T. *J. Org. Chem.* **1981**, *46*, 5237.

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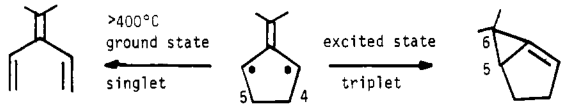
undergo secondary photolysis. However, as was established by light-filtering experiments, this pathway would require that the absorption spectrum of **10** extend toward the red as far as 315 nm.

Bicyclic hydrocarbon **4** is already known[16] to be a minor product (15–20%) of the photolysis of diazene **3** at 77 K, where it probably arises from ring closure of the short-lived singlet state of biradical **1**. Compound **4** also seems to be formed in the present experiments as a photolysis product of triplet **1**, but it cannot be a source of the other monomeric hydrocarbons under these conditions because it has only end absorption in the ultraviolet region, and is photochemically stable to 3000-Å radiation.

A parallel study[12] shows that the thermally produced (presumably singlet) intermediate **1** uses the internal energy it has acquired at 400 °C for the exothermic destruction of the C_4–C_5 bond. In contrast, the photochemically excited triplet **1** generated here uses its ~90 kcal/mol of excitation energy to stitch up a weak C–C bond (C_5–C_6 of **10** and probably C_1–C_4 of **4**), a reaction that would be endothermic[17] in the ground state.



9 1 10

Acknowledgment. We thank the National Science Foundation (CHE-8011399) and the National Institutes of Health (GM-23375) for support of this work. We also thank the National Science Foundation (CHE 7916210) for its support of the NSF Northeast Regional NMR Facility at Yale University. Acknowledgement is made to the donors of the Petroleum Research Fund, sponsored by the American Chemical Society, for partial support of this work. Dr. R. F. Salinaro made a helpful contribution in an early phase of this project.

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(16) (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, *104*, 2209.

(17) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2217.

High-Temperature Pathways on the Energy Surface Connecting a Vinylidene and a Trimethylenemethane. Gas-Phase Generation of a Bicyclo[3.1.0]hex-1-ene and a Novel Cyclization of a 1,2,5-Triene

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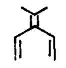
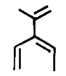
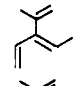
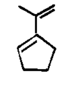
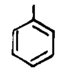
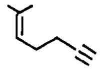
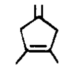
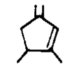
Although the thermal chemistry of the trimethylenemethane biradical **1** at moderate temperatures is almost entirely intermolecular (dimerization or cycloaddition with olefins),[3] we have found a richly detailed set of novel intramolecular transformations at higher temperature.

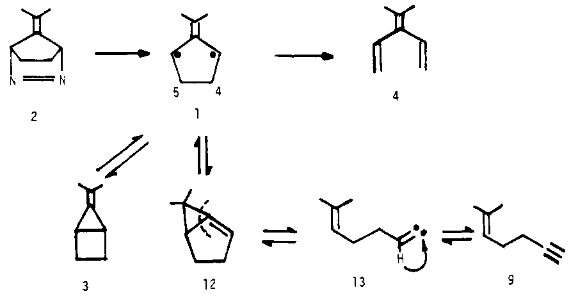
Flash vacuum pyrolysis of the diazene **2** at temperatures above 400 °C and pressures of 10^{-3}–10^{-4} torr gave the products shown in Table I. Control experiments established the occurrence of the reactions **4** → **5** + **6** (+**7**?); **5** ⇌ **6**; **5**, **6**, or **7** → **4**; **5** or **6** → **4**; and **7** → **4**–**6**. These processes were slow enough to permit the identification of the primary pyrolysis products as **4** and **7**–**9**.

Table I. Products of Flash Vacuum Pyrolysis[b] of Diazene **2** and Eneyne **9**[a–c]

product		% yield from reactant	
		diazene 2	enyne 9
4		10	31
5		25	10
6		30	10
7		5	1
8		10	32
9		1	
10		0	6
11[d]		0	b

[a] At 700 °C, 10^{-3}–10^{-4} torr, residence time ~0.02 s. [b] Experimental details given in supplementary material. [c] Unless otherwise noted, all products were identified by isolation. [d] Identified by gas chromatographic retention time.

Scheme I



Scheme I shows proposed mechanisms for the formation of **4** and **9**, in which no attempt is made to decide the extremely subtle question of whether the actual pathways originate from the biradical **1** or the bicyclic hydrocarbon **3**.

The enyne **9** apparently arises by a route beginning with cyclization of **1** to the bicyclo[3.1.0]hex-1-ene **12**. This compound suffers *thermal* vinylidene cycloreversion to the carbene **13**, which then undergoes a well-documented[4] type of hydrogen shift. The possibility that the **12** → **9** reaction may be concerted cannot be evaluated on the basis of the present experiments.

Reversal of the entire cyclization sequence was observed in the pyrolysis of the enyne **9** (Table I), which gave the same group of trienes **4**–**6** obtained from diazene **2**. Another major product from **9** was toluene (**8**), which also was observed from diazene **2**, probably as a secondary product via **9**. The formation of **8** can be rationalized by several mechanisms which we have not yet been able to distinguish experimentally.

Products **10** and **11**, although superficially seeming to resemble

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(1) Humphrey Chemical Co. Fellow, 1981–1982.

(2) Harkness Fellow of the Commonwealth Fund, 1973–1975.

(3) (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. (b) Berson, J. A. In "Diradicals"; Borden, W. T. Ed.; Wiley-Interscience: New York, 1982.

(4) Brown, R. F. C.; Harrington, K. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1175 et seq.

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