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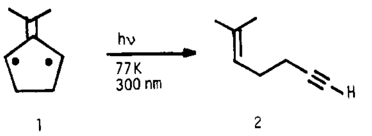
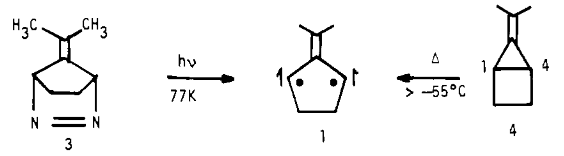
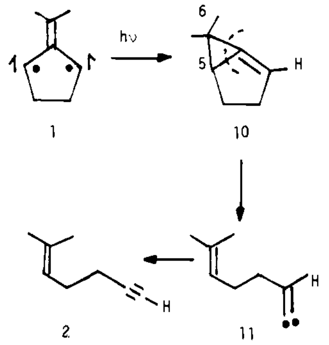
The literature of photochemistry provides few descriptive examples of the excited-state behavior of non-Kekulé molecules.[3] The present study of 2-isopropylidenecyclopentane-1,3-diyl (1) has uncovered a remarkable light-induced rearrangement to 2-methylhept-2-en-6-yne (2).

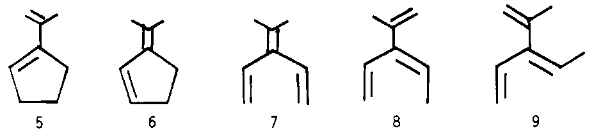


Biradical 1 in its triplet ground state[4,5] is generated by photodeazetation of the diazene 3 in glassy matrices at 77 K,[4] and its electron paramagnetic resonance (EPR) signal persists under these conditions for at least 1 h after irradiation is terminated. Melting the matrix produces high yields 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





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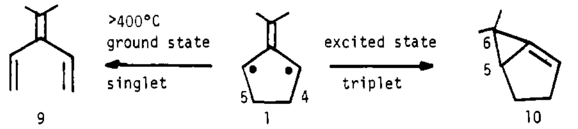
undergo secondary photolysis. However, as was established by light-filtering experiments, this pathway would require that the absorption spectrum of **10** extend toward the red as far as 315 nm.

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.



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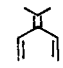
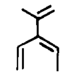
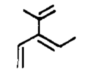
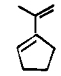
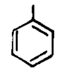
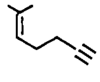
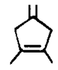
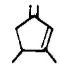
Although the thermal chemistry of the trimethylenemethane biradical **1** at moderate temperatures is almost entirely intermolecular (dimerization or cycloaddition with olefins),[3] we have found a richly detailed set of novel intramolecular transformations at higher temperature.

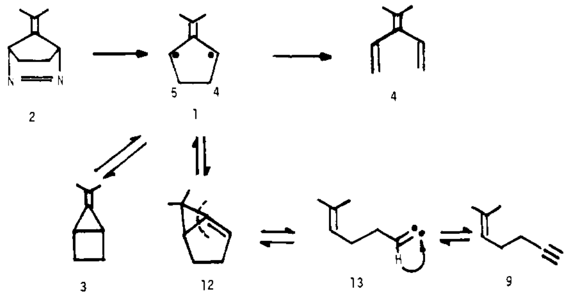
Flash vacuum pyrolysis of the diazene **2** at temperatures above 400 °C and pressures of 10^{-3}–10^{-4} torr gave the products shown in Table I. Control experiments established the occurrence of the reactions **4** → **5** + **6** (+**7**?); **5** ⇌ **6**; **5**, **6**, or **7** → **4**; **5** or **6**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