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Communications

Photochemical Generation of a Novel Eight-Membered-Ring Silene

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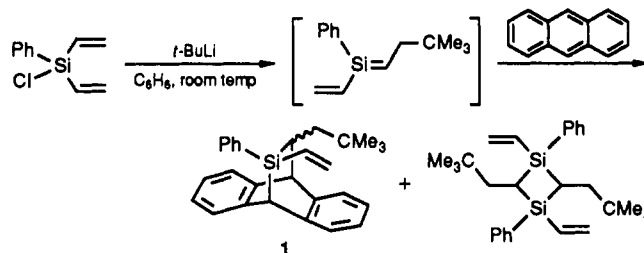
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Summary: Photolysis of the silabicyclo[2.2.2]octadiene **1** in the presence of methanol, methanol-*d*, or methoxytrimethylsilane gives products arising from trapping a silaallylic 1,6-biradical, 1-phenyl-1-vinyl-2-neopentylsilene, and a cyclic eight-membered-ring silene, **B**, formed by the novel ring closure of the 1,6-biradical.

The generation of silene intermediates by photolysis of suitable precursors has received considerable attention.⁴ Silene and disilene adducts to anthracene have also been shown to be stereospecific thermal precursors to the corresponding intermediates. We report herein evidence for the formation of the first example of a silene contained in a bicyclic eight-membered ring, formed by the photolysis of 7-phenyl-7-vinyl-8-neopentyl[2,3:5,6]dibenzo-7-silabicyclo[2.2.2]octane (**1**).

Compound **1** was prepared by the anthracene addition of the silene generated from the reaction of *tert*-butyllithium with chlorophenyldivinylsilane in benzene.⁵ In addition to a 24% yield of (*E*)-**1** and a 2% yield of (*Z*)-**1**,⁶

a 6% yield of the head-to-tail silene dimers was obtained along with polymeric material:



Irradiation (254 nm) of **1** in a sealed quartz tube at room temperature, with cyclohexane as the solvent and methanol, methanol-*d*, or methoxytrimethylsilane as trapping agents gave three major products, 4-substituted 3-phenyl-3-methoxy-6,6-dimethyl-3-silahept-1-ene, (**2a-c**;

(6) The stereochemistry of (*E*)-**1** and (*Z*)-**1** was assigned on the basis of the shielding of the methylene and *tert*-butyl protons, which is greater for the *Z* isomer.⁵ Characterization data for (*E*)-**1** are as follows: ¹H NMR (δ , ppm downfield from tetramethylsilane): 0.89, s, 9 H, C(CH₃)₃; 1.42, d, $J = 5$ Hz, 2 H, CH₂; 1.57, dt, $J = 3, 5$ Hz, 1 H, CH; 4.02, s, 1 H, and 4.34, d, $J = 3$ Hz, 1 H, benzyl hydrogens; 5.55, dd, $J = 4, 20$ Hz, 1 H, 5.70, dd, $J = 20, 15$ Hz, 1 H, and 6.03, dd, $J = 4, 15$ Hz, vinyl hydrogens; 6.88–7.23, m, 13 H, aryl hydrogens. ¹³C NMR (δ): 24.67, CH; 29.97, C(CH₃)₂; 32.03, C(CH₃)₃; 44.47, CH₂; 40.50 and 54.18, benzyl carbons; 124.61–143.13, 16 peaks, aryl and vinyl carbons. Characterization data for (*Z*)-**1** are as follows. ¹H NMR: δ 0.79, s, 9 H, C(CH₃)₃; 1.32–1.48, m, 3 H, CH and CH₂; 3.92, s, 1 H and 4.31, d, $J = 3$ Hz, 1 H, benzyl hydrogens; 5.47, dd, $J = 4, 20$ Hz, 1 H, 5.91, dd, $J = 4, 15$ Hz, 1 H, and 6.16, dd, $J = 15, 20$ Hz, vinyl hydrogens; 6.87–7.23 m, 13 H, aryl hydrogens. ¹³C NMR (δ) 25.10, CH; 29.76, C(CH₃)₂; 32.03, C(CH₃)₃; 44.17, CH₂; 40.59 and 54.39, benzyl carbons; 125.24–143.15, 16 peaks, aryl and vinyl carbons. MS for both isomers (m/z (relative intensity)): 394 (9, M⁺), 178 (20), 159 (100), 133 (22), 107 (19). Anal. Calcd for C₂₈H₃₀Si: C, 85.22; H, 7.66. Found: C, 85.23; H, 7.77.

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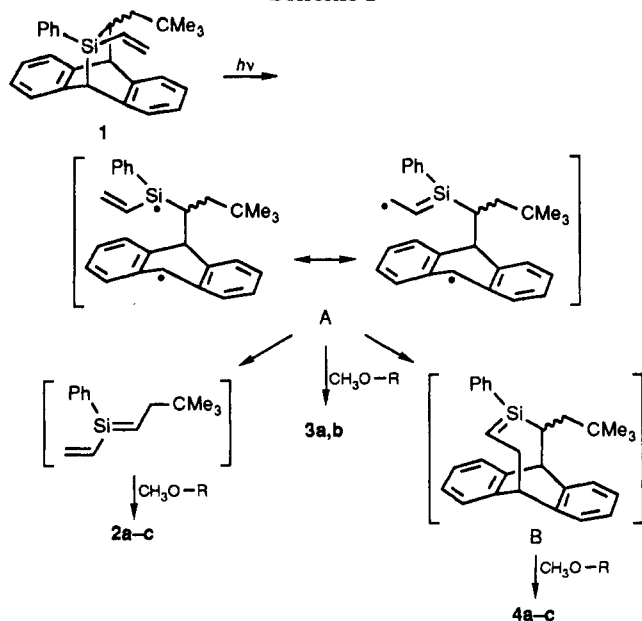
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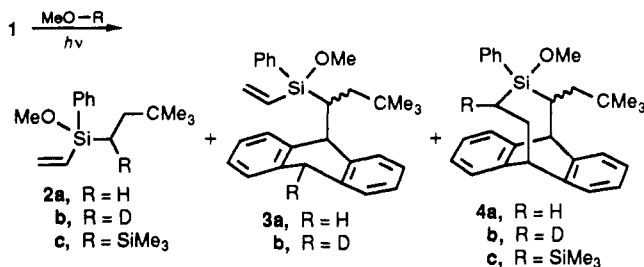
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Scheme I



two diastereomers), two diastereomers of 10-substituted 9-(1-(methoxyphenylvinylsilyl)-3,3-dimethylbutyl)-9,10-dihydroanthracene (**3a,b**), and, most significantly, the *E* and *Z* isomers of 4-substituted 2-neopentyl-3-methoxy-3-phenyldibenzo[7.8.9.10]-3-silabicyclo[4.2.2]decane (**4a-c**). The results are summarized in Table I.



When a 92:8 mixture of (*E*)-**1** and (*Z*)-**1** was irradiated (254 nm) for 10 h in the presence of either CH₃OH or CH₃OD, the adducts to 1-phenyl-1-vinyl-2-neopentylsilene **2a,b** were obtained in low yield.⁷ The major products were two diastereomers of **3a,b**, formed in 36% and 38% yields, respectively.⁸ Methanol is known to be an efficient bi-

(7) Characterization data for **2a** are as follows. ¹H NMR (δ): 0.82, s, 9 H, C(CH₃)₃; 0.88–0.94, m, 2 H, CH₂; 1.37–1.42, m, 2 H, CH₂; 3.37, s, 3 H, OCH₃; 5.90, dd, *J* = 4, 20 Hz, 1 H, 6.05, dd, *J* = 4, 15 Hz, 1 H, and 6.25, dd, *J* = 15, 20 Hz, 1 H, vinyl H; 7.15–7.66, m, 5 H, aryl H. ¹³C NMR (δ): 8.41, Si-CH₂; 28.84, C(CH₃)₃; 31.10, C(CH₃)₃; 37.05, CH₂; 50.93, OCH₃; 128.18–136.61, 8 peaks, aryl and vinyl carbons. MS (*m/z* (relative intensity)): 248 (3) M⁺, 163 (100), 137 (12), 107 (21), 91 (12), 59 (32). Anal. Calcd for C₁₆H₂₄O₂Si: C, 72.52; H, 9.74. Found: C, 72.31; H, 9.66.

(8) Characterization data for **3a** (diastereomer 1) are as follows. ¹H NMR (δ): 0.67, s, 9 H, C(CH₃)₃; 1.78–2.00, m, 3 H, CH and CH₂; 3.16, s, 3 H, OCH₃; 3.54 and 4.19, d, *J* = 18 Hz, 2 H, benzylic CH₂; 4.30, d, *J* = 8 Hz, 1 H, benzylic CH; 5.50, dd, *J* = 14, 21 Hz, 5.73, dd, *J* = 4, 21 Hz, 5.88, dd, *J* = 4, 14 Hz, vinyl H; 6.92–7.69 m, 13 H, aryl H. ¹³C NMR (δ): 29.07, CH; 29.83, C(CH₃)₃; 31.42, C(CH₃)₃; 39.60, CH₂; 35.20 and 49.17, benzylic carbons; 49.97, OCH₃; 125.82–142.02, 16 peaks, aryl and vinyl carbons. Characterization data for **3a** (diastereomer 2) are as follows. ¹H NMR (δ): 0.65, s, 9 H, C(CH₃)₃; 1.76–2.01, m, 3 H, CH and CH₂; 3.13, s, 3 H, OCH₃; 3.50 and 4.06, d, *J* = 18 Hz, 2 H, benzylic CH₂; 4.31, d, *J* = 8 Hz, 1 H, benzylic CH; 5.72, dd, *J* = 6, 19 Hz, 5.89, dd, *J* = 15, 19 Hz, 6.00, dd, *J* = 6, 15 Hz, vinyl H; 6.95–7.59, m, 13 H, aryl H. ¹³C NMR (δ): 28.43, CH; 29.83, C(CH₃)₃; 31.91, C(CH₃)₃; 39.32, CH₂; 36.47 and 49.03, benzylic carbons; 50.49, OCH₃; 125.81–141.56, 16 peaks, aryl and vinyl carbons. MS for both diastereomers (*m/z* (relative intensity)): 426 (2) M⁺, 179 (100), 178 (44), 163 (21), 107 (15), 59 (15). Anal. Calcd for C₂₀H₂₄O₂Si: C, 81.64; H, 8.03. Found for a mixture of both diastereomers: C, 80.77; H, 7.74.

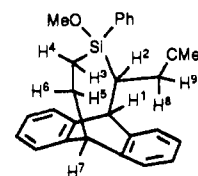
radical trap.^{9,10} It seems reasonable that **3** arises from methanol trapping of a 1,6-biradical intermediate formed by cleavage of the benzylic C–Si bond in **1**. The stereochemistry of one of the chiral centers of **3** is established in the precursor **1**. Because the ratio of the two diastereomers obtained differs from the ratio of *E* and *Z* isomers of the starting material, a direct insertion of methanol in the benzylic C–Si bond to form **3** is ruled out.

Most significant is the isolation of the *E* and *Z* stereoisomers of the unexpected eight-membered-ring products **4a,b**, obtained in 17% and 20% yields, respectively. The stereochemistry of these products was established by detailed analysis of the ¹H NMR coupling constants.¹¹ The most likely precursor to **4** is the cyclic silene intermediate B. In order to test for the presence of B, the photolysis was carried out in the presence of methoxytrimethylsilane, which is known to be an efficient silene trap.¹² Thus, irradiation of a cyclohexane solution of **1** with excess methoxytrimethylsilane at room temperature for 28 h gave 90% decomposition. Two diastereomeric adducts to 1-vinyl-1-phenyl-2-neopentylsilene¹³ and two isomeric ring-expanded products, (*E*)-**4c** and (*Z*)-**4c**,¹⁴ were obtained.

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Characterization data for (*E*)-**4a** are as follows. ¹H NMR (δ): 0.50, ddd, *J*³⁴ = 15, *J*³⁵ = 13, *J*³⁶ = 6 Hz, H³; 0.80, dt, *J*⁴³ = 15, *J*⁴⁵ ≈ *J*⁴⁶ = 4 Hz, H⁴; 0.86, s, 9 H, C(CH₃)₃; 1.68, dd, *J*⁸² = 2, *J*⁸⁹ = 15 Hz, H⁸; 1.74, dt, *J*²⁹ = 8 Hz, *J*²¹ ≈ *J*²⁸ = 2 Hz, H²; 2.05, dd, *J*⁸² = 8, *J*⁸⁶ = 15 Hz, H⁹; 2.19, dddd, *J*⁶⁶ = 14, *J*⁶³ = 13, *J*⁶⁴ = 4, *J*⁶⁷ = 2 Hz, H⁶; 2.43, dtd, *J*⁶⁵ = 14, *J*⁶⁹ ≈ *J*⁶⁷ = 6, *J*⁶⁴ = 4 Hz, H⁶; 2.87, s, 3 H, OCH₃; 4.20, dd, *J*⁷⁶ = 6, *J*⁷⁵ = 2 Hz, H⁷; 4.39, d, *J*¹² = 2 Hz, H¹; 6.97–7.53, m, 13 H, aryl H. ¹³C NMR (δ): 11.69, Si-CH₂; 30.24, C(CH₃)₃; 32.64, C(CH₃)₃; 34.88, SiCH₂-CH₂; 39.77, Si-CH; 41.67, CH₂-C(CH₃)₃; 46.31 and 47.28, benzylic carbons; 51.02, OCH₃; 126.09–141.29, 16 peaks, aryl and vinyl carbons. Characterization data for (*Z*)-**4a** are as follows. ¹H NMR (δ): 0.52, ddd, *J*³⁴ = 15, *J*³⁵ = 12, *J*³⁶ = 6 Hz, H³; 0.73, ddd, *J*⁴³ = 15, *J*⁴⁶ = 5, *J*⁴⁵ = 4 Hz, H⁴; 1.08, s, 9 H, C(CH₃)₃; 1.68, dd, *J*⁸⁹ = 18, *J*⁸² = 6 Hz, H⁸; 2.00, dddd, *J*⁶⁶ = 13, *J*⁶⁹ = 12, *J*⁶⁴ = 4, *J*⁶⁷ = 2 Hz, H⁶; 2.01, dd, *J*⁸² = 8, *J*⁸⁶ = 18 Hz, H⁹; 2.02, ddd, *J*²⁹ = 8, *J*²⁸ = 6, *J*²¹ = 1 Hz, H²; 2.29, dddd, *J*⁶⁶ = 13, *J*⁶⁷ = 7, *J*⁶³ = 6, *J*⁶⁴ = 5 Hz, H⁶; 3.07, s, 3 H, OCH₃; 4.09, dd, *J*⁷⁶ = 7, *J*⁷⁵ = 2 Hz, H⁷; 4.35, d, *J*¹² = 1 Hz, H¹; 6.82–7.50, m, 13 H, aryl H. ¹³C NMR (δ): 10.83, Si-CH₂; 30.57, C(CH₃)₃; 32.99, Si-CH₂-CH₂; 33.00, C(CH₃)₃; 39.84, Si-CH; 41.98, CH₂-C(CH₃)₃; 46.27 and 47.36, benzylic carbons; 50.20, OCH₃; 126.25–141.50, 16 peaks, aryl and vinyl carbons. Anal. Calcd for a mixture of (*E*)- and (*Z*)-**4a** (C₂₀H₂₄O₂Si): C, 81.64; H, 8.03. Found: C, 80.81; H, 8.03.

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(13) Chemical shifts for the minor diastereomer of **2c** are given in parentheses. ¹H NMR (δ): 0.18 (0.16), s, 9 H, Si(CH₃)₃; 0.36 (0.35), dd, *J* = 3, 6 Hz, methine H; 0.81 (0.82), s, 9 H, C(CH₃)₃; 1.54 (1.49), dd, *J* = 3, 14 Hz, one of the methylene hydrogens; 1.85 (1.84), dd, *J* = 6, 14 Hz, the other methylene hydrogen; 3.30 (3.28), s, 3 H, OCH₃; 5.85 (5.91), dd, *J* = 4, 20 Hz; 6.10 (6.11), dd, *J* = 4, 15 Hz, and 6.36 (6.36) dd, *J* = 15, 20 Hz, vinyl hydrogens; 7.19–7.67, m, 5 H, aryl hydrogens. ¹³C NMR (δ): 0.55 (0.60), Si(CH₃)₃; 8.99 (8.45), CH; 29.81 (29.81), C(CH₃)₃; 31.93 (31.87), C(CH₃)₃; 37.61 (37.31), CH₂; 51.23 (50.93), OCH₃; 127.59, 129.74, 129.80, 135.06, 135.11, 135.26, 135.34, 135.50, 135.79, 136.70, 136.90, aryl and vinyl carbons. MS for both isomers (*m/z* (relative intensity)): 305 (53) [M – Me]⁺, 263 (34), 163 (100), 157 (43), 133 (21), 107 (39), 73 (49), 59 (62), 57 (22). Anal. Calcd for C₁₈H₂₂Si₂O: C, 67.43; H, 10.06. Found: C, 67.09; H, 9.95.

A pathway that is consistent with these results is illustrated in Scheme I. Photolysis of 1 gives cleavage of the benzylic carbon-silicon bond to form the silylallyl 1,6-biradical intermediate A. This intermediate can either dissociate to give the vinylsilene, which leads to products 2, or ring close to give the ring-expanded cyclic silene B, leading to products 4. These results indicate the free silene intermediates 1-phenyl-1-vinyl-2-neopentylsilene and the

Table I. Product Yields and Distributions^a for the Photolysis of 1 in the Presence of Various Trapping Reagents

R-OMe	2	3	(E)-4	(Z)-4
R = H (a)	3	36 ^b	10	7
R = D (b)	4	38 ^c	12	8
R = Me ₃ Si (c)	12 ^d	0	23	6

^a Determined by GLC with use of internal standard methods. ^b A 69:31 mixture of two diastereomers. ^c A 68:32 ratio of two diastereomers. ^d An 83:17 ratio of two diastereomers.

eight-membered bicyclic silene B are formed under our photolysis conditions. The fact that the yields of 2 and 4 increase and that 3 is not found in the photolyses in the presence of methoxytrimethylsilane is consistent with our suggestion that the biradical A is the precursor of all the products observed.¹⁵ The formation of B from A represents the first demonstrated example of a radical ring-closure reaction giving rise to a silene. Attempts to trap B with use of 2,3-dimethyl-1,3-butadiene were unsuccessful, giving rise only to polymeric products. Further investigations of the chemistry of B are in progress.

(15) In response to a reviewer's suggestion an attempt to intercept the biradical intermediate A with tri-*n*-butyltin hydride was carried out. When the photolysis was carried out to 75% decomposition in the presence of excess hydride, only polymeric products were obtained, as is the case for the photolysis of 1 in the absence of a trap. The rate of decomposition was faster in the presence of tri-*n*-butyltin hydride, suggesting that ring closure to re-form 1 is another competing reaction of A.

(14) The numbering for the hydrogens in 4c is the same as that used for 4a.¹¹ Characterization data for (E)-4c are as follows. ¹H NMR (δ): -0.11, s, 9 H, Si(CH₃)₃; 0.47, t, *J*³⁶ = *J*³⁶ = 6 Hz, H³; 1.05, s, 9 H, C(CH₃)₃; 1.87, dd, *J*⁸² = 5, *J*⁸⁸ = 17 Hz, H⁸; 2.03, dd, *J*⁹² = 2, *J*⁹⁸ = 17 Hz, H⁹; 2.09, ddd, *J*²¹ = 2, *J*²⁹ = 2, *J*²⁸ = 5 Hz, H²; 2.52, dd, *J*⁶³ = 6, *J*⁶⁷ = 5 Hz, H⁶; 2.53, dd, *J*⁸³ = 6, *J*⁶⁷ = 5 Hz, H⁶; 2.96, s, 3 H, OCH₃; 4.09, t, *J*⁷⁵ = *J*⁷⁶ = 5 Hz, H⁷; 4.22, d, *J*¹² = 2 Hz, H¹; 6.94-7.48, m, 13 H, aryl hydrogens. ¹³C NMR (δ): 0.92, Si(CH₃)₃; 12.21, SiCH₂; 30.22, C(CH₃)₃; 33.06, C(CH₃)₃; 36.00, Si-CH₂CH₂; 40.77, Si-CH; 42.94, CH₂-C(CH₃)₃; 47.34 and 49.07, benzyl carbons; 51.62, OCH₃; 126.18-141.28, 16 peaks, aryl and vinyl carbons. Characterization data for (Z)-4c are as follows. ¹H NMR (δ): -0.26, s, 9 H, Si(CH₃)₃; 0.85, dd, *J*⁴⁶ = 13, *J*⁴⁶ = 5 Hz, H⁴; 0.87, s, 9 H, C(CH₃)₃; 1.45, dd, *J*⁸² = 6, *J*⁸⁸ = 10 Hz, H⁸; 1.99, ddd, *J*²¹ = 2, *J*²⁸ = 6, *J*²⁹ = 7 Hz, H²; 2.07, dd, *J*⁹² = 7, *J*⁹⁸ = 10 Hz, H⁹; 2.37, ddd, *J*⁶⁴ = 13, *J*⁶⁶ = 14, *J*⁶⁷ = 2 Hz, H⁶; 2.68, ddd, *J*⁸⁴ = 5, *J*⁸⁷ = 8, *J*⁸⁶ = 14 Hz, H⁸; 2.75, s, 3 H, OCH₃; 4.33, dd, *J*⁷⁶ = 2, *J*⁷⁶ = 8 Hz, H⁷; 4.48, d, *J*¹² = 2 Hz, H¹; 6.91-7.53, m, 13 H, aryl hydrogens. ¹³C NMR (δ): 0.08, Si(CH₃)₃; 11.82, SiCH₂; 30.78, C(CH₃)₃; 32.81, C(CH₃)₃; 37.40, Si-CH₂CH₂; 39.31, SiCH; 45.78, CH₂-C(CH₃)₃; 46.61 and 47.54, benzyl carbons; 51.42, OCH₃; 125.85-143.22, 16 peaks, aryl and vinyl carbons. For a mixture of (E)- and (Z)-4c, data are as follows. MS (*m/z* (relative intensity)): 441 (4) [M - *t*-Bu]⁺, 398 (27), 235 (23), 220 (15), 178 (30), 163 (100), 73 (35), 59 (30). Anal. Calcd for C₃₂H₄₂Si₂O: C, 77.05; H, 8.49. Found: C, 77.85; H, 8.36.

Novel Pathway of a Molybdenum-Mediated Cyclization Reaction

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Summary: Synthesis of the new molybdenum η^4 -tri-methylene cationic complex CpMo(CO)₂(η^4 -MeC₄H₅)BF₄ (4) has been described. Deprotonation of 4 gives CpMo(CO)₂(η^3 -2-vinylallyl), which undergoes an unusual cyclization with TCNE and PhCHO (BF₃ catalyzed) to afford six-membered-ring products. The molecular structure of a bicyclic product based on this cyclization has been described.

Transition-metal-mediated cyclization of organic substrates is recognized to be an important methodology in modern organic chemistry.¹⁻⁶ This synthetic approach has proved effective in the construction of basic skeletons of complex pericyclic natural products. Recently, there has been considerable interest in the utilization of organo-

molybdenum complexes in organic reactions;⁶⁻⁹ complexes of the type CpMoL₂(η^3 -allyl) represent one case in which the organic moiety has exhibited interesting chemical reactivity. Nevertheless, as noted in early papers,⁹⁻¹¹ the scope of investigation has been limited mainly to use of a metal fragment as a chiral auxiliary, and the aspect of the chemistry of cyclization has been neglected.¹² In this paper, we wish to report a novel pathway of molybde-

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