

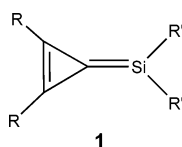
Synthesis of a Silene from 1,1-Dilithiosilole and 2-Adamantanone

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Silenes, compounds with silicon-carbon double bonds, are of considerable interest, but methods of synthesis are limited. Stable silenes have been made by photolysis of α -acylsilanes,¹ 1,2-dehalometalation of 1-halogen-2-metalloalkanes,² and via a sila-Peterson-type reaction.³ The latter route was employed by Kira and co-workers to prepare the 4-silatriafulvene, **1**.⁴



We report here a new silene synthesis from 1,1-dilithium-2,3,4,5-tetraphenylsilole **2**⁵ and 2-adamantanone **3**, leading to the first example of a 5-silapentafulvene, **4**.^{6,7} (Scheme 1).

The ²⁹Si NMR spectrum of **4** exhibited a single line at 83.4 ppm, assigned to the silicon resonance of the doubly bonded silicon. In the ¹³C NMR a signal was observed for the sp² carbon at 167.5 ppm. These resonances may be compared with those reported by Apeloig and co-workers for a silene with a somewhat related structure, **4a**, which had δ ²⁹Si = 51.7 ppm and δ ¹³C = 196.8 ppm.^{3b} After 24 h at room temperature the NMR signals belonging to silene **4** disappeared, and a complicated NMR spectrum of a reaction mixture was observed.

Reactions of **4** with water led to the formation of the trapping adduct silanol **5**⁸ (Scheme 1). The structure of **5** was confirmed by X-ray analysis (Figure 1) and ¹H, ¹³C, and ²⁹Si spectra.

A probable mechanism for the reaction leading to **4** is presented in Scheme 2. The first step involves a nucleophilic addition of the silole dianion to the carbonyl group with the formation of an intermediate α -lithioalkoxysilole anion **6**. 1,2-Elimination of Li₂O from the intermediate **6** leads to silene **4** (Scheme 2).

Intermediate **6** was not isolated, but evidence for the formation of this intermediate was obtained in the reaction of **2** with excess ketone **3**. In this case, hydrolysis of the reaction mixture led to 1,1-di-adamantanol-2,3,4,5-tetraphenylsilole **8**,⁹ whose structure was verified by X-ray crystallography (Figure 2).

We propose that this product arises from an intermediate **7**, probably resulting from the reaction of **6** with **3** (Scheme 3).

The reaction of the silene **4** with excess of 2-adamantanone yields a product **10**¹⁰ (Figure 3), in which one of the Ph rings is linked to an adamantyl substituent forming a second, boat-shaped six-membered heterocycle including Si and O atoms. The formation of **10** can be explained by a ring expansion reaction of the siloxetane **9** (Scheme 4). Similar ring expansions reactions of a "silene-ketone" adduct were described by Brook.¹¹

In the three structures, **5**, **8**, and **10**, the five-membered heterocycle is planar within 0.03 Å with a tetrahedral Si atom. The heterocycle "bite" angle about the Si atom is ~91(2)° in all cases. The corresponding Si-O and Si-C distances in **5**, **8**, and **10** agree well among themselves and with the literature data. The geometries

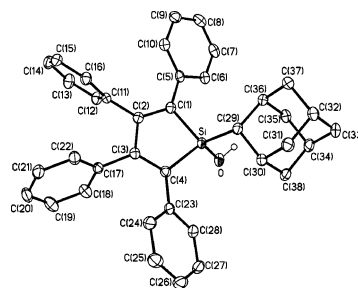


Figure 1. A molecular drawing of silanol **5** shown with 50% probability thermal ellipsoids. All H atoms except the hydroxyl HO have been omitted for clarity. Selected bond distances (angstroms) and angles (deg): Si-O 1.6496(10), Si-C(29) 1.8758(13), Si-C(1) 1.8806(13), Si-C(4) 1.8869(13); O-Si-C(29) 109.97(5), O-Si-C(1) 113.51(5), C(29)-Si-C(1) 112.53(6), O-Si-C(4) 113.05(6), C(29)-Si-C(4) 114.65(6), C(1)-Si-C(4) 92.24(6).

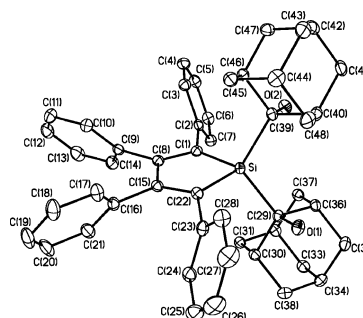
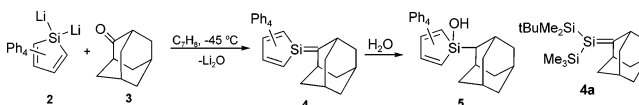
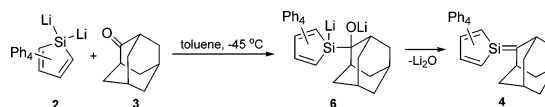


Figure 2. A molecular drawing of dicarbinol **8** shown with 30% probability thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (angstroms) and angles (deg): Si-C(1) 1.9045(17), Si-C(22) 1.9045(17), Si-C(29) 1.9301(17), Si-C(39) 1.9373(18); C(1)-Si-C(22) 91.22(8), C(1)-Si-C(29) 122.78(7), C(22)-Si-C(29) 103.97(7), C(1)-Si-C(39) 103.90(7), C(22)-Si-C(39) 123.08(7), C(29)-Si-C(39) 111.80(8).

Scheme 1. Reaction of Silole Dianion **2** with Ketone **3**



Scheme 2. Mechanism of the Formation of Silene **4**



of adamantyl substituents are normal. There is no preferred orientation of the Ph rings on the heterocyclic carbon atoms, with the interplanar dihedral angles between Ph rings and the plane of the five-membered ring varying between 38.4(9) and 77.0(4)°. Further details on the crystal structures are given in the Supporting Information.

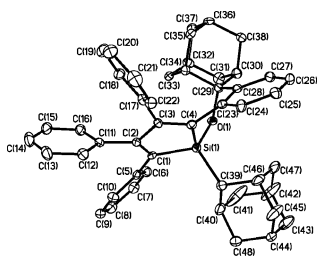
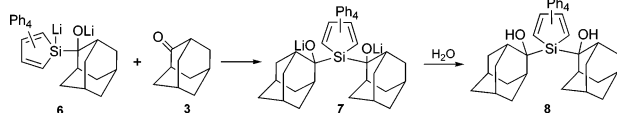
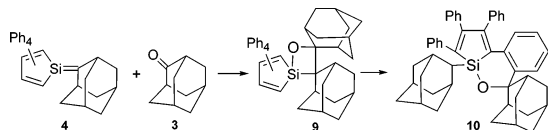


Figure 3. A molecular drawing of **10** shown with 30% probability thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (angstroms) and angles (deg): Si(1)–O(1) 1.657(6), Si(1)–C(4) 1.848(11), Si(1)–C(39) 1.867(6), Si(1)–C(1) 1.882(10); O(1)–Si(1)–C(4) 101.4(13), O(1)–Si(1)–C(39) 118(8), C(4)–Si(1)–C(39) 122(12), O(1)–Si(1)–C(1) 119.1(2), C(4)–Si(1)–C(1) 91.5(2), C(39)–Si(1)–C(1) 114.3(2). There are two symmetry-independent molecules in the lattice of **10**; thus the above values are averaged parameters for the two molecules.

Scheme 3. Reaction of an Intermediate **6** with Ketone **3**



Scheme 4. Reaction of Silene **4** with Ketone **3**



Conclusions

The reaction of 1,1-dilithio-2,3,4,5-tetraphenylsilole **2** with 2-adamantanone **3** proceeds with the formation of a novel-type silene **4**, the first example of a silapentafulvene. It appears that the formation of the silicon–carbon double bond occurs as a result of 1,2-elimination of lithium oxide from an intermediate α -lithioalkoxysilole anion **6** (Scheme 2). No similar reactions of silole (or germole) dianions with ketones were known previously.

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Supporting Information Available: Crystal data and structure refinement (text format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Experimental. 2-Adamantanone, diphenylacetylene, and lithium were purchased from Aldrich and used without further purification. Solvents were distilled from sodium benzophenone ketyl. All procedures with air- and moisture-sensitive compounds were carried out using a Schlenk line under a nitrogen or argon atmosphere. Dilithiotetraphenylsilole (**2**) was prepared from 1,1-dichloro-2,3,4,5-tetraphenylsilole as described previously. NMR spectra were recorded at 20 °C on a Varian INOVA spectrometer at 500 MHz for ^1H , 127.75 MHz for ^{13}C , 99.38 MHz for ^{29}Si , and on a Varian UNITY-500 spectrometer at 499.625 MHz for ^1H , 125.714 MHz for ^{13}C , 99.326 MHz for ^{29}Si . Reaction mixtures were purified by column and thin-layer chromatography using silica gel 60 Geduran from EM Science and silica gel GF (uniplate 1500 mm) from Analtech.
- Preparation of **4**. To 1,1-dilithio-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**2**) (2.2 mmol) in 10 mL of toluene a solution of 2-adamantanone (**3**) (2.2 mmol) in 10 mL of toluene was added at $-78\text{ }^\circ\text{C}$. The color of the reaction mixture changed from dark red to bright yellow, and a white precipitate was formed. The reaction mixture was warmed to room temperature over 1.5 h, and solvent was removed in a vacuum. ^1H NMR: δ = 1.26–2.48 (m, Ad), 6.55–7.64 (m, Ar). ^{13}C NMR: δ = 167.5 (C=Si), 20.55–46.92 (m, Ad), 124.11–130.41 (m, Ar). ^{29}Si NMR: δ = 83.6 (Si=C). Since the ^{13}C signal of the carbonyl carbon of ketone **3** at 214.62 ppm completely disappeared, we suggest that the yield of **4** is quantitative.
- Preparation of **5**. A solution of **4** in toluene prepared as described above was treated with 0.5 mL of H_2O in 5 mL of toluene. The inorganic layer was washed with 5 mL of Et_2O three times, and the combined organic fraction was dried with MgSO_4 . After evaporation of solvents, the solid reaction mixture was purified by column chromatography and TLC (eluent hexanes–ether (10:1)). The product **5** was obtained as yellow crystals from hexane (yield 50%, based on starting ketone **3**). ^1H NMR: δ = 1.09–2.32 (m, 15H, Ad), 6.61–8.11 (m, 20H, Ar). ^{13}C NMR: δ = 35.98–41.36 (m, Ad), 128.2–132.7 (m, Ar), 135.1–148.1 (m, silole carbones). ^{29}Si NMR: δ = –21.85. X-ray crystal data. $\text{C}_{38}\text{H}_{36}\text{OSi}$, $P1$, a = 11.8025(12) Å, b = 11.8154(12) Å, c = 11.9960(12) Å, α = 73.134(2)°, β = 63.641(2)°, γ = 85.474(2)°, V = 1432.0(3) Å³, T = 100(2) K, D_{calc} = 1.245 Mg/m³, $R(F)$ = 4.34% for 5801 [$R(\text{int})$ = 0.0310] independent reflections ($1.80 \leq \theta \leq 26.39^\circ$).
- Preparation of **8**. To **2** (2.2 mmol) in 10 mL of toluene, a solution of 2-adamantanone (**3**) (4.4 mmol) in 15 mL toluene was added at $-78\text{ }^\circ\text{C}$. The color of the reaction mixture changed from dark red to bright yellow, and a white precipitate was formed. The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 4 h, and then raised to room temperature and hydrolyzed with 0.5 mL of H_2O in 5 mL of toluene. The inorganic layer was washed with Et_2O three times, and the combined organic fractions were dried with MgSO_4 . After evaporation of solvents, the crude reaction mixture was purified by column chromatography and TLC (eluent hexanes–ether (10:1)). The product **8**, yield 30%, was collected and crystallized from hexanes– Et_2O (5:1) mixture. Selected NMR data for **8** as follows. ^1H NMR: δ = 1.56–2.36 (m, 28H, Ad), 6.62–7.31 (m, 20H, Ar). ^{13}C NMR: δ = 30.6–43.1 (m, Ad), 128.6–132.9 (m, Ar), 140.7–157.6 (m, silole carbones). ^{29}Si NMR: δ = 4.8. X-ray crystal data for **8**: $\text{C}_{38}\text{H}_{36}\text{O}_2\text{Si}$, monoclinic, $P2_1/c$, a = 17.9305(10) Å, b = 10.7556(6) Å, c = 20.4058(11) Å, β = 109.201(1)°, V = 3716.4(4) Å³, T = 173(2) K, D_{calc} = 1.228 Mg/m³, $R(F)$ = 5.15% for 7220 [$R(\text{int})$ = 0.0310] independent reflections ($2.06 \leq \theta \leq 26.38^\circ$).
- Preparation of **10**. To **2** (2.2 mmol) in 10 mL of toluene, a solution of 2-adamantanone (**3**) (4.4 mmol) in 15 mL of toluene was added at $-78\text{ }^\circ\text{C}$. The color of the reaction mixture changed from dark red to yellow, and a white precipitate was formed. The reaction mixture was warmed to room temperature during 1.5 h and stirred at room temperature for 2.5 h. After hydrolysis of the reaction mixture with 0.5 mL of H_2O in 5 mL of toluene, the organic layer was dried with MgSO_4 . The solvent was evaporated, and the crude reaction mixture was purified by column chromatography and TLC (eluent hexanes–ether (10:1)). The product **10** was collected and crystallized from hexanes– Et_2O (5:1) mixture (yield 31%). Selected NMR data for **10** as follows. ^1H NMR: δ = 1.16–3.19 (m, 29H, Ad), 6.82–7.57 (m, 19H, Ar). ^{13}C NMR: δ = 85.8 (O–C), 29.88–42.70 (m, Ad), 129.1–130.04 (m, Ar), 141.1–144.6 (m, silole carbones). ^{29}Si NMR: δ = 3.48. HRMS (MALDI) Calcd for $\text{C}_{48}\text{H}_{48}\text{OSi}$ 668.98; found, 669.1. X-ray data: $\text{C}_{48}\text{H}_{48}\text{OSi}$, triclinic, $P1$, a = 14.2755–(17) Å, b = 15.4092(18) Å, c = 19.496(2) Å, α = 97.471(2)°, β = 104.111(2)°, γ = 115.452(2)°, V = 3618.0(7) Å³, T = 173(2) K, D_{calc} = 1.228 Mg/m³, $R(F)$ = 8.49% for 10989 [$R(\text{int})$ = 0.0598] independent reflections ($1.12 \leq \theta \leq 24.00^\circ$).
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