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Preparation, Structure, and Photochemistry of 2-Disilanyl-1,4-benzoquinones

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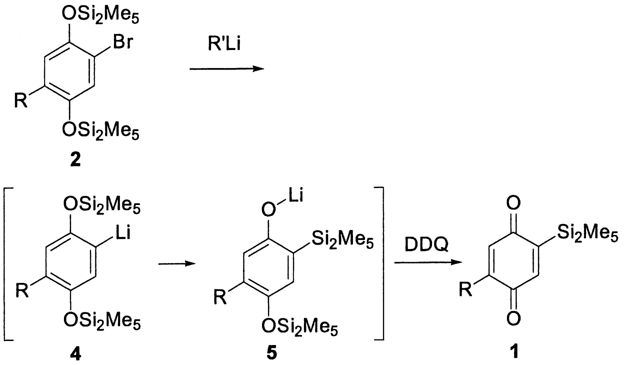
We synthesized 5-chloro- and 5-bromo-substituted 2-(pentamethyldisilanyl)-1,4-benzoquinones **1a** and **1b**, respectively. Their electronic absorption spectra showed significant intramolecular charge-transfer interaction between disilane and 1,4-benzoquinone moieties. The intramolecular σ(SiSi)–π* transition energies of **1a** and **1b** were lower than that of 2-(pentamethyldisilanyl)-5-*t*-butyl-1,4-benzoquinone (**1c**). X-ray crystallographic analysis of chloro-substituted derivative **1a** revealed that the angle between the Si–Si bond and the quinone ring was 74° and also that the structure of **1a** in the solid state was also advantageous for CT interaction. Photoreaction of **1a** and **1b** gave *α*-sila-*m*-quinonemethide derivatives **3a** and **3b**, respectively, which were trapped by acetone. Matrix isolation of **3a**, **3b**, and their 2-methyltetrahydrofuran-complexes were accomplished in glass matrixes.

Photochemical reactions of organosilicon compounds that involve intermolecular charge-transfer (CT) interaction have been receiving a lot of attention from the viewpoints of both synthesis and mechanisms.[1] However, relatively few photo-induced intramolecular CT reactions of organosilicon compounds have been reported.[1–4] Previously we have reported on the preparation and photoreactions of 2-(pentamethyldisilanyl)-5-*t*-butyl-1,4-benzoquinone (**1c**),[3,4] an interesting class of organosilicon compounds containing both strong electron-withdrawing (1,4-benzoquinone)[5] and strong electron-releasing (disilane) groups connected directly to each other that show notable CT interaction.[6] Photochemical reactions of **1c** resulted in the formation of novel *α*-sila-*m*-quinonemethide intermediate **3c** as described below.[3,4] In this paper, we describe the preparation, structure, and photoreactions of 5-chloro- and 5-bromo-substituted 2-(pentamethyldisilanyl)-1,4-benzoquinone derivatives, **1a** and **1b**, respectively. These compounds should have greater σ(SiSi)–π intramolecular CT interaction than that in **1c** because of an electronegative halogen atom substituted on the quinone ring. The photogeneration and complexation of *α*-sila-*m*-quinonemethides **3a** and **3b**, produced by the photoreaction of **1a** and **1b**, are also described.

Results and Discussion

Preparation of 2-(Pentamethyldisilanyl)-1,4-benzoquinones 1. Compound **1b** was prepared by modifying the procedure used to prepare **1c**, as shown in Scheme 1.[3] Partial lithiation of 2,5-dibromo-1,4-bis[(pentamethyldisilanyl)oxy]benzene (**2b**) was done by using *n*-BuLi at −78 °C in ether and the resulting anion **4b** was allowed to warm slowly to room temperature. In the course of warming, there was a spontaneous rearrangement resulting in the formation of **5b**. Without being isolated, **5b** was oxidized by using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to generate **1b** in a yield of 31% based on **2b**. Chloro-substituted derivative **1a** was obtained from **2a** by a similar procedure in a yield of 53%.



a: R = Cl, **b**: R = Br, **c**: R = *t*-Bu

Scheme 1.

Physical Properties of 2-Disilanyl-1,4-benzoquinones 1a and 1b. The absorption maxima of 2-disilanyl-1,4-benzoquinones **1a–c** and 2-(trimethylsilyl)-5-chloro-1,4-benzoquinone (**6a**) are summarized in Table 1. These quinones had two π–π* absorption bands at ca. 250 and 300 nm and one *n*–π* absorption band at ca. 485 nm. Also, **1a–c** had another broad absorption band around 360 nm, the presence of which can be explained by a σ(SiSi)–π* charge-transfer (CT) transition. The absorption maxima of the CT transitions in **1a** (370 nm) and **1b** (371 nm) were red-shifted in a greater extent

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Table 1. Properties of Silyl-Substituted 1,4-Benzoquinones

Quinone	UV (hexane) λ_{max}/nm (ε)	IR ν/cm^{-1} (C=O)
1a	257 (11100), 307 (2440), 370 (918), 481 (186)	1660, 1637
1b	262 (8720), 316 (2830), 371 (721), 483 (150)	1660, 1637
1c	252 (11700), 296 (2010), 353 (900), 488 (90)	1653, 1639
6a	262 (14200), 309 (342), 480 (30)	1664, 1637

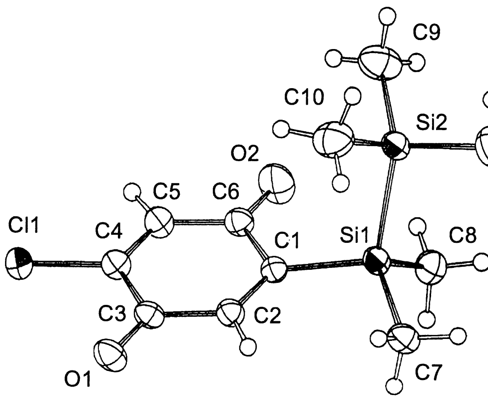


Fig. 1. ORTEP drawing of **1a**. Selected bond lengths (Å): Cl1–C4 = 1.740(4), Si1–Si2 = 2.349(2), S1–C1 = 1.92(4), O1–C3 = 1.223(6), O2–C6 = 1.219(7), C1–C2 = 1.348(7), C1–C6 = 1.497(7), C2–C3 = 1.475(7), C3–C4 = 1.487(7), C5–C6 = 1.480(7).

than the maximum in **1c** (353 nm).[3] These values indicate that intramolecular CT interactions in **1a** and **1b** were more effective than that in **1c**. In contrast, the IR spectra of all the compounds had two similar carbonyl absorption bands at 1653–1660 and 1637–1639 cm^{-1}, as shown in Table 1. The effects of the disilanyl group on the carbonyl group did not differ from those of the trimethylsilyl group in the IR spectra.

X-ray Crystallographic Analysis of 2-Disilanyl-5-chloro-1,4-benzoquinone 1a. A solid state structure of **1a** was revealed by X-ray crystallographic analysis. A single crystal of **1a** suitable for the X-ray crystallographic analysis was obtained from a hexane solution. An ORTEP drawing of **1a** is shown in Fig. 1. The crystal data are summarized in Table 2. The selected bond lengths and angles of **1a** are summarized in Table 3. In Table 4, the bond lengths in the quinone ring of **1a** are shown as compared with those of **6a**,[8] 2,5-dichloro-1,4-benzoquinone (**7**),[9] 2-chloro-1,4-benzoquinone (**8**),[10] and 1,4-benzoquinone (**9**).[11] Table 4 indicates that the bond lengths of **1a** were within the range of normal values when those of compared to the other 1,4-benzoquinones. In the disilanyl moiety, the torsion angles of Si2–Si1–C1–C2 and Si2–Si1–C1–C6 were 73.7(4)° and 101.5(4)°, respectively. Also, we found that C1 carbon was pyramidarized in the opposite direction of the Si–Si bond: the line of the C1–Si1 bond intersected the C1–C2–C6 plane at an angle of 4.1°. This geometrical feature is favorable for intramolecular CT interaction.

Photochemical Generation and Reactions of *α*-Sila-*m*-quinonemethide 3. a) Photoreaction of 1 in the Presence of Acetone: Because of the characteristic intramolecular CT interaction, 2-disilanyl-1,4-benzoquinone derivatives **1** are photochemically reactive. As reported earlier, irradiation of **1c**

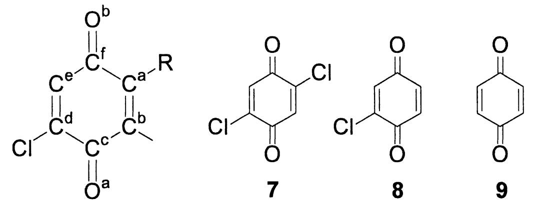
Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for **1a**

Mol formula	$C_{11}H_{17}ClO_2Si_2$
Mol wt	272.89
Cryst size, mm^3	0.25 × 0.20 × 0.25
Cryst system	triclinic
Space group	$P\bar{1}$
Cell dimens	
a/Å	7.834(1)
b/Å	13.654(2)
c/Å	6.850(8)
α/deg	93.36(0)
β/deg	92.19(0)
χ/deg	86.17(1)
V/Å^3	729.4(1)
Z	2
D_{calcd}/g cm^{-3}	1.24
μ/cm^{-1}	4.067
Diffractometer	Rigaku AFC 5R graphite monochromater rotating, anode (45 kV, 200 mA)
Temp/K	170
Radiation/Å	0.71069 (Mo $K\alpha$)
Scan type	ω–2θ
Scan speed/deg min^{-1}	8
Scan width/deg	1.00 + 0.30 tan2θ
No. of unique reflns	3206 ($2\theta_{max}$ = 50 deg)
No. of obsd reflns [$|F_o| > 3\sigma(F_o)$]	2004
No. of parameters refined	214
R	0.0614
R_w	0.0670

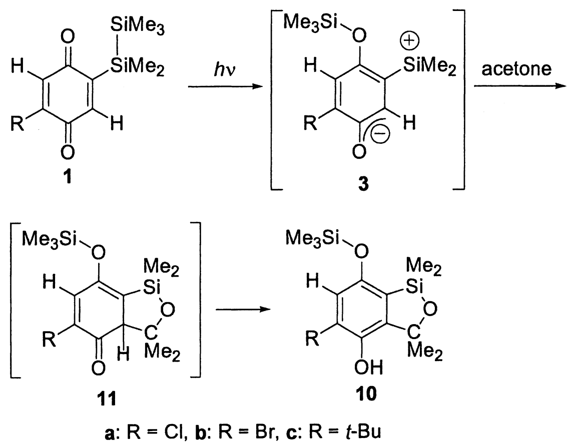
Table 3. Selected Bond Lengths (Å) and Angels (deg) for **1a** with Their Eds's in Parentheses

Cl1–C4	1.740(4)	Si2–Si1–C1	107.7(1)
Si1–Si2	2.349(2)	Si1–C1–C2	122.9(3)
Si1–C1	1.902(4)	Si1–C1–C6	119.0(3)
O1–C3	1.223(6)	C2–C1–C6	117.9(4)
O2–C6	1.219(7)	C1–C2–C3	123.6(4)
C1–C2	1.348(7)	O1–C3–C2	121.7(4)
C1–C6	1.497(7)	O1–C3–C4	121.4(4)
C2–C3	1.475(7)	C2–C3–C4	116.8(4)
C3–C4	1.487(7)	Cl1–C4–C3	116.6(3)
C4–C5	1.334(7)	Cl1–C4–C5	121.9(4)
C5–C6	1.480(7)	C3–C4–C5	121.5(4)
		C4–C5–C6	120.6(4)
		O2–C6–C1	120.8(4)
		O2–C6–C5	119.7(4)
		C1–C6–C5	119.4(4)

Table 4. Selected Bond Lengths (Å) of 1,4-Benzoquinones



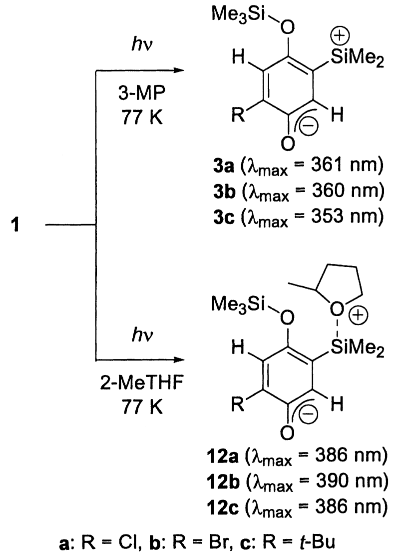
	1a	6a	7	8	9
C^a–C^f	1.497	1.494	1.503	1.487	1.467
C^b–C^c	1.475	1.479	1.470	1.479	1.467
C^c–C^d	1.487	1.499	1.503	1.505	1.467
C^e–C^f	1.480	1.478	1.470	1.473	1.467
C^a–C^b	1.348	1.345	1.340	1.340	1.312
C^d=C^e	1.334	1.326	1.340	1.346	1.312
O^a=C^c	1.223	1.217	1.222	1.226	1.218
O^b=C^f	1.219	1.224	1.222	1.227	1.218
Si–C^a	1.902	1.892			



Scheme 2.

in a hexane solution in the presence of acetone gave adduct **10c** in a quantitative yield (Scheme 2).[3] This reaction was explained in terms of the intermediacy of α-sila-*m*-quinonemethide **3c**, which gave **10c** via 1,3-adduct **11c** as a result of reaction with acetone. Irradiation ($\lambda > 350$ nm) of **1a** and **1b** in the presence of acetone also gave **10a** and **10b** in good yields, respectively. These results indicate that photoreactions of **1a** and **1b** generate α-sila-*m*-quinonemethides **3a** and **3b** as reactive intermediates.

b) Matrix Isolation of α-Sila-*m*-quinonemethide 3 and Their 2-MeTHF Complexes 12 at 77 K: Key intermediates **3a** and **3b** were isolated in glass matrixes at 77 K, in a procedure similar to that used to isolate **3c** (Scheme 3).[3] For example, a 3-methylpentane (3-MP) solution of **1a** was irradiated ($\lambda > 480$ nm) at 77 K and the change in the electronic absorption was monitored, as shown in Fig. 2. New peaks centered at 230 and 360 nm appeared with the progress of irradiation and the matrix turned yellow. The yellow species was identified as intermediate **3a**. The absorption maxima of **3a–c**[3] are summarized in Scheme 3.



Scheme 3.

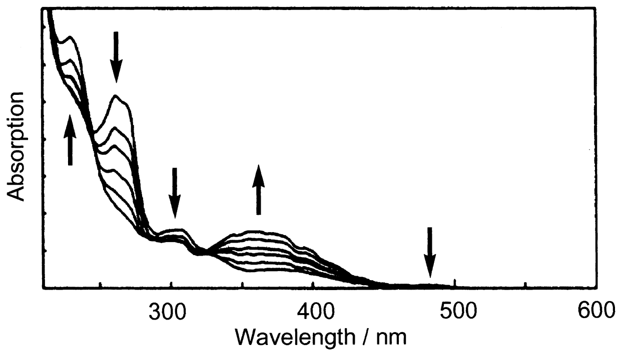


Fig. 2. Changes of absorption spectra of **1a** in a 3-MP matrix at 77 K during photolysis.

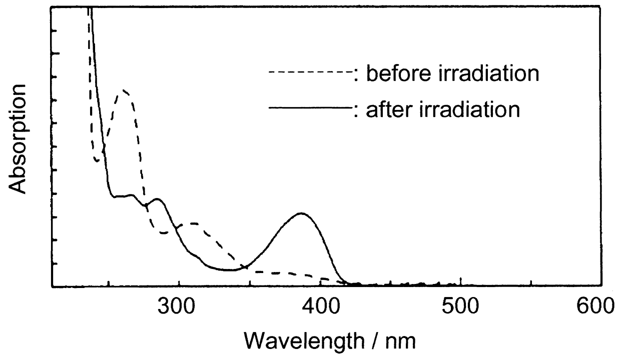


Fig. 3. Absorption spectral changes before and after photolysis of **1a** in a 2-MeTHF matrix in 77 K.

Interestingly, the irradiation ($\lambda > 480$ nm) of **1a** in a 2-methyltetrahydrofuran (2-MeTHF) solution resulted in the formation of an intermediate with red-shifted absorption (386 nm) compared to the irradiation of **1a** in a 3-MP solution (Scheme 3, Fig. 3). Because a similar red-shifted band was observed by the irradiation of **1a** in a 3-MP/2-MeTHF (100/1) solution at 77 K, the new species must be α-sila-*m*-quinonemethide–(2-MeTHF) complex **12a**.[11,12] Because the intermediates **3** have a silyl cation moiety which interacts with THF efficiently, 2-disilanyl-1,4-benzoquinone can be a photochemical initiator of cationic polymerization of THF.[13]

Experimental

Apparatus. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC300-P FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS D-300 mass spectrometer. Electronic absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrometer. Gas-liquid chromatography (GLC) analysis was carried out with a Shimadzu GC-8A gas chromatograph. IR spectra were recorded on a JEOL JIR-3505/3510 system.

Solvents. THF and Et_2O were dried over sodium benzophenone ketyl and distilled just before use. 3-Methylpentane (3-MP) and 2-methyltetrahydrofuran (2-MeTHF) were dried over $LiAlH_4$ and distilled before use. Hexane (for UV spectra), C_6D_6, and $CDCl_3$ were purchased from Aldrich and used without further purification.

Preparation of 2-Bromo-5-chloro-1,4-bis[(pentamethyldisilanyl)oxy]benzene (2a). To a THF (60 mL) solution of 2-bromo-5-chlorohydroquinone (1.50 g, 6.72 mmol) and $Me_3SiSiMe_2Cl$ (2.30 g, 13.8 mmol) was added a THF (40 mL) solution of Et_3N (1.42 g, 14.0 mmol) at room temperature. The mixture was stirred under reflux for 1 h and then filtered. The filtrate was concentrated and distillation gave **2a** (2.95 g, 6.12 mmol, 91%). **2a**: a colorless oil; bp 110–140 °C/0.11 mmHg; ^{1}H NMR (C_6D_6) δ 0.06 (s, 9H), 0.07 (s, 9H), 0.266 (s, 6H), 0.274 (s, 6H), 7.00 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (C_6D_6) δ −2.26, −2.19, 0.10, 0.16, 113.67, 121.55, 124.96, 124.96, 147.50, 148.46; ^{29}Si NMR (C_6D_6) δ −21.16, −21.10, 21.81, 22.11; HRMS *m*/*z* Found: 482.0322, Calcd for $C_{16}H_{32}BrClO_2Si_4$, 482.0351; Anal. Found: C, 39.66; H, 6.93%, Calcd for $C_{16}H_{32}BrClO_2Si_4$,: C, 39.69; H, 6.66%.

Preparation of 2-(Pentamethyldisilanyl)-5-chloro-1,4-benzoquinone (1a). To a Et_2O (50 mL) solution of **2a** (1.54 g, 3.19 mmol) was added a hexane solution of *n*-BuLi (6.51 mmol) at 0 °C. The mixture was stirred at 0 °C for 25 min and at room temperature for 40 min. Then a Et_2O solution of DDQ (0.934 g, 4.12 mmol) was added to the solution at 0 °C. After the mixture was stirred at 0 °C for 30 min and at room temperature for 110 min, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexane/toluene as the eluent to give **1a** (0.462 g, 1.69 mmol, 53%). **1a**: orange crystals; mp 73.8–74.3 °C; ^{1}H NMR (C_6D_6) δ 0.056 (s, 9H), 0.064 (s, 6H), 6.35 (s, 1H), 6.64 (s, 1H); ^{13}C NMR (C_6D_6) δ −4.67, −2.10, 134.66, 142.30, 143.78, 154.25, 177.79, 188.42; ^{29}Si NMR (C_6D_6) δ −22.20, −17.64; UV (hexane) λ_{max}/nm (ε) 257 (11100), 307 (2440), 370 (918), 481 (186); IR (KBr) ν/cm^{-1} 1660, 1637 (C=O); HRMS *m*/*z* Found: 272.0452, Calcd for $C_{11}H_{17}ClO_2Si_2$, 272.0456; Anal. Found: C, 48.13; H, 6.38%, Calcd for $C_{11}H_{17}ClO_2Si_2$: C, 48.42; H, 6.28%.

Preparation of 2,5-Dibromo-1,4-bis[(pentamethyldisilanyl)oxy]benzene (2b).[3] To a THF solution (150 mL) of 2,5-dibromohydroquinone (2.02 g, 7.53 mmol) and $Me_3SiSiMe_2Cl$ (2.53 g, 15.2 mmol) was added a THF (150 mL) solution of Et_3N (1.56 g, 15.4 mmol) at room temperature. After the mixture was stirred under reflux for 2 h, workup similar to that for **2a** gave **2b** (3.86 g, 7.34 mmol, 97%). **2b**: a colorless waxy solid; bp 110–115 °C/0.08 mmHg; mp 35–37 °C; ^{1}H NMR (C_6D_6) δ 0.07 (s, 18H), 0.28 (s, 12H), 7.16 (s, 2H); ^{13}C NMR (C_6D_6) δ −2.14, 0.20, 114.38, 124.38, 148.66; ^{29}Si NMR (C_6D_6) δ −21.10, 21.85; HRMS *m*/*z* Found: 525.9891, Calcd for $C_{16}H_{32}Br_2O_2Si_4$, 525.9846; Anal. Found: C, 36.20; H, 6.03%, Calcd for $C_{16}H_{32}Br_2O_2Si_4$: C, 36.36; H, 6.10%.

Preparation of 2-(Pentamethyldisilanyl)-5-bromo-1,4-benzoquinone (1b). To a Et_2O (120 mL) solution of **2b** (4.12 g, 7.79 mmol) was added a hexane solution of *n*-BuLi (16.6 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h and at room temperature for 15 min. To the reaction mixture was added a Et_2O solution of DDQ (1.52 g, 6.71 mmol) at −78 °C and this mixture was stirred for 15 min at the same temperature. The mixture was warmed to room temperature and workup similar to that for **1a** gave **1b** (0.765 g, 2.42 mmol, 31%). **1b**: orange crystals; mp 64.7–66.2 °C; ^{1}H NMR (C_6D_6) δ 0.05 (s, 9H), 0.06 (s, 6H), 6.666 (s, 1H), 6.673 (s, 1H); ^{13}C NMR (C_6D_6) δ −4.70, −2.09, 137.41, 139.10, 141.95, 153.96, 177.68, 187.96; ^{29}Si NMR (C_6D_6) δ −22.18, −17.67; UV (hexane) λ_{max}/nm (ε) 262 (8720), 316 (2830), 371 (721), 483 (150); IR (KBr) ν/cm^{-1} 1660, 1637 (C=O); HRMS *m*/*z* Found: 315.9950, Calcd for $C_{11}H_{17}BrO_2Si_2$, 315.9950; Anal. Found: C, 41.93; H, 5.53%, Calcd for $C_{11}H_{17}BrO_2Si_2$: C, 41.63; H, 5.40%.

Preparation of 2-(Pentamethyldisilanyl)-5-*t*-butyl-1,4-benzoquinone (1c).[3] To a THF (100 mL) solution of 2-bromo-5-*t*-butyl-1,4-[(pentamethyldisilanyl)oxy]benzene (2.00 g, 3.96 mmol) was added a hexane solution of *t*-BuLi (4.60 mmol) at −60 °C. The mixture was stirred at −50 °C for 2 h and at 10 °C for 5 min. To the reaction mixture was added a benzene (10 mL) solution of DDQ (1.05 g, 4.63 mmol) at −50 °C and this mixture was stirred for 20 min at the same temperature. The mixture was warmed to room temperature and workup similar to that for **1a** gave **1c** (0.496 g, 1.69 mmol, 43%). **1c**: orange crystals; mp 74–75 °C; ^{1}H NMR (C_6D_6) δ 0.13 (s, 9H), 0.16 (s, 6H), 1.08 (s, 9H), 6.47 (s, 1H), 6.76 (s, 1H); ^{13}C NMR (C_6D_6) δ −4.59, −2.00, 28.88, 34.90, 132.63, 145.56, 151.63, 155.64, 186.43, 191.66; ^{29}Si NMR (C_6D_6) δ −23.81, −18.19; MS (70 eV) *m*/*z* 354 (M^+); Anal. Found: C, 60.87; H, 8.70%, Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.17; H, 8.90%.

Preparation of 2-Bromo-5-chloro-1,4-bis(trimethylsiloxy)-benzene (14a). To a Et_2O (60 mL) solution of 2-bromo-5-chlorohydroquinone (1.50 g, 6.73 mmol) and Me_3SiCl (1.77 g, 16.3 mmol) was added a Et_2O (100 mL) solution of Et_3N (1.80 g, 17.8 mmol) at room temperature. After the mixture was stirred under reflux for 1 h, workup similar to that for **2a** gave **14a** (2.36 g, 6.42 mmol, 95%). **14a**: colorless crystals; mp 57–58 °C; ^{1}H NMR (C_6D_6) δ 0.09 (s, 9H), 0.11 (s, 9H), 6.95 (s, 1H), 7.15 (s, 1H); ^{13}C NMR (C_6D_6) δ 0.06, 0.13, 113.76, 121.77, 125.07, 125.16, 146.72, 147.71; ^{29}Si NMR (C_6D_6) δ 22.78, 22.99; HRMS *m*/*z* Found: 365.9866, Calcd for $C_{12}H_{20}BrClO_2Si_2$, 365.9874; Anal. Found: C, 39.05; H, 5.66%, Calcd for $C_{12}H_{20}BrClO_2Si_2$: C, 39.19; H, 5.48%.

Preparation of 2-Chloro-5-(trimethylsilyl)-1,4-benzoquinone (6a). To a Et_2O (100 mL) solution of **14a** (2.36 g, 6.64 mmol) was added a hexane solution of *n*-BuLi (13.3 mmol) at 0 °C. The mixture was stirred at 0 °C for 15 min and at room temperature for 15 min. A benzene solution of DDQ (1.51 g, 6.67 mmol) was added to the reaction mixture at 0 °C. The mixture was stirred at 0 °C for 10 min and warmed to room temperature. Workup similar to that for **1a** gave **6a** (0.666 g, 3.11 mmol, 47%). **6a**: yellow crystals; mp 98 °C; ^{1}H NMR (C_6D_6) δ 0.03 (s, 9H), 6.29 (s, 1H), 6.51 (s, 1H); ^{13}C NMR (C_6D_6) δ −2.00, 134.76, 142.36, 143.36, 151.81, 178.26, 188.17; ^{29}Si NMR (C_6D_6) δ −3.51; UV (hexane) λ_{max}/nm (ε) 262 (14200), 309 (342), 480 (30); IR (KBr) ν/cm^{-1} 1664, 1637 (C=O); HRMS *m/z* Found: 214.0217, Calcd for $C_9H_{11}ClO_2Si$, 214.0217; Anal. Found: C, 50.04; H, 5.35%, Calcd for $C_9H_{11}ClO_2Si$: C, 50.34; H, 5.16%.

Photoreaction of 1a in the Presence of Acetone. A hexane (4 mL) solution of **1a** (19.3 mg, 7.07×10^{-5} mol) and acetone (60.1 mg, 1.03 mmol) in a Pyrex tube (ϕ 10 mm) was irradiated ($\lambda > 350$ nm) for 10 min to give adduct **10a** (22.5 mg, 6.82×10^{-5} mol, 96%). **10a**: ^{1}H NMR (C_6D_6) δ 0.06 (s, 9H), 0.43 (s, 6H), 1.79 (s, 6H), 5.0 (brs, 1H), 6.72 (s, 1H); ^{13}C NMR (C_6D_6) δ 0.39, 0.95, 28.99, 84.13, 116.30, 121.79, 127.39, 128.31, 140.64, 144.58, 150.63; ^{29}Si NMR (C_6D_6) δ 19.07, 23.41; HRMS *m/z* Found: 330.0845, Calcd for $C_{14}H_{23}ClO_3Si_3$, 330.0874.

Photoreaction of 1b in the Presence of Acetone. A hexane (4 mL) solution of **1b** (27 mg, 8.5×10^{-5} mol) and acetone (105 mg, 1.8 mmol) in a Pyrex tube (ϕ 10 mm) was irradiated ($\lambda > 350$ nm) for 45 min to give adduct **10b** (27 mg, 7.2×10^{-5} mol, 85%). **10b**: ^{1}H NMR (C_6D_6) δ 0.05 (s, 9H), 0.43 (s, 6H), 1.80 (s, 6H), 5.1 (brs, 1H), 6.87 (s, 1H); ^{13}C NMR (C_6D_6) δ 0.17, 1.24, 29.44, 84.42, 113.06, 119.49, 129.16, 142.29, 145.71, 151.64; ^{29}Si NMR (C_6D_6) δ 19.12, 23.38; HRMS *m/z* Found: 374.0364, Calcd for $C_{14}H_{23}BrO_3Si_2$, 374.0369.

Photoreaction of 1c in the Presence of Acetone.[3] A hexane (10 mL) solution of **1c** (45 mg, 1.53×10^{-5} mol) and acetone (460 mg, 7.93 mmol) in a Pyrex tube (ϕ 20 mm) was irradiated ($\lambda > 520$ nm) for 60 min to give adduct **10c** (33 mg, 9.35×10^{-6} mol, 61%). **10c**: ^{1}H NMR (C_6D_6) δ 0.21 (s, 9H), 0.49 (s, 6H), 1.34 (s, 9H), 1.72 (s, 6H), 4.20 (s, 1H), 6.82 (s, 1H); ^{13}C NMR (C_6D_6) δ 0.55, 1.43, 30.13, 30.18, 34.50, 83.39, 115.61, 125.70, 139.88, 144.32, 146.50, 151.85; ^{29}Si NMR (C_6D_6) δ 16.46, 22.11; HRMS *m/z* Found: 352.1892, Calcd for $C_{18}H_{32}O_3Si_2$, 352.1890.

X-ray Crystallographic Analysis of 1a.[14,15] A suitable single crystal of **1a** was obtained by recrystallization from hexane. Crystal data were described above. Data collection were done at 170 K using a Rigaku AFC-5R diffractometer, graphite monochromatized Mo-$K\alpha$ ($\lambda = 0.71069$ Å) radiation. Reflections with $I > 3\sigma(I)$ were used in the least-squares refinement. The structure was solved by RANTAN81 direct method. The non-hydrogen atoms were refined anisotropically. Atomic scattering factors were applied from the literature. The ACOS 2200 computer at Tohoku University performed all calculations using UNICS III Package System.

Observation of α-Sila-*m*-quinonemethide 3 and Their 2-MeTHF Complex 12 at 77 K in Glass Matrixes by UV-Vis Spectroscopy. **1** and 3-MP, 2-MeTHF, or 3-MP/2-MeTHF (100/1) mixed solvent were placed in a sealed tube with a quartz cell. The solution was irradiated at 77 K and monitored by UV-vis spectroscopy.

Supporting Information Available. Ordering information is given on any current masthead page. Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factors for compound **1a** and **6a** (33 pages) are available. The crystallographic data for two crystals are deposited as Document No. 75053 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 192721 and 192722.

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