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Headline Articles

Synthesis, Structure, and Photochemistry of 2,3,5,6-Tetrasilyl-1,4-benzoquinones and Related Compounds

Shinobu Tsutsui,[#] Kenkichi Sakamoto,[*,†,##] Keisuke Ebata,[†] Chizuko Kabuto,[†] and Hideki Sakurai[*,†]

Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN),
519-1399 Aoba, Aramaki, Aoba-ku, Sendai 980-0845

†Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

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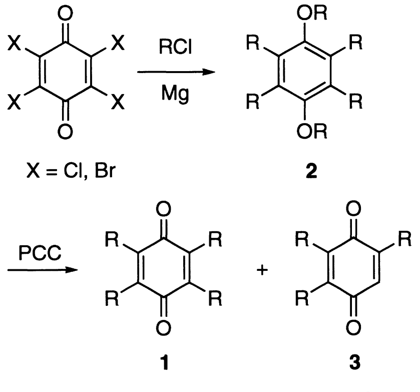
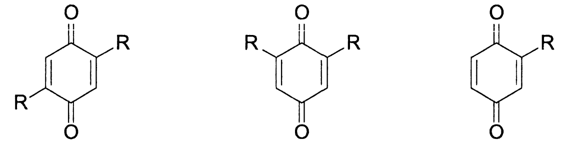
2,3,5,6-Tetrasilyl- and 2,3,5,6-tetragermyl-1,4-benzoquinones were obtained by oxidation of the corresponding 1,4-dimetaloxybenzene derivatives with pyridinium chlorochromate. X-ray crystallographic analysis revealed that the quinone ring of 2,3,5,6-tetrakis(trimethylsilyl)-1,4-benzoquinone (**1a**) was distorted into a chair form. The deformed quinone ring allowed a $\sigma(C_{quinone}\text{-}Si)$–$\pi^*$ electronic transition in **1a**. Photolysis of **1a** resulted in an isomerization, creating a ketene derivative, 4-carbonyl-2,3,5,5-tetrakis(trimethylsilyl)-2-cyclopenten-1-one.

Silyl groups perturb various π-electron systems electronically and sterically.[1] Fully silylated π-electron systems such as tetrasilylethene, hexasilylbenzene, pentasilylcyclopentadienyl, hexasilylbicyclopropenyl, and tetrasilylcyclobutadiene have previously been reported.[2–5] These compounds exhibit quite unusual properties due to the perturbation of silyl groups. 1,4-Benzoquinone is one of the most interesting fundamental π-electron systems due to properties such as high electron affinity.[6–8] In the present study we report the preparation and properties of 2,3,5,6-tetrasilyl-1,4-benzoquinones and related compounds as new fully silylated π-electron systems.[9]



a: R = Me_3Si, **b**: R = HMe_2Si, **c**: R = $(H_2C{=}CH)Me_2Si$, **e**: R = Me_3Ge

Scheme 1.



4b (R = HMe_2Si)
4c [R = $(H_2C{=}CH)Me_2Si$]
4e (R = Me_3Ge)
4f (R = $PhMe_2Si$)

5a (R = Me_3Si)
5b (R = HMe_2Si)

6a (R = Me_3Si)
6b (R = HMe_2Si)

Chart 1.

Results and Discussion

Preparation of Silyl- and Germyl-1,4-benzoquinones. The synthesis of 2,3,5,6-tetrakis(trimethylsilyl)-1,4-benzoquinone (**1a**) was carried out as shown in Scheme 1. Chloranil was reacted with trimethylchlorosilane and magnesium[10] using a mixture of THF and HMPA as the solvent (THF/HMPA = 10/1) to give 1,4-bis(trimethylsiloxy)-2,3,5,6-tetrakis(trimethylsilyl)benzene (**2a**) in 51% yield. Compound **2a** was also obtained by the reaction of 2,3,5,6-tetrabromo-1,4-benzoquinone with trimethylchlorosilane in the presence of magnesium in THF, even though the yield was lower (18%). The compound was then oxidized using pyridinium chlorochromate (PCC), producing **1a** (72%) as deep red crystals.[11] 2,3,5-Tris(trimethylsilyl)-1,4-benzoquinone (**3a**) was obtained in 9% yield as a by-product of the reaction. Preparation of **1b**, **1c**, and **1e** was achieved using similar procedures. This method was applicable to the preparation of 2,5-disilyl- and 2,5-digermyl-1,4-benzoquinones (**4**), 2,6-disilyl-1,4-benzoquinones (**5**), and 2-silyl-

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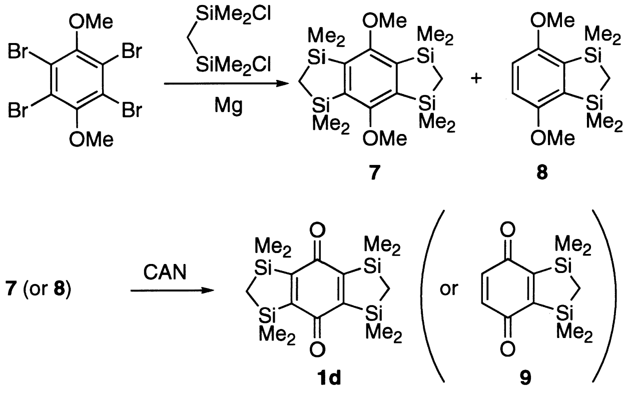
[#] Tohoku University
[##] RIKEN

1,4-benzoquinones (**6**) (Chart 1). However, attempts to prepare 2,3,5,6-tetrakis(dimethylphenylsilyl)-1,4-benzoquinone and 2,3,5,6-tetrakis(*t*-butyldimethylsilyl)-1,4-benzoquinone under similar conditions were not successful.

In addition, we have found that 1,4-dimethoxybenzene derivatives are useful precursors of silyl-1,4-benzoquinone derivatives.[12] Thus, preparation of tricyclic 2,3,5,6-tetrasilyl-1,4-benzoquinone (**1d**) was performed as shown in Scheme 2. The reaction of 2,3,5,6-tetrabromo-1,4-dimethoxybenzene with 1,3-dichloro-1,1,3,3-tetramethyl-1,3-disilapropane in the presence of magnesium in THF provided tricyclic dimethoxybenzene (**7**) and bicyclic dimethoxybenzene (**8**) in 5 and 3% yields, respectively. Oxidation of **7** and **8** using cerium(IV) ammonium nitrate (CAN) in CH_3CN provided **1d** and **9** in 37 and 69% yields, respectively.



Scheme 2.

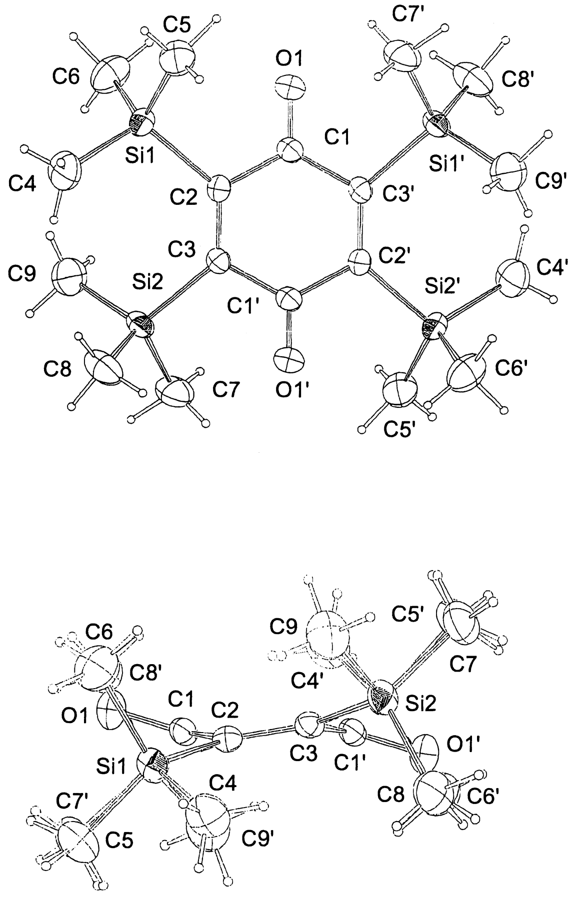


Fig. 1. ORTEP drawings of **1a**: upper, top view; lower, side view.

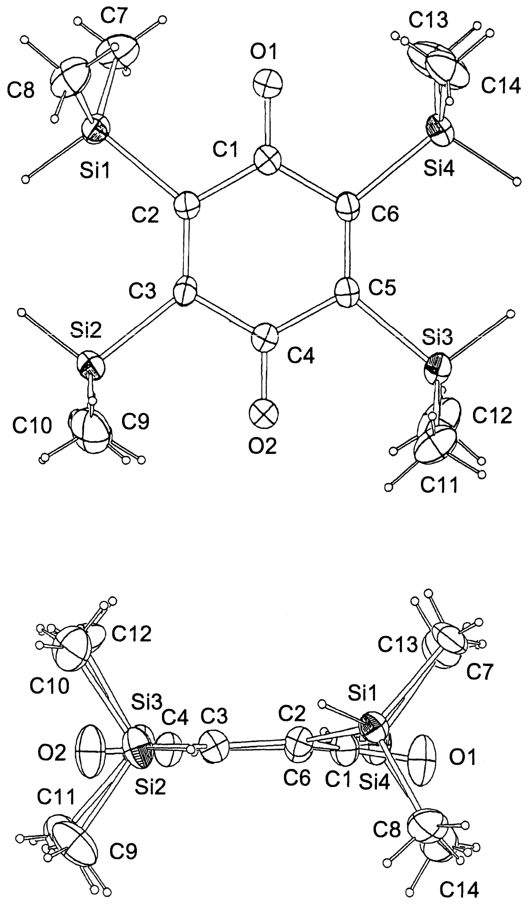


Fig. 2. ORTEP drawings of **1b**: upper, top view; below, side view.

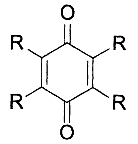
Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **1a** with Their Esd's in Parentheses

	Bond lengths		
Si1–C2	1.910(2)	C1–C6	1.499(4)
Si2–C3	1.911(2)	C2–C3	1.354(4)
O1–C1	1.225(4)	C3–C1′	1.499(3)
C1–C2	1.491(4)		
	Bond angles		
O1–C1–C2	118.0(2)	Si1–C2–C1	111.8(2)
O1–C1–C3′	118.2(2)	Si1–C2–C3	131.3(2)
C2–C1–C3′	123.4(2)	Si2–C3–C1′	116.3(2)
C1–C2–C3	116.9(2)	Si2–C3–C2	
C2–C3–C1′	116.3(2)		
	Torsion angles		
Si1–C2–C3–Si2	−17.3(4)	O1′–C1′–C3–Si2	−29.1(3)
O1–C1–C2–Si1	27.9(3)	C1–C2–C3–C1′	−20.0(3)

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **1b** with Their Esd's in Parentheses

Bond lengths			
Si1–C2	1.891(3)	C1–C2	1.491(4)
Si2–C3	1.896(3)	C1–C6	1.499(4)
Si3–C5	1.892(3)	C2–C3	1.353(4)
Si4–C6	1.895(3)	C3–C4	1.500(4)
O1–C1	1.214(4)	C4–C5	1.500(4)
O2–C4	1.215(4)	C5–C6	1.349(4)
Bond angles			
O1–C1–C2	118.4(3)	C1–C6–C5	118.6(2)
O1–C1–C6	118.9(2)	Si1–C2–C1	113.1(2)
C2–C1–C6	122.7(2)	Si1–C2–C3	128.4(2)
C1–C2–C3	118.4(2)	Si2–C3–C2	129.2(2)
C2–C3–C4	118.5(2)	Si2–C3–C4	112.3(2)
O2–C4–C3	118.8(2)	Si3–C5–C4	112.5(2)
O2–C4–C5	118.6(2)	Si3–C5–C6	129.0(2)
C3–C4–C5	122.6(3)	Si4–C6–C1	112.3(2)
C4–C5–C6	118.4(2)	Si4–C6–C5	129.0(2)
Torsion angles			
Si1–C2–C3–Si2	−4.9(5)	O1–C1–C2–Si1	13.2(4)
Si3–C5–C6–Si4	−0.6(5)	O1–C1–C6–Si4	−10.6(4)
C1–C2–C3–C4	−6.0(5)	O2–C4–C5–Si3	2.0(4)
C4–C5–C6–C1	1.4(5)	Si2–C3–C4–O2	1.1(4)

Table 3. Selected Averaged Bond Lengths (Å) of 1,4-Benzoquinones



R	C–C	C=C	C=O	Ref.
Me_3Si	1.503	1.354	1.225	This Work
HMe_2Si	1.498	1.351	1.215	This Work
i-$Pr_2(O=)P$	1.494	1.349	—	13a
Me	1.492	1.341	1.232	13b
Cl	1.490	1.344	1.211	13c
H	1.474	1.334	1.222	13d

X-ray Crystallographic Analysis of 1a and 1b. Crystal structures of **1a** and **1b** were revealed by X-ray crystallographic analysis. Single crystals of **1a** and **1b** suitable for X-ray crystallographic analysis were obtained from hexane solutions. ORTEP drawings of **1a** and **1b** are shown in Figs. 1 and 2, respectively. The selected bond lengths, bond angles, and torsion angles of **1a** and **1b** are summarized in Tables 1 and 2, respectively. In Table 3, the bond lengths in the quinone ring of **1a** and **1b** are shown and compared with those of other 1,4-benzoquinones.[13]

Figure 1 shows that the quinone ring of **1a** was significantly distorted into a chair conformation by the steric repulsion between the pairs of vicinal trimethylsilyl groups. The torsion angles for Si1–C2–C3–Si2 and C1–C2–C3–C1′ were 17.3 and 20.0°, respectively; the sp^2 carbon atoms C2 and C3 remained in near-planar geometries. As shown in Table 3, bond lengths of **1a** for C1–C2 (1.503 Å) and C2–C3 (1.354 Å) were slightly longer than the corresponding lengths for unsubstituted 1,4-benzoquinone (1.474 and 1.334 Å, respectively).[13d] The bond angles of **1a** for Si1–C2–C3 and Si2–C3–C2 were 131.3 and 131.1°, respectively, suggesting steric repulsion between vicinal trimethylsilyl groups. The angle between the planes defined by C1–C2–C3′ and C2–C3–C2′–C3′ was 19.1°, larger than the corresponding planes in 2,3,5,6-tetraphenyl-1,4-benzoquinone (7.0°)[13e] and 2,3,5,6-tetrakis(diisopropylphosphoryl)-1,4-benzoquinone (17.8°).[13a] The angle between the C1–O1 bond and the C1–C2–C3′ plane of **1a** (7.2°) was also larger than the corresponding angle in 2,3,5,6-tetrakis(diisopropylphosphoryl)-1,4-benzoquinone (1.3°).[13a]

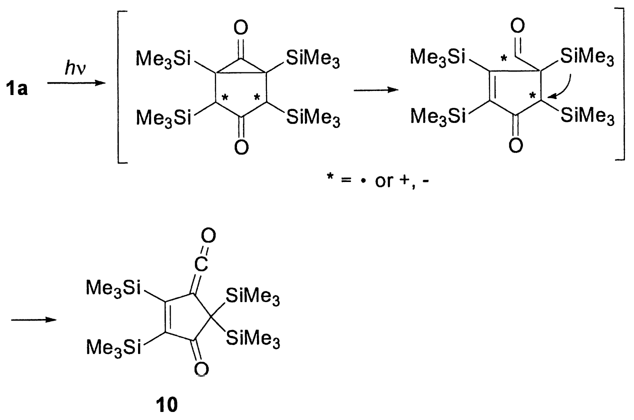
In contrast to the structure of **1a**, **1b** displays an almost planar quinone ring with silicon atoms almost coplanar to the quinone ring (Fig. 2). The torsion angles for Si1–C2–C3–Si2, Si3–C5–C6–Si4, C1–C2–C3–C4, and C4–C5–C6–C1 were 4.9, 0.6, 6.0, and 1.4°, respectively. The Si–H bond of **1b** was directed not towards the C=O group but towards another Si–H bond of the vicinal silyl group. The intramolecular distances of SiH···HSi of the vicinal silyl groups were 2.09–2.20 Å; this is shorter than the sum of two van der Waals radii for hydrogen (2.4 Å). Also, angles for Si–C=C of **1b** were large (128.2–129.2°). These results indicate that even the less-hindered dimethylsilyl groups interact with each other sterically, but the steric hindrance is insufficient to distort the quinone ring.

Physical Properties of 2,3,5,6-Tetrasilyl-1,4-benzoquinones and Related Compounds. The electronic absorption maxima and IR absorption frequencies of the C=O unit in silyl- and germyl-1,4-benzoquinones are summarized in Table 4. In the electronic absorption spectra of all the 1,4-benzoquinones in hexane, three bands were observed at about 250, 300, and 500 nm. The first and second bands are assignable to π–π^* transitions and the third one is assignable to a n–π^* transition. In addition, **1a** showed a broad band centered at 403 nm (ε = 123) assignable to a $\sigma(C_{quinone}\text{-}Si)$–$\pi^*$ transition. This transition is usually forbidden for planar quinones. In the distorted structure of **1a**, however, the π-orbitals of the quinone ring and the $\sigma(C_{quinone}\text{-}Si)$ bonds are not orthogonal to each other and hence the σ–π^* transition is allowed. A similar σ–π^* transition was observed at 417 nm (ε = 54) for **3a**. Since a similar steric repulsion between vicinal trimethylsilyl groups occurs in **3a**, its quinone ring should be similarly distorted. In contrast, 2,5-bis(trimethylsilyl)-1,4-benzoquinone (**4a**) having a planar ring showed no σ–π^* transition.[7c] The σ–π^* band was also observed for **1b** (λ_{max} = 426 nm, ε = 33) and **1d** (λ_{max} = 433 nm, ε = 10), but these absorptivities were smaller than that of **1a**. These results indicate that absorptivity of the σ–π^* band in these systems depends on the planarity of the quinone ring.

The IR spectrum of **1a** showed a peak at 1618 cm^{-1} assignable to the carbonyl group. Other 2,3,5,6-tetrasilyl- and 2,3,5,6-tetragermyl-1,4-benzoquinones also showed peaks at about 1620 cm^{-1}, such values are much lower than those of unsubstituted 1,4-benzoquinone (1668 and 1656 cm^{-1}).[14] With increasing number of silyl and germyl substituents, the peak shifted to lower frequencies, as shown in Table 4. These results showed that silyl and germyl groups acted as electron-donating substituents.

Table 4. Physical Properties of Silyl- and Germyl-1,4-benzoquinones

Quinone	UV (hexane) λ_{max}/nm (ε)			IR ν/cm^{-1} (C=O)
	π–π^*	n–π^*	n–π^*	
1a	265 (9260), 289 (4620), 327 (sh, 190)	403 (122)	527 (29)	1618
1b	266 (12300), 322 (sh, 300)	426 (33)	553 (48)	1624
1c	266 (8140), 291 (4750)	403 (119)	531 (35)	1620
1e	266 (9290), 286 (7790), 327 (sh, 223)	405 (90)	536 (37)	1620
1d	266 (10300), 315 (sh, 354)	433 (10)	562 (18)	1626
3a	258 (11400), 273 (sh, 5990), 328 (723)	417 (54)	539 (94)	1635, 1625
3e	263 (8120), 328 (sh, 490)	418 (33)	526 (67)	1635, 1628
4a	252 (14600), 296 (sh, 360)		504 (25)	1645
4b	252 (14000), 298 (390)		499 (20)	1645
4c	252 (13400), 306 (sh, 385)		499 (26)	1643
4d	255 (12800), 295 (sh, 968)		508 (28)	1643
4f	255 (12400), 306 (sh, 396)		501 (27)	1643
5a	253 (14500), 303 (562)		497 (24)	1651, 1626
5b	252 (13700), 306 (497)		492 (16)	1653, 1628
9	250 (13700), 312 (962)		511 (11)	1643



Scheme 3.

Photochemistry of 1a. The distorted structure of **1a** led to a novel photochemical reactivity of quinone. Photolysis of **1a** ($\lambda > 250$ nm) in hexane resulted in a transformation of the quinone ring: an isomer of **1a**, 4-carbonyl-2,3,5,5-tetrakis(trimethylsilyl)-2-cyclopenten-1-one (**10**) was obtained in 21% yield as pale yellow crystals (Scheme 3). Compound **10** was isolated by column chromatography on silica gel using hexane/benzene as the eluent, although **10** gradually decomposed in air. The structure of **10** was determined by NMR, IR, and mass spectra. The IR spectrum of **10** showed two peaks at 2089 and 1630 cm^{-1}, which are assignable to the ketene and ketone moieties, respectively. ^{13}C NMR and ^{29}Si NMR spectra of **10** indicated that **10** has three kinds of trimethylsilyl groups.

Biradical or zwitterionic species are plausible intermediates in this reaction, as shown in Scheme 3.[15] Attempts to trap the intermediates by *t*-BuOH and acetone failed. 2,5-Bis(trimethylsilyl)-1,4-benzoquinone (**4a**), 2,6-bis(trimethylsilyl)-1,4-benzoquinone (**5a**), 2,3,5,6-tetrakis(dimethylsilyl)-1,4-benzoquinone (**1b**) and 2,3,5,6-tetrakis(trimethylgermyl)-1,4-benzoquinone (**1e**) did not undergo a similar photoreaction. Thus, isomerization is driven by the large steric hindrance between silyl substituents and finishes with migration of a silyl substituent. Irradiation of **1a** at the n–π^* band ($\lambda > 500$ nm) also gave **10**, even though the reaction was very slow. Usually, irradiation of 1,4-benzoquinones gives n–π^* triplet excited states, which undergo radical reactions such as hydrogen abstraction.[6] However, no such reaction was observed in the photolysis of **1a**.

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.

Materials. THF, Et_2O, and benzene were dried over sodium benzophenone ketyl and distilled just before use. HMPA was dried over $LiAlH_4$ and distilled before use. CH_3CN and CH_2Cl_2 were dried over CaH_2 and distilled before use. Hexane (for UV spectra), C_6D_6, $CDCl_3$, Me_3SiCl, HMe_2SiCl, $PhMe_2SiCl$, $(H_2C{=}CH)Me_2SiCl$, chloranil, Mg, and PCC were purchased from Aldrich and used without further purification. 2,3,5,6-Tetrabromo-1,4-benzoquinone was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Me_3GeCl was purchased from AZmax Co., Ltd. and used without further purification. CAN, $NaHCO_3$, and Na_2SO_4 were purchased from Nacalai tesque Inc. and used without further purification. 2-Bromo-1,4-benzoquinone,[16a] 2,5-dibromo-1,4-benzoquinone,[16b] 2,6-dibromo-1,4-benzoquinone,[16c] 1,4-dimethoxy-2,3,5,6-tetrabromobenzene,[16d] and $(ClMe_2Si)_2CH_2$[16e] were made following the procedures described in the literature.

Preparation of 1,4-Bis(trimethylsiloxy)-2,3,5,6-tetrakis(trimethylsilyl)benzene (2a). Method A: To a THF (100 mL) solution of Me_3SiCl (47.1 g, 434 mmol), Mg (10.6 g, 43.5 mmol), and HMPA (9.5 mL) was added a THF (150 mL) solution of chloranil (11.8 g, 48.1 mmol) at room temperature. After stirring at room temperature for 1 night, the mixture was hydrolyzed with a saturated aqueous solution of $NaHCO_3$. 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 Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexane/benzene as the eluent to give **2a** (13.2 g, 24.3 mmol, 51%). **2a**: colorless crystals; mp 240 °C; ^1H NMR (C_6D_6) δ 0.18 (s, 18H), 0.42 (s, 36H); ^{13}C NMR (C_6D_6) δ 0.94, 4.04, 141.97, 162.21; ^{29}Si NMR (C_6D_6) δ −5.75, 19.23; HRMS found: *m/z* 542.2740, calculated for $C_{24}H_{54}O_2Si_6$: 542.2737; Anal. Found: C, 53.04; H, 9.96%, Calcd for $C_{24}H_{54}O_2Si_6$: C, 53.07; H, 10.02%.

Method B: To a THF (80 mL) solution of Me_3SiCl (37.2 g, 342 mmol) and Mg (8.14 g, 33.5 mmol) was added a THF (150 mL) solution of 2,3,5,6-tetrabromo-1,4-benzoquinone (23.6 g, 55.6 mmol) at room temperature. After stirring at room temperature for 2 days, a workup similar to that in Method A described above gave **2a** (5.56 g, 10.2 mmol, 18%).

Preparation of 2,3,5,6-Tetrakis(trimethylsilyl)-1,4-benzoquinone (1a). A CH_2Cl_2 (2 mL) solution of **2a** (1.01 g, 1.86 mmol) and PCC (0.825 g, 3.83 mmol) was stirred under reflux for 1.5 h. The resulting mixture was concentrated and chromatographed on silica gel using hexane as the eluent to give **1a** (0.529 g, 1.34 mmol, 72%) and 2,3,5-tris(trimethylsilyl)-1,4-benzoquinone (**3a**) (56 mg, 0.17 mmol, 9.3%). **1a**: deep red crystals; mp 182 °C; ^1H NMR (C_6D_6) δ 0.29 (s, 36H); ^{13}C NMR (C_6D_6) δ 1.54, 167.50, 198.99; ^{29}Si NMR (C_6D_6) δ −5.36; UV (hexane) λ_{max}/nm (ε) 207 (18900), 265 (9260), 289 (4620), 327 (sh, 190), 403 (122), 527 (29); IR (CCl_4) ν/cm^{-1} 1618 (C=O); HRMS found: *m/z* 396.1794, calculated for $C_{18}H_{36}O_2Si_4$: 396.1792; Anal. Found: C, 54.38; H, 9.01%, Calcd for $C_{18}H_{36}O_2Si_4$: C, 54.48; H, 9.14%. **3a**: deep red crystals; mp 140–140.5 °C; ^1H NMR (C_6D_6) δ 0.10 (s, 9H), 0.28 (s, 9H), 0.33 (s, 9H), 6.64 (s, 1H); ^{13}C NMR (C_6D_6) δ −1.94, 1.76, 1.82, 144.21, 153.08, 163.30, 168.36, 189.88, 196.17; ^{29}Si NMR (C_6D_6) δ −4.71, −4.45, −4.31; UV (hexane) λ_{max}/nm (ε) 258 (11400), 273 (sh, 5990), 328 (723), 417 (54), 539 (94); IR (CCl_4) ν/cm^{-1} 1635, 1625 (C=O); HRMS found: *m/z* 324.1393, calculated for $C_{15}H_{28}O_2Si_3$: 324.1397; Anal. Found: C, 55.70; H, 8.55%, Calcd for $C_{15}H_{28}O_2Si_3$: C, 55.50; H, 8.69%.

Preparation of 2,6-Bis(trimethylsilyl)-1,4-benzoquinone (5a).[7f] The compound was prepared from 2,6-dibromo-1,4-benzoquinone using a procedure similar to that for **1a**. **5a**: 7.9% yield; orange crystals; mp 54.5–55.5 °C; ^1H NMR (C_6D_6) δ 0.08 (s, 18H), 6.75 (s, 2H); ^{13}C NMR (C_6D_6) δ −1.84, 143.55, 153.37, 185.29, 194.40; ^{29}Si NMR (C_6D_6) δ −3.86; UV (hexane) λ_{max}/nm (ε) 253 (14500), 303 (562), 497 (24); IR (CCl_4) ν/cm^{-1} 1651, 1626 (C=O); MS (70 eV) *m/z* 252 (M^+).

Preparation of 2-(Trimethylsilyl)-1,4-benzoquinone (6a).[7e] The compound was prepared from 2-bromo-1,4-benzoquinone using a procedure similar to that for **1a**. **6a**: 7.4% yield; orange crystals; mp 63.5–64 °C; ^1H NMR (C_6D_6) δ 0.06 (s, 9H), 6.07 (m, 2H), 6.61 (s, 1H); ^{13}C NMR (C_6D_6) δ −1.96, 135.93, 137.28, 143.24, 151.42, 186.11, 190.59; ^{29}Si NMR (C_6D_6) δ −3.73; UV (hexane) λ_{max}/nm (ε) 246 (15400), 297 (630), 470 (28); IR (CCl_4) ν/cm^{-1} 1662, 1651 (C=O); MS (70 eV) *m/z* 180 (M^+).

Preparation of 1,4-Bis(dimethylsiloxy)-2,3,5,6-tetrakis(dimethylsilyl)benzene (2b). To a THF (50 mL) solution of HMe_2SiCl (15.3 g, 161 mmol) and Mg (3.93 g, 157 mmol) was added a THF (70 mL) solution of 2,3,5,6-tetrabromo-1,4-benzoquinone (7.38 g, 17.4 mmol) at room temperature. After the mixture was stirred at room temperature for 8 days, a workup similar to that for **2a** gave **2b** (2.50 g, 5.46 mmol, 31%). **2b**: colorless crystals; mp 112–112.5 °C; ^1H NMR (C_6D_6) δ 0.13 (d, *J* = 2.9 Hz, 12H), 0.54 (d, *J* = 3.8 Hz, 24H), 4.91 (sept., *J* = 3.8 Hz, 4H), 5.17 (sept., *J* = 2.9 Hz, 2H); ^{13}C NMR (C_6D_6) δ −1.57, −1.26, 138.40, 161.14; ^{29}Si NMR (C_6D_6) δ −20.76, 6.22; IR (KBr) ν/cm^{-1} 2160, 2141 (Si–H); HRMS found: *m/z* 458.1815, calculated for $C_{18}H_{42}O_2Si_6$: 458.1801; Anal. Found: C, 47.02; H, 8.96%, Calcd for $C_{18}H_{42}O_2Si_6$: C, 47.10; H, 9.22%.

Preparation of 2,3,5,6-Tetrakis(dimethylsilyl)-1,4-benzoquinone (1b). A mixture of **2b** (5.83 g, 12.7 mmol), PCC (5.48 g, 25.4 mmol), and CH_2Cl_2 (180 mL) was stirred under reflux for 1 h. A workup similar to that for **1a** gave **1b** (4.11 g, 12.1 mmol, 95%). **1b**: purple crystals; mp 103 °C; ^1H NMR (C_6D_6) δ 0.35 (d, *J* = 3.5 Hz, 24H), 4.62 (sept., *J* = 3.5 Hz, 4H); ^{13}C NMR (C_6D_6) δ −3.20, 162.55, 192.15; ^{29}Si NMR (C_6D_6) δ −22.09; UV (hexane) λ_{max}/nm (ε) 266 (12300), 322 (sh, 300), 426 (33), 553 (48); IR (CCl_4) ν/cm^{-1} 2156 (Si–H), 1624 (C=O); HRMS found: *m/z* 340.1167, calculated for $C_{14}H_{28}O_2Si_4$: 340.1167; Anal. Found: C, 49.10; H, 8.13%, Calcd for $C_{14}H_{28}O_2Si_4$: C, 49.35; H, 8.28%.

Preparation of 2,5-Bis(dimethylsilyl)-1,4-benzoquinone (4b). The compound was prepared from 2,5-dibromo-1,4-benzoquinone using a procedure similar to that for **1b**. **4b**: 52% yield; orange crystals; mp 28–29 °C; ^1H NMR (C_6D_6) δ 0.13 (d, *J* = 3.8 Hz, 12H), 4.28 (sept., *J* = 3.8 Hz, 2H), 6.70 (s, 2H); ^{13}C NMR (C_6D_6) δ −4.85, 145.20, 149.57, 189.27; ^{29}Si NMR (C_6D_6) δ −18.63; UV (hexane) λ_{max}/nm (ε) 252 (14000), 298 (390), 499 (20); IR (CCl_4) ν/cm^{-1} 2131 (Si–H), 1645 (C=O); HRMS found: *m/z* 224.0695, calculated for $C_{10}H_{16}O_2Si_2$: 224.0689; Anal. Found: C, 53.64; H, 7.22%, Calcd for $C_{10}H_{16}O_2Si_2$: C, 53.52; H, 7.19%.

Preparation of 2,6-Bis(dimethylsilyl)-1,4-benzoquinone (5b). The compound was prepared from 2-bromo-1,4-benzoquinone using a procedure similar to that for **1a**. **5b**: 34% yield; an orange oil; ^1H NMR (C_6D_6) δ 0.08 (d, *J* = 3.8 Hz, 12H), 4.25 (sept., *J* = 3.8 Hz, 2H), 6.73 (s, 2H); ^{13}C NMR (C_6D_6) δ −4.81, 144.43, 150.92, 184.72, 193.79; ^{29}Si NMR (C_6D_6) δ −18.47; UV (hexane) λ_{max}/nm (ε) 252 (13700), 306 (497), 492 (16); IR (CCl_4) ν/cm^{-1} 2131 (Si–H), 1653, 1628 (C=O); HRMS found: *m/z* 224.0689, calculated for $C_{10}H_{16}O_2Si_2$: 224.0689; Anal. Found: C, 53.39; H, 6.53%, Calcd for $C_{10}H_{16}O_2Si_2$: C, 53.52; H, 7.19%.

Preparation of 2-(Dimethylsilyl)-1,4-benzoquinone (6b). The compound was prepared from 2-bromo-1,4-benzoquinone using a procedure similar to that for **1b**. **6b**: 83% yield; an orange oil; ^1H NMR (C_6D_6) δ 0.07 (d, *J* = 3.8 Hz, 6H), 4.22 (sept., *J* = 3.8 Hz, 1H), 6.06 (d, *J* = 1.8 Hz, 1H), 6.07 (s, 1H), 6.62 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (C_6D_6) δ −4.90, 136.09, 136.99, 143.98, 149.38, 185.85, 190.34; ^{29}Si NMR (C_6D_6) δ −18.38; IR (CCl_4) ν/cm^{-1} 2131 (Si–H), 1666, 1650 (C=O); HRMS found: *m/z* 166.0450, calculated for $C_8H_{10}O_2Si$: 166.0434; Anal. Found: C, 58.09; H, 5.93%, Calcd for $C_8H_{10}O_2Si$: C, 57.80; H, 6.06%.

Preparation of 2,3,5,6-Tetrakis(dimethylvinylsilyl)-1,4-benzoquinone (1c). The compound was prepared from 2,3,5,6-tetrabromo-1,4-benzoquinone using a procedure similar to that for **1b**. **1c**: 3.3% yield; deep red crystals; mp 71.5 °C; ^1H NMR (C_6D_6) δ 0.38 (s, 24H), 5.68 (dd, *J* = 3.4, 20.4 Hz, 4H), 5.91 (dd, *J* = 3.4, 14.6 Hz, 4H), 6.38 (dd, *J* =14.6, 20.4 Hz, 4H); ^{13}C NMR (C_6D_6) δ −0.03, 133.02, 139.30, 166.54, 198.33; ^{29}Si NMR (C_6D_6) δ −12.96; UV (hexane) λ_{max}/nm (ε) 266 (8140), 291 (4750), 403 (119), 531 (35); IR (CCl_4) ν/cm^{-1} 1620 (C=O); HRMS found: *m/z* 444.1793, calculated for $C_{22}H_{36}O_2Si_4$: 444.1793; Anal. Found: C, 59.22; H, 7.94%, Calcd for $C_{22}H_{36}O_2Si_4$: C, 59.40; H, 8.16%.

Preparation of 2,5-Bis(dimethylvinylsilyl)-1,4-benzoquinone (4c). The compound was prepared from 2,5-dibromo-1,4-benzoquinone using a procedure similar to that for **1b**. **3c**: 41%

yield; orange crystals; mp 110.5–111 °C; ^{1}H NMR (C_6D_6) δ 0.21 (s, 12H), 5.64 (dd, J = 3.6, 20.2 Hz, 2H), 5.90 (dd, J = 3.6, 14.6 Hz, 2H), 6.18 (dd, J =14.6, 20.2 Hz, 2H), 6.74 (s, 2H); ^{13}C NMR (C_6D_6) δ −3.66, 134.10, 135.93, 145.18, 150.30, 189.71; ^{29}Si NMR (C_6D_6) δ −11.66; UV (hexane) $\lambda_{\max}$/nm (ε) 252 (13400), 306 (sh, 385), 499 (26); IR (CCl_4) ν/cm^{-1} 1643 (C=O); MS (70 eV) m/z 276 (M^{+}); HRMS found: m/z 276.0997, calculated for $C_{14}H_{20}O_2Si_2$: 276.1002; Anal. Found: C, 60.54; H, 7.43%, Calcd for $C_{14}H_{20}O_2Si_2$: C, 60.82; H, 7.29%.

Preparation of 2,5-Bis(dimethylphenylsilyl)-1,4-benzoquinone (4f). The compound was prepared from 2,5-bromo-1,4-benzoquinone using a procedure similar to that for **1b**. **4f**: 35% yield; orange crystals; mp 115–117 °C; ^{1}H NMR (C_6D_6) δ 0.39 (s, 12H), 6.65 (s, 2H), 7.1–7.2 (m, 6H), 7.4–7.5 (m, 4H); ^{13}C NMR (C_6D_6) δ −3.29, 128.54, 129.87, 134.58, 135.45, 145.70, 150.29, 189.66; ^{29}Si NMR (C_6D_6) δ −8.75; UV (hexane) $\lambda_{\max}$/nm (ε) 255 (12800), 295 (sh, 968), 508 (28); IR (CCl_4) ν/cm^{-1} 1643 (C=O); HRMS found: m/z 376.1314, calculated for $C_{22}H_{24}O_2Si_2$: 376.1315; Anal. Found: C, 70.01; H, 6.36%, Calcd for $C_{22}H_{24}O_2Si_2$: C, 70.16; H, 6.42%.

Preparation of 2,8-Dimethoxy-4,4,6,6,10,10,12,12-octamethyltricyclo[7.3.0.0^{3,7}]dodeca-4,6,10,12-tetrasila-1,3(7),8-triene (7). To a THF (100 mL) solution of $(ClMe_2Si)_2CH_2$ (13.6 g, 67.6 mmol) and Mg (3.29 g, 13.6 mmol) was added to a THF (50 mL) solution of 2,3,5,6-tetrabromo-1,4-dimethoxybenzene (10.0 g, 22.0 mmol) at room temperature. After the mixture was stirred at room temperature for 1 day, a workup similar to that for **2a** gave **7** (0.439 g, 1.11 mmol, 5.1%) and 2,5-dimethoxy-7,9-disila-7,7,9,9-tetramethyl-bicyclo[4.3.0]nona-1,3,5-triene (**8**) (0.194 g, 0.729 mmol, 3.3%). **7**: colorless crystals; mp 195–196.5 °C; ^{1}H NMR (C_6D_6) δ −1.03 (s, 4H), 0.47 (s, 24H), 3.55 (s, 6H); ^{13}C NMR (C_6D_6) δ −0.19, 1.38, 62.72, 145.78, 166.85; ^{29}Si NMR (C_6D_6) δ 7.84; HRMS found: m/z 394.1630, calculated for $C_{18}H_{34}O_2Si_4$: 394.1636; Anal. Found: C, 54.56; H, 8.53%, Calcd for $C_{18}H_{34}O_2Si_4$: C, 54.76; H, 8.68%. **8**: colorless crystals; mp 117.5–120.5 °C; ^{1}H NMR (C_6D_6) δ −0.05 (s, 2H), 0.52 (s, 12H), 3.37 (s, 6H), 6.51 (s, 2H); ^{13}C NMR (C_6D_6) δ −2.10, 0.73, 55.19, 111.39, 139.95, 158.32; ^{29}Si NMR (C_6D_6) δ 10.38; HRMS found: m/z 266.1155, calculated for $C_{13}H_{22}O_2Si_2$: 266.1158; Anal. Found: C, 58.69; H, 8.19%, Calcd for $C_{13}H_{22}O_2Si_2$: C, 58.59; H, 8.32%.

Preparation of 4,4,6,6,10,10,12,12-Octamethyl-4,6,10,12-tetrasilatricyclo[7.3.0.0^{3,7}]dodeca-1(9),3(7)-diene-2,8-dione (1d). To a CH_3CN (20 mL) solution of **7** (0.147 g, 0.373 mmol) was added a H_2O (20 mL) solution of CAN (1.71 g, 3.72 mmol) at room temperature. After the mixture was stirred under reflux for 12 h, a workup similar to that for **1a** gave **1d** (0.050 g, 0.14 mmol, 37%). **1d**: purple crystals; mp 254.5–255 °C; ^{1}H NMR (C_6D_6) δ −0.39 (s, 4H), 0.35 (s, 24H); ^{13}C NMR (C_6D_6) δ −3.57, 0.01, 166.75, 191.15; ^{29}Si NMR (C_6D_6) δ 12.95; UV (hexane) $\lambda_{\max}$/nm (ε) 266 (10300), 315 (sh, 354), 433 (10), 562 (18); IR (CCl_4) ν/cm^{-1} 1626 (C=O); HRMS found: m/z 364.1161, calculated for $C_{16}H_{28}O_2Si_4$: 364.1167; Anal. Found: C, 52.90; H, 7.80%, Calcd for $C_{16}H_{28}O_2Si_4$: C, 52.69; H, 7.74%.

Preparation of 7,7,9,9-Tetramethyl-7,9-disilabicyclo[4.3.0]-nona-1(6),3-diene-2,5-dione (9). To a CH_3CN (10 mL) solution of **8** (85.8 mg, 3.22 × 10^{-4} mol) was added a H_2O (12 mL) solution of CAN (0.752 g, 1.63 mmol) at room temperature. After the mixture was stirred at room temperature for 3 h, a workup similar to that for **1a** gave **9** (52.6 mg, 0.223 mmol, 69%). **9**: pale orange crystals; mp 81–81.5 °C; ^{1}H NMR (C_6D_6) δ −0.43 (s, 2H), 0.28 (s, 12H), 6.12 (s, 2H); ^{13}C NMR (C_6D_6) δ −3.92, −0.17, 137.53, 164.36, 189.14; ^{29}Si NMR (C_6D_6) δ 13.47; UV (hexane) $\lambda_{\max}$/nm (ε) 250 (13700), 312 (962), 511 (11); IR (CCl_4) ν/cm^{-1} 1643 (C=O); HRMS found: m/z 236.0685, calculated for $C_{11}H_{16}O_2Si_2$: 236.0689; Anal. Found: C, 55.60; H, 6.85%, Calcd for $C_{11}H_{16}O_2Si_2$: C, 55.88; H, 6.82%.

Preparation of 1,4-Bis(trimethylgermyloxy)-2,3,5,6-tetrakis(trimethylgermyl)benzene (2e). To a THF (20 mL) solution of Me_3GeCl (2.87 g, 18.7 mmol) and Mg (0.460 g, 18.9 mmol) was added a THF (15 mL) solution of 2,3,5,6-tetrabromo-1,4-benzoquinone (1.30 g, 3.06 mmol) at room temperature. After the mixture was stirred at room temperature for 36 h, a workup similar to that for **2a** gave **2e** (84.8 mg, 1.05 × 10^{-4} mol, 3.4%). **2e**: colorless crystals; mp 264–265 °C; ^{1}H NMR (C_6D_6) δ 0.31 (s, 18H), 0.58 (s, 36H); ^{13}C NMR (C_6D_6) δ 1.56, 4.42, 142.33, 163.23; Anal. Found: C, 35.71; H, 6.64%, Calcd for $C_{24}H_{54}Ge_6O_2$: C, 35.57; H, 6.71%.

Preparation of 2,3,5,6-Tetrakis(trimethylgermyl)-1,4-benzoquinone (1e). A mixture of **2e** (72.0 mg, 8.90 × 10^{-5} mol), PCC (39.0 mg, 0.181 mmol), and CH_2Cl_2 (15 mL) was stirred under reflux for 1 h. A workup similar to that for **1a** gave **1e** (40.5 mg, 6.98 × 10^{-5} mol, 79%) and 2,3,5-tris(trimethylgermyl)-1,4-benzoquinone (**3e**) (4.1 mg, 9.0 × 10^{-4} mol, 10%). **1e**: deep red crystals; mp 220 °C; ^{1}H NMR (C_6D_6) δ 0.43 (s, 6H); ^{13}C NMR (C_6D_6) δ 1.93, 169.03, 193.89; UV (hexane) $\lambda_{\max}$/nm (ε) 266 (9290), 286 (7790), 327 (sh, 223), 405 (90), 536 (37); IR (CCl_4) ν/cm^{-1} 1620 (C=O); HRMS found: m/z 579.9571, calculated for $C_{18}H_{36}O_2{}^{74}Ge_4$: 579.9563; Anal. Found: C, 37.75; H, 6.21%, Calcd for $C_{18}H_{36}Ge_4O_2$: C, 37.60; H, 6.31%. **3e**: deep red crystals; mp 128–130 °C; ^{1}H NMR (C_6D_6) δ 0.23 (s, 9H), 0.43 (s, 9H), 0.49 (s, 9H), 6.72 (s, 1H); ^{13}C NMR (C_6D_6) δ −2.04, 2.19, 2.25, 143.46, 156.46, 165.74, 169.63, 187.34, 192.74; UV (hexane) $\lambda_{\max}$/nm (ε) 263 (8120), 328 (sh, 490), 418 (33), 526 (67); IR (CCl_4) ν/cm^{-1} 1635, 1628 (C=O); HRMS found: m/z 455.9707, calculated for $C_{15}H_{28}O_2{}^{72}Ge_3$: 455.9752.

Preparation of 1,4-Bis(trimethylgermyloxy)-2,5-bis(trimethylgermyl)benzene (11e). To a THF (5 mL) solution of Me_3GeCl (1.00 g, 6.53 mmol) and Mg (0.258 g, 10.6 mmol) was added a THF (5 mL) solution of 2,5-dibromo-1,4-benzoquinone (0.390 g, 1.47 mmol) at room temperature. After the mixture was stirred for 18 h at room temperature and under reflux for 2.5 h, a workup similar to that for **2a** gave **11e** (0.293 g, 0.507 mmol, 34%). **11e**: colorless crystals; mp 160–161.5 °C; ^{1}H NMR (C_6D_6) δ 0.38 (s, 18H), 0.56 (s, 18H), 6.88 (s, 2H); ^{13}C NMR (C_6D_6) δ −0.95, 1.56, 121.79, 132.65, 156.77; HRMS found: m/z 573.9758, calculated for $C_{18}H_{38}{}^{72}Ge_4O_2$: 573.9755; Anal. Found: C, 37.44; H, 6.34%, Calcd for $C_{18}H_{38}Ge_4O_2$: C, 37.47; H, 6.64%.

Preparation of 2,5-Bis(trimethylgermyl)-1,4-benzoquinone (4e). A mixture of **11e** (121 mg, 2.10 × 10^{-4} mol), PCC (91.0 mg, 4.22 × 10^{-4} mol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. A workup similar to that for **1a** gave **4e** (71.3 mg, 2.10 × 10^{-4} mol, 99%). **4e**: orange crystals; mp 190.5–191 °C; ^{1}H NMR (C_6D_6) δ 0.26 (s, 18H), 6.75 (s, 2H); ^{13}C NMR (C_6D_6) δ −1.99, 143.89, 154.91, 188.50; UV (hexane) $\lambda_{\max}$/nm (ε) 255 (12400), 306 (sh, 396), 501 (27); IR (CCl_4) ν/cm^{-1} 1643 (C=O); HRMS found: m/z 339.9901, calculated for $C_{12}H_{20}O_2{}^{72}Ge_2$: 339.9905; Anal. Found: C, 42.14; H, 6.01%, Calcd for $C_{12}H_{20}Ge_2O_2$: C, 42.20; H, 5.90%.

X-ray Crystallographic Analysis of 1a.[17,18] Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) with graphite-monochromatized Cu-Kα radiation (λ = 1.54178 Å). Crystals for X-ray analysis were obtained from a hexane solution. The data collection was carried out at 170 K on a crystal of dimensions 0.25 × 0.20 ×

0.25 mm^3. A total of 1929 reflections with $2\theta_{\max} = 128°$ were collected. Crystal data: MF = $C_{18}H_{36}O_2Si_4$; MW = 396.83; orthorhombic; a = 12.184(1), b = 18.696(2), c = 10.562(1) Å; V = 2405.9(3) Å^3; space group = $Pbca$; Z = 4; D_c = 1.10 g/cm^3. The structure was solved by the direct method and refined anisotropically for Si, O, and C atoms and isotropically for H atoms. All calculations were performed using the UNICS Ⅲ package system and RANTAN81 program. The final R factor was 0.0376 (R_w = 0.0469) for 1735 reflections with $F_o > 3\sigma(F_o)$.

X-ray Crystallographic Analysis of 1b.[17,18] Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) with graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å). Crystals for X-ray analysis were obtained from a hexane solution. The data collection was carried out at 150 K on a crystal of dimensions 0.20 × 0.20 × 0.3 mm^3. A total of 5062 reflections with $2\theta_{\max} = 60°$ were collected. Crystal data: MF = $C_{14}H_{28}O_2Si_4$; MW = 340.72; monoclinic; a = 9.452(4), b = 17.702(5), c = 12.690(4) Å; V = 2046.5(24) Å^3; space group = $P2_1/c$; Z = 4; D_c = 1.11 g/cm^3. The structure was solved by the direct methods and refined anisotropically for Si, O, and C atoms and isotropically for H atoms. All calculations were performed using the UNICS Ⅲ package system and RANTAN81 program. The final R factor was 0.0628 (R_W = 0.0626) for 3967 reflections with $F_o > 3\sigma(F_o)$.

Photoisomerization of 1a. A hexane (7 mL) solution of **1a** (101 mg, 2.55×10^{-4} mol) in a Pyrex tube (ϕ 11 mm) was irradiated ($\lambda > 250$ nm) for 20 h at room temperature. The mixture was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexane/benzene as the eluent to give 4-carbonyl-2,3,5,5-tetrakis(trimethylsilyl)-2-cyclopenten-1-one (**10**) (21 mg, 5.3×10^{-5} mol, 21%). 7 mg (1.8×10^{-5} mol, 7%) of **1a** was recovered. **10**: Pale yellow crystals; mp 56–60 °C; ^{1}H NMR (C_6D_6) δ 0.13 (s, 18H), 0.19 (s, 9H), 0.39 (s, 9H); ^{13}C NMR (C_6D_6) δ −1.81, 0.91, 1.06, 47.51, 55.03, 149.10, 173.30, 197.60, 206.72; ^{29}Si NMR (C_6D_6) δ −7.6, −3.1, 4.7; IR (KBr, cm^{-1}) 2089 (C=C=O), 1630 (C=O); HRMS found: m/z 396.1791, calculated for $C_{18}H_{36}O_2Si_4$: 396.1792; UV (hexane) $\lambda_{\max}$/nm (ε) 281 (6340), 338 (6500).

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 compounds **1a** and **1b** (40 pages) are available. The crystallographic data for two crystals are deposited as Document No. 75054 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 192669 and 192670.

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