Synthesis, Structure, and Photochemistry of Tetrakis(trimethylsilyl)-*p*-benzoquinone

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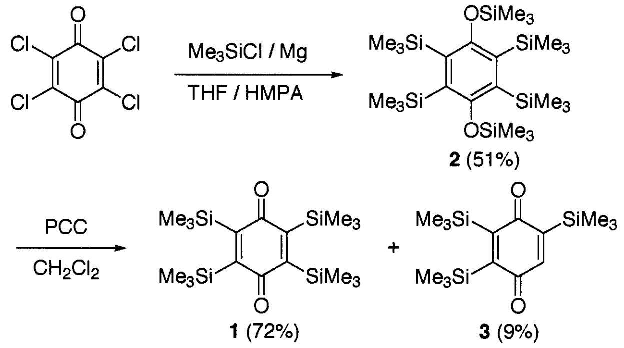
Tetrakis(trimethylsilyl)-*p*-benzoquinone (**1**) was obtained by oxidation of hexakis(trimethylsilyl)hydroquinone with pyridinium chlorochromate. X-Ray crystallographic analysis of **1** showed the quinone ring was distorted into a chair form by steric hindrance. Photolysis resulted in a rearrangement of the quinone ring and produced a ketene derivative.

We have reported on the chemistry of fully silylated π-electron systems such as tetrasilylethylene,[1,2] hexasilylbenzene,[3] pentasilylcyclopentadienyl,[4] and haxasilylbicyclopropenyl.[5] π-Systems are strongly perturbed by silyl groups. Such compounds thus exhibit quite unusual properties. Quinone is one of the most interesting fundamental π-electron systems because of properties such as its high electron affinity and photoreactivity.[6] Therefore, tetrakis(trimethylsilyl)-*p*-benzoquinone (**1**) was expected to be an interesting compound.[7]



Scheme 1.

The synthesis of **1** was carried out as shown in Scheme 1. Chloranil was subjected to the reaction with trimethylchlorosilane and magnesium[8] using a mixture of THF and HMPA as a solvent (THF/HMPA = 10/1) to give hydroquinone **2**. The compound was then oxidized using pyridinium chlorochromate (PCC) producing **1** (72%) as deep red crystals.[9,10] The main byproduct was tris(trimethylsilyl)-*p*-benzoquinone (**3**, 9%).[11] X-Ray crystallographic analysis showed that the quinone ring of **1** had been remarkably distorted into a chair form by steric repulsion between a couple of vicinal trimethylsilyl groups as shown in Figure 1.[12-14] 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. The bond lengths for C1-C2 (1.503 Å) and C2-C3 (1.354 Å) were slightly longer than the equivalent lengths for unsubstituted *p*-benzoquinone (1.474 and 1.334 Å, respectively).[15]

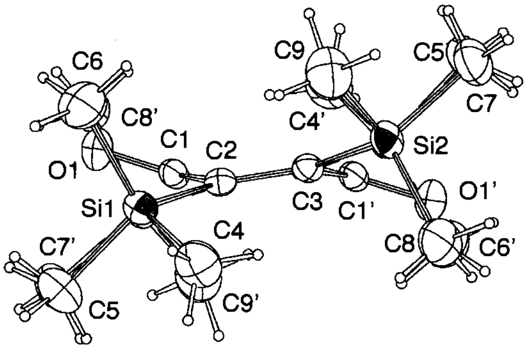


Figure 1. ORTEP drawing of **1**.

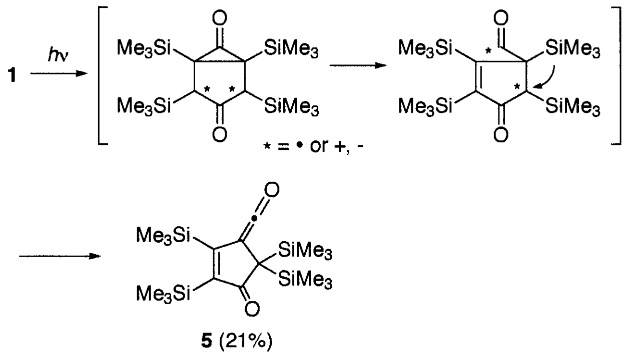
A broad band centered at 403 nm (ε = 123) was observed in the electronic absorption spectrum of **1** in hexane, along with the usual absorption bands of π–π* and n–π* transitions (Table 1). This stems from a σ(C$_{quinone}$–Si)–π* transition. Such a σ–π* transition would usually be forbidden. However, in the distorted structure of **1**, the π–orbitals of the quinone ring and the σ(C–Si) bonds are not orthogonal to each other, and hence the σ-π* transition is allowed. Since a similar steric repulsion between vicinal trimethylsilyl groups occurs in **3**, its quinone ring should be similarly distorted. In fact, a similar σ-π* transition was observed at 417 nm. In contrast, 2,5-bis(trimethylsilyl)-*p*-benzoquinone (**4**) with a planar ring showed no σ–π* transition.[7a]

Table 1. Absorption maxima of *p*-benzoquinones in hexane

Compound	λ$_{max}$/nm (ε)		
	π-π*	σ-π*	n-π*
1	265 (9240), 289 (4600), 326 (sh, 190)	403 (123)	530 (28)
3	258 (11400), 273 (sh, 5990), 328 (7230)	417 (54)	539 (94)
4[a]	253 (14500), 303 (562)	—	497 (24)

[a]Ref. 7a.

The distorted structure of **1** led to a novel photochemical reactivity of quinone. Photolysis of **1** (λ > 250 nm) in hexane resulted in a transformation of the quinone ring; an isomer of **1**, 4-carbonyl-2,3,5,5-tetrakis(trimethylsilyl)-2-cyclopenten-1-one (**5**) was obtained in 21% yield.[16,17] Biradical or zwitterionic species is a plausible intermediate of this reaction as shown in Scheme 2.[18] Because disilylquinone **4** did not undergo the similar photoreaction, the isomerization would be driven by the large steric hindrance and finished with migration of a silyl substituent.



Scheme 2.

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10 **1**: Deep red crystals; mp 182 °C; ^{1}H NMR (C_6D_6, δ) 0.29 (s, 36 H); ^{13}C NMR (C_6D_6, δ) 1.54, 167.50, 198.99; ^{29}Si NMR (C_6D_6, δ) -5.4; IR (KBr, cm^{-1}) 1614; HRMS Found: 396.1794, Calcd for $C_{18}H_{36}O_2Si_4$: 396.1792.

11 **3**: Deep red crystals; mp 140-140.5 °C; ^{1}H NMR (C_6D_6, δ) 0.10 (s, 9 H), 0.28 (s, 9 H), 0.33 (s, 9 H), 6.64 (s, 1 H); ^{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) -4.7, -4.4, -4.3; IR (KBr, cm^{-1}) 1633, 1620; HRMS Found: 324.1393, Calcd for $C_{15}H_{28}O_2Si_3$: 324.1397.

12 Diffraction data were collected on a Rigaku Denki AFC-5R diffiactometer 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 x 0.20 x 0.25 mm^3. A total of 1929 reflections with $2\theta_{max}$ = 128° was 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_{calcd} = 1.10 g/cm^3. The structure was solved by the direct methods and refined anisotopically for Si, O, and C atoms and isotropically for H atoms. All calculations were performed using UNICS III package system and RANTAN81 program. The final R factor was 0.0376 (R_W = 0.0469) for 1735 reflections with $F_0 > 3\sigma(F_0)$.

13 Selected structural parameters of **1** are as follows: bond lengths (Å) Sil-C2 = 1.910(2), C1-O1 = 1.225(4), C1-C2 = 1.503(4), C2-C3 = 1.354(4), C3-C1' = 1.499(3); bond angles (deg) Sil-C2-C1 = 111.8(2), Sil-C2-C3 = 131.3(2), Si2-C3-C1' = 112.6(2), O1-C1-C2 = 118.0(2), C1-C2-C3 = 116.9(2), C2-C1-C3' = 123.4(2); torsion angles (deg) Sil-C2-C3-Si2 = 17.3(4), O1-C1-C2-Sil = 27.9(3), C1-C2-C3-C1' = 20.0(3).

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16 **5**: Pale yellow crystals; mp 56-60 °C; ^{1}H NMR (C_6D_6, δ) 0.13 (s, 18 H), 0.19 (s, 9 H), 0.39 (s, 9 H); ^{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: 396.1791, Calcd for $C_{18}H_{36}O_2Si_4$: 396.1792; UV (hexane) λ_{max}/nm (ε) 281 (6340), 338 (6500).

17 Irradiation of **1** at the n-π* band (λ > 500 nm) also gave **5**, even though the reaction was very slow. Usually irradiation of quinones 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 **1**.

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