

Silylene-transfer reactions of cyclic organosilanes induced by phenanthraquinone triplet

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Abstract

On irradiation cyclic organosilanes **1a–b**, **7** and **8** react with phenanthraquinone (PQ) to afford corresponding dioxasilolenes **2a–b** as silylene-transfer products. The quenching experiment by anthracene reveals that PQ should act as triplet (³PQ*) to undergo radical displacement at the silicon atom of **1a–b**. In polar solvents, electron-transfer from **1a–b** to ³PQ* would generate PQ radical anion and the coupling of the radical ion pair formed would cause the Si–Si bond cleavage followed by intramolecular O–Si bond formation to give silylene transfer product **2a–b**. Since the photolysis of PQ with **1a–b** in the presence of CCl₄ gives dichlorooligosilanes, intermediacy of oligosilanyl radicals is highly probable. The quenching rate constant *k_q* of ³PQ* by cyclic organosilane **1b** has been determined by laser flash photolysis. In a mixed solvent of CH₃CN and CH₂Cl₂, ³PQ* is readily quenched by the addition of **1b** with the formation of PQ radical anion. On the other hand, since PQ radical anion has not been observed on the laser photolysis, the quenching of ³PQ* with **1b** in benzene should be less efficient. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oligosilane; Silylene transfer; Phenanthraquinone; Radical ion; Photo-induced electron-transfer; Radical displacement

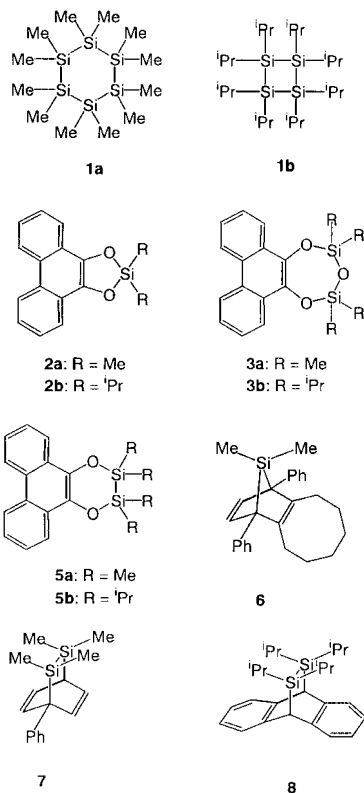
1. Introduction

Much attention has been drawn to the electron-transfer chemistry of organosilicon compounds since C–Si and Si–Si σ -bonds have much lower ionization potentials than those of the corresponding σ -C–C bonds [1]. It is of particular interest that the electron-donor property of oligosilanes increases as the chain length increases as a result of σ conjugation of Si–Si bonds [2]. In the meantime, several research groups investigated electron-transfer reactions of organosilanes with some kinds of electron deficient ketones as electron acceptors [3,4]. Previously, we reported that photoreactions of *p*-benzoquinone with carbocycles

having disilyl and digermanyl units resulted in the insertion of *p*-benzoquinone into Si–Si and Ge–Ge bonds [3]. Furthermore, benzylsilane has been shown to react with *p*-benzoquinone to give the corresponding benzylated quinone [4]. While a lot of examples of electron-transfer reactions of *p*-quinones acting as acceptors have been reported, those of *o*-quinones have been rather sparse. In the course of our continuous studies on electron-transfer chemistry of organometallic compounds, we have demonstrated that on irradiation cyclic organosilanes undergo novel silylene-transfer to phenanthraquinone (PQ), for which we have proposed a mechanism involving PQ triplet (³PQ*) without definite photophysical evidence [5]. In this paper, coupled with the quenching studies by laser flash photolysis we describe the novel photo-induced silylene-transfer reaction of organosilanes **1a–b**, **7** and **8** to ³PQ* with experimental details.

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2. Result and discussion

2.1. Photo-induced silylene-transfer reaction of cyclosilanes

Irradiation of a solution of **1a** [6a] (1.1×10^{-2} M) and PQ (3.5×10^{-2} M) in a mixed solvent ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2 = 4/1$) with two 500 W tungsten-halogen lamps (passing through an aqueous NaNO_2 solution filter, cutoff < 400 nm) produced **2a** and **3a**, as silylene-transfer products. Under similar reaction conditions **1b** [6b] afforded silylene-transfer product **2b** whereas it is noteworthy that another type of product **3b** was not obtained as shown in Table 1. Although ultraviolet photolysis of **1a** is well known to produce free

dimethylsilylene, which can be trapped readily by α -diketones to afford the corresponding dioxasilolene derivatives [7], **1a** is inert to the light source employed in the present photolyses. Furthermore, the photochemical reaction above does not seem to involve free dimethylsilylene because the photolysis of **1a** and PQ in the presence of Et_3SiH , a common silylene trap, did not give expected $\text{Et}_3\text{SiSiMe}_2\text{H}$ at all [7b].

On the other hand, since the silylene-transfer was efficiently quenched by the addition of anthracene, the triplet PQ ($^3\text{PQ}^*$) should be the key intermediate as judged by the comparison of the singlet and the triplet energies of PQ ($E_S = \text{ca. } 54$, $E_T = \text{ca. } 48$ kcal mol⁻¹) [8] and those of anthracene ($E_S = \text{ca. } 76$, $E_T = \text{ca. } 43$ kcal mol⁻¹) [9]. Meanwhile, the consumption of **1a** was suppressed by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), which has a lower oxidation potential ($E_{\text{ox}} = +0.70$ V vs. SCE) than that of **1a** ($E_{\text{ox}} = +1.45$ V vs. SCE). Table 2 indicates the free energy changes (ΔG) calculated by the Rehm–Weller equation [10] for the electron-transfer from cyclosilanes to $^3\text{PQ}^*$. These data suggest that the reaction may proceed a partial or complete electron-transfer from the cyclosilanes to $^3\text{PQ}^*$ at least in a polar solvent, such as acetonitrile. In fact, the silylene-transfer reaction proceeds substantially faster in acetonitrile than in benzene as shown in Table 1.

Based on previous observation that the ketone triplet cleaves a Si–Si bond of oligosilanes via $\text{S}_{\text{H}2}$ type radical displacement at the silicon atom [11], we depicted the plausible reaction scheme as exemplified by the case of **1a** (Scheme 1). Thus, $^3\text{PQ}^*$ attacks one of the silicon atoms of **1a** to afford diradical **4**. Prior to the formation of **4**, a partial or complete electron-transfer from **1a** to $^3\text{PQ}^*$ is likely to occur, at least in polar solvents, as mentioned above. Subsequently, intramolecular O–Si bond formation in **4** would lead to **2a**. The yields of **2a** indicate that a molecule of **1a** donates more than one silylene unit to PQ. After careful separation from the photolysate by HPLC, we obtained polymeric products containing silylene units, which might be arise from the fragmentation of the starting materials. In addition, the

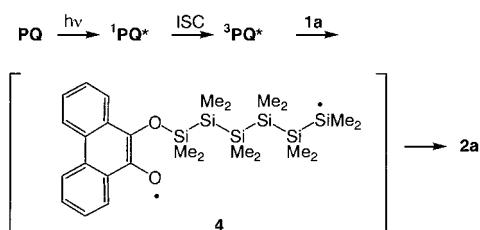
Table 1
Photo-induced silylene-transfer reactions of cyclosilanes to PQ

Silane	Condition	Time (h)	Conv. (%)	Product (yield (%)) ^a
1a	$h\nu/\text{PQ}-\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$	4.5	61	2a (138), 3a (33)
1a	$h\nu/\text{PQ}-\text{C}_6\text{H}_6$	10.5	49	2a (161), 3a (31)
1b	$h\nu/\text{PQ}-\text{CH}_2\text{Cl}_2$	0.5	70	2b (82)
1b	$h\nu/\text{PQ}-\text{C}_6\text{H}_6$	1.5	70	2b (57)
7	$h\nu/\text{PQ}-\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$	0.5	89	2a (28), 3a (11), biphenyl (100)
7	$h\nu/\text{PQ}-\text{C}_6\text{H}_6$	1.5	65	2a (62), 3a (13), biphenyl (94)
8	$h\nu/\text{PQ}-\text{CH}_3\text{CN}$	3.0	100	2b (85), anthracene (97)
8	$h\nu/\text{PQ}-\text{C}_6\text{H}_6$	18.0	70	2b (69), anthracene (100)

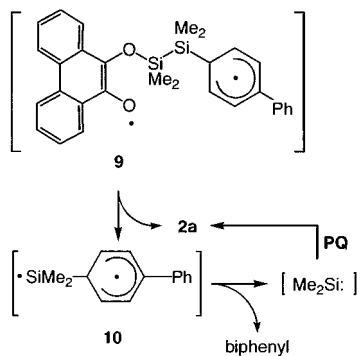
^a Yields were determined based on the amounts of consumed silanes.

Table 2
The free energy changes (ΔG) for the electron-transfer from cyclotetrasilanes to PQ

	E_{ox} (V vs. SCE)	ΔG (kcal mol ⁻¹)	
		in CH ₃ CN	in C ₆ H ₆
1a	+1.45	-1.4	+17.8
1b	+1.00	-11.8	+7.5
7	+0.42	-25.2	-6.0
8	+1.17	-7.9	+11.4



Scheme 1.



Scheme 2.

photolysis of **1a** and PQ in the presence of CCl₄ gave Cl(Me₂Si)_nCl ($n = 4-6$), which would substantiate the mechanism above involving silyl radical intermediates such as **4a** [12]. Under the reaction condition, the formation of Cl(Me₂Si)₆Cl may indicate the electron-transfer from **1a** to ³PQ*, and this affords the corresponding radical cation **1a**⁺• which readily reacts with CCl₄ to give Cl(Me₂Si)₆Cl [12b].

While the pathway leading to **3a** has not been clarified, it was proposed that an intermediate **5a**, which may arise from intramolecular cyclization of **4**, would undergo atmospheric oxidation to give **3a**. However, the intermediate **5a** was never detected in the photolysates. Further, several trapping experiments for free dimethylsilylene and dimethylsilanone [13], which could react with **2a** to afford **5a** and **3a**, respectively, have been unsuccessful. The residual molecular oxygen would be responsible for the formation of **3a**. In fact, when the photolysis was carried out after saturation of

molecular oxygen, the yield of **3a** increased while that of **2a** decreased somewhat. Since **2a** is stable in the air, it is suggested molecular oxygen should be incorporated probably by way of some radical intermediates to afford **3a** during the photoreactions. Meanwhile, photolysis of 7-silanorbornadiene **6** [14] with PQ gave **2a** and **3a** under similar reaction conditions. This result indicates that transfer of silylene units proceeds stepwise to produce **3a**, possibly by way of **2a**. Since the photoreaction of **1b** having more bulky isopropyl groups did not afford **3b** as mentioned above, conversion of **2b** to **3b** may be prevented by the steric restriction caused by isopropyl groups.

Recently, it has been demonstrated that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes such as **7** [15a,b] and **8** [15c], which are known as good disilene precursors [13], also serve as efficient electron donors [16]. Therefore, it was expected that selective disilanylene not silylene transfer to PQ might take place when **7** and **8** were employed as electron donors. However, the photolysis of **7** in the presence of PQ afforded silylene addition product **2a** together with **3a**, but expected **5a** was not detected in the photolysate. Similarly, under the same conditions **8** was photolyzed to yield only **2b**, **3b** was not detected in the reaction mixture as the case of **1b**. As proposed for the case of **1a-b**, this result should be interpreted reasonably in terms of the reaction scheme involving a diradical intermediate **9** (Scheme 2). Then, **9** might collapse to give biphenyl and free dimethylsilylene, which could contribute to the formation of **2a** and **3a**. Participation of free dimethylsilylene was suggested by the fact that Et₃SiSiMe₂H was obtained in the photolysis of **2a** and PQ in the presence of Et₃SiH. In contrast no concrete evidence for free diisopropylsilylene was obtained, and the co-photolysis of **8** and PQ in the presence of Et₃SiH did not give the trapped product Et₃SiSiPr₂H.

2.2. Laser flash photolysis

In order to gain more insight into the reaction mechanism discussed above, we investigated quenching of ³PQ* by oligosilane **1b** by means of laser flash photolysis. Fig. 1a shows the transient absorption spectra obtained after laser excitation of a solution (CH₃CN-CH₂Cl₂ = 4/1) of PQ at room temperature, in which triplet-triplet (T-T) absorption appeared around 450 nm [17]. In the presence of cyclotetrasilane **1b**, the T-T absorption of ³PQ* decayed faster due to quenching with **1b** and at the same time a new band around 520 nm assignable to PQ radical anion [17b] became intense as shown in Fig. 1b. From the dependence of lifetime of ³PQ* upon the concentration of **1b**, the quenching rate constant (k_q) was calculated to be 4.35×10^9 (M⁻¹ s⁻¹). These results indicate that the photo-induced electron-transfer reaction takes place from **1b** to

$^3\text{PQ}^*$ to give the corresponding radical ion pair. Same types of electron transfer should take place on irradiation of **1a**, **7**, and **8** as suggested by ΔG values in Table 2. Coupling of the radical ion pair thus formed would result in the formation of a diradical intermediate such

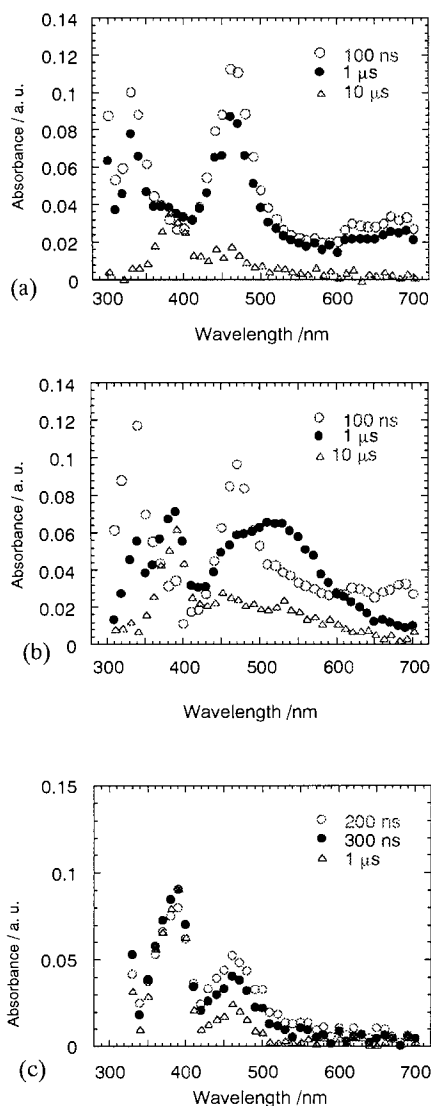
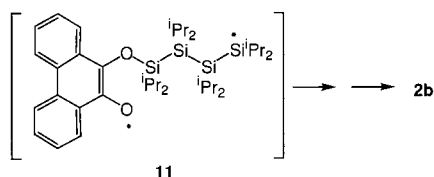
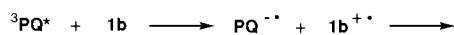


Fig. 1. Transient Absorption Spectra Obtained by Laser Excitation of PQ. (a) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. (b) in the presence of **1b** in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. (c) in the presence of **1b** in C_6H_6 .



Scheme 3.

as **11** and finally afford the product **2b** as in the case of **2a** (Scheme 3).

On the other hand, electron-transfer does not seem to operate efficiently in benzene, a less polar solvent. As shown in Fig. 1c, PQ radical anion was not observed on laser irradiation of PQ and **1b** in benzene. Furthermore, the k_q value was found to be $8.17 \times 10^8 \text{ (M}^{-1} \text{s}^{-1}\text{)}$, much smaller than that obtained for $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ solution. This is consistent with the experimental result that the present photoreaction proceeds faster in $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ than in benzene (Table 2). These solvent effects clearly indicate that some alternative process other than electron-transfer may be responsible for the quenching of $^3\text{PQ}^*$, at least in benzene. As discussed above, $\text{S}_{\text{H}2}$ -type radical substitution is a plausible rationale for the quenching process in non-polar media. Formation of an exciplex from $^3\text{PQ}^*$ and **2b** should be also considered, whereas no exciplex emission has been observed on irradiation of PQ and **2b** in benzene.

3. Experimental

3.1. General procedure

NMR spectra were recorded with a Varian Unity-plus 500 spectrometer. Deuterated CHCl_3 and C_6H_6 were used as the solvents. Mass spectral data were obtained on a Shimadzu QP-1000 mass spectrometer. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. UV-vis spectra were obtained with a Hitachi U-3300 spectrometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrometer. GLC analyses were carried out on a Shimadzu GC-14A equipped with an FID detector and a $0.25 \text{ mm} \times 25 \text{ m}$ CBP1 capillary column. Preparative GLC was performed on an Ohkura Riken 802 gas chromatograph with a TCD detector and a $3 \text{ mm} \times 1.7 \text{ m}$ SE-30 (10%) packed column. Gel permeation chromatography was also used for separation of reaction products using a series of JAIgel 1H and 2H columns with a flow of toluene on an LC-908 liquid chromatograph of Japan Analytical Industry Co. Ltd. Cyclic voltammograms of cyclosilanes were obtained in $0.1 \text{ M } n\text{-Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ (vs. SCE; scan rate, 200 mV s^{-1} ; Hokuto Denko Ltd, a potentiostat/galvanostat HA-501 and a function generator HB-104). The ΔG values were calculated according to the Rehm-Weller equation [10] ($\Delta G \text{ (kcal mol}^{-1}\text{)} = 23.06[E(D/D^+) - E(A^-/A) - \Delta E_{\text{excit.}} + \Delta E_{\text{coul.}}]$). The reduction potential of PQ is -0.66 V (vs. SCE), and the triplet energy of PQ (48 kcal mol^{-1}) was used as the excitation energy ($\Delta E_{\text{excit.}}$) [8]. The Coulomb interaction energies ($\Delta E_{\text{coul.}}$) are -0.06 and $+0.78 \text{ eV}$ for MeCN and C_6H_6 , respectively [10b]. PQ (Wako Pure Chemical) was commer-

cially available and used as received. Compounds **1a** [6a], **1b** [6b], **6** [14], **7** [15a,b], and **8** [15c] were prepared according to the literatures.

3.2. Photoreactions of cyclosilanes

A typical procedure is exemplified as follows. A degassed solution of **1a** (1.1×10^{-2} M) and PQ (3.5×10^{-2} M) in a mixed solvent ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2 = 4/1$) was irradiated with two 500 W tungsten-halogen lamps (passing through an aqueous NaNO_2 solution filter, cutoff < 400 nm) at room temperature (r.t.). The silylene adducts **2a** and **3a** were obtained by preparative GLC and HPLC. The yields of **2a** and **3a** were determined by analytical GLC. Photolyses of **1b**, **6**, **7**, and **8** were conducted in the same procedure and the results were summarized in Table 1. **2a**. $^1\text{H-NMR}$ (C_6D_6): δ 8.54 (d, 2H, $J = 8.0$ Hz), 8.46 (d, 2H, $J = 8.0$ Hz), 7.53 (t, 2H, $J = 8.0$ Hz), 7.40 (t, 2H, $J = 8.0$ Hz), 0.20 (s, 6H); $^{13}\text{C-NMR}$ (CDCl_3): δ 139.35 (s), 127.38 (s), 126.97 (d), 125.39 (s), 124.81 (d), 123.50 (d), 121.06 (d), -0.80 (q). MS (70 eV); m/z (%): 266 [M^+ , 6], 252 (21), 210 (100), 181 (34), 152 (35), 43 (20). Found: 266.0780. Exact mass Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Si}$: 266.0763. **3a**. $^1\text{H-NMR}$ (CDCl_3): δ 8.62 (d, 2H, $J = 8.0$ Hz), 8.16 (d, 2H, $J = 8.0$ Hz), 7.62–7.58 (m, 4H), 0.36 (s, 12H); $^{13}\text{C-NMR}$ (CDCl_3): δ 135.43 (s), 129.00 (s), 127.73 (s), 126.65 (d), 125.20 (d), 122.39 (d), 122.14 (d), -0.90 (q). MS (70 eV); m/z (%): 340 [M^+ , 100], 325 (30), 266 (82), 236 (44), 133 (58), 73 (21). Found: 340.0927. Exact mass Calc. for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{Si}_2$: 340.0951. **2b**. $^1\text{H-NMR}$ (CDCl_3): δ 8.67 (d, 2H, $J = 8.0$ Hz), 8.15 (d, 2H, $J = 8.0$ Hz), 7.65–7.53 (m, 4H), 1.43 (sept, 2H, $J = 7.5$ Hz), 1.16 (d, 12H, $J = 7.5$ Hz); $^{13}\text{C-NMR}$ (CDCl_3): δ 139.66 (s), 126.55 (s), 126.46 (d), 124.63 (s), 124.25 (d), 120.88 (d), 120.71 (d), 15.80 (q), 13.04 (d). MS (70 eV); m/z (%): 322 [M^+ , 100], 236 (28), 208 (10), 43 (20). Exact mass Calc. for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Si}$: 322.1389. Found: 322.1388.

3.3. Laser flash photolysis

Laser flash photolysis experiments were performed on nitrogen-bubbled solutions at r.t. by using the third harmonic (355 nm) of a Nd:YAG laser as an exciting light source. The concentrations of substrates employed were 4.80×10^{-4} M for PQ, 4.40×10^{-3} , 2.20×10^{-3} , 1.10×10^{-3} , 4.40×10^{-4} , and 2.20×10^{-4} M for **1b**, respectively, in a mixed solvent ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2 = 4/1$). In C_6H_6 , the concentrations were 4.80×10^{-4} M for PQ, 3.30×10^{-3} , 1.00×10^{-3} , and 3.00×10^{-4} M for **1b**, respectively.

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