# Photo-induced silylene-transfer reactions of cyclic organosilanes to phenanthraquinone

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Cophotolysis of cyclic organosilanes 1–4 with phenanthraquinone gave silylene insertion products *via* radical displacement at the silicon atoms of organosilanes by the photochemically excited phenanthraquinone.

Electron-transfer reactions of heavier group 14 organometallic compounds have been studied extensively from the mechanistic and synthetic viewpoints.[1] For these reactions, electron-deficient carbonyl compounds, especially *p*-benzoquinones, are frequently used as electron acceptors.[2,3] We and the other groups found that the photoreactions of some disilane and digermane derivatives with *p*-benzoquinones underwent electron-transfer processes to produce *O*-silylated and *O*-germylated *p*-benzoquinones.[2] On the other hand, it was reported that the photolysis of α-diketones with alkyl and allylic stannanes afforded exclusively the alkylated and allylated α-ketols without giving any stannylated products.[3] These previous results prompted us to investigate the photoreaction of organosilanes and *o*-benzoquinones, which serve as good silylene traps due to their s-*cis* α-diketone structures.[4] We now report the photoreaction of cyclic organosilanes **1–4** with phenanthraquinone (PQ), providing the first example of silylene transfer reactions induced by photoexcited triplet *o*-benzoquinones.
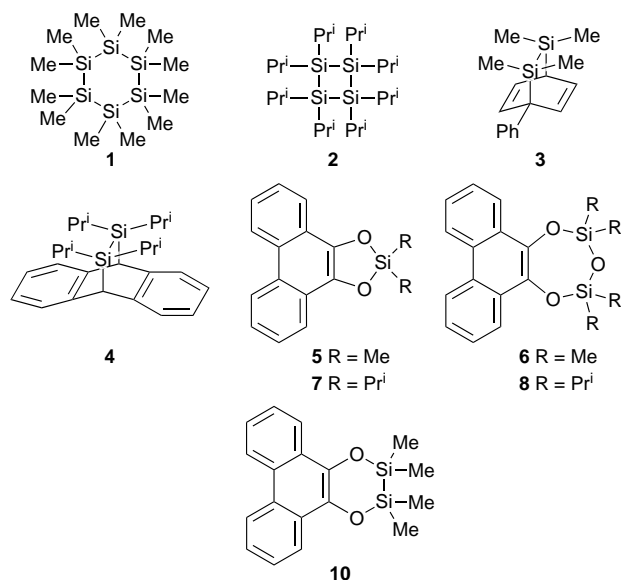
Irradiation of a solution (MeCN–CH₂Cl₂ = 4 : 1) of dodecamethylcyclohexasilane **1** (1.1×10^{-2} M) and PQ (3.5×10^{-2} M) in a sealed tube with two 500 W tungsten-halogen lamps (passing through an aqueous NaNO₂ filter, cutoff < 400 nm) afforded dioxasilolene **5**,† as a silylene adduct of PQ, along with a minor amount of trioxadisilepine **6**. In the case of photolysis of cyclotetrasilane **2**, dioxasilolene **7** was produced, whereas the corresponding trioxadisilepine **8** was not formed at all, as summarized in Table 1. We detected no other product derived

from PQ while substantial amounts of PQ were recovered after the photolyses.

It is well-known that ultraviolet photolysis of **1** produces free dimethylsilylene, which can be trapped readily by α-diketones to afford trioxadisilepine derivatives.[4] However, **1** is entirely inert to the visible light employed in the present photolyses. Furthermore, the present reaction does not seem to involve free dimethylsilylene because the cophotolysis of **1** and PQ in the presence of Et₃SiH, a common silylene trap, did not give any Et₃SiMe₂SiH.[4b]

Since the reaction was efficiently quenched by addition of anthracene, the triplet PQ is suggested to be the key intermediate as judged by the comparison of the singlet and the triplet energies of PQ ($E_S = ca.$ 54, $E_T = ca.$ 48 kcal mol⁻¹)[5] and those of anthracene ($E_S = ca.$ 76, $E_T = ca.$ 43 kcal mol⁻¹).[6] Meanwhile, the consumption of **1** was suppressed by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), which has a lower oxidation potential ($E_{ox} = +0.70$ V *vs.* SCE) than that of **1** ($E_{ox} = +1.45$ V *vs.* SCE). The free energy changes (ΔG) for the electron-transfer from cyclosilanes to the triplet PQ are given in Table 2.‡ These data suggest that the reaction may proceed *via* a partial or complete electron-transfer from the cyclosilanes to the photoexcited PQ at least in a polar solvent, such as MeCN. In fact, the silylene-transfer reactions were found to proceed substantially faster in MeCN than in benzene, as shown in Table 1.

We propose the following mechanism on the basis of Pedulli's result that photoexcited ketones are capable of cleaving Si–Si bonds of polysilanes *via* S_H2 type radical displacement at the silicon atoms.[8] Thus, the photochemically

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

Silane	Conditions	t/h	Conversion (%)	Product (% yield)[a]
1	hv/PQ/CH₃CN/ CH₂Cl₂	4.5	61	**5** (138), **6** (33)
1	hv/PQ/C₆H₆	10.5	49	**5** (161), **6** (31)
2	hv/PQ/CH₂Cl₂l	0.5	70	**7** (82)
2	hv/PQ/C₆H₆	1.5	70	**7** (57)
3	hv/PQ/CH₃CN/ CH₂Cl₂	0.5	89	**5** (28), **6** (11), biphenyl (100)
3	hv/PQ/C₆H₆	1.5	65	**5** (62), **6** (13), biphenyl (94)
4	hv/PQ/CH₃CN	3.0	100	**7** (85), anthracene (97)
4	hv/PQ/C₆H₆	18.0	70	**7** (69), anthracene (100)

[a] Based on the consumption of silanes.

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

	E_{ox}/V *vs.* SCE	ΔG/kcal mol⁻¹ in MeCN	in C₆H₆
1	+1.45	−1.41	+17.84
2	+1.00	−11.79	+7.47
3	+0.42	−25.16	−6.0
4	+1.17	−7.9	+11.4

excited PQ attacks one of the silicon atoms of **1** to afford a biradical intermediate **9**. At the initial interaction, a partial or complete electron-transfer from **1** to the triplet PQ may take place in polar solvents as mentioned above. Subsequent intramolecular O–Si bond formation in **9** would provide **5** as illustrated in Scheme 1. The yields of **5** indicate that a molecule of **1** donates more than an equimolar amount of silylene units to PQ. We obtained polymeric products containing silane fragments in these reactions, which might have arisen from framentation of the starting materials. In addition, the photoreaction of **1** and PQ in the presence of CCl_4 gave $Cl(Me_2Si)_nCl$ (n = 4–6), which would substantiate the present mechanism involving the silyl radical intermediates.[9]

There seemed to be three possible pathways leading to **6**: (i) intramolecular cyclization in **9** could afford **10**, which would be susceptible to atmospheric oxidation to give **6**, (ii) addition of free dimethylsilylene to **5** could give rise to **6** *via* **10**, and (iii) dimethylsilanone,[10] if formed in the course of reaction, could insert into **5** to produce **6**. However, the intermediate **10** was never detected in the photolysates while all trapping experiments for free dimethylsilylene and dimethylsilanone were not successful. When the reaction was carried out under an aerobic atmosphere, the yields of **6** increased while those of **5** decreased. The residual molecular oxygen plays an important role in the formation of **6**. Since **5** is stable in the air, it is suggested that molecular oxygen should be incorporated, probably as some radical species, to afford **6** during the photoreactions. Further investigations are in progress to clarify the mechanism.

Recently, it has been demonstrated that 7,8-disilabicyclo[2.2.2]octa-2,5-diene **3**, which is known as a disilene precursor,[10] also acts as a good electron donor.[11] Therefore, we anticipated that cophotolysis of **3** with PQ would produce selectively the corresponding disilanylene adduct **10**. Interestingly, the silylene adduct **5** was obtained along with **6** instead of **10**. Moreover, in contrast to the case of **1**, the intermediacy of free dimethylsilylene was evidenced by the formation of Et_3SiMe_2SiH in the cophotolysis of **3** with PQ in the presence of

Et_3SiH. Based on the mechanism proposed for **1**, the reaction of **3** is interpreted as shown in Scheme 2. The initially formed adduct **11** would collapse to afford **5**, **12**, free dimethylsilylene and biphenyl successivley. It should be noted that free dimethylsilylene could contribute to the formation of **5** and **6**. Compound **4** gave a similar result, although no trioxadisilepine **8** was obtained as the case of **2**.

In summary, we have indicated that silylene-transfer reactions take place between cyclic organosilanes **1**–**4** and the photochemically excited triplet PQ. The formation of free dimethylsilylene is noteworthy since there has been no precedent of generation of free silylenes induced by photoexcited carbonyl compounds as far as we know.
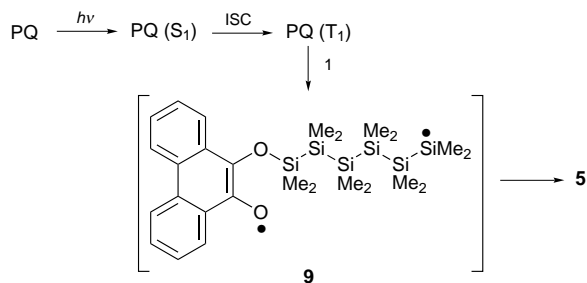
Footnotes

† *Selected spectral data* for **5**: ^{1}H NMR (C_6D_6): δ 8.54 (d, 2H, J 8.0 Hz), 8.46 (6, 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}C NMR (CDCl_3): δ 139.35 (s), 127.38 (s), 126.97 (d), 125.39 (s), 124.81 (s), 123.50 (d), 121.06 (q), −0.80 (q); *m/z* 266 (M+, 6%), 252 (21), 210 (100), 181 (34), 152 (35), 43 (20). For **6**: ^{1}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}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); *m/z* 340 (M+, 100%), 325 (30), 266 (82), 236 (44), 133 (58), 73 (21). For **7**: ^{1}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}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); *m/z* 322(M+, 100%), 236 (28), 208 (10), 43 (20).

‡ The ΔG values were calculated according to the Rehm–Weller equation (ref. 7) {ΔG/kcal mol^{-1} = 23.06[$E(D/D^+)−E(A^{-}/A)−\Delta E_{excit.}$ + $\Delta E_{coul.}$]}. The reduction potential of PQ is −0.66 V (*vs.* SCE) and the triplet energy of PQ was used as the excitation energy ($\Delta E_{excit.}$) (ref. 5). The Coulomb interaction energies ($\Delta E_{coul.}$) are −0.06 and +0.78 eV for MeCN and benzene, respectively [ref. 7(*b*)].
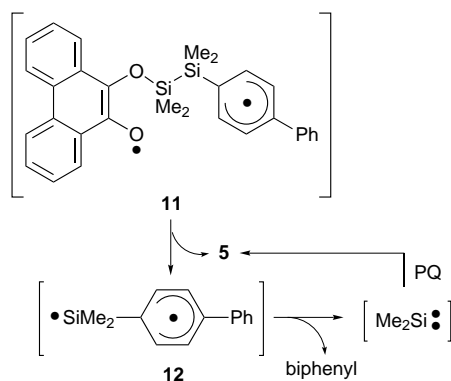
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Scheme 1

Scheme 2

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