Tetrahedron Vol. 48, No. 16, pp. 3283-3292, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Photo-induced Electron Transfer Oxygenation of 1,2-Disiletene[1]

Takeshi Akasaka, Kazuma Sato, Masahiro Kako, and Wataru Ando*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

(*Received in Japan* 13 *January* 1992)

Abstract: Photo-induced electron transfer oxygenation of 3-phenyl-1,1,2,2-tetramesityl-1,2-disilet-3-ene (1) in acetonitrile-methylene chloride afforded the corresponding 1,2-dioxa-3,6-disilin (2) in moderate yield as a dioxygen insertion product into a silicon-silicon σ-bond together with 1-oxa-2,5-disilolene (3). The results are reasonably accounted for by an electron transfer from disiletene 1 to the excited singlet state of the sensitizer to form a radical ion pair followed by addition of oxygen. Interestingly, a remarkable solvent effect was observed in the product ratio of dioxadisilin 2 and oxadisilolene 3 as a monooxygenated product. The solvent acetonitrile, acting as a nucleophile, participates for predominant formation of 2. Meanwhile, in the absence of acetonitrile, 3 was afforded as a major product. The conceivable mechanism is proposed.

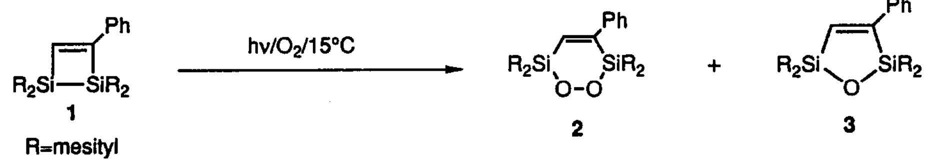
Introduction

Much attention has been drawn to the reaction of organosilicon compounds with molecular dioxygen in recent years. It is well known that strained silicon-silicon σ-bonds are oxidized exothermically with molecular dioxygen to afford disiloxanes as monooxygenated products.[2,3] In spite of the significance of aerobic oxygenation of organosilicon compounds, few mechanistic investigations were carried out.[2,3] Recently we have found that oxygenation by singlet oxygen[4,5] and charge-transfer induced photooxygenation[6] of the disilacyclopropane derivatives give the corresponding peroxides as dioxygen insertion products into a silicon-silicon σ-bond. Our continuous interest in the photochemical oxygenation[7] has led us to investigate electron transfer oxygenation of a silicon-silicon σ-bond. We report here the first example of dioxygen insertion into a silicon-silicon σ-bond in photo-induced electron transfer oxygenation of 1,2-disiletene to give the corresponding 1,2-dioxa-3,6-disilin.

Results and Discussion

In a typical experiment, irradiation of 3-phenyl-1,1,2,2-tetramesityl-1,2-disilet-3-ene[8] (**1**, 1.7×10^{-2}M) in a mixed solvent of acetonitrile ($\varepsilon=35.9$)[9] and methylene chloride ($\varepsilon=8.9$)[9] (1:1) in the presence of 9,10-dicyanoanthracene (DCA, 1.3×10^{-3}M)[10] with 500W tungsten-halogen lamps resulted in formation of 4-phenyl-1,2-dioxa-3,6-disilin (**2**) in 69 % yield together with 3-phenyl-1-oxa-2,5-disilolene (**3**, 13% yield)(Table I). These products were isolated by silica gel flash column chromatography using hexane-methylene chloride as eluent. Very similar results were also obtained in photo-induced electron transfer oxygenation by using methylene blue (MB^+)[11] and 2,4,6-triphenyl-pyrilium perchlorate ($TPPY^+$)[12] as sensitizer. The structures of **2** and **3** were assigned on the basis of spectroscopic data and elemental analyses. Interestingly, **2** was gradually decomposed at room temperature to afford 5-mesityloxy-3-phenyl-2,2,5-

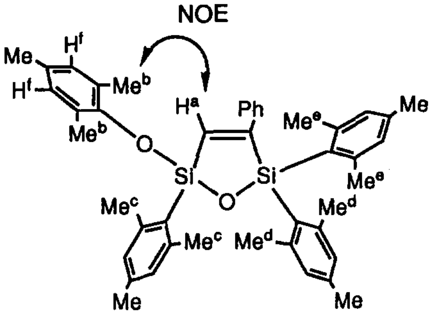
Table I. Photosensitized Oxygenation of 1



Sensitizer[a]	solvent	Products and Yields(%)[b] 2	 3
DCA	CH_3CN/CH_2Cl_2(1:1)	69	13
	CH_2Cl_2	4	21
	CH_3NO_2	5	33
	$CH_2Cl_2/C_6H_5S(O)CH_3$(200eq)	61	26
MB^+	CH_3CN/CH_2Cl_2(1:1)	35	19
	CH_2Cl_2	5	14
$TPPY^+$	CH_3CN/CH_2Cl_2(1:1)	51	19
	CH_2Cl_2	4	41
TPP		no reaction	
$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$/-78°C[c]	CH_3CN/CH_2Cl_2(1:1)	61	39
	CH_2Cl_2	6	23

[a]DCA; 9,10-dicyanoanthracene, MB^+; methylene blue, $TPPY^+$; 2,4,6-triphenylpyrilium perchlorate, TPP; tetraphenylporphine. [b]Conversion yields. [c]The reaction was carried out in dark.

trimesityl-1-oxa-2,5-disilolene (4) in 28% yield via Criegee type rearrangement.[4,5,13] Reduction of 2 with triphenylphosphine easily took place giving 3 in 50% yield with the phosphine oxide (90% yield). The stereochemistry of the rearranged product formed in the thermal reaction of 2 was assigned by a difference NOE experiment. Low-power irradiation of the vinylic proton (a) resulted in intensity enhancements at methyl protons (b) and (c), allowing assignment of the product as 4. Verification of this assignment was provided by irradiation of the methyl protons (b), which resulted in intensity enhancements at vinylic proton (a) and aromatic protons (f). Very similar results were also obtained in irradiation of the methyl protons (c). A reasonable NOE between the olefinic proton and protons of *o*-Me in O-mesityl (δ 7.20 and δ 2.70) also appeared on a NOESY spectrum (Fig.1). The structure of 4 was finally confirmed by X-ray crystal analysis as shown in Fig. 2. The structure of 4 was solved by direct methods and refined by full-matrix least-squares refinement for data with $Fo^2>3\sigma(Fo^2)$. Bond distances and angles for 4 are given in Table II. It is apparent that Criegee rearrangement occurred at the less hindered Si(1) atom of 2. The bond lengths around the central pentagonal core are all in the range of normal values for Si-C, Si-O, and C-C bonds. The structure of 4 is similar to that of benzobisoxadisilolene (5)[14] reported previously; the endocyclic Si-O-Si, O-Si-C, and Si-C-C bond angles are well consistent with those of 5. The C(1)-C(2) π bond is slightly twisted, the Si(1)-C(1)-C(2)-Si(2) torsional angle being 3.7°, whereas the Si atoms are coplanar with aromatic carbons in the case of 5. The oxygen atom is also displaced from the Si(1)-C(1)-C(2)-Si(2) plane as is evident from the torsional angles of -8.82° for O(1)-Si(1)-C(1)-C(2) and 2.83° for O(1)-Si(2)-C(2)-C(1), respectively. On the whole, deviation of the central C_2Si_2O ring from planarity is larger than that of 5.



4

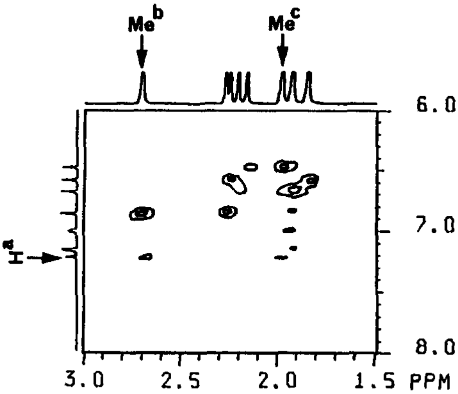
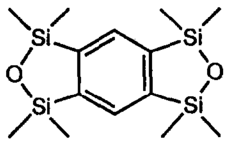
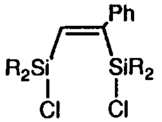


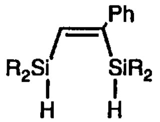
Fig. 1. NOESY spectrum of 4



5



6



7

R=mesityl

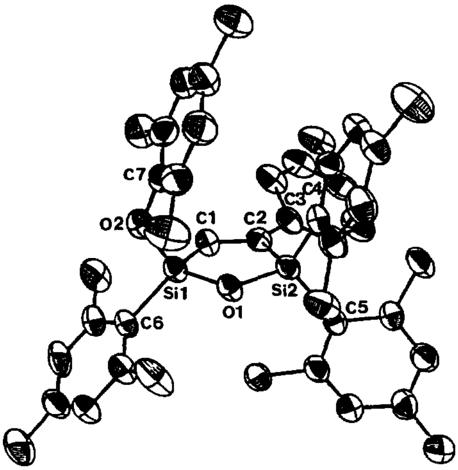


Fig. 2. ORTEP drawing of 4

Table II. Bond Distances (Å) and Angles (deg) for 4

Si1-O1	1.640(6)	Si2-C4	1.889(9)
Si1-O2	1.641(7)	Si2-C5	1.882(9)
Si1-C1	1.89(1)	C1-C2	1.36(1)
Si1-C6	1.895(9)	C2-C3	1.50(1)
Si2-O1	1.665(6)	C7-O2	1.38(1)
Si2-C2	1.900(9)		
Si1-O1-Si2	118.0(4)	C2-Si2-O1	97.4(4)
Si1-O2-C7	126.6(6)	C2-Si2-C4	118.3(4)
Si1-C1-C2	113.0(7)	C4-Si2-C5	111.9(4)
C1-Si1-O1	97.8(4)	C5-Si2-O1	112.7(4)
C1-Si1-O2	112.5(4)	C1-C2-Si2	112.7(6)
C6-Si1-O1	112.5(4)	C1-C2-C3	121.9(9)
C6-Si1-O2	104.0(4)	C3-C2-Si2	125.3(6)

The reaction did not occur without the sensitizer under the conditions. The free energy changes (ΔG) are -17.8, -10.4 and -32.3 kcal/mol for DCA, MB^+ and $TPPY^+$, respectively, indicative of exothermic electron-transfer from **1** to the excited singlet state of the sensitizer.[16] In order to confirm this process, the following DCA-sensitized oxygenations were carried out. The DCA fluorescence was efficiently quenched with **1** (k_q=3.60x$10^9 M^{-1}s^{-1}$). The rate of disappearance of **1** was enhanced by addition of $Mg(ClO_4)_2$.[17] Meanwhile, addition of 1,2,4,5-tetramethoxybenzene (E_{ox}=0.79 V vs. SCE) and diazabicyclo[2.2.2]octane (E_{ox}=0.70 V vs. SCE), each of which has a lower oxidation potential and is unreactive to DCA-sensitized photooxygenation, and also 2,4,6-tri-tert-butylphenol, a radical scavenger, quenches the oxidation of **1**. The reaction does not seem to involve singlet oxygen, since **1** is stable under the photooxygenation conditions in the presence of tetraphenylporphine (TPP) as singlet oxygen sensitizer. Intervention of the silyl radical cation ($1^{+\cdot}$) is also rationalized by the following experiment.[16a] Irradiation of **1** in a mixed solvent of acetonitrile and carbon tetrachloride in the presence of DCA resulted in chlorinative cleavage of the silicon-silicon bond which gave the corresponding chlorosilane (**5**) in 46% yield. Reduction of **6** with $LiAlH_4$ afforded **7** quantitatively.

A proposed mechanism for photo-induced electron transfer oxygenation of **1** is shown in eqs. (1)-(8). The photochemically generated cation radical ($1^{+\cdot}$) is attacked by either $O_2^{-\cdot}$ or $^3O_2$, giving directly **2** or the intermediate $[1{\bullet}O_2]^{+\cdot}$. In the latter case, the electron transfer from $sens^{-\cdot}$ or **1** to $[1{\bullet}O_2]^{+\cdot}$ affords **2**. This mechanism might be supported by the following facts: (1) It is well known that $O_2^{-\cdot}$ can be formed by the electron transfer (ΔG=-0.9 kcal/mol) from $DCA^{-\cdot}$ to $^3O_2$ (eq. (3)).[18] The electron transfer from both MB and TPPY to $^3O_2$ is, however, an unfavourable process based on thermochemistry; ΔG=15.9 and 15.0 kcal/mol for MB and TPPY, respectively.[18] (2) The reaction of **1** with $^3O_2$ in the presence of a catalytic amount of tris(p-bromophenyl)aminium hexachloroantimonate ($(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$),[19] in a mixed solvent of acetonitrile and methylene chloride in the dark gave **2** and **3** in 61% and 39% yields, respectively (Table I). This result suggests that $1^{+\cdot}$ which is formed by the electron transfer from **1** to the amine cation radical can be converted into **2** in the presence of $^3O_2$ via the pathways of eqs. (5) and (7).

$$
\begin{array}{lclcclcl}
{}^1\mathrm{sens}^* & + & 1 & \longrightarrow & \mathrm{sens}^{-\cdot} & + & 1^{+\cdot} & (1) \\
\mathrm{sens}^{-\cdot} & + & 1^{+\cdot} & \longrightarrow & \mathrm{sens} & + & 1 & (2) \\
\mathrm{sens}^{-\cdot} & + & {}^3O_2 & \longrightarrow & \mathrm{sens} & + & O_2^{-\cdot} & (3) \\
1^{+\cdot} & + & O_2^{-\cdot} & \longrightarrow & 2 & & & (4) \\
1^{+\cdot} & + & {}^3O_2 & \longrightarrow & [1{\bullet}O_2]^{+\cdot} & & & (5) \\
[1{\bullet}O_2]^{+\cdot} & + & \mathrm{sens}^{-\cdot} & \longrightarrow & 2 & + & \mathrm{sens} & (6) \\
[1{\bullet}O_2]^{+\cdot} & + & 1 & \longrightarrow & 2 & + & 1^{+\cdot} & (7) \\
[1{\bullet}O_2]^{+\cdot} & \xrightarrow{+e^-} & \longrightarrow & \longrightarrow & 3 & & & (8)
\end{array}
$$

To obtain further insight into the electron transfer oxygenation actually occurring, the following experiments were carried out. The relative ratio for the formation of **2** and **3** strongly depends on the solvent composition. In methylene chloride and nitromethane (ε=35.9)[9] the formation of **3** predominates instead of **2** under both photosensitized and aminium cation radical-catalyzed oxygenation conditions (Table I). Very similar results are also obtained in methylene chloride in the presence of methyl phenyl sulfoxide. More supporting data for the oxidation mechanism is provided by experiments in which the solvent composition in acetonitrile and methylene chloride was changed as shown in Fig. 3 and 4. These results might be rationalized in terms of the participation of acetonitrile[20] as shown in Scheme I. The solvent acetonitrile acts as the nucleophile toward $1^{+\bullet}$ to give A followed by addition of $^3O_2$ and then elimination of acetonitrile affording the oxidized product 2. Eq. (9) may be preferable to eq. (5) in the presence of acetonitrile. The role of the sulfoxide might be also explained by the same manner. Meanwhile, in the absence of acetonitrile, $^3O_2$ adds to $1^{+\bullet}$ to give B (eq. (5)) followed by ring-closure affording C. Loss of oxygen from C could afford 3. This may mean that $[1\bullet O_2]^{+\bullet}$ (B and C)is not responsible for formation of 2.

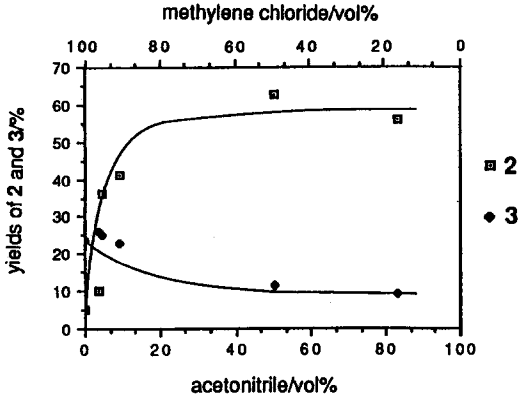


Fig. 3. Effect of the solvent composition on the DCA-sensitized oxygenation of 1 in acetonitrile-methylene chloride.

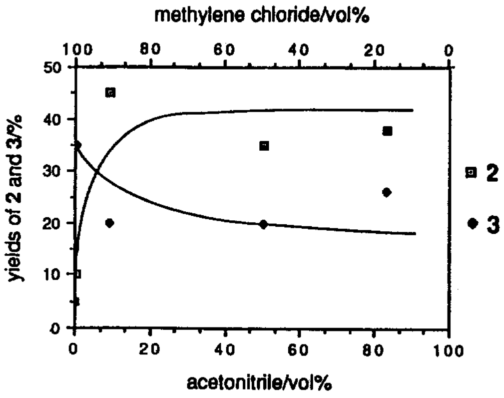
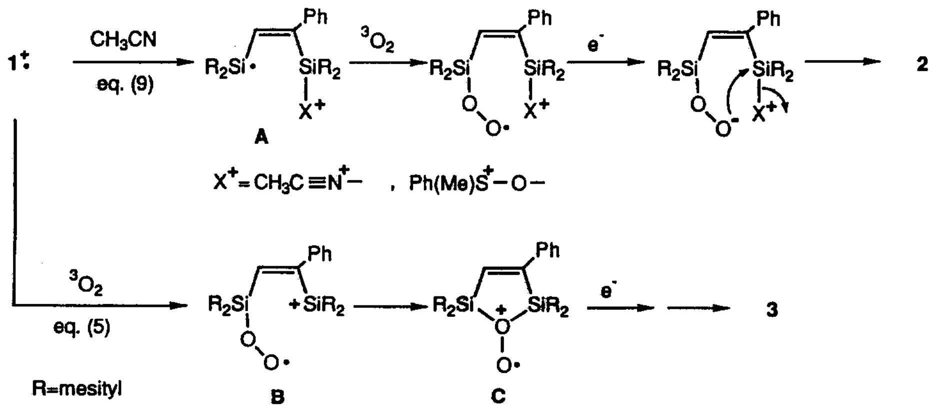


Fig. 4. Effect of the solvent composition on the MB^+-sensitized oxygenation of 1 in acetonitrile-methylene chloride.

Scheme I



Experimental

All melting points are uncorrected. IR spectra were recorded with a JASCO FT-IR5000 infrared spectrometer, ^1H-, ^{13}C- and ^{29}Si-NMR spectra recorded with a JEOL JNM-EX90 and a Bruker AM-500 spectrometer. Deuteriated chloroform and benzene were used as the solvent. Chemical shift values are reported (δ) relative to internal tetramethylsilane standard. Mass spectral data were obtained on a Hitachi RMU-6M mass spectrometer and exact mass data on a JEOL LMS-D300 mass spectrometer. HPLC analysis was done on a Jasco Trirotor-VI HPLC system, equipped with a 20cm x 5mm stainless steel column packed with Finepack SIL C_{18}. Gel permeation chromatography (preparative HPLC) was performed on a series of JAIGEL 1H and 2H columns with a flow of chloroform on a LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd. The light source was two 500-W tungsten-halogen lamps. Irradiations were carried out in Pyrex tubes at 15°C while oxygen was passed through. Reagent-grade solvents were used for the experiments in acetonitrile and methylene chloride. Acetonitrile was at first distilled in the presence of phosphoric anhydride and then distilled in the presence of calcium hydride before use. Methylene chloride was washed with water, dried over calcium chloride and then distilled. Nitromethane was distilled in the presence of calcium hydride. Deuteriated solvents for spectroscopy, TPP (Strem Chemicals), MB^+ (Kanto Chemical), and DCA(Tokyo Kasei) were used as received. 1,4-Diazabicyclo[2.2.2]octane was used after purification by sublimation. $TPPY^+$[21], $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$[22] and 1,2,4,5-tetramethoxybenzene[23] were prepared according to the literature procedure. **1** was prepared by addition of tetramesityldisilene to phenylacetylene.[8] **1**: mp 170-173°C; ^1H-NMR(C_6D_6) δ 8.09(s,1H), 7.43-7.44(m,2H), 6.98-7.07(m,3H), 6.66(s,4H), 6.62(s,4H), 2.41(s,12H), 2.32(s,12H), 2.07(s,6H), 2.04(s,6H) ppm; ^{13}C-NMR(C_6D_6) δ 170.42(s), 158.95(d), 145.02(s), 145.00(s), 144.62(s), 138.95(s), 138.55(s), 134.02(s), 133.90(s), 129.38(d), 129.25(d), 128.53(d), 127.38(d), 126.67(d), 25.47(q), 25.03(q), 21.01(q) ppm; ^{29}Si-NMR (C_6D_6) δ 5.62, -13.23 ppm. Calcd for $C_{44}H_{50}Si_2$: C, 83.22; H, 7.94. found: C, 83.00, H, 8.24.

Physical Properties of 1

Cyclic voltammograms of substrate **1** were obtained on 0.1 M $n\text{-}Bu_4NClO_4/CH_2Cl_2$ solution (vs. SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., Potentiostat/Galvanostat Model HZ-301). Oxidation potential (E_{ox}) of **1** is 1.2V.

The ΔG values were calculated according to the Rehm-Weller equation ($\Delta G(\text{kcal/mol})=23.06[E(D/D^+)-E(A^-/A)-e_0^2/\varepsilon a-\Delta E_{0,0}]$)[15] by using the excited singlet energies of DCA(2.89V), MB^+(1.84 V) and $TPPY^+$ (2.83 V), the reduction potentials of DCA(-0.98 V vs. SCE),[24] MB^+(-0.25 V vs. SCE)[25] and $TPPY^+$(-0.29 V vs. SCE),[26] and 0.06eV for $e_0^2/\varepsilon a$.[15] The free-energy changes of an electron-transfer process from $sens^{-\bullet}$ to $^3O_2$ is given by $\Delta G(\text{kcal/mol})=23.06[E(sens^{-\bullet}/sens)-E(O_2^-/O_2)]$, which contains the reduction potential of $^3O_2$ (-0.94V vs. SCE in CH_3CN).[18]

The rate constant (k_q) for DCA fluorescence quenching with **1** was measured by using a JASCO fluorescence spectrometer. The k_q value was calculated from the literature value of τ (15.3 ns) for DCA.[24]

DCA-sensitized Oxygenation of 1

In a typical experiment, **1** (1.7×10^{-2}M) was dissolved in a mixed solvent of acetonitrile and methylene chloride with DCA (1.3×10^{-3}M) as a sensitizer. After separation of the reaction mixture by silica gel flash column chromatography using hexane-methylene chloride as eluent, **2** was obtained in 69% yield, accompanied by **3** (13% yield). **2**: mp 127-130°; IR(C_6D_6) 1020, 1060 cm^{-1}; ^{1}H-NMR(C_6D_6) δ 7.30 (s,1H), 7.09-7.11(m,2H), 6.95-6.97(m,3H), 6.69(s,8H), 2.42(s,12H), 2.35(s,12H), 2.07(s,6H), 2.06 (s,6H); ^{13}C-NMR(C_6D_6) δ 159.69(s), 148.14(d), 144.80(s), 144.56(s), 144.05(s), 139.82(s), 139.74(s), 131.57(s), 130.68(s), 129.72(d), 129,70(d), 128.31(d), 128.02(d), 127.07(d), 24.77(q), 23.99(q), 21.11 (q), 21.04(q); ^{29}Si-NMR(C_6D_6) δ -6.99, -8.09; MS m/e 666(M^+). Anal. Calcd for $C_{44}H_{50}O_2Si_2$: C, 79.23; H, 7.56. Found: C, 79.45; H, 7.73. **3**: mp 250-252°; IR(C_6D_6) 1018, 1060 cm^{-1};^{1}H-NMR(C_6D_6) δ 7.66 (s,1H), 7.25-7.27(m,2H), 6.98-7.06(m,3H), 6.67(s,4H), 6.65(s,4H), 2.44(s,12H), 2.28(s,12H), 2.07 (s,6H), 2.04(s,6H); ^{13}C-NMR(C_6D_6) δ 165.52(s), 154.07(s), 145.91(s), 144.06(s), 143.94(s), 139.45(s), 139.22(s), 134.14(s), 132.67(s), 129.57(d), 129.56(d), 128.36(d), 127.60(d), 126.96(d), 24.58(q), 23.42 (q), 21.10(q), 21.02(q); ^{29}Si-NMR(C_6D_6) δ -6.51, -7.47; MS m/e 650(M^+). Anal. Calcd for $C_{44}H_{50}O_1Si_2$: C, 81.17; H, 7.74. Found: C, 81.01; H, 7.69.

Reduction of 2 with Triphenylphosphine

A 1.7x10^{-2}M acetonitrile-methylene chloride (1:1) solution of **1** containing DCA as a sensitizer was photooxygenated. After disappearance of **1** and formation of **2** were monitored by HPLC, triphenylphosphine (1.7x10^{-2}M) was added to the reaction mixture at room temperature and then kept to stand for overnight in dark. When the reaction mixture was separated by preparative HPLC, **3** was isolated in 58% yield, together with triphenylphosphine oxide (90%yield).

Rearrangement of 2 to 3

A 1.7x10^{-2}M acetonitrile-methylene chloride (1:1) solution of **1** containing DCA as a sensitizer was photooxygenated and then the resulting mixture was left to stand for overnight at room temperature. After separation of the reaction mixture by preparative HPLC, **4** was obtained in 28% yield. **4**: mp 155-156°; IR(KBr) 1031, 1079 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 7.20(s,1H), 7.13-7.14(m,3H), 6.97-7.02(m,2H), 6.84 (s,2H), 6.66(s,2H), 6.56(s,2H), 6.46(s,2H), 2.70(s,6H), 2.26(s,3H), 2.24(s,3H), 2.20(s,3H), 2.15 (s,3H), 1.97(s,6H), 1.92(s,6H), 1.84(s,6H); ^{13}C-NMR(C_6D_6) δ 169.55(s), 149.05(s), 148.93(s), 144.90 (s), 144.48(s), 144.24(s), 143.75(s), 140.09(s), 139.86(s), 139.25(s), 134.22(s), 131.65(s), 130.85(s), 130.06(s), 129.54(s), 129.16(d), 129.08(d), 128.52(d), 128.49(d), 127.48(d), 127.44(d), 24.55(q), 24.48 (q), 24.41(q), 21.19(q), 21.15(q), 21.02(q), 20.67(q), 17.50(q); ^{29}Si-NMR($CDCl_3$) δ -11.72, -25.43. Anal. Calcd for $C_{44}H_{50}O_2Si_2$: C, 79.23; H, 7.56. Found: C, 79.41; H, 7.56.

Photosensitized Oxygenation of 1

A 1.7x10^{-2}M acetonitrile-methylene chloride (1:1) solution of **1** containing a sensitizer was photooxygenated in the presence of an additive or under the several reaction conditions. The reactions were monitored by means of HPLC. The results obtained are summarized in Table I. The results on effect of the solvent composition on the DCA- and MB^+-sensitized oxygenation of **1** in acetonitrile-methylene chloride were also shown in Fig. 3 and 4.

DCA-sensitized Oxygenation of 1 in an Acetonitrile-Carbon Tetrachloride Solution

1 (1.7x10^{-2}M) was dissolved in a mixed solvent of acetonitrile and carbon tetrachloride (1:1) with DCA as a sensitizer. After consumption of **1**, the solvent was removed under reduced pressure and the residue was dissolved in tetrahydrofuran. Formation of **6** was confirmed by means of Mass analysis (**6**: MS m/e 704 (M^+)). The solution of the reaction mixture was reduced with lithium aluminium hydride at 0°C. **7** was obtained in 46% yield. **7**: IR($CDCl_3$) 2166 cm^{-1}; ^1H-NMR($CDCl_3$) δ 7.13(d, 1H,J=6.8Hz), 7.06-7.09 (m,5H), 6.74(s,4H), 6.67(s,4H), 5.69(s,1H), 5.52(d,1H,J=6.8Hz), 2.24(s,12H), 2.21(s,6H), 2.17(s,6H), 2.08(s,12H); ^{13}C-NMR($CDCl_3$) δ 157.21(s), 148.71(d), 144.78(s), 144.65(s), 144.24(s), 138.88(s), 138.85(s), 130.22(s), 129.94(s), 128.70(d), 128.65(d), 127.67(d), 127.23(d), 126.35(d), 23.89(q), 23.72 (q), 21.10(q), 21.08(q). Exact Mass Calcd for $C_{44}H_{52}Si_2$: 636.3608. Found: 636.3630.

Amine Cation Radical-Catalyzed Oxygenation of 1

To an acetonitrile-methylene chloride (1:1) solution of **1** was added 0.3 equiv. of $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ at -78°C in dark while oxygen was passed through. By means of HPLC analysis, **2** and **3** were afforded in 61% and 39% yields, respectively. When methylene chloride was used as a sole solvent, **2** and **3** were obtained in 6% and 23% yields, respectively.

X-ray Crystal Analysis of 4

Intensity data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite monochromated Mo-Kα radiation. A total of 3859 unique reflections within $2\theta<50°$ were measured by the ω-2θ scan method within a scan rate of 1-5°/min. The structure was solved by direct methods and refined by full-matrix least-squares refinement. Convergence on 2585 reflections [$Fo^2>3.0\sigma$] and 443 parameters resulted in R=0.071, Rw=0.081. The molecular structure is shown in Fig. 2. Crystal data for **4**: $C_{44}H_{50}O_2Si_2$, orthorhombic space group $P2_12_12_1$, a=11.790(2)Å, b=12.733(3)Å, c=25.887(6)Å, Z=4.

Acknowledgment: This work was supported by the Ministry of Education, Science and Culture in Japan and in part by a grant from ICI Japan Technical Centre.

Supplementary Material Available: Detailed information on the X-ray crystal analysis of **4** (4 pages); listing of observed and calculated structure factors for **4** (31 pages). Ordering information is given on any current masthead page.

References

1. Part of this work was reported as a preliminary communication: Akasaka, T.; Sato, K.; Kako, M.; Ando, W.*Tetrahedron Lett.* **1991**, *32*, 6605.
2. (a) Carberry, E.; West, R. *J. Organometal. Chem.* **1966**, *6*, 582; (b) Ishikawa, M.; Kumada, M. *J. Chem. Soc.,Chem. Commun.* **1970**, 612; (c) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organometal. Chem.* **1971**, *31*, 17; (d) Atwell, W. H.; Uhlmann, J. G.*ibid.* **1973**, *52*, C21; (e) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *ibid.* **1978**, *162*, C43; (f) Seyferth, D.; Vick, S. C. *ibid.* **1977**, *125*, C11; (g) Masamune, S.; Tobita, H.; Murakami, S. *J. Am. Chem. Soc.* **1983**, *105*, 6524; (h) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *ibid.* **1985**, *107*, 5552; (i) Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organometal. Chem.* **1980**, *187*, 297; (j)

Weidenbruch, M.; Schafer, A. *ibid.* **1984**, *269*, 231; (k) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1985**, 643.

3. Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.
4. Ando,W.; Kako, M.; Akasaka,T.; Nagase, S.; Kawai, T.; Nagai, Y.; Sato, T. *Tetrahedron Lett.* **1989**, *30*, 6705.
5. Ando, W.; Kako, M.; Akasaka, T.; Kabe, Y. *Tetrahedron Lett.* **1990**, *31*, 4177.
6. Akasaka, T.; Kako, M.; Nagase, S.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1990**, *112*, 7804.
7. (a) Akasaka, T.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 1260; (b) Akasaka, T.; Yabe, A.; Ando, W. *ibid.* **1987**, *109*, 8085; (c) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *ibid.* **1988**, *110*, 494; (d) Akasaka, T.; Nagase, S.; Yabe, A.; Ando, W. *ibid.* **1988**, *110*, 6270.
8. De Yong, D. J.; West, R. *Chem. Lett.* **1986**, 883.
9. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents*, Jhon Wiley & Sons: New York, 1986.
10. (a) Foote, C. S. *Tetrahedron*, **1985**, *41*, 2221; (b) Lewis, F. D. In *Photoinduced Electron Transfer*; Fox, M. A.; Chanon, M., Ed.; Elsevier: Amsterdam, 1988, Chapter 4.1, p 38.
11. (a) Manring, L.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275; (b) Mizuno, K.; Murakami, K.; Kamiyama, N.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 462; (c) Akasaka, T.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 1260; (d) Hatsui, T.; Takeshita, H. *Chem. Lett.* **1990**, 1253.
12. Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1262.
13. Alexandrov, Y. A. *J. Organometal. Chem.* **1982**, *238*, 1.
14. Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1973**, 2474.
15. Rehm. D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
16. Polysilanes have been known to act as good σ-electron donors to undergo photo-induced electron transfer reactions with electron deficient sensitizers such as DCA and acridinium ion; (a) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781; (b) Watanabe, H.; Kato, M.; Tabei, E.; Kawabata, H.; Hirai, N.; Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1662; (c) Kyushin, S.; Ehara, Y.; Nakadaira, Y.; Ohashi, M. *ibid.* **1989**, 279; (d) Mizuno, K.; Nakanishi, K.; Chosa, J.; Nguyen, T.; Otsuji, Y. *Tetrahedron Lett.* **1989**, *30*, 3689; (e) Fukuzumi, S.; Kitano, T.; Mochida, K. *Chem. Lett.* **1989**, 2177; (f) Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *ibid.* **1991**, 327.
17. (a) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron*, **1985**, *41*, 2207; (b) Mizuno, K.; Ichinose, N.; Otsuji, Y. In The Role of Oxygen in Chemistry and Biochemistry, Ando, W.; Moro-oka, Y. Eds.; Elsevier: Amsterdam, 1988; p79.
18. (a) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083; (b) Steichen, J.; Foote, C. S. *ibid.* **1981**, *103*, 1855.
19. Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 369. references cited therein.

20. (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973; (b) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.
21. Balaban, A. T.; Toma, C. *Tetrahedron Suppl.* **1966**, *7*, 1.
22. Baker, T. N.; Doherty, W. P.; Kelley, W. S.; Newmeyer, W.; Rogers, J. E.; Spalding, R. E.; Walter, R. I. *J. Org. Chem.* **1965**, *30*, 3714.
23. Benington, F.; Morin, R. D.; Clark, Jr., L. C. *J. Org. Chem.* **1955**, *20*, 102.
24. Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.
25. Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275.
26. Saeva, F. D.; Olin, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 299.