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FORMATION OF 1,2,3,6-DIOXADISILIN IN PHOTO-INDUCED ELECTRON TRANSFER OXYGENATION OF 1,2-DISILETENE[1]

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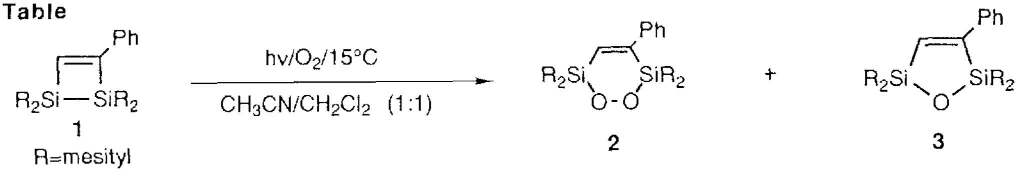
Summary: Photo-induced electron transfer oxygenation of 3-phenyl-1,1,2,2-tetramesityl-1,2-disiletene (**1**) in acetonitrile-methylene chloride afforded the corresponding 1,2,3,6-dioxadisilin (**2**) in moderate yield as a dioxygen insertion product into a silicon-silicon σ-bond together with 1,2,5-oxadisilolene (**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.

Much attention has been drawn to the reaction of organosilicon compounds with molecular oxygen in recent years. It is well known that strained silicon-silicon σ-bonds are oxidized exothermically with molecular oxygen 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 singlet oxygenation[4,5] and charge-transfer photooxygenation[6] of the disilacyclopropane derivatives to 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 1,2,3,6-dioxadisilin.

Irradiation of 3-phenyl-1,1,2,2-tetramesityl-1,2-disiletene[8] (**1**, 1.7×10^{-2}M) in a mixed solvent of acetonitrile and methylene chloride (1:1) in the presence of 9,10-dicyanoanthracene (DCA, 1.3×10^{-3}M) with two 500W tungsten-halogen lamps resulted in formation of 4-phenyl-1,2,3,6-dioxadisilin (**2**)[9] in 69 % yield[10] together with 3-phenyl-1,2,5-oxadisilolene[9] (**3**, 13% yield[10])(Table). Very similar results were also obtained in photo-induced electron transfer oxygenation by using methylene blue (MB^+) and 2,4,6-triphenylpyrilium perchlorate ($TPPY^+$) as sensitizer. Interestingly, **2** was gradually decomposed at room temperature to afford siloxane **4**[9,11] in 28% yield via Criegee type rearrangement.[4,5,12] Reduction of **2** with triphenylphosphine easily took place giving **3** in 50% yield with the phosphine oxide (90% yield).

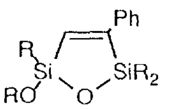
The free energy changes (ΔG) are -18.4, -10.6 and -32.5kcal/mol for DCA, MB^+ and $TPPY^+$, respectively, indicative of exothermic electron-transfer from **1** to the excited singlet state of the sensitizer.[13,14] The DCA fluorescence was efficiently quenched with **1** ($k_q=3.60\times10^9M^{-1}s^{-1}$).[15] The rate of disappearance of **1** was enhanced by addition of $Mg(ClO_4)_2$.[16] 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.[13a] 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**)[9] in 46% yield. Reduction of **5** with $LiAlH_4$ afforded **6**[9] quantitatively.

Table



Sensitizer[a]	Products and Yields(%)[b] 2	3
DCA	69 (4)[c]	13 (21)[c]
MB^+	35 (5)[c]	19 (14)[c]
$TPPY^+$	51 (4)[c]	19 (41)[c]
TPP	no reaction	
$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$/-78°C[d]	61 (6)[c]	39 (23)[c]

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



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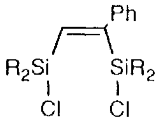

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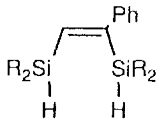


6

R=mesityl

A proposed mechanism for photo-induced electron transfer oxygenation of **1** is shown in eqs. (1)-(9). The photochemically generated cation radical ($1^{+\bullet}$) is attacked by either $O_2^{-\bullet}$ or $^3O_2$, giving directly **2** or the intermediate $[1\bullet O_2]^{+\bullet}$. In the latter case, the electron transfer from $sens^{-\bullet}$ or **1** to $[1\bullet O_2]^{+\bullet}$ affords **2**. This mechanism might be supported by the following facts: (1) It is well known that $O_2^{-\bullet}$ can be formed by the electron transfer (ΔG=-2.3kcal/mol) from $DCA^{-\bullet}$ to $^3O_2$ (eq. (3)).[17] The electron transfer from both MB and TPPY to $^3O_2$ is, however, an unfavourable process based on thermochemistry; ΔE_0=-0.67 and -0.65 V for MB and TPPY, respectively.[14] (2) The reaction of **1** with $^3O_2$ in the presence of a catalytic amount of tris(p-bromophenyl)aminium hexachloroantimonate ($(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$),[18] gave **2** and **3** in 61% and 39% yields, respectively (Table). This result suggests that $1^{+\bullet}$ 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).

The relative ratio for the formation of **2** and **3** strongly depends on the solvent composition (Fig. 1). In methylene chloride the formation of **3** predominates instead of **2** under both photosensitized and amine cation radical-catalyzed oxygenation conditions (Table). These results might be rationalized in terms of the participation of acetonitrile as shown in Scheme.[19] 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. Meanwhile, in the absence of acetonitrile, $^3O_2$ adds to $1^{+\cdot}$ to give **B** (eq. (5)) followed by ring-closure affording **C**. Loss of oxygen from **C** could afford **3**.

Further mechanistic studies on electron transfer photooxygenation of polysilanes are in progress.

$$^1\text{sens}^* + 1 \longrightarrow \text{sens}^{-\cdot} + 1^{+\cdot} \qquad (1)$$

$$\text{sens}^{-\cdot} + 1^{+\cdot} \longrightarrow \text{sens} + 1 \qquad (2)$$

$$\text{sens}^{-\cdot} + {}^3O_2 \longrightarrow \text{sens} + O_2^{-\cdot} \qquad (3)$$

$$1^{+\cdot} + O_2^{-\cdot} \longrightarrow 2 \qquad (4)$$

$$1^{+\cdot} + {}^3O_2 \longrightarrow [1\cdot O_2]^{+\cdot} \qquad (5)$$

$$[1\cdot O_2]^{+\cdot} + \text{sens}^{-\cdot} \longrightarrow 2 + \text{sens} \qquad (6)$$

$$[1\cdot O_2]^{+\cdot} + 1 \longrightarrow 2 + 1^{+\cdot} \qquad (7)$$

$$[1\cdot O_2]^{+\cdot} \xrightarrow{+e^-} \longrightarrow \longrightarrow 3 \qquad (8)$$

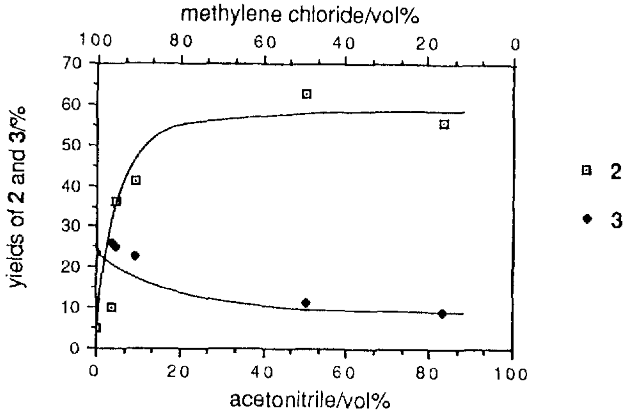
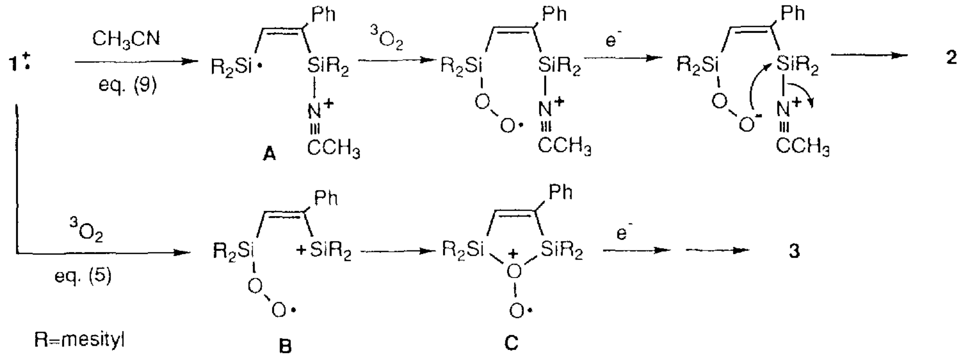


Fig. 1. Effect of the solvent composition on the DCA-sensitized oxygenation of **1** in acetonitrile-methylene chloride.

Scheme



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