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Electron Transfer Oxygenation of Oxadisiliranes

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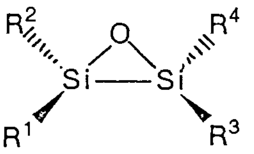
Electron-transfer photooxygenation of oxadisiliranes afforded the corresponding 1,2,4,3,5-trioxadisilolanes as dioxygen insertion products in reasonable yields. Stereochemical aspects of the oxygenation suggested formation of a peroxidic open intermediate.

The electron-transfer chemistry of organometallic compounds has been attracting much interest from the mechanistic and synthetic viewpoints.[1,2] The properties of organosilicon radical cations, however, have not been fully characterized. We have reported that disiletene and digermetene were oxygenated under electron-transfer conditions to afford the corresponding cyclic peroxides.[3] More recently, the singlet oxygen ($^1O_2$) oxidation of oxadisilirane has been found to be stereospecific.[4] As a part of our studies on the oxidation of organometallic compounds,[5] it is of particular interest to investigate the stereochemistry of the non-$^1O_2$ oxidation. We now report the stereochemical studies of electron-transfer oxygenation of oxadisilirane **1a** and **1b**, providing evidence for a peroxidic open intermediate.



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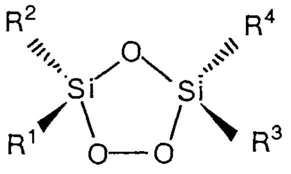

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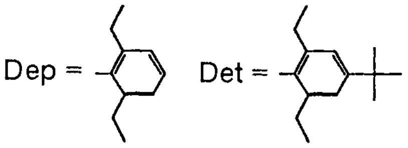
1a; $R^1 = R^2 = R^3 = R^4 =$ Dep
cis-**1b**; $R^1 = R^3 =$ Dep, $R^2 = R^4 =$ Det
trans-**1b**; $R^1 = R^4 =$ Dep, $R^2 = R^3 =$ Det

2a; $R^1 = R^2 = R^3 = R^4 =$ Dep
cis-**2b**; $R^1 = R^3 =$ Dep, $R^2 = R^4 =$ Det
trans-**2b**; $R^1 = R^4 =$ Dep, $R^2 = R^3 =$ Det



Electron-transfer oxygenation of oxadisilirane **1a** (1.0 x 10^{-2}M) was carried out in a mixed solvent of acetonitrile and methylene chloride (1:1) in the presence of 9,10-dicyanoanthracene (DCA, 1.3 x 10^{-3} M)[6] as sensitizer. Irradiation with two 500 W tungsten-halogen lamps passing through a sodium nitrite filter solution (cut off < 400 nm) under an oxygen flow resulted in the formation of 1,2,4,3,5-trioxadisilolane **2a**[4] in 50% yield

(Table 1, Entry 1). The free energy change (ΔG) is -23.0 kcal/mol, indicative of exothermic electron-transfer from **1a** to $^1DCA^*$.[7] The DCA fluorescence[8] was efficiently quenched with **1a** ($k_q = 1.12 \times 10^{10}$ $M^{-1}s^{-1}$). The reaction did not occur without the sensitizer and **1a** was recovered quantitatively. Similar results were also obtained in photosensitized oxygenation by using 2,4,6-triphenylpyrylium tetrafluoroborate ($TPPBF_4$)[9] as shown in Entry 2. The reaction of **1a** with $^3O_2$ in the presence of 10 mol% of $(p\text{-}BrC_6H_4)_3NSbCl_6$,[10] a single electron transfer reagent, gave **2a** in 58% yield (Entry 3). A proposed mechanism for photo-induced electron transfer oxygenation of **1a** is shown in Scheme 1. Cation radical ($1a^{+\bullet}$) is attacked by either $O_2^{-\bullet}$ or $^3O_2$, giving directly **2a** or the intermediate $[1a \cdot O_2]^{+\bullet}$. In the latter case, the electron transfer from $sens^{-\bullet}$ or **1a** to $[1a \cdot O_2]^{+\bullet}$ affords **2a**. It should be noted that $O_2^{-\bullet}$ is not involved in the $TPPBF_4$ and $(p\text{-}BrC_6H_4)_3NSbCl_6$ oxygenation.[9,10] These results are in good agreement with those of 1,2-disiletene.[3]

$$\begin{array}{lclcl}
{}^1\text{sens}^* & + & 1a & \longrightarrow & \text{sens}^{-\bullet} + 1a^{+\bullet} \\
\text{sens}^{-\bullet} & + & 1a^{+\bullet} & \longrightarrow & \text{sens} + 1a \\
\text{sens}^{-\bullet} & + & {}^3O_2 & \longrightarrow & \text{sens} + O_2^{-\bullet} \\
1a^{+\bullet} & + & O_2^{-\bullet} & \longrightarrow & 2a \\
1a^{+\bullet} & + & {}^3O_2 & \longrightarrow & [1a \cdot O_2]^{+\bullet} \\
[1a \cdot O_2]^{+\bullet} & + & \text{sens}^{-\bullet} & \longrightarrow & 2a + \text{sens} \\
[1a \cdot O_2]^{+\bullet} & + & 1a & \longrightarrow & 2a + 1a^{+\bullet}
\end{array}$$

Scheme 1. sens = sensitizer

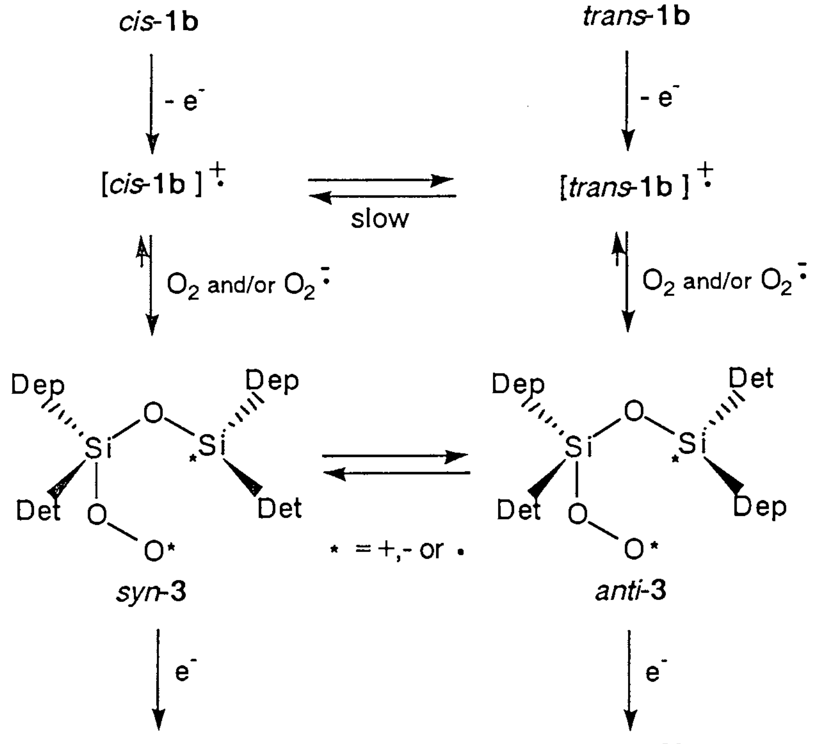
Table 1. Electron-transfer- and Charge-transfer- Oxygenation of Oxadisiliranes **1a** and **1b**

Entry	Oxadisilirane	Condition	Product[a)]	*cis/trans*
1	**1a**	$h\nu(\lambda>400nm)/O_2/DCA/CH_3CN/CH_2Cl_2$	**2a** (50)	-
2	**1a**	$h\nu(\lambda>400nm)/O_2/TPPBF_4/CH_3CN/CH_2Cl_2$	**2a** (68)	-
3	**1a**	$(p\text{-}BrC_6H_4)_3NSbCl_6/O_2/\text{-}78°C/CH_2Cl_2$	**2a** (58)	-
4	*cis*-**1b**	$h\nu(\lambda>400nm)/O_2/DCA/CH_3CN/CH_2Cl_2$	**2b** (51)	68/32
5	*trans*-**1b**	$h\nu(\lambda>400nm)/O_2/DCA/CH_3CN/CH_2Cl_2$	**2b** (35)	41/59
6	*cis*-**1b**	$h\nu(\lambda>400nm)/O_2/TPPBF_4/CH_3CN/CH_2Cl_2$	**2b** (13)	80/20
7	*trans*-**1b**	$h\nu(\lambda>400nm)/O_2/TPPBF_4/CH_3CN/CH_2Cl_2$	**2b** (22)	15/85
8	*cis*-**1b**	$(p\text{-}BrC_6H_4)_3NSbCl_6/O_2/\text{-}78°C/CH_2Cl_2$	**2b** (88)	66/34
9	*trans*-**1b**	$(p\text{-}BrC_6H_4)_3NSbCl_6/O_2/\text{-}78°C/CH_2Cl_2$	**2b** (95)	42/58
10	*cis*-**1b**	$h\nu(300nm<\lambda<400nm)/O_2/C_6H_6$	**2b** (79)	65/35
11	*trans*-**1b**	$h\nu(300nm<\lambda<400nm)/O_2/C_6H_6$	**2b** (83)	47/53

a)Isolated yields(%) are in parentheses.

The stereochemistry of the electron-transfer oxygenation was investigated with *cis*- and *trans*-**1b**,[4] which would give insight into the geometry of transient intermediates. The oxygenation was conducted under the same condition described above. DCA-sensitized photooxygenation of *cis*-**1b** and *trans*-**1b** gave 68:32 and 41:59

mixtures of *cis*- and *trans*-**2b**, respectively (Entry 4, 5), in contrast to the case of $^1O_2$ oxidation.4) The ratio of *cis/trans* was determined by comparing the relative peak intensities in the ^{13}C-NMR spectra, in which methyl resonances of ethyl groups appear at δ 15.66, 15.46 for *cis*-**2b** and those at δ 15.80, 15.34 for *trans*-**2b**.4) $TPPBF_4$-sensitized photooxygenation and $(p\text{-}BrC_6H_4)_3NSbCl_6$ oxygenation of **1b** also gave mixtures of *cis*- and *trans*- **2b** as summarized in Entry 6-9. In addition, the ^{13}C-NMR analysis confirmed that no *cis-trans* isomerization of the substrate **1b** took place at partial conversion (50 - 70%) in these reactions. **1b** did not isomerize under an argon atmosphere. This result suggests that cation radical rotation is far slow to isomerize **1b**$^{+\bullet}$ if at all under oxygenation conditions and that oxygen-addition reversal should be slow compared to cyclization. Therefore, we can safely conclude that an open intermediate **3** is involved in these reactions, and that rotation about Si-O-Si moiety is fairly competitive with its closure to **2b** (Scheme 2).4) $^1O_2$ mechanism is excluded in the cases of $TPPBF_4$9) and $(p\text{-}BrC_6H_4)_3NSbCl_6$10) oxygenation. Since $(p\text{-}BrC_6H_4)_3NSbCl_6$ and DCA oxygenation of **1b** gave similar stereochemical features, participation of $^1O_2$ might be negligible also in the latter system.11) But it is still unclear why the configuration was more retained in the $TPPBF_4$ oxygenation than others. We have already shown that an open intermediate similar to **3** was formed in the contact charge-transfer photooxygenation of **1a** on the basis of the IR spectroscopic observation in a cryogenic oxygen matrix together with *ab initio* calculation.5d) Thus, the contact charge-transfer photooxygenation of **1b** was non-stereospecific as expected, while the configuration of **1b** recovered at partial conversion was retained. (Entry 10, 11)



Scheme 2.

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