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Electron-Transfer Reaction of 1,2-Disila-3,5-cyclohexadienes

Masahiro Kako, Hideki Takada, and Yasuhiro Nakadaira*

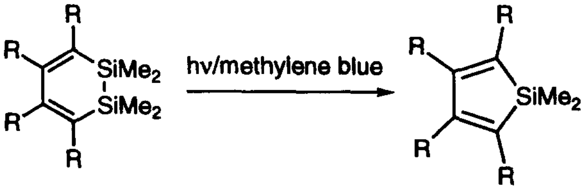
Department of Chemistry, The University of Electro-Communications,
Chofu, Tokyo 182, Japan

Abstract: Photolysis of 1,2-disila-3,5-cyclohaxadienes **1a-b** in the presence of methylene blue as a sensitizer led to efficient formation of the corresponding siloles as ring contraction products. The reaction mechanism is best rationalized by electron-transfer from **1a-b** to the excited state of methylene blue. Semiempirical molecular orbital calculation was also carried out to characterize the geometric and electronic structure of radical cation **1a**$^{+\bullet}$. © 1997 Elsevier Science Ltd.

1,2-Disila-3,5-cyclohexadiene (**1**) is an attractive compound in relation to the well-studied silacyclopentadiene (silole), one of the most fundamental silacycles.$^{1)}$ So far, **1** has been already reported to show unique reactivities such as photochemical rearrangement and ring contraction with a transition metal complex.$^{2)}$ However, the potential donor properties of **1** in electron-transfer reactions have been hitherto overlooked while silole **2** has been revealed to act as a good electron donor.$^{3)}$ As a part of our continuing studies of the electron-transfer chemistry of organometallic compounds,$^{4)}$ we now report the novel electron-transfer-induced ring contraction of **1**, which would constitute a novel electron donor. In addition, the structural and electronic aspects of **1** and the corresponding radical cation **1**$^{+\bullet}$ have been investigated by semiempirical molecular orbital calculation, which provides insight into the reaction mechanism.

1,2-disila-3,5-cyclohexadienes **1a** and **1b** have fairly low oxidation potentials (**1a**: E_{ox} = + 0.81 V vs SCE, **1b**: E_{ox} = + 1.03 V vs SCE), which are lower than those of siloles **2a** (E_{ox} = +1.31 V vs SCE) and **2b** (E_{ox} = +1.24 V vs SCE). Since **1a** and **1b** have intense absorption bands up to the visible region, methylene blue (MB)$^{5)}$ was chosen as a sensitizer for selective excitation. Irradiation of a CH_2Cl_2 solution of **1a** (1.4 x 10^{-2} M) in the presence of MB (1.4 x 10^{-3} M) with two 500 W tungsten-halogen lamps (passing through a

Scheme 1.



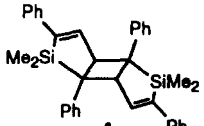
1a: R = Ph
1b: R = H

2a: R = Ph
2b: R = H

Toshiba Y-47 glass filter) afforded silole **2a** in 19% yield (Scheme 1 and Table 1). The reaction did not occur without MB or under dark conditions, and was suppressed by addition of 1,4-diazabicyclo[2.2.2]octane (E_{ox} = +0.70 V vs SCE) as an electron donor. According to the Rehm-Weller equation,[6] the free energy changes (ΔG) of the electron-transfer process from **1** to ^{1}MB* and ^{3}MB* are calculated to be -19.4 and -11.0 for **1a**, and -14.3 and -5.9 kcal/mol for **1b**, respectively. These negative ΔG values indicate that the exothermic electron-transfer from **1a** and **1b** to the excited states of MB should be expected. Treatment of **1a** with $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$,[7] a well-known oxidizing reagent, under dark conditions also produced **2a** in 47% yield, which result supports the electron-transfer mechanism. Considering the singlet and the triplet energies of MB (E_S = 42.8 kcal/mol, E_T = 34.4 kcal/mol),[5b] tetracene (E_S = 60.7 kcal/mol, E_T = 29.3 kcal/mol)[8] could act as a quencher of ^{3}MB*. Actually, the reaction was not suppressed by addition of tetracene. Therefore, the ring contraction of **1** would proceed through ^{1}MB* sensitization.

Table 1. Ring Contraction of 1,2-Disila-3,5-cyclohexadienes **1a** and **1b**

substrate	condition	product (yield/%)
1a	hν/MB/CH_3CN	**2a**(17)
1a	hν/MB/CH_2Cl_2	**2a**(19)
1a	hν/MB/CH_3CN/CH_3OH	**2a**(79)
1a	hν/MB/CH_2Cl_2/CH_3OH	**2a**(79)
1a	hν/MB/CH_3CN/$Bu_4N^+BF_4^-$	**2a**(59)
1a	$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$/$CH_2Cl_2$	**2a**(47)
1a	$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$/$Bu_4N^+BF_4^-$/$CH_2Cl_2$	**2a**(57)
1b	hν/MB/CH_3CN/CH_3OH	**2b**(13), **4**~**6**(7)
1b	hν/MB/CH_3CN/$Bu_4N^+BF_4^-$	**2b**(6), **4**~**6**(5)
1b	$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$/$CH_2Cl_2$	**2b**(72)



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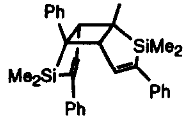

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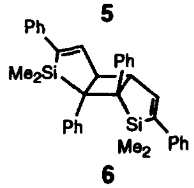

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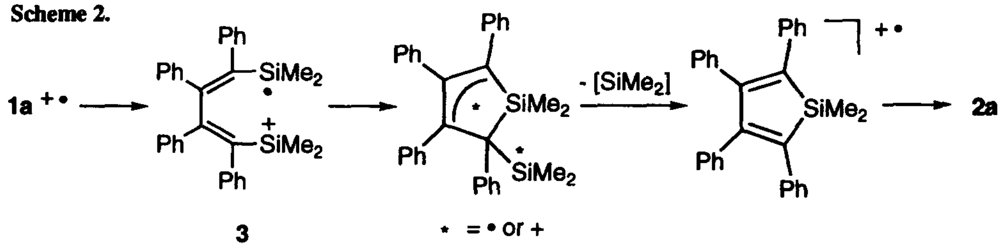
From these results, we propose a possible mechanism for the ring contraction of **1a** as depicted in Scheme 2. Initially, **1a** is readily oxidized by ^{1}MB* to give radical cation **1a**$^{+\bullet}$, in which the Si-Si bond is possibly cleaved to give an open intermediate **3**. Then, subsequent intramolecular addition of one of the silyl groups to the diene moiety followed by elimination of a dimethylsilylene unit and back-electron-transfer gives rise to **2a**, although none of the eliminated dimethylsilylene part could be trapped even in the presence of common silylene traps such as 2,3-dimethyl-1,3-butadiene or Et_3SiH. These results invoke the formation of dibenzosilole in the photoexcitation of the charge-transfer complex between dibenzodisilacyclohexadiene and tetracyanoethylene, where the dibenzodisilacyclohexadiene radical cation was suggested as the key intermediate.[10]

Scheme 2.



It is noteworthy that addition of MeOH as a part of the solvent improves the yield of **1a** as shown in Table 1. Since it has been well documented that alcohols assist cleavage of Si-Si σ radical cations in many electron-transfer reactions,[11] the solvent effect for the formation of **2a** suggests similar participation of MeOH in the bond cleavage stage involved in Scheme 2. A recent report has demonstrated that fluoride anions could cleave the Si-Si bonds of organosilicon radical cations when n-$Bu_4N^+BF_4^-$ was used as a fluoride source.[12] In fact, the yields of **2a** increased in the presence of n-$Bu_4N^+BF_4^-$.

Under the photosensitized conditions, the yields of **2b** are lower than those of **2a** because the product **2b** is also photolabile to give a small amount of the dimers **4**~**6**.[9] By examining the effects of DABCO and tetracene as additives, it is likely that an electron-transfer mechanism might operate also in the reaction of **2b**. However, we have not found the reason why **2b** is reactive whereas **2a** is not. Meanwhile, **2b** is inert toward $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ as expected from comparison of oxidation potentials of **2b** and $(p\text{-}BrC_6H_4)_3N$ (E_{ox} = + 1.16 V vs SCE).

Semiempirical molecular orbital calculation of **1a** and **1a**$^{+\bullet}$ was performed by the MOPAC PM3[13] system, and important structural parameters are shown in Table 2. Optimization of **1a** led to a geometry of approximate C_2 symmetry with the C_2 axis bisecting S1(1)-Si(2) and C(2)-C(3) bonds (Figure 1). Non-planarity of the Si_2C_4 ring might be ascribable to the sterical constraint caused by the four phenyl groups since the optimized structure of unsubstituted disilacyclohexadiene is planar. As seen in Figure 1, the following structural changes from **1a** to **1a**$^{+\bullet}$ should be noted: (i) the elongation of the Si-Si bond, (ii) the flattening of both the Si(1) and the Si(2) atoms (sum of angles, C(1)-Si(1)-C(5), C(1)-Si(1)-C(6), and C(5)-Si(1)-C(6) being 350.0°; sum of angles, C(4)-Si(2)-C(7), C(4)-Si(2)-C(8), and C(7)-Si(2)-C(8) being 350.1°). Similar

Table 2. Selected Bond Distances(Å) and Angles(°) of **1a** and **1a**$^{+\bullet}$

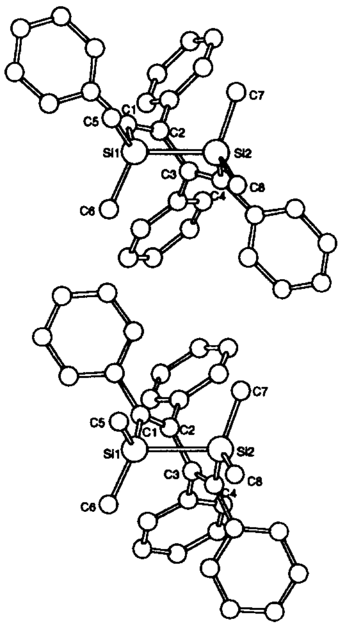
	1a	**1a**$^{+\bullet}$
Si(1)-Si(2)	2.447	2.575
Si(1)-C(1)	1.868	1.810
Si(2)-C(4)	1.860	1.810
C(1)-C(2)	1.344	1.360
C(2)-C(3)	1.493	1.469
C(3)-C(4)	1.344	1.360
Si(2)-Si(1)-C(1)	96.25	83.39
Si(1)-Si(2)-C(4)	95.04	83.33
Si(1)-C(1)-C(2)	117.18	121.69
C(1)-C(2)-C(3)	122.65	120.93
C(2)-C(3)-C(4)	124.49	120.94
C(3)-C(4)-Si(2)	117.26	121.69

Table 3. Charge and Spin Density of **1a**$^{+\bullet}$

atom	charge	(Δcharge*)	spin density
Si(1)	+0.6038	(+0.3052)	+0.2806
Si(2)	+0.6058	(+0.2668)	+0.2761
C(1)	-0.2056	(-0.0038)	+0.0735
C(2)	+0.0775	(+0.0572)	+0.1089
C(3)	+0.0795	(+0.0563)	+0.1028
C(4)	-0.2069	(-0.0126)	+0.0802

*Changes of the charge from the neutral to the cation radical.

Figure 1. Calculated Structures of **1a**(top) and **1a**$^{+\bullet}$(bottom)



structural deformation has been reported by Glidewell for $[Me_3SiSiMe_3]^{+\bullet}$ obtained by the PM3 calculation.14) Meanwhile, HOMO of **1a** was calculated to be a combination of those of the Si-Si σ- and the 1,3-butadiene π-systems, suggesting that these sites are susceptible to the initial one-electron oxidation. Additional electronic features of the optimized radical cation are also shown in Table 3, which indicate that the positive charge is concentrated at the Si atoms whereas the spin is dispersed throughout the molecule. These findings suggest that the Si-Si bond cleavage would take place easily in $\mathbf{1a}^{+\bullet}$, especially with assistance of nucleophilies. Further work is in progress to disclose the novel aspects of **1a** and **1b** as electron donors.

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REFERENCES

1) For reviews, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu R. J. P.; Lheureux, M. *Ibid.* **1990**, *90*, 265.
2) (a) Nakadaira, Y.; Kanouchi, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974**, *96*, 5623. (b) Nakadaira, Y.; Kobayashi, T.; Sakurai, H. *J. Organomet. Chem.* **1979**, *165*, 399.
3) (a) Kyushin, S.; Ohkura, Y.; Nakadaira, Y.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1718. (b) Nakadaira, Y.; Ohkura, Y.; Kyushin, S.; Ohashi, M.; Ueno, K.; Kanouchi, S.; Sakurai, H. *Tetrahedron Lett.* **1992**, *33*, 4013. (c) Kyushin, S.; Ohkura, Y.; Nakadaira, Y.; Ohashi, M.; Yasui, M.; Iwasaki, F. *Chem. Lett.* **1991**, 883. (d) Kyushin, S.; Baba, Y.; Nakadaira, Y.; Ohashi, M. *Main Gruop Metal Chemistry* **1995**, 299.
4) (a) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781. (b) Kyushin, S.; Ehara, Y.; Nakadaira, Y.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 279. (c) Kyushin, S.; Masuda, Y.; Matsushita, K.; Nakadaira, Y.; Ohashi, M. *Tetrahedron Lett.* **1990**, *31*, 6395. (d) Nakadaira, Y.; Gomi, Y.; Hosoe, H.; Kyushin, S; Kako, M.; Hatakenaka, K.; Ohashi, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 344. (e) Kako, M.; Kakuma, S.; Hatakenaka, K.; Nakadaira, Y.; Yasui, M.; Iwasaki, F. *Tetrahedron Lett.* **1995**, *35*, 6293. (f) Kako, M.; Mori, M.; Hatakenaka, K.; Kakuma, S.; Nakadaira, Y.; Yasui, M.; Iwasaki, F. *Tetrahedron* **1997**, *53*, 1265.
5) (a) Hatsui, T.; Takeshita, H.; *Chem. Lett.* **1990**, 1253. (b) *Idem, Ibid.* **1993**, 129. (c) *Idem, J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 257. (d) Das, S.; Thanulingam, T. L.; Rajesh, C. S.; George, M. V. *Tetrahedron Lett.* **1995**, *36*, 1337. (e) Akasaka, T.; Sato, K.; Kako, M.; Ando, W. *Tetrahedron Lett.* **1991**, *32*, 6605. (f) *Idem, Tetrahedron*, **1992**, *48*, 3283; (g) Ando, W.; Kako, M.; Akasaka, T. *Chem. Lett.* **1993**, 1679.
6) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
7) Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269, and references cited therein.
8) Murov, S. L. *Handbook of Photochemistry;* Marcel Dekker: New York, 1973.
9) (a) Barton, T. J.; Nelson, A. T. *Tetrahedron Lett.* **1969**, 5037. (b) Nakadaira, Y.; Sakurai, H. *Ibid.* **1971**, 1183.
10) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1213.
11) (a) Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327. (b) Nakadaira, Y.; Otani, S.; Kyushin, S.; Ohashi, M.; Sakurai, H.; Funada, Y.; Sakamoto, K.; Sekiguchi, A. *Ibid.* **1991**, 601. (c) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (d) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *Tetrahedron Lett.* **1993**, *34*, 2863. (e) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 151. (f) Watanabe, H.; Kato, M.; Tabei, E.; Kuwabara, H.; Hirai, N.; T. Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1662.
12) Becker, J. Y.; Shakkour, E.; West, R. *Tetrahedron Lett.* **1992**, *33*, 5633.
13) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) *Idem, QCPE Bull.* **1989**, *9*, 10.
14) Glidewell, C. *J. Organomet. Chem.* **1993**, *461*, 15.

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