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Cycloreversion of 2,3-Disilabicyclo[2.2.2]octa-5,7-dienes Induced by Electron-Transfer

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Synopsis. Photolysis of 1-phenyl-2,2,3,3-tetramethyl-2,3-disilabicyclo[2.2.2]octa-5,7-diene (**1**) with 9,10-dicyanoanthracene as a sensitizer yielded biphenyl as a tetramethyldisilene extrusion product. The mass spectrum of **1** provides access to the understanding of the reaction mechanism involving cycloreversion of a cation radical of **1**.

2,3-Disilabicyclo[2.2.2]octa-5,7-dienes **1**—**3** are known to produce transient Si–Si double bonds (disilenes)[1)] on thermolysis.[2)] Meanwhile, it has been demonstrated that **2** is photochemically reactive to undergo both disilene extrusion and intramolecular rearrangement.[3)] Recently, it has been reported that anion-catalyzed extrusion of disilene units from some derivatives of **1** yields ordered and monodispersed polysilane high polymers.[4)] However, no attention has been focused on their electron-donating characteristics. As a part of our continuing research for the electron transfer chemistry of organosilicon compounds,[5)] we now report a novel cycloreversion of **1**—**3** induced by electron transfer.

By cyclic voltammetry, it is shown that **1**—**3** are fairly good electron donors compared with usual allylsilanes (Table 1).[6)] Irradiation of **1** in a mixed solvent of CH_3CN/CH_2Cl_2 in the presence of 9,10-dicyanoanthracene (DCA) with two 500 W tungsten-halogen lamps in a Pyrex tube produced biphenyl (**4**) in a quantitative yield and a complex polymeric mixture containing silylmethyl units. Since the reaction did not occur without DCA, it is clear that DCA should be excited first by irradiation and acts as a sensitizer. Very similar results were obtained with **2** and **3**. The free energy changes (ΔG) calculated by the Rehm-Weller equation[7)] are indicative of highly exothermic electron transfer from **1**—**3** to the excited singlet state of DCA. Furthermore, the DCA fluorescence was efficiently quenched by **1**—**3** with diffusion-controlled rates (Table 1). In addition, when 10 mol% of $(p\text{-}BrC_6H_4)_3NSbCl_6$,[8)] an one-electron oxidizing reagent, was added to **1**—**3** in CH_2Cl_2 under a N_2 atmosphere caused the cycloreversion to give **4**—**6**, respectively (Table 2). Thus it is indicated that electron-transfer process affording cation radicals of **1**—**3** is operative in the cycloreversion. However, every effort of trapping the extruded disilene units using benzophenone,[9)] bis(trimethylsilyl)acetylene,[2b,3c,10)] and 2,3-dimethylbutadiene,[11)] which are usual traps for transient disilenes, was unsuccessful. Although the electron-transfer cleavage of Si–Si σ bonds with CCl_4 has been reported previously,[5a)] DCA-sensitized photoreaction of **1** in the presence of CCl_4 afforded none of identifiable chlorinated products (Chart 1).

Meanwhile, addition of an equimolar amount of tetracyanoethylene (TCNE) to **1**—**3** in CH_2Cl_2 at room temperature also resulted in the cycloreversion affording **4**, **5**, and **7** (a TCNE adduct of **6**),[12)] respectively. Many examples of charge-transfer (CT) complexes between organosilicon compounds and TCNE have been reported.[13)] Whereas a CT band of **3** and TCNE in CH_2Cl_2 appeared at 649 nm as expected, those of **1** and **2** could not be observed probably due to rapid decomposition of **1** and **2** induced by electron transfer. These results are rationalized by electron transfer from **1**—**3** to TCNE induced by the CT complexing.[14)] In the case of **1**, a tetrasiladioxane derivative **8**[15)] was obtained. Although the mechanism of the formation of **8** remains unclear at this moment, one possible explanation involves hydrolysis of **1** with a trace amount of H_2O under the reaction conditions and subsequent condensation since the yield of **8** increased when a mixture of THF/H_2O was used as a solvent.

To gain insight into the reaction mechanism, mass spectral fragmentations of **1**—**3** were investigated.[5g,5h)] As shown in Scheme 1 and Table 3, the mass spectra of **1**—**3** show moderate intensities of the peaks due to $M^{+\bullet}$, ($Me_2SiSiMe_2$; **9**)$^{+\bullet}$ as reported by Roark and Peddle.[2a)] The presence of two fragmentation processed, namely, $M^{+\bullet}$ to $\mathbf{9}^{+\bullet}$, $\mathbf{9}^{+\bullet}$ to (Me_3Si; **10**)$^+$ and ($Me_2SiSiMe$; **11**)$^+$, are indicated by linked scanning (both B^2/E and B/E constant spectra).[5g,5h)] This fragmentation suggests that disilene cation radical $\mathbf{9}^{+\bullet}$ is

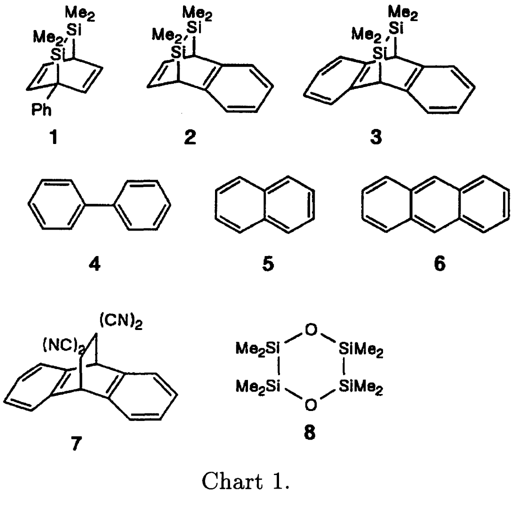


Chart 1.

Table 1. Oxidation Potentials, Calculated ΔG values for the One-Electron Transfer Process from **1**—**3** to ^{1}DCA*, and Rate Constants for the Fluorescence Quenching of DCA

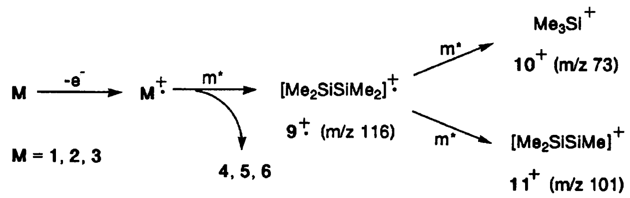
Substrate	E_{ox}[a]/V	ΔG[b]/kJ mol^{-1}	k_q[c]×10^{-10}/dm^3 mol^{-1} s^{-1}
1	0.42	−170.3	2.50
2	0.60	−153.1	2.10
3	0.80	−133.9	1.43

a) Oxidation potentials vs. SCE in CH_3CN. b) Free energy changes calculated by the Rehm–Weller equation.[7] c) Rate constants for fluorescence quenching calculated from the Stern–Volmer plots.

Table 2. Electron Transfer Induced Cycloreversion of **1**—**3**

Substrate	Condition	Time	Conversion/%	Products (Yields/%)[a]
1	$h\nu$/DCA/CH_3CN/CH_2Cl_2	15 min	100	**4** (85)
2	$h\nu$/DCA/CH_3CN/CH_2Cl_2	1 h	39	**5** (100)
3	$h\nu$/DCA/CH_3CN/CH_2Cl_2	1 h	30	**6** (61)
1	(p-$BrC_6H_4)_3NSbCl_6$/CH_2Cl_2/−78°C	3 h	100	**4** (73)
2	(p-$BrC_6H_4)_3NSbCl_6$/CH_2Cl_2/−78°C	3.5 h	76	**5** (88)
3	(p-$BrC_6H_4)_3NSbCl_6$/CH_2Cl_2/−78°C	3.5 h	21	**6** (100)
1	TCNE/CH_2Cl_2	10 min	100	**4** (96)
2	TCNE/CH_2Cl_2	10 min	100	**5** (100)
3	TCNE/CH_2Cl_2	1.5 h	23	**7** (100) [b]

a) Conversion yields determined by GLC. b) By NMR.



Scheme 1.

Table 3. MS peak intensities of **1**—**3**

M	m/z 116	m/z 73	m/z 101
1	100	36	13
2	100	40	12
3	100	32	9

the probable intermediate in the electron transfer induced cycloreversion of **1**—**3**. These selective C–Si bond cleavages of **1**—**3** are of particular interest since one electron oxidation of polysilane usually results in the facile Si–Si cleavage.[5a,5b,5g,16)]

Experimental

NMR spectra were recorded with a JEOL JNM-GX270 spectrometer. Deuteriated chloroform and benzene were used as the solvent. Mass spectral data were obtained on a Shimadzu QP-1000 and a Hitachi M-80B mass spectrometers. UV-visible spectra were obtained with a JASCO Ubest 30 spectrometer. GLC-analyses were carried out on a Shimadzu GC-14A equipped with a 0.25 mm × 25 m CBP1 capillary column. Cyclic voltammograms of **1**—**3** were obtained on 0.1 M n-Bu_4NClO_4/CH_2Cl_2 solution (1 M=1 mol dm^{-3}) (vs. SCE; scan rate, 200 mV s^{-1}; Nikkoh Keisoku Ltd., a potentiostat/galvanostat NPGS-301 and a potential sweeper NPS-2). The ΔG values were calculated according to the Rehm-Weller equation (ΔG(kcal mol^{-1})=23.06-[$E(D/D^+)-E(A^-/A)-e_0^2/\varepsilon a-\Delta E_{o,o}$])[7] by using the excited singlet energies of DCA (2.89 V), the reduction potentials of DCA (−0.98 V vs. SCE),[17] and 0.06 eV for $e_0^2/\varepsilon a$.[7] The rate constants (k_q) for DCA fluorescence quenching with **1**—**3** were measured by using a JASCO FP-550 fluorescence spectrometer. The k_q values were calculated from the literature value of τ (15.3 ns) for DCA.[17] Irradiation was carried out by two 500-W tungsten-halogen lamps using a Pyrex filter in a water bath while N_2 passed through the photolysate.

Materials. DCA (Tokyo Kasei) and (p-$BrC_6H_4)_3NSbCl_6$ (Aldrich) were used as received. TCNE (Tokyo Kasei) was used after sublimination. Compounds **1**—**3** were prepared according to the literature.[2a]

DCA-Sensitized Photoreactions of 1—3. In a typical experiment, **1** (1.7×10^{-2} M) was dissolved in a mixed solvent of CH_3CN and CH_2Cl_2 (4 : 1) with DCA (1.3×10^{-3} M) as a sensitizer, and this solution was photolyzed. The reaction was monitored by GLC. Formation of **4** was confirmed by comparison of its retention time on GLC with that of the authentic sample and GC-MS analysis, and the yield of **4** was also determined by GLC.

Reactions of 1—3 with (p-$BrC_6H_4)_3NSbCl_6$. In a typical experiment, 10 mol% of (p-$BrC_6H_4)_3NSbCl_6$ in CH_2Cl_2 (5 ml) was added to a CH_2Cl_2 (20 ml) solution of **1** (0.5 mmol) at −78°C in the dark under a N_2 atmosphere. After stirring 3 h, **1** was completely consumed. The yield of **4** was determined by GLC analysis by comparing with the authentic samples.

Reactions of 1—3 with TCNE. In a typical experiment, an equimolar amount of TCNE was added to a CH_2Cl_2 (20 ml) solution of **1** (0.5 mmol) at room temperature in the dark under a N_2 atmosphere. After stirring

10 min, and the yield of **4** was determined by GLC. The formation of **7**[12)] and **8**[15)] (in the cases of **1** and **3**, respectively) was confirmed by comparison of the NMR spectra with those of authentic samples.

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