Pergamon

Tetrahedron Letters 40 (1999) 1133–1136

TETRAHEDRON
LETTERS

Photoinduced Electron-transfer Reaction of 7,8-Disilabicyclo[2.2.2]octa-2,5-dienes

Masahiro Kako,* Kaname Hatakenaka, Seiji Kakuma, Masumi Ninomiya, Yasuhiro Nakadaira,*
Masanori Yasui,[†] Fujiko Iwasaki,[†] Masanobu Wakasa,[††] and Hisaharu Hayashi[††]

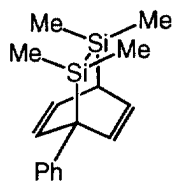
Department of Chemistry and [†]Department of Applied Physics and Chemistry,
The University of Electro-Communications, Chofu, Tokyo 182, Japan
[††]Molecular Photochemistry Laboratory, The Institute of Physical and Chemical Research (RIKEN),
Wako, Saitama 351-01, Japan

Received 6 August 1998; accepted 27 November 1998

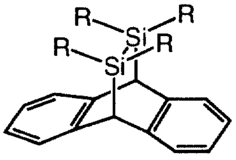
Abstract: 9,10-Dicyanoanthracene-sensitized irradiation of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes **1**-**3** in the presence of MeOH resulted in the formation of dimethoxydisilanes and the corresponding aromatic compounds. A stepwise mechanism involving C-Si bond cleavage by MeOH is proposed.

Electron-transfer chemistry of group 14 organometallic compounds has been attracting considerable interest from the mechanistic and synthetic viewpoints.[1)] Recently, the well-known disilene precursor 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene **1** has been revealed to have remarkable electron donor properties which are readily ascribable to efficient σ-π conjugation between the Si-C σ bonds and the C-C π bonds.[2)] Thus, one-electron oxidation of **1** resulted in the quantitative formation of biphenyl by facile cycloreversion, but the fate of the disilanylene unit eliminated has remains unclarified.[2a)] We now report the electron-transfer reaction of compounds **1**-**3** in the presence of nucleophiles to disclose the cycloreversion mechanism.

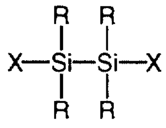
Irradiation of a solution of **1** (1.3×10^{-2} M) and 9, 10-dicyanoanthracene (DCA, 1.3×10^{-3} M) in a mixed solvent of CH_2Cl_2 and MeOH (4/1) with two 500 W tungsten-halogen lamps led to formation of $MeOMe_2SiSiMe_2OMe$ (**4**) and biphenyl. The photolysis of compounds **2** and **3** under similar conditions gave the corresponding dimethoxydisilanes **4** and **5**, respectively, together with anthracene. Interestingly, in the case of **3**, a dimer **6**[3)] was also formed along with **5**, and the molecular structure of **6** was determined unequivocally by X-ray crystal analysis (Figure 1).[4)] Photolysis of **6** also afforded **5** and anthracene. On the other hand, when **1**-**3** were irradiated with 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) as a sensitizer,[5)] difluorodisilanes **10** and **11** were obtained together with the corresponding arenes as indicated in Table 1, but no dimeric product was detected in these cases. Similarly, the photo-induced fluorinative cleavage



1



2: R = Me
3: R = ^{i}Pr



$XR_2Si{-}SiR_2X$

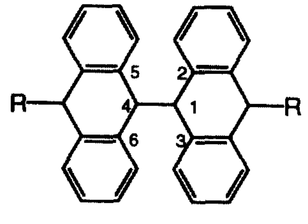
4: R = Me, X = OMe
5: R = ^{i}Pr, X = OMe
10: R = Me, X = F
11: R = ^{i}Pr, X = F

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)02546-5

did not proceed without light, and was inhibited by addition of 1,4-diazabicyclo[2.2.2]octane (DABCO). Furthermore, the ΔG values estimated by the Rehm-Weller equation[6] are indicative of exothermic electron-transfer from **1**-**3** to the excited singlet state of TPP$^+$BF$_4^-$, and the fluorescence of the pyrylium salt is efficiently quenched with **1**-**3**. Thus, the fluorinative cycloreversion should proceed also through the corresponding radical cations **1**$^{+\bullet}$-**3**$^{+\bullet}$ formed by the initial electron-transfer to the excited singlet state of the sensitizer, TPP$^+$BF$_4^-$. As expected, the fluorinative cleavage took place on irradiation in the presence of Bu$_4$N$^+$BF$_4^-$ using DCA as a sensitizer.[1,7]

Table 1. Photolysis of **1**-**3** in the presence of electron acceptors

Substrate	Condition	Products and Yields(%)
1	hv/DCA/CH$_2$Cl$_2$/MeOH	**4**(70), biphenyl(100)
2	hv/DCA/CH$_2$Cl$_2$/MeOH	**4**(35), anthracene(80)
3	hv/DCA/CH$_2$Cl$_2$/MeOH	**5**(55), **6**(16), anthracene(55)
1	hv/TPPBF$_4$/CH$_2$Cl$_2$	**10**(62), biphenyl(100)
2	hv/TPPBF$_4$/CH$_2$Cl$_2$	**10**(39), anthracene(90)
3	hv/TPPBF$_4$/CH$_2$Cl$_2$	**11**(21), anthracene(70)
1	hv/DCA/Bu$_4$NBF$_4$/CH$_2$Cl$_2$	**10**(50), biphenyl(89)
2	hv/DCA/Bu$_4$NBF$_4$/CH$_2$Cl$_2$	**10**(25), anthracene(42)
3	hv/DCA/Bu$_4$NBF$_4$/CH$_2$Cl$_2$	**11**(20), anthracene(53)



6: R = Si^{i}Pr$_2$Si^{i}Pr$_2$OMe

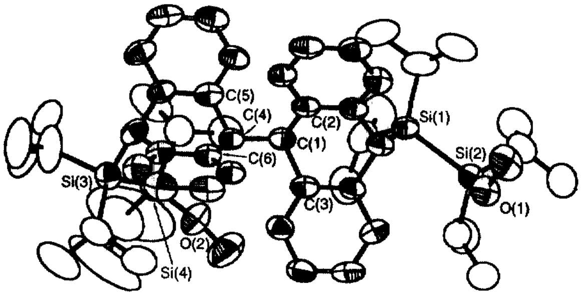
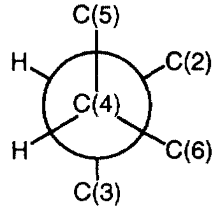


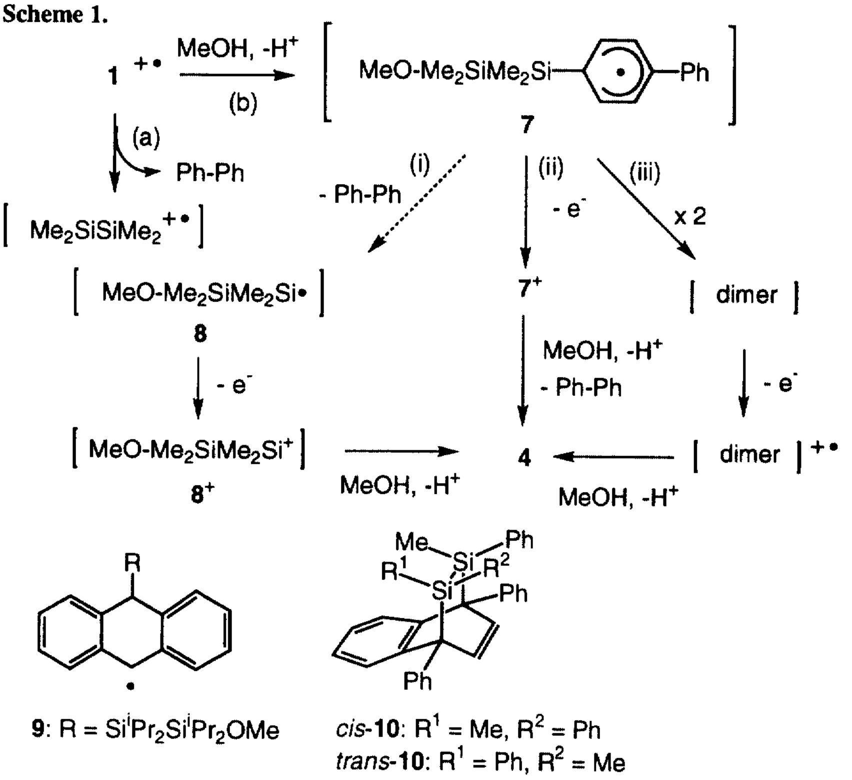
Figure 1. ORTEP Drawing of **6**.



Representation of **6** by Newman projection.

1$^{+\bullet}$ would be expected to undergo facile cycloreversion to afford initially the disilene radical cation [Me$_2$SiSiMe$_2$]$^{+\bullet}$ (path a in Scheme 1), but this is not likely because [Me$_2$SiSiMe$_2$]$^{+\bullet}$ would not afford **4** but rather MeOMe$_2$SiSiMe$_2$H in the presence of MeOH.[8] On the basis of well-recognized nucleophilic assistance to the cleavage of Si-Si and Si-C σ bonds of the organosilane radical cations,[9] **1**$^{+\bullet}$ is regarded to undergo facile C-Si bond cleavage by addition of the nucleophile MeOH to afford cyclohexadienyl radical **7** (path b). Three possible pathways are conceivable for the formation of **4** from **7**: (i) with elimination of biphenyl, **7**[10] collapses to a silyl radical MeOMe$_2$SiSiMe$_2$• (**8**), which is readily oxidized[11] and trapped by MeOH to give **4**, (ii) after one-electron oxidation of **7**, the *ipso*-C-Si bond becomes more susceptible to the nucleophile and this gives **4**, and (iii) as in the case of **3**, **7** dimerises at first, and then oxidation followed by methanolysis leads to **4**. However, for **7**, path (iii) may be less likely since **7** would be less persistent than **9** and reluctant to dimerize due to the steric hindrance around the radical center. Meanwhile, DCA-sensitized irradiation of *cis*-**10** and *trans*-**10**[12] was carried out to obtain streochemical information on the Si-C bond cleavage of **7** and this afforded two diastereomers of *meso*- and *dl*- PhMe(MeO)SiSi(OMe)MePh, stereospecifically. Although the configurations of the diastereomeric pair have not been determined yet, this result shows that the cleavage of the two Si-C bonds should proceed consecutively with either retention-retention or inversion-inversion. These experimental facts should rule out the possibility (i) for the Si-C bond fission. At the same time, intervention of a disilene radical cation should be excluded in view of the nonstereospecific addition of a neutral disilene with alcohol.[13)]

Scheme 1.



We carried out laser flash photolysis of **1** and DCA in a mixed solvent of CH_3CN/CH_2Cl_2 to observe the electron-transfer process. Nd:YAG laser third harmonic pulse (354 nm, pulse width 5 ns) was used as an exciting light source. An intense transient absorption band was observed at 330 nm[14)] (delay time of 10 μs after laser excitation) along with that of the DCA radical anion (450 ~ 500 nm) as shown in Figure 2. This transient absorption band at 330 nm was not observed in the absence of CH_3CN, but it developed more intensely as the concentration of CH_3CN increased. Neither disilene $Me_2SiSiMe_2$ nor $\mathbf{1}^{+\bullet}$ could be assigned to these absorption bands, which were not quenched by addition of alcohols as common trapping reagents for disilenes[4)] and organosilane radical cations.[5)] It is suggested that the transient might be some radical species since it was quenched by introducing gaseous oxygen into the sample solution. A similar absorption band was observed when MeOH was used instead of CH_3CN. Based on the observation of facile Si-C bond cleavage of organosilane radical cations by MeOH and CH_3CN, these transient peaks might be resulted from addition of MeOH and CH_3CN to $\mathbf{1}^{+\bullet}$.

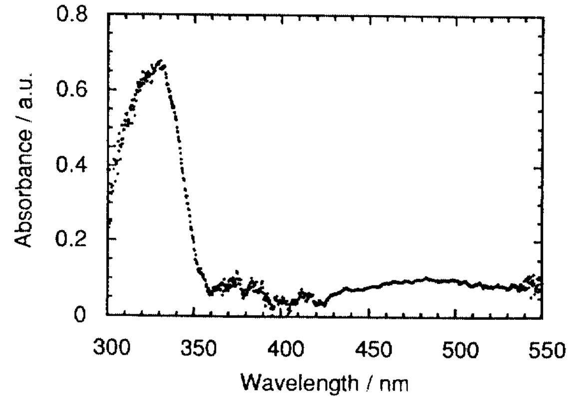


Figure 2. Transient absorption spectrum of **1** with DCA in CH_3CN/CH_2Cl_2 (4:1) at room temperature.

ACKNOWLEDGMENT: This work was supported in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture in Japan. We thank Toshiba Silicone Co. Ltd. for a gift of organosilicon reagents.

REFERENCES AND NOTES

1) Kako, M.; Kakuma, S.; Hatakenaka, K.; Nakadaira, Y.; Yasui, M.; Iwasaki, F. *Tetrahedron* **1997**, *53*, 1265, and references cited therein.
2) (a) Nakadaira, Y.; Gomi, Y.; Hosoe, H.; Kyushin, S; Kako, M.; Hatakenaka, K.; Ohashi, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 344. (b) Kyushin, S.; Ikarugi, M.; Takatsuna, K.; Goto, M.; Matsumoto, H. *J. Organomet. Chem.* **1996**, *510*, 121.
3) **6**: colorless crystals; mp 161~166 °C; ^{1}H-NMR(CDCl$_3$) δ 7.44~7.33(m, 6H), 7.14(t, 2H, J=7Hz), 7.00(t, 2H, J=7Hz), 6.98(t, 2H, J=7Hz), 6.58(t, 2H, J=7Hz), 6.42(d, 2H, J=7Hz), 5.30(s, 2H), 4.52(s, 2H), 3.50(s, 6H), 1.40~0.80(m, 56H); ^{13}C-NMR(CDCl$_3$) δ 141.24(s), 140.68(s), 138.79(s), 134.74(s), 130.56(d), 127.21(d), 125.65(d), 125.33(d), 124.89(d), 124.65(d), 123.23(d), 52.18(q) 40.65(d), 20.14(q), 19.71(q), 19.60(q), 19.47(q), 19.04(q), 18.94(q), 18.67(q), 16.57(d), 16.45(d), 15.19(d), 14.72(d); Anal. Calcd for $C_{54}H_{82}O_2Si_4$: C, 74.08; H, 9.44. Found: C, 73.92; H, 9.27. Also in solution, the conformer shown in Figure 1 may be favorable based on the decreased equivalency of signals observed in the ^{13}C-NMR spectrum. Variable-temperature ^{1}H-NMR measurement showed coalescence of methyl and aromatic proton signals, reflecting conformational change of the molecule.
4) Crystal data for **6**; $C_{54}H_{82}O_2Si_4$ (fw 875.5), monoclinic $P2_1/n$; a= 33.834(4) Å; b = 14.759(2) Å; c= 10.546(1) Å; β= 91.786(8)°, V=5264(2) Å^3; Z=4. Data were collected with Cu Kα radiation (graphite monochrometer λ=1.54184 Å) on a Rigaku AFC-4 diffractometer. A total of 9825 reflections within 2θ = 130° by the 2θ - ω scan method with a scan rate of 4°/min. The final R factor was 0.084 (R_w= 0.126) for 5351 reflections of Fo> 3σ (Fo). Atomic coordinates, bond lengths and thermal parameters were deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No.1.
5) Miranda, M. A.; García, H. *Chem. Rev.* **1994**, *94*, 1063.
6) Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259.
7) Becker, J. Y.; Shakkour, E.; West, R. *Tetrahedron Lett.* **1992**, *33*, 5633.
8) Raabe, G.; Michl, J. in "*The Chemistry of Organosilicon Compounds*" Patai, S.; Rappoport, Z., Eds.; Wiley, New York **1989**, Chapter 17, p. 1015.
9) (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) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.
10) Probably, **7** is formed as a protonated form, which may be transformed to **4**.
11) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.
12) Sakurai, H.; Nakadaira, Y.; Kobayashi, T. *J. Am. Chem. Soc.* **1979**, *101*, 487.
13) Addition of neutral disilenes with alcohols has been reported to be nonstereospecific at higher concentration of alcohol. Sekiguchi, A.; Maruki, I.; Sakurai, A. *J. Am. Chem. Soc.* **1993**, *115*, 11460.
14) Decay kinetics could not be determined since neither first- nor second- order kinetics fitted the decay curve.