© 2000 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 73, 2403—2422 (2000) 2403

Accounts

Photo-Induced Electron-Transfer Reactions of Cyclic Organosilanes and Related Compounds

Masahiro Kako and Yasuhiro Nakadaira*

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585

(Received June 22, 2000)

Under photo-induced ET conditions in the presence of CCl_4 and BF_4^-, a Si–Si σ-bond readily undergoes chlorinative and fluorinative cleavage, and gives the corresponding chloro- and fluoro-silanes in good yields. In contrast co-photolysis of an aromatic nitrile with a disilane and a tetraalkyl group 14 metal effects selective silylation and alkylation of the nucleus at the position where spin density is high on its radical anion. Chlorination with CCl_4 and the intra-molecular trap with the hydroxy group have clarified the radical cationic nature of the intermediate in the photo-induced electron transfer reactions of organooligosilanes. On the other hand, on photo-induced electron transfer, 7-silabicyclo[2.2.1]heptadiene derivatives undergo skeletal rearrangement to give 2-silabicyclo[3.2.0]heptadiene and 1-silabicyclo[2.2.1]heptadiene derivatives which are also the products from the direct photolysis. 7,8-Disilabicyclo[2.2.2]octadiene derivatives afford 1,2-dimethoxydisilane and 1,2-difluorodisilane, respectively on photo-induced electron transfer in the presence of methanol and BF_4^-. 1, 2-Disilacyclohexadiene derivatives undergo ring contraction to give the corresponding silacyclopentadienes under photo-induced electron transfer conditions. Structural and electronic characteristics of the radical cation derived from these cyclic unsaturated organosilanes by MO calculations have been discussed.

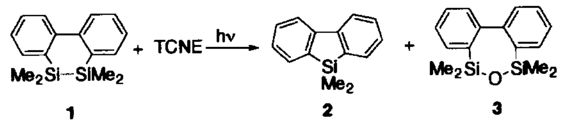
Since silicon and carbon belong to the same family, namely group 14 elements in the periodic chart, in addition to penta- and hexa-valent compounds and silicates, a silicon atom is able to form the same type of tetravalent compounds as carbon. However, silicon is a third row element but carbon belongs to the second row, so the silicon atom is much more positive and hence, in terms of ionization energy (IE), a Si–Si σ bond is rather similar to a C–C π-bond but not to a C–C σ-bond. Thus, a Si–Si σ-bond has been known to show formally analogous chemical reactivity with that of a C–C π-bond, and is able to conjugate with itself (σ–σ conjugation) and with π-systems such as C–C π-system (σ–π conjugation) as well. A Si–C σ-bond has higher IE than that of a Si–Si σ-bond, but the value is still low enough to be able to conjugate with a C–C π-bond effectively.[1] These characteristics of a Si–Si and a Si–C σ-bonds have made the electron-transfer (ET) chemistry of organosilicon and related compounds quite attractive and productive.[3—8]

In general, organosilicon compounds having Si–Si or somewhat activated Si–C bonds serve as good electron donors. Interaction with a strong electron acceptor, such as tetracyanoethylene (TCNE) gives charge transfer (CT) bands in absorption spectra. For example, in CH_2Cl_2 containing TCNE, permethylpolysilanes $Me(Me_2Si)_nMe$ ($n \geq 2$) are well-known to show the absorption maxima of CT bands which shift to longer wavelengths as the polysilanyl chain increases (λ_{max} 417 nm (n = 2), 474 nm (n = 3), 510 nm (n = 4), and 543 nm (n = 5)).[9,10] In fact, irradiation of the CT band induces ET and gives ESR signals assigned to TCNE radical anion.[10]

A certain acceptor such as 9,10-dicyanoanthracene (DCA) is not strong enough to cause effective electronic interaction with a donor in the ground state. Yet, on irradiation with an appropriate light source, the acceptor can be excited to the excited singlet state and its electron accepting ability is highly enhanced.[11] Now ET between the two components occurs exothermally. In addition to the brief description on CT reactions without light, we have reviewed principally our recent work on the photo-induced ET reactions of cyclic organosilanes and related compounds. The present review will give an emphasis on the Si–Si and Si–C bond cleavage coupled with the structure and reactivity of the key intermediate, a silyl radical cation.

1. Charge-Transfer Reactions of Organosilicon and Related Compounds without Light Generally, intra- and inter-molecular CT interactions do not induce any chemical reaction but often produce a CT absorption band. Irradiation of the CT band causes only efficient back-and-forth ET within the donor–acceptor pair. In the case of dibenzodisilacyclohexadiene **1** having a Si–Si σ-bond activated by ring strain, it shows CT bands (559 and 420 nm) in the presence of TCNE in CH_2Cl_2. Interestingly, irradiation of **2** and an equimolar amount of TCNE in CH_2Cl_2 with a Na lamp at room temperature has been reported to form silafluorene **2** and disiloxane **3** (Eq. 1).[12]

On the other hand, 3,4,7,8-tetrametala-1,5-octadiynes **4a-c** contain group 14 elements as key metal atoms and show characteristic electronic properties which are rationalized by through-bond conjugation among the two in-plane π-orbitals of ethynylenes and the two σ-orbitals of M–M (M = Si and Ge) bonds.[13—16] As expected, **4a-c** act as efficient electron donors to form CT complexes with electron acceptors such as TCNE and become colored on mixing with TCNE in CH_2Cl_2 to give characteristic intermolecular CT absorptions within the visible region (Eq. 1, Table 1). The absorption maxima of the CT spectra are red shifted in the order of **4b**, **4c**, and **4a** as the IE value of the donor decreases.



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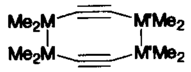


4a: M = M' = Si
4b: M = M' = Ge
4c: M = Si, M' = Ge

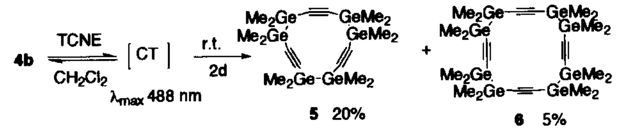
A Ge–Ge σ-bond is more susceptible to electrophiles, in fact, TCNE is inserted into the Ge–Ge σ-bond of polygermanes to give a 1 : 1 adduct under mild conditions.[16] Unlike the polygermane, **4b** turns out to be oligomerized in the presence of TCNE in CH_2Cl_2 at room temperature, possibly via a CT complex, to give higher homologues **5** and **6** in 20% and 5% yields, respectively (Eq. 2).[16] Interestingly, in the more polar solvent CH_3CN containing a catalytic amount of TCNE, **4b** and **4c** undergo ring-opening polymerization to give **7** and **8**, respectively, in almost quantitative yields (Eqs. 3 and 4).[16] However, under the reaction conditions **4a** shows only the CT absorption maximum which is stable on prolonged standing even on irradiation of the CT band. In GPC analysis, polymers **7** and **8** both give one peak with $M_n = 5.0\times10^3$ ($M_w/M_n = 1.4$) and 4.4×10^3 ($M_w/M_n = 1.3$) respectively, based on the polystyrene standard.

On mixing with another acceptor dichlorodicyanobenzoquinone (DDQ) in CH_2Cl_2, 3,4,7,8-tetrametala-1,5-octadiynes **4a-c** also show characteristic intermolecular CT absorption maxima even at longer wavelengths (Table 1). However, in contrast to the case with TCNE above, a CH_2Cl_2 solution of **4a** and DDQ leads to the formation of [2+6] cycloadduct **9** on standing at ambient temperature (Eq. 5). Under similar conditions, **4b** and **4c** with DDQ yield the corresponding bridged adducts **10—12**. The cycloaddition of **4b** proceeds quantitatively, and more smoothly than those of **4a** and **4c**. Accordingly, **4c** forms the cycloadducts **11** and **12** in a 1 : 2 ratio. However, simple linear 1,2-diethynyltetramethyldisilane and 1,2-diethynyltetramethyldigermane do not undergo the cycloaddition with DDQ in CH_2Cl_2.

Table 1. Ionization Energies (IE), Intermolecular Charge-Transfer Absorptions (λ_{CT}) and UV Absorption Maxima (λ_{max}) of **4a**, **4b**, and **4c**

Compound	IE/eV[a]	λ_{CT}/nm[b]	λ_{CT}/nm[c]	λ_{max}/nm(ε)[d]
4a	8.18, 9.48	462	516	251 (18500) 237 (sh 13900)
4b	8.00, 9.17	488	536	238 (17000) 228 (sh 11100)
4c	8.15, 9.36	467	519	244 (18200) 232 (sh 10900)

a) Determined by PE spectroscopy.[16] b) With TCNE in CH_2Cl_2. c) With DDQ in CH_2Cl_2. d) In cyclohexane.



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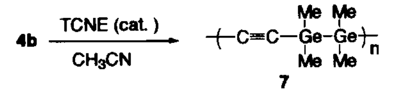
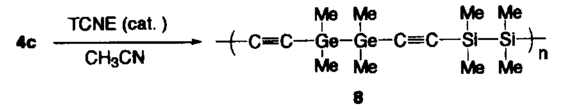
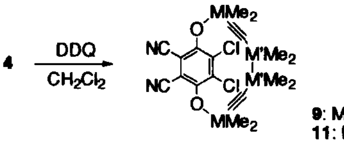


$$\mathbf{4b} \xrightarrow[CH_3CN]{\text{TCNE (cat.)}} -\!\!\left(C{\equiv}C-\overset{Me}{\underset{Me}{Ge}}-\overset{Me}{\underset{Me}{Ge}}\right)\!\!-_n \quad \mathbf{7} \qquad (3)$$



$$\mathbf{4c} \xrightarrow[CH_3CN]{\text{TCNE (cat.)}} -\!\!\left(C{\equiv}C-\overset{Me}{\underset{Me}{Ge}}-\overset{Me}{\underset{Me}{Ge}}-C{\equiv}C-\overset{Me}{\underset{Me}{Si}}-\overset{Me}{\underset{Me}{Si}}\right)\!\!-_n \quad \mathbf{8} \qquad (4)$$



(5)

9: M = M' = Si, **10**: M = M' = Ge,
11: M = Si, M' = Ge, **12**: M = Ge, M' = Si

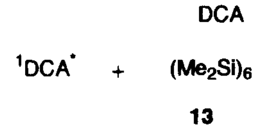
2. Photo-Induced Si–Si and Si–C Bond Cleavage by Electron Transfer

2.1 Chlorinative Si–Si Bond Cleavage. The first clear example of photo-induced ET of silicon-silicon bonded species has been reported for dodecamethylcyclohexasilane (**13**).[2b] Namely, irradiation of **13** (λ_{max} 255 nm, ε 2000) in a mixed solvent of CCl_4–CH_2Cl_2 in the presence of DCA results in the formation of 1,6-dichlorohexasilane **14** in 60—80% yields together with hexachloroethane (Eq. 6). The reaction does not occur without DCA under these conditions and DCA should be excited first by light of wavelength longer than 300 nm. Furthermore, the free energy change (ΔG) of ET from **13** to the excited singlet state of DCA ($^1DCA^*$) is calculated to be −17 kcal/mol by the Rehm–Weller equation.[18] These are indications of exothermic ET from cyclic silane **13** to $^1DCA^*$. This is substantiated by the fact that the fluorescence of DCA in CH_2Cl_2 is quenched by **13** at a diffusion-controlled rate (quenching rate constant, $k_q = 1.51 \pm 0.13\times10^{10}$ $M^{-1}s^{-1}$ (in CH_2Cl_2), $1.75 \pm 0.13\times10^{10}$ $M^{-1}s^{-1}$(in CH_3CN)). Linear permethylpolysilanes are also chlorinatively cleaved in general under similar irradiation conditions. Thus, decamethyltetrasilane gives a mixture of 1-chloroheptamethyltrisilane, chloropentamethyldisilane, and chlorotrimethylsilane without significant regioselectivity in the Si–Si bond cleavage.[19a] In this regard, the rate of the photodecomposition of poly(methylphenylsilane) has been reported to increase on addition of a halogenated sensitizer such as 1,4-bis(trichloromethyl)benzene.[20] As expected, a similar chlorinative cleavage of a Si–Si bond is effected by the treatment of polysilanes with tris(4-bromophenyl)ammoniumyl hexachloroantimonate [$(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$] in CH_2Cl_2.[21–23] From these results, the reaction sequence depicted in Scheme 1 has been proposed as a plausible reaction pathway for the photo-induced chlorinative Si–Si bond cleavage.[2b,19a] Thus, ET from **13** to $^1\text{DCA}^*$ gives radical ion pair composed of $\mathbf{13}^{+\bullet}$ and $\text{DCA}^{-\bullet}$. Then, radical cation $\mathbf{13}^{+\bullet}$ abstracts a chlorine atom from CCl_4 to give silyl cation $\mathbf{15}^+$ and $\text{CCl}_3^\bullet$. Back ET from DCA^-. to $\mathbf{15}^+$ affords silyl radical **15**, which abstracts again a chlorine from CCl_4 to give dichlorosilane **14** and $\text{CCl}_3^\bullet$, which finally couple with each other to give hexachloroethane. Thus, the radical nature of the key intermediate is evidenced by the formation of both dichlorosilane **14** and hexachloroethane in the presence of CCl_4. At the same time, the cationic nature of the intermediate is also substantiated with the intramolecular trap of the hydroxy group as mentioned below.

$$\underset{\mathbf{13}}{(\text{Me}_2\text{Si})_6} \xrightarrow[\text{DCA / CCl}_4\text{-CH}_2\text{Cl}_2]{h\nu\ (\lambda > 300\ \text{nm})} \underset{\mathbf{14}}{\text{Cl}-(\text{SiMe}_2)_6-\text{Cl}} + \text{Cl}_3\text{C}-\text{CCl}_3 \quad (6)$$

$$\underset{\mathbf{16}}{(\text{Si}i\text{-Pr}_2)_4} \xrightarrow[\text{DCA / EtOH-CH}_3\text{CN}]{h\nu} \underset{\mathbf{17}}{\text{EtOSi}i\text{-Pr}_2(\text{Si}i\text{-Pr}_2)_2\text{Si}i\text{-Pr}_2\text{H}} \quad (7)$$

$\underset{\mathbf{18}}{\text{HO}-(\text{CH}_2)_4-(\text{SiMe}_2)_2\text{R}}$ **a**: R = Me, **b**: R = C_6H_5, **c**: R = p-Me-C_6H_4, **d**: p-MeO-C_6H_4, **e**: R = p-CF_3-C_6H_4



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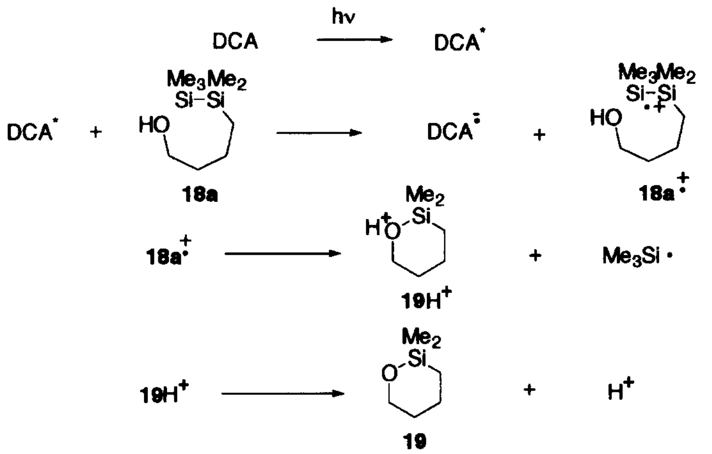
2.2. Si–Si Bond Cleavage by Oxy-Nucleophile.

Now, trapping at the cationic silicon center of the transient intermediate such as $\mathbf{13}^{+\bullet}$ by a nucleophilic solvent such as an alcohol is rather difficult under the reaction conditions. This is thought to be partly due to the extremely short lifetime of the most probable intermediate, silyl radical cation and/or rapid back ET from the DCA radical anion. Meanwhile highly strained cyclic oligosilanes with bulky substituents such as **16** have been reported to undergo nucleophilic cleavage with EtOH to afford the corresponding alkoxysilane **17** under photo-induced ET conditions (Eq. 7).[24] In this case, the lifetime of the silyl radical cation generated may be lengthened by steric protection.

To increase the efficiency of the nucleophilic trap, molecules containing both nucleophilic and cationic centers such as polysilanylalkanols **18** are employed. Photolysis of 4-(disilanyl)-1-butanol **18a** in CH_3CN containing a small amount of DCA with a medium pressure (MP) Hg lamp through a Pyrex filter causes cleavage of the Si–Si bond by intramolecular participation of the hydroxy group to give a six-membered cyclic silyl ether **19** (Eq. 8, Scheme 2). Similarly, DCA sensitized photoreaction of 4-[tetramethyl(phenyl)disilanyl]-1-butanol (**18b**) gives silyl ether **19** in high yields together with concomitant evolution of dimethyl(phenyl)silyl radical. Interestingly, the fate of dimethyl(phenyl)silyl moiety is quite dependent on the reaction media employed. Thus in CH_2Cl_2–CCl_4, chlorodimethyl(phenyl)silane (91%, with **19**, 96%), in benzene, dimethyldiphenylsilane (22%, with **19**, 53%), and in EtOH–CH_3CN (1 : 3), ethoxydimethyl(phenyl)silane (100% with **19**, 100%) are obtained, respectively. These results can be accounted for as shown in Scheme 2. ET from **18a** to $^1\text{DCA}^*$ generates the geminate radical ions composed of DCA radical anion and polysilanyl radical cation $\mathbf{18a}^{+\bullet}$, in which the hydroxy group attacks the cationic site intramolecularly to give protonated cyclic silyl ether $\mathbf{19H}^+$ and trimethylsilyl radical. Finally, deprotonation of $\mathbf{19H}^+$ yields cyclic silyl ether **19**. It is noteworthy that intramolecular nucleophilic trapping prevails over the intermolecular variety. Another piece of chemical evidence for intervention of the silyl radical is provided by the photolysis of **18b** in benzene containing a small amount of DCA; namely, the formation of dimethyl(diphenyl)silane in benzene is readily rationalized by the reaction of dimethyl(phenyl)silyl radical with the solvent benzene.[25] This is substantiated further

$$\begin{array}{lllll}
 & \text{DCA} & \xrightarrow{h\nu} & {}^1\text{DCA}^* & \\
{}^1\text{DCA}^* & + \underset{\mathbf{13}}{(\text{Me}_2\text{Si})_6} & \longrightarrow & \text{DCA}^{\bar{\bullet}} & + \underset{\mathbf{13}^{\dot{+}}}{(\text{Me}_2\text{Si})_6^{\dot{+}}} \\
\mathbf{13}^{\dot{+}} & + \text{CCl}_4 & \longrightarrow & \underset{\mathbf{15}^+}{\overset{+}{\text{Me}_2\text{Si}}-(\text{SiMe}_2)_5-\text{Cl}} & + \ \bullet\text{CCl}_3 \\
\mathbf{15}^+ & + \text{DCA}^{\bar{\bullet}} & \longrightarrow & \underset{\mathbf{15}}{\overset{\bullet}{\text{Me}_2\text{Si}}-(\text{SiMe}_2)_5-\text{Cl}} & + \ \text{DCA} \\
\mathbf{15} & + \text{CCl}_4 & \longrightarrow & \underset{\mathbf{14}}{\text{Cl}-(\text{SiMe}_2)_6-\text{Cl}} & + \ \bullet\text{CCl}_3 \\
 & 2\ \bullet\text{CCl}_3 & \longrightarrow & \text{Cl}_3\text{C}-\text{CCl}_3 &
\end{array}$$

Scheme 1. Mechanism for the photo-induced chlorinative cleavage of a Si–Si σ-bond.



Scheme 2. Intramolecular trapping of a transient silyl radical cation with a nucleophile.

by the efficient formation of chlorodimethyl(phenyl)silane on the photolysis in CH_2Cl_2–CCl_4. Chlorodimethyl(phenyl)silane should arise from dimethyl(phenyl)silyl radical by abstraction of a chlorine from CCl_4. On the other hand, the formation of ethoxydimethyl(phenyl)silane is not straightforward. Since silyl radicals have been reported to have quite low IEs (for examples, $^•SiMe_3$ 6.20 eV, $SiHMe_2$ 6.62 eV, $^•SiHPh_2$ 6.81 eV),[26] the possibility remains that the silyl radical is transformed into the silyl cation by means of ET to the ground state of DCA, followed by trapping with EtOH to give ethoxydimethyl(phenyl)silane. A similar oxidation process is assumed for the fluorinative cleavage reaction described below. Addition of the radical to CH_3CN, followed by ethanolysis, is another possibility.

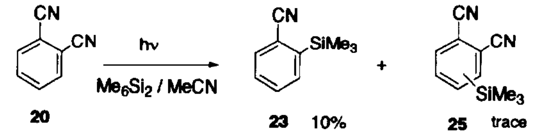
The relative reaction rates among **18b**—**e** have been obtained by competitive photolysis in CH_3CN–MeOH containing a small amount of DCA; the values obtained are $k_{18b} : k_{18c} : k_{18d} : k_{18e} = 1.0 : 1.2 : 1.9 : 0.68$. The logarithm of these relative rates against substituent constants σ^+ displays a good linear relationship, where reaction constant ρ is -0.32 ($r = 0.996$). The small but negative ρ value is consistent with the view that the Si–Si bond acts as an electron donor. The quenching rate constants of DCA fluorescence with **18b-e** also depend on the substituent on the phenyl group (Table 2). Thus, the quenching rate increases with increasing electron-donating nature of substituents and *vice versa*. Similar trends are observed in the oxidation potentials and the calculated free energy change on ET (Table 2).

Table 2. DCA Fluorescence Quenching with 4-(Aryldisilyl)-1-butanols **18b**—**e**

Compound	$k_q/10^{10}$ mol^{-1} s^{-1} a)	$E^{b)}_{ox}$	ΔG/kcal mol^{-1} c)
18d (R=p-$MeOC_6H_4$)	1.36	1.26	−21.4
18c (R=p-MeC_6H_4)	0.97	1.68	−11.7
18b (R=C_6H_5)	0.70	1.76	−9.9
18e (R=$CF_3C_6H_4$)	0.60	1.82	−8.5

a) Rate constants for fluorescence quenching of DCA in CH_3CN obtained by Horiba NAES-1000 time resolved fluorimeter. b) Oxidation peak potentials obtained by cyclic voltammetry: Pt electrode, tetrabutylammonium perchlorate in CH_3CN vs. SCE. c) Calculated free energy changes on electron transfer in CH_3CN.[18]

2.3 Photo-Induced Silylation and Alkylation. Photo-induced ET reactions of good electron-accepting aromatic nitriles have been studied extensively,[27] and various types of electron donors have been employed. i.e., π-donors such as aromatic compounds,[28,29] ethylene derivatives,[30] and allyl and benzyl metalloidals[31]; n-donors such as amines[32] and ethers[33]; σ-donors such as strained hydrocarbons.[34—36] Irradiation of aromatic nitriles in the presence of excess amounts of hexamethyldisilane causes a novel photochemical silylation of the aromatic nitriles via photo-induced ET.[2c] Thus, co-irradiation of benzonitrile and hexamethyldisilane affords selectively o- and p-trimethylsilylbenzonitriles but only in poor yields, and the corresponding m-isomer is not detected at all among isolable products. This is in contrast with the selectivity usually observed in electrophilic aromatic substitution. In the cases of dicyanobenzenes **20**—**22**, the position of trimethylsilyl group introduced is highly dependent on the substitution pattern of the aromatic nucleus. Thus, in o- and p-isomers **20** and **22**, silylation occurs exclusively on the ring carbon bearing the cyano substituent and expels the cyano group to yield **23** and **24**, respectively, together with trace amounts of **25** and **26** (Eqs. 9 and 11). In contrast, in case of the m-isomer **21**, the silyl group is introduced only to the 4-position to give **27** (Eq. 10). Furthermore, in 1,2,4,5-tetracyanobenzene **28**, one of the cyano groups is expelled exclusively to give a silylated product **29** and desilylated **30** similar to the cases of **20** and **22** (Eq. 12). A minor amount of methylated product **31** is also formed unexpectedly, **31** apparently being formed by the reaction of **28** and CH_3CN.[37] The M–C σ bonds (M = Si, Ge, Sn) of tetraalkyl- silane, germane, and stannane, have been found to act also as effective σ electron donors and hence on irradiation, tetraalkylated group 14 metals also undergo a novel alkylation of aromatic nitriles.[2d] Thus, in these photo-induced alkylations, one of cyano groups of aromatic nitriles is displaced regioselectively by a butyl group, for example, **22** gives **32** together with trace amounts of n-octane (Eq. 13). The alkyl group is not introduced into other positions of aromatic nitriles, in contrast with the photo-alkylation with organoborates.[38] The positions alkylated here are noted to be the same as those silylated by the photo-induced ET reaction with alkyldisilane. The relative reactivity of the tetraalkylated organometals decreases in the order of Sn > Ge > Si as expected (Eq. 13). The phenanthrene-sensitized irradiation of various allyl and benzyl group 14 organometals has resulted in similar types of photo-induced allylation and benzylation of dicyanobenzene.[32] Further, polysilylation of m-dicyanobenzene has been effected by using a mediator such as phenanthrene.



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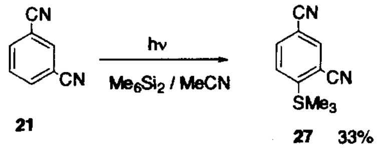

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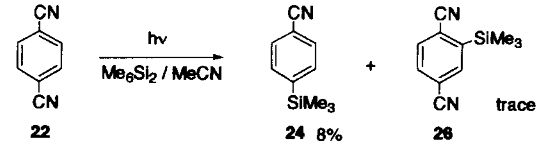

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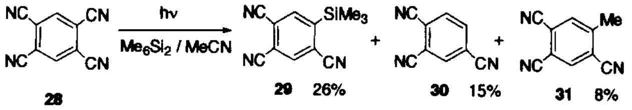

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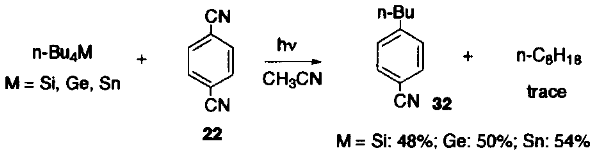
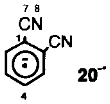
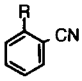
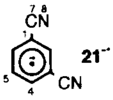
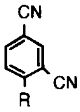
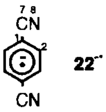
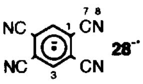
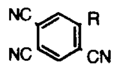


(13)

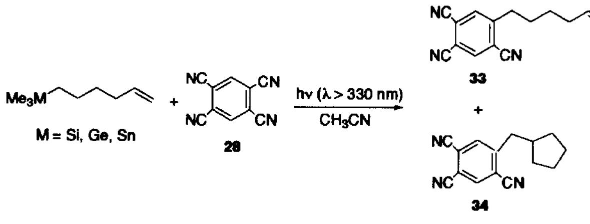
Although a CT interaction between aromatic nitriles, and hexamethyldisilane and tetraalkyl group 14 metals was not detected in the UV region, the fluorescence of **20**—**22** and **28** is quenched by these electron donors at nearly diffusion-controlled rates in CH_3CN. Coupled with a negative ΔG values calculated for ET from these σ-electron donors to **20**—**22** and **28**, the results are reasonably accounted for by ET from the σ-electron donor to the excited singlet state of the aromatic nitrile to form a radical-ion pair. It is interesting that the position of silylation and alkylation is in accord with that having maximum spin density on the benzene nucleus of cyanobenzene radical anions, which may be simply calculated by the Hückel and McLachlan MO methods and estimated by ESR spectroscopy (Table 3). For example, the spin density is largest on C(1) in $(\mathbf{20})^{-\bullet}$, C(4) in $(\mathbf{21})^{-\bullet}$, and C(1) in $(\mathbf{22})^{-\bullet}$. These are just the positions of silylation and alkylation with these σ-donors under photo-induced ET conditions. The similar photo-alkylation by tetraalkyl 14 group metals occurs on the pyrylium nucleus selectively at the position having high spin densities.[39]

The chemical behavior of the radical cation generated by ET has been examined by use of a radical clock.[42] On irradiation of 5-hexenyltrimethyl -silane, germane, and stannane in the presence of **28**, both acyclic product **33** and cyclic product **34** are formed (Eq. 14). The ratio of **33** to **34** decreases successively as the group 14 metal is varied from Sn to Si. The formation of **34** shows that a free 5-hexenyl radical should be generated from the radical cation of tetraalkylated group 14 metals before the alkylation of the aromatic ring of the nitrile. On the other hand, the formation of **33** is explained either by considering that the radical cation attacks the radical anion with concomitant elimination of the group 14 metal cation or that 5-hexenyl radical combines with the radical anion before cyclization to cyclopentylmethyl radical. The formation of **33** cannot be attributed only to free 5-hexenyl radical because the ratios of **33** to **34** are quite different among the group 14 organometals. These results show that the radical cation is responsible, in part, for the formation of **33**, and that the contribution is larger in the case of silane and smaller in the case of stannane. On the other hand, the bond strength of the σ M–C bond decreases in the order of Si > Ge > Sn, and this relationship may be valid in the corresponding radical cationic species. Thus, the radical cation of the stannane is more readily cleaved to give 5-hexenyl radical, and this favors the radical process to afford **34**.

Table 3. Correlation between the Position of Silyl and Alkyl Groups Introduced and the Spin Density of Radical Anions

Radical anion	Photo-product	ρ_{calcd}(Hückel)	ρ_{obs}(ESR)[a]
		1 0.2006[a]	
		3 0.0107	3 0.0177
		4 0.1393	4 0.1743
		7 0.0637	
		8 0.0858	
		1 0.1417[b]	
		2 0.0000	2 0.0608
		4 0.2417	4 0.3498
		5 0.0000	5 <0.004
		7 0.0510	
		8 0.0655	
		1 0.2088[b]	1 0.248
		2 0.0727	2 0.0672
		7 0.0609	
		8 0.0848	
		1 0.1606[b]	
		3 0.0000	
		7 0.0344	
		8 0.055	

a) Ref. 40 b) Ref. 41



(14)

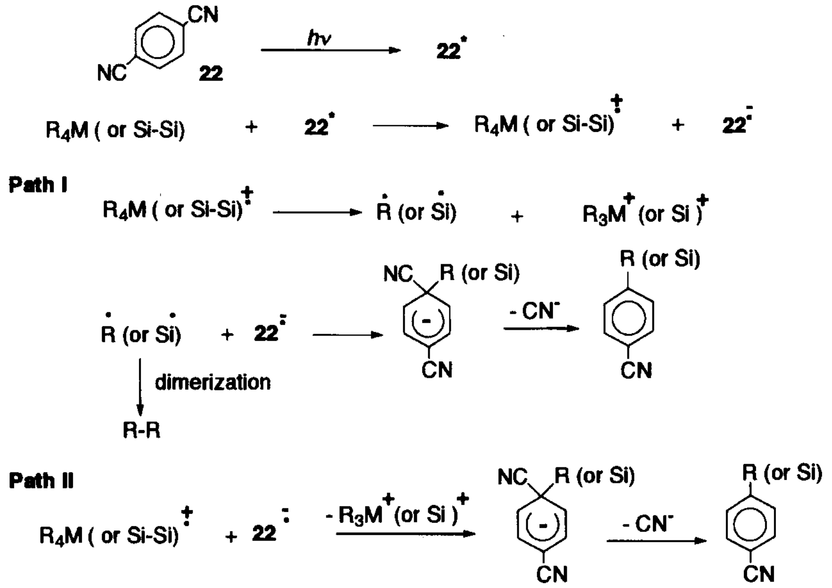
33 : 34 = 62 : 38 (M = Si, 61%), 49 : 51(M = Ge, 78%), 29 : 71 (M = Sn, 84%)

These findings strongly indicate that the photo- silylation and alkylation of aromatic nitriles and electron-deficient alkenes should proceed by way of ET. In Scheme 3, the possible mechanism is exemplified in the case of *p*-dicyanobenzene **22**. ET from the σ-electron donor to the excited singlet state of aromatic nitrile gives a radical ion pair. The radical cation is dissociated to the corresponding cation and radical, probably with the assistance of a nucleophile.[44,45] The radical thus generated bonds to the radical anion at the ring carbon bearing a cyano group where the spin density is maximum. Thus, elimination of a cyanide ion leads to the silylated or alkylated nitrile (Path I). Another mechanism assumes that prior to dissociation the radical cation attacks the radical anion of the aromatic nitrile, followed by elimination of group 14 metal cation either in a contact ion pair or a solvent-separated ion pair (Path II). From the result of the radical clock and the consideration of carbon-metal bond energy, Path I may be preferred in stannanes, while Path II may be favored in silanes.

2.4. Fluorinative Si–Si Bond Cleavage. Peralkylated oligosilanes are effective electron donors, and undergo chlorinative cleavage reactions of Si–Si σ-bonds in CCl_4 solutions initiated by photo-induced ET as described.[2b] Si–Si σ bonds of oligosilanes and phenyldisilanes also undergo fluorinative cleavage via photo-induced ET.[3]

Thus, irradiation of cyclic silanes **13** and **16** in CH_2Cl_2 in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) with tungsten–halogen (W) lamps causes fluorinative Si–Si bond cleavage and gives the corresponding α,ω-difluorohexasilanes **35** and **36**, respectively, as main products (Eq. 15). Prolonged irradiation results in further fluorinative cleavage of the product formed to give the corresponding difluorodisilane and difluorotetrasilane. Recently, electrochemical oxidation of cyclic peralkylsilanes using *n*-$Bu_4N^+BF_4^-$ as supporting electrolyte has been reported to undergo Si–Si bond cleavage reaction with tetrafluoroborate anion to form α,ω-difluorosilanes.[46] The photo-induced cleavage reaction does not proceed without light and pyrylium salt, and is inhibited by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO, oxidation potential (E_{ox}) is +0.70 V vs. SCE). ΔG values estimated from the Rehm–Weller equation indicate exothermic ET from polysilanes **13** and **16** to the excited singlet state of the sensitizer (ΔG: $Bu_4N^+BF_4^-$; **13**, −21.9 kcal/mol; **16**, −31.4 kcal mol^{-1}).[18] The fluorescence of the pyrylium salt is efficiently quenched with polysilanes ($k_q\tau$: **13**, 140 M^{-1}; **16**, 160 M^{-1}). The sensitized irradiation of **13** and **16** with DCA in the presence of tetrabutylammonium tetrafluoroborate ($Bu_4N^+BF_4^-$) also gives the corresponding α,ω-difluorooligosilanes. Fluorination occurs even in the absence of the tetrafluoroborate, and difluorosilanes are produced on irradiation of **13** and **16** in the presence of DCA and diethyl ether–boron trifluoride (1/1). Upon irradiation in the presence of $TPP^+BF_4^-$, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (**37a**), 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**37b**), 1-benzyl-1,1,2,2,2-pentamethyldisilane (**37c**), and octamethyltrisilane (**37d**) undergo fluorinative Si–Si bond cleavage to yield the corresponding fluorosilanes in reasonable yields (Table 4 and Eq. 16). Furthermore, under these reaction conditions hexamethyldisilane is also converted to give fluorotrimethylsilane.

Accounts of these fluorinative cleavage reactions are shown in Scheme 4, using **13** as an example. Similar to the chlorinative cleavage, the first step of the reaction should

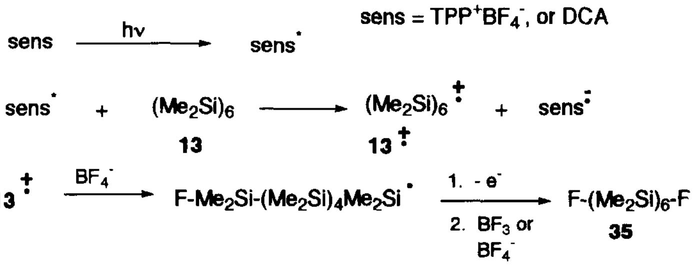


Scheme 3. A possible mechanism for photoalkylation (silylation) of an aromatic nitrile.

Table 4. Photo-induced Fluorinative Cleavage of Phenyldisilanes **37a** and **37b**, Benzyldisilane **37c**, and Trisilane **37d**

Substrate	Reaction condition[a]	Time/min	Conv./%	Product and Yield (%)	
37a	$TPP^+BF_4^-$ [b]	60	84	Ph_2MeSiF (100)	
37a	$DCA/Bu_4N^+BF_4^-$ [c]	60	58	Ph_2MeSiF (52)	
37b	$TPP^+BF_4^-$ [b]	30	72	$PhMe_2SiF$ (100)	
37b	$DCA/Bu_4N^+BF_4^-$ [c]	240	50	$PhMe_2SiF$ (85)	
37c	$TPP^+BF_4^-$ [d]	30	61	$PhCH_2Me_2SiF$ (53)	Me_3SiF[e]
37c	$DCA/Bu_4N^+BF_4^-$ [c]	120	33	$PhCH_2Me_2SiF$ (22)	Me_3SiF[e]
37d	$TPP^+BF_4^-$ [d]	30	55	$Me_3SiSiMe_2F$ (58)	Me_3SiF[e]
37d	$DCA/Bu_4N^+BF_4^-$ [c]	120	49	$Me_3SiSiMe_2F$ (55)	Me_3SiF[e]

a) On irradiation with a tungsten-halogen lamp. b) In a mixed solvent of CH_3CN and CH_2Cl_2. c) In CH_2Cl_2. d) In CH_3CN. e) Yield is not determined.



Scheme 4. Reaction mechanism for fluorinative Si–Si bond cleavage.

be one ET from organosilane **13** to the excited singlet state of the sensitizer ($TPP^+BF_4^-$ and DCA) to form a radical ion pair, namely, radical cation $\mathbf{13}^{+\bullet}$ and the radical of the sensitizer. This is substantiated by negative ΔG values, and efficient quenching of the fluorescence of sensitizers. Then, nucleophilic attack of BF_4^- on $\mathbf{13}^{+\bullet}$ causes Si–Si bond fission to give diflurosilane **35**, followed by oxidation and another fluorination possibly, by BF_4^- or BF_3.

$$(R_2Si)_n \xrightarrow[BF_4^-]{h\nu} F(R_2Si)_nF \qquad (15)$$

13: R = Me, n = 6 **35**: R = Me, n = 6
16: R = *i*-Pr, n = 4 **36**: R = *i*-Pr, n = 4

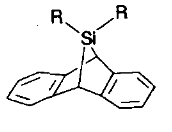
$$R_{3-n}Me_nSi\text{-}SiMe_nR'_{3-n} \xrightarrow[BF_4^-]{h\nu} R_{3-n}Me_nSiF + FSiMe_nR'_{3-n} \qquad (16)$$

37

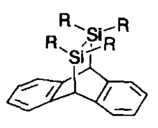
a; R = R' = Ph, n = 1, **b**; R = R' = Ph, n = 2
c; R = $PhCH_2$, R' = Me, n = 2, **d**; R = Me_3Si, R' = Me, n = 2

3. Skeletal Rearrangement via Photo-Induced Electron Transfer

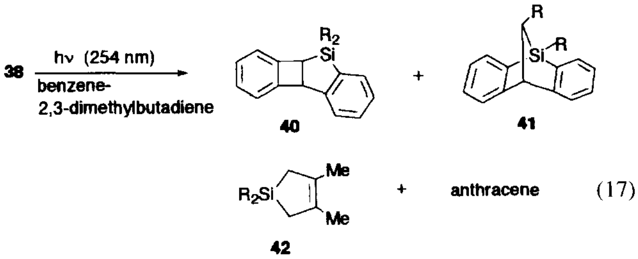
Silanorbornadienes **38a**—**b** have fairly low oxidation potentials (**38a**: $E_{ox} = +1.45$ V vs. SCE, **38b**: $E_{ox} = +1.40$ V vs. SCE in CH_2Cl_2). Upon mixing **38a** and TCNE in CH_2Cl_2, an intense coloration with an absorption maximum at 467 nm develops immediately. Previously, **39a**—**c** and TCNE have been reported to form CT complexes with absorption maxima at 630—650 nm, and the donor properties of **39a**—**c** are attributed to the effective overlapping of π-orbitals of aromatic ring with the benzylic Si–C σ-bonds.[43,44] Meanwhile, in comparison with **39**, such σ–π conjugation in **38** should be less effective because the dihedral angle between the π-orbital of the anthracene moiety and the benzylic Si–C σ bond is 43° (calculated by MOPAC PM3 method),[49] much larger than that of **39c** (17°).[48]



38a: R = 2,6-dimethylphenyl, **38b** : R = mesityl



39a: R = Me, **39b**: R = *i*-Pr, **39c**: R = $CH_2{}^tBu$

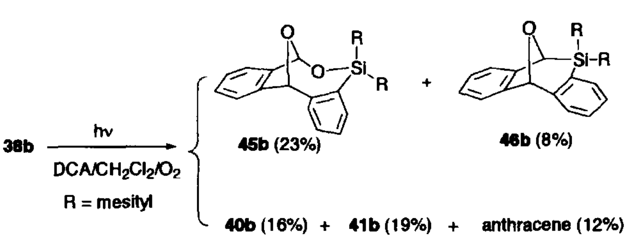


Direct irradiation of silanorbornadiene **38** with a MP Hg arc lamp in the presence of a silylene trapping reagent gives skeletal rearranged products **40** and **41** accompanied by anthracene and the corresponding silylene adduct **42** (Eq. 17).[50] On the other hand, since the effective σ–π conjugation of **38** should cause photo-induced ET on the irradiation in the presence of the weak electron acceptor, such as DCA, the photochemical behaviors of **38** may be different from those observed under direct irradiation conditions. However, irradiation of a solution of **38** and DCA in degassed dry CH_2Cl_2 with W lamps (passing through an aqueous $NaNO_2$ solution filter, cutoff < 400 nm) gives the same rearranged products **40** and **41** together with anthracene in the similar product ratio to that obtained in direct irradiation.[51] The photoreaction of **38** occurs also in CH_3CN, but proceeds slowly in benzene. No reaction takes place when **38** was irradiated with longer wavelength light > 400 nm in the absence of the sensitizer.

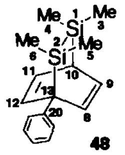
Meanwhile, addition of DABCO, which has a lower oxidation potential than that of **38**, suppresses the consumption of **38**. A ΔG value of -12.9 kcal mol^{-1} indicates exothermic ET from **38** to ^{1}DCA*. The fluorescence of DCA is efficiently quenched with **38** ($k_q = 7.9\times10^9$ M^{-1}s^{-1}). Incidentally, neither exciplex emission nor CT absorption is observed between **38** and DCA. So, the photo-rearrangement in the presence of the sensitizer would be reasonably accounted for by the stepwise process initiated by photo-induced ET from **38** to ^{1}DCA* outlined in Scheme 5.

Probably, the ET occurs from the bridge C–Si bond to form a radical cation **38**$^{+\bullet}$. Then, **38**$^{+\bullet}$ would collapse to give **43** by cleavage of one of the C–Si bonds, and isomerize to another key intermediate **44** by migration of one of the aromatic groups to the cationic center. Ring closure and subsequent back-ET leads to **40**. Meanwhile, the formation of **41** would be accounted for by the two-fold 1,2-migration of two aromatic groups, followed by ring closure and back ET. In these reduction steps, DCA$^{-\bullet}$ or neutral **38** probably serves as electron sources. Formation of anthracene in substantial yields under all the reaction conditions employed suggests that the second C–Si bond cleavage in **43** or spontaneous extrusion of the R_2Si moiety from **38**$^{+\bullet}$ would occur. However, no product derived from the R_2Si unit eliminated is detected so far even in the presence of 2,3-dimethyl-1,3-butadiene, which is an efficient trapping reagent for silylene.

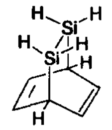
To obtain further insight into the rearrangement mechanism, **38b** is photolyzed in the presence of molecular oxygen, which has been reported to trap various radical cations efficiently.[6a,b,52–54] DCA-sensitized photolysis of **38b** under bubbling oxygen affords an oxygen-adduct **45b** (23%) accompanied by decrease of yields of **40b** and **41b** (16% and 19%, respectively) (Eq. 18). With careful analysis of spectral data, the structure of the oxygen-adduct is assigned to be **45b** instead of highly reactive endoperoxide **47**, since it is thermally stable and is not reduced by Ph_3P. In fact, **40** and **41** are inert under the oxygenation conditions. So the intermediate **44** would be trapped by $O_2^{-\bullet}$ to give **47** which is likely to undergo isomerization via the O–O bond cleavage. It should be noted that, as another route, **47** could be formed by O_2 addition to **44b** followed by reduction (Scheme 6). To our knowledge, the isomerization described here represent the first example of a photosensitized skeletal rearrangement of organosilicon compounds under ET conditions. From the considerations of radical cations such as **43**, the key intermediate in the photo-induced ET reaction, the results from the sensitized irradiation suggest that intramolecular ET from the bridge Si–C bond to the π-system may constitute a key step in the direct photolysis.[55]



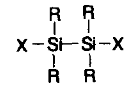
(18)



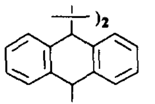
48



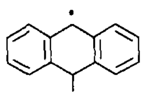
48a



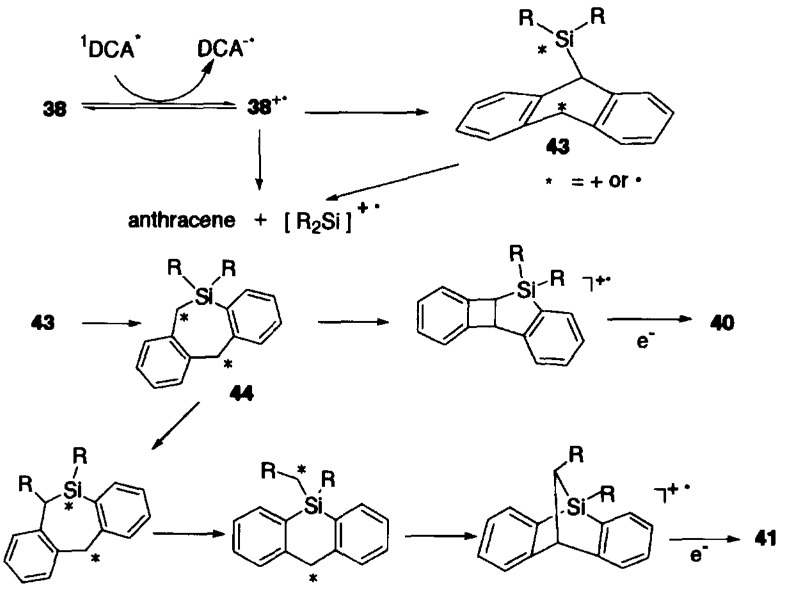
49: R = Me, X = OMe
50: R = *i*-Pr, X = OMe
52: R = Me, X = F
53: R = *i*-Pr, X = F



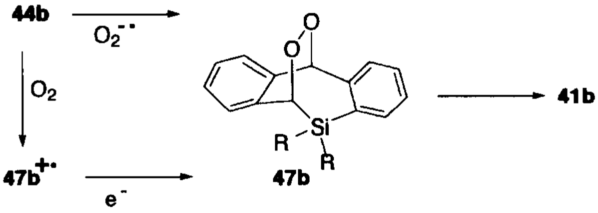
i-Pr_2SiSi*i*-Pr_2OMe
51



i-Pr_2SiSi*i*-Pr_2OMe
56



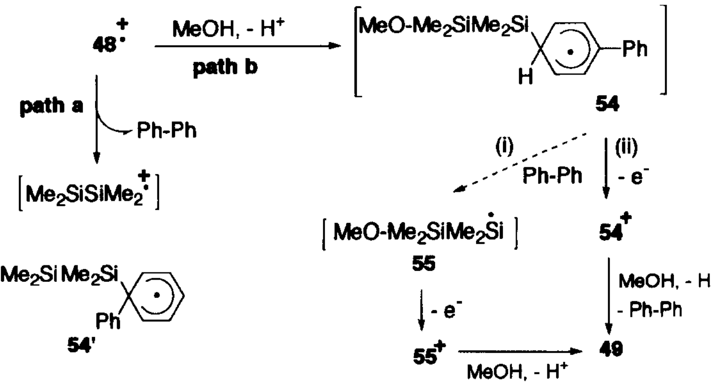
Scheme 5. Mechanism for the skeletal rearrangement via electron transfer.



Scheme 6. Photo-oxygenation of **38b** in the presence of the sensitizer.

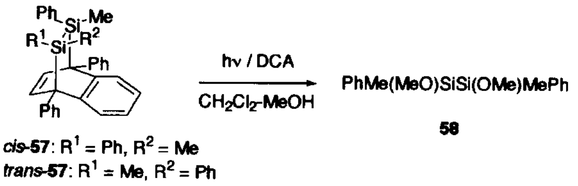
The well-known disilene precursor 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene **48** has been revealed to have remarkable electron donor properties which are readily ascribable to efficient σ–π conjugation between the Si–C σ-bonds and the C–C π-bonds.[47a,48] Thus, irradiation of a solution of **48** and DCA in a mixed solvent of CH_2Cl_2 and CH_3OH (4/1) with W lamps leads to formation of 1,2-dimethoxydisilane **49** and biphenyl. The photolysis of compounds **39a** and **39b** under similar conditions also gives the corresponding dimethoxydisilanes **49** and **50**, respectively, together with anthracene. Interestingly, in the case of **39b**, a dimer **51** is also formed along with **50**. Photolysis of **51** also affords **50** and anthracene under similar conditions. On the other hand, when **48**, **39a**, and **39b** are irradiated with $TPP^+BF_4^-$ as a sensitizer,[56] difluorodisilanes **52** and **53** are obtained together with the corresponding arenes, but no dimeric product is detected in these cases. Similarly, the photo-induced fluorinative cleavage does not proceed without light, and is inhibited by addition of DABCO. Furthermore, the ΔG values estimated by the Rehm–Weller equation[18] are indicative of exothermic ET from **48**, **39a** and **39b** to the excited singlet state of $TPP^+BF_4^-$, and the fluorescence of the pyrilium salt is efficiently quenched with them. Thus, the fluorinative cycloreversion should proceed also through the corresponding radical cations $\mathbf{48}^{+\bullet}$, $\mathbf{39a}^{+\bullet}$ and $\mathbf{39b}^{+\bullet}$ formed by the initial ET to the excited singlet state of the sensitizer, $TPP^+BF_4^-$. As expected, the fluorinative cleavage takes place also on irradiation in the presence of $Bu_4N^+BF_4^-$ using DCA as a sensitizer.[46,57]

$\mathbf{48}^{+\bullet}$ would be expected to undergo facile cycloreversion to afford initially the disilene radical cation $[Me_2SiSiMe_2]^{+\bullet}$ (path a in Scheme 7), but this is not likely because this radical cation would not afford **49** but rather $MeOMe_2SiSiMe_2H$ in the presence of CH_3OH.[58] On the basis of well-recognized nucleophilic assistance to the cleavage of Si–Si and Si–C σ bonds of organosilicon radical cations,[8] $\mathbf{48}^{+\bullet}$ is regarded to undergo facile C–Si bond cleavage by addition of the nucleophile CH_3OH to afford cyclohexadienyl radical **54** (path b), which may be formed as a protonated form at first. The participation of another type of cyclohexadieneyl radical **54′** is less likely from the consideration of the optimized structure of radical cation $\mathbf{48a}^{+\bullet}$ illustrated in Fig. 4 (below). Unlike the case of **39b**, dimerization of **54** is highly improbable due to the steric hindrance around the radical center. So the two possible pathways remain to be considered for the formation of **49** from **54**: (i) with elimination of biphenyl, **54** collapses to a silyl radical **55**, which is readily oxidized[26] and trapped by CH_3OH to give **49**. (ii) After one-electron oxidation of **54**, the ipso-C–Si bond becomes more susceptible to nucleophilic attack and this leads to formation of **49**. To obtain stereochemical information on the Si–C bond cleavage of **54** and to differentiate these two possible routes (i) and (ii), DCA-sensitized irradiation of *cis*-**57** and *trans*-**57**[59] has been carried out and this affords two diastereomers of *meso*- and *dl*-**58**, stereospecifically (Eq. 19). 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. Considering the fact that C–C bond fission of arylcyclopropane radical cation with a nucleophile proceeds with inversion of configuration, the inversion-inversion process will be most probable also in the case of **57**.[60] 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 also in view of the nonstereospecific addition of a neutral disilene with



Scheme 7. Plausible reaction pathway for photo-induced methanolysis of **48**.

alcohol.[61]



(19)

Laser flash photolyses of **48** and DCA have been carried out in a mixed solvent of CH_3CN and CH_2Cl_2 to observe the ET process. Nd : YAG laser third harmonic pulse (354 nm, pulse width 5 ns) is used as an exciting light source. An intense transient absorption band has been observed at 330 nm along with that of DCA radical anion (450—500 nm) (decay time of 10 μs after laser excitation) as shown in Fig. 1. This transient absorption band at 330 nm is not observed in the absence of CH_3CN, but it develops more intensely as the concentration of CH_3CN increases. Neither disilene $Me_2Si{=}SiMe_2$ nor $\mathbf{48}^{+\bullet}$ could be assigned to the absorption band, which is not quenched by addition of alcohol as a common trapping reagent for disilene and organosilane radical cation. It is suggested that the transient might be some species having a radical nature, since it is quenched by introducing gaseous oxygen into the sample solution. A similar absorption band is observed when MeOH is used instead of CH_3CN. If one considers facile Si–C bond cleavage of organosilane radical cation by MeOH and CH_3CN, the transient absorption at 330 nm is reasonably assigned due to that of **54**.

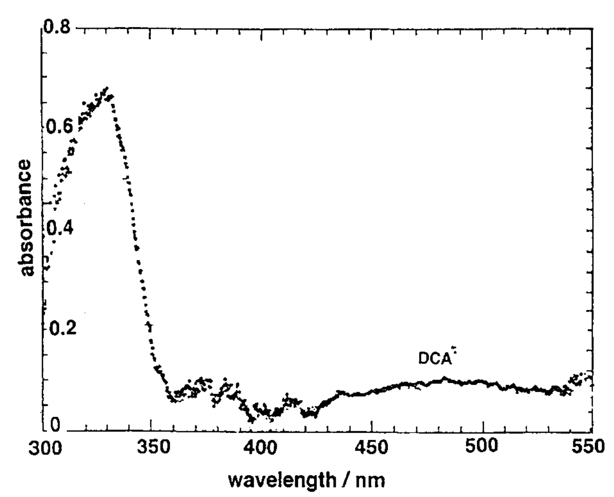
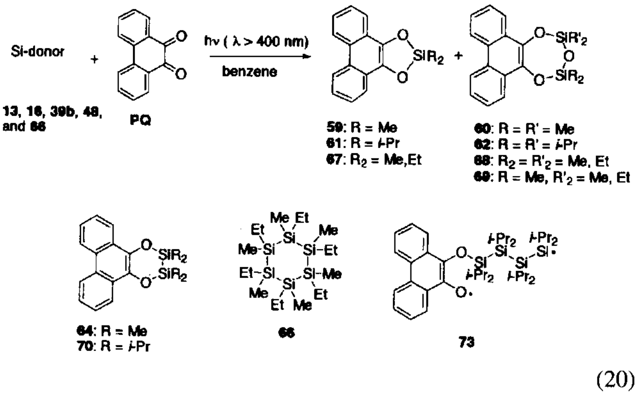


Fig. 1. Transient absorption spectrum of **48** with DCA in CH_3CN/CH_2Cl_2 (4 : 1) at room temperature.

4. Photo-Induced Silylene-Transfer Reaction of Cyclic Organosilanes

For ET reactions of heavier group 14 organometallic compounds, electron-deficient carbonyl compounds, especially *p*-benzoquinones, are frequently used as electron acceptors.[16,62,63] The irradiation of some disilane and digermane derivatives with *p*-benzoquinones induces ET to produce O-silylated and O-germylated *p*-hydroquinones.[16,62] On the other hand, the photolysis of α-diketones with alkyl and allylic stannanes affords exclusively the alkylated and allylated α-ketols without any stannylated products.[63] Furthermore, *o*-benzoquinones, such as phenanthraquinone (PQ) serve as good silylene traps due to their *s-cis*-α-diketone structures.[64] In addition, with cyclic organosilanes PQ has been found to undergo novel silylene-transfer reactions induced by way of its photo-excited triplet.[64] Namely, irradiation of a mixed solution of CH_3CN and CH_2Cl_2 (4/1) of cyclohexasilane **13** and PQ with W lamps (passing through an aqueous $NaNO_2$ filter, cutoff < 400 nm) affords dioxasilolene **59**, as a silylene-transfer product, along with a minor amount of trioxasilepin **60** (Eq. 20). In the case of photolysis of cyclotetrasilane **16**, 1,3,2-dioxasilolene **61** was produced (Eq. 20), whereas the corresponding 1,3,5,2,4-trioxadisilepin **62** is not formed at all, as summarized in Table 5.



(20)

Although on ultraviolet irradiation **13** is well known to evolve free dimethylsilylene, which can be trapped readily by α-diketones to afford the corresponding dioxasilolene

Table 5. Photolysis of **13**, **16**, **39b**, and **48** in the Presence of PQ

Substrate	Reaction condition[a]	Time/h	Conv./%	Product and Yield (%)
13	hν/PQ/CH_3CN/CH_2Cl_2	4.5	61	**59** (138), **50** (33)
13	hν/PQ/C_6H_6	10.5	49	**59** (161), **60** (31)
16	hν/PQ/CH_2Cl_2	0.5	70	**61** (82)
16	hν/PQ/C_6H_6	1.5	70	**61** (57)
39b	hν/PQ/CH_3CN	3.0	100	**61** (85), anthracene (97)
39b	hν/PQ/C_6H_6	18.0	70	**61** (69), anthracene (100)
48	hν/PQ/CH_3CN/CH_2Cl_2	0.5	89	**59** (28), **60** (11), biphenyl (100)
48	hν/PQ/C_6H_6	1.5	65	**59** (62), **60** (13), biphenyl (94)

a) On irradiation with a tungsten-halogen lamp.

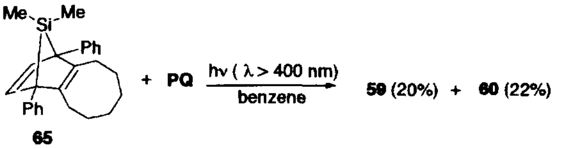
derivatives,[64] **13** is entirely inert to the visible light employed. Furthermore, the photochemical reaction above is not likely to involve free dimethylsilylene because the co-photolysis of **13** and PQ in the presence of Et_3SiH, a common silylene trapping reagent, does not give any expected Et_3SiMe_2SiH at all.[64]

On the other hand, since the silylene-transfer is efficiently quenched by addition of anthracene, the triplet PQ is suggested to be a key intermediate as judged by the comparison of singlet and triplet energies of PQ (E_S = ca. 54, E_T = ca. 48 kcal mol^{-1})[66] and those of anthracene (E_S = ca. 76, E_T = ca. 43 kcal mol^{-1}).[67] Meanwhile, the consumption of **13** is suppressed by addition of DABCO, which has a lower oxidation potential ($E_{OX} = +0.70$ V vs. SCE) than that of **13** ($E_{OX} = +1.45$ V vs. SCE in CH_3CN). For ET from cyclosilanes to PQ triplet, ΔG values estimated are given in Table 6.[18] These data suggest that the silylene-transfer may proceed via a partial or complete ET from the cyclosilanes to photo-excited PQ at least in a polar solvent, such as CH_3CN. In fact, the silylene-transfer reaction proceeds substantially faster in CH_3CN than in benzene, as shown in Table 5.

Since photo-excited ketones are capable of cleaving a Si–Si bond of polysilanes via S_H2 type radical displacement at the silicon atoms,[68] the photochemically excited PQ attacks one of the silicon atoms of **13** to afford a biradical intermediate **63** (Scheme 8). Prior to the formation of **63**, a partial or complete ET from **13** to the triplet PQ may take place in polar solvents. Subsequently, intramolecular O–Si bond formation in **63** would provide **59** as illustrated in Scheme 8. The yields of **59** indicate that a molecule of **59** donates more than one silylene unit to PQ. In addition, the photolysis of **13** and PQ in the presence of CCl_4 affords $Cl(SiMe_2)_nCl$ (n = 4—6), which substantiates that the mechanism involves the silyl radical intermediates such as **63**.[2a,b]

Table 6. The Free Energy Changes (ΔG) for the Electron-Transfer from Cyclosilanes to PQ

Substrate	E_{OX}/V vs. SCE	ΔG/kcal mol^{-1}	
		in CH_3CN	in C_6H_6
13	+1.45	−1.4	+17.8
16	+1.00	−11.8	+7.5
39b	+1.17	−7.9	+11.4
48	+0.42	−25.2	−6.0



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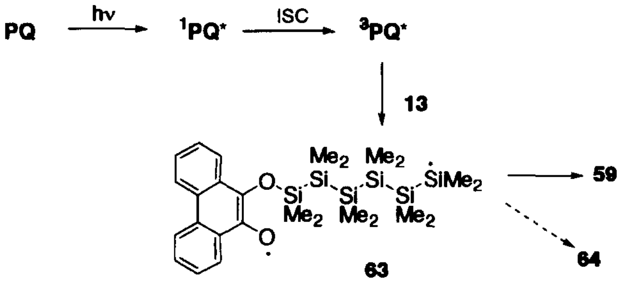
(21)

Intramolecular cyclization in **63** could afford **64** also, which would be susceptible to atmospheric oxidation to give **60**. However, intermediate **64** has not been detected in the photolysates. Furthermore, either free dimethylsilylene or dimethylsilanone[58] can be a candidate for the key intermediate, which could undergo insertion reaction into **59** to afford **64** or **60**, respectively, although no trapping experiments for these species have given any expected trapped product so far. The residual molecular oxygen in the reaction mixture would be responsible for the formation of **60**. In fact, when the photolysis is carried out after saturation of molecular oxygen, the yield of **60** increases while that of **59** decreases somewhat. Since **59** is stable in the air, molecular oxygen should be incorporated probably by way of some radical species containing oxygen, to afford **60** during the photoreaction. Meanwhile, photolysis of 7-silanorbornadiene **65**[69] with PQ gives **59** and **60** under similar reaction conditions (Eq. 21). This result indicates that the silylene-transfer proceeds stepwise to produce **60**, possibly by way of **59**, but this does not necessarily exclude the participation of **64** in formation of **60**. In accord with this, the photoreaction with **16** having more bulky isopropyl instead of methyl groups affords only **61**, as mentioned. Finally, the cross-experiment with PQ employing **13** and **66** has been carried out, and this gives all possible five products, **59**, **67**, **60**, **68**, and **69** in the ratio of ca. 1 : 2 : 1 : 1 : 2, respectively.

As mentioned above, disilene precursor 7,8-disilabicyclo[2.2.2]octa-2,5-diene **48** acts also as a good electron donor.[47a,70] Therefore, selective disilene not silylene transfer to PQ is the expected formally to take place when **48** and **39b** are employed as electron donors. However, photolysis of **48** in the presence of PQ affords silylene addition product **59** together with **60**, but expected **64** has not been detected in the photolysate. Similarly, under the same conditions **39b** is photolyzed to yield only **61** and, as the case of **48**, **70** has not been detected in the reaction mixture.

Interestingly, in contrast to the case of cyclic oligosilane **13**, the intermediacy of free dimethylsilylene is evidenced by formation of Et_3SiMe_2SiH in the co-photolysis of **48** with PQ in the presence of Et_3SiH. Based on the mechanism



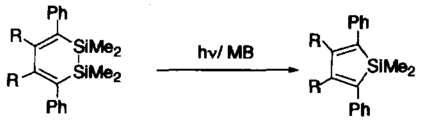
Scheme 8. Plausible reaction pathway for silylene-transfer reaction of cyclic silane **13**.

proposed for **13**, the reaction of **48** is interpreted as shown in Scheme 9. The initially formed adduct **71** would be cleaved in the two ways, firstly the oxy-radical attacks the silicon atom as shown by the arrow a, and this gives **59** and diradical **72**, which readily evolves dimethylsilylene with concomitant elimination of biphenyl. The silylene undergoes insertion to PQ to give **59**, and at the same time this may insert into **59** to afford **60**, followed by oxidation. Secondly, as shown by the arrow b the radical may be able to attack another silicon atom to afford **64**, of which the Si–Si bond is readily oxidized to give **60**. In contrast, no concrete evidence for free di-isopropylsilylene has been obtained in the co-photolysis of **39b** and PQ in the presence of Et_3SiH. Absence of **62** and probably free diisopropylsilylene also in the photoreactions of **16** and **39b** with PQ may be due to steric restriction caused by isopropyl groups, both on the cyclization of the expected intermediates such as **73** and on the insertion of diisopropylsilylene unit to **61**.

The photo-induced ET from organosilanes, **13**, **16**, **48**, and **39b** to $^3PQ^*$ should take place at least in polar solvent, as suggested from ΔG values in Table 6. Coupling of the radical ion pair thus formed results in formation of a biradical intermediate such as **73** and finally this affords **61** for example, in the case of **16** (see Scheme 8). On the other hand, ET does not seem to operate efficiently in benzene, a less polar solvent judging from the ΔG values shown in Table 6.

5. Electron-Transfer Reaction of 1,2-Disila-3,5-cyclohexadiene

1,2-Disila-3,5-cyclohexadiene **74** is an attractive compound in relation to the well-studied silacyclopentadiene (silole **75**), one of the most fundamental silacycles.[71] So far, **74** has been already reported to show unique reactivities, such as photochemical rearrangement and ring contraction with a transition metal complex.[72] However, the potential donor properties of **74** in ET reactions have been hitherto overlooked, while silole **75** has been revealed to act as good electron donors.[2e,2f,2g] Recently, under photo-induced ET conditions **74** has been reported to undergo novel ET induced ring contraction reactions.[73] 1,2-Disila-3,5-cyclohexadienes **74a** and **74b** have fairly low oxidation potentials (**74a**: E_{ox} = +0.81 V vs. SCE, **74b**: E_{ox} = +1.03 V vs. SCE in CH_3CN), which are lower than those of siloles (**75a**: E_{ox} = +1.31 V vs. SCE, **75b**: E_{ox} = +1.24 V vs. SCE in CH_3CN). Since **74a** and **74b** have intense absorption bands up to the visible region, Methylene Blue (MB)[74] has been chosen as a sensitizer for selective excitation. Irradiation of a CH_2Cl_2 solution of **74a** in the presence of MB with W lamps (passing through a Toshiba Y-47 glass filter) affords silole **75a** in 79% yield (Eq. 22 and Table 7). The reaction does not occur without MB or under dark conditions, and is suppressed by addition of DABCO as an electron donor. According to the Rehm–Weller equation,[18] ΔG values of ET process from **74** to $^1MB^*$ and $^3MB^*$ are calculated to be −19.4 and −11.0 for **74a**, and −14.3 and −5.9 kcal mol^{-1} for **74b**, respectively. These negative ΔG values indicate that exothermic ET from **74a** and **74b** to the excited states of MB should be expected. Treatment of **74a** with $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$,[54] a well-known oxidizing reagent, under dark conditions also produced **75a** in 47% yield, such a result supports ET mechanism. Considering the singlet and the triplet energies of MB (E_S = 42.8 kcal mol^{-1}, E_T = 43.4 kcal mol^{-1}),[75] tetracene (E_S = 60.7 kcal mol^{-1}, E_T = 29.3 kcal mol^{-1})[60] could act as a quencher of $^3MB^*$. Actually, the reaction is not suppressed by addition of tetracene. Therefore, the ring contraction of **74** would proceed though $^1MB^*$ sensitization.



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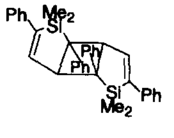
74a: R = Ph
74b: R = H

75a: R = Ph
75b: R = H



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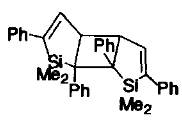

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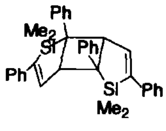

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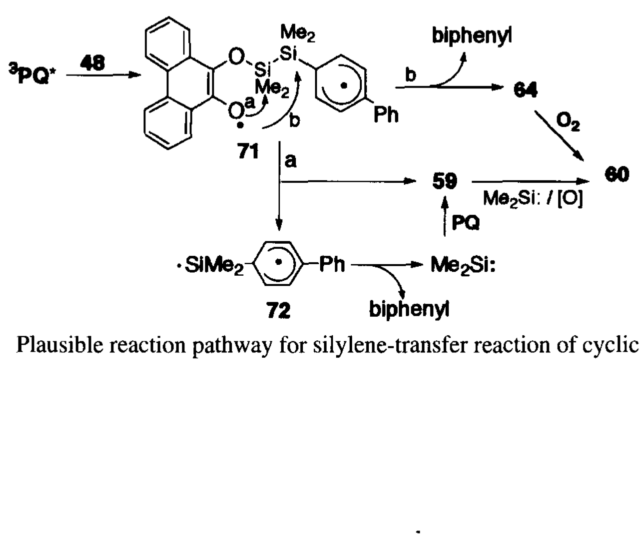
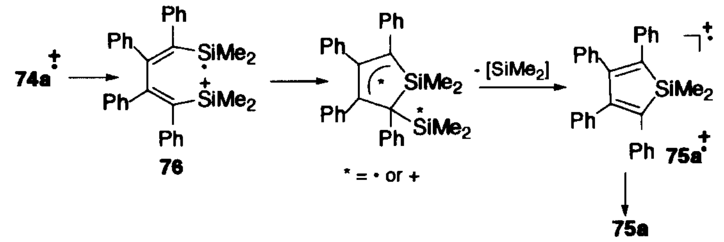
From these results, we propose a possible mechanism for the ring contraction of **74a** as depicted in Scheme 10. Initially, **74a** is readily oxidized by $^1MB^*$ to give radical cation **74a**$^{+\bullet}$, in which the Si–Si bond is cleaved to give an open intermediate **76**. Then, subsequent intramolecular addition of one of the silyl groups to the diene moiety, followed by elimination of a dimethylsilylene unit, and back-ET gives rise to **75a**, although at this moment none of the eliminated dimethylslylene part can be trapped even in the presence of common silylene trapping reagents such as 2,3-dimethyl-1,



Scheme 9. Plausible reaction pathway for silylene-transfer reaction of cyclic silane **48**.

Table 7. Ring Contraction of 1,2-Disilacyclo-3,5-diene **74**

Substrate	Reaction condition	Product and Yield (%)
74a	hν/MB/CH_3CN/CH_3OH	**75a** (79)
74a	hν/MB/CH_2Cl_2/CH_3OH	**75a** (79)
74a	hν/MB/CH_3CN/$Bu_4N^+BF_4^-$	**75a** (59)
74a	(p-$BrC_6H_4)_3N^+SbCl_6^-$/CH_2Cl_2	**75a** (47)
74a	(p-$BrC_6H_4)_3N^+SbCl_6^-$/$Bu_4N^+BF_4^-$/CH_2Cl_2	**75a** (57)
74b	hν/MB/CH_3CN/$CH_3OHC_6H_6$	**75a** (13), **77**—**79** (7)
74b	hν/MB/$Bu_4N^+BF_4^-$/CH_3CN	**75b** (6), **77**—**79** (5)
74b	(p-$BrC_6H_4)_3N^+SbCl_6^-$/CH_2Cl_2	**75b** (72)



Scheme 10. Plausible reaction pathway for ring contraction of **74**.

3-butadiene and Et_3SiH. These results invoke the formation of **2** in the photoexcitation of the CT complex between **1** and TCNE, where radical cation $\mathbf{1}^{+\bullet}$ has been suggested as the key intermediate (see, Eq. 1).[2a]

It is noteworthy that addition of CH_3OH as a part of the solvent improves the yield of **75a** as shown in Table 7. Since it has been well documented that alcohols assist cleavage of Si–Si σ radical cations in many ET reactions,[8] the solvent effect for formation of **75a** suggests similar participation of CH_3OH in the bond cleavage stage involved in Scheme 10. 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.[3]

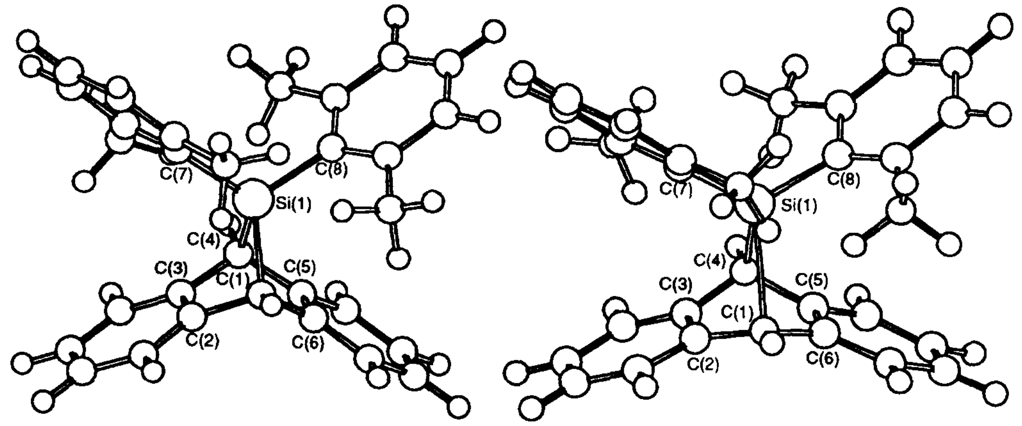
Under photosensitized conditions, the yields of **75b** are lower than those of **75a** because the product **75b** is also photolabile to give a small amount of the dimers **77**—**79**.[76] By examining the effects of DABCO and tetracene as additives, we conclude that an ET mechanism might operate also in the reaction of **75b**.

6. Structural Characteristics of Some Cyclic Silyl Radical Cations

In recent times, the chemistry of a free silyl cation (silylium ion) has been argued about intensively from experimental and theoretical points of views.[77] Since silicon is more positive than carbon, the silyl cation should be more thermodynamically stable than its carbon analogue. However, the trivalent silyl cation is readily formed in the vapor phase, such as in an ion chamber of a mass spectrometer,[3,78] this is not true in condensed phase. In fact, the silyl cation is extremely sensitive toward Lewis bases and is coordinated even with toluene and a carbon-carbon double bond.[79] After many attempts to isolate the free silyl cation in condensed phases, finally $[(\mathrm{mesity})_3Si]^+[B(C_6F_5)_4]^-$ has been prepared and its spectroscopic data are reasonably interpreted as showing no interaction with an aromatic solvent.[80] On the other hand, since silyl radical cations should have both radical and cationic characters, a silyl radical cation is thought to be more reactive than the corresponding silyl cation. In fact, a silyl radical cation is seldom trapped intermolecularly by an alcohol without sterically crowded substituents on the cationic silicon center.[2b,8a,8b,8e,19a] Hence, only a limited number of structural studies on the silicon centered radical cation have been reported so far.[81,82] We have examined some structural characteristics of newly generated silyl radical cations, $\mathbf{38a}^{+\bullet}$, $\mathbf{48}^{+\bullet}$, and $\mathbf{74a}^{+\bullet}$ primarily by simple MO calculations.

In addition to efficient fluorescence quenching of the sensitizer and exothermic ET from the σ-donor to the excited singlet state of the sensitizer, the radical cationic nature of the key intermediate is evidenced by chemical trapping experiments, as shown in Eqs. 6 and 8. Now, to reveal structural characteristics of so far elusive key intermediate silyl radical cations, an investigation by combination of X-ray crystallographic analysis and MOPAC calculation has been done.

The optimized structures of **38a** and radical cation $\mathbf{38a}^{+\bullet}$ are obtained by the MOPAC PM3 method,[49] these structures are shown in Fig. 2 with selected geometrical parameters. To verify relevance of the calculation, the structure of **38a** in crystals has been determined by X-ray crystallographic analysis, and the selected bond lengths and angles obtained are shown also in the bottom of Fig. 2.[57] The bond lengths and angles are fairly close to those reported for related silanorbornadiene derivatives.[83] The bridge Si–C bonds are slightly longer than normal Si–C bonds.[84] Similar bond elongation in silanorbornadiene skeleton has been reported and explained in terms of σ–π conjugation of the bridge Si–C σ-bond with the π system of anthracene moiety.[82b] Adiabatic ionization energies (IE) of **38a** and **38b** are also estimated to be 7.42 and 7.36 eV, respectively, by calculating the gap of heats of formation between the neutral and the radical cation. As shown in Table 8, these values are reasonable since the IE values calculated for Me_3SiCH_2-substituted benzenes as related compounds show good consistency with those measured by photoelectron spectroscopy.[85] The calculated HOMO draw-



	X-ray data[a]	Calculated data[b]			X-ray data[a]	Calculated data[b]	
	38a	**38a**	**38a**$^{+\bullet}$		**38a**	**38a**	**38a**$^{+\bullet}$
Si(1)–C(1)	1.94	2.02	2.60	C(4)–Si(1)–C(8)	110.5	114.13	114.92
Si(1)–C(4)	1.93	2.03	1.98	C(7)–Si(1)–C(8)	113.0	111.72	117.58
Si(1)–C(7)	1.91	1.88	1.82	Si(1)–C(1)–C(6)	97.8	95.64	82.08
Si(1)–C(8)	1.87	1.88	1.84	Si(1)–C(1)–C(2)	97.0	95.64	83.15
C(1)–Si(1)–C(4)	80.4	78.38	70.75	Si(1)–C(4)–C(5)	96.4	96.49	97.05
C(4)–Si(1)–C(7)	119.2	117.88	123.27	Si(1)–C(4)–C(3)	97.1	96.24	99.12

a) The standard deviations are omitted for the simplicity.[57] b) Calculated by MOPAC PM3.[49]

Fig. 2. Optimized structures of **38a** (left) and its radical cation **38a**$^{+\bullet}$ (right), and selected bond distances (Å) and angles (°).

Table 8. Ionization Energies (IE) of **38a**, **38b**, and Some Benzylic Silanes

Silane	IE/eV[a]
$Me_3SiCH_2C_6H_5$	8.06 (8.35)
1,2-$(Me_3SiCH_2)_2C_6H_4$	7.71 (8.05)
1,4-$(Me_3SiCH_2)_2C_6H_4$	7.63 (7.75)
38a	7.42
38b	7.36

a) Experimental values are in parentheses.[85]

ing of **38a** is illustrated in Fig. 3. The HOMO has surely delocalized both the aromatic π systems and the benzylic C–Si bonds.

Some distinct structural features of **38a**$^{+\bullet}$ can be drawn from the careful examination of data in Fig. 2. Firstly, one of the bridge Si–C bond (Si(1)–C(1), 2.60 Å) is much longer compared to the other (Si(1)–C(4), 1.98 Å) and to those of neutral species **38a** (Si(1)–C(1), 2.02 Å; Si(1)–C(4), 2.03 Å). On ET, Si(1)–C(1) bond is revealed to be elongated by around 30%, but in contrast the other Si(1)–C(4) bond shows a little shrinkage in its bond length. This means that the radical cationic nature generated may be localized on a particular bond: in this case, Si(1)–C(1). Secondly, the marked flattening of the configuration of Si(1) is observed on the formation of **38a**$^{+\bullet}$ from **38a** (sum of angles, C(7)–Si(1)–C(8), C(4)–Si(1)–C(7), and C(4)–Si(1)–C(8) being 343.7° in **38a**, and 355.8° in **38a**$^{+\bullet}$). So, cleavage of the longer Si(1)–C(1) bond by the nucleophile is expected to occur readily from the back side of C(1)–Si(1) and not from that of C(4)–Si(1) bond, and this leads to the inversion of the configuration of the silicon center (see, Eq. 19). Some electronic properties of the optimized radical cation are summarized in Table 9. A significant population of the positive charge is observed at the Si(1) atom, whereas the spin population is more predominant at the anthracene unit than at the silicon atom and the 2,6-dimethylphenyl group, as shown. This means that Si(1)–C(1) bond of **38a**$^{+\bullet}$ is cleaved in the direction to give a cationic silicon and a radical carbon sites. Similar structural and electronic aspects have been reported for radical cation [*t*-Bu_3SiH]$^{+\bullet}$ calculated from the MOPAC AM1 method.[49,82] In addition to the HOMO of **38a**, the findings described above indicate that one electron is removed from one of the bridge C–Si bonds, which would be weakened subsequently

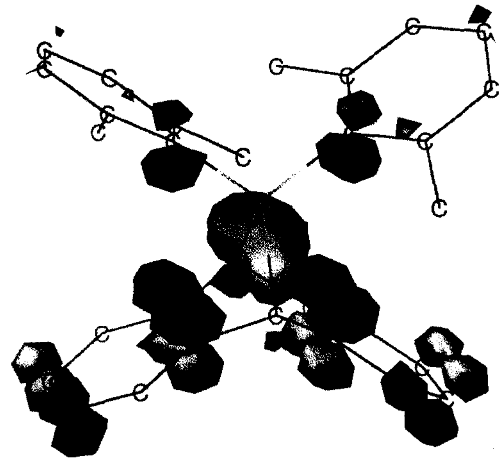


Fig. 3. HOMO orbital for **38a** calculated at the MOPAC PM3 level.

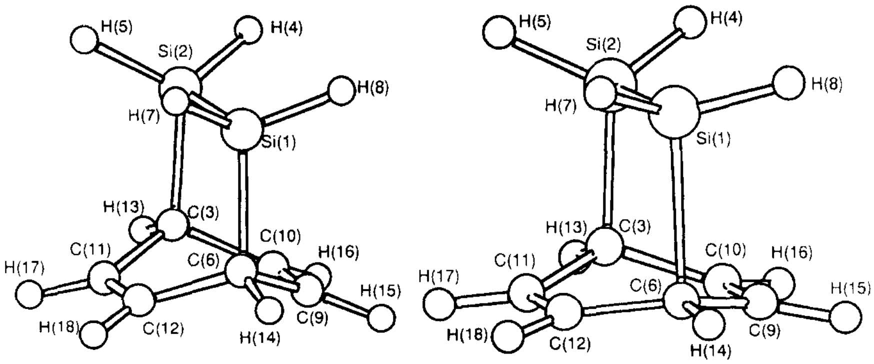
Table 9. Charge and Spin Density of Radical Cation **38a**$^{+\bullet}$

Atom or fragment	Charge	(ΔCharge)[a]	Spin density
Si(1)	+0.91	(+0.44)	+0.20
C(1)	−0.07	(−0.01)	−0.15
C(2)	−0.06	(−0.00)	+0.47
C(3)	−0.07	(−0.02)	−0.42
C(4)	−0.06	(+0.03)	+0.63
C(5)	−0.07	(−0.02)	−0.43
C(6)	−0.06	(+0.00)	+0.50
C(7)	−0.26	(−0.06)	−0.16
C(8)	−0.26	(−0.07)	−0.11
Fragment			
Si atom	+0.90	(+0.44)	+0.20
2,6-$(CH_3)_2(C_6H_3)$	−0.13	(+0.18)	+0.02
anthracene	+0.23	(+0.38)	+0.78

a) Change of the charge from neutral **38a** to cation radical **38a**$^{+\bullet}$.

to form the relaxed form of **38a**$^{+\bullet}$, as depicted in Fig. 2. The presence of nucleophiles such as alcohol and fluoride ion should accelerate the cleavage of the Si–C bond.

On DCA sensitized irradiation in CH_2Cl_2–MeOH, 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**48**) is readily photolyzed to give 1,2-dimethoxy-1,1,2,2-tetramethyldisilane along with biphenyl as mentioned (Scheme 7).[66,70] The structure of silyl radical cation **48**$^{+\bullet}$ intervened has been primarily examined by the MOPAC PM3. In addition, optimized structures of its parent compound, 7,8-disilabicyclo[2.2.2]octa-2,5-diene (**48a**) and its radical cation **48a**$^{+\bullet}$ have been also calculated by *ab initio* MO RHF/6-31G* and UHF/6-31G*, respectively. Thus, the geometrical (bond distances and angles) and electronic (charge density and spin density) data obtained by both methods are summarized in Fig. 4 and Tables 10, 11, and 12. From examination of these data, some structural and electronic features of the silyl radical cations **48a**$^{+\bullet}$ and **48**$^{+\bullet}$ have been revealed. First of all, unexpectedly on ET the Si–Si bond distances of **48a** and **48** change in only negligible amounts, but one of the Si–C (bridge head) bonds show appreciable bond elongation (Si(1)–C(6) 1.932 Å in **48a** and 2.230 Å in **48a**$^{+\bullet}$; Si(2)–C(13) 1.980 Å in **48** and 2.307 Å in **48**$^{+\bullet}$) as the case of **38a**. This may be ascribable to the nature of HOMO, which is composed of σ-orbitals of the Si–C (bridgehead) bonds and π-orbitals of the C–C double bonds, as depicted in Fig. 5. So, one electron should be removed from either the σ-Si–C or the π-carbon double bonds. The MO calculations show that the Si–Si σ-orbitals of **48a** and **48** contribute principally to the MO, which is located below the next HOMO. Secondly, along with elongation of Si(1)–C(6) in **48a** and Si(2)–C(13) bond in **48**, the marked flatterings of the configurations of Si(1) and C(6) in **48a**$^{+\bullet}$ and those of Si(2) and C(13) in **48**$^{+\bullet}$ are worthy of remark among structural changes on ET (sum of angles, Si(2)–Si(1)–H(8), Si(2)–Si(1)–H(7), and H(7)–Si(1)–H(8) being 351.3°, C(9)–C(6)–C(12), C(12)–C(6)–H(14), and C(9)–C(6)–H(14) being 354.7° in **48a**$^{+\bullet}$; C(5)–Si(2)–C(6), C(5)–Si(2)–Si(1), and C(6)–Si(2)–Si(1) being 349.6°, and C(8)–C(13)–C(12), C(8)–C(13)–C(20), and C(12)–C(13)–C(20) being 356.6° in **48**$^{+\bullet}$). Thus, preliminary MO calculations so far have indicated that on ET the geometry around only one of the two silicon atoms, namely



	48a	**48a**$^{+\bullet}$		**48a**	**48a**$^{+\bullet}$
Si(1)–Si(2)	2.35	2.37	H(7)–Si(1)–H(8)	107.9	111.2
Si(1)–C(6)	1.93	2.23	H(4)–Si(2)–H(5)	107.9	112.7
Si(2)–C(3)	1.93	1.97	Si(1)–Si(2)–H(5)	114.7	111.9
C(3)–C(10)	1.52	1.49	Si(1)–Si(2)–H(4)	114.7	111.9
C(6)–C(9)	1.52	1.44	C(10)–C(3)–C(11)	109.3	113.2
C(9)–C(10)	1.32	1.37	C(10)–C(3)–H(13)	111.7	113.3
Si(2)–Si(1)–C(6)	96.3	95.9	C(11)–C(3)–H(13)	111.7	113.3
Si(1)–Si(2)–C(3)	96.3	95.6	C(9)–C(6)–C(12)	109.3	118.8
Si(2)–Si(1)–H(7)	114.7	120.1	C(9)–C(6)–H(14)	111.7	118.0
Si(2)–Si(1)–H(8)	114.7	120.0	C(12)–C(6)–H(14)	111.7	118.0

Fig. 4. Optimized structures of **48a** (left) and its radical cation **48a**$^{+\bullet}$ (right) at ab initio MO RHF/6-31G* and UHF/6-31G* levels, and selected bond distances (Å) and angles (°).

Table 10. Selected Bond Distances (Å) and Angles (°) of **48**

	48	**$48^{+\bullet}$**		**48**	**$48^{+\bullet}$**
Si(1)–Si(2)	2.46	2.48	Si(1)–C(10)–H(4)	111.60	109.82
Si(1)–C(10)	1.94	1.97	C(3)–Si(1)–C(4)	110.95	113.84
Si(2)–C(13)	1.98	2.30	C(3)–Si(1)–Si(2)	111.66	109.71
C(13)–C(8)	1.49	1.44	C(4)–Si(1)–Si(2)	114.22	112.63
C(8)–C(9)	1.34	1.36	C(5)–Si(2)–C(6)	110.99	113.48
C(13)–C(20)	1.49	1.46	C(5)–Si(2)–Si(1)	108.95	116.59
Si(1)–Si(2)–C(13)	95.68	95.54	C(6)–Si(2)–Si(1)	114.00	119.51
Si(2)–Si(1)–C(10)	94.66	93.45	C(8)–C(13)–C(12)	111.09	116.89
Si(1)–C(10)–C(9)	102.81	101.43	C(8)–C(13)–C(20)	113.34	120.25
Si(1)–C(10)–C(11)	104.30	101.37	C(12)–C(13)–C(20)	112.24	119.43
Si(2)–C(13)–C(8)	101.65	94.13	C(9)–C(10)–C(11)	111.50	114.60
Si(2)–C(13)–C(12)	102.49	89.01	C(11)–C(10)–H(4)	112.98	113.94
Si(2)–C(13)–C(20)	115.10	104.99	C(9)–C(10)–H(4)	112.86	113.97

Table 11. Charge and Spin Density of Radical Cation **$48^{+\bullet}$**

Atom	Charge	(ΔCharge)[a]	Spin density
Si(1)	+0.50	(+0.24)	+0.16
Si(2)	+0.53	(+0.27)	+0.17
C(8)	−0.13	(+0.01)	−0.32
C(9)	−0.05	(−0.08)	+0.49
C(10)	−0.18	(−0.06)	−0.12
C(11)	−0.05	(+0.08)	+0.52
C(12)	−0.12	(+0.01)	−0.31
C(13)	−0.01	(+0.03)	+0.35

a) Change of the charge from the neutral to the cation radical.

Table 12. Selected Charge and Spin Density of Radical Cation **$48a^{+\bullet}$**

Atom	Charge	(ΔCharge)[a]	Spin density
Si(1)	+0.56	(+0.03)	+0.17
Si(2)	+0.59	(+0.06)	+0.11
C(3)	−0.56	(−0.06)	−0.16
C(6)	−0.49	(+0.01)	+0.46
C(9)	−0.14	(+0.03)	−0.46
C(10)	−0.12	(+0.05)	+0.69
C(11)	−0.12	(+0.05)	+0.69
C(12)	−0.14	(+0.03)	−0.46

a) Change of the charge from the neutral to the cation radical.

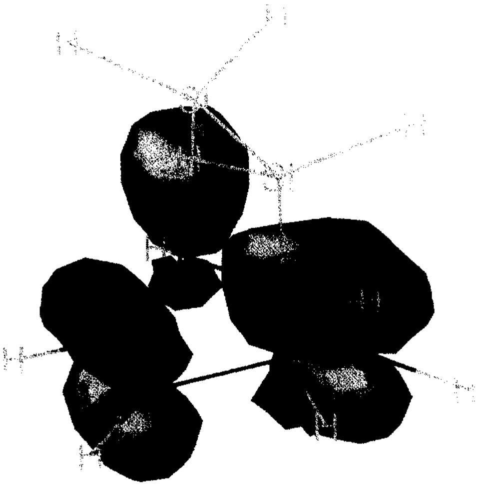
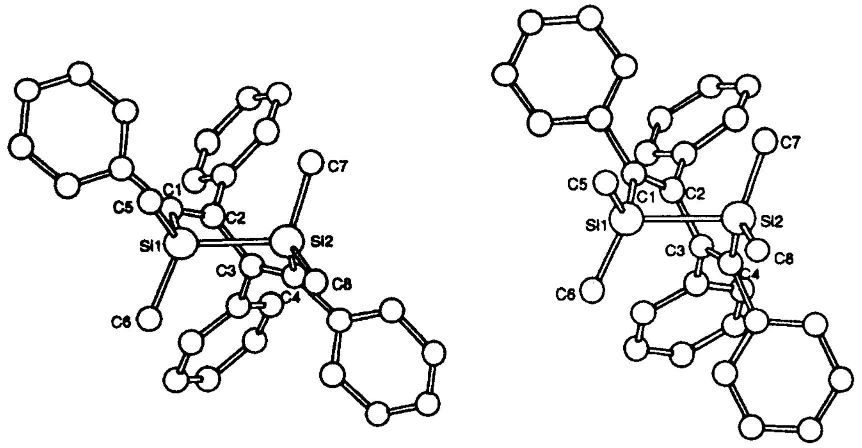


Fig. 5. HOMO orbital for **48a** calculated at the RHF/6-31G* level.

Si(1) in **48a** and Si(2) in **48** changes notably, accompanied by the change of the configuration of the bridged carbon atom bonded to the silicon atom. From consideration of the oxophilicity of silicon atoms, nucleophilic attack may occur on the silicon atom having longer the Si–C bond from the backside, and this leads the inversion of configuration of the silicon atom. This is consistent with the experimental results described (Eq. 19). Furthermore, on the silyl radical cation, the positive charge may be mainly distributed between two silicon atoms, and in contrast, a radical spin may be mainly on the olefinic double bonds of **48** and **48a**.

A semiempirical molecular orbital calculation of **74a** and **$74a^{+\bullet}$** has been performed also by the MOPAC PM3[49] system, and important structural parameters are summarized in the bottom of Fig. 6. Optimization of **74a** leads to a geometry of approximate C_2 symmetry with the C_2 axis bisecting Si(1)–Si(2) and C(2)–C(3) bonds (Fig. 6). Non-planarity of the Si_2C_4 ring may be ascribable to the steric constraint caused by the four phenyl groups since the optimized structure of unsubstituted disilacyclohexadiene is planar. As seen from Fig. 6, the following structure changes from **74a** to **$74a^{+\bullet}$** 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 structural deformation has been reported for $[Me_3SiSiMe_3]^{+\bullet}$ obtained by the PM3 calculation.[81] Meanwhile, HOMO of **74a** is calculated to be a combination of those of the Si–Si σ- and the 1, 3-butadiene π-system, suggesting that these sites are susceptible to the initial one-electron oxidation. This accords with elongation of Si–Si σ-bond on ET. Additional electronic features of the optimized radical cation are also summarized in Table 13, these indicate that the positive charge in 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 on **$74a^{+\bullet}$**, especially with



	74	$74^{+\cdot}$		74	$74^{+\cdot}$
Si(1)–Si(2)	2.45	2.58	Si(2)–Si(1)–C(1)	96.3	83.4
Si(1)–C(1)	1.87	1.81	Si(1)–Si(2)–C(4)	95.0	83.3
Si(2)–C(4)	1.86	1.81	Si(1)–C(1)–C(1)	117.2	121.7
C(1)–C(2)	1.34	1.36	C(1)–C(2)–C(3)	122.7	120.9
C(2)–C(3)	1.49	1.47	C(2)–C(3)–C(4)	124.5	120.9
C(3)–C(4)	1.34	1.36	C(3)–C(4)–Si(2)	117.3	121.7

Fig. 6. Calculated structures of **74a** (left) and its radical cation $\mathbf{74a}^{+\bullet}$ (right) at the MOPAC PM3 level, and selected bond distances (Å) and angles (°).

Table 13. Charge and Spin Density of Radical Cation $\mathbf{74}^{+\bullet}$

Atom	Charge	(ΔCharge)[a)]	Spin Density
Si(1)	+0.60	(+0.31)	+0.28
Si(2)	+0.61	(+0.27)	+0.28
C(1)	−0.21	(−0.00)	+0.07
C(2)	+0.08	(+0.06)	+0.11
C(3)	+0.08	(+0.06)	+0.10
C(4)	−0.21	(−0.13)	−0.01

a) Change of the charge from the neutral to the cation radical.

assistance of nucleophiles.

7. Concluding Remarks

A Si–Si σ-bond undergoes readily chlorinative and fluorinative cleavage under photo-induced ET conditions in the presence of CCl_4 and BF_4^-, and gives the corresponding chloro- and fluoro-silanes in good yields, respectively. Cophotolysis of aromatic nitrile with a disilane and a tetraalkyl group 14 metal effects selective silylation and alkylation of the nucleus at the position where spin density is high on its radical anion. On the other hand, on photo-induced ET, bridged organosilanes, such as 7-silabicyclo[2.2.1]heptadiene **38** and 7, 8-disilabicyclo[2.2.2]octadiene **48** give rise to radical cations $\mathbf{38}^{+\bullet}$ and $\mathbf{48}^{+\bullet}$ with evolution of one electron from one of the bridged Si–C bonds activated by effective σ–π conjugation. The former radical cation shows the skeletal rearrangement that is also observed on direct irradiation. Interestingly, from MO calculations of structures of these radical cations, one of the bridged Si–C bonds is estimated to be elongated more than the other in appreciable amounts and this seems to be the one cleaved by a nucleophile, probably with inversion of the configuration. This geometrical feature of these radical cations may bring about disadvantages in the concerted elimination of silylene and disilene units from **38** and **48**, respectively.

We are indebted to the co-workers whose names are cited in the references. We also gratefully acknowledge financial supports at various times from the Ministry of Education, Science, Sports and Culture.

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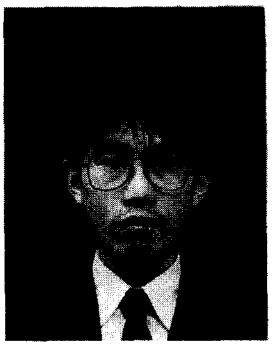

Masahiro Kako gained B. S. (1986) and Ph. D (1991) degrees from the University of Tsukuba. He joined the research group of Prof. Nakadaira of the University of Electro-Communications as a research associate. His research interests lie on organosilicon chemistry, organometallic chemistry, photochemistry and electron-transfer chemistry of organometallic compounds. His current researches include transition-metal complex mediated reactions of organometallic compounds involving group 14 elements.

Yasuhiro Nakadaira, Professor of Department of Applied Physics and Chemistry, the University of Electro-Communications, was born in 1935. He graduated from Tokyo Kyoiku University in 1960, and entered the Graduate School of Tohoku University, to work under the supervision of Professor K. Nakanishi. After receiving a degree of Doctor of Science he worked as a postdoctoral fellow with Professor H. H. Wasserman at Yale University about one year from 1965 to 1966. He became Research Associate at Department of Chemistry, Tohoku University in 1967, and after a few years he started to work with Professor H. Sakurai. He became Associate Professor of Tohoku University in 1972 and moved to the University of Electro-Communications as Professor in 1986. His recent interests are chemistry of organo-silicon and germanium compounds including photochemistry, preparations of novel compounds, reactions with transition metal complexes, and highly reactive species, such as silylene, germylene, and disilene.