

Formation and Cycloreversion of 2-Silacyclobuta[2.3]cyclophanes via Photoinduced Electron Transfer

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Irradiation of an acetonitrile solution containing dimethylbis(4-vinylphenylmethyl)silane **1a** in the presence of 9,10-dicyanoanthracene leads to formation of the intramolecular photocycloadduct, 2-sila-cyclobuta[2.3]cyclophane (**2a**). In contrast, prolonged irradiation gave insoluble polymeric material. The photocycloreversion of **2a** occurs efficiently (quantum yields exceeds unity) by use of redox-type photosensitization in the presence of magnesium perchlorate. The transient absorption spectra generated by pulse radiolysis and gamma-radiolysis show that the radical cation species generated from **1a** is different from that arising from **2a**.

key words: photoinduced electron transfer, photocycloaddition, photocycloreversion, bis(4-vinylphenylmethyl)silane, cyclobutacyclophane, radical cation, pulse radiolysis

INTRODUCTION

Photoinduced electron transfer reactions involving group 14 organometallic compounds have received much attention from mechanistic and synthetic viewpoints [1]. From the synthetic viewpoints, we have developed photoinduced electron transfer photoallylation and photobenzoylation reactions of aromatic nitriles and electron-deficient alkenes with allylic and benzylic substituted group 14 organometallic compounds [2]. Group 14 organometallic compounds act as good electron donors in the photoinduced electron transfer reactions. However, little is known about the photocycloaddition and photocycloreversion of group 14 organometallic compounds because of photolability of carbon-metal bonds [3].

Direct irradiation or triplet sensitization promoted photocyclodimerization reactions of styrene and its derivatives have been thoroughly investigated [4]. Photocyclodimerization processes of aromatic vinyl compounds, such as *N*-vinylcarbazole, phenyl vinyl ether, indene, and *p*-methoxystyrene, occurring via dimer radical cations, also have been reported [4c,5]. In addition, the redox-photosensitized ring cleavage of cyclobutane

derivatives has been studied extensively from the viewpoints of structure-reactivity relationship [6].

Here, we report the results of a mechanistic investigation of photocycloaddition reactions of group 14 organometallic compounds bearing the styrene chromophore and photoinduced electron transfer ring cleavage reactions of 2-silacyclobuta[2.3]cyclophanes.

DISCUSSION

Photocycloaddition via Photoinduced Electron Transfer

We have previously reported the results of our studies of photocycloaddition reactions of group 14 organometallic compounds bearing the styrene chromophores [3a]. These photoreactions proceed in both the singlet and triplet excited state manifold and can also be promoted under photoinduced electron transfer reaction conditions. For example, irradiation of an acetonitrile solution containing dimethylbis(4-vinylphenylmethyl) silane **1a** and a catalytic amount of phenanthrene (Phen) and 1,4-dicyanobenzene (*p*-DCB) with a 300W high pressure Hg lamp through Pyrex filter (>280 nm) under nitrogen atmosphere leads to formation of the [2 π +2 π] cycloadduct **2a**, 2-silacyclobuta[2.3]cyclophane [7], and insoluble polymeric material. The efficiency of this process is lower when the irradiated solution does not contain the photosensitizer (Scheme 1). This photoreaction also occurs when *p*-DCB or 9,10-dicyanoanthracene (DCA) are used as sensitizers. However, prolonged irradiation in these cases leads to production of

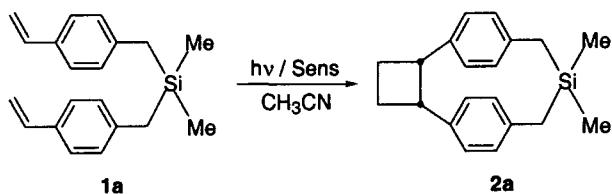
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Scheme 1.

Table 1. Effect of Sensitizers on the Photoreaction of **1a**^a

Sensitizer	Φ_{rel}^b
none	1.0
1,4-Dicyanobenzene (<i>p</i> -DCB)	0.48
<i>p</i> -DCB+Phenanthrene (Phen)	0.31
1,4-Dicyanonaphthalene (1,4-DCN)	~0 ^c
2,3-Dicyanonaphthalene (2,3-DCN)	~0 ^c
9-Cyanoanthracene (CA)	0.14
9,10-Dicyanoanthracene (DCA)	0.80

^aNitrogen-purged solutions containing **1a** (14 mg) and sensitizers (5×10^{-3} mol/dm³) in acetonitrile (3 mL) were irradiated through Pyrex filter by use of merry-go-round apparatus.

^bRelative quantum yield for the formation of **2a**, determined by GLC.

^cInsoluble polymer was obtained.

large amounts of insoluble polymers. 1,4-Dicyanonaphthalene (1,4-DCN) and 2,3-dicyanonaphthalene (2,3-DCN) sensitized reactions of substrate **1a** do not yield **2a**, but only insoluble polymers. The results are summarized in Table 1.

Photocycloreversion via Photoinduced Electron Transfer

Irradiation of an acetonitrile solution containing **2a**, Phen, and *p*-DCB with a 300W high pressure Hg lamp through a Pyrex filter ($\lambda > 280$ nm) under a nitrogen atmosphere leads to production of the ring cleaved product **1a** (Scheme 2). Prolonged irradiation led to complete consumption of **2a** and formation of insoluble polymer. Phen and *p*-DCB were recovered almost quantitatively even after prolonged irradiation. The time course of the photoreaction of **2a** is shown in Figure 1. In Figure 2 is shown the relationship between quantum yields for the formation of **1a** and the concentration of **2a**. Based on these data, a limiting quantum yield for the formation of **1a** of 20 can be calculated. Similarly, photoinduced ring cleavage of

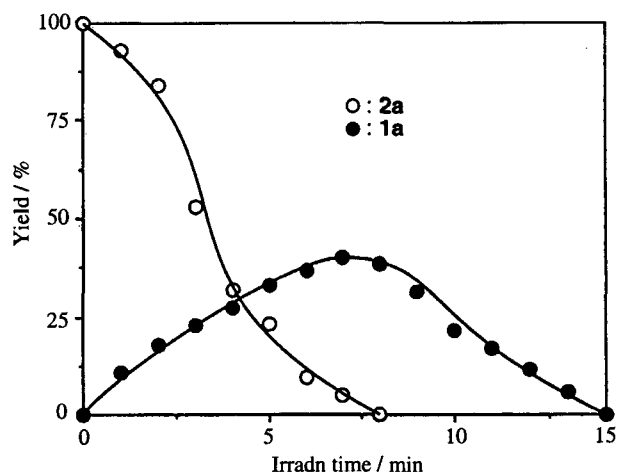


Figure 1. Plots of the distribution of **2a** and **1a** versus irradiation time in the photoreaction of **2a** sensitized by *p*-DCB and Phen in acetonitrile.

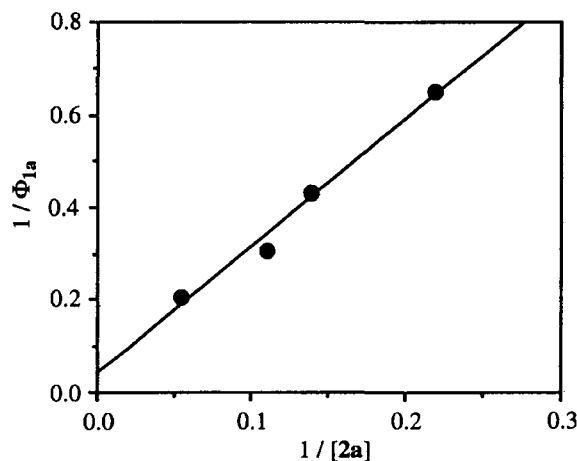
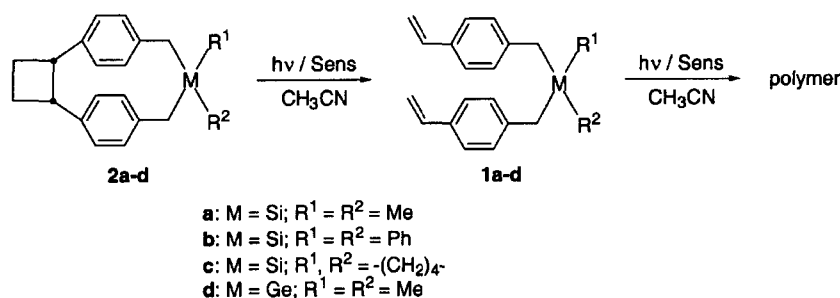


Figure 2. Double reciprocal plot of $1/[2a]$ versus $1/\Phi_{1a}$.

2b-d occurred efficiently to give styrene derivatives **1b-d**. Further irradiation in these cases also gave insoluble polymers. These photoreactions can be efficiently sensitized by *p*-DCB, 1,4-DCN, and DCA. In all cases, *p*-DCB-Phen was the most effective photosensitizer. The results are summarized in Table 2.

The quantum yields for the formation of **1a** were found to



Scheme 2.

Table 2. Effect of Sensitizers and Magnesium Perchlorate in the Photoreaction of **2a**^a

Sensitizer	Additive	Φ_{rel}^b
none	none	1.0
<i>p</i> -Dicyanobenzene (<i>p</i> -DCB)	none	3.5
<i>p</i> -DCB	Mg(ClO ₄) ₂ ^c	5.7
<i>p</i> -DCB+Phenanthrene (Phen)	none	12.4
<i>p</i> -DCB+Phen	Mg(ClO ₄) ₂ ^c	37.1
1,4-Dicyanonaphthalene (1,4-DCN)	none	2.7
1,4-DCN	Mg(ClO ₄) ₂ ^c	4.8
9,10-Dicyanoanthracene (DCA)	none	5.0
DCA	Mg(ClO ₄) ₂ ^c	15.7

^aNitrogen-purged solutions containing **2a** (4.6×10^{-4} mol/dm³) and sensitizers (5×10^{-3} mol/dm³) in acetonitrile (3 mL) were irradiated through Pyrex filter by use of merry-go-round apparatus.

^bRelative quantum yield for the formation of **1a**, determined by GLC.

^cMg(ClO₄)₂ (3 mg) was added.

increase by the addition of Mg(ClO₄)₂ into the reaction systems [1f,8]. In the absence of a photosensitizer, the photoreaction also occurred, but the rate of disappearance of **2a** was much smaller than that in the presence of a sensitizer. The photoreaction proceeded efficiently in polar solvents, and slowly in nonpolar solvents.

Structure of Cyclobutacyclophane **2a**

The ¹H NMR spectrum of **2a** exhibited two AB quartets at δ 6.33 and 6.58 ppm ascribable to the arene ring protons. These signals did not change in the temperature range from -60 to 80 °C. The results indicate that rotation of aromatic rings of **2a** is restricted by the structural demand. The *cis* configuration of substituents on the cyclobutane ring was confirmed by the X-ray crystallographic analysis of **2a** (Figure 3). The greater C_A-C_B bond distance (1.599 Å) in the cyclobutane ring of **2a**, as compared to simple monocyclic cyclobutanes (1.52-1.56 Å), is due perhaps to the structural requirements of the cyclophane.

Pulse Radiolysis and Gamma-Radiolysis

In order to gain information about the mechanism of the

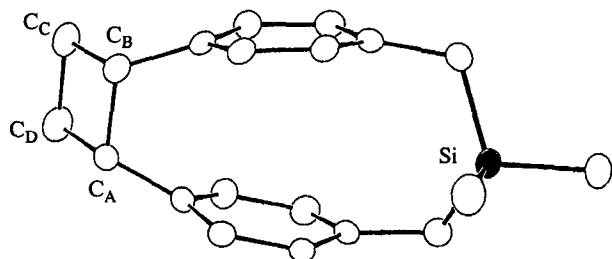


Figure 3. ORTER drawing of **2a**. All hydrogens are omitted for clarity. Selected bond lengths; C_A-C_B: 1.599(10) Å, C_B-C_C: 1.536(10) Å, C_C-C_D: 1.511(11) Å, C_D-C_A: 1.543(10) Å.

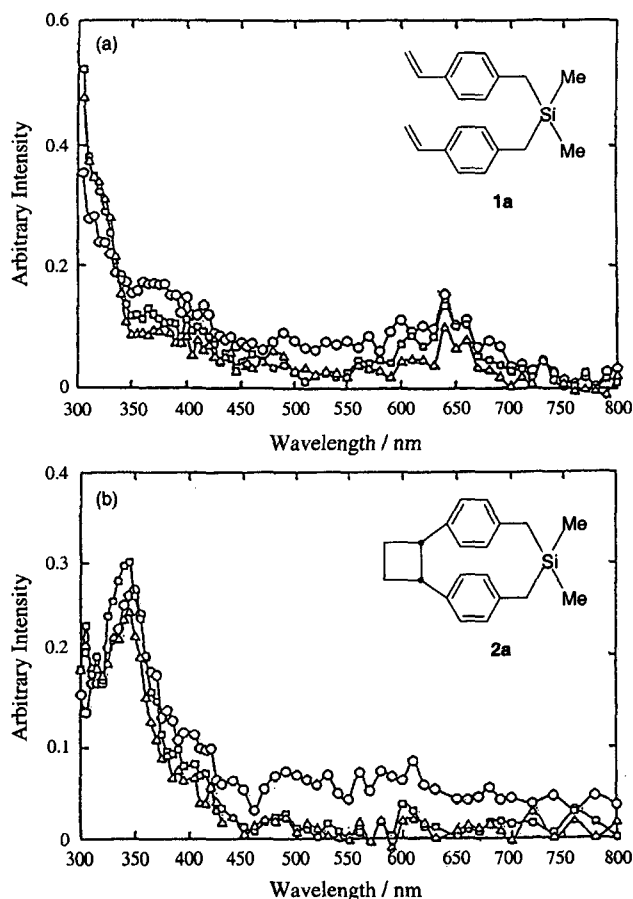


Figure 4. Transient absorption spectra in pulse radiolysis of (a) **1a** and (b) **2a**.

photochemical processes described above, we have investigated the transient absorption spectra of intermediates formed by pulse radiolysis at room temperature and gamma-radiolysis in low-temperature matrices [9]. The results are shown in Figures 4 and 5. Observable in the transient absorption spectra, arising from pulse radiolysis of **1a** in 1,2-dichloroethane at room temperature (Figure 4(a)), is a relatively long-lived reactive species, which possesses absorption maxima at 320 and 650 nm. On the other hand, a relatively short-lived species, with an absorption maximum at 340 nm was observed upon pulse radiolysis of **2a** (Figure 4(b)). Gamma-radiolysis of **1a** in the low temperature matrix gave more clear spectra. Absorption bands of 650 nm and 500 nm (Figure 5(a)) are assigned to the simultaneously disappearing monomer radical cation of the styrene moiety of **1a** and forming intramolecular dimer radical cation of **1a**. However, absorption bands for the dimer radical cation are not observable in spectra obtained by pulse radiolysis at room temperature (Figure 4(a)), a probable result of rapid polymerization. Spectra from pulse radiolysis of **2a** at room temperature (Figure 4(b)) only contained an absorption band at 350 nm, assigned to the benzyl radical generated by the C-Si bond cleavage of the radical cation of **2a**.

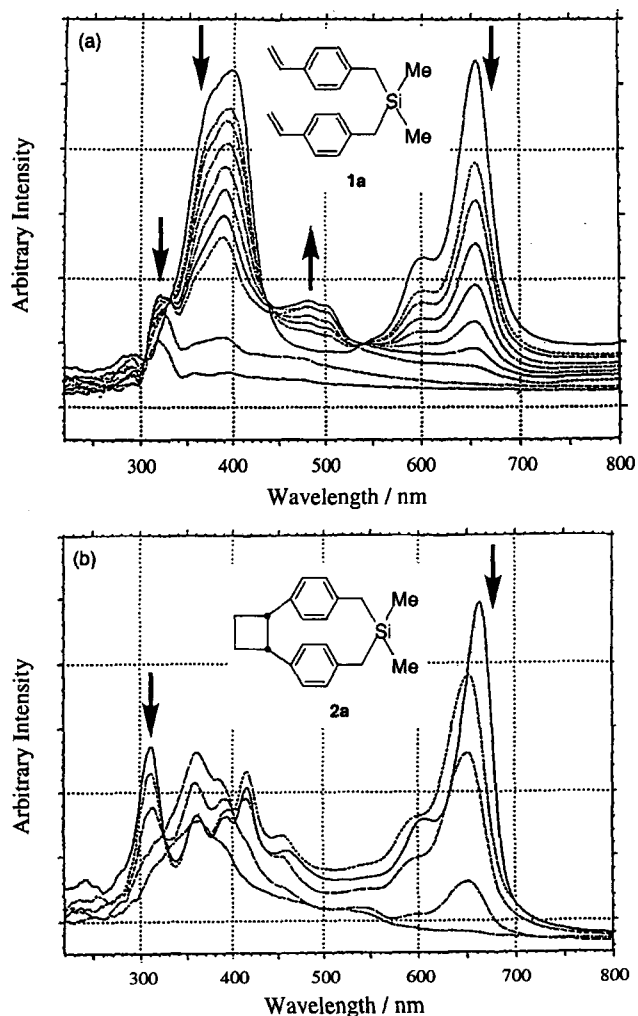
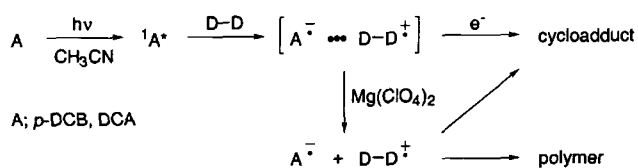


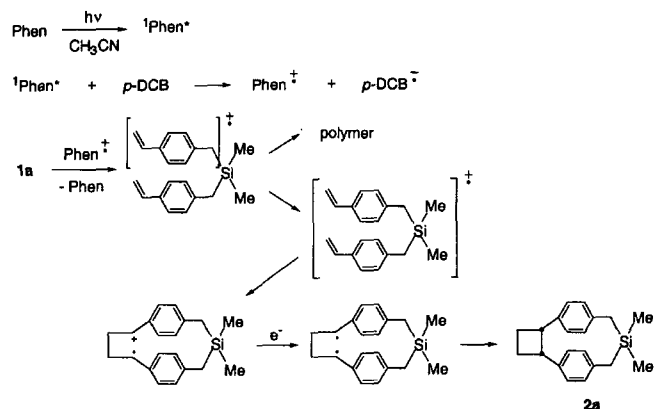
Figure 5. Low temperature matrix gamma-radiolysis of (a) **1a** and (b) **2a**.

Mechanism for the Photocycloaddition

Based on the results presented above, we propose the mechanism for the photocycloaddition and the photocycloreversion shown in Schemes 3-5. In reactions using *p*-DCB or DCA as a photosensitizer (Scheme 3), the first step is one-electron transfer from the styrene derivatives having group 14 elements (D-D) to the excited singlet states of cyano aromatic compounds ($^1A^*$), giving a radical ion pair [$A^{\cdot-} \cdots D-D^{\cdot+}$]. This radical ion pair produces cycloadducts. In the presence of metal salts, the radical ion pair smoothly dissociates to the



Scheme 3.



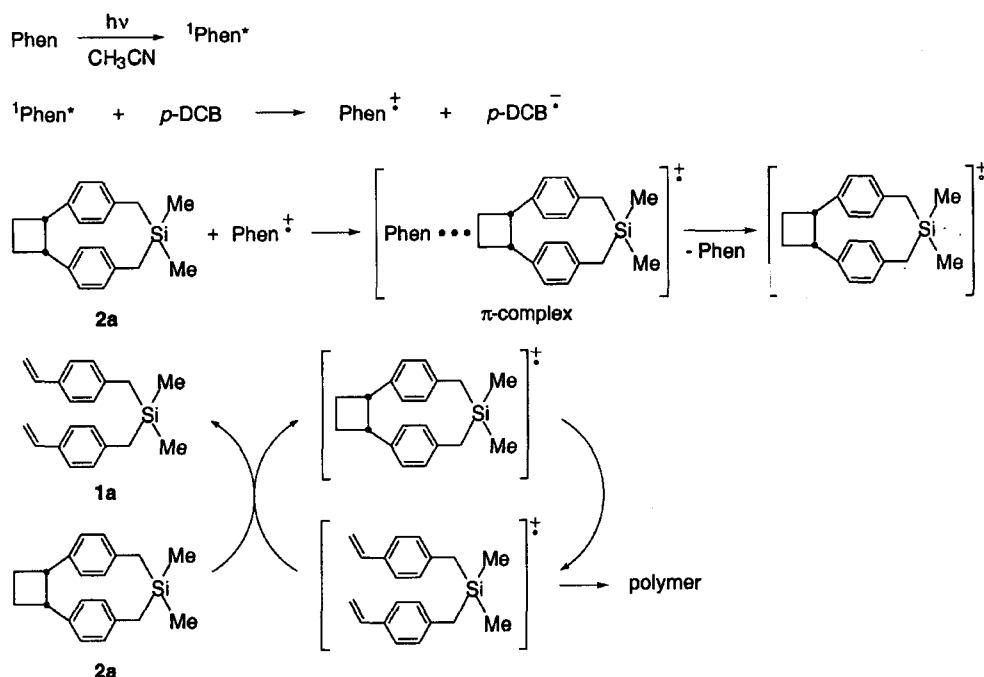
Scheme 4.

free radical ions [8]. The free radical $D-D^{\cdot+}$ reacts to form polymers. Related to the reactions promoted by redox-photosensitizer (Phen-*p*-DCB) (Scheme 4), we observed that the fluorescence of Phen was efficiently quenched by *p*-DCB, but not by **1a**. Thus, the first step in the redox-photosensitized process involves one-electron transfer from the excited singlet state of Phen ($^1\text{Phen}^*$) to the ground state of *p*-DCB, giving radical ions, $\text{Phen}^{\cdot+}$ and $p\text{-DCB}^{\cdot-}$. The second step is a secondary electron transfer from D-D to $\text{Phen}^{\cdot+}$, producing $D-D^{\cdot+}$ and neutral Phen. From results of the pulse radiolysis and gamma-radiolysis experiments, we know that the initially formed radical cation $D-D^{\cdot+}$ is a styrene localized monomer radical cation. The monomer radical cation interacts with another styrene intramolecularly or intermolecularly, giving the dimer radical cation or polymerized products. The dimer radical cation then cyclizes to form cycloadduct through a pathway shown in Scheme 4.

Mechanism for Photocycloreversion

The quantum yield for the formation of **1a** from **2a** in the redox-photosensitized reaction is greater than unity. Therefore, the photocleavage reaction of **2a** must proceed via a chain mechanism. We propose the following mechanism for the photocycloreversion of **2a** (Scheme 5). The first step is one-electron transfer from the excited singlet state of Phen ($^1\text{Phen}^*$) to the ground state of *p*-DCB, giving radical ions, $\text{Phen}^{\cdot+}$ and $p\text{-DCB}^{\cdot-}$. This is followed by formation of the π -complex [$\text{2a} \cdots \text{Phen}^{\cdot+}$], which dissociates to produce the radical cation $\text{2a}^{\cdot+}$ (closed form) and the neutral Phen. Ring opening of the radical cation generates the opened form of $\text{2a}^{\cdot+}$. Electron transfer from neutral **2a** to the opened form of $\text{2a}^{\cdot+}$ produces $\text{2a}^{\cdot+}$ (closed form) and neutral **1a**, then it becomes a chain process.

In conclusion, the electron transfer promoted photocycloaddition of **1a** afforded 2-silacyclobuta[2.3]cyclophane. Photocycloreversion of the 2-sila- and 2-germa-cyclobuta[2.3]cyclophanes also occurred under the same reaction conditions with quantum yields which exceed unity. Prolonged irradiation of these



Scheme 5.

substrates gave insoluble polymers. Pulse radiolysis and gamma-radiolysis of **1a** and **2a** gave rise to valuable information about the radical cation species generated from **1a** and **2a**.

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7. **Data for 1a:** oil; ^1H NMR (270 MHz, CDCl_3) δ -0.01 (s, 6 H), 2.14 (s, 4 H), 5.45 (dd, $J = 11$, 1 Hz, 2 H), 5.71 (dd, $J = 16$, 1 Hz, 2 H), 6.72 (dd, $J = 16$, 11 Hz, 2 H), 7.15 (ABq, $\Delta\nu = 86$ Hz, $J = 8$ Hz, 8 H); ^{13}C NMR (67 MHz, CDCl_3) δ -3.8, 25.1, 112.2, 126.2, 128.3, 133.7, 136.8, 139.7; IR (neat) 849, 903, 990, 1249, 1510, 1607, 1630, 2960 cm^{-1} ; MS (EI) $m/z = 43$, 59, 91, 117, 133, 145, 159, 175, 277, 292 (M^+). **Data for 2a:** mp 100-102°C; ^1H NMR (270 MHz, CDCl_3) δ 0.26 (s, 3 H), 0.28 (s, 3 H), 2.07 (s, 4 H), 2.44-2.52 (m, 2 H), 4.04-4.08 (m, 2 H), 6.33 (ABq, $\Delta\nu = 62$ Hz, $J = 8$ Hz, 4 H), 6.58 (ABq, $\Delta\nu = 14$ Hz, $J = 8$ Hz, 4 H); ^{13}C NMR (67 MHz, CDCl_3) δ -0.33, 25.8, 29.7, 47.1, 128.1, 131.1, 136.6, 137.5; IR (KBr) 712, 837, 1245, 1510, 1605, 2926 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{Si}$: C, 82.12; H, 8.27%. Found: C, 82.29; H, 8.38%.
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9. **Pulse Radiolysis:** A 5 mmol dm^{-3} 1,2-dichloroethane solution of **1a** or **2a** was saturated with Ar by bubbling for 10 minutes and sealed in a 40×10×10 mm^3 rectangular Suprasil cell. A transient absorption spectrum was measured at room temperature using a conventional nanosecond pulse radiolysis system using an electron LINAC (energy, 28 MeV; pulse width, 8 ns; dose, 0.8 kGy/pulse). **Low Temperature Matrix Measurements:** A sample solution (5 mmol dm^{-3}) was sealed in a 40×10×1 mm^3 Suprasil cell under high vacuum. γ -Ray irradiation was carried out in liquid nitrogen with a ^{60}Co source (3.7×10^{14} Bq, dose 700 Gy). The absorption spectrum was measured in liquid nitrogen with a rectangular quartz Dewar vessel and a multichannel spectrometer.