

# Photochemical carbon–silicon bond forming reaction on electron-deficient alkenes by disilanes and polysilanes via photoinduced electron transfer

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## Abstract

The phenanthrene-sensitized photoreaction of electron-deficient alkenes with disilanes in acetonitrile gave silylated alkanes in high yields. The photosilylation occurred in a highly regioselective manner at the position  $\beta$  to the electron-withdrawing groups of the alkenes. With asymmetrically substituted disilanes and polysilanes, silyl groups bearing more bulky substituents were preferentially introduced to the alkenes. The photoreactions were sensitized by aromatic hydrocarbons such as phenanthrene and triphenylene, but not by pyrene or anthracene. In the absence of aromatic hydrocarbons, the photoreactions were not appreciable. The key step of the photoreactions was the reaction with the radical anions of electron-deficient alkenes of silyl radicals, which were generated by a nucleophile-assisted cleavage of the radical cations of disilanes and polysilanes. The mechanistic features of the photoreaction are discussed.

*Key words:* Silyl; Silane; Alkene; Photochemistry; Electron transfer; Group 14

## 1. Introduction

Photoinduced electron-transfer reactions of organo-silicon compounds have received considerable attention in recent years in various fields of chemistry as well as in the development of advanced materials [1,2]. A characteristic property of these compounds is that their oxidation potentials are lower, especially in polysilanes, compared with the corresponding carbon analogues. Actually, charge transfer complexes are formed between polysilanes and tetracyanoethene in organic solvents in the dark [3]. Photosilylation of cyanobenzenes [4] and acridinium salts [5] with polysilanes takes place via photoinduced electron-transfer. In these photoreactions, the Si–Si bond of polysilanes is cleaved via their radical cations to produce silyl radicals and silyl cations [6]. In some cases, these radical and cationic fragments can be trapped by reactions with carbon tetrachloride and alcohols, respectively [7]. However, little is known about photoreaction of alkenes with polysilanes. We now report efficient photosilylations of electron-deficient alkenes by disilanes and polysilanes via photoinduced electron-transfer.

The photoreactions take place in a highly regioselective fashion, and efficiency can be enhanced by utilizing additive and solvent effects. Mechanistic and reactivity features are discussed.

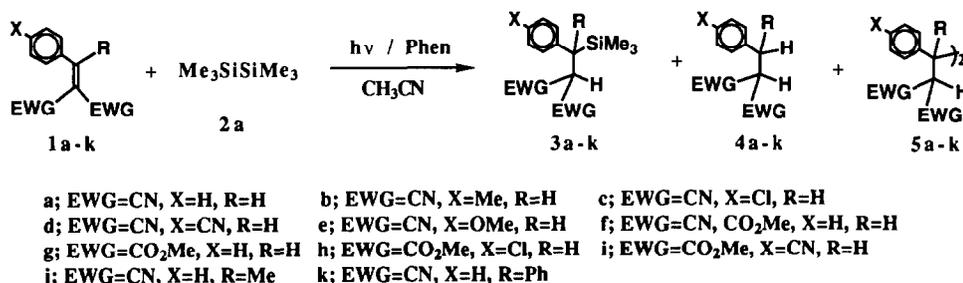
## 2. Results and discussion

### 2.1. Photoreaction with hexamethyldisilane

Irradiation with  $> 280$  nm light under nitrogen atmosphere of an acetonitrile solution containing 1,1-dicyano-2-phenylethene (**1a**) and hexamethyldisilane (**2a**) in the presence of phenanthrene (Phen) gave 1,1-dicyano-2-phenyl-2-trimethylsilylethane (**3a**) in good yield, along with a small amount of 1,1-dicyano-2-phenylethane (**4a**). The photoreaction of electron-deficient alkenes **1b–k** with **2a** gave silylated products **3b–k**. The trimethylsilyl group was introduced regioselectively at the carbon  $\beta$  to the electron-withdrawing groups of alkenes. The reduction products **4b–k** were by-products. In some cases, the reductive dimerization products **5** were formed. The results are in Table 1.

The products were isolated by column chromatography on silica gel, and the structures of the products

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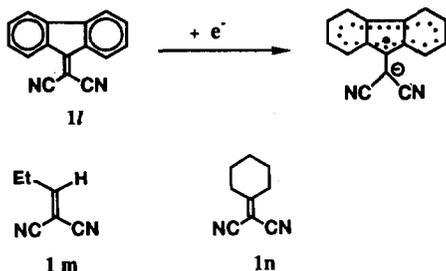
TABLE 1. Photosilylation of electron-deficient alkenes by **2a**<sup>a</sup>

Alkene ( $E_{p/2}^{\text{red}}/\text{V}^{\text{a}}$ )	Irradn time/h	Products (yield/%)
<b>1a</b> (-1.45)	43	<b>3a</b> (75), <b>4a</b> (10)
<b>1b</b> (-1.51)	45	<b>3b</b> (80), <b>4b</b> (8)
<b>1c</b> (-1.37)	46	<b>3c</b> (54), <b>4c</b> (32)
<b>1d</b> (-1.13)	80	<b>3d</b> (84), <b>4d</b> (6)
<b>1e</b> (-1.59)	50	<b>3e</b> (10), <b>4e</b> (trace)
<b>1f</b> (-1.61)	48	<b>3f</b> (67), <b>4f</b> (18)
<b>1g</b> (-1.85)	53	<b>3g</b> (56), <b>4g</b> (10)
<b>1h</b> (-1.76)	34	<b>3h</b> (45), <b>4h</b> (trace), <b>5h</b> (2)
<b>1i</b> (-1.62)	70	<b>3i</b> (68), <b>4i</b> (trace), <b>5i</b> (14)
<b>1j</b> (-1.51)	126	<b>3j</b> (40), <b>4j</b> (20)
<b>1k</b> (-1.38)	46	<b>3k</b> (trace), <b>4k</b> (70)
<b>1l</b> (-0.96)	> 100	no reaction
<b>1m</b>	> 100	no reaction
<b>1n</b>	> 100	no reaction

<sup>a</sup> Oxidation potential of **2a**: 1.20 V vs. Ag/Ag<sup>+</sup>.<sup>b</sup> Reduction potentials vs. Ag/Ag<sup>+</sup> in CH<sub>3</sub>CN.

were determined from their spectral properties and elemental analyses (see Experimental section).

The efficiency of the photoreaction depended on the structures of the electron-deficient alkenes. A higher efficiency was obtained for 1,1-dicyanoethenes (**1a-d**, EWG = CN) than for 1,1-dimethoxycarbonyl ethenes (**1f-i**, EWG = CO<sub>2</sub>Me). With the tetra-substituted ethene **1k**, the formation of the reduction product **4k** predominated. No reaction occurred with **1l-n**. It is noteworthy that the radical anion of **1l** is a stabilized radical anion in which the radical centre is delocalized over the planar fluorene ring.



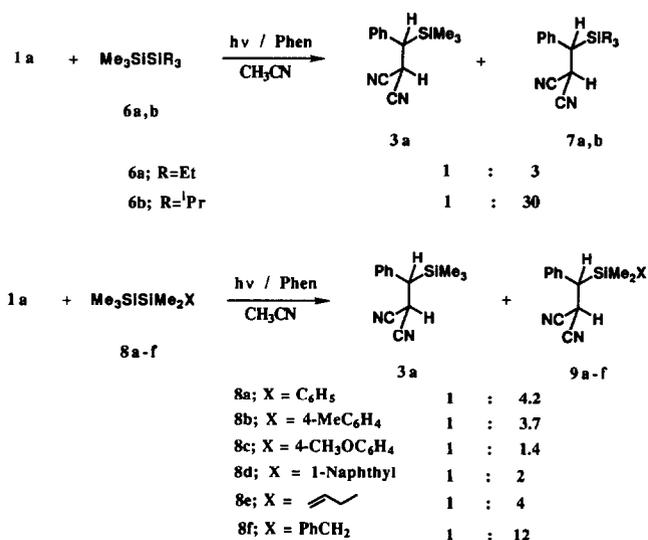
## 2.2. Photoreaction with asymmetrically substituted disilanes

The photoreaction of electron-deficient alkenes with asymmetrically substituted disilanes gave two kinds of silylated alkanes. For example, irradiation of an acetonitrile solution of **1a** and 1,1,1-triethyl-2,2,2-trimethyldisilane (**6a**) in the presence of Phen gave a mixture of trimethylsilylated alkane **3a** and triethylsilylated alkane **7a** in a 1:3 ratio. The photoreaction of **1a** with 1,1,1-trimethyl-2,2,2-tris(1-methylethyl)disilane (**6b**) gave **3a** and tris(1-methylethyl)silyl-substituted alkane (**7b**) in a 1:30 ratio. In the photoreaction of **1a** with arylpentamethyldisilanes **8a-d**, the formation of aryl dimethylsilyl-substituted alkanes **9a-d** predominated. In the photoreaction of **1a** with **8c**, a small amount of 1,1,2,2-tetramethyl-1,2-bis(4-methoxyphenyl)disilane (**10**) was a by-product, formed via a coupling of dimethyl(4-methoxyphenyl) silyl radical. The significant feature here is that more bulky silyl groups in the asymmetrical disilanes are introduced preferentially to the electron-deficient alkenes at the  $\beta$ -carbon to the electron-withdrawing groups.

Previously, we reported that the photoreaction of allylic and benzylic silanes with electron-deficient alkenes gives allylated and benzylated alkanes in high yields [9]. Key intermediates of this photoreaction are allylic and benzylic radicals that are generated by the cleavage of the C-Si bond of radical cations of silicon compounds. However, the photoreaction of **1a** with **8e-f**, which bear allyl and benzyl substituents on the silicon atom, give exclusively the silylated alkanes **3a** and **9e-f** without production of allylated or benzylated alkanes. This indicates that Si-Si bond cleavage occurs in preference to C-Si bond cleavage in the radical cations of **8a-f**. In these cases, more bulky silyl groups were preferentially introduced to the alkenes.

## 2.3. Photoreaction with cyclic disilane

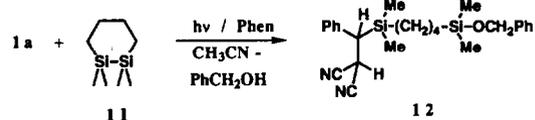
The photoreaction of **1a** with 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**11**) in acetonitrile in the presence of benzyl alcohol gave the silylated products **12** in



**Me<sub>2</sub>ArSiSiMe<sub>2</sub>Ar**

**10**; Ar = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

which the benzyloxy group was incorporated at the terminal silyl group (Table 2). In the photoreaction in the presence of ethanol, the formation of ethoxy group-incorporated compound was detected by the IR spectrum of the reaction mixture. But the compound was unstable and could not be isolated in a pure form; the IR spectrum of the isolated compound showed an absorption associated with the Si–O–Si bond.



#### 2.4. Photoreactions with polysilanes

The photoreaction of **1a** with octamethyltrisilane (**13**) under similar conditions gave the monosilyl-sub-

TABLE 2. Photosilylation of **1a** with asymmetrically substituted disilanes, cyclic disilane, and polysilanes

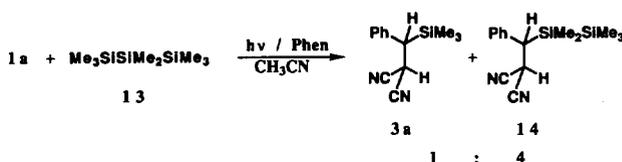
Silane ( $E_{p/2}^{\text{ox}}/\text{V}^{\text{a}}$ )	Irradn time/h	Product(s) (yield(s)/%)	$\Phi_{\text{ref}}^{\text{b}}$
<b>2a</b> (1.20)	43	<b>3a</b> (75), <b>4a</b> (10)	1.0
<b>6a</b> (1.08)	33	<b>3a</b> (14), <b>7a</b> (44)	2.1
<b>6b</b> (1.02)	10	<b>3a</b> (2), <b>7b</b> (61)	3.0
<b>8a</b> (1.05)	30	<b>3a</b> (14), <b>9a</b> (54)	
<b>8b</b> (0.93)	10	<b>3a</b> (13), <b>9b</b> (44)	
<b>8c</b> (0.82)	10	<b>3a</b> (17), <b>9c</b> (26)	
<b>8d</b> (1.08)	11	<b>3a</b> (16), <b>9d</b> (31)	
<b>8e</b>	17	<b>3a</b> (9), <b>9e</b> (37)	
<b>8f</b>	19	<b>3a</b> (4), <b>9f</b> (53)	
<b>11</b> (0.98) <sup>c</sup>	20	<b>12</b> (30)	
<b>13</b> (1.17)	14	<b>3a</b> (14), <b>14</b> (55)	
<b>15</b> (0.92)	5	<b>3a</b> (3), <b>14</b> (24), <b>16</b> (6)	
<b>17</b> (1.12)	5	<b>3a</b> (trace), <b>18</b> (80)	

<sup>a</sup> Oxidation potentials *vs.* Ag/Ag<sup>+</sup> in CH<sub>3</sub>CN.

<sup>b</sup> Relative quantum yields for the formation of silylated products.

<sup>c</sup> In CH<sub>3</sub>CN-PhCH<sub>2</sub>OH = 7:1.

stituted compound **3a** and the disilyl-substituted compound **14** in a 1:4 ratio, 69% total yield.



From **1a** and dexamethyltetrasilane (**15**), a mixture of **3a**, **14**, and the trisilyl-substituted compound **16** was obtained in a 1:8:2 ratio, 33% total yield. The predominant formation of **14** indicates that the Si–Si bond cleavage of the radical cation of tetrasilane occurs efficiently at the middle of the tetrasil group. The mode of the bond dissociation of radical cations of polysilanes will be discussed in detail below. The photoreaction of **1a** with permethylpentasilane and permethylhexasilane afforded complex mixtures containing mono-, di-, tri-, and tetra-silyl substituted compounds. However, the photoreaction of **1a** with tetrakis(trimethylsilyl)silane (**17**) gave predominantly **18** in good yield, along with a trace amount of **3a**. The reactivity of

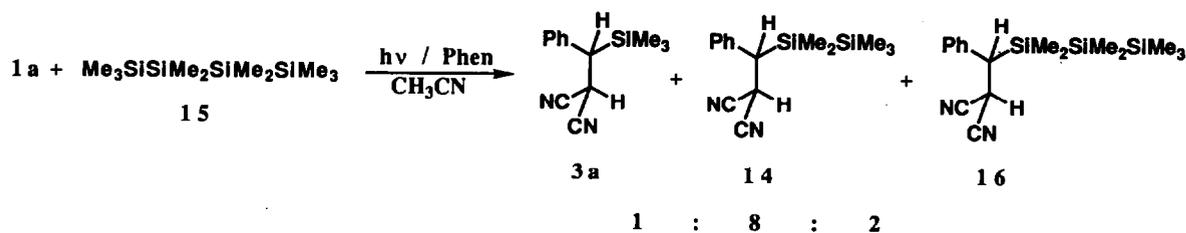


TABLE 3. Effect of solvents on the photosilylation of **1a** with **2a**

Solvent	$\epsilon^a$	$\Phi_{\text{rel}}^b$
CH <sub>3</sub> CN	37.5	1.0
CH <sub>3</sub> OH	32.6	0.3 <sup>c</sup>
CH <sub>3</sub> CN-CH <sub>3</sub> OH (8:1)		0.4 <sup>c</sup>
CH <sub>3</sub> CN-CH <sub>3</sub> CO <sub>2</sub> H (8:1)		0.4 <sup>c</sup>
CH <sub>3</sub> CN-H <sub>2</sub> O (8:1)		0.04 <sup>c</sup>
CH <sub>3</sub> CO <sub>2</sub> Et	6.0	~ 0
C <sub>6</sub> H <sub>6</sub>	2.3	~ 0

<sup>a</sup>  $\epsilon$ ; Dielectric constant.

<sup>b</sup> Relative quantum yields for the formation of **3a**.

<sup>c</sup> In these cases, the reduction product **4a** was produced as a major product.

polysilanes increased with decreasing the oxidation potentials of the compounds. The results are also given in Table 2.

### 2.5. Effect of solvents

Photosilylation of **1a** with **2a** was carried out in various solvents in the presence of Phen (Table 3). The quantum yield for the formation of **3a** increased with increasing solvent polarity. In less polar and nonpolar solvents such as ethyl acetate and benzene, the photoreaction occurred inefficiently. In protic polar solvents such as methanol, the quantum yield for the formation of **3a** decreased, but that for the formation of **4a** increased. The addition to acetonitrile of methanol, acetic acid, and water as proton donor also caused the decrease in the quantum yield for the formation of **3a** and the increase in the quantum yield for the formation of **4a**. The addition of a small amount of CCl<sub>4</sub> suppressed the formation of **3a**, giving a complex mixture.

### 2.6. Effect of additives

(1) Aromatic hydrocarbons: The photoreaction of **1a** with **2a** did not occur appreciably when the photoreaction was carried out in the absence of aromatic hydrocarbons. The photosilylation was sensitized by aromatic hydrocarbons such as Phen, triphenylene (Tri) and

TABLE 4. Effect of additives on the photosilylation of **1a** with **2a** and free energy changes ( $\Delta G$ )

Additive	$E_{p/2}^{\text{ox}}/V^a$	$\Delta G^b/kJ\ mol^{-1}$	$\Phi_{\text{rel}}^c$
Phenanthrene (Phen)	1.17	-99.1	1.0
Triphenylene (Tri)	1.29	-90.0	2.5
<i>p</i> -Terphenyl ( <i>p</i> -Ter)	1.32	-	0.5
Naphthalene (Nap)	1.22	-132.8	0.9
Pyrene (Py)	0.78	-112.0	~ 0
Anthracene (Anth)	0.75	-112.4	~ 0
None	-	-	~ 0

<sup>a</sup> Oxidation potentials vs. Ag/Ag<sup>+</sup> in CH<sub>3</sub>CN.

<sup>b</sup> Free energy changes [10] for single electron transfer from the excited singlet <sup>1</sup>ArH\* to **1a** ( $E_{p/2}^{\text{red}} = -1.45\text{ V}$ ).

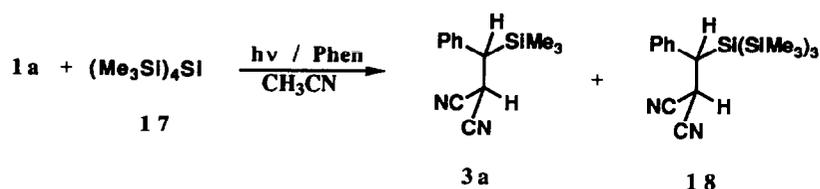
<sup>c</sup> Relative quantum yield for the formation of **3a**.

*p*-terphenyl (*p*-Ter). However, pyrene (Py) and anthracene (Anth) were not effective sensitizers for this photoreaction (Table 4). The photosilylation of **1a** with tetrasilane **15** was sensitized by Py to give **3a**, **14**, and **16** in 3, 24, and 6% yields. The photosilylation of **1a** with cyclohexasilane was effectively sensitized by Py. The role of aromatic hydrocarbons will be discussed later.

(2) Metal salts: The effect of metal salts on the photosilylation of **1a** with **2a** in the presence of Phen was studied. Addition of metal salts such as Mg(ClO<sub>4</sub>)<sub>2</sub>, LiClO<sub>4</sub>, KClO<sub>4</sub>, Bu<sub>4</sub>NClO<sub>4</sub>, and NaBF<sub>4</sub> did not influence the photosilylation of **1a**. The formation of **4a** was suppressed by adding these metal salts, especially NaBF<sub>4</sub>.

### 2.7. Fluorescence quenching and redox potentials

The fluorescence of aromatic hydrocarbons was quenched by electron-deficient alkenes at a rate which was approximately controlled by diffusion, but it was not quenched by disilanes or polysilanes. Table 4 shows the oxidation potentials (vs. Ag/Ag<sup>+</sup>) of aromatic hydrocarbons in acetonitrile, and the free energy changes ( $\Delta G$ ) for a single electron-transfer process from the excited singlet states of aromatic hydrocarbons to **1a**, which were estimated by the Rehm-Weller equation [10].

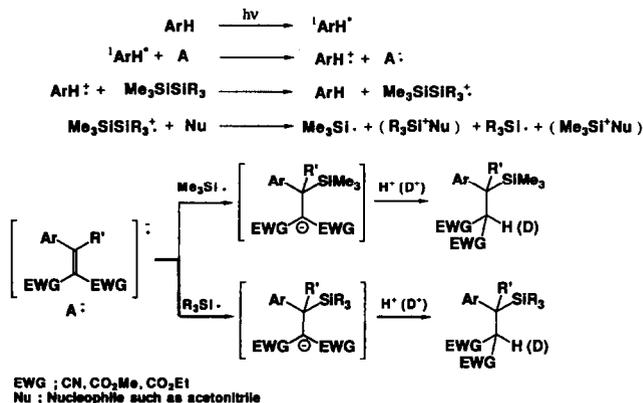


### 2.8. Effect of sensitizers

The difference in the oxidation potential between aromatic hydrocarbon (ArH) and organosilicon compound (D) is an important factor in determining the efficiency of photoreaction. For example, the photosilylation of **1a** with **2a** was sensitized by *p*-Ter, Tri, Phen, and Nap, but not by Py or Anth. The photosilylation of **1a** with tetrasilane was sensitized by both Phen and Py. When the difference in the oxidation potentials between D and ArH is less than 0.3–0.4 V, electron transfer from D to ArH<sup>+</sup> can occur smoothly to produce D<sup>+</sup> and ArH. However, when the difference is more than 0.4 V, electron transfer can hardly occur. In this case, the radical cations are rather deactivated by a rapid back-electron transfer from A<sup>-•</sup> to ArH<sup>+</sup>.

### 2.9. Mechanism

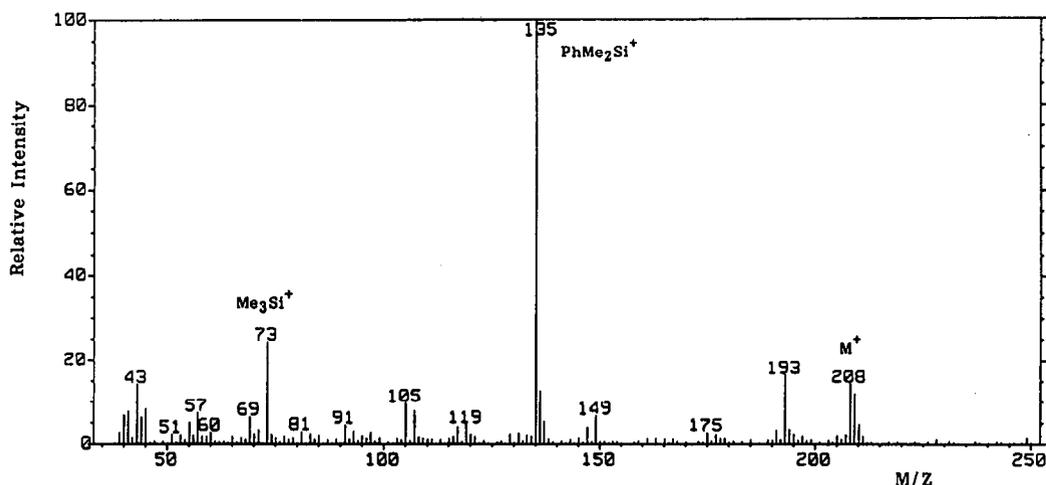
The proposed mechanism for the photosilylation of electron deficient alkenes by disilanes and polysilanes is shown in Scheme 1. The first step is a one-electron transfer from the excited singlet <sup>1</sup>ArH\* to the electron-deficient alkenes (A) to give the radical ion pair [ArH<sup>+</sup> ··· A<sup>-•</sup>] [11]. This process is exothermic as predicted by fluorescence quenching experiments of ArH and by the negative Δ*G* values for a one-electron transfer from <sup>1</sup>ArH\* to A. The radical ion pair mostly decays by rapid back-electron transfer to the ground states of ArH and A and partly dissociates to the free radical cation of ArH<sup>+</sup> and the radical anion A<sup>-•</sup>. The second step is the formation of radical cations of disilanes by a secondary electron transfer from the disilanes to ArH<sup>+</sup> to produce radical cations of disilanes and neutral ArH. This is consistent with the fact that the quantum efficiency for the photosilylation



Scheme 1.

increases with decreasing oxidation potential of disilanes (Table 2).

A key step of the photoreaction is the coupling of A<sup>-•</sup> with a trialkylsilyl radical that is produced by cleavage of the Si–Si bond of the radical cations of disilanes. This process would be assisted by a nucleophilic attack of nucleophiles such as acetonitrile on the Si atom. A nucleophile-assisted cleavage of the C–Si bond in organosilicon compounds is proposed by several groups [7,12,13]. Dinnocenzo found that the decay rate of (*p*-methoxybenzyl)trialkylsilane radical cation in acetonitrile decreases with increasing bulk of the substituent on the silicon atom [12a]. Nakadaira and Sakurai reported an intramolecular addition of OH group to the radical cations of disilanes, accompanying cleavage of the Si–Si bond [7]. In the photosilylation of electron-deficient alkenes with asymmetrically substituted disilanes, a more bulky silyl group was

Fig. 1. Mass spectrum of **8a**.

selectively introduced to the alkenes. This can be rationalized by assuming that the cleavage of the radical cations of disilanes to silyl radical and silyl cation is assisted by nucleophilic attack that occurs at the less hindered site of the radical cations of disilanes. Hence, the trimethylsilyl cation ( $\text{Me}_3\text{Si}^+\text{Nu}^-$ ) and the more bulky silyl radical ( $\text{R}_3\text{Si}^\cdot$ ) are predominantly produced.

The mass spectra of asymmetrically substituted disilanes and polysilanes are shown in Table 5 and Fig. 1 [14]. In the mass spectroscopy, the major fragment ion is the more bulky silyl cation which is stabilized by conjugation or delocalization interaction with substituents. The less hindered silyl cation would be attacked by a nucleophile to eliminate the more bulky silyl radical. These results support the hypothesis that the Si-Si bond cleavage of the radical cations occurs by assistance of nucleophiles in solution.

The regioselectivity of the photosilylation can be explained in terms of the charge and spin densities of the radical anions of electron-deficient alkenes, which are calculated by the PM-3 RHF calculation [15]. The photosilylation occurs at the position of highest spin density and the protonation occurs at that of highest negative charge density (Table 6). When the photoreaction of **1a** with **2a** was carried out in the presence of  $\text{D}_2\text{O}$  or  $\text{CH}_3\text{OD}$ , 1,1-dicyano-1-deuterio-2-phenyl-2-trimethylsilylethane was obtained. In the photosilylation with cyclic disilane in the presence of benzyl alcohol, the benzyloxy group was incorporated at the terminal silyl atom. The photosilylation of **1a** with (4-methoxyphenyl)pentamethyldisilane (**8c**) gave 1,1,2,2-tetramethyl-1,2-bis(4-methoxyphenyl)disilane (**10**) as a by-product by the coupling of free aryl dimethylsilyl radical. In protic solvents, a large amount of the reduction and/or reductive dimerization products were produced. These results are also consistent with the reac-

TABLE 5. Fragments of silyl cation species generated from mass spectroscopy and photosilylation of 1,1-dicyano-2-phenylethene

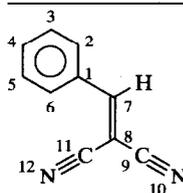
Silane	Mass fragment in gas phase <sup>a</sup>		Fragment ratio in solution <sup>b</sup>	
	$\text{Me}_3\text{Si}^+$	$\text{R}_3\text{Si}^+$	$\text{Me}_3\text{Si}^+$	$\text{R}_3\text{Si}^+$
$\text{Et}_3\text{SiSiMe}_3$	35	100	75	25
$\text{PhMe}_2\text{SiSiMe}_3$	25	100	97	3
$(4\text{-MeC}_6\text{H}_4)_2\text{Me}_2\text{SiSiMe}_3$	19	100	80	20
$(4\text{-MeOC}_6\text{H}_4)_2\text{Me}_2\text{SiSiMe}_3$	13	100	77	23
$\text{NapMe}_2\text{SiSiMe}_3$	12	100	63	37
$(\text{cyclohexyl})_2\text{Me}_2\text{SiSiMe}_3$	50	100	80	20
$\text{Me}_3\text{SiSiMe}_2\text{SiMe}_3$	87	100	80	20
$\text{Si}(\text{SiMe}_3)_4$	71	100	95	5

<sup>a</sup> Mass fragment intensity.

<sup>b</sup> Fragment ratios were estimated from the product ratios in the photosilylation of 1,1-dicyanoethene by disilanes and polysilanes.

TABLE 6. Calculated spin densities and negative charge densities of the radical anion of 1,1-dicyano-2-phenylethene by PM-3 RHF calculations [15]

Atom	Spin density	Negative charge density	Atom	Spin density	Negative charge density
1	0.0666	-0.0307	7	0.2639	-0.1178
2	0.0969	-0.1546	8	0.1822	-0.1191
3	0.0095	-0.0852	9	0.0160	-0.0029
4	0.1296	-0.2359	10	0.0594	-0.2431
5	0.0056	-0.0879	11	0.0158	-0.0188
6	0.0993	-0.1728	12	0.0553	-0.2454



tive species being the radical anion of alkene and the silyl radical.

### 3. Experimental details

#### 3.1. General

<sup>1</sup>H NMR spectra were recorded on a JEOL PMX-GX 270 (270 MHz) spectrometer for  $\text{CDCl}_3$  solutions using tetramethylsilane as an internal standard. <sup>13</sup>C NMR spectra were recorded on a JEOL PMX-GX 270 (67 MHz) spectrometer for solutions in  $\text{CDCl}_3$  using chloroform ( $\delta$  77.05) as an internal standard. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. UV/Vis spectra were recorded on a JASCO UVIDEK-670 spectrometer, fluorescence and excitation spectra on a JASCO FP-770 spectrometer and mass spectra with a Shimadzu LKB9000 instrument. Elemental analyses were performed with a Yanaco MT-3 CHN Corder instrument. GLC analyses were performed with Hitachi 163 and 164 instruments using a 1 m  $\times$  3 mm glass column packed with 5% Silicone-OV 17 on Shimalite W. An Eikosha PIH-300 300 W high pressure mercury lamp was the light source.

#### 3.2. Materials

Acetonitrile was distilled three times over  $\text{P}_2\text{O}_5$  and once over  $\text{CaH}_2$  before use. Spectral grade benzene, cyclohexane and ethyl acetate were used without further purification. Aromatic and aliphatic electron-deficient alkenes were prepared by the methods described [15–18]. Hexamethyldisilane, disilane derivatives, cyclic disilanes, polysilanes, and cyclohexasilane were prepared by literature methods [19–27]. Other organic chemicals were purchased and purified by distillation

or recrystallization before use. Inorganic chemicals were purchased and used without further purification.

### 3.3. General procedure for photoreaction of electron-deficient alkenes with disilane derivatives

Preparative photoreactions were carried out by using a 300 W Eikosha high pressure mercury lamp with a Pyrex filter. A solution containing an electron-deficient alkene and a disilane was purged with nitrogen before irradiation. The progress of photoreaction was monitored by GLC. When over 95% of the electron-deficient alkene had been consumed, the photoirradiation was ceased and the solvent was removed under reduced pressure. The residue was analyzed on the basis of its  $^1\text{H}$  NMR spectral data, from which the product ratio was determined by integration of the signals. The products were isolated by flush column chromatography on silica gel and purified by recrystallization or distillation and their structures determined by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, MS spectra and elemental analyses.

### 3.4. Typical procedure for photosilylation of electron-deficient alkenes with disilanes

A nitrogen-purged solution of 1,1-dicyano-2-phenylethene (**1a**, 100 mg, 0.65 mmol), hexamethyldisilane (**2a**, 180 mg, 1.23 mmol), and phenanthrene (Phen, 50 mg, 0.28 mmol) in acetonitrile (8 cm<sup>3</sup>) was irradiated with > 280 nm light. The photoreaction was monitored by GLC (SE-30 10%). After the peak of alkene had almost disappeared (43 h), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel. 1,1-Dicyano-2-phenylethane (**4a**, 10 mg, 10%) was obtained from hexane-benzene (1:1) eluent, and 1,1-dicyano-2-phenyl-2-trimethylsilylethane (**3a**, 106 mg, 75%) from hexane-benzene (2:3) eluent. 1,1-Dicyano-2-phenyl-2-trimethylsilylethane (**3a**); oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.16 (s, 9H), 2.64 (d, 1H,  $J = 8$  Hz), 4.08 (d, 1H,  $J = 8$  Hz), 7.14–7.37 (m, 5H);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.1, 25.2, 37.9, 113.1, 127.9, 128.2, 129.2, 129.3; IR (neat) 1257, 2260 cm<sup>-1</sup>; MS  $m/z$  228(M<sup>+</sup>), 155; Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>Si: C, 68.37; H, 7.06; N, 12.27. Found: C, 68.36; H, 7.21; N, 12.32%.

**3b**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.12 (s, 9H), 2.28 (s, 3H), 2.50 (d, 1H,  $J = 8$  Hz), 3.97 (d, 1H,  $J = 8$  Hz), 6.97–7.10 (m, 4H); IR (neat) 2256 cm<sup>-1</sup>; MS  $m/z$  242(M<sup>+</sup>), 169.

**3c**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.16 (s, 9H), 2.63 (d, 1H,  $J = 8$  Hz), 4.06 (d, 1H,  $J = 8$  Hz), 7.24 (ABq, 4H,  $\Delta\nu = 52$  Hz,  $J = 8$  Hz);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.3, 24.9, 37.0, 113.0, 128.7, 129.9, 131.8, 133.1, 135.7; IR (neat) 2344, 2364 cm<sup>-1</sup>; Anal. Calcd.

for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>ClSi: C, 59.41; H, 5.75; N, 10.66. Found: C, 59.80; H, 5.70; N, 10.73%.

**3d**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  -0.03 (s, 9H), 2.77 (d, 1H,  $J = 8$  Hz), 4.08 (d, 1H,  $J = 8$  Hz), 7.69 (ABq, 4H,  $\Delta\nu = 15$  Hz,  $J = 8$  Hz); MS  $m/z$  253 (M<sup>+</sup>), 180.

**3e**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.07 (s, 9H), 2.61 (d, 1H,  $J = 8$  Hz), 3.85 (s, 3H), 4.33 (d, 1H,  $J = 8$  Hz), 7.79 (ABq, 4H,  $\Delta\nu = 12$  Hz,  $J = 8$  Hz); MS  $m/z$  258 (M<sup>+</sup>), 185.

**3f**, **3f'**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  -0.10 (s, 9H), 2.56 (d, 1H,  $J = 8$  Hz), 2.64 (d, 1H,  $J = 8$  Hz), 3.54 (s, 3H), 3.56 (s, 3H), 3.69 (d, 1H,  $J = 8$  Hz), 6.84–7.33 (m, 5H); IR (neat) 1726, 2256 cm<sup>-1</sup>; MS  $m/z$  261 (M<sup>+</sup>), 188.

**3g**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  -0.03 (s, 9H), 3.04 (d, 1H,  $J = 10$  Hz), 3.50 (s, 3H), 4.05 (d, 1H,  $J = 10$  Hz), 7.25–7.58 (m, 5H); MS  $m/z$  294 (M<sup>+</sup>), 221.

**3h**; powder;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  -0.06 (s, 9H), 3.08 (d, 1H,  $J = 8$  Hz), 3.47 (s, 3H), 3.76 (s, 3H), 3.97 (d, 1H,  $J = 8$  Hz), 7.33 (ABq, 4H,  $\Delta\nu = 62$  Hz,  $J = 8$  Hz);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.2, 36.2, 52.5, 52.8, 53.8, 128.4, 129.3, 131.1, 139.3, 168.9, 169.1; IR (KBr) 1740, 2364 cm<sup>-1</sup>; Anal. Calcd. for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>SiCl: C, 54.78; H, 6.44. Found: C, 55.01; H, 6.68%.

**3i**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  -0.06 (s, 9H), 3.08 (d, 1H,  $J = 12$  Hz), 3.47 (s, 3H), 3.76 (s, 3H), 3.97 (d, 1H,  $J = 12$  Hz), 7.32 (ABq, 4H,  $\Delta\nu = 107$  Hz,  $J = 8$  Hz);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.56, 37.1, 52.2, 53.0, 108.9, 118.6, 128.4, 131.8, 147.0, 168.3, 168.5; IR (neat) 1605, 1740, 2230 cm<sup>-1</sup>; MS  $m/z$  319 (M<sup>+</sup>), 246; Anal. Calcd. for C<sub>16</sub>H<sub>21</sub>NO<sub>4</sub>Si: C, 60.16; H, 6.63; N, 4.39. Found: C, 60.25; H, 6.72; N, 4.44%.

**3j**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.07 (s, 9H), 1.72 (s, 3H), 4.33 (s, 1H), 7.10–7.40 (m, 5H); MS  $m/z$  242 (M<sup>+</sup>), 169.

**4k**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  4.37 (d, 1H,  $J = 8$  Hz), 4.59 (d, 1H,  $J = 8$  Hz), 7.28–7.39 (m, 10H); MS  $m/z$  232 (M<sup>+</sup>).

**6b**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.73 (q, 6H,  $J = 8$  Hz), 0.94 (t, 9H,  $J = 8$  Hz), 2.75 (d, 1H,  $J = 8$  Hz), 4.07 (d, 1H,  $J = 8$  Hz), 7.15–7.75 (m, 5H); IR (neat) 2226 cm<sup>-1</sup>; MS  $m/z$  270 (M<sup>+</sup>), 155.

**6c**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.05–1.28 (m, 21H), 2.98 (d, 1H,  $J = 7$  Hz), 4.18 (d, 1H,  $J = 7$  Hz), 7.31–7.49 (m, 5H); IR (neat) 2226 cm<sup>-1</sup>; MS  $m/z$  312 (M<sup>+</sup>), 155.

**8a**; oil;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ),  $\delta$  0.41 (s, 3H), 0.44 (s, 3H), 2.77 (d, 1H,  $J = 8$  Hz), 3.82 (d, 1H,  $J = 8$  Hz), 7.12–7.53 (m, 10H);  $^{13}\text{C}$  NMR (67 MHz,  $\text{CDCl}_3$ )  $\delta$  -3.16, -4.39, 25.3, 37.9, 113.3, 127.5, 127.9, 128.2, 128.5, 129.1, 129.2, 130.5, 134.2; IR (neat) 2256 cm<sup>-1</sup>;

MS  $m/z$  290 ( $M^+$ ), 155, 135; Anal. Calcd. for  $C_{18}H_{18}N_2Si$ : C, 74.57; H, 6.25; N, 9.65. Found: C, 74.57; H, 6.22; N, 9.61%.

**8b**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.33 (s, 3H), 2.36 (s, 3H), 2.76 (d, 1H,  $J = 7$  Hz), 3.82 (d, 1H,  $J = 7$  Hz), 7.16–7.71 (m, 5H), 7.28 (ABq, 4H,  $\Delta\nu = 14$  Hz,  $J = 8$  Hz); IR (neat) 2208  $cm^{-1}$ ; MS  $m/z$  304 ( $M^+$ ), 155.

**8c**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.04 (s, 3H), 0.33 (s, 3H), 2.75 (d, 1H,  $J = 8$  Hz), 3.82 (s, 3H), 4.06 (d, 1H,  $J = 8$  Hz), 7.14–7.69 (m, 5H), 7.16 (ABq, 4H,  $\Delta\nu = 23$  Hz,  $J = 8$  Hz); MS  $m/z$  320 ( $M^+$ ), 155.

**8d**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.47 (s, 3H), 0.50 (s, 3H), 3.14 (d, 1H,  $J = 7$  Hz), 3.72 (d, 1H,  $J = 7$  Hz), 7.20–7.69 (m, 5H), 7.32–7.95 (m, 7H);  $^{13}C$  NMR (67 MHz,  $CDCl_3$ )  $\delta$  -2.6, -1.3, 25.2, 37.4, 112.9, 113.3, 125.4, 126.0, 126.7, 126.8, 127.5, 128.2, 129.1, 129.8, 131.4, 131.7, 133.6, 135.7, 136.3, 136.6; IR (neat) 2205  $cm^{-1}$ ; Anal. Calcd. for  $C_{22}H_{20}N_2Si$ : C, 77.60; H, 5.92; N, 8.23. Found: C, 77.74; H, 6.28; N, 7.91%.

**8e**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.22 (s, 6H), 1.65 (d, 2H,  $J = 8$  Hz), 2.73 (d, 1H,  $J = 8$  Hz), 4.16 (d, 1H,  $J = 8$  Hz), 4.92–4.98 (m, 2H), 5.65–5.80 (m, 1H), 7.19–7.42 (m, 5H); MS  $m/z$  254 ( $M^+$ ), 155.

**8f**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.06 (s, 3H), 0.20 (s, 3H), 2.19 (s, 2H), 2.65 (d, 1H,  $J = 8$  Hz), 3.95 (d, 1H,  $J = 8$  Hz), 6.94–7.37 (m, 10H); MS  $m/z$  304 ( $M^+$ ), 155.

**12**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.04 (s, 9H), 0.36 (s, 6H), 2.71 (d, 1H,  $J = 8$  Hz), 4.05 (d, 1H,  $J = 8$  Hz), 7.17–7.37 (m, 5H);  $^{13}C$  NMR (67 MHz,  $CDCl_3$ )  $\delta$  -5.0, -4.1, -2.5, 25.7, 36.2, 113.1, 113.3, 127.2, 128.0, 128.9, 137.6; IR (neat) 700, 799, 837, 1077, 1251, 1456, 1497, 2226, 2898, 2954  $cm^{-1}$ ; MS  $m/z$  286 ( $M^+$ ), 213, 73; Anal. Calcd. for  $C_{15}H_{22}N_2Si_2$ : C, 62.87; H, 7.74; N, 9.78. Found: C, 62.81; H, 8.02; N, 9.67%.

**14**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.02 (s, 6H), 0.10 (s, 6H), 0.38 (s, 6H), 2.65 (d, 1H,  $J = 7$  Hz), 4.13 (d, 1H,  $J = 7$  Hz), 7.23–7.45 (m, 5H);  $^{13}C$  NMR (67 MHz,  $CDCl_3$ )  $\delta$  -0.53, -1.28, 0.28, 27.36, 40.19, 114.6, 129.0, 129.3; MS  $m/z$  344 ( $M^+$ ), 271.

**16**; oil;  $^1H$  NMR (270 MHz,  $CDCl_3$ ),  $\delta$  0.07 (s, 27H), 2.97 (d, 1H,  $J = 5$  Hz), 3.91 (d, 1H,  $J = 5$  Hz), 7.16–7.52 (m, 5H);  $^{13}C$  NMR (67 MHz,  $CDCl_3$ )  $\delta$  1.7, 2.7, 29.7, 34.5, 113.1, 126.5, 128.5, 129.1, 129.7; IR (neat) 2206  $cm^{-1}$ ; MS  $m/z$  402 ( $M^+$ ).

### 3.5. Effect of solvents

A nitrogen-purged solution of **1a** (20 mg, 0.13 mmol), **2a** (73 mg, 0.50 mmol), and Phen (10 mg, 0.056 mmol) in organic solvent (acetonitrile/other solvent = 8/1 v/v) was irradiated, and the yield of **3a** was then determined by GLC in a similar manner as above.

### 3.6. Effect of aromatic hydrocarbons

Nitrogen-purged solutions of **1a** (20 mg, 0.13 mmol), **2a** (73 mg, 0.50 mmol), and an aromatic hydrocarbon (0.056 mmol) in acetonitrile (4  $cm^3$ ) was irradiated, and the yield of **3a** was then determined by GLC.

### 3.7. Effect of salts

A nitrogen-purged solution of **1a** (20 mg, 0.13 mmol), **2a** (73 mg, 0.50 mmol), Phen (10 mg, 0.056 mmol), and a metal salt (0.08 mmol) in acetonitrile (4  $cm^3$ ) was irradiated, and the yield of **3a** was determined by GLC.

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