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Reaction of phenyl(trimethylsilyl)silylene with chloromethanes; Insertion into the C–Cl bond and abstraction of chlorine and HCl

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Abstract

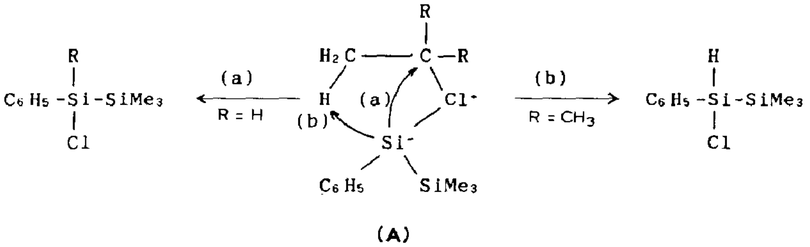
Photolysis of tris(trimethylsilyl)phenylsilane in chloromethanes, $Cl_nCX_{(4-n)}$, ($n = 1$–4, X = H, alkyl, and Cl) produced phenyl(trimethylsilyl)silylene as a major intermediate, which afforded three types of products: 1,1-dichloro-1-phenyltrimethyldisilane via abstraction of two chlorine atoms, 1-alkyl-1-chloro-1-phenyltrimethyldisilane via insertion into the C–Cl bond, and 1-chloro-1-phenyl-2,2,2-trimethyldisilane via abstraction of HCl. Possible reaction mechanisms for the formation of these products were discussed based on initial formation of an 1,2-zwitterionic intermediate. A small amount of a radical-reaction product, 2-chloro-2-phenylhexamethyltrisilane, and a product considered to be a cyclohexadienyl derivative were detected in all cases as minor products.

Introduction

A number of studies on reactions of photochemically produced silylene species have been reported [1]. Silylenes have been believed to exist as a singlet ground state undergoing only insertion reactions into certain single bonds and addition reactions to unsaturated bonds. Recently, formation of a 1,2-zwitterionic intermediate was confirmed to play an important role in the reaction of silylenes with various kinds of Lewis bases [2]. Most of the reactions of silylenes with compounds having lone pair electrons could be explained in terms of formation of this intermediate [3].

The reaction of phenyl(trimethylsilyl)silylenes (**1**) with alkyl chlorides ($R_2(Cl)CCH_3$), weak Lewis bases, yields two kinds of products; an HCl-abstraction product ($R = CH_3$) and a C–Cl-insertion product (R = H) via the zwitterionic intermediate **A** as depicted in Scheme 1 [4–6]. However, controlling factors determining the reaction path are still obscure.

In addition, a third type of product, apparently produced via abstraction of two chlorine atoms, was found in the reaction of dimethylsilylene with chloromethanes



Scheme 1

(eq. 1) [7], although phenylmethylsilylene was reported not to react with 1,2-dichloroethane [8].

$$(CH_3)_2Si: \xrightarrow[-CCl_3]{CCl_4} (CH_3)_2\dot{S}iCl \xrightarrow[-CCl_3]{CCl_4} (CH_3)_2SiCl_2 \qquad (1)$$

Thus the reaction of silylenes with C–Cl bonds seems to vary greatly depending on the nature of both the silylene itself and the substrate. Therefore, a detailed study on the factors controlling these reaction paths would be important for a better understanding of the reactivity of silylenes in general. Selection of reaction of silylene $C_6H_5(Me_3Si)Si:$ (1) with chloromethanes is relevant for this purpose, since results can be checked on the basis of information available in the previous results [4–6,9–12].

We report here that the reaction of silylene 1 with chloromethanes $Cl_nCX_{(4-n)}$ (X = Cl, alkyl, and H) yields an insertion product into the C–Cl bond, a chlorine abstraction product and an HCl abstraction product, and how these reaction paths depend on the nature of the substrate involved.

Results and discussion

GLPC and GC-MS analyses of a photo-irradiated solution of tris(trimethylsilyl)-phenylsilane (**2**, 0.14 mmol) in CCl_4 (0.5 ml)/pentane (5 ml) solution in a quartz tube under argon revealed the production of hexamethyldisilane (**3**), 1,1-dichloro-1-phenyltrimethyldisilane (**4**), and hexachloroethane (**5a**) as major products and trimethylchlorosilane (**6**) and 2-chloro-2-phenylhexamethyltrisilane (**7**) as minor ones. The time profile of the reaction is shown in Fig. 1.

Under the experimental conditions, **2** absorbs the irradiating light 120 times more effectively than CCl_4, suggesting that the excitation of **2** is far more important than primary decomposition of CCl_4 into chlorine atoms and trichloromethyl radicals [13]. The production of **3** in high yield indicates clearly that the formation of silylene species **1** is the major course of this reaction, and thus **4** is almost exclusively produced via the reaction initiated by silylene **1** (Scheme 2). The close similarity of the yields of **3** and **4** support this mechanism. However, the yield of **5a** was twice as large as the amount of **4**. Thus, a reaction producing **6** and **7**, a free-radical reaction product of **2** with a chlorine atom [14], must contribute to the formation of **5a**.

Photolyses of **2** in 1-chloropentane and 1-chloroheptane produced 1-alkyl-1-chloro-1-phenyltrimethyldisilanes (**8**) and **3** as major products, but **4**, **6**, **7** and

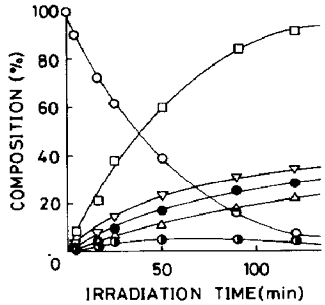
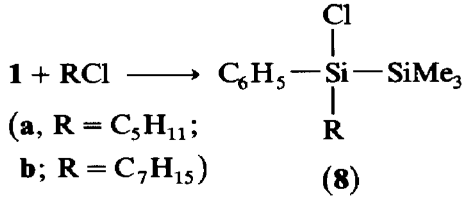


Fig. 1. Photolysis of tris(trimethylsilyl)phenylsilane (**2**) (0.14 mmol) and CCl_4 (0.5 ml) in pentane (5 ml). **2** (○), hexamethyldisilane (**3**) (▽), 1,1-dichloro-1-phenyltrimethyldisilane (**4**) (●), hexachloroethane (**5a**) (□), trimethylchlorosilane (**6**) (△), 2-chloro-2-phenylhexamethyltrisilane (**7**) (◑).

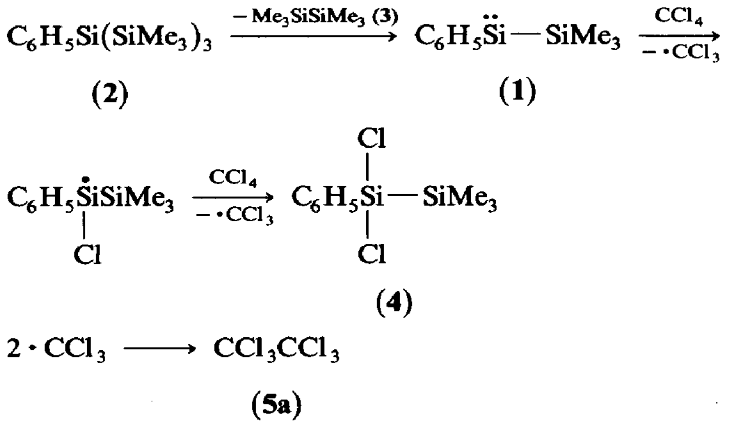
1-chloro-1-phenyl-2,2,2-trimethyldisilane (**9**) were detected as minor ones. The reaction profile (Fig. 2) excludes the path of conversion **8** to **4**. The high yield of **3** implies that the silylene **1** is the major intermediate producing **8**. The result is, thus, explained by the mechanism reported by Ishikawa et al. [4–6] that an insertion of the silylene **1** into the C–Cl bond produces **8** (eq. 2). The production of **9** in low yield will be discussed later.



$$\mathbf{1} + RCl \longrightarrow C_6H_5-\overset{\displaystyle Cl}{\underset{\displaystyle R}{Si}}-SiMe_3 \qquad (2)$$

$(\mathbf{a}, R = C_5H_{11};$ $\mathbf{b}; R = C_7H_{15})$ $(\mathbf{8})$

It is noted that an insertion into the C–Cl bond (path a in Scheme 1) and an abstraction of chlorine atoms (Scheme 2) were major processes in the reaction of the silylene **1** with alkyl chlorides and CCl_4, respectively. This dual nature of the reaction must be attributed to the absence and presence of the second chlorine atom in these substrates. To examine the effect of the extra chlorine atoms on the reaction of the silylene **1**, photolyses of **2** in some polychlorinated compounds were carried out. The results are summarized in Table 1.



$$\underset{(\mathbf{2})}{C_6H_5Si(SiMe_3)_3} \xrightarrow{-Me_3SiSiMe_3\ (\mathbf{3})} \underset{(\mathbf{1})}{C_6H_5\ddot{S}i-SiMe_3} \xrightarrow[-\cdot CCl_3]{CCl_4}$$

$$C_6H_5\underset{\displaystyle Cl}{\dot{S}i}SiMe_3 \xrightarrow[-\cdot CCl_3]{CCl_4} \underset{(\mathbf{4})}{C_6H_5\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Si}}-SiMe_3}$$

$$2\cdot CCl_3 \longrightarrow \underset{(\mathbf{5a})}{CCl_3CCl_3}$$

Scheme 2

Table 1

Photolysis of tris(trimethylsilyl)phenylsilane (2) in chloromethanes

2 (mmol)	$Cl_nCX_{(4-n)}$	Irradiation time(min)	Conversion of 2 (%)	Product yield (%) [a]						
				4	7	5	6	3	8	9
0.3	CCl_4 [b]	35	80.0	47.6	14.4	340	172	ND [d]	ND [d]	ND [d]
0.3	CCl_4 [b]	60	96.1	48.2	4.2	370.1	193	ND [d]	ND [d]	ND [d]
0.14	CCl_4 [c]	120	92.3	38.4	4.3	91.4	24	39.8	ND’[d]	ND [d]
0.14	$CHCl_3$ [b]	60	95.8	31.6	<1	17.8	[e]	43.8	15.2	ND [d]
0.15	CH_2Cl_2 [b]	60	92.3	17.4	<1	8.7	[e]	38	14.2	ND [d]
0.14	$C_5H_{11}Cl$ [b]	150	89.3	4.3	<1	ND [d]	[e]	59.2	9.3	1.7
0.1	$C_7H_{15}Cl$ [f]	70	91.8	3.2	1.3	ND [d]	[e]	52.3	19.2	2.6
0.1	Cl_3CCH_3 [f]	30	95.4	34.2	<1	[e]	[e]	53.7	[d]	4.3
0.05	Cl_2CHCH_3 [f]	30	95.1	35.1	<	[e]	[e]	62.3	(12.8) [g]	3.8
0.05	$(CH_3)_2CCl_2$ [f]	35	96.8	24.3	1.3	[e]	[e]	69.6	ND [e]	15.4
0.05	$(CH_3)_3CCH_2CHCl_2$ [f]	30	95.9	28.3	<1	[e]	[e]	49.3	(12.9) [g]	3.8
0.1	$ClCH_2CH_2Cl$ [b]	90	95.8	12.6	1.7	12.5	[e]	66.6	21.6	3.2

[a] Based on consumed 2. [b] Reaction in neat chloromethane. [c] Reaction with 0.5 ml of chloromethane in 5 ml pentane. [d] Not detected. [e] Detected by GCMS but the yield was estimated to be less than 1%. [f] Reaction with 1 ml of chloromethanes in 5 ml pentane. [g] Sum of two isomers.

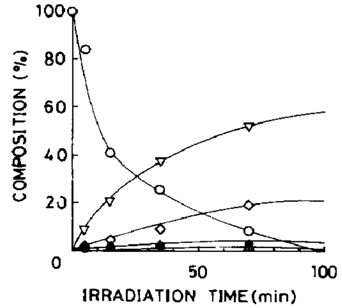


Fig. 2. Photolysis of tris(trimethylsilyl)phenylsilane (**2**) (0.1 mmol) in $C_7H_{15}Cl$(1 ml) and pentane (5 ml). **2** (○), hexamethyldisilane (**3**) (▽), 1,1-dichloro-1-phenyltrimethyldisilane (**4**) (●), 2-chloro-2-phenylhexamethyltrisilane (**7**) (△), 1-chloro-1-heptyl-1-phenyltrimethyldisilane (**8b**) (◇).

Photolysis of **2** in $CHCl_3$ yielded **4**, 1-chloro-1-dichloromethyl-1-phenyltrimethyldisilane (**8c**), 1,1,2,2-tetrachloroethane (**5b**) in addition to **3** as major products; **6** and **7** were very minor products (< 1%). The production of **3** in high yield and **6** in low yield indicates again that silylene **1** was the only main intermediate producing the above major products. The reaction profile, shown in Fig. 3, indicates that both **4** and **8c** are primary products and that the conversion of **8c** into **4** is not important. Thus the ratio of yields of **4** to **8c** (ca. 2/1) reflects the ratio of the two reaction rates of silylene **1**, i.e., the chlorine abstraction reaction from $CHCl_3$ vs. the insertion reaction into the C–Cl bond (Scheme 3). Here, one may suspect that **5b**, the dimerization product of dichloromethyl radicals (eq. 3), would be produced via

$$2\cdot CHCl_2 \longrightarrow \underset{(\mathbf{5b})}{Cl_2CH{-}CHCl_2} \qquad (3)$$

primary photo-dissociation of $CHCl_3$. But the fact that **2** absorbs most of the irradiation light (> 200 times more than $CHCl_3$ at 253.7 nm) in the reaction system excludes the mechanism. A silylene mechanism as shown in Scheme 3 could explain the formation of all the products.

Photolysis of **2** in CH_2Cl_2 also yielded **3**, **4**, 1-chloro-1-chloromethyl-1-phenyltrimethyldisilane (**8d**), and 1,2-dichloroethane (**5c**) as major products. The ratio of the yields of the chlorine abstraction product **4** to the C–Cl insertion product (**8d**) is

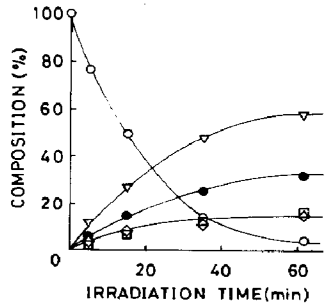
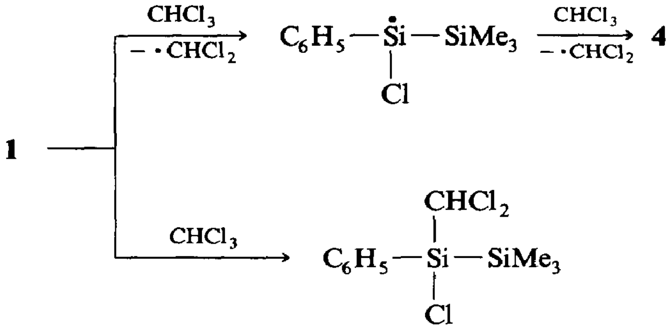


Fig. 3. Photolysis of tris(trimethylsilyl)phenylsilane (**2**) (0.14 mmol) in $CHCl_3$ (5 ml). (**2**) (○), hexamethyldisilane (**3**) (▽), 1,1-dichloro-1-phenyltrimethyldisilane (**4**) (●), 1,1,2,2-tetrachloroethane (**5b**) (□), 1-chloro-1-dichloromethyl-1-phenyltrimethyldisilane (**8c**) (◇).



(8c)

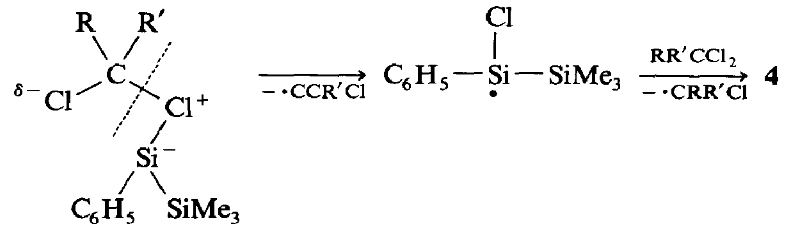
Scheme 3

smaller than that in the reaction with $CHCl_3$. Both experiments therefore imply that the formation of **4** may be attributed to the presence of at least a second chlorine atom in the substrate. As shown in Table 1 it is obvious that the yield of **4** increases with increasing number of chlorine atoms in the substrate.

The mechanistic interpretation of both the C–Cl bond-insertion and the HCl abstraction has already been given in Scheme 1 [4]. Although the factor(s) determining the reaction path have not been discussed [4–6], the formation of the HCl abstraction product can undoubtedly be attributed to the presence of an alkyl moiety on the same carbon atom that has the chlorine atom; as shown in Table 1 the production of **9** was observed only when a chloromethane had an alkyl group. This fact suggests that a steric repulsion between the negatively charged silicon and the alkyl moiety is the factor driving the reaction to path (b) in Scheme 1. Here, it should be noted that both reactions in Scheme 1 are intramolecular processes.

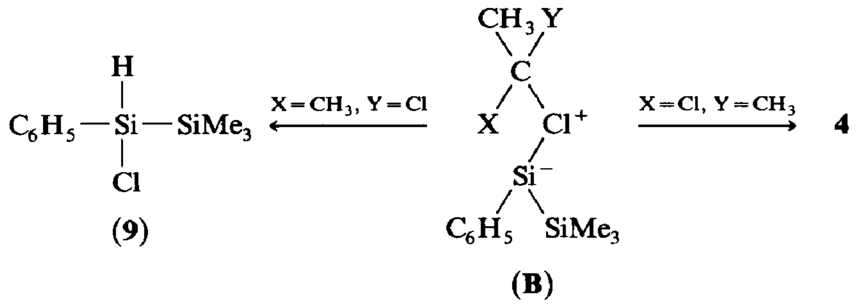
Intramolecular attack at the second chlorine atom by the negatively charged silicon in the zwitterionic intermediate, however, seems inadequate as a mechanism for the formation of **4**, since the electronegative chlorine atom of the chloromethyl moiety must repel the anionic silicon atom. Instead, we now consider this electrostatic repulsion as a driving force of a C–Cl bond rupture resulting in intermediary formation of the chloromethyl and chlorinated silyl radicals (Scheme 4). The second step of this mechanism is, in contrast to the steps in Scheme 1, an intermolecular process.

From the above discussion it is concluded that the presence of an alkyl group and an extra chlorine atom in the substrate is the factor determining the product originating from HCl abstraction and chlorine abstraction as in Schemes 1 (path b)



(B)

Scheme 4



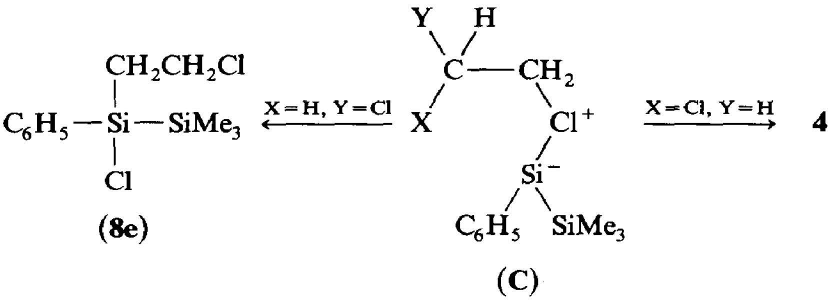
Scheme 5

and 4, respectively. On the basis of this conclusion, a reaction of **1** with 2,2-dichloropropane is predicted to afford both an intramolecular HCl abstraction product and an intermolecular chlorine abstraction product, since two methyl groups and two chlorine atoms would constitute the determining factors of Schemes 1 (path b) and 4, respectively. Indeed, photolysis of **2** with 2,2-dichloropropane in pentane yielded **4** and **9**, the later product being also reported to be formed in the reaction of **1** with 2-chloro-2-methylpropane [6]. Furthermore, the production of **4** and **9** by the reaction of **1** with 1,1,1-trichloroethane in pentane confirmed the above prediction. The results of the reactions of **1** with 2,2-dichloropropane and 1,1,1-trichloroethane indicate clearly that the relative yields of **4** and **9** depend on the number of alkyl groups and chlorine atoms in the substrates.

Here, products **4** and **9** reflect the mutual disposition of the second chlorine atom and the methyl group in the intermediate **B**. When a chlorine atom occupies the position X the intermediate **B** decomposes (Scheme 5) into chloromethyl radicals and chlorosilyl radicals which finally produce dimer **5** and chlorine abstraction product **4**, respectively. When a methyl group occupies the position X, the anionic silicon atom abstracts a hydrogen atom (path b in Scheme 1), instead of attacking the carbon atom to which the cationic chlorine is attached.

The probability of a methyl group occupying position X in **B** (Scheme 5) is twice that for a chlorine atom in the reaction with 2,2-dichloropropane and half that in the reaction of 1,1,1-trichloroethane. This predicts that **9** and **4** are predominant products in the reaction with 2,2-dichloropropane and 1,1,1-trichloroethane, respectively. The higher yield of **9** in 2,2-dichloropropane than in 1,1,1-trichloroethane indicates the importance of the steric effect due to methyl groups. However, **4** is the major product even in the reaction with 2,2-dichloropropane, indicating that repulsion of electrons by the chlorine atom is more influential in determining the product than the steric effect of the methyl group.

If the electronic repulsion causes a rapid rotation around the C–Cl bond in intermediate **B**, the probability of formation of a conformer in which the methyl group occupies the position X would increase with increasing number of chlorine atoms of the substrate and would result in an increase of the yield of **9**. As described above, the result in Table 1 is in contrast to this expectation, viz., the yield of **9** is smaller in the reaction with 1,1,1-trichloroethane than that with 2,2-dichloroethane. The electronic repulsion thus causes fast C–Cl bond rupture rather than change of conformation. Therefore, the number of chlorine atoms and methyl groups would



Scheme 6

give an indication of the likely site where the substrate would be attacked by silylene **1** when forming the intermediate **B**.

Concerning the mechanism for the formation of C–Cl bond insertion product, it is noteworthy that the product is produced only when the substrate has a hydrogen atom at the same carbon atom as that to which the chlorine atom is attached (Table 1). The hydrogen atom at position X has neither steric nor electronic repulsion, so that the anionic silicon attacks the carbon atom attached to the positively charged chlorine atom yielding the C–Cl bond insertion product.

Interestingly, the second chlorine atom at a vicinal carbon atom has similar influence on the determination of reaction product to that at a geminal one in chloromethanes; photolysis of **2** in 1,2-dichloroethane yielded both **4** and an insertion product, 1-chloro-1-(2-chloroethyl)-1-phenyltrimethyldisilane (**8e**). This result suggests that an intermediate **C** also plays an important role in the determinant of a reaction path (Scheme 6).

The ratio of yields of **4** to **8** in the reaction with 1,2-dichloroethane (0.58) and 1,1-dichloroethane (2.74) must reflect the efficiency of the electronic repulsion by the chlorine atoms at vicinal and geminal positions; the chlorine atom at the geminal position is about 5 times more effective in repulsion than that at the vicinal position.

As shown in Table 1, nearly the same yields of **9**, the HCl abstraction product, were observed in the reactions of **2** with primary alkyl chlorides (chloromethanes with one alkyl group); all of the alkyl groups appear to have the similar magnitude of steric hindrance per one alkyl moiety in intermediate **B**. An alkyl group at position X in intermediate **B** (Scheme 5) protects the carbon atom to which the positively charged chlorine atom is attached from intramolecular attack by the anionic silicon, which therefore ultimately attacks a hydrogen atom of the alkyl group at position X.

Finally, we have to note that **7** and a product having the same molecular ion as **2** but showing a different mass-spectral fragmentation pattern were detected in the GC-MS analyses of all photolysis experiments. The former suggests that photolysis of **2** inevitably involves a homolysis path [14]. The latter, which is considered to be a cyclohexadienyl derivative as in the photolysis of phenyldisilanes [15], suggests the concominant formation of a silene species in the photolysis of **2**.

Experimental

Instrument. GLPC analysis was made with an HP 5890A machine equipped with a flame ionization detector, and a quartz capillary column (J & W DB5 30 m, ϕ

0.53 mm) was used. Quantities of the products were calculated based on their areas using an HP 3396A integrator. Mass spectra were taken with a JEOL DX302 gaschromatograph-mass spectrometer (ionized at 70 eV). UV spectra were measured with a Hitachi 323 spectrophotometer. A 20 W low pressure Hg lamp (SEN UVB-20) emitted light at 253.7 nm (determined by a UNISOKU PCS-400 photon-counting spectrophotometer). Identification of the products was mainly based on mass spectra or on gas-chromatographic retention times. Boiling points were uncorrected. A200 J (200 W) ultrasonic cleaner from Kaijo Electronic K.K. was used. Preparative gas-chromatography was carried out using a Varian Aerograph 1700 equipped with a thermal conductivity detector and a 10′ × 3/8″ aluminum column packed with 30% SE 30 on Celite 545.

Preparation of tris(trimethylsilyl)phenylsilane (2). Compound **2** was prepared by modifying the reported method [5]. Into a 1 l flask immersed in an ultrasound cleaner bath was placed 500 ml of dried THF and lithium tips. A mixture of phenyltrichlorosilane and trimethylchlorosilane (1/3.5 molar ratio) was added dropwise into this flask with agitating by ultrasound at $< 10\,^\circ$C. Work-up followed by distillation gave **2** in 51% yield (b.p. 132°C/1.5 Torr (Lit. [5] 135–137°C/3 Torr)); MS (m/z, ion, %): (324, M^+, 39.5), (309, $\mathrm{M-CH_3}$, 15), [251, $\mathrm{M-SiMe_3}$, 20.5], (236, 18), (174, 100), (135, $C_6H_5SiMe_2$, 55), (73, $SiMe_3$, 72.6). Compound **2** containing some tetrakis(trimethylsilyl)silane was purified by silica gel column chromatography with hexane eluent (purity > 99.5%).

Reagents. Chloromethanes were dried over Molecular Sieves and then used after distillation. THF and cyclohexane were purified by distillation after drying with lithium aluminium hydride. Other reagents were of commercial grade.

General procedure of photolysis of 2 in chloromethanes and determination of products. A defined amount of **2**, octamethylcyclotetrasiloxane to be used as an internal standard for GLPC analysis, a chloromethane and pentane were placed in a quartz vessel with a Teflon valve and a silicon rubber septum, from which aliquots were periodically removed for GLPC analysis. After the reaction vessel had been deaerated by conventional freeze-and-thaw cycles on a vacuum line, argon gas was introduced (ca. 1.1 atm). The sample was subjected to photo-irradiation for a defined time. The irradiated sample was subjected to GLPC and GC-MS analysis. Finally the sample was treated by a methyl alcohol/pyridine mixture to convert the Si–Cl moiety to $\mathrm{Si{-}OCH_3}$ for mass spectral identification.

Products **4** [16] (NMR δ 0.27(s), 9H, δ 7.4–7.8(m), 5H, MS: (m/z, ion, %), (248, M^+, 8.2), (135, $C_6H_5SiMe_2$, 18.6), (73, $SiMe_3$, 100)) and **7** (NMR: δ 0.19(s), 18H, δ 7.35–7.76(m), 5H. MS: (286, M^+, 4.5), (193, 61.3), (178, $C_6H_5SiSiMe_3 = \mathrm{M} - Me_3SiCl$, 84.4), (163, $C_6H_5SiSiMe_2$, 20.6), (135, $C_6H_5SiMe_2$, 100), (105, 16.5), (73, $SiMe_3$, 50.2)) were isolated by preparative GLPC from a reaction mixture of **2** and *N*-chlorosuccinimide and used as authentic materials. Treatment of **4** and **7** with methyl alcohol and pyridine yielded 1,1-dimethoxy-1-phenyltrimethyldisilane [17] (MS: (240, M^+, 7.8), (225, $M-CH_3$, 100), (195, $C_6H_5Si(OH)SiMe_3$, 81), (167, $M-SiMe_3$, 75.5), (135, $C_6H_5SiMe_2$, 55.2), (107, 31.3), (91, $C_6H_5CH_2$, 47.3), (73, $SiMe_3$, 35.0)) and 2-methoxy-2-phenylhexamethyltrisilane (MS: (282, M^+, 19.2), (267, $\mathrm{M-CH_3}$, 73.7), (209, $M-SiMe_3$, 23.4), (193, $C_6H_5Si(CH_3)SiMe_3$, 35.2), (178, $C_6H_5SiSiMe_3$, 100), (163, $C_6H_5SiSiMe_2$, 52), (135, $C_6H_5SiMe_2$, 78.8)), respectively. The other products were not isolated by preparative GLPC but identified and measured from their MS spectra and the MS spectra of their methoxylated derivatives.

Photolysis of 2 and CCl_4 in pentane. GLPC and GC-MS analysis of an irradiated mixture of **2** (0.14 mmol) and CCl_4 (0.5 ml) in pentane (5 ml) indicated the production of **3**, **4**, and **5a** (MS: (199, $M-Cl$, 54.5%), (164, $M-Cl_2$, 31.8%), (129, C_2Cl_3, 11.8%), (117, CCl_3, 100)) as major product and **6** and **7** as minor ones. Aliquots of the irradiation mixture were removed periodically from the quartz vessel for GLPC analysis. The progress of reaction is shown in Fig. 2.

Photolysis of 2 in $C_5H_{11}Cl$. GLPC and GC-MS analysis of an irradiated mixture of **2** (0.14 mmol) in $C_5H_{11}Cl$ (5 ml) identified **3**, **8a** (MS: (284, M^+, 8), (269, $M-CH_3$, 5), (176, 44), (148, 44), (135, $C_6H_5SiMe_2$, 72), (105, 28.3), (98, 100), (73, $SiMe_3$, 83.4)) and **4**, as the main products. Small amounts of **9** and **7** and, after treatment with methyl alcohol/pyridine, their methoyxlated derivatives were also found (MS spectra; see section of $(CH_3)_2CCl_2$).

Photolysis of 2 in $C_7H_{15}Cl$. GLPC and GC-MS analyses of an irradiated mixture of **2** (0.1 mmol) and $C_7H_{15}Cl$ (0.5 ml) in pentane (5 ml) identified **3** and **8b** (MS: (312, M^+, 6.2), (297, $M-CH_3$, 2.7), (175, 72.5), (141, 57.5), (135, $C_6H_5SiMe_2$, 79.0), (126, 48.4)). A small amount of **7** was also found by GC-MS analysis. Treatment of the mixture with methyl alcohol and pyridine gave 1,1-dimethoxy-1-phenyltrimethyldisilane, 2-methoxy-2-phenylhexamethyltrisilane, and 1-heptyl-1-methoxy-1-phenyltrimethyldisilane (MS: (308, M^+, 4.2), (293, $M-CH_3$, 8.2), (235, $M-SiMe_3$, 9.6), (195, 100), (137, 69.0), (135, 24.3), (107, 18.6), (73, 13.4)). Small amounts of **9** and its methoxylated product were also observed (MS spectra; see section of $(CH_3)_2CCl_2$).

Photolysis of 2 in $CHCl_3$. GLPC and GC-MS analyses of a photolysis mixture of **2** (0.14 mmol) in $CHCl_3$ (5 ml) identified the following products: **3**, **4**, **8c** (MS: (296, M^+, 0.16), (213, $M-SiMe_2Cl$, 17.8), (188, $M-Me_3SiCl$, 26.3), (135, $C_6H_5SiMe_2$, 40.0), (73, $SiMe_3$, 100)), and **5b** (MS: (166, M^+, 11.4), (83, $CHCl_2$, 100)). Treatment of the irradiated mixture with methyl alcohol and pyridine gave 1,1-dichloromethyl-1-methoxy-1-phenyltrimethyldisilane (MS: (292, M^+, 4.1), (209, $M-SiMe_2Cl$, 92), (184, $M-Me_3SiCl$, 45), (135, $C_6H_5SiMe_2$, 60), (91, $C_6H_5CH_2$, 51), (73, $SiMe_3$, 100), (59, 78)) and 1,1-dimethoxy-1-phenyltrimethyldisilane. A small amount of **7** (< 1%) was detected by GC-MS analysis.

Photolysis of 2 in CH_2Cl_2. GLPC and GC-MS analyses of an irradiated mixture of **2** (0.15 mmol) in CH_2Cl_2 (5 ml) indicated the presence of **3**, **4**, 1,2-dichloroethane, and **8c** (MS: (262, M^+, 0.2), (247, $M-CH_3$, 6.0), (211, 10.6), (154, 57.6), (135, $C_6H_5SiMe_2$, 25.1), (105, C_6H_5Si, 11.1), (91, $C_6H_5CH_2$, 62.5), (73, $SiMe_3$, 100)). Treatment of the mixture with methyl alcohol and pyridine gave 1-chloromethyl-1-methoxy-1-phenyltrimethyldisilane (MS: (258, M^+, 10.1), (243, $M-CH_3$, 30.3), (207, 83.3), (150, 38.7), (135, $C_6H_5SiMe_2$, 67.8), (73, $SiMe_3$, 100)).

Photolysis of 2 and $CH_3C(Cl)_2CH_3$ in pentane. GLPC and GC-MS analyses of an irradiated mixture of **2** (0.05 mmol) and $CH_3CCl_2CH_3$ (0.5 ml) in pentane (5 ml) indicated the formation of **3**, **4** and **9** [9] (MS: (214, M^+, 10), (199, $M-CH_3$, 3.1), (135, $C_6H_5SiMe_2$, 14.8), (121, 6.2), (105, C_6H_5Si, 8.8), (73, $SiMe_3$, 100)). Treatment of the mixture with methyl alcohol and pyridine gave 1,1-dimethoxy-1-phenyltrimethyldisilane and 1-methoxy-1-phenyl-2,2,2-trimethyldisilane (MS: (210, M^+, 9.4), (195, $M-CH_3$, 100), (179, 11.8), (167, 19), (136, 23.3), (107, 15.0), (73, 63.3), (59, 62.8)).

Photolysis of 2 and Cl_3CCH_3 in pentane. GLPC and GC-MS analyses of the irradiated mixture of **2** (0.05 mmol) and Cl_3CCH_3 (0.5 ml) in pentane (5 ml) indicated the presence of **3**, **4**, and **9**. Treatment of the irradiated mixture with methyl alcohol and pyridine yielded 2-methoxy-2-phenylhexamethyltrisilane and 1-methoxy-1-phenyl-2,2,2-trimethyldisilane.

Photolysis of 2 in Cl_2CHCH_3. GC-MS analysis of an irradiated mixture of **2** (0.05 mmol) and Cl_2CHCH_3 (0.5 ml) in pentane (5 ml) identified **3**, **4**, **7** ($< 1\%$), **9**, 2,3-dichlorobutane (MS: (125, $M - H$, 19.5), (97, $M - C_2H_5$, 100), (63, $CHClCH_3$, 20)) and two products having molecular ions corresponding to the insertion product of **1** into the C–Cl bond, 1-chloro(1-chloroethyl)-1-phenyltrimethyldisilane, (product of the shorter retention time, MS: (276, M^+, 0.6), (261, $M - CH_3$, 4.5), (236, 4.7), (213, $M - ClCHCH_3$, 16.1), (168, $M - Me_3SiCl$ 85.1), (140, C_6H_5SiCl, 66.8), (135, $C_6H_5SiMe_2$, 77.8), (105, C_6H_5Si, 40.8), (73, $SiMe_3$, 100)) and the product of the longer retention time (MS: (276, M^+, 1.0), (261, $M - CH_3$, 3.8), (211, $M - ClCHCH_3$, 14.1), (168, $M - Me_3SiCl$, 100), (140, C_6H_5SiCl, 71), (135, $C_6H_5SiMe_2$), (105, C_6H_5Si, 41.5), (73, $SiMe_3$, 83.3)). Treatment of the mixture with methyl alcohol and pyridine yielded methoxylated **4**, **7**, **9** and a product attributed as 1-(1-chloroethyl)-1-methoxy-1-phenyltrimethyldisilane (MS: 272, M^+, 7.1), (275, $M - CH_3$, 36.8), (209, $M - CHClCH_3$, 94.0), (164, 88.0), (135, $C_6H_5SiMe_2$, 95.7), (73, $SiMe_3$, 70.7), (59, $SiMe_2H$, 100)). Since the insertion product is expected to have asymmetric centres at silicon and carbon atoms, the two products having similar MS spectra were tentatively attributed to the stereoisomers.

Photolysis of 2 and $CHCl_2CH_2C(CH_3)_3$ in pentane. GLPC and GC-MS analyses of an irradiated mixture of **2** (0.05 mmol) and $CHCl_2CH_2C(CH_3)_3$ (0.5 ml) in pentane (5 ml) identified **3**, **4**, **7** ($< 1\%$), **9** and compounds attributable as products of the insertion of **1** into the C–Cl bond of $CHCl_2CH_2C(CH_3)_3$ (MS: (233, 2.8), (224, $M - SiMe_3$), (213, $M - CHClCH_2C(CH_3)_3$, 23.4), (167, 100), (135, $C_6H_5SiMe_2$, 26.1), (105, C_6H_5Si, 12.8), (73, $SiMe_3$, 55.7)). Two GC peaks having MS spectra corresponding to the dimer of 1-chloro-3,3-dimethylbutyl radicals were also detected. Treatment of the mixture with methyl alcohol and pyridine yielded methoxylated derivatives of **7**, **4**, **9** and compounds attributable as 1-(1-chloro-3,3-dimethylbutyl)-1-methoxy-1-phenyltrimethyldisilane (MS: (328, M^+, 0.2), (313, $M - CH_3$, 1.5), (271, 6.8), (229, 9.3), (209, 57.1), (163, 100), (135, 44.1), (73, 233.7)).

Photolysis of 2 in $ClCH_2CH_2Cl$. GLPC and GC-MS analyses of an irradiated-mixture of **2** (0.1 mmol) and $ClCH_2CH_2Cl$ (5 ml) indicated the presence of **3**, **4**, **7** ($< 2\%$), **8e** (MS: (213, $M - CH_2CH_2Cl$, 3.0), (168, 29.0), (155, 5.8), (140, 71.1), (135, $C_6H_5SiMe_2$, 45.5), (105, C_6H_5Si, 12.5), (73, $SiMe_3$, 100)) and **9**. Treatment of the irradiated mixture with methyl alcohol and pyridine showed mass spectra of the corresponding methoxylated product of **4**, **7** and **8e** (MS; (272, M^+, 1.6), (229, $M - CH_3 - C_2H_4$, 80.3), (171, $C_6H_5SiCl(OCH_3)$, 83.6), (136, 81.6), (135, $C_6H_5SiMe_2$, 79.8), (73, $SiMe_3$, 80.6), (59, 100)) and **9**.

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