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Photolysis of Bis(organosilyl)imines

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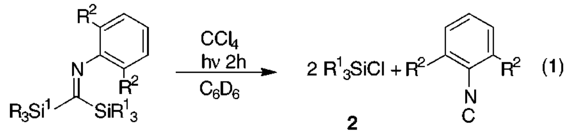
Photolysis of acylsilanes involves two types of reactions.[1] One is a homolytic scission of the silicon−carbonyl bond in carbon tetrachloride to afford a pair of radicals.[2] The organosilyl radical thus generated abstracts a chlorine atom from carbon tetrachloride to yield an organosilyl chloride. Another reaction is a migration of the organosilicon group to the carbonyl oxygen in methanol, resulting in the formation of an acetal via the corresponding silyloxycarbene intermediate.[3]

However, photolysis of bis(organosilyl)ketones is different from that of the acylsilanes. For instance, bis(triphenylsilyl)ketone, which is a red-violet solid with UV absorption around 550 nm, is not stable in solution and rapidly undergoes photolysis in solution to afford hexaphenyldisilane and carbon monoxide.[4]

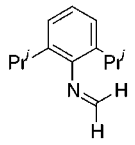
On the other hand, *N*-substituted bis(organosilyl)imines, the preparation of which has been found by us,[5] are stable not only in the solid state but also in solution. Bis(organosilyl)imines also exhibit red-shifted UV absorption around 400 nm with relatively large extinction coefficients (150−200), which is ascribed to n-π* absorption.[6] Now, we find that bis(organosilyl)imines undergo photolysis in a different manner from the ketone analogue. Herein, we report new photochemistry of 2,6-xylyl bis(organosilyl)imines.

A high-pressure mercury lamp was used as a light source for all the photoreactions. UV irradiation of bis(organosilyl)imine (**1**) for 2 h in benzene-d_6 containing carbon tetrachloride led to a complete conversion, giving a 2:1 mixture of organosilyl chloride and the corresponding isocyanide together with its derivatives (eq 1). In the reaction of **1c,** the minor byproducts **4c** (5.9%),[7] **5c** (5.6%),[7] and **6c**[8] (6.3%)[7] were separated and identified by GC-MS analysis. The present reaction did not proceed in refluxing benzene containing carbon tetrachloride without irradiation. Photolysis of some bis(organosilyl)imines having various silicon substituents (SiR^1_3) and alkyl groups (R^2) is summarized in eq 1.



2 **3**

1a SiR^1_3 = $SiMe_2Ph$, R_2 = *i*-Pr
b $SiMe_2Ph$ Me
c $SiMe_3$ *i*-Pr
d $SiMe_3$ Me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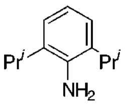
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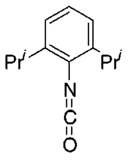
6c

These results might suggest that the photolysis of *N*-substituted bis(organosilyl)imines involved a stepwise elimination of the two organosilyl radicals.[9] However, this hypothesis was ruled out by following results. No reaction of bis(silyl)imines took place under irradiation for several hours in benzene and acetonitrile. The photolysis of the bis(organosilyl)imines in the presence of styrene and methyl methacrylate in benzene-d_6 did not give any adducts. Radical trapping experiments with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) during the photolysis have also failed.

In contrast, irradiation of **1b** with alkyl iodides in benzene-d_6 gave organosilyl iodide, which was readily hydrolyzed to the corresponding siloxane, along with the aromatic isocyanide. The photolysis of **1b** with ethyl iodide in the presence of TEMPO afforded dimethylphenylsilyl-TEMPO adduct **7** together with a small amount of dimethylphenylsilyl iodide **8** and ethyl-TEMPO adduct **9** (eq 2). The same reaction proceeded with isopropyl iodide and iodobenzene. No charge-transfer complex formation in the ground state was observed between **1b** and iodobenzene.[10]

An exciplex intermediate may be involved prior to the reaction with carbon tetrachloride or alkyl iodides. An exciplex formation has also been proposed for the photolysis of acylsilanes.[11] Organic halides were not decomposed by irradiation under the same condition, suggesting that the reaction of **1** was not promoted by the photolysis of organic halides.

Photoinduced electron transfer (PET) may be involved after the exciplex formation.[12] Single electron transfer could occur from bis(organosilyl)imines to organic halide

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[7] The yield is based on GC analysis. The isocyanide **3c** was produced in 82.2% yield.

[8] The formation of aromatic isocyanates by photochemical oxidation with an aromatic isocyanides has been reported. Boyer, J. H.; Ramakrishnan, V. T.; Srinivasan, K. G.; Spak, A. J. *Chem. Lett.* **1981**, 43−46.

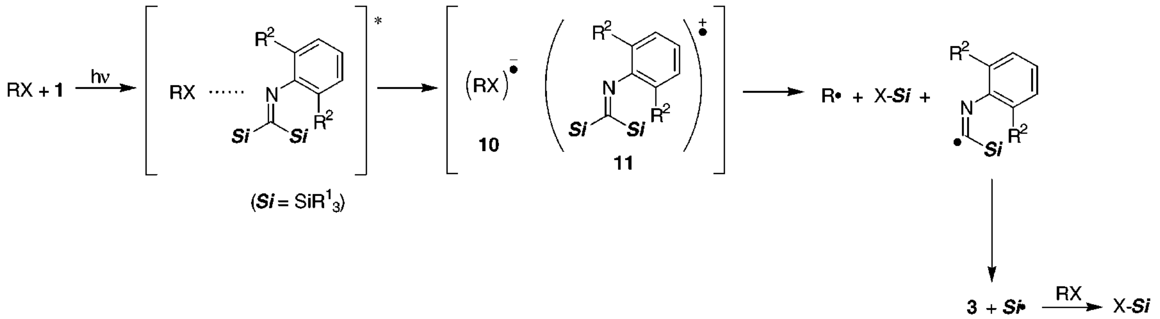
[9] The formation of alkyl radicals and isocyanides from imidoyl radicals has been reported. (a) Kaba, R. A.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6202−6203 (b) Nanni, D.; Pareschi, P.; Tundo, A. *Tetraheadron Lett.* **1996**, *37*, 9337−9340.

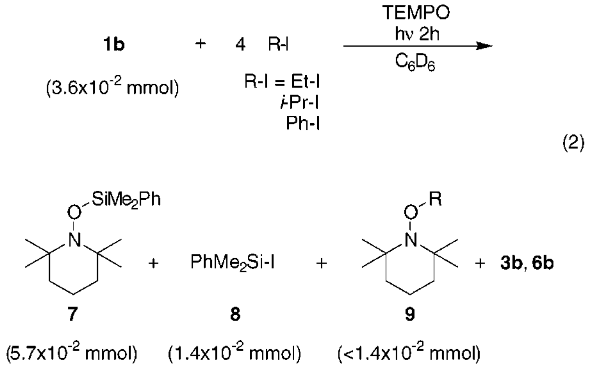
[10] UV spectra of **1b** did not depend on polarity of solvent used. In addition, no UV change was observed when iodobenzene was added to a solution of **1b** in acetonitrile and *n*-hexane. The mathematical sum of UV spectra of **1b** and iodobenzene measured separately was in good agreement with UV spectra of a mixture of **1b** and iodobenzene.

[11] Porter, N. A.; Iloff, P. M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6200−6202.

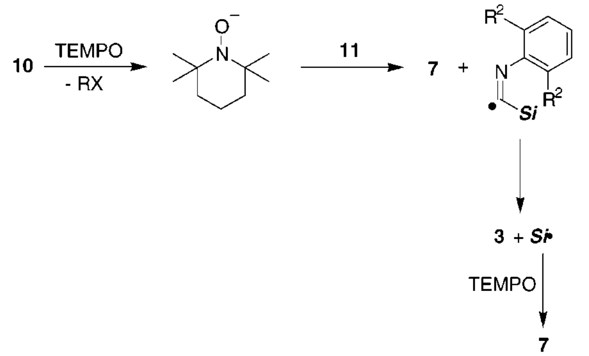
10.1021/jo991443s CCC: $19.00

Scheme 1





Scheme 2



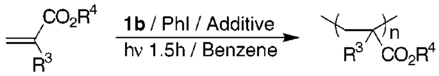
to yield pairs of an anion radical **10** and a cation radical **11** (Scheme 1). The former would give an alkyl radical (R•) and a halide anion, which would produce 1 equiv of organosilyl halide by an attack at the cationic organosilicon in **11**.[13] An imidoyl radical thus generated gives an isocyanide **3** and an organosilyl radical,[9] which abstracts a halogen atom to afford another 1 equiv of organosilyl halide.[14]

The photolysis of **1** proceeds quantitatively in the presence of benzoquinone in stead of organic halides, giving a complex mixture containing isocyanide derivatives **3**–**6** and hydroquinone silyl ethers. However, no reaction took place when a benzene-d_6 solution of benzoquinone in the absence of **1** was irradiated under the same condition.

The formation of nearly 2 equiv of **7** in the photolysis of **1b** with ethyl iodide in the presence of TEMPO may suggest that TEMPO is operating as an electron acceptor in the PET mechanism[15] (Scheme 2). Single electron transfer from **10** to TEMPO could occur to yield 2,2,6,6-tetramethylpiperidine-1-oxide, which can afford 1 equiv of **7** by a reaction with a cationic organic silicon. On the other hand, the imidoyl radical can give the isocyanide and the organosilyl radical, which affords another 1 equiv of **7** by trapping the silyl radical with TEMPO.

The organosilyl radical as well as the alkyl radical thus generated photochemically promoted radical polymerization of methyl methacrylate (MMA) (eq 3). Irradiation of a mixture of **1b** (0.1 mmol) and iodobenzene (0.4 mmol) in MMA (1.0 mL) and benzene (2.0 mL) for 1.5 h produced poly(methyl methacrylate) (PMMA) in 9% yield (Table 1, entry 1). The low yield may be due to inhibition of the polymerization by the isocyanide generated during irradiation. The inhibition by 2,6-xylyl isocyanide was also observed in the polymerization of MMA initiated by AIBN. The radical polymerization of MMA (20 mmol) with 0.08 mmol of AIBN in the presence of 4 mmol of 2,6-xylyl isocyanide was carried out at 65 °C for 15 min, affording only trace amounts of PMMA (0.2%, M_n = 2.17×10^4, M_w/M_n = 1.25).[16]

Table 1. Photoinduced Polymerization Initiated by 1b and PhI



(3)

entry	R^3	R^4	additive	yield (%)	M_n ($\times 10^4$)	M_w/M_n
1	Me	Me	none	9	0.95	1.55
2	Me	Me	CuBr	20	2.31	1.33
3	Me	Me	TEMPO	np[a]		
4	H	Me	CuBr	50	2.87	1.82
5	Me	CH_2Ph	CuBr	28	1.00	2.62

[a] No polymerization.

Irradiation of MMA in the presence of TEMPO did not give PMMA (Table 1, entry 3), indicating that this polymerization reaction proceeded in a radical fashion. Irradiation of MMA in the presence of iodobenzene without bis(organosilyl)imines did not induce the polymerization either, suggesting that the photolysis of bis(organosilyl)imines was crucial for an initiation of the polymerization reaction. Intervention of organosilyl radical as well as phenyl radical, which worked as an initiating species, was confirmed by ^{1}H NMR analysis of PMMA indicating that both of the dimethylphenylsilyl

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(12) PET reactions of organosilanes are well-known. For example, see Steinmetz, M. G. *Chem. Rev.* **1995**, *95*, 1527–1588 and references therein.

(13) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973–8975.

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(15) (a) Belonogova, O. V.; Likhtenstein, G. I.; Krinichnyi, V. I. *J. Photochem. Photobiol. A: Chem.* **1997**, *107*, 35–42. (b) Vogel, V. R.; Rubtsova, E. T.; Likhtenstein, G. I.; Hideg, K. *J. Photochem. Photobiol. A: Chem.* **1994**, *83*, 229–236 and references therein.

(16) In the absence of 2,6-xylyl isocyanide, PMMA was obtained in 7% yield (M_n = 4.75×10^4, M_w/M_n = 1.08) under the same condition.

group and the phenyl group were included in the ratio of 60:40, respectively, as terminal groups of the PMMA polymer chains.

It is worthwhile to note that the yield of PMMA produced in the photochemically promoted radical polymerization was increased up to 20% in the presence of copper(I) salts (Table 1, entry 1 and 2). Probably, isocyanide generated was trapped and deactivated by complexation with Cu(I). No polymerization of MMA occurred in the presence of **1b** and iodobenzene together with CuBr at ambient temperature without irradiation. Similarly, the photochemically induced radical polymerization of methyl acrylate and benzyl methacrylate proceeded in the presence of **1b**, iodobenzene, and CuBr in benzene, giving poly(methyl acrylate) and poly(benzyl methacrylate) in 50% and 28% yield, respectively (Table 1, entry 4 and 5).

In summary, bis(organosilyl)imines, which are stable toward UV light unlike the ketone analogue, undergo photolysis in the presence of carbon tetrachloride and organic iodides to afford organosilyl halides and isocyanides. PET mechanism is proposed for the reaction. Generation of the organosilyl radical as well as the alkyl radical was demonstrated by polymerization of acrylates and methacrylates.

Experimental Section

General Methods. All photochemical reactions were carried out with RIKO UVL-100HA (100W) and Pyrex glassware. Reagents and solvents were handled with standard syringe techniques. Solvents were distilled in the presence of appropriate drying agents before use. Methyl methacrylate, methyl acrylate, and benzyl methacrylate were distilled prior to use. Other commercially available reagents were used without further purification.

Photolysis of 1 with Carbon Tetrachloride in Benzene-*d*$_6$. In benzene-d_6 (0.8 mL) were dissolved **1c** (0.0360 mmol) and carbon tetrachloride (0.144 mmol). The solution was irradiated under air for 2 h in a water bath at ambient temperature. Trimethylsilyl chloride and isocyanide derivatives **3c**−**6c** were observed by ^{1}H NMR and GC-MS. Photolysis of **1a**, **1b**, and **1d** were carried out according to the same procedure.

Photolysis of 1b with Alkyl Iodide in the Presence of TEMPO. In benzene-d_6 (0.8 mL) were dissolved **1b** (0.0358 mmol), ethyl iodide (0.143 mmol), and TEMPO (0.0716 mmol). The solution was irradiated under nitrogen atmosphere for 2 h in a water bath at ambient temperature. Structures of the products were identified by ^{1}H NMR and GC-MS. Structural data of **7** was identical in all respect with an authentic sample prepared by the reported procedure.[17] Photolysis of **1b** with other alkyl iodides was carried out according to the same procedure.

Physical and spectral data for 1-(dimethylphenylsilyloxy)-2,2,6,6-tetramethylpiperidine **7**: bp 100−105 °C (0.5 mmHg); ^{1}H NMR (C_6D_6) δ 0.51 (s, 6H), 1.08 (s, 6H), 1.16 (s, 6H), 1.00−1.22 (m, 2H), 1.26−1.47 (m, 4H), 7.17−7.27 (m, 3H), 7.64−7.69 (m, 2H); ^{13}C NMR (C_6D_6) δ 0.2, 17.2, 19.4, 33.9, 40.0, 59.8, 129.3, 133.7, 140.5; HRMS calcd for $C_{17}H_{29}ONSi$ 291.2017, found 291.2011.

Photoinduced Polymerization with 1b and Iodobenzene. A mixture of **1b** (0.1 mmol) and iodobenzene (0.4 mmol) in 1.0 mL of MMA and 2.0 mL of benzene was irradiated under nitrogen atmosphere for 1.5 h in a water bath at ambient temperature. After volatile compounds were removed under reduced pressure, the reaction mixture was poured into 50 mL of methanol. PMMA precipitated was collected by filtration and dried. The molecular weight was determined by GPC analysis with polystyrene standard. The ratio of the terminal groups ($PhMe_2Si$ vs Ph) was calculated on the basis of the integration ratio of the peaks at δ 0.02 (bs, 6H [$PhMe_2Si$]) and at δ 7.18−7.57 (m, 5H [$PhMe_2Si$] + 5H [Ph]) in ^{1}H NMR (DMSO-d_6). A similar polymerization of MMA was carried out in the presence of either TEMPO (0.4 mmol) or CuBr (0.4 mmol) under the same condition. Copper compounds precipitated were removed by filtration using Celite after the irradiation. Polymerization of methyl acrylate and benzyl methacrylate was conducted according to the similar procedure.

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