New Generation of Organosilyl Radicals by Photochemically Induced Homolytic Cleavage of Silicon−Boron Bonds

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Unlike bis(diethylamino)organosilylboranes, bis(diisopropylamino)organosilylboranes, which have UV absorption at longer wavelength than 300 nm, undergo photolysis to afford pairs of an organosilyl radical and a bis(diisopropylamino)boryl radical by homolytic scission of the silicon−boron bonds. Generation of organosilyl radical and organoboryl radical was confirmed by trapping experiments using TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl). The organosilyl radical thus generated induces not only silylation of mono-olefins and silylative cyclization of dienes but also polymerization to afford polymers bearing organosilyl termini. On the other hand, the bis(diisopropylamino)boryl radical generated is not incorporated into the olefin adducts.

Introduction

Combination of an organotin hydride and a conventional radical initiator has been widely utilized in organic synthesis.[1] However, the use of organotin derivatives is not desired from the environmental viewpoint. In addition, it is often difficult to remove any organotin impurities from the product.[2] Although some attempts using a catalytic amount of organotin hydride have been reported,[3] development of the alternatives may be recommended in synthetic organic chemistry.

On the other hand, usefulness of organosilyl radicals in organic synthesis has also been reported,[4] suggesting that organotin radicals may be replaced with organosilyl radicals. Unlike organotin radicals, however, generation of organosilyl radical intermediates has not been practically convenient. Organosilyl radicals are often generated by treatment of organosilyl hydride with a stoichiometric amount of peroxide. Since a hydrogen atom of an organosilyl hydride is, however, resistant to abstraction by a carbon-centered radical, organosilyl hydrides unlike organotin hydrides are not usually involved in a radical chain process.[5] Polarity-reversal catalyst is reported to promote the efficient radical chain cycle.[6] On the other hand, it has been recently found that some organosilyl hydrides such as tris(trimethylsilyl)silane (TTMSS) provide the corresponding tris(trimethylsilyl)silyl radical intermediates via hydrogen atom abstraction without the catalyst, which are utilized in organic synthesis.[7] Herein, we describe new and useful photochemical generation of dimethylphenylsilyl radical from organosilylboranes, which can promote stereoselective silicon−carbon bond formation.

The silicon−boron σ-bonds in organosilylboranes had been considered to be thermally inert.[8] However, the silicon−boron bond activation catalyzed by transition metal complexes has been recently utilized in organic synthesis, e.g., some silaborations of carbon−carbon multiple bonds catalyzed by Pd, Pt, and Ni complexes create both of silicon−carbon bonds and boron−carbon bonds stereoselectively and regioselectively.[9]

However, photochemistry of organosilylboranes has not been investigated well. To our knowledge, a photochemical generation of triphenylsilylboranediyl (Ph_3SiB:) from bis- or tris(organosilyl)boranes has been noted.[10]

Results and Discussion

UV spectra of a series of bis(dialkylamino)organosilylboranes revealed that UV absorption of **1d** was very similar to that of **1f**, suggesting no significant electronic contribution of dialkylamino groups to UV absorption.[11] Of note is, however, that sterically bulky substituents on either silicon or boron atoms remarkably affected UV absorption of bis(dialkylamino)organosilylboranes. The silylborane **1c** bearing a triphenylsilyl group absorbed UV light up to around 320 nm (Figure 1). The charac-

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[11] It has been reported that aminoboranes exhibit UV absorption ascribed to π-bonding between boron and nitrogen: (a) Lappert, M. F.; Pedley, J. B.; Riley, P. N. K.; Tweedale, A. *Chem. Commun.* **1966**, *21*, 788−789. (b) Fuss, W. *Z. Naturforsch., Teil B* **1974**, *29*, 514−523.

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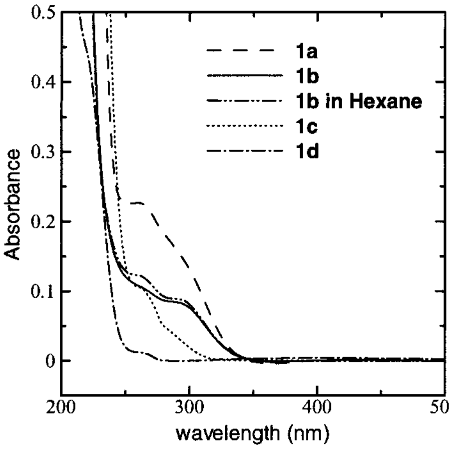


Figure 1. UV spectra of **1a**–**d** in acetonitrile and **1b** in *n*-hexane at 5.0 × 10^{-5} M.

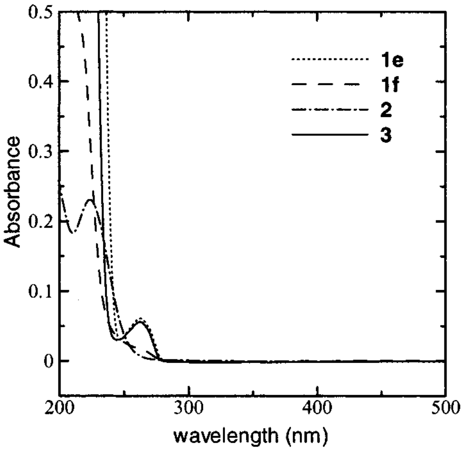
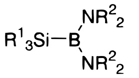
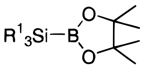


Figure 2. UV spectra of **1e**–**f**, **2**, and **3** in acetonitrile at 5.0 × 10^{-5} M.

teristic tailing of the UV absorption was not observed for a pinacol derivative **1e** (Figure 2).



1	R^1_3Si	R^2
1a	Ph_3Si	^iPr
1b	$PhMe_2Si$	^iPr
1c	Ph_3Si	Et
1d	$PhMe_2Si$	Et



1	R^1_3Si
1e	Ph_3Si
1f	$PhMe_2Si$

The similar substituent effect at the boron was also observed in the UV spectra of **1a** and **1b** having diisopropylamino groups, which exhibited higher intensities than those of **1c** and **1d**, respectively. The UV absorption of the silylboranes was not influenced by the polarity of the solvent (Figure 1), suggesting that the ground state does not involve a charge-transfer character.

It may be remarked that the characteristic UV absorption was not observed for the two reference compounds $ClB(N^iPr_2)_2$ (**2**)[11] and Ph_3SiMe (**3**) (Figure 2). The origin of the absorption is not clear at present,[12] but the effect of the substituents at boron was also seen in ^{11}B NMR. The ^{11}B chemical shifts of **1a**,**b** appeared in downfield compared to those of **1c**–**e** (Table 1).[13]

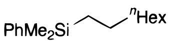
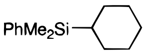
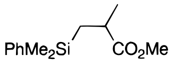
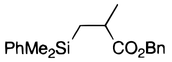
On irradiation with a high-pressure mercury lamp, **1a** and **1b** underwent photolysis in benzene-d_6 quantitatively for 1.5 h at ambient temperature to afford a complex product mixture, in which bis(diisopropylamino)borane[14] and $R^1_3Si-C_6D_5$ were detected by ^1H, ^{13}C NMR, and GC-MS. However, although **1c** underwent sluggish photolysis, no reaction took place under the same condition with **1d**–**f**, which have very weak, if any, UV absorption at >280 nm. It is noted that photolysis of **1b** in the presence of TEMPO in benzene-d_6 gave $PhMe_2$-Si–TEMPO adduct **4** and $(^iPr_2N)_2B$–TEMPO adduct **5** in a quantitative yield, indicating generation of pairs of an organosilyl radical and an organoboryl radical (eq 1). These reactions do not occur without irradiation. Moreover, organosilylboranes **1** are thermally stable and do not decompose even at 180 °C.

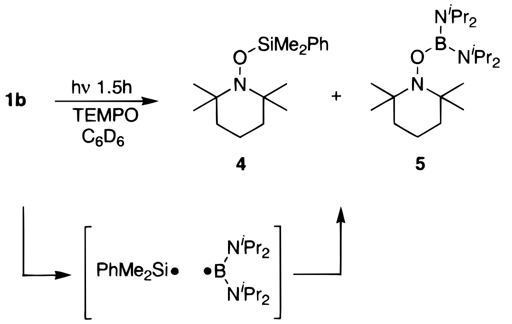
Table 1. ^{11}B Chemical Shifts of Organosilylboranes 1

compound	chemical shift (ppm)[a]	compound	chemical shift (ppm)[a]
1a	39.5	**1d**	36.5[b]
1b	41.2	**1e**	34.1
1c	35.5		

[a] Measured in C_6D_6 with $BF_3{\cdot}Et_2O$ as external reference. [b] Reported in ref 8e.

Table 2. Photochemical Reaction of 1b with Olefins

olefin (equiv)	solvent	product		yield (%)
1-octene (4.0)	*n*-hexane		**6**	56
cyclohexene (4.0)	*n*-hexane		**7**	56
MMA (2.0)	benzene		**8**	46
BnMA (2.0)	benzene		**9**	45



(1)

The high reactivity of organosilyl radicals toward carbon–carbon multiple bonds is well-known.[4] Indeed, irradiation of a mixture of **1b** and olefins led to addition of organosilyl radicals across the carbon–carbon double bonds to give silylated products (eq 2 and Table 2). UV irradiation of **1b** with 1-octene and cyclohexene in

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(12) Some organosilylboranes have been reported to have UV absorption around 400 nm: Pillot, J.-P.; Birot, M.; Bonnefon, E.; Dunogues, J.; Rayez, J.-C.; Rayez, M.-T.; Liotard, D.; Desvergne, J.-P. *Chem. Commun.* **1997**, 1535–1536.

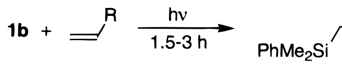
(13) ^{11}B NMR chemical shifts of some bis(dialkylamino)organosilylboranes reported so far are 33–36 ppm; see refs 8c, 8d, and 8e.

(14) Structural identity of bis(diisopropylamino)borane was confirmed by comparison (^1H, ^{13}C NMR) with an authentic sample prepared from **2** and $LiAlH_4$: see Chavant, P. Y.; Vaultier, M. *J. Organomet. Chem.* **1993**, *455*, 37–46.

(15) Steric congestion of bis(diisopropylamino)boryl groups has been discussed. See ref 14.

(16) Oxidation of *β*-boryl ester; see (a) Rasset, C.; Vaultier, M. *Tetrahedron* **1994**, *50*, 3397–3406. (b) Matteson, D. S.; Michnick, T. J. *Organometallics* **1990**, *9*, 3171–3177.

n-hexane afforded dimethyl(*n*-octyl)phenylsilane (**6**) and dimethyl(*cyc*-hexyl)phenylsilane (**7**), respectively. No regioisomeric adduct was obtained in the reaction of 1-octene. Photochemical reaction with α,β-unsaturated esters such as methyl methacrylate (MMA) and benzyl methacrylate (BnMA) in benzene also produced the corresponding β-silyl carboesters **8** and **9** along with some methacrylate oligomers. Hydrogen atoms, which terminate the radical reactions, may have mainly come from the diisopropylamino group. Irradiation of **1b** (1.0 equiv) with MMA (2.0 equiv) in THF-d_8, ^{2}H donor solvent, yielded **8**, in which 20% of ^{2}H was incorporated at the carbon α to the ester moiety. These reactions may involve radical intermediates since the presence of TEMPO in the reaction mixture completely inhibited the formation of silylated products, afforing TEMPO-adducts **4** and **5** in good yields.



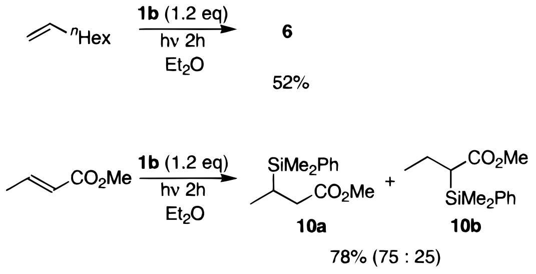
(2)

In contrast to the reactive organosilyl radical, the organoboryl radical, which may have been simultaneously generated, does not apparently participate in the reaction with olefins. The organoboryl radical did not add to olefins, probably due to the steric hindrance.[15] In the case of the reaction with BnMA, oxidation of the reaction mixture using hydrogen peroxide in the presence of sodium hydroxide afforded **9** in 44% yield without giving the corresponding β-hydroxy carboester, which might have arisen from a possible formation of the β-boryl carboester.[16] Monitoring the photochemical reaction with MMA in benzene-d_6 by ^{1}H NMR revealed that neither of boryl enolates nor silyl enolates were formed throughout the photochemical reaction. Only bis(diisopropylamino)borane, which could be produced via hydrogen abstraction by the bis(diisopropylamino)boryl radical,[14] was identified as one of the products derived from the boryl group.[17] No reaction proceeded without irradiation in all cases.

Trialkylboranes are known as a radical initiator in the presence of a trace of oxygen (O_2).[18] However, oxygen cannot initiate any reaction of **1a**,**b**. Under dry air atmosphere, **1b** in benzene-d_6 was not decomposed at all. Photochemical reactions of **1a**,**b** are unlikely to proceed with the radical chain mechanism. Heating a mixture of **1b** (1.0 equiv) and benzoyl peroxide (0.2 equiv) in benzene-d_6 at 95 °C for 2 h in a sealed tube led to partial decomposition of **1b**, giving a mixture of **1b** and small amounts of unidentified products. However, the photolysis products such as $PhMe_2Si-C_6D_5$ and bis(diisopropylamino)borane were not observed in the mixture. We assume that the BPO-induced decomposition of **1b** may be caused by hydrogen abstraction from the diisopropylamino groups by the benzoyloxy radical. Moreover, irradiation of a mixture of **1b** and **1d** in benzene-d_6 resulted in the consumption of **1b**, leaving **1d** unchanged. This finding may exclude a mechanistic possibility of sensitization of **1b** followed by radical chain reaction.

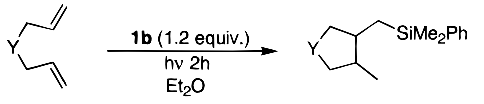
The generation of trivalent boron-centered radical in the present work deserves to be noted. Organoboryl radicals ($R_2B\bullet$) have been so far detected by some spectroscopic studies[19] and proposed as transient intermediates.[20] Trapping of organoboryl radical with TEMPO described in the present paper provides the first and unambiguous evidence for a nonligated boryl radical intermediate.[21]

Next, we attempted to demonstrate the usefulness of the photochemical reaction of **1b** in organic synthesis. Hydrosilylation of olefins shown in eq 2 was carried out in the presence of excess amounts of olefins. Use of a stoichiometric amount of olefins in the hydrosilylation resulted in low yields. However, the chemical yield was improved by choice of ether solvent, which served as hydrogen donor and terminated the radical reaction effectively. Regioselective hydrosilylation of olefins took place by irradiating a 1:1 mixture of **1b** and 1-octene in diethyl ether (eq 3). Similarly, methyl crotonate also underwent the hydrosilylation by UV irradiation to afford **10** in a good yield.



(3)

Photochemical reaction of **1b** with dienes induced organosilylative cyclization. Irradiation of 1,6-dienes (**11**) in the presense of **1b** afforded 5-exo cyclized products (**12**) exclusively in a stereoselective manner without using conventional radical initiators (eq 4). Various functional groups such as ether, ester, silyl ether, and amide are tolerated in this reaction. Not only cyclopentane derivatives but also heterocycles such as tetrahydrofurans and pyrrolidines can be constructed by using organosilylborane **1b**. In contrast, radical-induced cyclization using TTMSS in the presence of Et_3B as a radical initiator yields an undesired product mixture including bicyclic compounds.[22]



(4)

11 **12**

11a	Y=O	**12a** (67%, *cis*/*trans*=79/21)
b	$C(CO_2Et)_2$	**b** (67%, 87/13)
c	$C(CH_2OSiMe_2Bu\text{-}t)_2$	**c** (57%, 87/13)
d	CH_2	**d** (53%, 84/16)
e	NAc	**e** (58%, 69/31)

Organosilyl radicals are also highly reactive for halogen abstraction. The organosilylborane **1b** promotes a reductive cyclization of 1-bromo-5-hexene (**13**) to give methylcyclopentane (**14**). Halogen abstraction by the silyl radical and subsequent cyclization was followed by hydrogen abstraction to give the product. This finding is

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(17) Attempts to isolate bis(diisopropylamino)borane from the reaction mixture have all failed because it was highly moisture sensitive. Usually, a complex mixture of boryl compounds was produced in the photochemical reaction, probably due to the hydrogen abstraction from the isopropyl groups.

(18) Brown, H. C.; Midland, M. M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 692–700.

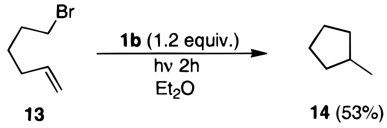
(19) (a) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. London, Ser. A* **1967**, *298*, 142–159. (b) Rehorek, D.; Herzschuh, R.; Hennig, H. *Inorg. Chim. Acta* **1980**, *44*, L75–L76.

(20) Hancock, K. G.; Uriarte, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 6374–6376, and references therein.

Table 3. Photochemically Induced Radical Polymerization with 1b

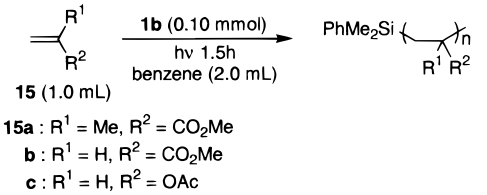
monomer (**15**)	yield (%)	M_n	M_w/M_n
15a	23	3.11×10^3	1.67
15b	94	3.08×10^4	2.41
15c	51	9.36×10^3	5.17

indicating that organosilylborane **1b** may function as an alternative of organotin hydride−radical initiator (eq 5).



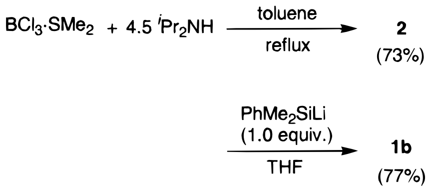
(5)

The organosilylborane **1b** can promote a radical polymerization. Irradiation of **1b** with large excess of monomers (**15**) in benzene afforded polymers (eq 6 and Table 3). Not only methyl methacrylate (**15a**) and acrylate (**15b**) but also vinyl acetate (**15c**) was polymerized with **1b**. ^{1}H NMR analysis showed that the polymers contained dimethylphenylsilyl groups at the polymer termini. Addition of TEMPO inhibited the polymerization completely, indicating that the polymerization took place in a radical fashion. It is needless to say that no polymer was obtained without irradiation.



(6)

Organosilylborane **1b** is easily prepared via two steps (eq 7). Treatment of excess diisopropylamine with $BCl_3 \cdot SMe_2$ yielded **2** without formation of $(^iPr_2N)_3B$.[23] Organosilylborane **1b** was obtained by a reaction of dimethylphenylsilyllithium and **2**. Organosilylborane **1b** is stable enough for storage for months under dry atmosphere. Synthetic availability of organosilylborane **1b** may enhance the utilities of the present photochemical reactions in organic synthesis.



(7)

Conclusion

Steric congestion in organosilylborane is crucial for the bathochromic UV absorption, which causes homolytic scission of Si−B bonds on UV irradiation. Utility of organosilylboranes is also demonstrated. Organosilylborane **1b** serves as a good photolatent dimethylphenylsilyl radical in organic synthesis. This reagent can be an alternative for organotin hydrides−conventional radical initiators. In addition, **1b** is useful as a radical initiator for polymerization.

Experimental Section

General. All reactions were carried out under dry nitrogen, unless otherwise mentioned. Reagents and solvents were handled with standard syringe techniques. Solvents were purified by distillation in the presence of appropriate drying agents under nitrogen. All photochemical reactions were carried out with a high-pressure mercury lamp (100 W) and Pyrex glassware. Methyl methacrylate, methyl acrylate, benzyl methacrylate, and vinyl acetate were distilled prior to use. Other commercially available reagents were used without further purification.

Synthesis of Organosilylboranes (1). To a mixture of lithium (0.56 g, 80 mmol) and THF (20 mL) was added $PhMe_2SiCl$ (3.36 mL, 20 mmol) dropwise. After the mixture was stirred at room temperature for 6 h, the resulting supernatant solution of $PhMe_2SiLi$ was added dropwise to $ClB(N^iPr_2)_2$ [23] (4.75 g, 19.3 mmol) in *n*-hexane (20 mL), and then the mixture was stirred at room temperature overnight. After the produced precipitates were filtered off, the filtrate was evaporated and distilled to afford **1b** (5.13 g, 77% yield). The same procedure was applied for the synthesis of $Ph_3SiB(N^iPr_2)_2$ (**1a**).

Triphenylsilylbis(diisopropylamino)borane (1a): bp 190 °C at 0.1 mmHg; ^{1}H NMR (C_6D_6) δ 1.07 (d, $J = 7.0$ Hz, 24H), 3.94 (hept, $J = 7.0$ Hz, 4H), 7.15−7.29 (m, 9H), 7.80−7.92 (m, 6H); ^{13}C NMR (C_6D_6) δ 25.4, 50.2, 127.9, 128.3, 136.8, 140.2; ^{11}B NMR (C_6D_6) δ 39.5. Anal. Calcd for $C_{30}H_{43}BN_2Si$: H, 9.21; C, 76.57; N, 5.95. Found: H, 9.40; C, 76.30; N, 5.88.

Dimethylphenylsilylbis(diisopropylamino)borane (1b): bp 140 °C at 0.2 mmHg; ^{1}H NMR (C_6D_6) δ 0.51 (s, 6H), 1.14 (d, $J = 6.8$ Hz, 24H), 3.85 (hept, $J = 6.8$ Hz, 4H), 7.15−7.32 (m, 3H), 7.62−7.70 (m, 2H); ^{13}C NMR (C_6D_6) δ 1.0, 25.4, 49.2, 127.9, 128.3, 134.4, 144.2; ^{11}B NMR (C_6D_6) δ 41.2; HRMS Calcd for $C_{20}H_{39}BN_2Si$ (M+1) 347.3054, found 347.3059.

Silylboranes **1c**−**f** were prepared by the reported procedures.[24,25] Physical and spectral data for new compounds are given below.

Triphenylsilylbis(diethylamino)borane (1c): bp 170 °C at 0.1 mmHg; ^{1}H NMR (C_6D_6) δ 0.84 (t, $J = 6.9$ Hz, 12H), 2.93 (q, $J = 6.9$ Hz, 8H), 7.16−7.25 (m, 9H), 7.82−7.87 (m, 6H); ^{13}C NMR (C_6D_6) δ 15.3, 43.5, 128.6, 136.6, 140.1; ^{11}B NMR (C_6D_6) δ 35.5.

Triphenylsilylpinacolborane (1e): ^{1}H NMR (C_6D_6) δ 1.01 (s, 12H), 7.15−7.24 (m, 9H), 7.82−7.88 (m, 6H); ^{13}C NMR (C_6D_6) δ 24.8, 83.9, 128.3, 129.4, 135.7, 136.6; ^{11}B NMR (C_6D_6) δ 34.1; HRMS Calcd for $C_{24}H_{27}BO_2Si$ (M − C_6H_5) 309.1482; found 309.1494.

Photolysis of Organosilylborane 1b with TEMPO. In 5.0 mL of C_6D_6 were dissolved **1b** (0.308 mmol) and TEMPO (0.925 mmol). The solution was irradiated for 1.5 h at ambient temperature in a water bath. Structures of products **4** and **5** were identified by ^{1}H NMR. Structual data of **4** was identical in all respect with an authentic sample prepared by the reported procedure.[26] After evaporation of the reaction mixture, the resulting residue was subjected to a column chromatography on silica gel to give **5** in 51% yield.

1-Dimethylphenylsilyloxy-2,2,6,6-tetramethylpiperidine (4): bp 100−105 °C at 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.

1-Bis(diisopropylamino)boryloxy-2,2,6,6-tetramethylpiperidine (5): ^{1}H NMR (C_6D_6) δ 1.23−1.33 (m, 36H), 1.39−1.54 (m, 6H), 3.39 (hept, $J = 6.8$ Hz, 2H), 4.62 (hept, $J = 7.1$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 17.5, 21.9, 24.6, 25.2, 33.4, 40.3, 46.1, 47.0, 59.5; HRMS calcd for $C_{21}H_{46}BN_3O$ 367.3734, found 367.3728.

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(23) Synthesis of **2** has been reported in ref 14.

(24) Synthesis of organosilylbis(dialkylamino)boranes; see ref 8e.

(25) Synthesis of organosilylpinacolboranes; see Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics*, in press.

(26) Armbrecht, M.; Maringgele, W.; Meller, A.; Noltemeyer, M.; Sheldrick, G. M. *Z. Naturforsch., Teil B* **1985**, *40*, 1113−1122.

(27) Fleming, I.; Lee, D. *J. Chem. Soc., Perkin. Trans. 1* **1998**, 2701−2710.

Photolysis of 1b with Benzyl Methacrylate. A solution of **1b** (0.293 mmol) and benzyl methacrylate (0.586 mmol) in benzene (30 mL) was irradiated for 1.5 h at ambient temperature in a water bath. After the reaction mixture was evaporated, the residue was subjected to a column chromatography on silica gel to give **9** in 45% yield.

Benzyl 3-(dimethylphenylsilyl)-2-methylpropionate (9): ^{1}H NMR (CDCl$_3$) δ 0.30 (s, 3H), 0.31 (s, 3H), 0.95 (dd, J = 7.2, 14.7 Hz, 1H), 1.18 (d, J = 7.2 Hz, 3H), 1.34 (dd, J = 7.5, 14.7 Hz, 1H), 2.55−2.67 (m, 1H), 4.97 (d, J = 12.6 Hz, 1H), 5.04 (d, J = 12.6 Hz, 1H), 7.30−7.41 (m, 8H), 7.48−7.55 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −2.6, 20.5, 20.6, 35.6, 66.0, 127.8, 128.1, 128.5, 129.0, 133.6, 136.2, 138.7, 177.3. Anal. Calcd for $C_{19}H_{24}O_2Si$: H, 7.74; C, 73.03. Found: H, 8.00; C, 73.31.

Photolysis of **1b** with MMA was carried out in the same manner. The spectral data of the product **8** has been reported in the literature.[27] For reactions with 1-octene and cyclohexene, a mixture of **1b** and olefins in *n*-hexane was irradiated for 3 h at ambient temperature in a water bath.

Dimethy(*n*-octyl)phenylsilane (6): ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 6H), 0.74 (t, J = 7.8 Hz, 2H), 0.88 (t, J = 6.8 Hz, 3H), 1.14−1.40 (m, 12H), 7.33−7.39 (m, 3H), 7.48−7.56 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −3.1, 14.0, 15.6, 22.6, 23.8, 29.2, 31.9, 33.5, 127.7, 128.7, 133.6, 139.9. Anal. Calcd for $C_{16}H_{28}Si$: H, 11.36; C, 77.34. Found: H, 11.32; C, 77.13.

Cyclohexyldimethylphenylsilane (7): ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 6H), 0.72−0.88 (m, 1H), 0.97−1.33 (m, 5H), 1.56−1.81 (m, 5H), 7.31−7.41 (m, 3H), 7.44−7.56 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −5.2, 25.8, 26.9, 27.4, 28.0, 127.6, 128.7, 133.9, 138.7. Anal. Calcd for $C_{14}H_{22}Si$: H, 10.15; C, 76.99. Found: H, 10.38; C, 76.71.

Hydrosilylation of 1-octene with 1b in Diethyl Ether. A solution of **1b** (0.386 mmol) and 1-octene (0.322 mmol) in 39 mL of dry diethyl ether was irradiated under nitrogen atmosphere for 1.5 h at ambient temperature with a high-pressure mercury lamp. After evaporation of the reaction mixture, the residue was treated with 5 mL of *n*-hexane and filtered to remove the resultant precipitates with Celite. The filtrate was concentrated under reduced pressure and then subjected to a column chromatography on silica gel to give dimethyl(*n*-octyl)phenylsilane (**6**) in 52%. Hydrosilylation of methyl crotonate was carried out in the same manner.

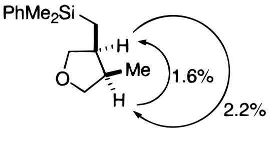
Methyl 3-(dimethylphenylsilyl)butyrate (10a, major isomer): ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 6H), 0.97 (d, J = 7.5 Hz, 3H), 1.37−1.51 (m, 1H), 2.06 (dd, J = 11.1, 15.3 Hz, 1H), 2.39 (dd, J = 4.2, 15.3 Hz, 1H), 3.61 (s, 3H), 7.33−7.39 (m, 3H), 7.46−7.53 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −5.5, −5.1, 14.4, 16.4, 36.6, 51.3, 127.8, 129.2, 133.9, 137.3, 174.5. Anal. Calcd for $C_{13}H_{20}O_2Si$: H, 8.53; C, 66.05. Found: H, 8.77; C, 66.25.

Methyl 2-(dimethylphenylsilyl)butyrate (10b, minor isomer): ^{1}H NMR (CDCl$_3$) δ 0.34 (s, 3H), 0.36 (s, 3H), 0.88 (t, J = 6.9 Hz, 3H), 1.42 (ddt, J = 20.6, 6.9, 3.0 Hz, 1H), 1.79 (ddt, J = 20.6, 11.6, 6.9 Hz, 1H), 2.12 (dd, J = 11.6, 3.0 Hz, 1H), 3.55 (s, 3H), 7.32−7.41 (m, 3H), 7.45−7.54 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −4.9, −4.0, 15.0, 20.4, 39.5, 50.9, 127.9, 129.5, 133.9, 136.4, 175.7. Anal. Calcd for $C_{13}H_{20}O_2Si$: H, 8.53; C, 66.05. Found: H, 8.69; C, 66.25.

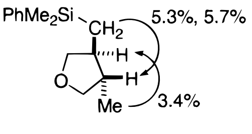
Radical Cyclization of Diallyl Ether (11a) with 1b. A diene cyclization reaction was conducted in the same procedure with the hydrosilylation. A column chromatography on silica gel afforded the product **12a** as a mixture of two stereoisomers. The ratio of the isomers was determined by capillary GC. Each isomer was isolated by HPLC.

***cis*-12a (major, polar isomer):** ^{1}H NMR (CDCl$_3$) δ 0.30 (s, 6H), 0.71 (dd, J = 14.4, 9.6 Hz, 1H), 0.88 (d, J = 6.9 Hz, 3H), 0.89 (dd, J = 14.4, 5.4 Hz, 1H), 2.07−2.19 (m, 1H), 2.20−2.33 (m, 1H), 3.25 (dd, J = 8.1, 8.1 Hz, 1H), 3.45 (dd, J = 8.0, 3.6 Hz, 1H), 3.78 (dd, J = 8.1, 8.1 Hz, 1H), 3.85 (dd, J = 8.0, 6.0 Hz, 1H), 7.33−7.39 (m, 3H), 7.48−7.54 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −2.50, −2.47, 13.2, 13.3, 37.3, 38.3, 73.2, 75.0, 127.8, 129.0, 133.4, 139.0. Anal. Calcd for $C_{14}H_{22}OSi$: H, 9.46; C, 71.73. Found: H, 9.58; C, 71.84. The stereochemistry was determined by NOE in C_6D_6.

***trans*-12a (minor, less polar isomer):** ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 6H), 0.63 (dd, J = 14.9, 10.3 Hz, 1H), 0.95 (d, J = 6.3 Hz, 3H), 1.13 (dd, J = 14.9, 3.5 Hz, 1H), 1.62−1.83 (m, 2H), 3.19 (dd, J = 8.5, 8.5 Hz, 1H), 3.25 (dd, J = 8.5, 8.5 Hz, 1H), 3.87 (dd, J = 8.4, 6.9 Hz, 1H), 3.93 (dd, J = 8.4, 6.9 Hz, 1H), 7.32−7.38 (m, 3H), 7.46−7.53 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −2.7, −2.5, 15.2, 18.0, 43.2, 74.6, 75.2, 127.9, 129.1, 133.5, 139.0. Anal. Calcd for $C_{14}H_{22}OSi$: H, 9.46; C, 71.73. Found: H, 9.52; C, 71.47. The stereochemistry was determined by NOE in CD_3OD.



cis-**12a**



trans-**12a**

Radical cyclization of **11b**−**e** was carried out with the same procedure. All **12b**−**e** were isolated as a mixture of two stereoisomers, the ratio of which was determined by capillary GC. However, isolation as a single isomer with HPLC failed.

12b: ^{1}H NMR (CDCl$_3$) δ 0.30 (s, 6H), 0.62−0.95 (m, 5H), 1.21 (t, J = 7.1 Hz, 6H), 1.81−2.18 (m, 4H), 2.25−2.40 (m, 2H), 4.07−4.21 (m, 4H), 7.28−7.38 (m, 3H), 7.45−7.56 (m, 2H); HRMS calcd for $C_{21}H_{32}O_4Si$ 376.2070; found 376.2074. Anal. Calcd for $C_{21}H_{32}O_4Si$: H, 8.57; C, 66.98. Found: H, 8.58; C, 67.27.

12c: ^{1}H NMR (CDCl$_3$) δ 0.00 (s, 12H), 0.28 (s, 6H), 0.87 (s, 18H), 0.55−1.18 (m, 7H), 1.40−2.11 (m, 4H), 3.28−3.43 (m, 4H), 7.29−7.37 (m, 3H), 7.46−7.54 (m, 2H); HRMS Calcd for $C_{29}H_{56}O_2Si_3$ 520.3588; found 520.3577. Anal. Calcd for $C_{29}H_{56}O_2Si_3$: H, 10.83; C, 66.85. Found: H, 11.07; C, 66.56.

12d: ^{1}H NMR (CDCl$_3$) δ 0.276 (s, 6H, minor isomer), 0.279 (s, 6H, major isomer), 0.52−0.94 (m, 5H), 1.00−1.98 (m, 8H), 7.30−7.38 (m, 3H), 7.47−7.56 (m, 2H); HRMS Calcd for $C_{15}H_{24}Si$ 232.1647; found 232.1637. Anal. Calcd for $C_{15}H_{24}Si$: H, 10.41; C, 77.51. Found: H, 10.26; C, 77.68.

12e: ^{1}H NMR (CDCl$_3$) δ 0.29−0.33 (m, 6H), 0.52−1.21 (m, 5H), 1.50−2.17 (m, 5H), 2.68−3.82 (m, 4H), 7.30−7.40 (m, 3H), 7.42−7.57 (m, 2H); HRMS Calcd for $C_{16}H_{25}NOSi$ 275.1705; found 275.1701. Anal. Calcd for $C_{16}H_{25}NOSi$: H, 9.15; C, 69.76; N, 5.08. Found: H, 9.15; C, 69.83; N, 5.03.

Radical Cyclization of 1-Bromo-5-hexene (13) with 1b. A solution of **1b** (0.354 mmol), 1-bromo-5-hexene (**13**) (0.295 mmol), and *n*-octane (26.0 mg) in 35 mL of diethyl ether was irradiated under nitrogen atmosphere for 1.5 h with a high-pressure mercury lamp. During the irradiation, the reaction flask was kept at ambient temperature by a cooling water bath. The yield of methylcyclopentane (**14**) was determined by capillary GC with *n*-octane as an internal reference.

Photochemically Induced Polymerization with 1b. A solution of **1b** (0.10 mmol) in 1.0 mL of monomer (**15**) and 2.0 mL of benzene was irradiated under nitrogen atmosphere for 1.5 h with a high-pressure mercury lamp. During irradiation, the apparatus are kept at ambient temperature by a cooling water bath. After the reaction mixture was evaporated under reduced pressure, the viscous residue was poured into 50 mL of methanol (for PMMA and PMA) or *n*-hexane (for PVAc). Precipitates produced were collected by filtration and dried. The molecular weight of the polymer was determined by GPC analysis with a polystyrene standard. ^{1}H NMR indicated that the polymerization products thus prepared contained the dimethylphenylsilyl groups at the polymer ends. The dimethylphenylsilyl terminal of the polymer (^{1}H NMR in CDCl$_3$):

Poly(methyl methacrylate): δ 0.28 (bs, 6H), 7.26−7.50 (m, 5H).

Poly(methyl acrylate): δ 0.25 (bs, 6H), 7.26−7.50 (m, 5H).

Poly(vinyl acetate): δ 0.28−0.42 (m, 6H), 7.28−7.62 (m, 5H).

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