Persistent Tris(*t*-butyldimethylsilyl)silyl Radical and Its New Generation Methods

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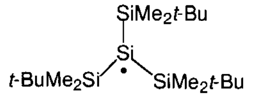
A persistent silyl radical, tris(*t*-butyldimethylsilyl)silyl radical, (t-BuMe$_2$Si)$_3$Si• (**1**), was produced by two new methods in addition to a conventional hydrogen abstraction from the corresponding hydrosilane: one-electron oxidation of (t-BuMe$_2$Si)$_3$SiNa (**2**) by NO$^+$BF$_4^-$ and one-electron reduction of (t-BuMe$_2$Si)$_3$SiBr (**3**) by sodium.

Although silyl radicals have been recognized as important reactive intermediates in organosilicon chemistry since 1940s,[1] they have never been isolated so far. Lately, much attention has been focused on stable silyl radicals and many efforts have been devoted to generate persistent silyl radicals stabilized by bulky substituents.[2] Quite recently, Matsumoto et al. have demonstrated that persistent silyl radicals with bulky trialkylsilyl substituents are produced in solution at room temperature by hydrogen abstraction from the corresponding hydrosilanes by *t*-butoxy radicals, which are generated through photolysis of di-*t*-butyl peroxide, or by photochemical Si-Si bond cleavage of the corresponding disilanes.[3] Kira et al. have independently planned to generate a similar stable tris(trialkylsilyl)silyl radical using electron-transfer type reactions.[4] While it is well known that silyl radicals are involved as reactive intermediates during one-electron oxidation of silylmetals[5] and one-electron reduction of bromosilanes,[6] these two processes have never been applied to generation of persistent silyl radicals. We wish herein to report ESR studies of persistent tris(*t*-butyldimethylsilyl)silyl radical (**1**) generated by these oxidation and reduction of the corresponding silicon compounds, and by the hydrogen abstraction of the corresponding hydrosilane.



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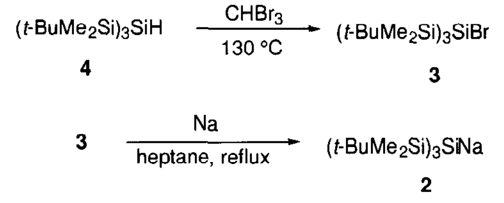
As precursors of silyl radical **1**, (t-BuMe$_2$Si)$_3$SiNa (**2**)[7] and bromosilane (t-BuMe$_2$Si)$_3$SiBr (**3**)[8] were synthesized via the corresponding hydrosilane, (t-BuMe$_2$Si)$_3$SiH (**4**),[9] which was prepared by a reductive coupling reaction of HSiCl$_3$ with t-BuMe$_2$SiCl using Li, as shown in Scheme 1.



Scheme 1.

Radical **1** was generated by one-electron oxidation of **2** in heptane using various oxidizing agents such as NO$^+$BF$_4^-$ and Ph$_3$C$^+$BPh$_4^-$ (Method A, Eq. 1). In a typical experiment, to a mixture of NO$^+$BF$_4^-$ purified by sublimation (29 mg, 0.25 mmol) and **2** (101 mg, 0.25 mmol) was introduced dry heptane (1 ml) in vacuo at 77 K. Warming up the mixture to room temperature gave a yellow solution with precipitates. The supernatant of the mixture was transferred into an ESR sample tube (5 mmϕ). An ESR spectrum of the sample measured at room temperature showed an intense sharp line at g = 2.0055 with satellite hyperfine splitting (hfs) lines due to central (α-Si) and substituent ^{29}Si nuclei (β-Si) (Figure 1); two hfs constants due to α-Si and β-Si were determined as 5.71 and 0.81 mT, respectively. Hyperfine splitting due to *t*-butyl and methyl protons were resolved using low modulation frequency. The experimental spectrum was well reconstructed by computer simulation with the hfs constants of 0.033 and 0.011 mT for *t*-butyl and methyl protons, respectively.

$$\mathbf{2} \xrightarrow[\text{heptane, -80 °C ~ rt}]{\text{An oxidizing agent}} \mathbf{1} \qquad (1)$$

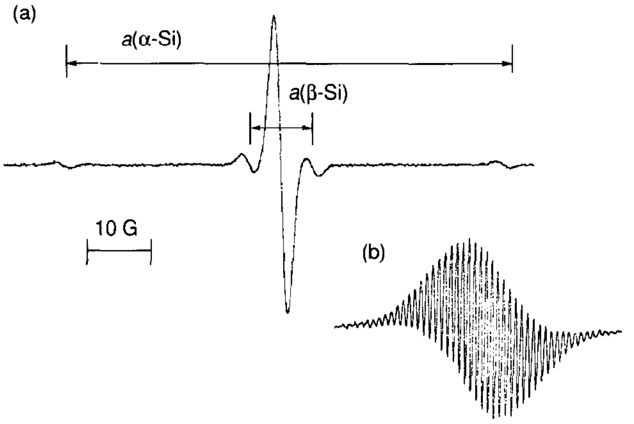
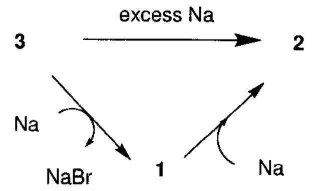


Figure 1. (a) An ESR spectrum of **1** during oxidation of **2** by NO$^+$BF$_4^-$ in heptane at room temperature. (b) Central part of the spectrum recorded using low modulation frequency.

During the reduction of bromosilane **3** with sodium to silylsodium **2**, silyl radical **1** should be involved as an intermediate (Scheme 2). Therefore, **1** may be generated as a persistent radical by careful reduction of **3** with an equimolar amount of sodium. As expected, addition of **3** (45 mg, 0.10 mmol) to sodium (2.6 mg, 0.11 mmol) in dry heptane followed by heating at 110 °C for 12 h gave a yellow solution together with white precipitates of sodium bromide (Method B); an ESR spectrum of the solution gave intense signals due to **1**, which were superimposable with that observed during the oxidation of **2**.



Scheme 2.

Silyl radical **1** was generated also by the hydrogen abstraction of hydrosilane **4** by *t*-butoxy radical produced by photolysis of di-*t*-butyl peroxide (Method C, Eq. 2).[3] The g-values and hfs values of silyl radical **1** generated by the three different methods were essentially identical with each other.

$$4 \xrightarrow[t\text{-BuOO}t\text{-Bu}]{h\nu} 1 \qquad (2)$$

ESR parameters of **1** and several related silyl radicals are compared in Table 1. The ^{29}Si hfs constant due to α-Si [a(α-Si)] of **1** is much smaller than that of $Me_3Si\bullet$ and close to that of $(i\text{-}Pr_3Si)_3Si\bullet$, whose geometry around the central silicon is reported to be nearly planar.[3b] Since a(α-Si) values reflect the s-character of the singly occupied molecular orbital (SOMO), the planarity around silicon of a silyl radical will be estimated by comparing the a(α-Si) values.[10] The a(α-Si) value of **1** is much smaller than that of $Me_3Si\bullet$ but comparable to those of tris(trialkylsilyl)silyl radicals shown in Table 1, suggesting the high planarity of **1**; the origin is ascribed to the electropositive effects of trialkylsilyl substituents, which decrease the s-character of the SOMO.[11] Small but significant differences of a(α-Si) values between $(Me_3Si)_3Si\bullet$ and the other bulky tris(trialkylsilyl)silyl radicals may be an indication of the effects of steric bulkiness of trialkylsilyl substituents on the planarity, as discussed by Matsumoto et al.[3a] In this context, the planarity of **1**, $(Et_3Si)_3Si\bullet$, and $(i\text{-}Pr_3Si)_3Si\bullet$ is almost the same with each other. The g value of **1** is characteristic as those of tris(trialkylsilyl)silyl radicals and much larger than that of trimethylsilyl radical.

The half-life ($\tau_{1/2}$) of **1** was dependent on the generation methods, as has been shown by Matsumoto et al. for other tris(trialkylsilyl)silyl radicals;[3a] $\tau_{1/2}$ = ca. 1 day at 15 °C for **1** generated by Methods A and B, while 10 h by Method C at the same temperature.[13] Silyl radical **1** generated by Method C reacted with CCl_4 slowly at room temperature to give $(t\text{-}BuMe_2Si)_3SiCl$ in 90% yield, in contrast to $(i\text{-}Pr_3Si)_3Si\bullet$, which does not react with CCl_4.[3b,14]

Table 1. ^{29}Si hyperfine splitting constants of silyl radicals

silyl radical	solvent	T / °C	*g*	a (α-Si) [a]	a (β-Si) [a]
$Me_3Si\bullet$ [b]	–	–	2.0031	18.3	–
$(Me_3Si)_3Si\bullet$ [c]	–	–	2.0050	6.5	0.62
$(Et_3Si)_3Si\bullet$ [d]	pentane	15	2.0063	5.72	0.79
1 [e]	heptane	15	2.0055	5.71	0.81
1 [f]	benzene	rt	2.0060	5.69	0.80
$(i\text{-}Pr_3Si)_3Si\bullet$ [g]	pentane	15	2.0061	5.56	0.81

[a] mT. [b] Refs. 2d and 10. [c] Refs. 10 and 12. [d] Ref. 3a. [e] Methods A and B. [f] Method C. [g] Ref. 3b.

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7 A mixture of **3** (2.40 g, 5.29 mmol) and sodium (0.660 g, 28.7 mmol) in heptane (10 ml) was kept at 100 °C for 4 h in a Schlenk tube. Recrystallization from the greenish supernatant of the reaction mixture gave 1.20 g of solids, which contained **2** in 95% purity as determined by NMR spectroscopy. **2**: yield, 50%; slight yellow crystals; ^1H NMR (C_6D_6, δ) 0.45 (s, 18 H), 1.17 (s, 27 H); ^{13}C NMR (C_6D_6, δ) 3.2, 19.3, 29.4; ^{29}Si NMR (C_6D_6, δ) -196.0, 7.9.

8 A reaction of a mixture of **4** (3.17 g, 8.46 mmol) and bromoform (37.5 g, 148 mmol) at 100 – 120 °C for 20 h followed by Kugel-rohr distillation (70 °C/0.03 mmHg) gave **3** in 82%. **3**: colorless crystals; mp 60-62 °C; ^1H NMR(C_6D_6, δ) 0.35 (s, 18 H), 1.05 (s, 27 H); ^{13}C NMR (C_6D_6, δ) -2.2, 19.8, 28.7; ^{29}Si NMR(C_6D_6, δ) -20.1, 2.2; MS (EI, 70 eV) *m*/*z*(%) 452 (M^+, 8), 437(6), 395 (18), 258 (100), 73(74). Found: C, 47.89; H, 9.70%. Calcd for $C_{18}H_{45}Si_4Br$: C, 47.64; H, 10.00%.

9 **4**: colorless crystals; mp 126-128 °C; ^1H NMR(C_6D_6, δ) 0.26 (s, 18 H), 1.02 (s, 27 H), 2.70 (s, 1 H); ^{13}C NMR (C_6D_6, δ) -0.7, 18.6, 27.9; ^{29}Si NMR(C_6D_6, δ) -130.3, 3.0; MS (EI, 70 eV) *m*/*z*(%) 374 (M^+, 21), 359(12), 317(94), 73 (100). Found: C, 57.71; H, 12.07%. Calcd for $C_{18}H_{46}Si_4$: C, 57.67; H, 12.37%.

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13 Shorter life time of **1** generated by Method C may be ascribed to the efficient trapping of **1** by radicals and compounds formed by the decomposition of *t*-butoxyl radical;[3a] no such trapping reactions are expected for **1** generated by Methods A and B.

14 A similar reaction of **1** generated by Method A with CCl_4 gave the corresponding chlorosilane in at most 40% yield, indicating less efficient generation of **1** by Method A. No similar experiment has been carried out for Method B because of the incompletion of the one-electron oxidation.