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Highly Stable Silyl Radicals $(Et_nMe_{3-n}Si)_3Si^\bullet$ (n = 1−3)

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Summary: Silyl radicals $(Et_nMe_{3-n}Si)_3Si^\bullet$ *(**1**, n = 1; **2**, n = 2; **3**, n = 3) were generated by hydrogen abstraction from* $(Et_nMe_{3-n}Si)_3SiH$ *(**4**, n = 1; **5**, n = 2; **6**, n = 3) with di-tert-butyl peroxide and by photolysis of* $(Et_nMe_{3-n}Si)_4Si$ *(**7**, n = 1; **8**, n = 2; **9**, n = 3) and* $(Et_nMe_{3-n}Si)_3SiSi(SiMe_{3-n}Et_n)_3$ *(**10**, n = 1; **11**, n = 2; **12**, n = 3) and observed by ESR spectroscopy. These silyl radicals are considerably stable at room temperature; the half-lives of **1**, **2**, and **3** generated from **10**−**12** are 3 h, 1 day, and 1.5 months at 15 °C, respectively.*

Silyl radicals are one of the important reactive intermediates in organosilicon chemistry, and their formation, reactions, and properties have been investigated extensively since 1960s.[1] Silyl radicals are highly reactive species which usually can be observed only at low temperatures.[2] Stabilization of silyl radicals by the introduction of bulky substituents such as *tert*-butyl,[3] mesityl,[4] 3,5-di-*tert*-butylphenyl,[5] trimethylsilyl,[6] and other groups[7] has been attempted. However, only two examples of the formation of stable silyl radicals have been reported. In 1974, Hudson, Lappert, and co-workers showed that the reaction of $Cl_3SiSiCl_3$ with $(Me_3Si)_2CHLi$ and subsequent irradiation afforded $[(Me_3Si)_2CH]_3Si^\bullet$ which has a half-life of *ca.* 10 min at 30 °C.[8] In 1988, Michl and co-workers reported that the irradiation of poly(di-*n*-alkylsilane)s $(R_2Si)_n$ in solution led to polysilanylsilyl radicals $(-R_2Si)_2RSi^\bullet$ which are stable for hours or days.[9] As part of an ongoing investigation of the chemistry of polysilane oligomers,[10] we began to explore the possibility of generating persistent silyl radicals from highly branched precursors $(Et_nMe_{3-n}Si)_3SiH$, $(Et_nMe_{3-n}Si)_4Si$, and $(Et_nMe_{3-n}Si)_3SiSi(SiMe_{3-n}Et_n)_3$ (n = 1−3). Prior to our work, Ishikawa and co-workers reported that the photolysis of $(Me_3Si)_3SiSi(SiMe_3)_3$ produced silylenes in the main photochemical pathways but the formation of $(Me_3Si)_3Si^\bullet$ was also involved to some extent.[11] Pannell and co-workers reported that the central Si−Si bond of $(Me_3Si)_3SiSiMe_2SiMe_2Si(SiMe_3)_3$ is most prone to photochemical cleavage.[12] We report herein the for-

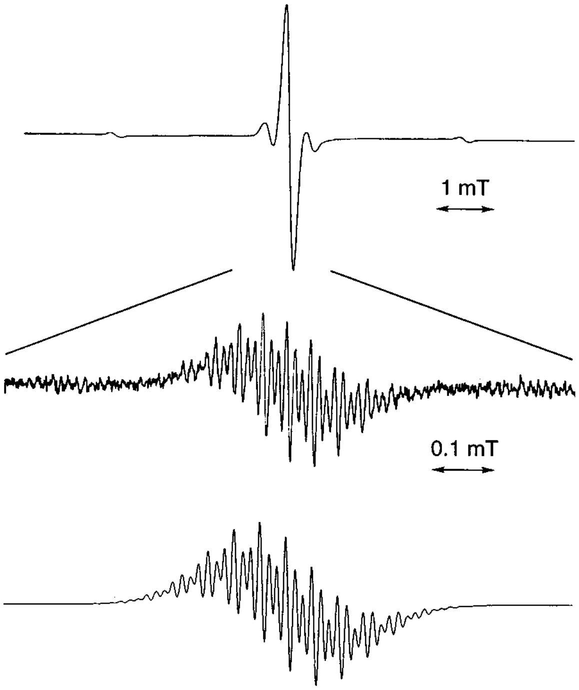
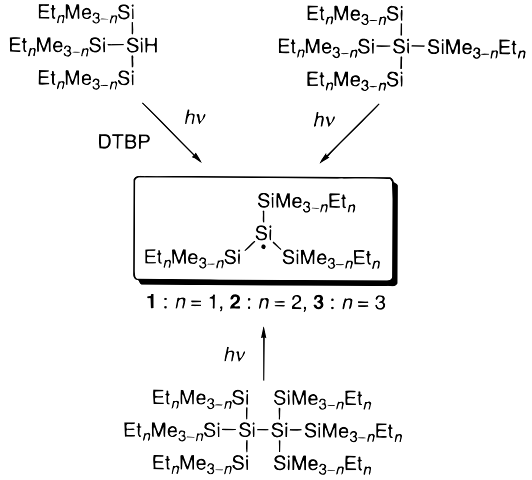


Figure 1. ESR spectrum of **1** in pentane at room temperature (top). An enlargement of the central part of the ESR spectrum showing the hyperfine structure is recorded at lower field modulation width (middle). A simulated spectrum is shown at the bottom.

Scheme 1



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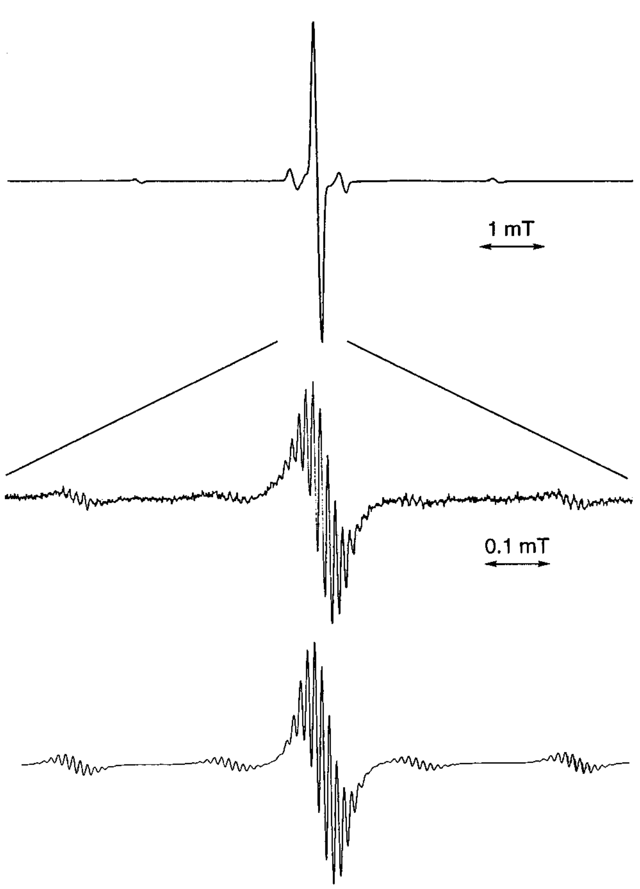
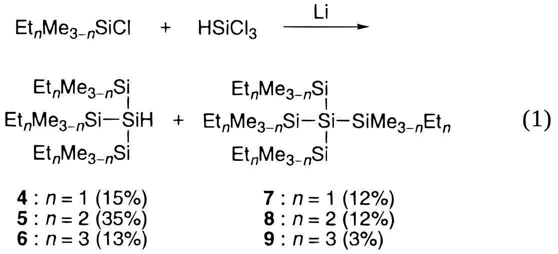


Figure 2. ESR spectrum of **3** in pentane at room temperature (top). An enlargement of the central part of the ESR spectrum showing the hyperfine structure is recorded at lower field modulation width (middle). A simulated spectrum is shown at the bottom.

mation and ESR study of highly stable silyl radicals $(Et_nMe_{3-n}Si)_3Si^\bullet$ (**1**, $n = 1$; **2**, $n = 2$; **3**, $n = 3$).

Tris(trialkylsilyl)silanes **4**–**6** were prepared by a modification of a previously reported method.[13] Condensation of $Et_nMe_{3-n}SiCl$ ($n = 1$–3) and trichlorosilane with lithium under reflux of tetrahydrofuran (THF) produced **4**–**6**, eq 1. In these reactions, tetrakis(trialkylsilyl)silanes **7**–**9** were also formed, which are also precursors of silyl radicals **1**–**3** (vide infra). Both types of compounds (**4**–**6** and **7**–**9**) were separated easily by distillation.[14]



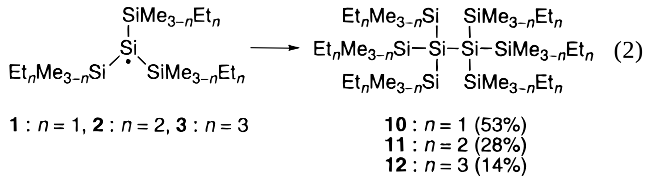
$$Et_nMe_{3-n}SiCl + HSiCl_3 \xrightarrow{Li} Et_nMe_{3-n}Si-\overset{Et_nMe_{3-n}Si}{\underset{Et_nMe_{3-n}Si}{Si}}H + Et_nMe_{3-n}Si-\overset{Et_nMe_{3-n}Si}{\underset{Et_nMe_{3-n}Si}{Si}}-SiMe_{3-n}Et_n \qquad (1)$$

4 : $n = 1$ (15%)
5 : $n = 2$ (35%)
6 : $n = 3$ (13%)

7 : $n = 1$ (12%)
8 : $n = 2$ (12%)
9 : $n = 3$ (3%)

Silyl radicals **1**–**3** were generated by irradiation of solutions containing **4**–**6** and di-*tert*-butyl peroxide (DTBP) with a high-pressure mercury lamp (Scheme 1).[15] In the ESR spectrum, each radical shows a signal with two kinds of satellites, as shown in Figures 1 and 2 (top). The intensity of the satellites shows that the satellites with the larger splitting constant are due to a ^{29}Si nucleus at the α-position, and those with a smaller splitting constant correspond to three ^{29}Si nuclei at the *β*-positions. When the ESR spectra were recorded at lower field modulation width, splitting due to protons was observed, as shown in Figures 1 and 2 (middle). The ESR spectrum of **1** is well-simulated with hyperfine splitting constants by 18 equivalent methyl protons and 6 equivalent ethyl protons at the *δ*-positions (Figure 1 (bottom)). Similarly, the ESR spectra of **2** and **3** are simulated with hyperfine splitting constants by 9 equivalent methyl protons and 12 equivalent ethyl protons at the *δ*-positions (**2**) and 18 equivalent ethyl protons at the *δ*-positions (**3**) (Figures 2 (bottom)). In the cases of **2** and **3**, splitting due to ^{13}C nuclei at the *γ*-positions also was observed. The splitting constants and *g* values are summarized in Table 1. As the methyl groups of $(Me_3Si)_3Si^\bullet$ are progressively replaced by ethyl groups, $a(^{29}Si(\alpha))$ tends to decrease and $a(^{29}Si(\beta))$ slightly increases. The observed trends are explained by assuming that the structure around the radical center of $(Me_3Si)_3Si^\bullet$, which has been reported to have a nearly planar structure,[6] becomes more planar with the successive ethyl substitution and that the spin density on the radical center is delocalized to the silyl substituents more effectively. The tendency of *g* values to increase along the series $(Me_3Si)_3Si^\bullet$ < **1** < **2** < **3** also supports the effective interaction of spin with silyl substituents.

Several features of silyl radicals **1**–**3** are noted. (1) ESR spectra of **1**–**3** can be observed at room temperature. The stability is remarkable because ESR spectra of $(Me_3Si)_3Si^\bullet$ have been reported to be observed at −70[6a] and −25 °C.[6c] The steric effect of methyl groups and ethyl groups seems significantly different in $(R_3Si)_3Si^\bullet$ systems. (2) After irradiation was stopped and ESR signals had almost disappeared, the reaction mixtures were separated by HPLC to give hexakis(trialkylsilyl)disilanes **10**–**12**, eq 2.[14] The formation of **10**–**12** shows that dimerization of **1**–**3** occurs to some extent, al-



$$\overset{SiMe_{3-n}Et_n}{\dot{Si}}(Et_nMe_{3-n}Si)(SiMe_{3-n}Et_n) \longrightarrow Et_nMe_{3-n}Si-\overset{Et_nMe_{3-n}Si}{\underset{Et_nMe_{3-n}Si}{Si}}-\overset{SiMe_{3-n}Et_n}{\underset{SiMe_{3-n}Et_n}{Si}}-SiMe_{3-n}Et_n \qquad (2)$$

1 : $n = 1$, **2** : $n = 2$, **3** : $n = 3$

10 : $n = 1$ (53%)
11 : $n = 2$ (28%)
12 : $n = 3$ (14%)

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[14] For experimental details for the synthesis of **4**–**12** and their spectroscopic data, see the Supporting Information.

[15] A reviewer suggested that some experiments based on thermally-generated *tert*-butoxyl radicals may give some further information. Although thermal reactions are less favorable for the generation of stable silyl radicals than photochemical reactions, we are also interested in the thermal behavior of **1**–**3** and it is a future subject of our research.

Table 1. ESR Parameters of 1−3 and $(\mathrm{Me_3Si})_3\mathrm{Si}^\bullet$

silyl radical	*T*, °C	*g*	$a(^{29}\mathrm{Si}(\alpha))$, mT	$a(^{29}\mathrm{Si}(\beta))$, mT	$a(^{13}\mathrm{C}(\gamma))$, mT	$a(\mathrm{H}(\delta))$, mT	ref
$(\mathrm{Me_3Si})_3\mathrm{Si}^\bullet$	−25	2.0053	6.38	0.71		0.043	6c
1	15	2.0060	6.28	0.71		0.037 (Me), 0.014 (Et)	this work
2	15	2.0060	6.03	0.73	0.32	0.027 (Et), 0.015 (Me)	this work
3	15	2.0063	5.72	0.79	0.30	0.012	this work

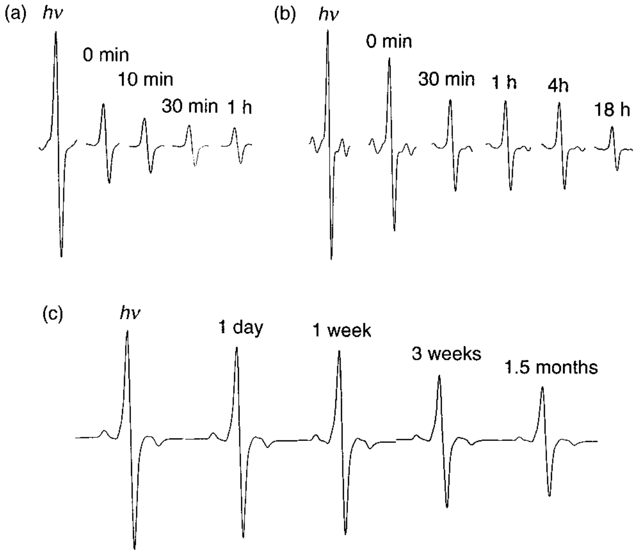

Figure 3. Decay of the ESR signals of **3** at 15 °C after the light was shut off. Radical **3** was generated by (a) hydrogen abstraction from **6** with DTBP and by photolysis of (b) **9** and (c) **12**. Only the central signals are shown in each case.

though yields of the dimers are medium to low under these conditions.

Silyl radicals **1**−**3** can also be generated from tetrakis(trialkylsilyl)silanes **7**−**9** and hexakis(trialkylsilyl)disilanes **10**−**12**, as shown in Scheme 1. When solutions of **7**−**12** in pentane were irradiated with a high-pressure mercury lamp, the identical ESR spectra of silyl radicals **1**−**3** were observed at room temperature (Figures 1 and 2). The generation of **1**−**3** is due to cleavage of one of the Si−Si bonds of **7**−**12**. In spite of the identical ESR spectra, the decay time of silyl radicals **1**−**3** generated by these methods is considerably different, as exemplified by **3** in Figure 3. When silyl radicals **1**−**3** were generated from **4**−**6** by hydrogen abstraction with DTBP, the ESR signals were reduced immediately after the light was shut off. However, the ESR signals of **1**−**3** generated by photolysis of **7**−**9** were reduced more slowly; the half-lives of **1**, **2**, and **3** are 3 min, 1 h, and 1 min at 15 °C, respectively. When silyl radicals **1**−**3** were generated by photolysis of **10**−**12**, much slower decay was observed; the half-lives of **1**, **2**, and **3** are 3 h, 1 day, and 1.5 months at 15 °C, respectively. Hence, these silyl radicals, especially **3**, are remarkably persistent at room temperature when generated from **10**−**12**. The change of the decay time of **1**−**3** by the generation methods is explained by the following consideration. In the hydrogen abstraction with DTBP, several kinds of radicals and compounds such as $\mathrm{CH_3}^\bullet$, $\mathrm{CH_3COCH_2}^\bullet$, and acetone are formed by the decomposition of the *tert*-butoxyl radical.[16] Silyl radicals **1**−**3** are trapped quite rapidly by these reactive species. Of course, the trapping process competes with dimerization of **1**−**3**. Consequently, the yields of **10**−**12** are relatively low and decrease in the order **10** > **11** > **12** as dimerization rates of silyl radicals decrease (**1** > **2** > **3**). In the photolysis of **7**−**9**, such reactive species are not present except for $\mathrm{Et}_n\mathrm{Me}_{3-n}\mathrm{Si}^\bullet$ ($n = 1-3$), which are formed together with **1**−**3**, and the decay of **1**−**3** becomes relatively slow. In the photolysis of **10**−**12**, only signals of **1**−**3** were observed in the ESR spectrum, as mentioned above. Other probable radicals such as $(\mathrm{Et}_n\mathrm{Me}_{3-n}\mathrm{Si})_3\mathrm{Si}\dot{\mathrm{Si}}(\mathrm{SiMe}_{3-n}\mathrm{Et}_n)_2$ ($n = 1-3$) were not detected. Furthermore, after irradiation was stopped and the ESR signals of **1**−**3** disappeared, dimers **10**−**12** were obtained almost quantitatively. These results suggest that **1**−**3** are generated cleanly in the photolysis of **10**−**12**, and **1**−**3** gradually disappear by dimerization to **10**−**12** without capture by other species. The reaction pathway is in contrast with a previously reported result on the photolysis of $(\mathrm{Me_3Si})_3\mathrm{SiSi}(\mathrm{SiMe_3})_3$ in which mainly silylenes are generated and the formation of silyl radicals is a minor process.[11] Since the stability of $(\mathrm{R_3Si})_3\mathrm{Si}^\bullet$ increases dramatically when the methyl groups of $(\mathrm{Me_3Si})_3\mathrm{Si}^\bullet$ are replaced by ethyl groups, it is probable that cleavage of the central Si−Si bonds of **10**−**12** occurs more easily than other pathways to give highly stable silyl radicals **1**−**3**.[17]

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Supporting Information Available: Text giving experimental details for the synthesis of **4**−**12**, the generation of **1**−**3**, and the spectroscopic data of **4**−**12**, ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **4** and **5**, ESR spectra of **2** and **3**, and tables of experimental details of the X-ray crystallography, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles of **12** (32 pages). Ordering information is given on any current masthead page.

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(17) The X-ray crystallographic analysis of **12** discloses the significant distortion of the central Si−Si bond due to the steric hindrance of bulky $\mathrm{Et_3Si}$ groups; the central Si−Si bond lengths are 2.417(1) and 2.445(1) Å, while the terminal Si−Si bond lengths are 2.376(1) and 2.396(1) Å at −120 °C. The central Si−Si bond length of $(\mathrm{Me_3Si})_3\mathrm{SiSi}(\mathrm{SiMe_3})_3$, a less crowded molecule, has been reported to be 2.390(2) Å at −120 °C.[18] The relief of the steric hindrance might be responsible for the cleavage of the central Si−Si bond of **12**. For details of X-ray crystallographic data of **12**, see the Supporting Information.

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