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1,2-Migration of the trimethylsilyl group in free radicals

Joanna M. Harris [a], Iain MacInnes [a], John C. Walton [a] and Bernard Maillard [b]

[a] *Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST (UK)*
[b] *Laboratoire de Chimie Organique et Organometallique, Université de Bordeaux 1, 33705, Talence Cedex (France)*

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Abstract

EPR spectroscopic observations and product studies showed that the trimethylsilyl group undergoes 1,2-migration from carbon to nitrogen in aminyl radicals, $Me_3SiCH_2NH^{\bullet} \rightarrow {}^{\bullet}CH_2NHSiMe_3$, and from carbon to oxygen in alkoxyl radicals, $Me_3SiCH_2O^{\bullet} \rightarrow {}^{\bullet}CH_2OSiMe_3$.

The ability of a group R_nX to undergo an intramolecular 1,2-migration in a free radical, $R_nX\text{–}Y\text{–}Z^{\bullet} \rightarrow {}^{\bullet}Y\text{–}Z\text{–}XR_n$, generally depends on the availability of a vacant, low-lying orbital on X to accommodate the unpaired electron during the transfer. For the Me_3Si group, the vacant Si *d*-orbitals are probably too high in energy [1] to stabilize the transition state. On the other hand, silicon easily expands its valence shell to become five coordinate, which would obviously favour group transfer. No examples of 1,2-migration of R_3Si groups from carbon to carbon are known [2–4]. Me_3Si migration from Si to C has been observed in the gas phase [5,6], but not in solution [7]. The only other known, 1,2-migrations of silyl groups are from Si to S [8], and from O to N [9]. It seemed to us that the high Si–N and Si–O bond strengths, as compared with the Si–C bond strength [10], might tilt the balance in favour of 1,2-silyl migration from C to N and from C to O. Evidence outlined below, from a study of several radicals generated from silylamines and β-silylalkoxy derivatives, indicates that both these migrations occur in solution at low temperatures.

Reaction of trimethylsilylmethylamine, **1**, with photochemically generated t-butoxyl radicals in solution (cyclopropane or t-butylbenzene) in the cavity of an EPR spectrometer, gave rise to the spectrum of the aminoalkyl radical **2** ($g = 2.003 \pm 0.001$, $a(H_\alpha) = 1.60$, $a(N) = 0.63$, $a(H_\beta) = 0.072$, $a(H_\beta) = 0.036$, $a(9H_\gamma) = 0.036$ mT at 220 K) [11 *] in the temperature range 150–230 K. t-Butoxyl radicals abstract hydrogen in primary amines from *both* the carbon adjacent to nitrogen and nitrogen to give a mixture of aminoalkyl and aminyl radicals [12], although the

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[*] Reference number with asterisk indicates a note in the list of references.

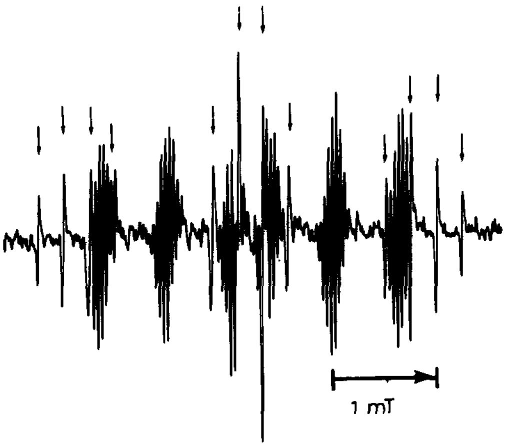


Fig. 1. 9.4 GHz EPR spectrum of radicals obtained on hydrogen abstraction from amine **1** by t-butoxyl radicals in solution at 260 K. Lines from the rearranged radical **4** are indicated by arrows; other lines are due to radical **2**.

latter cannot be detected by EPR spectroscopy in solution [13]. It is probable therefore that both radicals **2** and **3** are formed from **1** and that aminyl radical **3** is

$$\underset{(\mathbf{1})}{Me_3SiCH_2NH_2} \xrightarrow{{}^tBuO^\cdot} \underset{(\mathbf{2})}{Me_3Si\dot{C}HNH_2} + \underset{(\mathbf{3})}{Me_3SiCH_2NH^\cdot} \longrightarrow \underset{(\mathbf{4})}{{}^\cdot CH_2NHSiMe_3}$$

EPR "silent". Above 230 K a second radical appeared reaching full intensity at 260 K, see Fig. 1, where the ratio of its concentration to that of **2** was ca. 0.7. The EPR parameters ($g = 2.003 \pm 0.001$, $a(2H) = 1.63$, $a(N) = 0.24$, $a(1H) = 0.24$ mT at 260 K) [14 *] indicate that this spectrum is the aminoalkyl radical **4**, formed from **3** by a 1,2-migration of the Me_3Si group. At $T < 230$ K rearrangement of **3** is too slow, on the EPR timescale, but above this temperature Me_3Si migration is sufficiently rapid for the stationary concentration of **4** to come within the detection range of the EPR spectrometer. Corroborative evidence was obtained from the di-deuterio amine **5**. Radical **6** containing two D-atoms was detected at $T < 230$ K; both **6** and rearranged radical **7**, containing only a single D-atom, were detected at higher temperatures.

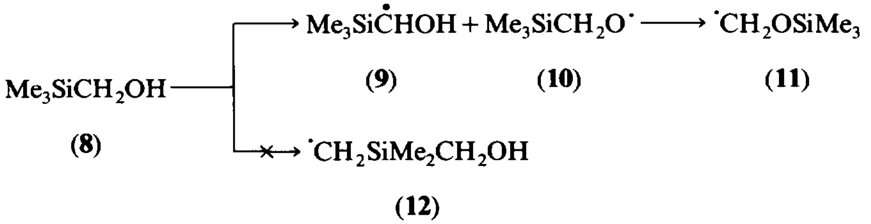
$$\underset{(\mathbf{5})}{Me_3SiCH_2ND_2} \xrightarrow{{}^tBuO^\cdot} \underset{(\mathbf{6})}{Me_3Si\dot{C}HND_2} + Me_3SiCH_2ND^\cdot \longrightarrow \underset{(\mathbf{7})}{{}^\cdot CH_2NDSiMe_3}$$

The main products from photolysis of **1** with di-t-butyl peroxide at 300 K were t-butanol, hexamethyldisiloxane, trimethylsilyl t-butyl ether, a black intractable solid and one possible combination product from **2** or **4**. These products seemed to indicate that trimethylsilyl radicals were released during the reaction; consequently **4** would be formed by β-elimination of $Me_3Si^\cdot$ from **3** followed by re-addition. Organosilyl radicals are good halogen abstractors, but when Me_3CCl was added to the reaction mixture no t-butyl radicals were detected. Similarly, when 1,3,5-trinitrobenzene, which is known to be a good trap for Me_3Si radicals [15] was used, none of the spin adduct was detected. Silyl amines are known to react with alcohols as follows [16]:

$$\mathrm{R'N(R)SiMe_3} + {}^{t}\mathrm{BuOH} \longrightarrow \mathrm{R'NHR} + {}^{t}\mathrm{BuOSiMe_3}$$

It is probable therefore that the rearrangement occurs intramolecularly, and that the silyl ether is formed as shown above from silyl amines derived from **4**, i.e. $CH_3NHSiMe_3$ and $Me_3SiNHCH_2CH_2NHSiMe_3$ and the product t-butanol. Silylamines are also readily converted to trimethylsilanol and hence to hexamethyldisiloxane in the presence of peroxides [16]. Traces of trimethylsilanol were identified along with the main products listed above. The observed products are consistant therefore with initial formation of silylamines from the rearranged radical, **4**.

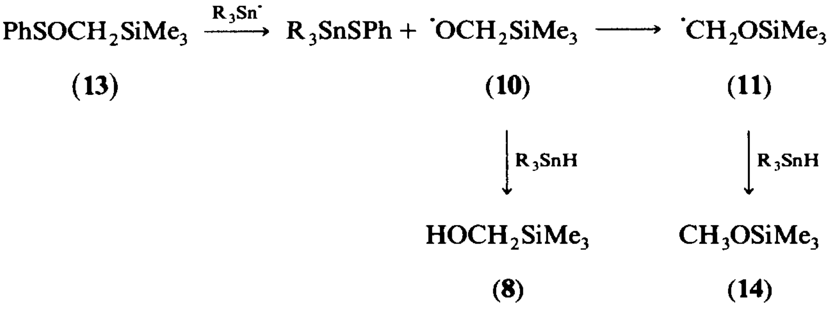
The EPR spectrum obtained from the reaction of trimethylsilylmethanol, **8**, with t-butoxyl radicals showed the presence of radical **9** [a(1H) = 1.87, a(1H) = 0.24, a(9H) = 0.03 mT at 220 K], together with a second species having EPR parameters identical to those in the literature [2] for trimethylsilyloxymethyl radicals, **11** [a(2H) = 1.91 mT at 220 K]. That this was not radical **12**, formed by H-abstraction from the trimethylsilyl group, was shown by the difference in the H_α hyperfine splitting (hfs) [2,17] and by the fact that γ-hfs are resolved in radicals like **12** (e.g. for $Me_3SiCH_2^{\bullet}$ a(2H) = 2.09, a(9H) = 0.04 mT) [2,17]. The observation of **11** at 190 K indicates that 1,2-migration of the Me_3Si group from carbon to oxygen in the alkoxyl radical **10** is extremely fast.



$$\mathrm{Me_3SiCH_2OH}\ (\mathbf{8}) \longrightarrow \mathrm{Me_3Si\dot{C}HOH}\ (\mathbf{9}) + \mathrm{Me_3SiCH_2O^{\bullet}}\ (\mathbf{10}) \longrightarrow {}^{\bullet}\mathrm{CH_2OSiMe_3}\ (\mathbf{11})$$

$$\mathrm{Me_3SiCH_2OH}\ (\mathbf{8}) \not\longrightarrow {}^{\bullet}\mathrm{CH_2SiMe_2CH_2OH}\ (\mathbf{12})$$

To confirm this conclusion we generated radical **10** by a specific, recently discovered, route for alkoxyl radicals [18]. When the benzenesulphenate **13** was treated with photochemically generated $Me_3Sn^{\bullet}$ radicals, alkoxyl radical **10** will initially be formed [18]. Study of this reaction by EPR spectroscopy showed rearranged radical **11**, together with a minor unidentified species, in the range 190–260 K. Similarly, treatment of **13** with tri-n-butyltin hydride under radical conditions [18] gave trimethylsilyl methyl ether, **14**, as the main product derived from **13**. Measurement of the rate of rearrangement from the ratio of unrearranged



$$\begin{tikzcd}[column sep=small] \mathrm{PhSOCH_2SiMe_3}\ (\mathbf{13}) \arrow[r, "\mathrm{R_3Sn^{\bullet}}"] & \mathrm{R_3SnSPh} + {}^{\bullet}\mathrm{OCH_2SiMe_3}\ (\mathbf{10}) \arrow[r] \arrow[d, "\mathrm{R_3SnH}"] & {}^{\bullet}\mathrm{CH_2OSiMe_3}\ (\mathbf{11}) \arrow[d, "\mathrm{R_3SnH}"] \\ & \mathrm{HOCH_2SiMe_3}\ (\mathbf{8}) & \mathrm{CH_3OSiMe_3}\ (\mathbf{14}) \end{tikzcd}$$

8 and rearranged products **14** was not possible because **8** was undetectable above ambient temperature. This shows that the 1,2-migration of Me_3Si from C to O is very rapid indeed and is consistent with the detection of the rearranged radical at temperatures as low as 190 K.

Thus, spectroscopic evidence and product studies indicate that the trimethylsilyl group can undergo 1,2-shifts from carbon to nitrogen or oxygen in free radical intermediates.

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