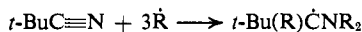


Table I. Epr Parameters for Long-Lived  $\alpha$ -Aminoalkyl Radicals at 23° (Hyperfine Couplings in Gauss)

Radical	$g^a$	$a^N$	$a^{H_{NH}}$	$a^{R_{NR}}$	$a^{R_{CR}}$	$a^{13C}$	$a^{H-t-Bu}$
$t\text{-Bu}_2\dot{C}NHSiMe_3$	2.0024	1.28	16.57	16.21 <sup>b</sup>		8.89 <sup>c</sup>	0.25
$t\text{-Bu}_2\dot{C}NHSi-n\text{-Bu}_3$	2.0024	1.24	15.25	$d$		$d$	0.23
$t\text{-Bu}_2\dot{C}N(Si-n\text{-Bu}_3)_2$		2.91 <sup>e</sup>					
$Ad(Me_3Si)\dot{C}N(SiMe_3)_2$	2.0022	2.0		23.5 <sup>b</sup>		36.5 <sup>f</sup>	
$(Me_3Si)_2\dot{C}N(SiMe_3)_2$	2.0025	2.05		20.5 <sup>b,g</sup>	14.3 <sup>b,g</sup>	2.0 <sup>g,h</sup>	0.20 <sup>i</sup>
$t\text{-Bu}_2\dot{C}NH[(EtO)_2PO]$	2.0023	3.30	23.58	57.79 <sup>i</sup>		10.46 <sup>c</sup>	0.35
$t\text{-Bu}_2\dot{C}N[(EtO)_2PO]_2$	2.0022	4.09		56.58 <sup>i</sup>		9.90 <sup>c</sup>	0.17
$t\text{-Bu}[(EtO)_2PO]\dot{C}N[(EtO)_2PO]_2$	2.0022	3.53		46.6 <sup>i</sup>	39.4 <sup>i</sup>		0.40

<sup>a</sup> Calculated from the Breit-Rabi equation. <sup>b</sup> <sup>29</sup>Si. <sup>c</sup>  $\gamma^{13C}$  of  $t\text{-Bu}$  groups, *i.e.*,  $(CH_3)_3C$ . <sup>d</sup> Could not be determined because of strong signal attributed to  $t\text{-Bu}_2\dot{C}N(Si-n\text{-Bu}_3)_2$ . <sup>e</sup> The presence of other long-lived radicals allowed only the N coupling to be measured. <sup>f</sup>  $\alpha\text{-}^{13C}$ . <sup>g</sup> Estimated using computer simulation. <sup>h</sup> Six <sup>13C</sup>, presumably due to  $Me_3Si$  groups on C rather than to those on N. <sup>i</sup>  $a^H$  of  $Me_3Si$ , presumably the  $Me_3Si$  groups on C. <sup>j</sup> <sup>31</sup>P.

to give the expected triadduct, the trimethylsilyl radical



replaces the *tert*-butyl group and gives a tetraadduct.

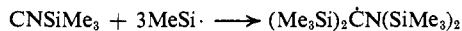


This same radical is produced by addition of  $Me_3Si\cdot$  to benzyl cyanide and isopropyl cyanide. It is the longest lived of all the radicals reported here (as we might expect from a comparison of  $(Me_3Si)_3\dot{C}$  and  $t\text{-Bu}_3\dot{C}$  radicals).<sup>4</sup> For example, a *ca.*  $10^{-3}$  M solution (from benzyl cyanide) decayed to *ca.*  $3 \times 10^{-4}$  M in 5 days at 25° while a *ca.*  $10^{-5}$  M solution (from  $t\text{-BuC}\equiv\text{N}$ ) had not observably decayed in 3 weeks at 25°. In contrast,  $t\text{-Bu}_2\dot{C}N[(EtO)_2PO]_2$  at *ca.*  $10^{-4}$  M had a half-life of *ca.* 8 hr;  $t\text{-Bu}[(EtO)_2PO]\dot{C}N[(EtO)_2PO]_2$  decayed with first-order kinetics and a half-life of 29 min, and the  $t\text{-Bu}_2\dot{C}NHR$  radicals decay in less than 1 sec.

With 1-adamantyl cyanide only a triadduct was obtained (Table I), while acetonitrile yielded an extremely stable radical containing no nitrogen.<sup>13</sup> Since only "stabilized" alkyl groups are lost the most probable route to tetra(trimethylsilyl)aminomethyl involves  $\alpha$ -scission of the iminoyl radical<sup>14,15</sup> formed in the initial step.



The isocyanide then adds<sup>18</sup> three  $Me_3Si\cdot$  radicals, one after the other.



Several features of Table I deserve comment. Thus, although the  $a^N$  values are similar to those found in analogous unhindered  $\alpha$ -aminoalkyl radicals (normally  $4 < a^N < 7$  G) the  $a^{H_{NH}}$  values are very much larger than normal ( $0 < a^{H_{NH}} < 6$  G).<sup>19</sup> According to Lyons and Symons,<sup>8</sup> the unhindered  $\alpha$ -aminoalkyls are most probably planar at the  $\alpha$ -C and close to planar at N. They adopt conformation 1 since interaction of the unpaired electron with the lone pair dominates conformation. The spin density on N is presumably positive while that on the amino H is presumably negative.<sup>8</sup>

(13) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 6203 (1974).

(14) For first epr identification of iminoyl's see W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **95**, 6872 (1973).

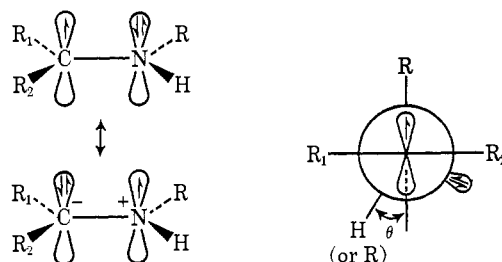
(15) The  $\beta$ -scission of such radicals is known.<sup>16-18</sup>

(16) H. Ohta and K. Tokamaru, *Chem. Commun.*, 1601 (1970).

(17) T. Saegusa, Y. Ito, N. Yasuda, and T. Hotaka, *J. Org. Chem.*, **35**, 4238 (1970).

(18) L. A. Singer and S. S. Kim, *Tetrahedron Lett.*, 861 (1974).

(19) For example,  $\dot{C}H_2NHCH_3$ ,  $a^N = 5.84$ ,  $a^{H_{NH}} = 6.35$  G;  $\dot{C}H_2NHC_2H_5$ ,  $a^N = 6.3$ ,  $a^{H_{NH}} \approx 0$  G;  $CH_3\dot{C}HNHC_2H_5$ ,  $a^N = 4.8$ ,  $a^{H_{NH}} \approx 0.9$  G;  $CH_3\dot{C}HN(C_2H_5)_2$ ,  $a^N = 5.18$  G.<sup>5</sup>



1,  $R_1$ ,  $R_2$ , and  $R$  small 2,  $R_1$ ,  $R_2 = t\text{-Bu}$ , etc;  $R = Me_3Si$ , etc

For all our radicals, the splitting constants are virtually independent of temperature (40 to  $-90^\circ$ ), suggesting that they exist in a "locked" conformation. Since steric effects should dominate all other interactions (*cf.*  $t\text{-Bu}_2\dot{C}CH_2R$ ),<sup>2,3</sup> these radicals should adopt conformation 2.<sup>20</sup> The  $\alpha$ -C should be planar (*cf.* the  $a^{13C_\alpha}$  value for  $Ad(Me_3Si)\dot{C}N(SiMe_3)_2$ ) and the N pyramidal, but probably not tetrahedral, *i.e.*,  $0^\circ < \theta < 60^\circ$ . The N may even be inverting rapidly. The spin density on N will now be negative and that on the amino H large and positive. In  $R_1R_2\dot{C}N(R)H$  the R group is optimally positioned for hyperconjugative interaction with the unpaired electron, yet the extent of hyperconjugation (as measured by  $a^{R_{NR}}$ )<sup>2,3</sup> is only about half of that found in structurally related  $t\text{-Bu}_2\dot{C}CH_2R$  radicals.<sup>21</sup> This may reflect specific differences between the two types of radical (*e.g.*, the greater electronegativity of N or the presence of its lone pair). Further epr studies on a wider variety of  $\alpha$ -aminoalkyls would be desirable.

(20) The low  $g$  values found for some of our radicals also support this conformation. See, *e.g.*, T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972); T. Kawamura, D. J. Edge, and J. K. Kochi, *ibid.*, **94**, 1752 (1972).

(21) For example,  $t\text{-Bu}_2\dot{C}CH_2SiMe_3$ ,  $a^{Si} = 35.02$  G;  $t\text{-Bu}_2\dot{C}CH_2P(OEt)_2O$ ,  $a^P = 109.4$  G.

(22) N.R.C.C. Postdoctorate Fellow 1973-1974.

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## Novel Routes to New, Long-Lived 1,1,2,2-Tetrasubstituted Ethyl Radicals of Unusual Conformation<sup>1</sup>

Sir:

We wish to report the formation of some highly hindered 1,1,2,2-tetrasubstituted ethyl radicals. Not

(1) Issued as N.R.C.C. No. 14248.

Table I. Epr Parameters for Some 1,1,2,2-Tetrasubstituted Ethyl Radicals at 25° (Coupling Constants in Gauss)

Radical	<i>g</i>	<i>a</i> <sup>13</sup> C <sub>α</sub>	<i>a</i> <sup>29</sup> Si <sub>β</sub>	<i>a</i> <sup>29</sup> Si <sub>γ</sub>	<i>a</i> <sup>H</sup> <sub>β</sub> <sup>a</sup>	<i>a</i> <sup>H</sup> <sub>γ</sub> <sup>b</sup>	<i>a</i> <sup>13</sup> C <sub>γ</sub> <sup>b</sup>
1 (Me <sub>3</sub> Si) <sub>2</sub> ĊCH(SiMe <sub>3</sub> ) <sub>2</sub>	2.0024	<i>c</i>	13.71	27.59	≤ 0.27 <sup>d</sup>	<i>d</i>	4.88 (6) <sup>e</sup>
2 (Me <sub>3</sub> Si)( <i>t</i> -Bu)ĊCH(SiMe <sub>3</sub> ) <sub>2</sub>	2.0023	<i>c</i>	14.8	29.07	< 2.0	~0.3 <sup>f</sup>	9.65 (3)
3 ( <i>t</i> -Bu) <sub>2</sub> ĊCH(SiMe <sub>3</sub> ) <sub>2</sub>	2.0023	42.89		30.74	< 2.0	~0.16 <sup>f</sup>	10.2 (6)
4 ( <i>t</i> -Bu) <sub>2</sub> ĊCH( <i>t</i> -Bu) <sub>2</sub>	2.0023	45.77			< 3.5	<i>g</i>	11.8 (6)
Me <sub>2</sub> ĊCHMe <sub>2</sub> <sup>h</sup>	2.0025	<i>i</i>			10.77	22.92 <sup>i</sup>	<i>i</i>
( <i>t</i> -Bu) <sub>2</sub> ĊCH <sub>2</sub> (SiMe <sub>3</sub> ) <sup>k</sup>	2.0024	46.35		35.02	15.76	0.36	10.23 (6)
(Me <sub>3</sub> Si) <sub>3</sub> Ċ <sup>l</sup>	2.0027	~26	13.5			0.38	5.2 (9)

<sup>a</sup> When < sign is used, value quoted is  $\Delta H_{pp}$  of central line. <sup>b</sup> Due to Me groups of *t*-Bu or Me<sub>3</sub>Si attached to  $\alpha$ -carbon. <sup>c</sup> Not resolved but probably  $\leq 28$ –29 G. <sup>d</sup> See text. <sup>e</sup> From [(CD<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>ĊCH[Si(CD<sub>3</sub>)<sub>3</sub>]<sub>2</sub>. <sup>f</sup> Partly resolved. <sup>g</sup> Not resolved. <sup>h</sup> Via photolysis of (Me<sub>2</sub>CH)<sub>2</sub> in *t*-BuOO-*t*-Bu at -60°. <sup>i</sup> Not detected. <sup>j</sup> Due to  $\alpha$ -Me groups. <sup>k</sup> Reference 2. <sup>l</sup> Reference 9.

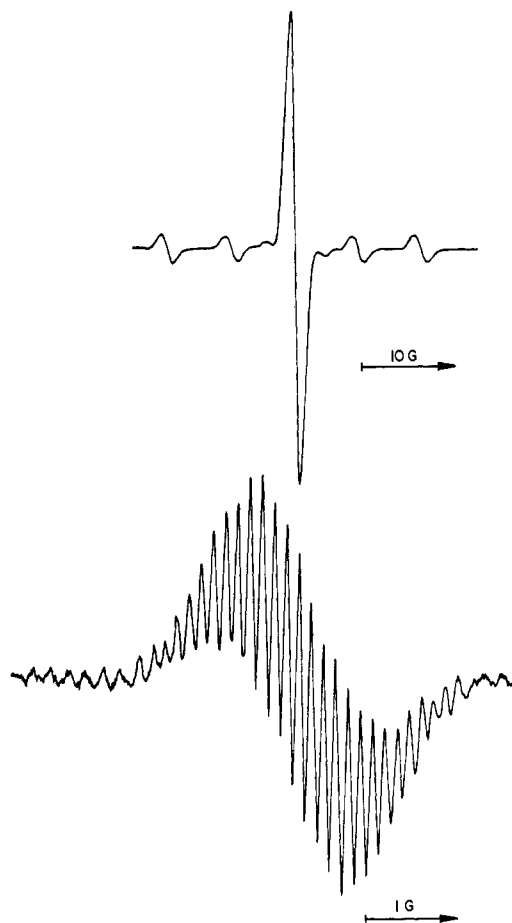


Figure 1. First derivative epr spectrum of 1: Top, full spectrum slightly over modulated; bottom, central line at optimum resolution.

surprisingly<sup>2-4</sup> these radicals are remarkably long lived. Their principal interest lies, however, in the number and diversity of the routes by which they are obtained and in the conformation they adopt which makes the lone  $\beta$ -hydrogen "invisible" in their epr spectra. That is, hyperfine splitting by this hydrogen is less than the line width, so its presence can only be inferred, and the radicals were therefore identified only with some difficulty. In this communication we confine ourselves to ethyl radicals having trimethylsilyl groups and *tert*-butyl (*t*-Bu) groups.

The (Me<sub>3</sub>Si)<sub>2</sub>ĊCH(SiMe<sub>3</sub>)<sub>2</sub> radical, 1, has been pre-

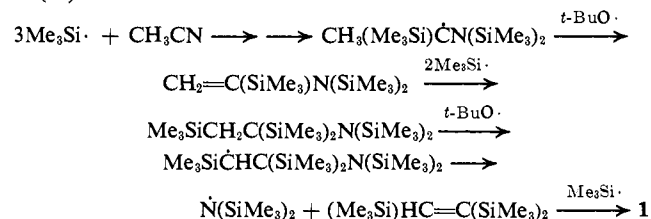
(2) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973).

(3) G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 2441 (1974).

(4) R. A. Kaba, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 6202 (1974).

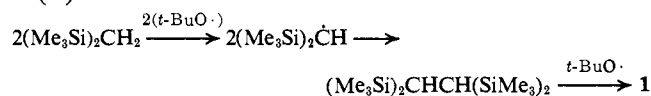
pared by prolonged photolysis of the following solutions in the cavity of an epr spectrometer at 25°: (A) Me<sub>3</sub>SiH, *t*-BuOO-*t*-Bu, and acetonitrile (1:1:1 v/v),<sup>5</sup> (B) (Me<sub>3</sub>Si)<sub>2</sub>CH<sub>2</sub> (10% v/v) in *t*-BuOO-*t*-Bu, (C) Me<sub>3</sub>SiH, *t*-BuCH=CH-*t*-Bu, and *t*-BuOO-*t*-Bu (1:1:2 v/v), (D) Me<sub>3</sub>SiH, *t*-BuC≡CH, and *t*-BuOO-*t*-Bu (1:2:4 v/v). While any mechanism must be somewhat speculative the following routes are suggested.

(A)



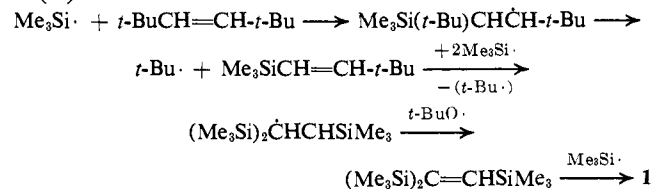
This route is consistent with the initial formation of a variety of nitrogen containing radicals and with our data<sup>4</sup> on Me<sub>3</sub>Si· additions to other nitriles and to imines.

(B)



This is consistent with the initial formation and very rapid dimerization of (Me<sub>3</sub>Si)<sub>2</sub>ĊH radicals.<sup>6</sup>

(C)



A number of long-lived radicals were produced in this system, but after standing for 2 days in the dark at room temperature only 1 remained. The facile loss of *t*-Bu· from the  $\beta$  position of the radical intermediates is consistent with the short lifetimes and first-order decay of radicals such as (*t*-Bu)<sub>2</sub>CHĊ(*t*-Bu)<sub>2</sub> (see below).

Half-lives for 1 depended very much on the exact experimental conditions, presumably because 1 frequently decays by reaction with minor impurities. Method A gave the longest half-life, *viz.*, 120 hr at 50°. The most stable unconjugated alkyl radical we have

(5) Prolonged photolysis of solutions of Me<sub>3</sub>SiH (10% v/v) in *t*-BuOO-*t*-Bu gave only Me<sub>3</sub>Si·.

(6) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3422 (1973).

