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

Radical	ga	a^{N}	a ^H NH	a ^R NR	a ^R CR	a ¹³ C	a ^H -t-Bu
t-Bu ² ĊNHSiMe ³	2.0024	1.28	16.57	16.21		8,89°	0.25
t-Bu2CNHSi-n-Bu3	2.0024	1.24	15.25	d		d	0.23
$t-Bu_2CN(Si-n-Bu_3)_2$		2.91*					
Ad(Me ₃ Si)CN(SiMe ₃) ₂	2.0022	2.0		23.5 ^b		36.5 ⁷	
(Me ₃ Si) ₂ CN(SiMe ₃) ₂	2.0025	2.05		20.5 ^{b,g}	14.30.0	$2.0^{g,h}$	0.20^{i}
t-Bu ₂ CNHI(EtO) ₂ PO]	2,0023	3.30	23.58	57.79 <i>i</i>		10.46°	0.35
$t-Bu_2CN[(EtO)_2PO]_2$	2.0022	4.09		56.58i		9.90°	0.17
t-Bu[(EtO) ₂ PO]ĊN[(EtO) ₂ PO] ₂	2.0022	3.53		46.6 ⁱ	39 .4 <i>i</i>		0.40

^a Calculated from the Breit-Rabi equation. ^{b 29}Si. ^c γ^{13} C of t-Bu groups, *i.e.*, (CH₃)₃C. ^d Could not be determined because of strong signal attributed to t-Bu₂CN(Si-n-Bu₃)₂. ^e The presence of other long-lived radicals allowed only the N coupling to be measured. ^f α -¹³C, ^e Estimated using computer simulation. ^h Six ¹³C, presumably due to Me₃Si groups on C rather than to those on N. ⁱ a^{H} of Me₃Si, presumably the Me₃Si groups on C. i^{31} P.

to give the expected triadduct, the trimethylsilyl radical

$$t$$
-BuC \equiv N + 3 $\dot{R} \longrightarrow t$ -Bu(R) \dot{C} NR₂

replaces the tert-butyl group and gives a tetraadduct.

$$t$$
-BuC \equiv N + 4Me₃Si · \longrightarrow (Me₃Si)₂ČN(SiMe₃)₂

This same radical is produced by addition of Me_3Si . 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 (Me₃Si)₃C and t-Bu₃C radicals).⁴ 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-BuC \equiv N) had not observably decayed in 3 weeks at 25°. In contrast, t-Bu₂CN[(EtO)₂PO]₂ at ca. 10^{-4} M had a half-life of ca. 8 hr; t-Bul(EtO)₂PO)CN[(EtO)₂-POl₂ decayed with first-order kinetics and a half-life of 29 min, and the t-Bu₂CNHR 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.13 Since only "stabilized" alkyl groups are lost the most probable route to tetra(trimethylsilyl)aminomethyl involves α scission of the iminoyl radical^{14,15} formed in the initial step.

t-BuC \equiv N + Me₃Si · \longrightarrow t-BuCNSiMe₃ \longrightarrow t-Bu · + CNSiMe₃

The isocyanide then adds¹⁸ three Me₃Si · radicals, one after the other.

 $CNSiMe_3 + 3MeSi \rightarrow (Me_3Si)_2\dot{C}N(SiMe_3)_2$

Several features of Table I deserve comment. Thus, although the a^{N} values are similar to those found in analogous unhindered α -aminoalkyl radicals (normally $4 < a^{\text{N}} < 7$ G) the a^{H}_{NH} values are very much larger than normal $(0 < a^{H}_{NH} < 6 \text{ G})$.¹⁹ According to Lyons and Symons,⁸ the unhindered α -aminoalkyls are most probably planar at the α -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.⁸

(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, $\dot{C}H_2NHCH_3$, $a^N = 5.84$, $a^H_{NH} = 6.35 \text{ G}^6$; $\dot{C}H_2$ - $\text{NHC}_{2}\text{H}_{5}, a^{\text{N}} = 6.3, a^{\text{H}}_{\text{NH}} \sim 0 \text{ G}^{5}; \text{ CH}_{3}\text{CHNHC}_{2}\text{H}_{5}, a^{\text{N}} = 4.8, a^{\text{H}}_{\text{NH}} \sim$ 0.9 G⁵; CH₃ĊHN(C₂H₅)₂, $a^{N} = 5.18$ G.⁵



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

For all our radicals, the splitting constants are virtually independent of temperature (40 to -90°), suggesting that they exist in a "locked" conformation. Since steric effects should dominate all other interactions $(cf. t-Bu_2CCH_2R)$,^{2,3} these radicals should adopt conformation 2.²⁰ The α -C should be planar (cf. the $a^{1^{3}C_{\alpha}}$ value for Ad(Me₃Si)ĊN(SiMe₃)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})^{2,3} is only about half of that found in structurally related t-Bu₂CCH₂R radicals.²¹ 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 α -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, 3 t-Bu₂CCH₂SiMe₃, $a^{Si} = 35.02$ G; t-Bu₂CCH₂P- $(OEt)_2O$, $a^P = 109.4$ G.

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

R. A. Kaba,²² D. Griller,²² K. U. Ingold* Division of Chemistry, National Research Council of Canada Ottawa, Ontario, Canada KIA OR9 Received April 24, 1974

Novel Routes to New, Long-Lived 1,1,2,2-Tetrasubstituted Ethyl Radicals of Unusual Conformation¹

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,

⁽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 β-scission of such radicals is known.¹⁰⁻¹⁸
(16) H. Ohta and K. Tokamaru, Chem. Commun., 1601 (1970).

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

_	Radical	g	$a^{1^{1^{2}C}\alpha}$	a ²⁹ Siß	$a^{2^{9}\mathrm{Si}\gamma}$	a ^{Hβ a}	a ^{Hy b}	a ¹⁸ Cy b
1	(Me ₃ Si) ₂ ĊCH(SiMe ₃) ₂	2.0024	с	13.71	27.59	<0.27 ^d	d	4.88 (6)*
2	$(Me_3Si)(t-Bu)CCH(SiMe_3)_2$	2.0023	с	14.8	29.07	<2.0	$\sim 0.3^{f}$	9.65 (3)
3	$(t-Bu)_2CCH(SiMe_3)_2$	2.0023	42.89		30.74	<2.0	~0.16/	10.2(6)
4	$(t-Bu)_2\dot{C}CH(t-Bu)_2$	2.0023	45.77			<3.5	8	11.8 (6)
	Me ₂ CCHMe ₂ ^h	2.0025	i			10.77	22.92 <i>i</i>	i
	$(t-Bu)_2\dot{C}CH_2(SiMe_3)^k$	2.0024	46.35		35.02	15.76	0.36	10.23 (6)
	(Me₃Si)₃Ċ ⁱ	2.0027	~ 26	13.5			0.38	5.2(9)

^a When < sign is used, value quoted is ΔH_{pp} of central line. ^b Due to Me groups of *t*-Bu or Me₃Si attached to α -carbon. ^c Not resolved but probably $\leq 28-29$ G. ^d See text. ^e From [(CD₃)₃Si]₂CCH[Si(CD₃)₃]₂. ^f Partly resolved. ^e Not resolved. ^h Via photolysis of (Me₂-CH)₂ in *t*-BuOO-*t*-Bu at -60° . ⁱ Not detected. ⁱ Due to α -Me groups. ^k Reference 2. ⁱ Reference 9.



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

surprisingly ²⁻⁴ 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 β 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 tertbutyl (t-Bu) groups.

The (Me₃Si)₂CCH(SiMe₃)₂ radical, 1, has been pre-

pared by prolonged photolysis of the following solutions in the cavity of an epr spectrometer at 25°: (A) Me₃SiH, t-BuOO-t-Bu, and acetonitrile (1:1:1 v/v),⁵ (B) (Me₃Si)₂CH₂ (10% v/v) in t-BuOO-t-Bu, (C) Me₃SiH, t-BuCH=CH-t-Bu, and t-BuOO-t-Bu (1:1:2 v/v), (D) Me₃SiH, 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.

$$3Me_{3}Si_{\cdot} + CH_{3}CN \longrightarrow CH_{3}(Me_{3}Si)\dot{C}N(SiMe_{3})_{2} \xrightarrow{t-BuO_{\cdot}} CH_{2}=C(SiMe_{3})N(SiMe_{3})_{2} \xrightarrow{2Me_{3}Si_{\cdot}} Me_{3}SiCH_{2}C(SiMe_{3})_{2}N(SiMe_{3})_{2} \xrightarrow{t-BuO_{\cdot}} Me_{3}Si\dot{C}HC(SiMe_{3})_{2}N(SiMe_{3})_{2} \longrightarrow \dot{N}(SiMe_{3})_{2} + (Me_{3}Si)HC=C(SiMe_{3})_{2} \xrightarrow{Me_{3}Si_{\cdot}} 1$$

This route is consistent with the initial formation of a variety of nitrogen containing radicals and with our data⁴ on Me₃Si · additions to other nitriles and to imines.

$$2(Me_3Si)_2CH_2 \xrightarrow{2(t-BuO+)} 2(Me_3Si)_2\dot{C}H \xrightarrow{--+}$$

t-BuO (Me₃Si)₂CHCH(SiMe₃)₂ · → 1

This is consistent with the initial formation and very rapid dimerization of (Me₃Si)₂ĊH radicals.⁶

$$Me_{3}Si_{\cdot} + t-BuCH = CH-t-Bu \longrightarrow Me_{3}Si(t-Bu)CHCH-t-Bu \longrightarrow t-Bu_{\cdot} + Me_{3}SiCH = CH-t-Bu \xrightarrow{+2Me_{3}Si_{\cdot}} - (t-Bu_{\cdot})$$

$$(Me_{3}Si)_{2}CHCHSiMe_{3} \xrightarrow{t-Bu()} (Me_{3}Si)_{2}C = CHSiMe_{3} \xrightarrow{Me_{3}Si_{\cdot}} 1$$

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 β position of the radical intermediates is consistent with the short lifetimes and first-order decay of radicals such as $(t-Bu)_2$ CHC $(t-Bu)_2$ (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

⁽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).}

⁽⁵⁾ Prolonged photolysis of solutions of Me₈SiH (10% v/v) in t-BuOO-t-Bu gave only MeaSi.

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

examined previously is $(Me_3Si)_3C$ which has a halflife of only 2 hr at this temperature^{3,6}

(D) The t-Bu(Me₃Si) $\dot{C}CH(SiMe_3)_2$ radical, 2, was prepared by photolysis of t-BuC=CH, Me₃SiH, and t-BuOO-t-Bu (1:2:4 v/v). At 50° the half-life of 3 \times 10^{-6} M 2 was 23 hr. Storage of a much more concentrated solution of 2 for many hours at 50° left a residue of 1 (about 3% based on the initial 2).

 $Me_{3}Si \cdot + t \cdot BuC = CH$ $Me_{3}Si \cdot + t \cdot BuC = CH$ $Me_{3}Si(t \cdot Bu)C = \dot{C}H \rightarrow t \cdot Bu \cdot + Me_{3}SiC = CH$ $\frac{^{3}Me_{3}Si}{t \cdot Bu} + Me_{3}SiC = CH$

The $(t-Bu)_2\dot{C}CH(SiMe_3)_2$ radical, 3, was generated by $Me_3Si \cdot addition$ to $(t-Bu)_2C = CH_2$ via the intermediate $(t-Bu)_2$ ČCH₂SiMe₃ radical² and by Me₃Si · addition to $(t-Bu)_2C = CH-t-Bu$ (presumably via the $(t-Bu)_2CH$ -(t-Bu)SiMe₃ radical which was too short lived to be positively identified). The latter method of preparation gave 3 which, at concentrations in the range 2 \times 10^{-4} to 2 \times 10⁻⁵ M, decayed with first-order kinetics and had a half-life of 2.3 hr at 50°.

$$Me_{3}Si + (t \cdot Bu)_{2}C \Longrightarrow CH_{2} \longrightarrow (t \cdot Bu)_{2}CCH_{2}SiMe_{3}$$

$$(t \cdot Bu)_{2}C \Longrightarrow CHSiMe_{3} \xrightarrow{Me_{3}Si} 3$$

$$\int -(t \cdot Bu)_{2}C \Longrightarrow CHSiMe_{3} \xrightarrow{Me_{3}Si} 3$$

$$Me_{3}Si + (t \cdot B_{2})_{2}C \Longrightarrow CHSiMe_{3} \xrightarrow{Me_{3}Si} 3$$

 $Me_3Si + (t \cdot Bu)_2C \Longrightarrow CHt \cdot Bu \longrightarrow (t \cdot Bu)_2CCH(t \cdot Bu)SiMe_3$

The $(t-Bu)_2 CCH(t-Bu)_2$ radical, 4, was prepared by hydrogen abstraction by t-BuO· from the parent hydrocarbon.³ This radical also decays with first-order kinetics, $\tau_{1/2} = 9.8$ sec at 25°.

The stability of the foreging radicals decreases from 1 to 4. Radicals 1, 2, and 3 probably decay by CH_3 elimination from an α -substituent, such a process occurring more readily from t-Bu than from Me₃Si. Radical 4 probably loses a β -(t-Bu·). Unless 1 decays by a bimolecular process at high concentrations (i.e., a disproportionation), we see no reason why it should not be isolated if a more convenient source is discovered.

The epr parameters of 1, 2, 3, and 4 are listed in Table I. Values of $a^{H\beta}$ are so low that they are within the line width for 2, 3, and 4. That is, proton splittings are not completely resolved in these radicals and so they all yield a single line epr spectrum that is flanked only by the appropriate ¹³C and/or ²⁹Si satellites. Only for radical 1 are the protons on the α -substituents fully resolved (see Figure 1). The principal multiplet of 1 can be reproduced extremely well by computer simulation using at least four combinations of proton coupling constants, a line width $(\Delta H_{pp}) = 0.1$ G, and a^{13C} $(6^{13}C) = 4.88 \text{ G}, viz:$ (i) $a^{\text{H}}(9 \text{ H}) = 0.135, a^{\text{H}}(9 \text{ H}) =$ 0.27, a^{H} (1 H) = 0.675 G; (ii) a^{H} (9 H) = 0.135, a^{H} (9 H) = 0.405 G; (iii) $a^{\text{H}} (10 \text{ H}) = 0.135, a^{\text{H}} (9 \text{ H}) =$ 0.405 G; (iv) a^{H} (9 H) = 0.135, a^{H} (1 H) = 0.27, a^{H} (9 H) = 0.405 G. The hyperfine coupling to the lone β -H must therefore be uniquely small,⁷ and in fact possibility (i) was eliminated by treating $(CD_3)_3Si$ with The resulting $[(CD_3)_3Si]_2\dot{C}CH[Si(CD_3)_3]_2$ CH₃CN. radical had no resolvable deuteron couplings and the width $(\Delta H_{\rm pp})$ of the principal line was only 0.48 G. The β -H coupling in 1 must therefore be ≤ 0.27 G.

In substituted ethyl radicals, values of $a^{H_{\beta}}$ can be approximately described by the empirical relation,^{2,10} $a^{H\bar{\beta}} = A + B \cos^2{\theta}$, where θ is the angle between $C_{\alpha}2_{p_{\alpha}}$ axis and the C_{α} , C_{β} , H_{β} plane. For the constants, A and B values of 0-5 and 40-45 G have been suggested.¹⁰ The very small value of $a^{H_{\beta}}$ for 1 (and also for 2, 3, and 4) implies that $\theta = 90^{\circ}$ (*i.e.*, $a^{H_{\beta}} = A$).



These radicals must be locked into this conformation by steric factors.^{11,12} The relatively large values of $a^{2^9 \text{Si}\gamma}$ also support this conformational assignment.¹¹ Moreover, since R_{α} and R'_{α} are always magnetically inequivalent, our general failure to resolve splittings due to protons on α -Me₃Si and α -(t-Bu) groups is not surprising.

The variety of ways in which these and other 2-4,13long-lived carbon centered radicals (not necessarily containing Me₃Si or t-Bu· groups)¹³ can be obtained suggests that they are far more ubiquitous in freeradical chemistry than has previously been supposed.

(9) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).
(10) See, e.g., H. Fischer in "Free Radicals," Vol. 2, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 19.
(11) For a discussive of the second s

(11) For a discussion of the conformational effect in substituted ethyl radicals see ref 2, and references cited therein.

(12) For comparison, the less hindered Me₂CCHMe₂ radical shows a much weaker preference for this conformation (Table I), but the preference does become more pronounced as the temperature is lowered, *i.e.*, $a^{H\beta} = 11.9 \text{ G}$ at 20° and 9.8 G at -120° (in cyclopropane). (13) D. Griller and K. U. Ingold, unpublished results.

(14) N.R.C.C. Postdoctoral Fellow 1973-1974.

D. Griller,¹⁴ K. U. Ingold*

Division of Chemistry, National Research Council of Canada Ottawa, Ontario, Canada KIAOR9 Received June 4, 1974

Ozonolysis of cis- and trans-Diisopropylethylene with Added Oxygen-18 Acetaldehyde

Sir:

Three proposals for the mechanism of the reaction of ozone with alkenes in solution have received prominent attention: the Criegee mechanism,1 the syn-anti zwitterion mechanisms,^{2,3} and the aldehyde interchange mechanism.⁴ It is well known that aldehydes added to alkene solutions may be incorporated into final ozonides produced via ozonization. The alde-

(1) R. Criegee, Rec. Chem. Progr., 18, 11 (1957).

(2) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, J. Amer. Chrm. Soc., 90, 1822 (1968).

(3) (a) R. P. Lattimer, C. W. Gillies, and R. L. Kuczkowski, J. Amer. Chem. Soc., 95, 1348 (1973); (b) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, ibid., 96, 348 (1974).

(4) (a) P. R. Story, R. W. Murray, and R. D. Youssefyeh, J. Amer. Chem. Soc., 88, 3144 (1966); (b) R. W. Murray, R. D. Youssefyeh, and P. R. Story, ibid., 89, 2429 (1967).

⁽⁷⁾ The lowest $a^{H\beta}$ for a tetrasubstituted ethyl in solution known to us is 3.68 G for 9,9'-bifluorenyl-9-yl.⁸ The exceptionally low value of $a^{H\beta}$ in 1 may, in part, be a consequence of the known ability of α -silicon substituents to "mop-up" a good deal of electron density.9

⁽⁸⁾ F. A. Neugebauer and R. W. Groh, Tetrahedron Lett., 1005 (1973).