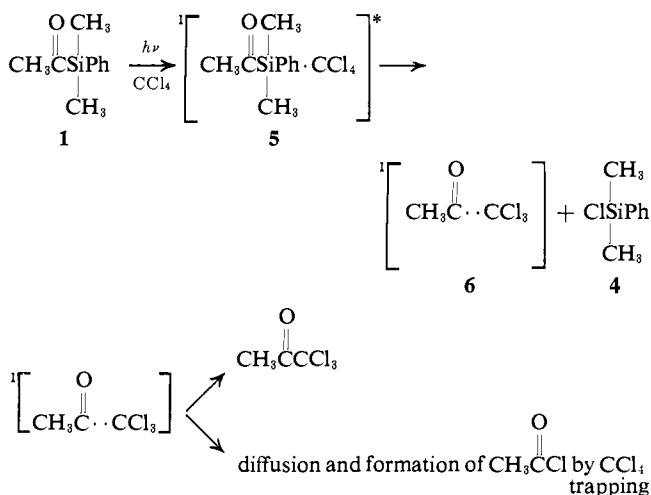


Scheme II



leading only to the acetyl-trichloromethyl pair at the expense of any silyl-trichloromethyl pair.^{11a}

The mechanism proposed in Scheme II for acylsilyl photolysis is analogous to one proposed earlier for the photolysis of diisopropyl ketone (DIK) in CCl_4 .^{12,13} The favored mechanism in the DIK studies involves nonradiative decay of a complex from DIK (Si) and CCl_4 (exciplex). The $\text{DIK} \cdot \text{CCl}_4$ exciplex selectively collapses to form acetyl chloride and an isopropyl-trichloromethyl singlet radical pair.

Regardless of the mechanism for its formation, the key intermediate in Scheme II is the singlet acetyl-trichloromethyl radical pair **6**. Cage recombination of **6** should yield trichloroacetone which exhibits enhanced absorption (as is observed). The cage escaped product, acetyl chloride, is observed in the CIDNP spectrum in emission, as predicted by application of the CKO rules.^{9,10} The product distribution temperature dependence is also accommodated by this scheme. At low temperatures, the cage recombination product of **6**, trichloroacetone, is favored. At higher temperatures, cage escape is favored, as expected,¹⁴ and the relative proportion of escape product, acetyl chloride, increases accordingly.

The photolysis of **1** in solvents other than CCl_4 takes an entirely different course. Photolysis of **1** in benzyl chloride, for example, results in a complex product mixture as well as a complex CIDNP spectrum. However, the signals from the methyl groups of the silyl compound **4**, which were observed unpolarized during the photolysis of **1** in CCl_4 , clearly exhibit emission during the photolysis of **1** in benzyl chloride. This observation is consistent with a mechanism involving formation of an authentic silyl-acyl triplet pair, from which the silyl chloride is an escape product.

Our observations force the conclusion that CCl_4 plays an active role in the photochemistry of acylsilyl compounds. In fact, it seems likely that the type I cleavage to radicals is

(11a) NOTE ADDED IN PROOF. Professor A. G. Brook has informed us that fluorescence quenching of acyl silanes by CCl_4 has recently been observed in his laboratories. This is further support of the exciplex mechanism.

(12) (a) J. A. denHollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Lett.*, **10**, 430 (1971); (b) J. A. denHollander, *Chem. Ind. (Belge)*, **36**, 1083 (1971).

(13) See also T. DoMinh, *Chem. Ind. (Belge)*, **36**, 1080 (1971).

(14) For a comprehensive review of the chemistry of "caged" radicals, see J. P. Lorand, *Prog. Inorg. Chem.*, **17**, 207 (1972).

avoided when CCl_4 is used as a solvent for these photolyses.

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Ned A. Porter,* P. M. Iloff, Jr.

Paul M. Gross Chemical Laboratories, Duke University
Durham, North Carolina 27706

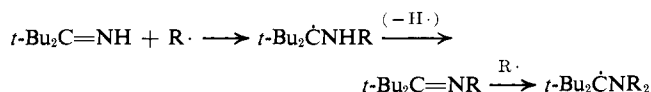
Received June 21, 1974

Some Unusually Long-Lived α -Aminoalkyl Radicals¹

Sir:

We have recently shown that long-lived alkyl radicals can be prepared by addition of a wide variety of simple radicals to 1,1-di-*tert*-butylethylene.² The resulting 2-substituted 1,1-di-*tert*-butylethyl radicals have provided important insights into problems of alkyl radical conformation³ and kinetics.⁴ As a logical outgrowth of this work, we have generated a number of long-lived α -aminoalkyls by radical additions to di-*tert*-butylimine, $t\text{-Bu}_2\text{C}=\text{NH}$, and pivalonitrile, $t\text{-BuC}\equiv\text{N}$. Some of the radicals produced had quite unexpected structures and some have epr hyperfine couplings that are quite different from those expected from earlier epr studies of simple α -aminoalkyl radicals.⁵⁻⁹

A number of radicals that add readily to $t\text{-Bu}_2\text{C}=\text{CH}_2$ gave no epr signals attributable to addition to the imine (e.g., $\text{C}_6\text{H}_5\cdot$, $\text{C}_6\text{F}_5\cdot$, and $\dot{\text{C}}\text{Cl}_3$) or nitrile (e.g., $\text{C}_6\text{H}_5\cdot$, CF_3 , $\text{CF}_3\text{O}\cdot$, and $\dot{\text{S}}\text{iCl}_3$).^{10,11} However, both trimethylsilyl, $\text{Me}_3\text{Si}\cdot$, and diethoxyphosphonyl, $(\text{EtO})_2\dot{\text{P}}\text{O}$,¹² added readily to yield the radicals listed in Table I. Addition to the imine gives initially a monoadduct, as expected. What were not expected, were the diadducts produced after a few minutes of photolysis.



The diadduct structure is certain for $\text{R} = (\text{EtO})_2\dot{\text{P}}\text{O}$ but with Me_3Si a number of long-lived radicals were formed that so complicated the spectra that structural assignment was impossible. However, with $\text{R} = n\text{-Bu}_3\text{Si}$ a radical containing nitrogen that we believe was the diadduct was identified.

Although the phosphonyl radical adds to $t\text{-BuC}\equiv\text{N}$

(1) Issued as N.R.C.C. No. 14249.

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

(3) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, in press.

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

(5) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970); *ibid.*, **53**, 3932 (1970).

(6) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 738 (1971).

(7) R. O. C. Norman and N. H. Anderson, *J. Chem. Soc. B*, 993 (1971).

(8) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 502 (1972).

(9) For epr spectra of radicals from amino acids and amides see, e.g., H. Paul and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 972 (1969); R. Poupko, A. Lowenstein, and B. L. Silver, *J. Amer. Chem. Soc.*, **93**, 580 (1971).

(10) A referee has pointed out that addition may occur but remain unobserved by epr because the adduct radical is unstable. Such processes might be probed by chemical analysis.

(11) We were also unsuccessful in attempts to add $(\text{CH}_3)_3\text{C}\cdot$ and $(\text{CH}_3)_3\text{Sn}\cdot$ to these compounds.

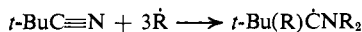
(12) Generated by photolysis of di-*tert*-butyl peroxide solutions containing Me_3SiH or $(\text{EtO})_2\text{POH}$.

Table I. Epr Parameters for Long-Lived α -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 ^b		8.89 ^c	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 ^e					
$Ad(Me_3Si)\dot{C}N(SiMe_3)_2$	2.0022	2.0		23.5 ^b		36.5 ^f	
$(Me_3Si)_2\dot{C}N(SiMe_3)_2$	2.0025	2.05		20.5 ^{b,g}	14.3 ^{b,g}	2.0 ^{g,h}	0.20 ⁱ
$t\text{-Bu}_2\dot{C}NH[(EtO)_2PO]$	2.0023	3.30	23.58	57.79 ^j		10.46 ^c	0.35
$t\text{-Bu}_2\dot{C}N[(EtO)_2PO]_2$	2.0022	4.09		56.58 ^j		9.90 ^c	0.17
$t\text{-Bu}[(EtO)_2PO]\dot{C}N[(EtO)_2PO]_2$	2.0022	3.53		46.6 ^j	39.4 ⁱ		0.40

^a Calculated from the Breit-Rabi equation. ^b ²⁹Si. ^c γ^{13C} of t -Bu groups, *i.e.*, $(CH_3)_3C$. ^d Could not be determined because of strong signal attributed to $t\text{-Bu}_2\dot{C}N(Si-n\text{-Bu}_3)_2$. ^e The presence of other long-lived radicals allowed only the N coupling to be measured. ^f $\alpha\text{-}^{13C}$. ^g 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. ^j ³¹P.

to give the expected triadduct, the trimethylsilyl radical



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

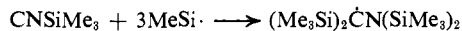


This same radical is produced by addition of Me₃Si· to benzyl cyanide and isopropyl cyanide. It is the longest lived of all the radicals reported here (as we might expect from a comparison of $(Me_3Si)_3\dot{C}$ and $t\text{-Bu}_3\dot{C}$ radicals).⁴ For example, a *ca.* 10^{-3} M solution (from benzyl cyanide) decayed to *ca.* 3×10^{-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.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.



The isocyanide then adds¹⁸ three Me₃Si· 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 α -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).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

(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).

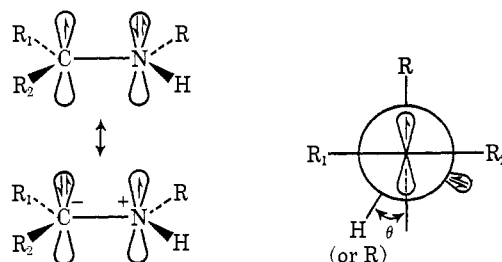
(15) The β -scission of such radicals is known.¹⁶⁻¹⁸

(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; $CH_2\dot{C}HNHC_2H_5$, $a^N = 4.8$, $a^{H_{NH}} \approx 0.9$ G; $CH_2\dot{C}HN(C_2H_5)_2$, $a^N = 5.18$ G.⁵



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°), suggesting that they exist in a "locked" conformation. Since steric effects should dominate all other interactions (*cf.* $t\text{-Bu}_2\dot{C}CH_2R$),^{2,3} these radicals should adopt conformation 2.²⁰ The α -C should be planar (*cf.* the a^{13C} 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 $a^{R_{NR}}$)^{2,3} is only about half of that found in structurally related $t\text{-Bu}_2\dot{C}CH_2R$ 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 $t\text{-Bu}_2\dot{C}CH_2SiMe_3$, $a^{Si} = 35.02$ 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.

R. A. Kaba,²² D. Griller,²² K. U. Ingold*

Division of Chemistry, National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R9

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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.