Silylaminyl Radicals. Part 3.[1] Electron Spin Resonance Studies of Alkyl(trialkylsilyl)aminyl Radicals

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A series of *N*-alkyl-*N*-trialkylsilylaminyl radicals $R^1\dot{N}SiR^2_3$ (R_3^2Si = Me_3Si, Et_3Si, Pr^i_3Si, or Bu^tMe_2Si) have been generated photochemically in solution and characterised using e.s.r. spectroscopy. The radicals $Ph\dot{N}SiBu^tMe_2$ and $Bu^t\dot{N}GeMe_3$ were also studied. The well resolved spectra and low magnitudes of a(N) (*ca.* 12.5 G) indicate that these aminyls are π radicals and this is confirmed by the magnitudes of the β-proton splittings for a series of radicals in which the conformation about the C–N bond may be inferred on the basis of steric considerations. The $+I/-M$ substituent effect of the trialkylsilyl ligand is thus insufficient to bring about a switch from a π to a σ SOMO. However, the *g*-factors for the alkyl(silyl)aminyls (2.0061—2.0075) are significantly larger than those of dialkylaminyls (typically 2.0047) and also increase with the bulk of the substituents at nitrogen. This effect is interpreted in terms of increased effectiveness of spin–orbit coupling for the unpaired electron on nitrogen in $R\dot{N}SiR_3$, as a result of a reduction in the energy required to promote a σ lone-pair electron into the π SOMO. These conclusions are supported by the results of MNDO molecular orbital calculations. The lifetimes of the alkyl(silyl)aminyls increase with the extent of steric shielding of the nitrogen radical centre. The aminyl cyclo-$C_4H_7\dot{N}SiBu^tMe_2$ undergoes rapid ring-opening at 195 K, whilst the cyclopentyl analogue does not rearrange at 265 K.

In Part 1[2] we reported e.s.r. studies of the generation and reactions of bis(trialkylsilyl)aminyl radicals in fluid solution. These radicals, the e.s.r. spectra of which have not yet been observed, were shown to be much more reactive than dialkylaminyl radicals and to abstract hydrogen from hydrocarbons very readily. The latter reaction is a propagation step in the free radical chain halogenation of hydrocarbons by bis(trialkylsilyl)halogenoamines and, in Part 2,[1] the regioselectivity of $(R_3Si)_2N^{\bullet}$ in hydrogen atom abstraction was investigated using product analysis techniques.

In the present paper we describe e.s.r. studies of a range of alkyl(trialkylsilyl)aminyl radicals and compare their spectra with those of analogous dialkylaminyl radicals. The e.s.r. spectra of $Bu^t\dot{N}SiMe_3$ and $Bu^t\dot{N}SiMe_2Bu^t$ were reported in a preliminary communication[3] in which we showed that an earlier claim[4] to have identified the former radical was erroneous.

Results

E.s.r. spectra were monitored during continuous u.v.–visible (λ > 240 nm) photolysis of static liquid samples in the spectrometer cavity, using techniques that have been described previously.[5] Two general methods were used for production of alkyl(trialkylsilyl)aminyl radicals. The first involves direct photochemical cleavage of the N–Cl bond in an alkyl(trialkylsilyl)chloroamine, usually in the presence of norbornene, ethylene, or hexamethyldisilane which act as scavengers of the chlorine atoms formed simultaneously [equation (i)].

$$R(R_3Si)NCl \xrightarrow{h\nu} R\dot{N}SiR_3 + Cl^{\bullet} \qquad (i)$$

The second method involves homolytic displacement (*via* an intermediate phosphoranyl radical) from an aminophosphine by photochemically generated t-butoxyl or bis(trimethylsilyl)aminyl[1] radicals [equations (ii) and (iii), X = Bu^tO or $(Me_3Si)_2N$]. For comparative purposes, a number of dialkylaminyl radicals were also generated by analogous displacement from aminophosphines of the type $R_2NP(OEt)_2$ or $(R_2N)_3P$.[6] The main disadvantage of the phosphine route is that the phosphoranyl radical intermediate (**1**) does not break down readily to give $R\dot{N}SiR_3$ unless the nitrogen carries relatively bulky ligands and competing β-scission to give alkyl radicals can be a problem, especially when X = Bu^tO [equations (iv) and (v)]. Since even $Me_2N\dot{P}(OEt)_2OBu^t$ breaks down very readily to give $Me_2N^{\bullet}$, these observations imply that the N–P bond is stronger in $R(R_3Si)N\dot{P}(OR)_3$ than in $R_2N\dot{P}(OR)_3$ and, in general, it appears that the N–Y bond is stronger in $R(R_3Si)N–Y$ than in $R(R_3C)N–Y$.[1,2]

$$X–X \xrightarrow{h\nu} 2X^{\bullet} \qquad (ii)$$

$$X^{\bullet} + R(R_3Si)NP(OEt)_2 \longrightarrow \underset{(\mathbf{1})}{R(R_3Si)N\dot{P}(OEt)_2X} \longrightarrow R\dot{N}SiR_3 + XP(OEt)_2 \qquad (iii)$$

$$R(R_3Si)N\dot{P}(OEt)_2N(SiMe_3)_2 \longrightarrow R(R_3Si)NP(O)(OEt)N(SiMe_3)_2 + Et^{\bullet} \qquad (iv)$$

$$R(R_3Si)N\dot{P}(OEt)_2OBu^t \longrightarrow R(R_3Si)NP(O)(OEt)_2 + Bu^{t\bullet} \qquad (v)$$

Photolysis of some silylchloroamines initiated chain reactions leading to rapid depletion of these reagents and to the build-up of secondary radical products. Cleaner spectra of the shorter lived silylaminyl radicals could often be obtained with a Pyrex filter (cut off *ca.* 290 nm) positioned in the photolysing beam.

E.s.r. parameters for the alkyl(silyl)aminyl radicals generated in this work are presented in Table 1 and Table 2 gives data for a number of dialkylaminyl radicals, some of which have not been reported previously.

t-Butyl(trialkylsilyl)aminyl Radicals.—The radical $Bu^t\dot{N}SiMe_3$ proved the most difficult to detect, on account of its short lifetime and large peak-to-peak linewidth (ΔB_{p-p} 3.8 G at 188 K). This radical appeared to be reactive in hydrogen abstraction and, when derived from the chloroamine, the intensity of its e.s.r. spectrum was irreproducible and seemed to depend markedly on the presence of trace impurities. These problems were not encountered for the longer lived radicals containing more bulky trialkylsilyl groups and strong spectra were obtained for $Bu^t\dot{N}SiEt_3$, $Bu^t\dot{N}SiMe_2Bu^t$, and $Bu^t\dot{N}SiPr^i_3$

Table 1. E.s.r. parameters for alkyl(trialkylsilyl)aminyl radicals in cyclopropane

Radical	Source [b]	T/K	g-Factor	Hyperfine splittings (G) a(N)	$a(H_\beta)$ [b]	Others [b]
$Me\dot{N}SiMe_2Bu^t$	A	154	2.0063 [c]	12.3	32.1 [c] (3)	
		177	2.0063 [c]	12.3	32.1 [c] (3)	
$Bu^tCH_2\dot{N}SiMe_2Bu^t$	A	153	2.0063 [c]	12.1	48.0 [c] (2)	
		234	2.0063 [c]	12.1	46.4 [c] (2)	
$Pr^i\dot{N}SiMe_2Bu^t$	C	189	2.0063	12.3	12.3 (1)	
		255	2.0063	12.3	12.8 (1)	
cyclo-$C_5H_9\dot{N}SiMe_2Bu^t$	A,C	189	2.0061	12.0	12.6 (1)	
		243	2.0061	12.0	13.1 (1)	
$Bu^t\dot{N}SiMe_3$	A,B,C	160	2.0066	12.2		
		187	2.0066	12.2		*d*
$Bu^t\dot{N}SiEt_3$	A,C	150	2.0069	12.4		2.8 (3H)
		184	2.0069	12.4		*e*
$[^2H_9]Bu^t\dot{N}SiEt_3$	A	150	2.0069	12.3		*e, f*
$Bu^t\dot{N}SiMe_2Bu^t$	A,B	150	2.0068	12.5		2.6 (3H)
		221	2.0068	12.5		*e, g*
$[^2H_9]Bu^t\dot{N}SiMe_2Bu^t$	A	149	2.0068	12.5		12.9 ($4\,^{13}C$), 12.9 ($1\,^{29}Si$) [h]
		220	2.0068	12.5		12.9 ($4\,^{13}C$), 12.9 ($1\,^{29}Si$) [h]
$Bu^t\dot{N}SiPr^i_3$	A,B	151	2.0075	12.7		*ca.* 2.2 (2H)
		239	2.0075	12.7		*e, i*
$[^2H_9]$-$Bu^t\dot{N}SiPr^i_3$	A	154	2.0074	12.7		2.0 (1H)
$Ph\dot{N}SiMe_2Bu^t$	B [j]	203	2.0041	7.35		6.00 ($2H_o$), 1.95 ($2H_m$), 7.80 ($1H_p$)

[a] A = Photolysis of the appropriate chloroamine in the presence of norbornene; B = photolysis of Bu^tOOBu^t in the presence of the appropriate aminophosphine; C = photolysis of $(Me_3Si)_2NN(SiMe_3)_2$ in the presence of the appropriate aminophosphine. [b] Numbers of equivalent nuclei shown in parentheses. [c] Corrected for higher order effects; calculated from measured line positions and the microwave frequency using Preston's program ESRLSQ.[15] [d] ΔB_{p-p} 3.9 G. [e] Fine structure not detectable at higher temperatures; line (envelope) width less than at lower temperatures. Presumably an exchange process which averages the resolved with (smaller) unresolved proton splittings is responsible for this narrowing. [f] ΔB_{p-p} 1.8 G; same linewidth at 200 K. [g] ΔB_{p-p} 3.2 G. [h] ΔB_{p-p} 1.9 G. [i] ΔB_{p-p} 5.0 G. [j] Diethyl peroxide gave a 'cleaner' spectrum (see Figure 5). With Bu^tOOBu^t as a primary radical source, more persistent unidentified radicals were also present.

Table 2. E.s.r. parameters for dialkylaminyl radicals and related species

Radical	Solvent [a]	T/K	g-Factor	Hyperfine splittings (G) a(N)	$a(H_\beta)$ [b]	Others [b]	Ref.
$Me_2N^\bullet$ [c]	A	167	2.0047 [d]	14.7 [d]	27.3 [d] (6)		*e, f*
$Me\dot{N}Bu^t$ [g]	A	154	2.0047 [d]	14.5 [d]	28.5 [d] (3)		*h*
$Bu^tCH_2\dot{N}Bu^t$	A	311	2.0048 [d]	14.6 [d]	39.2 [d,i] (2)		*j*
$Pr^i\dot{N}Bu^t$ [g]	A	166	2.0046	14.7			*h*
	A	258	2.0046	14.7	3.2 (1)	0.35 [k]	*h*
$Bu^t_2N^\bullet$	B	203	2.0045	14.2			*l*
$\overline{CH_2CH_2N}^{\bullet}$ [m]	A	163	2.0044 [d]	12.4 [d]	30.5 [d] (4)		*e, n*
$\overline{CH_2(CH_2)_2N}^{\bullet}$ [m]	A	162	2.0047 [d]	14.0 [d]	38.6 [d] (4)	0.55 (2H)	*e, n*
$\overline{CH_2(CH_2)_3N}^{\bullet}$	B	228	2.0046	14.4	39.1 (4)		*l*
$Me_2\overline{C(CH_2)_3CMe_2N}^{\bullet}$	C	200	2.0048	14.7		0.63 [k]	*o*
$Ph\dot{N}H$	D	300	2.0033	7.95		12.94 ($1H_\alpha$), 6.18 ($2H_o$), 2.01 ($2H_m$), 8.22 ($1H_p$)	*p*
$Ph\dot{N}Bu^t$	E	300	2.0035	9.70		5.84 ($2H_o$), 1.99 ($2H_m$), 7.09 ($1H_p$)	*q*

[a] A = Cyclopropane; B = solid solution in adamantane; C = isopentane; D = water; E = n-alkane. [b] Numbers of equivalent nuclei shown in parentheses. [c] From photolysis of Bu^tOOBu^t + $(Me_2N)_3P$. [d] Corrected for higher order effects; calculated from the measured line positions and the microwave frequency using Preston's program ESRLSQ.[15] [e] Remeasured for this work. [f] W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, 1970, **92**, 5235; W. C. Danen and R. C. Rickard, *ibid.*, 1972, **94**, 3254. [g] From photolysis of Bu^tOOBu^t + $R_2NP(OEt)_2$. [h] This work. [i] Decreases with increasing temperature. [j] B. P. Roberts and J. N. Winter, *J. Chem. Soc., Chem. Commun.*, 1978, 961. [k] Line spacing; complex multiplet due to splitting from the γ-protons. [l] Ref. 31. [m] From photolysis of Bu^tOOBu^t and the appropriate secondary amine. [n] W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 1971, 2247. [o] Ref. 33. [p] Ref. 21. [q] Ref. 20.

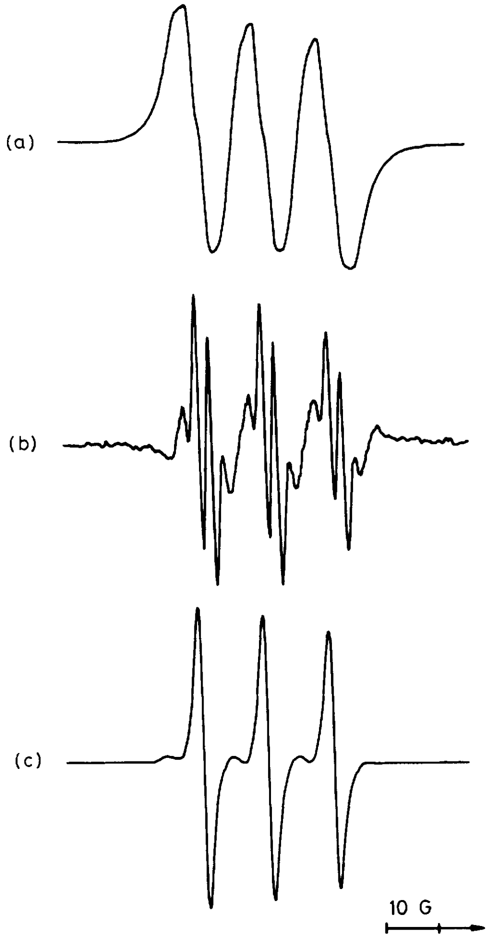

Figure 1. E.s.r. spectra in cyclopropane at 148 K of (a) $Bu^t\dot{N}SiMe_2Bu^t$ (first-derivative spectrum); (b) $Bu^t\dot{N}SiMe_2Bu^t$ (third-derivative spectrum); (c) $[^2H_9]Bu^t\dot{N}SiMe_2Bu^t$ (first-derivative spectrum)

using either the chloroamine or phosphine routes. The spectrum of $Bu^t\dot{N}SiMe_2Bu^t$ at 194 K appears as Figure 1 of ref. 3. Below *ca.* 160 K, the spectrum showed further resolution into 1:3:3:1 quartets (see Figures 1a and b) although above *ca.* 180 K this fine structure could not be detected. The quartet splitting was not apparent in the spectrum of $[^2H_9]Bu^t\dot{N}SiMe_2Bu^t$ (see Figure 1c) and ΔB_{p-p} was substantially less than for the protio-analogue. The splitting therefore arises from three protons in the *N*-t-butyl group, probably from one of the three methyl groups.

The satellite lines (Figure 1c), which represent *ca.* 9% of the total spectrum, are from radicals that contain ^{29}Si (I 1/2; natural abundance 4.7%) or that contain ^{13}C (I 1/2; natural abundance 1.1%) in either the α or β positions of the *N*-t-butyl group.*

Similar results were obtained for $Bu^t\dot{N}SiEt_3$ and $[^2H_9]$-$Bu^t\dot{N}SiEt_3$, but the spectrum of $Bu^t\dot{N}SiPr^i_3$ showed long-range splitting from only *two* protons (see Figure 2), while that of $[^2H_9]Bu^t\dot{N}SiPr^i_3$ showed a doublet splitting from a *single* proton. Hence, it appears that one proton from the *N*-t-butyl group and one isopropyl methine proton are responsible for the small splittings observed for $Bu^t\dot{N}SiPr^i_3$.

The *g*-factors of $Bu^t\dot{N}SiR_3$ increase significantly with the bulk of the trialkylsilyl group, being largest for $Bu^t\dot{N}SiPr^i_3$.

Secondary-alkyl(trialkylsilyl)aminyl Radicals.—Three radicals of the type $R^s\dot{N}SiMe_2Bu^t$, in which R^s = Pr^i, cyclo-C_4H_7, or cyclo-C_5H_9, were chosen for study. The *N*-isopropyl and *N*-cyclopentyl derivatives showed splittings of 12.3 and 12.6 G, respectively, from one β proton at 189 K and both these splittings increased with increasing temperature.† The spectrum of $Pr^i\dot{N}SiMe_2Bu^t$ is shown in Figure 3.

Although we found no evidence for ring-opening of cyclo-$C_5H_9\dot{N}SiMe_2Bu^t$ up to 265 K, even at 195 K the only spectrum detected when $(Me_3Si)_2NN(SiMe_3)_2$ was photolysed in the presence of cyclo-$C_4H_7N(SiMe_2Bu^t)\dot{P}(OEt)_2$ was one which we assign to the alkyl radical (**2**) [$a(2H_\alpha)$ 22.1, $a(2H_\beta)$ 29.3 G]. Evidently, cyclo-$C_4H_7\dot{N}SiMe_2Bu^t$ undergoes rapid ring opening at low temperatures [equation (vi)].

Photolysis of $Pr^iN(Cl)SiMe_2Bu^t$ (**3**) in cyclopropane at 170 K gave rise initially to the spectrum of the long lived t-butyl(isopropyl)aminyl radical (see Table 2), although after prolonged photolysis this became weaker and was partially replaced by that of $Pr^i\dot{N}SiMe_2Bu^t$. We suggest that during distillation (or, less likely, during the photolysis) of (**3**) a small amount of rearrangement takes place to give (**4**) [equation (vii)], which could undergo direct photolysis to yield $Pr^i\dot{N}Bu^t$. Alternatively, (**4**) could give $Pr^iN(Cl)Bu^t$ by halogen exchange with (**3**) and photolysis of this *N*-chlorodialkylamine would certainly give $Pr^i\dot{N}Bu^t$. A closely related 1,2-alkyl shift from silicon to nitrogen takes place during thermal rearrangement of (**5**) to (**6**) at 200 °C,[8] and a similar rearrangement of $Ph_3SiOOSiPh_3$ is known.[9] It is possible that a radical pair mechanism is operative in all three rearrangements.

Primary-alkyl(trialkylsilyl)aminyl Radicals.—The neopentyl- and methyl-(t-butyldimethylsilyl)aminyl radicals were studied and the spectrum of $Bu^tCH_2\dot{N}SiMe_2Bu^t$ is shown in Figure 4. Both radicals were generated only by the chloroamine route and a good quality spectrum of $CH_3\dot{N}SiMe_2Bu^t$ was difficult to obtain. The phosphoranyl radicals $CH_3N(SiMe_2Bu^t)\dot{P}(OEt)_2X$ [X = EtO, Bu^tO, or $(Me_3Si)_2N$] did not undergo α-scission to give $CH_3\dot{N}SiMe_2Bu^t$.[2] Whilst $a(3H_\beta)$ for $CH_3\dot{N}SiMe_2Bu^t$ was essentially independent of temperature, the much larger β proton splitting for the *N*-neopentyl analogue showed a negative temperature coefficient.

Phenyl-(t-butyldimethylsilyl)aminyl Radical.—The spectrum of this radical, along with a computer simulation obtained using the parameters listed in Table 1, is given in Figure 5. The nitrogen splitting and *g*-factor shown by this radical, which was obtained only by displacement from phosphorus, are both significantly smaller than the corresponding values for the *N*-alkyl analogues.

t-Butyl(trimethylgermyl)aminyl Radical.—For comparison we prepared $Bu^t\dot{N}GeMe_3$ by displacement from Bu^t-$N(GeMe_3)\dot{P}(OEt)_2$ using photochemically generated bis(trimethylsilyl)aminyl radicals. The spectrum consists of three broad lines [a(N) 12.6 G, ΔB_{p-p} 2.6 G, g 2.0052 in cyclopropane at 202 K] and it was not possible to detect satellites from $Bu^t\dot{N}{}^{73}GeMe_3$ present in natural abundance (7.8%; I 9/2).

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* In our preliminary communication[3] we omitted to consider the possibility of coupling with $^{13}C_\alpha$. Comparison with other *N*-t-butylaminyl radicals[2,7] indicates that $a(^{13}C_\alpha)$ and $a(^{13}C_\beta)$ will be of similar magnitude (although presumably of opposite sign).

† The accuracy of these measurements is not high because of incomplete resolution. From the observed 1:2:2:1 quartets, a(N) was taken as the separation between the central lines and the wing line separation as $2a(N) + a(1H)$. The results were checked by computer simulation of the spectra.

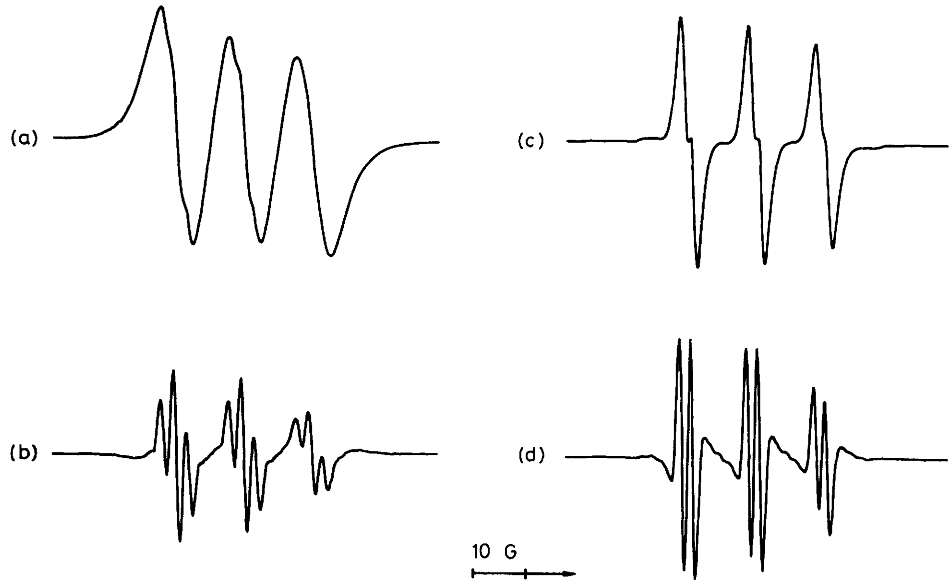


Figure 2. E.s.r. spectra in cyclopropane at 153 K of (a) $\mathrm{Bu^t\dot{N}SiPr^i_3}$ (first-derivative spectrum); (b) $\mathrm{Bu^t\dot{N}SiPr^i_3}$ (third-derivative spectrum); (c) $\mathrm{[^2H_9]Bu^t\dot{N}SiPr_3{}^i}$ (first-derivative spectrum); (d) $\mathrm{[^2H_9]Bu^t\dot{N}SiPr^i_3}$ (third-derivative spectrum)

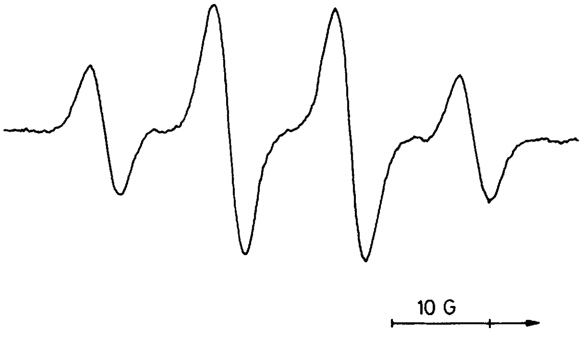
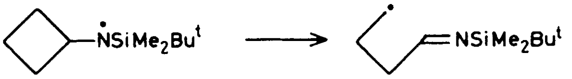


Figure 3. E.s.r. spectrum of $\mathrm{Pr^i\dot{N}SiMe_2Bu^t}$ in cyclopropane at 255 K



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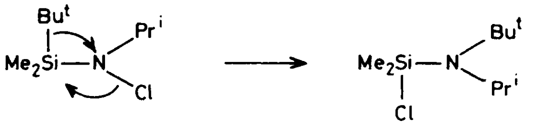
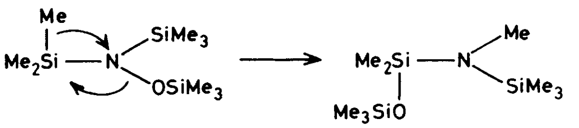


(3) (4) (vii)



(5) (6) (viii)

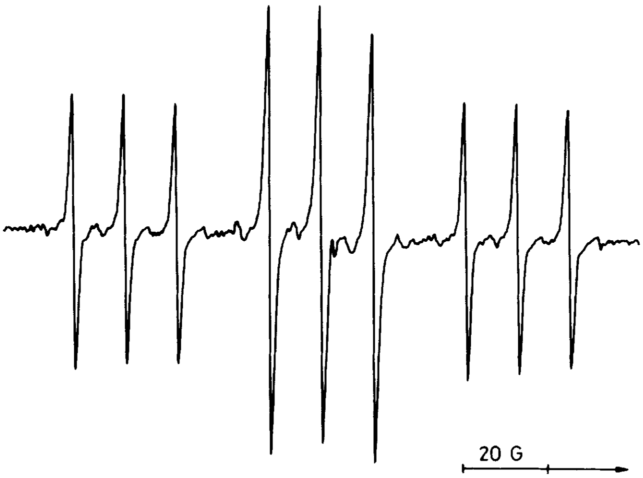


Figure 4. E.s.r. spectrum of $\mathrm{Bu^tCH_2\dot{N}SiMe_2Bu^t}$ in cyclopropane at 242 K

Rates of Radical Decay.—The radicals $\mathrm{Bu^t\dot{N}SiMe_2Bu^t}$, $\mathrm{Bu^t\dot{N}SiPr^i_3}$, $\mathrm{Bu^tCH_2\dot{N}SiMe_2Bu^t}$, and $\mathrm{Bu^t\dot{N}Pr^i}$ were chosen as representative examples and decay of each e.s.r. spectrum was monitored after interrupting photochemical generation at 230 K. Under the conditions employed, $\mathrm{Bu^t\dot{N}SiMe_2Bu^t}$ and $\mathrm{Bu^t\dot{N}SiPr_3{}^i}$ decayed by first-order (or pseudo-first-order) processes, whilst second-order decay was observed for the shorter lived $\mathrm{Bu^tCH_2\dot{N}SiMe_2Bu^t}$. The dialkylaminyl radical $\mathrm{Bu^t\dot{N}Pr^i}$ exhibited mixed first- and second-order decay kinetics. The rate constants and lifetimes are given in Table 3.

The Colour of Alkyl(trialkylsilyl)chloroamines.—The chloroamines investigated in this work are pale yellow-green liquids [$\mathrm{MeN(Cl)SiMe_2Bu^t}$ is a solid] which each exhibit one optical absorption maximum in the near u.v. region above 225 nm. Values of $\lambda_{max.}$ for solutions in $\mathrm{CF_2ClCCl_2F}$ at 293 K are given in Table 4, and it can be seen that the band shifts towards the visible with increasing bulk of the ligands attached to nitrogen.

Discussion

(i) *Electronic Configuration of Alkyl(trialkylsilyl)aminyl Radicals.*—All these radicals must be bent at nitrogen, since they give rise to well resolved e.s.r. spectra in fluid solution. If

Table 3. Rate constants for decay of selected radicals in cyclopropane at 230 K

Radical	Source [a]	Kinetic order of decay	Initial [radical]/M	k_t/s^{-1}	$2k_t$/l mol^{-1} s^{-1}	Lifetime [b] (s)
$Bu^tCH_2\dot{N}SiMe_2Bu^t$	A	Second	1.6×10^{-6}		2×10^7	0.005 [c]
$Bu^t\dot{N}SiMe_2Bu^t$	A	First	3.4×10^{-5}	0.49		2.0
$Bu^t\dot{N}SiPr^i_3$	A	First	5.8×10^{-5}	0.42		2.4
$Bu^t\dot{N}SiPr^i_3$	B	First	6.7×10^{-5}	0.31		3.2
$Pr^i\dot{N}Bu^t$	B	Complex	2.2×10^{-5}			*ca.* 5

[a] A = photolysis of the appropriate chloroamine in the presence of norbornene; B = photolysis of Bu^{t}OOBu^t in the presence of the appropriate amino(diethoxy)phosphine. [b] Equal to $1/k_t$ or $1/2k_t[R^\bullet]$, as appropriate. [c] For $[R^\bullet] = 1 \times 10^{-5}$ M.

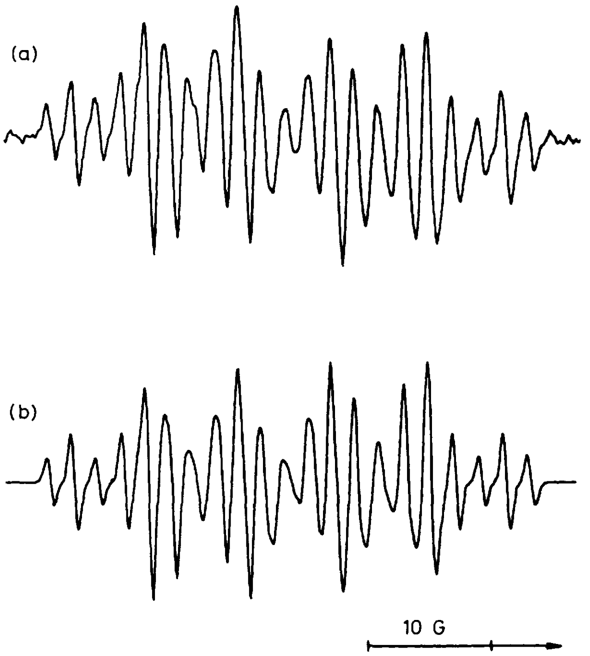
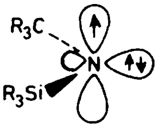


Figure 5. (a) E.s.r. spectrum of $Ph\dot{N}SiMe_2Bu^t$ in cyclopropane at 203 K; (b) computer simulation of the spectrum using the coupling constants given in Table 1 and a gaussian lineshape



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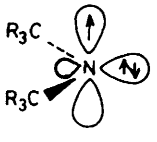

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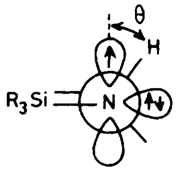


(9)

they were linear (or quasi-linear) at nitrogen, the resulting orbital degeneracy (or near-degeneracy) would lead to extreme line broadening, of the type predicted for alkoxyl radicals RO$^\bullet$ in solution.[10] The small nitrogen splitting (12—13 G) indicates that the N-2*s* contribution to the SOMO is close to zero and hence that the alkyl(silyl)aminyls must be π radicals (**7**), like the dialkylaminyl analogues (**8**),[11] rather than σ radicals. This conclusion receives strong support from consideration of the magnitudes and temperature dependencies of the hyperfine splittings from β-protons in the *N*-alkyl groups. Similar arguments based on β-proton coupling constants have shown conclusively that amidyl radicals $R\dot{N}C(O)R$ have π- rather than σ-type SOMOs,[12,13] although twisting about the N–C bond is an additional complication for these species.

Table 4. U.v. spectra of chloroamines in CF_2ClCCl_2F at room temperature under nitrogen

Compound	$\lambda_{max.}$[a]/nm	ε/mol l^{-1} cm^{-1}
$Bu^tN(Cl)SiMe_3$	295	126
$Bu^tN(Cl)SiMe_2Bu^t$	301	81
$Bu^tN(Cl)SiEt_3$	303	95
$Bu^tN(Cl)SiPr^i_3$	309	66
$Pr^iN(Cl)SiMe_2Bu^t$	297	65
$Bu^tCH_2N(Cl)SiMe_2Bu^t$	299	62
$MeN(Cl)SiMe_2Bu^t$	297	96

[a] Error ±1 nm.

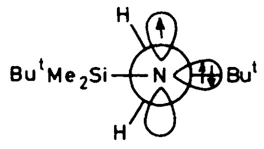
Unpaired spin density on the β-proton in (**9**) is expected to arise principally through a hyperconjugative interaction and to be related to the π spin population (ρ^π_N) on nitrogen according to the usual Heller–McConnell equation (ix),[14] where *A* and

$$a(H_\beta) = (A + B\cos^2\theta)\rho^\pi_N \qquad \text{(ix)}$$

B are constants and the former is relatively small. Assuming free rotation ($\bar{\theta}$ = 45°) about the N–C bond in $CH_3\dot{N}SiMe_2Bu^t$ and taking *A* to be zero, $B\rho^\pi_N$ is calculated to be 64.2 G. It is also reasonable to assume that ρ^π_N is very similar, and fairly close to unity, for all the alkyl(silyl)aminyl radicals. The β-proton splitting for $CH_3\dot{N}SiMe_2Bu^t$ (32.1 G) may be compared with the values of $a(H_\beta)$ for $(CH_3)_2\dot{C}H$,[15] $(CH_3)_2N^\bullet$, $CH_3\dot{N}C(O)Bu^t$,[13] $CH_3\dot{N}SO_2Me$,[16] $(CH_3)_2O^{+\bullet}$,[17] and $CH_3O^\bullet$[18] which are 24.7, 27.4, 29.2, 29.7, 43.0, and 52 G, respectively. Hyperconjugation is apparently more important for $CH_3\dot{N}SiMe_2Bu^t$ than for $CH_3\dot{N}R$ but less than for $(CH_3)_2O^{+\bullet}$ or $CH_3O^\bullet$, as expected if this interaction increases as the effective electronegativity of X in CH_3X increases,[19] that is as the SOMO energy decreases to match more closely that of the filled π group orbital of the CH_3 moiety.

On steric grounds, the most stable conformation of $Bu^tCH_2\dot{N}SiMe_2Bu^t$ would be predicted to be (**10**) and both the magnitude and negative temperature dependence of $a(2H_\beta)$ are consistent with this structure. Making the assumptions discussed above, the calculated value of $\bar{\theta}$ at 153 K is 30°, equal to that expected for (**10**).

The β-proton splittings for $Pr^i\dot{N}SiMe_2Bu^t$ and cyclo-$C_5H_9\dot{N}SiMe_2Bu^t$ are both smaller than that for the *N*-methyl analogue and both show a positive temperature coefficient. For $Pr^i\dot{N}SiMe_2Bu^t$ at 189 K the value of $a(1H_\beta)$ corresponds to $\bar{\theta}$ = 64°, close to that expected for the conformation (**11**) which represents a compromise between the demands of hyperconjugative and steric interactions. The barrier to rocking between (**11a** and **b**) could be relatively small but, because of steric repulsion between the methyl and trialkylsilyl groups, the barrier to full rotation about the C–N bond would be much larger. The endocyclic β-CH_2 groups in cyclo-$C_5H_9\dot{N}SiMe_2Bu^t$ are 'tied back' and their effective size is smaller than that of the



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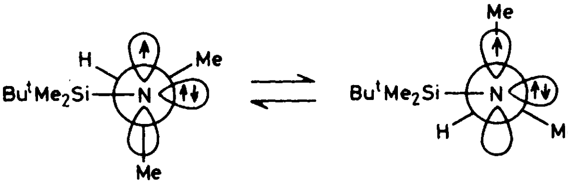
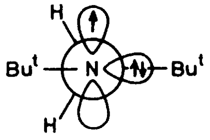


(x)

(11a) (11b)



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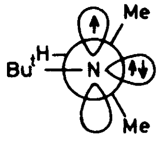


(13)

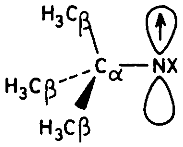
methyl groups in (**11**), leading to a smaller value of $\bar{\theta}$ and hence to a larger value of $a(1H_\beta)$, at a given temperature, for the former radical.

The most stable conformation of the dialkylaminyl radical $Bu^tCH_2\dot{N}Bu^t$ is clearly (**12**), analogous to (**10**) (see Table 2), but the increased steric repulsion between the *N*-t-butyl group and the two β-methyl groups of the *N*-isopropyl moiety forces $Pr^i\dot{N}Bu^t$ to adopt the conformation (**13**),* in which $\bar{\theta}$ is close to 90°, rather than one analogous to (**11**).

The ring proton splittings for $Ph\dot{N}SiMe_2Bu^t$ are very similar to those shown by the π radicals $Ph\dot{N}Bu^t$ and $Ph\dot{N}H$.[20,21] The benzene ring in the phenyl(silyl)aminyl radical must lie in the CNSi plane and a(N) and g are both reduced, relative to the corresponding values for the *N*-alkyl derivatives, as a result of conjugative delocalisation of the unpaired electron from nitrogen on to the ring.

(ii) ^{13}C-, ^{29}Si-, *and Long-range Proton Splittings.*—The values of $a(^{13}C_\alpha)$, and $a(^{13}C_\beta)$ for $Bu^t\dot{N}SiMe_2Bu^t$ (**14**; X = Bu^tMe_2Si) may be compared with those[7b] (9.9 and 8.0 G, respectively) for [**14**; X = $(EtO)_2P(O)O$] and with the similar values[2,7a] for (**14**; X = Bu^tO or Me_3SiO). The mechanism of spin transmission to C_β is presumably hyperconjugative, whilst σ–π spin polarisation is responsible for the coupling to C_α. Likewise, the coupling to $^{29}Si_\alpha$ is probably mainly the result of spin polarisation and its magnitude is similar to that observed for $Me_3Si\dot{N}OSiMe_3$ (11.6 G)[2] and that for $(Me_3Si)_3C^\bullet$ (13.5 G),[22] although delocalisation of the unpaired electron on to silicon (see below) would give rise to a *positive* contribution to the spin density in the Si-3*s* orbital.

For $Bu^t\dot{N}SiMe_2Bu^t$ and $Bu^t\dot{N}SiEt_3$ the long-range proton splitting originates from one methyl group in the N-Bu^t substituent, whereas for $Bu^t\dot{N}SiPr^i_3$ the resolved splitting is due to one proton in the N-Bu^t group and one proton in an isopropyl group. By analogy with the assignment of long-range splittings from γ-protons in the neopentyl radical,[23] we suggest the following interpretation.



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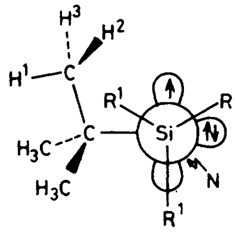

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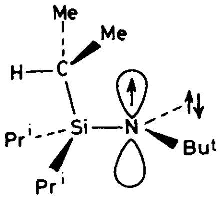

(16)

For steric reasons, the t-butyl(silyl)aminyl radicals adopt the conformation (**15**; $R^1 = R^2$ = Et or Pr^i; R^1 = Me, R^2 = Bu^t) in which rotation about the C–N and Si–N bonds is slow on the e.s.r. time scale and even rocking about these bonds, which could render equivalent two of the *C*-methyl groups or the two groups R^1 on silicon, is prevented by interlocking of the N-Bu^t and $N\text{-}R^1{}_2R^2Si$ groups. For $Bu^t\dot{N}SiMe_2Bu^t$ and $Bu^t\dot{N}SiEt_3$, the three protons of the eclipsing *C*-methyl group give rise to the resolved splitting[23] and these protons are rendered magnetically equivalent by rapid rotation about the H_3C–C bond. However, this rotation must be hindered in $Bu^t\dot{N}SiPr^i_3$ such that only one of the methyl protons, probably H^1 which is in the W-plan position, gives rise to resolvable splitting. We might expect that this single proton splitting would be significantly larger than the (averaged) three proton splitting in the less bulky radicals and the precise conformation of $Bu^t\dot{N}SiPr^i_3$ is therefore likely to be somewhat different from that of the other two derivatives. The single isopropyl proton which gives rise to resolvable splitting is probably that in the eclipsing *Si*-alkyl group and, on steric grounds, this proton would be expected to occupy the W-plan position as shown in (**16**).

(iii) *Substituent Effect of the* R_3Si *Group.*—Compared with an alkyl group, a trialkyl group is a σ electron donor (+*I* effect) but it is also a π electron acceptor (−*M* effect).[24] On the basis of qualitative considerations, we have proposed that the energy difference ΔE_{lp} between the π SOMO and the σ HOMO (essentially a nitrogen lone pair) of (**8**) will decrease upon replacement of R_3C by R_3Si, even if the angle at nitrogen remains unchanged.[2] The silylaminyl will be a π radical so long as the σ orbital remains lower in energy than the π orbital. For both (**7**) and (**8**), as the angle (φ) at nitrogen increases towards 180° the energy of the σ HOMO will increase whilst that of the π SOMO will remain fairly constant and hence ΔE_{lp} will decrease, towards zero in the limit of linearity. In fact, as discussed in Part 1,[2] replacement of R_3C by R_3Si is expected to be accompanied by widening of the angle at nitrogen and thus, on two counts, ΔE_{lp} should be smaller for $R_3C\dot{N}SiR_3$ than for $(R_3C)_2N^\bullet$.

To put these qualitative conclusions on to a firmer basis, we have carried out semi-empirical MNDO molecular orbital calculations[25,26] for the *anions* $(H_3C)_2N^-$, $H_3C\bar{N}SiMe_3$,

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* This is because the Si–C and Si–N bonds are longer than the corresponding bonds to carbon.

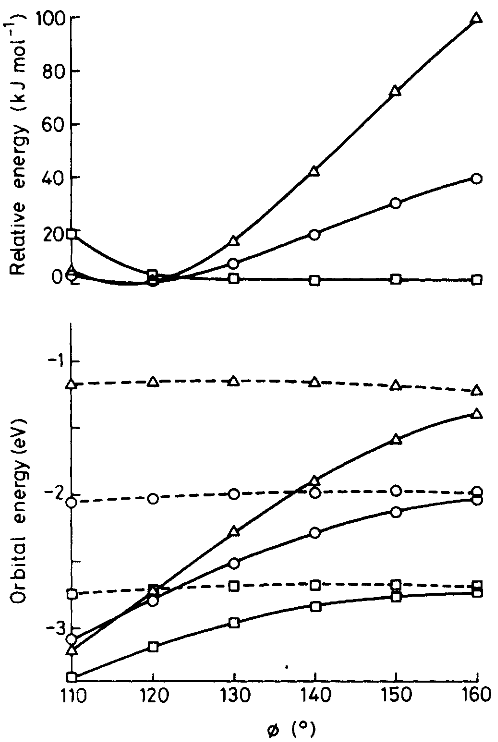
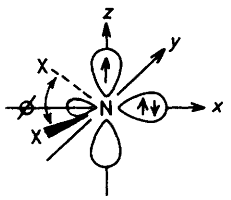


Figure 6. Relative total energies and orbital energies for $(CH_3)_2N^-$ (△), $CH_3\bar{N}SiH_3$ (○), and $(H_3Si)_2N^-$ (□) as a function of the bond angle at nitrogen, obtained by MNDO calculations. The dashed line refers to the HOMO and the full line to the NHOMO; the zero of relative total energy is different for each anion. The C–H and Si–H bond lengths were fixed at 1.090 and 1.487 Å, respectively

$(H_3Si)_2N^-$, $(Me_3C)_2N^-$, and $Me_3C\bar{N}SiMe_3$.* The anions were chosen in preference to the corresponding radicals because of interpretative difficulties associated with spin-unrestricted calculations for the open-shell species.† For each anion, fixed standard values were used for the C–H, Si–H, C–C, and Si–C bond lengths and bond angles other than φ were taken to be 109.5°. For each value of φ the C–N and/or Si–N bond lengths and the torsional angles about these bonds were optimised. The results for the first three anions are given in Figure 6, which shows the total energies and the energies of the HOMO and NHOMO (essentially π and σ lone pairs on nitrogen, respectively) as a function of φ. The anion HOMO and NHOMO are analogous to the radical SOMO and HOMO, respectively, and the energy of the anion HOMO should approximate to the negative of the radical electron affinity (Koopmans' theorem). The corresponding results for $(Me_3C)_2N^-$ and $Me_3C\bar{N}SiMe_3$ were very similar, except that for $\varphi < 133°$ the σ NHOMO of the latter was higher in energy than that of the former. We conclude that replacement of R_3C in $(R_3C)_2N^{\bullet}$ by R_3Si has the following consequences.

(a) The energy of the π SOMO is lowered considerably.

(b) There is a smaller effect on the energy of the σ HOMO, whether it is raised or lowered in energy depends on φ and on the nature of R. The $+I$ destabilising effect of one R_3Si group and its $-M$ stabilising effect will be more equal in magnitude for the σ orbital than for the π, and for values of φ in the range 110—125° the two effects approximately cancel for the former orbital. As φ approaches 180° the distinction between σ and π orbitals is lost.



(17)

(c) The energy separation between the π SOMO and σ HOMO, ΔE_{lp}, is reduced.

(d) The ease of bending at nitrogen is greatly increased. Full structural optimisation for $(H_3C)_2N^-$, $H_3C\bar{N}SiH_3$, and $(H_3Si)_2N^-$ gave values for φ of 117, 115, and 121°, respectively.‡ Similarly, MNDO-UHF calculations[26] for $(Me_3C)_2N^{\bullet}$ and $Me_3C\dot{N}SiMe_3$ ($\varphi_{opt.}$ 139 and 143°, respectively) indicated that it costs more than four times less energy to increase φ for the silylaminyl radical.

(iv) g-*Factors.*—There are two possible (and related) reasons for the appreciably higher *g*-factors of $R_3C\dot{N}SiR_3$ as compared with $(R_3C)_2N^{\bullet}$ (see Tables 1 and 2). The spin–orbit coupling constant (ζ_{Si}) for an Si-3*p* electron is significantly greater than ζ_C and hence delocalisation of the unpaired electron on to silicon could account for some of the observed increase in *g*-factor. However, the *g*-factors of $Me_3M\dot{C}H_2$ and $(Me_3M)_3C^{\bullet}$ (M = C or Si) are all 2.0026 ± 0.0001,[22,28] and hence this explanation is unlikely to be correct.§ Moreover, on the basis of this explanation there is no obvious reason why the *g*-factors of $R_3C\dot{N}SiR_3$ should be so markedly dependent on the bulk of the R_3Si group.

We propose that the higher *g*-factors of $R_3C\dot{N}SiR_3$ compared with $(R_3C)_2N^{\bullet}$ arise because of more effective spin–orbit coupling for the unpaired electron on nitrogen in the former radicals. Consider a bent aminyl radical (**17**) in which the unpaired electron is confined to the $2p_z$ orbital on nitrogen. When the magnetic field is aligned along the *z*-direction the *g*-factor (g_z) will be close to the free spin value (g_e 2.0023), but both g_x and g_y would be expected to be greater than g_e by δg_x and δg_y, respectively. The magnitude of δg_x will depend mainly on $\zeta_N/\Delta E_{N-X}$, where ΔE_{N-X} is the energy required to promote a β-spin electron into the SOMO from a filled N–X σ bonding orbital; δg_y will depend similarly on $\zeta_N/\Delta E_{N-X}$ but, in addition, it will reflect coupling of the SOMO with the lone pair orbital and its magnitude will also increase with $\zeta_N/\Delta E_{lp}$, where $\Delta E_{lp} = E_{SOMO} - E_{lone\ pair}$.[29] The average *g*-factor measured in solution (g_{av}) will, therefore, also be greater than 2.0023. When the XNX angle is *ca.* 120° or greater, the lone pair will be higher in energy than the N–X σ orbital and g_{av} will be determined mainly be g_y.[17,30] Effects which act to reduce ΔE_{lp}, such as the replacement of R_3C in $(R_3C)_2N^{\bullet}$ by R_3Si as discussed above, will increase g_y and thus g_{av}.

The *g*-value of $Bu^t\dot{N}SiPr^i{}_3$ is significantly larger than that of $Bu^t\dot{N}SiMe_3$, presumably because the angle at nitrogen is greater in the former radical as a result of steric interference between

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* Very recently, Glidewell and Thomson[27] have published an *ab initio* molecular orbital study of $(CH_3)_2N^-$, $CH_3\bar{N}SiH_3$, and $(H_3Si)_2N^-$ and have reported the calculated structures and proton affinities of these species. The information required for our purpose and summarised in Figure 6 was not reported.

† MNDO-UHF calculations for $H_3C\dot{N}SiH_3$ and $Me_3C\dot{N}SiMe_3$ predict both species to be bent π radicals, in agreement with experiment.

‡ The corresponding angles calculated by Glidewell and Thomson[27] are 106, 125, and 120° and these are probably more realistic than our values. However, MNDO calculations should provide reliable estimates of the relative ease of bending at nitrogen.

§ This argument is not unequivocal, because of possible differences in the accessibilities of excited states of $Me_3M\dot{N}R$ and $Me_3M\dot{C}R_2$.

the bulky $Pr^i{}_3Si$ group and the Bu^t group. The angle φ in alkyl(silyl)aminyl radicals is probably rather sensitive to steric effects, since bending at nitrogen requires little expenditure of energy (see above).

The question arises[31] as to why the *g*-factors of dialkylaminyl radicals do not fall appreciably when the angle at nitrogen is constrained to be much less than 120° by incorporation into a small ring (see Table 2). Thus, the *g*-value of aziridinyl (2.0044), although less than that of $Me_2N^{\bullet}$ (2.0047), is not as small as might be expected.[31] We suggest that as ΔE_{lp} *increases*, because of the greater N-2*s* character of the lone pair orbital as the XNX angle decreases from *ca.* 120° to 60°, this is offset by a concomitant *decrease* in ΔE_{N-X} which leads to an increase in g_x, because of the greater N-2*p* character of the N–X σ bonding orbitals. Hence g_{av} for $(R_3C)_2N^{\bullet}$ changes only slightly as the angle at nitrogen decreases from *ca.* 120° to 60°.

(v) *The Colour of* $R(R_3Si)NCl$.—A related explanation can be offered for the red shift in the low energy optical absorption band of $R(R_3Si)NCl$, which tails into the visible region and is responsible for the yellow-green colour, as the bulk of the *N*-alkyl and *N*-trialkylsilyl groups increase. This absorption probably results from an electronic transition to the N–Cl σ^* LUMO from the HOMO, which will be the nitrogen lone pair orbital or the π^* symmetry-allowed combination of this orbital with a chlorine lone pair orbital.[32] As the CNSi angle widens because of steric interaction between alkyl and trialkylsilyl groups, the N-2*s* character of the N–Cl σ and σ^* orbitals will decrease and the latter orbital will decrease in energy. The HOMO energy should be much less sensitive to the bond angle at nitrogen and thus the HOMO$\longrightarrow$LUMO transition energy will decrease as the bulk of the ligands increases.

(vi) *Radical Lifetimes.*—The primary-alkyl(silyl)aminyl radical $Bu^tCH_2\dot{N}SiMe_2Bu^t$ decays with second-order kinetics at 230 K, presumably by combination to give the corresponding hydrazine and by disproportionation [equation (xi)] to give

$$2Bu^tCH_2\dot{N}SiMe_2Bu^t \longrightarrow Bu^tCH_2N(H)SiMe_2Bu^t + Bu^tCH{=}NSiMe_2Bu^t \qquad (xi)$$

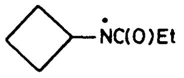
imine and silylamine. The rate constant is less than expected for a diffusion-controlled process and the relatively bulky ligands evidently afford some protection to the radical centre. Such steric shielding is more effective for the tertiary-alkyl(silyl)-aminyl radicals $Bu^t\dot{N}SiMe_2Bu^t$ and $Bu^t\dot{N}SiPr^i{}_3$, which are much longer lived and decay by first-order processes. The lifetime of $Bu^t\dot{N}SiPr^i{}_3$ is similar whether it is produced by the chloroamine or phosphine routes, suggesting that the β-scission process (xii) (*cf.* the β-scission of $Bu^tO^{\bullet}$) or intramolecular

$$Bu^t\dot{N}SiR_3 \longrightarrow Me^{\bullet} + Me_2C{=}NSiR_3 \qquad (xii)$$

1,4-hydrogen transfer from an *Si*-alkyl group[1] may be involved, rather than abstraction of hydrogen from the various other species present in each system. However, further speculation is not justified at this time.

Decay of $Bu^t\dot{N}Pr^i$ is kinetically complex and, as might be expected, its lifetime is intermediate between those of $Pr_2{}^iN^{\bullet}$ and the cyclic di-t-alkylaminyl radical $Me_2\overline{CCH_2CH_2CH_2\dot{N}}CMe_2$.[33] The latter radical undergoes first-order decay in hydrocarbon solvents (probably by hydrogen abstraction) and shows no sign of dimerising even at 153 K.[33]

Whilst rearrangement of cyclo-$C_5H_9\dot{N}SiMe_2Bu^t$ could not be detected, the cyclobutyl analogue underwent rapid ring opening, even at low temperatures, and thus it behaves more like the amidyl radical (**18**)[34] than the dialkylaminyl radical (**19**).[35] The latter undergoes ring opening more slowly and the rate constant and activation parameters for the rearrangement have been measured using e.s.r. spectroscopy.[35]



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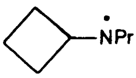

(19)

(viii) *t-Butyl(trimethylgermyl)aminyl Radical.*—The e.s.r. spectrum of $Bu^t\dot{N}GeMe_3$ is very similar to that of the silicon analogue, except that the former has a somewhat smaller *g*-factor. Our attempts to generate the corresponding tin-containing radical have been unsuccessful so far. The Me_3Ge group will be a less good π-acceptor than the Me_3Si ligand and thus the lower *g*-value of $Bu^t\dot{N}GeMe_3$ might be explained in terms of the increasing value of ΔE_{lp} for $Bu^t\dot{N}MMe_3$ along the series M = Si < Ge < C (see above). However, other factors may also be important since ζ_{Ge} is larger than ζ_{Si} and in this connection we note that although *g* for $Me_3Ge\dot{C}H_2$ is 2.0023 that for $Me_3Sn\dot{C}H_2$ (2.0008) is appreciably less than the free-spin value.[28]

Experimental

N.m.r. (in C_6D_6) and u.v. spectra were obtained using Varian XL-200 and Pye–Unicam SP8-400 instruments, respectively. E.s.r. spectra were obtained using either Varian E-4 or E-109 spectrometers, equipped for *in situ* photolysis of samples, using techniques which have been described previously.[5] Third derivative spectra were obtained using a Telmore Instruments sub-harmonic generator.

Semi-empirical MNDO molecular orbital calculations were carried out using the computer program written by Bischof.[26]

Materials.—Cyclopropane (Cambrian) was used as received. Norbornene was dissolved in isopentane, dried over molecular sieves and, after removal of the solvent, was distilled at atmospheric pressure, b.p. 99 °C. Di-t-butyl peroxide (Koch–Light) was treated with aqueous acidic potassium iodide to remove t-butyl hydroperoxide, dried ($MgSO_4$), and passed down a column of basic alumina (activity 1) before being distilled, b.p. 51—52 °C at 90 Torr. Tetrakis(trimethylsilyl)hydrazine[2] and the compounds $Bu^t(Me_3Si)NH$,[36] $Bu^t(Me_3Si)NCl$,[37] and $Me(Bu^tMe_2Si)NH$[38] were prepared according to published procedures. $Bu^t(Et_3Si)NH$[39] was prepared by the reaction of triethylchlorosilane with the lithium salt of t-butylamine in ether–hexane solvent. $[^2H_9]Bu^tNH_2$ was prepared from $[^2H_9]Bu^tOD$ (Aldrich) using the method of Charelli and Rassat.[40] Mass spectroscopic analysis (12 eV) showed the product to consist of $C_4D_9NH_2$ (81%), $C_4D_8HNH_2$ (16%), and $C_4D_7H_2NH_2$ (3%). The new compounds prepared in this work are listed in Table 5; the N-$[^2H_9]Bu^t$ derivatives were prepared from $[^2H_9]Bu^tNH_2$ using the methods described below for the protio-analogues. All compounds gave satisfactory ^1H n.m.r. spectra. All preparations were carried out under dry nitrogen.

Alkyl(trialkylsilyl)amines.—These were prepared by lithiation of the amine, using n-butyl-lithium in hexane, and subsequent reaction of the lithium amide with the appropriate trialkylchlorosilane. The more sterically crowded the compound, the more forcing the conditions required for its preparation and an equimolar amount of *NNN'N'*-tetramethylethylenediamine (TMEDA) was added for the preparation of $Bu^t(Pr^i{}_3Si)NH$, which is described in detail below.

Table 5. B.p.s and elemental analyses for the new compounds prepared in this work

Compound	B.p. (° C/Torr)	Elemental analysis [calculated (%)/found (%)] C	H	N	Cl	P
$Bu^t(Me_3Si)NP(OEt)_2$	83/4	49.8	10.6	5.3		11.7
		50.0	10.7	5.5		12.0
$Bu^t(Et_3Si)NCl$	36/0.1	54.1	10.9	6.3	16.0	
		54.2	10.7	6.2	15.9	
$Bu^t(Et_3Si)NP(OEt)_2$	74/0.04	54.7	11.2	4.6		10.1
		54.9	10.9	5.0		10.5
$Bu^t(Pr^i_3Si)NH$	72—74/0.7	68.0	13.6	6.1		
		67.9	13.9	6.0		
$Bu^t(Pr^i_3Si)NCl$	75/0.2	59.2	11.5	5.3	13.4	
		59.6	11.6	5.2	13.4	
$Bu^t(Pr^i_3Si)NP(OEt)_2$	110—113/0.02	58.4	11.5	4.0		8.9
		58.1	11.2	4.0		8.9
$Bu^t(Bu^tMe_2Si)NH$	44—46/5	64.1	13.5	7.5		
		64.1	13.1	7.3		
$Bu^t(Bu^tMe_2Si)NCl$	60/1	54.1	10.9	6.3	16.0	
		54.1	10.7	6.3	16.0	
$Bu^t(Bu^tMe_2Si)NP(OEt)_2$	71—73/0.2	54.7	11.2	4.6		10.1
		55.0	11.0	4.6		*a*
$Pr^i(Bu^tMe_2Si)NH$	33—34/5	62.4	13.4	8.1		
		62.7	13.7	8.2		
$Pr^i(Bu^tMe_2Si)NCl$	34/1	52.0	10.7	6.7	17.1	
		52.0	10.8	6.7	17.2	
$Pr^i(Bu^tMe_2Si)NP(OEt)_2$[b]	67—70/0.1	53.2	11.0	4.8		10.6
		53.2	10.9	5.0		10.9
cyclo-$C_4H_7(Bu^tMe_2Si)NH$	68—70/7	64.8	12.5	7.6		
		a	*a*	*a*		
cyclo-$C_4H_7(Bu^tMe_2Si)NP(OEt)_2$[c]	91/1	55.1	10.6	4.6		10.1
		55.1	10.3	4.7		10.1
cyclo-$C_5H_9(Bu^tMe_2Si)NH$	78—81/7	66.3	12.6	7.0		
		66.2	12.6	7.1		
cyclo-$C_5H_9(Bu^tMe_2Si)NCl$	66/0.5	56.5	10.4	6.0	15.2	
		56.6	10.3	6.1	15.2	
cyclo-$C_5H_9(Bu^tMe_2Si)NP(OEt)_2$	80—83/0.05	56.4	10.7	4.4		9.7
		56.4	10.6	4.4		9.6
$Bu^tCH_2(Bu^tMe_2Si)NH$	49—51/3	65.6	13.5	7.0		
		65.8	13.7	7.0		
$Bu^tCH_2(Bu^tMe_2Si)NCl$	46/0.3	56.0	11.1	5.9	15.0	
		56.7	11.0	6.0	15.0	
$Me(Bu^tMe_2Si)NCl$	65/20 [d]	46.8	10.1	7.8	19.7	
		45.7	9.7	7.6	20.1	
$Ph(Bu^tMe_2Si)NH$	87—90/0.4	69.5	10.2	6.8		
		69.2	10.2	6.9		
$Ph(Bu^tMe_2Si)NP(OEt)_2$	87/0.1	58.7	9.2	4.3		9.5
		58.9	9.2	4.3		9.7
$Bu^t(Me_3Ge)NH$	27/4	44.3	10.1	7.4		
		a	*a*	*a*		
$Bu^t(Me_3Ge)NP(OEt)_2$[e]	88/5	42.6	9.1	4.5		10.0
		42.5	8.7	4.2		*a*
$Bu^t(Me)NP(OEt)_2$	42—43/1	52.2	10.7	6.8		15.0
		52.1	10.6	6.6		15.3
$Bu^t(Pr^i)NP(OEt)_2$	34—35/0.03	56.2	11.1	6.0		13.2
		56.4	11.4	5.9		13.1

[a] Not analysed. [b] $\delta^{31}P$ 159.3 (downfield from external 85% aqueous H_3PO_4). [c] $\delta^{31}P$ 159.2. [d] Solidified on cooling, m.p. 30 °C, making analysis difficult. [e] $\delta^{31}P$ 165.2.

t-Butyl(tri-isopropylsilyl)amine.—n-Butyl-lithium in hexane (74 ml, 1.72M) was added dropwise with stirring at room temperature to a solution of t-butylamine (9.2 g, 0.13 mol) in benzene (50 ml). The reaction mixture was stirred for a further 30 min and tri-isopropylchlorosilane (24.3 g, 0.13 mol) in benzene (50 ml) was added, followed by TMEDA (14.6 g, 0.13 mol). Most of the hexane was distilled off, leaving benzene as the solvent, and the mixture was then refluxed for a total of 26 h. The precipitated lithium chloride was removed by filtration, the solvent was removed under reduced pressure, and the residue distilled to give $Bu^t(Pr^i_3Si)NH$ as a viscous liquid (see Table 5).

Alkyl(trialkylsilyl)chloroamines.—These were prepared by reaction of t-butyl hypochlorite with the appropriate alkyl-(trialkylsilyl)amine in dichloromethane, following the method used by Wiberg and Raschig[37] for synthesis of $Bu^t(Me_3Si)NCl$ and $(Me_3Si)_2NCl$.

[*Alkyl(trialkylsilyl)amino*]*diethoxyphosphines*.—These were prepared by reaction of the lithium salt of the appropriate alkyl(trialkylsilyl)amine with freshly distilled diethyl chlorophosphite in diethyl ether solvent. The preparation of $Bu^t(Pr^i_3Si)NP(OEt)_2$ is described in detail below.

[*t-Butyl(tri-isopropylsilyl)amino*]*diethoxyphosphine*.—n-Butyl-lithium in hexane (4.4 ml, 1.80M) was added dropwise with stirring and at ambient temperature to a solution of $Bu^t(Pr^i_3Si)NH$ (1.8 g, 8 mmol) in diethyl ether (10 ml). The reaction mixture was stirred at room temperature for a further 30 min. and then diethyl chlorophosphite (1.2 g, 8 mmol) in ether (4 ml) was added dropwise without cooling. Lithium chloride was precipitated immediately and the mixture was stirred for a further 2 h before filtration, removal of the solvent, and distillation to give the aminophosphine as an oil (see Table 5).

Photolysis of the silylated amines or of the aminophosphines alone in cyclopropane gave rise to no e.s.r. spectra, with the exception of $Bu^t(Me_3Ge)NP(OEt)_2$ which afforded a weak spectrum assigned to $(EtO)_2P^{\bullet}$[41] [a(P) 79.4 G at 178 K]. A very weak spectrum of $Ph\dot{N}SiMe_2Bu^t$ was obtained when di-t-butyl peroxide was photolysed in the presence of $Ph(Bu^tMe_2Si)NH$, but the signal was much stronger when this was replaced by $Ph(Bu^tMe_2Si)NP(OEt)_2$.

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References

1 Part 2, M. D. Cook, B. P. Roberts, and K. Singh, *J. Chem. Soc., Perkin Trans. 2*, 1983, 635.

2 J. C. Brand, B. P. Roberts, and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1983, 261.

3 J. C. Brand, M. D. Cook, A. J. Price, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1982, 151.

4 I. Gümrükçü, A. Hudson, M. F. Lappert, M. J. Slade, and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1980, 776.

5 J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 161.

6 R. W. Dennis and B. P. Roberts, *J. Organomet. Chem.*, 1972, **43**, C2; *J. Chem. Soc., Perkin Trans. 2*, 1975, 140.

7 (*a*) H. Woynar and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 3813; (*b*) M. Negareche, M. Boyer, and P. Tordo, *Tetrahedron Lett.*, 1981, **22**, 2879.

8 R. West and P. Boudjouk, *J. Am. Chem. Soc.*, 1971, **93**, 5901.

9 A. K. Shubber and R. L. Dannley, *J. Org. Chem.*, 1971, **36**, 3784.

10 M. C. R. Symons, *J. Am. Chem. Soc.*, 1969, **91**, 5924.

11 W. C. Danen and F. Neugebauer, *Angew. Chem. Int. Ed. Engl.*, 1975, **14**, 783.

12 J. Lessard, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 3262.

13 R. Sutcliffe, D. Griller, J. Lessard, and K. U. Ingold, *J. Am. Chem. Soc.*, 1981, **103**, 624.

14 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535; J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189.

15 D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975.

16 W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, 1980, **102**, 3264; R. Sutcliffe, M. Anpo, A. Stolow, and K. U. Ingold, *ibid.*, 1982, **104**, 6064.

17 J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1981, **103**, 6994.

18 M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, 1978, **100**, 1964.

19 T. A. Claxton, S. A. Fieldhouse, R. E. Overill, and M. C. R. Symons, *Mol. Phys.*, 1975, **29**, 1453.

20 S. F. Nelson, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Am. Chem. Soc.*, 1972, **94**, 1610.

21 P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.

22 A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 1970, 559.

23 K. U. Ingold and J. C. Walton, *J. Am. Chem. Soc.*, 1982, **104**, 616.

24 K. J. Shea, R. Gobeille, J. Bramblett, and E. Thompson, *J. Am. Chem. Soc.*, 1978, **100**, 1611.

25 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907; M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *ibid.*, 1978, **100**, 3607.

26 P. Bischof and G. Friedrich, *J. Comput. Chem.*, 1982, **3**, 486.

27 C. Glidewell and C. Thomson, *J. Comput. Chem.*, 1982, **3**, 495.

28 Landolt-Börnstein New Series, Vol. 9b, 'Magnetic Properties of Free Radicals,' eds. H. Fischer and K.-H. Hellwege, Springer-Verlag, Berlin, 1977.

29 P. W. Atkins and M. C. R. Symons, 'The Structures of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

30 J. H. Mackey, J. W. Boss, and M. Kopp, *Phys. Chem. Glasses*, 1970, **11**, 205.

31 D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 1971, **75**, 3486.

32 R. E. Bailey and R. West, *J. Organomet. Chem.*, 1965, **4**, 430.

33 J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 3228.

34 R. Sutcliffe and K. U. Ingold, *J. Am. Chem. Soc.*, 1982, **104**, 6071.

35 Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 328.

36 R. M. Pike, *J. Org. Chem.*, 1961, **26**, 232.

37 N. Wiberg and F. Raschig, *J. Organomet. Chem.*, 1967, **10**, 15.

38 J. R. Bowser, R. H. Nelson, and R. L. Wells, *Inorg. Chem.*, 1978, **17**, 1882.

39 B. N. Dolgov, V. P. Kharitonov, and M. G. Voronkov, *Zhur. Obshch. Khim.*, 1954, **24**, 678.

40 R. Charelli and A. Rassat, *Tetrahedron*, 1971, **29**, 3639.

41 D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 554; K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1973, 420.

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