

E.S.R. Studies of the Bis(triethylsilyl)aminyl Radical and Trialkylsilyl(t-butyl)aminyl Radicals: a Reinvestigation

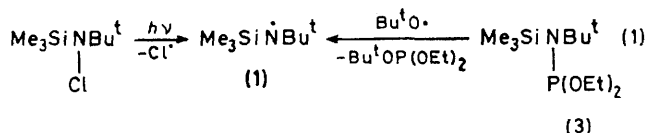
John C. Brand, Malcolm D. Cook, Allan J. Price, and Brian P. Roberts*

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

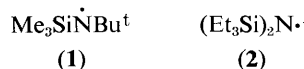
The radicals $(\text{Et}_3\text{Si})_2\dot{\text{N}}\cdot$, $\text{Me}_3\text{Si}\dot{\text{N}}\text{Bu}^t$, and $\text{Bu}^t\text{Me}_2\text{Si}\dot{\text{N}}\text{Bu}^t$ have been generated photochemically and studied using e.s.r. spectroscopy; previous assignments of spectra to the first two radicals appear to be incorrect.

Both e.s.r.^{1,2} and chemical³ studies have shown that the bis-(trimethylsilyl)aminyl radical $(\text{Me}_3\text{Si})_2\dot{\text{N}}\cdot$ is much more reactive than a dialkylaminyl radical and will even abstract hydrogen rapidly from cyclopropane at 140 K, implying that

the N-H bond in $(\text{Me}_3\text{Si})_2\text{NH}$ is significantly stronger than that in Me_2NH .¹ Recently, however, Hudson, Lappert, and coworkers⁴⁻⁶ have reported that a number of trialkylsilyl- and trialkylgermyl-aminyl radicals, including $\text{Me}_3\text{Si}\dot{\text{N}}\text{Bu}^t$ (**1**)

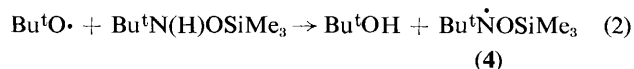


and $(\text{Et}_3\text{Si})_2\text{N}\cdot$ (2) have lifetimes of *ca.* 1 s in *n*-hexane at 298 K. The e.s.r. spectra attributed to (1) and (2) were considered to indicate that these species were π radicals and it was suggested that the low reactivity of (2) compared with $(\text{Me}_3\text{Si})_2\text{N}\cdot$ might be accounted for if the latter is a σ radical.⁴ That the electronic configuration of $(\text{R}_3\text{Si})_2\text{N}\cdot$ might be dependent on the nature of R is certainly an interesting possibility, however, in view of the results which we report here, the previous assignments⁴⁻⁶ of e.s.r. spectra to (1) and (2) appear to be in error.



Photolysis of a cyclopropane solution containing *t*-butyl-(trimethylsilyl)chloramine and norbornene or hexamethyldisilane (which act as scavengers of $\text{Cl}\cdot$) gave rise to an e.s.r. spectrum showing a 1:1:1 triplet splitting [$a(\text{N})$ 12.2 G, g 2.0066 at 160 K]. At 150 K, decay of the spectrum when photolysis ceased was complete within ≤ 0.5 s. The same spectrum was detected during photolysis of di-*t*-butyl peroxide (DTBP; a source of $\text{Bu}^t\text{O}\cdot$) in the presence of the silylaminophosphine (3).† We assign this e.s.r. spectrum to (1), formed by photolytic cleavage of the N-Cl bond or by displacement from phosphorus (*via* an intermediate phosphoranyl radical) as shown in equation (1).

No e.s.r. signals were detected during photolysis of a deoxygenated solution of the chloramine and norbornene in hexane at 295 K.‡ However, repetition of this experiment in the presence of oxygen afforded a weak spectrum consisting of a 1:1:1 triplet [$a(\text{N})$ 14.6 G, g 2.0051] which persisted for several seconds after the light was shuttered.§ This spectrum was also obtained by photolysis of $\text{Bu}^t\text{N}(\text{H})\text{OSiMe}_3$, either alone or (stronger) with DTBP and we assign it to the *t*-butyl(trimethylsilyloxy)aminyl radical (4) (*cf.* ref. 7 $\text{Bu}^t\dot{\text{N}}\text{O}-\text{Bu}^t$).¶



The nitrogen splitting for (4) is very similar to that (14.4 G) ascribed to (1) by Hudson, Lappert, *et al.*, but the g -factor of (4) is lower than that (2.007) reported previously.⁴ We have repeated Hudson and Lappert's experiment, which involved photolysis of $[\text{Me}_3\text{Si}(\text{Bu}^t\text{N})_2]\text{Ge}$, and find that a nominally degassed solution of this germanium(II) compound in cyclopropane or hexane shows a weak e.s.r. spectrum similar to that of (4), even before u.v. photolysis. When a small

† Satisfactory analytical and spectroscopic data have been obtained for this and the other new compounds discussed herein.

‡ Studies of the radical chain bromination of hydrocarbons by $\text{Me}_3\text{Si}(\text{Bu}^t\text{N})\text{Br}$ have shown that (1) is more reactive in hydrogen abstraction than a dialkylaminyl radical (*ref.* 3).

§ Three other 1:1:1 triplets were also observed in this experiment. The strongest spectrum of the four [$a(\text{N})$ 29.0 G, g 2.0055 at 295 K] was also detected during generation of $\text{Me}_3\text{Si}\cdot$ in the presence of Bu^tNO_2 and is assigned to $\text{Bu}^t\dot{\text{N}}(\text{O})\text{OSiMe}_3$.

¶ Rearrangement of (4) to give $\text{Bu}^t(\text{Me}_3\text{Si})\text{NO}\cdot$ was not detected. In contrast, rearrangement of $\text{Me}_3\text{Si}\dot{\text{N}}\text{OSiMe}_3$ [$a(\text{N})$ 11.6 G, g 2.0068 at 190 K] to give $(\text{Me}_3\text{Si})_2\text{NO}\cdot$ may be monitored readily using e.s.r. spectroscopy (*ref.* 8).

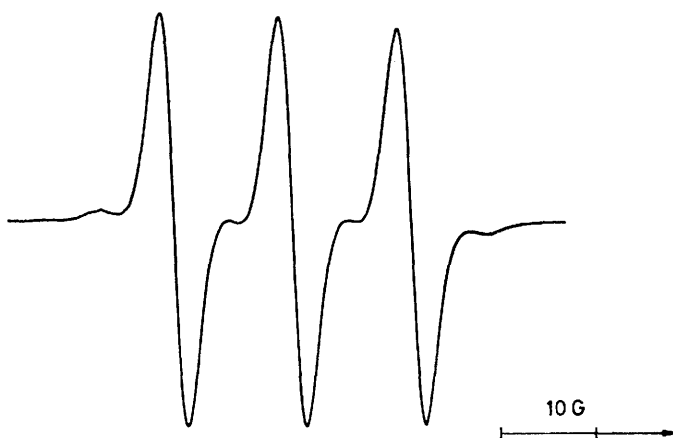
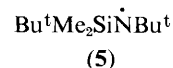


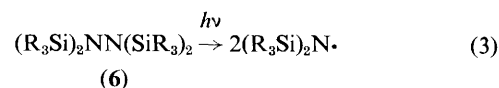
Figure 1. E.s.r. spectrum of the radical $\text{Bu}^t\text{Me}_2\text{Si}\dot{\text{N}}\text{Bu}^t$ in cyclopropane at 194 K obtained by photolysis of $\text{Bu}^t\text{Me}_2\text{Si}(\text{Bu}^t)\text{NCl}$ in the presence of norbornene. The satellite lines (*ca.* 8% of the total spectrum) are tentatively ascribed to radicals containing ^{13}C (natural abundance 1.1%) in the methyl groups of the *N*-*t*-butyl substituent and to radicals containing ^{29}Si (natural abundance 4.7%): $a(^{13}\text{C}) = \text{ca. } a(^{29}\text{Si}) = \text{ca. } 13$ G.

amount of air was admitted to the sample tube this spectrum [$a(\text{N})$ 14.4 G, g 2.0049 at 296 K.] became much stronger and when the solution was photolysed the spectrum assigned previously⁶ to $[\text{Me}_3\text{Si}(\text{Bu}^t\text{N})_2]\text{Ge}\cdot$ was observed in addition to the triplet. We presume that this triplet was also detected by Hudson and Lappert, but that the g -factor given in *ref.* 4 is in error. The radical responsible for the triplet spectrum is probably very similar to (4) and of the type $\text{Bu}^t\dot{\text{N}}\text{OM}$, where M is a germanium or silicon ligand of unknown structure.

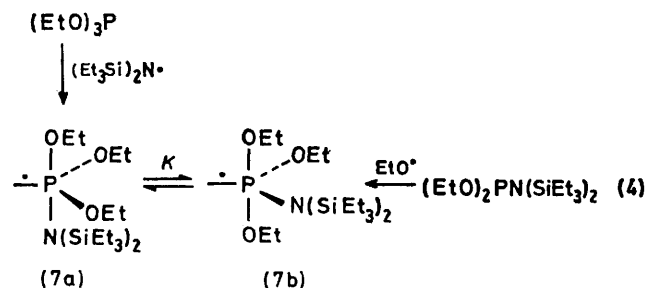


The silylaminy radical $\text{Bu}^t\text{Me}_2\text{Si}\dot{\text{N}}\text{Bu}^t$ (5) [$a(\text{N})$ 12.5 G, g 2.0068 at 194 K] was also generated from the appropriate chloramine and phosphine, as shown for (1) in equation (1), and its e.s.r. spectrum is given in Figure 1. The spectrum of (5) decayed with a half-life of *ca.* 7 min when photochemical generation from the chloramine in the presence of norbornene was interrupted at 150 K and this radical is thus much longer-lived than (1), presumably because of greater steric protection of the radical centre in (5).

We have shown previously that u.v. photolysis of tetrakis(trimethylsilyl)hydrazine (6; R = Me) provides a clean source of $(\text{Me}_3\text{Si})_2\text{N}\cdot$.¹



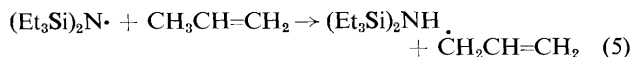
We now report that photolysis of (6; R = Et) similarly gives rise to $(\text{Et}_3\text{Si})_2\text{N}\cdot$ (2), which shows reactivity similar to



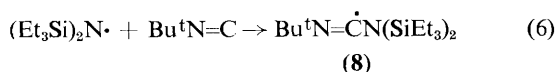
that of $(\text{Me}_3\text{Si})_2\text{N}\cdot$. We have not yet detected a spectrum attributable to (2) and in none of our experiments with (6; R = Et) have we observed the spectrum reported by Hudson, Lappert, and coworkers and assigned to (2).

Photolysis of (6; R = Et) in the presence of triethyl phosphite at 178 K gave rise to the same equilibrium mixture ($K = 0.55 \pm 0.02$) of the phosphoranyl radicals (7a) and (7b) as was obtained during photochemical generation of EtO \cdot (from EtOOEt) in the presence of $(\text{EtO})_2\text{PN}(\text{SiEt}_3)_2$ [equation (4)].**

Photolysis of (6; R = Et) in propene, even at 130 K, gave rise to the spectrum of the allyl radical showing that reaction (5) proceeds readily. Addition of (2) to t-butyl isocyanide



afforded the relatively long-lived imidoyl radical (8) [$a(\text{NSi}_2)$ 11.6, g 2.0016 at 228 K].



We conclude that (2), like $(\text{Me}_3\text{Si})_2\text{N}\cdot$, is much more reactive than a dialkylaminyl radical and would be extremely short-lived in hexane at 298 K. Whether (2) is effectively linear or bent at nitrogen and, if bent, whether it has a σ or π ground state is not known at present since its e.s.r. spectrum has not been detected.

The trialkylsilyl(t-butyl)aminyl radicals (1) and (5) are presumably bent at nitrogen, since they give rise to well-defined e.s.r. spectra in fluid solution.⁹ The small nitrogen

splittings are more consistent with a π electronic configuration for both, but the g -values are significantly greater than that of $\text{Bu}^t_2\text{N}\cdot$ (2.0045)¹⁰ and we suggest that this is a consequence of a smaller separation between σ and π states of the silyl-(alkyl)aminyl as compared with the dialkylaminyl radicals.

Stabilisation of the σ configuration relative to the π for $\text{R}_3\text{Si}\overset{\cdot}{\text{N}}\text{R}$ would be expected on account of the σ -donor/ π -acceptor properties of the R_3Si group and the associated increase in the $\text{Si}\overset{\wedge}{\text{N}}\overset{\wedge}{\text{C}}$ angle compared with the $\text{C}\overset{\wedge}{\text{N}}\overset{\wedge}{\text{C}}$ angle in $\text{R}_2\text{N}\cdot$.

We thank the S.R.C. for financial support and Dr. J. N. Winter for carrying out some initial experiments with $\text{Me}_3\text{Si}\overset{\cdot}{\text{N}}\text{Bu}^t$.

Received, 26th October 1981; Com. 1249

References

- 1 B. P. Roberts and J. N. Winter, *J. Chem. Soc., Chem. Commun.*, 1978, 545.
- 2 B. P. Roberts and K. Singh, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1549.
- 3 B. P. Roberts and C. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 752; B. P. Roberts and K. Singh, unpublished work.
- 4 I. Gümrükçü, A. Hudson, M. F. Lappert, M. J. Slade, and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1980, 776.
- 5 M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, and M. M. Riviere-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
- 6 A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1976, 2369.
- 7 H. Woyнар and K. U. Ingold, *J. Am. Chem. Soc.*, 1980, **102**, 3813.
- 8 R. West and P. Boudjouk, *J. Am. Chem. Soc.*, 1971, **93**, 5901; *ibid.*, 1973, **95**, 3983; J. C. Brand, B. P. Roberts, and J. N. Winter, unpublished work.
- 9 M. C. R. Symons, *J. Am. Chem. Soc.*, 1969, **91**, 5924.
- 10 D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 1971, **75**, 3486.

** The e.s.r. parameters for (7a) are $a(\text{P})$ 835.7, $a(\text{N})$ 27.0 G, g 2.0025 and for (7b) are $a(\text{P})$ 850.5, $a(\text{N})$ ca. 3 G, g 2.0021 in cyclopropane at 178 K.