Unstable Intermediates. Part 202. The Use of Spin Traps to Study Trialkylsilyl and Related Radicals

By **Harish Chandra, Iain M. T. Davidson,** and **Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

Exposure of trimethylsilane, containing Me_3CNO molecules in low concentration, to ^{60}Co γ-rays at 77 K gave $Me_3Si\cdot$ radicals, characterized by their e.s.r. spectra. On annealing, these reacted with Me_3CNO to give $Me_3Si\dot{N}(O)CMe_3$ radicals (A_N 9.75 G), which have not been reported previously. However, these proved to be short-lived and could not be detected when $Me_3Si\cdot$ and related radicals were generated by standard procedures at ambient temperatures. We conclude that Me_3CNO is unsuitable as a trap for such radicals. In contrast, nitrone traps such as $PhCH=N(O)CMe_3$ gave relatively stable radicals with $R_3Si\cdot$, the alkyl derivatives being more stable than the aryl derivatives. These radicals were characterized by a relatively large β-proton hyperfine coupling and a coupling to ^{29}Si of *ca.* 13 G. 2,6-Di-t-butyl-*p*-benzoquinone also gave relatively stable adducts but these are less readily characterized and we were unable to detect well defined ^{29}Si hyperfine features. The structures of these adducts and the formation of other species are discussed.

SILICON-centred radicals, $R_3Si\cdot$, have been widely studied in solid and in fluid solutions.[1-5] Nevertheless, for some types of mechanistic study, especially for gas-phase radicals, it is desirable to use effective spin traps.[6]

One of the most popular traps is the molecule Me_3CNO formed reversibly from the dimer in dilute solution. This adds to radicals, $R\cdot$, to give nitroxide radicals, $Me_3C\dot{N}(O)R$, having characteristic e.s.r. spectra. These are frequently persistent and can be studied without the need of special techniques or precautions. However, although $(R_3Si)_2\dot{N}O$ radicals have been reported,[7] we know of no reported data for $Me_3C\dot{N}(O)SiR_3$ radicals. One of our aims has been to characterise such radicals by e.s.r. spectroscopy, and to estimate their suitability for trapping studies.

In contrast, nitrone traps, $RCH=N(O)R'$, have been used successfully by Wan and his co-workers [8] and by Lappert and his co-workers [9] to trap specific $R_3Si\cdot$ radicals, although proof that such trapping occurred was incomplete since no ^{29}Si features were reported. However, the new species thought to be the silyl adducts $RCH(SiR_3)\dot{N}(O)R'$ did exhibit unusually large hyperfine coupling to the β-proton. No explanation for this was offered but it can perhaps be taken as characteristic of such adducts. Our aim has been to characterize these species more firmly by estimating their ^{29}Si hyperfine coupling constants, and to compare their stabilities with those derived from RNO traps.

Adeleke *et al.* have also used 2,6-di-t-butyl-*p*-benzoquinone as a trap for silyl radicals,[10] so we have investigated these traps for comparative purposes.

EXPERIMENTAL

2-Methyl-2-nitrosopropane, α-phenyl-t-butyl nitrone, di-t-butyl peroxide, phenyl-, diphenyl-, and triphenyl-silanes, and trimethylsilane were used as supplied. 2,6-Di-t-butyl-*p*-benzoquinone was used after purification by vacuum sublimation. Spectrograde n-hexane was dried over calcium hydride.

In each experiment *ca.* 0.02M-spin trap and *ca.* 0.05M-silane were dissolved in solvent. In some experiments di-t-butyl peroxide was used as solvent. The solutions were thoroughly degassed at *ca.* 10^{-4}—10^{-5} Torr.

E.s.r. spectra were recorded on a Varian E-3 spectrometer with 100 KHz modulation, usually at ambient temperatures. In our irradiation studies, samples were exposed to ^{60}Co γ-rays at 77 K, and e.s.r. spectra were recorded at this temperature and at increasing temperatures until liquid-phase spectra were obtained.

Mass spectra were measured on a micromass 16B instrument, and n.m.r. spectra were measured on a JEOL PS-100 spectrometer.

RESULTS AND DISCUSSION

Nitroso-traps.—Since all our liquid-phase studies were inconclusive, giving no nitroxide radicals that were clearly novel (see below), we decided to use a solid-state procedure in which $R_3Si\cdot$ radicals were generated by radiolysis. We have previously shown [1] that radiolysis of trimethylsilane gives $Me_3Si\cdot$ radicals at 77 K which are well characterized by their e.s.r. spectra, including satellite features from ^{29}Si. These results were reproduced in the present work, in the presence or absence of Me_3CNO molecules or their dimers. On annealing to the m.p., isotropic spectra for nitroxide radicals appeared (Figure 1), one of which was clearly novel, having $A(^{14}N)$ 9.75 G. At high gain, two sets of satellite features were detected, one of which is assigned to ^{13}C from the methyl groups of the CMe_3 unit, and the other to radicals containing ^{29}Si (^{29}Si has $I = \frac{1}{2}$ and is 4.7% abundant). (In both cases, the apparent intensities were slightly less than expected relative to the main lines, but the linewidths were increased, presumably because of extra anisotropies.) The magnitude of the ^{29}Si coupling (5.4 G) is close to expectation for an α-silicon atom in a system having *ca.* 50% spin density on nitrogen. (This value of the spin density was estimated from solid-state spectra for normal dialkyl nitroxides: it probably does not change greatly for the present species, as indicated below.) Thus, for example, $(R_3Si)_2\dot{N}O$ radicals have $A(^{29}Si)$ 5.9 G.[7]

Empirically, the $A(^{14}N)$ value of 9.75 G is also close

Hyperfine coupling constants assigned to silyl derivatives of spin-traps in n-hexane

Trap	Radical	Hyperfine coupling constants (G) [a] $^{14}N \pm 0.1$	$^{1}H \pm 0.1$	$^{13}C(CH_3)$	^{29}Si	g value $\pm$ 0.0002
Me_3CNO	$Me_3Si\cdot$	9.75		3.75	5.4	2.0082 *
$PhCH{=}N(O)CMe_3$	$Me_3Si\cdot$	14.50	6.00	*ca.* 3.7	13.0	2.0057
	Me_2SiH	14.75	7.00			
	$MeSiH_2$	14.18	4.62			2.0059 †
	$Ph_3Si\cdot$	14.50	5.50			2.0057
	Ph_2SiH	14.75	7.75			2.0057
	$PhSiH_2$	14.87	8.00			2.0057

* Relative to di-t-butyl nitroxide. † Relative to acyl nitroxide. Other g values are relative to butoxy-adduct of nitrone.

[a] G = 10^{-4} T.

to expectation. Thus, dialkyl nitroxides give *ca.* 15 G whilst disilyl radicals give *ca.* 6.5 G. The average, 10.75 G, is close to the present value of 9.75 G. It is not clear to us, however, why replacing carbon by silicon should cause such a large fall in $A_{iso}(^{14}N)$.

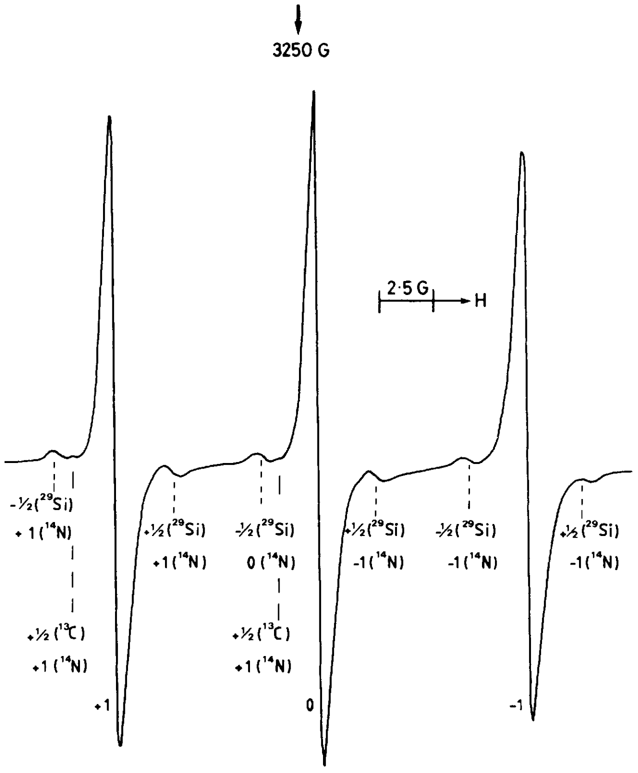


FIGURE 1 First-derivative X-band e.s.r. spectrum assigned to the nitroxide $(Me_3Si)_2NO(CMe_3)$. High- and low-field satellite lines assigned to ^{29}Si and ^{13}C are indicated

On further annealing, the signals assigned to the silyl adduct rapidly faded, being undetectable at *ca.* 180 K. Thus it seems that there is an efficient decomposition pathway which clearly renders these species unsuitable for detecting silyl radicals. All our attempts to detect these species in standard liquid-phase experiments failed.

Nitrone Adducts.—We have confirmed that relatively long-lived nitroxides, with characteristically high proton hyperfine coupling constants, are formed under conditions in which $R_3Si\cdot$ radicals should be formed. Thus, for example, photolysis of di-t-butyl peroxide (Bu^tOOBu^t) in the presence of R_3SiH should give $R_3Si\cdot$ radicals.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2\ Bu^tO\cdot \qquad (1)$$

$$Bu^tO\cdot + R_3SiH \longrightarrow Bu^tOH + R_3Si\cdot \qquad (2)$$

In the presence of $PhCH{=}N(O)CMe_3$ traps, both $Bu^tO\cdot$ and $R_3Si\cdot$ radicals add to give nitroxide radicals as shown in Figure 2. At high gain, two sets of doublet satellite features were detected, with $A(1)$ *ca.* 3.7 G and $A(2)$ = 13 G. The former splitting is about that expected for ^{13}C from the CMe_3 methyl groups, so the latter is assigned to $A(^{29}Si)$. The intensities of these satellite features followed those of the main lines assigned to the $R_3Si\cdot$ adducts. Other weak outer features were sometimes detected, but these were not symmetrically distributed about the main features and hence are assigned to other nitrogen-centred radicals present in low abundance (see below). Again, the intensities of both sets of satellites were about half those expected for ^{13}C and ^{29}Si, but the lines were broader than the central features, presumably reflecting the extra anisotropy.

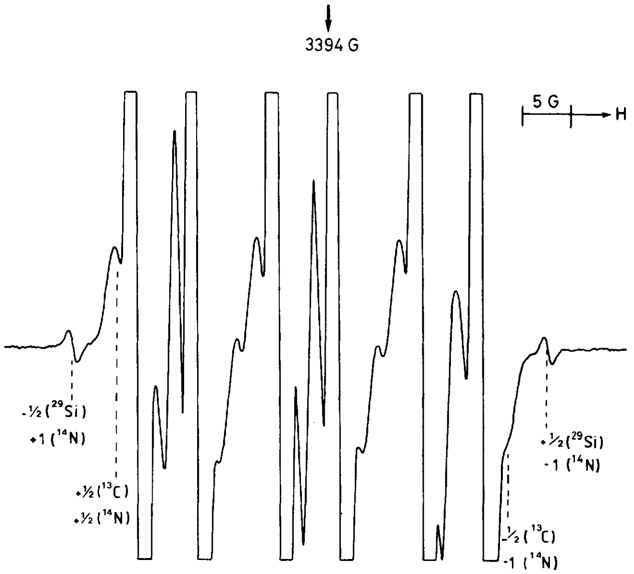
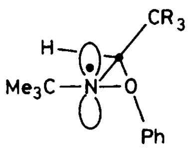


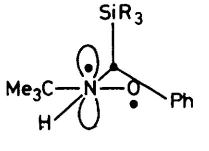
FIGURE 2 First-derivative X-band e.s.r. spectrum assigned to the nitroxide $Me_3Si(Ph)CH{-}\dot{N}O(CMe_3)$. The outermost ^{29}Si and ^{13}C features are indicated. The inner features are obscured by features for other nitroxide radicals in low abundance

Solutions of the Me_3Si derivative were stable for several days at room temperature. The Me_2SiH derivative decayed slowly during *ca.* 4 h, whilst the phenyl derivatives decayed rapidly in the absence of light. We were unable to detect adducts from silicon radicals containing α-chloro- or α-bromo-derivatives, but observed the formation of white precipitates even before illumination. These systems have been discussed by Lappert and his co-workers.[9]

It is of interest to consider the source of the large proton and ^{29}Si hyperfine coupling constants. At first sight it seemed contradictory that both should be large on replacing R_3C by R_3Si groups. However, we suggest that the following conformational considerations adequately explain the changes. For normal alkyl derivatives the proton hyperfine coupling of 3—4 G is low.



(I)

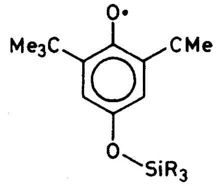


(II)

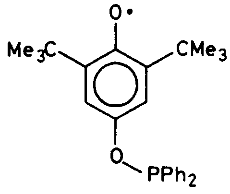
Thus, for $\left[\begin{smallmatrix}R\\R\end{smallmatrix}\!\!>\dot{N}\text{-}CH_3\right]^+$ groups, the methyl proton coupling is *ca.* 27 G, so for 50% spin density on nitrogen, an average (θ 45°) value might be in the region of 13 G. For the limiting structure (I), this should fall to *ca.* 0 G, whilst for (II) (θ 30°) it should be *ca.* 9 G. We therefore suggest that the phenyl alkyl derivatives have preferred conformations close to (I), presumably for steric reasons, whereas the silyl derivatives have conformations approaching (II).

This explains the increase in $A(^1H)$ on silicon substitution. That (II) should be favoured is expected because it is the most favourable structure for σ–π delocalisation (hyperconjugation) between the semi-occupied π*-orbital and the C–Si σ-orbital. Krusic and Kochi[11] have shown that this conformation is favoured for $R_2\dot{C}\text{-}CH_2(SiR_3)$ radicals, and we established independently that such conformations lead to unusually large heavy-atom hyperfine coupling constants.[12] More recently, Sakurai *et al.*[13] have reported values of *ca.* 35 G for $A(^{29}Si)$ and 15.6 G for $A(^1H)$ for radicals $(Me_3C)_2\dot{C}CH_2SiR_3$. Our ^{29}Si coupling is *ca.* 45% of this value, as also are our ^1H coupling constants. This leads us to suggest that the spin-density on nitrogen is *ca.* 45%, in good agreement with expectation.

Quinone Traps.—Our studies confirm that relatively stable radicals can be formed using 2,6-di-t-butyl-*p*-benzoquinone, which are probably the adducts (III). (The isomers in which addition occurs to the alternative oxygen atom are never more than minor products). However, for the normal spectra there are no clear identification features except the two ring proton coupling constants, and it is difficult to predict how these should vary with the nature of the substituents. Adeleke *et al.*[8] reported the detection of ^{29}Si satellite features for the triphenylsilyl derivative, but unfortunately we have not been able to confirm this. Their coupling constant of 11.5 G is unexpectedly large, and we believe that we could readily detect such features unless broadening were very marked. In our view, the coupling is probably no greater than *ca.* 1 G. That 11.5 G is too high can be seen by comparison with the clearly authentic coupling to ^{31}P for the phosphine derivative (IV).[9] This coupling of 3.1 G is equivalent to a coupling of 0.94 G for ^{29}Si for the same 3*s*-character. Whilst there is no reason for these to be equal, they are unlikely to differ by a factor of *ca.* 10.



(III)



(IV)

We conclude that the quinone derivatives are about as stable as the nitrone derivatives, those with phenyl substituents being somewhat more stable, and those with alkyl substituents being somewhat less stable. However, the nitrone derivative spectra are more characteristic, and ^{29}Si features can be detected.

Other Radicals.—During the course of this work, many other radical features were detected, thereby rendering the technique less satisfactory than might have been expected. Some of these features were due to trapping of other expected radicals, such as $Me_3CO\cdot$ from $Me_3CO\text{-}OCMe_3$, and methyl radicals, probably formed from the decomposition of $Me_3CO\cdot$ radicals. Others were formed from low concentrations of reactive impurities. In the case of Me_3CNO traps, $(Me_3C)_2\dot{N}O$ radicals were almost unavoidable despite the fact that care was taken to prevent photolysis.

In the particular case of the halogen derivatives using Me_3CNO as a trap, the signals due to $(Me_3C)_2\dot{N}O$ radicals faded rapidly after mixing, with the formation of a precipitate. At this stage new e.s.r. features grew in. One set, having $A(^{14}N)$ 7.5 G, are assigned to acyl nitroxide radicals, $RCO\dot{N}OR'$. These species have been widely studied, and are frequently detected in spin-trap studies involving nitroxide radicals.[6,14] No simple explanation for their formation has yet been forthcoming, and we are reluctant to indulge in further speculation.

Another radical, having the spectrum shown in Figure 3, was formed from the chlorinated derivatives, $R_3Si\text{-}Cl$. Only compounds containing Si–Cl bonds gave this reaction, and Si–H bonds were not necessary. There appears to be three sets of six lines having A_{iso} *ca.* 0.9 G and it is possible that chlorine nuclei make some contribution to this. (^{35}Cl and ^{37}Cl have $I = \frac{3}{2}$ and similar magnetic moments.) Mass spectrometric and

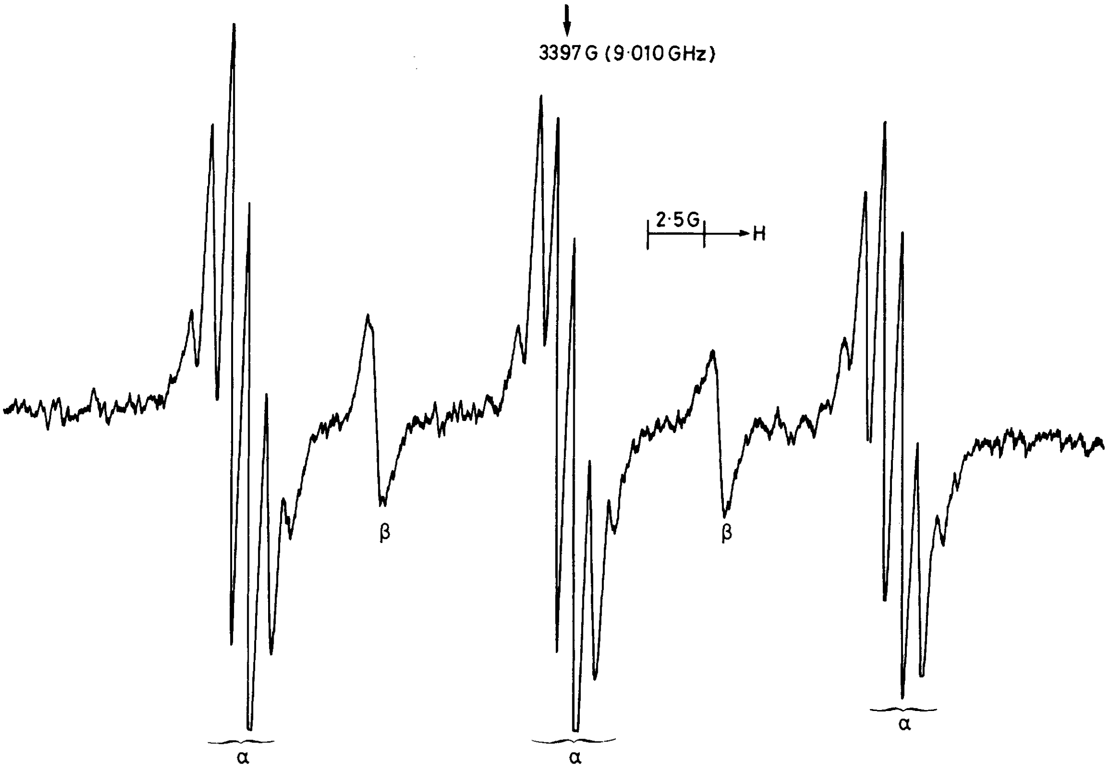


FIGURE 3 First-derivative X-band e.s.r. spectrum for a nitroxide radical formed in the reaction between Me_3NO and Me_3SiCl, possibly exhibiting hyperfine coupling to chlorine nuclei (α). Features (β) are assigned to acyl nitroxide radicals

n.m.r. analysis showed that the precipitate was the hydroxylamine, $(Me_3C)_2NOH$, suggesting that the initial act was hydrogen atom abstraction. Despite these clues, we have not been able to derive a compelling identification for these radicals.

Finally, in our studies with $PhCH{=}N(O)CMe_3$ traps weak outer features for a species having $A(^{14}N)$ 27.5 G were often obtained. Wan and his co-workers[8] also detected such features, and suggested that the radicals $Me_3C\dot{N}(O){-}OCMe_3$ were responsible. Certainly such nitro-derivatives exhibit large $A(^{14}N)$ coupling constants in this region, and they are readily formed from nitroso-traps. It is difficult to understand why they should be formed in the present systems. Another possibility is the formation of iminoxyl radicals, $R_2C{=}\dot{N}O$, but it is again difficult to formulate a clear mechanism for their formation.

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