EPR spectroscopic studies of *N*-alkyl-*N*-trialkylsilylmethylaminyl radicals in solution

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Photochemically-generated trialkylsilyl radicals $R_3Si^{\bullet}$ (R = Me, Et, Pr^i) add rapidly to *N*-methylene-*tert*-butylamine ($H_2C{=}NBu^t$) to give silylmethylaminyl radicals $R_3SiCH_2\dot{N}Bu^t$ which have been studied by EPR spectroscopy. These aminyl radicals prefer conformations in which the β-C–Si bond eclipses the N-2p_π orbital, formally occupied by the unpaired electron, and lineshape effects resulting from hindered rotation about the R_3SiCH_2–N bond are evident in the EPR spectra. The aminyl radicals $Me_3SiCH_2\dot{N}Bu^t$ and $Me_3SiCH_2\dot{N}Me$ have been generated by displacement from aminophosphanes of the type $(EtO)_2PN(R)$-CH_2SiMe_3 using photochemically-generated alkoxyl radicals. The proposal in the literature that $Me_3SiCH_2\dot{N}R$ (R = Me or Bu^t) rearranges to give $^{\bullet}CH_2N(R)SiMe_3$ has been confirmed and this process has been monitored by EPR spectroscopy. Since no free silyl radicals could be trapped by $Bu^t_2C{=}CH_2$, the rearrangement probably proceeds by an intramolecular 1,2-shift of the Me_3Si group from carbon to nitrogen. The rearranged radicals $^{\bullet}CH_2N(R)SiMe_3$ have been generated independently by hydrogen-atom abstraction from the corresponding aminosilanes $Me_3SiN(R)CH_3$.

The key role of silicon compounds in organic chemistry, particularly in synthesis, is now well established.[1–4] The substituent effects of silyl groups on structure, thermochemistry and reactivity in free radical chemistry have been investigated over a number of years,[4–11] but are still subjects of current interest.[12–19]

In a recent paper, Harris *et al.*[20] reported an EPR spectroscopic study of the radicals produced by hydrogen-atom abstraction from a number of β-silyl-substituted amines **1** by *tert*-butoxyl radicals. The α-aminoalkyl radicals **2** were detected directly at low temperatures, but it was also proposed that

$$\underset{\mathbf{1}}{Me_3SiCHR^1{-}NHR^2} \xrightarrow[-Bu^tOH]{Bu^tO^{\bullet}} \underset{\mathbf{2}}{Me_3Si\dot{C}R^1{-}NHR^2} + \underset{\mathbf{3}}{Me_3SiCHR^1{-}\dot{N}R^2} \quad (1)$$

competing hydrogen-atom abstraction from nitrogen occurred to give trimethylsilylalkylaminyl radicals of the type **3**. The EPR spectra of **3** were not detected, but the presence of these aminyl radicals was inferred because spectra assigned to the radicals **4** were observed at higher temperatures, when **3** was believed to rearrange by a 1,2-silyl migration from carbon to nitrogen [eqn. (2)].[20,21]

$$\underset{\mathbf{3}}{Me_3SiCHR^1{-}\dot{N}R^2} \longrightarrow \underset{\mathbf{4}}{H\dot{C}R^1{-}NR^2SiMe_3} \quad (2)$$

Several years ago, we reported that homolytic addition to *N*-methylene-*tert*-butylamine (MTBA) gives aminyl radicals of the type **5** which may be readily detected by EPR spectroscopy [eqn. (3)].[22,23] One of the adducts we described was the aminyl

$$X^{\bullet} + H_2C{=}NBu^t \longrightarrow \underset{\mathbf{5}}{XCH_2\dot{N}Bu^t} \quad (3)$$

radical $Et_3SiCH_2\dot{N}Bu^t$ ($X^{\bullet}$ = $Et_3Si^{\bullet}$) and thus we were very intrigued by the failure of Harris *et al.* to detect the EPR spectra of similar silylmethylaminyl radicals. As a consequence, we were prompted to extend our earlier work on the addition of trialkylsilyl radicals to MTBA and also to generate silylmethylaminyl radicals independently by displacement from trivalent phosphorus[11,24] in order to examine these species in detail using EPR spectroscopy. In the course of this work, we have also shown that EPR spectra of silylmethylaminyl radicals **3** are, in fact, observable in two of the systems studied previously[20] and we have confirmed that these aminyl radicals rearrange as shown in eqn. (2) to give carbon-centred radicals, the identities of which we have proved by generating them by independent routes.

Results and discussion

Radical addition to MTBA

Simple formaldimines (methanimines) of the type $H_2C{=}NR$ are unstable with respect to cyclo-trimerization or polymerization unless the steric bulk or electronic properties of the *N*-alkyl group militate against this.[25,26] Some confusion exists in the literature regarding the relative stabilities of MTBA and its cyclic trimer **6**. This imine was prepared first in 1952 by Hurwitz,[25] using the condensation reaction between *tert*-butylamine and aqueous formaldehyde, who reported that monomeric MTBA (bp 63–65 °C/760 Torr) was stable at room temperature. On the other hand, in 1984 Müller *et al.*[27] claimed to have isolated only the trimer **6** (bp 82 °C/0.05 Torr) from this condensation, although 10 years earlier Murray and Cromwell[28] had reported the isolation of monomeric MTBA after the same reaction. However, the ^{1}H NMR spectroscopic analysis given by the latter authors[28] is clearly incorrect and the spectrum of an approximately equimolar[29] mixture of MTBA and the trimer **6** appears to have been interpreted as if it corresponded to that of the pure monomer. In fact, a reasonably definitive NMR spectroscopic study of the reversible trimerization shown in eqn. (4) was reported as early as 1970 by Mauzé *et al.*[29] These

$$3\ H_2C{=}NBu^t \rightleftharpoons \underset{\mathbf{6}}{\text{1,3,5-tri-tert-butyl-1,3,5-triazacyclohexane}} \quad (4)$$

Table 1 EPR parameters for trialkylsilylmethylaminyl radicals in cyclopropane

Radical	Source[a]	T/K	g-Factor	Hyperfine splittings[b]/G	$da(2H_\beta)/dT$ (mG K^{-1})
$Me_3SiCH_2\dot{N}Bu^t$ **7**	A, B, C	262	2.0047	22.42 ($2H_\beta$), 14.57 (N), 30.3[c] (^{29}Si)	+4.7
$Et_3SiCH_2\dot{N}Bu^t$ **8**	A	259	2.0047	22.88 ($2H_\beta$), 14.58 (N), 27.0[d] (^{29}Si)	+9.1
$Pr^i_3SiCH_2\dot{N}Bu^t$ **9**	A	259	2.0047	25.38 ($2H_\beta$), 14.60 (N), 21.0[e] (^{29}Si)	+16.3
$Me_3SiCH_2\dot{N}Me$ **19**	B, C	259	2.0047	17.98 ($2H_\beta$), 14.48 (N), 25.02 ($3H_\beta$)	*ca.* +8
$Me_3CCH_2\dot{N}Bu^t$[f]	D	311	2.0048	39.2 ($2H_\beta$), 14.6 (N)	−8
$Me_2\dot{N}$[g]	B	167	2.0047	27.3 ($6H_\beta$), 14.7 (N)	—
$Me_3C\dot{N}Me$[g]	B	154	2.0047	28.5 ($3H_\beta$), 14.5 (N)	—

[a] A = silyl radical addition to MTBA; B = homolytic displacement from $(EtO)_2PN(R)CH_2SiMe_3$, $(Me_2N)_3P$ or $(EtO)_2PN(Me)Bu^t$, as appropriate; C = hydrogen-atom abstraction from the corresponding silylmethylamine; D = *tert*-butyl radical addition to MTBA. [b] Generally ±0.05 G; nuclei indicated in parentheses. [c] At 230 K; 31.0 G at 170 K. [d] At 264 K; the value given in ref. 22 is incorrect. [e] Tentative value at 269 K; identification of the satellite lines is uncertain. [f] Data from ref. 22. [g] Data from ref. 11.

authors showed that although essentially pure monomer is obtained immediately following distillation of the condensation product at atmospheric pressure, the neat liquid undergoes almost complete conversion to the trimer within 72 h at room temperature.† In solution, the mole fraction of monomer at equilibrium is strongly dependent on the polarity and, in particular, on the hydrogen-bond donor properties of the solvent. Polar solvents, especially alcohols, selectively stabilize the monomer which is more polar than the saturated trimer.[29]

In the present work gaseous monomeric MTBA was transferred at room temperature using a vacuum line and condensed directly into the EPR sample tube. The trimer **6** could be readily cracked by heating it with alumina as catalyst under reduced pressure: in the absence of a catalyst, the rate of monomer formation was very much slower. After addition of the other reagents and the solvent, the sample tube was sealed and stored in liquid nitrogen until required. The sample was thawed and mixed by repeated inversion in a solid CO_2–ethanol bath immediately prior to examination by EPR spectroscopy.

Samples containing di-*tert*-butyl peroxide (DTBP, *ca.* 15% v/v), MTBA (*ca.* 1 mol dm^{-3}) and trimethyl-, triethyl- or triisopropyl-silane (*ca.* 1 mol dm^{-3}) in cyclopropane solvent were irradiated with UV light while positioned in the microwave cavity of the EPR spectrometer, as described previously.[30] Photochemically-generated *tert*-butoxyl radicals abstract hydrogen from the silane to give the corresponding silyl radical, which adds to MTBA to produce the trialkylsilylmethylaminyl radicals **7**–**9** [eqns. (5)–(7)].[22] The EPR

$$Bu^tO_2Bu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \quad (5)$$

$$Bu^tO^\bullet + R_3SiH \longrightarrow Bu^tOH + R_3Si^\bullet \quad (6)$$

$$R_3Si^\bullet + H_2C{=}NBu^t \longrightarrow R_3SiCH_2\dot{N}Bu^t \quad (7)$$

7 R = Me
8 R = Et
9 R = Pr^i

spectrum of the radical **9** is shown in Fig. 1 and the spectroscopic parameters for all the silylmethylaminyl radicals detected in this work are given in Table 1. Addition to the imine is evidently very rapid, because the EPR spectrum of $R_3Si^\bullet$ was not detected alongside that of the aminyl radical adduct.

The central lines of the β-proton triplet [$M_I(2H_\beta) = 0$] in the EPR spectrum of **9** at 251 K are broadened significantly relative to the lines corresponding to $M_I(2H_\beta) = \pm 1$ [see Fig. 1(*b*)]. This selective broadening becomes more marked as the temperature is lowered, until by *ca.* 200 K the lines associated with $M_I(2H_\beta) = 0$ are almost undetectable above the noise. As the temperature is increased above 251 K, the lines become of more equal width until by *ca.* 310 K the 1:2:1 amplitude ratio is approached for the β-proton triplet [see Fig. 1(*a*)]. Similar alternating linewidth effects are evident in the spectra of **7** and **8** and indicate that the β-protons in **7**–**9**, although instantaneously non-equivalent, undergo exchange on the EPR timescale. The individual β-proton splittings, required for computer simulation of the lineshape effects, could not be determined because spectra of adequate quality could not be obtained at sufficiently low temperature in the slow exchange region. In conjunction with evidence derived from the magnitudes and temperature dependences of the average β-proton splittings (see later), these results show that a conformation close to the idealized 'eclipsed' structure **10** is preferred by the aminyl radicals **7**–**9** and that the two β-protons are exchanged by hindered rotation about the N–C_β bond, with the R_3Si group presumably taking the less sterically demanding route past the nitrogen lone pair.

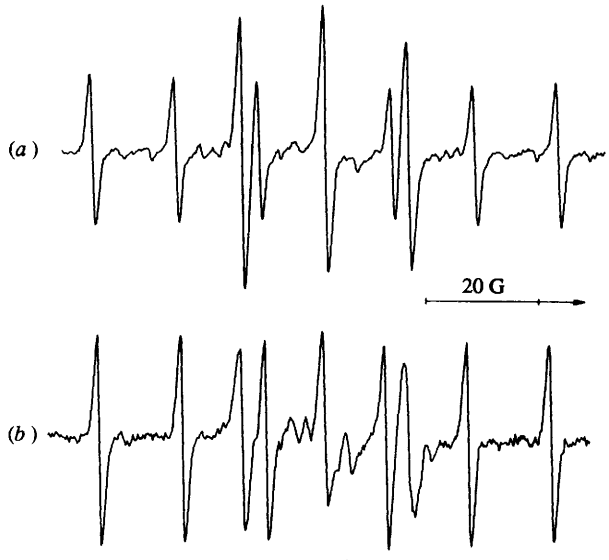
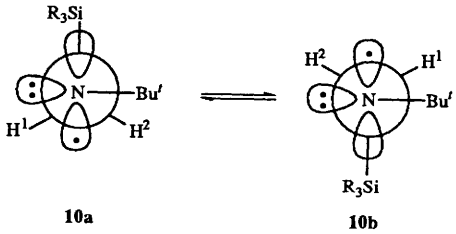


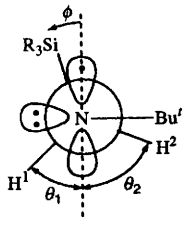
Fig. 1 EPR spectra of $Pr^i_3SiCH_2\dot{N}Bu^t$ **9** produced by radical addition to MTBA in cyclopropane at (*a*) 308 K and (*b*) 251 K



10a **10b** (8)

† Our own observations suggest that the rate of trimerization is rather irreproducible and is often much more rapid than this, probably because of the presence of adventitious catalysts (*vide infra*).

An electronic preference for a conformation in which the β-C–Si bond eclipses the N-2p_π orbital, formally occupied by the unpaired electron, would be expected by analogy with the preferred conformations of β-silylalkyl radicals[14,31–34] and of isoelectronic aminyl–borane radicals of the type $R_3SiBH_2{\leftarrow}\dot{N}R_2$.[35] The preference for the eclipsed conformation **10** presumably reflects the greater energetic advantage of a hyperconjugative interaction between the unpaired electron and the β-C–Si bond, as compared with the β-C–H bond, because of the lower electronegativity of silicon in comparison to hydrogen.‡[,32,36,37] However, this electronic effect which favours eclipsing ($\phi = 0°$ in the time-averaged conformation **11**) is opposed by steric repulsion between the R_3Si group and the *N-tert*-butyl group which will tend to increase ϕ.



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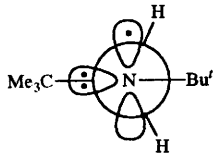


12

When the silicon atom in **7** is replaced by carbon to give $Me_3CCH_2\dot{N}Bu^t$, hyperconjugative effects become relatively unimportant and the preferred conformation is now **12**, because of the dominance of steric repulsion between the two *tert*-butyl groups.[22]

Hyperfine coupling between the unpaired electron and the β-protons in **7**–**9** is also a consequence of hyperconjugation and the magnitude of $a(H_\beta)$ should be approximated by eqn. (9),

$$a(H_\beta) = (A_N + B_N \cos^2 \theta)\rho_N^\pi \qquad (9)$$

which is analogous to the Heller–McConnell equation applicable to carbon-centred radicals.[35,39,40] Here θ is the dihedral angle between the β-C–H bond and the axis of the N-2p_π orbital, ρ_N^π is the unpaired electron population in this orbital, and A_N and B_N are constants, with the former probably very small.[19]

For the conformation **11** with its time-averaged dihedral angles, the observed averaged value of $a(2H_\beta)$ will be proportional to $(\cos^2\theta_1 + \cos^2\theta_2)$, if A_N is neglected. Hence, $a(2H_\beta)$ will be at a minimum when $\phi = 0°$ ($\theta_1 = \theta_2 = 60°$, if $\theta_1 + \theta_2 = 120°$) and this coupling constant will increase (because $\cos^2\theta_1 + \cos^2\theta_2$ increases) as φ increases. The observation that, at a given temperature, $a(2H_\beta)$ increases in the order $R_3Si = Me_3Si < Et_3Si < Pr^i{}_3Si$ can thus be understood in terms of a steric effect which increases the average value of ϕ. The potential function describing torsional motion about the N–C_β bond will be asymmetric and the energetic cost of increasing ϕ will be less than that of decreasing it by the same amount, because of the presence of the repulsive steric interaction between the R_3Si and *N*-Bu^t groups. Hence, the time-averaged value of ϕ for a given silylmethylaminyl radical will increase as the temperature increases, and thus $a(2H_\beta)$ should show a positive temperature dependence, as observed (see Table 1). Similar reasoning explains the negative temperature dependence of the relatively large ^{29}Si splitting constant observed for the aminyl radical **7** and the decrease in $a(^{29}Si)$ along the series $R_3Si = Me_3Si > Et_3Si > Pr^iSi$.

‡ Additional factors are thought to be important in determining the conformational preferences of the related aminoxyl radicals R_3Si-$CH_2N(\dot{O})Bu^t$.[38]

The electronic preference of the R_3Si substituent for the eclipsing position means that this group is already in what is probably the stereoelectronically favoured site for 1,2-migration from carbon to nitrogen. The transition state for migration could be reached simply by increasing and supplementing the 'bridging' hyperconjugative interaction already present in the ground state of the aminyl radical [however, a transition state of this structure would not appear to correlate effectively with the conjugatively stabilized ground state geometry of the product aminoalkyl radical (see below)].

Displacement of silylmethylaminyl radicals from trivalent phosphorus

We have shown previously[24] that alkoxyl radicals react rapidly with dialkylaminophosphanes to displace dialkylaminyl radicals. Thus, photolysis of a dialkyl peroxide ($R^1O_2R^1$) in the presence of $(EtO)_2PNR_2$ provides a general route to $R_2N^\bullet$ for EPR studies [eqn. (10a)]. The alkyl radical $R^{1\bullet}$ may also be formed as a minor product of β-scission of the intermediate phosphoranyl radical **13** or, as a secondary reaction product, by β-scission of the phosphoranyl radical **14** [eqn. (11)]. The extent to which the EPR spectrum of $R^{1\bullet}$ appears alongside and corrupts that of $R_2N^\bullet$ thus increases with the duration of

$$(EtO)_2PNR_2 \xrightarrow{R^1O^\bullet} R^1O(EtO)_2\dot{P}NR_2 \quad \textbf{13}$$

$$\xrightarrow{\text{major}} R_2N^\bullet + (EtO)_2POR^1 \qquad (10a)$$

$$\xrightarrow{\text{minor}} R^{1\bullet} + (EtO)_2P(O)NR_2 \qquad (10b)$$

photolysis and with the degree of stabilization of $R^{1\bullet}$. Hence, this problem can be quite annoying when DTBP is the primary radical source, but is not significant with diethyl peroxide (DEP).§ Di-*tert*-pentyl peroxide ($EtMe_2CO_2CMe_2Et$; DTPP) and dicumyl peroxide ($PhMe_2CO_2CMe_2Ph$; DCP), like DTBP, both give rise to tertiary alkyl radicals $R^{1\bullet}$, but the spectra of these are less obtrusive than the spectrum of Bu$^{t\bullet}$.¶ Tris(dialkylamino)phosphanes $(R_2N)_3P$ are sometimes preferable as sources of $R_2N^\bullet$ because, unlike $(EtO)_2PNR_2$, the phosphorus(III) product of the initial displacement reaction also yields $R_2N^\bullet$ on subsequent reaction with $R^1O^\bullet$ [*cf.* eqn. (11)].

$$(EtO)_2POR^1 \xrightarrow{R^1O^\bullet} (EtO)_2\dot{P}(OR^1)_2 \longrightarrow R^{1\bullet} + (EtO)_2P(O)OR^1 \qquad (11)$$

14

The *N-tert*-butyl- and *N*-methyl-aminophosphanes **17** and **18** were prepared from the corresponding silylmethylamines **15** and **16** as shown in Scheme 1; it is noteworthy that the equilibrium between the lithium salts $Me_3SiCH_2\bar{N}R\ Li^+$ and $Me_3SiN(R)\bar{C}H_2\ Li^+$ favours the former[41] almost exclusively when R is a simple alkyl group and no isomeric phosphanes $Me_3SiN(R)CH_2P(OEt)_2$ were detected in the products.

UV photolysis of the peroxides DTBP, DEP, DTPP or DCP in the presence of the aminophosphane **17** afforded a good quality EPR spectrum of the silylmethylaminyl radical **7** (see

§ Diethyl peroxide can react heterolytically with phosphorus(III) compounds and this can cause complications at higher temperatures.

¶ The lines in the EPR spectrum of the *tert*-pentyl radical are both more numerous and broader than those of Bu$^{t\bullet}$. The EPR spectrum of the cumyl radical also consists of a relatively large number of lines and these are easily saturated.

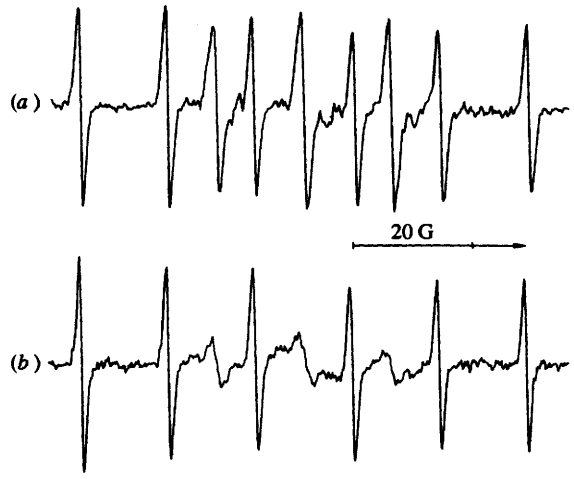


Fig. 2 EPR spectra of $Me_3SiCH_2\dot{N}Bu^t$ **7** produced by reaction of cumyloxyl radicals with the aminophosphane **17** in cyclopropane at (*a*) 281 K and (*b*) 240 K

$$Me_3SiCH_2Cl \xrightarrow{i} Me_3SiCH_2NHR$$

15 R = Bu^t
16 R = Me

ii, iii

$$(EtO)_2PN(R)CH_2SiMe_3$$

17 R = Bu^t
18 R = Me

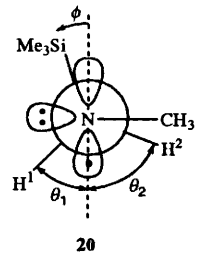
Scheme 1 *Reagents and conditions:* i, excess RNH_2, heat under pressure; ii, BuLi; iii, $(EtO)_2PCl$

Fig. 2) with spectroscopic parameters identical to those of the radical produced by addition of $Me_3Si^\bullet$ to MTBA. The temperature-dependent linewidth effects referred to before are clearly evident in the spectrum, but attempts to determine the individual β-proton splittings were frustrated by the appearance at low temperatures of broad features of an unidentified spectrum which obscured the regions where the separated $M_I(2H_\beta) = 0$ lines should appear in the slow exchange limit. Furthermore, at very low temperature, the rate of generation of the aminyl radical by α-scission of the phosphoranyl radical **13** [eqn. (10a)] becomes slow, the spectrum of **7** is therefore weaker and the spectrum of **13** becomes apparent.[24]

The EPR spectrum of the *N*-methyl-*N*-trimethylsilylmethylaminyl radical **19** was obtained in a similar manner

$Me_3SiCH_2\dot{N}Me$

19



20

by photolysis of a dialkyl peroxide in the presence of the aminophosphane **18**. The spectrum at 259 K is shown in Fig. 3, along with a computer simulation using the parameters given in Table 1. As for the radicals **7**–**9**, an alternating linewidth effect is observed such that the lines corresponding to $M_I(2H_\beta) = 0$ are broader than those associated with $M_I(2H_\beta) = \pm 1$, and this has been accounted for in the simulation. The spectroscopic

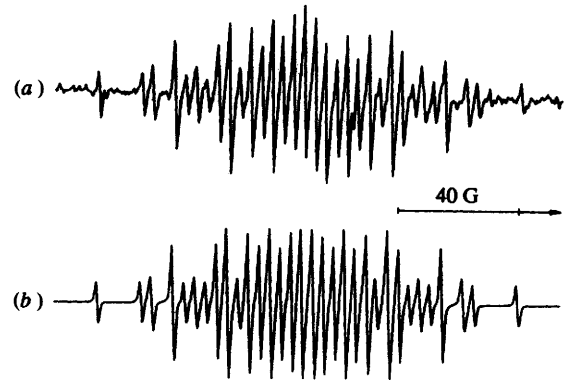


Fig. 3 (*a*) EPR spectrum of $Me_3SiCH_2\dot{N}Me$ **19** produced by reaction of *tert*-butoxyl radicals with the aminophosphane **18** in cyclopropane at 259 K. (*b*) Computer simulation of the spectrum using the parameters given in Table 1; the widths of the $M_I(2H_\beta) = 0$ and ±1 lines are 1.25 and 1.00 G, respectively.

parameters indicate that the preferred conformation of the radical is as shown in structure **20** for which, at a given temperature, the time-average angle ϕ is presumably closer to zero than for the *N*-*tert*-butyl analogue **7**, because of the smaller steric repulsion between the Me_3Si and *N*-Me groups. The value of $\langle a(2H_\beta)\rangle$ at a particular temperature should then be smaller for **19** than for **7**, as observed, and a corollary would be that the magnitudes of the individual β-proton splittings $a(H^1)$ and $a(H^2)$ are more similar for **19** than for **7**.

The nitrogen and *N*-methyl proton splittings for **19** are similar to those observed for the dialkylaminyl radicals $Me_2N^\bullet$ and $Me\dot{N}Bu^t$ (see Table 1). On the basis of eqn. (9), it might be expected that the individual β-proton splittings for **19** would both be about half as large as the *N*-methyl proton splitting because, if ϕ is *ca.* 0°, $\cos^2\theta_1 \approx \cos^2\theta_2 \approx 0.25$ while $\langle\cos^2\theta\rangle = 0.5$ for the freely-rotating methyl group. However, $\langle a(2H_\beta)\rangle$ for **19** (18.0 G at 259 K) is appreciably greater than half the value of $a(CH_3N)$ (25.0 G), suggesting that the same value of B_N is not applicable to both the *N*-CH_3 and *N*-CH_2SiMe_3 groups. In fact, it would be expected[15,32,35,37] that the value of $B_N^{CH_2SiMe_3}$ would be greater than that of $B_N^{CH_3}$, because of the lower electronegativity of Si as compared with H and the consequent greater electron donor ability of the $-CH_2SiMe_3$ group compared with $-CH_3$.

Mechanism of 1,2-trialkylsilyl group migration

Having characterized the silylmethylaminyl radicals **7** and **19** by EPR spectroscopy, we set out to confirm the conclusion[20] that these radicals undergo rearrangement by 1,2-migration of the trimethylsilyl group from carbon to nitrogen [eqns. (12) and (13)]. Fig. 4(*a*) shows the EPR spectrum of the authentic radical

$Me_3SiCH_2\dot{N}Bu^t$ → $H{\cdot}C(H)(SiMe_3)-N(Bu^t)$ (12)

7 **21**

$Me_3SiCH_2\dot{N}Me$ → $H{\cdot}C(H)(SiMe_3)-N(Me)$ (13)

19 **22**

21 generated in *tert*-butylbenzene by hydrogen-atom abstraction from $Me_3SiN(Bu^t)Me$ using photochemically produced *tert*-butoxyl radicals; the spectroscopic parameters for the carbon-centred radicals described in this work are collected in Table 2. When the aminyl radical **7** was generated by photolysis of DCP in the presence of the aminophosphane **17** in *tert*-

Table 2 EPR parameters for carbon-centred radicals

Radical	Solvent[a]	T/K	g-Factor	Hyperfine splittings[b,c]/G
$^{\bullet}CH_2N(Bu^t)SiMe_3$ **21**	B	350	2.0029	14.85 (2 H), 3.48 (N), 0.25 (9 H) [14.8 (2 H), 3.7 (N) at 300 K]
$^{\bullet}CH_2N(Me)SiMe_3$ **22**	B	325	2.0030	15.05 (1 H), 14.51 (1 H), 3.30 (N), 4.20 (3 H)
$Me_3Si\dot{C}HNHBu^t$ **27**	C	225	2.0029	15.13 (1 H), 6.57 (N), 1.92 (N*H*), 0.32 (18 H)[d] [15.0 (1 H), 7.2 (N), 2.5 (N*H*), 0.34 (9 H) at 225 K]
$Me_3Si\dot{C}HNHMe$ **28**	C	190	2.0029	14.21 (1 H), 5.70 (N), 6.37 (3 H), 2.97 (N*H*), 0.35 (9 H) [16.0 (1 H), 6.3 (N), 0.3 (9 H) at 240 K]

[a] C = cyclopropane; B = *tert*-butylbenzene. [b] Nuclei indicated in parentheses. [c] Values in square brackets taken from ref. 20. [d] At 267 K the difference between the two nine-proton splittings (0.28 and 0.36 G) could be resolved and the fine structure could be simulated as a decet of decets.

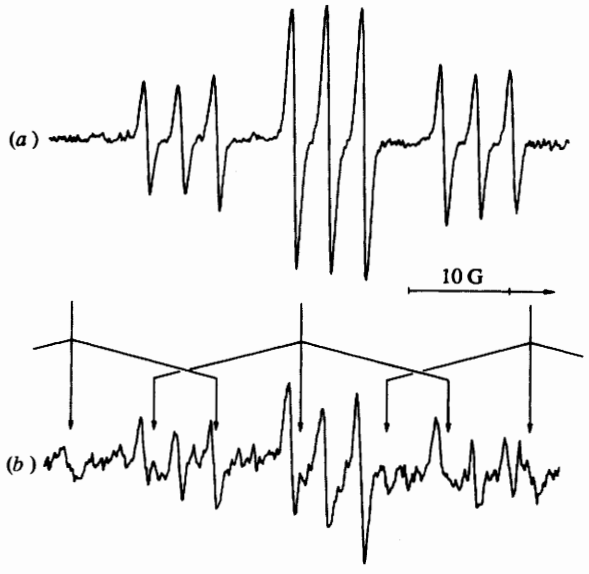


Fig. 4 (*a*) EPR spectrum of the radical **21** produced by reaction of *tert*-butoxyl radicals with $Me_3SiN(Bu^t)Me$ in *tert*-butylbenzene at 350 K. (*b*) EPR spectrum observed during reaction of cumyloxyl radicals with the aminophosphane **17** in *tert*-butylbenzene at 350 K. The arrows indicate the positions of seven of the nine lines from $Me_3SiCH_2\dot{N}Bu^t$ (*cf.* Fig. 2).

butylbenzene above *ca.* 310 K, the EPR spectrum of **21** was detected alongside that of **7** and the ratio [**21**]:[**7**] increased as the temperature increased. The spectrum at 350 K is reproduced in Fig. 4(*b*) and shows the presence of both radicals in approximately equal concentration (*ca.* 2–3 × 10^{-7} mol dm^{-3}), indicating[42] that the rate constant for the rearrangement is 10^3–10^4 s^{-1} at this temperature (provided that the product radical **21** is removed by diffusion-controlled radical–radical reactions which have rate constants of[43] *ca.* 10^{10} dm^3 mol^{-1} s^{-1} in *tert*-butylbenzene). This rate constant for 1,2-silyl migration is about an order of magnitude larger than the value which can be calculated from the approximate Arrhenius parameters proposed by Harris *et al.*[20]

Qualitatively similar observations were made for the rearrangement of **19** to **22**. The EPR spectrum of the authentic radical **22** [see Fig. 5(*a*)], generated by hydrogen-atom abstraction from Me_3SiNMe_2, clearly shows the non-equivalence of the α-protons, as a result of the presence of a significant barrier to rotation about the C_α–N bond.‖ This barrier arises because of delocalization of the unpaired electron onto nitrogen which is maximized when the H_2C–N(C)Si skeleton is planar (see structures **23a** and **b**).

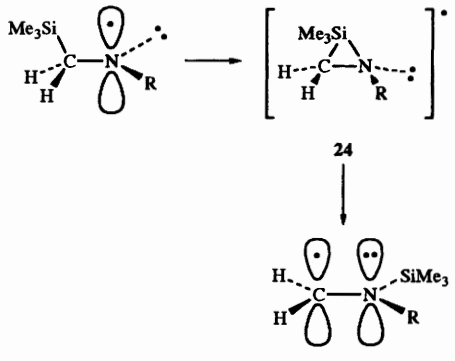
23a **23b**

UV photolysis of DCP in the presence of the aminophosphane **18** in *tert*-butylbenzene at temperatures above *ca.* 280 K afforded the EPR spectrum of **22** [see Fig. 5(*c*)] in addition to that of the aminyl radical **19**, providing clear evidence for the rearrangement proposed by Harris *et al.*[20] As judged from the temperature dependence of the relative intensities of the spectra of **19** and **22** (the concentrations of **19** and **22** were approximately equal at *ca.* 310 K), the rearrangement of the former proceeds more readily than the corresponding rearrangement of the *N*-*tert*-butyl analogue **7**, in accord with the suggestion[20] that the rate of 1,2-migration of the Me_3Si group in aminyl radicals of the type $Me_3SiCH_2\dot{N}R$ decreases as the bulk of the *N*-alkyl group R increases.

As discussed by Harris *et al.*,[20] the 1,2-migration of the silyl group might occur by a dissociative mechanism [eqn. (14)] or

$$Me_3SiCH_2\dot{N}R \rightleftharpoons Me_3Si^{\bullet} + H_2C{=}NR \longrightarrow H_2\dot{C}{-}N(R)SiMe_3 \quad (14)$$

could be an intramolecular process which proceeds *via* a transition state or intermediate **24** containing five-coordinate silicon [eqn. (15)]. It is noteworthy that the development



(15)

of conjugative stabilization of the type represented by **23a** ⟷ **23b** would appear to be hindered in the structure **24**, for stereoelectronic reasons. Since such stabilization of the product radical appears to be significant, as evidenced by the relatively large barrier to rotation about the C–N bond in α-aminoalkyl radicals,[44] there would appear to be a sizeable stereoelectronic contribution to the activation energy for 1,2-silyl migration.**

The intermolecular pathway [eqn. (14)] represents a real

‖ Analogous non-equivalence was not resolved in the spectrum of **21** for which the linewidth is much greater.

** This stereoelectronic effect is relevant to many related 1,2-rearrangements, *e.g.* $Me_3SiCH_2O^{\bullet} \longrightarrow {}^{\bullet}CH_2OSiMe_3$ and $H_3CO^{\bullet} \longrightarrow H_2\dot{C}OH$.[21,45]

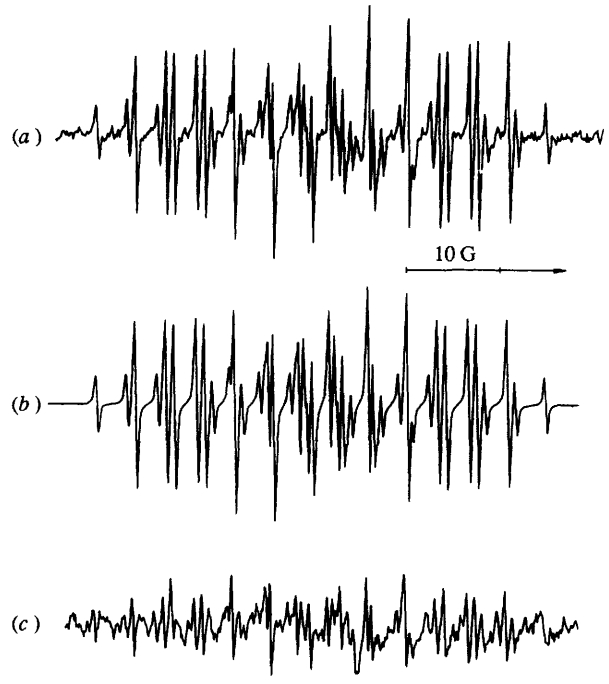


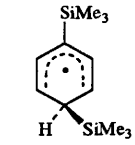
Fig. 5 (*a*) EPR spectrum of the radical **22** produced by reaction of *tert*-butoxyl radicals with Me_3SiNMe_2 in *tert*-butylbenzene at 325 K. (*b*) Computer simulation of the spectrum shown in (*a*) using the parameters given Table 2. (*c*) EPR spectrum observed during reaction of cumyloxyl radicals with the aminophosphane **18** in *tert*-butylbenzene at 325 K; some (much broader) lines from the aminyl radical **19** are just detectable alongside the narrower lines from the rearrangement product **22**.

possibility. Although we have shown that the silylmethylaminyl radical is the kinetically-controlled product of addition of trialkylsilyl radicals to an imine $H_2C{=}NR$, addition to nitrogen would yield the more stable isomeric silylaminomethyl radical and the rate of this mode of addition will increase as the bulk of the *N*-alkyl group decreases. However, attempts by Harris *et al.*[20] to detect free trimethylsilyl radicals, by their reactions with *tert*-butyl chloride or with 1,3,5-trinitrobenzene, failed for the rearrangement of **7** to **21**.

Trimethylsilyl radicals are known to add rapidly to 1,1-di-*tert*-butylethylene to form the persistent radical **25** which is readily detected by EPR spectroscopy.[34] Trapping with this alkene was used by Sakurai *et al.*[46] to demonstrate that trimethylsilyl radicals add reversibly to aromatic rings, by

$$Me_3Si^{\bullet} + Bu^t{}_2C{=}CH_2 \longrightarrow \underset{\mathbf{25}}{Bu^t{}_2\dot{C}{-}CH_2SiMe_3} \quad (16)$$

showing that they are readily eliminated from the four-coordinate carbon atom of the cyclohexadienyl radical **26**. When DCP was photolysed in the presence of either aminophosphane **17** or **18** and $Bu^t{}_2C{=}CH_2$ (0.6 mol dm^{-3}) under the conditions used to obtain Figs. 4(*b*) and 5(*c*), respectively, or at higher temperatures (up to 375 K), no spectrum of **25** was detectable alongside the spectrum of the appropriate rearrangement product **21** or **22**. However, an intense EPR spectrum of **25** was observed when DCP was photolysed in the presence of $Bu^t{}_2C{=}CH_2$ and Me_3SiH in *tert*-butylbenzene at temperatures up to 375 K. We conclude that the rearrangement of trialkylsilylmethylaminyl radicals probably occurs by an intramolecular pathway, as shown in eqn. (15), since it seems likely that some trimethylsilyl radicals would escape from a solvent caged pair [$Me_3Si^{\bullet}$ + $H_2C{=}NR$] before re-addition to the nitrogen atom.



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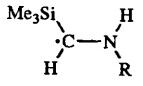

27 R = Bu^t
28 R = Me

Hydrogen-atom abstraction from *N*-alkyl-*N*-trimethylsilylmethylamines

The conclusions drawn by Harris *et al.*[20] and referred to in the previous sections were based on EPR spectra observed during reactions of photochemically generated *tert*-butoxyl radicals with silylmethylamines Me_3SiCH_2NHR. From the reaction with $Me_3SiCH_2NHBu^t$ only the *C*-centred radicals $Me_3SiCH{-}NHBu^t$ and $^{\bullet}CH_2N(Bu^t)SiMe_3$ (the latter presumed to arise from the 1,2-silyl-group migration) were detected. For the reaction of Me_3SiCH_2NHMe, none of the product radicals was conclusively identified, although some lines in the 'extremely weak and complex spectrum' were tentatively assigned to $Me_3SiCHNHMe$ [the three coupling constants $a(1H_{\alpha})$ 16.0, a(N) 6.3 and a(9H) 0.3 G at 240 K were reported]. Having fully characterized the silylmethylaminyl radicals **7** and **19** and their rearrangement products **21** and **22**, we considered it appropriate to reexamine the reactions of alkoxyl radicals with the amines.

UV irradiation of a cyclopropane solution containing DTBP (15% v/v) and *N*-methyltrimethylsilylmethylamine **16** (*ca.* 1 mol dm^{-3}) at 240 K afforded the EPR spectra reproduced in Figs. 6(*a*) and (*c*) (only the low-field half is shown). Fig. 6(*a*) was recorded with a microwave power of 5 mW and a modulation amplitude of 1.25 G and it is dominated by the spectrum of the aminyl radical **19** [*cf.* Fig. 3 and the computer simulation shown in Fig. 6(*b*)]. Fig. 6(*c*) was recorded using the same sample over the same magnetic field range, but with a microwave power of 1 mW and a modulation amplitude of 0.25 G. Under the latter conditions the sharp-lined and more easily-saturated spectrum of the radical **28** is revealed.†† The complete spectrum (stronger at lower temperatures) of **28** at 190 K is shown in Fig. 7, along with a computer simulation obtained using the parameters given in Table 2. Clearly hydrogen-atom abstraction, presumably mainly by $Bu^tO^{\bullet}$,‡‡ takes place from both nitrogen and carbon. Similar results were obtained from *N*-*tert*-butyltrimethylsilylmethylamine **15**, which gave rise to overlapping EPR spectra of the aminyl radical **7** and the carbon-centred radical **27**, the latter as reported by Harris *et al.*[20] However, our analysis differs from that given by these authors in that the spectrum at 225 K could only be satisfactorily simulated by including a splitting of 0.32 G from 18 protons, rather than from

†† The *E*-rotamers of the captodatively stabilized radicals **27** and **28** are presumably favoured over the *Z*-rotamers for steric reasons. Although the barrier to rotation about the C_{α}–N bond is probably sufficiently large that the rotamers would not exchange on the EPR timescale below 225 K,[47] only one spectrum, attributed to the *E*-rotamer (or conceivably to both rotamers if their EPR parameters were indistinguishable) was detected.

‡‡ It is not impossible that the silylmethylaminyl radicals **7** and **19** also abstract hydrogen from carbon in the parent amine to a small extent and thereby provide a minor route to **27** and **28**.

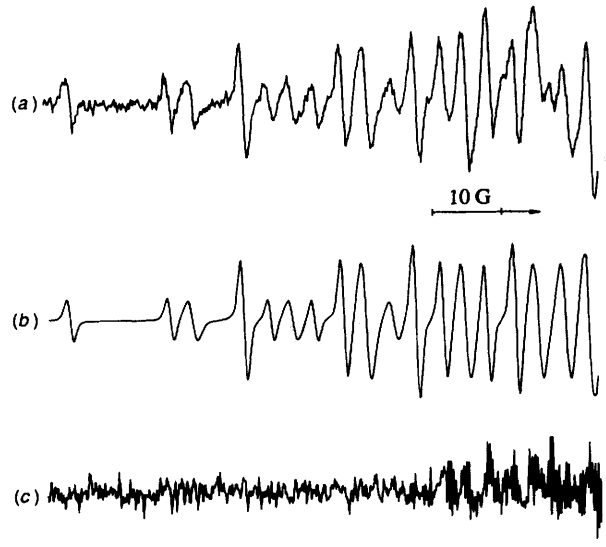

Fig. 6 (*a*) Low-field half of the EPR spectrum recorded during photolysis of DTBP in the presence of Me_3SiCH_2NHMe in cyclopropane at 240 K; the microwave power was 5 mW and the modulation amplitude was 1.25 G. The dominant spectrum is that of the silylmethylaminyl radical **19**. (*b*) Computer simulation of the spectrum of **19** [$a(3H_\beta)$ 25.09, a(N) 14.52 and $a(2H_\beta)$ 17.70 G]; the widths of the $M_I(2H_\beta) = 0$ and ± 1 lines are 1.45 and 1.00 G, respectively. (*c*) As (*a*), except the microwave power was 1 mW and the modulation amplitude was 0.25 G. The major spectrum apparent is now that of the radical **28**.

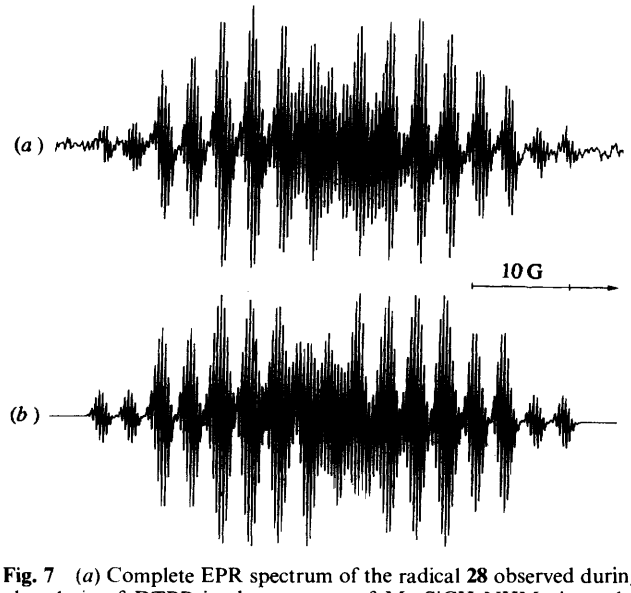

Fig. 7 (*a*) Complete EPR spectrum of the radical **28** observed during photolysis of DTBP in the presence of Me_3SiCH_2NHMe in cyclopropane at 190 K. (*b*) Computer simulation using the parameters given in Table 2. Some minor differences between the simulated spectrum and the (very complex) experimental spectrum are evident. However, the simulated spectrum, especially towards the centre, is very sensitive to the precise values of the splitting constants and changing any of these by as little as 0.01 G alters the appearance of the spectrum.

9 protons as reported previously. Thus, it appears that the protons of both the *tert*-butyl and trimethylsilyl groups give rise to similar splittings. At 267 K, under optimum instrumental conditions, the fine structure could be resolved as a decet of decets corresponding to separate 9-proton splittings of 0.28 and 0.36 G. At low temperatures (< *ca.* 250 K) the spectrum of an unidentified and relatively persistent radical was also detected in experiments with **15**.

Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert inside the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz, as described previously.[30] The microwave frequency was measured using a frequency counter (Hewlett-Packard 5350B) and the magnetic field was measured with an NMR gaussmeter calibrated to account for the field difference between the sample and the NMR probe using the pyrene radical anion (g 2.002 71) as a standard.[48] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (4 mm o.d., 3 mm i.d.).

Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[49] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

Materials

^1H and ^{13}C (proton decoupled) NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^1H). The solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si: J-values are quoted in Hz. Cyclopropane (Union Carbide), trimethylsilane (Fluorochem) and other silanes (Aldrich) were used as received. Butyllithium in hexanes (Aldrich, nominally 2.5 mol dm^{-3}) was standardized by titration with 2,5-dimethoxybenzyl alcohol;[50] the concentration was found to be 2.36 mol dm^{-3}.

Di-*tert*-butyl peroxide (98%, Aldrich) was passed down a column of basic alumina (activity 1) and distilled (bp 46–47 °C/76 Torr) (1 Torr ≈ 133.3 Pa). Diethyl peroxide,§§[51] di-*tert*-pentyl peroxide (bp 38 °C/7 Torr)[52] and 1,1-di-*tert*-butylethylene (bp 43–44 °C/12 Torr)[53] were prepared using published methods. Dicumyl peroxide (Aldrich, 98%) was recrystallized from 95% ethanol (mp 39–40 °C).

***N*-Methylene-*tert*-butylamine (MTBA).**[25] Aqueous formaldehyde (37% w/v, 60.0 cm^3, 0.80 mol) was added dropwise to *tert*-butylamine (48.0 g, 0.66 mol) with vigorous mechanical stirring. The temperature of the reaction mixture was kept below *ca.* 45 °C by external cooling using a water bath and after the addition was complete the mixture was stirred for a further 1 h. Potassium hydroxide pellets (*ca.* 10 g) were added to aid separation of the liquid layers; the upper organic phase was dried over KOH pellets and distilled at atmospheric pressure to give the imine (43.2 g, 77%), bp 63–65 °C. Monomeric MTBA shows δ_H 1.20 (9 H, s), and 7.27 and 7.40 (2 H, AB q, J = 16.0); δ_C 26.7, 80.9, 147.5; the trimer shows δ_H 1.12 (27 H, s) and 3.52 (6 H, br s). Traces of unidentified impurities (possibly including $MeOCH_2NHBu^t$) were present in the imine.

On standing, the viscosity of the liquid increased and monomeric MTBA could no longer be removed by trap-to-trap distillation at room temperature using a vacuum line, indicating that trimerization had taken place. However, the ^1H NMR spectrum obtained from this liquid in $CDCl_3$ showed the presence of mainly monomer, because the trimer undergoes rapid partial dissociation in this solvent.[29] To obtain monomeric MTBA for EPR experiments, the trimer (*ca.* 2.0 g) was mixed with neutral alumina (Merck 90, activity 1, 70–230 mesh, *ca.* 1.0 g) in a 10 cm^3 round-bottomed flask containing a PTFE-coated magnetic stirrer bar and then attached to the vacuum line. The mixture was degassed using two freeze–pump–thaw cycles and

§§ This was purified by trap-to-trap distillation at room temperature using a vacuum line and was not distilled at atmospheric pressure as described previously.[51]

then stirred and heated with a hot-air blower. Gaseous monomeric MTBA was evolved and was condensed directly into the EPR sample tube using liquid nitrogen. Other reagents were then added without allowing the monomeric MTBA to melt and, after being sealed, the sample tube was kept in liquid nitrogen until required, when the contents were thawed and mixed by repeated inversion of the tube in a solid CO_2–ethanol bath.

***N*-Methyltrimethylsilylmethylamine 16.**[54] A mixture of methylamine (*ca.* 60 cm^3, *ca.* 1.3 mol) and chloromethyltrimethylsilane (16.0 g, 0.13 mol) was stirred in a PTFE-lined autoclave (Berghof, capacity 125 cm^3) for 5 h at *ca.* 85 °C (internal temperature) and under autogenous pressure. The cooled reaction mixture was washed out of the autoclave with pentane and a solution of potassium hydroxide pellets (12.0 g) in water (30 cm^3) was added with stirring. The organic phase was separated and the aqueous phase extracted with pentane (3 × 30 cm^3). The combined organic phases were washed with saturated brine (80 cm^3) and then dried over K_2CO_3. The majority of the pentane was removed carefully at room temperature using a rotary evaporator and the residue was distilled at atmospheric pressure from calcium hydride to yield the amine (8.90 g, 59%), bp 100–102 °C (lit.,[54] 101.6 °C/735 Torr): δ_H −0.02 (9 H, s), 0.61 (NH, br s), 1.99 (2 H, s) and 2.42 (3 H, s); δ_C −2.7, 41.5 and 43.2.

***N*-*tert*-Butyltrimethylsilylmethylamine 15.**[38] This was prepared in the same way as **16** from *tert*-butylamine (26 cm^3, 0.25 mol) and chloromethyltrimethylsilane (10.0 g, 0.082 mol); stirring was continued for 8 h at an internal temperature of *ca.* 118 °C. After a work-up as described for **16**, the amine (7.80 g, 59%) was purified by distillation, bp 40–42 °C/20 Torr (lit.,[38] 65–77 °C/90 Torr): δ_H −0.01 (9 H, s), 0.32 (NH, br s), 1.01 (9 H, s, Bu^t) and 1.93 (2 H, s); δ_C −2.7, 28.4, 31.4 and 51.0.

***N*-*tert*-Butyl-*N*-trimethylsilylmethylamino(diethoxy)phosphane 17.** Butyllithium in hexanes (2.36 mol dm^{-3}, 13.2 cm^3, 0.031 mol) was added dropwise under nitrogen to a stirred solution of *N*-*tert*-butyltrimethylsilylmethylamine (4.94 g, 0.031 mol) in dry diethyl ether (30 cm^3) cooled in an ice–water bath. After the addition was complete, the ice bath was removed and the mixture was stirred for a further 1 h. The ice bath was replaced and a solution of diethyl chlorophosphite (4.85 g, 0.031 mol) in dry pentane (40 cm^3) was added dropwise during 40 min; the ice bath was removed and the mixture was stirred for a further 2 h at room temperature. Precipitated lithium chloride was removed by filtration through Celite and the solvents were removed from the filtrate under reduced pressure. The residual oil was distilled to yield the aminophosphane **17** (5.20 g, 60%) as a colourless liquid, bp 60–62 °C/0.02 Torr (Found: C, 51.2; H, 10.7; N, 4.7. $C_{12}H_{30}NO_2PSi$ requires C, 51.6; H, 10.8; N, 5.0%); δ_H 0.02 (9 H, s), 1.21 (6 H, t, J = 7.0, CH_3CH_2O), 1.24 (9 H, d, J_{HP} = 1.6, Bu^t), 2.39 (2 H, d, J_{HP} = 6.6) and 3.67 (4 H, m, CH_3CH_2O); δ_C −1.2, 17.1, 30.5 (d, J_{CP} = 12.9), 31.1, 54.6 (d, J_{CP} = 17.3) and 59.2 (d, J_{CP} = 20.8).

***N*-Methyl-*N*-trimethylsilylmethylamino(diethoxy)phosphane 18.** This aminophosphane (2.82 g, 52%) was prepared in a similar way to **17** starting from *N*-methyltrimethylsilylmethylamine (2.65 g, 0.023 mol), bp 60–62 °C/0.5 Torr (Found: C, 45.6; H, 10.1; N, 5.7. $C_9H_{24}NO_2PSi$ requires C, 45.5; H, 10.2; N, 5.9%); δ_H 0.04 (9 H, s), 1.20 (6 H, t, J = 7.1, CH_3CH_2O), 2.41 (2 H, d, J_{HP} = 8.6), 2.56 (3 H, d, J_{HP} = 8.1) and 3.65 (4 H, m, CH_3CH_2O); δ_C −1.2, 17.0, 34.4 (d, J_{CP} = 15.3), 38.9 (d, J_{CP} = 19.7) and 58.9 (d, J_{CP} = 16.7).

***N*-*tert*-Butyl-*N*-methylaminotrimethylsilane.** Butyllithium in hexanes (2.36 mol dm^{-3}; 12.9 cm^3, 0.030 mol) was added dropwise under nitrogen to a stirred solution of *N*-methyl-*tert*-butylamine (2.62 g, 0.030 mol) in dry diethyl ether (20 cm^3) with cooling in an ice–water bath. After the addition was complete, the ice bath was removed and the mixture was stirred for a further 2 h at room temperature. The ice bath was replaced and chlorotrimethylsilane (3.26 g, 0.030 mol) in pentane (20 cm^3) was added dropwise during 1 h. After the addition was complete, the mixture was stirred for 2 h at room temperature, filtered through Celite under nitrogen and the solvents were removed from the filtrate under reduced pressure. Distillation of the residue gave the aminosilane (3.15 g, 66%), bp 76–78 °C/70 Torr (Found: C, 60.1; H, 13.4; N, 8.4. $C_8H_{21}NSi$ requires C, 60.3; H, 13.3; N, 8.8%); δ_H 0.12 (9 H, s), 1.16 (9 H, s, Bu^t) and 2.42 (3 H, s); δ_C 3.6, 29.8, 31.1 and 53.3.

Acknowledgements

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