Trialkylsilylaminyl Radicals. Part 1. Electron Spin Resonance Studies of the Photolysis of Silylated Hydrazines, Hydroxylamines, Triazenes, and Tetrazenes

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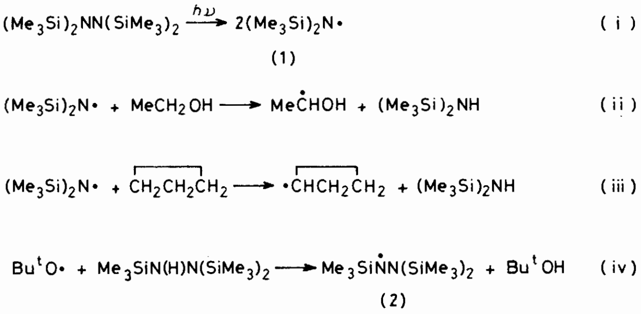
Radicals produced by liquid-phase u.v. photolysis of a number of trialkylsilylated hydrazines, hydroxylamines, triazenes, and tetrazenes have been studied using e.s.r. spectroscopy. The bis(trimethylsilyl)aminyl radical $(Me_3Si)_2N^\cdot$, generated by photolysis of $(Me_3Si)_2NN(SiMe_3)_2$, $(Me_3Si)_2NOSiMe_3$, or $(Me_3Si)_2NN{=}NN(SiMe_3)_2$, is much more reactive than a dialkylaminyl radical. It abstracts hydrogen from aliphatic C–H groups, adds to ethylene, t-butyl isocyanide, and trialkyl phosphites; the bis(triethylsilyl)aminyl radical behaves similarly. Differences between $(R_3Si)_2N^\cdot$ and $(R_3C)_2N^\cdot$ are attributed to the σ-donor–π-acceptor substituent effect of the trialkylsilyl ligand. The reactivity of $(R_3Si)_2N^\cdot$ is generally similar to that of $Bu^tO^\cdot$, although the steric congestion at the radical centre in the former results in a preference for attack at less hindered sites. For example, whilst $Bu^tO^\cdot$ and $H_2N^\cdot$ both react with isobutane to give mainly $Bu^{t\cdot}$, $(Me_3Si)_2N^\cdot$ gives mainly $Bu^{i\cdot}$ below room temperature. The trimethylsilyl(methyl)aminyl radical was generated by photolysis of $Me_3SiN(Me)OSiMe_3$ or $Me_3SiN(Me)N{=}NMe$ and, although its e.s.r. spectrum was not detected, it could be trapped by trialkyl phosphites to give the phosphoranyl radicals $Me_3SiN(Me)\dot{P}(OR)_3$, implying a reactivity greater than that of $Me_2N^\cdot$. Hydrogen abstraction from $R_3SiN(H)OSiR_3$ affords $R_3Si\dot{N}OSiR_3$ which rearranges to $(R_3Si)_2NO^\cdot$, but $R\dot{N}OSiR_3$ does not rearrange to $R_3Si(R)NO^\cdot$. The e.s.r. spectra of $R\dot{N}OR$, $R\dot{N}OSiR_3$, and $R_3Si\dot{N}OSiR_3$ are compared and differences are accounted for in terms of the π-acceptor nature of the R_3Si group.

There is continued interest in the changes in properties of organic molecules consequent upon replacement of key carbon atoms by silicon. In preliminary communications [1,2] we have reported that bis(trialkylsilyl)aminyl radicals $(R_3Si)_2N^\cdot$ are much more reactive than their carbon analogues $(R_3C)_2N^\cdot$. We have also shown [2] that previous reports [3] of e.s.r. spectra assigned to $(Et_3Si)_2N^\cdot$ and to $Me_3Si\dot{N}CMe_3$ are in error. In the present paper we give a full account of our e.s.r. studies of the reactions of silylaminyl radicals, generated by photochemical decomposition of *N*-silylated hydrazines, hydroxylamines, triazenes, and tetrazenes.



$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} 2(Me_3Si)_2N\cdot \qquad (i)$$

(1)

$$(Me_3Si)_2N\cdot + MeCH_2OH \longrightarrow Me\dot{C}HOH + (Me_3Si)_2NH \qquad (ii)$$

$$(Me_3Si)_2N\cdot + CH_2CH_2CH_2 \longrightarrow \cdot CHCH_2CH_2 + (Me_3Si)_2NH \qquad (iii)$$

$$Bu^tO\cdot + Me_3SiN(H)N(SiMe_3)_2 \longrightarrow Me_3Si\dot{N}N(SiMe_3)_2 + Bu^tOH \qquad (iv)$$

(2)

Results

The general techniques used in similar investigations have been described previously.[4] E.s.r. spectra were monitored during continuous u.v. photolysis of static liquid samples in the cavity of the spectrometer. The solvent was usually cyclopropane. E.s.r. spectra attributable to silylaminyl radicals were not obtained in this work and evidence for their formation rests on the detection of radicals produced by their subsequent reactions. The results are sub-divided according to the primary photochemical sources of radicals.

(i) *Tetrakis(trimethylsilyl)hydrazine* (*TTMH*).—This substance was prepared by the exhaustive silylation of hydrazine.[5] It is a colourless, thermally stable, crystalline solid sufficiently resistant to hydrolysis to be handled easily on the open bench. It is very soluble in hydrocarbons and, in iso-octane, exhibits weak u.v. absorption with a shoulder at 280 nm (ε 1.9 l mol^{-1} cm^{-1}). For comparison, in iso-octane at 290 K, tetramethylhydrazine and di-t-butyl peroxide (DTBP) show ε_{280} 2.0 and 4.4 l mol^{-1} cm^{-1}, respectively.

A strong e.s.r. spectrum of the 1-hydroxyethyl radical was detected during u.v. photolysis (*ca.* 260—340 nm) of a cyclopropane solution containing TTMH (*ca.* 0.2M) and ethanol (10% v/v). The bis(trimethylsilyl)aminyl radical (1), formed by cleavage of the N–N bond, abstracts hydrogen from the methylene group of the alcohol [equations (i) and (ii)]. A spectrum of similar intensity was obtained when the TTMH was replaced by DTBP, implying a high quantum efficiency for the photochemical cleavage of the hydrazine. In general, concentrations of transient radicals obtained from TTMH were relatively high (10^{-7}—10^{-8}M) *provided that the hydrazine was not screened* by other substances present. Attempts to sensitise the cleavage of TTMH using *p*-methoxyacetophenone, which is an effective sensitiser for DTBP,[6] were unsuccessful.

Photolysis of TTMH alone in cyclopropane afforded an e.s.r. spectrum of the cyclopropyl radical, even at 150 K, and thus reaction (iii) must be rapid at very low temperatures implying that it is probably exothermic or at least thermoneutral. *D*(C–H) in cyclopropane is 421 kJ mol^{-1},[7] and thus *D*(N–H) in hexamethyldisilazane is probably $\geqslant$421 kJ mol^{-1}.

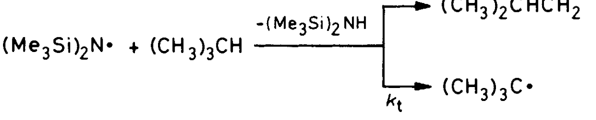
Photolysis of TTMH alone in $CFCl_3$ or CF_2Cl_2 afforded a spectrum of the persistent tris(trimethylsilyl)hydrazyl radical (2) [*a*(1N) 11.0, *a*(1N) 4.3 G, *g* 2.0050 at 178 K]. A stronger spectrum was obtained by photolysis of tris(trimethylsilyl)hydrazine either alone or with DTBP [equation (iv)], as reported by West and Bichlmeir.[8] The route for formation of (2) from TTMH in Freon is unclear; perhaps C–Cl bond cleavage in the solvent is sensitised by excited TTMH (compare similar sensitisation by excited DTBP [9]). Chlorine

Table 1. Radicals detected during the reactions of the bis(trimethylsilyl)aminyl radical [a]

Reactant	Solvent [b]	Product radicals	E.s.r. parameters of novel product radicals [c]
EtOH	A	$\mathrm{Me\dot{C}HOH}$	
$\mathrm{Pr^iOH}$	A	$\mathrm{Me_2\dot{C}OH}$	
$\mathrm{Me_2O}$	A	$\mathrm{H_2\dot{C}OMe}$	
$\mathrm{Et_2O}$	A	$\mathrm{Me\dot{C}HOEt}$	
cyclo-$\mathrm{C_3H_6}$	A	cyclo-$\mathrm{C_3H_5^{\bullet}}$	
cyclo-$\mathrm{C_5H_{10}}$	B	cyclo-$\mathrm{C_5H_9^{\bullet}}$	
$\mathrm{Me_3CH}$	B	$\mathrm{Me_2CH\dot{C}H_2 + Me_3C\cdot}$	
$\mathrm{CH_3CH{=}CH_2}$	B	$\mathrm{CH_2{=}CH\dot{C}H_2}$	
$\mathrm{H_4B^-}$	C	$\mathrm{H_3B^{-\bullet}}$	
$\mathrm{O_2}$ [d]	D	$\mathrm{(Me_3Si)_2NO^{\bullet}}$	
$\mathrm{CH_2{=}CH_2}$	B	$\mathrm{(Me_3Si)_2NCH_2\dot{C}H_2}$	$a(2\mathrm{H}_\alpha)$ 21.9, $a(2\mathrm{H}_\beta)$ 31.2, $a(\mathrm{N})$ 2.5, g 2.0025 at 212 K [e]
$\mathrm{Bu^tN{=}C}$	A	$\mathrm{Bu^tN{=}\dot{C}N(SiMe_3)_2}$	$a(\mathrm{N})$ 11.5, $a(^{13}\mathrm{C}_\alpha)$ 95.2, g 2.0017 at 170 K.
$\mathrm{(EtO)_3P}$	A	$\mathrm{(EtO)_3\dot{P}N(SiMe_3)_2}$ [f,g]	$a(\mathrm{P})$ 841.5, $a(\mathrm{N})$ *ca.* 2, g 2.0022 at 170 K
$\mathrm{Et_3P}$	A	$\mathrm{Et\cdot}$	

[a] Temperature range investigated usually *ca.* 170—270 K. [b] A = cyclopropane, B = reactant, C = dimethyl ether–t-pentyl alcohol (1.6 : 1 v/v), D = cyclopentane. [c] Coupling constants in gauss. [d] Unsealed tube. [e] $\mathrm{d}|a(2\mathrm{H}_\beta)|/\mathrm{d}T = -26$ mG K^{-1}. [f] Isomer with an equatorial nitrogen ligand, see text. [g] Undergoes fragmentation (β-scission) to give $\mathrm{Et^{\bullet} + (EtO)_2P(O)N(SiMe_3)_2}$ at higher temperatures (>*ca.* 220 K).

$$\mathrm{(Me_3Si)_2N\cdot + [O] \longrightarrow \underset{(3)}{(Me_3Si)_2NO\cdot}} \qquad \text{(v)}$$



$$\mathrm{(Me_3Si)_2N\cdot + (CH_3)_3CH \xrightarrow{-(Me_3Si)_2NH}} \begin{cases} \xrightarrow{k_i} \mathrm{(CH_3)_2CH\dot{C}H_2} \\ \xrightarrow{k_t} \mathrm{(CH_3)_3C\cdot} \end{cases} \qquad \text{(vi)}$$

atoms could react with TTMH to yield (2) directly or abstract hydrogen to give HCl which would then react with TTMH to give tris(trimethylsilyl)hydrazine. Alternatively, electron transfer from excited TTMH to Freon could give $[\mathrm{TTMH}]^{+\bullet}$, $\mathrm{Cl^-}$, and $\mathrm{^{\bullet}CFCl_2}$ (from $\mathrm{CFCl_3}$) or $\mathrm{^{\bullet}CF_2Cl}$ (from $\mathrm{CF_2Cl_2}$), and subsequent reaction of $[\mathrm{TTMH}]^{+\bullet}$ with $\mathrm{Cl^-}$ could then yield (2) and $\mathrm{Me_3SiCl}$.

A number of other reactions of (1) were investigated by photolysis of TTMH in the presence of the desired reactant and the results are summarized in Table 1. Hydrogen abstraction from cyclopentane gives the cyclopentyl radical, but in the presence of oxygen, bis(trimethylsilyl) nitroxide[10] (3) [$a(\mathrm{N})$ 6.5, $a(^{29}\mathrm{Si})$ 5.9 G, g 2.0093 at 221 K] is detected.

The silylaminyl radical (1) abstracts hydrogen from isobutane and gives rise to spectra of both the isobutyl and t-butyl radicals, with that of the former predominating below room temperature. The relative concentrations of the two alkyl radicals were measured between 170 and 280 K and, assuming that $[\mathrm{Bu^{i\bullet}}]/[\mathrm{Bu^{t\bullet}}]$ is equal to (k_i/k_t),[11] the temperature dependence of the latter may be expressed by equation (vii).* At 170 K the value of (k_i/k_t) is *ca.* 2.4.

$$(k_i/k_t) = (0.37 \pm 0.05)\exp(2.66 \pm 0.50)/RT\ \mathrm{kJ\ mol^{-1}} \qquad \text{(vii)}$$

This selectivity was compared with that of $\mathrm{Bu^tO^{\bullet}}$ in experiments where DTBP replaced TTMH and the t-butyl radical

$$\mathrm{[(CH_3)_2CHCH_2C(O)]_2O_2 \xrightarrow{h\nu} 2(CH_3)_2CH\dot{C}H_2 + 2CO_2} \qquad \text{(viii)}$$

$$\mathrm{(Me_3Si)_2N\cdot + H_4B^- \longrightarrow H_3B^{\overline{\bullet}} + (Me_3Si)_2NH} \qquad \text{(ix)}$$

was found to be the major product at all temperatures investigated ($[\mathrm{Bu^{i\bullet}}]/[\mathrm{Bu^{t\bullet}}]$ = *ca.* 0.02 at 170 K). Photolysis of di-isovaleryl peroxide[12] in isobutane over the temperature range 166—281 K afforded only the spectrum of the isobutyl radical [equation (viii)], confirming that $\mathrm{Bu^{i\bullet}}$ does not abstract hydrogen from isobutane to give $\mathrm{Bu^{t\bullet}}$ under the conditions employed.

Similar differences in selectivity between (1) and $\mathrm{Bu^tO^{\bullet}}$ were found in intermolecular competition experiments involving ethanol and propan-2-ol at 198 K. Thus, photolysis of TTMH in the presence of a mixture of the alcohols ($[\mathrm{EtOH}]/[\mathrm{Pr^iOH}] = 1.00$) in cyclopropane afforded spectra of both α-hydroxyalkyl radicals with that from ethanol predominating ($[\mathrm{Me\dot{C}HOH}]/[\mathrm{Me_2\dot{C}OH}] = 7.1 \pm 0.5$). However, with the same alcohol mixture when DTBP replaced TTMH, the 1-hydroxy-1-methylethyl radical predominated ($[\mathrm{Me\dot{C}HOH}]/[\mathrm{Me_2\dot{C}OH}] = 0.44 \pm 0.04$).

Photolysis of TTMH in the presence of tetra-n-butylammonium borohydride in t-pentyl alcohol–dimethyl ether solvent (1 : 1.6 v/v) afforded an intense spectrum of the borane radical anion,[13] showing that hydrogen abstraction from $\mathrm{BH_4^-}$ occurs rapidly [equation (ix)].

Hydrogen abstraction, rather than addition to the double bond, takes place with propene to give the allyl radical, but addition to ethylene to give (4) was readily detectable (see Figure 1).

A variety of radicals, including $\mathrm{Bu^tO^{\bullet}}$ [equation (xi)], add readily to alkyl isocyanides to form imidoyl radicals.[14] Similarly, (1) adds to t-butyl isocyanide to give the relatively persistent ($t_{\frac{1}{2}}$ *ca.* 90 s at 250 K) imidoyl radical (6), the spectrum of which is shown in Figure 2. Since $a(^{13}\mathrm{C}_\alpha)$ for (6) is similar to that (108.0 G) for (5; R = $\mathrm{Bu^t}$), the degree of bending at C_α is probably also similar in these two σ-radicals.[14] Because $a(\mathrm{N})$ for (5) is very small, we assign the large $^{14}\mathrm{N}$ splitting shown by (6) to the three-co-ordinate nitrogen.

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* This equation differs somewhat from that given in a preliminary communication[1] because the microwave power level used in the earlier work (1 mW) was insufficiently low to avoid selective saturation of the signal from the t-butyl radical. In the present work, the power level was 0.25 mW and the spectrum of neither radical was saturated.

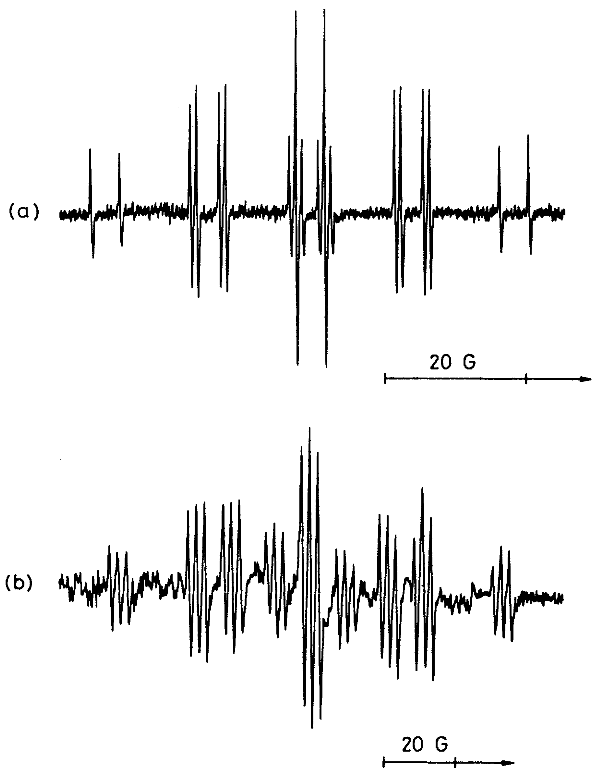

Figure 1. (a) E.s.r. spectrum of the allyl radical produced by photolysis of TTMH in propene at 150 K. (b) E.s.r. spectrum of the radical (4) produced by photolysis of TTMH in ethylene at 195 K

$$(\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{CH_2{=}CH_2} \longrightarrow (\mathrm{Me_3Si})_2\mathrm{NCH_2\dot{C}H_2} \quad \text{(x)}$$

(4)

$$\mathrm{Bu^tO}\cdot + \mathrm{RN{=}C} \longrightarrow \mathrm{RN{=}\dot{C}OBu^t} \quad \text{(xi)}$$

(5)

$$(\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{Bu^tN{=}C} \longrightarrow \mathrm{Bu^tN{=}\dot{C}N(SiMe_3)_2} \quad \text{(xii)}$$

(6)

The radical (1) also adds readily to phosphorus(III) compounds to give phosphoranyl radicals.[15] The adduct from triethylphosphine is too unstable to detect by e.s.r. spectroscopy and undergoes rapid α-scission to give the ethyl radical and $\mathrm{Et_2PN(SiMe_3)_2}$. However, the phosphoranyl adducts from trialkyl phosphites are readily observable. Trimethyl or triethyl phosphite gave (7a; R = Me or Et); the isomers (7b; R = Me or Et) were not detected directly, but lineshape effects evident in the spectra of (7a) showed that exchange with the minor isomer (7b) was occurring on the e.s.r. time scale above *ca.* 180 K.[15] The phosphoranyl radical (7; R = Et) was also generated during photolysis of diethyl peroxide in the presence of $\mathrm{(EtO)_2PN(SiMe_3)_2}$ and the spectrum was identical from the two sources.

To allow comparison of the reactivities of (1) and $\mathrm{Me_2N^{\cdot}}$, all the above experiments were repeated replacing TTMH by tetramethyltetrazene as a photochemical source[16] of the dialkylaminyl radical [equation (xiv)]. With each reactant, except oxygen and $\mathrm{Bu_4{}^nNBH_4}$,* only $\mathrm{Me_2N^{\cdot}}$ was detected by e.s.r. spectroscopy, providing clear evidence for the much greater reactivity of (1).

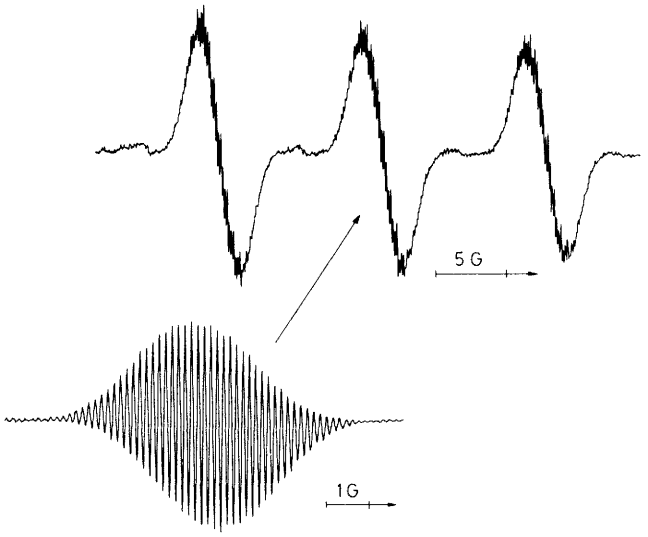

Figure 2. E.s.r. spectrum of the imidoyl radical (6) produced by photolysis of TTMH in the presence of t-butyl isocyanide in cyclopropane at 269 K. The fine structure, which was not analysed in detail, results from coupling to the two-co-ordinate nitrogen and to the protons of the t-butyl and trimethylsilyl groups (compare ref. 14)

U.v. photolysis of tetramethylhydrazine in cyclopropane or cyclopropane–ethanol[17] (5 : 1 v/v) did not give a detectable concentration of $\mathrm{Me_2N^{\cdot}}$ or of any other radical. Presumably the excited $\mathrm{Me_2NNMe_2}$ molecule can dissipate energy in ways other than by N–N fission, possibly because the relatively small bulk of the substituents at nitrogen permits rotation about the N–N bond.

(ii) *Tetrakis(trimethylsilyl)tetrazene (TTMT)*.—This compound (an air-stable solid like TTMH) was investigated as an alternative source of (1) [equation (xv)], since TTMT absorbs more strongly than TTMH in the near u.v. region.[18] U.v. photolysis of TTMT in benzene at 298 K has been reported to give $\mathrm{(Me_3Si)_2NH}$, $\mathrm{N_2}$, $\mathrm{(Me_3Si)_3N}$, and $\mathrm{Me_3SiN_3}$,[18] and the first two products probably arise from the cleavage shown in equation (xv). E.s.r. studies have confirmed the formation of (1), but the use of TTMT did not result in greater concentrations of radicals than could be obtained from TTMH.

Photolysis of TTMT in isobutane at 230 K gave rise to isobutyl and t-butyl radicals in the same relative concentration ($[\mathrm{Bu^{i\cdot}}]/[\mathrm{Bu^{t\cdot}}] = 1.5$) as was obtained when (1) was generated from TTMH. Photolysis of TTMT in ethylene afforded a spectrum of the adduct (4) (Figure 1), but when trimethyl phosphite was also present this was replaced by spectra of *two* phosphoranyl radicals, (7a; R = Me) and one showing *a*(P) 853.7, *a*(1N) 23.7 G, *g* 2.0026 at 175 K. Whilst (7a; R = Me) was short-lived and present immediately after beginning photolysis at 147 K, the second phosphoranyl radical was much longer-lived ($t_{\frac{1}{2}}$ *ca.* 3 min) and *ca.* 10 min photolysis was required before its concentration reached a steady-state value. The second spectrum was weaker at higher temperatures and we tentatively assign it to the phosphoranyl radical (8), formed by trapping of the 1,1-bis(trimethylsilyl)-triazenyl radical (9) which would be produced by one-bond

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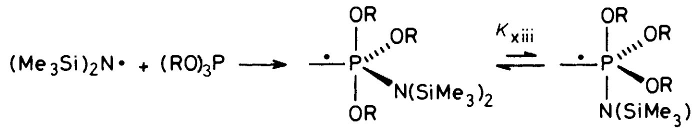
* No spectra were obtained during photolysis of tetramethyltetrazene in the presence of tetra-n-butylammonium borohydride, but these two compounds appear to react directly on mixing at 200 K.

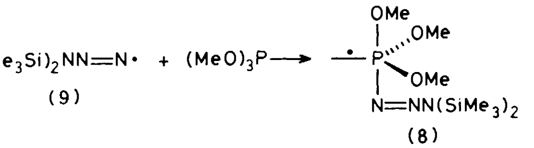


(7a) (7b) (xiii)

$$\mathrm{Me_2NN{=}NNMe_2} \xrightarrow{h\nu} 2\,\mathrm{Me_2N}\cdot + \mathrm{N_2} \qquad \text{(xiv)}$$

$$(\mathrm{Me_3Si})_2\mathrm{NN{=}NN(SiMe_3)_2} \xrightarrow{h\nu} 2(\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{N_2} \qquad \text{(xv)}$$

$$\underset{(10)}{(\mathrm{Me_3Si})_2\mathrm{NOSiMe_3}} \xrightarrow{h\nu} (\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{Me_3SiO}\cdot \qquad \text{(xviii)}$$



(9) (8) (xvi)

$$(\mathrm{Me_3Si})_2\mathrm{NN{=}N}\cdot \longrightarrow (\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{N_2} \qquad \text{(xvii)}$$

cleavage of the photo-excited TTMT. Although (9) is probably very short-lived with respect to loss of nitrogen [equation (xvii)], reaction (xvi) is probably also extremely rapid.[19] No e.s.r. evidence was found for rearrangement of (9) by the 1,3-shift of an $\mathrm{Me_3Si}$ group, which would give the known 1,3-bis(trimethylsilyl)triazenyl radical $\mathrm{Me_3Si\overline{N\dot{N}N}SiMe_3}$.[17] The 1,3-shift of an $\mathrm{R_3Si}$ group in the triazenes $\mathrm{R_3SiN(Me)N{=}NMe}$ gives rise to lineshape effects in their n.m.r. spectra.[20]

(iii) *Tris(trimethylsilyl)hydroxylamine* (10).—Photolysis of fully silylated hydroxylamine proved to be a less useful source of (1) than TTMH, since the trimethylsiloxyl radical[21] is formed simultaneously [equation (xviii)]. For example, at 190 K in the presence of triethyl phosphite in cyclopropane, e.s.r. spectra of both (7; R = Et) and $\mathrm{Me_3SiO\dot{P}(OEt)_3}$ [a(P) 881.3 G, g 2.0019] * were observed.

After a few minutes' photolysis of (10) alone in cyclopropane at 200 K, the cyclopropyl radical was detected but, initially, the spectrum of the trimethylsilyl(trimethylsiloxy)aminyl radical [along with that of (3), see below] was observed. This radical is presumably formed from a trace of *NO*-bis(trimethylsilyl)hydroxylamine, present as an impurity in the sample of (10).

(iv) *Tetrakis(triethylsilyl)hydrazine* (*TTEH*).—This compound behaved in a similar way to TTMH and its u.v. photolysis afforded the bis(triethylsilyl)aminyl radical (11). Photolysis in propene at 130 K and above gave rise to the spectrum of the allyl radical, showing that reaction (xx) proceeds readily at very low temperatures. Above *ca.* 150 K the spectrum of the very long-lived tris(triethylsilyl)hydrazyl radical [a(1N) 10.6, a(1N) 4.3 G, g 2.0052 at 208 K] was observed. The origin of the hydrazyl is not clear, because it is so persistent that a very small rate of production would result in the observed steady-state concentration. Indeed, we cannot eliminate the possibility that it arises from a minute amount of tris(triethylsilyl)hydrazine trapped in the crystalline TTEH, but there were strong indications that the hydrazyl could be formed as a result of reaction of (11) with TTEH itself. Thus, the spectrum of the hydrazyl was very much stronger in the absence of compounds which react rapidly with (11), for example when TTEH was photolysed alone in cyclopropane.

Photolysis of TTEH (*ca.* 0.2M) in cyclopropane containing triethyl phosphite (0.3—1.2M) at 178 K gave rise to spectra (see Figure 3) which we assign to isomers (a and b) of the phosphoranyl radical (12) in which the nitrogen ligand is either equatorial or apical [for (12a), a(P) 850.5, a(N) *ca.* 3 G, g 2.0021, and for (12b), a(P) 835.7, a(N) 27.0 G, g 2.0025]. The phosphoranyl radicals (12a and b) decayed with a half-life of *ca.* 3 s at 150 K and must be present in their equilibrium concentrations[15] ($K_{\mathrm{xxi}} = 1.6 \pm 0.2$ at 178 K). The same equilibrium mixture was obtained during photolysis of diethyl peroxide (as a source of EtO•) in the presence of $\mathrm{(EtO)_2PN(SiEt_3)_2}$. The larger value of K_{xxi} compared with K_{xiii} (see above) is presumably a consequence of the greater bulk of the $\mathrm{(Et_3Si)_2N}$ ligand.† At very low temperatures a third phosphorus-centred radical was also detected (see Figure 3) and, assuming that phosphorus and nitrogen splittings are present a(P) = 885.6, a(N) = *ca.* 26.5 G, and g = 2.0027 at 178 K. Its concentration relative to those of (12a and b) was independent of the source of radicals and, when generated from TTEH, was also independent of the phosphite concentration. It therefore seems likely to be an isomer of (12) and the relatively large nitrogen splitting would be consistent with the σ*(P–N) phosphoranyl radical[19] $\mathrm{(EtO)_3P\dot{-}N(SiEt_3)_2}$.

The bis(triethylsilyl)aminyl radical, like (1), added to t-butyl isocyanide to give an imidoyl radical [a(1N) 11.6 G, g 2.0016 at 228 K in cyclopropane]. It also reacted with oxygen to yield bis(triethylsilyl) nitroxide [a(1N) 6.5, a(^{29}Si) 5.3 G, g 2.0095 at 199 K in cyclopentane].

(v) NO-*Bis(trimethylsilyl)hydroxylamine* (13).—West and Boudjouk[10] have reported that photolysis of DTBP and (13) in toluene gives rise to the e.s.r. spectrum of bis(trimethylsilyl) nitroxide (3) and they proposed that the trimethylsilyl(trimethylsiloxy)aminyl radical (14), although undetected in their experiments down to 193 K, was formed initially and subsequently rearranged [equation (xxii)]. We have found that, using cyclopropane solvent and high photolysing light intensities, the radical (14) may be readily detected up to *ca.* 240 K. Figure 4 shows the spectrum obtained at 204 K using the full light intensity obtainable with our equipment. The value of [(14)]/[(3)] decreased with increasing temperature and, at a fixed temperature, with decreasing incident light intensity,

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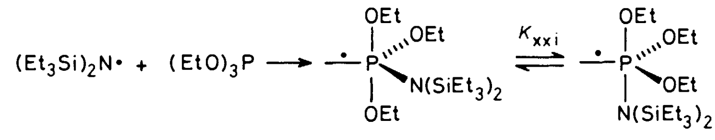
* This phosphoranyl radical was also detected during photolysis of $\mathrm{Me_3SiOOSiMe_3}$ in the presence of $\mathrm{(EtO)_3P}$ or of EtOOEt in the presence of $\mathrm{(EtO)_2POSiMe_3}$; $\mathrm{d}a(\mathrm{P})/\mathrm{d}T = +116$ mG K^{-1}.

† No evidence was found for exchange of (12a) with (12b) on the e.s.r. time scale up to 210 K. At this temperature and above the ethyl radical, formed along with $\mathrm{(EtO)_2P(O)N(SiEt_3)_2}$, by β-scission of (12), was also detected. The radical (7; R = Et) undergoes similar β-scission.[15]

$$(Et_3Si)_2NN(SiEt_3)_2 \longrightarrow \underset{(11)}{2(Et_3Si)_2N^\bullet} \qquad (xix)$$

$$(Et_3Si)_2N^\bullet + CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH\dot{C}H_2 + (Et_3Si)_2NH \qquad (xx)$$



(12a) (12b) (xxi)

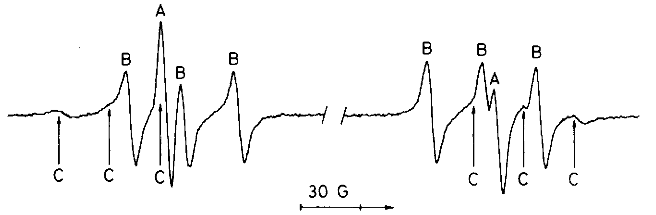


Figure 3. E.s.r. spectra of the phosphoranyl radicals (12a) (lines marked A) and (12b) (lines marked B) produced by photolysis of TTEH in the presence of triethyl phosphite in cyclopropane at 179 K. For discussion of the lines marked C see text

$$\underset{(13)}{Me_3SiN(H)OSiMe_3} \xrightarrow[-Bu^tOH]{Bu^tO^\bullet} \underset{(14)}{Me_3Si\dot{N}OSiMe_3} \longrightarrow \underset{(3)}{(Me_3Si)_2NO^\bullet} \qquad (xxii)$$

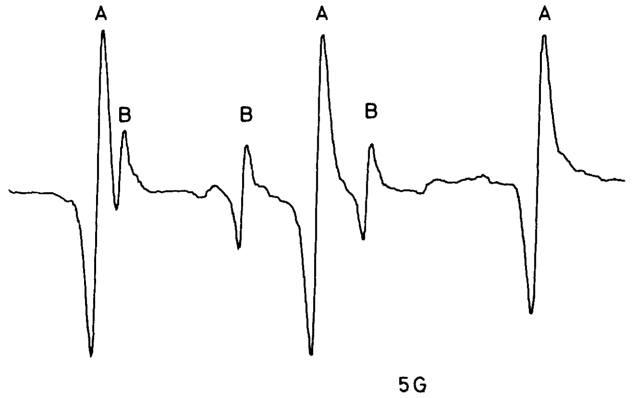


Figure 4. E.s.r. spectra of $Me_3Si\dot{N}OSiMe_3$ (14) (lines marked A) and $(Me_3Si)_2NO^\bullet$ (3) (lines marked B) produced by photolysis of $Me_3SiN(H)OSiMe_3$ (13) in cyclopropane at 204 K

as expected if (14) and (3) are not in equilibrium under the experimental conditions.* The e.s.r. parameters of (14) and of other siloxyaminyl radicals are gathered in Table 2.

The radicals (14) and (3) were also detected when (13) was photolysed alone in cyclopropane and evidently N–O cleavage [equation xxiii)] takes place to give $Me_3SiO^\bullet$ and $Me_3Si\dot{N}H$ which then abstract hydrogen from (13). This was confirmed by conducting the photolysis in the presence of triethyl phosphite when the phosphoranyl radicals $Me_3SiN(H)\dot{P}(OEt)_3$ [a(P) 853.8, a(1N) *ca.* 2 G, g 2.0021 at 188 K] and $Me_3SiO\dot{P}(OEt)_3$ (see above) were detected.

(vi) NO-*Bis*(*triethylsilyl*)*hydroxylamine* (15).—This compound behaved similarly to the methyl analogue (13). Photolysis of a cyclopropane solution containing (15) (*ca.* 0.8M) and DTBP (*ca.* 15% v/v) at 162 K afforded $Et_3Si\dot{N}OSiEt_3$ (see Table 2), the rearrangement of which to $(Et_3Si)_2NO^\bullet$ [a(N) 6.5, $a(^{29}Si)$ 5.8 G, g 2.0095 at 195 K] could be monitored in the temperature range 175—195 K.

(vii) N-*Methyl*-NO-*bis*(*trimethylsilyl*)*hydroxylamine* (16).—This compound was investigated as a potential photochemical source of the methyl(trimethylsilyl)aminyl radical (17). However, when (16) was photolysed alone in cyclopropane the only spectrum observed was one which we assign to the methyl(trimethylsiloxy)aminyl radical (18) (see Table 2). The same spectrum was observed when $MeN(H)OSiMe_3$ (19) was photolysed alone or (stronger) along with DTBP. Although great care was taken to ensure that (16) was not hydrolysed during purification or sample preparation, we cannot exclude the possibility that (16) was contaminated with a trace of (19) which would be sufficient to give rise to (18). Once photolysis of (16) has commenced, Me_3SiOH will be formed from $Me_3SiO^\bullet$ and the silanol could then react with (16) to give more (19).

Despite these difficulties, photochemical formation of (17) was shown to occur by conducting the photolysis of (16) in the presence of trialkyl phosphites as traps for the reactive radicals. Thus, with triethyl phosphite in cyclopropane photolysis of (16) afforded the phosphoranyl radicals $Me_3SiO\dot{P}(OEt)_3$ and (20; R = Et) [a(P) 848.8, a(1N) *ca.* 3 G, g 2.0021 at 178 K]. The same aminophosphoranyl radical was generated by addition of $EtO^\bullet$ (from EtOOEt) to $(EtO)_2PN(Me)SiMe_3$. Addition of (17) to trimethyl phosphite yielded the less massive (20; R = Me) for which the nitrogen splitting was better resolved [a(P) 846.1, a(1N) 2.4 G, g 2.0021 at 188 K]. Dimethylaminyl radicals do not add to trialkyl phosphites under similar conditions and, in fact, $R_2N^\bullet$ is readily displaced from $(RO)_2PNR_2$ by $RO^\bullet$ in a reaction involving the unstable intermediate phosphoranyl radical $(RO)_3\dot{P}NR_2$.[22]

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* At 218 K when photolysis was interrupted the approximate half-lives for decay of (3) and (14) were 7 and <0.25 s, respectively.

Table 2. E.s.r. parameters of trialkylsiloxyaminyl radicals and related species in cyclopropane

Radical	T/K	g Factor	Hyperfine splittings/G a(N)	 Others [a]	Ref.
$\mathrm{Me_3Si\dot{N}OSiMe_3}$	186	2.0068	11.6	11.6 (^{29}SiN), 3.1 (^{29}SiO or ^{13}CSiN) [b]	This work
$\mathrm{Et_3Si\dot{N}OSiEt_3}$	164	2.0071	11.6	11.3 (^{29}SiN)	This work
$\mathrm{Me\dot{N}OSiMe_3}$	175	2.0052	14.9	23.3 (3H)	This work
$\mathrm{Me\dot{N}OBu^t}$	183	2.0048	14.5	21.5 (3H)	*c*
$\mathrm{Bu^t\dot{N}OSiMe_3}$ [d]	221	2.0051	14.6	9.7 (^{13}CN), 7.4 (^{13}CCN)	This work
$\mathrm{Bu^t\dot{N}OBu^t}$ [e]	297	2.0049	14.1	9.1 (^{13}CN), 7.0 (^{13}CCN)	*f*
$\mathrm{Bu^t\dot{N}OP(O)(OEt)_2}$ [e]	303	2.0047	14.9	9.9 (^{13}CN), 8.0 (^{13}CCN)	*g*
$\mathrm{Me_2N^{\cdot}}$	183	2.0044	14.8	27.4 (6H)	*h*

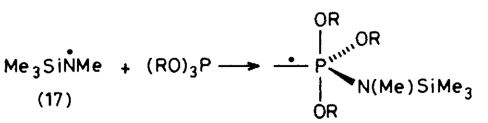
[a] Number of equivalent nuclei shown in parentheses. [b] Assignment uncertain. [c] Ref. 56. [d] Generated by photolysis of $\mathrm{Bu^tN(H)OSiMe_3}$ either alone or along with DTBP, see ref. 2. This siloxyaminyl radical was relatively persistent ($t_{\frac{1}{2}}$ *ca*. 3 min at 220 K) and was the only radical detected in experiments between 150 K (in cyclopropane) and 338 K (in n-hexane). [e] Benzene solvent. [f] Ref. 54. [g] Ref. 55. [h] Ref. 16.

$$\underset{(15)}{\mathrm{Me_3SiN(H)OSiMe_3}} \xrightarrow{h\nu} \mathrm{Me_3Si\dot{N}H} + \mathrm{Me_3SiO\cdot} \qquad \text{(xxiii)}$$

$$\underset{(21)}{\mathrm{Me_3SiN(Me)N{=}NMe}} \xrightarrow{h\nu} \underset{(17)}{\mathrm{Me_3Si\dot{N}Me}} + \mathrm{Me\cdot} + \mathrm{N_2} \qquad \text{(xxvii)}$$

$$\underset{(16)}{\mathrm{Me_3SiN(Me)OSiMe_3}} \xrightarrow{h\nu} \underset{(17)}{\mathrm{Me_3Si\dot{N}Me}} + \mathrm{Me_3SiO\cdot} \qquad \text{(xxiv)}$$

$$\mathrm{Bu^tO\cdot} + \underset{(19)}{\mathrm{MeN(H)OSiMe_3}} \longrightarrow \underset{(18)}{\mathrm{Me\dot{N}OSiMe_3}} + \mathrm{Bu^tOH} \qquad \text{(xxv)}$$



(17) (20) (xxvi)

$$\mathrm{Me_3Si\dot{N}Me} + \mathrm{(RO)_3P} \longrightarrow \dot{\mathrm{P}}\mathrm{(OR)_3N(Me)SiMe_3}$$

(viii) 1-*Trimethylsilyl*-1,3-*dimethyltriazene* (21).—This compound was studied in the hope that its photolysis might provide a useful source of (17), without simultaneous formation of a reactive oxyl radical [equation (xxvii)]. However, photolysis of (21) alone in cyclopropane afforded only weak spectra of the methyl and 1,3-dimethyltriazenyl [23] radicals, the latter perhaps formed by photochemical cleavage of the N–Si bond, and (17) was not detected. The silylaminyl radical was, however, also being formed during the photolysis, since it could be trapped by trimethyl phosphite at 200 K to give (20; R = Me).*

(ix) 1-*Trimethoxysilyl*-1,3-*dimethyltriazene* (22).—Photolysis of (22) alone in cyclopropane also afforded spectra of $\mathrm{Me\overset{\cdot}{\overline{NNN}}Me}$ and $\mathrm{Me^{\cdot}}$, and no spectrum assignable to $\mathrm{(MeO)_3Si\dot{N}Me}$ was detected. However, in the presence of trimethyl phosphite this aminyl radical could be trapped to give the phosphoranyl radical (23) [a(P) 845.4, a(1N) 2.8 G, g 2.0019 at 198 K].*

Discussion

A variety of methods are available for the generation of aminyl radicals.[25] For e.s.r. studies of dialkylaminyl radicals, u.v. photolysis of tetra-alkyltetrazenes [16] and the reactions of alkoxyl radicals with dialkylaminophosphines [22] or with certain dialkylamines [26] provide the best methods for generation. It has been reported that t-butoxyl radicals attack the methyl groups of hexamethyldisilazane to give the radical (24).[27]

The bis(trialkylsilyl)- and trialkylsilyl(methyl)-aminyl radicals investigated in this work are significantly more reactive than dialkylaminyl radicals. There appear to be two reasons for this. Firstly, the N–X bonds in $\mathrm{(R_3Si)_2NX}$ and $\mathrm{R_3Si(R)NX}$ are stronger than that in $\mathrm{R_2NX}$. For example, *D*(N–H) in $\mathrm{(Me_3Si)_2NH}$ is probably $\geqslant 421$ kJ mol^{-1}, compared to 397 kJ mol^{-1} in $\mathrm{Me_2NH}$.[7] The parent aminyl radical $\mathrm{H_2N^{\cdot}}$ is also much more reactive in hydrogen abstraction than is $\mathrm{Me_2N^{\cdot}}$, presumably in part because the N–H bond in $\mathrm{H_3N}$ is also stronger (439 kJ mol^{-1}) than that in $\mathrm{Me_2NH}$,[28] although $\mathrm{H_2N^{\cdot}}$ is probably less reactive than (1). Secondly, $\mathrm{(R_3Si)_2N^{\cdot}}$ and $\mathrm{R_3Si(R)N^{\cdot}}$ are probably more electrophilic than $\mathrm{R_2N^{\cdot}}$. Whilst addition of (1) to ethylene occurs readily at low temperatures, addition of $\mathrm{Me_2N^{\cdot}}$ is undetected under our conditions, although this reaction is probably exothermic. The slow addition of $\mathrm{H_2N^{\cdot}}$ and $\mathrm{R_2N^{\cdot}}$ to unconjugated alkenes has been attributed to the destabilising effect on the transition state of repulsion between electrons in the filled π-orbital of the alkene and the non-bonding electron pair of the aminyl radical.[29] Addition of $\mathrm{Me_2N^{\cdot}}$ to ring-substituted α-methylstyrenes at 298 K shows a Hammett ρ-value of $+0.69$, indicating that the aminyl radical behaves as a *nucleophile* in this reaction.[30] However, the zinc chloride-complexed dimethylaminyl radical is *electrophilic* (ρ -0.98) in the addition reaction,[30] as is the uncomplexed radical in hydrogen abstraction reactions.[31] Complexation with zinc chloride or protonation of a dialkylaminyl radical would both be expected to increase electrophilicity. Like $\mathrm{(R_3Si)_2N^{\cdot}}$, $\mathrm{R_2\dot{N}H^+}$ is much more reactive than $\mathrm{R_2N^{\cdot}}$ in hydrogen abstraction.[32] Replacement of R in $\mathrm{R_2N^{\cdot}}$ by $\mathrm{R_3Si}$ appears to provide an intramolecular analogue of protonation of $\mathrm{R_2N^{\cdot}}$ or its complexation with Lewis acids.

The rate constants at 300 K for hydrogen abstraction by $\mathrm{H_2N^{\cdot}}$ from alkane C–H groups increase in the order $\mathrm{RCH_2{-}H} < \mathrm{R_2CH{-}H} < \mathrm{R_3C{-}H}$ and the corresponding activation energies decrease along this series.[28] At this temperature the yield of $\mathrm{Bu^{t\cdot}}$ from the reaction of $\mathrm{H_2N^{\cdot}}$ with isobutane is about ten times that of $\mathrm{Bu^{i\cdot}}$.[33] This regioselectivity

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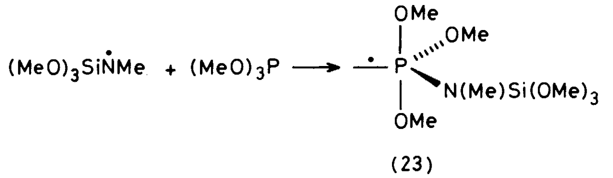
* The phosphoranyl radical $\mathrm{Me\dot{P}(OMe)_3}$ [a(P) 783.7, a(3H) 1.0 G, g 2.0019 at 203 K] was also detected in these experiments.[24]

$$(MeO)_3SiN(Me)N{=}NMe \xrightarrow{h\nu} (MeO)_3Si\dot{N}Me + Me\cdot + N_2 \qquad (xxviii)$$

(22)

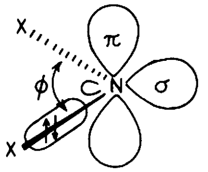


$$(MeO)_3Si\dot{N}Me + (MeO)_3P \longrightarrow \cdot P(OMe)_3N(Me)Si(OMe)_3 \qquad (xxix)$$

(23)

$$Bu^tO\cdot + (Me_3Si)_2NH \longrightarrow \cdot CH_2Si(Me_2)N(H)SiMe_3 + Bu^tOH \qquad (xxx)$$

(24)



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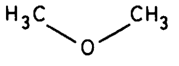

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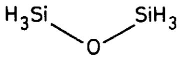

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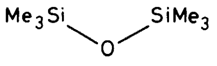

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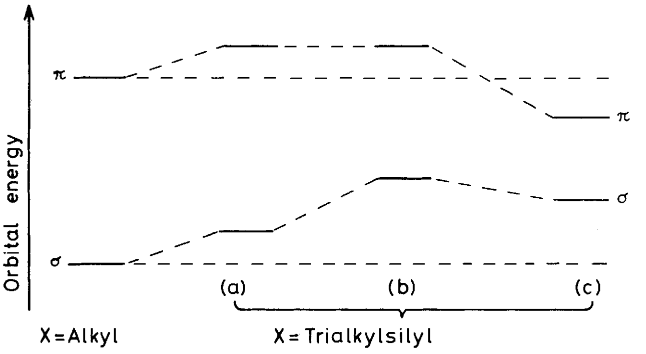

Figure 5. Qualitative changes in orbital energies brought about by replacement of alkyl by trialkylsilyl ligands in the aminyl radical (25). For explanation of (a)—(c), see text

is reversed in the reaction of (1) with isobutane and the activation energy for abstraction from the tertiary C–H group is now slightly *greater* than that for reaction at the primary C–H group. We attribute these differences in selectivities of (1) and $H_2N^\cdot$ to the large bulk of the former, which acts to decrease the rate of attack at more hindered C–H groups. Aminium radical cations in which the nitrogen is sterically congested [*e.g.* $Pr^i_2\dot{N}H^+$ or $Me_2C(CH_2)_3CMe_2\dot{N}H^+$] can show even greater selectivity in attacking primary rather than tertiary C–H groups.[34] The different regioselectivities of (1) and $Bu^tO^\cdot$ in their reactions with isobutane and with mixtures of ethanol and propan-2-ol may also be explained in terms of the relatively large steric demands of (1).

In general, however, the reactivity of (1) resembles that of $Bu^tO^\cdot$ [$D(Bu^tO–H)$ [35] 440 kJ mol^{-1}]. A similar preference for hydrogen abstraction from propene over addition to the C=C bond is shown by (1) and by the t-butoxyl radical.

The differences in properties of alkyl- and silyl-aminyl radicals may be understood in a qualitative way in terms of the σ-donor–π-acceptor substituent effects of the R_3Si group.[36,37] There are three electrons to be distributed between the σ and π orbitals of the bent aminyl radical (25). In dialkylaminyl radicals ($X = R_3C$) the unpaired electron occupies the higher-energy π (essentially N-2*p*) orbital and the *sp*-hybrid σ orbital is doubly occupied.[25] However, replacement of one or both alkyl substituents by σ-donor–π-acceptor R_3Si groups would be expected to reduce the energy difference between the σ and π orbitals, even if the angle φ remains unaltered. The orbital energy changes are illustrated qualitatively in Figure 5.

Replacement of an alkyl group by a σ donor ligand will, neglecting orbital overlap, raise the energies of the σ and π orbitals by equal amounts, as shown in (a). Inclusion of orbital overlap in the NX_2 plane will, as shown in (b), leave the energy of the π orbital unchanged but will further increase the energy of the σ orbital, because the Si–N σ bonding orbital is doubly occupied. Interaction with empty π-type (Si-3*d* and/or σ*Si–C group [38]) orbitals of the R_3Si ligand will stabilise both π and σ orbitals (the latter by pseudo-π overlap), but better overlap and energy matching with the former will result in a greater stabilisation of this orbital, as shown in (c). Hence, replacement of R_3C by R_3Si should stabilise the π orbital relative to the σ and could, in principle, even result in a π orbital lower in energy than the σ and, consequently, in a σ SOMO for the silylaminyl radical.

The above discussion assumes that the bond angle at nitrogen is not affected by the replacement of R_3C by R_3Si. However, analogy with diamagnetic molecules suggests that φ would in fact increase.[37] Thus, the bond angles in (26),[39] (27),[40] and (28) [40] are 112, 142, and 148°, respectively, and the barriers to inversion of (27) and (28) through linear transition states are extremely small.[41] Indeed, the SiOSi grouping in crystalline $(PhCH_2)_3SiOSi(CH_2Ph)_3$ is linear.[42,] * As φ in (25) increases, the energies of the σ and π orbitals will move together and in the limit of $\varphi = 180°$ they would be degenerate (assuming three-fold rotational symmetry about the SiNSi axis). However, silylaminyl radicals are unlikely to be linear at nitrogen in the ground vibrational state since such a structure, with its off-axis arrangement of *Si*-alkyl groups, would be subject to a Jahn–Teller distortion which removes the

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* E.s.r. studies of $(R_3Si)_2O^{+\cdot}$ and $R_3Si(R)O^{+\cdot}$ in rigid matrices (*cf.* ref. 43) could be very informative.

orbital degeneracy and, on energetic grounds, bending at nitrogen appears to be a likely distortion to occur. However, the radicals could be quasi-linear[44] with a very low barrier to inversion through a linear transition state.

The total effect of replacing R_3C by R_3Si will thus be to bring the σ and π orbitals closer together in energy and inversion of $(R_3Si)_2N^{\bullet}$ through a linear transition state probably occurs much more readily than for $(R_3C)_2N^{\bullet}$.

The N–H bonds in $(R_3Si)_2NH$ and $R_3Si(R_3C)NH$ appear to be significantly stronger than that in $(R_3C)_2NH$; replacement of R_3C by R_3Si must increase the energy difference between the parent amine and the aminyl radical. Bis(silylated) amines are planar at nitrogen whilst dialkylamines are pyramidal.[36,37] The ionisation energy of $(H_3Si)_3N$ (9.7 eV)[45] is greater than that of Me_3N (8.5 eV), which corresponds to removal of a lone pair electron from nitrogen. Similarly, the ionisation energy of $(Me_3Si)_2NH$ (8.79 eV) is greater than that of $Me_3Si(Me_3C)NH$ (8.41 eV).[46] These effects of replacing R_3C by R_3Si as substituent at nitrogen in an amine have been interpreted in terms of delocalisation of the lone pair onto the π acceptor silyl ligand.[36] Planarity at nitrogen has also been attributed to the polar nature of the $Si^{\delta+}{-}N^{\delta-}$ σ bond.[37]

The strength (ΔH_{xxxi}) of the N–H bond in X_2NH may be expressed by equation (xxxv) in terms of the enthalpy changes involved in reactions (xxxii)—(xxxiv). Hence, the N–H bond in $(R_3Si)_2NH$ will be stronger than that in $(R_3C)_2NH$, provided

$$X_2NH \longrightarrow X_2N\bullet + H\bullet \qquad \text{(xxxi)}$$

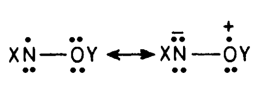
$$X_2N\bullet + H^+ \longrightarrow X_2\overset{\bullet}{N}H^+ \qquad \text{(xxxii)}$$

$$X_2NH \longrightarrow X_2\overset{\bullet}{N}H^+ + e^- \qquad \text{(xxxiii)}$$

$$H\bullet \longrightarrow H^+ + e^- \qquad \text{(xxxiv)}$$

$$\Delta H_{xxxi} = \Delta H_{xxxiii} - \Delta H_{xxxii} - \Delta H_{xxxiv} \qquad \text{(xxxv)}$$

that $(R_3Si)_2N^{\bullet}$ is not sufficiently *less* basic than $(R_3C)_2N^{\bullet}$ so as to compensate for the differences in ionisation energies. If $(R_3Si)_2N^{\bullet}$ is a π-radical,* the energy of the σ lone pair should be higher than for $(R_3C)_2N^{\bullet}$ (see Figure 5) and this could result in a *greater* basicity for $(R_3Si)_2N^{\bullet}$ compared with $(R_3C)_2N^{\bullet}$.† The angle at nitrogen (φ) is likely to decrease significantly upon protonation of $(R_3Si)_2N^{\bullet}$, but the energy required to change φ is probably relatively small (see above). Although this argument based on equation (xxxv) is necessarily circular, the relatively high strength of the N–H bond in $(R_3Si)_2NH$ may be readily understood in terms of the (known) high ionisation energy of the silylamine and the (predicted) high basicity of $(R_3Si)_2N^{\bullet}$.‡



(29a) (29b)

$$X\dot{\underset{\cdot\cdot}{N}}{-}\underset{\cdot\cdot}{\ddot{O}}Y \longleftrightarrow X\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}{-}\overset{+}{\underset{\cdot\cdot}{\dot{O}}}Y$$

Silylaminyl radicals would be expected to be more electrophilic than the alkyl analogues because, as shown in Figure 5, the SOMO energy of the former is probably lower than that of the latter.[49] Electron addition to $(R_3Si)_2N^{\bullet}$ will occur more readily than to $(R_3C)_2N^{\bullet}$. A similar decrease in SOMO energy and increase in electrophilicity occurs upon complexation with $ZnCl_2$ or protonation of a dialkylaminyl radical. Because of the greater electronegativity of oxygen compared with that of nitrogen, $RO^{\bullet}$ is also more electrophilic than $R_2N^{\bullet}$. The similar magnitudes of $a(^{13}C_\alpha)$ for $Bu^tN{=}\dot{C}N(SiMe_3)_2$ and $Bu^tN{=}\dot{C}OBu^t$ also suggest[14] that the electronegativities of the $(Me_3Si)_2N$ and Bu^tO groups are similar.

So far we have been unable to detect e.s.r. spectra for radicals of the type $(R_3Si)_2N^{\bullet}$ in fluid solution.§ One reason for this failure is probably their very high reactivity, but even if a reasonably large steady-state concentration (*ca.* 10^{-7}—10^{-8}M) could be achieved detection might still prove difficult on account of a substantial spectral linewidth. This would be expected for quasi-linear radicals which have unquenched orbital magnetism[50] and for bent radicals in which the energy separation between σ and π orbitals is small and, consequently, *g*-factor anisotropy is large. In sharp contrast, di-t-alkylaminyl radicals are relatively persistent[51] and $(Me_3C)_2N^{\bullet}$, the carbon analogue of (1), shows a well resolved e.s.r. spectrum typical of a dialkylaminyl radical [*a*(N) 14.2 G, *g* 2.0045].[52]

Although e.s.r. spectra of $Me_3Si\dot{N}Me$ and $(MeO)_3Si\dot{N}Me$ were also not detected in this work, spectra of other silyl(alkyl)aminyl radicals generated by different routes have been observed in fluid solution.[2,53] The present results show that $R_3Si\dot{N}Me$ is more reactive than $Me_2N^{\bullet}$ in addition to trialkyl phosphites, probably because the silylaminyl radical is the more electrophilic and forms the stronger bond to phosphorus.

The e.s.r. parameters of the siloxyaminyl radicals may be compared with those of $Bu^t\dot{N}OBu^t$[54] and $Bu^t\dot{N}OP(O)(OEt)_2$[55] (see Table 2). The values of *a*(N) and the *g*-factors for $Bu^t\dot{N}OY$ [Y = Bu^t, R_3Si, $(EtO)_2P(O)$] are rather similar, indicating that the extent of delocalisation onto oxygen [see (29a and b; X = Bu^t)] is also similar. The magnitude of $a(H_\beta)$ for $Me\dot{N}OSiMe_3$ is 4.1 G less than that for $Me_2N^{\bullet}$, but 1.8 G greater than for $Me\dot{N}OBu^t$,[56] implying that delocalisation of the unpaired electron onto Me_3SiO by conjugation is less effective than that onto Me_3CO, but more effective than delocalisation onto Me by hyperconjugation. However, when X is a π-acceptor R_3Si group, the structure (29b)

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* Even if $(R_3Si)_2N^{\bullet}$ is a σ radical, the π configuration will probably be close in energy.

† $(Me_3Si)_2O$ is a weaker Lewis base than $(Me_3C)_2O$;[41] however, the energy of the HOMO of the latter is probably higher than that of the former and protonated dialkyl ethers are pyramidal at oxygen.

‡ The N–H bond in $Me_2\overset{+}{N}H_2$ is also stronger than that in Me_2NH (413 and 397 kJ mol^{-1}, respectively).[47] This conclusion may also be reached by consideration of reactions (A)—(C) from which it

$$R_2\overset{\bullet}{N}H^+ + R_2NH \longrightarrow R_2\overset{+}{N}H_2 + R_2N\bullet \qquad \text{(A)}$$

$$R_2NH + H^+ \longrightarrow R_2\overset{+}{N}H_2 \qquad \text{(B)}$$

$$R_2N\bullet + H^+ \longrightarrow R_2\overset{\bullet}{N}H^+ \qquad \text{(C)}$$

follows that $\Delta H_A = \Delta H_B - \Delta H_C$. A dialkylaminyl radical is less basic than the parent amine R_2NH, because of the lower energy of the lone pair in the former. Using the pK_a values[48] of $Me_2\overset{+}{N}H_2$ and $Me_2\overset{\bullet}{N}H^+$ determined in aqueous solution at 298 K and assuming $\Delta S_B = \Delta S_C$, ΔH_A may be calculated to be *ca.* −21 kJ mol^{-1}.

§ In the liquid phase, the precursor of $(R_3Si)_2N^{\bullet}$ will always provide a source of abstractable hydrogen. The best chance of detecting (1) would be if this radical could be isolated in a rigid inert matrix at low temperatures to reduce SiNSi bending motion and to retard possible rearrangement to (24), by intramolecular 1,3-hydrogen shift from C to N.

becomes relatively more important and this is reflected by a reduction in nitrogen splitting and by an increase in the *g*-factor, the latter because of the larger spin–orbit coupling constant of oxygen compared with that of nitrogen.

The rearrangement of $R_3Si\dot{N}OSiR_3$ to $(R_3Si)_2NO^{\bullet}$ has been reported by West and Boudjouk.[10] It is not surprising that $Bu^t\dot{N}OBu^t$ does not rearrange to $Bu^t_2NO^{\bullet}$,[54] but we had hoped to observe the rearrangement of $R\dot{N}OSiR_3$ to $R_3Si(R)NO^{\bullet}$. Although it now appears that trialkylsilyl(alkyl) nitroxides may be too unstable to detect readily,[57] their decay products might still be observable. Our results indicate that the *N*-silyl group facilitites the 1,2-shift of R_3Si from O to N in $R_3Si\dot{N}OSiR_3$. It is noteworthy that both $R_3Si\dot{N}OSiR_3$ and $R\dot{N}OSiR_3$ rearrange by 1,2-shift of R_3Si from O to N.[58]

Experimental

The techniques used for the photochemical generation and detection by e.s.r. spectroscopy of transient free radicals in solution have been described previously.[4,14] Large coupling constants (from ^{31}P or ^{13}C) and the associated *g*-factors were calculated using the Breit–Rabi equation.[59]

Materials.—Isobutane (Matheson Instrument Grade) was used as received. All compounds containing Si–N or Si–O bonds were prepared under an atmosphere of dry nitrogen.

NO-Bis(trimethylsilyl)hydroxylamine (13),[60] *NO*-bis(triethylsilyl)hydroxylamine (15),[61] tris(trimethylsilyl)hydroxylamine (10),[62] *N*-methyl-*O*-trimethylsilylhydroxylamine (19),[63] *N*-methyl-*NO*-bis(trimethylsilyl)hydroxylamine (16),[63] tetrakis(trimethylsilyl)tetrazene (TTMT),[18] 1,3-dimethyl-1-trimethylsilyltriazene (21),[64,65] and 1,3-dimethyl-1-trimethoxysilyltriazene (22)[65] were prepared by published methods. Di-isovaleryl peroxide,[66] tetramethyltetrazene,[67] tetramethylhydrazine,[68] and tetra-n-butylammonium borohydride[69] were also prepared using established procedures.

Tetrakis(trimethylsilyl)hydrazine (TTMH) was prepared from tris(trimethylsilyl)hydrazine[70] using a modification of the published method.[5] n-Butyl-lithium in hexane (112 ml, 0.18 mol) was added dropwise with stirring to tris(trimethylsilyl)hydrazine (44.6 g, 0.18 mol) and *NNN'N'*-tetramethylethylenediamine (TMEDA) (20.8 g, 0.18 mol) in toluene (200 ml). An exothermic reaction took place, the temperature of the mixture rose to 40 °C and a solid was precipitated. The mixture was heated in an oil-bath at 100 °C for 1 h during which time some of the hexane distilled off and the precipitate dissolved, although this reappeared on cooling to *ca.* 30 °C. Chlorotrimethylsilane (25.0 g, 0.23 mol) was then added dropwise with stirring during 5 min and the precipitate dissolved towards the end of the addition to give a clear solution. After 1 h at *ca.* 30 °C, a precipitate (LiCl) had formed and the mixture was then heated for a further 4 h at 100—110 °C. The mixture was allowed to cool, filtered, and the volatiles were removed first at 40 °C using a rotary evaporator (*ca.* 15 Torr) and then at 25 °C for 0.5 h under high vacuum (0.1 Torr). The semi-crystalline residue was dissolved in pentane (200 ml), the solution was filtered to remove some LiCl, and then passed down a column (30 × 2 cm) of basic alumina. Further pentane (100 ml) was passed through the column and the solvent was evaporated from the combined eluate to yield the crystalline TTMH which was further purified by recrystallisation from acetone [yield 36.4 g, 63%; m.p. (sealed capillary), 290—292 °C (lit.,[70] 286 °C)]. The ^1H n.m.r. spectrum (in C_6D_6) showed a singlet, δ 0.20, downfield from Me_4Si.

Tetrakis(*triethylsilyl*)*hydrazine* (TTEH) has been reported previously[70] as an involatile liquid, b.p. 103 °C at 0.001 Torr, prepared by thermal decomposition of $Et_3SiN{=}NSiEt_3$. We prepared it as a crystalline solid by a procedure similar to that used for TTMH. To bis(triethylsilyl)hydrazine[71] (15.9 g) in benzene (75 ml) was added an equimolar amount of n-butyl-lithium in hexane. The mixture was heated under reflux for 1 h, cooled, and equimolar amounts of chlorotriethylsilane and TMEDA were added. After heating under reflux for 1 day, the mixture was cooled, the precipitated lithium chloride was removed by filtration, and the tris(triethylsilyl)hydrazine (47%), b.p. 140—142 °C at 0.01 Torr, was isolated by distillation. Silylation of the lithium salt of this hydrazine with Et_3SiCl in toluene solvent at 100 °C for 1 day, as described above for the methylsilyl analogue, yielded crude TTEH which was recrystallised from ethanol, m.p. 267 °C (Found: C, 58.8; H, 12.3; N, 5.7. $C_{24}H_{60}N_2Si_4$ requires C, 58.9; H, 12.4; N, 5.7%), *m/e* 488 (M^+, 11.6%) and 115 (Et_3Si^+, base peak).

N-*t*-*Butyl*-O-*trimethylsilylhydroxylamine* (63%), b.p. 64—65 °C at 45 Torr, was prepared from *N*-t-butylhydroxylamine[72] using the method described by Smrekar and Wannagat[63] for the *N*-methyl analogue (Found: C, 52.1; H, 11.8; N, 8.8. $C_7H_{19}NOSi$ requires C, 52.1; H, 11.9; N, 8.7%).

Silylaminophosphines.—Bis(trimethylsilyl)amino(diethoxy)phosphine was prepared as described previously.[73] *Bis*(*triethylsilyl*)*amino*(*diethoxy*)*phosphine* (75%), b.p. 100—101 °C at 0.005 Torr, was prepared in a similar way from hexaethyldisilazane[36] (Found: C, 52.6; H, 11.1; N, 3.8; P, 8.6. $C_{16}H_{40}NO_2PSi_2$ requires C, 52.6; H, 11.0; N, 3.8; P, 8.5%). The proton-decoupled ^{31}P n.m.r. spectrum (in C_6D_6) showed a singlet at δ 163 p.p.m. downfield from external 85% H_3PO_4.

[*Trimethylsilyl*(*methyl*)*amino*](*diethoxy*)*phosphine* (53%), b.p. 40—42 °C at 0.1 Torr, was prepared similarly from methyl(trimethylsilyl)amine[74] (Found: C, 43.3; H, 9.9; N, 6.4; P, 13.8. $C_8H_{22}NO_2PSi$ requires C, 43.1; H, 9.9; N, 6.3; P, 13.9%).

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