Electron Spin Resonance Studies of the Structures and Reactions of Trialkoxysilyl Radicals

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Photochemically generated t-butoxyl radicals abstract hydrogen from the silanes $(RO)_3SiH$ (R = Me, Bu^t, or Me_3Si) to give the corresponding silyl radicals $(RO)_3Si^{\cdot}$, which have been studied in liquid solution using e.s.r. spectroscopy. All three silyl radicals are strongly pyramidal at silicon, as judged from the magnitudes of the ^{29}Si hyperfine splittings, and the values of $a(^{29}Si)$ accord reasonably well with those predicted from a previously established linear relationship between $a(^{29}Si)$ for $X_3Si^{\cdot}$ and $^1J(^{29}Si-H)$ for X_3SiH. Trialkoxysilyl radicals abstract halogen rapidly from alkyl bromides and less readily from alkyl chlorides; the relative reactivities of Bu^tBr and $PrBr$ towards $(Bu^tO)_3Si^{\cdot}$ and $Me_3Si^{\cdot}$ are similar. Addition of $(Bu^tO)_3Si^{\cdot}$ to carbonyl compounds is somewhat slower than addition of $Me_3Si^{\cdot}$. Addition of $(RO)_3Si^{\cdot}$ to ethylene and to 1,1-di-t-butylethylene takes place readily to give β-silylalkyl radicals. Non-equivalence of the β-protons in $(Bu^tO)_3SiCH_2\overset{\cdot}{C}H_2$ is attributed to chirality of the $(RO)_3Si$ group and lineshape analysis provides Arrhenius parameters for the process exchanging the environments of the two protons; this process is identified as hindered rotation about the Si–O bonds.

The structures of silyl radicals $X_3Si^{\cdot}$ and their reactions with organic compounds have been investigated extensively over many years.[1–3] However, although e.s.r. studies of many different types of silyl radical have been described, spectra of trialkoxysilyl radicals have never been reported.

t-Butoxyl radicals react with silane and with alkylsilanes R_nSiH_{4-n} (n = 0–3) predominantly by hydrogen-atom abstraction from silicon to yield the corresponding silyl radicals $R_n\overset{\cdot}{S}iH_{3-n}$.[4,5] However, $(EtO)_3Si^{\cdot}$ was not detected by e.s.r. spectroscopy when t-butoxyl radicals were generated in the presence of triethoxysilane,[4,6] because hydrogen transfer from silicon is slower[6] than for R_3SiH and abstraction takes place preferentially from the methyleneoxy groups to give the radical (1) [equation (1).][4,6]

$$Bu^tO^{\cdot} + (EtO)_3SiH \longrightarrow Me\overset{\cdot}{C}HOSi(OEt)_2H + Bu^tOH \quad (1)$$

$$(1)$$
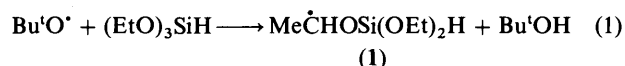
It seemed to us that the rather obvious expedient of using trialkoxysilanes which do not contain C–H groups activated by an adjacent oxygen atom or in which such C–H groups are less reactive than those in $(EtO)_3SiH$, might divert attack to the Si–H function. This turned out to be so and we report here e.s.r. studies of the properties of trialkoxysilyl radicals produced in this manner.

Results and Discussion

E.s.r. spectra were recorded during continuous u.v. irradiation of cyclopropane solutions containing di-t-butyl peroxide (DTBP) (*ca.* 15% v/v) and the silane, while the sample was in the microwave cavity of the e.s.r. spectrometer.[7] Consistent with the greater strength of primary as compared with secondary C–H bonds, competing hydrogen abstraction from carbon and from silicon was observed with trimethoxysilane (*ca.* 1.5 mol dm^{-3}) between 150 and 200 K [equations (2)–(4)]. The e.s.r. spectrum

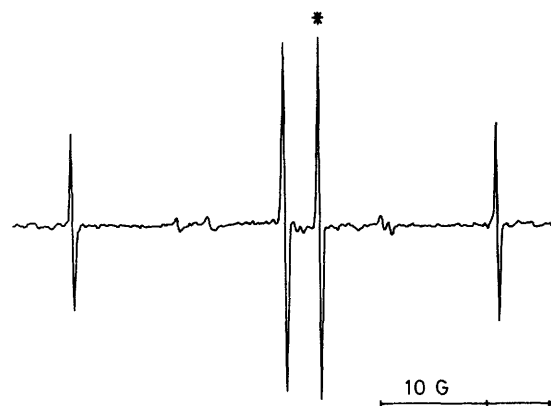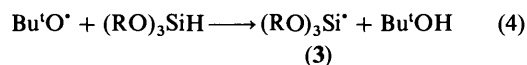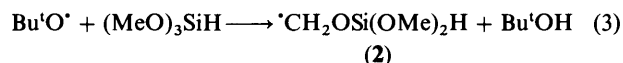$$Bu^tOOBu^t \xrightarrow{hv} 2\,Bu^tO^{\cdot} \quad (2)$$

Figure 1. E.s.r. spectrum recorded during photolysis of DTBP in the presence of trimethoxysilane at 156 K. The single line marked with an asterisk is assigned to (3; R = Me).

$$Bu^tO^{\cdot} + (MeO)_3SiH \longrightarrow {}^{\cdot}CH_2OSi(OMe)_2H + Bu^tOH \quad (3)$$

$$(2)$$

$$Bu^tO^{\cdot} + (RO)_3SiH \longrightarrow (RO)_3Si^{\cdot} + Bu^tOH \quad (4)$$

$$(3)$$

(see Figure 1) consisted of a 1:2:1 triplet [*a*(2 H) 19.9 G and *g* 2.0033 at 195 K], which we assign to the radical (2), along with a narrow singlet (*g* 2.0012) which we attribute to the trimethoxysilyl radical (3; R = Me). Immediately after commencement of photolysis, the steady-state concentrations of (2) and (3) were comparable, but the relative concentration of the silyl radical decreased during prolonged u.v. irradiation and, as with the other trialkoxysilanes studied, spectra of secondary-product radicals built up with time.

Tri-t-butoxysilane does not contain C–H groups activated by an adjacent oxygen atom and hydrogen abstraction now takes place almost exclusively from silicon. The e.s.r. spectrum shown in Figure 2 was recorded during u.v. irradiation of a cyclopropane solution containing DTBP and $(Bu^tO)_3SiH$ (1.0 mol dm^{-3}) at 221 K. The central multiplet (*g* 2.0014) is ascribed to the tri-t-butoxysilyl radical (3; R = Bu^t) and the fine
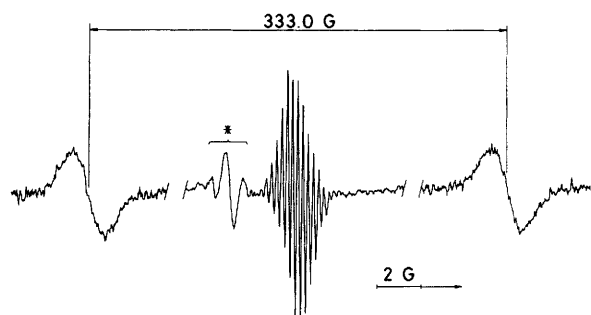
Figure 2. E.s.r. spectrum of the tri-t-butoxysilyl radical (**3**; R = Bu^t) at 221 K; the ^{29}Si satellites are shown recorded at higher gain. The lines marked with an asterisk arise from a persistent secondary-product radical.

structure can be satisfactorily simulated as resulting from a 0.23 G coupling to 27 equivalent protons. Less well-resolved satellites arising from (**3**; R = Bu^t) which contains ^{29}Si in natural abundance (4.7%, I 1/2) were also detected [$a(^{29}$Si) (−)330.9 G at 197 K]; ^{29}Si satellites could also be located for (**3**; R = Me).
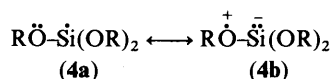
Tris(trimethylsiloxy)silane similarly afforded the corresponding silyl radical (**3**; R = Me$_3$Si), the magnitude of $a(^{29}$Si) for which is significantly larger than the values for (**3**; R = Me or Bu^t) (see Table 1). For comparison, the trimethylsilyl radical Me$_3$Si$^{\cdot}$ shows a(9 H) 6.28, $a(^{29}$Si) (−)181.1 G, and g 2.0031 at 153 K.[4,5]

The large increase in the magnitude of $a(^{29}$Si) on going from Me$_3$Si$^{\cdot}$ to (RO)$_3$Si$^{\cdot}$ parallels the increase in ligand electronegativity and reflects the increase in the Si-3s contribution to the SOMO and in the deviation from planarity at silicon.[8] The effective electronegativity of the Me$_3$SiO group could be greater than that of an R$_3$CO ligand, because the silicon substituent can behave as a π acceptor towards the electron pairs on an attached oxygen atom.[9]

A linear relationship has been shown[10] to exist between $a(^{29}$Si) for X$_3$Si$^{\cdot}$ and $^1J(^{29}$Si–H) for the silane X$_3$SiH, similar to that established previously[11,12] for phosphorus-centred radicals and their protic parents. Such correlations exist, because the contribution of the central-atom valence s-orbital to the SOMO of L$_n$M$^{\cdot}$ is linearly related, and probably similar to, its contribution to the M–H σ-bonding orbital in L$_n$MH. For silyl radicals which do not contain α-Si or -Cl substituents capable of delocalising the unpaired electron, equation (5) was found to

$$a(^{29}\text{Si})/\text{G} = 1.625\ ^1J(^{29}\text{Si–H})/\text{Hz} + 123.9 \qquad (5)$$

hold.[10] The experimentally determined values of $a(^{29}$Si) for (**3**; R = Me, Bu^t, or Me$_3$Si) are fairly close to those predicted from the nuclear spin–spin coupling constants (see Table 1), implying that delocalisation of the unpaired electron onto oxygen is not substantial for (**3**). However, a small amount of unpaired-electron delocalisation by the conjugative mechanism implied by the inclusion of structure (**4b**) may occur for (**3**; R = Me or Bu^t), because the value of $a(^{29}$Si) predicted for (**3**; R = Me$_3$Si) is significantly smaller than that observed, in accord with the reduced donating ability of oxygen in an Me$_3$SiO ligand (see before).

$$\text{R}\ddot{\text{O}}\text{-}\overset{\cdot}{\text{S}}\text{i(OR)}_2 \longleftrightarrow \text{R}\overset{+}{\text{O}}\text{=}\overset{-}{\text{S}}\text{i(OR)}_2$$
$$\text{(4a)} \qquad\qquad \text{(4b)}$$

The tri-t-butoxysilyl radical is isoelectronic with the alane radical anion (Bu^{t}O)$_3$Al$^{-\cdot}$, which we have studied previously,[13] and the structures of these two species are clearly similar. Thus, the ^{29}Si and ^{27}Al hyperfine splittings correspond[14] to ca. 27 and

31% unpaired electron population of the central-atom 3s orbital, respectively.

The low g-factors found for (**3**) compared with that for Me$_3$Si$^{\cdot}$ can also be associated with the greater deviation from planarity of the former. Analogous trends are shown by the alane radical anions[13] and by carbon-centred radicals.[15]
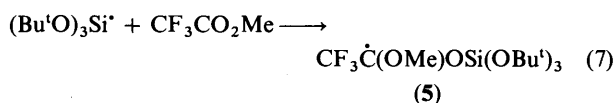
Chemical Reactions of (**3**).—A number of chemical reactions of (**3**; R = Me, Bu^t, or Me$_3$Si) have been investigated by including the chosen reactant along with the appropriate silane and DTBP in cyclopropane.

Halogen abstraction from alkyl halides by trialkylsilyl radicals is well documented and is a standard method of generating specific alkyl radicals from bromoalkanes for study in solution using e.s.r. spectroscopy.[16] Between 180 and 250 K in the presence of PrBr or Bu^{t}Br (each ca. 1 mol dm^{-3}), the spectrum of (**3**; R = Bu^t) was replaced completely by that of the corresponding alkyl radical [equation (6)]. A similar result was

$$(\text{Bu}^t\text{O})_3\text{Si}^{\cdot} + \text{RHal} \longrightarrow (\text{Bu}^t\text{O})_3\text{SiHal} + \text{R}^{\cdot} \qquad (6)$$
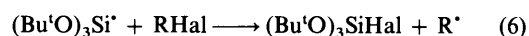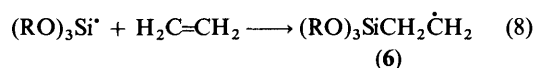
obtained with Bu^{t}Cl above ca. 200 K, but as the temperature was lowered quenching of the spectrum of (**3**; R = Bu^t) became progressively less complete. With PrCl no spectrum of the propyl radical was apparent alongside that of (**3**) until the temperature was raised above ca. 240 K. Relative rates of halogen-atom abstraction from t-butyl and propyl bromides were determined in competition experiments.[7] At 203 K, ($k_{\text{Bu}^t\text{Br}}/k_{\text{PrBr}}$) was found to be 2.9, effectively the same as the value of 3.1 found for bromine abstraction by Me$_3$Si$^{\cdot}$ when the (Bu^{t}O)$_3$SiH was replaced with Me$_3$SiH (cf. the value of 3.4 reported previously[17]).

Trialkylsilyl radicals add readily to a variety of types of unsaturated organic molecules[3] and many of these reactions have been investigated using e.s.r. spectroscopy. The reactivity of (**3**; R = Bu^t) towards ketones and esters appears to be somewhat less than that[18] of Me$_3$Si$^{\cdot}$. Thus, while addition of Me$_3$Si$^{\cdot}$ to acetone[18a] (ca. 1 mol dm^{-3}) was complete at 210 K, as judged by e.s.r. spectroscopy, the spectrum of (**3**; R = Bu^t) was still strong under similar conditions. Neither (**3**; R = Bu^t) nor[18b] trialkylsilyl radicals undergo detectable addition to ethyl acetate (1 mol dm^{-3}) up to 260 K but, like[18b,19] Me$_3$Si$^{\cdot}$, (**3**; R = Bu^t) adds more readily to methyl trifluoroacetate (1 mol dm^{-3}) [equation (7)]. While addition of Me$_3$Si$^{\cdot}$ was complete at 188

$$(\text{Bu}^t\text{O})_3\text{Si}^{\cdot} + \text{CF}_3\text{CO}_2\text{Me} \longrightarrow$$
$$\text{CF}_3\overset{\cdot}{\text{C}}(\text{OMe})\text{OSi(OBu}^t)_3 \qquad (7)$$
$$\text{(5)}$$

K,[19] the spectrum of (**3**; R = Bu^t) was only partially replaced by that of (**5**) and addition of (**3**) was not complete until 233 K. At 273 K the spectrum of (**5**) could be analysed in terms of a(3 F) 17.70, a(3 H) 1.24 G, and g 2.0032, but as the temperature was lowered the lines corresponding to M_I(3 F) = ±0.5 broadened selectively and were barely detectable at 188 K. We attribute this lineshape effect to the existence of hindered rotation about the CF$_3$–C bond in the adduct (**5**), which is pyramidal at the radical centre.[19]

U.v. irradiation of a cyclopropane solution containing DTBP, (MeO)$_3$SiH, and ethylene afforded superimposed e.s.r. spectra of (**2**) and of the radical (**6**; R = Me), the latter produced by addition of (**3**) to the alkene [equation (8)]. The spectroscopic

$$(\text{RO})_3\text{Si}^{\cdot} + \text{H}_2\text{C=CH}_2 \longrightarrow (\text{RO})_3\text{SiCH}_2\overset{\cdot}{\text{C}}\text{H}_2 \qquad (8)$$
$$\text{(6)}$$

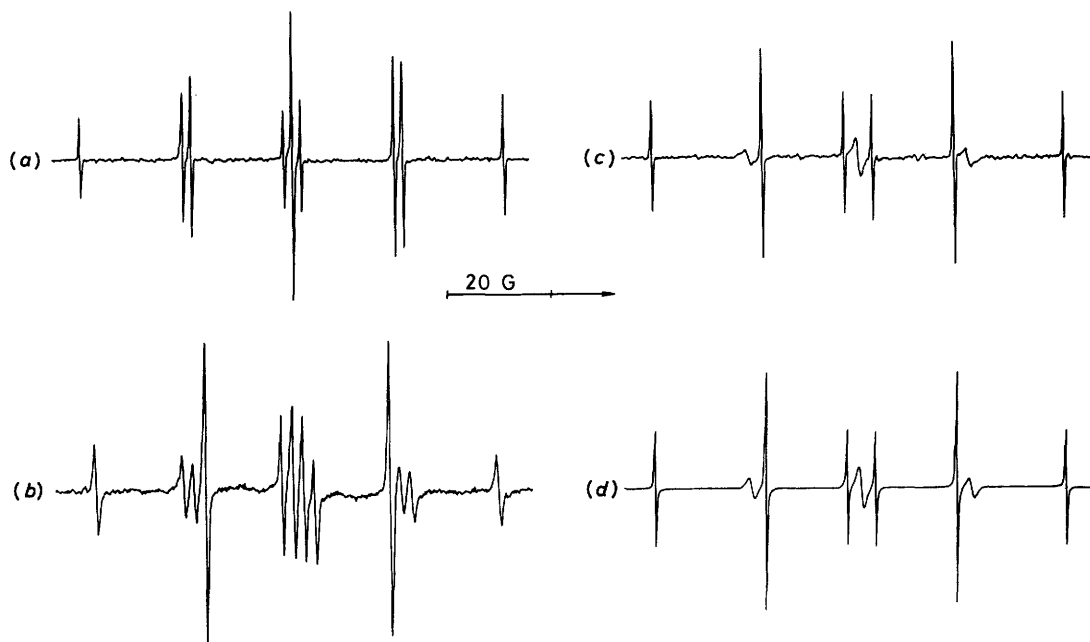parameters for (**6**; R = Me) are given in Table 2; the e.s.r.

Figure 3. E.s.r. spectra of the β-silylethyl radical (6; R = Buᵗ) (a) at 238 K, (b) at 141 K, and (c) at 170 K. A computer simulation of (c), obtained with k_{exch} = 2.0 × 10⁷ s⁻¹, is shown in (d); the individual β-proton splittings used were 17.41 and 19.50 G.

Table 1. E.s.r. parameters for silyl radicals $(RO)_3Si^•$ (3) in cyclopropane.

R	T/K	g-Factor	$a(^{29}Si)/G$ [a,b]	$[d\|a(^{29}Si)\|]/dT$ /mG K⁻¹	$^1J(Si-H)/Hz$ [b,c]	Calculated [b,d] $a(^{29}Si)/G$
Me	194	2.0012	339.0	+77	289.2	346.1
Buᵗ	197	2.0014	330.9 [e]	+61	280.2	331.4
Me₃Si	199	2.0011	363.3 [f]	+44	291.1	349.1

[a] Computed from the line positions and the microwave frequency using the Breit–Rabi equation. [b] Because the magnetogyric ratio of ²⁹Si is negative, the signs of $a(^{29}Si)$ and $^1J(^{29}Si-H)$ will also be negative. [c] Measured for this work in C_6D_6; values in the literature [29,30] are very similar. [d] Calculated using equation (5). [e] Further splitting of 0.23 G from 27 equivalent protons detected at 221 K. [f] Further splitting of 0.13 G from 27 equivalent protons detected at 221 K.

Table 2. E.s.r. parameters for the radicals $(RO)_3SiCH_2\dot{C}H_2$ (6) in cyclopropane.

			Hyperfine splittings (G)		
R	T/K	g-Factor	$a(2\ H_\alpha)$	$a(2\ H_\beta)$	$a(^{29}Si)$ [a]
Me	222	2.0027	21.46	19.40	
	156	2.0027	21.42	18.70	
Buᵗ	238	2.0026	21.24	19.64	
	141	2.0026	21.24	16.91,[b] 19.00 [b]	46.1
Me₃Si	240	2.0027	21.52	19.66	
	138	2.0027	21.51	18.26	48.9

[a] Calculated using the Breit–Rabi equation, the sign of $a(^{29}Si)$ is presumed to be negative. [b] Splitting from one proton (see the text).

spectrum showed no selective line-broadening down to 137 K. The tri-t-butoxysilyl radical underwent similarly ready addition to ethylene to give (6; R = Buᵗ), but now the e.s.r. spectrum was strongly temperature dependent (see Figure 3). At high temperatures [e.g. Figure 3(a)] the β-protons are equivalent on the e.s.r. timescale, but as the temperature is decreased the lines corresponding to $M_I(2\ H_\beta)$ = 0 at first broaden and then, below ca. 160 K, split into doublets arising from coupling to non-equivalent β-protons [Figure 3(b)]. E.s.r. spectra of (6; R = Buᵗ)

in the intermediate exchange region were computer simulated using the program ESREXN,[20] with the assumption that the temperature coefficient for both of the β-proton splittings was the same as that (+17 mG K⁻¹) for the average β-proton splitting between 140 and 240 K. Simulation of spectra obtained between 150 and 220 K [see e.g. Figure 3(c) and (d)] yielded rate coefficients for β-proton exchange which give a good fit to the Arrhenius equation (9) (θ = 2.303RT kJ mol⁻¹).

$$\log_{10}(k_{exch}/s^{-1}) = 12.5 - 16.9/\theta \qquad (9)$$

The low values of $a(2\ H_\beta)$ found for (6) indicate [21] that the conformation (7), in which the C_β–Si bond eclipses the axis of the C_α–2p_π SOMO is preferred, as it is for the corresponding adduct of $Me_3Si^{•}$.[3,22] This is because steric interference is thereby minimised and (more importantly) hyperconjugative interaction between the unpaired electron and the C_β–Si bond is maximised. We suggest that the non-equivalence of the β-protons in (6; R = Buᵗ) arises because of restricted rotation around the Si–O bonds in a preferred conformation shown idealised in (8). In structure (8) the β-protons are diastereotopic and intrinsically non-equivalent,[23] but their environments can be exchanged by concerted rotation (or a series of consecutive rotations) about the Si–O bonds. For steric reasons, the barrier to such an exchange process should be smaller for (6; R = Me), as is observed.

Table 3. E.s.r. parameters for the radicals $X_3SiCH_2\dot{C}Bu^t_2$ (9) in cyclopropane.

| X	T/K	g-Factor	Hyperfine splittings/G			$^1J(Si-H)/Hz$ for X_3SiH^b
			$a(2\ H_\beta)$	$a(18_\gamma)$	$a(^{29}Si)^a$	
MeO	274	2.0026	15.68	0.39	43.7	289.2^d
	173	2.0026	15.6	c		
Bu^{t}O	275	2.0025	15.60	0.37	45.9	280.2^d
	165	2.0025	13.3,^{e} 17.2^e	c	47.3^f	
Me$_3$SiO	274	2.0025	15.57	0.38	46.6	291.1^d
	165	2.0025	15.4	c		
Me^g	298^h	2.0024	15.76	0.36	35.02	184.0^i
Bu^g	298	2.0024	15.78	c	30.87	179.2^{i,j}
Cl^g	298^h	2.0030	14.58	0.43	77.24	362.9^i

^{a} Calculated using the Breit–Rabi equation; the sign of $^a(^{29}Si)$ is presumed to be negative. ^{b} The sign of $^1J(^{29}Si-H)$ is negative. ^{c} Not resolved. ^{d} Measured for this work in C_6D_6. ^{e} Splitting from one proton (see the text). ^{f} At 183 K. ^{g} Data from ref. 25. ^{h} The solvent was DTBP. ^{i} Data from ref. 31. ^{j} Value for Et_3SiH.
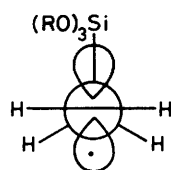
(7)
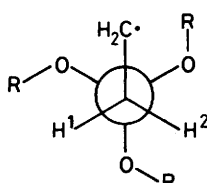
(8)
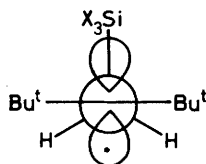
(9)

The tris(trimethylsiloxy)silyl radical adds to ethylene to give (6; R = Me₃Si), the e.s.r. spectrum of which shows no selective line broadening down to 138 K. The barrier to β-proton exchange must therefore be smaller than for (6; R = Buᵗ) and, although steric interactions may be reduced in (6; R = Me₃Si) because of the larger covalent radius of silicon, we attribute this difference mainly to the greater ease of rotation about the Si–OSiMe₃ bond as compared with the Si–OCMe₃ bond. This would be anticipated, since the bond angle at oxygen is greater and more readily increased to 180° in disiloxanes than in silyl alkyl ethers.[9] (Compare[24] also the much lower barrier to α-proton exchange for Me₃SiOĊH₂ compared with that for Me₃COĊH₂).

Addition of (3) to 1,1-di-t-butylethylene[25] affords the relatively persistent adducts (9; X = MeO, Buᵗ O, or Me₃SiO), which must for steric reasons be rigidly held in the eclipsed conformation shown. The e.s.r. parameters for (9; X = RO) are given in Table 3, along with those for other silyl radical adducts of the type (9) which have been reported previously.[25] At high temperatures (ca. 270 K) the β-protons in (9; X = RO) are apparently equivalent, but as the temperature is decreased, broadening of the central component of the triplet is observed when X = Buᵗ O and non-equivalence of the β-protons is clearly

resolved at 165 K. No line-shape effects were observed for (9; X = MeO or Me₃SiO) down to 165 K.

It can be seen from Table 3 that the magnitude of the ²⁹Si splitting for (9) increases with the electronegativity of the substituent X and with the value of $^1J(^{29}Si-H)$ for the silane X₃SiH. Even if the extent of hyperconjugative delocalisation of the unpaired electron into the C_β–Si bond remains roughly constant as X changed, this increase in $a(^{29}Si)$ would be expected[26] because the Si–3s contribution to the C_β–Si σ-bonding orbital will also increase with increasing electronegativity of X (cf. ref. 25).

We have found previously[26] that for analogous radicals which contain a β-phosphorus(v) substituent an approximate linear relationship exists between $a(^{31}P)$ and $^1J(^{31}P-H)$ in the corresponding phosphorus compound L_nPH. However, in general for a radical of the type $L_nMCH_2\dot{C}Bu^t_2$, the extent of hyperconjugative delocalisation will decrease as the difference in energy between the C_β–M σ-bonding orbital and the C_α–2p$_\pi$ orbital increases with ligand electronegativity.[27,28] Thus, an increase in ligand electronegativity should result in decreased unpaired electron delocalisation into a C_β–M σ orbital of increased M–3s character and consequently, in general, a linear relationship between $a(M)$ and $^1J(M-H)$ in L_nMH would not be expected. For the radicals listed in Table 3 a plot of $a(^{29}Si)$ against $^1J(^{29}Si-H)$ is far from being a straight line, although as pointed out before, the magnitudes of both do increase as the ligand electronegativity increases.

Experimental

The techniques used for photochemical generation of radicals in liquid solution for study by e.s.r. spectroscopy have been described previously.[7]

Trimethoxysilane (Aldrich) and tris(trimethylsiloxy)silane (Petrarch) were carefully distilled before use, the former from calcium hydride, and were handled under dry nitrogen. Tri-t-butoxysilane was prepared by the reaction of t-butyl alcohol with trichlorosilane in the presence of pyridine, as described by Newton and Rochow.[29] The values of $^1J(^{29}Si-H)$ for (RO)₃SiH were measured from the ¹H n.m.r. spectra (Varian VXR-400, C₆D₆ solvent) and found to be in good agreement with values in the literature.[29-31]

Cyclopropane and ethylene (both Argo International) were used as received and 1,1-di-t-butylethylene was prepared from di-t-butyl ketone using the published method.[32] All other reagents were commercially available materials which were distilled before use.

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