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AN ELECTRON SPIN RESONANCE STUDY OF TRI-ISOPROPYLSILYL AND TRI-t-BUTYLSILYL RADICALS

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Summary

Tri-isopropylsilyl and tri-t-butylsilyl radicals have been prepared by hydrogen abstraction from the corresponding organosilicon hydrides, using intermittent illumination and output signal phase inversion to remove the ESR signals arising from persistent radicals. Tri-t-butylsilyl radicals are not markedly persistent. The variation in β-hydrogen coupling constants in the series trimethylsilyl, triethylsilyl, tri-isopropylsilyl is tentatively interpreted in terms of conformational preference, with a larger coupling constant for a C–H bond *gauche* to the singly occupied orbital on silicon than for the *anti* conformation.

Simple organosilicon free radicals can be prepared by hydrogen abstraction from the corresponding organosilicon hydride by t-butoxyl radicals in the cavity of an ESR spectrometer [1–3], but for more complex organosilicon hydrides the signal due to transient organosilicon free radicals is often obscured by intense signals due to persistent free radicals which build up rapidly during the experiment. We recently described a technique to overcome this problem, involving modulation of the light source, output signal phase inversion, and a long time constant to remove the ESR signals arising from persistent free radicals [4]. In this paper, we apply this technique to the study of tri-isopropylsilyl and tri-t-butylsilyl radicals.

Results and discussion

Trialkylsilyl radicals such as trimethylsilyl [1–3] and triethylsilyl [5] have been shown to have non-planar geometry at the silicon radical centre and are not persistent. The extension of this series to tri-isopropylsilyl and tri-t-butylsilyl is of interest, since the increasing bulk of the alkyl groups should tend to flatten the silicon centre, and might make the radicals persistent if the steric hindrance became sufficient to inhibit radical combination reactions.

We attempted to make tri-isopropylsilyl and tri-t-butylsilyl radicals by the normal

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route of hydrogen abstraction from the hydride by t-butoxyl radicals. Strong signals due to persistent radicals were obtained in both cases, but the spectra could not be analysed. However, by modulating the UV light source at 3–5 Hz, inverting the phase of the output signal during the dark period, and using a long time constant (~ 1 s) we were able to cancel the spectra due to the persistent radical impurities and observe the spectrum of tri-isopropylsilyl as a quartet, and tri-t-butylsilyl as a singlet. By overmodulation of the latter spectrum, ^{29}Si and ^{13}C satellites were observed but the quartet structure of the tri-isopropylsilyl radical thwarted our efforts to identify the silicon satellites of this radical.

Coupling constants of these radicals, along with tri-n-propylsilyl radicals which were prepared normally, and literature values for trimethylsilyl and triethylsilyl radicals are collected in Table 1.

There is a modest tendency towards planarity in silicon-centred radicals as the substituent groups vary from methyl to t-butyl as evidenced by the fall in ^{29}Si coupling constants which reflects the decreasing proportion of *s* character in the orbital containing the unpaired electron: this is most simply explained as a steric effect.

The tri-t-butylsilyl radicals are not persistent (over a period of several seconds or more) though our experiments do not rule out the possibility of persistence for periods of ~ 0.1 s. Inspection of space-filling models indicates that it is unlikely that tri-t-butylsilyl radicals dimerize readily, and the absence of β-hydrogen prevents the normal radical disproportionation mechanism for destruction of radicals. It is likely that tri-t-butylsilyl radicals are lost by hydrogen abstraction from C–H bonds of compounds present in the system.

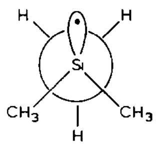
The change in proton coupling constants in the series is tentatively attributed to a conformational effect. For trimethylsilyl **A**, the three rotational conformations will have equal populations and the observed coupling will be an average of the two *gauche* and one *anti* protons. For triethylsilyl and tri-isopropylsilyl, it will be expected that conformations of types **B** and **D** respectively will be preferred: the fall in coupling constant on going from trimethylsilyl to tri-isopropylsilyl indicates that protons with the *gauche* orientation have a higher coupling constant than do *anti* protons. If it is assumed that the geometry at silicon does not change in this series, that all the *gauche* interactions between alkyl groups in **B C D** and **E** are the same, and that the coupling constants due to a particular orientation are the same in the three radicals, values of the *gauche* and *anti* coupling constants are derived to be 8.34 and 2.22 G respectively, and the energy difference between **C** and **B** (or **E** and **D**) to be 2.2 kJ mol^{-1}.

TABLE 1

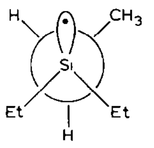
ESR PARAMETERS FOR ORGANOSILYL RADICALS[a]

Radical	$a_{\beta\text{-H}}$	$a_{^{29}Si}$	g	Reference
$Me_3Si\cdot$	6.3	181, 183	2.0031	1,2,3
$Et_3Si\cdot$	5.7	170	2.0030	2,3,5
$n\text{-}Pr_3Si\cdot$	5.8			this work
$i\text{-}Pr_3Si\cdot$	4.6		2.0027	this work
$t\text{-}Bu_3Si\cdot$	–	163[b]		this work

[a] Couplings in Gauss. [b] $a_{^{13}C}$ 43 G.



(A)



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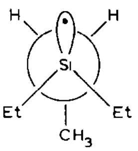
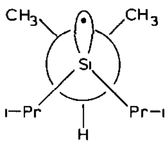


(C)



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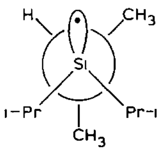

(E)

This energy difference corresponds to a single alkyl–alkyl *gauche* interaction, and is somewhat smaller than that found for all-carbon systems such as the 1,2-dimethylcyclohexanes, for which values of 3.1–3.8 kJ mol^{-1} for the *gauche* interaction have been derived [6]. The smaller value in the C–Si system seems reasonable in view of the longer C–Si bond length.

On the other hand, the β-C–H coupling constant [7] in bicyclo[2.2.2]-1-sila-octyl in which the β protons are locked in approximately *gauche* orientations is only 1.53 G, which implies that the *anti* conformation would have a much higher value. However, if this is the case, to account for the β-C–H couplings in triethylsilyl and tri-isopropylsilyl, it would be necessary to assume a smaller energy difference between **E** and **D** than between **C** and **B**, or a change in couplings due to the change in geometry at the silicon atom. Both for acyl RCO$^{\cdot}$ radicals [8] and for α,α-difluoroalkyl radicals [9], the ESR spectra have been interpreted in terms of a maximum coupling constant for a 180° dihedral angle (*anti*) between the β-C–H bond and the singly occupied orbital, with a smaller value for the 60° dihedral angle (*gauche* conformation).

A more extensive study of silicon-centred radicals to include radicals with locked conformations will be needed to test the relationship between dihedral angle and the β-C–H coupling constant.

Experimental

Tri-n-propylsilane, b.p. 172–173°C (lit. 10 172.3°C) and tri-isopropylsilane, b.p. 168–170°C (lit. 10 169–170°C) had purities > 99% by GLC. Tri-t-butylsilane [11], b.p. 100°C/0.5 mmHg (lit. 11 142–146°C/100 mmHg), purity by GLC > 98%, was made via di-t-butylchlorosilane and di-t-butylfluorosilane. The ESR measurements were carried out at −40°C on 1/3 v/v mixtures of organosilane with t-butyl peroxide as described previously [4].

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