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# AN ELECTRON SPIN RESONANCE STUDY OF SOME SILICON-CENTRED FREE RADICALS WITH A TRIS(TRIMETHYLSILYL)METHYL SUBSTITUENT

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## Summary

Silicon-centred radicals with one bulky trisyl (= tris(trimethylsilyl)methyl = Tsi) substituent and all six combinations of hydrogen, methyl, and phenyl as the other two substituents have been formed by hydrogen abstraction from the corresponding silanes. Coupling constants are in the expected ranges, and no evidence for radical rearrangements was obtained. $TsiSiH(OMe)_2$ gives a mixture of $Tsi\dot{S}i(OMe)_2$ and $TsiSiH(OMe)OCH_2\cdot$radicals.

The ESR spectra were obscured by the presence of persistent radicals, but the signals of these were selectively removed by the technique of using intermittent UV light (3–5 Hz) to form the radicals, inverting the phase of the ESR spectrometer output each time the UV beam was interrupted or restored, and employing a relatively long time constant of 1–2 seconds.

## Introduction

UV irradiation of tris(trimethyl)methyl (trisyl, Tsi) substituted iodides in various solvents gave some products in which rearrangement had taken place, for example TsiSiPhMeI in $C_5H_{12}$ rearranged to $(Me_3Si)_2C(SiPhMe_2)SiMe_2I$, and it was postulated that free radicals could have been involved in some of these reactions [1]. Pyrolysis of compounds of this type also gives products explicable on the basis of migration of a methyl group in the first-formed radical $(Me_3Si)_3CSiPhMe$ to give $Me_2\dot{S}i(Me_3Si)_2CSiPhMe_2$ [2]. In view of these results, it was of interest to study radicals of this type by electron spin resonance, and to see whether rearrangement can take place under ESR conditions.

## Results and discussion

We endeavoured to make the trisyl-substituted silicon-centred radicals shown in Table 1 by abstraction of hydrogen from the silicon hydride by photolytically

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produced t-butoxyl radicals in the cavity of the ESR spectrometer [3,4], but (as often happens in such experiments with relatively complex organosilicon hydrides), the spectra were obscured by intense signals from persistent radicals. This problem was overcome by modulating the UV light source by a rotating sector with equal open and opaque sections, operating at a frequency of 3–5 Hz, with a trigger operated by the sector to change the phase of the output signal each time the light was interrupted or restored. By using a time constant of 1 or 2 seconds to damp the spectrometer response, the signal due to persistent radicals averages to zero (see Fig. 1), whereas the signal due to transient radicals averages to approximately one half the value expected for continuous illumination.

By this means we obtained spectra of the trisyl-substituted silicon-centred radicals with the six possible combinations of hydrogen, methyl and phenyl as the other substituents on the silicon atom, as shown in Table 1.

The α-hydrogen splittings in $\mathrm{Tsi\dot{S}iH_2}$ and $\mathrm{Tsi\dot{S}iMeH}$ are similar, and fall between the values of 11.8–12.1 and 17.0–17.3 found for $\mathrm{Me\dot{S}iH_2}$ and $\mathrm{Me_2\dot{S}iH}$ respectively [4,5]. The value for $\mathrm{Tsi\dot{S}iPhH}$ is considerably smaller. A smaller value is to be expected if free spin is delocalized into the phenyl ring, but in view of the evidence that such delocalization has a rather small effect on the stability of aryl-substituted silyl radicals [6], the extent of the decrease of coupling constant of the α-H is surprising.

The marked variation in α-proton coupling constants observed in methyl-substituted silyl radicals have been discussed by Sharp and Symons [7]. As the $^{29}$Si couplings for the series $\mathrm{Me}_n\mathrm{H}_{3-n}\mathrm{Si}\bullet$ are essentially constant, they suggested that the

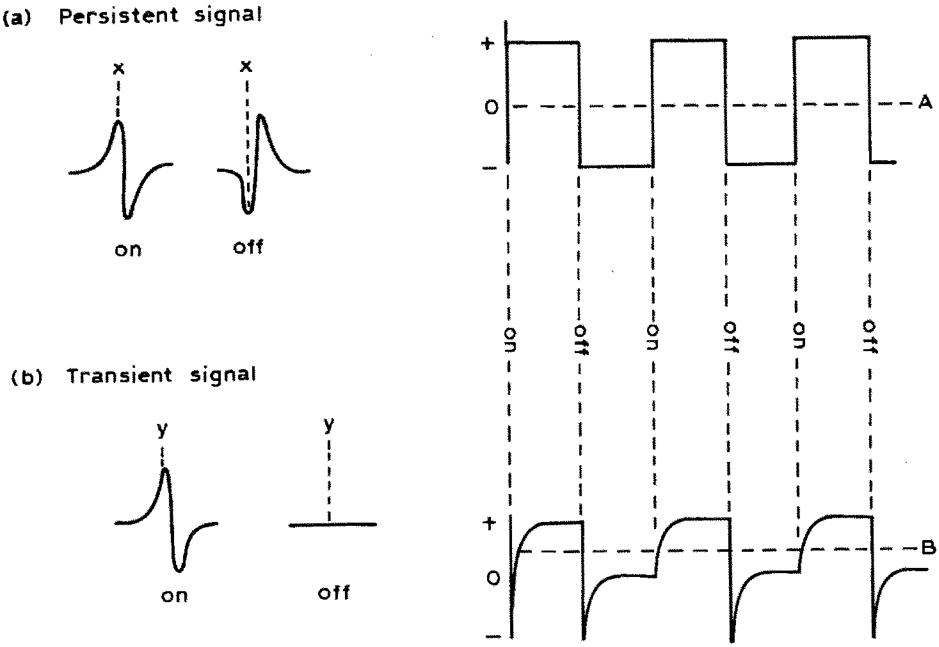

Fig. 1. A: output signal (at point x) averages to zero for long time constant; B: output signal (at point y) averages to ~ $\frac{1}{2}$ maximum value for long time constant; "on" and "off" refer to the UV light; Output signal: ——— short time constant. ------ long time constant.

TABLE 1

ESR PARAMETERS FOR TRISYL RADICALS[a]

| Radical | $a_H$ | $a_{Me}$ |
|---|---|---|
| $\mathrm{Tsi\dot{S}iH_2}$ | 14.3 | – |
| $\mathrm{Tsi\dot{S}iMeH}$ | 13.9 | 7.1 |
| $\mathrm{Tsi\dot{S}iPhH}$ | 9.8 | – |
| $\mathrm{Tsi\dot{S}iMePh}$ | – | 6.8 |
| $\mathrm{Tsi\dot{S}iMe_2}$ | – | 6.5 |
| $\mathrm{Tsi\dot{S}iPh_2}$[b] | – | – |

[a] Couplings in Gauss. [b] Singlet.

changes are related to small variations in bond angles which leave the 3*s* to 3*p* ratio constant in the singly occupied orbital. The $\alpha$-proton coupling is known to be very sensitive to small changes in the bond angles in the region where the coupling is small. The analysis is complicated by uncertainty about the signs of the $\alpha$-H couplings, although they are probably positive [7].

No couplings from aromatic hydrogen atoms were resolved in any of the phenyl-substituted radicals studied. The *ortho-* and *para*-hydrogen coupling constants for tris(3,5-di-t-butylphenyl)silyl radicals have been reported as 0.95 and 1.17 G, respectively [8], and the *meta* coupling constants in trimesitylsilyl radicals as 0.7 G [9]: if similar couplings are involved in our radicals, they may have been obsured by the greater complexity of the splitting pattern and high modulation amplitudes (up to 2 G) needed to get acceptable signal/noise in our samples.

The trend of methyl coupling constants, falling slightly from $\mathrm{Tsi\dot{S}iMeH}$ to $\mathrm{Tsi\dot{S}iMe_2}$ is similar to that for the series $\mathrm{Me\dot{S}iH_2}$ (8.0, 8.2) > $\mathrm{Me_2\dot{S}iH}$(7.2, 7.3) > $\mathrm{Me_3Si\bullet}$(6.3 G) [4,5]. The methyl coupling constant of $\mathrm{Tsi\dot{S}iMePh}$ falls between those of $\mathrm{Tsi\dot{S}iMeH}$ and $\mathrm{Tsi\dot{S}iMe_2}$. Overall, the results do not indicate a very large change in geometry in the radicals when methyl is replaced by trisyl, in spite of the great steric demands of the latter.

$\mathrm{TsiSiH(OMe)_2}$ gives a four line spectrum, analysable in terms of a 1/2/1 triplet with a superimposed singlet at higher field than the central line of the triplet. We assign the triplet (19.3 G) to $\mathrm{TsiSiH(OMe)OCH_2\bullet}$ (compare $\mathrm{Me_3SiOCH_2\bullet}$ $a_H$ 19.1 G) [10] and the singlet to $\mathrm{TsiSi(OMe)_2^{\bullet}}$. Triethoxysilane undergoes hydrogen abstraction only at the methylene groups [4,11]: the methoxy groups of our compounds should be less susceptible to hydrogen abstraction than the $\mathrm{CH_2}$ of the ethoxy groups, giving rise to a mixture of radicals from C–H and Si–H abstraction. The two electronegative oxygen atoms may be responsible for the lower *g* value of the silicon-centred radical (0.0017 lower than for the carbon-centred radical); for example $g = 2.0022$ has been reported for the $\mathrm{Me_2\dot{S}iF}$ radical [12], and two oxygen substituents have been shown to produce a lowering of the *g* value in carbon-centred radicals; this is associated with increased bending at the radical centre [13].

Solutions of TsiPhMeI, $\mathrm{TsiSiPh_2I}$ and $\mathrm{TsiSiMe_2I}$ in hexane were also photolysed in the cavity of the ESR spectrometer. No signals attributable to transient radicals were observed.

In spite of the presence of the bulky trisyl group, which might be expected to inhibit radical combination, none of the radicals described above was markedley persistent. Our sectoring indicates that the processes involved in removal of these radicals have half-life values shorter than about 0.3 seconds. No evidence for rearrangement of any of the transient radicals was obtained, but this does not, of course, rule out rearrangements in the unidentified persistent radicals.

## Experimental

### *Trisyl compounds*

*$TsiSi(OMe)_2H$.* A solution of ICl (2.30 g, 0.0142 mmol) in $CCl_4$ (250 cm$^3$) was added dropwise to $TsiSi(OMe)H_2$ [14] (4.15 g, 0.0142 mmol) in $CCl_4$ (40 cm$^3$) with stirring at room temperature. The solvent was removed under vaccum and the solid residue shaken with aqueous sodium thiosulphate. Extraction with $CH_2Cl_2$ and evaporation of the extract gave a solid, which was recrystallized from MeOH to yield trisyl(iodo)methoxysilane, TsiSi(OMe)(I)H, (4.51 g, 76%) m.p. 290°C (sealed tube); $^1$H NMR ($CCl_4$), $\delta$ 0.32 (s, 27H, $SiMe_3$), 3.45 (s, 3H, OMe), 5.81 (s, 1H, SiH). Some of the product (2.0 g) was refluxed with anhydrous MeOH (25 cm$^3$) for 3 h, then the solvent was removed under reduced pressure, and the solid residue was sublimed (125°C/0.2 mmHg) to give trisyl(dimethoxy)silane, $TsiSi(OMe)_2H$ (1.1 g, 71%), m.p. 227°C; $^1$H NMR, $\delta$($CCl_4$) 0.19 (s, 27H, $SiMe_3$), 3.66 (s, 6H, OMe), 4.60 (s, 1H, SiH).

*Trisyl(methyl)silane.* $TsiSiMeH_2$ was made from TsiSiMe(H)Cl as described in ref. 15, and the preparations of the remaining compounds were as described in ref. 14.

### *Electron spin resonance*

UV light from a 1 kW Hanovia high pressure Hg-Xe lamp was focussed in the plane of a rotating disc with two opposed 90° cut out sectors, and again on the cavity of the ESR spectrometer by a second 75 mm diameter quartz lens. A small secondary incandescent lamp and a photodiode were fixed on opposite sides of the disc 180° away from the UV beam; this secondary beam was used, via intermediate circuitry, to trigger the phase inversion of the output of the Varian 104A ESR spectrometer. Samples consisted of saturated solutions of the silanes in t-butyl peroxide, and the spectra were run at about $-40$°C. Calibration was carried out by the central two lines of $Mn^{++}$, 84.0 G apart [16]. The Si–H hydrogen coupling in $Tsi\dot{S}iMeH$ is approximately twice that of the methyl quartet: the figures quoted in Table 1 were obtained by varying the coupling constants in this region near the 2/1 ratio and optimizing the match between the computed and the experimental spectrum [17].

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