Tris[bis(trimethylsilyl)methyl]tin(III), $R_3Sn\cdot$, an Unusually Stable Stannyl Radical, from Photolysis of R_2Sn

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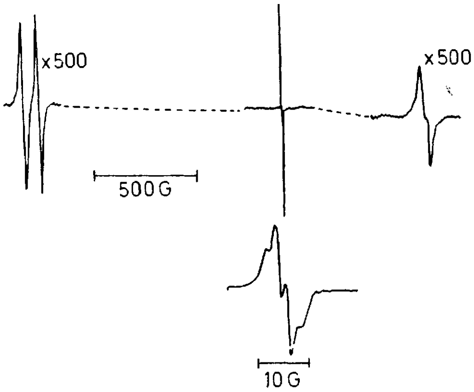
Summary Photolysis of R_2Sn [$R = (Me_3Si)_2CH$] with visible light in benzene at ambient temperature yields the stable radical $R_3Sn\cdot$, which has an e.s.r. solution spectrum showing coupling with the methine protons and ^{119}Sn and ^{117}Sn nuclei.

We report the preparation and e.s.r. spectrum of a novel organotin radical $R_3Sn\cdot$ [$R = (Me_3Si)_2CH$]. This species is readily formed in high concentration (10^{-2} to 10^{-3} M) by the photolysis with visible light [R_2Sn has λ_{max} at 495, 332, and 239 nm in n-C_6H_{14}] of deoxygenated solutions of R_2Sn,[1] at ambient temperatures in solvents such as hexane or benzene, possibly by reactions (1) and (2).

$$R_2Sn \xrightarrow{h\nu} R\cdot + RSn\cdot \qquad (1)$$

$$R\cdot + R_2Sn \rightarrow R_3Sn\cdot \qquad (2)$$

The overall process is thus viewed as a novel photochemical disproportionation: $2M^{II} \rightleftharpoons M^{I} + M^{III}$. The evidence rests on the unequivocal characterisation (see below) of $R_3Sn\cdot$ and the failure to observe deposition of a tin mirror even under u.v. irradiation; by contrast, under those conditions R_2Pb (ref. 1) yields metallic lead. The Sn^I species, or its decomposition products, have yet to be identified. Equation (2) shows $R_2\ddot{S}n$ functioning as a spin-trap. It is established that it can behave as a good ligand,[1] but attempts to generate $R_2SnX\cdot$ [$X = Bu^tO$, $Me_2(CN)C$, galvinoxyl, or Ph_3C; R_2Sn affords non-radical products with the precursors of the first three] have so far been unsuccessful. Alternatively, the products of equations (1) and (2) may arise from a bimolecular reaction between singlet and triplet R_2Sn.



FIGURE

The main feature of the e.s.r. spectrum of the $R_3Sn\cdot$ species is (Figure) a binomial quartet centred at $g = 2{\cdot}0094$ ($g_\perp = 2{\cdot}016$, $g_\parallel = 1{\cdot}994$]. The hyperfine coupling of 0·21 mT attributed to an interaction with three methine protons is comparable with the 0·275 mT splitting found[2] in $Me_3Sn\cdot$. Under higher gain, satellite spectra from the $I = \frac{1}{2}$ nuclei ^{119}Sn and ^{117}Sn were detectable in natural abundance (Figure). An exact solution of the Brëit-Rabi equation gives $a(^{117}Sn) = 169{\cdot}8$ mT and $a(^{119}Sn) = 177{\cdot}6$ mT. The ratio of these splittings is in excellent agreement with the value of 1·046 from the ratio of the nuclear moments. We are not aware of any previous reports of coupling to ^{117}Sn and ^{119}Sn in the solution e.s.r. spectrum of a tin-centred radical; indeed only $Me_3Sn\cdot$ has been characterised in solution.[2] Our coupling constants are intermediate between the two sets of data reported for $Me_3Sn\cdot$ observed in the solid state.[3] Their magnitude indicates that, like $Me_3Sn\cdot$, the radical is markedly non-planar. A further point of interest in the e.s.r. spectrum is the extreme width of the satellite lines. Although the calculated intensity of each line is about $\frac{1}{25}$ of that of the central quartet, it was necessary to use 500 times more amplifier gain in order to achieve comparable signal amplitudes in the illustrated spectrum measured in benzene at 40°. This broadening is associated with incomplete averaging of the anisotropic g- and hyperfine tensors by rotational diffusion; the satellite lines become sharper at higher temperatures. This behaviour is not unexpected in view of the large size of the ^{117}Sn and ^{119}Sn coupling constants; it serves to emphasise the difficulties inherent in finding satellite lines in solution for less stable species such as $Me_3Sn\cdot$.

Tris[bis(trimethylsilyl)methyl]tin is remarkably stable; a degassed solution in benzene showed no decrease in e.s.r. signal intensity after being kept in the dark for 750 h at room temperature. Its stability is attributed to reluctance to dimerise or hydrogen-abstract. The high steric requirement of R does not allow for bond angles close to tetrahedral at Sn (*cf.*, R_2Sn),[1] (and in any event the low Sn–H bond strength does not encourage H-abstraction from solvent). It is probable that $(Me_3Si)_2CH$ and related ligands[4] will frequently be found to favour 3-co-ordination for a metal [*cf.*, the isoelectronic $(Me_3Si)_2N$]. Other bulky Group IV radicals $(Me_3Si)_3C\cdot$ and $(Me_3C)_3C\cdot$ have high stability and decay by first-order processes.[5]

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