Novel Transient Tin-centred Radical Tris-(2-phenyl-2-methylpropyl)stannyl

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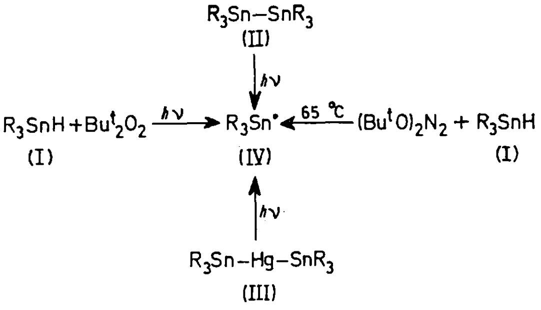
Summary The novel radical $R_3Sn^{\cdot}$ ($R = PhMe_2CCH_2$), generated from the new compounds R_3SnH, $R_3Sn{-}SnR_3$, and $R_3Sn{-}Hg{-}SnR_3$, is shown to be pyramidal by e.s.r. measurements between -80 and $+120$ °C [a_H (CH_2) = 3·1 G, $g = 2{\cdot}013$, a (^{117}Sn) = 1325 and a (^{119}Sn) = 1380 G, $\tau_{\frac{1}{2}} < 0{\cdot}1$ s], the rotation around the Sn–C bonds being hindered.

STANNYL radicals, $R_3Sn^{\cdot}$, which have been widely used as reagents during the last 15 years,[1] cannot normally be observed in solution and only $Me_3Sn^{\cdot}$ has been detected by e.s.r. spectroscopy.[2] The radical $[(Me_3Si)_2CH]_3Sn^{\cdot}$ is the only reported example which persists in solution.[3] In order to investigate the relative reactivities of radicals $R_3Sn^{\cdot}$ we sought radicals with bulky R groups which could be detected by e.s.r. spectroscopy. We report that the radical $R_3Sn^{\cdot}$ (IV; $R = PhMe_2CCH_2$) is suitable for this purpose and can easily be observed at room temperature. We generated (IV) by four independent methods. The e.s.r. signals were always identical, the method involving photolysis of (I) and $Bu^t_2O_2$ giving the most intense signal.

Compounds (I)–(III) (Scheme) have not been reported previously and were prepared as follows. Treatment of R_3SnBr with $LiAlH_4$ gave colourless crystals of (I), m.p. 42—43 °C, b.p. 200 °C at 0·05 Torr, 69% yield, ν_{Sn-H} (C_6H_{12}) 1820 cm^{-1}. Colourless crystals of (II), m.p. 146—147 °C (decomp.), were obtained in 78% yield by treating (I) with an equimolar amount of azobisisobutyronitrile. Following the general procedure,[4] (III) was prepared from R_3SnH and Bu^t_2Hg as a yellow crystalline compound, m.p. 114 °C.†



Scheme. R = $PhMe_2CCH_2$.

The e.s.r. spectrum of (IV) shows the expected septet, as illustrated in the Figure with a_H (CH_2) = 3·1 G, g = 2·013, and a (^{117}Sn) = 1325 and a (^{119}Sn) = 1380 G. The high value of the tin splitting shows that there is considerable s-character in the orbital of the lone electron. The radical is not planar, the angles C–Sn–C being 116°, and the out-of-plane angles being 12° (assuming A_0 = 15,400[5]). The radical decays in cyclopropane at −91 °C following strictly second-order kinetics, $k = 2{\cdot}98 \times 10^7$ ($\pm$ 2·6%) l mol^{-1} s^{-1}.[6]

Although the e.s.r. spectrum of (IV) remains unchanged in the range 0—120 °C, an alternating linewidth effect appears below 0 °C (in n-hexane, see Figure) and is complete at −40 °C indicating restricted rotation around Sn–C bonds caused by the bulky R groups. This steric hindrance might be considered as the main reason for the relatively high stationary concentration of (IV), caused by retarded recombination.

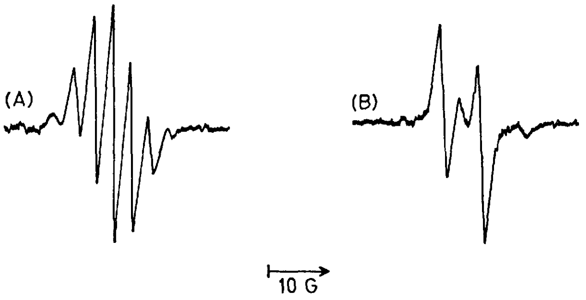


Figure. E.s.r. spectrum of the radical (IV), generated by irradiating R_3SnH and $Bu^t_2O_2$ with unfiltered light of an Hg-Xe compact arc lamp (Hanovia 977 B-1), using a system of quartz lenses. (A) In n-nonane at 120 °C. (B) In n-hexane at −20 °C.

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† Compounds (I)—(III) were characterised by spectroscopic (i.r., n.m.r., and mass) data and combustion analysis.

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[3] J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1974, 651. In addition, a persistent radical of the type $(X_2N)_3Sn\cdot$ is described here.

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[6] P. Blum and A. G. Davies, personal communication.