# Unstable Intermediates. Part CXLVII.[1] Electron Spin Resonance Spectra of Radicals in Irradiated Organotin Compounds: the Radicals $R_3Sn$, $R_4Sn^-$, $R_5Sn$, $R_3SnCl^-$, $Ph_6Sn_2^-$, $H_2\dot{C}Sn(Me)_2SnMe_3$, and $H_2\dot{C}Sn(Me)_2Cl$

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Exposure of the following compounds or their solutions to $^{60}$Co γ-rays at 77 K gave e.s.r. spectra which are interpreted in terms of the radicals in parentheses: $Me_4Sn$ ($Me_3\dot{S}n$, $Me_4\dot{S}n^-$, $Me_5Sn$, $H_2\dot{C}SnMe_3$); $Et_4Sn$ ($Et_3\dot{S}n$, $Me\dot{C}HSnEt_3$, $H_2\dot{C}CH_2SnEt_3$); $Bu_4Sn$ ($Bu_3\dot{S}n$, $Et\dot{C}HCH_2SnBu_3$, $R\dot{C}HSnBu_3$); $Me_3S\dot{n}Cl$ ($Me_3\dot{S}nSCl^-$, $Me_3\dot{S}n$ $H_2\dot{C}SnMe_2Cl$); $Bu_3SnCl$ ($Bu_3\dot{S}n$, $Et\dot{C}HCH_2SnBu_2Cl$, $Pr\dot{C}HSnBu_2Cl$); $Me_6Sn_2$ ($Me_2\dot{S}nSnMe_3$, $H_2CSnMe_2$-$SnMe_3$); $Ph_6Sn_2$ ($Ph_6Sn_2^-$); and $Ph_3SnH$ ($Ph_3Sn\cdot$). Interesting aspects of these results include the pyramidal character of $R_3\dot{S}n$ radicals and the low spin density on tin for $Me_5\dot{S}n$, which is thought to have $D_{3h}$ symmetry with major spin density on the axial methyl groups. The absence of hyperfine interaction from the β-Cl or β-$SnMe_3$ groups for $H_2\dot{C}Sn(Me)_2Cl$ and $H_2\dot{C}Sn(Me)_2SnMe_3$ suggests that these groups lie near the nodal plane of the half-occupied 2*p* (carbon) orbital, in complete contrast with the preferred conformation for the corresponding carbon radicals, $H_2\dot{C}CR_2Cl$ and $H_2\dot{C}CR_2SnMe_3$.

IT is now well established that, although alkyl radicals, $R_3C\cdot$, are planar,[2] or nearly so,[3] silyl radicals $R_3Si$ are pyramidal.[4-6] We have shown[7] that on going across the Periodic Table from $R_3Al^{-\cdot}$ to $R_3P^{+\cdot}$ radicals there is a considerable flattening, which is in good accord with predictions based on Pauling's electronegativity rules.[8]

We initiated this study to probe structural changes for $R_3\dot{M}$ radicals on going down the Periodic Table. Since then Jackel and Gordy[9] have reported an e.s.r. spectrum assigned to $^{117/119}SnH_3$, Schmidt *et al.*[10] detected signals assigned to $Ph_3Sn\cdot$ and $Bu^i_3Sn\cdot$, and Watts and Ingold[11] detected $Me_3Sn\cdot$ radicals in the liquid phase. However, in the last two studies, satellite lines from $^{117/119}$Sn were not detectable.

When our studies were almost complete, Bennett and Howard[12] reported the formation of $Me_3Sn\cdot$ and $Me_3Pb\cdot$ radicals by reaction (1) on a rotating cryostat at 77 K.

$$Me_3MCl + Na \longrightarrow NaCl + Me_3M\cdot \qquad (1)$$

Their well defined e.s.r. spectra were unambiguously assigned and have been of assistance in the interpretation of our more complicated e.s.r. spectra resulting from high energy irradiation.

Also after this work was complete, a paper by Lloyd and Rogers describing the effect of γ-rays on $Me_4Sn$, $Me_3SnCl$, $Me_2SnCl_2$, and $MeSnCl_3$ appeared.[13] These authors used both the pure substrates and 'solutions' in adamantane, but in general did not report the species described in the present study. Coupling to $^{117/119}$Sn was only observed for $Me_3Sn\cdot$ radicals. This radical in adamantane gave an isotropic spectrum, but the very high coupling to $^{119}$Sn (1983 G) was derived by a second-order procedure which is unfortunately not satisfactory for such large coupling constants.

Also of interpretative use have been our own results for the radicals $Ph_3\dot{P}bCl^-$ and $Ph_3\dot{P}bBr^-$ which show hyperfine features for $^{207}$Pb as well as $^{35/37}$Cl and $^{79/81}$Br nuclei.[14] We have also detected a species thought to be $Ph_4\dot{A}s$, which is isostructural with $Me_4\dot{S}n^-$, thought to be one of the products in the present study.[15]

In the radiation chemistry of trialkylphosphines, the

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[1] Part CXLVI, S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1973, **70**, 1280

[2] M. C. R. Symons, *Nature*, 1969, **224**, 686; *Mol. Phys.*, 1972, **24**, 461; *Tetrahedron Letters*, 1973, 207.

[3] D. E. Wood, L. F. Williams, and R. F. Sprecher, *J. Amer. Chem. Soc.*, 1972, **94**, 6241.

[4] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3084.

[5] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 3938.

[6] S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc.* (*A*), 1970, 348.

[7] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290.

[8] L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1928, **14**, 349; *J. Chem. Phys.*, 1969, **51**, 2767.

[9] G. S. Jackel and W. Gordy, *Phys. Rev.*, 1968, **176**, 443.

[10] V. Schmidt, K. Kabitzke, K. Markau, and W. P. Neumann, *Chem. Ber.*, 1965, **98**, 3827.

[11] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

[12] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[13] R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2459.

[14] O. P. Anderson, S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Mol. Phys.*, 1973, **26**, 1561.

[15] S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Chem. Phys. Letters*, 1973, **23**, 508.

' dimerisation ' process (2) occurs readily.[16] The present

$$R_3P^{\cdot +} + R_3P \longrightarrow R_3P\text{–}PR_3^{+} \qquad (2)$$

studies were therefore extended to include the molecules $(Me_3Sn)_2$ and $(Ph_3Sn)_2$, which might be expected to form similar species by electron capture. Our results for $H_2\dot{C}SnMe_3$ have been reported,[17] and compared with those of Mackey and Wood.[18] The present results for the related $H_2\dot{C}Sn(Me)_2Cl$ and $H_2\dot{C}Sn(Me)_2SnMe_3$ radicals are of significance in the light of recent studies of strongly interacting β-groups (X) in the analogous carbon radicals, $R_2\dot{C}C(R)_2X$.[19-23] Hoppner and Lassmann[24] also studied the radicals $H_2\dot{C}SnMe_3$ and $H_2\dot{C}SnMe_2Cl$ in *X*-irradiated $SnMe_4$ and $Me_3SnCl$.

It is also of interest to compare the present results for covalent tin(IV) compounds with those previously reported for radicals loosely described as ' $Sn^{3+}$ ' obtained from more ionic tin(II) and tin(IV) complexes.[25]

E.s.r. data for various organotin radicals

| | | Hyperfine coupling constants (G)[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $^{119}Sn$[b] | | | | | | |
| Source | Radical | $A_{\parallel}$ | $A_{\perp}$ | $A_{iso}$ | $2B$ | $^1H$ and others | *g* Values | $a_{5s}$[c] |
| $Me_4Sn$ | $Me_3Sn\cdot$ | 1950 ± 50 | 1350 ± 20 | 1550 | 400 | $a_{Me}$ 2·75[e] | $g_{\parallel}$ 2·000<br>$g_{\perp}$ 2·027 | $0{\cdot}15_5$ |
| $Me_6Sn_2$ | $Me_3Sn\cdot$ | | | | | | $g_{av}$ 2·017[e] | |
| $Me_3SnCl$ | $Me_3Sn\cdot$ | | 1415 | | | | | |
| $Me_3SnCl$[d] | $Me_3Sn\cdot$ | 2157 | 1262 | 1611 | | | $g_x$ 1·995<br>$g_y$ 2·0243<br>$g_z$ 2·0296 | $0{\cdot}16_1$ |
| $Et_4Sn$ | $Et_3Sn\cdot$ | 1950 ± 60 | 1350 ± 30 | 1550 | 400 | | $g_{av}$ *ca.* 2·0 | $0{\cdot}15_5$ |
| $Bu_4Sn$ | $Bu_3Sn\cdot$ | 1950 ± 100 | 1350 ± 50 | 1550 | 400 | | $g_{av}$ *ca.* 2·0 | $0{\cdot}15_5$ |
| $Ph_3SnH$ | $Ph_3Sn\cdot$ | 1950 ± 100 | 1350 ± 50 | 1550 | 400 | | $g_{av}$ *ca.* 2·0 | $0{\cdot}15_5$ |
| $Me_3SnCl$ | $Me_2\dot{S}nCl$ * | 2037 ± 50 | 1626 ± 30 | 1780 | 307 | (Cl) ~ 0 ± 10 *<br>($A_{Cl}$ = 9·7) | $g_{av}$ *ca.* 2·0 | $0{\cdot}17_8$ |
| $Me_6Sn_2$ | $Me_2\dot{S}n(1)Sn(2)Me_3$ | (1) 1681 ± 50<br>(2) 250 ± 10 | 916 ± 20 | 1171<br>250 | 510 | ($^1H$) 4·5 ± 0·5 | | $0{\cdot}11_7$ |
| $Me_4Sn$ | $Me_4Sn^{-\cdot}$ | 2101 | 1672 | 1815 | 286 | | $g_{av}$ *ca.* 2·0 | $0{\cdot}18_2$ |
| $Me_3SnCl$ | $Me_3SnCl^-$ | 2696 ± 60 | 2280 ± 40 | 2419 | 277 | (Cl) *ca.* 30 ± 10[f] | | $0{\cdot}24_2$ |
| $Me_4Sn$ | $Me_5Sn\cdot$ | 650 | 400 | 483 | 167 | *ca.* 18 | | $0{\cdot}04_8$ |
| $Me_4Sn$ | $H_2\dot{C}SnMe_3$[g] | 164 | 128 | 140 | 24 | ($^1H$) ∥ 26·7<br>⊥ 18·7 | $g_x$ 1·996<br>$g_y$ 2·000<br>$g_z$ 2·003 | $0{\cdot}01_4$ |
| $Me_3SnCl$ | $H_2\dot{C}SnMe_2Cl$ | 155 | 120 | 132 | 23 | ($^1H$) ∥ 26<br>⊥ 19<br>(Cl) ~ 0 ± 3 | *g* 2·000<br>$g_{\perp}$ 2·003 | $0{\cdot}01_3$ |
| $Me_6Sn_2$ | $H_2\dot{C}Sn(1)Sn(2)Me_3$<br>$H_2\dot{C}Sn(1)Me_2Sn(2)Me_3$ | (1) 152<br>(2) 0 ± 4 | 120 | 131 | 21 | | | |
| $Et_4Sn$ | $H_2\dot{C}CH_2SnEt_3$ | *ca.* 409[h] | | | | $^1H(\alpha)$ ~ 20<br>$^1H(\beta)$ ~ 13 | $g_{av}$ *ca.* 2·006[h]<br>$g_{av}$ *ca.* 2·006[h] | $0{\cdot}04_1$ |
| $Bu_4Sn$ | $Et\dot{C}HCH_2SnBu_3$ | *ca.* 420[h] | | | | | $g_{av}$ *ca.* 2·006[h] | $0{\cdot}04_2$ |
| $Bu_3SnCl$ | $Et\dot{C}HCH_2SnBu_2Cl$ | *ca.* 679[h] | | | | | $g_{av}$ *ca.* 2·006[h] | $0{\cdot}06_8$ |
| $Ph_6Sn_2$ | $Ph_6Sn_2^-$ | 1730 ± 50 | 1462 ± 20 | 1551 | 179 | | $g_{av}$ *ca.* 2·006[h] | $0{\cdot}015_5$ |

[a] 1G = $10^{-4}$mT. Data estimated using the Breit–Rabi equations when necessary. [b] $^{117}Sn$ Features were generally resolved and the resulting data agreed well with those reported for $^{119}Sn$. [c] Deduced from $A_{iso}$ ($^{119}Sn$) by dividing by $A^0$, the calculated value for unit spin density in the 5*s* atomic orbital. We have found that the most reasonable value to use is *ca.* 10,000 G.[25] [d] By interacting with sodium, taken from ref. 12. [e] Ref. 11. [f] Individual features not clearly resolved. [g] Data for $Me\dot{C}HSnEt_3$ from $Et_4Sn$, $Pr\dot{C}HSnBu_3$ ($Bu_4Sn$), and $Pr\dot{C}HSnBu_2Cl$ ($Bu_3SnCl$) were the same, within experimental error. [h] No clearly defined anisotropy. [i] On each Sn atom.

## EXPERIMENTAL

Tetramethyltin and trimethyltin chloride were obtained from B.D.H., hexaphenylditin and triphenylstannane from Alpha Inorganics, and tetraethyltin, tetrabutyltin, tributyltin chloride, and hexamethylditin from K and K. Hexamethylditin and triphenylstannane were purified by vacuum distillation and subsequent manipulations were performed in a nitrogen glove-bag. Hexaphenylditin was recrystallised from chloroform–ethanol and all other samples were used as received.

Samples in the form of glassy beads or finely ground powders were irradiated for 1—2 h, at 77 K, in a Vickrad γ-ray source (nominal dose rate 4 Mrad $h^{-1}$). E.s.r. spectra were obtained at 77 K using a quartz Dewar insert to a Varian E3 spectrometer. Annealing studies were carried out by warming for increasing time intervals followed by quenching and measuring at 77 K.

## RESULTS AND DISCUSSION

The major results are summarised in the Table and the Figures.

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[16] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1589.

[17] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1063.

[18] J. H. Mackey and D. E. Wood, *Mol. Phys.*, 1970, **18**, 783.

[19] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

[20] A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 622.

[21] A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1971, **93**, 7330.

[22] A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Letters*, 1970, **5**, 552.

[23] T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 1752.

[24] K. Hoppner and G. Lassmann, *Z. Naturforsch.*, 1968, **A23**, 1758.

[25] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J. Phys. Chem.*, 1972, **76**, 141; R. J. Booth, R. S. Eachus, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2233.

*Tetramethylstannane*.—In addition to features in the central region, which are due, primarily, to a single asymmetric line from $Me_3\dot{S}n$ radicals together with characteristic features for $H_2\dot{C}SnMe_3$ radicals previously discussed,[17] high- and low-field satellite lines were detected (Figure 1) which are assigned to species containing $^{117}Sn$ or $^{119}Sn$ [$^{117}Sn$ ($I = 1/2$) 7·67%, $^{119}Sn$($I = 1/2$) 8·68%]. One set (A) clearly falls in the regions found by Bennett and Howard[12] for $Me_3Sn\cdot$ and we accept their assignment except that our species, after slight annealing, had the axial symmetry expected for this radical.

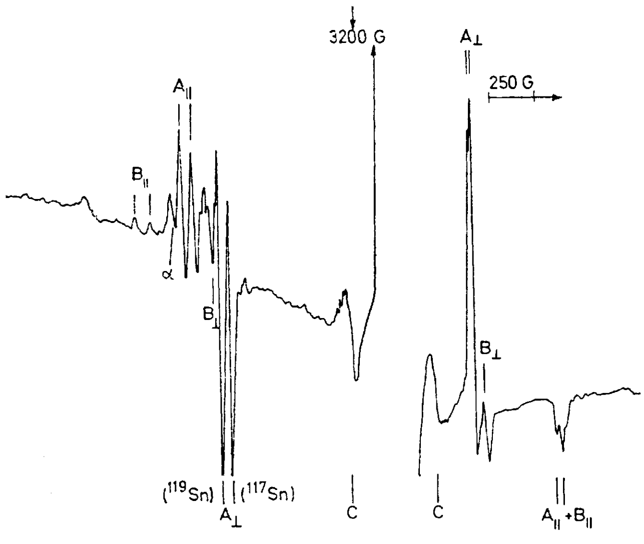

FIGURE 1 First derivative e.s.r. spectrum for tetramethylstannane after exposure to $^{60}Co$ $\gamma$-rays at 77 K and slight annealing. A, B, and C are features assigned to $^{117/119}SnMe_3$, $^{117/119}SnMe_4^-$, and $^{117/119}SnMe_5$ respectively. The line marked $\alpha$ remains unidentified. This was lost selectively on further annealing, prior to the loss of features assigned to $Me_4Sn^-$ (B)

The other centre (B), which probably also has near axial symmetry, was lost on slight annealing above 77 K. We tentatively suggest that this species is the previously unknown radical $Me_4\dot{S}n^-$. This radical is expected, by comparison with isostructural $\cdot PL_4$ radicals, to have two near axial methyl groups and two equatorial methyl groups, the *s–p* hybridised orbital of the unpaired electron taking up in a formal sense the third equatorial position of a pseudo-trigonal bipyramid.[26,27] Unfortunately, apart from the radical $\dot{P}H_4$,[28] which, if correctly identified, has anomalous properties,[29] no $R_4P\cdot$ ($R = H$ or alkyl) radicals are known. However, we have introduced an empirical but convincing extrapolative procedure which enables us to predict $A_{iso}(^{31}P)$ to be in the region of 500 G.[29] Our recent results assigned to $Ph_4As\cdot$ radicals[15] lend weight to this suggestion. After conversion, in the normal approximate manner,[30] into orbital populations, this predicts an *s* orbital spin density of *ca.* 14%, which, reconverted into gauss for $^{119}Sn$, corresponds to *ca.* 1060 G. This approximate value is based on the $A^0$ value of *ca.* 7577 G for $^{119}Sn$, calculated from the wavefunctions of Froese:[31] it is probable that the $A^0$ value should be increased to nearer 10,000 G,[32] which would increase the predicted coupling to *ca.* 1400 G. Our value of $A_{iso}$ of *ca.* 1815 G for $\dot{S}nMe_4^-$ accords reasonably well with this prediction, but suggests that there is a real increase in *s* character on going from phosphorus to tin. Coupling to the protons of the methyl groups is expected to be small,[26] as is the case for $Me_3Sn\cdot$,[11] and we would not expect to detect this in our solid state studies. [It should be pointed out that the precise magnitude of our quoted data for $Me_4Sn^{-\cdot}$ and $Me_3Sn\cdot$ hinges very much upon the method used to correct for non-linearity. We have used an adaptation of the Breit–Rabi equation for axial symmetry, previously described,[25] which gives fair agreement with the values of Bennett and Howard for $Me_3Sn\cdot$, given in the Table. Certainly the *g* values estimated from the outer lines agree reasonably with those obtained from the central features for radicals containing non-magnetic tin isotopes. The results for $Me_4Sn^{-\cdot}$ suggest that the central line for this species more or less coincides with that for $Me_3Sn\cdot$.]

After annealing, a doublet (C in Figure 1) became better defined and split into multiplets having defined parallel and perpendicular components. Under higher resolution these appeared to be quintets or septets with a separation of *ca.* 18 G. To explain the results (Table), we require a structure which would have two methyl groups giving a relatively strong interaction with the unpaired electron and a tin atom with a relatively low interaction, both with respect to *s* and *p* orbitals. A reasonable candidate, both from mechanistic and structural viewpoints, is $Me_5\dot{S}n$. The most favourable structure for this radical would probably place three strongly bonded methyl groups trigonally in a plane, with two more weakly bonded groups axial and equivalent. These would share two electrons in a three-centre bonding orbital comprising $5p_z$ on tin, leaving the unpaired electron in a (nearly) non-bonding orbital on the two methyl groups.

This qualitative description accords well with the extended Hückel calculations of Hoffmann *et al.*[33] for $\dot{P}H_5$ and with the *ab initio* calculations in $\dot{P}H_5$ by Rauk *et al.*[34] These authors stress that the $D_{3h}$ molecule is likely to be most stable, with the outermost 'non-bonding' $2a_1'$ orbital well removed from the filled

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[26] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[27] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.

[28] C. A. McDowell, K. A. R. Mitchell, and P. Raghunathan, *J. Chem. Phys.*, 1972, **57**, 1699.

[29] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

[30] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[31] Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[32] J. H. Mackey and D. E. Wood, *J. Chem. Phys.*, 1970, **52**, 4914.

[33] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

[34] A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 3035.

bonding orbitals. Hence, loss of an electron should be from this level, and there seems to be no compelling reason for any consequent distortion.

These considerations rule out $H\dot{S}nMe_4$ for species C since a very large hyperfine coupling to the added proton would be expected, and none is apparent. However, our results are quite reasonable for $Me_5\dot{S}n$. The proton coupling, which is probably positive, can be compared with that found for the methyl protons in a $\dot{P}bMe^{2+}$ species formed in irradiated lead acetate,[35] which was *ca.* 21 G, with an experimental reason for favouring a positive sign. We estimated the spin density on methyl to be *ca.* 40% for this radical so our present result of *ca.* 18 G accords well with the spin being largely on two methyl groups. Again in agreement with the model, the coupling to $^{117/119}Sn$ is very much less than that for $^{207}Pb$ in $\cdot PbMe^{2+}$ despite the fact that the $A^0$ values are similar for these metals. Indeed, the observed hyperfine coupling to tin may well arise largely from spin polarisation of inner bonding electrons rather than from direct delocalisation onto tin, although this is possible *via* the 5*s* or $5d_{z^2}$ orbitals.

*Tetraethyl- and Tetra-n-butyl-stannane.*—In both cases, the centre regions were dominated by features for the α-radicals, $R\dot{C}HSnR_3$. These were normal and will not be discussed further. In addition, strong features from β-radicals, $R\dot{C}HCH_2SnR_3$, were detected (Figure 2, B), as described previously.[20] In addition, however, high- and low-field features were detected (Figure 2, A) which we assign to $R_3Sn\cdot$ radicals. These have $^{117}Sn$ and $^{119}Sn$ coupling constants indistinguishable from those for the trimethyl derivative (Table) within the error caused by the increased linewidth. No features assignable to the molecular anions were detected for these compounds, nor could we distinguish features for $R_5Sn\cdot$ radicals. This is not surprising, however, since their features would be masked by intense doublets from the β-Sn species.[20]

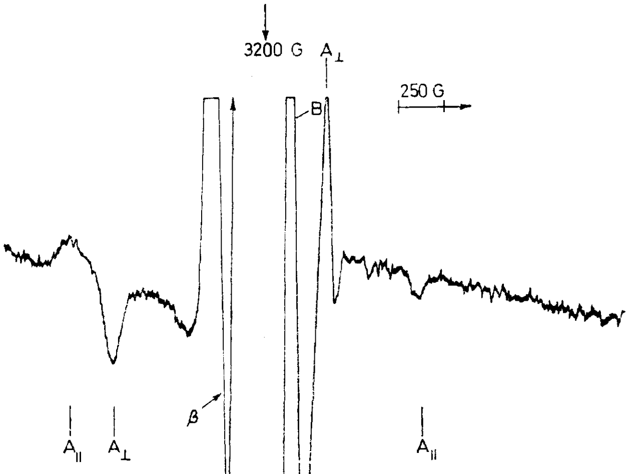

FIGURE 2 First derivative e.s.r. spectrum for tetraethylstannane after exposure to $^{60}Co$ γ-rays at 77 K, showing features A assigned to $Et_3Sn\cdot$ radicals and B assigned to $\dot{C}H_2CH_2SnEt_3$ radicals

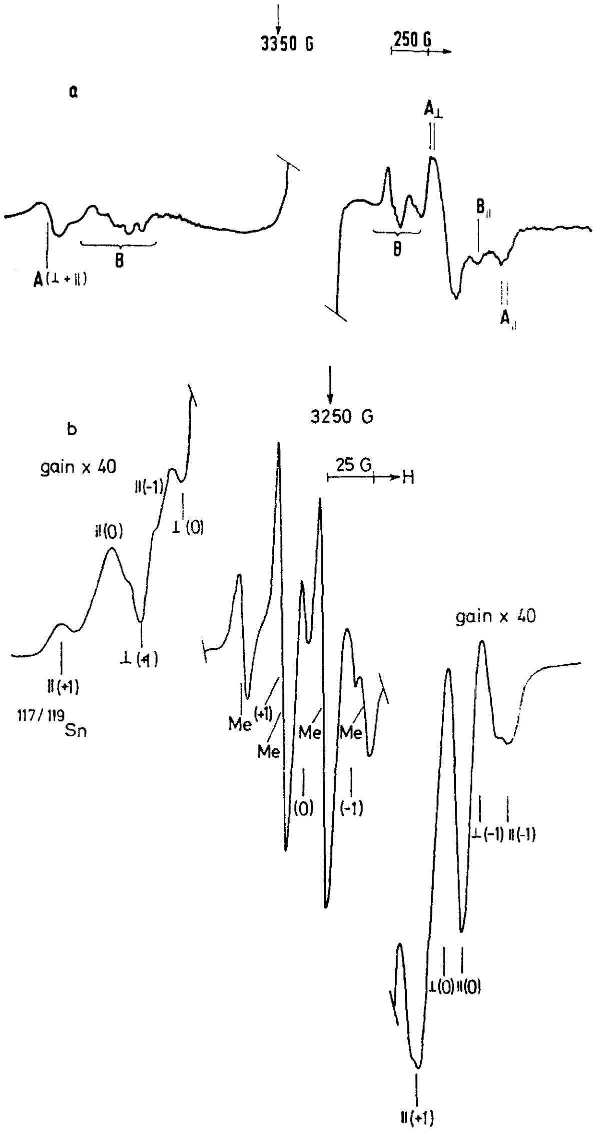

FIGURE 3 First derivative e.s.r. spectrum for trimethyltin chloride after exposure to $^{60}Co$ γ-rays at 77 K, showing a, outer features assigned to $(Me_3{}^{117/119}SnCl)^-$ (A) and $Me_2{}^{117/119}SnCl$ (B) and b, central features assigned to $H_2\dot{C}SnMe_2Cl$. Features from trapped methyl radicals are also indicated

*Trimethyl- and Tri-n-butyl-tin Chloride.*—The most significant result for the methyl derivative was the appearance of a pair of hyperfine features (Figure 3, A) clearly removed from the positions expected for $Me_3Sn\cdot$ radicals, containing $^{117/119}Sn$. In view of Bennett and Howard's results,[12] we had expected to detect $Me_3Sn\cdot$ radicals as major products, but our work on $Ph_3PbCl$ and $Ph_3PbBr$[14] showed that under our conditions the anions $Ph_3PbHal^-$ are favoured. The results obtained for $Me_3SnCl$ are in good agreement with the latter interpretation, except that there was no clear resolution of the expected small coupling to $^{35/37}Cl$. In contrast,

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[35] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 638.

solutions in methanol gave clear features for $Me_3Sn\cdot$. Thus it seems that simple addition of an electron gives $Me_3\dot{S}nCl^-$ initially, but that in the presence of $Na^+$ or methanol molecules this loses chloride ion to give $Me_3Sn\cdot$. The fact that no anion was detected for $Bu_3SnCl$ but $Bu_3Sn\cdot$ radicals were clearly formed, shows how delicate the balance must be at 77 K.

The increase in the hyperfine coupling parameters for $Me_3\dot{S}nCl^-$ relative to $Me_4\dot{S}n^-$ is in accord with Pauling's rules[8] and ties in closely with experience for phosphoranyl radicals.[26] Thus the structure of $Me_3\dot{S}nCl^-$ is probably closer to that envisaged for dihalides such as $\dot{S}O_2Cl_2^-$,[36] rather than to the $\sigma^*$ structure envisaged for the anions of various *N*-halogenoamides.[37]

The central features for irradiated $Me_3SnCl$ (Figure 3b) are assignable to $H_2\dot{C}SnR_3$ type radicals, together initially, with low concentrations of methyl radicals. These results are important in that, even after careful annealing, no hyperfine coupling to $^{35/37}Cl$ could be detected, in agreement with a previous report.[24] This is in marked contrast with results for $R_2\dot{C}C(R)_2Cl$ radicals,[21,24] and suggests either that the chlorine atom lies near to the radical plane making $\sigma$–$\pi$ overlap impossible or that, for some reason, such overlap does not result in a large coupling to $^{35/37}Cl$ in this instance. Since, in our view,[21] the hyperfine coupling and the preferred orientation are closely linked, the former seems to be more probable.

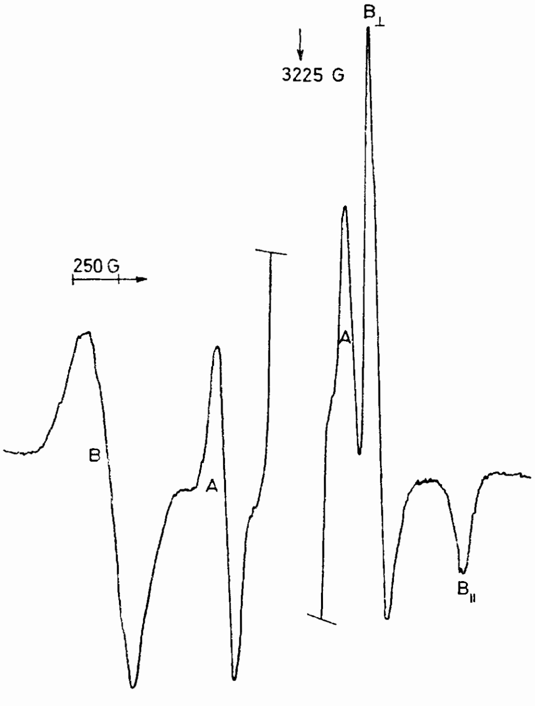
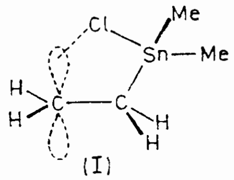


FIGURE 4 First derivative e.s.r. spectrum for tri-n-butyltin chloride after exposure to $^{60}Co$ $\gamma$-rays at 77 K, showing broad features B assigned to $Bu_3{}^{117/119}Sn\cdot$ radicals together with an isotropic doublet A assigned to $Et\dot{C}HCH_2Sn(Cl)Bu_2$ radicals

In the case of $Bu_3SnCl$, extra, narrow doublet, features separated by *ca.* 680 G were obtained (Figure 4, A). The most probable assignment is the β-radical $Et\dot{C}HCH_2Sn(Bu)_2Cl$, which, by analogy with our other results is most likely to be formed. If we accept this identification, then we need to explain the considerable increase in $A_{iso}(^{117/119}Sn)$ from that of *ca.* 400 G normally found for such β-radicals.[20]

We suggest that this increase can be related to that also observed for $A(^{117/119}Sn)$ for the $H_2\dot{C}Sn(Me)_2Cl$ radicals relative to that for $H_2\dot{C}SnMe_3$ radicals (Table). We postulate an indirect effect which is linked to Pauling's electronegativity rule.[8] We suggest that the bond between tin and carbon gains more 5*s* character when methyl is replaced by the far more electronegative chlorine atom. This increase in 5*s* character is then reflected as an increase in $A_{iso}$, either for the spin polarisation effect envisaged for $H_2\dot{C}SnR_3$ radicals[17] or the hyperconjugative effect for $R_2\dot{C}C(R)_2SnR_3$ radicals. In the latter case, however, an alternative mode of interaction involving the chlorine atom directly, as in (I), is possible, though we would have expected this to result in well-defined $^{35/37}Cl$ hyperfine structure.



(I)

*Hexaphenyldistannane*.—The centre of the spectrum (Figure 5a) comprises a feature associated with some outer satellite lines, together with shoulders (A) and other poorly defined central lines The outer features (Figure 5b, B) are indicative of hyperfine coupling to $^{117}Sn$ and $^{119}Sn$. Although the hyperfine coupling displays near axial symmetry the *g* tensor components in this case do not (Table).

We would expect to obtain both $(Ph_6Sn_2)^+$ and $(Ph_6Sn_2)^-$ radical ions initially from this compound and the latter could break down to give $Ph_3Sn\cdot$ [reaction (3)].

$$Ph_3Sn\dot{-}SnPh_3^- \longrightarrow Ph_3Sn^- + Ph_3Sn\cdot \qquad (3)$$

However, the reverse of this step was observed for certain trialkylphosphines[16] [equation (2)], and hence we expected these tin anions to be stable. They should be structurally similar to $R_3P$–$PR_3^+$ radicals, with the extra electron in the Sn–Sn $\sigma^*$ orbital, but since only one tin atom is likely to be magnetic this would result in a coupling considerably reduced from that for $R_3Sn\cdot$ radicals. However, since the bond angle for each $Ph_3Sn$– unit should be closer to the tetrahedral value than that for $R_2Sn\cdot$ radicals, the anisotropic coupling should be reduced more than the isotropic coupling. This is just what is observed for species B in Figure 5b, as is shown by the derived hyperfine parameters and the estimated orbital populations (Table). We are, therefore, fairly confident about this identification. This

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[36] K. V. S. Rao and M. C. R. Symons, *J.C.S. Dalton*, 1973, 9.

[37] G. W. Neilson and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1582.

result means that a tin–tin σ-bond is a good electron trap. Unfortunately, we were unable to detect signals from species containing two magnetic tin isotopes because of lack of sensitivity.

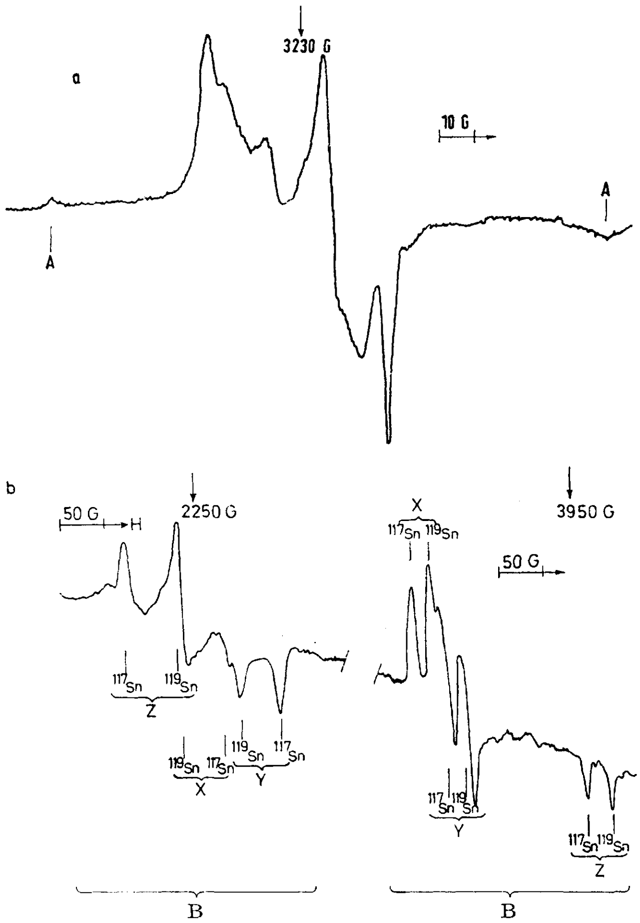


FIGURE 5 First derivative e.s.r. spectrum for hexaphenyldistannane after exposure to $^{60}Co$ γ-rays at 77 K, a, showing central features for $Ph_6Sn_2^-$ together with unassigned features and satellites A, and b, showing outer $^{117/119}Sn$ satellites B assigned to $(Ph_6Sn_2)^-$ anion radicals

We would anticipate that electron loss would also occur with some facility from the tin–tin σ-bond. This would leave one electron shared between the two tin atoms and hence the tendency towards local planarity at the tin centres would be very large. This would lead to hyperfine tensor components from $^{117/119}Sn$ exhibiting a relatively large anisotropy and a greatly reduced isotropy. We therefore considered that the shoulders separated by *ca.* 160 G (Figure 5a, A) might be associated with the cation. However, a search for a second set of satellite lines from radicals containing two magnetic tin isotopes established that no such features with the predicted relative intensities, were present. Thus, this species is probably not the symmetrical radical cation, and we are unable to offer any firm identification.

*Triphenylstannane.*—Only broad satellite features in the regions expected for $Ph_3Sn\cdot$ containing $^{117/119}Sn$ were observed (see Table) and the central (*g* 2) region was dominated by strong features assignable to cyclohexadienyl radicals. No clear features for the radical anions were obtainable.

*Hexamethyldistannane.*—Of the two sets of outer features (A and B) in Figure 6a, B are clearly due to $Me_3Sn\cdot$ radicals. Set A are remarkably similar and we suggest that they are due to $Me_2\dot{S}nSnMe_3$ radicals. The radical anions $(Me_3Sn{-}SnMe_3)^-$ are clearly not trapped under these conditions.

The species $Me_2\dot{S}nSnMe_3$ should exhibit a second pair of satellite lines for the weakly interacting α-tin atom, and we suggest that the features (A) showing extra structure (obtained after slight annealing) in Figure 6b are the required lines. This extra (proton) structure is not resolved on the outermost features, but this is precluded by their increased width. The central features for radicals containing non-magnetic tin isotopes are also partially resolved (A) although they are considerably overlapped by the perpendicular feature for $Me_3Sn\cdot$ (B). We have ascertained, using a Du Pont curve resolver,

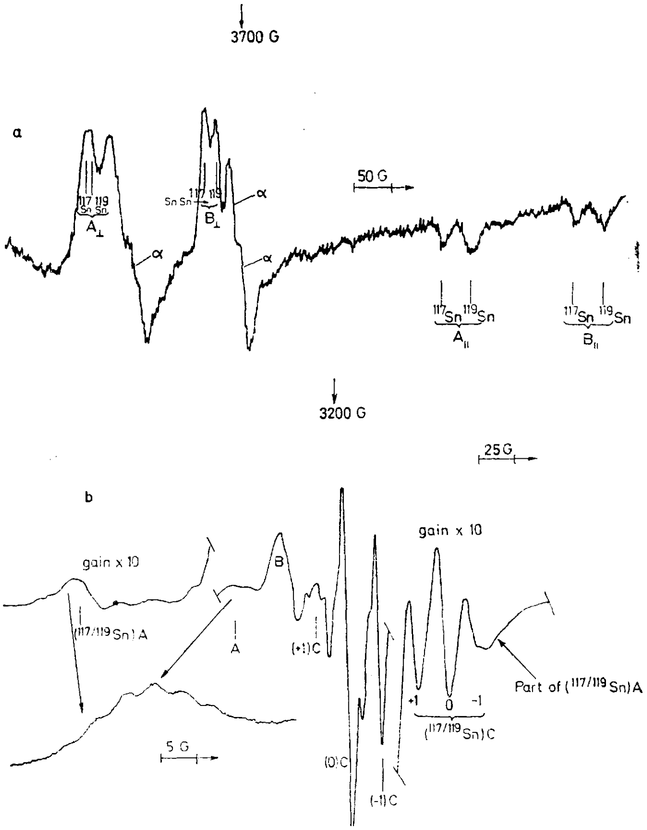
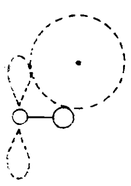


FIGURE 6 First derivative e.s.r. spectrum for hexamethyldistannane after exposure to $^{60}Co$ γ-rays at 77 K. a Shows outer $^{117/119}Sn$ satellites in the high field region assigned A, to $Me_2Sn(1)\dot{S}n(2)Me_3$ containing $^{117/119}Sn(1)$ and non-magnetic Sn(2) atoms (α features probably indicating non-axial symmetry were lost selectively on annealing), and B, to $Me_3Sn\cdot$ radicals. b Shows central features for both these radicals, with satellite lines from $Me_2\dot{S}n(1)Sn(2)Me_3$ radicals containing $^{117/119}Sn(2)$: A, enlarged in the insert to illustrate the resolution of proton hyperfine features, a broad perpendicular feature for $Me_3Sn\cdot$ radicals B, and sets of lines and satellites C assigned to $H_2\dot{C}Sn(Me)_2SnMe_3$ radicals

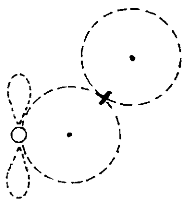
that there are seven hyperfine components rather than ten, which means that it is the protons of the $Me_2\dot{S}n$ function rather than those of the $SnMe_3$ group that are coupled to the electron spin.

It is of interest to compare these results with those for $Me_3Sn\cdot$ radicals in the liquid phase, which displayed a proton coupling of 2·75 G.[11] Our increased coupling of 4·5 G, taken together with the fall in $A_{iso}(^{117/119}Sn)$, strongly suggests that replacement of Me by $Me_3Sn$ results in a flattening at the radical centre. (This argument is only valid if the proton coupling is positive, which is certainly expected on theoretical grounds.)

The other result of interest is that the e.s.r. spectrum assigned to $H_2\dot{C}Sn(Me)_2SnMe_3$ radicals (Figure 6b, C) is almost identical with that for $H_2\dot{C}SnMe_3$ (Table). The absence of a large hyperfine interaction with the β-tin atom is in accord with our results for the corresponding chloro-derivative and again suggests that the $SnMe_3$ group lies close to the plane of the radical. These two results suggest that the gain in stability exhibited by $R_2\dot{C}CR_2{-}X$ radicals, when X is a ' heavy ' atom or group such as $PR_3^+$ or $SnR_3$ is greatly reduced or even completely destroyed on replacing the intervening $CR_2$ group by another group containing a heavy atom. We suggest that the cause is related to the relatively large radius of the α-heavy atom, as illustrated in the models (II) and (III). It would be of interest to see if there are mechanistic consequences of this result, since, as has been shown by Eaborn *et al.*[38] and Traylor *et al.*,[39] heavy atom ' hyperconjugation ' can have a marked effect on rates of electrophilic substitutions.



(II)



(III)

*Structure of* $R_3Sn\cdot$ *Radicals.*—Uncertainties in the experimental 2*B* values (Table) and in the calculated $2B^0$ values for $^{117/119}Sn$ (*ca.* 350 G) are such that no good *p* orbital population can be derived. The relatively large values for these radicals nevertheless demonstrate that the unpaired electron is largely confined to the tin atom, as expected. This is especially noteworthy for $Ph_3Sn\cdot$ radicals, which show no evidence for delocalisation onto the aromatic rings.

Our isotropic coupling constants to $^{117/119}Sn$ for $R_3Sn\cdot$ radicals are considerably smaller than the values recently reported for the stable radical tris[bis(trimethylsilyl)-methyl]tin ($A_{iso}$ $^{119}Sn$ 1776 G).[40] This seems to imply that there is a greater deviation from planarity in the latter species, but that is opposite to expectation on electronegativity or steric grounds. The difference is not great, however, in contrast with the results assigned [9] to $\cdot SnH_3$ ($A$ $^{119}Sn$ *ca.* 380 G). However, results for the latter radical must be treated with reserve since the features depicted in the published spectrum [9] are very poorly defined.

*Aspects of Mechanism.*—As usual, we start with the premise that the initial damage process is electron ejection (4) and possibly electron trapping (5). We

$$Me_4Sn \longrightarrow Me_4Sn^{+\cdot} + e^- \tag{4}$$

$$Me_4Sn + e^- \longrightarrow Me_4Sn^{-\cdot} \tag{5}$$

expect the radical cations to be very unstable and to break down either by proton loss, as with hydrocarbon cations, or by loss of methyl [reactions (6) and (7)].

$$Me_4Sn^{+\cdot} \longrightarrow (H^+) + H_2\dot{C}SnMe_3 \tag{6}$$

$$Me_4Sn^{+\cdot} \longrightarrow Me_3Sn^+ + Me\cdot \tag{7}$$

Path (7) is not normally postulated for hydrocarbons, but would be a favourable route for tin(IV) compounds. Since only traces of methyl radicals were detected at 77 K we suggest that they abstract a hydrogen atom from a neighbour [reaction (8)]. However, for tin there

$$Me\cdot + Me_4Sn \longrightarrow CH_4 + H_2\dot{C}SnMe_3 \tag{8}$$

is an alternative, namely addition (9). Neither process

$$Me\cdot + Me_4Sn \longrightarrow Me_5Sn\cdot \tag{9}$$

(8) or (9) explains the formation of $Me_3Sn\cdot$ which is clearly a significant product. Since neither of the primary ions can break down reasonably to give this product, we suggest that the reverse step (10) is of

$$Me_4Sn^{+\cdot} + e^- \longrightarrow Me_4Sn^* \longrightarrow Me\cdot + Me_3Sn\cdot \tag{10}$$

importance (where $Me_4Sn^*$ is an electronically excited molecule).

For $Ph_6Sn_2$, it seems probable that the primary anions are relatively stable. However, this is not the case for $Me_6Sn_2$, which gives $Me_3Sn\cdot$ as a major product. This may reasonably be formed from either cation or anion [reactions (11) or (12)] and we are unable to make

$$(Me_6Sn_2)^{+\cdot} \longrightarrow Me_3Sn^+ + Me_3Sn\cdot \tag{11}$$

$$(Me_6Sn_2)^{-\cdot} \longrightarrow Me_3Sn^- + Me_3Sn\cdot \tag{12}$$

a clear choice. Arguing by analogy, $Me_2\dot{S}nSnMe_3$ is probably formed from an excited state [reaction (13)

$$(Me_6Sn_2)^{+\cdot} + e^- \longrightarrow (Me_6Sn_2)^* \longrightarrow Me\cdot + Me_2\dot{S}nSnMe_3 \tag{13}$$

followed by (14)].

$$Me\cdot + Me_6Sn_2 \longrightarrow CH_4 + H_2\dot{C}Sn(Me)_2SnMe_3 \tag{14}$$

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[38] C. Eaborn, *J. Chem. Soc.*, 1956, 4858; M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1969, **20**, 49; 1970, **24**, 293.

[39] W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 7476.

[40] P. J. Davidson, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 829.