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SULPHUR SUBSTITUTED ORGANOTIN COMPOUNDS.

X *. PREPARATIONS AND REACTIONS OF $Ph_3Sn(CH_2)_nSOC_6H_4Me$-*p* ($n = 3$ OR 4) AND $Ph_3Sn(CH_2)_nSO_2C_6H_4Me$-*p* ($n = 2$, 3 OR 4)

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Summary

The preparations of $Ph_3Sn(CH_2)_nSOC_6H_4Me$-*p* (II) ($n = 3$ or 4) and $Ph_3Sn(CH_2)_nSO_2C_6H_4Me$-*p* (III) ($n = 3$ or 4) were achieved by the controlled oxidation of $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* (I) ($n = 3$ or 4) using *m*-chloroperbenzoic acid. Similar reactions with I ($n = 2$) failed to produce the corresponding sulphoxide or sulphone; III ($n = 2$) was, however, prepared by the reaction of Ph_3SnH and $CH_2{=}CHSO_2C_6H_4Me$-*p*. Triphenyltin hydride did not add to $CH_2{=}CHSO$-C_6H_4Me-*p*, but instead catalysed the decomposition of Ph_3SnH to $Ph_3SnSnPh_3$. The reactions of II or III with iodine, bromine or mercury(II) chloride all led to phenyltin bond cleavage, to give $Ph_2XSn(CH_2)_nSO_mC_6H_4Me$-*p* (X = I, Br or Cl; $m = 1,2$).

Introduction

Various sulphidoalkyltin compounds have been prepared and studied; included among these are compounds of the types $R_3Sn(CH_2)_nSR'$ ($n = 1$ [2,3], $n = 2$ [2,4,5], $n = 3$ [6,7] and $n = 4$ [6]), $R_3SnCR'(SR^2)_2$ [8] (including, 1,3-dithianes [8a] and 1,3,5,7-tetrathiocane derivatives [8b]), $R_3SnC(SR')=CR^2_2$ [9], $R_3SnCH=CHSR'$ [10] and $R_3SnCH_2CH(SR')_2$. Sulphinyl- and sulphonyl-alkyltins have not been as fully studied, although $Bu_3SnC(SOPh)=CH_2$ [9a], and $Bu_3SnCH_2SO_2R$ [3] have been reported. In addition, $Bu_3SnCH_2SO_mPh$ ($m = 1$ [11] or 2 [12]) and $Me_3Sn(CH_2)_nSO_2R$ ($n = 2$ or 3) [13] have been mentioned in patents.

As a follow up to our work with $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* (I) we wish to report preparations and some reactions of $Ph_3Sn(CH_2)_nSOC_6H_4Me$-*p* (II) ($n = 3$ or 4) and $Ph_3Sn(CH_2)_nSO_2C_6H_4Me$-*p* (III) ($n = 2$, 3 or 4) with electrophilic reagents.

Experimental

Tin compounds, $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* ($n = 2$, 3 or 4) were prepared as described previously [6].

* For part IX see ref. 1.

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Preparation of [3-(p-toluenesulphinyl)propyl]triphenyltin, $Ph_3SnCH_2CH_2CH_2SOC_6H_4Me$-p

To a stirred solution of $Ph_3SnCH_2CH_2CH_2SC_6H_4Me$-*p* (2.80 g, 0.00543 mol) in dichloromethane (20 ml) at 0°C, was added dropwise a solution of *m*-chloroperbenzoic acid (0.936 g, 0.00543 mol) in dichloromethane (40 ml), and the mixture stirred overnight. The reaction solution was washed twice with sodium bicarbonate solution (5%) and the organic layer dried over magnesium sulphate. After filtering, the solvent was removed under reduced pressure to yield an oily solid, which was recrystallised from methanol to give a white crystalline solid, m.p. 84–86°C, yield 72%. ν(SO) 1048(s) cm^{-1}.

Analysis. Found: C, 63.1; H, 5.4; S, 6.0. $C_{28}H_{28}OSSn$ calcd.: C, 63.3; H, 5.3; S, 6.0%.

^1H NMR ($CDCl_3$, 30°C): 7.90 (m, 19H), Ph_3 and SOC_6H_4Me-*p*, 3.07 (t, 2H, $SOCH_2$, *J* 5.0 Hz), 2.38 (s, 3H, Me), 2.28 (m, 4H, $SnCH_2CH_2$).

^{13}C NMR ($CDCl_3$, 30°C): δ 141.6–123.94 (aryl C), 60.84 ($SOCH_2$), 21.35 ($CH_2CH_2CH_2$), 19.87 (Me), 9.93 ($SnCH_2$).

Mass spectrum (70 eV): $[M]^+$(0.9%); $[M-(CH_2)_3]^+$, (1.0%); $[M-Ph]^+$ (4%); $[PhSn(CH_2)_3SOC_6H_4Me\text{-}p]^+$ (5.5%); $[Ph_3Sn]^+$ (100%), $[Ph_2Sn]^+$ (3.5%); $[PhSn]^+$ (20%).

Preparation of [4-(p-toluenesulphinyl)butyl]triphenyltin, $Ph_3SnCH_2CH_2CH_2CH_2SOC_6H_4Me$-p

This was prepared from $Ph_3SnCH_2CH_2CH_2CH_2SC_6H_4Me$-*p* (4.0 g, 0.00756 mol) and *m*-chloroperbenzoic acid (1.340 g, 0.00756 mol) in an analogous manner to that used for $Ph_3SnCH_2CH_2CH_2SOC_6H_4Me$-*p*.

$Ph_3SnCH_2CH_2CH_2CH_2SOC_6H_4Me$-*p*, m.p. 68–69°C, yield 82%, δ(SO) 1048s cm^{-1}.

Analysis. Found: C, 63.8; H, 5.4; S, 5.9. $C_{29}H_{30}OSSn$ calcd.: C, 63.8; H, 5.5; S, 5.9%.

Mössbauer data: IS 1.33 mm sec^{-1}.

^1H NMR ($CDCl_3$, 30°C): δ 7.80–6.80 (m, 19H, Ph_3 and SOC_6H_4Me), 2.70 (t, 2H, $SOCH_2$, *J* 6.0 Hz), 2.37 (s, 3H, Me), 2.00–1.1 (m, 6H, $CH_2CH_2CH_2Sn$).

^{13}C NMR ($CDCl_3$, 30°C): δ 141.16–124.03 (aryl C), 56.50 ($SOCH_2$), 26.20 and 25.90 ($SnCH_2CH_2CH_2$), 21.35 (Me), 10.43 ($SnCH_2$).

Mass spectrum (20 eV): $[M]^+$ (0.1%), $[M-O]^+$ (0.1%), $[M-Ph]^+$ (5%), $[Ph_2SnCH_2CH_2CH_2CH_2SC_6H_4Me\text{-}p]^+$ (3%), $[Ph_3Sn]^+$ (100%), $[Ph_2Sn]^+$ (4%).

Attempted preparation of $Ph_3Sn(CH_2)_2SOC_6H_4Me$-p

By oxidation of [2-(p-tolylthio)ethyl]triphenyltin. To a stirred solution of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (3.0 g, 0.0059 mol) in methanol (100 ml) at 0°C was added a solution of hydrogen peroxide (30%, 0.0059 mol). The mixture was stirred overnight. Chloroform (100 ml) and sodium chloride (4.0 g, 0.0683 mol) were added. The chloroform layer was collected, dried over magnesium sulphate, and the solvent removed under reduced pressure to leave an oily solid. The ^1H NMR spectrum of the residue showed that there were no methylene protons present, and hence none of the desired product had been formed.

Failure was also met using the following oxidants, H_2O_2/SeO_2, *m*-$ClC_6H_4CO_3H$, $NaIO_4$ or $K_2S_2O_8$.

By reaction of triphenyltin hydride and vinyl p-tolyl sulphoxide. To vinyl *p*-tolyl sulphoxide (1.71 g, 0.0114 mol), prepared from 2-bromoethyl *p*-tolyl sulphoxide, and triphenyltin hydride (4.0 g, 0.0114 mol) was added a small amount of azo-bis-isobutyronitrile (AIBN) and the mixture heated at 80–90°C for 5 min. Although vigorous gas evolution occurred, the ^{1}H NMR spectrum of the reaction mixture indicated that the starting material had not reacted. Hexaphenylditin was isolated from the reaction mixture.

Preparation of [2-(p-toluenesulphonyl)ethyl]triphenyltin, $Ph_3SnCH_2CH_2SO_2C_6H_4Me$-p

To triphenyltin hydride, prepared from triphenyltin chloride (8.0 g, 0.0207 mol) was added vinyl *p*-tolyl sulphone [14] (2.6 g, 0.01428 mol) and a little AIBN. The mixture was heated at 80–95°C for 0.5 h. On cooling in ice/water, an oily solid was produced and which was crystallised from methanol to give colourless crystals, m.p. 120–121°C, yield 67%.

Analysis. Found: C, 60.7; H, 4.7; S, 6.1. $C_{27}H_{26}SO_2Sn$ calcd.: C, 60.8; H, 4.9; S, 6.0%. $\nu(SO_2)$ 1311 and 1144 cm^{-1}.

^{1}H NMR ($CDCl_3$, 30°C): δ 7.72 (d, 2H, A portion of AB system, $SO_2C_6H_4Me$), 7.26–7.60 (m, 17H, Ph_3 and B portion of AB system, $SO_2C_6H_4Me$), 3.30 (m, 2H, SO_2CH_2), 2.38 (s, 3H, Me), 1.71 (m, 2H, $SnCH_2$) ^{13}C NMR. ($CDCl_3$, 30°C): δ 144.60–127.57 (aryl C), 54.51 (SO_2CH_2) 21.63 (Me), 2.42 ($SnCH_2$).

Mass spectrum (20 eV): $[M - 28]^+$ (1.5%), $[M - Ph]^+$ (5.5%), $[Ph_2SnSO_2C_6H_4Me\text{-}p]^+$ (1%), $[Ph_2SnCH_2CH_2SO_2]^+$ (8%), $[Ph_3Sn]^+$ (100%), $[Ph_2Sn]^+$ (4%).

Preparation of [3-(p-toluenesulphonyl)propyl]triphenyltin, $Ph_3SnCH_2CH_2CH_2SO_2C_6H_4Me$-p

To a solution of [3-(*p*-tolylthio)propyl]triphenyltin (2.553 g, 0.00495 mol) in dichloromethane (20 ml) at 0°C, was added dropwise with stirring, *m*-perchlorobenzoic acid (2.214 g, 0.0109 mol) in dichloromethane (20 ml) and the mixture stirred overnight. The reaction mixture was washed with sodium bicarbonate solution (5%) (twice) and the organic layer dried over magnesium sulphate. After filtering, the solvent was removed under reduced pressure to yield an oily solid, which was recrystallised from methanol to give a white crystalline solid, m.p. 108.5–109.5°C, yield 78%.

Analysis. Found: C, 61.4; H, 5.0; S, 5.9. $C_{28}H_{28}O_2SSn$ calcd.: C, 61.5; H, 5.1; S, 5.9%. $\nu(SO_2)$ 1311 and 1140 cm^{-1}.

^{1}H NMR ($CDCl_3$, 30°C): 7.80–7.00 (m, 19H, Ph_3 and $SO_2C_6H_4Me$), 3.08 (t, 2H, SO_2CH_2, *J* 8.0 Hz), 2.40 (s, 3H, Me), 2.07 (m, 2H, $CH_2CH_2CH_2$), 1.45 (t, 2H, CH_2Sn, *J* 7.0 Hz).

^{13}C NMR ($CDCl_3$, 30°C): 144.39–127.43 (aryl C), 59.56 (SO_2CH_2), 21.55 ($CH_2CH_2CH_2$), 20.56 (Me), 9.43 ($SnCH_2$).

Mass spectrum (20 eV): $[M]^+$ (0.1%), $[M - Ph]^+$ (35%), $[Ph_2Sn(CH_2)_3SC_6H_4Me\text{-}p]^+$ (0.4%), $[Ph_3Sn]^+$ (100%), $[Ph_2Sn]^+$ (0.5%).

Preparation of [4-(p-toluenesulphonyl)butyl]triphenyltin, $Ph_3SnCH_2CH_2CH_2CH_2SO_2C_6H_4Me$-p

This was prepared, similarly to $Ph_3SnCH_2CH_2CH_2SO_2C_6H_4Me$-*p*, from $Ph_3SnCH_2CH_2CH_2CH_2SC_6H_4Me$-*p* (1.994 g, 0.00376 mol) and *m*-chloroperbenzoic acid (1.431 g, 0.00829 mol).

$Ph_3SnCH_2CH_2CH_2CH_2SO_2C_6H_4Me$-*p*, m.p. 88.5–89.5°C, yield 72%; $\nu(SO_2)$ 1300 and 1141 cm^{-1}.

Analysis. Found: C, 62.0; H, 5.2; S, 5.8. $C_{29}H_{30}O_2SSn$ calcd.:C, 62.0; H, 5.4; S, 5.7%.

Mössbauer data: IS 1.30 mm sec^{-1}

^1H NMR. ($CDCl_3$, 30°C): δ 7.67 (d, 2H, A portion of AB system, $SO_2C_6H_4Me$-*p*), 7.60–7.20 (m, 17H, Ph_3 and B portion of AB system, $SO_2C_6H_4Me$), 3.00 (t, 2H, SO_2CH_2, *J* 8.0 Hz), 2.39 (s, 3H, Me), 2.06–1.50 (m, 4H, $CH_2CH_2CH_2CH_2$ 1.46 (t, 2H, CH_2Sn, *J* 7.0 Hz).

^{13}C NMR. ($CDCl_3$, 30°C): δ 138.35–127.38 (aryl C), 55.91 (SO_2CH_2), 27.25 ($SnCH_2CH_2CH_2CH_2$), 25.39 (Me), 21.63 ($SnCH_2CH_2$), 10.1 ($SnCH_2$).

Mass spectrum (20 eV): $[M]^+$ (0.5%), $[M - Ph]^+$ (36%), $[Ph_3Sn]^+$ (100%).

Reactions

With bromine or iodine. To a stirred solution of the sulphinyl- or sulphonyl-alkyltin compound in CCl_4 solution was added dropwise a dilute solution of the halogen (equimolar) in CCl_4 (Br_2 at 0°C; I_2 at room temperature). The aryl halide, PhBr or PhI, was identified as the major volatile product and the yield determined by GLC.

GLC conditions: 2 m glass columns O.D. 6.0 mm; 2.5% silicone gum rubber (E301) on Chromosorb G-AW-PMCS, 80–100 mesh, oven temperature 90°C.

With mercury chloride. A solution of the tin compound, $Ph_3Sn(CH_2)_n$-$SO_mC_6H_4Me$-*p* and equimolar mercury chloride in ethanol was stirred at 50°C for 3 h. On cooling, phenylmercury chloride was collected by filtration. The solvent was removed from the filtrate under reduced pressure. The resulting oily residue was crystallised from chloroform/petroleum ether (b.p. 60–80°C) to give $Ph_2(Cl)Sn(CH_2)_nSO_mC_6H_4Me$-*p*.

The following compounds were obtained from the mercury chloride reactions.

[3-(p-Toluenesulphinyl)propyl]diphenyltin chloride, m.p. 72°C, yield 63%; ν(SO) 975 cm^{-1} (Nujol mull).

Analysis. Found: C, 53.7; H, 4.5; S, 6.5; Cl, 7.1. $C_{22}H_{23}ClOSSn$ calcd.: C, 53.9; H, 4.7; S, 6.5; Cl, 7.3%.

^1H NMR ($CDCl_3$, 30°C): 7.94 (m, 4H, *ortho* H of phenyl groups, *J* ($^{119}Sn-^1H$) 29 Hz), 7.50–7.28 (m, 6H, *meta* and *para* H of phenyl groups), 7.20 (s, 4H, SOC_6H_4Me), 2.94 (m, 1H) and 2.71 (t, *J* 8.8 Hz, 1H), ($SOCH_2$), 2.35 (m, 5H, Me and $CH_2CH_2CH_2$), 1.94 (m, 2H, CH_2Sn).

^{13}C NMR ($CDCl_3$, 30°C): δ 142.64–124.41 (aryl C), 55.50 (CH_2SO), 23.99 ($CH_2CH_2CH_2$), 21.74 (Me), 21.39 (CH_2Sn).

Mass spectrum (20 eV): $[M]^+$ (0.8%), $[M - O]^+$ (0.2%), $[M - Cl]^+$ (1.5%), $[M - Ph]^+$ (9%), $[M - (Ph + O)]^+$ (5.5%), [355] (11%), $[Ph_2SnCl]^+$ (100%), $[PhSnCl]^+$ (1.5%).

[4-(p-Toluenesulphinyl)butyl]diphenyltin chloride, m.p. 67°C, yield 74%; ν(SO) 980 cm^{-1} (Nujol mull).

Analysis. Found: C, 50.8; H. 4.4; S, 6.0; Cl, 6.3. $C_{23}H_{25}ClOSSn$ calcd.: C, 50.6; H, 4.6; S, 5.9; Cl, 6.5%.

Mössbauer data: IS 1.32 mm sec^{-1}, QS 3.11 mm sec^{-1} (Γ0.84, 0.98)

^1H NMR ($CDCl_3$, 30°C): δ 7.65 (m, 4H, *ortho* H of phenyl groups, $J(^{119}Sn-^1H)$ 29 Hz), 7.46–7.10 (m, 10H, *meta* and *para* H of phenyl groups and aryl protons of

SOC_6H_4Me), 2.75 (t, 2H, $SOCH_2$, J 5 Hz), 2.39 (s, 3H, Me), 2.20–1.50 (m, 6H, $SnCH_2CH_2CH_2$).

Mass spectrum (20 eV): $[M]^+$ (0.6%), $[M-O]^+$ (2%), $[M-(CH_2)_4]^+$ (1.5%), $[M-Ph]^+$ (11%), $[M-(Ph+O)]^+$ (2.5%), $[Ph_2SnCl]^+$ (100%), $[PhSn]^+$ (7%).

[2-(p-Toluenesulphonyl)ethyl]diphenyltin chloride, m.p. 74–75°C, yield 45%; $\nu(SO_2)$ 1285, 1295, and 1130 cm^{-1} (Nujol mull).

Analysis. Found: C, 47.4; H, 3.7; S, 5.9; Cl, 6.4. $C_{21}H_{21}ClO_2SSn$ calcd.: C, 47.3; H, 3.9; S, 6.0; Cl, 6.7%.

^1H NMR ($CDCl_3$, 30°C): δ 7.85 (m, 4H, *ortho* H of phenyl groups, J ($^{119}Sn-^1H$) 30.8 Hz), 7.57–7.23 (m, 8H, *meta* and *para* H of phenyl groups + A portion of AB system, $SO_2C_6H_4Me$), 7.16 (d, 2H, B portion of AB system, $SO_2C_6H_4Me$, J 6.6 Hz), 3.42 (t(br) 2H, SO_2CH_2, J(H–H) 5.5 Hz, J($^{119}Sn-^1H$) 47 Hz), 2.33 (s, 3H, Me), 1.87 (t(br) 2H, CH_2Sn, J(H–H) 5.5 Hz, J($^{119}Sn-^1H$) 32 Hz).

^{13}C NMR ($CDCl_3$, 30°C): δ 145.66–127.13 (aryl C), 53.74 (SO_2CH_2), 21.62 (Me), 12.05 (CH_2Sn).

[3-(p-Toluenesulphonyl)propyl]diphenyltin chloride, m.p. 72–73°C, yield 67%; $\nu(SO_2)$ 1295 and 1133 cm^{-1} (CH_2Cl_2 solution).

Analysis. Found: C, 47.2; H, 4.2; S, 5.6; Cl, 6.2. $C_{22}H_{23}ClO_2SSn$ calcd.: C, 47.1; H, 4.1; S, 5.7; Cl, 6.3%.

^1H NMR ($CDCl_3$, 30°C): δ 7.67 (m, 4H, *ortho* H of phenyl groups, J($^{119}Sn-^1H$) 30 Hz), 7.54 (d, 2H, A portion of AB system $SO_2C_6H_4Me$-*p*, J 6.6 Hz), 7.42 (m, 6H, *meta* and *para* H of phenyl groups), 7.26 (d, 2H, B portion of AB system, $SO_2C_6H_4Me$-*p*, J 6.6 Hz), 3.13 (t, 2H, SO_2CH_2, J 6 Hz), 2.38 (s, 3H, Me), 2.26 (q, 2H, $CH_2CH_2CH_2$, J 6 Hz, J($^{119}Sn-^1H$) 47 Hz), 1.81 (t, 2H, CH_2Sn, J 6 Hz, J($^{119}Sn-^1H$) 27 Hz).

^{13}C NMR ($CDCl_3$, 30°C): δ. 144.93–127.49 (aryl C), 58.19 (SO_2CH_2), 21.61 (Me), 19.50 ($CH_2CH_2CH_2$), 17.42 (CH_2Sn).

Mass spectrum (20 eV): $[M]^+$ (0.6%), $[M-O]^+$ (0.1%), $[M-2O]$ (1.0%), $[M-Ph]^+$ (35%), $[Ph_2SnCl]^+$ (100%), $[PhSnCl]^+$ (1.5%).

[*4*-(*p*-Toluenesulphonyl)butyl]diphenyltin chloride, m.p. 81–82°C, yield 71%; $\nu(SO_2)$ 1295 and 1132 cm^{-1} (CH_2Cl_2 solution).

Analysis. Found: C, 53.2; H, 4.7; S, 6.2; Cl, 6.7. $C_{23}H_{25}ClO_2SSn$ calcd.: C, 53.1; H, 4.8; S. 6.2; Cl. 6.8%.

Mössbauer spectra were obtained as previously described [15], the isomer shifts are relative to SnO_2.

Results and discussion

Controlled oxidation of γ-sulphidopropyl- and δ-sulphidobutyl-triphenyltin compounds by *m*-chloroperbenzoic acid in CH_2Cl_2 solution gave the sulphinyl and sulphonyl derivatives in good yield. However the β-substituted ethyltin derivatives could not be prepared by this route. Reaction of I ($n = 2$) with, *m*-$ClC_6H_4CO_3H$

$$\underset{(I)}{Ph_3Sn(CH_2)_nSC_6H_4Me\text{-}p} \xrightarrow[1\ eq]{m\text{-}ClC_6H_4CO_3H} \underset{(II)}{Ph_3Sn(CH_2)_nSOC_6H_4Me\text{-}p} \qquad (1)$$

$$\underset{(III)}{Ph_3Sn(CH_2)_nSC_6H_4Me\text{-}p} \xrightarrow[2\ eq]{m\text{-}ClC_6H_4CO_3H} \underset{(III)}{Ph_3Sn(CH_2)_nSO_2C_6H_4Me\text{-}p} \qquad (2)$$

under comparable conditions employed for I ($n = 3$ or 4) did not give any oxidation product but instead led to decomposition of I ($n = 2$). The ^{1}H NMR spectra indicated loss of all methylene protons, i.e. ethylene had been eliminated. Reactions of I ($n = 2$) with a number of other oxidizing agents, including H_2O, H_2O_2/SeO_2, $NaIO_4$ and $K_2Cr_2O_8$ were also unsuccessful, either leading to decomposition of I ($n = 2$) or being insufficiently reactive under the conditions used.

Addition of organotin hydrides has been found to occur to a variety of substituted alkenes [16,17]. It was found in this study that Ph_3SnH added to vinyl *p*-tolyl sulphone, at 80–90°C, in the presence of AIBN (eq. 3), but however not to vinyl *p*-tolyl sulphoxide. Despite varying the reaction temperature, reagent propor-

$$Ph_3SnH + CH_2{=}CHSO_2C_6H_4Me\text{-}p \xrightarrow[80\text{–}90°C]{AIBN} Ph_3Sn(CH_2)_2SO_2C_6H_4Me\text{-}p \qquad (3)$$

tions and free radical initiator, all attempts to prepare III ($n = 2$) by the $Ph_3SnHCH_2{=}CHSOC_6H_4Me$-*p* route failed. In each case, after a rapid evolution of gas (hydrogen), Ph_3SnH was found to be completely consumed. The reaction mixture was shown to contain hexaphenylditin and unreacted $CH_2{=}CHSOC_6H_4$-Me-*p*. It is significant that Ph_3SnH adds to $CH_2{=}CHSC_6H_4Me$-*p* and $CH_2{=}CHSO_2C_6H_4Me$-*p* but not to the more basic $CH_2{=}CHSOC_6H_4Me$-*p*, under comparable reaction conditions. Amines have been found to act as catalysts for the decomposition of organotin hydrides to tin–tin bonded species [18]. It appears that sulphoxides too may act similarly.

Attempts to isolate R_3SnCH_2SOR' (and $R_3SnCH_2SO_2R'$) by direct oxidation of R_3SnCH_2SR' have also been reported to fail [2,3] however oxidation of $Bu_3SnC(SPh){=}CH_2$ using *m*-chloroperbenzoic acid at −78°C apparently succeeded [9a]. The preparation of Bu_3SnCH_2SOMe could also not be achieved from Bu_3SnCl and $MeSOCH_2Li$ [3]. In contrast, $Bu_3SnCH_2SO_2R$ compounds could be obtained from the related reactions of Bu_3SnCl and RSO_2CH_2M (M = Li or MgX) [3].

Reactions

Reactions of II and III with bromine, iodine or mercury(III) chloride were studied. All reactions led to phenyltin bond cleavage (see Table 1).

TABLE 1

PERCENTAGE YIELDS FROM REACTIONS OF $Ph_3Sn(CH_2)_nS(O)_mC_6H_4Me$-*p* WITH ELECTROPHILES

Compound	Reactant (product)		
	Iodine (PhI) [a]	Bromine (PhBr) [a]	$HgCl_2$ ($Ph_2SnCl(CH_2)_nSO_mC_6H_4Me$-*p*) [b]
$Ph_3Sn(CH_2)_3SOC_6H_4Me$-*p*	94	93	63
$Ph_3Sn(CH_2)_4SOC_6H_4Me$-*p*	97	92	74
$Ph_3Sn(CH_2)_2SO_2C_6H_4Me$-*p*	98	67	45
$Ph_3Sn(CH_2)_3SO_2C_6H_4Me$-*p*	99	96	67
$Ph_3Sn(CH_2)_4SO_2C_6H_4Me$-*p*	95	98	71

[a] By GLC. [b] Isolated crystalline material.

$$II + E\text{–}Y \rightarrow Ph_2Sn(Y)(CH_2)_nSOC_6H_4Me\text{-}p + PhE \quad (4)$$

($n = 3$ or 4)

$$III + E\text{–}Y \rightarrow Ph_2Sn(Y)(CH_2)_nSO_2C_6H_4Me\text{-}p + PhE \quad (5)$$

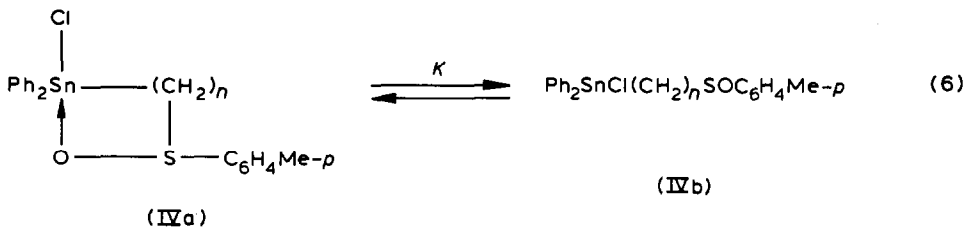
($n = 2$, 3 or 4)

(E–Y = I–I, Br–Br, ClHg–Cl)

The halogen reactions produced phenyl halides in yields greater than 92%. Table 1, except for the reaction of III ($n = 2$) with bromine for which a 67% yield of PhBr was determined. In this case, the ^1H NMR spectrum indicated additional reaction products. These additional reactions were not pursued. The products from the mercury chloride reactions could not be monitored by GLC and were isolated from the reaction solutions; although the isolated yields of crystalline material were in the range 45–74% no other reaction was indicated by the ^1H NMR spectra. While the substituents has little or no effect on the site of reaction, they had a great influence on the reactivities. The relative reactivities [19] of II and III have been established towards iodine from competition reactions with tetra(*p*-tolyl)tin. Considerable differences in reactivities were found, especially reactive was II ($n = 3$).

Cleavage products from reaction with mercury(II) chloride

Sulphoxide products, $Ph_2SnCl(CH_2)_nSOC_6H_4Me\text{-}p$ (IV). In the solid state ν(SO) in Nujol mulls, are at 975s and 980s cm^{-1} for IV ($n = 3$) and IV ($n = 4$), respectively. These show significant changes from ν(SO) 1040 cm^{-1} for both II ($n = 3$) and II ($n = 4$) in which the SO group is not coordinated. The lower ν(SO) values and the presence of ν(Sn–O) at 428 and 424 cm^{-1} for IV ($n = 3$) and IV ($n = 4$), clearly



indicate chelate structures, e.g. IVa, in the solid state. Intermolecular complexation of sulphoxides, R_2SO, with tin halides have been frequently reported; both $R_2SO : R'_x\ SnCl_{4-x}$ and $2R_2SO : IR'_xSnCl_{4-x}$ ($x = 0$–3) stoichiometries have been isolated [20–25]. In all cases, complexation via oxygen is indicated by the lowering of ν(SO) compared to the value in the free sulphoxide, and the presence of Sn–O absorptions (ca. 410–430 cm^{-1}) (see Table 2).

The Mössbauer data of IV ($n = 4$) (IS 1.32 mm sec^{-1}, QS 3.11 mm sec^{-1}) are similar to those reported for intermolecular complexes of R_3SnCl and sulphoxides [26].

The solid state IR spectra of IV showed no free ν(SO) absorptions and point to complete complexation. However in CH_2Cl_2 solution, some dissociation is indicated by the presence of free ν(SO) at 1040 cm^{-1}, as well as ν(SO) complexed at 980 cm^{-1}. Considerably greater dissociation occurs with IV ($n = 4$) than with IV ($n = 3$). This is expected for intramolecular complexation, since a six-membered ring should be

TABLE 2

IR DATA FOR TIN HALIDE-SULPHOXIDE COMPLEXES (cm^{-1})

Compound	ν(SO)complexed	$\Delta\nu$(SO) [a]	ν(Sn–O)	Reference
Solid state				
$Ph_3SnCl \cdot Me_2SO$	956, 946	91, 101	405	29, 31
$Ph_2SnCl(CH_2)_3SOC_6H_4Me$-*p*	975 [b]	73 [b]	428	This study
$Ph_2SnCl(CH_2)_4SOC_6H_4Me$-*p*	980 [c]	68 [c]	424	This study
In solution				
$Ph_2SnCl(CH_2)_3SOC_6H_4Me$-*p*	980 [d]	60 [d]		This study
$Ph_2SnCl(CH_2)_4SOC_6H_4Me$-*p*	980 [d]	60 [d]		This study
$Me_3SnCl \cdot (CH_2)_4SO$	1007 [e]	30.5 [e]		26

[a] $\Delta\nu$(SO) = $\Delta\nu$(SO) free $-\Delta\nu$(SO) complexed. [b] ν(SO) for $Ph_3Sn(CH_2)_3SOC_6H_4Me$-*p* 1048 cm^{-1} [c] ν(SO) for $Ph_3Sn(CH_2)_4SOC_6H_4Me$-*p* = 1048 cm^{-1}. [d] In CH_2Cl_2 solution. [e] In CCl_4 solution.

more stable than a seven-membered ring. (For intermolecular complexation in both compounds little difference would be expected.) Equilibrium constants K = [IVa]/[IVb] were calculated in CH_2Cl_2 solution at 30°C to be ca. 10 and 1, for $n = 3$ and $n = 4$, respectively. These values are somewhat imprecise since the relative extinction coefficients of ν(SO) free and ν(SO) complexed for IV could not be directly obtained and were assumed from values for related compounds. The nitrogen donor, phen, successfully competes with the internal sulphoxide donor for the tin centre; this is shown by increases in the intensity of ν(SO) free and decreases in that of ν(SO) complexed on addition of phen to solutions of IV in CH_2Cl_2.

Drago and coworkers [27] have measured equilibrium constants for trimethyl and triethyl-tin chloride-tetramethylenesulphoxide and -Me_2SO interactions,

$$R_3SnCl + R'_2SO \rightleftharpoons R_3SnCl \cdot OSR'_2 \qquad (7)$$

$$K = [R_3SnCl : OSR_2'] / [R_3SnCl][R_2'SO]$$

Some values of K (l mol^{-1}) are 5.5 for Me_3SnCl: tetramethylene sulphoxide at 35°C in CCl_4 solution and 9 for $Me_3SnCl \cdot Me_2SO$ at 26°C in CCl_4 solution.

Another pointer to the intramolecular coordination in IV ($n = 3$) in solution came from the ^1H NMR study in $CDCl_3$ solution. The spectrum indicated the non-equivalence of the γ protons (δ 2.70 and 2.92) of $Ph_2SnClCH_2CH_2CH_2SOC_6H_4Me$-*p*. In addition the pattern for the α proton was much more complex than the triplet expected for a simple coupling with the β protons in an open-chain structure. A number of other organotin halides containing inbuilt donor groups have been reported to undergo intramolecular coordination, including *o*-$Me_2NCH_2C_6H_4$-CH_2SnR_2X [28], $Cl_3SnCH_2CH_2CO_2R$ and $Cl_2Sn(CH_2CH_2CO_2R)_2$ [29], $Me_2SnCl(CH_2)_nCOR$ ($n = 3$ or 4) [30], $Ph_xY_{3-x}Sn(CH_2)_3COMe$ ($x = 1$ or 2, Y = Br or Cl [31], and $Ph_2ClSn(CH_2)_3CMe{=}NOH$ [31].

The greater dissociation of IV ($n = 4$) in solution prevented any NMR study of the chelate in solution.

Sulphone products, $Ph_2SnCl(CH_2)_nSO_2C_6H_4Me$-p. The $\nu(SO_2)$ values in III and in V (in the solid state) were only slightly different. However it should be realised that

complexation of sulphones even by $SnCl_4$ only results in small changes in $\nu(SO_2)$ [32]. Significantly ν(Sn–O) could not be observed for V. We feel certain that little intra- (or even inter-) molecular complexation, at the most, is occurring in the solid state, and therefore too in solution. While various organotin halide complexes with the sulphoxides have been isolated the number of tin halide-sulphone complexes are few [33]. Indeed only tin tetrahalides form sulphone complexes [32].

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33 See for example the compilation of compounds in Ref. 26.