Sulphur-substituted Organotin Compounds. Part 8.[1] Preparation and Reactions of 3-(*p*-Tolylthio)propyl- and 4-(*p*-Tolylthio)butyltriphenyltin. Interactions with Tetracyanoethylene †

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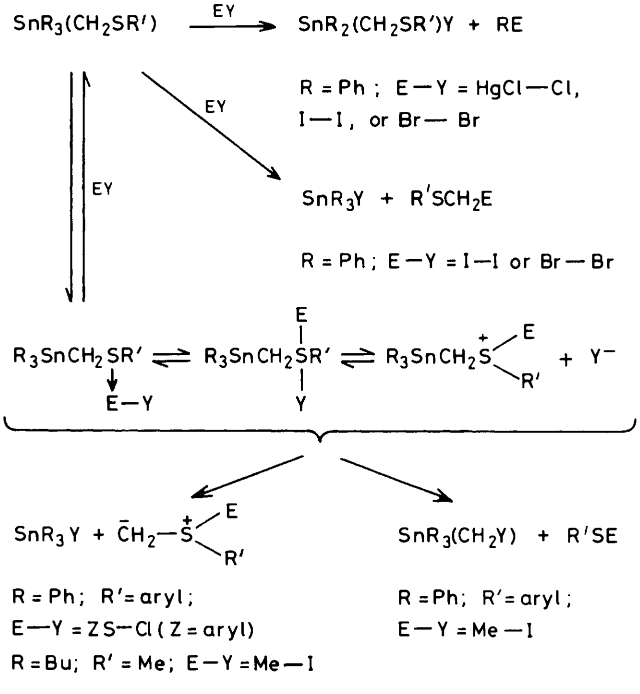
The reactions of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 3 or 4) with mercury(II) chloride, bromine, and iodine lead to phenyl–tin bond cleavage. In contrast, reactions with methyl iodide provide $SnPh_3[(CH_2)_nI]$ and $MeSC_6H_4Me\text{-}p$. Charge-transfer adducts are formed between $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 1—4) and tetracyanoethylene or *p*-bromoanil. The values of $\lambda_{max.}$ of the complexes indicate similar donor character for $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 2, 3, or 4); however, the compound $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ is a stronger donor.

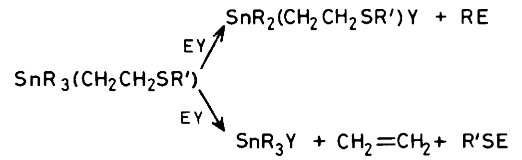
The preparations and reactions of α- and β-organotin substituted sulphides, such as $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ and $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$, have been reported.[1-7] The α-substituted compounds, $SnR_3(CH_2SR')$, show a considerable array of reaction types with electrophiles, EY (Scheme 1).

For β-substituted compounds, $SnR_3(CH_2CH_2SR')$, two reaction types were recognised (Scheme 2) for example when R = Ph, phenyl–tin bond cleavage (by $HgCl_2$ and iodine) and ethylene elimination [by ZSCl (Z = aryl) and MeI] were obtained; bromine reacted by both pathways.

We have extended our work to the γ- and δ-organotin alkyl sulphides, $SnPh_3[(CH_2)_3SC_6H_4Me\text{-}p]$ and $SnPh_3[(CH_2)_4SC_6H_4Me\text{-}p]$ and wish to report our findings. In addition to the preparations and reactions of these compounds with electrophiles, interactions with π-acceptors $(CN)_2C{=}C(CN)_2$ are also reported.



Scheme 1.



Scheme 2.

Experimental

Organotin Compounds.—Triphenyl(p-*tolylthiomethyl*)*tin*, $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. This complex was prepared according to a published procedure,[3] from $SnPh_3(CH_2I)$ and $Na(SC_6H_4Me\text{-}p)$; m.p. 111—112 °C (lit.,[3] 112—113 °C) (Found: C, 64.0; H, 4.8; S, 6.5. Calc. for $C_{26}H_{24}SSn$: C, 63.9; H, 4.9; S, 6.5%). ^1H N.m.r. spectra (220 MHz, CD_2Cl_2, 30 °C): δ 7.45—7.80 (m, *o*-phenyl protons, 6 H); 7.30—7.40 (m, *p*- and *m*-phenyl protons, 9 H); 7.22 (d, A portion of AB system, $SC_6H_4Me\text{-}p$, 2 H, J 8.8 Hz); 7.07 (d, B portion of AB system, J 8.8 Hz); 2.91 [CH_2, 2 H, $J(^{119}Sn-^1H)$ 24.2 Hz]; 2.27 (s, Me, 3 H).

Triphenyl[2-(p-*tolythio*)*ethyl*]*tin*, $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$. This complex was prepared according to a published procedure, namely[3] from $p\text{-}MeC_6H_4CH{=}CH_2$ and $SnPh_3H$, yield 50%; m.p. 73—74 °C (lit.,[3] 73—74 °C) (Found: C, 64.6; H, 5.2; S, 6.4. Calc. for $C_{27}H_{26}SSn$: C, 64.7; H, 5.2; S, 6.4%). ^{13}C N.m.r. spectra ($CDCl_3$, 30 °C): δ 131.11—127.38 (aryl C); 33.08 (CH_2S); 20.98 (Me); 11.60 (CH_2Sn).

(3-*Hydroxypropyl*)*triphenyltin*, $SnPh_3(CH_2CH_2CH_2OH)$. This was prepared by heating allyl alcohol (20.0 g, 0.345 mol) and triphenyltin hydride[8] (0.104 mol) at 80—95 °C for 3 h in the presence of azobisisobutyronitrile (aibn); m.p. 104—105 °C (lit.,[9] 105 °C), yield 58%.

(3-*Chloropropyl*)*triphenyltin*, $SnPh_3(CH_2CH_2CH_2Cl)$. A solution of (3-hydroxypropyl)triphenyltin (5.68 g, 0.014 mol) and triphenylphosphine (3.65 g, 0.014 mol) in carbon tetrachloride (20 cm^3) was refluxed overnight, then cooled, concentrated, and chromatographed on alumina using carbon tetrachloride as eluant to yield a white solid. This was recrystallised from light petroleum (b.p. 60—80 °C) to give colourless crystals of $SnPh_3(CH_2CH_2CH_2Cl)$; m.p. 44 °C, yield 63%.

Preparation of Triphenyl[3-(p-*tolylthio*)*propyl*]*tin*, $SnPh_3(CH_2CH_2CH_2SC_6H_4Me\text{-}p)$. This was prepared using the route: $SnPh_3H \longrightarrow SnPh_3(CH_2CH_2CH_2OH) \longrightarrow SnPh_3(CH_2CH_2CH_2Cl) \longrightarrow SnPh_3(CH_2CH_2CH_2SC_6H_4Me\text{-}p)$. To a stirred solution, made up from sodium (0.23 g. 0.01 mol) and *p*-toluenethiol (1.247 g, 0.01 mol) in ethanol (25 cm^3), was added a solution of (3-chloropropyl)triphenyltin (4.275 g,

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† *Non-S.I. units employed*: 1 eV ≈ 1.60×10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.

0.01 mol) in ethanol (40 cm^3) and the mixture heated for 3 h. The mixture was cooled and the sodium chloride filtered off. The ethanol was removed under reduced pressure and the resulting clear oily solid recrystallised from methanol to give a white solid on cooling in ice–water; m.p. 42—43 °C, yield 83% (Found: C, 65.3; H, 5.3; S, 6.1. Calc. for $C_{28}H_{28}SSn$: C, 65.2; H, 5.4; S, 6.2%). ^{1}H N.m.r. spectra (100 MHz, $CDCl_3$, 30 °C): δ 7.22—8.00 (m, Ph_3, 15 H); 7.15 (d, A portion of AB system, SC_6H_4Me-*p*, *J* 7.0 Hz, 2 H); 6.98 (d, B portion of AB system, 2 H); 2.89 (t, CH_2S, *J* 7 Hz, 2 H); 2.26 (s, Me, 3 H); 1.76—2.10 (m, $CH_2CH_2CH_2$, 2 H); 1.57 (m, CH_2Sn, 2 H). ^{13}C N.m.r. spectra ($CDCl_3$, 30 °C) δ: 127.29—138.61 (aryl C); 38.40 (SCH_2); 26.28 ($CH_2CH_2CH_2$); 20.97 (Me); 9.96 ($SnCH_2$). Mass spectrum (20 eV): M^+ 0.4%; $(M - 42)^+$ 0.6%; $(M - Ph)^+$ 100%; Ph_3Sn^+ 60%. Mössbauer data: isomer shift 1.267(11) mm s^{-1}, Γ = 0.88(4).

Triphenyl[4-(p-*tolylthio*)*butyl*]*tin*, $SnPh_3(CH_2CH_2CH_2CH_2SC_6H_4Me\text{-}p)$. This was prepared by two routes (below).

$$(a)\ SnPh_3(CH_2CH_2CH{=}CH_2) \longrightarrow SnPh_3(CH_2CH_2CH_2CH_2SC_6H_4Me\text{-}p)$$

$$(b)\ p\text{-}MeC_6H_4CH_2CH_2CH{=}CH_2 \longrightarrow SnPh_3(CH_2CH_2CH_2CH_2SC_6H_4Me\text{-}p)$$

Route (*a*). To a solution of but-3-enyltriphenyltin (prepared from $SnPh_3Cl$ and the Grignard reagent from 4-bromobutene in tetrahydrofuran, m.p. 72—75 °C, 4.256 g, 0.0105 mol) and *p*-toluenethiol (1.135 g, 0.0191 mol) in carbon tetrachloride (20 cm^3) was added a little aibn and the mixture refluxed for 3 h. After cooling, the solvent was removed under reduced pressure to give a clear oily solid. The product mixture was chromatographed on a silica gel column using light petroleum (b.p. 60—80 °C)–chloroform (9 : 1) as eluant. Triphenyl[4-(*p*-tolylthio)butyl]tin was collected as colourless crystals; m.p. 74—75 °C, yield 14% (Found: C, 65.6; H, 5.6; S, 6.0. Calc. for $C_{29}H_{30}SSn$: C, 65.8; H, 5.7; S, 6.0%). ^{1}H N.m.r. spectra (100 MHz, $CDCl_3$, 30 °C): δ 7.17—7.82 (m, Ph_3 and A portion of AB system, SC_6H_4Me-*p*); 6.99 (d, B portion of AB system, J_{AB} 8.0 Hz, 2 H); 2.81 (t, SCH_2, *J* 7.0 Hz, 2 H); 2.26 (s, Me, 3 H); 1.34—1.98 (m, $CH_2CH_2CH_2Sn$, 6 H). ^{13}C N.m.r. spectra ($CDCl_3$, 30 °C): δ 127.29—138.73 (aryl C); 33.70 (SCH_2); 25.71 ($CH_2CH_2CH_2CH_2$); 20.91 (Me); 10.45 ($SnCH_2$). Mass spectrum (20 eV) : $(M - Ph)^+$ 0.3%; $(Ph_2Sn)^+$ 100%.

Route (*b*). *But*-3-*enyl* p-*tolyl sulphide*.[10] To a solution, made up of sodium (1.702 g, 0.074 mol) and *p*-toluenethiol (9.174 g, 0.074 mol) in ethanol (100 cm^3), was added dropwise, a solution of 4-bromobutene (9.900 g, 0.074 mol) in ethanol (10 cm^3). The mixture was stirred at room temperature for 3 h, and refluxed for 1 h. The mixture was cooled, the sodium bromide filtered off, and the ethanol removed under reduced pressure. The resulting pale yellow oil was chromatographed on an alumina column with light petroleum (b.p. 60—80 °C) as eluant, yielding a colourless oil, which was used as such for the next stage.

Triphenyl[4-(p-*tolylthio*)*butyl*]*tin*. To triphenyltin hydride (prepared from triphenyltin chloride) (13.184 g, 0.0342 mol) was added but-3-enyl *p*-tolyl sulphide (3.044 g, 0.0171 mol) and aibn. The resulting mixture was heated for 30 min at 95 °C and then cooled in ice–water. A white solid was collected and recrystallised from methanol to yield colourless crystals, m.p. 74—75 °C, yield 56%. Samples produced by this route were identical to those obtained from $SnPh_3(CH_2CH_2CH{=}CH_2)$ and $p\text{-}MeC_6H_4SH$ [route (*a*)].

Organic Sulphides.—Methyl *p*-tolyl sulphide was from a previous study.[1] Other alkyl *p*-tolyl sulphides were prepared [11] by carefully adding a solution of the alkyl bromide (0.08 mol) in ethanol (10 cm^3) to a solution made up from sodium (0.08 mol) and *p*-toluenethiol (0.08 mol) in ethanol (50 cm^3) at 0 °C. After heating for about 2 h, the sodium bromide was filtered off and the solvent removed under reduced pressure. The residual oil was purified by distillation.

Ethyl p-*tolyl sulphide*. B.p. 204 °C (Found: C, 70.8; H, 8.0; S, 21.0. Calc. for $C_9H_{12}S$: C, 70.9; H, 7.9; S, 21.1%).

n-Propyl p-*tolyl sulphide*. B.p. 220 °C (Found: C, 71.0; H, 8.4; S, 19.2. Calc. for $C_{10}H_{14}S$: C, 72.2; H, 8.5; S, 11.3%).

n-Butyl p-*tolyl sulphide*. B.p. 96 °C at 6 mmHg (Found: C, 73.1; H, 8.7; S, 17.9. Calc. for $C_{11}H_{16}S$: C, 73.3; H, 8.9; S, 17.8%).

Reagents.—Methyl iodide was treated with dilute base and redistilled prior to use. *o*-Nitrobenzenesulphenyl chloride was prepared by bubbling chlorine gas through a suspension of bis(*o*-nitrophenyl) disulphide (11.084 g, 0.036 mol) and iodine (0.5 g, 0.001 96 mol) in carbon tetrachloride (150 cm^3) for 1.5 h. The solution was filtered and the solvent removed under reduced pressure to give *o*-nitrobenzenesulphenyl chloride, which was purified by recrystallisation from light petroleum (b.p. 60—80 °C) to give yellow needles, m.p. 51—52 °C (lit.,[12] 51.5—53 °C), yield 5.2 g (72%).

Tetracyanoethylene was sublimed at low pressure prior to use. *p*-Bromoanil (tetrabromo-*p*-benzoquinone) was a gift from Dr. O. C. Musgrave. Solvents and other reagents were commercial samples.

Reactions.—*With methyl iodide*. A solution of the organotin-containing sulphides, $SnPh_3[(CH_2)_nC_6H_4Me\text{-}p]$ (n = 2, 3, or 4), in methyl iodide (10 cm^3) was refluxed for 48 h. The yields of methyl *p*-tolyl sulphide were determined by g.l.c. using iodobenzene as an external standard, with due allowance made for the different response factors of PhI and $MeSC_6H_4Me$-*p*. Conditions: 2-m glass column (outside diameter 6 mm); 2.5% silicone gum rubber (E301) on Chromosorb-G-AW-PMCS, 80—100 mesh; oven temperature 90 °C. Yields of $MeSC_6H_4Me$-*p* were 89, 93, and 93% from $SnPh_3[(CH_2)_nC_6H_4Me\text{-}p]$ for n = 2, 3, and 4 respectively. Work up of the reaction products led to the isolation of $SnPh_3[(CH_2)_nI]$.

With bromine. To a stirred solution of the organotin-containing sulphide, $SnPh_3[(CH_2)_nC_6H_4Me\text{-}p]$ (n = 2, 3, or 4) (0.001 mol), in carbon tetrachloride (2.0 cm^3) at 0 °C was added dropwise, bromine (0.001 mol) in carbon tetrachloride solution. The bromine reacted immediately. Bromobenzene was identified as a major product and the yield determined by g.l.c. (using iodobenzene as an external standard and the same conditions as used for methyl *p*-tolyl sulphide). Yields of bromobenzene were 37, 97, and 98% for $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 2, 3, and 4).

With iodine. (*a*) To a stirred solution of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 2, 3, or 4) (0.001 mol) in carbon tetrachloride (2 cm^3) was added dropwise a solution of iodine (0.001 mol) in carbon tetrachloride (5 cm^3). After adding all the iodine, the solutions were left until they became colourless. Iodobenzene was identified as the major volatile product and the yield determined by g.l.c. (using bromobenzene as the external standard). Yields of iodobenzene were 98, 99, and 99% for $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ (n = 2, 3, and 4).

(*b*) To a solution of $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ (0.095 g, 0.000 19 mol) in carbon tetrachloride (0.3 mol) was added iodine (0.0482 g, 0.000 19 mol) and the solution left for 12 h. The ^{1}H n.m.r. spectrum indicated the formation of $SnPh_2(CH_2CH_2SC_6H_4Me\text{-}p)I$, from the changes in the aromatic region and shifts of $\delta(CH_2S)$ to 3.27, $\delta(CH_2Sn)$ to 2.10, and δ(Me) to 2.30 p.p.m.

With mercury(II) *chloride*. To a boiling solution of $SnPh_3$-

Table. Charge-transfer maxima for complexes between tetracyanoethylene and sulphides (CH_2Cl_2, 30 ± 0.1 °C)

	$SnPh_3[(CH_2)_nSC_6H_4Me$-*p*]					$H(CH_2)_nSC_6H_4Me$-*p*				$SnPh_2[(CH_2)_3SC_6H_4Me$-*p*]X					
n	$\lambda^1_{max.}$/nm	$\lambda^2_{max.}$/nm	$\varepsilon_2/\varepsilon_1$ [a]	$10^2\varepsilon_1K$ [b]	i.p.[c]/eV	$\lambda^1_{max.}$/nm	$\lambda^2_{max.}$/nm	$\varepsilon_2/\varepsilon_1$ [a]	i.p.[c]/eV	X	$\lambda^1_{max.}$/nm	$\lambda^2_{max.}$/nm	$\varepsilon_2/\varepsilon_1$ [a]	$10^2\varepsilon_1K$ [b]	i.p.[c]/eV
1	634 (579) [d]	384	0.71	22.5	7.86	610	382	0.36	7.94	Cl	598	381	1.13	6.5	7.99
2	610 [e] (550) [d]	390 [e]	1.13	16.0	7.94	610	384	0.36	7.94	I	602	398	*ca.* 3.5	8.0	7.97
3	611 (551) [d]	392	0.84	14.1	7.94	611 (552) [d]	384	0.36	7.94						
4	611 (551) [d]	392	0.73	15.3	7.94	611	—	—	7.94						

[a] ε_1 and ε_2 are absorption coefficients of the longer and shorter wavelength charge transfer absorptions respectively. [b] *K* is the formation constant for the charge-transfer complex at 30 ± 0.1 °C. [c] Ionisation potentials (i.p.) calculated from the relationship $\nu^1(cm^{-1}) = 7\,331$ i.p. $- 41\,830$ and using $1/(\lambda^1_{max.})$ values. [d] Values for interaction with *p*-bromoanil. [e] Unstable solutions.

$$SnPh_3H \xrightarrow{(i)} SnPh_3[(CH_2)_3OH] \xrightarrow{(ii)} SnPh_3[(CH_2)_3Cl] \xrightarrow{(iii)} SnPh_3[(CH_2)_3SC_6H_4Me\text{-}p]$$

Scheme 3. (*i*) CH_2=$CHCH_2OH$, 80—85 °C, aibn; (*ii*) PPh_3, CCl_4; (*iii*) HSC_6H_4Me-*p*

$[(CH_2)_nSC_6H_4Me$-*p*] (*n* = 2, 3, or 4) (0.005 mol) in ethanol (100 cm^3) was added a solution of mercury(II) chloride (0.005 mol) in ethanol (20 cm^3) and the solution refluxed for 4 h. The solvent was removed under reduced pressure to yield a clear oily solid which was partially dissolved in $CHCl_3$. The white solid, phenylmercury chloride, was filtered off, m.p. 253—256 °C (lit.,[13] 255—256 °C). Isolated yields of HgPhCl were greater than 70% from each organotin substituted sulphide.

Reaction of $SnPh_3(CH_2CH_2CH_2SC_6H_4Me$-*p*) *and* $HgCl_2$. After collecting the HgPhCl, the filtrate from the $SnPh_3$-($CH_2CH_2CH_2SC_6H_4Me$-*p*)–$HgCl_2$ (0.013 mol) reaction was concentrated under reduced pressure to yield a clear oily solid, which was redissolved in chloroform and filtered to remove a little more HgPhCl. The chloroform was removed from the filtrate to give a residue which was crystallised from chloroform–light petroleum (b.p. 60—80 °C) (1 : 1); the solid was diphenyl[3-(*p*-tolylthio)propyl]tin chloride, m.p. 78—79 °C, yield 68% (Found: C, 55.9; H, 4.7; Cl, 7.5; S, 6.7. Calc. for $C_{22}H_{23}ClSSn$: C, 55.7; H, 4.8; Cl, 7.4; S, 6.8%). ^1H N.m.r. spectra (220 MHz, $CDCl_3$, 30 °C): δ 7.44—7.80 [m, *o*-H of Ph_3Sn; $J(^{119}Sn-^1H)$ 30.8 Hz, 4 H]; 7.18—7.40 (m, *p*- and *m*-H of Ph_3Sn, 6 H); 6.80—7.00 (m, SC_6H_4Me, 4 H); 2.88 (t, *J* 4.4 Hz, SCH_2, 2 H); 2.21 (s, Me, 3 H); 2.09 (quart., *J* 4.4 Hz, $CH_2CH_2CH_2$, 2 H); 1.80 [t, *J* 4.5 Hz, $J(^{119}Sn-^1H)$ 28.6 Hz, CH_2Sn, 2 H]. ^{13}C N.m.r. spectra ($CDCl_3$, 30 °C): δ 128.89—139.21 (aryl C); 37.82 (CH_2S); 24.94 ($CH_2CH_2CH_2$); 20.99 (Me); 17.39 (CH_2Sn). Mass spectrum (20 eV): M^+ 0.8%; $(M - Cl)^+$ 8.5%; $[M - (CH_2)_3]^+$ 2%; $(M - Ph)^+$ 56%; (352) 6.5%; $(Ph_2SnCl)^+$ 21%; $[(CH_2)_3SC_6H_4Me]^+$ 100%. Mössbauer spectrum: isomer shift 1.406(7) mm s^{-1}, quadrupole splitting 3.015(7) mm s^{-1}, Γ 0.81(2) and 0.81(2).

Reaction of $SnPh_3(CH_2CH_2CH_2CH_2SC_6H_4Me$-*p*) *and* $HgCl_2$. After removing the HgPhCl, the filtrate from the reaction of $SnPh_3(CH_2CH_2CH_2CH_2SC_6H_4Me$-*p*) and $HgCl_2$ (both 0.0094 mol) in ethanol was concentrated under reduced pressure to yield a clear oily solid, to which was added chloroform. After filtering, the chloroform was removed under reduced pressure to leave a clear oil. Despite many attempts it was found to be impossible to crystallise this oil. ^1H N.m.r. spectrum (100 MHz, $CDCl_3$, 30 °C): δ 6.60—8.00 (m, aryl protons, 14 H); 2.79 (t, *J* 7 Hz, CH_2S, 2 H); 2.23 (s, Me, 3 H); 1.20—2.20 (m, $CH_2CH_2CH_2Sn$, 6 H).

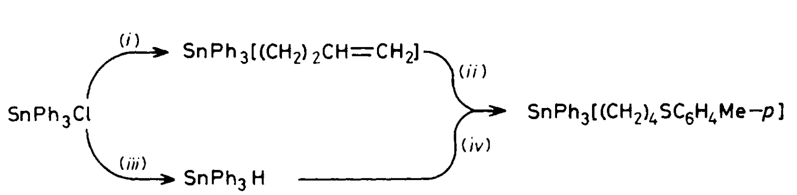
Formation of $SnPh_2(CH_2CH_2CH_2SC_6H_4Me$-*p*)I. This was prepared by halogen exchange from $SnPh_2(CH_2CH_2CH_2SC_6H_4Me$-*p*)Cl and sodium iodide in acetone solution.

Interactions with Tetracyanoethylene.—U.v. spectra. Solutions of $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] (*n* = 1—4), $SnPh_2[(CH_2)_3SC_6H_4Me$-*p*]I, or $H(CH_2)_nSC_6H_4SMe$-*p* (*n* = 1—4) and the π-acceptors were made up in dry oxygen-free dichloromethane and the u.v.-visible spectra recorded at 30 ± 0.1 °C. As wide a range of concentrations of each sulphide as possible was taken with a constant concentration of tetracyanoethylene. The $\lambda_{max.}$ values are quoted in the Table. No attempt was made to decompose the lower wavelength charge-transfer absorptions for the tetracyanoethylene interactions although some overlap with other bands was probable.

Results and Discussion

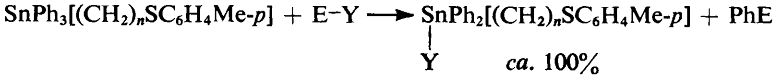
Preparations.—The γ- and δ-organotin substituted sulphides were prepared as shown in Schemes 3 and 4. Poller and co-workers [14] previously reported the preparation of some $SnR_3(CH_2CH_2CH_2SR')$ compounds. Attempts to prepare $SnPh_3(CH_2CH_2CH_2SC_6H_4Me$-*p*) using $SnPh_3H$ and CH_2=$CHCH_2SC_6H_4Me$-*p* failed despite the complete consumption of $SnPh_3H$. It is well established that allylic halides do not undergo tin hydride additions,[15] but rather produce alkenes by hydrogen–chlorine exchange and a similar situation could be occurring with the allyl sulphide. Reaction of the but-3-enyl sulphide, CH_2=$CHCH_2CH_2SC_6H_4Me$-*p*, with $SnPh_3H$ in contrast proceeded readily (Scheme 4); only the δ-sulphidoalkyltin species was isolated.

Reactions.—The α- and β-sulphidoalkyltin compounds, $SnPh_3(CH_2SC_6H_4Me$-*p*) and $SnPh_3(CH_2CH_2SC_6H_4Me$-*p*), undergo the variety of reactions shown in Schemes 1 and 2. The γ- and δ-sulphidoalkyltin species both undergo the same type of reactions; namely Ph–Sn bond cleavage [equation (1)] by the electrophilic species, Br_2, I_2, or $HgCl_2$, and formation of $MeSC_6H_4Me$-*p* from reaction with MeI, probably *via* the sulphonium salt, equation (2). Normally, phenyl–tin bonds are found to be more easily cleaved by electrophiles than alkyl–tin bonds, except for certain α-substituted alkyl–tin compounds, *e.g.* $SnPh_3[CH_2SC_6H_4Me$-*p*] (Scheme 1). Reaction (2) is a typical reaction of organic sulphides, see for



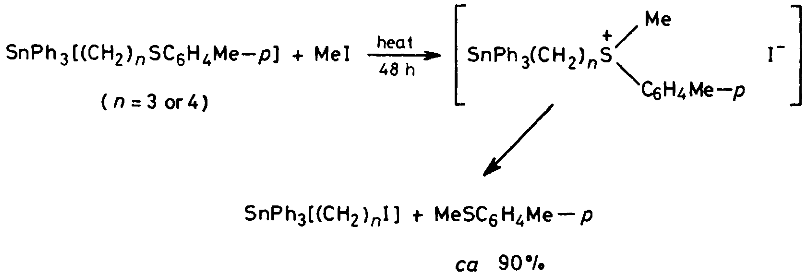
Scheme 4. (*i*) CH_2=$CH(CH_2)_2MgBr$; (*ii*) aibn, HSC_6H_4Me-*p*; (*iii*) $LiAlH_4$; (*iv*) CH_2=$CH(CH_2)_2C_6H_4Me$-*p*, aibn

example ref. 16. Formation of $MeSC_6H_4Me$-*p* was found for all the $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] compounds studied (n = 1—4). Methyl iodide has been found usually to be too weak an electrophile to break such simple carbon–tin bonds as are present in the compounds used here.* Sulphenyl halides react with $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] (n = 1 or 2), Schemes 1 and 2. However with $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] (n = 3 or 4) very little reaction occurred; even after prolonged reaction times, very little product, that could be unambiguously ascribed to reaction of the sulphenyl halide with the organotin compound, was present. At this stage considerable decomposition of the sulphenyl halide had occurred.



$$SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p] + E\text{-}Y \longrightarrow \underset{\displaystyle Y}{\underset{|}{Sn}}Ph_2[(CH_2)_nSC_6H_4Me\text{-}p] + PhE \quad ca.\ 100\% \qquad (1)$$

n = 3 or 4; E–Y = Br–Br, I–I, or HgCl–Cl



(2)

Complexation.—From the reactions with iodine, it was apparent from the new intense u.v.-visible absorptions that iodine–$SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] complexes were present. However the ensuing reactions prevented much study of the complexes. As we wished to gain some insight into the donor abilities of the sulphides $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] we turned to acceptors other than iodine and found that the π-acceptor, tetracyanoethylene, was suitable. Charge-transfer complexes of arenes with π-acceptors have been frequently studied,[18] including charge-transfer complexes of $(CN)_2C$=$C(CN)_2$ with totally organic aryl sulphides.[19-23] There are differences between iodine (a σ-acceptor) and $(CN)_2C$=$C(CN)_2$ (a π-acceptor) as acceptors towards sulphur substituted aryl donors,[19] but both acceptors can provide useful information regarding the donor ability.

The values of $\lambda_{max.}$ for π-complexes of $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*] and the corresponding alkyl *p*-tolyl sulphides with $(CN)_2C$=$C(CN)_2$ are given in the Table. Two charge-transfer absorptions are observed in the u.v.-visible region for each complex. This is as expected for $(CN)_2C$=$C(CN)_2$ complexes of substituted benzenes,[20] such as $SnPh_3[(CH_2)_nSC_6H_4Me$-*p*].

While the maxima of the longer wavelength absorption can be readily assigned, those of the shorter wavelength bands are generally more difficult to locate precisely due to overlapping absorption bands. Additional charge-transfer absorptions may arise from the Ph_3Sn unit (or from one of the phenyl groups) as donor and, as the ionisation potential (i.p.) of the Ph_3Sn group should be about that of benzene,† the additional bands would be at *ca.* 380—400 nm. A complete resolution of the lower wavelength bands was not achieved in our study and the overall or resultant maxima ($\lambda^2_{max.}$) are simply reported as obtained.

Attempts to calculate formation constants, K [equation (3)], were made using the Benesi–Hildebrand procedure.[24] However, the charge-transfer complexes were too weak and with the concentration ranges available to us it was not possible to obtain sufficiently accurate values of K. Compound terms, $\varepsilon_1 K$ (ε_1 = absorption coefficient of longer wavelength band) however could be obtained. Such compound terms may not be too significant; as shown in the Table, there are only slight differences for all the sulphides studied. Using equation (4), values of the first ionization potentials of each organo-tin containing sulphide were calculated (see Table). The values for $H(CH_2)_nSC_6H_4Me$-*p* are also given.

$$SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p] + (CN)_2C\text{=}C(CN)_2 \overset{K}{\rightleftharpoons} SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]\cdot(CN)_2C\text{=}C(CN)_2 \qquad (3)$$

$$\nu(\mathrm{cm}^{-1}) = 7\,331\ \mathrm{i.p.} - 41\,830 \qquad (4)$$

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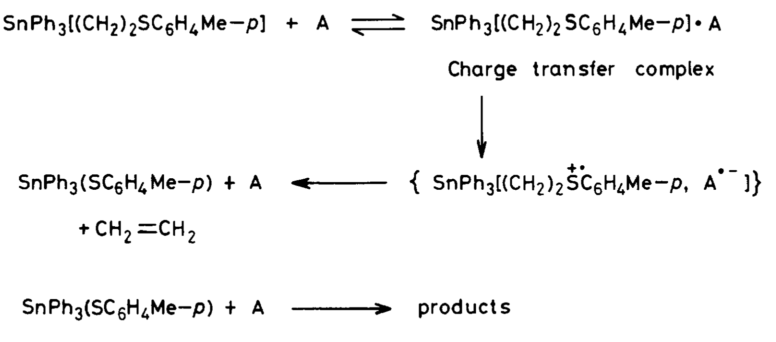
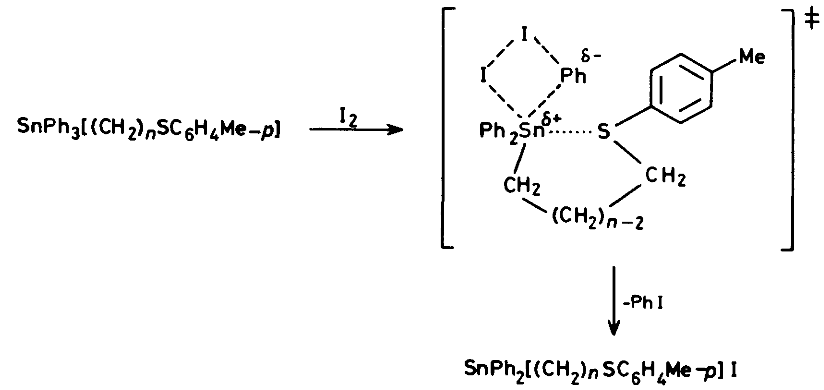
* Radical reactions of halogenoalkanes with organotin compounds are known, however.[17]

† The i.p. of $SnPh_3H$ and $SnPh_3Cl$ are 9.13 and 9.29 eV respectively compared to that of benzene = 9.24 eV. From the values of the charge-transfer frequencies, it is possible to calculate the i.p. using empirical relationships,[21] such as equation (4). Of further interest, the $(CN)_2C$=$C(CN)_2$ adduct of Ph_2CHSPh exhibits charge-transfer bands at 560 and 400 nm (due to −SPh acting as donor) and at 420 nm (Ph_2CH− as donor).[19]



Scheme 5. A = π-acceptor



Scheme 6. Simplified mechanism of reaction of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ with iodine

It can be seen from the Table that the Ph_3Sn substituent only has an impact on $\lambda_{max.}$ when at an α-methylene group, *i.e.* for $n = 1$ in $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$. For all other values of n, all the $\lambda_{max.}$ values (and therefore the i.p.) are the same, *i.e.* the donor abilities of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ ($n = 2$—4) are the same at least towards π-acceptors.

In contrast to the constant $\lambda_{max.}$ value for the $(CN)_2C{=}C(CN)_2{\cdot}Ph_3Sn(CH_2)_nSC_6H_4Me\text{-}p$ ($n = 2$—4) complexes, different $\lambda_{max.}$ values are obtained for complexes of $SnPh_2[(CH_2)_3SC_6H_4Me\text{-}p]X$ (Table). This is despite the separation of the X group from the $SC_6H_4Me\text{-}p$ group. We interpret this as being due to intramolecular Sn ⟶ S co-ordination in $SnPh_2[(CH_2)_3SC_6H_4Me\text{-}p]X$ which reduces the electron density of the sulphur and thereby results in a poorer π-donor group for co-ordination to the π-acceptor.

Stability of Complexes.—The charge-transfer adducts were stable for all $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ except for $n = 2$. The $SnPh_3[CH_2CH_2SC_6H_4Me\text{-}p]$ adduct ($\lambda_{max.}$ 610 and 390 nm) with $(CN)_2C{=}C(CN)_2$ underwent subsequent reaction. This was shown by (*i*) development of very intense visible absorption ($\lambda_{max.}$ 557 nm in CH_2Cl_2) and (*ii*) complete elimination of $CH_2{=}CH_2$ with conversion of all the $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ present to other species. The intensity of the initial charge-transfer adducts was considerably less than that for the products of the ensuing reaction. We have shown that $SnPh_3(SC_6H_4Me\text{-}p)$ and related compounds also react with an equivalent of $(CN)_2C{=}C(CN)_2$ and that the tin-containing products of this reaction are the same as those from reaction of equimolar $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ and $(CN)_2C{=}C(CN)_2$. We envisage the initial reactions of $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ with π-acceptors (A) to be as shown in Scheme 5.* The critical step is the development of positive charge on the sulphur atom. In keeping with this, the ethylene elimination in interactions of $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ with acceptors proceeds at a faster rate with the most powerful acceptor, *e.g.* the rate of ethylene elimination increases in the sequence *p*-bromoanil ⩽ dichlorodicyano-*p*-benzoquinone < $(CN)_2C{=}C(CN)_2$ (E_a values are 1.37, 1.95, and 2.2, respectively).

Relative Reactivity of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$.—We have shown[25] that the reactivity of $SnPh_3[(CH_2)_nSC_6H_4Me\text{-}p]$ towards iodine [relative to $Sn(C_6H_4Me\text{-}p)_4$] in CCl_4 solution at 30 ± 0.1 °C is 0.26 ± 0.03, 1.16 ± 0.12, and 0.23 ± 0.023 for $n = 2$, 3, and 4 respectively. This is despite the constant donor ability of the sulphides as found towards $(CN)_2C{=}C(CN)_2$ (and without doubt too towards iodine). As there are no steric differences any differences in reactivity must stem from transition state effects and in particular from the ability of the sulphur to interact with the developing positive character of the tin atom in the transition state. This appears to be most significant for $SnPh_3[(CH_2)_3SC_6H_4Me\text{-}p]$ in which a five-membered chelate ring can be formed (Scheme 6). Whilst this effect is not so pronounced with sulphides, it becomes really significant[25] for sulphoxides and sulphones, $SnPh_3[(CH_2)_nS(O)C_6H_4Me\text{-}p]$ and $SnPh_3[(CH_2)_nS(O)_2C_6H_4Me\text{-}p]$.

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* Previously we have indicated that development of positive charge on the sulphur in $SnPh_3(CH_2CH_2SC_6H_4Me\text{-}p)$ (as in reactions with electrophilic species, such as MeI, or on electron impact in the mass spectrum) results in elimination of $CH_2{=}CH_2$.

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