Sulphur-substituted Organometallic Compounds. Part IV.[1] Reactions of *p*-Tolylthiomethyltriphenyltin with Electrophilic Reagents and Oxidants. Comparison of Reactions of the Oxygen, Selenium, and Germanium Analogues

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Reactions of $SnPh_3(CH_2ZC_6H_4Me$-*p*) (Z = O, S, and Se) with Br_2, I_2, $HgCl_2$, and PhSCl generally give Sn–Ph and Sn–CH_2 bond cleavage. The following conclusions are reached: (*i*) all reactions of $SnPh_3(CH_2OC_6H_4Me$-*p*) lead only to Sn–Ph cleavage; (*ii*) no Sn–Ph bond cleavage occurs in the PhSCl reactions; (*iii*) the halogens give both types of cleavage on reaction with the sulphur and selenium compounds; and (*iv*) all reactions of $HgCl_2$ give only Sn–Ph bond cleavage. In contrast, the reactions of $SnPh_3(CH_2SC_6H_4Me$-*p*) with EtI and $Na[IO_4]$ each lead to $SnPh_3(CH_2I)$. While attempts to prepare the tin sulphoxide, $Ph_3SnCH_2S(O)C_6H_4Me$-*p*, have failed, the germanium analogue has been prepared using Br_2 in aqueous methanol as the oxidant. The effect on the halogen reactions of changing the aryl groups (R) in $SnR_3(CH_2SR)$ has been briefly studied, as have reactions of $GePh_3$-$(CH_2SC_6H_4Me$-*p*).

RECENTLY we reported[1,2] reactions of β-sulphur-substituted organotin compounds, $SnPh_3(CH_2CH_2SR)$ (I) and $SnPh_3(CHClCH_2SR)$ (II) (R = aryl), with electrophilic reagents (EY), including halogens, arenesulphenyl compounds, mercury(II) salts, and alkyl halides. Two types of initial reaction, (1) and (2), were evident.

$$SnPh_3(CHXCH_2SR) + EY \longrightarrow SnPh_2(CHXCH_2SR)Y + PhE \quad (1)$$

X = H; E–Y (solvent) = HgCl–Cl (EtOH) or I–I (CCl_4)
X = Cl; E–Y (solvent) = HgCl–Cl (EtOH), I–I ($ClCH_2CH_2Cl$), or Br–Br ($CHCl_3$)

$$SnPh_3(CHXCH_2SR) + EY \longrightarrow SnPh_3Y + CHX{=}CH_2 + [ESR] \quad (2)$$

X = H; E–Y (solvent) = RS–X′(CCl_4) (X′ = Cl or Br), Me–I, or Br–Br (CCl_4)
X = Cl; E–Y (solvent) = RS–X′(CCl_4) (X′ = Cl or Br)

It is clear from the above examples that only minor changes in the electrophile [*cf.* reaction of (II) with Br_2 and I_2] bring about major changes in the reaction types of these β-substituted sulphides.

A natural extension of this work is to reactions of α-sulphur-substituted compounds, $SnPh_3(CH_2SR)$, with the same electrophiles. In this paper, we report our findings for reactions not only of $SnPh_3(CH_2SC_6H_4Me$-*p*) (III) but also of the oxygen, $SnPh_3(CH_2OC_6H_4Me$-*p*) (IV), the selenium, $SnPh_3(CH_2SeC_6H_4Me$-*p*) (V), and the germanium, $GePh_3(CH_2SC_6H_4Me$-*p*) (VI), analogues. Some attempts to oxidise (III) are also reported.

RESULTS AND DISCUSSION

This section is divided into two parts dealing with first a comparison of reactions of $SnPh_3(CH_2ZC_6H_4Me$-*p*) (Z = O, S, or Se) as well as those of $GePh_3(CH_2SC_6H_4Me$-*p*) (VI) and other electrophilic reactions of (III), and secondly the attempts to oxidise (III) and (VI).

[1] Part III, R. D. Taylor and J. L. Wardell, *J. Organometallic Chem.*, 1975, **94**, 15.
[2] J. L. Wardell, *J.C.S. Dalton*, 1975, 1786.

Comparison of the Primary Reactions of $MPh_3(CH_2ZC_6H_4Me\text{-}p)$ *with the Electrophiles* I_2, Br_2, $HgCl_2$, *and* PhSCl.—As with the β-sulphides, (I) and (II), two initial reactions of the tin derivatives were observed, phenyl–tin bond [equation (3)] and tin–methylene bond cleavages [equation (4)]. Four general conclusions can be made: (*i*) all reactions of $SnPh_3(CH_2OC_6H_4Me\text{-}p)$ led only to Sn–Ph bond cleavage; (*ii*) no Sn–Ph bond cleavage occurred in the PhSCl reactions; (*iii*) the halogens gave both types of cleavage with the sulphur and selenium analogues; and (*iv*) all reactions of $HgCl_2$ gave only Sn–Ph bond cleavage.

$$SnPh_3(CH_2ZC_6H_4Me\text{-}p) + EY \nearrow SnPh_2(CH_2ZC_6H_4Me\text{-}p)Y + PhE \qquad (3)$$

$$SnPh_3(CH_2ZC_6H_4Me\text{-}p) + EY \searrow SnPh_3Y + p\text{-}MeC_6H_4ZCH_2E \qquad (4)$$

The differences between (IV) and the S and Se analogues with respect to reaction (4) can be rationalised by considering the stabilities of the carbanions $p\text{-}MeC_6H_4ZCH_2^-$, that of the oxygen derivative being very much less than those of the other two. Thus a reaction in which charge separation in the $\equiv Sn{-}CH_2$ bond ($\equiv \overset{\delta+}{Sn}{-}\overset{\delta-}{CH_2}$) is required, as in $\equiv Sn{-}CH_2$ bond cleavages, will be much more favoured for the sulphur and selenium compounds. As a result of these carbanion stabilities, any reaction of (IV) with the electrophiles, EY, will be at the Sn–Ph bond. Unlike the halogens and mercury(II) chloride, arenesulphenyl halides do not cleave Sn–Ph bonds,[3] and the consistent lack of such cleavages in the $SnPh_3(CH_2ZC_6H_4Me\text{-}p)$–PhSCl reactions is in accord with this finding. No direct reaction of PhSCl with (IV) occurred, even after a period of 2 weeks in the dark in carbon tetrachloride solution. During this period, some decomposition of PhSCl to diphenyl disulphide and chlorine occurred; the chlorine then reacted with (IV) as shown by the presence of a little chlorobenzene.* The reactions of PhSCl with the other compounds, (III) and (V), were fast [in the order, (III) > (V)] and led to a number of organic products, as shown by t.l.c.

For the halogen reactions with (III) and (V), both Sn–Ph and Sn–CH_2 bond cleavages generally occurred. Specifically for (III)–I_2 interactions, it was found that the solvent had an effect on the relative amounts of the two cleavage processes (Table) as well as on the rate of consumption of iodine. Some kinetic studies of iodination of trialkylaryltin compounds have shown that different processes operate in methanol (in which an overall second-order reaction occurs)[4] and in CCl_4 (an overall third-order reaction).[5] Clearly in these electrophilic reactions of (III) and (V), as well as of (I) and (II), there is more to consider than just the ground-state charge separations in the Sn–Ph and Sn–CH_2 bonds, since the operation of this single factor would lead to a consistent cleavage ratio. Other factors to consider are different solvation effects and different electronic demands of transition states occurring at different places along the reaction paths. As well as these, the different extents of co-ordination of the heteroatoms and the electrophile, EY, must also be considered. Such co-ordination has been extremely well documented; for example with halogens, crystal structures of both the molecule complex type [*e.g.* $Se(CH_2)_4$–I–I,[6] $S(CH_2Ph)$–I–I,[7] $C_4H_8O_2{:}Br_2$[8]] and the oxidative-addition type [$Se(C_6H_4Me\text{-}p)_2X_2$ (X = Cl or Br),[9] $S(C_6H_4Cl\text{-}p)Cl_2$[10]] have been determined, while in solution equilibrium constants, particularly for iodine molecular complexes,

Percentage of reaction of $SnPh_3(CH_2ZSR)$ with electrophiles leading to Sn–Ph bond cleavage

(a) Reagent/solvent	$SnPh_3(CH_2OC_6H_4Me\text{-}p)$	$SnPh_3(CH_2SC_6H_4Me\text{-}p)$	$SnPh_3(CH_2SC_6H_4Cl\text{-}p)$	$SnPh_3(CH_2SeC_6H_4Me\text{-}p)$
Br_2/CCl_4 [a]	100 [b]	10 [b]	20 [b]	17 [b]
$I_2/CHCl_3$	100 [b]	64 [b]	67 [b]	21 [b]
$HgCl_2$/EtOH	90 [c]	87 [c]		86 [c]
$PhSCl/CCl_4$	0	0		0

(b) Compound	Reagent/solvent			
	$I_2/CHCl_3$	I_2/CCl_4	I_2/MeCOMe	I_2/MeOH
$SnPh_3(CH_2SC_6H_4Me\text{-}p)$	64 [b]	19 [b]	13 [b]	33 [b]
$Sn(C_6H_4Me\text{-}p)_3(CH_2SC_6H_4Me\text{-}p)$	100 [b,d]			

[a] For $GePh_3(CH_2SC_6H_4Me\text{-}p)$, the percentage was 0. [b] Yields calculated from g.l.c. [c] Yields based on isolated yields. [d] Yield of $p\text{-}MeC_6H_4I$.

* Any direct reaction of PhSCl with $SnPh_3(CH_2ZC_6H_4Me\text{-}p)$ would have given PhSPh and not PhCl.

[3] (*a*) J. L. Wardell and S. Ahmed, *J. Organometallic Chem.*, 1974, **78**, 395; (*b*) J. L. Wardell and D. W. Grant, *ibid.*, 1969, **20**, 91.

[4] R. W. Bott, C. Eaborn, and J. A. Waters, *J. Chem. Soc.*, 1963, 681.

[5] O. Buchman, M. Grosjean, and J. Nasielski, *Helv. Chim. Acta*, 1964, **47**, 1679.

[6] H. Hope and J. D. McCullough, *Acta Cryst.*, 1964, **17**, 712.

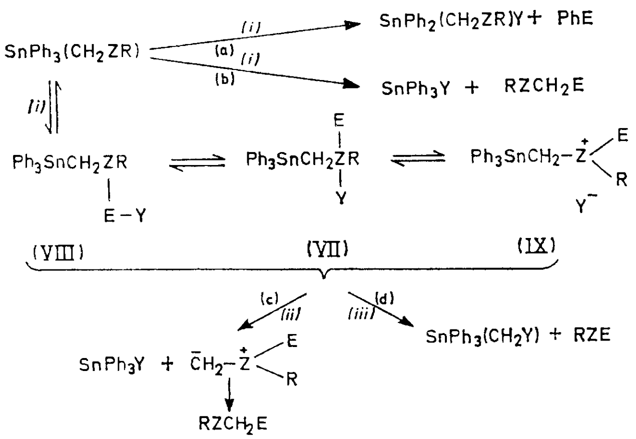
[7] C. Rømming, *Acta Chem. Scand.*, 1960, **14**, 2145.

[8] O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 873.

[9] J. D. McCullough and R. E. Marsh, *Acta Cryst.*, 1950, **3**, 41.

[10] N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, 1969, **91**, 5749.

have been calculated.[11,12] We thus propose the general reaction Scheme below. While we have found no



SCHEME (*i*), EY; (*ii*), attack of Y^- at Sn; (*iii*), attack of Y^- at the α carbon

concrete evidence for ylide formation, step (c), in the halogen, sulphenyl chloride, and mercury(II) chloride reactions, Peterson[13] has reported the formation of $\bar{C}H_2-\overset{+}{S}Me_2$ from the reaction of $SnBu_3(CH_2SMe)$ and MeI, *via* the intermediate $SnBu_3(CH_2\overset{+}{S}Me_2I^-)$. An unresolved feature of our reactions is the complexity of products from the sulphenyl halide, RSX, reactions with (II) (see also ref. 14). The simple $Sn-CH_2$ cleavage products, *p*-$MeC_6H_4SCH_2SR$, did not react further under the reaction conditions and so could not be the source of the additional products. It is tempting to speculate on the formation of ylides and their subsequent reactions in these reactions.

Furthermore, there is no evidence for any of the $HgCl_2$, Br_2, I_2, or RSCl reactions proceeding *via* step (d) in the Scheme. Some products, such as di-*p*-tolyl disulphides and diselenides, isolated from the reactions, could have arisen from *p*-MeC_6H_4ZE (Z = S or Se; E = Cl or Br) if this was formed, but could equally well have arisen from other sources. Further, $SnPh_3(CH_2Y)$ was neither isolated nor spectroscopically (n.m.r.) identified from any of the reactions of these electrophiles. However, the much slower reaction of (III) with EtI, on the other hand, did produce some $SnPh_3(CH_2I)$ (see later). There is, in fact, a precedent[15] for nucleophilic attack of an α carbon to tin, namely the reaction of I^- with $SnMe_3(CH_2Cl)$ to give $SnMe_3(CH_2I)$. Nucleophilic attack of Y^- on an α-carbon atom carrying a positive substituent should be even more favourable.

The effects of changing the aryl groups in $SnR_3(CH_2SR)$ were briefly studied. Bromination and iodination of $SnPh_3(CH_2SC_6H_4Cl$-*p*) gave essentially the same result as did (III); there was just a little more Sn–Ph bond cleavage with the former. The remoteness of the Cl and Me substituents from the reaction sites would of necessity limit their effect; the enhancement of the carbanion *p*-$XC_6H_4SCH_2^-$ ability and the reduction of the donor ability * of the sulphur on changing X from Me to Cl would have, in any case, opposing influences on the two cleavage processes. A more detailed study of the effects of substituents, X, on the rates and products of reactions of $SnPh_3(CH_2SC_6H_4X$-*p*) is currently underway.

Altering the other aryl group to give $Sn(C_6H_4Me$-*p*$)_3(CH_2SC_6H_4Me$-*p*) resulted in complete tin–aryl cleavage by iodine in $CHCl_3$. The increased reactivity of the Sn–C_6H_4Me-*p* bond compared to the Sn–Ph bond towards iodine (by a factor of 7.5 in CCl_4[5] and 5 in MeOH solutions[4]) completely upset the balance of the two cleavage processes. Such a balance was also upset in the $GePh_3(CH_2SC_6H_4Me$-*p*)–Br_2 system, in which no Ge–Ph cleavage occurred. The latter generally occurs much less readily than does Sn–Ph cleavage (*e.g.* by a factor of 10^4 towards $HClO_4$ in aqueous alcohol[16]) and so any co-ordinating role of the sulphur in directing attack to the M–CH_2SR bond becomes relatively more significant. There was no reaction of (VI) with iodine in refluxing carbon tetrachloride.

All three $SnPh_3(CH_2ZC_6H_4Me$-*p*) compounds, as well as the two types of β-sulphides, gave Sn–Ph cleavage on reaction with $HgCl_2$ in ethanol. In this solvent, the product, HgPhCl, is only sparingly soluble and this factor is possibly a driving force in these reactions. Complexes of sulphides, particularly dialkyl sulphides,[17–19] with $HgCl_2$ are known but these are extensively dissociated in ethanolic solution.[17] Complexes of alkyl aryl sulphides are less strong and would be even more dissociated in solution, and hence most, if not all, of the $HgCl_2$ and the tin-substituted sulphides, (I)—(III), would remain uncomplexed in these systems. As a result there would be little tendency for the reaction to occur *via* steps (c) and (d) in the Scheme. However, why reaction does not occur to give Sn–CH_2 cleavage *via* step (b) remains unclear.

The reaction of MeI and $SnBu_3(CH_2SMe)$, reported by Peterson,[13] was mentioned earlier. In contrast, the products from the slow reaction of EtI and (III) are as shown in equation (5) (R′ = Et). The intermediacy of

* The reduced basicity of S in (II) compared to (I) was considered to be the reason why fewer electrophilic reactions of (II) occurred in the sulphur-substituted alkyl group.

[11] S. Santini, G. Reichenbach, S. Sorriso, and A. Ceccon, *J.C.S. Perkin II*, 1974, 1056; V. Mancini, O. Piovesana, and S. Santini, *Z. Naturforsch.*, 1974, **B29**, 815; J. van der Veen and W. Stevens, *Rec. Trav. chim.*, 1963, **82**, 287.

[12] J. D. McCullough and B. A. Eckerson, *J. Amer. Chem. Soc.*, 1945, **67**, 707; J. D. McCullough and M. K. Barsh, *ibid.*, 1949, **71**, 3029; J. D. McCullough and B. A. Eckerson, *ibid.*, 1951, **73**, 2954; N. W. Tideswell and J. D. McCullough, *ibid.*, 1957, **79**, 1031; J. D. McCullough and D. Mulvey, *J. Phys. Chem.*, 1960, **64**, 264; J. D. McCullough and I. C. Zimmermann, *ibid.*, p. 1084.

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[16] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1961, 3715.

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[18] P. Biscarini and G. D. Nivellini, *J. Chem. Soc. (A)*, 1969, 2206.

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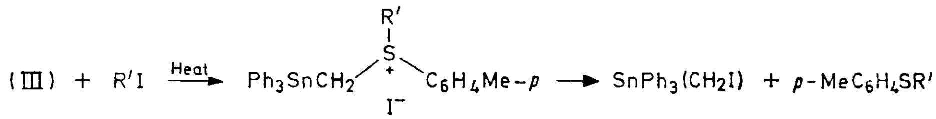
the sulphonium salt is expected following the isolation of $SnBu_3(CH_2\overset{+}{S}Me_2X^-)$ ($X^- = I^-$ or $SMeO_4^-$) by Peterson. Such differences in the products of the overall $SnR'_3(CH_2SR^2)$–R'I reactions are more a consequence of the different R^2 groups than of different $SnR^1_3(CH_2)$ and R' groups. There are a number of examples of related exchanges of organic groups on sulphur (*i.e.* $R^1R^2S + R'I \longrightarrow R^1R'S + R^2I$).[20]



Initially we used a commercial unpurified sample of MeI with (III). This resulted in products expected from HI rather than MeI. The decision to pursue these alkyl iodide reactions with pure EtI rather than MeI was taken so as to remove any doubts about the course of the reaction. (Formation of p-MeC_6H_4SMe could stem from protonolysis of the Sn–CH_2 bond as well as from MeI attack at the sulphur, whereas p-MeC_6H_4SEt formation could only arise from R'I attack at sulphur.)

The amounts of halogenobenzenes quoted in the Table were determined by g.l.c., while the yields quoted for HgPhCl were based on isolated products. Not all the products formed either in reaction (3) or (4) were isolated; the existence of some was based on spectroscopic (n.m.r.) information. Compounds of the type $SnPh_2(CH_2ZC_6H_4Me$-$p)Y$ were difficult to isolate, oils rather than crystalline solids being the rule.

Many of the initial sulphur and selenium products were prone to further reaction, especially on work-up. An example of this is p-$MeC_6H_4SCH_2Br$ which could be collected from the reaction by fractional distillation, but which on SiO_2 t.l.c. stationary phases broke down to give $CH_2(SC_6H_4Me$-$p)_2$. This change was also monitored in a sealed n.m.r. tube (see Experimental section). Hydrolysis of $EtSCH_2Cl$ to give $CH_2(SEt)_2$, HCHO, and HCl has been previously reported.[21] While in our reactions there might be sufficient water present with the SiO_2 to cause an analogous hydrolysis, it is also a possibility that the stationary phase is acting as an acid.

Attempts to Oxidise (III).—A typical property of an organic sulphide is oxidation to a sulphoxide. A variety of oxidants have been successfully used, $Na[IO_4]$ being particularly useful.[22] However, reaction of $Na[IO_4]$ with (III) gave $SnPh_3(CH_2I)$ and p-$MeC_6H_4SO_3H$ (or possibly p-$MeC_6H_4SO_2H$), instead of the sulphoxide $Ph_3SnCH_2SOC_6H_4Me$-p. It is probable that the sulphoxide was initially formed but had only limited stability in the mixed dichloromethane–water solvent system. Peterson[13] reported unsuccessful attempts to oxidise $SnR_3(CH_2SMe)$ and that no Bu_3SnCH_2SOMe was formed from $SnBu_3Cl + MeS(O)CH_2Li$. Sulphites are known[23] to reduce iodates to iodine or iodides, which suggests that the p-$MeC_6H_4SO_3H$ arose from oxidation by iodate of a bivalent sulphur species, such as the sulphenic acid p-$MeC_6H_4S(O)H$ which could be formed from hydrolysis of the sulphoxide.

No reaction occurred between $Na[IO_4]$ and $GePh_3(CH_2SC_6H_4Me$-$p)$. However, the use of another oxidising system,[24] Br_2 in aqueous methanol, did lead to some sulphoxide $Ph_3GeCH_2S(O)C_6H_4Me$-p. The reactivity of tin–carbon bonds was too great for successful use of this oxidant with (III). A silicon-substituted sulphoxide, $Me_3SiCH_2S(O)Me$ has also been produced; it is thermally labile and chemically reactive.[25]

EXPERIMENTAL

Organometallic Compounds.—The compounds $SnPh_3(CH_2SC_6H_4Me$-$p)$, $SnPh_3(CH_2OC_6H_4Me$-$p)$, and $GePh_3(CH_2SC_6H_4Me$-$p)$ were prepared as previously described.[26] The new compounds $SnPh_3(CH_2SeC_6H_4Me$-$p)$, $SnPh_3(CH_2SC_6H_4Cl$-$p)$, and $Sn(C_6H_4Me$-$p)_3(CH_2SC_6H_4Me$-$p)$ were prepared analogously from reaction of the triaryliodotin and the sodium salt of the thiol or selenol: $SnPh_3(CH_2SC_6H_4Cl$-$p)$, m.p. 99—101 °C (Found: C, 59.9; H, 4.5. Calc. for $C_{25}H_{21}ClSSn$: C, 59.4; H, 4.2%), ^1H n.m.r. spectrum (in $CDCl_3$ at 30 °C) τ 1.80—2.80 (m) (19 H) and 7.12 (s) (2 H) [$J(^{119}Sn$–$^1H)$ 49 Hz]; $SnPh_3(CH_2SeC_6H_4Me$-$p)$, m.p. 97—98.5 °C (Found: C, 58.3; H, 5.1; Se, 14.6. Calc. for $C_{26}H_{24}SeSn$: C, 58.5; H, 4.5; Se, 14.8%), ^1H n.m.r. spectrum (100 MHz, in $CDCl_3$ at 30 °C) τ 2.20—3.05 (m) (19 H), 7.20 (s) (2 H) [$J(^{119}Sn$–$^1H)$ 44 Hz], and 7.72 (s) (3 H); $Sn(C_6H_4Me$-$p)_3(CH_2SC_6H_4Me$-$p)$, m.p. 110—112 °C (Found: C, 65.7; H, 5.8; S, 6.1. Calc. for $C_{29}H_{30}SSn$: C, 65.8; H, 5.7; S, 6.05%), ^1H n.m.r. spectrum (100 MHz, in $CDCl_3$ at 30 °C) τ 1.16—2.65 (m) (16 H), 7.32 (s) (2 H) [$J(^{119}Sn$–$^1H)$ 48 Hz], 7.71 (s) (9 H), and 7.77 (s) (3 H). The new compound $Sn(C_6H_4Me$-$p)_3(CH_2I)$ was prepared according to the method of Seyferth,[27] from $Sn(C_6H_4Me$-$p)_3I$ and CH_2I_2 in the presence of a zinc–copper couple, m.p. 82—84 °C, ^1H n.m.r. spectrum τ 2.42—2.91 (m) (12 H), 7.63 (s) (2 H), and 7.70 (s) (9 H). p-Tolueneselanol was a gift from Dr. W. McFarlane of the City of London Polytechnic.

Other Reagents and Solvents.—Iodine, bromine, mercury(II) chloride, $Na[IO_4]$, and all the solvents were the purest commercial grades available. The solvents were dried (over CaH_2) and distilled prior to use. Benzenesulphenyl

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[24] K. Uneyama and S. Torii, *Tetrahedron Letters*, 1971, 329; R. H. Baker, R. M. Dodson, and B. Riegel, *J. Amer. Chem. Soc.*, 1946, **68**, 2636; U. Miotti, G. Modena, and L. Sedea, *J. Chem. Soc.* (*B*), 1970, 802.
[25] A. G. Brook and D. G. Anderson, *Canad. J. Chem.*, 1968, **46**, 2115.
[26] R. D. Taylor and J. L. Wardell, *J. Organometallic Chem.*, 1974, **77**, 311.
[27] D. Seyferth and S. B. Andrews, *J. Organometallic Chem.*, 1971, **30**, 151.

chloride was prepared as published.[28] Ethyl iodide was purified by washing successively with dilute aqueous potassium hydroxide solution and water, refluxing over anhydrous calcium chloride, and finally distilling.

Determination of Bromo- and Iodo-benzenes, and p-*Iodotoluene*.—A Perkin-Elmer F11 g.l.c. instrument was employed to determine the percentages of PhBr, PhI, and *p*-MeC_6H_4I; an E_{301} column was used. A known weight of toluene was added to the particular reaction solution and the peak areas (or weights) in the chromatogram of PhMe and aryl halide were determined. With due account taken of the response factors, the yield of aryl halide, based on the molarity of the tin compound, was calculated.

Other Instruments.—^{1}H N.m.r. spectra were recorded on Varian HA 100D and Perkin-Elmer R 12A spectrometers.

Reactions of Bromine.—*With* $SnPh_3(CH_2SC_6H_4Me$-*p*). (1) To a cooled solution of $SnPh_3(CH_2SC_6H_4Me$-*p*) (6.0 g, 12.4 mmol) in CCl_4 (100 cm^3) was added dropwise with stirring a solution of bromine (2.0 g, 12.5 mmol) in CCl_4 (100 cm^3). The bromine reacted immediately on addition. After complete addition, the solvent was removed under reduced pressure and on adding light petroleum (b.p. 60—80 °C) to the oily residue $SnBrPh_3$ was precipitated. This was collected and recrystallised from light petroleum (b.p. 60—80 °C), m.p. 121—123 °C (lit.,[29] 121 °C), yield 3.9 g (82%). The filtrate was divided into two parts. (*a*) One half was fractionally distilled and bromoethyl *p*-tolyl sulphide was collected, b.p. 71—72 °C (0.1 mmHg),* yield 0.65 g (50%) (Found: C, 44.0; H, 4.2; Br, 36.7; S, 15.0. Calc. for C_8H_9BrS: C, 44.2; H, 4.15; Br, 36.9; S, 14.8%). (*b*) The other half of the filtrate was evaporated and the residue chromatographed [t.l.c. SiO_2: light petroleum (b.p. 60—80 °C)–$CHCl_3$ (17 : 3) eluant]. Bis(*p*-tolylthio)methane was collected as an oil and crystallised from ethanol as white needles, m.p. 29 °C (lit.,[30] 30 °C), yield 0.52 g (65%) (Found: C, 69.0; H, 5.8. Calc. for $C_{15}H_{16}S_2$: C, 69.3; H, 6.1%).

(2) To a further cooled solution of $SnPh_3(CH_2SC_6H_4Me$-*p*) (51.5 mg, 0.106 mmol) in CCl_4 (0.3 cm^3) was carefully added an equimolar quantity of Br_2 [0.3 cm^3 of a solution of Br_2 (0.562 g in 10 cm^3)]. The bromine colour was immediately dispelled. The ^{1}H n.m.r. spectrum (100 MHz in CCl_4 solution) of the reaction solution indicated the presence of a little $SnPh_2(CH_2SC_6H_4Me$-*p*)Br [τ (CH_2) 7.17] as well as the major product *p*-$MeC_6H_4SCH_2Br$ [τ (CH_3) 5.33] in the ratio 1 : 9. Using g.l.c. the yield of PhBr was calculated to be 10%.

Some silica (Merck G.F.254) was added to the total solution in an n.m.r. tube and the tube was then sealed. The subsequent reaction at room temperature was monitored by n.m.r. spectroscopy; the absorption at τ 5.33 (*p*-$MeC_6H_4SCH_2Br$) gave way to peaks at τ 5.90 [$CH_2(SC_6H_4Me$-*p*)] and 5.06 (CH_2Br_2) in a ratio of *ca.* 3 : 2 respectively.

With $SnPh_3(CH_2SeC_6H_4Me$-*p*). To a cooled solution of $SnPh_3(CH_2SeC_6H_4Me$-*p*) (0.468 g, 0.88 mmol) in CCl_4 was carefully added dropwise a Br_2 solution [0.6 cm^3 of a solution containing Br_2 (2.32 g) in CCl_4 (10 cm^3)]. Reaction was immediate. The ^{1}H n.m.r. spectrum (100 MHz in CCl_4 solution) of the reaction solution indicated the presence of *p*-$MeC_6H_4SeCH_2Br$ [τ (CH_2) 5.44, $J(^{77}Se-^1H)$ 14 Hz] and $SnPh_2(CH_2SeC_6H_4Me$-*p*)Br [τ (CH_2) 7.28] in a ratio of *ca.* 6 : 1. The amount of PhBr present was calculated, using g.l.c., as 17%. Silica (Merck G.F.254) was added and the reaction was followed by ^{1}H n.m.r. spectroscopy at room temperature. Loss of the peak at τ 5.44 (*p*-$MeC_6H_4SeCH_2Br$) was accompanied by new absorptions at τ 5.88 [$CH_2(SeC_6H_4Me$-*p*)] and τ 5.05 (CH_2Br_2) in a ratio of *ca.* 3 : 1. The completion of the reaction was hastened on heating. Use of t.l.c. on SiO_2, with light petroleum (b.p. 60—80 °C)–chloroform (9 : 1) as eluant, allowed collection of $CH_2(SeC_6H_4Me$-*p*$)_2$ [^{1}H n.m.r. (60 MHz in $CDCl_3$) τ 2.50—3.00 (q) (4 H), 5.87 (s) (2 H) [$J(^{77}Se-^1H)$ 14 Hz], and 7.66 (q) (3 H)] and (*p*-$MeC_6H_4Se)_2$.

With $SnPh_3(CH_2OC_6H_4Me$-*p*). A solution of Br_2 (46.2 mg, 0.29 mmol) in CCl_4 was added to a solution of $SnPh_3(CH_2OC_6H_4Me$-*p*) (0.137 g) in CCl_4; the reaction occurred quickly. The amount of PhBr was calculated to be 100%. The solvent and PhBr were removed under reduced pressure to leave a very viscous residue. The ^{1}H n.m.r. spectrum at 60 MHz (in CCl_4) [τ 2.10—3.30 (m) (10 H), 5.10 (s) (2 H), and 7.70 (s) (3 H)] indicated the presence of $SnPh_2(CH_2OC_6H_4Me$-*p*)Br.

With $SnPh_3(CH_2SC_6H_4Cl$-*p*). A Br_2 solution [1.0 cm^3 of a solution containing Br_2 (0.068 g) in CCl_4 (20 cm^3) ($\equiv$ 0.02 mmol)] was added to $SnPh_3(CH_2SC_6H_4Cl$-*p*) (0.0153 g, 0.03 mmol). After reaction was complete the amount of PhBr was calculated as 20%, based on Br_2 added.

With $GePh_3(CH_2SC_6H_4Me$-*p*). (1) A solution of bromine (0.18 g, 1.1 mmol) in CCl_4 (10 cm^3) was added dropwise to a stirred solution of $GePh_3(CH_2SC_6H_4Me$-*p*) (0.5 g, 1.1 mmol) in CCl_4 (25 cm^3) and the resulting red-orange solution was heated under reflux for 2 h. The solvent was removed and light petroleum (b.p. 60—80 °C) was added to the residue to precipitate $GeBrPh_3$, which was crystallised from light petroleum (b.p. 60—80 °C), m.p. 134—137 °C (lit.,[31] 138 °C), yield 0.31 g (70%). The solvent from the filtrate was removed and the products in the oily residue separated by t.l.c. [light petroleum (b.p. 60—80 °C)–benzene (7 : 3) as eluant]. The compound with the largest R_F was bis(*p*-tolylthio)methane, yield 36 mg. The ^{1}H n.m.r. spectrum, τ 2.60—3.00 (8 H), 5.80 (2 H, s), and 7.70 (6 H, s), was identical to that of the sample obtained from the reaction of Br_2 with $SnPh_3(CH_2SC_6H_4Me$-*p*). Also present, and shown by comparison of R_F data, were di(*p*-tolyl) disulphide and starting material, $GePh_3(CH_2SC_6H_4Me$-*p*) (19 mg).

(2) A solution of Br_2 (47.7 mg, 0.298 mmol) in CCl_4 (2.0 cm^3) was added to $GePh_3(CH_2SC_6H_4Me$-*p*) (134 mg, 0.304 mmol) in CCl_4 (2.0 cm^3). No PhBr was formed. The solution had a slight thiol-like odour and also fumed slightly in air. The ^{1}H n.m.r. spectrum (in $CDCl_3$) showed absorptions at τ 5.23 [*p*-$MeC_6H_4SCH_2Br$], 5.56, 6.76, and 6.94 [$GePh_3(CH_2SC_6H_4Me$-*p*)] in a ratio of 18 : 3 : 4 : 6.

(3) A solution of bromine (4.75 g, 30 mmol) in methanol–water (1 : 1, 250 cm^3 total) was prepared and slowly added to a stirred solution of $GePh_3(CH_2SC_6H_4Me$-*p*) (0.5 g, 1.1 mmol) in diethyl ether (25 cm^3). The red colour of the bromine solution disappeared *ca.* 0.5 min after the addition of each aliquot portion. The reaction was monitored by t.l.c. After *ca.* 25 cm^3 of bromine solution (3 mmol) had been added, the reaction was stopped. The organic layer was collected, dried with anhydrous sodium sulphate, and

* 1 mmHg ≈ 13.6 × 9.8 Pa.

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the solvent removed under reduced pressure. The products in the residual viscous oil were separated by t.l.c. using chloroform as eluant. (*p*-Tolylsulphinylmethyl)triphenylgermanium was collected and crystallised from ethanol, m.p. 145—147 °C, yield 0.15 g (Found: C, 70.0; H, 5.8; S, 7.4. Calc. for $C_{26}H_{24}GeOS$: C, 68.4; H, 5.3; S, 7.4%), ν(SO) at 1 030 cm^{-1} [lit.,[32] for RS(O)R generally, ν(SO) at 1 045—1 025 cm^{-1}], ^1H n.m.r. spectrum τ 2.20—3.05 (m) (19 H), 6.70—6.75 (d) (2 H), and 7.65 (s) (3 H).

Reactions of Iodine.—With $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. (1) A solution of iodine (0.21 g, 0.83 mmol) in CCl_4 (75 cm^3) was added dropwise to a solution of $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (0.4 g, 0.83 mmol) and the mixture stirred overnight at room temperature. During this time the reaction solution changed from purple to pale yellow. The solvent was removed and the compounds in the residual oil were separated by t.l.c. [light petroleum (b.p. 60—80 °C)–benzene (7 : 3) as eluant]. In order of increasing R_F, there were four bands A, B, C, and D, plus base-line material ($SnPh_3I$): A, recovered $SnPh_3(CH_2SC_6H_4Me\text{-}p)$, yield 27 mg, identified from its ^1H n.m.r. spectrum; B, $CH_2(SC_6H_4Me\text{-}p)_2$, yield 20 mg, ^1H n.m.r. in $CDCl_3$ τ 2.60—3.00 (m) (4 H), 5.80 (s) (1 H), and 7.70 (s) (3 H); C ($p\text{-}MeC_6H_4)_2S_2$, yield 30 mg, ^1H n.m.r. τ 2.50—3.00 (m) (8 H) and 7.70 (s) (3 H); D, PhI.

(2) From separate experiments, the amounts of PhI obtained from reaction of I_2 and $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (equimolar amounts) in different solvents were determined in the usual manner. The solvent, yield (%), and reaction conditions required to give complete consumption of iodine were: CCl_4, 22, minutes at 25 °C; $CHCl_3$, 64, minutes at 25 °C; Me_2CO, 15, hours at 40 °C; MeOH, 31, hours at reflux. From reaction of I_2 (0.06 mmol) and $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (0.11 mmol) in $CDCl_3$, the amount of PhI produced was 64%, ^1H n.m.r. τ 5.54 ($p\text{-}MeC_6H_4SCH_2I$), 6.84 [$SnPh_2(CH_2SC_6H_4Me\text{-}p)I$], and 7.07 [$SnPh_3(CH_2SC_6H_4Me\text{-}p)$] in a ratio of *ca.* 1 : 1 : 1. However, on addition of I_2 (0.042 mmol), the absorptions at τ 6.84 and 7.07 disappeared to leave only an absorption at τ 5.52.

With $SnPh_3(CH_2SC_6H_4Cl\text{-}p)$. Equimolar amounts of I_2 and $SnPh_3(CH_2SC_6H_4Cl\text{-}p)$ (0.1 mmol) in $CHCl_3$ gave, after several minutes at room temperature, 67% PhI.

With $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$. On addition of a solution of I_2 (33.0 mg, 0.13 mmol) in $CDCl_3$ to a solution of $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$ (70.1 mg, 0.13 mmol) in $CDCl_3$ an orange-brown solution was produced. The iodination reaction was complete within 1 h. The yield of PhI was calculated to be 22%. The solution was left for 2 weeks and the only CH_2 absorption in the ^1H n.m.r. spectrum was at τ 5.77 [$J(^{77}Se-^1H)$ 16 Hz] ($p\text{-}MeC_6H_4SeCH_2I$).

With $SnPh_3(CH_2OC_6H_4Me\text{-}p)$. Reaction of I_2 (56.6 mg, 0.233 mmol) and $SnPh_3(CH_2OC_6H_4Me\text{-}p)$ (105 mg, 0.233 mmol) in $CDCl_3$ produced 100% PhI. On evaporation of all the volatiles, the only methylene absorption in the ^1H n.m.r. spectrum in $CDCl_3$ solution was at τ 5.12 [$SnPh_2(CH_2OC_6H_4Me\text{-}p)I$] [$J(^{119}Sn-^1H)$ 10 Hz].

With $Sn(C_6H_4Me\text{-}p)_3(CH_2SC_6H_4Me\text{-}p)$. The reaction of I_2 (10.5 mg, 0.041 mmol) and $Sn(C_6H_4Me\text{-}p)_3(CH_2SC_6H_4Me\text{-}p)$ (21.9 mg, 0.041 mmol) in $CDCl_3$ was fast and gave 100% $p\text{-}MeC_6H_4I$. The ^1H n.m.r. spectrum in $CDCl_3$ showed an absorption at τ 5.75 [$CH_2(SC_6H_4Me\text{-}p)_2$].

Reactions of $HgCl_2$.*—With* $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. A solution of mercury(II) chloride (0.12 g, 0.41 mmol) in ethanol (15 cm^3) was added slowly to a boiling solution of $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (0.2 g, 0.41 mmol) in ethanol (8 cm^3). After about half the $HgCl_2$ had been added, a white precipitate appeared. When the addition was complete, the solution was cooled to −10 °C and the HgPhCl was collected and recrystallised from ethanol, m.p. 250—258 °C (lit.,[33] 250 °C), yield 105 mg (87%) (Found: C, 23.7; H, 2.1; Cl, 11.6. Calc. for C_6H_5ClHg: C, 23.2; H, 1.9; Cl, 11.4%).

With $SnPh_3(CH_2OC_6H_4Me\text{-}p)$. Similarly to the $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ reaction, $SnPh_3(CH_2OC_6H_4Me\text{-}p)$ (3.90 g, 8.1 mmol) and $HgCl_2$ (2.19 g, 8.1 mmol) gave HgPhCl (2.29 g, 90%). The filtrate, after collection of HgPhCl, gave an oil on evaporation. The ^1H n.m.r. spectrum τ 2.22—3.1 (m) (19 H), 5.19 (s) (2 H), and 7.78 (s) (3 H), suggested the product was $SnPh_3(CH_2OC_6H_4Me\text{-}p)Cl$ [$J(^{119}Sn-^1H)$ 12 Hz]. The oil did not crystallise on standing.

With $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$. Similarly to the $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ reaction, $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$ (0.534 g, 1 mmol) and $HgCl_2$ (0.272 g, 1 mmol) gave HgPhCl (0.268 g, 90%). The filtrate from the crystallisation gave an oil on evaporation, ^1H n.m.r. τ 7.08 (*J* 10 Hz) [$SnPh_2(CH_2SeC_6H_4Me\text{-}p)Cl$?]. Attempts to isolate a crystalline product failed; instead decomposition occurred and among the decomposition products were ($p\text{-}MeC_6H_4Se)_2$, $CH_2(SeC_6H_4Me\text{-}p)$ {^1H n.m.r. (in $CDCl_3$) τ 2.44—3.00 (q) (4 H), 5.85 (s) (2 H) [$J(^{77}Se-^1H)$ 13 Hz], and 7.68 (s) (3 H)}, and $SnPh_3Cl$.

Reactions of Benzenesulphenyl Chloride.—With $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. Benzenesulphenyl chloride (31.1 mg, 0.215 mmol) in CCl_4 was added to $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (105 mg, 0.216 mmol) in CCl_4. Immediate decolouration occurred. The compound PhSPh was shown not to be present by g.l.c. The ^1H n.m.r. spectrum showed major peaks at τ 5.86 and minor absorption at τ 6.93 and 7.14 (starting material). On SiO_2 t.l.c. stationary phases several products were shown to be present. Addition of light petroleum (b.p. 60—80 °C) to the oily residue, left after evaporation of the solvent, caused precipitation of $SnPh_3Cl$.

With $SnPh_3(CH_2OC_6H_4Me\text{-}p)$. The compound PhSCl (32.9 mg, 0.227 mmol) in CCl_4 was added to $SnPh_3(CH_2OC_6H_4Me\text{-}p)$ (108 mg, 0.227 mmol) in CCl_4. The vessel was sealed and left for several weeks in the dark. Even after 3 weeks the solution was still yellow in colour, indicating the presence of PhSCl. G.l.c. showed the absence of PhSPh, but the presence of PhSSPh and PhCl. On evaporation of the solvent, the remaining PhSCl decomposed to leave a colourless oil. The ^1H n.m.r. spectrum of the residue showed that considerable $SnPh_3(CH_2OC_6H_4Me\text{-}p)$ (>75%) was left.

With $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$. The compound PhSCl (33.7 mg, 0.233 mmol) in CCl_4 was added to $SnPh_3(CH_2SeC_6H_4Me\text{-}p)$ (124 mg, 0.233 mmol) in CCl_4. The colour of the solution deepened somewhat initially, but then quickly became colourless. No PhSPh was detected by g.l.c. The ^1H n.m.r. spectrum (in $CDCl_3$ solution) showed absorption at τ 5.29 ($p\text{-}MeC_6H_4SeCH_2Cl$?), 5.90, 7.15, and 7.25 [$SnPh_3(CH_2SeC_6H_4Me\text{-}p)$] in a ratio of 1 : 7 : 3 : 4.

Reactions of $Na[IO_4]$.*—With* $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. A solution of $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (1.0 g, 2.1 mmol) in dichloromethane (10 cm^3) was mixed with $Na[IO_4]$ (0.44 g, 2.1 mmol) dissolved in water (10 cm^3). The mixture was stirred vigorously overnight. The organic layer was then collected, dried over sodium sulphate, and the solvent

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removed under reduced pressure. Ethanol was added to the residue and (iodomethyl)triphenyltin was collected by filtration and crystallised from ethanol, m.p. 86.5—87.5 °C (lit.,[25] m.p. 86—87 °C), ^{1}H n.m.r. τ 2.20—2.90 (m) (15 H) and 7.55 (s) (2 H) (Found: C, 46.7; H, 3.4; I, 25.5. Calc. for $C_{19}H_{17}ISn$: C, 46.4; H, 3.5; I, 25.9%). The aqueous layer was acidic.

With $GePh_3(CH_2SC_6H_4Me\text{-}p)$. A mixture of $Na[IO_4]$ (0.25 g, 1.2 mmol) in water (10 cm^3) and $GePh_3(CH_2SC_6H_4\text{-}Me\text{-}p)$ (0.5 g, 1.2 mmol) in dichloromethane (10 cm^3) was stirred vigorously overnight. Work-up of the organic layer led to the complete recovery of $GePh_3(CH_2SC_6H_4Me\text{-}p)$.

Reactions of Ethyl Iodide.—With $SnPh_3(CH_2SC_6H_4Me\text{-}p)$. The ethyl iodide was a purified commercial sample. A solution of $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (0.2 g, 0.41 mmol) in EtI (5 cm^3) was heated under reflux for 5 d, after which time all the $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ had reacted (as shown by t.l.c.). The excess of EtI was removed under reduced pressure and two products in the residue were separated by t.l.c. [light petroleum (b.p. 60—80 °C)–chloroform (19 : 1) as eluant]. There were two bands, A and B, in order of increasing R_F: A, $SnPh_3(CH_2I)$, m.p. 85—87 °C (lit.,[25] 86—87 °C), ^{1}H n.m.r. τ 2.20—2.90 (m) (15 H) and 7.55 (s) (2 H); B, p-MeC_6H_4SEt, yield, 33 mg, τ 2.65—3.00 (m) (4 H), 6.90—7.36 (q) (2 H), 7.70 (s) (3 H), and 8.60—8.82 (t) (3 H).

With $GePh_3(CH_2SC_6H_4Me\text{-}p)$. A solution of $GePh_3\text{-}(CH_2SC_6H_4Me\text{-}p)$ (0.2 g, 0.46 mmol) in purified EtI (20 cm^3) was heated under reflux for 1 week. Although the solution became red in colour, the only species detected by t.l.c. in solution was the starting material.

Reaction of $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ *and Impure Methyl Iodide.*—An impure commercial sample of methyl iodide (0.35 g, 25 mmol) and $SnPh_3(CH_2SC_6H_4Me\text{-}p)$ (0.4 g, 0.83 mmol) in n-butanol (20 cm^3) were heated under reflux overnight. The solvent was removed and from the residual pale yellow oil, on standing, $SnPh_3I$ crystallised out. Light petroleum was added to the residue and the crystals were collected by filtration, m.p. 121—124 °C (lit.,[34] 120—121 °C), yield 0.15 g. The materials (A, B, C, and D) in the filtrate were separated by t.l.c. using light petroleum–benzene (3 : 1) as eluant: A, $SnPh_3(CH_2SC_6H_4Me\text{-}p)$, 24 mg, ^{1}H n.m.r. τ 2.20—3.00 (m) (19 H), 7.05 (s) (2 H), and 7.70 (s) (3 H); B, unidentified, 7 mg; C, p-MeC_6H_4SMe, 50 mg, ^{1}H n.m.r. τ 2.70—2.90 (m) (4 H), 7.55 (s) (3 H), and 7.70 (s) (3 H); D, $(p\text{-}MeC_6H_4S)_2$, 16 mg, ^{1}H n.m.r. τ 2.50—3.00 (m) (4 H) and 7.70 (s) (3 H). A, B, and D were identical with authentic samples.

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