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SULPHUR-CONTAINING ORGANOMETALLIC COMPOUNDS: PREPARATION AND SOME PHYSICAL PROPERTIES OF (*p*-TOLYLTHIOMETHYL)-TRIPHENYL-TIN AND -GERMANIUM, $Ph_3MCH_2SC_6H_4Me$-*p* (M = Ge, Sn) AND [2-(*p*-TOLYLTHIO)ETHYL] TRIPHENYLTIN, $Ph_3SnCH_2CH_2SC_6H_4Me$-*p*

ROBIN D. TAYLOR and JAMES L. WARDELL
Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE (Great Britain)
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Summary

The preparation and properties of $Ph_3MCH_2SC_6H_4Me$-*p* (M = Ge and Sn) and of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* are reported. Two synthetic methods have been found for the α-sulphur substituted organometallic compounds; reaction of (1) Ph_3MLi with $ClCH_2SC_6H_4Me$-*p* and (2) Ph_3MCH_2X with $NaSC_6H_4Me$-*p* (X = I, Cl). For the β-sulphur substituted compounds three routes are possible; reaction of (1) $Ph_3SnCH{=}CH_2$* with HSC_6H_4Me-*p* in the presence of AIBN, (2) Ph_3SnH with $CH_2{=}CHSC_6H_4Me$-*p* also in the presence of AIBN and (3) $(Ph_3Sn)_2Mg$ + $BrCH_2CH_2SC_6H_4Me$-*p*. The $Ph_3MCH_2SC_6H_4Me$-*p* compounds exhibit in most solvents temperature-dependent ^1H NMR spectra, while the spectrum of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* is essentially temperature-independent in carbon disulphide but not in carbon tetrachloride.

Introduction

There have been very few reports of α- and β-sulphur substituted alkyltin compounds; the first publication [1] of an α-sulphur substituted alkyltin was in 1971. This reported the preparation and some properties of R_3SnCH_2SMe and $R_3SnCH_2SO_2Y$ (R = Bu, Ph; Y = alkyl, aryl and NMe_2). In the next year, Brasington and Poller [2] gave the preparation and some physical properties of $(RSCH_2)_4Sn$ (R = Bu and Ph) and $Bu_{4-n}Sn(CH_2SPh)_n$ (n = 1, 2). The only report [3] of β-sulphur substituted alkyltin compounds was concerned with the preparation of $Bu_3SnCH_2CH_2SH$ and $Bu_3SnCH_2CH_2SC(O)Me$. No mention of an α-sulphur substituted alkylgermanium compound could be found in the literature.

We now wish to report the preparation and properties of the three related compounds: $Ph_3SnCH_2SC_6H_4Me$-*p*, $Ph_3GeCH_2SC_6H_4Me$-*p* and $Ph_3SnCH_2CH_2$-SC_6H_4Me-*p*.

Results and discussion

Preparation of (p-tolylthiomethyl)triphenyltin

No compounds of the type (arylthiomethyl)triphenyltin have been reported in the literature, although the related compounds, Bu_3SnCH_2SMe [1] and Bu_3SnCH_2SPh [2] have been. The method of preparation in each case was from the reaction of the appropriate lithiated methyl sulphide with tributyltin chloride (eqn. 1). The yield of Bu_3SnCH_2SPh was 59% while that of the Me derivative was unquoted.

$$(RSCH_3 \rightarrow)RSCH_2Li + Bu_3SnCl \rightarrow RSCH_2SnBu_3 \qquad (1)$$

Several attempts were initially made in this study to prepare (*p*-tolylthiomethyl)triphenyltin by this reaction, but all were unsuccessful. When this compound had been prepared by other methods it was in fact shown to react under mild conditions with an organolithium compound to give products arising from cleavage of the tin—methylene carbon bond (eqn. 2).

$$Ph_3SnCH_2SC_6H_4Me\text{-}p + n\text{-}BuLi \rightarrow n\text{-}BuSnPh_3 + LiCH_2SC_6H_4Me\text{-}p \qquad (2)$$

Addition of acetone to the n-BuLi/$Ph_3SnCH_2SC_6H_4Me$-*p* reaction mixture led, after hydrolysis, to 2-(*p*-tolylthiomethyl)propan-2-ol (eqn. 3); other products

$$LiCH_2SC_6H_4Me\text{-}p + Me_2CO \rightarrow p\text{-}MeC_6H_4SCH_2CMe_2OH \qquad (3)$$

isolated were hexaphenylditin, methyl *p*-tolyl sulphide and n-butyltriphenyltin. The methyl *p*-tolyl sulphide could arise from hydrolysis of $LiCH_2SC_6H_4Me$-*p*, possibly from water in the acetone. A route to the hexaphenylditin could be as follows:

$$Ph_3SnCH_2SC_6H_4Me\text{-}p + n\text{-}BuLi \rightarrow Ph_3SnLi + BuCH_2SC_6H_4Me\text{-}p$$
$$Ph_3SnLi \rightarrow Ph_3SnH \rightarrow (Ph_3Sn)_2$$

i.e. cleavage of the Sn—CH_2 bond in the opposite direction. However, the other product of this particular cleavage, $BuCH_2SC_6H_4Me$-*p*, was not definitively found. Another possibility is from the decomposition of $Ph_3SnCHLiSC_6H_4Me$-*p*:

$$Ph_3SnCH_2SC_6H_4Me\text{-}p + n\text{-}BuLi \rightarrow BuH + Ph_3SnCHLiSC_6H_4Me\text{-}p$$

The fact that an organolithium compound does react readily with (*p*-tolylthiomethyl)triphenyltin implies that eqn. 1 would be, at least, an inefficient one to use for its preparation. Hence the lack of success of preparing this compound from *p*-$MeC_6H_4SCH_2Li$ and Ph_3SnCl can be accounted for.

The routes to (*p*-tolylthiomethyl)triphenyltin subsequently found were (A) and (B) below.

$$\text{(A)}\quad p\text{-}MeC_6H_4S(O)CH_3 \xrightarrow[Et_2O]{HCl} p\text{-}MeC_6H_4SCH_2Cl \qquad (4)$$

$$p\text{-}MeC_6H_4SCH_2Cl + Ph_3SnLi \xrightarrow{THF} Ph_3SnCH_2SC_6H_4Me\text{-}p \qquad (5)$$

$$\text{(B)}\quad Ph_3SnCl \xrightarrow{ICH_2ZnI} Ph_3SnCH_2I \qquad (6)$$

$$Ph_3SnCH_2I + p\text{-}MeC_6H_4SNa \xrightarrow{EtOH} Ph_3SnCH_2SC_6H_4Me\text{-}p \qquad (7)$$

In the first of these routes (A), each of the two steps proceded readily in ca. 60% yield. It is of interest to note that Ph_3SnLi obviously does not react with the final product as does BuLi. For the preparation of a series of arylthiomethyltin compounds, this however would be a laborious route if each $ArSCH_2Cl$ had to be prepared from the appropriate thiol, ArSH. For such a series, (B) is by far the better one if starting from the thiols*. The pure product from route (B) was easily obtained from the reaction mixture in an excellent yield. The reaction was simply effected by refluxing for a few hours the ethanolic solution of the sodium salt of the thiol and Ph_3SnCH_2I, prepared essentially by Seyferth and Andrew's method [4], and on cooling the reaction mixture, the (*p*-tolylthiomethyl)triphenyltin crystallised out. During the course of our work, Brasington and Poller [2] published a similar method to (B) for the formation of $(RSCH_2)_4Sn$ from $(BrCH_2)_4Sn$.

Preparation of (p-tolylthiomethyl)triphenylgermanium

Having tried unsuccessfullly to prepare (*p*-tolylthiomethyl)triphenyltin from Ph_3SnCl and $LiCH_2SC_6H_4Me$-*p*, the analogous germanium reaction was not attempted. As with $Ph_3SnCH_2SC_6H_4Me$-*p*, $Ph_3GeCH_2SC_6H_4Me$-*p* was prepared from the reaction of the triphenylmetallithium compound with $ClCH_2SC_6H_4$-Me-*p* in 60% yield. The same objections already put forward to this method for the preparation of a series of arylthiomethyltin compounds, of course, apply for the germanium analogue. An attempt was made to prepare Ph_3GeCH_2I by the reaction of ICH_2ZnI and Ph_3GeCl but was not successful. In place of this, the following preparation of Ph_3GeCH_2Cl was adopted.

$$GeCl_4 + CH_2N_2 \rightarrow ClCH_2GeCl_3 \xrightarrow{PhBr/Mg} ClCH_2GePh_3 \qquad (8)$$

The (chloromethyl)triphenylgermanium was then treated with the sodium thiolate.

$$Ph_3GeCH_2Cl + NaSC_6H_4Me\text{-}p \xrightarrow{EtOH} Ph_3GeCH_2SC_6H_4Me\text{-}p \qquad (9)$$

The major difference in the work-up of the germanium reaction (9) and the tin reaction (7) was that NaCl, unlike NaI, is only sparingly soluble in ethanol and thus had to be removed before allowing the (*p*-tolylthiomethyl)triphenylgermanium to crystallise out (in ca. 65% yield).

Preparation of [2-(p-tolylthio)ethyl] triphenyltin

The possible methods of preparation of this compound can be put into two categories: homolytic and heterolytic reactions. Among the homolytic reactions are that of triphenyltin hydride with *p*-tolyl vinyl sulphide and that of triphenylvinyltin with *p*-toluenethiol.

$$Ph_3SnCH{=}CH_2 + HSC_6H_4Me\text{-}p \xrightarrow{AIBN} Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \qquad (10)$$

$$Ph_3SnH + CH_2{=}CHSC_6H_4Me\text{-}p \xrightarrow{AIBN} Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \qquad (11)$$

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* A series of compounds $Ph_3SnCH_2SC_6H_4X$-*p* (X = H, Et, t-Bu, OMe, NH_2, Cl, Br, NO_2) has been prepared in this way.

In the first of these, eqn. 10, various means of initiation were tried before deciding upon azobisisobutyronitrile, AIBN. These included using UV light (from different types of lamp and with different reaction times) and benzoyl peroxide. Success was almost negligible with these initiators, while a small quantity of AIBN using a short reaction time was successful. The ^{1}H NMR spectra of the AIBN catalysed reaction indicated the presence of at least 60% of the desired product. However, much less pure product was actually isolated, due to difficulties of separating the products. In the other reaction, eqn. 11, the same initiator was finally used, with another low yield of pure isolated product. This low yield also arose from difficulties of separating the products. Photochemical additions of hydrogen sulphide (at —70°) and thioacetic acid to triphenylvinyltin have been previously shown to give β-sulphur substituted alkyltin compounds, $Bu_3SnCH_2CH_2SH$ and $Bu_3SnCH_2CH_2SCOMe$ [3].

Three heterolytic reactions to [2-*p*-tolylthio)ethyl] triphenyltin were attempted (eqns. 12—14).

$$Ph_3SnLi + BrCH_2CH_2SC_6H_4Me\text{-}p \rightarrow Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \quad (12)$$

$$(Ph_3Sn)_2Mg + BrCH_2CH_2SC_6H_4Me\text{-}p \rightarrow Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \quad (13)$$

$$Ph_3SnCH_2I + LiCH_2SC_6H_4Me\text{-}p \rightarrow Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \quad (14)$$

Of these three, only eqn. 13 was successful. The lack of the desired product from eqn. 14 could be due to its reaction with organolithium compounds as happens to $Ph_3SnCH_2SC_6H_4Me$-*p*. While some product was obtained from eqn. 13, the yield was poor and this method is inferior to the two successful homolytic reactions.

An interesting β-sulphur substituted alkyltin, $Ph_3SnCHClCH_2SC_6H_4NO_2$-*o*, has been obtained from the electrophilic reaction of *o*-nitrobenzenesulphenyl chloride and triphenylvinyltin. Cleavage of the vinyl—tin bond also occurred but the other possible addition product, $Ph_3SnCH(SC_6H_4NO_2\text{-}o)CH_2Cl$ was not obtained [5].

Properties

General

The three compounds, $Ph_3SnCH_2SC_6H_4Me$-*p*, $Ph_3GeCH_2SC_6H_4Me$-*p* and $Ph_3SnCH_2CH_2SC_6H_4Me$-*p*, are all thermally stable solids. The m.p.'s of $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* ($n = 0, 1, 2$) are 103—105° [6], 112—113° and 73—74° respectively; the latter is lower than expected from a consideration of the other two values and could be a result of a greater degree of intramolecular association in the latter compound.

No decomposition of $Ph_3SnCH_2SC_6H_4Me$-*p* occurred on heating at 60° for 2 days in the presence of cyclohexene, while $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* was unaffected after heating at 100° for several hours.

The tin—alkylcarbon stretching frequencies were within the expected range [7], $Ph_3SnCH_2C_6H_4Me$-*p* at 567 cm^{-1}, $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* at 579 cm^{-1}. No assignment could be made for the metal—carbon frequency in $Ph_3GeCH_2SC_6H_4Me$-*p* (Table 1).

In the Mössbauer spectra of the tin compounds no quadrupole splittings were observed: the isomer shifts (relative to β-tin) were 1.33, 1.30 and 1.28 mm/sec for $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p*, $n = 0, 1, 2$, respectively (the quadrupole splitting for the compound with $n = 0$ was 1.54 mm/sec [6]).

TABLE 1

VIBRATIONAL SPECTRA IN THE 800 to 250 cm^{-1} REGION

$n = 0$		$n = 1$		$n = 2$	
IR [a]	Raman [b]	IR [a]	Raman [b]	IR [a]	Raman [b]
(i) $Ph_3Sn(CH_2)_nSC_6H_4Me$-p					
225 (sh)					
266 s	266 m	260 s	260 m	262 s	260 m
271 s					
294 m	296 s		305 m		
				338 w	333 m
362 s	360 s	366 vw	360 w		360 vw
374 m	372 m				
386 m	384 s				
396 vw		400 vw	398 vw	400 w	395 w
410 vw					
444 s	448 w	442 s	440 vw	440 s	440 w
450 s		449 s		448 s	
454 s	452 w	451 s		452 vs	
				460 s	
499 s		490 s	488 w	506 s	506 w
		567 m	567 m	583 m	576 s
617 w	618 w	613 vw	616 m	618 w	615 m
626 m	627 w	625 vw			
	638 m		632 m		635 m
660 m	655 s	658 m	652 m	655 s	654 s
				660 s	
695 s	700 w	695 s	700 w	698 s	695 s
730 s	738 w	728 s	730 w	730 vs	728 w
760 vw		760 m	762 w		
795 w	800 m	795 (sh)	795 m	800 (sh)	797 s
(ii) $Ph_3Ge(CH_2)_nC_6H_4Me$-p					
275 m	268 m	260 (sh)	265 w		
		292 m	288 w		
	300 w		304 w		
310 m	315 m		316 m		
325 s		326 s			
	360 w		363 w		
372 w	375 m	370 w			
385 m	391 s		390 w		
405 s		408 w			
461 s		460 s			
465 s		467 s			
474 s		472 s			
		492 m	495 w		
504 s	498 w	500 m			
	612 m	609 m	615 s		
619 w	620 w	621 m			
629 w	632 m	630 w	632 m		
666 w	662 s	668 (sh)	666 s		
676 m		674 m			
698 s	695 w	697 s	698 w		
736 s	720 w	731 s			
741 s		748 w	740 w		
		772 w	772 s		
798 m	792 s	795 (sh)	795 s		

[a] Measured in CsI discs on a Perkin—Elmer 457 Grating Infrared Spectrometer. [b] Measured with solid samples on a Cary Raman 83 Spectrometer.

Mass spectra

Molecular ion clusters of $[Ph_3MCH_2SC_6H_4Me\text{-}p]^+$ (M = Ge, Sn) were obtained in low intensities (2.5 and 7.5% respectively) in the mass spectra of $Ph_3MCH_2SC_6H_4Me$-*p* at 70 eV (Table 2). The base peak clusters were due to $[Ph_3M]^+$. No

TABLE 2

MASS SPECTRA AT 70 eV FOR $Ph_3Sn(CH_2)_nSC_6H_4Me$-*p* (*n* = 0—2) AND $Ph_3Ge(CH_2)_nSC_6H_4Me$-*p* (*n* = 0 and 1)[a]
Ions in abundance above 1%: M^+ (%).

$Ph_3SnSC_6H_4Me$-p	$Ph_3SnSC_6H_4Me$-*p* (11); $Ph_2SnC_6H_4Me$-*p* (2); $PhSnC_6H_4Me$-*p* (1); $C_{19}H_{17}Sn$ (3); Ph_3Sn (100); Ph_2Sn (1.5); $SnSC_6H_4Me$-*p* (5); PhSnS (2); PhSn (82); Sn(28).
$Ph_3SnCH_2SC_6H_4Me$-p	$Ph_3SnCH_2SC_6H_4Me$-*p* (7.5); $C_{19}H_{17}Sn$ (1); Ph_3Sn (100); Ph_2Sn (1.5); PhSn (25); Sn (18).
$Ph_3Sn(CH_2)_2SC_6H_4Me$-p	$Ph_3SnSC_6H_4Me$-*p* (13); $Ph_2SnSC_6H_4Me$-*p* (2.5); Ph_3Sn (100); Ph_2Sn (2); $SnSC_6H_4Me$-*p* (2); PhSn (29); Sn (20).
$Ph_3GeSC_6H_4Me$-p	$Ph_3GeSC_6H_4Me$-*p* (25); Ph_3Ge (100); Ph_2Ge (1).
$Ph_3GeCH_2SC_6H_4Me$-p	$Ph_3GeCH_2SC_6H_4Me$-*p* (2); Ph_3GeCH_2S (4.5); Ph_3Ge (100); $C_{13}H_{11}Ge$ (1.5); Ph_2Ge (25); $PhGeCH_2S$ (7.5); PhGe (95).

[a] Recorded on an AEI MS30 Instrument.

molecular ion clusters were found in the mass spectrum of $Ph_3SnCH_2CH_2SC_6H_4$-Me-*p* (Table 2). The highest *m/e* clusters corresponded to $[Ph_3SnSC_6H_4Me\text{-}p]^+$, i.e. loss of ethylene. The base peaks again were $[Ph_3Sn]^+$ and there were no really intense clusters containing the central CH_2 units. However, a very low intensity cluster, $[Ph_2SnCH_2CH_2SC_6H_4Me\text{-}p]^+$, was just discernible ($< 0.2\%$).

NMR spectra

$Ph_3MCH_2SC_6H_4Me$-p (M = Ge and Sn). The ^{117}Sn—H and ^{119}Sn—$^1H[CH_2]$ coupling constants were 47.5 and 50.0 Hz respectively. By a heteronuclear double resonance technique, the ^{119}Sn chemical shift was found to be 118 ppm (to high field of Me_4Sn). The ^{13}C chemical shifts of the CH_2 carbons were 12.03 and 16.84 ppm (relative to $CDCl_3$) for M = Sn and Ge respectively.

The ^1H 100 MHz NMR spectra of $Ph_3MCH_2SC_6H_4Me$-*p* in solvents such as CS_2 exhibit interesting temperature effects (Fig. 1). As the temperature is altered, so changes are seen in the resonances of the protons in the *p*-disubstituted ring, C_6H_4, the rest of the spectra remaining essentially unchanged. For $Ph_3SnCH_2SC_6H_4$-Me-*p*, for example, at 30° in CS_2, these four protons constitute an AA'BB' system giving essentially a quartet spectrum. On lowering the temperature, the splitting between the central lines of the 'quartet' decreases until at —44°, only a singlet is present. This is clearly a chemical shift change rather than an equilibrium effect, since there is no increase in the line widths. The proton-coupling does not alter either. At the higher temperature, there must be sufficient differences in the electronic effects of the $(Ph_3SnCH_2)S$ and CH_3 substitutents for the protons in the *p*-disubstituted ring to have different chemical shifts; that of the protons *ortho* to the sulphur being downfield to that of the protons *ortho* to the methyl group. As the temperature is lowered, the four protons eventually become equivalent and resonate as a singlet. At equivalence, the chemical shift is that initially observed for the protons *ortho* to the methyl group. This effect can be explained by assuming association between tin and sulphur of either an inter-(I) or intra-molecular (II) nature, which increases as the temperature is lowered. This increase in association would result in a greater withdrawal of electrons from

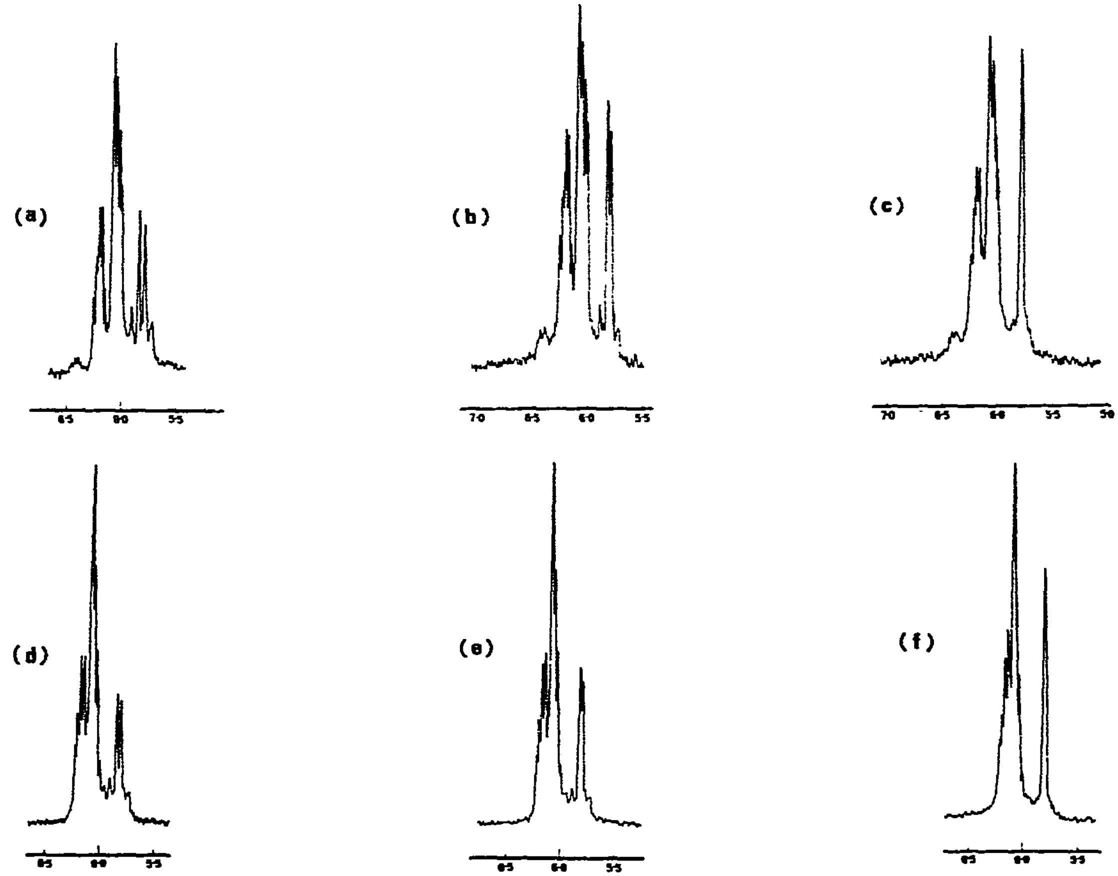
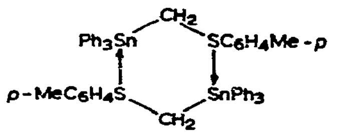


Fig. 1. Aromatic region in the ^{1}H NMR spectra (100 MHz) in CS_2 solution of $Ph_3SnCH_2SC_6H_4Me$-*p* at (a) 30°, (b) —14° and (c) —44° and of $Ph_3GeCH_2SC_6H_4Me$-*p* at (d) 30°, (e) 0° and (f) —30°.

sulphur with attendent changes in the electronic effect on its *ortho* hydrogens. The choice between I and II is difficult to make; both in fact might be present.



(I)

(II)

Further lowering of the solution temperature below —40°, to see whether a further chemical shift change occurred, unfortunately brought about crystallisation of the tin compound. Other solvents, such as carbon tetrachloride, tetrachloroethylene, $CDCl_3$, CD_3NO_2, benzene-d_6, were used; the largest changes were in carbon disulphide solution. Suitable solvents were quite limited in number since they had to be liquid over a large temperature range and able to dissolve the tin compounds in this range.

A similar discussion could be put forward for the variable $Ph_3GeCH_2SC_6H_4$-Me-*p* spectra.

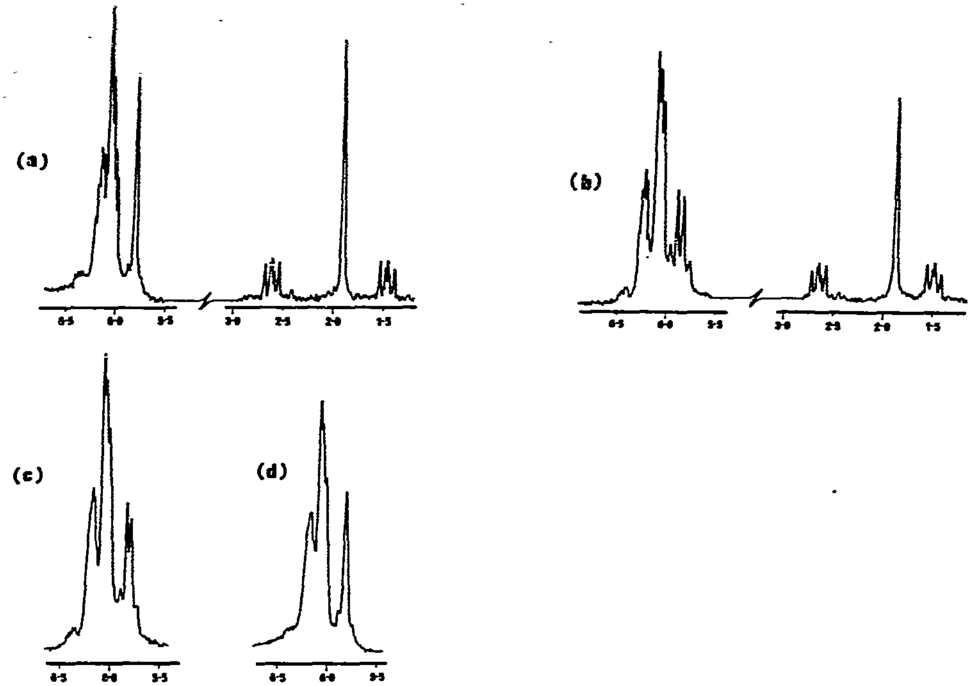
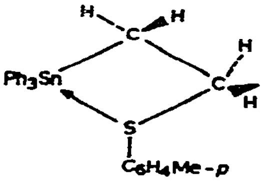


Fig. 2. ^1H NMR spectra (100 MHz) of $Ph_3SnCH_2CH_2SC_6H_4Me$-*p* (a) in CS_2 solution at 30° and in CCl_4 solution at (b) 60°, (c) 30° and (d) —5°.

$Ph_3SnCH_2CH_2SC_6H_4Me$-p. The ^1H 100 MHz NMR spectrum of Ph_3SnCH_2-$CH_2SC_6H_4Me$-*p* in CS_2 was essentially temperature-independent [at 30°, 0° and —30°]. At 30°, the four protons in the *p*-disubstituted ring were almost equivalent, resonating as a broad singlet, and the only change on lowering the temperature to —30° was a sharpening of this singlet. However, in CCl_4 solution, this portion of the spectrum was more temperature-dependent. (Fig. 2) Changing the temperature from 60° to —5° caused the distinct AA′BB′ quartet to collapse to a singlet.

An interesting feature of the ^1H NMR spectrum in all solvents was that the two CH_2 units did not resonate as triplets but as multiplets. [In $CDCl_3$ solution: the CH_2 α to the tin at 8.05—8.35 γ and that β to the Sn at 6.60—6.90 γ; the multiplets are mirror images]. From an inspection of a model, it can be seen that the sulphur can approach very close to the tin without much strain and so an intramolecular structure III is possible. If this does happen in solution, it would result in each proton in each CH_2 being inequivalent.



(III)

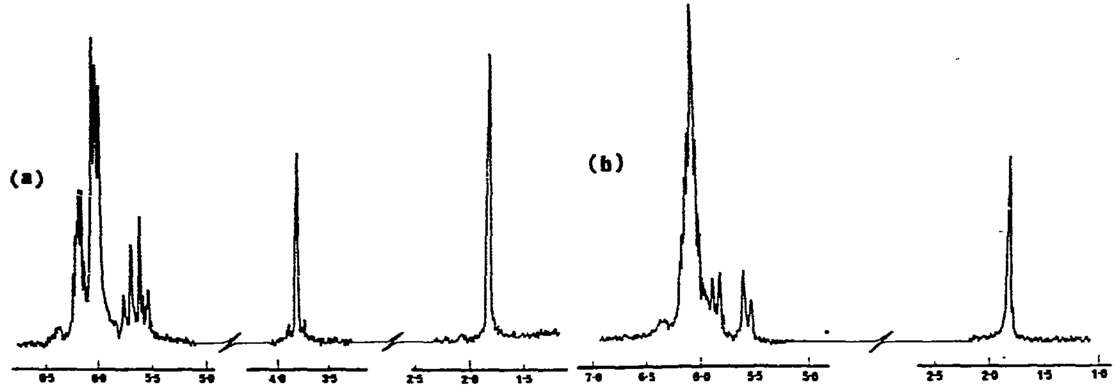


Fig. 3. ^{1}H NMR spectra (100 MHz) in CS_2 solution of (a) $Ph_3SnCH_2OC_6H_4Me$-*p* and (b) $Ph_3SnSC_6H_4$-Me-*p*.

Interestingly, $Ph_3SnCH_2OC_6H_4Me$-*p* and $Ph_3SnSC_6H_4Me$-*p* (Fig. 3) both have temperature-invariable ^{1}H NMR spectra; in each case, the *p*-disubstituted aromatic ring always constitutes an AA'BB' system. This is also found in the organometallic *p*-tolyl sulphides $M(SC_6H_4Me\text{-}p)_n$ (M = Sb, $n = 3$; M = PhHg, $n = 1$; M = Bu_3Sn, Me_3Sn, Bu_3Ge, Ph_3Pb, $n = 1$; M = Me_2Sn, $n = 2$).

Experimental

Triphenyltin *p*-tolyl sulphide was a sample from a previous study [6]. Chloromethyl *p*-tolyl sulphide [8] b.p. 80°/4 mm; (chloromethyl)trichlorogermane [10]; (chloromethyl)triphenylgermanium [11], m.p. 117–118.5° (lit. [11], m.p. 116–118°); triphenylvinyltin [14], m.p. 38–39° (lit. [14] m.p. 39°), were prepared according to published procedures.

Methyl p-tolyl sulphoxide

A solution of sodium metaperiodate (12.7 g, 0.06 mole) in water (80 ml) and methyl *p*-tolyl sulphide (8.0 g, 0.058 mole) were stirred at 0° overnight [9]. The mixture was filtered to remove the sodium iodate, which was well washed with methylene chloride (3 × 20 ml). The organic layer of the combined washings and filtrate was collected, dried with sodium sulphate and the solvent removed. Methyl *p*-tolyl sulphoxide was distilled, b.p. 119°/0.2 mm, yield 6.4 g, 71%.

(Iodomethyl)triphenyltin

To the zinc/copper couple, from cupric acetate monohydrate (0.09 g) granular zinc (6.5 g, 0.1 mole) and acetic acid (10 ml), in tetrahydrofuran was added slowly diiodomethane (27.0, 0.1 mole) in tetrahydrofuran (30 ml). The mixture was stirred at room temperature for 3 h after which time all the zinc had reacted. The pale purple solution was cooled in an ice-bath and rapidly filtered through glass wool into a dry, nitrogen-filled flask. To this solution was added triphenyltin chloride (18.1 g, 0.047 mole) in tetrahydrofuran (80 ml) and the solution was stirred at ca. 40° for 3 h. To the almost colourless solution so formed was added hydrochloric acid (75 ml, 5%), then benzene (50 ml). The layers were separated and the organic layer further extracted with hydrochloric acid (3 × 75 ml, 5%). The organic layer was dried with sodium sulphate, the solvents removed to yield (iodomethyl)triphenyltin, which was crystallised from light petroleum, m.p. 85—86.5° (lit. [4] m.p. 86—87°), yield 19.8 g (86%).

2-Bromoethyl p-tolyl sulphide

In accord with a basic method of Schneider [12], bromine (16.0 ml, 0.1 mole) was added to a stirred carbon tetrachloride solution of *p*-toluenethiol (12.4 g, 0.1 mole) at —25°. Ethylene was bubbled through the dark red solution for 1½ h while the temperature was raised to 10°, forming a pale yellow solution. The solvent was removed and the 2-bromoethyl *p*-tolyl sulphide purified by distillation, b.p. 126—127°/0.8 mm, n_D^{22} 1.5940, yield 11.8 g, 50%.

p-Tolyl vinyl sulphide

In accord with a general method [13], 2-bromoethyl *p*-tolyl sulphide (7.0 g, 0.03 mole) was added to a boiling solution of sodium (0.7 g, 0.03 mole) in n-amyl alcohol. A precipitate of sodium bromide formed immediately on mixing. After heating under reflux for 40 min the precipitate was removed and the filtrate distilled to give initially n-amyl alcohol and subsequently *p*-tolyl vinyl sulphide, b.p. 104—106°/20 mm.

Triphenyltin hydride

To a rigorously stirred suspension of magnesium (2.0 g) in tetrahydrofuran (50 ml) was added a solution of triphenyltin chloride (5.0 g, 0.013 mole) in tetrahydrofuran (20 ml). A white precipitate was formed, which gradually disappeared to give a dark grey-green coloured solution of bis(triphenyltin)magnesium [15]. This was quickly filtered through glass wool and hydrolysed with a saturated ammonium chloride solution. The organic layer was separated, dried with sodium sulphate and the solvent removed to leave triphenyltin hydride.

Preparation of (p-tolylthiomethyl)triphenylgermanium

(a). From triphenylgermyllithium and chloromethyl p-tolyl sulphide. A mixture of triphenylgermanium bromide (3.84 g, 0.01 mole) and pieces of lithium wire (0.69 g, 0.1 mole) in tetrahydrofuran (50 ml) was stirred for 3 h. The dark, red-brown coloured solution of triphenylgermyllithium thus formed was filtered quickly through glass wool.

To this solution was added dropwise, with stirring, chloromethyl *p*-tolyl sulphide (1.73, 0.01 mole) in tetrahydrofuran. The reaction was exothermic and the solution changed colour from dark red-brown to pale brown. After being stirred overnight, the solution was hydrolysed with a saturated ammonium chloride solution and the organic layer was collected and dried over sodium sulphate. The solvent was removed to yield (*p*-tolylthiomethyl)triphenylgermanium, which was recrystallised from 95% ethanol, m.p. 147—148.5°, yield 3.0 g, 65%. (Found, C, 70.8; H, 5.3; S, 7.3. $C_{26}H_{24}GeS$ calcd.: C, 70.8; H, 5.3; S, 7.25%.)

(b). From (chloromethyl)triphenylgermanium and p-toluenethiol. To a solution of sodium ethoxide, prepared from sodium (0.033 g, 0.0014 mole) and ethanol (100 ml), was added *p*-toluenethiol (0.18 g, 0.0014 mole), then (chloromethyl)triphenylgermanium (0.5 g, 0.0014 mole). The reaction mixture was heated under reflux overnight. The sodium chloride precipitate was removed and the solvent removed from the filtrate to give (*p*-tolylthiomethyl)triphenylger-

manium, which was recrystallised from ethanol, m.p. 148—149°, yield 0.43 g, 64%. ^{1}H NMR (100 MHz) ($CDCl_3$ 30°): τ 2.20—3.05 (19 H, m), 6.93 (2H, s), 7.71 (3H, s).

Preparation of (p-tolylthiomethyl)triphenyltin

(a). From triphenyltinlithium and chloromethyl p-tolyl sulphide. A solution of triphenyltinlithium in tetrahydrofuran was prepared from triphenyltin chloride (4.95 g, 0.013 mole) and lithium (0.9 g, 0.13 mole). To this solution was added, dropwise with stirring, chloromethyl *p*-tolyl sulphide (2.25 g, 0.013 mole) in tetrahydrofuran (100 ml). The reaction was exothermic and the solution changed colour from dark green to dark brown. After stirring for 1 h the solution was hydrolysed with saturated ammonium chloride solution and the organic layer was collected and dried with sodium sulphate. The solvent was removed and the (*p*-tolylthiomethyl)triphenyltin was precipitated from the oily residue on addition of 95% ethanol. Recrystallisation was from ethanol, m.p. 112°, yield 4.20 g, 64%. It was identical with the sample formed below.

(b). From (iodomethyl)triphenyltin and p-toluenethiol. *p*-Toluenethiol (0.25 g, 0.002 mole), then (iodomethyl)triphenyltin (1.0 g, 0.002 mole) were added to a solution of sodium (0.047 g, 0.002 mole) in ethanol and the mixture heated under reflux overnight. On cooling, (*p*-tolylthiomethyl)triphenyltin precipitated and was recrystallised from ethanol, m.p. 112—113°, yield 0.86 g, 86%. (Found, C, 64.0; H, 4.8; S, 6.5. $C_{26}H_{24}SnS$ calcd.: C, 63.9; H, 4.9; S, 6.5%.) ^{1}H NMR (100 MHz) ($CDCl_3$ 30°): τ 1.80—3.00 (19H, m), 7.09 (2H, s), 7.70 (2H, s).

Preparation of [2-(p-tolylthio)ethyl] triphenyltin

(a) From bis(triphenyltin)magnesium and 2-bromoethyl p-tolyl sulphide. To a tetrahydrofuran solution of bis(triphenyltin)magnesium, from triphenyltin chloride (5.0 g, 0.013 mole) and magnesium (2.0 g) was added with stirring a solution of 2-bromoethyl *p*-tolyl sulphide (1.5 g, 0.0065 mole) in tetrahydrofuran. The reaction was exothermic and there was a colour change from dark grey-green to grey. The mixture was warmed for 1½ h, stirring at room temperature overnight, then hydrolysed with saturated ammonium chloride solution. The organic layer was collected and dried with sodium sulphate. The solvent was removed to yield an oily solid. Light petroleum was added to the residue and the insoluble hexaphenylditin collected by filtration. Removal of the solvent from the solution yielded an oil from which [2-(*p*-tolylthio)ethyl] triphenyltin was isolated by several careful crystallisations from methanol, m.p. 73—74°, yield 20%. (Found: C, 64.3; H, 5.3; S, 6.4. $C_{27}H_{26}SSn$ calcd.: C, 64.6; H, 5.2; S, 6.4%.)

(b). From triphenylvinyltin and p-toluenethiol. Triphenylvinyltin (5.0 g, 0.013 mole) and *p*-toluenethiol (1.6 g, 0.013 mole) were mixed and a small quantity of azobisisobutyronitrile (AIBN) added. The mixture was heated at 80—100° for about 15 min, during which time a gas was evolved. An ^{1}H NMR spectrum taken of the reaction mixture at this stage indicated that ca. 60% of the mixture was [2-(*p*-tolylthio)ethyl] triphenyltin, which was obtained, with some difficulty, by successive careful crystallisations from methanol, m.p. 71—73°, ^{1}H NMR and IR spectra were identical to those of an authentic sample of [2-(*p*-tolylthio)ethyl] triphenyltin.

(c). From triphenyltin hydride and p-tolyl vinyl sulphide. Unpurified triphenyltin hydride (1.0 g), *p*-tolyl vinyl sulphide (0.4 g) and a little AIBN were heated at 80—95° for 40 min, after which time the IR spectrum showed that all the triphenyltin hydride had reacted. The ^{1}H NMR spectrum of the mixture showed it to be composed of *p*-tolyl vinyl sulphide and the desired product, [2-(*p*-tolylthio)ethyl] triphenyltin. The components were separated by preparative TLC, using light petroleum/chloroform, (80/20), as eluant. The band with the lowest R_F value was [2-(*p*-tolylthio)ethyl]triphenyltin. ^{1}H NMR (100 MHz): in $CDCl_3$ solution: τ 1.80—2.95 (19H, m), 6.60—6.90 (2H, m), 7.70 (3H), 8.05—8.35 (2H, m).

Reaction of (p-tolylthiomethyl)triphenyltin with n-butyllithium

n-Butyllithium (0.16 g, 0.0025 mole) in dry hexane (2 ml) was added dropwise to a stirred suspension of (*p*-tolylthiomethyl)triphenyltin (1.0 g, 0.0021 mole) in dry hexane (75 ml) and the solution was gently heated for 90 min. Anhydrous acetone (0.15 g) in hexane (10 ml) was then added dropwise and the mixture was refluxed for 90 min. On cooling, hexaphenylditin separated out and was collected. It was recrystallised from benzene, m.p. 226—229° (Lit. [16] m.p. 229—331°) yield 0.4 g. To the filtrate, saturated ammonium chloride solution was added and the organic layer was collected and dried over sodium sulphate. The solvent was removed and the residue was separated by preparative TLC, using light petroleum/chloroform (1/1) as eluant. This separated the mixture into two components, 2-(*p*-tolylthiomethyl)propan-2-ol, 0.19 g, (^{1}H NMR: τ 2.60—3.00 (4H, m) 6.95 (2H, s); 7.60 (1H, s): IR: 3420 [free OH] and 800 cm^{-1} [*p*-disubstituted aromatic ring]) and a group of products with a larger R_F value. These latter products were eventually separated by TLC (light petroleum/benzene (65/35) as eluant) into three components (in order of increasing R_F value): *(i)* n-butyltriphenyltin, m.p. 60—62°; ^{1}H NMR (100 MHz): τ 2.30—3.00 (15H, m), 8.30—9.40 (9H, m); yield 0.30 g; *(ii)* methyl *p*-tolyl sulphide; ^{1}H NMR 100 MHz: τ 2.70—2.90 (4H, m), 7.55 (3H, s), 7.70 (3H, s); yield 0.165 g; *(iii)* unknown; ^{1}H NMR 100 MHz: τ 2.30—2.85 (2H, m), 8.20—9.40 (6H, m).

Preparation of (p-tolyloxymethyl)triphenyltin

(Iodomethyl)triphenyltin (1.0 g, 0.022 mole) was added to a solution of sodium (0.047 g, 0.002 mole) and *p*-cresol (0.22 g, 0.002 mole) in ethanol (10 ml). The reaction mixture was refluxed overnight, cooled and the solvent removed. (*p*-Tolyloxymethyl)triphenyltin was separated by TLC from the residue. The product was crystallised from ethanol, m.p. 66.5—67.5°, yield 0.40 g, 42%. ^{1}H NMR 100 MHz; in $CDCl_3$ solution τ 1.80—3.30 [19H, m), 5.30 (2H, s), 7.70 (3H, s).

Preparation of triphenylgermanium p-tolyl sulphide

To a solution of triphenylgermanium bromide [17] (5.0 g, 0.013 mole) and triethylamine (1.4 g, 0.014 mole) in CCl_4 (80 ml) was added *p*-toluenethiol (1.5 g, 0.013 mole) in CCl_4 (15 ml). After heating under reflux for 2½ h, the precipitate of triethylamine hydrochloride (2.4 g, 100%) was collected. Evaporation of the solvent from the filtrate gave crude triphenylgermanium *p*-tolyl sulphide, which was recrystallised from light petroleum, m.p. 91—92.5°, yield 3.6 g, 65%. (Found, C, 70.8; H, 5.5; S, 7.7. $C_{25}H_{22}GeS$ calcd.: C, 70.4; H, 5.2; S, 7.5%.)

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