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THE PREPARATION OF DI- AND TRI-PHENYLSTANNYL ESTERS OF AROMATIC DITHIO ACIDS, AND SOME OF THEIR REACTIONS

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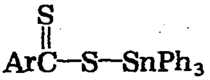
Summary

Some crystalline di- and tri-phenylstannyl esters [$\mathrm{ArCS_2SnPh_3}$ and $\mathrm{(ArCS_2)_2SnPh_2}$] of aromatic dithio acids have been prepared in good yields and characterized. Preferential cleavage of the Sn—S bond of the ester was observed by treating them with primary and secondary amines as well as with phenacylidenetetramethylenesulfurane.

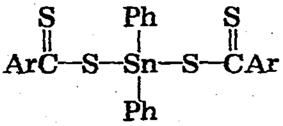
Introduction

In a previous report [1], we described the preparation and spectral properties of some trimethyl—Group IVb metal esters of dithio acids. The present paper describes the preparation of crystalline di- and tri-phenylstannyl esters (I and II) of aromatic dithio acids and their reaction with some nucleophiles.



$$\mathrm{Ar}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}S{-}SnPh_3}$$

(I).



$$\mathrm{Ar}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}S{-}}\underset{\underset{\mathrm{Ph}}{|}}{\overset{\overset{\mathrm{Ph}}{|}}{\mathrm{Sn}}}\mathrm{{-}S{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{Ar}$$

(II)

Results and discussion

Preparation

Di- and tri-phenylstannyl esters were obtained in good yields by slightly modifying our previous procedures [1]: (a) replacement of petroleum ether by dichloromethane as solvent; (b) the use of a Soxhlet extractor, and diethyl

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ether as solvent for the separation of the stannyl esters and piperidinium chloride. For example, when an equimolar amount of piperidinium *p*-methyldithiobenzoate was treated with chlorotriphenylstannane in dichloromethane at room temperature for 3 h, pure (*p*-methylthiobenzoylthio)triphenylstannane (Ib) was obtained in a yield of 68%. Analogous treatment of piperidinium salts of other substituted-dithiobenzoates with chlorotriphenylstannane gave the corresponding stannyl esters (Ia, Ic—Ig). Reactions of these salts with dichlorodiphenylstannane gave bis(thioaroylthio)diphenylstannanes (II) in good yield (Table 1). As shown in Table 1, in the UV and visible spectra two characteristic absorption maxima are observed at 310—350 nm (ϵ 8000—33000) and 490—510 nm (ϵ 150—300). The former band can be ascribed to the π—π^* and the latter one to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. The absorption maxima in both the UV and visible region appeared for the *para* isomers at longer wavelength than the ones given by the *ortho* isomers. In contrast, the molecular extinction coefficients for the π—π^* transition of the *para* isomer were larger than those of the *ortho* isomer, while those of $n \rightarrow \pi^*$ transition with the exception fo the methoxy substituted species exhibited an opposite behavior. The larger hypsochromic shifts of the absorption maxima of the *ortho* isomer can be interpreted in terms of steric hindrance of resonance caused by the *ortho*-substituent.

Reactions

The stannyl esters I and II were quite stable, and unreactive toward methanol even when refluxed for 24 h. However, the stannyl ester Ib readily reacted with a variety of amines at room temperature. The reaction conditions and the yields of the products are summarized in Table 2. The products of this reaction were bis(triphenylstannyl) sulfide (III), thioamides, and amine salts or their decomposition products (thioamide and hydrogen sulfide). The isolation of piperidinium or cyclohexylammonium *p*-methyldithiobenzoates with no evolution of hydrogen sulfide indicates that the ester Ib was preferentially cleaved at the carbon—sulfur bond by the attack of amines*.

These results could be rationalized as follows (Scheme 1): the reaction proceeds via a four center transition state (A) in the interaction of the stannyl esters I with amines, resulting in the formation of corresponding dithio acids V and the aminostannane VI: the dithio acids formed react immediately further with the amine to yield amine salts VII, which, in some cases, decompose to the thioamide and hydrogen sulfide [2, 3], while the reactive intermediate, aminostannane VI, readily reacts with the remaining Ib to give bis(triphenylstannyl) sulfide.

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* If direct attack of piperidine on the thiocarbonyl carbon in the ester Ib occurs, evolution of hydrogen sulfide should be observed according to the following equation:

$p\text{-}CH_3C_6H_4CS_2SnPh_3 + C_5H_{10}NH \rightarrow Ph_3SnSH + p\text{-}CH_3C_6H_4C(S)NC_5H_{10}$

$2\ Ph_3SnSH \rightarrow (Ph_3Sn)_2S + H_2S$

However, we observed no evolution of H_2S in this reaction. Moreover, it was found that bis(*p*-methylthiobenzoyl) disulfide [$(p\text{-}CH_3C_6H_4CS_2)_2$] readily reacted with piperidine with no evolution of hydrogen sulfide to give piperidinium *p*-methyldithiobenzoate in quantitative yield. The salt also decomposed above its melting point to give *p*-methylthiobenzpiperidide and hydrogen sulfide in a similar high yield.

TABLE 1. YIELDS AND CERTAIN PHYSICAL PROPERTIES OF DI- AND TRI-PHENYLSTANNYL ESTERS OF AROMATIC DITHIO ACIDS

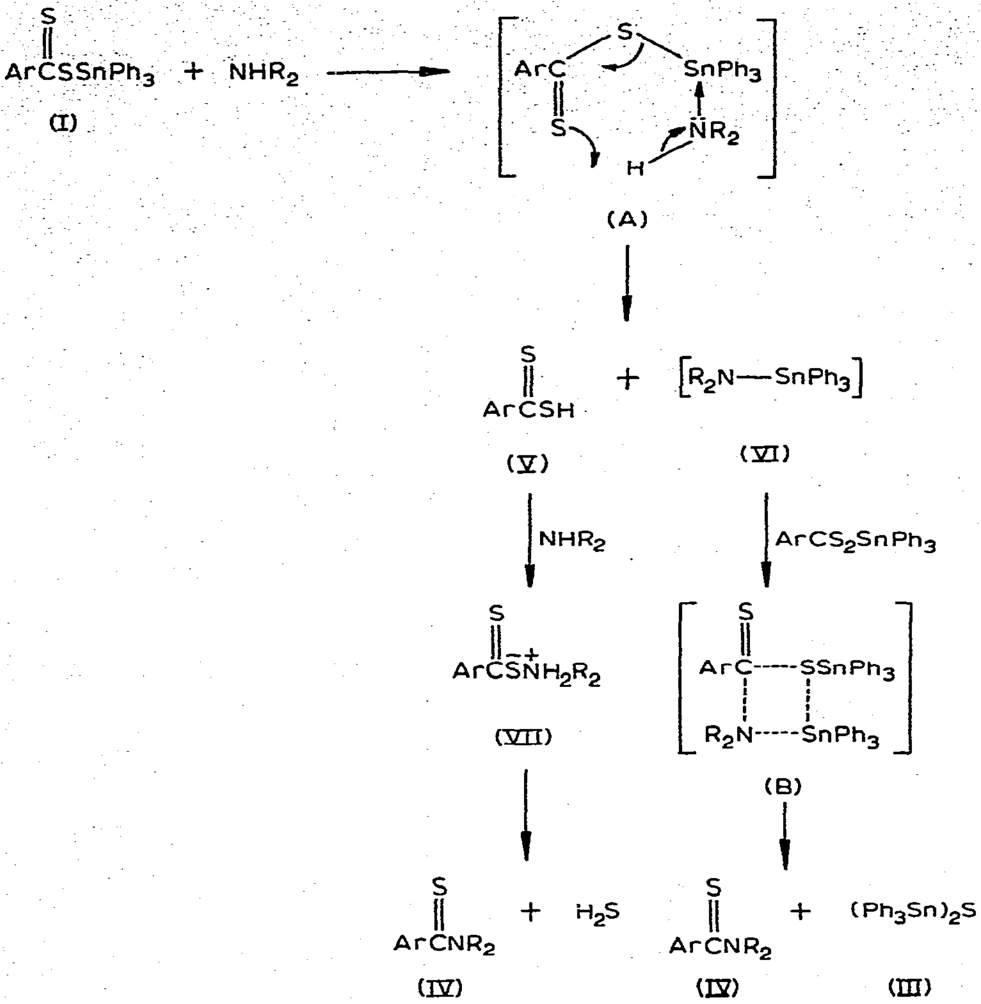
No.	Compound	M.p. (°C)	Color	Yield (%)	NMR ($CDCl_3$) (δ, ppm)		IR (KBr) ν(C=S) (cm^{-1})	UV ($CHCl_3$) λ_{max} (nm)(ε)
Ia	$C_6H_5CS_2SnPh_3$	98.0—100.5	Red	64		7.33 (aromatic, m, 20H)	1217	312 (20200) 508 (151)
Ib	p-$CH_3C_6H_4CS_2SnPh_3$	119.0—122.0	Red	68	2.28 (CH_3, s, 3H)	7.40 (aromatic, m, 19H)	1218	328 (32600) 504 (243)
Ic	o-$CH_3C_6H_4CS_2SnPh_3$	99.0—100.5	Orange	72	2.24 (CH_3, s, 3H)	7.38 (aromatic, m, 19H)	1235	324 (12200) 493 (295)
Id	p-$CH_3OC_6H_4CS_2SnPh_3$	108.5—111.5	Red	56	3.78 (OCH_3, s, 3H)	7.50 (aromatic, m, 19H)	1237	349 (27500) 504 (250)
Ie	o-$CH_3OC_6H_4CS_2SnPh_3$	106.0—108.0	Orange	52	3.82 (OCH_3, s, 3H)	7.40 (aromatic, m, 19H)	1233	337 (8000) 496 (172)
If	p-$ClC_6H_4CS_2SnPh_3$	113.5—115.0	Red	48		7.45 (aromatic, m, 19H)	1210	321 (19600) 512 (156)
Ig	o-$ClC_6H_4CS_2SnPh_3$	106.5—108.0	Orange	67		7.50 (aromatic, m, 19H)	1230	309 (13000) 496 (271)
IIa	$(C_6H_5CS_2)SnPh_2$	151.0—152.5	Orange	83		7.34 (aromatic, m, 20H)	1218	320 (43100) 462 (620)
IIb	$(p$-$CH_3C_6H_4CS_2)_2SnPh_2$	171.0—172.0	Orange	93	2.38 (CH_3, s, 6H)	7.00—8.32 (aromatic, m, 18H)	1223	336 (44200) 460 (780)
IIc	$(p$-$ClC_6H_4CS_2)_2SnPh_2$	158.0—160.0	Orange	88		7.43 (aromatic, m, 18H)	1230	330 (45000) 465 (680)

TABLE 2. REACTION OF (p-METHYLTHIOBENZOYLTHIO)TRIPHENYLSTANNANE (Ib) AND BIS(p-METHYLTHIOBENZOYLTHIO)DIPHENYLSTANNANE (IIb) WITH AMINES

Tin esters	Amines	Mol. Ratio Ib or IIb/amine	Solv.	Temp. (°C)	Time (h)	Products (%) [a]				
						$(Ph_3Sn)_2S$	$(Ph_2SnS)_3$	Amine Salts	Thio-amides	H_2S
$(p$-$CH_3C_6H_4CS_2SnPh_3$ (Ib)	NH_3	excess	Ether	R.T.	3	94.8		14	78.5	evolution
	p-$CH_3C_6H_4NH_2$	1/1	Ether	R.T.	24	96.8			92.6	evolution
	cyclo-$C_6H_{10}NH_2$	1/1	Ether	R.T.	3	94.4		43.6	45.6	
	$C_5H_{10}NH$	1/1	Ether	R.T.	2	98.0		45.3	43.0	
	Ph_2NH	1/1	THF	66	24		no reaction			
	$PhNHNH_2$	1/1	Ether	R.T.	24	92.0			94.6	evolution
	$HOCH_2$-CH_2NH_2	1/1	Toluene	90	2	84.0			84.0	evolution
$(p$-$CH_3C_6H_4CS_2)_2SnPh_2$ (IIb)	p-$CH_3C_6H_4NH_2$	1/2	Ether	R.T.	50		94.0 [b]		91.5 [b]	evolution
	$C_5H_{10}NH$	1/2	Ether	R.T.	2		96.5 [b]	44.0	47.4 [b]	

[a] Based on the tin ester Ib, according to Scheme 1. [b] Based on the tin ester IIb, according to Scheme 2.

SCHEME 1



On the other hand, the reaction of bis(*p*-methylthiobenzoylthio)diphenylstannane (IIb) with two equivalents of piperidine under similar conditions gave trimeric diphenyltin sulfide (VIII), the piperidinium *p*-methyldithiobenzoate and *p*-methylthiobenzpiperidide. The reaction with toluidine, however, afforded, with evolution of hydrogen sulfide, trimer VIII and *p*-methylthiobenzpiperidide (Table 2). A plausible explanation for the formation of these reaction products is given in Scheme 2.

It is not obvious whether or not the direct attack of the amine on the thiocarbonyl carbon takes place during the reactions of dithio esters with primary or secondary amines. However, the fact that the amine salts of dithio acids were isolated from the reactions mentioned above suggests that in the first step, at least, the thiocarbonyl carbon of the tin esters I and II was not directly attacked by the amines. Therefore, we investigated the reaction with ylides which have an isoelectronic structure with the amines used in this study.

SCHEME 2

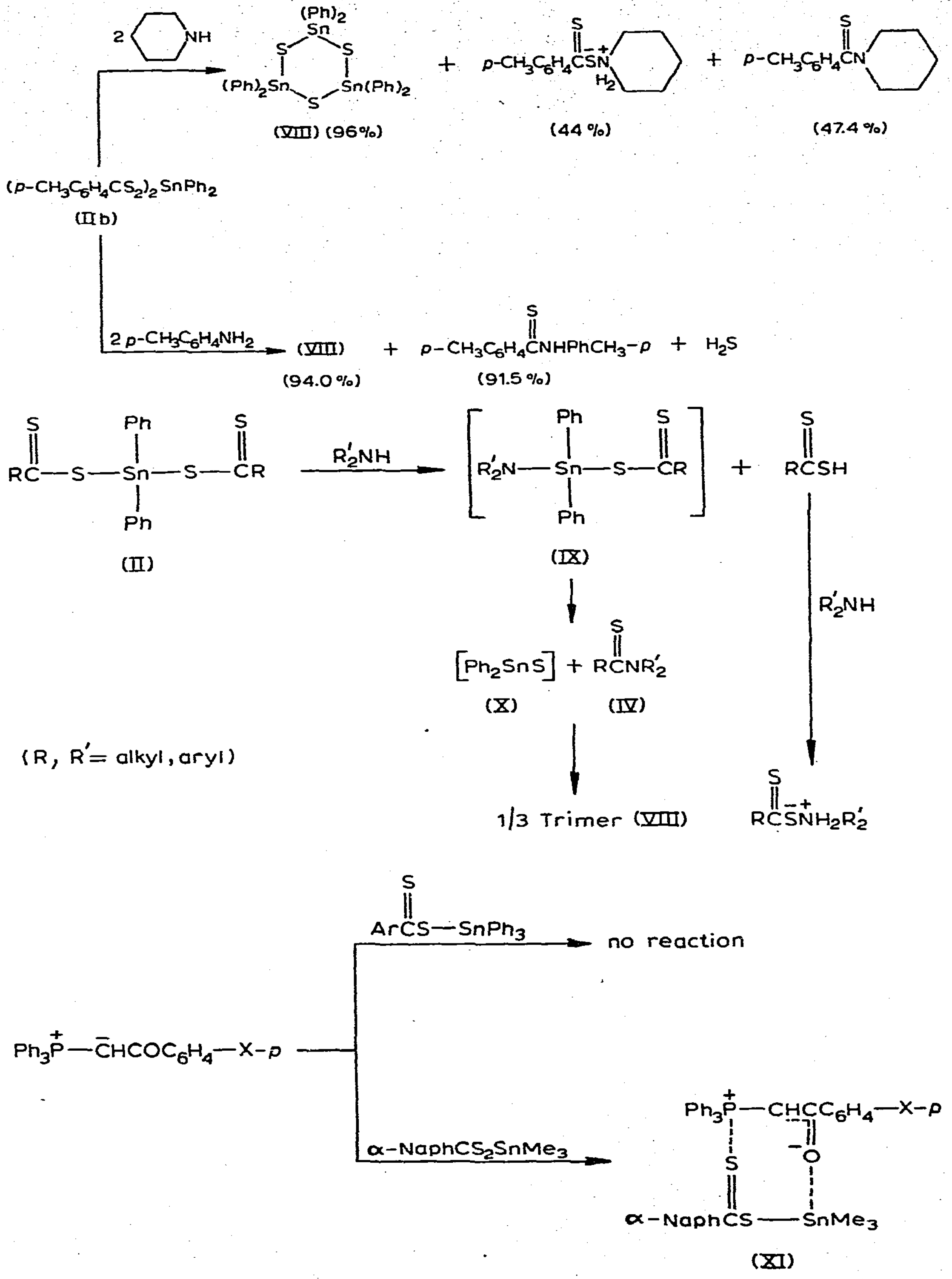
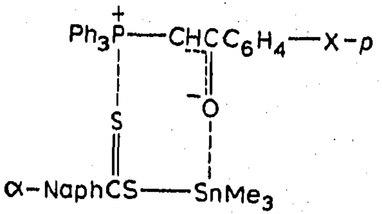

2 NH
(Ph)$_2$ Sn S S (Ph)$_2$Sn Sn(Ph)$_2$ S
(VIII) (96%)
+ p-CH$_3$C$_6$H$_4$CSN H$_2$
(44 %)
+ p-CH$_3$C$_6$H$_4$CN
(47.4 %)
(p-CH$_3$C$_6$H$_4$CS$_2$)$_2$SnPh$_2$
(IIb)
2 p-CH$_3$C$_6$H$_4$NH$_2$
(VIII) + p-CH$_3$C$_6$H$_4$CNHPhCH$_3$-p + H$_2$S
(94.0 %)
(91.5 %)
RC—S—Sn—S—CR Ph Ph
(II)
R'$_2$NH
R'$_2$N—Sn—S—CR Ph Ph
(IX)
+ RCSH
R'$_2$NH
[Ph$_2$SnS] + RCNR'$_2$
(X)
(IV)
1/3 Trimer (VIII)
RCSNH$_2$R'$_2$
(R, R' = alkyl, aryl)
ArCS—SnPh$_3$
no reaction
Ph$_3$P—CHCOC$_6$H$_4$—X-p
α-NaphCS$_2$SnMe$_3$
Ph$_3$P—CHCC$_6$H$_4$—X-p
O
S
α-NaphCS—SnMe$_3$
(XI)

TABLE 3

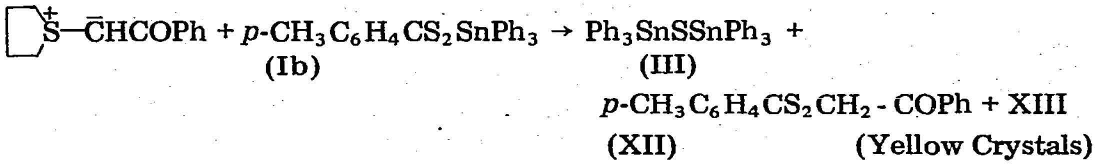
YIELDS AND PHYSICAL PROPERTIES OF THE ADDUCTS (XI)



No.	Adduct Group X	M.p. (°C)	Yield (%)	Color	IR (KBr) ν(C=O)(cm^{-1})	UV (CHCl$_3$) λ_{max} (nm) (ϵ)	NMR (CDCl$_3$) (δ, ppm)	J(Hz)
XIa	H	124 –126	95.7	Red	1460	329 (16900) 503 (196)	0.68 (CH_3—Sn, s, 9H) 4.38 (CH, d, 1H) 7.20–8.00 (aromatic, m, 27H)	57.5 (^{119}Sn—C—H)
XIb	CH$_3$	103.5–105.5	87.5	Red	1480	329 (18000) 502 (201)	0.67 (CH_3—Sn, s, 9H) 2.34 (CH_3, s, 3H) 4.35 (CH, d, 1H) 7.00–7.90 (aromatic, m, 26H)	58.0 (^{119}Sn—C—H) 55.0 (^{117}Sn—C—H)
XIc	Cl	115 –117	85.6	Red	1495	329 (24000) 502 (177)	0.66 (CH_3—Sn, s, 9H) 4.34 (CH, d, 1H) 7.18–8.02 (aromatic, m, 26H)	58.0 (^{119}Sn—C—H) 55.5 (^{117}Sn—C—H)

Esters of type I did not react with phenacylidenetriphenylphosphoranes under a variety of conditions; only starting materials were recovered. However, when a solution of (α-thionaphthoylthio)trimethylstannane in THF was treated with the same phosphorane at room temperature for 6 h, the monomeric 1/1 adduct (XIa, X = H) was obtained in 96% yield as stable brownish crystals. In the IR spectrum of XI the extremely low carbonyl stretching frequency at 1460 cm^{-1} suggests the possibility of strong coordination of the carbonyl oxygen to the trimethyltin moiety in these adducts. Additional spectral data of XIa together with those of the other adducts (XIb, X = CH_3 and XIc, X = Cl) are summarized in Table 3.

Analogous treatment of the tin ester Ib with phenacylidenetetramethylenesulfurane gave a 49% yield of XII, the phenacyl ester of p-methyldithiobenzoate formed by cleavage of the sulfur—tin bond of the ester, a 15% yield of bis(triphenylstannyl) sulfide and compound XIII (yellow crystals, m.p. 140—141°)



which contained tin, sulfur, carbon and hydrogen. Analogous products were obtained also from the reaction with (p-chlorothiobenzoylthio)triphenylstannane (If).

To our knowledge, this result is the first example of the cleavage of a sulfur—tin bond by an ylide. So far, we are unable to explain the origin of the methylene proton in the formation of phenacyl p-methyldithiobenzoate. Attempts to elucidate the structure of XIII on the basis of elemental analysis and spectral data (IR, UV, NMR and Mass) were not successful. An X-ray study, to be presented in a later paper, will hopefully determine the structure of this compound.

Treatment of Ib with sodium methoxide afforded good yields of sodium p-methyldithiobenzoate and methoxytriphenylstannane, indicating attack of the methoxy anion on the tin atom. Formation of bis(triphenylstannyl) sulfide was not observed.

$$p\text{-}CH_3C_6H_4CS_2SnPh_3 + CH_3\overset{-}{O}\overset{+}{Na} \rightarrow p\text{-}CH_3C_6H_4C\overset{-}{S_2}\overset{+}{Na} + CH_3OSnPh_3$$

In conclusion, although attempts to isolate the expected intermediates (A, B, VI and IX) in the reactions mentioned above were unsuccessful, it seems that direct attack at the thiocarbonyl carbon in the esters I and II was negligible. The tin or sulfide sulfur atoms were predominantly attacked, resulting in cleavage of the Sn—S bond.

Experimental

All melting points are uncorrected. The IR spectra were measured on a JASCO grating IR spectrophotometer IR-G. The UV and visible spectra were obtained from a Hitachi 124 spectrophotometer. The NMR spectra were recorded either on the JEOL C-60HL or a Hitachi R-22 (90 MHz) with tetramethylsilane as internal standard. Analyses were carried out by the Elemental Analyses Center of Kyoto University, and their data were in excellent agreement with all new structures (Ia—Ig, IIa—IIc and IXa—IXc).

Materials

Piperidinium *p*-substituted dithiobenzoates were prepared according to the procedures described previously [2, 3]. The *o*-substituted isomers were prepared by an analogous method. Yields and physical properties are summarized in Table 4. Chlorotriphenyl- and dichlorodiphenyl-stannane were prepared according to Kozeschkow's method [4]. *para*-Substituted phenacylidenetriphenylphosphoranes [5], and phenacylidenetetramethylenesulfurane [6] were prepared by previously described methods. (α-Thionaphthoylthio)trimethylstannane (m.p. 105—107°) was synthesized by the standard procedure. The amines were dried over potassium hydroxide and distilled before use. All solvents were carefully dried and also distilled before use.

Preparation of (substituted thiobenzoylthio)triphenyl- (I) and bis(substituted thiobenzoylthio)diphenyl-stannanes (II)

Two typical preparations are presented. The yields and physical properties are summarized in Table 1.

(p-Methylthiobenzoylthio) triphenylstannane (Ib). A mixture of 0.96 g (0.0025 mol) of chlorotriphenylstannane and 0.64 g (0.0025 mol) of piperidinium *p*-methyldithiobenzoate in dichloromethane (20 ml) was stirred at room temperature for 3 h. After removal of the solvent in vacuo, and extraction of the residue with petroleum ether (b.p. <40°) in a Soxhlet extractor and subsequent cooling to —25° of the extracts gave 1.20 g of the ester Ib as reddish microfine crystals, which can be recrystallized from the same solvent.

Bis(p-methylthiobenzoylthio)diphenylstannane (IIb). Piperidinium *p*-methyldithiobenzoate (2.52 g, 0.01 mol) was added to a solution of dichlorodiphenylstannane (1.72 g, 0.005 mol) in dichloromethane and stirred at room temperature for 5 h, during which a color change of the solution from dark red to dark orange was observed. After the vacuum distillation of the solvent, the residue was extracted (Soxhlet extractor for 3 days) with ether until it remained colorless. Removal of the ether and subsequent recrystallization of the solids from ether/petroleum ether (b.p. < 40°) gave 2.88 g of the ester IIb as reddish orange crystals.

Reaction of (p-methylthiobenzoylthio)triphenylstannane (Ib) or bis(p-methylthiobenzoylthio)diphenylstannane (IIb) with amines

A typical example is given below. The structures of all of the obtained products were confirmed by comparison of their melting points and IR spectra with

TABLE 4

YIELDS AND PHYSICAL PROPERTIES OF PIPERIDINIUM *o*-SUBSTITUTED DITHIOBENZOATES ($X\text{-}C_6H_5CS_2^-\overset{+}{N}H_2C_5H_{10}$)

o-Substituent	M.p. (°C)	Yield (%)	Color	IR (KBr) $\nu(C{=}S)$ (cm^{-1})
CH_3	122.0—124.0	54	Orange	1013
CH_3O	84.0— 86.5	77	Orange	998
Cl	115.0—118.0	48	Orange	1018

those of the authentic samples; bis(triphenylstannyl) sulfide [7], trimeric diphenyl tin sulfide [8], and thioamides [2] were prepared by heating an equimolar mixture of *p*-methyldithiobenzoic acid and the amine in a glass ampule.

Reaction of ammonia with Ib. A large excess of ammonia was introduced into a solution of 1.04 g (0.002 mol) of Ib in dry ether (40 ml) at room temperature for 3 h. A red solid was filtered and gave 0.043 g (14%, based on Ib) of ammonium *p*-methyldithiobenzoate, m.p. 60—64° (authentic sample m.p. 63—66°). On the other hand, careful vacuum evaporation of small amount of the solvent from the filtrate and filtration of the resulting precipitates gave 0.69 g (94.8%) of bis(triphenylstannyl) sulfide (III), m.p. 142—145° (authentic sample, m.p. 144—146°). In addition, evaporation of the solvent from the ether solution followed by removal of III in vacuum and subsequent recrystallization of the residue from chloroform/petroleum ether (b.p. $< 40°$) gave 0.29 g (78.5%) of *p*-methylthiobenzamide as yellow crystals, m.p. 162—165° (authentic sample, m.p. 166—168°).

Reaction of (α-thionaphthoylthio)trimethylstannane with para-substituted phenacylidenetriphenylphosphoranes

A typical example is described below. The yields and physical properties are summarized in Table 3.

Equimolar amounts of (α-thionaphthoylthio)trimethylstannane (0.74 g, 0.002 mol) and phenacylidenetriphenylphosphorane (0.76 g, 0.002 mol) in THF (25 ml) were stirred at room temperature for 6 h. Removal of the solvent under reduced pressure and recrystallization of the residue from acetone gave 1.42 g of the 1/1 adduct (XIa).

Reaction of (thiobenzoylthio)triphenylstannane (Ia) with phenacylidenetriphenylphosphorane

Equimolar amounts of (thiobenzoylthio)triphenylstannane (1.11 g, 0.002 mol) and phenacylidenetriphenylphosphorane (0.76 g, 0.002 mol) in THF (30 ml) were stirred at 50° for 20 h. Removal of the solvent under reduced pressure and extraction of the residue with petroleum ether (b.p. $< 40°$) led to recovery of 0.62 g of the starting phosphorane (81%). Upon cooling of the extracts at —25°, 0.80 g of Ia, a crystalline stannyl ester, was obtained (82%).

Reaction of (p-methylthiobenzoylthio)triphenylstannane (Ib) with phenacylidenetetramethylenesulfurane

Equimolar amounts of Ib (1.29 g, 0.0025 mol) and phenacylidenetetramethylenesulfurane (0.52 g, 0.0025 mol) in THF were stirred at room temperature for 5 h. The color of the solution changed from red to orange yellow. After evaporation of the THF in vacuo, the residue was repeatedly extracted with petroleum ether (b.p. $< 40°$). Removal of the solvent from the extracts gave 0.56 g (55% based on Ib) of phenacyl *p*-methyldithiobenzoate (XII) which was identified by comparison of its melting point and its IR spectrum with those of an authentic sample (m.p. 129—130°). The extracted residue (1.10 g) was chromatographed on a 60 g-silica gel column. The eluent with n-hexane gave 0.31 g of bis(triphenylstannyl) sulfide after evaporation of the solvent. Subsequently, changing the eluent to n-hexane/ether (1/1) gave 0.36 g of yellow crystals of compound XIII after evaporation of the solvent and recrystallization from dichloromethane/n-hexane, m.p. 142—143°; IR (KBr), 1615 [ν(C=O)?], 1180 cm^{-1} [ν(C=S)?]. NMR ($CDCl_3$): δ 1.95 (3H, s, CH_3), 6.90—7.78 (29H, m, aromatic). Mass spectrum *m/e* 268$^+$; elemental analysis; C, 41.24; H, 2.97; S, 10.92%. Finally, upon eluting with ether/ethanol (1/1), 0.40 g of an intractable brown oil was obtained.

Reaction of (p-methylthiobenzoylthio)triphenylstannane (Ib) with sodium methoxide

A methanolic solution (1.2 ml) of sodium methoxide (0.006 mol) was added dropwise to *p*-methyldithiobenzoyltriphenylstannane (2.3 g, 0.005 mol) in ether (75 ml) and stirred while refluxing for 2 h. After evaporation of the solvents under reduced pressure, 20 ml of petroleum ether (b.p. $< 40°$) was added. Filtration of the resulting precipitate and recrystallization from dichloromethane/n-hexane gave 0.76 g (80.3%) of sodium *p*-methyldithiobenzoate*. Its IR spectrum exactly agreed with that of an authentic sample. Removal of the petroelum ether from the filtrate gave 1.58 g (75.8%, m.p. 64—65°) of methoxytriphenylstannane which was identified by comparison of its melting point and IR spectrum with those of an authentic sample [9].

Moreover, no bis(triphenylstannyl) sulfide was detected by carefully chromatographing the filtrate (n-hexane) on silica gel.

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* This compound shows no definite melting point even after repeated recrystallization.