Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

II*. REACTIONS BETWEEN (BROMOMETHYL)TIN COMPOUNDS AND SODIUM THIOLATES

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(Received February 10th, 1972)

SUMMARY

Compounds containing $RSCH_2Sn\leqslant$ groups have been prepared by two routes:

$$RSNa + BrCH_2Sn\leqslant \rightarrow RSCH_2Sn\leqslant + NaBr \qquad (1)$$

$$RSCH_2Li + ClSn\leqslant \rightarrow RSCH_2Sn\leqslant + LiCl \qquad (2)$$

the former method is preferred. Reactions between RSNa and $(BrCH_2)_2SnBr_2$ give $(RSCH_2)_2Sn(SR)_2$. Properties, including the Mössbauer spectra, of these compounds are reported.

INTRODUCTION

For an examination of the relationship between the structure of compounds and their ability to stabilize poly(vinyl chloride) we wished to synthesise certain functionally substituted organotin compounds. In a previous paper[1] we showed that stannylalkyl sulphides could be prepared by additions of thiols to alkenyltin compounds. We now describe two other methods of preparing this type of compound, these are (*i*) displacement of bromide ion with RS^- ion in (bromomethyl)tin compounds and (*ii*) reactions between phenylthiomethyllithium and chlorotin compounds.

RESULTS AND DISCUSSION

Tetrakis(bromomethyl)tin (I), prepared from stannic bromide and diazomethane[2] was treated with sodium benzenethiolate and sodium butanethiolate to give, respectively, tetra(phenylthiomethyl)tin (II, R = Ph) and tetra(butylthiomethyl)tin (II, R = Bu).

$$\underset{}{4\,RSNa} + \underset{\text{(I)}}{(BrCH_2)_4Sn} \rightarrow \underset{\text{(II)}}{(RSCH_2)_4Sn} + 4\,NaBr \qquad R = Ph, Bu$$

Bis(bromomethyl)tin dibromide (III) was readily prepared from (I) by treat-

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* For Part I see ref. 1.

ment with two moles of bromine. This method was found to be more convenient than the published procedure[2] based on reaction between stannic bromide and a controlled amount of diazomethane followed by fractional distillation of the product. Compound (III) was characterized by formation of its 2,2'-bipyridine adduct. Also, it was shown that, by careful hydrolysis using the stoichiometric quantity of alkali, bis(bromomethyl)tin oxide (IV) was obtained as an infusible white powder. The physical properties of (IV) and its Mössbauer spectrum (see Table 1) are characteristic of R_2SnO compounds and rule out alternative formulations such as $(HOCH_2)_2SnBr_2$.

Treatment of (III) with sodium benzenethiolate or sodium butanethiolate causes replacement of bromine bound to carbon as well as bromine bound to tin to give, respectively, bis(phenylthiomethyl)bis(benzenethiolato)tin (V, R = Ph) and bis(butylthiomethyl)bis(butanethiolato)tin(V,R = Bu). Compound (V, R = Ph), on treatment with aqueous alkali, gave bis(phenylthiomethyl)tin oxide (VI) as an infusible white solid which showed a Mössbauer effect at room temperature characteristic of polymeric tin compounds[4]. Treatment of compound (VI) with acetic acid failed to give the expected diacetate. Instead, a high-melting-point crystalline solid was obtained which was shown by analysis and NMR measurements to contain equal numbers of phenylthiomethyl and acetate groups. It appears that cleavage of a phenylthiomethyl group by acetic acid has occurred to give the (phenylthiomethyl)stannoxane acetate $[PhSCH_2Sn(O)OCOCH_3]_x$. This structure was confirmed by the Mössbauer spectrum of this compound (Table 1) which showed a characteristically[4] low isomer shift. A similar reaction occurred when bis(bromomethyl)tin oxide (IV) was treated with acetic acid to give $[BrCH_2Sn(O)OCOCH_3]_x$.

$$4\,RSNa + \underset{(III)}{(BrCH_2)_2SnBr_2} \rightarrow \underset{(V)}{(RSCH_2)_2Sn(SR)_2} + 4\,NaBr$$

$$(R = Ph,\ Bu)$$

$$(PhSCH_2)_2SnO + 2\,CH_3COOH \not\rightarrow (PhSCH_2)_2Sn(OCOCH_3)_2 + H_2O$$

Using the *N,N,N',N'*-tetramethylethylenediamine (TMED) complex of butyllithium, thioanisole can be converted to the phenylthiomethyllithium TMED complex in high yield (*cf.* ref. 6) and the latter was used to prepare (phenylthiomethyl)tin

TABLE 1

MÖSSBAUER MEASUREMENTS MADE AT 78 K

Units are mm/s, isomer shifts refer to tin(IV) oxide.

No.	*Compound*	*δ*	*Δ*	*Ref.*
(II) (R = Ph)	$(PhSCH_2)_4Sn$	1.62	0	This work
(II) (R = Bu)	$(BuSCH_2)_4Sn$	1.29	0	This work
	Bu_3SnCH_2SPh	1.51	0	This work
	$[PhSCH_2Sn(O)OCOCH_3]_x$	0.62	2.0	This work
	$[PhSn(O)OCOC(CH_3)_3]_x$	0.59	2.0	4
(VI)	$(PhSCH_2)_2SnO$	1.12	2.0	This work
(IV)	$(BrCH_2)_2SnO$	1.03	1.85	This work
	Bu_2SnO	1.15	2.08	5

compounds as indicated by the following equations.(Since this work was completed the preparation of $\mathrm{Bu_3SnCH_2SCH_3}$ by a similar method was reported[7].)

$$\mathrm{PhSCH_2Li \cdot TMED + Bu_3SnCl \rightarrow Bu_3SnCH_2SPh + LiCl + TMED}$$

$$\mathrm{2\ PhSCH_2Li \cdot TMED + Bu_2SnCl_2 \rightarrow Bu_2Sn(CH_2SPh)_2 + 2\ LiCl + 2\ TMED}$$

$$\mathrm{4\ PhSCH_2Li \cdot TMED + SnCl_4 \rightarrow (PhSCH_2)_4Sn + 4\ LiCl + 4\ TMED}$$

This alternative method of preparing (II) (R = Ph) was less satisfactory as the NMR spectrum of the product from the lithium reagent showed a $\mathrm{C_6H_5/CH_2}$ ratio higher than 1/1. This is thought to be caused by contamination of the $\mathrm{PhSCH_2Li}$ reagent by traces of PhSLi since partial cleavage of alkyl sulphides by organolithium compounds is known to occur[8]. Because of this difficulty this method of preparing (phenylthiomethyl)tin compounds was abandoned in favour of the use of (bromomethyl)tin compounds.

All of the compounds containing $\mathrm{RSCH_2Sn}$ groups decomposed slowly on storage. As noted earlier, when bis(phenylthiomethyl)bis(benzenethiolato)tin (IV, R = Ph) was treated with alkali the $\mathrm{PhSCH_2{-}Sn}$ bonds survived yet these same bonds were attacked, under mild conditions, when $\mathrm{(PhSCH_2)_2SnO}$ was treated with acetic acid. These observations are consistent with enhanced carbanion character of the tin-bound carbon atom due to the participation of the resonance structures:

$$\mathrm{RSCH_2{-}Sn}\leqslant \ \leftrightarrow\ \mathrm{RSCH_2^{\ominus}}\,\overset{\oplus}{\mathrm{Sn}}\leqslant \ \leftrightarrow\ \mathrm{R}\overset{\ominus}{\mathrm{S}}{=}\mathrm{CH_2}\,\overset{\oplus}{\mathrm{Sn}}\leqslant$$

involving *d* orbitals on sulphur[7,9].

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere[10]. NMR spectra were measured using a Perkin–Elmer R 10 60 MHz instrument, IR measurements were made with Perkin–Elmer 237 and 325 spectrometers. The reactions were monitored, and all products shown to be homogeneous, by thin-layer chromatography[1].

Tetrakis(bromomethyl)tin (τ 7.0), m.p. 59–62° (lit.[2] m.p. 57°), was made by a published procedure[2].

Bis(bromomethyl)tin dibromide

Bromine (18.2 g, 0.11 mole) in carbon tetrachloride (200 ml) was added dropwise to a solution of tetrakis(bromomethyl)tin (28.0 g, 0.057 mole) in carbon tetrachloride which was boiling under reflux. The addition was complete in 4 h giving a colourless solution from which the solvent was removed on a rotary evaporator. The residue was crystallised from carbon tetrachloride to give pure bis(bromomethyl)tin dibromide (20.0 g, 76%), m.p. 87–89.5° (lit.[2] m.p. 87°). (Found: C, 5.3; H, 1.0. $\mathrm{C_2H_4Br_4Sn}$ calcd.: C, 5.2; H, 0.9%.)

Treatment of a benzene solution of bis(bromomethyl)tin dibromide with one equivalent of 2,2′-bipyridine in the same solvent gave the adduct as white crystals, m.p. 210° decomp. (Found: C, 23.4; H, 1.9; N, 4.5. $\mathrm{C_{12}H_{12}Br_4N_2Sn}$ calcd.: C, 23.2; H, 1.9; N, 4.5%.)

Bis(bromomethyl)tin oxide

A solution of sodium hydroxide (0.343 g, 0.0086 mole) in water (6.8 ml) was added dropwise to a solution of bis(bromomethyl)tin dibromide (2.00 g, 0.0043 mole) in ethanol (50 ml). The resulting suspension was allowed to stand overnight. Removal of the liquid phase using a centrifuge and washing the powdery product with water and methanol gave bis(bromomethyl)tin oxide (1.2 g, 87%) which began to decompose, without melting, when heated above 164°. (Found: C, 7.6; H, 1.2. $C_2H_4Br_2OSn$ calcd.: C, 7.5; H, 1.2%.)

Tetrakis(phenylthiomethyl)tin

Benzenethiol (3.6 g, 0.033 mole) was added to a solution of sodium (0.74 g, 0.032 mole) in anhydrous ethanol (100 ml). Tetrakis(bromomethyl)tin (4.0 g, 0.0081 mole) was then added and the mixture boiled under reflux for 16 h. The cooled suspension was filtered and the white residue washed in turn with water, methanol and light petroleum (b.p. 30–40°) to give tetrakis(phenylthiomethyl)tin (3.3 g, 61%) m.p. 60–61°, the analytical specimen was crystallised from light petroleum (b.p. 60–80°) to give white crystals, m.p. 59.5–60°. (Found: C, 54.2; H, 4.75; S, 21.1; Sn, 19.4. $C_{28}H_{28}S_4Sn$ calcd.: C, 55.0; H, 4.6; S, 21.0; Sn, 19.4%.)

Tetrakis(butylthiomethyl)tin

This compound was obtained in a similar manner in 73% yield as a clear oil, n_D^{25} 1.5380 (R_f 0.7). (Found: C, 45.3; H, 8.3. $C_{20}H_{44}S_4Sn$ calcd.: C, 45.2; H, 8.4%.) After keeping for 3 weeks this oil had solidified to give material having R_f 0.0.

Bis(phenylthiomethyl)bis(benzenethiolato)tin

Benzenethiol (3.2 g, 0.029 mole) was added to a solution of sodium (0.62 g, 0.027 mole) in anhydrous ethanol (50 ml). Bis(bromomethyl)tin dibromide (3.33 g, 0.0071 mole) in anhydrous ethanol (50 ml) was added dropwise and the mixture stirred and boiled under reflux for 20 h. The sodium bromide was removed by filtration, after concentration on a rotary evaporator it was necessary to filter again to remove further sodium bromide. Complete evaporation gave bis(phenylthiomethyl)bis(benzenethiolato)tin (3.5 g, 84%) as a clear yellow liquid. (Found: C, 53.7; H, 4.0; S, 21.5. $C_{26}H_{24}S_4Sn$ calcd.: C, 53.5; H, 4.1; S, 22.0%.)

Bis(butylthiomethyl)bis(butanethiolato)tin

This compound was obtained in a similar manner in 25% yield as a clear colourless viscous liquid. (Found: C, 42.8; H, 8.3. $C_{18}H_{40}S_4Sn$ calcd.: C, 43.0 H, 8.0%.)

Bis(phenylthiomethyl)tin oxide

Bis(phenylthiomethyl)bis(benzenethiolato)tin which had been prepared by the above method from bis(bromomethyl)tin dibromide (2.0 g, 0.0043 mole) was boiled with a solution of sodium hydroxide (3.0 g, 0.075 mole) in water (50 ml) for 15 min. The aqueous layer was decanted off and the residue boiled again with a similar amount of aqueous sodium hydroxide. The resultant suspension was filtered and the precipitate washed consecutively with water, ethanol and light petroleum (b.p. 30–40°) to give bis(phenylthiomethyl)tin oxide as a white powder (1.0 g, 61%) which decomposed at 320°. (Found: C, 43.4; H, 3.7; Sn, 30.8. $C_{14}H_{14}OS_2Sn$ calcd.: C, 44.1; H, 3.7; Sn, 31.2%.)

(Phenylthiomethyl)stannoxane acetate

A solution of glacial acetic acid (0.63 g, 0.011 mole) in benzene (5 ml) was added to a suspension of bis(phenylthiomethyl)tin oxide (2.0 g, 0.0052 mole) in benzene (20 ml). After stirring for 2 h the mixture was filtered and the filtrate allowed to stand overnight. The colourless fine needle crystals which had formed were filtered and dried giving (phenylthiomethyl)stannoxane acetate (0.4 g, 24%), m.p. 258–260°. (Found: C, 34.1; H, 3.3; S, 10.5; Sn, 37.8. $C_9H_{10}O_3SSn$ calcd.: C, 34.1; H, 3.2; S, 10.1; Sn, 37.4%.)

(Bromomethyl)stannoxane acetate

The compound was obtained from bis(bromomethyl)tin oxide in a similar manner in 81% as a white crystalline solid, m.p. 120–123°. (Found: C, 13.2; H, 1.9. $C_3H_5BrO_3Sn$ calcd.: C, 12.5; H, 1.7%.)

Dibutylbis(phenylthiomethyl)tin

Thioanisole (25.0 g, 0.20 mole) was added to a suspension of the *N,N,N',N'*-tetramethylethylenediamine adduct of butyllithium (0.12 mole) in light petroleum (b.p. 30–40°) and the mixture was stirred overnight. A solution of dibutyltin dichloride (18.0 g, 0.059 mole) in light petroleum (100 ml, b.p. 30–40°) was added dropwise and the mixture boiled under reflux for 3½ h. The mixture was shaken with saturated aqueous ammonium chloride (100 ml), the organic layer was then separated, dried and the solvent removed on a rotary evaporator. Distillation of the residue under reduced pressure gave first thioanisole followed by pure dibutylbis(phenylthiomethyl)-tin (8.0 g, 28%) as a pale yellow liquid, b.p. 141–147°/0.02 mm. (Found: C, 55.05; H, 6.9; Sn, 24.8. $C_{22}H_{32}S_2Sn$ calcd.: C, 55.1; H, 6.7; Sn, 24.8%.)

Tributyl(phenylthiomethyl)tin

This compound was prepared similarly in 59% yield from BuLi·TMED and tributyltin chloride and obtained as a pale yellow liquid, b.p. 133–143°/0.002 mm, n_D^{25} 1.5407. (Found: C, 55.4; H, 8.3; S, 7.8. $C_{19}H_{34}SSn$ calcd.: C, 55.2; H, 8.3; S, 7.8%.)

Reaction between BuLi·TMED, thioanisole and tin(IV) chloride gave crude tetrakis(phenylthiomethyl)tin in 69% yield. This material was purified by column chromatography using a silica gel adsorbent and eluting with benzene to give tetrakis(phenylthiomethyl)tin as an oil which crystallised on keeping for 2 days. (Found: C, 54.6; H, 4.6; S, 21.1. $C_{28}H_{28}S_4Sn$ calcd.: C, 55.0; H, 4.6; S, 21.0%.) As the NMR spectrum of this material indicated that some impurity was still present, this method of synthesis was rejected in favour of the reaction between $(BrCH_2)_4Sn$ and PhSNa described earlier.

ACKNOWLEDGEMENT

We thank the Science Research Council for a C.A.P.S. award and Messrs. Albright and Wilson for generous support.

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