Journal of Organometallic Chemistry, 117 (1976) 329—338

SYNTHESIS AND REACTIVITY OF ω-HALOALKYLTIN COMPOUNDS

E.J. BULTEN *, H.F.M. GRUTER and H.F. MARTENS
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)
(Received January 16th, 1976)

Summary

ω-Haloalkyltin trihalides, $X(CH_2)_nSnX_3$ ($n \geqq 3$; X = halogen) can readily be prepared in high yields by the direct reaction of stannous halides with α,ω-dihaloalkanes, catalysed by trialkylantimony compounds. The compounds are versatile starting materials for the synthesis of a variety of ω-functionally-substituted organotin compounds $R_{3-m}X_mSn(CH_2)_nY$ (R = alkyl, phenyl; m = 0—3; X = Cl, Br, O; Y = Br, NMe_2, NEt_2, COOH, CHOHR, R_3Sn).

^{1}H-NMR spectral data for a series of such compounds are presented. The trends observed in the chemical shifts and the ^{119}Sn—methyl proton coupling constants of $Me_{3-m}Br_mSn(CH_2)_nBr$ (m = 0—3; n = 3—5) are discussed in terms of inductive effects. Intramolecular coordination between the ω-bromine atom and tin could not be demonstrated.

Introduction

Information on ω-haloalkyltin compounds $R_{3-m}X_mSn(CH_2)_nY$ (R = alkyl; X,Y = halogen; m = 0—3) is rather scanty due to a lack of synthetic methods. Only the halomethyltin compounds (n = 1; m = 0—3) are readily accessible by reaction of the corresponding alkyltin halide with diazomethane [1] or with iodomethylzinc iodide [2]. Haloethyltin compounds have been obtained by Gielen and Topart [3], according to eq. 1:

$$R_3SnH \xrightarrow{CH_2=CH(CH_2)_nOH} R_3Sn(CH_2)_{n+2}OH \xrightarrow{Ph_3P/CCl_4} R_3Sn(CH_2)_{n+2}Cl \qquad (1)$$

Seyferth obtained the first 3-halopropyltin compounds by addition of chloroform or carbon tetrachloride to triethylvinyltin [4] (eq. 2):

$$Et_3SnCH{=}CH_2 \xrightarrow{XCCl_3} Et_3SnCHXCH_2CCl_3 \qquad (2)$$

(X = H, Cl)

ω-Haloalkyltin dihalides or trihalides, $R_{3-m}X_mSn(CH_2)_nY$ ($m = 2,3$) with $n > 1$ have not yet been described in the literature.

Recently we reported a convenient synthesis of alkyltin trihalides based on the direct reaction of stannous halides with alkyl halides in the presence of trialkylantimony catalysts [5]. As will be discussed in the present paper the analogous reaction of stannous halides with α,ω-dihaloalkanes (eq. 3) is highly suitable for the synthesis of ω-haloalkyltintrihalides. The latter compounds

$$SnX_2 + X(CH_2)_nX \xrightarrow{R_3Sb} X_3Sn(CH_2)_nX \qquad (3)$$

are versatile starting materials for the synthesis of other types of functionally-substituted organotin compounds.

Results and discussion

Syntheses

As reported in a preceding paper [5] the catalytic activity of trialkylantimony compounds in reactions according to eq. 4 increases markedly with decreasing

$$SnX_2 + RX \xrightarrow{R_3Sb} RSnX_3 \qquad (4)$$

chain length of the alkyl groups bound to antimony. Furthermore, the reaction rate decreases in the order X = Br > X = Cl, so, in the present study, reactions were generally performed with the bromine derivatives and with triethylantimony as the catalyst.

Reactions were carried out without solvents, an excess of the dihaloalkane being used as the reaction medium. Progress of the reaction can be monitored by titrimetric determination of the ionic bromine present in solution [5] or by filtration of the residual stannous halide.

Methylene bromide failed to react with $SnBr_2$ after heating for 14 h at 97°C. Reaction with methylene iodide, however, was complete after 5 h at 120°C or 0.5 h at 150°C. Attempted distillation of the reaction product resulted in extensive decomposition. Methylation of a freshly-prepared reaction mixture (ratio $CH_2I_2/SnBr_2 = 3$) and subsequent ^1H NMR analysis showed the presence of only some 10% of the mono-insertion product, Br_2ISnCH_2I, and as much as 90% of the bis-insertion product, $(Br_2ISn)_2CH_2$. With the ratio of reactants $CH_2I_2/SnBr_2 = 1.25$ exclusively bis-insertion was observed. It should be noted

$$SnBr_2 \xrightarrow[Et_3Sb;\ 120°C]{3CH_2I_2} \underset{(10\%)}{ICH_2SnBr_2I} + \underset{(90\%)}{(IBr_2Sn)_2CH_2} \qquad (5)$$

that this remarkable preference for bis-insertion is not observed in the reaction of tin bis(acetylacetonate) with CH_2I_2. The latter reaction is homogeneous and occurs in the absence of catalysts [6].

$$Sn(acac)_2 \xrightarrow[benzene;\ 20°C]{2CH_2I_2} ICH_2Sn(acac)_2I \qquad (6)$$

Reaction with 1,2-dibromoethane gave only 7% conversion of $SnBr_2$ after 72 h at 131°C. With 1,2-dibromopropane as the substrate 95% of $SnBr_2$ had

been consumed after 7 h at 150°C. During the reaction propene was evolved. Distillation gave tin tetrabromide as the main product.

$$SnBr_2 + BrCH_2CHRBr \rightarrow SnBr_4 + CH_2{=}CH{-}R \quad (7)$$

(R = H, Me)

In neither of these reactions were indications obtained of the intermediate formation of insertion products, $Br_3Sn{-}\overset{|}{C}{-}\overset{|}{C}{-}Br$, which may be expected to be thermally rather unstable as a result of the ease of β-elimination.

When used in a 200—400% excess α,ω-dibromoalkanes, $Br(CH_2)_nBr$, $n \geqslant 3$ react readily with $SnBr_2$ to give high yields of the mono-insertion products, only small amounts of bis-insertion products being detectable.

$$SnBr_2 + Br(CH_2)_nBr \rightarrow Br_3Sn(CH_2)_nBr \quad (8)$$

($n \geqslant 3$)

Thus, reaction of stannous bromide with 4.5 equivalents of 1,3-dibromopropane gave (as determined by ^{1}H-NMR spectrometry after methylation) (3-bromopropyl)-tin tribromide. With equimolar amounts of reactants the product mixture $Br_3Sn(CH_2)_3Br/Br_3Sn(CH_2)_3SnBr_3 = 0.55$ is obtained.

Purification of the ω-bromoalkyltin tribromides by regular distillation is hampered by thermal degradation according to the reverse of eq. 8. As a result the distillation yields (mercury diffusion pump vacuum) decrease rapidly with increasing chain length: $n = 3$, 74%; $n = 4$, 37%; $n = 5$, 0%. By using a high vacuum molecular distillation device a 64% yield of pure (5-bromopentyl)tin tribromide could be isolated. However, the crude products, generally obtained in semi-quantitative yield after evaporation of the excess of α,ω-dibromoalkane, can be used very effectively as such for the preparation of a large variety of other types of functionally-substituted organotin compounds (Scheme 1). The physical constants, yields and analysis data of the newly-prepared compounds are compiled in Table 1.

ω-Bromoalkylstannonic acid derivatives can be prepared in high yields by careful hydrolysis of the ω-bromoalkyltin tribromides in the presence of diethyl amine. The more conventional procedure involving hydrolysis with three

$$Br_3Sn(CH_2)_nBr \xrightarrow{H_2O/Et_2NH} HOOSn(CH_2)_nBr \quad (9)$$

($n = 3, 4$)

equivalents of sodium hydroxide [7] resulted in the formation of impure products containing varying amounts of stannic oxide.

Quite unexpectedly, the tin—carbon bond of the γ-bromopropyltin derivative and to a lower extent that of the δ-bromobutyltin compound are susceptible to cleavage by bases. Reaction of γ-bromopropyltin tribromide with an excess of aqueous 4 *N* sodium hydroxide solution at room temperature is complete within one minute, yielding stannic oxide and cyclopropane. Under similar conditions the tin—carbon bond of unsubstituted alkyltin trihalides is completely stable [7].

(continued on p. 334)

SCHEME 1

THE SYNTHESIS OF SOME NEW FUNCTIONALLY-SUBSTITUTED ORGANOTIN COMPOUNDS STARTING FROM (ω-BROMOALKYL)TIN TRIBROMIDES

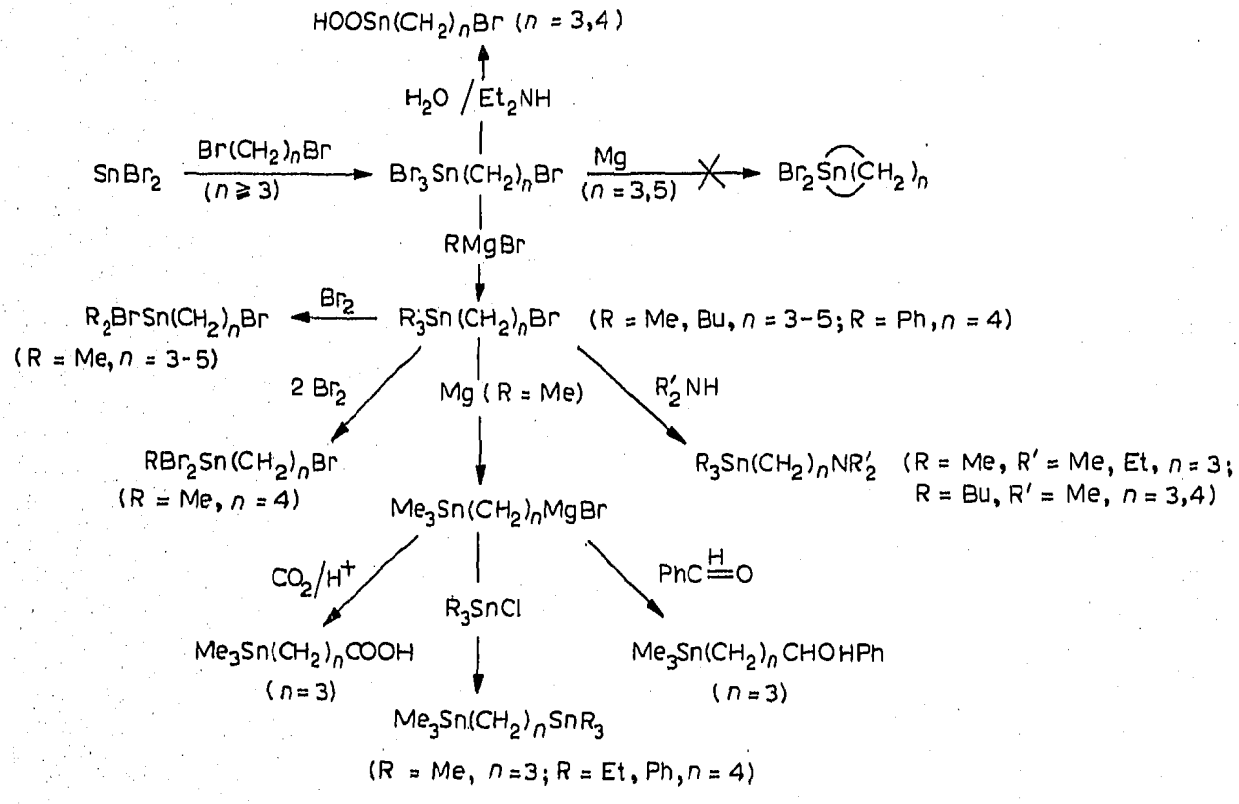

TABLE 1

PHYSICAL CONSTANTS, YIELDS AND ANALYSIS DATA OF SOME NEW ORGANOTIN COMPOUNDS $R_{3-m}X_mSn(CH_2)_nY$

Compound	B.p. (°C/mmHg)	n_D^{20}	Yield (%)	Analysis found (calcd.) (%)			
				C	H	Sn	Br
$Me_3SnCH_2SnMe_3$	88– 92/15	1.5056	48	24.9 (24.61)	6.1 (5.90)	68.6 (69.49)	
$Bu_3SnCH_2SnBu_3$	160–164/0.3	1.4976	60	50.3 (50.25)	9.3 (9.50)	39.4 (39.96)	
$Br_3Sn(CH_2)_3Br$	111–112/0.1	1.6568	74 [a]	7.7 (7.50)	1.3 (1.26)		66.2 (66.53)
$Br_3Sn(CH_2)_4Br$	123–124/0.1	1.6353	51 [a]	9.9 (9.72)	1.8 (1.63)	23.9 (24.01)	64.7 (64.65)
$Br_3Sn(CH_2)_5Br$		1.6207	64 [a]	12.0 (11.81)	1.9 (1.98)		62.9 (62.87)
$HOOSn(CH_2)_3Br$	>260 [b]	—	90	—	—	43.1 (43.37)	29.0 (29.20)
$HOOSn(CH_2)_4Br$	>260 [b]	—	88	—	—	40.7 (41.25)	27.2 (27.8)
$Me_3Sn(CH_2)_3Br$	83– 85/12	1.5090	74	25.8 (25.22)	5.6 (5.29)	—	
$Me_3Sn(CH_2)_4Br$	97– 99/10	1.5042	88	28.2 (28.04)	5.8 (5.72)		
$Me_3Sn(CH_2)_5Br$	60– 62/0.3	1.5012	88	30.2 (30.62)	6.2 (6.1)		
$Bu_3Sn(CH_2)_3Br$	112–115/0.12	1.4998	84	44.0 (43.73)	8.3 (8.07)	28.8 (28.81)	
$Bu_3Sn(CH_2)_4Br$	122–126/0.12	1.4572	90	45.3 (45.11)	8.6 (8.28)	27.9 (27.86)	18.6 (18.75)
$Ph_3Sn(CH_2)_4Br$	64– 67 [b]	—	60	55.0 (54.37)	4.8 (4.77)	—	
$Me_2BrSn(CH_2)_3Br$	104–106/0.9	1.5724	83	17.3 (17.13)	3.6 (3.45)	—	
$Me_2BrSn(CH_2)_4Br$	97– 98/0.9	1.5582	74	—	—	32.4 (32.54)	
$Me_2BrSn(CH_2)_5Br$	132–136/2.0	1.5524	79	21.2 (22.20)	4.1 (4.26)		
$MeBr_2Sn(CH_2)_4Br$	131–134/0.1	1.6046	57	14.4 (13.98)	2.8 (2.58)	—	
$Me_3Sn(CH_2)_3NMe_2$	73– 74/11	1.4706	63	38.7 (38.44)	8.7 (8.47)	47.0 (47.49) [c]	
$Me_3Sn(CH_2)_3NEt_2$	55– 56/0.6	1.4715	26	43.3 (43.21)	9.3 (9.06)	42.4 (42.69) [d]	
$Bu_3Sn(CH_2)_3NMe_2$	104–106/0.12	1.4785	86	54.5 (54.29)	10.2 (10.44)	31.6 (31.56) [e]	
$Bu_3Sn(CH_2)_4NMe_2$	109–112/0.11	1.4784	81	55.4 (55.41)	10.8 (10.59)	30.4 (30.41) [f]	
$Me_3Sn(CH_2)_3COOH$		1.4839	52	—	—	47.0 (47.31)	
$Me_3Sn(CH_2)_3CHOHPh$	99–102/0.03	1.5323	50	—	—	38.3 (37.92)	
$Me_3Sn(CH_2)_3SnMe_3$	60– 64/0.1	1.5002	80	28.8 (29.24)	6.6 (6.54)	64.0 (64.21)	
$Me_3Sn(CH_2)_4SnEt_3$	108–110/0.07	1.5016	40	36.4 (36.67)	7.7 (7.58)	—	
$Me_3Sn(CH_2)_4SnPh_3$	~240/0.1 (dec.)	1.5980	40	52.6 (52.69)	5.7 (5.66)	41.4 (41.65)	

[a] After careful distillation; crude product yield 100%. [b] M.p. [c] N, 5.8 (5.60). [d] N, 5.2 (5.03). [e] N, 3.7 (3.72). [f] N, 3.5 (3.48).

$$Br_3Sn(CH_2)_3Br \xrightarrow{NaOH/H_2O} \underset{CH_2}{CH_2{-}CH_2} + SnO_2 + NaBr \qquad (10)$$

The mechanism of this first example of a base-catalyzed 1,3-elimination in organotin chemistry will be investigated further. Recently, Davis et al. reported 1,3-eliminations observed with (γ-hydroxyalkyl)trimethyltin compounds in the presence of acetic acid [8]. Attempts to prepare 1,1-dibromo-1-stannacyclobutane and -hexane by reaction of magnesium with (3-bromopropyl)tin tribromide and (5-bromopentyl)tin tribromide, respectively, failed [9].

Reaction of (ω-haloalkyl)tin tribromides with Grignard or organolithium reagents gives high yields of the corresponding (ω-haloalkyl)triorganotin compounds The latter compounds in turn are suitable starting materials for the synthesis of a variety of other types of functionally-substituted organotin compounds. For example, substitution of the ω-halogen atoms by dialkylamino groups gives the corresponding (ω-dialkylaminoalkyl)triorganotin compounds. Furthermore, via the Grignard reagents $R_3Sn(CH_2)_nMgBr$, other types of functional substituents can be introduced, such as carboxylate groups, alcohol functions, different organometallic moieties, etc. (cf. Scheme 1 and Table 1).

Bromodemetallation reactions of (ω-bromoalkyl)trimethyltin compounds afforded the first well-defined examples of (ω-haloalkyl)dialkyltin halides and (ω-haloalkyl)alkyltin dihalides, viz. $Me_2BrSn(CH_2)_nBr$ (n = 3—5) and $MeBr_2$-$Sn(CH_2)_4Br$.

¹H NMR data

The ¹H NMR spectral data of the new compounds prepared are given in Table 2.

In various papers on functionally-substituted organotin compounds structures involving intramolecular coordination between the functional group and the tin atom have been discussed. Thus, the groups of Matsuda [10], of Poller [11] and of Kuivila [12] reported evidence for intramolecular coordination between the carbonyl oxygen and the tin atom in ketoorganochlorostannanes of the type $\geqslant Sn(CH_2)_nC(O)R$, coordination being stronger when $n = 2$ than when $n = 3$ (cf. Fig. 1).

As regards the compounds $Me_3Sn(CH_2)_nBr$, the chemical shift and the $^{117/119}Sn$ coupling constants of the methyltin protons and also the chemical shifts of the CH_2Br protons show only minor differences in the series n = 3—5. Therefore, the occurrence of intramolecular bromine—tin coordination in this series is highly unlikely, as was to be expected for these tetraorganotin compounds.

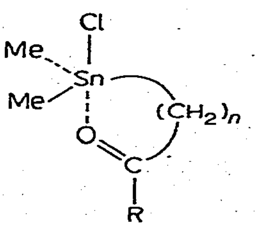

Fig. 1. (n = 2, 3).

TABLE 2

^{1}H NMR DATA OF SOME NEW COMPOUNDS $R_{3-m}X_mSn(CH_2)_nY$ IN CCl_4 SOLUTION

Compound	δ (ppm) [a]		$J(^{117/119}Sn-Me)$ (Hz)	Other data [b]
	CH_3-Sn	$-CH_2-Y$		
$Me_3SnCH_2SnMe_3$ [c]	0.08(s)		51/53	$\delta(CH_2-Sn) = -0.22$ ppm(s), $J(^{117/119}Sn-CH_2) = 58/60$ Hz
$Bu_3SnCH_2SnBu_3$				$\delta(CH_2-Sn) = -0.42$ ppm(s), $J(^{117/119}Sn-CH_2) = 54/56$ Hz
$Br_3Sn(CH_2)_3Br$		3.51(t)		
$Br_3Sn(CH_2)_4Br$		3.42(t)		
$Br_3Sn(CH_2)_5Br$		3.37(t)		
$Me_3Sn(CH_2)_3Br$	0.09(s)	3.33(t)	50/52	
$Me_3Sn(CH_2)_4Br$	0.07(s)	3.37(t)	50/52	
$Me_3Sn(CH_2)_5Br$	0.05(s)	3.35(t)	50/52	
$Ph_3Sn(CH_2)_4Br$		3.30(t)		
$Me_2BrSn(CH_2)_3Br$	0.78(s)	3.45(t)	55/57	$\delta(Sn-CH_2) = 1.44$ ppm(t); $\delta(C-CH_2-C) = 2.22$ ppm(t)
$Me_2BrSn(CH_2)_4Br$	0.72(s)	3.39(t)	53/55	
$Me_2BrSn(CH_2)_5Br$	0.71(s)	3.41(t)	53/55	
$MeBr_2Sn(CH_2)_4Br$	1.39(s)	3.43(t)	59/61.5	
$Me_3Sn(CH_2)_3NMe_2$	0.05(s)	2.14(t)	50/52	$\delta(Sn-CH_2) = 0.80$ ppm(t); $\delta(-C-CH_2-C) = 1.62$ ppm(q); $\delta(NMe_2) = 2.10$ ppm(s)
$Me_3Sn(CH_2)_3NEt_2$	0.05(s)	2.30(t)	50/52	$\delta(Sn-CH_2) = 0.76$ ppm(t); $\delta(-C-CH_2-C) = 1.58$ ppm(q); $\delta[N(-CH_2-C)_2] = 2.42$ ppm(qua); $\delta(N-C-CH_3) = 0.96$ ppm(t)
$Me_3Sn(CH_2)_3COOH$	0.07(s)	2.30(t)	50/52	$\delta(COOH) = 11.8$ ppm(s)
$Me_3Sn(CH_2)_3CHOHPh$	0.03(s)	4.49(t)	50/52	$\delta(-CH-O) = 4.49$ ppm(t); $\delta(C-OH) = 2.92$ ppm(s)
$Me_3Sn(CH_2)_4SnEt_3$	0.04(s)		50/52	
$Me_3Sn(CH_2)_4SnPh_3$	−0.05(s)		50/52	
Me_3SnPr	0.04		49/51.5	
Me_3SnBu	0.04		49/51.5	
$Me_3SnPent$	0.05		50/52	
$Me_2BrSnPr$	0.70		52/54	
$Me_2BrSnBu$	0.67		51.5/53.5	
$Me_2BrSnPent$	0.69		52/54	
$MeBr_2SnBu$	1.34		57/59	

[a] Downfield from TMS; s = singlet; t = triplet; qua = quartet; q = quintet. [b] Unresolved broad signals have not been included. [c] Lit. [13]: $\delta(CH_3-Sn) = 0.06$ ppm, $J(^{117/119}Sn-CH_3) = 50.7/52.9$ Hz; $\delta(CH_2-Sn) = -0.28$ ppm, $J(^{117/119}Sn-CH_2) = 57.7/60.3$ Hz.

As regards the compounds $Me_2BrSn(CH_2)_nBr$ (n = 3—5), comparison of the ^1H NMR data with those of $Me_2BrSn(CH_2)_4H$ shows that introduction of the ω-bromine atom results in a small downfield shift of the methyltin resonances (n = 3: $\Delta\delta$ = 0.08 ppm; n = 4: $\Delta\delta$ = 0.05 ppm; n = 5: $\Delta\delta$ = 0.02 ppm). This feature may be better explained on the basis of the inductive effect of the ω-bromine atom rather than by involving intramolecular bromine—tin coordination since the latter effect would result in an upfield shift (cf. [11,12]). The small differences in the chemical shifts of the CH_2Br protons in the series $Me_2BrSn(CH_2)_nBr$ (n = 3—5) likewise are not in accordance with intramolecular coordination but the increase of the $^{117/119}Sn$—methyl coupling constants in the latter series (n = 3: ΔJ = 3 Hz; n = 4: ΔJ = 1.5 Hz; n = 5: ΔJ = 1 Hz) can be rationalized in either way (cf. [12]).

Inductive effects may also account for the differences between the ^1H NMR data of $MeBr_2(CH_2)_4H$ and $MeBr_2Sn(CH_2)_4Br$, viz. a small downfield shift of the methyltin resonance ($\Delta\delta$ = 0.05 ppm) and a slight increase of the $^{117/119}Sn$—methyl coupling constants (ΔJ = 2 Hz).

Comparisons of the chemical shifts of the CH_2Br protons of $Br_3Sn(CH_2)_nBr$ with those of $Me_3Sn(CH_2)_nBr$ shows an increasing downfield shift with decreasing chain length in the former series (n = 5: $\Delta\delta$ = 0.02 ppm; n = 4: $\Delta\delta$ = 0.12 ppm; n = 3: $\Delta\delta$ = 0.23 ppm). This feature may be explained equally well in terms of inductive effects or intramolecular bromine—tin coordination.

In summary, it can be stated that the ^1H NMR data of $Me_{3-m}Br_mSn(CH_2)_nBr$ (m = 0—3; n = 3—5) do not provide conclusive evidence for the occurrence of intramolecular bromine—tin coordination in this type of compound.

Experimental

All reactions were performed under dry, oxygen-free nitrogen. Unless otherwise indicated, the starting materials were prepared according to published procedures or purchased. All materials were purified under nitrogen before use. Typical experiments are described below.

^1H NMR spectra were recorded using a Varian Associates HA 100 NMR spectrometer. Elemental analyses were carried out by the Element Analytical Section of this Institute.

Reaction of $SnBr_2$ with CH_2I_2 catalyzed by Et_3Sb: The synthesis of $R_3Sn-CH_2SnR_3$ (R = Me, Bu)

A mixture of 11.2 g (0.040 mol) of anhydrous $SnBr_2$, 32.3 g (0.120 mol) of CH_2I_2 and 0.82 g (0.004 mol) of Et_3Sb was stirred for 5 h at 120°C. Attempted distillation of the reaction mixture resulted in extensive decomposition. In a duplicate experiment the resulting clear orange liquid (100% conversion of $SnBr_2$) was treated with an excess of methyl magnesium bromide to give 5.2 g of crude $Me_3SnCH_2SnMe_3$ (n_D^{20} 1.5080). According to ^1H NMR spectrometry the product contained about 10% of Me_3SnCH_2I. Distillation gave 3.3 g (48%) of pure $Me_3SnCH_2SnMe_3$.

In a similar experiment the reaction product was treated with butylmagnesium bromide to give a 60% yield of $Bu_3SnCH_2SnBu_3$.

$Br_3Sn(CH_2)_nBr$ (n = 3—5)

A mixture of 111.6 g (0.40 mol) of anhydrous $SnBr_2$, 363 g (1.80 mol) of $Br(CH_2)_3Br$ and 4 ml (5.25 g, 0.025 mol) of Et_3Sb was stirred for 4.5 h at 150—160°C. The $SnBr_2$ had been completely converted. Evaporation in vacuo (14 mmHg) at 100°C gave 272 g (1.35 mol) of recovered $Br(CH_2)_3Br$, leaving 206 g of a brown, oily liquid. Distillation in vacuo (mercury diffusion pump) gave 141.6 g (74%) of pure $Br_3Sn(CH_2)_3Br$.

In a similar way $Br_3Sn(CH_2)_4Br$ and $Br_3Sn(CH_2)_5Br$ were prepared. Distillation of these compounds in vacuo is attended by thermal decomposition. In fact, $Br_3Sn(CH_2)_5Br$ could be isolated in the pure state only by high vacuum molecular distillation.

$HOOCSn(CH_2)_nBr$ (n = 3, 4)

To a solution of 2.42 g (0.005 mol) of $Br_3Sn(CH_2)_3Br$ in 15 ml of methanol at 0°C were added 1.57 ml (0.015 mol) of diethylamine. Under cooling at 0°C 15 ml of water were added drop-wise. The resulting white precipitate was filtered off and dried in vacuo over solid potassium hydroxide to give 1.23 g (90%) of (3-bromopropyl)stannonic acid.

In a similar way (4-bromobutyl)stannonic acid was obtained in 88% yield.

Reaction of $Br_3Sn(CH_2)_3Br$ with aqueous sodium hydroxide

A 100 ml reaction flask charged with 4.8 g (0.010 mol) of $Br_3Sn(CH_2)_3Br$ was cooled down to 0°C. At once 15 ml of a 4 *N* aqueous sodium hydroxide were added, resulting in a vigorous reaction. Within one minute 210 ml of gas (~0.010 mol) evolved. By IR spectrometry as well as by combined gas chromatography — mass spectrometry (GC—MS) the gas was proven to be pure cyclopropane.

$Me_3Sn(CH_2)_nBr$ (n = 3—5)

A solution of 20 g (0.042 mol) of $Br_3Sn(CH_2)_3Br$ in 100 ml of diethyl ether was added drop-wise to 80 ml of a 2.5 *N* solution of MeMgBr in diethyl ether. After reflux for 2 h the mixture was treated with a saturated aqueous solution of NH_4Cl and distilled to give 8.7 g (74%) of (3-bromopropyl)trimethyltin.

In a similar way were prepared: (4-bromobutyl)trimethyltin, (5-bromopentyl-trimethyltin, (3-bromopropyl)tributyltin, (4-bromobutyl)tributyltin and (4-bromobutyl)triphenyltin.

$Me_2BrSn(CH_2)_nBr$ (n = 3—5)

Over a period of 1 h 6.4 g (0.040 mol) of bromine was added drop-wise to a solution of 11.44 g (0.040 mol) of $Me_3Sn(CH_2)_3Br$ in 90 ml of anhydrous methanol, the reaction mixture being kept at —30°C. After 1 h at room temperature the mixture was distilled to give 12 g (83%) of (3-bromopropyl)dimethyltin bromide.

In a similar way were prepared: (4-bromobutyl)dimethyltin bromide and (4-bromobutyl)methyltin dibromide.

$Bu_3Sn(CH_2)_3NMe_2$

In a reaction vessel provided with a carbon dioxide condenser, a mixture of 6.18 g (0.015 mol) of $Bu_3Sn(CH_2)_3Br$ and 20 ml of Me_2NH was refluxed for 7 h.

The residue obtained after evaporation of the excess of Me_2NH was taken up in 30 ml of diethyl ether and treated for 15 min with 50 ml of a 10% aqueous solution of $NaHCO_3$. Distillation gave 4.95 g (86%) of (3-dimethylaminopropyl)tributyltin.

Analogously were prepared: (3-dimethylaminopropyl)trimethyltin, (3-diethylaminopropyl)trimethyltin, and (4-dimethylaminobutyl)tributyltin.

$Me_3Sn(CH_2)_3COOH$

A solution of 3.6 g (0.0125 mol) of $Me_3Sn(CH_2)_3Br$ in 6 ml diethyl ether was added dropwise to 0.35 g (0.015 mol) of magnesium in 6 ml diethyl ether. After reflux for 1.5 h the magnesium had been consumed and a positive Gilman test was obtained. The resulting solution was treated for 1 h with gaseous carbon dioxide, decomposed with 15 ml of a saturated aqueous solution of NH_4Cl and subsequently with 5 ml 1 *N* HCl. Evaporation of the solvent gave 1.6 g (52%) of $Me_3Sn(CH_2)_3COOH$. According to ^1H NMR spectrometry the product was slightly contaminated with $Me_3Sn(CH_2)_6SnMe_3$. The product was taken up in 5 ml 4 *N* NaOH and extracted with 5 ml of diethyl ether to give 0.3 g of $Me_3Sn(CH_2)_6SnMe_3$ [δ(Sn—Me) = 0.05 ppm]. The aqueous layer was treated with 4 *N* HCl (pH ~3) and extracted with 10 ml diethyl ether. Evaporation gave 0.8 g (26%) of pure $Me_3Sn(CH_2)_3COOH$.

In a similar way reaction of $Me_3Sn(CH_2)_nMgBr$ with benzaldehyde (n = 3), with triethyltin chloride (n = 4) and with triphenyltin chloride (n = 4) gave (4-phenyl-4-hydroxybutyl)trimethyltin, (4-triethylstannylbutyl)trimethyltin and (4-triphenylstannylbutyl)trimethyltin, respectively.

Acknowledgements

The authors wish to thank Mr. J.W. Marsman and Dr. J.G. Noltes for critical discussions. Financial support by the International Tin Research Council, London, is gratefully acknowledged.

References

1 D. Seyferth and E.G. Rochow, J. Amer. Chem. Soc., 77 (1955) 1302.
2 D. Seyferth, S.B. Andrews and R.L. Lambert, J. Organometal. Chem., 37 (1972) 69; D. Seyferth and S.C. Vick, Syn. React. Inorg. Met. Org. Chem., 4 (1974) 515.
3 M. Gielen and J. Topart, Bull. Soc. Chim. Belges, 80 (1971) 655.
4 D. Seyferth, J. Org. Chem., 22 (1957) 1252.
5 E.J. Bulten, J. Organometal. Chem., 97 (1975) 167.
6 K.D. Bos, E.J. Bulten and J.G. Noltes, J. Organometal. Chem., 99 (1975) 397.
7 J.G.A. Luijten, Rec. Trav. Chim. Pays-Bas, 85 (1966) 873.
8 D.D. Davis and R.H. Black, J. Organometal. Chem., 82 (1974) C30.
9 E.J. Bulten and H.A. Budding, J. Organometal. Chem., in the press.
10 S. Matsuda, S. Kikkawa and N. Kashiwa, Kogyo Kagaku Zasshi, 69 (1966) 1036.
11 S.Z. Abbas and R.C. Poller, J. Chem. Soc. Dalton, (1974) 1769.
12 H.G. Kuivila, J.E. Dixon, P.L. Maxfield, N.M. Scarpa, T.M. Topka, K.H. Tsai and K.R. Wusthorn, J. Organometal. Chem., 86 (1975) 89.
13 H.O. Kaesz, J. Amer. Chem. Soc., 83 (1961) 1514.