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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY

XXXIII*. HETEROCYCLIC TIN COMPOUNDS. THE SYNTHESIS OF 10,10-DIMETHYLPHENOXASTANNIN, 10,10-DIETHYLPHENOXASTANNIN AND 10,10-DIMETHYLPHENOTHIASTANNIN. THE CHARACTERIZATION OF A NEW TWELVE-MEMBERED ORGANOTIN HETEROCYCLE, $C_{28}H_{28}O_2Sn_2$

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SUMMARY

10,10-Dimethyl- and 10,10-diethylphenoxastannin have been prepared for the first time by the reaction of oxy-2,2′-bis(phenyllithium) with dimethyl- and diethyltin dichloride, respectively. The compound thought by Kupchik *et al.* to be dimeric 10,10-dimethylphenoxastannin has been found to be a twelve-membered organotin heterocycle, $C_{28}H_{28}O_2Sn_2$. PMR spectra in various solvents show this compound to be present in solution as an equilibrium mixture of conformational isomers. The PMR results for the tin-methyl protons emphasize the importance of conformational effects on both chemical shifts and coupling constants. Two magnetically non-equivalent methyl groups bound to one tin atom exhibit markedly different coupling constants (ΔJ 14.3 Hz). Reaction of 10,10-dimethylphenoxastannin with $SnCl_4$ affords the trimetallic species $C_{24}H_{16}O_2Cl_8Sn_3$.

10,10-Dimethylphenothiastannin has been obtained in good yield by the reaction of thio-2,2′-bis(phenyllithium) with dimethyltin dichloride. Oxidation of this compound with an excess of *m*-chloroperbenzoic acid resulted in the formation of 10,10-dimethylphenothiastannin 5,5-dioxide.

INTRODUCTION

Heterocyclic tin compounds containing a carbon–tin–carbon linkage and oxygen or sulfur in the ring have been described by Kupchik *et al.*[2,3]. These authors reported the preparation of a number of 10,10-dialkyl-, and 10,10-diphenylphenoxastannin and -phenothiastannin 5,5-dioxide derivatives by the reaction of oxy- or sulfonyl-2,2′-bis(phenyllithium), with dialkyl- and diphenyltin dichlorides. In connection with another investigation[4] we wished to prepare 10,10-dimethylphenoxastannin essentially by Kupchik's procedure. However, our experimental results revealed that Kupchik *et al.* did not isolate phenoxastannin derivatives. This paper reports the

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* For Part XXXII see ref. 1

preparation of 10,10-dimethylphenoxastannin, 10,10-diethylphenoxastannin and 10,10-dimethylphenothiastannin. The nature of the product thought by Kupchik *et al.* to be dimeric 10,10-dimethylphenoxastannin has been elucidated.

RESULTS AND DISCUSSION

10,10-*Dimethylphenoxastannin and the organotin heterocycle* $C_{28}H_{28}O_2Sn_2$

The reaction of oxy-2,2′-bis(phenyllithium) with dimethyltin dichloride, in a 1/1 molar ratio, afforded two reaction products, (I) and (II), in 31% and 4% yield, respectively. Both compounds analyzed for a composition $C_{14}H_{14}OSn$. However, (I) and (II) show great differences in physical properties, *e.g.* (I) melts at 49° and (II) at 255–257°. In contrast to (II), compound (I) is very soluble in organic solvents.

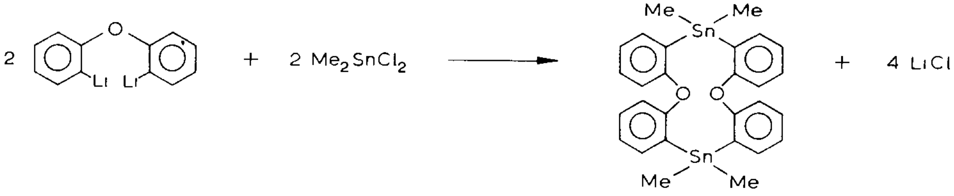
A molecular weight determination revealed the monomeric nature of compound(I) (found 318, calcd. for $C_{14}H_{14}OSn$ 317). Based on its mode of formation and the analytical and mol. wt. data we assign the phenoxastannin structure to this compound:

(I)

A dimeric molecular weight (found 674, calcd. for $C_{14}H_{14}OSn$ 317) was observed for compound (II). Both the mol. wt. and the melting point data show that (II) is identical with the only product isolated by Kupchik *et al.* (*cf.* refs. 2 and 3), who concluded that it was 10,10-dimethylphenoxastannin, which had dimerized via intermolecular tin–oxygen coordination. However, such tin–oxygen coordinative bonding must be considered highly unlikely in view of the lack of acceptor properties of the tin atom in tetraorganotin compounds. No other example of complex formation by tetraorganotin compounds is recorded in the literature. Therefore, we have investigated the nature of compound (II) in greater detail.

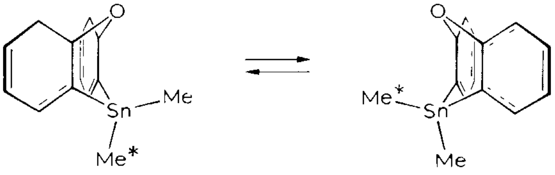
Mass spectra. 70 eV electron impact mass spectra of both (I) and (II) were recorded at identical ion-source temperatures. Compound (I) showed a relatively small molecular ion at *m/e* 318 [^{120}Sn], the base peak being the ion at *m/e* 303 (loss of $\cdot CH_3$). In the high mass region above *m/e* 318 no other peaks were observed. The mass spectrum of (II), however, showed several Sn-containing ions in the high mass region, of which an isotopic cluster with its most intense peaks at *m/e* 617, 619, 621 appeared to be composed of $C_{27}H_{25}O_2Sn_2$. Obviously this corresponds to loss of a methyl radical from the molecular ion $C_{28}H_{28}O_2Sn_2^{+\cdot}$ which was not observed. Fragmentation of $C_{27}H_{25}O_2Sn_2^+$ proceeds predominantly by loss of $C_{14}H_{14}OSn$ (metastable confirmed) leading to the same base peak as observed in the spectrum of (I) at *m/e* 303. All other peak intensities in the lower mass region showed a close resemblance to those of compound (I), apart from a cluster at *m/e* 165 [^{120}Sn] corresponding with $Sn(CH_3)_3^+$ ions. For a more detailed discussion on this subject we refer to ref. 5.

The analytical and molecular weight data, and in particular the presence of the $C_{27}H_{25}O_2Sn_2^+$ fragment ion in the mass spectrum of (II), lead to the conclusion that compound (II) does not consist of dimeric (I), but that it is a twelve membered heterocyclic ring compound formed by the reaction of two molecules of oxy-2,2'-bis-(phenyllithium) with two molecules of dimethyltin dichloride as follows:



(II)

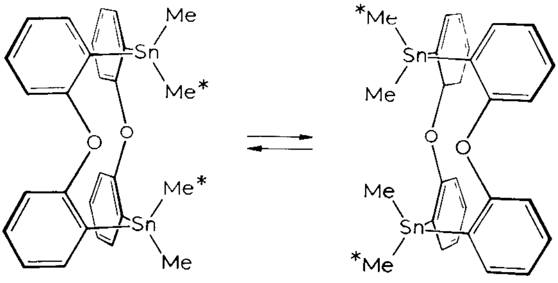
PMR spectra. In the PMR spectrum of (I), only one singlet due to tin methyl group protons is observed down to $-100°$ in methylene chloride or toluene-d_8 solution. Obviously the equilibrium between the two conformations (A_1) and (A_2) is rapid within the PMR time scale.



(A_1) (A_2)

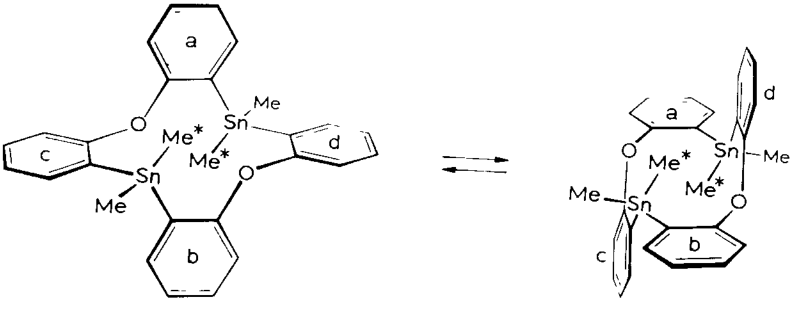
A similar behaviour has been observed for 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]-silin, -germin and -stannin^6.

The PMR spectrum of (II) is remarkably different, in that at 27° three methyl group signals are present at δ 0.31, 0.55 and 0.56 ppm in CCl_4 solution (intensity ratio 4/4/5). This can be explained by assuming the presence in solution of an equilibrium mixture of conformational isomers. The tin-methyl proton signal at δ 0.56 ppm may be attributed to an equilibrium mixture of conformers (B_1) and (B_2). Conformational exchange occurs at such a rate that even at $-100°$ in methylene chloride solution the tin-methyl groups Me and Me* are equivalent within the PMR time scale.



(B_1) (B_2)

The two equally intense tin-methyl group signals at δ 0.31 and 0.55 ppm point to the presence of conformers (C_1) and (C_2) in which two sets of magnetically inequivalent methyl groups are present.



(C_1) (C_2)

Contrary to the $(B_1)\rightleftharpoons(B_2)$ situation, the equilibrium $(C_1)\rightleftharpoons(C_2)$ does not result in the Me and Me* groups becoming magnetically equivalent, whatever the rate of this process. In (C_1) the signal due to Me* appears at higher field as a result of diamagnetic shielding of the two Me* groups by the aromatic rings a and b. The conformational change $(C_1)\rightarrow(C_2)$ does not result in a change of the magnetic environment of Me and Me*, the two Me* groups now being shielded by the aromatic rings d and c.

The isomer ratio (B)/(C) appears to be slightly solvent-dependent. In CCl_4 a ratio 5/8 is observed, whereas in the more polar solvent methylene chloride isomer (C) is more favoured as appears from the observed isomer ratio of 3/10. A high energy barrier exists for interconversion of (B) and (C). Upon heating a sample of (II) in hexachlorobutadiene solution only at 190° coalescence of the tin-methyl group signals was observed. At room temperature a methylene chloride solution of (II) shows methyl group signals at δ 0.27, 0.55 and 0.58 ppm with intensity ratio 5/3/5. On cooling to $-100°$ no marked changes in the PMR spectrum were initially observed. However, after about 10 minutes at temperatures below $-80°$ the methyl proton signals at δ 0.27 and 0.58 ppm disappeared, whereas the signal at δ 0.55 ppm remained unaffected. It appeared that a crystalline solid had deposited from the solution. Upon raising the temperature above $-60°$ the solid redissolved and the original PMR spectrum was observed. These results suggest that in the crystalline state compound (II) adopts conformation (C). This is confirmed by the observation that the PMR spectrum of a freshly prepared solution of (II) in CH_2Cl_2 at 0° shows only methyltin signals due to conformation (C), whereas after 15 min at 27° an equilibrium mixture of conformations (B) and (C) is present.

The presence of two magnetically non-equivalent methyl groups bound to one tin atom is not unprecedented. Various authors have studied the PMR behaviour of methyl groups on tin bound to a chiral carbon atom (refs. 7–9 and refs. cited therein) For example, Gielen *et al.*[8] in their study of a series of alkyldimethyl α-methylbenzyltin compounds observed non-equivalence of the tin-methyl groups by 0.04–0.15 ppm. Interestingly, the coupling constants $J(^{119}Sn\text{–}CH_3)$ for the diastereotopic methyl groups were found to be different by 0.2–0.9 Hz. In conformation (C) of compound (II) we observe a non-equivalence of the tin-methyl groups of 0.24 ppm. Surprisingly, the coupling constants $J(^{119}Sn\text{–}CH_3{}^*)$ (64.5 Hz) and $J(^{119}Sn\text{–}CH_3)$ (50.2 Hz) differ by as much as 14.3 Hz. For conformation (B) in which all tin methyl groups are equivalent as a result of rapid conformational exchange, $J(^{119}Sn\text{–}CH_3)$ is found to be 57.5 Hz, the mean value of the tin–methyl coupling constants in conformation (C). These results emphasize the importance of conformational effects on both chemical shifts and coupling constants, $J(\text{Sn–CH}_3)$. Similar effects on methyl, methylene and methinyl protons adjacent to chiral tin atoms have been described in recent communications[10–12].

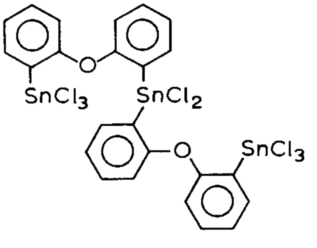
10,10-*Diethylphenoxastannin*

The reaction of oxy-2,2′-bis(phenyllithium) with diethyltin dichloride, in a 1/1 molar ratio, afforded 10,10-diethylphenoxastannin (III) as a colourless liquid, b.p. 116°/10^{-4} mm, in 23% yield. According to the results of both gas chromatographic and mass spectroscopic analyses the compound was (III), contaminated with 2% diphenyl ether and a trace of diethylbutyl(*o*-phenoxyphenyl)tin (*cf.* also ref. 5).

Recrystallisation of the distillation residue from 2-butanone, results in the isolation of a colourless product, with m.p. 158–160° in 2% yield, which apparently is identical with the only product, with m.p. 160–162°, isolated by Kupchik *et al.*[3]. We believe this product to be a twelve-membered heterocyclic ring compound, comparable to (II). Mass spectroscopy revealed that even after repeated recrystallizations from various solvents the compound was not absolute pure (see ref. 5).

$C_{24}H_{16}O_2Cl_8Sn_3$

An attempt to prepare 10,10-dichlorophenoxastannin, by the reaction of 10,10-dimethylphenoxastannin(I) with $SnCl_4$ in a 1/1 molar ratio, was unsuccessful. A crystalline solid (IV) was obtained, the mass spectrum of which showed an isotopic cluster of molecular ions at *m/e* 966–988. The observed isotopic distribution was in accordance with that calculated for $C_{24}H_{16}O_2Cl_8Sn_3$. The analytical data for (IV) are in agreement with this formulation. Based on these data we propose structure (IV) for this reaction product which has formed from (I) in a 2/3 molar reaction with $SnCl_4$.



(IV)

10,10-*Dimethylphenothiastannin and* 10,10-*dimethylphenothiastannin* 5,5-*dioxide*

The reaction of thio-2,2′-bis(phenyllithium) with dimethyltin dichloride afforded only one reaction product, which by C, H, Sn and S analysis and by molecular weight determination was found to be 10,10-dimethylphenothiastannin (V). Oxidation of this compound with an excess of *m*-chloroperbenzoic acid resulted in the formation of 10,10-dimethylphenothiastannin 5,5-dioxide (VI), which was found to be identical with the reaction product, obtained by Kupchik *et al.*, from the reaction of dimethyltin dichloride with sulfonyl-2,2′-bis(phenyllithium)[3].

PMR data for the various heterocyclic dimethyltin compounds described in this paper are given in Table 1.

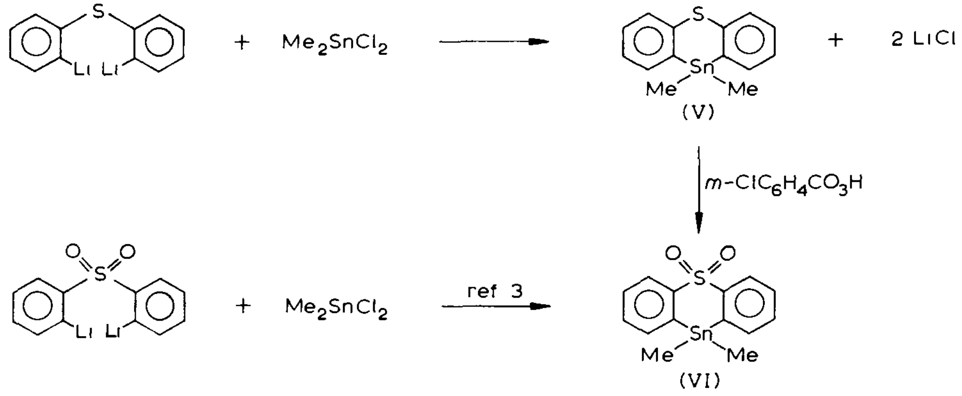


TABLE 1

PMR SPECTRAL DATA FOR THE HETEROCYCLIC DIMETHYLTIN COMPOUNDS (I), (II), (V) AND (VI) IN CCl_4 SOLUTION AT 27°

Compound	*Chemical shifts, δ*[a]		$J(^{119}Sn\text{-}CH_3)$[b]	$J(^{117}Sn\text{-}CH_3)$[b]
	Aromatic protons	*Sn-Me*		
(I)	6.80–7.50	0.50[c]	62.0	59.2
(II)	6.30–7.70	0 56[c,d]	57.5	55.0
		0.55[e]; 0.31[e]	50.2; 64.5	47.8; 61.5
(V)	7 00–7.30 7 30–7.50[f] 7.50–7.75[g]	0.54[c]	60.4	57.8
(VI)	7.20–7 48 7.48–7.60[f] 7.90–8 20[g]	0.67[c]	62 0	59 2

[a] Ppm downfield from TMS. [b] Hz. [c] Only one singlet observed, even at − 100° in CH_2Cl_2 solution [d] Conformation (B) [e] Conformation (C) [f] Protons in *ortho* position with respect to the carbon–tin–carbon linkage [g] Protons in *ortho* position with respect to the carbon–sulfur–carbon linkage.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Elemental analyses were carried out by Mr. W. J. Buys. PMR spectra were recorded by Mr. J. W. Marsman, using a Varian Associates HA-100 NMR spectrometer. Mass spectral data were collected on an AEI MS902 mass spectrometer, by Dr. J. K. Terlouw at the Laboratory for Analytical Chemistry of the State University of Utrecht. Molecular weights were measured by Miss M. E. Kurth on 0.2–0.5% solutions in benzene using a Mechrolab dynamic vapour pressure osmometer.

Preparation of 10,10*-dimethylphenoxastannin* (*I*)

A solution of 7.4 g (22.5 mmoles) of bis(2-bromophenyl) ether[13] in diethyl ether (75 ml) was dropwise added to a cooled (0°) stirred solution of 45.1 mmoles of

BuLi in hexane (25 ml) and diethyl ether (50 ml). After addition was complete the reaction mixture was refluxed for 1 h. The resulting solution of oxy-2,2'-bis(phenyllithium) and a solution of 5.0 g of dimethyltin dichloride (22.5 mmoles) in diethyl ether (150 ml) were dropwise added into a 500 ml reaction flask, equipped with two dropping funnels and a mechanical stirrer. From both dropping funnels reagents were added at the same rate. The reaction mixture was vigorously stirred, while being cooled with an ice-salt bath. After 1 h the addition was complete. The mixture was refluxed for 1 h, hydrolyzed with water, and filtered in order to remove 0.1 g of a colourless solid. The ether layer was separated, dried on mol. sieve 4A, and evaporated leaving a turbid yellowish oil, which upon distillation afforded 2.2 g of analytically pure 10,10-dimethylphenoxastannin (I), b.p. 110–120°/0.001 mmHg, m.p. 49°. (Found: C, 53.16; H, 4.56; mol. wt., 318. $C_{14}H_{14}OSn$ calcd.: C, 53.05; H, 4.45%; mol. wt., 317.). Yield 31%. Recrystallization of the distillation residue from 2-butanone afforded 0.3 g of a colourless crystalline solid (II), m.p. 255–257°. (Found: C, 52.72; H, 4.53; mol. wt., 674. $C_{28}H_{28}O_2Sn_2$ calcd.: C, 53.05; H, 4.45%; mol. wt., 634.). Yield 4%.

Preparation of 10,10-*diethylphenoxastannin* (*III*)

By the same procedure as described above 3.0 g of impure 10,10-diethylphenoxastannin (III) was obtained as a yellowish oil, b.p. 80–120°/10^{-4} mm, from 8.4 g (25.6 mmoles) of bis(2-bromophenyl) ether, 51.2 mmoles of BuLi and 6.3 g (25. 6 mmoles) of diethyltin dichloride. This crude product was purified by passing a hexane solution through a column of activated alumina. Subsequent, evaporation of the solvent results in the isolation of a colourless oil which upon distillation affords 2.0 g of 10,10-diethylphenoxastannin (III), b.p. 116°/10^{-4} mmHg (GLC, 98% (III), 2% diphenyl ether and a trace of diethylbutyl(*o*-phenoxyphenyl)tin. (Found: C, 57.00; H, 5.45; Sn, 33.01. $C_{16}H_{18}OSn$ calcd.: C, 55.70; H, 5.26; Sn, 34.41%.) Yield 23%.

Repeated recrystallizations of the original distillation residue from 2-butanone gave 0.2 g of a colourless solid, m.p. 158–160° (lit.[3] m.p. 160–162°). (Found: C, 55.96; H, 5.84. $C_{32}H_{36}O_2Sn_2$ calcd.: C, 55.70; H, 5.26%.) Yield 2.3%.

Preparation of $C_{24}H_{16}O_2Cl_8Sn_3$ (*IV*)

$SnCl_4$ (0.33 g, 1.3 mmoles) was added to 0.4 g (1.3 mmoles) of compound (I). The reaction mixture was heated for 1 h at 160° at 15 mmHg during which Me_2SnCl_2 (0.2 g) sublimed from the reaction mixture. Recrystallization from toluene of the purple-black residue afforded 0.2 g of a grey crystalline product, m.p. 220–222°, which analyzed for compound (IV). (Found: C, 30.17; H, 1.88; Cl, 28.97; Sn, 35.76. $C_{24}H_{16}Cl_8O_2Sn_3$ calcd.: C, 29.48; H, 1.64; Cl, 29.07; Sn, 36.42%.) Yield ≈45%.

Preparation of 10,10-*dimethylphenothiastannin* (*V*)

A solution of 20.0 g (57 mmoles) of bis(2-bromophenyl) sulphide[14] in diethyl ether (120 ml) was dropwise added to a cooled (0°) stirred solution of 114 mmoles of BuLi in hexane (65 ml) and diethyl ether (120 ml). After addition was complete the reaction mixture was refluxed for 1 h. The resulting solution of thio-2,2'bis(phenyllithium) was dropwise added to a solution of 12.5 g of dimethyltin dichloride (57 mmoles) in diethyl ether (100 ml). The reaction mixture was vigorously stirred, while being cooled with an ice-salt bath. After 1 h the addition was complete. The mixture was refluxed for 1 h, and subsequently hydrolyzed with water. The ether layer was separated, dried on mol. sieve 4A, and evaporated leaving a yellowish oil. Upon distillation, the fraction boiling at 125°/7 · 10^{-4} mmHg was recovered as a colourless solid, which was recrystallized from petroleum ether (40–60°) to give 10.7 g of 10,10-dimethylphenothiastannin (V), m.p. 95–96°. (Found: C, 50.75; H, 4.39; S, 9.60; mol. wt., 326. $C_{14}H_{14}SSn$ calcd.: C, 50.49; H, 4.24; S, 9.63%; mol. wt., 333.) Yield 56%

Preparation of 10,10-*dimethylphenothiastannin* 5,5-*dioxide* (*VI*)

To a solution of 1.0 g (3 mmoles) of 10,10-dimethylphenothiastannin (V) in chloroform (25 ml) was added a solution of 1.1 g (6 mmoles) of *m*-chloroperbenzoic acid in chloroform (25 ml). The clear solution was left overnight and thereupon the solvent was evaporated. The remaining colourless solid was dissolved in diethyl ether and in order to remove the *m*-chlorobenzoic acid this solution was treated with an aqueous solution of $NaHCO_3$. The ether layer was separated, dried on mol. sieves 4A, and evaporated leaving a colourless solid which upon recrystallization from methanol afforded 0.7 g of 10,10-dimethylphenothiastannin 5,5-dioxide, m.p. 164–166° (lit.[3] 164–165°). (Found: C, 45.89; H, 3.90; S, 8.68; mol. wt., 350. $C_{14}H_{14}O_2SSn$ calcd.: C, 46.06; H, 3.87; S, 8.78%; mol. wt., 365.) Yield 64%.

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