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THE SYNTHESIS AND CHARACTERIZATION OF SOME (AMINOMETHYL)TRIALKYL- AND (AMINOMETHYL)TRIPHENYL-TINS

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Summary

A range of aminomethyl substituted triorganotins have been prepared by four basic routes: by the direct action of (iodomethyl)trimethyltin or (iodomethyl)triphenyltin on primary and secondary amines in ether solution (method A), on primary and secondary amines in the presence of triethylamine (method B), on the potassium salts of amines in ether solution (method C), and finally by the reaction of *N,S*-acetals with various trialkyltinlithiums.

Introduction

In the course of our studies of the reactions of metal carbonyls with organotin bases [1], it was necessary to have access to (aminomethyl)trialkyltins as intermediates. At the outset of our investigation some (aminomethyl)trialkyltins had been reported [2-5]; but we sought to increase the range of compounds considerably, and where possible to improve the method and yield of previous syntheses.

In an initial report, Kostyanovskii et al. [2] demonstrated that mixtures of (chloromethyl)triethyltin and dimethylamine when heated in sealed tubes afforded good yields of (*N,N*-dimethylaminomethyl)triethyltin. They also showed that the potassium salts of aziridine and pyrrole underwent rapid reaction, with (chloromethyl)triethyltin to produce *N*-[(tri-ethylstannyl)methyl]aziridine and *N*-[(triethylstannyl)methyl]pyrrole respectively.

Subsequently [3] a solution of dimethylamine in ether was shown to undergo reaction with (chloromethyl)trimethyltin at room temperature to give the product in good yield after 13 d. Methylamine was reported to react similarly to give a mixture of (*N*-methylaminomethyl)trimethyltin and bis[(trimethylstannyl)methyl]methylamine, although 122 d reaction was necessary to obtain good yields.

More recently, Peterson [6-8] has demonstrated that *N*-[tri-n-butylstan-

nyl)methyl]amines are readily prepared by the reaction of tri-n-butyltinlithium with aminomethyl phenyl sulphides.

$$R_2NCH_2SC_6H_5 + (n\text{-}C_4H_9)_3SnLi \xrightarrow{THF} (n\text{-}C_4H_9)_3SnCH_2NR_2 + C_6H_5SLi$$

Results and discussion

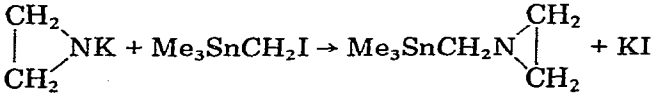
We have extended these methods of preparation using a number of modifications to synthesize a wide variety of (aminomethyl)triorganotins. Seyferth et al. [9] have developed an important straightforward method for the synthesis of (iodomethyl)trimethyltin (I), and this offers an attractive alternative to the chloromethyl analogue in amine synthesis, since the halogen atom in I might be expected to be more easily replaced than that in (chloromethyl)trimethyltin. Furthermore, the general procedure used in the preparation of (chloromethyl)-trimethyltin involves methylenation with diazomethane [10]; thus although this reaction proceeds in good yield the potential hazards associated with diazomethane restrict the scale of its application. The generally greater reactivity of I is demonstrated by its reaction with methylamine in anhydrous ether, which is complete within 4 h at room temperature:

$$Me_3SnCH_2I + MeNH_2 \xrightarrow{Et_2O} \begin{cases} \rightarrow Me_3SnCH_2NHMe & (54\%\ \text{yield}) \\ \rightarrow (Me_3SnCH_2)_2NMe & (38\%\ \text{yield}) \end{cases}$$

This increased reactivity facilitates the preparation of other amines by this route (method A). However, the rate of reaction falls rapidly as the size of the alkyl groups on the primary or secondary amine increases, and thus no reaction appears to take place between I and di-n-butylamine. Although somewhat less reactive than I, (iodomethyl)triphenyltin couples in an analogous fashion and for example (*N,N*-dimethylaminomethyl)triphenyltin may be obtained from reaction with dimethylamine.

The interaction of I with equimolar proportions of secondary amines in the presence of a large excess of triethylamine affords very good yields of (aminomethyl)trialkyltins (method B), and this method is of particular utility when the tertiary amine product is otherwise less readily available.

The reaction of I with the potassium salts of aziridine and pyrrole proceeds readily at low temperatures to give the desired products (method C).



We have also used this procedure to prepare *N*-[(triphenylstannyl)methyl]aziridine, but yields are much lower.

For the preparation of (aminomethyl)tri-n-butyltins we have found the interaction of tri-n-butyltinlithium with *N,S*-acetals to be by far the most useful synthetic route. The relative ease of preparation of *N,S*-acetals by the condensation of a secondary amine, benzenethiol and formalin makes the route particularly attractive. We have employed this method successfully (method D) to syn-

thesize a wide range of [(tri-n-butylstannyl)methyl]amines containing a variety of alkyl and aryl substituents on nitrogen. We have by this method synthesized the first reported tris[(trialkylstannyl)methyl]amine:

$$(C_6H_5SCH_2)_3N + 3\ (n\text{-}C_4H_9)_3SnLi \rightarrow [(n\text{-}C_4H_9)_3SnCH_2]_3N + 3\ C_6H_5SLi$$

The product tris[(tri-n-butylstannyl)methyl]amine, is an air-sensitive liquid which may be isolated and purified by column chromatography. The thermal instability of this and the majority of the [(tri-n-butylstannyl)methyl]amines precluded their isolation by distillation.

Experimental

All melting points and boiling points are uncorrected. NMR spectra were determined using a Perkin—Elmer R10 60 MHz or a Jeol JNM-MH-100 100 MHz spectrometer, either as neat liquids or as solutions in carbon tetrachloride or deuterochloroform. All reactions and manipulations were, as a matter of course, carried out under dry nitrogen and etherial solvents were redistilled from potassium/benzophenone immediately prior to use.

The following were prepared using reported procedures *N,N*-diethylaminomethyl phenyl sulphide [11]; *N*-[(phenylthio)methyl]piperidine [12]; *N*-methyl-*N*-phenylaminomethyl phenyl sulphide [13]; tris[(phenylthio)methyl]-amine [14] and (*N,N*-dimethylaminomethyl)tri-n-butyltin [6].

The method of Grillot et al. [11] was extended to prepare the following aminomethyl sulphides which were characterized by their integrated NMR spectra — *N,N*-di-n-propylaminomethyl phenyl sulphide, b.p. 98°C/0.06 Torr, τ 2.94 (m, 5 H, C_6H_5S), 5.63 (s, 2 H, SCH_2N), 7.62 (t, 4 H, *J* 8 Hz, NCH_2), 8.76 (m, 4 H, CCH_2C) and 9.34 ppm (t, 6 H, *J* 6.5 Hz, CH_3C); *N,N*-di-iso-propylaminomethyl phenyl sulphide, b.p. 90°C/0.1 Torr, τ 2.79 (m, 5 H, C_6H_5S), 5.54 (s, 2 H, SCH_2N), 6.90 (sept., 2 H, *J* 7 Hz, NCH) and 9.00 ppm [d, 12 H, *J* 7 Hz, $C(CH_3)_2$]; *N,N*-di-n-butylaminomethyl phenyl sulphide, b.p. 120°C/0.06 Torr, τ 2.81 (m, 5 H, C_6H_5S), 5.42 (s, 2 H, SCH_2N), 7.38 (t, 4 H, *J* 5.5 Hz, NCH_2), 8.68 (m, 8 H, CCH_2CH_2C) and 9.08 ppm (t, 6 H, *J* 6 Hz, CCH_3); *N,N*-di-iso-butylaminomethyl phenyl sulphide, b.p. 98°C/0.04 Torr, τ 2.73 (m, 5 H, C_6H_5S), 5.54 (s, 2 H, NCH_2S), 7.70 (d, 4 H, *J* 7 Hz, NCH_2C), 8.42 (m, 2H, CCHC) and 9.24 ppm [d, 12 H, *J* 6 Hz, $C(CH_3)_2$]; *N,N*-diphenylaminomethyl phenyl sulphide, m.p. 59-60°C, τ 3.07 [m, 15 H, $(C_6H_5)_2N$] and C_6H_5S and 4.98 (s, 2 H, NCH_2S); *N,N*-dicyclohexylaminomethyl phenyl sulphide, τ 2.78 (m, 5 H, C_6H_5S), 5.43 (s, 2 H, SCH_2N), 7.42 (m, 2H, NCH) and 8.64 ppm (m, 20 H, C_6H_{10}); *N*-methyl-*N*-cyclohexylaminomethyl phenyl sulphide, τ 2.82 (m, 5 H, C_6H_5S), 5.51 (s, 2 H, SCH_2N), 7.69 (s, 3 H, CH_3N), 7.47 (m, 1 H, NCH) and 8.62 ppm (m, 10 H, C_6H_{10}).

A detailed account of each of the four synthetic methods is given below. These and the other products prepared by the various methods are tabulated and characterized in Table 1.

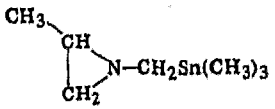
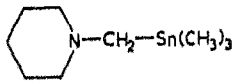
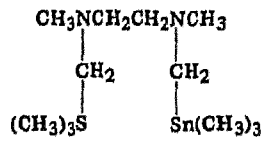
(N,N-Dimethylaminomethyl)trimethyltin (Method A)

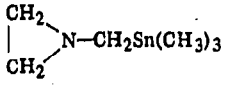
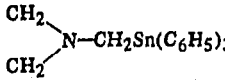
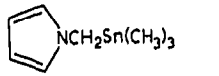
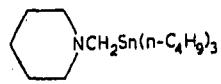
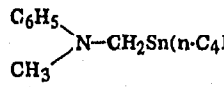
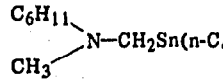
(Iodomethyl)trimethyltin [9] (15.3 g, 0.05 mol), anhydrous dimethylamine (22.5 g, 0.5 mol) and ether (80 ml) were stirred in a sealed vessel at room tem-

(continued on p. 164)

TABLE 1

CHARACTERIZATION OF THE (AMINOMETHYL)TRIORGANOTINS

Compound	Method of preparation	Yield (%)	B.p. (°C/Torr) [m.p.]	^{1}H NMR spectra: τ values (ppm), intensity, multiplicity, coupling (Hz) and assignments
$(CH_3)_2NCH_2Sn(CH_3)_3$	A	76	48-50/15	7.63 (2 H, s, J $^{119/117}$Sn—CH_2 25.4, NCH_2Sn), 7.84 [6 H, s, $(CH_3)_2N$], 9.90 [9 H, s, J ^{119}Sn—CH_3 52.9, J ^{117}Sn—CH_3 49.7, $(CH_3)_3Sn$]
$CH_3NHCH_2Sn(CH_3)_3$	A	54	59-60/30	7.50 (2 H, s, J $^{119/117}$Sn—CH_2 29.5, NCH_2Sn), 7.66 (3 H, s, CH_3N), 7.86 (1 H, s, NH), 9.92 [9 H, s, J ^{119}Sn—CH_3 52.8, J ^{117}Sn—CH_3 47.8, $(CH_3)_3Sn$]
$CH_3N[CH_2Sn(CH_3)_3]_2$	A	38	76/1	7.62 (4 H, s, J $^{119/117}$Sn—CH_2 22.7, NCH_2Sn), 7.87 (3 H, s, CH_3N), 9.92 [9 H, s, J ^{119}Sn—CH_3 52.8, J ^{117}Sn—CH_3 49.3, $(CH_3)_3Sn$]
$(C_2H_5)_2NCH_2Sn(CH_3)_3$	A	89	60/8	7.41 (2 H, s, J $^{119/117}$Sn—CH_2 21.6, NCH_2Sn), 7.67 (4 H, q, J 7.2, C—CH_2N), 9.02 (6 H, t, J 7.2, CH_3C), 9.89 [9 H, s, J ^{119}Sn—CH_3 52.0, J ^{117}Sn—CH_3 49.4, $(CH_3)_3Sn$]
$C_2H_5NHCH_2Sn(CH_3)_3$	A	37	58/16	7.44 (2 H, q, J 7.2, CCH_2N), 7.47 (2 H, s, J $^{119/117}$Sn—CH_2 31.6), 8.97 (3 H, t, J 7.2, CH_3C), 9.35 (1 H, s, NH), 9.92 [9 H, s, J ^{119}Sn—CH_3 51.5, J ^{117}Sn—CH_3 49.0, $(CH_3)_3Sn$]
	A	38	40/0.1	7.82 (2 H, s, J $^{119/117}$Sn—CH_2 29.5, NCH_2Sn), 8.73 (1 H, m, NCH), 9.07 (5 H, m, CH_3C, CH_2C), 9.90 [9 H, s, J ^{119}Sn—CH_3 54.0, J ^{117}Sn—CH_3 48.7, $(CH_3)_3Sn$]
$(CH_3)_2NCH_2Sn(C_6H_5)_3$	A	85	[81-83]	2.65 [15 H, m, $(C_6H_5)_3Sn$], 6.83 (2 H, s, J $^{119/117}$Sn—CH_2 21.7) 7.73 [6 H, s, $(CH_3)_2N$]
	B	65		7.72 (2 H, s, J $^{117/119}$Sn—CH_2 24.5, NCH_2Sn), 7.80 (4 H, m, NCH_2C), 8.66 [6 H, m, $C(CH_2)_3C$], 9.90 [9 H, s, J ^{119}Sn—CH_3 52.0, J ^{117}Sn—CH_3 49.5, $(CH_3)_3Sn$]
	B	32		7.51 (4 H, s, J $^{119/117}$Sn—CH_2 22.6, NCH_2Sn), 7.68 [4 H, s, $N(CH_2)_2N$], 7.84 (6 H, s, CH_3N), 9.86 [18 H, s, J ^{119}Sn—CH_3 52.9, J ^{117}Sn—CH_3 49.13, $(CH_3)_3Sn$]

	C	82	53/13	7.89 (2 H, s, J $^{119/117}$Sn—CH_2 30.2, NCH_2Sn), 8.63 (2 H, t, J 2.6, NCH), 9.19 (2 H, t, J 2.6, NCH), 9.86 [9 H, s, J ^{119}Sn—CH_3 53.7, J^{117}Sn—CH_3 50.3, $(CH_3)_3Sn$]
	C	21	[69-70]	2.58 [15 H, m, $(C_6H_5)_3Sn$], 7.23 (2 H, s, J $^{119/117}$Sn—CH_2 33.2, NCH_2Sn), 8.44 (2 H, t, J 2.4, NCH), 9.13 (2 H, t, J 2.4, NCH)
	C	70	44/0.01	3.76 (2 H, m, NCH) 4.14 (2 H, m, CCH), 6.54 (2 H, s, J $^{119/117}$Sn—CH_2 26.1), 10.04 [9 H, s, J ^{119}Sn—CH_3 53.9, J ^{117}Sn—CH_3 51.1, $(CH_3)_3Sn$]
$(C_2H_5)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	80		7.46 (2 H, s, J $^{119/117}$Sn—CH_2 21, NCH_2Sn), 7.70 (4 H, q, J 7, NCH_2C), 8.87 [27 H, m, $(C_4H_9)_3Sn$], 9.02 (6 H, t, J 7, CH_3CN)
$(n\text{-}C_3H_7)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	78		7.41 (2 H, s, J $^{119/117}$Sn—CH_2 16.4, NCH_2Sn), 7.79 (4 H, t, J 7, NCH_2C), 8.87 [37 H, m, $(C_4H_9)_3Sn$, CH_3CH_2CN]
$(i\text{-}C_3H_7)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	75		7.04 (1 H, sept, J 6.8, NCHC), 7.42 (2 H, s, J $^{119/117}$Sn—CH_2 21.6, NCH_2Sn), 8.92 [27 H, m, $(C_4H_9)_3Sn$], 9.02 [12 H, d, J 6.8 $(CH_3)_2C$]
$(n\text{-}C_4H_9)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	75		7.40 (2 H, s, J $^{119/117}$Sn—CH_2 20.7), 7.78 (4 H, m, NCH_2C) 8.90 (41 H, m, $(C_4H_9)_3Sn$, $CH_3CH_2CH_2C$)
$(i\text{-}C_4H_9)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	80		7.39 (2 H, s, J $^{119/117}$Sn—CH_2 15.5), 8.06 (4 H, m, NCH_2C) and 8.66 [41 H, m, $(C_4H_9)_3Sn$, $CCH(CH_3)_2$]
	D	73		7.45 (2 H, s, J $^{119/117}$Sn—CH_2 15.8, NCH_2Sn), 7.81 (4 H, m, NCH_2C), 8.72 [33 H, m, $(C_4H_9)_3Sn$, $C(CH_2)_3C$]
$(C_6H_5)_2NCH_2Sn(n\text{-}C_4H_9)_3$	D	75		3.08 [10 H, m, $(C_6H_5)_2N$], 6.43 (2 H, s, J $^{119/117}$Sn—CH_2 13.9), 8.94 [27 H, m, $(C_4H_9)_3Sn$]
	D	70		3.15 (5 H, m, C_6H_5N), 6.79 (2 H, s, J $^{119/117}$Sn—CH_2 14, $SnCH_2N$), 7.21 (3 H, s, CH_3N), 8.75 [27 H, m, $(C_4H_9)_3Sn$]
	D	71		7.64 (2 H, m, NCHC), 7.46 (2 H, s, J $^{119/117}$Sn—CH_2 14, NCH_2Sn), 7.82 (3 H, s, CH_3N), 8.75 [37 H, m, $(C_4H_9)_3Sn$, C_6H_{10}]
$(C_6H_{11})_2N—CH_2—Sn(n\text{-}C_4H_9)_3$	D	65		7.45 (2 H, s, J $^{119/117}$Sn—CH_2 15.3, NCH_2Sn), 7.77 (2 H, m, NCHC), 8.78 [47 H, m, $(C_4H_9)_3Sn$, C_6H_{10}]
$N[CH_2Sn(n\text{-}C_4H_9)_3]_3$	D	70		7.55 (6 H, s, J $^{119/117}$Sn—CH_2 29, NCH_2Sn), 8.84 [81 H, m, $(C_4H_9)_3Sn$]

perature for 48 h. Precipitated salt was removed by filtration, and the filtrate was fractionally distilled to give the product (76%), b.p. 48-50°C/15 Torr (lit. [5], b.p. 67.2-68.5°C/47 Torr). (Found: C, 33.1; H, 8.0; N, 6.27. Calcd.: C, 32.5; H, 7.7; N, 6.32%.)

N-[(Trimethylstannyl)methyl]piperidine (Method B)

(Iodomethyl)trimethyltin (3.06 g, 0.01 mol), piperidine (1.26 g, 0.015 mol) and triethylamine (15.2 g, 0.15 mol) were stirred in a sealed vessel at room temperature for 24 h. Salts were removed by filtration, and the filtrate was concentrated at 20°C/10 Torr. After further filtration to remove small traces of precipitated salt, the filtrate was kept at 30°C/0.01 Torr for ≈2 h to produce the product (65%). (This product is prone to decomposition when kept at temperatures >0°C for prolonged periods.)

N-[(Trimethylstannyl)methyl]aziridine (Method C)

N-Potassium aziridine was prepared by stirring a mixture of aziridine (10.7 g, 0.25 mol) and potassium (1.95 g, 0.05 mol) at 50°C for 3 h. Diethyl ether (30 ml) was added, the slurry was cooled to −78°C and a solution of (iodomethyl)trimethyltin (14.95 g, 0.049 mol) in ether (10 ml) was added dropwise with stirring. After warming to ambient temperature the suspension was filtered, and the filtrate was fractionally distilled to give the product (82%) b.p. 53°C/13 Torr (lit. [4], b.p. 56°C/20 Torr). (Found: C, 33.3; H, 7.1; N, 6.18. Calcd.: C, 32.8; H, 6.83; N, 6.37%.)

N-Potassium aziridine was allowed to react with (iodomethyl)triphenyltin [15] as above. After filtration the filtrate was concentrated and the residue recrystallized from hexane to give *N*-[(triphenylstannyl)methyl]aziridine (21%) m.p. 69-70°C.

N-[(Tri-n-butylstannyl)methyl]piperidine (Method D)

N-[(Phenylthio)methyl]piperidine (16.15 g, 0.0078 mol) was added dropwise to a stirred solution of tri-n-butyltinlithium (0.08 mol) in tetrahydrofuran (60 ml) cooled in ice. The resulting mixture was hydrolysed with water, washed with 10% aqueous sodium hydroxide dried ($MgSO_4$) and concentrated at reduced pressure (25°C/0.01 Torr). Chromatography of the concentrate on florisil, and elution with hexane afforded an initial fraction of hexa-n-butylditin, elution with hexane/diethyl ether (20/1) gave the product as a clear air-sensitive oil (73%). (Found: C, 55.1; H, 11.0; N, 3.97. Calcd.: C, 55.7; H, 10.1; N, 3.61%.)

The remaining *N*-(tri-n-butylstannyl)amines were prepared in a similar fashion except that (*N*,*N*-diphenylaminomethyl)tri-n-butyltin and (*N*-methyl-*N*-phenylaminomethyl)tri-n-butyltin were chromatographed on neutral alumina.

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