352. *Amino-derivatives of Metals and Metalloids. Part I. Preparation of Aminostannanes, Stannylamines, and Stannazanes*

By K. Jones and M. F. Lappert
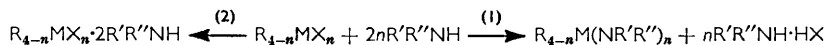
A representative series of amino-derivatives of tin(IV) have been prepared. These include aminostannanes $R_nSn(NR'_2)_{4-n}$, stannylamines $R_3Sn \cdot NHR$ and $(R_3Sn)_3N$, distannazanes $(R_3Sn)_2NR'$, and cyclotristannazanes $(R_2SnR)_3$. Synthetic methods have involved transmetallation, transamination, transamination/condensation, and transamination/elimination/cyclopolymerisation. It appears that steric effects play an important role in many of these systems, both in influencing the course of reactions (*e.g.*, the transamination displacement order is $H_2N > RHN > R_2N$), and in affecting the stability of products [*e.g.*, whilst $Bu^n_3Sn \cdot NHBu^t$ is stable, $Me_3Sn \cdot NHMe$ decomposes spontaneously to afford $(Me_3Sn)_2NMe$].

THIS Paper begins a series dealing with amino-derivatives of metals and metalloids, and specifically relates to derivatives of tin(IV); preliminary results have been published, both on preparative aspects [1] and on chemical reactions.[1,2]

The principal objective of the work here described was to prepare as wide as possible a range of tin amines (*i.e.*, primary, secondary, and tertiary acyclic and cyclic derivatives), in order subsequently (see later Papers) to study their structures and physical and chemical behaviour, so that proper comparisons with analogues of carbon, silicon, germanium, and lead may be made.

We have, so far, failed to make primary stannylamines, and of cyclic derivatives only report on the six-membered cyclostannazanes. The compounds that have been prepared are of structural interest, especially so in a comparative sense. For example, whereas trisilylamine, and therefore probably tris(trimethylsilyl)amine, has D_{3h} skeletal symmetry,[3] in accord with $2sp^2(N)-3sp^3(Si)$ σ-orbitals and $d_\pi-p_\pi$–Si–N interaction, tris(trimethylstannyl)amine is expected to be more nearly like an alkylamine with nitrogen in a pyramidal, approximately sp^3-situation. Similarly, the conformation of the cyclostannazanes will throw light on the nature of the bonding between nitrogen and the Group IV element. Other physicochemical aspects that are relevant to this problem are the relative strengths of the metal–nitrogen bond (predicted SiN > CN ⩾ GeN > SnN > PbN) and the basicity of the nitrogen (predicted CN > PbN > SnN > GeN > SiN) in its different environments; such studies are in hand.

At the outset of this work, very few compounds containing a $\geqslant$Sn–N$\leqslant$ bond had been characterised. This was undoubtedly due to the fact that aminostannanes could not generally be prepared by direct aminolysis of halostannanes.[4] Indeed, appropriate equations [5] to describe reactions of amines with Group IV halides are (1) for M = Si or Ge and (2) for M = Sn or Pb. With ammonia, on the other hand, dehydrochlorination of the intermediate complex has been reported [6] to produce species (X = Cl or Br) of types $X_3Sn \cdot NH_2$ and $X \cdot Sn(NH_2)_3$.

$$R_{4-n}MX_n \cdot 2R'R''NH \xleftarrow{\text{(2)}} R_{4-n}MX_n + 2nR'R''NH \xrightarrow{\text{(1)}} R_{4-n}M(NR'R'')_n + nR'R''NH \cdot HX$$

Imido- and sulphonamido-derivatives of tin(IV) are known.[7,8] We believe these to be

[1] Jones and Lappert, *Proc. Chem. Soc.*, 1962, 358.
[2] Jones and Lappert, *Proc. Chem. Soc.*, 1964, 22.
[3] Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford, 1963, p. 106.
[4] Ingham, Rosenberg, and Gilman, *Chem. Rev.*, 1960, **60**, 508, Table 21.
[5] Anderson, *J. Amer. Chem. Soc.*, 1952, **74**, 1421.
[6] Schwalz and Jeanmaire, *Ber.*, 1932, **64**, 1442; Bannister and Fowles, *J.*, 1958, 751, 4354.
[7] Luijten and van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, 1955.
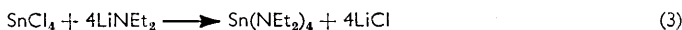[8] van der Kerk and Luijten, *J. Appl. Chem.*, 1956, **6**, 49; Mack and Parker, U.S.P. 2,618,625 (*Chem. Abs.*, 1953, **47**, 1977g); U.S.P. 2,634,281 (*Chem. Abs.*, 1954, **48**, 1420).

polymeric with 5-co-ordinate tin, since they are both water-stable (unlike the simple SnN compounds reported here) and have potentially bifunctional ligands, properties that they share with certain heterocyclic SnN compounds of that structure.[9,10] These compounds, being insoluble, were prepared by metathesis from their SnO-precursors and the free ligands, with elimination of water.

Organotin azides and pseudohalides of " iso "-structure are known.[9,11,12]

The conductometric titration of sodium in liquid ammonia with dimethylstannane afforded aminodimethylstannyl sodium,[13] $Me_2Sn(NH_2)\cdot Na$.
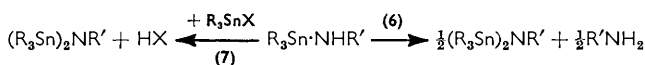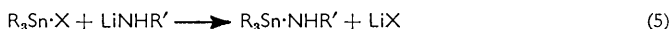
A major advance in SnN chemistry was the preparation of an aminostannane [see reaction (3)], by way of the lithium salt of the amine.[14] We have extended reaction (3) [see reaction (4), R, R′, and R″ = alkyl or aryl, X = Cl or Br, M = Li, and n = 1 2, 3, or 4] to the preparation by transmetallation of numerous derivatives.

$$SnCl_4 + 4LiNEt_2 \longrightarrow Sn(NEt_2)_4 + 4LiCl \tag{3}$$

$$R_4SnX_{4-n} + nLiNR'R'' \longrightarrow R_{4-n}Sn(NR'R'')_n + nMX \tag{4}$$

Since we began this work, reports by others have appeared on the following compounds [also using reaction (4), and in some cases with M = Na, K, or R‴Mg]: $MeSn(NMe_2)_3$, $Me_3Sn\cdot NMe_2$,[15] $Me_3Sn\cdot NHEt$,[16] $Me_3Sn\cdot NEt_2$, $Et_2Sn(NEt_2)_2$,[15] $Et_3Sn\cdot NEt_2$,[15,17] $Et_3Sn\cdot N(CH_2Ph)Tol$-o,[18,19] $Pr_3Sn\cdot NEt_2$,[17] $Bu_3Sn\cdot NEt_2$, $Ph\cdot Sn(NMe_2)_3$,[15] $(Me_3Sn)_3N$.[20]

Transmetallation with Lithium Salts of Secondary Amines.—Reaction (4) invariably proceeded smoothly. Although tetrakis(di-isopropylamino)- and tetrakis(di-n-butylamino)-stannanes were not obtained pure, this was due to decomposition during distillation.

Transmetallation with Lithium Salts of Primary Amines.—The monolithium salts of primary amines were prepared from n-butyl-lithium and the appropriate amine. Their reactions with trialkylhalogenostannanes were expected to proceed according to reaction (5). In the event, this was only one (for R = Me, R′ = Ph, or p-Tol; and R = Et, R′ = Ph) of alternative reaction paths that was observed; the other led to N-alkyldistannazanes, $(R_3Sn)_2NR'$ (for R = Me and R′ = Me or Et). The latter presumably were formed from N-alkyltrimethylstannylamine precursors, which then underwent condensation to the distannazanes, according to reaction (6) or, less likely, to reaction (7).

$$R_3Sn\cdot X + LiNHR' \longrightarrow R_3Sn\cdot NHR' + LiX \tag{5}$$

$$(R_3Sn)_2NR' + HX \underset{(7)}{\overset{+ R_3SnX}{\longleftarrow}} R_3Sn\cdot NHR' \overset{(6)}{\longrightarrow} \tfrac{1}{2}(R_3Sn)_2NR' + \tfrac{1}{2}R'NH_2$$

Transamination (R'_2NH–R''_2NH) *Reactions.*—Reaction (8) was essentially a volatility-controlled equilibrium. Thus, during continuous distillation the more volatile of the two amines, R'_2NH and R''_2NH, was removed first, and an example of a relative displacement series that was demonstrated is $Bu_2N > Et_2N > Me_2N$.

$$R_3Sn\cdot NR'_2 + R''_2NH \longrightarrow R_3Sn\cdot NR''_2 + R'_2NH \tag{8}$$
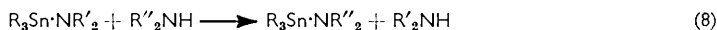
Transamination (R_2NH–$R'NH_2$) *Reactions.*—A second type of transamination is that involving primary as well as secondary amines, and it appears that in this event there is

[9] Luijten, Janssen, and van der Kerk, *Rec. Trav. chim.*, 1962, **81**, 202; van der Kerk, Luijten, and Janssen, *Chimia*, 1962, **16**, 10.
[10] Luijten and van der Kerk, *Rec. Trav. chim.*, 1963, **82**, 1181.
[11] Seyferth and Kahlen, *J. Amer. Chem. Soc.*, 1960, **82**, 1080; *J. Org. Chem.*, 1960, **25**, 809.
[12] Green, Sowerby, and Wihksne, *Chem. and Ind.*, 1960, 1306.
[13] Kettle, *J.*, 1959, 2936.
[14] Thomas, *Canad. J. Chem.*, 1961, **39**, 1386.
[15] Wiberg and Rieger, G.P. 1,121,050 (*Chem. Abs.*, 1962, **56**, 14328b).
[16] Abel, Brady, and Lerwill, *Chem. and Ind.*, 1962, 1333.
[17] Sisido and Kozima, *J. Org. Chem.*, 1962, **27**, 4051.
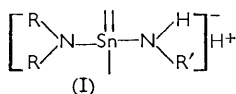[18] Neumann, Niermann, and Sommer, *Angew. Chem.*, 1961, **73**, 768.
[19] Neumann and Heyman, *Angew. Chem. Internat. Edn.*, 1963, **2**, 100.
[20] Lehn, *J. Amer. Chem. Soc.*, 1964, **86**, 305; Sisido and Kozimo, *J. Org. Chem.*, 1964, **29**, 907.

steric rather than volatility control. Thus, irrespective of boiling points, reactions (9) or (10) were realised. Steric effects are manifested in at least two ways, (i) in the displacement order, and (ii) in the choice as between reactions (9) and (10).

$$Me_3Sn\cdot NR_2 + R'NH_2 \longrightarrow Me_3Sn\cdot NHR' + R_2NH \qquad (9)$$

$$2Me_3Sn\cdot NR_2 + R'NH_2 \longrightarrow (Me_3Sn)_2NR' + 2R_2NH \qquad (10)$$

As to (i), the order (generally) $R'HN > R_2N$ must have a steric origin, whether it is the case that the SnN bond in $\equiv Sn\cdot NHR$ is thermochemically stronger than in $\equiv Sn\cdot NR_2$ (where there is greater F- and B-strain), or the reaction is one that is kinetically deter-mined. In the latter event, the transition state is presumably trigonal bipyramidal, as shown in (I), with tin using sp^3d-hybrid orbitals, and the relative ease of its formation, as expressed by collision probability between nitrogen and tin, will be greater when the nucleophile is a primary rather than a secondary amine. Factors affecting the displacement order in transamination of tin(IV) seem to be broadly similar to those operating for silicon [21] and boron.[22] Yet steric effects are evidently of somewhat less importance for tin than for boron, since the order $Me_2N > Bu^tHN$ is true for boron,[22] whilst the reverse (see below) is the case for tin. This is in accord with the relative radii of boron(III) and tin(IV); the size of the amine ($Bu^tNH_2 > Me_2NH$) will be more critical the smaller the reaction site.

The reaction of dimethylaminotrimethylstannane with aniline gave N-phenyltrimethyl-stannylamine [reaction (9)], and this could not be converted into N-phenylhexamethyl-distannazane, the expected product of reaction (10), even under forcing conditions with excess of dimethylaminotrimethylstannane.

Methylamine and ethylamine, on the other hand, reacted with dimethylaminotrimethyl-stannane according to scheme (10). There was no infrared spectral evidence for N-alkyl-trimethylstannylamine formation even under the mildest conditions, and it follows that condensation (reaction 11) must be very facile for lower N-alkyl derivatives. In accord with this, the distannazanes could not be converted into the N-alkyltrimethylstannyl-amines, by treatment with excess of amine.

$$2Me_3Sn\cdot NHR \longrightarrow (Me_3Sn)_2NR + RNH_2 \qquad (11)$$

The stability, with respect to reaction (11), of a secondary tin amine must therefore be governed by the nature of the hydrocarbon group R, since in the present experiments the trimethylstannyl group is a constant factor. To test whether steric effects played a major role, transamination with a sterically hindered primary aliphatic amine was carried out. Reaction of dimethylaminotrimethylstannane with excess of t-butylamine was inconclusive and complex; although dimethylamine was evolved, the residual organotin compound could not be characterised. However, N-t-butyltri-n-butylstannylamine was obtained as the only tin-bearing product in a related reaction ($Bu^n_3Sn\cdot NMe_2 + Bu^tNH_2 \longrightarrow Bu_3Sn\cdot NHBu^t$). Thus, it appears that steric effects, in the sense of (ii), are significant.
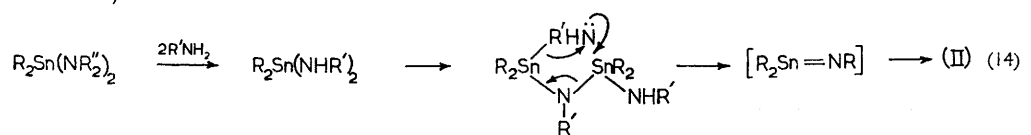
The formation of a distannazane from a secondary stannylamine may be generalised as in reaction (12). A clear extension (13; R = Me or Et) is to the synthesis of cyclo-stannazanes, by using a bifunctional organotin compound and a primary organic amine.

$$\equiv Sn\cdot N= \longrightarrow \equiv Sn\cdot N\cdot Sn\equiv \qquad (12)$$

$$nMe_2Sn(NMe_2)_2 + nRNH_2 \longrightarrow (Me_2SnNR)_n + 2nMe_2NH \qquad (13)$$

[21] Fessenden and Fessenden, *Chem. Rev.*, 1961, **61**, 361.
[22] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148; Aubrey, Lappert, and Majumdar, *J.*, 1962, 4088.

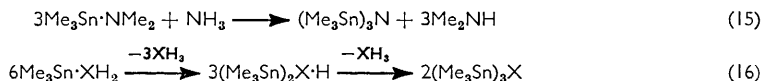The N-ethyl homologue was shown (mol. wt.) to be the cyclotristannazane (II). The molecular weight of the N-methyl derivative was not determined because of its low solubility in benzene, but it is presumed also to be the cyclic trimer.

It is probable, by analogy with the formation of borazines from aminoboranes,[23] that the mechanism of formation of cyclostannazane is a 4-step process (reaction 14), involving successively transamination, intermolecular condensation, 1:3-nucleophilic rearrangement and elimination, and cyclopolymerisation (multiply-bonded tin compounds are, of course, unknown).

$$R_2Sn(NR''_2)_2 \xrightarrow{2R'NH_2} R_2Sn(NHR')_2 \longrightarrow R_2Sn \cdots SnR_2 \longrightarrow [R_2Sn=NR] \longrightarrow (II) \quad (14)$$

Transamination ($R_2NH–NH_3$) *Reactions.*—A third type of transamination is that involving ammonia as the reagent. It was expected, on the basis of the steric argument, that the displacement series could be extended to $H_2N > RHN > R_2N$. The use of dimethylaminotrimethylstannane as substrate afforded a route (reaction 15) to tris(trimethylstannyl)-amine. No evidence was obtained that an intermediate primary or secondary stannyl-amine was formed.

There is a parallel with the stannylphosphines; thus,[24] interaction of bromotrimethylstannane and sodiophosphine afforded tris(trimethylstannyl)phosphine, $(Me_3Sn)_3P$. Presumably, in both cases, ready condensations of the type of reaction (16); ($X = N$ or P) occur.

$$3Me_3Sn \cdot NMe_2 + NH_3 \longrightarrow (Me_3Sn)_3N + 3Me_2NH \tag{15}$$

$$6Me_3Sn \cdot XH_2 \xrightarrow{-3XH_3} 3(Me_3Sn)_2X \cdot H \xrightarrow{-XH_3} 2(Me_3Sn)_3X \tag{16}$$

It has previously been suspected[25] that tris(trimethylstannyl)amine is formed in the reaction of trimethylstannylsodium with iodobenzene in liquid ammonia, and it has also recently been prepared[20] directly from the organotin chloride and lithium nitride; or sodamide in liquid ammonia.

Attempted Sn–C *Aminolysis.*—There are aspects of the chemistry of aluminium that somewhat closely resemble those of tin. Accordingly, by analogy with reaction (17),[26] it was possible that protodestannylation of a tetraorganostannane, by reaction with an amine, might be effected. Four systems ($Ph_4Sn–PhNH_2$, $Ph_4Sn–C_5H_{11}N$, $Me_4Sn–PhNH_2$, and $Me_4Sn–Bu_2NH$) were investigated, but in none was Sn–C cleavage achieved.

$$Ph_3Al + ArNH_2 \longrightarrow \tfrac{1}{4}(Ph_2AlNAr)_4 + 2C_6H_6 \tag{17}$$
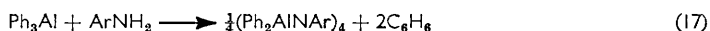
EXPERIMENTAL

Carbon, hydrogen, and nitrogen analyses were carried out in this Department and we thank Mr. V. Manohin and his staff for this work. Amino-group estimation was by steam-distillation of the liberated amine from an alkaline solution of the Sn–N compound into standard sulphuric acid and back-titration with standard sodium hydroxide. Halide was estimated by Volhard's method, after hydrolysis in aqueous alcoholic solutions. Tin was determined by total oxidation to tin(IV) oxide;[27] the atmosphere-sensitive organotin–nitrogen compound was weighed into a stoppered silica tube and kept open to the atmosphere until it decomposed; it was then oxidised with a mixture of fuming nitric and sulphuric acids, and the residue was ultimately ignited.

[23] Lappert and Majumdar, *Proc. Chem. Soc.*, 1963, 88.
[24] Brucker, Balashova, and Soborovskii, *Doklady Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, **135**, 843 (*Chem. Abs.*, 1961, **55**, 13301).
[25] Bullard and Robinson, *J. Amer. Chem. Soc.*, 1927, **49**, 1368.
[26] Idris Jones and McDonald, *Proc. Chem. Soc.*, 1962, 366.
[27] Gilman, Langham, and Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 1327.

Melting points were determined in sealed capillary tubes, to minimise contact with the atmosphere. Molecular weights were measured cryoscopically in benzene solution.

Diethyl ether and hydrocarbon solvents such as benzene, toluene, and petroleum fractions were dried over sodium wire. Methylamine, ethylamine, and dimethylamine were dried over sodium hydroxide, recondensed at $-78°$, and weighed into ampoules. Aniline and other higher boiling amines were fractionally distilled before use. Tin(IV) chloride and bromide, were commercial reagents and were satisfactory for preparing starting materials without further purification. Precautions were taken at all times to protect the reactants from atmospheric moisture.

Tetramethylstannane (from $SnCl_4$/MeMgI) and tetraethylstannane (from $SnCl_4$/EtMgBr) were obtained by standard methods,[28] whilst tetra-n-butylstannane (distilled before use) and tetraphenylstannane, were gifts from Pure Chemicals Ltd.

The organotin halides used were prepared by the Kocheshkov disproportionation reaction, by methods essentially the same as those previously described.[4,7] n-Butyltrichlorostannane was prepared by the Grignard reaction, and bromo-tri-n-butylstannane by the reaction of bromine with tetra-n-butylstannane.

A typical n-butyl-lithium solution was prepared from lithium sheet (13·9 g., 2 mol.), freshly cut under light petroleum (b. p. 30—40°; 300 ml.), and n-butyl chloride (92·6 g., 1 mol.), in the same solvent (300 ml.), run in at such a rate that gentle reflux was maintained.[26] After the reaction was complete, the mixture was filtered; the clear solution could be stored at 0° for long periods without decomposition. The concentration of the solution was determined before use by hydrolysing a portion of it with water and titrating it with standard acid.

Lithium salts of amines were invariably freshly prepared.

In experiments where we report lack of reaction, reagents were invariably recovered almost quantitatively and were fully characterised.

Preparation of Compounds by Transmetallation.—The conditions used in the synthesis of tin–nitrogen compounds by the reaction of lithium salts of amines with organotin halides are summarised in Table 1. Physical constants, yields, and analytical results are shown in Table 2. Typical procedures are given below.

TABLE 1

Amino-derivatives of tin: reaction conditions employed in syntheses by transmetallation

Compound	Halide Hal	Halide Wt. (g.)	Halide Mol.	Halide solvent Vol. (ml.)	Bu^{n}Li (1 mol.) Vol. (ml.)	Bu^{n}Li (1 mol.) Strength (M)	Dil. with Et$_2$O Vol. (ml.)	Amine Wt. (g.)	Amine Mol.	Reflux time (hr.)
Sn(NMe$_2$)$_4$	Cl	30·5	0·22	C$_6$H$_6$ 100	240	2·202	200	25·0	1·05	4 *
Sn(NEt$_2$)$_4$	Cl	31·0	0·24	C$_6$H$_6$ 100	300	1·687	200	37·0	1·0	3
Me$_3$SnNMe$_2$	Cl	28·0	0·94	Et$_2$O 50	95	1·587	150	7·0	1·04	3 *
Me$_3$SnNEt$_2$	Cl	14·5	0·73	Et$_2$O 50	56	1·794	100	7·7	1·05	2
Me$_3$SnNPr$^i_2$	Cl	15·0	0·75	Et$_2$O 50	56	1·794	100	10·3	1·01	3
Me$_3$SnNBu$^n_2$	Cl	12·5	0·86	Et$_2$O 50	49	1·520	100	10·0	1·01	1
Me$_3$SnN(C$_6$H$_{11}$)$_2$	Cl	9·1	0·92	Et$_2$O 50	33	1·518	100	9·1	1·00	1
Me$_3$SnN<C$_5$H$_{10}$	Cl	14·0	0·94	Et$_2$O 50	49	1·520	100	6·4	1·00	1
Me$_3$SnNMePh	Cl	14·5	0·73	Et$_2$O 50	56	1·794	100	10·7	1·00	2
Me$_3$SnNPh$_2$	Cl	9·0	0·91	Et$_2$O 50	28	1·794	100	8·5	1·00	1
Me$_2$Sn(NMe$_2$)$_2$	Cl	10·0	0·46	C$_6$H$_6$ 100	105	0·954	100	4·8	1·06	2
Me$_2$Sn(NEt$_2$)$_2$	Cl	45·0	0·41	C$_6$H$_6$ 100	385	1·298	100	37·0	1·00	3
Me$_2$Sn(NPr$^i_2$)$_2$	Cl	8·0	0·37	C$_6$H$_6$ 50	56	1·794	100	10·5	1·04	1
Et$_3$SnNMe$_2$	Br	18·0	0·95	Et$_2$O 50	74	0·900	100	3·1	1·03	2 *
Et$_3$SnNEt$_2$	Cl	46·0	0·96	Et$_2$O 100	109	1·841	100	14·6	1·00	2
Bu$^n_3$SnNMe$_2$	Cl	70·0	0·85	Et$_2$O 100	136	1·840	200	13·0	1·16	4
Bu$^n_2$Sn(NMe$_2$)$_2$	Cl	14·5	0·46	Et$_2$O 50	56	1·794	100	6·1	1·33	1
Bu^{n}Sn(NMe$_2$)$_3$	Cl	13·0	0·30	Et$_2$O 100	84	1·794	100	8·0	1·19	2
Ph$_3$SnNMe$_2$	Cl	14·5	0·75	Et$_2$O 100	28	1·794	100	2·4	1·11	4
Ph$_2$Sn(NMe$_2$)$_2$	Cl	14·0	0·41	Et$_2$O 50	56	1·794	100	5·0	1·12	1
PhSn(NMe$_2$)$_3$	Cl	14·0	0·29	Et$_2$O 100	108	1·400	150	7·0	1·04	2
(Me$_3$Sn)$_2$NMe	Cl	18·5	0·93	Et$_2$O 50	56	1·790	100	3·5	1·13	1
Me$_3$SnNHPh	Cl	14·0	0·70	Et$_2$O 50	56	1·794	100	9·3	1·00	2
Me$_3$SnNH·C$_6$H$_4$Me-p	Cl	13·8	0·70	Et$_2$O 50	91	1·090	100	10·7	1·00	1
Et$_3$SnNHPh	Br	14·0	0·98	Et$_2$O 50	46	1·090	100	4·65	1·00	1

* Set aside for 12 hr. at 20°.

[28] Ref. 7, p. 95.

TABLE 2

Amino-derivatives of tin: yields, physical constants, and analytical results

					Found						Required				
Compound	B.p. °/mm. (m.p.)	n_D^{20}	d_4^{20}	Yield (%)	C (%)	H (%)	N (%)	Sn (%)	M	Formula	C (%)	H (%)	N (%)	Sn (%)	M
$Sn(NMe_2)_4$	51/0·15	1·4774	1·687	60·2	33·0	7·6	18·6	40·0		$C_8H_{24}N_4Sn$	32·56	8·20	18·99	40·26	
$Sn(NEt_2)_4$	90/0·05	1·4800	1·1042	45·0	47·1	9·5	13·6			$C_{16}H_{40}N_4Sn$	47·18	9·90	13·76		
Me_3SnNMe_2	126/760	1·4572	1·2173	91·0	29·6	7·1	6·8	57·0	199	$C_5H_{15}NSn$	28·86	7·27	6·73	57·13	208
Me_3SnNEt_2	43/8	1·4618	1·1539	84·5	35·6	7·9	5·9		222	$C_7H_{19}NSn$	35·60	8·11	5·93		236
$Me_3SnNPr^i_2$	63/8	1·4645	1·1068	80·3	41·1	8·5	5·4			$C_9H_{23}NSn$	40·92	8·78	5·30		
$Me_3SnNBu^n_2$	74/2·5	1·4559	1·1972	81·0	45·2	9·3	4·5			$C_{11}H_{27}NSn$	45·23	9·32	4·80		
$Me_3SnN(C_6H_{11})_2$	96/0·2	1·5055		70·0	52·1	9·0	4·0			$C_{15}H_{31}NSn$	52·35	9·07	4·07		
$Me_3SnN{<}C_5H_{10}$	48/1·0			76·0	38·6	7·5	5·8			$C_8H_{20}NSn$	38·74	7·71	5·65		
$Me_3SnNMePh$	82/0·1	1·5757	1·3645	83·0	44·0	6·1	4·8			$C_{10}H_{17}NSn$	44·47	6·35	5·19		
Me_3SnNPh_2	108/0·1	1·6096	1·3176	85·0	54·1	5·6	4·1			$C_{15}H_{21}NSn$	54·26	5·76	4·22		
$Me_2Sn(NMe_2)_2$	138/760	1·4463	1·1482	68·0	31·0	7·7	35·8(Me_2N)			$C_6H_{18}N_2Sn$	30·4	7·66	36·15(Me_2N)		
$Me_2Sn(NEt_2)_2$	78/4	1·4685	1·1060	67·2	41·2	9·0	9·2			$C_{10}H_{26}N_2Sn$	40·97	8·95	9·56		
$Me_2Sn(NPr^i_2)_2$	66/0·05	1·4783		71·5	48·3	9·6	8·1			$C_{14}H_{34}N_2Sn$	48·15	9·82	8·02		
Et_3SnNMe_2	76/9	1·4724	1·1692	75·0	38·2	8·3	5·7			$C_8H_{21}NSn$	38·42	8·47	5·60		
Et_3SnNEt_2	72/2	1·4737	1·1247	87·2	43·1	9·6	5·2			$C_{10}H_{25}NSn$	43·18	9·07	5·04		
$Bu^n_3SnNMe_2$	86/0·1	1·4747		86·0	50·5	9·6	4·0		347	$C_{14}H_{33}NSn$	50·30	9·96	4·19		334
$Bu^n_2Sn(NMe_2)_2$	72/0·05			77·5	45·0	9·2	8·95			$C_{12}H_{30}N_2Sn$	44·86	9·42	8·72		
$Bu^nSn(NMe_2)_3$	67/0·1			71·0	40·1	8·6	13·5			$C_{10}H_{27}N_3Sn$	38·98	8·72	13·64		
Ph_3SnNMe_2	166/0·1 (62°)			81·0	61·0	5·5	3·6			$C_{20}H_{21}NSn$	60·94	5·37	3·55		
$Ph_2Sn(NMe_2)_2$	128/0·2	1·5296	1·3519	82·5	53·2	6·1	7·9			$C_{16}H_{22}N_2Sn$	53·20	6·14	7·76		
$PhSn(NMe_2)_3$	80/0·1	1·5331	1·5084	70·0	44·1	6·9	12·6		340	$C_{12}H_{23}N_3Sn$	43·92	7·07	12·81		
$(Me_3Sn)_3N$	70/0·2	1·4901	1·4794	82·5 *	21·9	5·4	2·7	70·0		$C_9H_{27}NSn_3$	21·37	5·38	2·77	70·45	
$(Me_3Sn)_2NMe$	64/3	1·4968	1·4805	64·5	23·4	5·7	3·8			$C_7H_{21}NSn_2$	23·56	5·93	3·93		356
$(Me_3Sn)_2NEt$	93/15		1·4255	90·0 *	26·0	6·1	3·5			$C_8H_{23}NSn_2$	25·90	6·25	3·78		
$Me_3SnNHPh$	77/0·05	1·5721	1·3536	82·3	42·7	5·7	5·3		277	$C_9H_{15}NSn$	42·22	5·90	5·47		256
$Me_3SnNH·C_6H_4Me\text{-}p$	106/0·5	1·5622		76·0	44·1	6·8	4·9			$C_{10}H_{17}NSn$	44·47	6·34	5·19		
$(Me_2SnNMe)_3$	114/0·2			62·5 *	20·7	5·3	8·0	66·2		$C_9H_{27}N_3Sn_3$	20·25	5·06	7·87	66·80	
$(Me_2SnNEt)_3$	104/0·05			63·5 *	26·3	5·9	7·2		596	$C_{12}H_{33}N_3Sn_3$	25·04	5·74	7·30		575
$Et_3SnNHPh$	100/0·2			82·0	48·4	7·0	4·8			$C_{12}H_{21}NSn$	48·36	7·10	4·70		
$Bu^n_3SnNHBu^t$	124/1	1·4773	1·0577	92·0 *	53·3	10·3	3·6			$C_{16}H_{37}NSn$	53·04	10·3	3·87		

* Transamination reaction.

TABLE 3

Amino-derivatives of tin: reaction conditions used in transamination reactions

Reactant Amine	Wt. (g.)	Reactant Sn cpd. (1 mol.)	Wt. (g.)	Mol.	Product Sn cpd.	Wt. (g.)	Yield (%)	Product Amine	Wt. (g.)	Yield (%)
Et_2NH	2·63	Me_3SnNMe_2	0·93	1·00	Me_3SnNEt_2	2·82	95	Me_2NH	0·55	96
Bu^n_2NH	2·47	Me_3SnNEt_2	1·35	1·00	$Me_3SnNBu^n_2$	2·79	92	Et_2NH	0·74	98
$C_5H_{10}NH$	1·63	Me_3SnNEt_2	0·59	1·00	$Me_3SnN{<}C_5H_{10}$	1·65	96·5	Et_2NH	0·50	99
$PhNH_2$	1·873	Me_3SnNEt_2	0·76	1·00	$Me_3SnNHPh$	1·83	90	Et_2NH	0·60	100
$MeNH_2$	2·53	Me_3SnNMe_2	1·04	Excess	$(Me_3Sn)_2NMe$	1·80	83	Me_2NH	†	
$EtNH_2$	6·05	Me_3SnNMe_2	2·01	Excess	$(Me_3Sn)_2NEt$	4·85	90	Me_2NH	†	
Bu^tNH_2	12·81	$Bu^n_3SnNMe_2$	3·45	1·33	$Bu^n_3SnNHBu^t$	12·80	92	Me_2NH	†	
$MeNH_2$	6·70	$Me_2Sn(NMe_2)_2$	1·79	2·10	$(Me_2SnNMe)_3$	3·26	62·5	Me_2NH	†	
$EtNH_2$	3·53	$Me_2Sn(NMe_2)_2$	1·60		$(Me_2SnNEt)_3$	1·80	63·5	Me_2NH	†	
NH_3	5·10	Me_3SnNMe_2 *	Excess		$(Me_3Sn)_3N$	3·40	82·5	Me_2NH	†	

* In light petroleum (b. p. 30—40°, 30 ml.). † Me_2NH detected by i.r.

3 R

(i) *Preparation of dimethylaminotrimethylstannane.* Dimethylamine (7·0 g., 1·04 mol.) at −78° was added to a solution of n-butyl-lithium (95 ml. of a 1·587M soln.; 1 mol.) in light petroleum (b. p. 30—40°) diluted with diethyl ether (100 ml.) at −78°. The mixture was allowed to attain room temperature to allow n-butane and excess of dimethylamine to evaporate off. Trimethylchlorostannane (28·0 g., 0·94 ml.) in diethyl ether (50 ml.) was added, the mixture refluxed for 1 hr. and was set aside for 12 hr. at 20°. It was then refluxed for a further 2 hr., lithium chloride (6·4 g., 100%) (Found: Cl, 83·5. Calc. for LiCl: Cl, 83·7%) was filtered off, and washed with light petroleum (2 × 20 ml.). Solvents were distilled off from the combined filtrate and washings at atmospheric pressure. Distillation of residual liquid gave *dimethyl-aminotrimethylstannane* (24·6 g., 91%), b. p. 126°, n_D^{20} 1·4572, d_4^{20} 1·2173 (Found: C, 29·6; H, 7·1; N, 6·8; Sn, 57·0. $C_5H_{15}NSn$ requires C, 28·9; H, 7·3; N, 6·7; Sn, 57·1%).

(ii) *Preparation of tetrakis(dimethylamino)stannane.* A procedure analogous to that described in (i), with dimethylamine (25·0 g., 1·05 mol.) and n-butyl-lithium (240 ml. of a 2·200M-solution; 1 mol.) afforded a solution (450 ml.) of dimethylaminolithium. To this, tin(IV) chloride (30·5 g., 0·22 mol.) in benzene (100 ml.) was added and, after refluxing for 4 hr., the mixture, worked-up as in (i), gave *tetrakis(dimethylamino)stannane* (20·5 g., 60·2%), b. p. 51°/0·15 mm., n_D^{20} 1·4774, d_4^{20} 1·1687 (Found: C, 33·0; H, 7·6; N, 18·6; Sn, 40·0. $C_8H_{24}N_4Sn$ requires C, 32·6; H, 8·2; N, 19·0; Sn, 40·3%).

(iii) *Preparation of* N-*phenyltrimethylstannylamine.* A procedure analogous to that described in (i), with aniline (9·30 g., 1·0 mol.) and n-butyl-lithium (56 ml. of a 1·794M-solution; 1 mol.) afforded a solution (210 ml.) of anilinolithium. To this, trimethylchlorostannane (14·0 g., 0·70 mol.) in diethyl ether (50 ml.) was added and, after being refluxed for 2 hr., the mixture, worked up as in (i), gave N-*phenyltrimethylstannylamine* (15·0 g., 82·3%), b. p. 77°/0·05 mm., n_D^{20} 1·5421, d_4^{20} 1·4255 (Found: C, 42·7; H, 5·7; N, 5·3; Sn, 46·6%; *M*, 277. $C_9H_{15}NSn$ requires C, 42·2; H, 5·9; N, 5·5; Sn, 46·4%; *M*, 256).

(iv) *Preparation of* N-*methylhexamethyldistannazane.* Similarly, methylamine (3·50 g., 1·13 mol.) and n-butyl-lithium (56 ml. of a 1·790M-solution; 1 mol.) afforded a solution (160 ml.) of methylaminolithium which, upon addition of trimethylchlorostannane (18·5 g., 0·93 mol.) in ether (50 ml.), refluxing for 1 hr., and working up as in (i), afforded N-*methylhexamethyldistannazane* (11·9 g., 64·5%), b. p. 64°/3 mm., n_D^{20} 1·4901 (Found: C, 23·4; H, 5·7; N, 3·8%; *M*, 340. $C_7H_{21}NSn_2$ requires C, 23·6; H, 5·9; N, 3·9%; *M*, 356).

Preparation of Compounds by Transamination.—Tin–nitrogen compounds prepared by transamination methods are listed, together with the reaction conditions, in Table 3. Physical constants and analytical results are included in Table 2. Typical procedures are given below.

(i) *Preparation of* N-*phenyltrimethylstannylamine.* To diethylaminotrimethylstannane (1·873 g., 1·0 mol.), aniline (0·76 g., 1·0 mol.) was added with cooling. Distillation at atmospheric pressure gave diethylamine (0·60 g., 100%), b. p. 56° (authentic spectrum), then, under reduced pressure, N-phenyltrimethylstannylamine (1·83 g., 90%), b. p. 77°/0·05 mm., n_D^{20} 1·5421.

(ii) *Preparation of* N-*ethylhexamethyldistannazane.* To dimethylaminotrimethylstannane (6·05 g., 1·0 mol.) at −78°, ethylamine (2·01 g., excess of 0·5 mol.) at −78° was added. The mixture was allowed to warm to room temperature, all volatile materials being collected in a trap at −78°. The infrared spectrum of the volatile materials showed the presence of a mixture of ethylamine and dimethylamine. Distillation of the residual liquid crude distannazane (5·40 g., 100%) gave N-*ethylhexamethyldistannazane* (4·85 g., 90%), b. p. 93°/15 mm., n_D^{20} 1·4968, d_4^{20} 1·4805 (Found: C, 26·0; H, 6·1; N, 3·5. $C_8H_{23}NSn_2$ requires C, 25·9; H, 6·2; N, 3·8%).

(iii) *Preparation of* NN′N″-*triethylhexamethylcyclotristannazane.* To bis(dimethylamino)-dimethylstannane (3·53 g., 1 mol.) at −78°, ethylamine (1·60 g., excess of 0·33 mol.) at −78° was added. The mixture was allowed to warm to room temperature and volatiles were trapped at −78°. The infrared spectrum showed the presence of a mixture of ethylamine and dimethyl-almine in the condensate. Distillation of the residual liquid crude cyclotristannazane (2·84 g., 100%) gave NN′N″-*triethylhexamethylcyclotristannazane* (1·80 g., 63·5%), b. p. 104°/0·05 mm. (Found: C, 26·3; H, 5·9; N, 7·2%; *M*, 596. $C_{12}H_{33}N_3Sn_3$ requires C, 25·0; H, 5·7; N, 7·3%; *M*, 575).

(iv) *Preparation of tris(trimethylstannyl)amine.* Ammonia was passed at a steady rate through a solution of dimethylaminotrimethylstannane (5·10 g., 1 mol.) in light petroleum (b. p. 30—40°, 30 ml.) for 15 min.; volatile material was trapped at −78°. As most of the light petroleum was carried over, the trap was allowed to warm to room temperature and volatile

material was again collected at $-78°$. Infrared examination of this trap showed the presence of almost pure dimethylamine. Distillation of the residual liquid gave *tris(trimethylstannyl)-amine* (3·40 g., 82·5%), b. p. $70°/0·2$ mm., n_D^{20} 1·5331 (Found: C, 21·9; H, 5·4; N, 2·7; Sn, 70·0. $C_9H_{27}NSn_3$ requires C, 21·4; H, 5·4; N, 2·8; Sn, 70·4%).

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