

## AMINO DERIVATIVES OF METALS AND METALLOIDS

## III\*. METAL AMINES AS REAGENTS FOR SYNTHESIS OF ORGANOMETALLICS; ESPECIALLY THE REACTIONS OF AMINOSTANNANES WITH PROTIC SPECIES

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## INTRODUCTION

This series of papers relates to the chemistry of amino derivatives of metals and metalloids, particularly of aminoorganometallanes; for example the present paper is concerned very largely with aspects of the chemistry of (dimethylamino)trimethylstannane.

Compounds of 3-co-ordinate nitrogen which have been investigated in the most detail are of elements of the short periods of the Periodic Table.

The alkali metal salts of amines are well-known as reagents in organic chemistry<sup>1</sup> and in transmetallation (*cf.* ref. 2). Beryllium-nitrogen compounds have been reported<sup>3</sup>, and aminomagnesium halides behave like Grignard reagents<sup>4</sup>. Boron-nitrogen chemistry has received considerable attention<sup>5</sup>, especially the cyclic derivatives, such as borazines<sup>5,6</sup>. Amino-aluminium compounds are generally oligo- or poly-meric<sup>7</sup>, with the nitrogen in a 4-co-ordinate environment; exceptions are found with compounds which are sterically-hindered<sup>8</sup>. The nitrogen chemistry of the Group IVB elements is one of great contrasts. The chemistry of the carbon compounds is of course extensive<sup>1</sup>, and that of silicon is expanding rapidly<sup>9</sup>. Germanium-nitrogen compounds have not as yet received much attention<sup>10</sup>, and the simple amino-tin(IV) compounds date only from 1961<sup>11</sup>, although there has been a spate of publications since then (*cf.* ref. 2). Compounds containing  $>N-N<$  units are the hydrazines<sup>12</sup>. Amino-phosphorus(III) and phosphorus(V) compounds have been studied<sup>13</sup> in some detail, but the phosphonitrilic compounds are not strictly (they are imino derivatives) within the present terms of reference. Amino-arsenic derivatives have also been examined<sup>15</sup>. Hydroxylamine derivatives are well-known<sup>16</sup> as are sulphenyl<sup>15,17</sup>, sulphiny<sup>15</sup>, and sulphonyl<sup>19</sup> amides, as well as inorganic sulphur-nitrogen compounds<sup>20</sup> (some of these are imino compounds). The *N*-haloamines represent Group VIIB<sup>21</sup>. Only a few amino derivatives of transition metals have been prepared; publications relate to compounds of uranium(IV)<sup>22</sup>, titanium(IV)<sup>23,24</sup>, zirconium(IV)<sup>23</sup>, vanadium(IV)<sup>23</sup>, niobium(IV) and

\* For Part I, see ref. 2; for Part II, see ref. 29.

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-(V)<sup>26</sup>, and tantalum(V)<sup>26</sup>. To summarise, the elements which are at present known to form amino derivatives are shown in Table I. It will be patently obvious that this is an area of chemistry ripe for further development.

TABLE I  
ELEMENTS KNOWN TO FORM AMINO DERIVATIVES

Period	Group														
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VII B
1	H														H
2	Li	Be									B	C	N	O	F
3	Na	Mg								Al	Si	P	S		Cl
4	K										Ge	As			Br
5	Rb			Ti	V						Sn				I
6				Zr	Nb										
7			U		Ta										

Our interest in amino derivatives of metals and metalloids has in the main so far been related to their preparation and reactivity. We noted<sup>25</sup> in 1962 that aminostannanes, *e.g.* Me<sub>3</sub>Sn-NMe<sub>2</sub>, have a high affinity for many unsaturated substrates and predicted that this would be characteristic of amino derivatives of metals and metalloids, generally. This theme, of aminostannanes as 1,2-dipolarophiles, was a principal feature of Part II of this series<sup>29</sup>, aminometallation reactions were also then surveyed.

In a brief communication<sup>3</sup>, we compared the reactivity of the amino derivatives of the more electropositive elements (these would have a weak and highly polar metal-nitrogen bond; preliminary measurement<sup>31</sup> of the Sn-N thermochemical bond strength in Me<sub>3</sub>Sn-NMe<sub>2</sub> as ~ 40 kcal/mole provides confirmation) with Grignard reagents. This was supported, in part, by experiments on tin(IV) and iron(II) compounds, with regard to their reactions with protic species, AH; which, in the cases where A is a hydrocarbon residue, provided a novel synthesis of organometallic compounds. In this paper, we present these results in more detail.

As well as combining with polar species which are either (i) unsaturated or (ii) protic, it is to be anticipated that amino derivatives of the more electropositive elements will react with (iii) saturated substrates such as halides of the elements, and (iv) donor molecules. With reactions of class (iv), molecular addition compounds will be expected, by virtue of the fact that the metal derivative is likely to have available unoccupied orbitals of low energy. For example, (diethylamino)trimethylstannane might have been anticipated to form a 5-co-ordinate complex with pyridine. In fact, no reaction, nor between tetrakis(dimethylamino)stannane and pyridine, was observed.

## DISCUSSION

Most of our experiments have been with (dialkylamino)trialkylstannanes, R<sub>3</sub>Sn-NR'<sub>2</sub>, and protic reagents and these results together with others from the literature, are summarised in Table 2.

TABLE 2

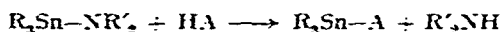
REACTIONS OF AMINOSTANNANES AND TRISTANNYLAMINES WITH PROTIC REAGENTS

Pr = *n*-propyl; Bu = *n*-butyl.

No.	Reactants	Products	Reference
1	$\text{Me}_3\text{Sn-NMe}_2 + 2\text{HCl}$ $\text{R}_3\text{Sn-NEt}_2 + 2\text{HCl}$ (R = Et, Pr, Bu)	$\text{Me}_3\text{Sn-Cl} + \text{Me}_2\text{NH}\cdot\text{HCl}$ $\text{R}_3\text{Sn-Cl} + \text{Et}_2\text{NH}\cdot\text{HCl}$	This work 32
2	$\text{Me}_3\text{Sn-NMe}_2 + \text{H}_2\text{O}$ $\text{Ph}_3\text{Sn-NMe}_2 + \text{H}_2\text{O}$ $(\text{Me}_2\text{Sn})_2\text{N} + 3\text{H}_2\text{O}$	$\text{Me}_3\text{Sn-OH} + \text{Me}_2\text{NH}$ $\text{Ph}_3\text{Sn-OH} + \text{Me}_2\text{NH}$ $3\text{Me}_3\text{Sn-OH} + \text{NH}_3$	This work This work 33
3	$2\text{Et}_3\text{Sn-NMe}_2 + \text{H}_2\text{O} + \text{CO}_2$ $2\text{R}_3\text{Sn-NEt}_2 + \text{H}_2\text{O} + \text{CO}_2$ (R = Et, Pr, Bu) $2(\text{R}_3\text{Sn})_2\text{N} + 3\text{H}_2\text{O} + 3\text{CO}_2$ (R = Et, Pr) $2\text{Et}_3\text{Sn-N}(\text{PhCH}_2)\text{-C}_6\text{H}_4\text{-CH}_3\text{-}p + \text{H}_2\text{O} + \text{CO}_2$	$(\text{Et}_3\text{Sn})_2\text{CO}_3 + 2\text{Me}_2\text{NH}$ $(\text{R}_3\text{Sn})_2\text{CO}_3 + 2\text{Et}_2\text{NH}$ $3(\text{R}_3\text{Sn})_2\text{CO}_3 + 2\text{NH}_3$ $(\text{Et}_3\text{Sn})_2\text{CO}_3 + p\text{-CH}_3\text{-C}_6\text{H}_4\text{-NHCH}_2\text{Ph}$	This work 32 33 34
4	$\text{Et}_3\text{Sn-NMe}_2 + \text{MeOH}$ $\text{Bu}_3\text{Sn-NMe}_2 + \text{MeOH}$ $\text{Ph}_3\text{Sn-NMe}_2 + \text{MeOH}$ $\text{Me}_3\text{Sn-NEt}_2 + \text{MeOH}$	$\text{Et}_3\text{Sn-OMe} + \text{Me}_2\text{NH}$ $\text{Bu}_3\text{Sn-OMe} + \text{Me}_2\text{NH}$ $\text{Ph}_3\text{Sn-OMe} + \text{Me}_2\text{NH}$ $\text{Me}_3\text{Sn-OMe} + \text{Et}_2\text{NH}$	This work This work 35 36
5	$\text{R}_3\text{Sn-NR}'_2 + \text{R}''_2\text{NH}$ R = Me and (i) R' = Me, R'' = Et, or (ii) R' = Et and R'' = Bu <sub>2</sub> or (CH <sub>2</sub> ) <sub>5</sub>	$\text{R}_2\text{Sn-NHR}'' + \text{R}'_2\text{NH}$	Part I (2)
6	$\text{R}_3\text{Sn-NR}'_2 + \text{R}''\text{NH}_2$ R = Me, R' = Et, and R'' = Ph; or R = Bu, R' = Me, and R'' = <i>tert</i> -Bu	$(\text{Me}_3\text{Sn})_2\text{NR}' + 2\text{R}_2\text{NH}$	Part I (2)
7	$2\text{Me}_3\text{Sn-NMe}_2 + \text{RNH}_2$ R = Me or Et	$(\text{Me}_2\text{SnNR})_3 + 6\text{Me}_2\text{NH}$	Part I (2)
8	$3\text{Me}_2\text{Sn}(\text{NMe}_2)_2 + 3\text{RNH}_2$ R = Me or Et	$(\text{Me}_3\text{Sn})_3\text{N} + 3\text{Me}_2\text{NH}$	Part I (2)
9	$3\text{Me}_2\text{Sn-NMe}_2 + \text{NH}_3$	$\text{R}_3\text{Sn-PPH}_2 + \text{Me}_2\text{NH}$	This work
10	$\text{R}_3\text{Sn-NMe}_2 + \text{Ph}_2\text{PH}$ R = Me or Et	$\text{R}_3\text{Sn-AsPh}_2 + \text{Me}_2\text{NH}$	This work
11	$\text{R}_3\text{Sn-NMe}_2 + \text{Ph}_2\text{AsH}$	$\text{Me}_3\text{Sn-C}\equiv\text{CR} + \text{Me}_2\text{NH}$	This work
12	$\text{Me}_3\text{Sn-NMe}_2 + \text{RC}\equiv\text{CH}$ R = Pr or Bu	$\text{R}_3\text{Sn-C}\equiv\text{CPh} + \text{Me}_2\text{NH}$	This work
13	$\text{R}_3\text{Sn-NMe}_2 + \text{PhC}\equiv\text{CH}$ R = Me, Et, or Ph	$\text{Bu}_3\text{Sn-C}\equiv\text{C-SnBu}_2 + 2\text{Me}_2\text{NH}$	This work
14	$2\text{Bu}_3\text{Sn-NMe}_2 + \text{HC}\equiv\text{CH}$	$[\text{Bu}_3\text{SnC}\equiv\text{C}]_n + 2n\text{Me}_2\text{NH}$	This work
15	$n\text{Bu}_2\text{Sn}(\text{NMe}_2)_2 + n\text{HC}\equiv\text{CH}$	$\text{R}_3\text{Sn-} \begin{array}{c} \diagup \\ \square \\ \diagdown \end{array} + \text{Me}_2\text{NH}$	This work
16	$\text{R}_3\text{Sn-NMe}_2 + \begin{array}{c} \diagup \\ \square \\ \diagdown \end{array}$ R = Me, Bu, or Ph	$\text{Me}_3\text{Sn-} \begin{array}{c} \diagup \\ \square \\ \diagdown \end{array} + \text{Me}_2\text{NH}$	This work
17	$\text{Ph}_3\text{Sn-NMe}_2 + \begin{array}{c} \diagup \\ \square \\ \diagdown \end{array}$	$\text{R}_3\text{Sn-CR}''\text{R}'''\text{-CN}(\text{?}) + \text{R}'_2\text{NH}$	This work
18*	$\text{R}_3\text{Sn-NR}'_2 + \text{R}''\text{R}'''\text{CH-CN}$	$\text{R}_3\text{Sn-CH}_2\text{NO}_2(\text{?}) + \text{R}'_2\text{NH}$	This work
19	$\text{R}_3\text{Sn-NR}'_2 + \text{CH}_3\text{NO}_2$	$(\text{R}_3\text{Sn})_2\text{O} + 2\text{R}'_2\text{NH} + (\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	This work
20	$2\text{R}_3\text{Sn-NMe}_2 + 2(\text{CH}_3)_2\text{CO}$ R = Me or Bu	$\text{R}'_2\text{N-COCH}_3 + (\text{R}_3\text{Sn})_2\text{O} + (\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	This work
21	$\text{R}_3\text{Sn-NR}'_2 + \text{CH}_2=\text{CMeOCOCH}_3$ R = Me, R' = Et; or R = Et, R' = Me	No reaction	This work
22	$\text{Me}_3\text{Sn-NMe}_2 + \text{Et}_3\text{SiH}$		

\* CH<sub>3</sub>CN and Et<sub>3</sub>Sn-NEt<sub>2</sub> or Bu<sub>3</sub>Sn-NMe<sub>2</sub>; PhCH<sub>2</sub>CN and Me<sub>3</sub>Sn-NMe<sub>2</sub>; Ph<sub>2</sub>CHCN and Me<sub>3</sub>Sn-NMe<sub>2</sub> or Et<sub>3</sub>Sn-NEt<sub>2</sub>.

It will be clear that these reactions, apart from the complications encountered in types 18-21, conform to a pattern expressed by the following equation:



Of these, types 1-9 are not especially surprising, since they have counterparts in other areas of amino-metal or -metalloid chemistry (*e.g.*, see refs. 9 and 37 for Si-N compounds); the others are quite novel, but are likely to prove of general significance for amino derivatives of the more electropositive elements. Furthermore, it is interesting that they proceed essentially quantitatively under mild conditions. This is likely to have synthetic value, partly because the metal-bearing product is the sole non-volatile component of reaction. This great facility for reactivity with protic species is undoubtedly due to the very weak metal-nitrogen bond. That the mechanism involves proton abstraction rather than hydride ion or hydrogen atom loss is further demonstrated by the non-reactivity of the Si-H bond (see, No. 22).

#### Reactions 2-9

It was noticed when preparing aminostannanes<sup>2</sup>, that the exclusion of atmospheric moisture was necessary to avoid their decomposition. When (dialkylamino)-trialkylstannanes, where the alkyl group on tin is ethyl or larger, are exposed to the atmosphere, hydrolysis is accompanied by condensation to the bis(trialkylstannyl) oxide, which in turn absorbs carbon dioxide to afford the carbonate. In the case of trimethylstannyl derivatives reaction stops at the hydroxide stage, presumably due to its dimeric nature<sup>28</sup>. On the other hand, organotin-nitrogen compounds derived from substituted imidazole and triazole residues are sufficiently stable to allow their preparation to be effected from organotin oxides and the free base, by azeotropic removal of water<sup>29</sup>; this stability has been attributed to their polymeric nature with tin in a 5-co-ordinate environment.

The ready alcoholysis of aminostannanes has been utilised for the preparation by this route of methoxytrimethylstannane<sup>36</sup>, a compound which it has been difficult to obtain pure by more conventional syntheses. Transamination reactions (see 5-9 in Table 2) have been discussed in Part I<sup>2</sup>. In summary, the displacement order of aminostannanes derived from secondary amines is  $Bu_2N > Et_2N > Me_2N$ ; whilst the order between ammonia and amines is  $H_2N > RHN > R_2N$ .

#### Reactions 10 and 11

4-Co-ordinate tin-phosphorus<sup>40</sup> and tin-arsenic<sup>41</sup> compounds have only recently been prepared. In view of the difficulties encountered with most of the earlier methods, reactions 10 and 11 offer simple and attractive routes to these derivatives. Of theoretical interest are the displacement orders: (i) phosphine > amine, and (ii) arsine > amine. Evidently tin(IV) is a class "b" acceptor<sup>42</sup>, with Sn-P and Sn-As stronger than Sn-N bonds; this is confirmed by chemical observations on Sn-O and Sn-S compounds<sup>29</sup> and by preliminary thermochemical data<sup>31</sup>. On the other hand, silicon appears to be a class "a" acceptor, since we found that the amino group of amino-silanes was not displaced upon treatment with diphenylphosphine. These observations are consistent with there being significant  $d_{\pi}-p_{\pi}$  interaction to stabilise the Si-N, but not the Sn-N, bond.

*Reactions 12-17 and others involving acidic hydrocarbons*

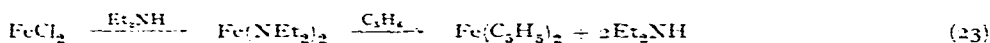
Organometallic compounds are generally obtained by transmetallation (*e.g.*,  $\text{SnCl}_4/\text{RLi}$ ) or hydrometallation (*e.g.*,  $\text{Et}_3\text{SnH}/\text{C}_2\text{H}_4$ ) methods. Reactions 12-17 provide another general procedure, applicable when the organic residue is acetylenic or is otherwise a stable anion. In these cases, the parent hydrocarbon is, of course, acidic and proton abstraction is an energetically-facile process. Among other hydrocarbons, which proved unreactive, were toluene, triphenylmethane, and  $\alpha$ -picoline.

An independent report of similar reactions of some alkoxy-stannanes with acetylenes has recently been published<sup>43</sup>.

*A new synthesis of ferrocene*

Among the available syntheses for ferrocene is the reaction of either iron(II) or iron(III) chloride with cyclopentadiene in the presence of an amine<sup>44</sup>. This procedure followed the prediction that the slightly acidic hydrogen of cyclopentadiene might be replaced by a metal atom from a metal halide, if proton abstraction was encouraged by the basic function of the amine. A recent discussion of the method<sup>45</sup> correlated the yield of ferrocene with the  $\text{p}K_{\text{a}}$  of the amine. Thus, the mechanism of ferrocene formation was believed to involve  $[\text{BaseH}]^+ [\text{C}_5\text{H}_5]^-$ .

It occurred to us that an alternative, and possibly more plausible, reaction sequence was feasible. In part, this was based on the observation that the earlier study<sup>45</sup> showed a correlation of ferrocene yield not only with amine basicity but, to us much more strikingly, with the structure of the amine; far and away the best yields were obtained with secondary amines. Furthermore, our studies, reported above, indicated that amino derivatives of iron were likely to be reactive derivatives. Thus, we proposed to investigate system 23 [shown for iron(II) chloride].



The first of these two steps has not yet been investigated; however, the second has been established. Iron(III) chloride in ether was treated with diethylaminolithium. Lithium chloride was filtered off and the diethylaminoiron solution, without being characterised as to oxidation state, on treatment with an excess (to allow for possible reduction,  $\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{II}}$ ) of cyclopentadiene, afforded ferrocene in high yield.

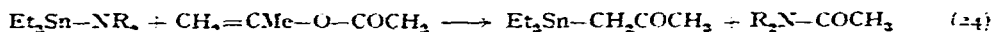
In this synthesis, ferrocene is the only relatively non-volatile product and this may be an advantageous feature, especially for more complex derivatives.

*Reactions 18-22*

Benzonitrile has been shown to react with (dimethylamino)trimethylstannane as a 1,2-dipolarophile, affording an amidinotrimethylstannane<sup>29</sup>. By contrast, nitriles having an  $\alpha$ -hydrogen atom appear to behave as protic species (see No. 18). Thus, from reactions with (dialkylamino)trialkylstannanes, the dialkylamine was isolated in almost quantitative yield, and the less-volatile residual liquids showed (infrared spectral evidence) the presence of  $-\text{CN}$  groups. Distillation invariably afforded a mixture of nitrile-containing products, suggesting thermal redistribution. This behaviour is similar to an observation in silicon chemistry; thus, acetonitrile, sodium, and chlorotrimethylsilane gave  $\text{Me}_4\text{Si}$  (6%),  $\text{Me}_3\text{Si}-\text{NC}$  (27%),  $\text{Me}_3\text{Si}-\text{CH}_2\text{CN}$  (2%),  $(\text{Me}_3\text{Si})_2\text{CHCN}$  (7%), and  $\text{Me}_3\text{Si}-\text{CH}=\text{C}=\text{CH}-\text{SiMe}_3$  (25%)<sup>46</sup>.

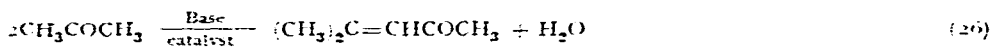
The reaction with nitromethane (No. 19) was also not fully elucidated, but the amine was again obtained in high yield.

Interaction with isopropenyl acetate (No. 21) was also complex. It is known that methoxytrimethylstannane reacts with isopropenyl acetate to give ethyl acetate and acetyltriethylstannane,  $\text{Et}_3\text{Sn}-\text{CH}_2\text{COCH}_3$ , and that the latter is readily hydrolysed to produce acetone and bis(triethylstannyl) oxide<sup>17</sup>. Analogous reaction schemes would be 24 and 25.

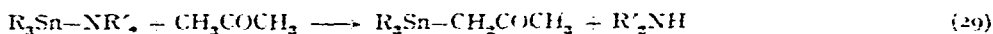


With neither pair of reagents were the anticipated organotin compounds isolated. On treating various (dialkylamino)trialkylstannanes with excess of isopropenyl acetate, the corresponding *N,N*-dialkylacetamide was, however, obtained. Apart from unidentified residues, the bulk of the trialkylstannyl group was traced to the acetate.

From the reaction of acetyltrialkylstannanes with secondary amines, acetone was invariably obtained, but also mesityl oxide, bis(trialkylstannyl) oxides, and unidentified residues. The formation of mesityl oxide indicates that condensation of acetone had occurred during the course of the reaction; the water eliminated would have been available for hydrolysis of the aminostannane to afford the bis(trialkylstannyl) oxide. Thus, equations contributing to the overall situation may well involve 25-28.



Reaction 20 can be accommodated within the same pattern. The aminostannane is either a catalyst as in scheme 26, or else scheme 29 must be invoked, whence the liberated amine is allowed to behave as in 26.



## EXPERIMENTAL

### General procedures

The preparation of starting materials, and the analytical and manipulative techniques were as described in Parts I and II<sup>2,29</sup>.

All products were identified by their infrared spectra, as well as by the methods specifically mentioned below. Those experiments which in the discussion have been referred to as leading to lack of reaction, are not described; however, in each case the mass balance and analyses were satisfactory.

*Reaction of (dimethylamino)trimethylstannane with hydrogen chloride*

Diethyl ether (20 ml), saturated with hydrogen chloride, was added dropwise to (dimethylamino)trimethylstannane (2.21 g, 1 mol.), also in diethyl ether (10 ml). The precipitated dimethylamine hydrochloride (0.85 g, 98.5 %) (Found: Cl, 43.4. C<sub>2</sub>H<sub>5</sub>ClN calcd.: Cl, 43.6 %) was filtered off. The solvent was removed from the filtrate at 20°/15 mm, and distillation of the residual liquid gave chlorotrimethylstannane (1.80 g, 89.7 %), b.p. 152°/760 mm, which on cooling crystallised, m.p. 37°. (Ref. 48 gives b.p. 152–154°/760 mm, m.p. 37–38°.)

*Reaction of (dimethylamino)triorganostannanes with water*

Water (0.14 g, 1.06 mol.) in diethyl ether (10 ml) was added dropwise to (dimethylamino)trimethylstannane (1.52 g, 1 mol.) in diethyl ether at 20°. Dimethylamine was evolved when the mixture was refluxed. After the solvent had been removed at 20°/15 mm, the white solid was dried at 20°/0.1 mm and was identified as hydroxytrimethylstannane (1.28 g, 96.6 %), sublimes 118°. (Ref. 48 cites m.p. 118°.)

Similarly, (dimethylamino)triphenylstannane (1.82 g, 1 mol.), on hydrolysis, gave hydroxytriphenylstannane (1.67 g, 98.5 %), m.p. 119°. (Ref. 48 gives m.p. 119–120°.)

*Reaction of (dimethylamino)triethylstannane with water and carbon dioxide*

Air was bubbled through (dimethylamino)triethylstannane (1.20 g, 1 mol.) until a solid was formed, and this was allowed to remain exposed to the atmosphere (2 h). Dimethylamine was evolved, leaving bis(triethylstannyli) carbonate (1.08 g, 95.4 %), m.p. 120°. (Ref. 48 gives m.p. 120°.)

*Reaction of (dimethylamino)trialkylstannane with methanol*

Methanol (0.30 g, 1.14 mol.) in diethyl ether (10 ml) was added dropwise to (dimethylamino)triethylstannane (2.05 g, 1 mol.) at 20°. Dimethylamine was evolved, and after the solvent had been removed at 20°/15 mm, distillation of the residual liquid gave methoxytriethylstannane (1.90 g, 97.5 %), b.p. 70°/12 mm,  $n_D^{20}$  1.4750. (Ref. 48 gives b.p. 73–74°/13 mm,  $n_D^{20}$  1.4760.)

Similarly, (dimethylamino)tri-*n*-butylstannane (2.1 g, 1 mol.), on treatment with methanol (0.25 g, 1.24 mol.), gave methoxytri-*n*-butylstannane (1.95 g, 96.6 %), b.p. 99°/0.8 mm. (Ref. 48 gives b.p. 101–102°/2 mm.)

*Reaction of (dialkylamino)trialkylstannane with diphenylphosphine*

Diphenylphosphine (1.94 g, 1 mol.) was added to (dimethylamino)trimethylstannane (2.16 g, 1 mol.) at 20°. Dimethylamine was immediately evolved, and the residual liquid (3.62 g, 100 %) was distilled under reduced pressure to give (diphenylphosphino)trimethylstannane (2.90 g, 80.0 %), b.p. 150°/0.8 mm. (Found: C, 51.4; H, 5.15. C<sub>15</sub>H<sub>19</sub>PSn calcd.: C, 51.61; H, 5.47 %.)

Similarly, diphenylphosphine (2.88 g, 1 mol.) was added to (diethylamino)triethylstannane (4.30 g, 1 mol.) at –78°. On allowing the mixture to attain room temperature, then warming slowly to 60°, diethylamine (1.05 g, 92.8 %) was evolved. Distillation of the residual liquid (6.05 g, 100 %) gave (diphenylphosphino)triethylstannane (4.24 g, 70.2 %) b.p. 170°/0.7 mm. (Ref. 40b gives b.p. 170°/0.7 mm.)

*Reaction of (dimethylamino)trimethylstannane with diphenylarsine*

Diphenylarsine (1.02 g, 1 mol.) was added to (dimethylamino)trimethylstannane (1.41 g, 1 mol.) at 20°. Dimethylamine was immediately evolved and distillation of the residual liquid afforded (diphenylarsino)trimethylstannane (1.20 g, 77%), b.p. 136°/0.05 mm.  $n_D^{20}$  1.6438.  $d_4^{20}$  1.4682 (Found: C, 45.0; H, 4.73. C<sub>15</sub>H<sub>19</sub>AsSn calcd.: C, 45.8; H, 4.88%).

*Reactions 18-22*

As was mentioned in the discussion of these reactions, this part of the investigation is incomplete. Not all the products have been characterised nor have some experiments given reproducible results. However, the following examples are included as evidence to support the equations which were postulated, and to indicate the nature of such experiments.

(i) *Reaction of (dialkylamino)trialkylstannane with acetonitrile.* Acetonitrile (2.07 g, 1 mol.) was added to (diethylamino)triethylstannane (14.04 g, 1 mol.) at 20°. After refluxing (½ h), the mixture was distilled giving diethylamine (2.78 g, 75.3%), b.p. 56°/760 mm. Distillation of the residual liquid gave fractions: (a) b.p. 84-90°/0.2 mm (1.5 g); (b) b.p. 95-140°/0.2 mm (2.0 g); (c) b.p. 156°/0.2 mm (3.0 g); (d) b.p. 160-180°/0.1 mm (1.5 g); (e) residue (4.8 g); and (f) a condensate at -78° (0.5 g), which was identified as a mixture of diethylamine and acetonitrile. Further purification of fractions (a)-(d) was attempted by distillation, but this led to further disproportionation and decomposition of the higher boiling fractions. Infrared spectra recorded on fractions (a)-(e) all showed absorption in the region 2200 cm<sup>-1</sup>, indicating the presence of -C≡N.

Similarly, acetonitrile (1.83 g, 2.32 mol.) was refluxed (1 h) with (dimethylamino)tri-*n*-butylstannane (6.36 g, 1 mol.), Excess acetonitrile and dimethylamine were removed at 20°/15 mm, and distillation of the residual liquid was attempted. After a short forerun, b.p. 70-100°/0.1 mm (0.8 g), the distillation was stopped at 180° when the residue began to decompose. Infrared spectra recorded on both distillate and residue showed absorption in the 2200 cm<sup>-1</sup> region due to -C≡N.

(ii) *Reaction of dimethylamino)trimethylstannane with phenylacetonitrile.* Phenylacetonitrile (1.56 g, 1 mol.) was added to (dimethylamino)trimethylstannane (2.77 g, 1 mol.) at 20°. Dimethylamine (0.50 g, 83.4%) was evolved. Distillation of the residual liquid gave a continuous fraction, b.p. 110-144°/0.4 mm (3.0 g), and a solid residue (0.65 g). Fractional distillation of the volatile fraction gave (a) phenylacetonitrile (0.55 g), b.p. 72°/0.6 mm; (b) b.p. 100-130°/0.6 mm (1.0 g); (c) b.p. 146°/0.6 mm (0.8 g); and (d) a residue (0.6 g).

(iii) *Reaction of (dialkylamino)trialkylstannane with diphenylacetonitrile.* Diphenylacetonitrile (2.40 g, 1 mol.) was added to (dimethylamino)trimethylstannane (2.59 g, 1 mol.) at 20°. On warming, dimethylamine (0.50 g, 89%) was evolved. The infrared spectrum of the residual liquid showed absorption at 2200 cm<sup>-1</sup>, indicating -C≡N, and also at 2040 cm<sup>-1</sup> suggestive of -N=C=N-. Attempted distillation at 0.1 mm led to decomposition.

Similarly, diphenylacetonitrile (4.58 g, 1 mol.) was added to (diethylamino)triethylstannane (6.59 g, 1 mol.) at 20°. Distillation of the mixture gave diethylamine (1.56 g, 90%), b.p. 55°/760 mm. The infrared spectrum of the residual liquid showed a doublet at 2200 cm<sup>-1</sup> indicating -C≡N. Distillation gave fractions: (a) b.p. 86°/0.2



mm (1.2 g); (b) b.p. 86–130°/0.2 mm (3.8 g); (c) b.p. 140°/0.3 mm (4.0 g); and (d) a residue (0.6 g).

(iv) *Reaction of (dimethylamino)trialkylstannane with acetone.* Acetone (2.65 g, 1.77 mol.) was added dropwise to (dimethylamino)tri-*n*-butylstannane (8.60 g, 1 mol.) at 20°. Dimethylamine (1.05 g, 90.6%), was evolved. The residual mixture was refluxed (1 h) at 80° and then distilled at 0.1 mm. The volatile products (2.1 g), collected at –78°, were then distilled at atmospheric pressure to give acetone (1.04 g), b.p. 57°/760 mm, and mesityl oxide (1.06 g, 84%), b.p. 129°/760 mm. The residual organotin compound (7.4 g, 96.5%) was identified as bis(tri-*n*-butylstannyl) oxide.

Similarly, acetone (0.87 g, 1 mol.) was added to (dimethylamino)trimethylstannane (3.12 g, 1 mol.) at 0°. The mixture was set aside overnight, whereafter the volatile products were distilled at 20°/15 mm into a trap at –78°. This fraction was then distilled at atmospheric pressure to give dimethylamine (0.6 g, 89.1%), acetone (0.1 g), and mesityl oxide (0.5 g, 68%), b.p. 129°/760 mm. Distillation of the residual liquid gave bis(trimethylstannyl) oxide (2.1 g, 82%), b.p. 75°/15 mm. (Ref. 48 gives b.p. 86°/24 mm.)

(v) *Reaction of (dialkylamino)trialkylstannane with isopropenyl acetate.* Isopropenyl acetate (3.96 g, 2 mol.) was added to (diethylamino)trimethylstannane (4.67 g, 1 mol.) at 20°. After refluxing (5 min), a white solid precipitated out on cooling. Light petroleum (b.p. 40–60°, 10 ml) was added, the solid filtered off, dried at 20°/0.1 mm and identified as acetoxytrimethylstannane (1.66 g). The solvent was removed from the filtrate at 20°/15 mm, and the residual liquid gave *N,N*-diethylacetamide (2.19 g, 95.4%), b.p. 54°/0.4 mm, and an unidentified fraction, b.p. 92–102°/0.4 mm (1.50 g). Further heating of the residue gave a white solid which sublimed above 130°/0.2 mm, and was identified as acetoxytrimethylstannane (0.5 g, total yield 48.8%).

Similarly, isopropenyl acetate (2.35 g, 1.02 mol.) was refluxed (½ h) with (dimethylamino)triethylstannane (5.76 g, 1 mol.). Distillation of the mixture gave *N,N*-dimethylacetamide (1.2 g, 56%), b.p. 64°/15 mm. The residual mixture was then cooled and light petroleum (b.p. 30–40°, 10 ml) added. A white solid was filtered off, dried at 20°/0.1 mm, and identified as acetoxytriethylstannane (3.40 g, 55.6%), m.p. 130°. The solvent was removed from the filtrate at 20°/15 mm, and the residual liquid was distilled at 0.5 mm giving an unidentified fraction, b.p. 74°/0.5 mm (1.30 g), and a tarry residue (3.3 g).

(vi) *Reaction of (triethylstannyl)acetone with dimethylamine.* Dimethylamine (2.2 g, 1 mol.) at –78° was added to (triethylstannyl)acetone (11.75 g, 1 mol.) also at –78°. The mixture was allowed to reflux (½ h) at 20°, and was then distilled to give dimethylamine (1.5 g, 74%), acetone (1.08 g, 41.7%), b.p. 57°/760 mm, and mesityl oxide (0.65 g, 35.8%), b.p. 129°/760 mm. The residual organotin compound (9.40 g, 98.4%) was identified as bis(triethylstannyl) oxide.

#### *Reaction of (dimethylamino)trimethylstannane with phenylacetylene*

Phenylacetylene (0.60 g, 1 mol.) was added to (dimethylamino)trimethylstannane (1.19 g, 1 mol.) at 20°. An exothermic reaction resulted, with evolution of dimethylamine. Distillation of the residual liquid gave (phenylethynyl)trimethylstannane (1.40 g, 92%), b.p. 68°/0.3 mm,  $n_D^{20}$  1.5695. (Found: C, 50.1; H, 5.1.  $C_{11}H_{14}Sn$  calcd.: C, 49.86; H, 5.33%.)

*Reaction of (dimethylamino)trimethylstannane with alkylacetylenes*

(i) *n*-Propylacetylene (1.58 g, 1 mol.) was added to (dimethylamino)trimethylstannane (5.42 g, 1 mol.) at 20°. The mixture was refluxed (4 h), during which time dimethylamine was steadily evolved. Distillation of the residual liquid at atmospheric pressure gave pentynyltrimethylstannane (6.0 g, 86%), b.p. 172°/760 mm,  $n_D^{20}$  1.4716. (Found: C, 40.5; H, 6.6.  $C_8H_{16}Sn$  calcd.: C, 41.6; H, 6.96%.)

(ii) Similarly, *n*-butylacetylene (1.32 g, 1 mol.) was refluxed (2 h) with (dimethylamino)trimethylstannane (3.34 g, 1 mol.), and dimethylamine was evolved. Distillation of the residual liquid gave hexynyltrimethylstannane (3.30 g, 90.2%), b.p. 82°/12 mm,  $n_D^{20}$  1.4714. Satisfactory analysis was not obtained.

The lower boiling tin-acetylene derivatives gave low carbon and hydrogen analysis. This could be due to the fact that the combustions were carried out using air instead of oxygen (as a precaution against the possible explosive nature of these compounds); this might have caused incomplete combustion.

*Reaction of (dimethylamino)tri-n-butylstannane with acetylene*

A slow stream of acetylene was bubbled through a solution of (dimethylamino)tri-*n*-butylstannane (13.99 g) in light petroleum (b.p. 30–40°, 50 ml) for 5 h. The volatile products were collected during this period, from which dimethylamine (1.60 g, 87%) was recovered. The solvent was removed from the mixture at 20°/1 mm, and the remaining colourless liquid was identified as bis(tri-*n*-butylstannyl)acetylene (12.00 g, 95%),  $n_D^{20}$  1.4861. (Found: C, 51.7; H, 8.8.  $C_{26}H_{54}Sn_2$  calcd.: C, 51.7; H, 9.01%.) The boiling point was not determined, as a precaution against a possible explosion at high temperature.

*Reaction of bis(dimethylamino)di-n-butylstannane with acetylene*

A slow stream of acetylene was bubbled through a solution of bis(dimethylamino)di-*n*-butylstannane (16.2 g) in light petroleum (b.p. 30–40°, 50 ml) for 1½ h, after which time the contents of the flask solidified. From the volatile products collected during this period, dimethylamine was isolated. The solid was filtered, washed with portions of light petroleum, and dried at 20°/0.1 mm to give a white solid material (9.0 g). The solvent from the combined filtrate and washings was removed at 20°/15 mm, leaving a colourless liquid (4.50 g) which was identified as unreacted bis(dimethylamino)di-*n*-butylstannane. The di-*n*-butyltinacetylene polymer (9.0 g, 94%) had softening point at 128°. (Found: C, 46.3; H, 7.2.  $(C_{10}H_{18}Sn)_n$  calcd.: C, 46.7; H, 7.05%.)

*Reaction of (dimethylamino)triethylstannane with phenylacetylene*

Phenylacetylene (0.84 g, 1 mol.) was added to (dimethylamino)triethylstannane (2.04 g, 1 mol.) at 20°. Dimethylamine was immediately evolved, and the residual liquid was distilled to give (phenylethynyl)triethylstannane (2.31 g, 92.3%), b.p. 88°/0.1 mm,  $n_D^{20}$  1.5525. (Ref. 43 gives b.p. 120–122°/2 mm,  $n_D^{20}$  1.5548.)

*Reaction of (dimethylamino)triphenylstannane with phenylacetylene*

Phenylacetylene (1.08 g, 1 mol.) was added to solid (dimethylamino)triphenylstannane (4.18 g, 1 mol.) at 20°. Dimethylamine was immediately evolved, and the residual liquid crystallised from ethanol. This product was filtered, dried at 20°/0.1

mm, and identified as (phenylethynyl)triphenylstannane (3.60 g, 75.2%), m.p. 62°. (Ref. 49 gives m.p. 62°.)

*Reaction of (dimethylamino)trimethylstannane with cyclopentadiene*

Cyclopentadiene monomer (1.78 g, 1 mol.) was added to (dimethylamino)trimethylstannane (5.61 g, 1 mol.) at 20°. The mixture was refluxed (1 h), during which time dimethylamine (1.1 g, 90%) was evolved. Distillation of the residual liquid gave a forerun of an unidentified liquid (0.5 g), b.p. 20–30°/1 mm, followed by a pale yellow liquid which went brown on standing, and was identified as cyclopentadienyltrimethylstannane (3.1 g, 50.2%), b.p. 56–60°/1 mm. (Found: C, 42.3; H, 5.9. C<sub>8</sub>H<sub>14</sub>Sn calcd.: C, 42.0; H, 6.16%.) (Ref. 50 gives b.p. 85°/10 mm.)

*Reaction of (dimethylamino)tri-*n*-butylstannane with cyclopentadiene*

Cyclopentadiene monomer (2.64 g, 1 mol.) was added to (dimethylamino)tri-*n*-butylstannane (13.34 g, 1 mol.) at 20°. Dimethylamine (1.70 g, 94.5%) was evolved and the residual liquid (14.0 g, 98.5%) was identified as cyclopentadienyltri-*n*-butylstannane, b.p. 134°/0.8 mm,  $n_D^{20}$  1.5047. (Ref. 50 gives b.p. 90°/0.001 mm.)

*Reaction of (dimethylamino)triphenylstannane with cyclopentadiene*

Cyclopentadiene monomer (3.5 g, excess of 1 mol.) was added to a solution of (dimethylamino)triphenylstannane (17.3 g, 1 mol.) in light petroleum (b.p. 80–100°, 150 ml). Dimethylamine was evolved while the mixture was refluxing (1 h). The solution was filtered hot, then cooled, and the product was allowed to crystallise out. The precipitate was filtered, dried at 20°/0.1 mm, and identified as cyclopentadienyltriphenylstannane (13.0 g, 71.3%), m.p. 129°. (Ref. 51 gives m.p. 130–131°.)

*Reaction of (dimethylamino)triphenylstannane with indene*

Indene (2.60 g, 1 mol.) was added to (dimethylamino)triphenylstannane (8.81 g, 1 mol.) in light petroleum (b.p. 60–80°, 50 ml). Dimethylamine was evolved during refluxing (½ h), and the solvent was removed at 50°/15 mm. The residual crystalline solid was recrystallised from the same solvent to give (1-indenyl)triphenylstannane (7.70 g, 74%), m.p. 129°. (Ref. 51 gives m.p. 129–130°.)

*Synthesis of ferrocene*

Diethylamine (7.3 g, 1 mol.) in diethyl ether (25 ml) was added to butyllithium (86 ml of a 1.16 *M* solution, 1 mol.) in the same solvent (100 ml) at 0°, at such a rate that *n*-butane was only slowly evolved. The solution was refluxed (½ h) and then allowed to attain room temperature, whereafter iron(III) chloride (5.40 g, 0.33 mol.) in diethyl ether (100 ml) was added during ½ h.

The mixture was set aside (3 h), the precipitated lithium chloride (4.20 g, 99%) (Found: Cl, 83.0. LiCl calcd.: Cl, 83.6%) was filtered off, and cyclopentadiene monomer (7.60 g, 1.15 mol.) was added to the filtrate.

After refluxing for 1 h, the solvents were removed at 20°/15 mm. The residual solid was extracted with light petroleum (4 × 50 ml, of b.p. 60–80°), and the combined extracts were evaporated to yield ferrocene (4.45 g, 71.6%), m.p. 172°. (Ref. 44 gives m.p. 172°.)

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## SUMMARY

(Dialkylamino)trialkylstannanes,  $R_3Sn-NR'_2$ , are very reactive reagents. With protic species HA, including hydrogen chloride, water, alcohols, ammonia and primary and secondary amines, diphenylphosphine, diphenylarsine, acetylene and mono-substituted acetylenes, cyclopentadiene and indene, they readily eliminate amine  $R'_2NH$  and afford organotin products of formula  $R_3Sn-A$ . Nitriles and nitro-compounds, with  $\alpha$ -hydrogen atoms, and acetone are believed to behave similarly in the primary step but side-reactions also are prominent.

The great facility of reaction is, in the main, attributed to a weak Sn-N bond and it is predicted that these reactions are capable of wide extension not only into the domain of organotin-amino compounds, but also into similar derivatives of other, particularly the more electropositive, metals. This is demonstrated by a synthesis of ferrocene from an iron diethylamide and cyclopentadiene.

The amino-derivatives of the elements are very briefly surveyed.

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