

54. *Reactions of Tin(IV) Halides with Ammonia Derivatives. Part III.*¹
The Reaction of Tin(IV) Halides with Aliphatic Amines.

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The reactions of tin(IV) chloride, tin(IV) bromide, and tin(IV) iodide with trimethylamine, dimethylamine, methylamine, and a number of higher primary amines have been investigated. Whereas simple 1 : 2 adducts are formed by all three halides with trimethylamine, and by tin(IV) chloride with dimethylamine, tin(IV) bromide and tin(IV) iodide react further with dimethylamine. The halides react with methylamine to give as final product a mixture of methylamine hydrohalide and the appropriate aminobasic tin(IV) halide, $\text{SnX}_2(\text{NHMe})_2, 2\text{NH}_2\text{Me}$.

The mechanism of the reactions and the structure of the products are discussed, and a number of anomalies in the literature are re-interpreted.

REACTIONS of tin(IV) halides with ammonia have recently been studied^{1,2} in some detail; the chloride, bromide, and iodide form simple diammoniates ($\text{SnX}_4, 2\text{NH}_3$) in gas-phase reactions, but are ammonolysed in liquid ammonia. The reactions of the tin(IV) halides with tertiary amines and several other nitrogen compounds have been examined by a number of workers, who obtained adducts of formula $\text{SnX}_4, 2\text{A}$ in most cases, for instance

¹ Part II, Bannister and Fowles, *J.*, 1958, 4374.

² Bannister and Fowles, *J.*, 1958, 751.

in reactions of tin(IV) chloride with trimethylamine,³ triethylamine,⁴ pyridine,^{3,5} pyrrole and substituted pyrroles,⁶ indole,⁷ and several nitriles,⁸ of tin(IV) bromide with trimethylamine,⁹ triethylamine,⁹ and substituted pyrroles,⁶ and of tin(IV) iodide with pyridine¹⁰ and aniline.¹¹ Corresponding tertiary phosphine and arsine compounds have also been reported.¹² In these simple adducts, the tin(IV) halide acts as a typical Lewis acid by accepting electrons from the nitrogen atoms of the ligands; in this way the tin atom achieves an octahedral configuration ($5s^2p^35d^2$). In presence of the amine hydrohalide, the hexahalogenostannate(IV) complex may be formed,^{13,14} e.g., $[\text{PhNH}_2]_2[\text{SnBr}_6]$.

Both tin(IV) chloride⁴ and tin(IV) bromide⁹ form tetra-aminates with triethylamine, so it appears that the tin atom might attain a covalency of eight under suitable conditions; this point is dealt with in the Discussion.

Much less is known of the reactions of the tin(IV) halides with secondary and primary aliphatic amines. George, Mark, and Wechster¹⁵ obtained diammines from the reaction of tin(IV) chloride with *sec.*-butylamine and *n.*-butylamine, and Trost¹⁶ obtained a hexaminate with ethylamine and tin(IV) chloride. Although the diammines can be considered simple adducts, the tin atom is unable to achieve a covalency of ten, so that the ethylamine product cannot be just an addition compound. With the primary and secondary amines, the presence of a nitrogen-hydrogen bond makes aminolysis of the tin(IV) halides probable, so that the ethylamine compound might be considered a mixture of ethylamine hydrochloride and an aminobasic tin(IV) chloride.

Since Trost's work is the only indication of the aminolysis of tin(IV) halides and the formation of covalent tin-nitrogen bonds, we have examined the reactions of the three tin(IV) halides with a number of aliphatic primary amines, and with dimethylamine. The reaction of trimethylamine with tin(IV) bromide and tin(IV) iodide has also been studied to make sure that only simple diammines are formed. (The work of Bohme and Boll⁹ on the tin(IV) bromide-trimethylamine system was published during our investigations).

EXPERIMENTAL

Materials.—Tin(IV) halides,^{1,2} mono-, di-, and trimethylamine,¹⁷ and ethylenediamine¹⁸ were purified as described previously. *n.*-Propylamine, *n.*-butylamine, and *n.*-pentylamine (Messrs. British Drug Houses) were all dried by distillation *in vacuo* from freshly-crushed barium oxide.

Analyses.—Tin, halogen, and nitrogen were estimated as usual,^{1,2} on weighed samples whenever possible, but where the product adhered very firmly to the sides of the reaction vessel, it was hydrolysed *in situ*; in such cases ratios only are quoted.

Reactions.—The appropriate tin(IV) halide and amine were allowed to react in the absence of solvents in the usual type of closed vacuum system.¹⁷ Initial experiments were carried out in a detachable jointed tube complete with stopcock, by condensing excess of amine on a weighed quantity of tin(IV) halide; after reaction for an hour or so (with shaking) at room temperature, excess of amine was pumped off and the tube reweighed. The amount of amine associated with the halide could therefore be determined.

To find out if further reaction would take place on standing, the tin(IV) halide and excess of

³ Laubengayer and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5985.

⁴ Trost, *Canad. J. Chem.*, 1952, **30**, 835.

⁵ Pfeiffer, *Z. anorg. Chem.*, 1910, **71**, 97.

⁶ Schmitz-Dumont, *Ber.*, 1929, **62**, B, 226.

⁷ Schmitz-Dumont and Motzkus, *Ber.*, 1929, **62**, B, 466.

⁸ Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, **B**, **17**, 21.

⁹ Böhme and Boll, *Z. anorg. Chem.*, 1957, **292**, 61.

¹⁰ Dimitriou, *Praktika*, 1927, **2**, 496.

¹¹ Cooper and Wardlaw, *J.*, 1930, 1141.

¹² Allison and Mann, *J.*, 1949, 2915.

¹³ Rosenheim and Aron, *Z. anorg. Chem.*, 1904, **39**, 170.

¹⁴ Richardson and Adams, *Amer. Chem. J.*, 1899, **22**, 446.

¹⁵ George, Mark, and Wechster, *J. Amer. Chem. Soc.*, 1950, **72**, 3896.

¹⁶ Trost, *Canad. J. Chem.*, 1952, **30**, 842.

¹⁷ Fowles and Pleass, *J.*, 1957, 1674.

¹⁸ Fowles, McGregor, and Symons, *J.*, 1957, 3329.

amine were sealed in ampoules and allowed to react (after 24 hours' mechanical shaking) for several months. The ampoules were then opened and the contents analysed after excess of amine had been pumped off. In some instances, the products were extracted with solvents before analysis, but unless this is stated the analytical figures refer to the total solid remaining after removal of amine. All experiments were carried out two or three times.

(i) *Reaction of trimethylamine with tin(IV) bromide and tin(IV) iodide.* The pale yellow solid initially formed by tin(IV) bromide had an overall composition $\text{SnBr}_4 \cdot 2 \cdot 0\text{NMe}_3$. After reaction with trimethylamine for several months in sealed ampoules, both tin(IV) bromide and tin(IV) iodide formed *diaminates* [Found: (a) Sn, 21.4; Br, 57.9; N, 5.05. $\text{SnBr}_4 \cdot 2\text{NMe}_3$ requires Sn, 21.3; Br, 57.4; N, 5.03%. (b) Sn : I : N = 1.00 : 4.00 : 2.00]. The pale yellow diaminate of tin(IV) bromide was insoluble in trimethylamine, but the brown compound formed by tin(IV) iodide was fairly soluble and gave an amber solution in the amine.

(ii) *Reaction of dimethylamine with tin(IV) halides.* In initial experiments, tin(IV) chloride and tin(IV) iodide both reacted with dimethylamine to give adducts $\text{SnCl}_4 \cdot 1.95\text{NHMe}_2$ and $\text{SnI}_4 \cdot 2.21\text{NHMe}_2$. The reaction of tin(IV) bromide and dimethylamine was very rapid and could not be examined by the weighed-vessel technique since the sudden pressure change invariably burst the vessel. The *diaminate* formed by tin(IV) chloride sublimed unchanged on heating *in vacuo* to 156° (Found: Sn, 34.1; Cl, 40.8; N, 7.92. $\text{SnCl}_4 \cdot 2\text{NHMe}_2$ requires Sn, 33.9; Cl, 40.4; N, 7.90%). In nitrogen, the sublimate melted to a brown liquid at 197°.

On reaction for several months in an ampoule, tin(IV) chloride still only formed the white diaminate, since the product again melted at 197° (Found: Cl, 39.8; N, 7.92%). With tin(IV) bromide, however, a pale yellow solid remained on removal of amine from the amber solution (Found: Sn, 21.5; Br, 57.8; N, 6.87%, *i.e.*, Sn : Br : N = 1.00 : 3.99 : 2.70). The yellow solution formed by tin(IV) iodide in dimethylamine deposited a white solid on cooling to -78°, but removal of amine left a heterogeneous brown solid $\text{SnI}_4 \cdot 3.8\text{NHMe}_2$; another similar product which was pumped for 4 hr. at 50° before analysis, gave Sn, 15.1; I, 64.3; N, 6.43%, *i.e.*, Sn : I : N = 1.00 : 3.98 : 3.61.

(iii) *Reaction of monomethylamine with tin(IV) halides.* In initial reactions, both tin(IV) chloride and tin(IV) bromide gave white products $\text{SnX}_4 \cdot 4.0\text{NH}_2\text{Me}$. When heated to 200° *in vacuo*, the tin(IV) chloride product turned yellow, evolved methylamine, and gave a substantial white sublimate; on prolonged heating virtually all the solid sublimed (Found: Sn : Cl : N = 1.00 : 3.96 : 2.01).

When sealed in ampoules, all three tin(IV) halides dissolved in the methylamine to give colourless solutions, which after some hours became cloudy and slowly formed a white deposit. This redissolved on warming. The white products obtained after reaction for several months had somewhat similar compositions (Found: Sn : Cl : N, 1.00 : 3.99 : 5.69; Sn : Br : N, 1.00 : 4.06 : 5.83; Sn : I : N, 1.00 : 4.00 : 5.60). When the iodide product was pumped at 50° for 2 hr. before analysis, the product was $\text{SnI}_4 \cdot 5.4\text{NH}_2\text{Me}$. It seemed likely that all those products were mixtures of aminobasic tin(IV) halides and the appropriate methylamine hydrohalide, and attempts were accordingly made to obtain pure substances by selective solvent extraction. Although nothing could be extracted from the tin(IV) chloride product by benzene, chlorobenzene, or chloroform, a small amount of solid was obtained by several extractions with nitromethane. Since this solid contained no tin (Found: N : Cl = 1.08 : 1.00), it was probably methylamine hydrochloride. However, its low solubility in nitromethane prevented its complete removal from the products and the isolation of a pure aminobasic tin(IV) chloride. The methylamine hydrohalides readily dissolved in methylamine, but in the case of the tin(IV) chloride and tin(IV) iodide products the tin-containing component of the mixture was too soluble for effective separation. With the tin(IV) bromide product, however, an appreciable amount of white solid still remained after several washings with 50 ml. of methylamine. After removal of excess of amine, the insoluble and soluble portions were hydrolysed *in situ* and analysed (Found: Sn : Br : N, 1.00 : 2.10 : 4.14, for insoluble; Sn : Br : N, 1.00 : 16.7 : 18.6, for soluble). Apparently the methylamine largely extracts methylamine hydrobromide, leaving a relatively insoluble aminobasic tin(IV) bromide, $\text{SnBr}_3(\text{NHMe})_2 \cdot 2\text{NH}_2\text{Me}$. Some of this tin compound is also found as expected in the soluble portion, where the overall analysis suggests a mixture of $\text{SnBr}_2(\text{NHMe})_2 \cdot 2\text{NH}_2\text{Me} + 14.6$ mol. of $\text{NH}_2\text{Me} \cdot \text{HBr}$.

(iv) *Reaction of tin(IV) iodide with ethylenediamine and higher primary aliphatic amines.* Tin(IV) iodide dissolved in *n*-propylamine, *n*-butylamine, and *n*-pentylamine to give yellow

solutions which did not change appreciably on standing for some months. When excess of amine was pumped away, the solutions became viscous yellow glasses from which the amine could only be removed very slowly even at 45°. The overall compositions of the products are tabulated.

Products of the reaction of tin(IV) iodide with aliphatic amines.

Amine	Product (A = amine)	Reaction time	Pumping before analysis
<i>n</i> -Propylamine ...	SnI ₄ .4.21A	Few hours	20 hr. at 45°
	SnI ₄ .4.71A	Several months	24 hr. at 45°
<i>n</i> -Butylamine	SnI ₄ .6.37A	Few hours	4 hr. at room temp.
	SnI ₄ .4.94A	Few hours	4 hr. at room temp. and 1 hr. at 45°
	SnI ₄ .4.80A	Several months	24 hr. at 45°
<i>n</i> -Pentylamine	SnI ₄ .8.8A	Several months	24 hr. at room temp.

Tin(IV) iodide reacted with ethylenediamine to give a white solid and a colourless solution. The solid was filtered off and washed with ethylenediamine (5 × 50 ml.) to remove any ethylenediamine hydriodide and pumped (Found: Sn : I : N, 1.00 : 0.96 : 3.62). A glass remained when excess of ethylenediamine was removed from the extract; this is characteristic of concentrated solutions in ethylenediamine.¹⁹

DISCUSSION

All three tin(IV) halides give the simple 1 : 2 adducts with trimethylamine, and even after several months' reaction there was no evidence for the formation of higher aminates. It is, therefore, surprising that a tetra-aminato is formed by triethylamine, because although triethylamine is a stronger base, its steric requirements are much greater, and its complexes are accordingly less stable.^{20,21} Probably the tin atom is not octacoordinated as suggested by Trost,⁴ who pointed out, however, that the tetra-aminato is unlikely to be a mixture such as SnX₂(NEt₂)₂ + 2NEt₃Cl; the sharp m. p. (90—92°⁹) supports this supposition. Böhme and Bolle suggested an ionic structure, [Sn(NEt₃)₄]⁴⁺4Br⁻, since the tetra-aminato has a completely different nature from the diaminate, for instance, in being soluble in water. They argue that since all the bromine is precipitated by silver nitrate, then it is entirely ionic. The bromine atoms would be labile in any structure, however, so that there is no evidence for the ionisation of all the tin-bromine bonds; this would, indeed, be unlikely as the preparation was made in an organic solvent. The properties are consistent with some measure of ionisation, however, and a structure [SnBr₂(NEt₃)₄]²⁺2Br⁻ is perhaps more likely, since it gives an octahedral configuration to the tin atom.

From an aqueous solution of the tetra-aminato, Böhme and Boll isolated [Sn(NEt₃)₆]⁴⁺4NO₃⁻. Complete ionisation is reasonable with a preparation made in aqueous solution, but since this product contains hexacoordinated tin it is reasonable to suppose the original tetra-aminato does also. We consider that both trimethylamine and triethylamine form simple diaminates, but that the more basic triethylamine can also force some ionisation of the tin-bromine bonds.

The reaction of dimethylamine with tin(IV) chloride again gives only a 1 : 2 adduct which sublimes unchanged *in vacuo*. The 1 : 2 di-*n*-butylamine compound reported by George *et al.*¹⁵ is evidently similar. With tin(IV) bromide and tin(IV) iodide, however, more dimethylamine is taken up on prolonged reaction, and the final products have compositions SnBr₄.2.7NHMe₂ and SnI₄.3.8NHMe₂ respectively. In view of their non-stoichiometric compositions and heterogeneous appearance, it seems reasonable to consider these products to be mixtures of di- and tetra-aminates. The nature of the tetra-aminato is again difficult to formulate, since although the dimethylamine molecule forms stronger

¹⁹ Fowles and McGregor, *J.*, 1958, 136.

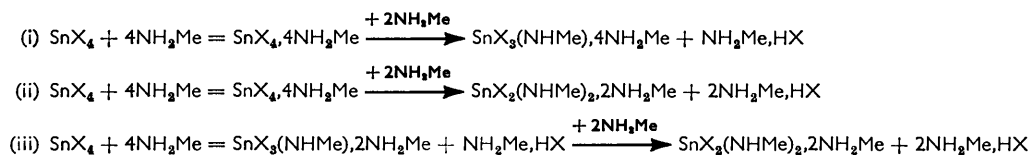
²⁰ Brown, Schlesinger, and Cardon, *J. Amer. Chem. Soc.*, 1942, **64**, 325.

²¹ Brown and Sujishi, *J. Amer. Chem. Soc.*, 1948, **70**, 2878.

complexes²² than does trimethylamine, it is still doubtful whether the tin(IV) halide can accept four dimethylamine molecules and give the tin atom an octaco-ordinated configuration. In any case, tin(IV) chloride should be a better Lewis acid than tin(IV) iodide, and yet it shows no tendency to accept more than two molecules of dimethylamine. Moreover, it seems odd that only part of the tin(IV) bromide should form a tetra-aminatate when the amine is present in such huge excess.

The two most likely structural possibilities are then either an ionic complex similar to that suggested for $\text{SnX}_4 \cdot 4\text{NEt}_3$, e.g., $[\text{SnX}_2(\text{NHMe}_2)_4]^{2+} 2\text{X}^-$ or a mixture of aminolysis products, e.g., $\text{SnX}_3(\text{NMe}_2) \cdot 2\text{NHMe}_2 + \text{NHMe}_2 \cdot \text{HX}$. Whereas the ionic formulation was considered correct for the triethylamine adduct, aminolysis is more likely with dimethylamine since a nitrogen-hydrogen bond is broken more readily than a nitrogen-carbon bond; this type of reaction has in fact been firmly established for several metal halide-dimethylamine reactions.^{17, 23} Moreover, in the case of the tin(IV) iodide product, the composition $\text{SnI}_4 \cdot 3 \cdot 8\text{NHMe}_2$ indicates almost quantitative formation of the tetra-aminatate, and yet the very heterogeneous nature of the product shows that it must be a mixture and not a single species as required by the ionic structure. It is also more feasible to consider the tin(IV) bromide product as resulting from an incomplete aminolysis rather than an incomplete ionisation.

With monomethylamine, the tin(IV) halides initially form a tetra-aminatate, but further reaction takes place after some hours, and a white precipitate begins to form; the eventual composition of the reaction product approximates to $\text{SnX}_4 \cdot 6\text{NH}_2\text{Me}$. While it seems fairly obvious that the second slow reaction is aminolytic, there are three possible explanations of the overall reaction:



Isolation of the aminobasic tin(IV) bromide $\text{SnBr}_2(\text{NHMe})_2 \cdot 2\text{NH}_2\text{Me}$ from the tin(IV) bromide product shows that reaction (i) is incorrect. It is difficult to choose between the other two possibilities, since it really amounts to deciding whether the tetra-aminatate is a simple adduct or a mixture. Although the adduct requires the tin atom to be octaco-ordinated, this is not perhaps so unreasonable with monomethylamine as the ligand. Moreover, the tetra-aminatate formed by tin(IV) chloride loses methylamine when heated *in vacuo* and forms the di-aminatate as a sublimate almost quantitatively. This di-aminatate could, however, result from the reaction $\text{SnCl}_3(\text{NHMe}) + \text{NH}_2\text{Me} \cdot \text{HCl} = \text{SnCl}_4 \cdot 2\text{NH}_2\text{Me}$. It is noteworthy that although the di-adducts of tin(IV) chloride with ammonia, methylamine, and dimethylamine are volatile, Laubengayer and Smith were unable to purify the analogous trimethylamine adduct by sublimation. That the composition of products of the prolonged reactions should fall rather below $\text{SnX}_4 \cdot 6\text{NH}_2\text{Me}$ is not unexpected, because two molecules of amine are attached to an aminobasic tin(IV) halide, and these replaced compounds will be much poorer Lewis acids than the halides themselves, and will tend to lose amine on pumping.

Trost observed that tin(IV) chloride added 6 mol. of ethylamine, 1.4 mol. of which were lost on heating *in vacuo* at 88°. It seems reasonable to suppose that Trost's product is also a mixture, $\text{SnCl}_2(\text{NH}_2\text{Et})_2 \cdot 2\text{NH}_2\text{Et} + 2\text{NH}_2\text{Et} \cdot \text{HCl}$, and that the two co-ordinately-bound ethylamine molecules will be lost on heating *in vacuo*. Although Trost only obtained 1.4 mol. of ethylamine, he did not apparently heat the product above 88°, and it is likely that the amine was incompletely removed under these conditions, since it would diffuse only slowly through the solid lattice.

²² Brown and Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 1332.

²³ Fowles and Pleass, *J.*, 1957, 2078.

n-Butylamine only gave a di-aminato according to George and his co-workers. Their compound being assumed to have the stated composition (the only analysis is for nitrogen), then it is apparent that solvolysis decreases as the alkyl group gets larger. Although the extension of our work to *n*-propylamine, *n*-butylamine, and *n*-pentylamine yielded only glasses from which free amine could be only incompletely removed, our figures show that much less reaction has occurred than with methylamine and ethylamine, so that the nature of the alkyl group does determine the reaction.

In the reaction of tin(IV) iodide with ethylenediamine, three of the tin-iodine bonds are aminolysed, and this we attribute to the highly basic nature of the ethylenediamine and to the possibility of chelate formation.

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