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# The Synthesis, Reactivity, and Physicochemical Properties of Compounds with a Tin-Nitrogen Bond

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Data on the methods of preparation, properties, and practical applications of organotin compounds with an Sn-N bond are reviewed.
The bibliography includes 343 references.

CONTENTS


| | | |
|---|---|---|
| I. | Introduction | 1132 |
| II. | Synthesis of compounds with a tin-nitrogen bond | 1132 |
| III. | The reactivity of compounds with a tin-nitrogen bond | 1138 |
| IV. | Chemical properties of organotin pseudohalides with a tin-nitrogen bond | 1142 |
| V. | Physicochemical properties and structures of nitrogen-containing organotin compounds | 1144 |
| VI. | Applications of nitrogen-containing organotin compounds | 1145 |


## I. INTRODUCTION

Organotin compounds with a covalent tin–nitrogen bond have attracted in recent years the continuous attention of investigators and workers in the field of applied chemistry. The study of their properties led to the discovery of new types of processes, for example the reaction involving the insertion of isocyanates in the Sn–N bond. The fields where these compounds have found practical applications are continuously expanding [1-9]. Several reviews [10-17] and a separate chapter in a monograph [18] have been devoted to this problem and the data have been partly surveyed in a book [19].

The aim of this paper is to review the available data on the synthesis, reactivity, physicochemical properties, and applications of organotin compounds with a tin–nitrogen bond, contained in monographs, journal articles, and patents published up to 1975. The main task is to draw the attention of Soviet chemists to this rapidly developing field of organoelemental chemistry, which is promising from both theoretical and practical points of view. The characteristics of the structures, physicochemical properties, and possible applications of nitrogen-containing organotin products have still been inadequately investigated.

These compounds can be divided into two groups [18]. The first includes aminostannanes $\equiv Sn-NR_2$ and the second organotin pseudohalides $\equiv Sn-N-R$ (R = C, N, or P). Compounds belonging to the first and second groups are synthesised by similar methods, but their physicochemical properties and reactivities are very different in certain cases.

The synthesis and properties of aminostannanes have been investigated in detail, while the studies which have been carried out on organotin pseudohalides are much less satisfactory.

## II. THE SYNTHESIS OF COMPOUNDS WITH A TIN–NITROGEN BOND

Organotin amines of the type $R_{4-n}Sn(NR'R'')_n$ ($n = 1-4$) cannot be synthesised by the reactions of amines with organotin halides, in contrast to the corresponding silicon and germanium compounds. The explanation is that the complexes formed in this reaction decompose on heating into the initial reactants [20-21]. The cases where the thermal stability of the complex is high are an exception. For example, triphenylstannylpurine can be synthesised from triphenylstannyl chloride and purine [22].

Organotin amines are obtained by transmetallation and transamination reactions as well as addition and exchange reactions.

### 1. Transmetallation Reactions

Whereas the syntheses of secondary and tertiary aminostannanes have been satisfactorily developed, an acceptable method for the synthesis of primary organotin amines of the type $R_3SnNH_2$ was not proposed until 1974 for t-butyl derivatives [23]. It involves the treatment of tris-(t-butyl)phenylstannane with a solution of potassium amide in liquid ammonia:

$$t\text{-}Bu_3SnPh + KNH_2 \xrightarrow{NH_3} t\text{-}Bu_3SnNH_2 + PhK \quad .$$

Secondary and tertiary aminostannanes are readily obtained by the reaction of lithium salts of amines with organotin halides [4,8,22,24-37]:

$$R_{4-n}SnX_n + n\,LiNR'R'' \rightarrow R_{4-n}Sn(NR'R'')_n + n\,LiX \quad ,$$

where R, R′, and R″ are alkyl or aryl groups and X is a halogen. The reaction proceeds readily and with high yields of the desired products in a dry inert solvent. At the same time the general method has certain characteristic features to which attention must be drawn. In particular, only the reaction of monolithium salts of primary aromatic amines leads to the formation of secondary organotin amines [27,38]:

$$R_3SnX + LiNHR' \rightarrow R_3SnNHR' + LiX \quad .$$

When organotin alkyl derivatives and salts of aliphatic amines were used, the products were the corresponding distannazanes. This can probably be accounted for by the successive transformations of (alkylamino)trialkylstannane:

$$\begin{aligned} 2R_3SnNHR' &\rightarrow (R_3Sn)_2NR' + H_2NR' \quad , \\ R_3SnNHR' + R_3SnX &\rightarrow (R_3Sn)_2NR' + HX \quad . \end{aligned} \qquad (1)$$

Lithium nitrides or amides are used in the synthesis of tris(trialkyl- and triarylstannyl)amines or hydrazine derivatives [33,39-41]:

$$3Me_3SnCl + Li_3N \rightarrow (Me_3Sn)_3N + 3LiCl \quad .$$

Different organotin amines and amides, including derivatives of sulphonamides and heterocyclic compounds (imidazoles, triazoles, etc.) are obtained via the corresponding sodium, potassium[2-4,42-45], and silver[46] salts and dialkylaminomagnesium bromide[47]. Together with organotin halides, the corresponding nitrates and acetates[48] as well as oxide derivatives[49,50] are used:

$$R_3SnX + MNH_2 \xrightarrow{NH_3} (R_3Sn)_2N \quad , \qquad (2)$$
$$X=Cl,\ OR,\ or\ OSnR_3;\ M=Li,\ Na,\ or\ K;$$

$$R_3SnCl + R'NAg \rightarrow R_3Sn{-}NR' + AgCl \quad ;$$
$$\qquad\qquad\quad NO_2 \qquad\quad NO_2$$
$$R_3SnCl + R'_2NMgBr \rightarrow R_3SnNR'_2 + MgBrCl \quad ;$$

Together with the tertiary amine, the secondary amine $(R_3Sn)_2NH$ was obtained in reaction (2).[51] The simultaneous formation of secondary and tertiary aminostannanes was also noted in the reaction of tricyclohexylphenylstannane and hexacyclohexyldistannane with potassium amide[52-54]:

$$2R_3SnC_6H_5 + KNH_2 \xrightarrow{NH_3} (R_3Sn)_2NH + C_6H_6 \quad ,$$

where R is the cyclohexyl group.

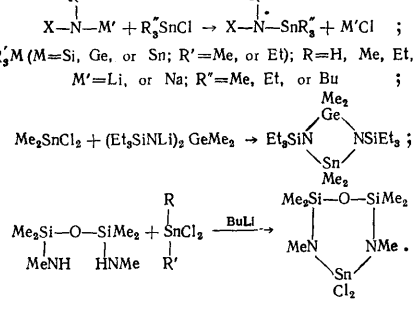
The use of organometallic derivatives and salts for the synthesis of aminostannanes is not restricted to Group I and II metals. Four- and six-membered cyclostannazanes[55] and dichlorostannoazosulphonylarenes, the first compounds containing a Sn–N bond[56], have been synthesised via tin(II) chloride:

$$ArSO_2NCl_2 + SnCl_2 \rightarrow ArSO_2{-}N{-}SnCl_3 \xrightarrow{SnCl_2} [ArSO_2N(SnCl_3)_2] \rightarrow$$
$$\qquad\qquad\quad Cl$$
$$\rightarrow ArSO_2N{=}SnCl_2 + SnCl_4 \quad .$$

However, there is some doubt about the existence of such products, which are allegedly fairly stable under the usual conditions. From our point of view, these derivatives probably have dimeric or trimeric structures [see reaction (3)].

The transmetallation reaction is widely used also in the synthesis of mixed organotin–organosilicon amines of the type $X{-}\underset{\displaystyle R}{\underset{|}{N}}{-}Y$,[29-31,36,57-61] including cyclic derivatives containing organoelemental germanium and silicon fragments[29,62]:

$$X{-}\underset{R}{\underset{|}{N}}{-}M' + R''_3SnCl \rightarrow X{-}\underset{R}{\underset{|}{N}}{-}SnR''_3 + M'Cl \quad ;$$
$$X=R'_3M\ (M=Si,\ Ge,\ or\ Sn;\ R'=Me,\ or\ Et);\ R=H,\ Me,\ Et,\ or\ X;$$
$$M'=Li,\ or\ Na;\ R''=Me,\ Et,\ or\ Bu \quad ;$$



Mixed organosilicon aminostannanes can be obtained also by the converse reaction, i.e. from the lithium salts of organic aminotin compounds and trialkyl derivatives of the chlorides of Group IVB elements[63] or from trialkylstannyl-lithium and *N*-bromohexamethyldisilazane[48].

Exchange reactions are quite suitable also for the synthesis of organotin pseudohalides. Trialkyl- and triaryl-stannyl isocyanates[64-68], trialkyl- and triarylstannyl isothiocyanates[64,69,70], dialkyl- and diaryl-tin di-isothiocyanates[71-74], the di-isocyanates, di-isothiocyanates, and hydroxide isothiocyanates of tetra-alkyldistannoxanes $R_2(SCN)SnOSn(NCS)R_2$ and $R_2(SCN)SnOSn.R_2(OH)$,[6,71,75] and triphenylstannyl *N*-selenocyanate[76] have been obtained in this way from organotin halides and cyanates or sodium, potassium, silver, and ammonium thiocyanates. Trialkylstannyl isocyanides, which are converted into isothiocyanates on heating with elemental sulphur[77], have been obtained via potassium cyanide[69]. Triphenyl- and tributyl-stannyl isocyanates may be synthesised also by treating organotin chlorides in xylene with a suspension of sodium *N*-ethylcarbamate[65]:

$$R_3SnCl + NaNHCOOC_2H_5 \rightarrow [R_3SnNHCOOC_2H_5] \rightarrow R_3SnNCO + C_2H_5OH \quad .$$

Trialkyl- and triaryl-stannyl azides[24,43,44,78,79,80,81] and hexa-alkyl-1,5-diazidotristannoxane $N_3Sn(R)_2{-}OSn(R)_2{-}OSn(R)_2N_3$[82] have been obtained by a corresponding procedure via azide salts.

Imino-derivatives of organotin compounds may be synthesised from trialkyltin salts and cyanoiodo-derivatives[28]:

$$Et_3SnLi + Me_2CI \rightarrow Et_3SnN{=}C{=}CMe_2 + LiI$$
$$\qquad\qquad\quad CN$$

or from immonium salts and organotin halides[83-85]. Triphenyl- and trimethyl-stannyldicyanamides and bis-(dicyanomido)dimethylstannane have been obtained similarly[41,86,87]:

$$Me_2SnCl_2 + 2NaN(CN)_2 \rightarrow Me_2Sn[N(CN)_2]_2 + 2NaCl \quad .$$

In order to elucidate the structure of organotin compounds containing the carbodi-imide fragment, *NN'*-bis-(triphenylstannyl)carbodi-imide was synthesised via the sodium salt of cyanamide, but the conditions of this reaction and the constants of the products are not quoted by the authors[43]. The syntheses of the corresponding alkyl derivatives[88-91] and of the tetrameric dibutylcarbodi-imidostannane were achieved subsequently[92]:

$$2Me_3SnCl + X_2NCN \rightarrow Me_3SnNCNSnMe_3 + 2XCl \quad ;$$
$$X=H,\ Na,\ or\ Ag \quad .$$

Organotin hyponitrites have also been obtained by the above procedures, but Beck et al.[93] are inclined to the idea, based on dipole moments and infrared spectra, that these compounds do not contain an Sn–N bond and the problem has therefore not been finally solved.

## 2. The Transamination Reaction

Organotin amines are frequently synthesised by exchange reactions between dialkylaminostannanes and secondary aliphatic amines, which proceed readily and quantitatively[26,27]:

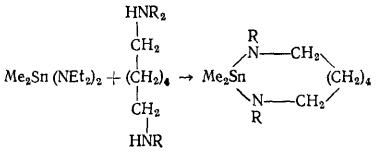
$$R_3SnNR'_2 + HNR''_2 \rightarrow R_3SnNR''_2 + HNR'_2 \quad ;$$
$$R,\ R'\ R''\ =\ alkyls.$$

The order of substitution of the amino-groups in simple aliphatic aminostannanes is[27]

$$NBu_2 > NEt_2 > NMe_2 \quad .$$

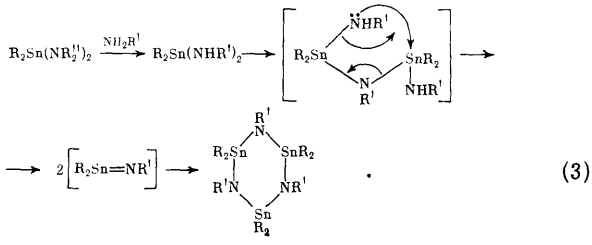
This method has also been used on a preparative scale to synthesise not only linear but also cyclic organotin

amines[94-99], for example:



Dialkylaminostannanes are transaminated by primary amines[26,27]. When t-butylamine and aniline were used in this reaction, t-butyl- and phenyl-aminostannanes were isolated respectively[100]. On the other hand, the reaction with methyl- or ethyl-amine leads to the formation of only the corresponding distannazanes even in the presence of an excess of the amine. This confirms yet again that the condensation of organotin amines of the type $R_3SnNHAlk$ to distannazanes via reaction (1) proceeds rapidly and irreversibly.

An interesting example of intramolecular transamination is the synthesis of six-membered[24,26,101] and four-membered[102] cyclostannazanes via primary amines. In the former case, the reaction is a four-stage process involving the transamination proper, intermolecular condensation, and nucleophilic 1,3-rearrangement with subsequent elimination and cyclopolymerisation:



(3)

Like amines, ammonia can be used successfully in the transamination reactions in order to obtain tertiary organotin amines, the ease of substitution decreasing in the sequence[27,103] $H_2N > RNH > R_2N$, where R is an alkyl group.

### 3. Reactions Involving the Addition of Organotin Compounds to Multiple Bonds

The addition of organotin compounds to multiple bonds is a preparatively convenient method of synthesis of organotin formamides, carbamates, amino- and imino-derivatives, substituted ureas, and related products. This section deals mainly with insertion reactions via the mdchanism

$$\equiv Sn{-}X + N{-}Y \rightarrow \equiv Sn{-}N{-}Y{-}X \quad ,$$

where N–Y is an unsaturated nitrogen compound and X = H, O, N, P, or As. These reactions can be conveniently considered separately for different X.

(a) Insertion in the Sn–H bond. The interaction of triethylstannane with dicyclohexylcarbodi-imide in the presence of azobisisobutyronitrile or zinc chloride leads to the formation of *N*-cyclohexyl-*N'*-triethylstannyl-*N'*-cyclohexylamidine[104]:

$$C_6H_{11}N{=}C{=}NC_6H_{11} + Et_3SnH \rightarrow C_6H_{11}N{=}CH{-}\underset{\displaystyle C_6H_{11}}{N}{-}SnEt_3 \quad .$$

The reaction with azomethines containing aromatic substituents proceeds similarly[104-107]:

$$n\text{-}R{-}C_6H_4N{=}CH{-}C_6H_5 + Et_3SnH \rightarrow Et_3Sn{-}\underset{\displaystyle CH_2C_6H_5}{N}{-}C_6H_4R \quad ;$$

R=H, or Me.

Similar reactions of azocarboxylic acid nitriles[28] and the dinitriles of alkylidenemalonic acids[108,109] also lead to the formation of an Sn–N bond:

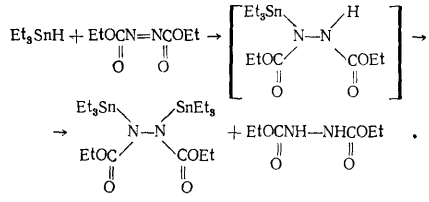
$$R{-}CH{=}\underset{\displaystyle C{\equiv}N}{C}{-}CN + R'_3SnH \rightarrow RCH_2{-}\underset{\displaystyle CN}{C}{=}C{=}NSnR'_3 \quad ;$$

R=CH$_3$, OC$_2$H$_5$, C$_6$H$_5$, *p*-CH$_3$OC$_6$H$_4$, *p*-ClC$_6$H$_4$, R'=C$_2$H$_5$, or C$_4$H$_9$.

Triphenyl- and triethyl-stannanes react with azeobenzene in different ways. While the former gives rise to *NN'*-diphenyl-*N*-triphenylstannylhydrazine, the corresponding addition product derived from the latter was not isolated. When aromatic azocompounds of the type RN=NXR' and RXN=NXR' (where X = $SO_2$ or $OCH_2$) are used in this reaction, there is no addition of triethylstannane[110], for example:

$$PhN{=}NSO_2Ph + Et_3SnH \rightarrow PhSO_2SnEt_3 + C_6H_6 + N_2 \quad .$$

In the reaction of triethylstannane with diethyl azodicarboxylate, the primary 1,2-addition product disproportionates to hydrazinedicarboxylate and bis(triethylstannyl)-bis(ethoxycarbonyl)hydrazine[111]:



The synthesis of trialkylstannylaniline and *N*-tributylstannylarenesulphonamides by the reaction of incompletely substituted stannanes with benzene- and arene-sulphonyl azides[63,112] is an example of the intermediate formation of products resulting from addition to the unsaturated nitrogen–nitrogen bond in the molecule of the incompletely substituted stannane:

$$RN_3 + R'_3SnH \rightarrow \left[\begin{array}{c} RN{=}N{=}N \\ \vdots \quad\quad \vdots \\ H{-}\!-\!SnR'_3 \end{array}\right] \rightarrow R'_3SnNHR + N_2 \quad ;$$

R=C$_6$H$_5$, *p*-CH$_3$C$_6$H$_4$SO$_2$, *p*-CH$_3$OC$_6$H$_4$SO$_2$, *p*-NO$_2$C$_6$H$_4$SO$_2$, or SO$_2$C$_6$H$_5$; R' = C$_2$H$_5$, or C$_4$H$_9$.

The analogous reaction of benzoyl azide is accompanied by the Curtius rearrangement and the formation of phenyl isocyanate, which in its turn gives rise to a urea derivative on interaction with the incompletely substituted stannane[113]. In contrast to the foregoing, when incompletely substituted arylstannanes were allowed to react with triphenylstannane azide, compounds with an Sn–N bond were not isolated[114]. There is no doubt that such products are formed as intermediates[16], but the authors apparently did not select conditions necessary for their isolation.

The reactions of trialkyl- and triaryl-stannanes with isocyanates and isothiocyanates are of greatest interest from the preparative and theoretical standpoints[115-117]. The composition of these products showed that, depending on the nature of the reactant, different types of addition are observed. The reaction between trialkylstannanes and aromatic isocyanates leads to the formation of

trialkyl-*N*-arylformamidostannanes [116]:

$$ArNCO + R_3SnH \rightarrow R_3SnN(Ar)\overset{\overset{O}{\|}}{C}H \ ;$$
$$Ar = C_6H_5,\ p\text{-}ClC_6H_4,\ \text{or}\ p\text{-}NO_2C_6H_4;\ R = C_2H_5,\ \text{or}\ C_4H_9.$$

The reactions of diethylstannane with two moles of phenyl isocyanate and of two moles of triethylstannane with *p*-phenylene di-isocyanate proceed similarly.

The same behaviour has been observed in the reactions of aliphatic isocyanates. For example, the addition of triethylstannane to cyclohexyl isocyanate leads to the formation of compounds with an Sn–N bond [118], although in an earlier study [115] the author believed that the process results in the formation of *N*-cyclohexylcarbamoyltriethylstannane only.

Allyl isocyanate reacts with tributylstannane, this being accompanied by the possible formation of a formamide derivative, which decomposes to tributylstannyl isocyanate and propene [119]. Alkyl and aryl isothiocyanates react with triethylstannane to form alkylstannylthiomethyleneimines. The hydrostannylation of arenesulphonyl isocyanates by tributylstannane takes place similarly [120]. It has been shown by infrared spectrophotometry and thermographically that the *N*-(tributylstannyloxymethylene)-arenesulphonamide (A) is involved in a tautomeric equilibrium with *N*-tributylstannylarenesulphonylformamide (B) [120]:

$$\underset{(A)}{ArSO_2N{=}C(H)OSnBu_3} \rightleftharpoons \underset{(B)}{ArSO_2N(SnBu_3)C(O)H} \ .$$

The use of an excess of triarylstannane in the reaction with aromatic isocyanates leads to the decomposition of the resulting organotin formamide and ultimately to the reduction of the isocyanates to *N*-arylformamides [121].

The study of the mechanism of the hydrostannylation of organic isocyanates and isothiocyanates has demonstrated the occurrence of nucleophilic attack by stannane hydrogen on the carbon atom of the isocyanate in the rate-determining stage of the reaction [117]. It is believed that the reaction proceeds via a polar mechanism [122,123]:

$$R_3SnH + R'N{=}C{=}X \rightarrow \left[\begin{array}{c} R'{-}N{\cdots}C{\cdots}X \\ \vdots \quad\ \vdots \\ H \quad\ \vdots \\ \vdots \\ SnR_3 \end{array}\right] \rightarrow$$
$$\rightarrow R_3Sn^{(+)} + \begin{cases} R'{-}\overset{(-)}{N}{-}CH{=}X & \xrightarrow{X=O} R'{-}N(SnR_3){-}C(O)H \\ R'{-}N{=}CH{-}\overset{(-)}{X} & \xrightarrow{X=S} R'{-}N{=}CH{-}S{-}SnR_3 \end{cases} .$$

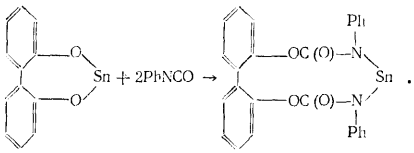
The proposed mechanism cannot apparently be unambiguous, because it does not take into account the possible tautomeric transformations of the products.

(b) Insertion in the Sn–O bond. These reactions are not of preparative importance alone. They are important for the understanding of the problem of the mechanism of the catalytic interaction of alcohols with isocyanates in the presence of organotin compounds, which still remains controversial [124–126].

The interaction of isocyanates and alkoxy-derivatives of organotin compounds results in the formation of *N*-stannylcarbamates [118,127–130]:

$$R_3SnOR' + R''NCO \rightarrow R_3SnN(R'')C(O)OR' \ ;$$
$$R = \text{alkyl};\ R' \text{ and } R'' = \text{alkyl or aryl}.$$

Ethyl and phenyl isocyanates react similarly with dibutyldimethoxystannane. The reaction proceeds stepwise with formation of 1 : 1 and 2 : 1 adducts in the first and second stages respectively. The latter adduct disproportionates on heating with dibutyldihalogenostannane, forming halogeno-substituted carbamates [131]. The synthesis of new heterocycles in which tin is bivalent constitutes an interesting example of the insertion of phenyl isocyanate in the Sn–O bond [132]:




The authors [132] give preference to the carbamate form of this compound.

It is noteworthy that the structure of the corresponding organotin imide rather than the carbamate has been attributed to the adduct of acetyl isocyanate and methoxytripropylstannane [133]:

$$CH_3{-}C{=}N{-}C(O)OCH_3 \ .$$
$$\quad\ |$$
$$\quad OSn(C_3H_7)_3$$

Presumably the imide is a result of the isomerisation of the carbamate form to the imide form as a result of the migration of the trialkylstannyl fragment. This idea has been put forward [118,129] but without any evidence for its occurrence. The possibility of the tautomeric transformations of organotin carbamates into imides was confirmed for products of the interaction of arenesulphonyl isocyanates and tributylmethoxystannane [134]:

$$p\text{-}RC_6H_4SO_2NC(O)OCH_3 \rightleftharpoons p\text{-}RC_6H_4SO_2N{=}C(OSn(C_4H_9)_3)OCH_3 \ ;$$
$$\quad\ |$$
$$Sn(C_4H_9)_3$$
$$R = H,\ CH_3,\ OCH_3,\ \text{or Cl}.$$

Organotin urea derivatives can be readily synthesised by the reaction of hexa-alkyldistannoxanes and alkyl or aryl isocyanates. The initial step involves the formation of trialkylstannyl *N*-alkyl(or aryl)-*N*-trialkylstannylcarbamates, which are decarboxylated to dialkyl(diaryl)-*NN'*-bis(trialkylstannyl)ureas and stannoxanes on heating [135–137]:

$$(R_3Sn)_2O + R'NCO \rightarrow R_3SnNR'C(O)OSnR_3 \ ;$$
$$2R_3SnNR'C(O)OSnR_3 \xrightarrow{-CO_2} R_3SnNR'{-}CO{-}NR'SnR_3 \ ;$$
$$R \text{ and } R' = \text{alkyl or aryl}.$$

Stannylureas are obtained also by the reaction of organotin carbamates with isocyanates on heating [137,138]:

$$R_3SnNR'C(O)OSnR_3 + R''NCO \rightarrow R_3SnNR'{-}CO{-}NR''SnR_3 + CO_2 \ .$$

When the reaction is carried out at room temperature, hexa-alkyldistannoxanes and organic isocyanurates are formed [125,138]. It is of interest that this type of reaction apparently constitutes the basis of the catalytic trimerisation of isocyanates, which occurs in the presence of organotin compounds [125,126].

Like the reactions of arenesulphonyl isocyanates with incompletely substituted stannanes and alkoxy-derivatives, the reaction of the above isocyanates with tributyltin oxide results in the isolation of a mixture of tautomeric compounds to which the structures of the corresponding carbamates and stannoxymethyleneimines [scheme (4)] has been attributed to the basis of infrared spectra. When the isocyanate and the oxide were used in proportions of 2 : 1, it was possible to obtain organotin disulphonylureas [139]:

$$n\text{-}RC_6H_4SO_2NCO + (Bu_3Sn)_2O \rightarrow \begin{cases} \rightarrow n\text{-}RC_6H_4SO_2N(SnBu_3)C(O)OSnBu_3 \\ \rightarrow n\text{-}RC_6H_4SO_2N{-}C(OSnBu_3)_2 \end{cases} ;$$
$$R = H,\ CH_3,\ OCH_3,\ \text{or Cl}. \qquad (4)$$

The attempt to synthesise triethylstannyl *N*-phenylcarbamate from triethyltin hydroxide and phenyl isocyanate was unsuccessful[136]. On the other hand, the reaction of arenesulphonyl isocyanates with triethyl- and triphenyltin hydroxides proceeds readily and in the case of the ethyl derivative results in formation of organotin arenesulphonamides and, in the presence of the phenyl derivative, a mixture of the corresponding arenesulphonamides and arenesulphonylcarbamates[140].

Organotin ureas can also be obtained by the interaction of hexa-alkyldistannoxanes or alkoxy-tin derivatives with carbodi-imides[94,141]. The latter are more reactive than isocyanates and isothiocyanates. Nitriles containing strong electron-accepting groups react with oxygen-containing organotin compounds to form substituted imides with an Sn–N bond[9,94,131]:

$$Bu_3SnOMe + CCl_3CN \rightarrow Bu_3SnN{=}C(CCl_3)OMe \ .$$

Diarylsulphodi-imides and *N*-sulphinamides readily react with alkylstannoxy derivatives; one or two N=S bonds are ruptured and intermediate products resulting from insertion in the Sn–O bond are formed[142-144]:

$$ArN{=}S{=}NAr + (Bu_3Sn)_2O \rightarrow Bu_3SnN(Ar)SON(Ar)SnBu_3 \ ;$$
$$ArSO_2NSO + R_3SnOR' \rightarrow R_3SnN(SO_2Ar){-}SO{-}OR' \ ;$$
$$Ar = C_6H_5, \text{ or } p\text{-}CH_3C_6H_4 \ .$$

The organotin sulphinyl diamides, sulphimates, and other compounds formed in these reactions are as a rule thermally unstable.

Finally, fairly stable t-butyl *N*-alkyl-*N*-triphenylstannylperoxycarbamates, $Ph_3SnN(Alk)C(O)OOBu\text{-}t$, have been obtained as a result of the reaction of t-butyl triphenylstannyl peroxide with alkyl isocyanates[145].

(c) Insertion in the Sn–N bond. The addition of unsaturated compounds to the Sn–N bond is the most typical example of the insertion reaction. It is used to synthesise organotin ureas, imines, imides, sulphinic diamides, and other compounds from aminostannanes and isocyanates, isothiocyanates, organic cyano-derivatives, carbodi-imides, and sulphinyl derivatives[12,26,108,146-149]:

$$Me_3SnNMe_2 \xrightarrow{PhNCO} Me_3SnN(Ph)C(O)NMe_2$$
$$\xrightarrow{PhCN} Me_3SnN{=}C(Ph)NMe_2$$
$$\xrightarrow{PhNCNPh} Me_3SnN(Ph)C(=NPh)NMe_2$$
$$\xrightarrow{PhNSO} Me_3SnN(Ph)S(O)NMe_2$$
$$\xrightarrow{PhNCS} Me_3SnN(Ph)C(S)NMe_2 \ .$$

The reactions proceed under mild conditions with nearly quantitative yields. Aromatic isocyanates are less reactive in these processes than the aliphatic compounds.

Phenyl isocyanate is capable of adding to *N*-tributylstannyl-*N*-methylformamide and *N*-tributylstannylacetamide, but the adduct obtained as a result of the latter reaction decomposes to tributylstannyl isocyanate and acetanilide[7,150]:

$$Bu_3SnNHC(O)Me + PhNCO \rightarrow [Bu_3SnN(Ph)C(O)NHC(O)Me] \rightarrow$$
$$\rightarrow Bu_3SnNCO + PhNHC(O)Me \ .$$

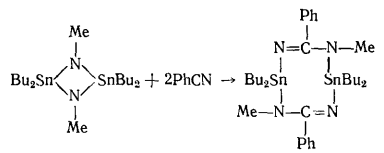
The reactions of aminostannanes with aromatic *N*-sulphinylsulphonamides[143] and of phenyl isocyanate with diethylaminodimethylstannyl chloride[151] also proceed with formation of unstable adducts. The interaction of alkyl or aryl isocyanates and isothiocyanates with *N*-tributyldiphenylmethyleneiminostannane leads to the formation of the corresponding organotin ureas and thioureas[152]:

$$Bu_3SnN{=}CPh_2 + RNCX \rightarrow Bu_3SnN(R)C(X)N{=}CPh_2 \ ;$$
$$R = Me, Et, Bu, \text{ or } Ph;\ X = O \text{ or } S \ .$$

The addition of heptamethylsilylstannazane to isocyanates and isothiocyanates has been studied in a number of investigations and it has been shown that the structures of the products thus obtained are different[12,153]. Thus the reaction with methyl isocyanate gives rise mainly to the iminoester

$$R_3SnN(CH_3)C\langle^{NCH_3}_{OSiR_3} \ ,$$

while the reaction with phenyl isocyanate gives rise to the urea derivative $R_3SnN(Ph)CON.(CH_3)SiR_3$. The reaction of silylstannazane with phenyl isothiocyanate leads to an equilibrium mixture of products with both structures. The reaction involving the insertion of isocyanates in the Sn–N bonds of organotin cyanamides has been used to synthesise organotin cyanoureas, which exhibit biological activity[154]. An interesting example of the addition reaction of the above type is the synthesis of eight-membered organotin heterocycles by the reaction of benzonitrile with diazostannetidines[102]:



A simple method has been proposed for the synthesis of trimethylstannyl *N*-methyl(trimethylstannyl)carbamate by passing carbon dioxide through a solution of heptamethyldistannazane[155]:

$$(Me_3Sn)_2NMe + CO_2 \rightarrow Me_3SnN(Me)C(O)OSnMe_3 \ .$$

(d) Insertion in the Sn–P and Sn–As Bonds. The interaction of isocyanates, isothiocyanates, and phenyl azide with triphenylstannyldiphenylphosphine and triphenylstannyldiphenylarsine may be classified as insertion reactions of the above type[156-158]:

$$Ph_3SnPPh_2 + PhNCX \rightarrow Ph_3SnN(Ph)C(X)PPh_2 \ ;$$
$$X = O \text{ or } S;$$
$$Ph_3SnYPh_2 + 2PhN_3 \rightarrow Ph_3SnN(Ph)Y(=NPh)Ph_2 \ ;$$
$$Y = P \text{ or } As;$$
$$Ph_3SnAsPh_2 + 3PhN_3 \rightarrow Ph_3SnN(Ph){-}As(Ph){-}N(Ph)SnPh_3 \ .$$
$$\|$$
$$NPh$$

## 4. Exchange and Substitution Reactions of Organotin Compounds

Exchange reactions of organotin oxides and hydroxides with nitrogen-containing reagents having an active hydrogen atom have been proposed for the synthesis of compounds with an Sn–N bond, which are fairly resistant to hydrolysis:

$$(R_3Sn)_2O + 2HN\langle \rightarrow 2R_3SnN\langle + H_2O \ .$$

Organotin derivatives of pyrrole, imidazole, benzotriazole[22,43-45], amido-compounds[118,159], nitroamines[46], and trialkylstannyltoluenesulphonamide[42,150] have been obtained via this mechanism. The reaction is used in the preparative methods for the synthesis of organotin isocyanates and isothiocyanates involving the interaction of trialkyl- or triaryl-tin oxides and hydroxides with urea,

biuret, thiourea, or their alkyl- or aryl-substituted derivatives on heating in the melt[69,159-161] or in solution in xylene and toluene[162,163] with simultaneous elimination of water:

$$(R_3Sn)_2O + 2(NH_2)_2CX \rightarrow 2R_3SnNCX + 2NH_3 + H_2O \quad ;$$
$$R=CH_3,\ C_2H_5,\ C_4H_9,\ C_6H_5,\ C_6H_5CH_2;\ X=O \text{ or } S \quad .$$

When dibutyltin oxide reacts with urea, the polymer $[R_2SnOSnR_2(NCO)_2]_n$ is obtained[160,161], while the reaction of hexaphenyldistannoxane with thiourea or its derivatives in boiling acetonitrile gives rise to *NN'*-bis(triphenylstannyl)carbodi-imide or *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide.[164,165] However, organotin derivatives of trialkyl- or triaryl-carbodi-imides can be obtained more simply and in high yields by the interaction of cyanamide with the corresponding oxides[90,91,166]:

$$(R_3Sn)_2O + 2NH_2CN \xrightarrow{-H_2O} 2R_3SnNHCN \rightarrow R_3SnNCNSnR_3 + NH_2CN \quad ;$$
$$R=Et,\ Bu,\ \text{or}\ Ph.$$

The first stage of the reaction can be used to synthesise aromatic organotin derivatives of cyanamide[167].

Organotin isocyanates can be obtained quantitatively by a similar procedure[160,162,168]:

$$(R_3Sn)_2O + 2HNCO \rightarrow 2R_3SnNCO + H_2O \quad ; \qquad (5)$$
$$R=Bu,\ \text{or}\ Ph.$$

The use of dialkyltin oxides and isocyanic or isothiocyanic acid makes it possible to synthesise the corresponding di-isocyanates and di-isothiocyanates of tetraalkylstannoxanes[6]. Organotin azides have been obtained similarly from alkyltin hydroxides and nitrous acid[80]. By altering the conditions of reaction (5) (by raising the temperature and eliminating the solvent), it is possible to obtain *N'*, *N''*, *N'''*-tris[trialkyl(or aryl)stannyl]isocyanurates—an interesting but extremely little studied class of organotin compounds—instead of organotin isocyanates[162]. When hexa-alkyl(or phenyl)distannoxanes are fused with cyanuric acid, the same compounds are obtained[159,160]. However, the authors of the review were unable to reproduce the latter reaction with aromatic derivatives. Organotin butyl isocyanurates have also been synthesised by heating tributyltin oxide or hydroxide with cyanuryl chloride[169]. The reactions of organotin oxides, hydroxides, and alkoxy-derivatives with ammonium thiocyanate[170] and of trialkyltin oxides with trimethylsilyl isothiocyanate[171] are also suitable for the synthesis of organotin isothiocyanates:

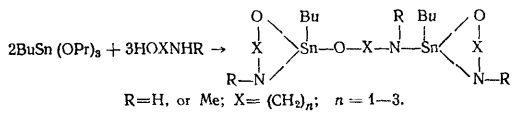
$$(R_3Sn)_2O + 2Me_3SiNCS \rightarrow 2R_3SnNCS + (Me_3Si)_2O \quad .$$

Organotin halides or alkoxy-derivatives can likewise be employed to obtain nitrogen-containing organotin compounds[118]:

$$R_3SnOCH_3 + R'NHC(O)R'' \rightarrow R_3SnN(R')C(O)R'' + CH_3OH \quad ;$$
$$R'=C_6H_5,\ R''=H,\ CH_3,\ \text{or}\ OCH_3;$$
$$R'=C_6H_{13},\ R''=H,\ \text{or}\ CH_3.$$

The stability of the amides depends on R'. Their decomposition results in the formation of the corresponding ureas or isocyanates[159,172].

Cyclic organotin derivatives with the OSn–N fragment have been synthesised by the reaction of butyl(tri-isopropoxy)stannane with sifferent hydroxyalkylamines[173]:



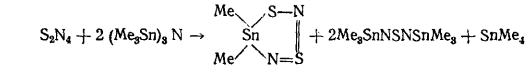
$$2BuSn(OPr)_3 + 3HOXNHR \rightarrow \quad ;$$

$$R=H,\ \text{or}\ Me;\ X=(CH_2)_n;\ n=1-3.$$

The synthesis of organotin isocyanates and isothiocyanates as a result of the interaction of trialkylstannyl chlorides with urea and thiourea[69,161], of partly substituted organotin hydrazines by the interaction of hydrazine with organotin chlorides[174], and of organotin ureas via organotin chlorides and carbamates[130-137,175] can also serve as examples of exchange reactions. At the same time there are many reactions unrelated to those described above whereby it is possible to synthesise organotin amines and their derivatives. In particular, the synthesis of tris(trimethylstannyl)amine and trimethylsodiostannane and iodobenzene in liquid ammonia[96], of aminodimethylsodiostannane from dimethyldisodiostannane and ammonia[176], and of organotin nitroamines from tetra-alkylstannanes and nitroamines[46] have been reported. The reaction involving the cleavage of the bond in tetra-alkyl(or aryl)-stannanes by thiocyanate, leading to the formation of trialkyl(or aryl)stannyl isothiocyanates[177], i.e.

$$R_3SnR' + (SCN)_2 \rightarrow R_3SnNCS + R'NCS \quad ;$$
$$R=CH_3,\ \text{or}\ C_6H_5;\ R'=C_3H_5,\ C_4H_7,\ CH{=}C{=}CH_2,\ \text{or}\ CH_2{-}C{\equiv}CH \quad .$$

as well as a new method for the simultaneous synthesis of five-membered cyclic and linear compounds containing tin, sulphur, and nitrogen[178], i.e.



$$S_2N_4 + 2(Me_3Sn)_3N \rightarrow \quad + 2Me_3SnNSNSnMe_3 + SnMe_4 \quad .$$

are promising from the standpoint of synthesis. A dimeric form has been proposed for the five-membered ring, but the overall formula does not reflect its true structure. There are probably no classical double bonds in this compound and all the bonds are to a large extent equalised. *NN'*-Bis(trimethylstannyl)sulphodi-imide was obtained similarly from diethylaminotrimethylstannane and sulphur nitride[179]. Organotin sulphuranes have been synthesised from aromatic sulphodi-imides and hexamethyldistannane[144]:

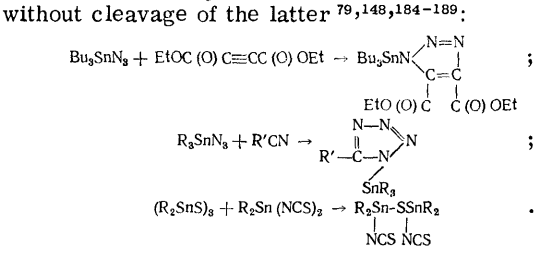
$$2n\text{-}CH_3C_6H_4NSNC_6H_4CH_3 + (CH_3)_3SnSn(CH_3)_3 \rightarrow$$
$$\rightarrow CH_3{-}N(CH_3C_6H_4){-}S{-}N(C_6H_4CH_3){-}Sn(CH_3)_2{-}Sn(CH_3)_2{-}N(C_6H_4CH_3){-}N(CH_3C_6H_4){-}CH_3 \quad .$$

When nitrogen compounds are inserted in the Sn–Sn bond, it is also possible to obtain nitrogen-containing organotin compounds, for example, isoselenocyanates[180], amines, and amides[181,182]:

$$Ph_3SnSnPh_3 + Se(SeCN)_2 \rightarrow 2Ph_3SnNCSe + Se$$
$$Bu_3SnSnBu_3 + RN_3 \rightarrow RN(SnBu_3)_2 + N_2 \quad ;$$
$$R=C_6H_5,\ C_6H_5CO,\ \text{or}\ C_6H_5SO_2.$$

The formation of compounds with an Sn–N bond is also possible with the aid of homolytic reactions. For example, when 1-aryltriazene, Ar–N=N–$NR_2$, was acted upon by $R_3Sn$ radicals, the amine $R_3SnNR_2$ was obtained[183].

More complex compounds of a similar type can be synthesised from simple derivatives with an Sn–N bond but without cleavage of the latter[79,148,184-189]:



$$Bu_3SnN_3 + EtOC(O)C{\equiv}CC(O)OEt \rightarrow \quad ;$$

$$R_3SnN_3 + R'CN \rightarrow \quad ;$$

$$(R_2SnS)_3 + R_2Sn(NCS)_2 \rightarrow \quad .$$

These reactions will be examined in greater detail in the next section.

## III. REACTIVITY OF COMPOUNDS WITH A TIN–NITROGEN BOND

It has been suggested that the reactions of organotin compounds with an Sn–N bond be divided into these with protic reagents, reactions with organoelemental hydrides, and exchange decomposition and addition reactions [18].

### 1. Reactions with Protic Reagents

The most characteristic property of organotin amines [33,44,47,147,182,190], imines [83,191,192], ureas [130,136], carbamates [127,128,129,145], triazenes [193], amides [112,140,159,182], sulphinic diamides [142], and triphenylstannyldicyanamide [86] is their hydrolytic instability:

$$\equiv Sn{-}N\!\!<\!\!\!\!\!\!\diagup \; + H_2O \rightarrow \equiv Sn{-}OH + HN\!\!<\!\!\!\!\!\!\diagup \; .$$

Aminostannanes containing less bulky substituents are more readily hydrolysed by water as a result of the steric factor [30]. When these reactions are performed in air, hydrolysis is accompanied by carboxylation of the aminostannanes, leading to organotin carbonates [33,47,106,155,194].

Various organotin amino-derivatives are readily cleaved at the Sn–N bond by hydrogen chloride or hydrochloric acid [47,49,145,147,194], hydrogen sulphide [127,129], and hydrogen cyanide [195]. The last reaction is used to synthesise organotin cyanides:

$$R_{4-n}Sn(NEt_2)_n + 2n\,HCN \rightarrow R_{4-n}Sn(CN)_n + n\,HNEt_2 \cdot HCN \; ;$$
$$R{=}Me,\ Et,\ \text{or}\ Bu,\ Ph;\ n = 2,\ 3.$$

When stannylamines [194,196], trialkylstannylketenimines [192], organotin carbamates [127,129,134,139], *NN'*-bis(trialkylstannyl)-sulphinic amides [142], and *NN*-bis(tributylstannyl)benzenesulphonamide [182] react with acetic acid, organotin acetates are formed quantitatively.

Alcohols react readily with aminostannanes [34,141,147,182,194,197,198], *N*-trialkylstannylketenimines [191,192], *NN'*-diaryl-*NN'*-bis(trialkylstannyl)sulphinic diamides [142], and stannyl carbamates [126,129,136,139,175,193] at the Sn–N bond under mild conditions, which leads to the formation of organotin alkoxides and amines. Such reactions are used, for example, to synthesise pure methoxytrimethylstannane [197]:

$$R_{4-n}Sn(NR'_2)_n + n\,R''OH \rightarrow R_{4-n}Sn(OR'')_n + n\,R'_2NH \; .$$

Butaneselenol [199,200], butanethiol [201], and silanol [34] react with aminostannanes similarly to alcohols.

The reactions of alcohol with organotin carbamates are particularly interesting from the standpoint of the explanation of the mechanism of the catalysis of the synthesis of urethanes by the latter [129,202]:

$$Bu_3SnOEt + PhNCO \rightarrow Bu_3SnN(Ph)C(O)OEt \xrightarrow{EtOH} Bu_3SnOEt + PhNH{-}C(O)OEt$$

or

$$PhNCO + EtOH \xrightarrow{Sn^{IV}} PhNH{-}C(O)OEt \; .$$

However, the lack of quantitative data, on the basis of which the rates of the known catalytic reactions put forward by Bloodworth and Davies [129] could be compared, precludes unambiguous inferences concerning this mechanism. One can only add that a different version of the mechanism of the catalytic formation of urethanes has been considered [124] and its validity demonstrated.

Organic hydroperoxides and peroxides react similarly with aminostannanes. The reaction of t-butyl hydroperoxide with a dialkylaminotrialkylstannane yields the trialkyl-t-butylperoxystannane and the dialkylamine. The main products of the reaction with benzoyl peroxide were the trialkylstannyl benzoate and the *NN*-dialkyl-*O*-benzoylhydroxylamine. The latter reaction does not have a free-radical mechanism despite the use of a typical free-radical generating agent–benzoyl peroxide [203].

Reactions involving the transamination of aminostannanes have already been partly discussed in Section II. It is of interest to consider here the interaction of methyl *N*-phenyl-*N*-tributylstannylcarbamate with ethylamine, the products of which are tributylmethoxystannane and *N*-ethyl-*N'*-phenylurea instead of the expected transamination products [129] [Eqn. (6)]. According to the authors [129], the reaction can proceed via two equally probable pathways. From our point of view, the second pathway is preferable, because the tributylethylaminostannane formed via the first pathway should condense with liberation of distannazanes [Eqn. (1)], which were not detected in the reaction:

$$Bu_3SnN(Ph)C(O)OMe + EtNH_2 \begin{cases} \rightarrow Bu_3SnNHEt + PhNH{-}C(O)OMe \\ \rightarrow MeOH + Bu_3SnNPh{-}CO{-}NHEt \end{cases} \rightarrow$$
$$\rightarrow PhNH{-}CO{-}NHEt + Bu_3SnOMe \; . \qquad (6)$$

When stannyl *N*-stannyl-*N*-sulphonylcarbamates react with diethylamine, the corresponding substituted ureas and tributyltin oxide are also obtained [139]. The transamination of bis(tributylstannyl)benzenesulphonamide with diethylamine proceeds in the standard manner [182]:

$$Bu_3Sn\,N(PhSO_2)C(O)OSn\,Bu_3 + Et_2NH \rightarrow PhSO_2NH{-}CO{-}NEt_2 + (Bu_3Sn)_2O \; ;$$
$$(Bu_3Sn)_2NSO_2Ph + Et_2NH \rightarrow Bu_3SnNHSO_2Ph + Bu_3SnNEt_2 \; .$$

Stannylamines react with halogenohydrocarbons in different ways depending on the nature of the halogen and the structure of its derivative. Thus when a dialkylaminotrialkylstannane was acted upon by chloroform, bromoform or chloroethylene derivatives, trihalogenomethyl derivatives of tin were obtained [131,204–207]:

$$R_3SnNR'_2 + HCX_3 \rightarrow R_3SnCX_3 + R'_2NH \; ;$$
$$R{=}Me,\ Et,\ Bu,\ \text{or}\ Ph;\ R'{=}Me\ \text{or}\ Et;\ X{=}Cl\ \text{or}\ Br.$$

The synthesis of pentafluorophenyltrimethylstannane was achieved by the reaction of dimethylaminotrimethylstannane with pentafluorobenzene in boiling benzene [208]. However, this reaction does not occur with iodo-, fluoro-, or mixed chlorofluoro-derivatives of methane of the type $HCFCl_2$.

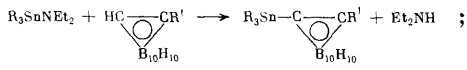
The reaction of aminostannanes with acetylene and its derivatives constitutes a preparative method for the introduction of an unsaturated bond into the molecule of an organotin compound. The reaction proceeds quantitatively which is promoted by the possibility of the effective elimination of the volatile alkylamine formed as a product [147,148,194,208,209,210,211]:

$$R_{4-n}Sn(NR'_2)_n + n\,HC{\equiv}CR'' \rightarrow R_{4-n}Sn(C{\equiv}CR'')_n + n\,HNR'_2 \; ;$$
$$n{=}1{-}4$$
$$R,\ R',\ \text{and}\ R'' = \text{hydrocarbon groups.}$$

In the reactions with amines of the type $R_2Sn(NR'_2)_2$ acetylene gives rise to a polymeric complex [147,194]. Cyclopentadiene, indene, and their derivatives react with aminostannanes similarly to acetylene [147,194,212].

Other compounds containing an active hydrogen atom attached to a carbon atom (nitriles, nitromethane) are also capable of involvement in proton exchange reactions with aminostannanes [194]. Thus diazomethane reacts with dimethylaminotrimethylstannane, which is followed by the substitution of two hydrogen atoms by organotin fragments [186,213,214], the reactivity of diazomethane derivatives

increasing in the sequence $MeCHN_2 < CH_2N_2 < CH[C(O).OEt]N_2$.[214-216]. *o*-, *m*-, and *p*-Carboranes react similarly[217,218]:



$R = Et$, or Bu; $R' = H$, $CH{=}CH_2$, or $SnR_3$ .

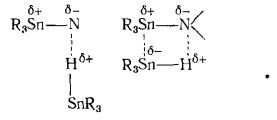
Although decaborane contains an active hydrogen atom, it reacts with aminostannane to form only a complex of the type $[Me_3Sn]^+[B_{10}H_{13}{\cdot}Me_2NH]^-$.[219] The mechanism of the reactions of aminostannanes with protic reagents has not been elucidated. However, one may postulate that it is based on electrophilic attack by the hydrogen atom of the protic reagent HA on the nitrogen atom of the aminostannane $\equiv Sn-N\lessdot$ followed by the coordination of the A fragment to the tin atom[18].

## 2. Reactions of Amino-Derivatives of Tin with Organoelemental Hydrides

Organotin hydrides react with aminostannanes[220-228], stannylhydrazines[117], and amides[111,226,229] to form di- and poly-stannanes in almost quantitative yields, for example:

$$R_3SnNEt_2 + R'_3SnH \rightarrow R_3SnSnR'_3 + Et_2NH \quad ;$$
$$n\,R_2Sn(NEt_2)_2 + n\,R_2SnH_2 \rightarrow (-SnR_2)_{2n} + 2n\,Et_2NH \quad .$$

The relative reactivity of $R_3SnH$ depends on R and increases in the following sequences[222,224]: t-Bu < iso-Bu < Bu < Ph and $R_3SnSnR_2H < R_3SnH < R_2SnH_2$. On the other hand, the reactivity of aminostannanes in these reactions increases with increasing basicity of nitrogen: $R_3SnNHR'' < R_3SnNR''_2$.[222] The study of the kinetics of the reaction of diethylaminotriethylstannene with triethylstannane showed that it is of second order overall and of first order with respect to each reactant[230]. $S_E2$ and $S_Ei$ mechanisms have been proposed for polar and non-polar solvents respectively[220], the intermediate states being of the following form:



The main reaction is sometimes accompanied by an exchange side reaction, which, however, may be reduced to a minimum[220,222,224]. For example, in the synthesis of compounds with more than two tin atoms, it is best to employ dialkylstannanes and not diaminostannane, because exchange reactions are more probable in the $R_3SnH/R'_2{\cdot}Sn(NEt_2)_2$ system[224].

Typical examples of the synthesis of compounds with a tin–element bond are the reactions of trialkyldimethylaminostannanes with triphenylgermanes[223,228], phosphines[147,194], arsines[103,147,231], and stibenes[103]:

$$R_3SnNR'_2 + Ph_nXH \rightarrow R_3SnXPh_n \quad ;$$
$X = P$, As, Sb, or Ge, $n = 2,3$.

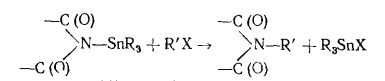
The reaction has been used to synthesise tin–germanium derivatives with functional groups by treating tin–germanium amines with water, phenols, acetylene derivatives, and other reagents[228]. At the same time, aminostannanes do not react with trialkylgermanes and trialkyl(or triaryl)silanes, apparently as a consequence of the lower activity of the hydrogen atom in these compounds[157,222,228].

Carbonyl and cyclopentadienyl derivatives of chromium, molybdenum, vanadium, manganese, rhenium, rhodium, platinum, and other metals containing active hydrogen also react with aminostannanes, which makes it possible to synthesise organometallic compounds containing Sn–Cr,[232,233] Sn–Mo,[232-235] Sn–W[232,233,236], Sn–Rh[79,233], Sn–Mn, Sn–Fe, Sn–Co, and Sn–Ni bonds[235]:

$$(\pi\text{-}C_5H_5)(CO)_3M{-}H + R_3SnNR'_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_3M{-}SnR_3 + HNR'_2 \quad ;$$
$M = Cr$, Mo, or W.

## 3. Substitution Reactions

The substitution reactions of aminostannanes involving the dissociation of the Sn–N bond can be regarded as amination reactions and the organotin amines can therefore be treated as aminating agents[18,237]. Reactions of this type include the alkylation or acylation of organotin derivatives of imides (phthalimide, succinimide, imidazole, and isatin) with the aid of alkyl or acyl halides[238], selective substitution of tributylstannyl groups in organotin tetrazoles by methyl iodide[239], and the synthesis of tris(benzoyl)isocyanurate on treatment of an organotin isocyanurate with benzoyl chloride[193,238]:



R – Alk; $R' =$ Alk, or Ac; X = Hal.

The interaction of tin-containing amino-derivatives with halogenohydrocarbons depends on the nature of the reactants. Thus the explosive reaction of bis(dimethylamino)dimethylstannane with carbon tetrachloride has been reported[240]. When tributyldiethylaminostannane was allowed to react with butyl chloride, tributylamine, triethylamine, and dibutylethylamine were isolated together with butyldiethylamine[241], while the reaction involving dimethylaminotrimethylstannane proceeds with dehydrochlorination and the formation of *cis*- and *trans*-but-2-enes[242]. This was also observed when pentachloroethane[204] and chloromethylacetylene were used[219]. On the other hand, on reaction with fluoroalkanes (or fluoroalkenes) and other fluorine compounds, aminostannanes behave in the usual manner[101,196,237,241,243-246]:

$$Me_3SnNMe_2 + YF \rightarrow Me_3SnF + YNMe_2 \quad ;$$
$Y = C_6F_5$, $C_6F_4Br$, $C_6F_4CN$, $CF{=}CFCl$, $BF_2(OC_2H_5)_2$, $PF_2$, $AsF_2$, $SbF_2$, or $TiF_3$.

Organoelemental and inorganic chloro-, bromo-, and iodo-derivatives react similarly[79,196,237,241,242,247]. In contrast to the reactions of aminostannanes with organoelemental hydrides discussed above, which lead to the formation of an element–element bond, metal hydrides and certain hydrogen-containing boron, aluminium, and silicon derivatives give rise to hydrogen-containing stannanes[46,196,237,242,248]:

$$R_{4-n}Sn(NR'_2)_n + R''H \rightarrow R_{4-n}SnH + R''NR'_2 \quad ;$$
$R = R' =$ Alk; $R'' = Et_3N{\cdot}BH_2$, $B_2H_5$, $Bu_4Al_2H$, or $Ph_2SiCl$.

Substitution reactions between aminostannanes and organoelemental alkyl and alkoxy-derivatives are known[49,196,237,249]:

$$R_3SnNMe_2 + R'_nM \rightarrow R_3SnR' + Me_2NMR_{n-1} \quad ;$$
$M = Li$, $R' = Me$, $n = 1$; $M = Al$, $R' = Et$, $n = 3$; $M = B$, $R' = Bu$, Ph, or OMe, $n = 3$.

The synthesis of disubstituted organoelemental alkylstannanes of the type $R_3SnC{\equiv}CMR_3$ (R = Me, Et, or Ph; M = Si, Ge, or Pb) on heating a mixture of a dialkylaminotrialkyl(or triaryl)stannane, sodium acetylide, and organic derivatives of the chlorides of Group IVB elements can also be included among the reactions of the type under consideration[250].

The interaction of a trialkyldiethylaminostannane with bis(trimethylsilyl)mercury, which leads to the formation of the hexa-alkyldistannane, the diethylaminotrimethylsilane, and metallic mercury is unusual[251].

Aminostannanes also react with esters, but these reactions have not been studied in detail and have not been fully explained[148,196,249,252]. It has been shown that the reactions with methyl methacrylate and alkyl and aryl acetates involve exchange and the dissociation of the bond between the carbon atom of the carbonyl group and the alkoxy-fragment[196,249]:

$$R_3SnNMe_2 + R'C(O)OR'' \rightarrow R_3SnOR'' + R'C(O)NMe_2;$$
R, R' = alkyl or aryl groups.

The similar reaction with vinyl acetate proceeds with formation of the trialkylstannyl acetate and the dissociation of the C–O bond in the alkoxy-group[252]. When aminostannanes were allowed to react with isopropenyl acetate, a trialkylstannyl acetate and dimethylacetamide were obtained[194,253]:

$$Et_3SnNMe_2 + MeC(O)OC(CH_3){=}CH_2 \rightarrow Et_3SnCH_2C(O)Me + CH_3C(O)NMe_2.$$

Certain aldehydes are also involved in the exchange reactions. Thus chloral cleaves the Sn–N bond in a dialkylaminotrialkylstannane, forming the trialkyl(trichloromethyl)stannane and the dialkylformamide[254,255]. The interaction of *N*-phenylhexabutyldistannazane with acetaldehyde proceeds under mild conditions with substitution of the oxygen of the carbonyl group and the formation of ethylideneamine[100]:

$$(R_3Sn)_2NR' + R''CH{=}O \rightarrow \left[\begin{array}{cc} R_3Sn{-}O & SnR_3 \\ | & | \\ R''CH{-}NR' & \end{array}\right] \rightarrow (R_3Sn)_2O + R''CH{=}NR'.$$

## 4. Addition Reactions of Aminostannanes

This section gives a systematic account of the reactions of stannylamines with unsaturated compounds which involve the cleavage of the Sn–N bond and the insertion of the unsaturated compounds in accordance with the general mechanism[26,148,155,249]:

$$\equiv Sn{-}N\!\!<\!\!\!\!\diagup\!\!\!\!\diagdown + A \rightarrow \equiv Sn{-}A{-}N\!\!<\!\!\!\!\diagup\!\!\!\!\diagdown$$
A = compounds with a multiple bond.

It has been shown that different versions of the reaction are possible, including 1,1-, 1,2-, 1,3-, and 1,4-insertion reactions.

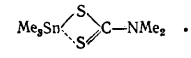
The interaction of dimethylaminotrimethylstannane with *p*-tolyl isocyanide is an example of the 1,1-insertion reaction[148,157]:

$$Me_3SnNMe_2 + p\text{-}CH_3C_6H_4N{=}C \rightarrow p\text{-}CH_3C_6H_4N{=}C\!\!<\!\!\!\!\diagup\!\!\!\!\diagdown^{SnMe_3}_{NMe_2}.$$

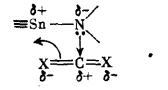
1,2-Insertion has been much more thoroughly investigated. The reactions of aminostannanes with carbon and sulphur dioxides, carbon disulphide, and carbon oxide sulphide are typical; they take place at room temperature and are accompanied by the formation of the corresponding organotin carbamates, thiocarbamates, and related products[26,146,151,155], for example:

$$Me_3SnNMe_2 + CX_2 \rightarrow Me_3SnXC(X)NMe_2;$$
X=O, or S.

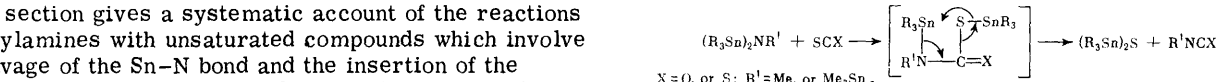
The oxygen-containing compounds are polymers in which the tin atom is coordinated to oxygen. The thioanalogues of carbamates are monomeric in benzene solution, but the tin in these compounds is likewise in a five-coordinated state:



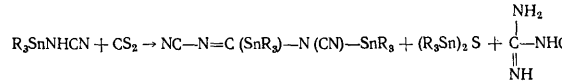
The reactivity of *N*-arylaminostannanes is much lower compared with that of the alkyl derivatives. For example, trimethylphenylaminostannane reacts with carbon dioxide much more slowly and trimethyldiphenylaminostannane does not react with $CO_2$ and $CS_2$ at all. This is consistent with the hypothesis that the mechanism of the insertion reaction involves initial nucleophilic attack by the nitrogen atom of the stannylamine on the positively charged carbon atom of the 1,2-dipole (in the present instance, O=C=O or S=C=S). The aromatic substituent delocalises the free electron pair of the nitrogen atom and hence hinders attack by this atom[146,155]:



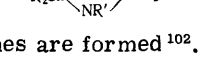
At the same time one should note that in certain cases these reactions do not stop at the first stage involving the formation of the insertion product. Thus the reaction of trimethylphenylaminostannane with carbon disulphide results in the formation of bis(trimethylstannyl) sulphide and *syn*-diphenylthiourea, while *N*-methylhexamethyldistannazane and tris(trimethylstannyl)amine react with COS and $CS_2$ to form bis(trimethylstannyl)sulphide and the corresponding organic or organotin isocyanates and isothiocyanates. It has been suggested that an unstable 1,2-adduct is formed only in the first stage of the reaction[155,254,256,257]:




The use of trialkyl(or triaryl)stannylcyanamide in these reactions leads to unexpected products[167]:

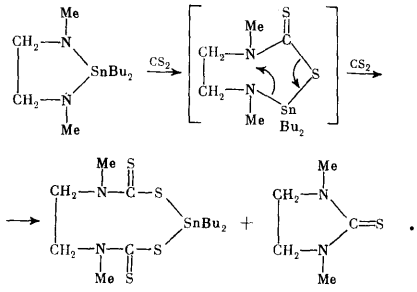



Bis(dialkylamino)stannanes reacts with carbon dioxide and carbon disulphide to form the corresponding biscarbamates and bisthiocarbamates. Tetrakis(dimethylamino)stannane reacts similarly with $CS_2$.[135] When the latter adds to diazostannetidines,

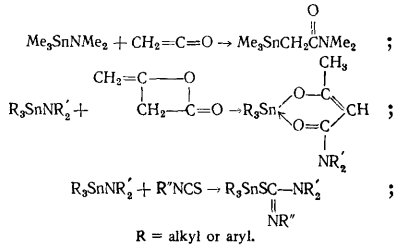


stable dithiostannetanes are formed[102]. The interaction of cyclic diaminostannanes, for example, a 2,2-dialkyl-1,3-diaza-2-stannacyclopentane, with carbon disulphide

proceeds via a 1,2-insertion mechanism, but is accompanied by the simultaneous decomposition of the 1,2-adduct to diazacyclopentanes [258]:

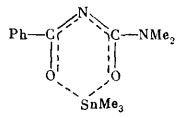


The reactions of amino-derivatives of tin with ketenes [18,146,253,259], diketen [260,261], isothiocyanates [26,146,148,262], isocyanates, and carbodi-imides [149,263,265] are also examples of the 1,2-insertion reaction:



R = alkyl or aryl.

The reaction of dimethylaminotrimethylstannane with benzoyl isocyanate, *N*-benzoyl-*N'*-t-butylcarbodiimide [149,263,264], and thiobenzoyl isocyanate [265] leads to six-membered rings owing to the intramolecular coordination of oxygen with the tin atom:



Processes involving the addition of stannylamines to double and triple carbon–carbon bonds activated by strong electron-accepting substituents belong to insertion reactions of the same type. Acrylate esters, acrylonitrile, acrolein, crotonaldehyde, diethyl acetylenedicarboxylate, 1-chloro-2-diphenylacetylene, etc. have been investigated as the activated reagents [148,243,249,252]. As a rule, the amino-group adds to the $\beta$-carbon atom and the organotin fragment adds to the $\alpha$-atom. The reactions proceed under mild conditions and give high yields of the desired products:

$$CH_2{=}CHC(O)OCH_3 + R_3SnNR'_2 \rightarrow R'_2NCH_2CH(SnR_3)C(O)OCH_3 \quad ;$$

$$C_6H_5C{\equiv}CCl + R_3SnNR'_2 \rightarrow R'_2NC(C_6H_5){=}C(Cl)SnR_3 \quad ;$$

R=R' — alkyl groups.

However, aldehydes with strong electron-accepting substituents add to stannylformamides and stannylureas with dissociation of their C=O bond [138,150]:

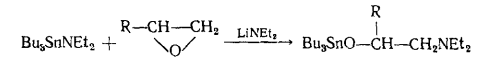
$$R_3SnN(R')C(O)R'' + CX_3C(O)H \rightarrow R_3SnOCH(CX_3)-N(R')C(O)R'' \quad ;$$

R=Bu, R'=Me, R''=H, X=Cl, or Br;

R=Et, R'=Ph, R''=H, X=Br; R=Bu,

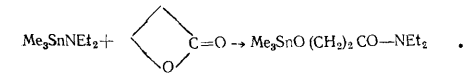
R'=H, R''=Me, X=Br.

Stannylamines and stannyl carbamates can also give rise to a 1,2-insertion product on interaction with acetic anhydride, but it could not be isolated [129,196,252]. Under certain conditions, the extremely weak Sn–N bond can be dissociated by ketones. Here the interaction is complex, as shown by the formation of a hexaalkyldistannoxane, organic amines, mesityl oxide, a trialkylstannylacetone, and other products in the reaction of alkylaminostannanes with acetone [194,296]. The possible pathways in this reaction and the influence on the latter by steric and electronic factors have been investigated [267]. On the other hand, hexafluoroacetone reacts with aminostannanes to form 1,1-adducts [268]. Analogous 1,2-addition products have been obtained in the reaction of trialkyldiethylaminostannane with cyclopentanone and cyclohexanone [244,269]. 1,3-Insertion reactions of aminostannanes have been observed in their interaction with epoxy-derivatives, including epoxybutane, phenyloxiran (styrene oxide), and epoxycyclohexane [270]:



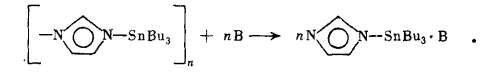
Thi-iran and methylthi-iran give rise to $R_3SnSCH(R'')CH_2.NR'_2$, where R = R' = R'' = Me or Et respectively [243].

The interaction of diethylaminotrimethylstannane with $\gamma$-butyrolactone and $\beta$-propiolactone, which involves ring opening, is an example of 1,4-insertion [271–273]:



## 5. Other Reactions of Aminostannanes

Aminostannanes can exhibit both electron-accepting (tin atom) and electron-donating (nitrogen atom) properties and can thus function both as aprotic acids and aprotic bases. However, such reactions are not characteristics of these compounds and few are known owing to the low strength of the Sn–N bond. *N*-Tributylstannylimidazole forms complexes with basic ligands [18,274] in which tin has a coordination number of five and behaves as a Lewis acid:

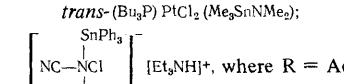


Another example of compounds in which tin exhibits electron-accepting properties is provided by organotin derivatives of nitroamine, which have a chelate structure [46].

The properties of aminostannanes as Lewis bases are characterised by the formation of complexes [18,256,275,276]:

$(Me_2N)_4Sn \cdot VOCl_3$; $[(Me_3Sn)_4N]^+Br^-$;

*trans*-$(Bu_3P)PtCl_2(Me_3SnNMe_2)$;



EtCO, Bz, MeOCO, EtOCO, or $PhSO_2$.

The reactions involving the photochemical decomposition of aminostannanes, whose study has only just begun, constitute a group separate from those enumerated above. It has now been shown that the photochemical decomposition of diethylaminotrimethylstannane, investigated by ESR, proceeds with the dissociation of the nitrogen–tin bond and

is a complex multistage process leading ultimately to the formation of hexamethyldistannane, diethylamine, and *N*-ethyliminoethane[277]:

$$Me_3SnNEt_2 \xrightarrow{h\nu} \begin{cases} Me_3SnH + MeCH{=}NEt \\ Me_3Sn^{\cdot} + Et_2N^{\cdot} \end{cases}$$
$$Me_3SnH + Me_3SnNEt_2 \rightarrow (Me_3Sn)_2 + Et_2NH$$
$$2Me_3Sn^{\cdot} \rightarrow (Me_3Sn)_2$$
$$2Et_2N^{\cdot} \rightarrow Me{-}CH{=}NEt + Et_2NH$$
$$Me_3Sn^{\cdot} + Et_2N^{\cdot} \rightarrow Me_3SnH + Me{-}CH{=}NEt \ .$$

## IV. CHEMICAL PROPERTIES OF ORGANOTIN PSEUDOHALIDES WITH A TIN–NITROGEN BOND

Bearing in mind the appreciable differences between the reactivities of aminostannanes and tin pseudohalides, we thought it useful to consider in this Section the specific chemical properties of typical examples of the latter, including organotin azides, isocyanates, isothiocyanates, carbodi-imides, imines, and related compounds.

Investigators noted in the first place the high thermal stabilities of the pseudohalides. Thus triphenylstannyl azide decomposes at a high temperature (>200°C), in contrast to organic analogues, with formation of tetraphenylstannane as the only tin-containing product[278]. Aromatic and aliphatic organotin isocyanates of the type $R_3SnNCO$ are distinguished by an enhanced stability. The latter are stable when acted upon by oxygen, ultraviolet radiation, and prolonged heat up to 200°C. The thermal decomposition of such isocyanates is a complex process, which probably involves both homolytic and heterolytic reactions. The decomposition of tributylstannyl isocyanate takes place at 250°C with the liberation of butane, butene, carbon dioxide, and carbon monoxide and the formation of metallic tin. In the decomposition of triphenylstannyl isocyanate, both disproportionation to tetraphenylstannane and diphenylstannyl di-isocyanate and its decomposition with formation of carbon dioxide and an organotin carbodi-imide were observed[91,163,279]:

$$(C_4H_9)_3SnNCO \begin{cases} \rightarrow C_4H_8 + C_4H_{10} + N_2 + Sn + CO \\ \rightarrow (C_4H_9)_3SnNCNSn(C_4H_9)_3 + CO_2 \end{cases} ;$$
$$(C_6H_5)_3SnNCO \begin{cases} \rightarrow (C_6H_5)_4Sn + [(C_6H_5)_2Sn(NCO)_2] \\ \rightarrow (C_6H_5)_3SnNCNSn(C_6H_5)_3 + CO_2 \end{cases} .$$

Organotin pseudohalides react in different ways with protic reagents. Under the influence of hydrogen chloride, the Sn–N bond in triphenylstannyl isocyanate is cleaved, but only triphenylstannyl chloride (44%) and tetraphenylstannane (33%) could be isolated from the reaction mixture[163]. On the other hand, *NN'*-bis(tributylstannyl)-carbodi-imide is involved in exchange processes with HCl and acetic and benzoic acids under mild conditions, forming the corresponding organotin derivatives and cyanamide[91,280,281]:

$$Bu_3SnNCNSnBu_3 + 2HX \rightarrow 2Bu_3SnR + H_2NCN \ ;$$
$$X{=}Cl,\ MeC(O)O,\ or\ PhC(O)O.$$

In contrast to aminostannanes, typical organotin pseudohalides (monoisocyanates and carbodi-imides) are as a rule comparatively resistant to hydrolysis, which makes it possible to synthesise them via reactions involving the elimination of water. Nevertheless, the hydrolysis of butyl and phenyl organotin di-isocyanate derivatives leads to high-molecular-weight compounds of the type $Bu_8Sn_4(NCO)_4O_2$, $Bu_8Sn_4(NCO)_2(OH)_2O_2$, and $Ph_4Sn(NCO)_2 \cdot (OH)_2$.[65]

Tributylstannyl isocyanate is wholly hydrolysed with formation of tributyltin hydroxide and urea derivatives only when acted upon by boiling water in the course of 28 h. Alkalis appreciably accelerate this process[91]. The Sn–N bond in *NN'*-bis(tributylstannyl)carbodi-imide is cleaved by water under the same conditions[282].

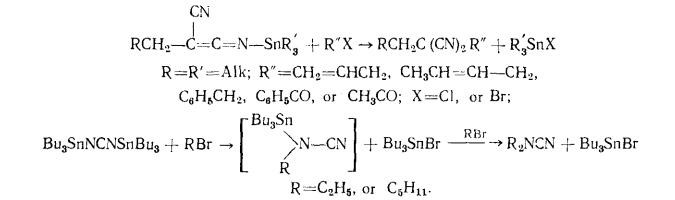
However, dimethyltin di-isocyanate is readily and completely decomposed by water[283]:

$$Me_2Sn(NCO)_2 + 3H_2O \rightarrow (Me_2SnO)_n + CO_2 + 2NH_3 \ .$$

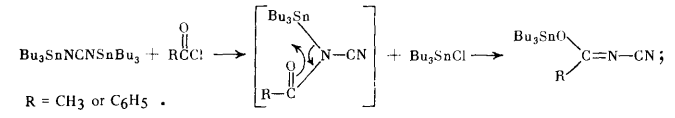
The report that tributylstannyl isocyanate reacts with alcohols and phenols to form organotin carbamates has been confirmed experimentally[160]. It was subsequently established that the adduct obtained when the isocyanate reacts with an excess of methanol or butanol contains the urethane group according to infrared spectroscopic data, but is unstable on heating and cannot be isolated by vacuum distillation[91,284]. When butaneselenol reacts with $Bu_3SnNCO$ in proportions of 2 : 1, the cleavage of the tin–nitrogen bond is accompanied by addition to the isocyanate group and the formation of butylselenourethane[285]:

$$Bu_3SnNCO + 2BuSeH \rightarrow BuSeSnBu_3 + BuSeCNH_2 \ .$$
$$\qquad\qquad\qquad

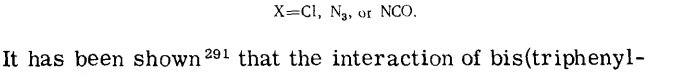
The reactions of tin pseudohalides with various halogeno-derivatives are of interest. Thus alkyl derivatives of organotin isocyanates exchange the isocyanate group for the halogen on heating with alkyl halides. On the other hand, the phenyl analogues are decomposed by ethyl bromide to triphenylstannyl bromide, the isocyanate fragment undergoing complex transformations, whose nature was not elucidated [133,163]. Chlorotrimethylsilane is involved in an exchange interaction with triphenylstannyl isocyanate, giving a high yield of the corresponding silyl isocyanate [172]. *N*-Trialkylstannylketenimines and *NN'*-bis(tributylstannyl)carbodi-imide react vigorously with organic halogeno-derivatives [91,191,280]. The reactions apparently proceed with transfer of the reaction centre:



When a stannylcarbodi-imide and equimolecular amounts of acetyl or benzoyl chloride are used, only one Sn–N bond in the carbodi-imide is cleaved and there is a simultaneous migration of the organotin group to the oxygen atom. As a result, *N*-[tributylstannoxy(methyl or phenyl)-methylidene]cyanamides were obtained instead of the expected *N*-acetyl(or benzoyl)-*N*-(tributylstannyl)cyanamides [289]:

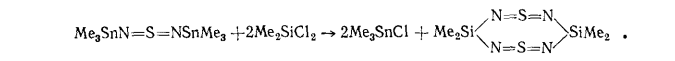


It is of interest that in the case of benzenesulphonyl chloride, azide, and isocyanate which exhibit pseudohalide properties, this process involves the exchange of only one $R_3Sn$ fragment regardless of the proportions of the reactants [181,290]:

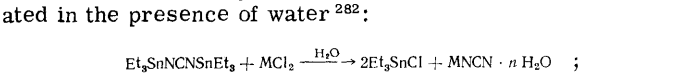


It has been shown [291] that the interaction of bis(triphenylstannyl)carbodi-imide with organic halogeno-derivatives proceeds somewhat differently. On heating with benzyl bromide, this reagent yields an isomerisation product—dibenzylcyanamide. When chlorotriphenylmethane, which has three bulky substituents, is used, the process is accompanied by the formation of a non-isomeric compound—*NN'*-bis(triphenylmethyl)carbodi-imide.

The usual exchange processes take place when *NN'*-bis(trimethylstannyl)sulphodi-imide is treated with chlorotrimethylsilane and dichlorodimethylsilane. In the latter case, the product is an eight-membered cyclic compound containing silicon, sulphur, and nitrogen atoms [179,292]:

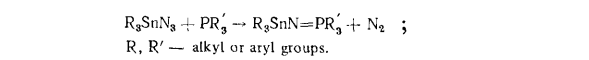


Group II–IV metal chlorides react with *NN'*-bis(triethylstannyl)carbodi-imide, forming triethylstannyl chloride and metal-cyanamides. The reaction is accelerated in the presence of water [282]:



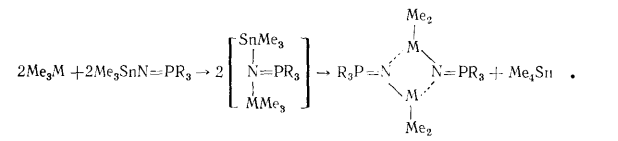
The interaction of organotin imines of the type $Me_3SnN=C(CF_3)_2$ with platinum, rhodium, and iridium halides is accompanied by the formation of metal alkylideneimides [293]. In contrast to this, triphenylstannyl azide forms 1 : 1 adducts with $BBr_3$ and $SnCl_4$. [294]

The reactions of trialkyl(aryl)stannyl azides with aliphatic and aromatic phosphines, which as a rule take place with formation of organotin phosphineimines, have been investigated in fair detail [79,295–297]:

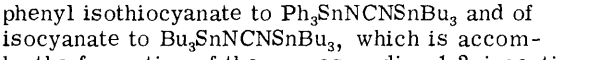


The reaction of $Me_3SnN_3$ with methyl-, ethyl-, and phenyl-phosphines is complicated by disproportionation reactions and also leads to the formation of *N*-azidodimethylstannyl(phosphine)imine, $Me_3Sn(N_3)-N=PR_3$, and tetramethylstannane [295]. Under mild conditions, $Ph_3SnN_3$ does not react with $Ph_3X$ (X = P, As, or Sb). [80]

Organotin phosphine imines are readily decomposed by triethylaluminium, triethylgallium, and triethylindium, which leads to the formation of the dimeric trialkyl-[(dimethylmetal)imino]phosphorane [298].



Bis(triethylgermyl)mercury undergoes an exchange interaction with tributylstannyl isocyanate [299]:



Insertion reactions, which are so typical for aminostannanes, are relatively uncharacteristic of organotin pseudohalides. An example of such reactions is the addition of phenyl isothiocyanate to $Ph_3SnNCNSnBu_3$ and of phenyl isocyanate to $Bu_3SnNCNSnBu_3$, which is accompanied by the formation of the corresponding 1,2-insertion adducts [291,300]. In the latter case, further successive cycloaddition of a second and third isocyanate molecule is observed, which ultimately leads to the formation of an organotin triphenylisoammelide. The addition of tributylstannyl azide to the triple bonds of nitriles and acetylenedicarboxylate esters has been fairly thoroughly investigated, but the reaction proceeds without the cleavage of the Sn–N bond and the function of the azide group under these conditions does not differ from that in organic azides [185,186,301].

In order to investigate the reactivity of the biradical $Ph_3SnN^{\cdot}$, a study was made of the photolysis of aromatic organotin azides, which proceeds with the cleavage of the Sn–N bond and not the N–N bond as suggested by Jappy and Preston [302]. Finally a characteristic property of trialkylstannyl isothiocyanates and dialkyltin di-isothiocyanates is their capacity for complex formation [71,303], with, among others, pyridine, 2,2-bipyridyl, 1,10-phenanthroline and other bases [233,304–306].

The different properties of the pseudohalides and amino-derivatives of tin examined can probably be accounted for by electron redistribution between the tin atom and the $-\ddot{N}=C<$ group, which is highly unsaturated and has lone electron pairs. As a result, the trialkylstannyl fragment passivates the N=C bond in nucleophilic substitution reactions. The addition of a second isocyanate group to the tin atom or of an electron-donating substituent to the nitrogen atom diminishes the degree of

redistribution and thereby increases the reactivity of the Sn–N bond in pseudohalides, which approaches that in aminostannanes. Examples of reactions of these compounds were given above. It is noteworthy that detailed studies have not been made of the influence of different substituents on the Sn–N=A linkage, where A = C, O, P or other elements. The available physicochemical data for the strength of the Sn–N bond are summarised in the next section.

## V. PHYSICOCHEMICAL PROPERTIES AND STRUCTURES OF NITROGEN-CONTAINING ORGANOTIN COMPOUNDS

Systematic investigations of the physicochemical properties of organoelemental compounds containing an Sn–N bond were begun comparatively recently. It is therefore not surprising that the published data are sometimes incomplete and contradictory. There are only isolated publications on many key problems concerning the molecular structures of these derivatives (the geometrical configurations of the molecules, the quantum-mechanical description and determination of the energetic parameters of the Sn-N bond). As a result, the available information about the mechanisms of reactions involving compounds of the above type is extremely limited. The physical characteristics quoted in papers on the synthesis of aminostannanes (melting and boiling points, refractive indices, and densities) can serve only for the estimation of the degrees of purity of the products. These parameters have been arranged systematically [18] and additional data have been published elsewhere [307,308].

The majority of nitrogen-containing organotin compounds are volatile liquids, which permitted the conclusion, also on the basis of infrared, Raman, and NMR spectroscopic data, that the Sn–N bond is covalent in products of this kind [33,103,198,309]. However, the problem of the degree of delocalisation of the unshared electron pair of nitrogen owing to the $d_\pi$–$p_\pi$ interaction still remains open. An attempt has been made [310] to solve it by relating it to the basicity of model compounds of the type $Me_3MNMe_2$ and $(Me_3M)_3N$ (where M = Sn, Ge, or Si).

The relative basicities of the above aminostannanes were investigated in the reactions with $CHCl_3$ and $CDCl_3$, which were regarded as pseudoacids. The shifts $\Delta\nu$(C–D) and $\Delta\nu$(C–H) of the frequencies in the infrared spectra of free $CHCl_3$ and $CDCl_3$ and of their complexes with aminostannanes were correlated with the basicities. It was shown that the basicity decreases in the sequence Sn > Ge > Si and for $Me_3SnNMe_2$ it proved to be equivalent to the basicity of the usual aliphatic amines [310]. On this basis, it was concluded that the lone electron pair of nitrogen is fully localised in aminostannanes. It has been noted [31] that the delocalisation of the electron pair of nitrogen in $Me_3MN(GeMe_3)Me$ (M = Si, Ge, Sn, or Pb), investigated by NMR, decreases in the sequence Si > Ge > Sn > Pb. The same sequence of decreasing basicities of aminostannanes has been found by Mack and Yoder [311]. The number of parameters correlated with the basicities has been extended, but unambiguous results have not been obtained [312,313]. This led to the conclusion that the experimental data fail to confirm the occurrence of $d_\pi$–$p_\pi$ conjugation in organotin amines [313]. However, the considerable polarity of the Sn–N bond has been explained by the delocalisation of the lone electron pair of nitrogen on the basis of measurements of the dipole moments ($\mu$ = 1.7) of the Sn–N bond in a large series of compounds having the general formula $R_{4-n}Sn(NR'_2)_n$ (R = $CH_3$, $C_2H_5$, $C_4H_9$, or $C_6H_5$; R′ = $CH_3$ or $C_2H_5$; $n$ = 1–4). [314] It has been shown that this effect makes a significant contribution to the energy of the Sn–N bond [315]. An appreciable shift of the lone electron pair of nitrogen has also been observed in aromatic fluoro-derivatives of aminostannanes [316].

The thermal stability of aminostannanes decreases in the sequence $R_3SnNR'_2 > RSn(NR'_2)_3 \simeq Sn(NR'_2)_4 > R_2Sn.(NR'_2)_2$. [244] The heat of combustion $-\Delta H^\circ_{c,L}$ = 1883 ± 1 kcal mole$^{-1}$ of liquid $(C_2H_5)_3SnN(C_2H_5)_2$ permitted the calculation of the standard heat of formation of this compound ($-\Delta H^\circ_{f,L}$ = 50 kcal mole$^{-1}$) and the average dissociation energy of the Sn–N bond [$\bar{D}$(Sn–N) = 62 kcal mole$^{-1}$] [317]. The last value is somewhat higher than those of $E$(Sn–N) obtained previously for $(CH_3)_3SnN(CH_3)_2$, $[(CH_3)_3Sn]_2NCH_3$, and $[(CH_3)_3Sn]_3N$, which are 43.5, 48.7, and 40.0 kcal mole$^{-1}$ respectively [11,18]. According to Zhuravlev et al. [318], the energies of the Sn–N bond in tributylstannyl isocyanate and *NN′*-bis(tributylstannyl)carbodi-imide are much greater, amounting to 102 ± 5 and 100 ± 5 kcal respectively, which indicates a differenee in the nature of these bonds in organotin isocyanates and carbodi-imides compared with aminostannanes. The dissociation energy of the M–N bond (M = Si, Ge, or Sn) decreases from Si to Sn [317] (79.9 kcal mole$^{-1}$, [319] 63.4 kcal mole$^{-1}$, [18] and 40 kcal mole$^{-1}$ [18]) which indicates a relatively weak Sn–N bond in aminostannanes.

The successful employment of infrared spectroscopy for the determination of the molecular structures of Sn–N derivatives [33,43,44,116,146,148] and for the investigation of the rates of reactions involving Sn–N bonds [111] has been noted. The absorption bands in spectra of compounds of the type $R_3SnNR'_2$, $(R_3Sn)_2NR'$, and $R_2Sn(NR'_2)_2$ have been calculated and assigned [320]. Nevertheless, it has still not been fully decided whether the stretching vibrations of the Sn–N bonds are characteristic and their bands have not been fully assigned. The frequency $\nu_{asym}$ for $(R_3Sn)_3N$ has been found in the range 712–728 cm$^{-1}$; $\nu_{sym}$ is believed to be below 400 cm$^{-1}$. [33] The 510 cm$^{-1}$ band in the spectrum of $Me_3SnN(Ph)CONMe_2$ has been assigned to $\nu$(Sn–N). [146] In the infrared spectra of $(CH_3)_3SnNH(C_6H_5)$ containing the $^{14}N$ and $^{15}N$ isotopes, the 843 and 835 cm$^{-1}$ bands correspond to $\nu$(Sn–$^{14}$N) and $\nu$(Sn–$^{15}$N) respectively; the 535 and 508 cm$^{-1}$ bands are believed to be due to the $\nu_{sym}$ and $\nu_{asym}$ vibrations of the $SnC_3$ skeleton [321]. Analysis of the infrared and Raman spectra showed in its turn that the skeleton has $C_{3v}$ pyramidal symmetry and not $D_{3h}$ [$C_{3h}$] symmetry [103]. The highly polarised band in the Raman spectrum at 514 cm$^{-1}$ has been assigned to $\nu_{sym}(Sn_3–N)$ and the 672 cm$^{-1}$ band has been assigned to $\nu_{asym}(Sn_3–N)$.

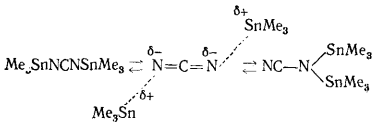
Other examples of the assignment of the bands to the stretching vibrations of the Sn–N bond are as follows: 596 and 592 cm$^{-1}$ for $Ph_3SnN(Ph)P(=NPh)Ph_2$ and $[Ph_3Sn.SnN(Ph)]_2P(=NPh)Ph$ [157]; 880 cm$^{-1}$ for $\nu_{asym}(Sn–N_2)$ in the spectra of $R_2Sn(NR'_2)_2$ [322]; 479, 480, and 472 cm$^{-1}$ for $Me_3SnN(SiMe_3)(CMe_3)$, $R_3SnN[CMe_2(SiMe_3)]$ and $Me_3C.(Me_3Si)NSnMe_2Cl$ respectively [32]; 480 cm$^{-1}$ for $Me_3Sn.NCO$ [323]; $\nu_{asym}$ = 690 cm$^{-1}$ and $\nu_{sym}$ = 602 cm$^{-1}$ in the spectra of $Bu_2Sn(NR_2)_2$ (where R = Me, Et, or Bu). [320] Similar information has also been published elsewhere [33,43,69,86,92,103,313]. One should note the virtually complete absence of publications devoted to studies of the band intensities in the vibrational spectra of nitrogen-containing organotin compounds.

Studies have been made on the NMR spectra of the compounds investigated [31,32,40,57–59,60,61,95,97,98,210,309,312,313,324–326] and on the Mössbauer effect [46,323,327–329]. In all cases, the interpretation of the spectra is consistent with

the proposed molecular structures. Data have also been published for $J_{119}Sn-H$ and $J_{117}Sn-H$ in the Sn–N–C–H systems [30,95,198,309]. For $R_nSn(NEt_2)_{4-n}$ (R = Ph or Me), such interaction was not observed in the range $0 \leq n \leq 3$ [198,309] and band splitting was not observed even at −50°C. [95] However, band splitting in the spectrum of $Et_3SnNMe_2$ was noted at low temperatures, disappearing at 150°C. [324]

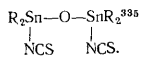
The physicochemical characteristics of nitrogen-containing organotin pseudohalides have been studied much less than the corresponding quantities for aminostannanes. Analysis of the Mössbauer spectra of alkyltin isocyanates has shown that the Sn–N bond is covalent, the tin atom is in the four-coordinated state, and the compounds have the iso-structure [323]. However, $Ph_3SnNCO$ is associated via bridging NCO groups and the tin atom is in the five-coordinated state [327].

Intermolecular coordination has also been suggested for *NN'*-bis(trimethylstannyl)carbodi-imide [330]. According to the authors [88,330], this compound has a structure intermediate between the carbodi-imide, cyanamide, and ionic forms:



However, the study of infrared spectra and dipole moments of organotin ethyl- and butyl-carbodi-imides indicates unambiguously a carbodi-imide structure of such products [90,308].

Investigation of the structures of organotin isothiocyanates by infrared and Mössbauer spectroscopy has shown that the compounds exist in the isocyanate form and that the tin atom is in the five-coordinated state [68,69,331–333]. The occurrence of intermolecular donor–acceptor interactions has been noted also for dimethyltin di-isocyanate, which is a polymer with chains of weakly linked molecules [334], for bis(dicyanamido)dimethylstannane, which has the carbodi-imide structure [86,87], for [polymeric] dibutyltin-carbodi-imidostannane [92], and for distannoxanes of the type



## VI. APPLICATIONS OF NITROGEN-CONTAINING ORGANOTIN COMPOUNDS

The use of nitrogen-containing organotin compounds is in many respects traditional for organotin derivatives, which are widely used in practice as herbicides, disinfectants, polymer stabilisers, and catalysts.

It has been suggested that triphenylstannyl and tributylstannyl isocyanates [1,336], and *NN'*-bis[trialkyl(aryl)-stannyl]carbodi-imides [337,338] be employed as stabilisers of poly(vinyl chloride). The stabilising effect of mixtures of organic phosphines with trialkyl(aryl)stannyl isocyanates and isothiocyanates in the thermal degradation of poly(vinyl chloride) has been studied in detail [339,340]. Aminostannanes are suitable for the stabilisation of rubbers [2,3] and as fungicides, bactericides, and herbicides [8,9,37], and plasticisers [7]. It has been suggested that organic carbodi-imides be synthesised via amino-derivatives of tin [262]. Numerous data have been obtained on the applications of the compounds under consideration in the catalysis of the reactions of isocyanates with compounds having an active hydrogen atom [4–6,341,342]. It has been shown [343] that, when the reaction of butyl isocyanate with phenol is acted upon jointly by organotin compounds and amines as catalysts, a synergistic effect is observed. The use of tin- and nitrogen-containing compounds as catalysts of the synthesis of urethanes [344] instead of the familiar organotin derivatives of aliphatic acids can be definitely economical in view of the low cost and high availability of initial nitrogen-containing products such as amines, urea, cyanuric acid, and their derivatives, compared with organic acids.

The applications of aminostannanes and their analogues have not been studied widely because convenient preparative methods for their synthesis became available comparatively recently.

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