975. *Organometallic Reactions. Part I.*[1] *The Addition of Tin Alkoxides to Isocyanates*

By A. J. Bloodworth and Alwyn G. Davies

Reactions involving the addition of a metallic compound (M–X) to a multiple bond (A=B) are reviewed, and it is suggested that processes of this type, where, *e.g.*, X = oxygen or nitrogen, are much more general than is commonly appreciated.

In preliminary experiments, adducts have been obtained between trialkyltin alkoxides or bis(trialkyltin) oxides (M = tin, X = oxygen), and the following acceptor molecules (A=B): isocyanates, isothiocyanates, aldehydes, nitriles, carbon dioxide, carbon disulphide, sulphur dioxide, carbodi-imides, and ketens.

The alkyl trialkylstannylcarbamates, obtained by adding trialkyltin alkoxides to isocyanates, are described in detail. Their rapid formation, and rapid reaction with protic reagents, may account in part for the catalytic action which tin compounds have on the formation of urethanes.

Equation (1) defines a reaction in which a metallic compound (M = a metal, X = a relatively electronegative group) adds to a multiply-bonded acceptor molecule (A=B), perhaps reversibly:

$$\text{M–X} + \text{A=B} \rightleftharpoons \text{M–A–B–X} \qquad (1)$$

Insofar as X is limited to carbon or to hydrogen, this is a very familiar process. For example, a Grignard reagent (M = magnesium, X = carbon) will add to a carbonyl group (A = oxygen, B = carbon) to give the precursor of an alcohol; or diborane (M = boron, X = hydrogen) will add to an olefin (A = B = carbon) to give an alkylborane.

Processes of this general type are much less familiar, however, when X is a more electronegative element such as oxygen, nitrogen, sulphur, or a halogen. Isolated examples can be quoted where the reaction follows, or appears to follow, equation (1), but these reactions have never been studied systematically, nor assumed the same synthetic importance as those of the metal alkyls or hydrides.

When the present work was started, the more important examples that we were aware of in the literature were as follows.

In Group IV, the addition of trialkylsilyldialkylamines to carbon dioxide and (reversibly) to carbon disulphide, giving trialkylsilyl *NN*-dialkylcarbamates (I) and *NN*-dialkyldithiocarbamates (II), had been demonstrated by Breederveld[2] [equation (2)]; in recent months, this has been extended to other acceptor molecules by other workers.[3] *

$$\underset{\text{(I)}}{Me_3Si{\cdot}O{\cdot}CO{\cdot}NEt_2} \xleftarrow{CO_2} Me_3Si{\cdot}NEt_2 \overset{CS_2}{\rightleftharpoons} \underset{\text{(II)}}{Me_3Si{\cdot}S{\cdot}CS{\cdot}NEt_2} \qquad (2)$$

Lutsenko and his co-workers had shown that trialkyltin alkoxides would add to keten

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* Very recently, in Groups V and VI, Oertel and his co-workers[4] have demonstrated the addition of the P–N and As–N bond to carbon disulphide, carbon dioxide, isocyanates, and isothiocyanates, and the S–N bond to carbon disulphide, isocyanates, and isothiocyanates.

[1] A preliminary account of some of this work has been given by A. J. Bloodworth and **A. G.** Davies, *Proc. Chem. Soc.*, 1963, 264, 315.

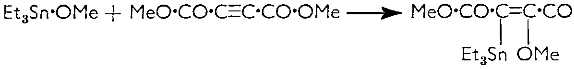
[2] H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 1126; 1962, **81**, 276.

[3] To isocyanates by (*a*) G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891; (*b*) W. Fink, *Chem. Ber.*, 1964, **97**, 1424, 1433; (*c*) J. F. Klebe, J. B. Bush, and J. E. Lyons, *J. Amer. Chem. Soc.*, 1964, **86**, 4400; (*d*) D. J. Zhinken, M. M. Morgunova, K. K. Popkov, and K. A. Andrianov, *Doklady Akad. Nauk, S.S.S.R.*, 1964, **158**, 641; to aldehydes by (*e*) D. L. Birkofer and H. Dickopp, *Angew. Chem. Internat. Ed.*, 1964, **3**, 514.

[4] G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891; G.P., **1,155,433** (*Chem. Abs.*, 1964, **60**, 2823); see also H. J. Vetter and H. Nöth, *Z. Naturforsch.*, 1964, **19**b, 167.

to give alkyl trialkylstannylacetates [equation (3)],[5] and to acetylenedicarboxylic esters to give the adducts (III).[6]

$$\mathrm{R_3Sn{\cdot}OR' + CH_2{=}C{=}O \longrightarrow R_3Sn{\cdot}CH_2{\cdot}CO{\cdot}OR'} \qquad (3)$$



$$\mathrm{Et_3Sn{\cdot}OMe + MeO{\cdot}CO{\cdot}C{\equiv}C{\cdot}CO{\cdot}OMe \longrightarrow MeO{\cdot}CO{\cdot}\underset{Et_3Sn}{C}{=}\underset{OMe}{C}{\cdot}CO{\cdot}OMe} \qquad (4)$$

(III)

In Group III there appears to be no clear-cut example of additions involving M–O or M–N bonds, although the Tischenko reaction can reasonably be interpreted in terms of a preliminary addition of an aluminium alkoxide to an aldehyde.[7] Additions involving boron–halogen bonds, however, are known, as illustrated in equations (5) [8] and (6).[9]

$$\mathrm{BCl_3 + O{=}CH{\cdot}CHCl_2 \longrightarrow B(O{\cdot}CHCl{\cdot}CHCl_2)_3} \qquad (5)$$

$$\mathrm{BCl_3 + PhN{=}C{=}O \longrightarrow ClB(NPh{\cdot}CO{\cdot}Cl)_2} \qquad (6)$$

In Group II, additions of the magnesium–nitrogen bond to carbon dioxide, aldehydes, and nitriles are known [equations (7)—(9)].[10]

$$\mathrm{PhMeN{\cdot}MgI + CO_2 \longrightarrow PhMeN{\cdot}CO_2MgI} \qquad (7)$$

$$\mathrm{PhHN{\cdot}MgBr + Ph{\cdot}CHO \longrightarrow Ph{\cdot}CH(O{\cdot}MgBr)NH{\cdot}Ph} \qquad (8)$$

$$\mathrm{Et_2N{\cdot}MgBr + Et_2N{\cdot}C{\equiv}N \longrightarrow Et_2NC({=}NMgBr)NEt_2} \qquad (9)$$

Compounds of mercury have received more attention and examples of the addition of mercuric acetate in methanol to olefins,[11] of mercuric methoxide to keten,[12] of methylmercuric oxide to carbon dioxide [13] and carbon disulphide,[14] and of phenylmercuric sulphide to carbon disulphide [15] are well established.

$$\mathrm{Hg(OAc)_2 + CH_2{=}CH_2 \xrightleftharpoons{MeOH} AcO{\cdot}Hg{\cdot}CH_2{\cdot}CH_2{\cdot}OMe} \qquad (10)$$

$$\mathrm{Hg(OMe)_2 + CH_2{=}C{=}O \longrightarrow Hg(CH_2{\cdot}CO{\cdot}OMe)_2} \qquad (11)$$

$$\mathrm{(MeHg)_2O + CO_2 \longrightarrow MeHg{\cdot}O{\cdot}CO{\cdot}O{\cdot}HgMe} \qquad (12)$$

$$\mathrm{(RHg)_2O + CS_2 \xrightarrow{MeOH} RHg{\cdot}S{\cdot}CS{\cdot}OMe} \qquad (13)$$

$$\mathrm{(PhHg)_2S + CS_2 \longrightarrow (PhHg{\cdot}S)_2CS} \qquad (14)$$

Allied to the addition reactions of equation (1) is a series of metathetical reactions of metallic compounds with singly-bonded reagents A–B. Equation (15) illustrates the reaction of a metallic compound M–X; equally the metallic compound could be the adduct between M–X and A=B.

$$\mathrm{M{-}X + A{-}B \longrightarrow M{-}A + B{-}X} \qquad (15)$$

Often A–B is a protic reagent (B = hydrogen), and the alkyls, hydrides, oxides, alkoxides, dialkylamines, dialkylphosphines, alkylsulphides, etc., of most non transition metals are susceptible to acidolysis under appropriate conditions.

Some typical examples of the less familiar case where X $\neq$ carbon, and B $\neq$ hydrogen, are illustrated in equations (16—21) (refs. 16—21, respectively).

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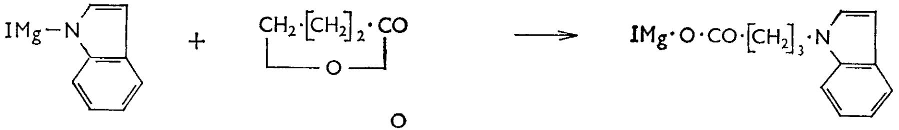
[5] I. F. Lutsenko and S. V. Ponomarev, *Zhur. obshchei Khim.*, 1961, **31**, 2025.
[6] I. F. Lutsenko, S. V. Ponomarev, and O. P. Petrii, *Zhur. obshchei Khim.*, 1962, **32**, 896.
[7] J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, 1961, **44—46**, 398.
[8] M. J. Frazer, W. Gerrard, and M. F. Lappert, *J.*, 1957, 739.
[9] M. F. Lappert and B. Prokai, *J.*, 1963, 4223.
[10] Reviewed by P. A. Petyunin, *Russ. Chem. Rev.*, 1962, **31**, 100.
[11] Reviewed by J. Chatt, *Chem. Rev.*, 1951, **48**, 7.
[12] I. F. Lutsenko, V. L. Foss, and I. L. Ivanova, *Proc. Acad. Sci.* (*U.S.S.R.*), 1961, **141**, 1270.
[13] D. Grdenic and F. Zabo, *J.*, 1962, 521.
[14] I. A. Koten and R. Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 2764.
[15] L. Pesci, *Gazzetta*, 1899, **29**, 394.
[16] J. Valade and M. Pereyre, *Compt. rend.*, 1962, **254**, 3693.
[17] R. C. Mehrotra and K. C. Pande, *Z. anorg. Chem.*, 1957, **290**, 95.
[18] A. G. Davies and J. E. Packer, *J.*, 1959, 3164.
[19] E. W. Abel, D. Brady, and B. R. Lerwill, *Chem. and Ind.*, 1962, 1333.
[20] F. N. Stepanov, Russ. P., 66,681 (*Chem. Abs.*, 1947, **41**, 2087.)
[21] A. J. Bloodworth and A. G. Davies, unpublished work.

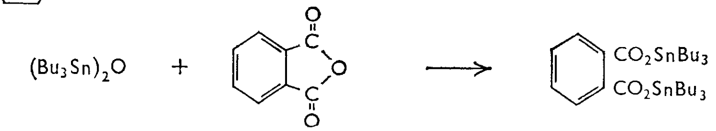
$$Bu_3Sn{\cdot}OMe + Cl{\cdot}CO{\cdot}Me \longrightarrow Bu_3Sn{\cdot}Cl + Me{\cdot}CO{\cdot}OMe \qquad (16)$$

$$Ti(OPr^i)_4 + (Me{\cdot}CO)_2O \longrightarrow Ti(OPr^i)_3{\cdot}O{\cdot}CO{\cdot}Me + Me{\cdot}CO{\cdot}OPr^i \qquad (17)$$

$$Cd(O{\cdot}OEt)_2 + o\text{-}C_6H_4(CO{\cdot}Cl)_2 \longrightarrow CdCl_2 + o\text{-}C_6H_4(CO{\cdot}O{\cdot}OEt)_2 \qquad (18)$$

$$Me_3Si{\cdot}NHEt + Me_3SnBr \longrightarrow Me_3SiBr + Me_3Sn{\cdot}NHEt \qquad (19)$$


(20)


(21)

We believe that addition reactions of the type defined by equation (1) (X = *e.g.*, O or N) are much more general than is commonly appreciated, and that they may provide synthetic methods comparable in importance with the established reactions of metal alkyls or metal hydrides. In this Paper we describe a preliminary investigation of the addition of trialkyltin alkoxides and of bis(trialkyltin) oxides to nine different types of acceptor molecule, and deal in detail with the adducts formed between trialkyltin alkoxides and isocyanates. In later Parts of this Series we hope to discuss some of the other addition processes, and similar reactions involving other metals.

DISCUSSION

The Reaction Sn–O + A=B $\rightleftharpoons$ Sn–A–B–O.—In preliminary experiments we established that the Sn–O bond of trialkyltin alkoxides or of bis(trialkyltin) oxides will add to isocyanates, isothiocyanates, aldehydes, nitriles, carbon dioxide, carbon disulphide, sulphur dioxide, carbodi-imides, and ketens, to give 1 : 1 adducts which apparently have the structures shown in Table 1.* The course of the reaction was usually followed by the disappearance of the strong infrared absorption of the multiply-bonded acceptor molecule, and, when appropriate, by the characteristic change in the proton magnetic resonance

TABLE 1

Products of the reactions Sn–O + A=B ⟶ Sn–A–B–O

A=B \ SnO	$R_3Sn{\cdot}OR'$	$R_3Sn{\cdot}O{\cdot}SnR_3$
R–N=C=O	$Et_3Sn{\cdot}NNp{\cdot}CO{\cdot}OEt$	$Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}OSnBu_3$
R–N=C=S	$Bu_3Sn{\cdot}S{\cdot}C(OMe)=NPh$	[a]
O=CH–R	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3)OMe$	$Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}OSnBu_3$
N≡C–R	$Bu_3Sn{\cdot}N=C(CCl_3)OMe$	$Bu_3Sn{\cdot}N=C(CCl_3)OSnBu_3$
O=C=O	$Bu_3Sn{\cdot}O{\cdot}CO{\cdot}OMe$	$Bu_3Sn{\cdot}O{\cdot}CO{\cdot}OSnBu_3$
S=C=S	$Bu_3Sn{\cdot}S{\cdot}CS{\cdot}OMe$	[b]
O=S=O	$Bu_3Sn{\cdot}O{\cdot}SO{\cdot}OMe$	$Bu_3Sn{\cdot}O{\cdot}SO{\cdot}OSnBu_3$
RN=C=NR	$Bu_3Sn{\cdot}NNp{\cdot}C(=NNp)OMe$	$Bu_3Sn{\cdot}NPhC(=NPh)OSnBu_3$
$R_2C=C=O$	$Bu_3Sn{\cdot}CH_2{\cdot}CO{\cdot}OMe$ [5, 22]	$Bu_3Sn{\cdot}CMe_2{\cdot}CO{\cdot}OSnBu_3$ [c]

Np = 1-Naphthyl.

[a] Bis(tributyltin) oxide gives bis(tributytin) sulphide and the oxide–phenyl isocyanate adduct [b] Oxygen–sulphur exchange again occurs, giving again bis(tributyltin) sulphide and an adduct of COS or CO_2. [c] From the dimethylmalonic acid–dimethylketen acylal.[23]

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* Our attention was drawn to the possibility of these reactions by the following facts: (*a*) bottles of bis(tributyltin) oxide and of tributyltin methoxide developed, round the stopper, crystals which had carbonyl-group absorption in the infrared; (*b*) Lutsenko[12] demonstrated the addition of mercuric methoxide to keten, and (*c*) tin compounds catalyse the addition of alcohols to isocyanates, which are isoelectronic with ketens.

[22] A. G. Davies and I. F. Graham, unpublished work.

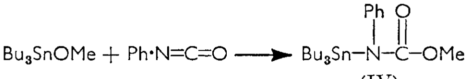
[23] G. Holder, personal communication.

spectrum. The additions, with the exception of those involving nitriles, occur very rapidly and exothermically at room temperature; the yields of the adducts are almost quantitative, and most of them have been isolated analytically pure.

A similar but less extensive series of reactions of the Sn–N bond in trialkyltin dialkylamines has been demonstrated by Jones and Lappert.[24] There is clearly a broad parallelism between the addition reactions of the Sn–O and Sn–N bonds, and those of the Mg–C bonds of Grignard reagents.

In this Paper we describe the addition of trialkyltin alkoxides to isocyanates to form alkyl *N*-trialkylstannylcarbamates; subsequent Parts of this Series will describe the other adducts.

The Reaction $R_3Sn{\cdot}OR' + R''N{=}C{=}O \longrightarrow R_3Sn{\cdot}NR''{\cdot}CO{\cdot}OR'$.—The reaction between trialkyltin alkoxides and isocyanates at room temperature is rapid and exothermic, and the stannylcarbamates [*e.g.*, (IV)] which are formed can be isolated pure by distillation under reduced pressure (see Table 2).



$$Bu_3SnOMe + Ph{\cdot}N{=}C{=}O \longrightarrow Bu_3Sn{-}\underset{}{\overset{Ph}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OMe \qquad (22)$$

(IV)

The reaction of dialkyltin dialkoxides is clearly similar, but the products have not yet been isolated analytically pure, partly because they appear to be more sensitive to moisture. Tributyltin phenoxide adds to phenyl isocyanate to give the phenyl trialkylstannylcarbamate, but this adduct is now thermally unstable, dissociating to its factors at 100° (bath)/0·01 mm.

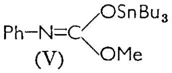
TABLE 2

Alkyl trialkylstannylcarbamates

Compound	B. p./mm.	Required C	Required H	Required N	Found C	Found H	Found N	$\nu_{C=O}$ cm.$^{-1}$
$Et_3Sn{\cdot}NBu{\cdot}CO_2Et$	57·5°/0·01	44·6	8·3	4·0	45·6	8·8	4·1	1635s 1690vs
$Et_3Sn{\cdot}NNp{\cdot}CO_2Et$	104—108/0·05 [a]	54·3	6·5	3·3	53·9	6·5	3·6	1650vs (broad)
$Bu_3Sn{\cdot}NPh{\cdot}CO_2Me$	98—100/0·01	54·6	8·0	3·2	54·4	8·1	3·3	1660vs 1690vs
$Bu_3Sn{\cdot}NNp{\cdot}CO_2Me$	120/0·01	58·8	7·6	2·9	58·8	7·9	3·0	1655vs 1690s
$Bu_3Sn{\cdot}NPh{\cdot}CO_2Ph$ [c]	Solid [b]	59·8	7·4	2·8	58·2	7·7	2·9	1675vs (broad)
$Bu_3Sn{\cdot}NEt{\cdot}CO_2Me$ [d]	89—90/0·05	49·0	9·0	3·55	49·7	9·15	2·0	1660vs 1695vs
$Bu_3Sn{\cdot}NMe{\cdot}Co_2Me$	101·5/0·05	47·65	8·8	3·7	48·45	9·15	3·95	1660vs 1695vs

[a] M. p. 86—93° (sealed tube). [b] Dissociates on distillation. [c] Sn, Found, 23·7. Required, 24·8%. [d] The product was identical with the analytically pure compound prepared by Mr. W. R. Symes. We cannot account for the poor nitrogen analysis.

In equation (22) and Table 2, we have assumed that the addition to the Sn–O bond occurs across the N=C group, rather than across the C=O group to give the isomeric structure, *e.g.*, (V). The evidence as to which is correct is in fact by no means clear. The adducts absorb strongly in the infrared at 1635—1690 cm.$^{-1}$ but this cannot be assigned with confidence to the N=C or C=O group, because the stretching frequency in model compounds overlaps, and little is known about the effect that the tin atom would have on these frequencies. Lappert and Prokai[9] suggested that the B–Cl bond added across the N=C group in isocyanates [equation (6)] and it is usually accepted that the Si–N bond adds in the same manner, but in neither case is the evidence very convincing.



(V)

In their reactions (see below) the alkyl stannylcarbamates behave as though they had the structure (IV) rather than (V) but chemical reactions may here be a particularly poor

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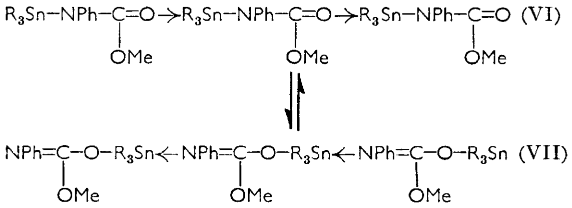
[24] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1962, 358; 1964, 22.

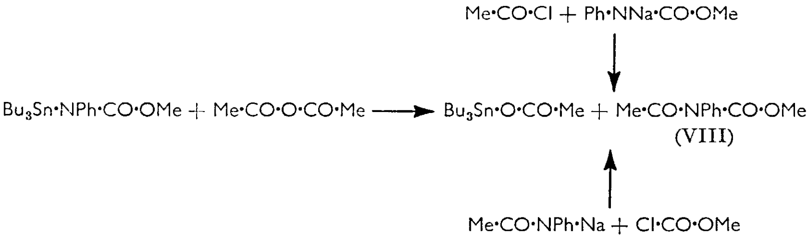
criterion of structure.* There is evidence that trialkyltin carboxylates, under some conditions, can associate through the carbonyl group giving the system a three-fold axis of symmetry about the trialkyltin group. If a similar association obtained with the stannylcarbamates, it could provide an easy route for the interconversion of the structures (VI) and (VII), or, in the extreme, render their two formulations equivalent.



$$\begin{array}{c} R_3Sn{-}NPh{-}\underset{\overset{|}{OMe}}{C}{=}O \rightarrow R_3Sn{-}NPh{-}\underset{\overset{|}{OMe}}{C}{=}O \rightarrow R_3Sn{-}NPh{-}\underset{\overset{|}{OMe}}{C}{=}O \quad \text{(VI)} \\ \Downarrow\!\Uparrow \\ NPh{=}\underset{\overset{|}{OMe}}{C}{-}O{-}R_3Sn \leftarrow NPh{=}\underset{\overset{|}{OMe}}{C}{-}O{-}R_3Sn \leftarrow NPh{=}\underset{\overset{|}{OMe}}{C}{-}O{-}R_3Sn \quad \text{(VII)} \end{array} \qquad (23)$$

Until evidence to the contrary may be forthcoming, we choose to regard the adducts as *N*-stannylcarbamates [*e.g.*, (IV)] recognising that the interconversion between this and the alternative structure [*e.g.*, (V)] is probably an easy process.

Reactions of the Stannylcarbamates.—Methyl *N*-phenyl-*N*-tributylstannylcarbamate reacted with acetic anhydride at room temperature to give methyl *N*-acetyl-*N*-phenylcarbamate which has unambiguously the structure (VIII) as it can be obtained both by treating acetyl chloride with the sodium derivative of methyl *N*-phenylcarbamate, or methyl chloroformate with the sodium derivative of acetanilide. This is a further example of a metathetical reaction of an organometallic compound, as generalised in equation (15).



$$\begin{tikzcd} & Me{\cdot}CO{\cdot}Cl + Ph{\cdot}NNa{\cdot}CO{\cdot}OMe \arrow[d] \\ Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}OMe + Me{\cdot}CO{\cdot}O{\cdot}CO{\cdot}Me \arrow[r] & Bu_3Sn{\cdot}O{\cdot}CO{\cdot}Me + Me{\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}OMe \ \text{(VIII)} \\ & Me{\cdot}CO{\cdot}NPh{\cdot}Na + Cl{\cdot}CO{\cdot}OMe \arrow[u] \end{tikzcd} \qquad (24)$$

The stannylcarbamates react very rapidly at the Sn–N bond with most protic reagents. All were very readily hydrolysed by water, and the adduct from dibutyltin dimethoxide and phenyl isocyanate appeared to be particularly reactive. This hydrolysis could be observed by the appearance of absorption bands at 3280 and 1710cm.$^{-1}$ if the specimen, on sodium chloride plates, was exposed to air.

Acetic acid, hydrogen sulphide, ethanol, and methanol similarly convert the *N*-stannylcarbamates into the corresponding tin derivatives and urethanes within a few seconds.

The reaction with ethylamine, however, was very slow, and involved fission of both the Sn–N and C–O bonds. In the course of 3 days, methyl *N*-phenyl-*N*-tributylstannylcarbamate and ethylamine gave *N*-ethyl-*N*′-phenylurea and tributyltin methoxide. The order in which the two metathetical processes occur is not clear, and either the combination shown in equation (25) or (26) would appear to be reasonable.

$$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}OMe + EtNH_2 \longrightarrow Bu_3Sn{\cdot}NHEt + PhNH{\cdot}CO{\cdot}OMe \longrightarrow PhNH{\cdot}CO{\cdot}NHEt + Bu_3Sn{\cdot}OMe \qquad (25)$$

$$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}OMe + EtNH_2 \longrightarrow Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}NHEt + MeOH \longrightarrow PhNH{\cdot}CO{\cdot}NHEt + Bu_3Sn{\cdot}OMe \qquad (26)$$

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* The reactions described here are metathetical processes which can be generalised by the equation $M{-}A{-}B{-}X + A'{-}B' \longrightarrow M{-}A' + B'{-}A{-}B{-}X$. We have also investigated a number of further addition processes represented by the equation $M{-}A{-}B{-}X + A' = B' \longrightarrow M{-}A'{-}B'{-}A{-}B{-}X$; [21, 25, 26] here too, the stannylcarbamates react through the structure (IV).

[25] A. J. Bloodworth and A. G. Davies, *Chem. Comm.*, 1965, 24.

[26] A. G. Davies and W. R. Symes, *Chem. Comm.*, 1965, 25.

The rapid reaction of the stannylcarbamates with alcohols [*e.g.*, equation (28) is particularly interesting in view of the known effect of tin compounds in catalysing the formation of urethanes from alcohols and isocyanates [*e.g.*, equation (29)].[27] For example, 10 moles-% of dibutyltin diacetate accelerates the reaction between n-butanol and phenyl isocyanate by a factor of 600,000, and in the Experimental section we describe a similar catalysis by tributyltin phenoxide and by bis(tributyltin) oxide on the addition of phenol.

The work reported here suggests that one possible mechanism for this catalysis, which does not appear to have been considered before, is that the tin compound reacts with the alcohol (or phenol) to give a small amount of the tin alkoxide; this then rapidly adds to the isocyanate to give the stannylcarbamate [*e.g.*, equation (27)] which rapidly undergoes protolysis forming the urethane and regenerating the catalytic alkoxide [equation (28)].*

$$Bu_3Sn{\cdot}OEt + PhNCO \longrightarrow Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}OEt \quad (27)$$

$$Bu_3Sn{\cdot}NPh{\cdot}CO{\cdot}OEt + EtOH \longrightarrow Bu_3SnOEt + PhNH{\cdot}CO{\cdot}OEt \quad (28)$$

$$PhNCO + EtOH \xrightarrow{Sn^{IV}} PhNH{\cdot}CO{\cdot}OEt \quad (29)$$

EXPERIMENTAL

Compounds containing the Sn–O or Sn–N bond were stored and manipulated under dry nitrogen.

Proton magnetic resonance spectra were recorded on a Perkin-Elmer instrument at 60 Mc./sec. The specimen, under dry nitrogen, was sealed in the sample tube by a self-sealing rubber cap, through which reagents could be injected by syringe.

Organotin Alkoxides.—Triethyltin ethoxide, b. p. 30°/0·2 mm., tributyltin methoxide, b. p. 75°/0·15 mm., n_D^{19} 1·4773, and dibutyltin dimethoxide, b. p. 119°/1·5 mm., were prepared as described by Alleston and Davies.[29] *Tributyltin phenoxide*, b. p. 124°/0·01 mm., was obtained in good yield by adding tributyltin chloride (32·5 g.) in benzene (30 c.c.) to sodium phenoxide [from sodium (2·3 g.), phenol (9·4 g.), and methanol (12 c.c.)] in benzene (Found: C, 56·4: H, 8·3. $C_{18}H_{32}OSn$ requires C, 56·4; H, 8·4%).

The Addition of Tin Alkoxides to Isocyanates.—The following preparation of *methyl* N-1-*naphthyl*-N-*tributylstannylcarbamate* is typical.

1-Naphthyl isocyanate (1·7 g.) was added to tributyltin methoxide (3·21 g.). Much heat was evolved, and the mixture became viscous; the infrared spectrum showed the absence of the isocyanate band at 4·4 μ. Distillation gave methyl *N*-1-naphthyl-*N*-tributylstannylcarbamate, b. p. 119°/0·01 mm., in 90% yield.

There was no obvious difference between the reactivities of alkyl or aryl isocyanates. Dibutyltin dimethoxide reacted, if anything, more readily than tributyltin methoxide; tributyltin phenoxide reacted less exothermically, but still very rapidly.

Details of the various trialkylstannylcarbamates, all of which are new compounds, are given in Table 2.

Preparation of Methyl N-*Acetyl*-N-*phenylcarbamate.*†—(a) *From methyl* N-*phenylcarbamate.* Methyl *N*-phenylcarbamate (5·0 g.) in benzene (50 c.c.) was heated under reflux with sodium (0·8 g.) for 1·5 hr. giving a white suspension of the sodium derivative. Acetyl chloride (1·1 g.) in benzene (40 c.c.) was slowly added with cooling and stirring, and the mixture then boiled under reflux for 15 min. The benzene was distilled off, and the residue extracted with benzene giving *methyl* N-*acetyl*-N-*phenylcarbamate* (1·6 g.) which was recrystallised from ethanol, m. p. 110·5° (Found: C, 62·2; H, 5·5. $C_{10}H_{11}NO_3$ requires C, 62·2; H, 5·7%), ν(C=O) 1750 and 1700 cm.$^{-1}$.

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* On the same basis, it might be expected that organotin compounds would catalyse the addition of suitable protic reagents to other of the acceptor molecules of Table 1, and we have demonstrated such catalysis in the reaction of alcohols with carbodi-imides.[28]

† We are grateful to Mr. R. N. Joanes for carrying out these two experiments.

[27] Reviewed by (*a*) A. Farkas and G. A. Mills, *Adv. Catalysis*, 1962, **13**, 363; (*b*) J. H. Saunders and K. C. Frisch, " Polyurethanes: Chemistry and Technology. Part I. Chemistry," Interscience, New York, 1962, ch. IV.

[28] A. J. Bloodworth, A. G. Davies, and J. A. Easterbrook, unpublished work.

[29] D. L. Alleston and A. G. Davies, *J.*, 1962, 2050.

(b) *From acetanilide.* Sodium (1 g.) reacted with acetanilide (6 g.) in boiling benzene (60 c.c.) during 1 hr. Methyl chloroformate (4·5 c.c.) in benzene (50 c.c.) was then added with cooling and stirring, then the mixture was heated under reflux for 15 min. The benzene was evaporated off, and the residue extracted with benzene giving methyl *N*-acetyl-*N*-phenylcarbamate, m. p. 106—109°, with an infrared spectrum identical with that of the previous specimen.

Reaction of Methyl N-*Phenyl*-N-*tributylstannylcarbamate with Acetic Anhydride.*—A slight excess of acetic anhydride (0·48 c.c.) was added to methyl *N*-phenyl-*N*-tributylstannylcarbamate [prepared from tributyltin methoxide (1·64 g.) and phenyl isocyanate (0·57 c.c.)]. The infrared spectrum of the mixture showed that a slow reaction occurred, and the mixture solidified during 3 days. The excess of acetic anhydride was removed under reduced pressure. A little light petroleum was added, and the solid filtered off and sublimed at 85—90° (bath)/0·02 mm. giving methyl *N*-acetyl-*N*-phenylcarbamate (0·48 g.), m. p. and mixed m. p. 108—109°, the identity of which was checked by the infrared and proton magnetic resonance spectra.

The filtrate was evaporated and the residue washed with light petroleum (1 c.c.) and then sublimed at 85° (bath)/0·02 mm. The first fraction was tributyltin acetate, which was recrystallised from light petroleum, and identified by its m. p. and mixed m. p. (85·5—86·5°), and by its infrared spectrum.

In contrast, methyl *N*-ethyl-*N*-tributylstannylcarbamate did not react with phthalic anhydride during 3 days, although tributyltin methoxide reacts rapidly and exothermically, giving methyl tributylstannylphthalate.

Reaction of Trialkylstannylcarbamates with Protic Reagents.—Methyl *N*-1-naphthyl-*N*-tributylstannylcarbamate in pentane was shaken with a few drops of water; methyl *N*-1-naphthylcarbamate, m. p. 124°, was precipitated within a few seconds. Acetic acid similarly gave the urethane (crude, m. p. 119—125°, recrystallised from chloroform, m. p. 121—123°), and tributyltin acetate, m. p. 84—84·5°. Ethanolysis, similarly, in a few seconds gave urethane and tributyltin ethoxide, b. p. *ca.* 98°/0·01 mm. (Found: C, 49·4; H, 9·1. Calc. for $C_{14}H_{32}OSn$: C, 50·2; H, 9·6%).

Hydrogen sulphide was bubbled through a solution of methyl *N*-phenyl-*N*-tributylstannylcarbamate in pentane. After about 1 min. methyl *N*-phenylcarbamate, m. p. 43—45°, was precipitated. The filtrate contained an evil-smelling oil, probably a mixture of bis(tributyltin) sulphide and tributyltin hydrosulphide; with acetic acid, it gave hydrogen sulphide and tributyltin acetate.

Reaction of Methyl N-*Phenyl*-N-*tributylstannylcarbamate with Ethylamine.*—Methyl *N*-phenyl-*N*-tributylstannylcarbamate (0·737 g.) in carbon tetrachloride (0·5 c.c.) was treated with ethylamine (0·0768 g.). The proton magnetic resonance spectrum showed that the reaction was complete after 3 days, and suggested that *N*-ethyl-*N'*-phenylurea was being formed. The solvent was removed under reduced pressure, and the mixture was cooled, when the urea (m. p. 100—101°, mixed m. p. 99—101°) slowly separated. The infrared spectrum of the remaining oil indicated the presence of tributyltin methoxide, which was identified by its reaction with phthalic anhydride.

It is interesting that the tributyltin methoxide confers solubility upon the urea and prevents its being precipitated from carbon tetrachloride. We confirmed that *N*-ethyl-*N'*-phenylurea (0·245 g.) is insoluble in carbon tetrachloride (1 c.c.) but readily dissolves in the presence of tributyltin methoxide (0·479 g.) when gently warmed.

Catalysis of Urethane Formation.—This is exemplified by the addition of phenol to phenyl isocyanate.

Phenol (0·81 g.) and phenyl isocyanate (1·03 g., 1 mol.) were mixed; the infrared spectrum showed that virtually no reaction occurred during 17 hr. Tributyltin phenoxide (3 drops) was then added. After 2—3 min. the flask became very hot, and the contents set to a solid mass. This was extracted with hot benzene, yielding phenyl *N*-phenylcarbamate, m. p. 124·5—125·5°. Bis(tributyltin) oxide had a similar catalytic effect.

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