1162. *Organometallic Reactions. Part II.*[1] *The Addition of Bistrialkyltin Oxides to Isocyanates*

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Bistrialkyltin oxides react exothermically with isocyanates giving trialkyltin *N*-trialkylstannylcarbamates. If these are treated with the appropriate primary amine and then carbon dioxide, the corresponding trialkyltin carbamate is formed.

$$(R_3Sn)_2O + R'{\cdot}NCO \longrightarrow R_3Sn{\cdot}NR'{\cdot}CO_2{\cdot}SnR_3 \xrightarrow[(2)\ CO_2]{(1)\ R'NH_2} 2R'NH{\cdot}CO_2{\cdot}SnR_3$$

The properties of both types of carbamate are described. Both are decarboxylated when heated to give bistrialkylstannylureas, $R_3Sn{\cdot}NR'{\cdot}CO{\cdot}NR'{\cdot}SnR_3$.

PART I [1] described the addition of trialkyltin alkoxides to isocyanates to give alkyl *N*-trialkylstannylcarbamates, $R_3Sn{\cdot}NR'{\cdot}CO{\cdot}OR''$. A similar reaction (equation 1) occurs between bistrialkyltin oxides and isocyanates, yielding trialkyltin *N*-trialkylstannylcarbamates (I).

$$(R_3Sn)_2O + R'NCO \longrightarrow \underset{(I)}{R_3Sn{\cdot}NR'{\cdot}CO_2{\cdot}SnR_3} \qquad (1)$$

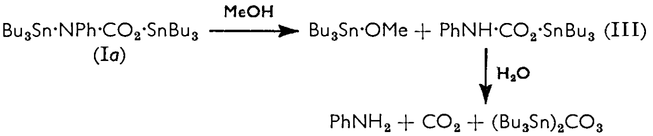
	R	R′		R	R′		R	R′
Ia	Bu	Me	Ic	Et	Ph	Ie	Bu	1-$C_{10}H_7$
Ib	Bu	Et	Id	Bu	Ph	If	Pr	Ph

As with alkoxides, the addition is rapid and exothermic, and the infrared spectrum shows that consumption of the isocyanate is quantitative. The products are oils or solids which decompose on distillation, but if the isocyanate is sufficiently volatile, the pure adducts can be isolated by carrying out the reaction with a slight excess of the isocyanate, then removing the excess under reduced pressure. By this procedure, the trialkyltin trialkylstannylcarbamates (Ia—e) were produced analytically pure, and the compound (If) was obtained but not analysed.

We discussed in Part I [1] the difficulty of deciding between an amide and an imidate structure for the stannylcarbamates. The infrared spectra of the pure liquid tin stannylcarbamates all show three strong bands at about 1550, 1590, and 1610 cm.$^{-1}$, which could reasonably be ascribed to the C=O group of (I), or the N=C group of (II). As in the case of the alkyl stannylcarbamates, the tin stannylcarbamates will take part in further reactions to give products containing unambiguously the amide unit, that is, as though they were derived from the structure (I), but this is of doubtful significance as it is probable that the structures (I) and (II) are readily interconvertible. We will again normally adopt the amide structure (I), unless contrary evidence is forthcoming.

$$\underset{(II)}{R'N{=}C(OSnR_3)_2}$$

Protic reagents react at the Sn–N bond; for example, infrared and proton magnetic resonance spectra indicated that methanol reacted very rapidly with the tin stannylcarbamate (I*a*) to give tributyltin methoxide and tributyltin *N*-phenylcarbamate (III) (equation 2). Attempts to separate these products were not successful, and therefore we looked for independent routes to the trialkyltin carbamates, $R'NH{\cdot}CO{\cdot}OSnR_3$.



$$\begin{array}{ccc} \underset{(Ia)}{Bu_3Sn{\cdot}NPh{\cdot}CO_2{\cdot}SnBu_3} & \xrightarrow{MeOH} & Bu_3Sn{\cdot}OMe + PhNH{\cdot}CO_2{\cdot}SnBu_3\ (III) \\ & & \Big\downarrow {\scriptstyle H_2O} \\ & & PhNH_2 + CO_2 + (Bu_3Sn)_2CO_3 \end{array} \qquad (2)$$

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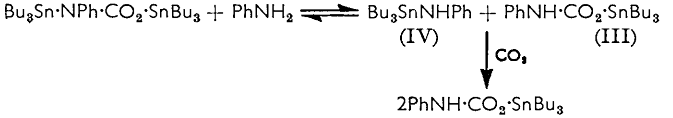
[1] Part I, A. J. Bloodworth and A. G. Davies, *J.*, 1965, 5238.

Treatment of tributyltin chloride with aqueous sodium *N*-phenylcarbamate was not successful because water hydrolyses the tin carbamate (III) to aniline, carbon dioxide, and bistributyltin carbonate. Similarly, an attempt to prepare triethyltin *N*-phenylcarbamate by adding triethyltin hydroxide to phenyl isocyanate [2] was a failure, the isocyanate dehydrating the hydroxide giving the carbonate and diphenylurea.*

A route to the tin carbamates, however, was devised, account being taken of the reactivity of the Sn–N bond in metathesis and addition. It appeared likely that tributyltin *N*-phenyl-*N*-tributylstannylcarbamate would react with aniline to give a mixture of tributyltin *N*-phenylcarbamate (III) and *N*-tributylstannylaniline (IV) and that the latter would add to carbon dioxide to give the tin carbamate (III) as the sole product.



$$\begin{tikzcd} Bu_3Sn{\cdot}NPh{\cdot}CO_2{\cdot}SnBu_3 + PhNH_2 \arrow[r, rightleftharpoons] & \underset{(IV)}{Bu_3SnNHPh} \arrow[d, "CO_2"] + \underset{(III)}{PhNH{\cdot}CO_2{\cdot}SnBu_3} \\ & 2PhNH{\cdot}CO_2{\cdot}SnBu_3 \end{tikzcd} \qquad (3)$$

By this procedure tributyltin *N*-phenylcarbamate was isolated as a crystalline solid, m. p. 41—43°. Tributyltin *N*-ethylcarbamate, m. p. 72—74°, was obtained similarly from tributyltin *N*-ethyl-*N*-tributylstannylcarbamate, ethylamine, and carbon dioxide; it is rather more stable towards hydrolysis than is the corresponding *N*-phenyl compound.

An alternative mechanism can be suggested in which the initial reaction is between aniline and carbon dioxide to give *N*-phenylcarbamic acid, which then reacts metathetically with the trialkyltin stannylcarbamate (equation 4).

$$\left.\begin{array}{r} PhNH_2 + CO_2 \rightleftharpoons PhNH{\cdot}CO_2H \\ Ph{\cdot}NH{\cdot}CO_2H + Bu_3Sn{\cdot}NPh{\cdot}CO_2{\cdot}SnBu_3 \longrightarrow 2PhNH{\cdot}CO_2{\cdot}SnBu_3 \end{array}\right\} \quad (4)$$

This mechanism is similar to that suggested by Breederveld for the interaction of silylamines and carbon dioxide.[4]

The proton magnetic resonance spectra appeared to indicate that a reaction occurred between the trialkyltin stannylcarbamate and aniline, *i.e.*, that the process described in equation (3) is correct. However, the n.m.r. (and i.r.) spectra of such mixtures must be interpreted with caution because strong interactions occur between the organic and metallic components, modifying the spectra of both. For exampe, if bistributyltin oxide is added to aniline in carbon tetrachloride, the proton resonance of the amino-group broadens and shifts downfield by about 0·35 p.p.m.[2]

Methyl *N*-phenyl-*N*-tributylstannylcarbamate reacts metathetically with acetic anhydride giving tributyltin acetate and methyl *N*-acetyl-*N*-phenylcarbamate.[1] The interaction of tributyltin *N*-phenyl-*N*-tributylstannylcarbamate and acetic anhydride was followed by proton magnetic resonance, and has a more complicated course. During 70 hr., the singlet of the acetic anhydride decayed and that of tributyltin acetate appeared; meanwhile the contour of the complex resonance of the phenyl group changed completely. The infrared spectrum of the solution then indicated the presence of tributyltin acetate and phenyl isocyanate. The nature of the products was confirmed in the case of the reaction between tributyltin *N*-ethyl-*N*-tributylstannylcarbamate and acetic anhydride, from which tributyltin acetate and ethyl isocyanate were isolated.

A number of reasonable pathways to these products can be suggested, but the most likely appears to be that in which the acetic anhydride first reacts metathetically with the tin

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* Triethylsilanol, on the other hand, reacts with aryl isocyanates during 1 hr. at 80—85° to give the corresponding triethylsilicon carbamates.[3]

[2] T. N. Mitchell, personal communication.

[3] V. V. Atakhin, I. P. Losev, and K. A. Andrianov, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 581 (*Chem. Abs.*, 1957, **51**, 14,582); M. F. Shostakovskii, V. N. Kotrelev, D. A. Kochkin, S. P. Kalinina, and V. V. Borisenko, *Zhur. priklad. Khim.*, 1958, **31**, 952.

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

stannylcarbamate in its imidate form (equation 5). The initial product (V) would be an adduct between tributyltin acetate and an isocyanate; we have failed to prepare stable adducts of this type by other routes, and would expect the adduct (V) to decompose to the products which are observed.

$$\begin{tikzcd}
 & \mathrm{Bu_3Sn{\cdot}NEt{\cdot}CO_2{\cdot}SnBu_3} \arrow[r, shift left] & \mathrm{EtN{=}C(OSnBu_3)_2} \arrow[l, shift left] \arrow[d, "\mathrm{Ac_2O}"] \\
\mathrm{EtN{=}C{=}O + Bu_3Sn{\cdot}OAc} & & \mathrm{EtN{=}C(OAc){\cdot}OSnBu_3 + Bu_3Sn{\cdot}OAc} \arrow[ll] \\
 & & \mathrm{(V)}
\end{tikzcd} \qquad (5)$$

Neither the tin stannylcarbamates (I) nor the tin carbamates (III) can be purified by distillation. At their melting points, the tin carbamates decompose (equation 6) to give the amine and carbon dioxide (or the equivalent ammonium carbamate) and the corresponding tin stannylcarbamate.

$$\mathrm{2RNH{\cdot}CO_2{\cdot}SnBu_3 \longrightarrow CO_2 + RNH_2 + Bu_3Sn{\cdot}NR{\cdot}CO_2{\cdot}SnBu_3} \qquad (6)$$

At a somewhat higher temperature, the tin stannylcarbamates then decarboxylate further (equation 7) giving bistributyltin oxide and another new class of organotin compounds, the bistributylstannylureas (VI).

$$\mathrm{2Bu_3Sn{\cdot}NR{\cdot}CO_2{\cdot}SnBu_3 \longrightarrow CO_2 + (Bu_3Sn)_2O + \underset{(VI)}{Bu_3Sn{\cdot}NR{\cdot}CO{\cdot}NR{\cdot}SnBu_3}} \qquad (7)$$

Tributyltin *N*-ethyl-*N*-tributylstannylcarbamate is more stable than the corresponding *N*-phenyl compound, and can be distilled with little decomposition at *ca.* 100°/0·05 mm. Both stages in the decomposition can thus be observed. With tributyltin *N*-phenyl-*N*-tributyl-stannylcarbamate, reaction (6) and (7) cannot be separated.

The stannylureas can be obtained more conveniently by a combination of reactions (1) and (7) in which the tin oxide and isocyanate are heated in the molar ratio of 1 : 2 (equation 8).

$$\mathrm{(Bu_3Sn)_2O + 2RNCO \longrightarrow CO_2 + Bu_3Sn{\cdot}NR{\cdot}CO{\cdot}NR{\cdot}SnBu_3} \qquad (8)$$

By reaction of this type *NN′* (or *NO*)bistributylstannyl-*NN′*-diphenyl- and -*NN′*-di-1-naphthyl-ureas have been obtained as thermally stable oils. In the air, they are very rapidly hydrolysed to the corresponding *NN′*-diarylureas.

The same bistrialkylstannylureas can be prepared by treating the bistrialkyltin oxides with a carbodi-imide (RN=C=NR), and by dehydrating a mixture of the tin oxide and the urea, RNH•CO•NHR. These compounds will be discussed more fully in a forthcoming Paper.

EXPERIMENTAL

General methods are described in Part I.[1] Unless otherwise stated, n.m.r. spectra were determined on solutions in carbon tetrachloride; infrared (i.r.) spectra are of neat liquids or of Nujol mulls.

Preparation of Trialkyltin N-*Trialkylstannylcarbamates* (I).—(*a*) Methyl isocyanate (0·76 g., 0·0133 mole) was mixed with bistributyltin oxide (5·713 g., 0·0096 mole) at 0°, whereupon an exothermic reaction occurred. The excess of isocyanate was immediately removed under reduced pressure, giving *tributyltin* N-*methyl*-N-*tributylstannylcarbamate* as an oil (Found: C, 47·8; H, 8·9; N, 2·3; Sn, 35·55. $C_{26}H_{57}NO_2Sn_2$ requires C, 47·8; H, 8·8; N, 2·15; Sn, 36·35%); $\nu_{max.}$ 1610vs, 1590vs, and 1550vs cm.$^{-1}$. The presence of a small peak in the i.r. spectrum at 1695 cm.$^{-1}$ indicated that a small amount of trimethyl isocyanurate is formed even under these very mild conditions.

(*b*) Ethyl isocyanate (0·365 g.) and bistributyltin oxide (2·783 g.) reacted exothermically at room temperature. The slight excess of the isocyanate was removed under reduced pressure; the i.r. spectrum of the residue (99·5% yield) showed the absence of the isocyanate group (at *ca.* 2275 cm.$^{-1}$) and of bistributyltin oxide (at 770 cm.$^{-1}$). *Bistributyltin* N-*ethyl*-N-*tributylstannylcarbamate* was obtained as an oil; $\nu_{max.}$ 1610vs, 1590vs, and 1550s cm.$^{-1}$ (Found: C, 48·8; H, 9·0; N, 2·2; Sn, 35·4. $C_{27}H_{59}NO_2Sn_2$ requires C, 48·6; H, 8·9; N, 2·1; Sn, 35·6%).

The following compounds were obtained by similar methods.

(*c*) [2] *Triethyltin* N-*phenyl*-N-*triethylstannylcarbamate*, m. p. 58—60°; $\nu_{max.}$ 1550vs, broad, 1590s, and 1600vs cm.$^{-1}$; τ 2·8—2·9 (aromatic), broad triplet centred at 8·77 (*J* = *ca.* 4 c./sec.) (CH_2 and CH_3) (Found: C, 41·6; H, 6·4; N, 2·6; Sn, 42·1. $C_{19}H_{35}NO_2Sn_2$ requires C, 41·8; H, 6·4; N, 2·6; Sn, 43·4%).

(*d*) *Tributyltin* N-*phenyl*-N-*tributylstannylcarbamate*, $\nu_{max.}$ 1550vs, 1590vs, and 1610vs cm.$^{-1}$ (Found: C, 51·9; H, 8·2; N, 2·0. $C_{31}H_{59}NO_2Sn_2$ requires C, 52·0; H, 8·3; N, 1·9%).

(*e*) *Tributyltin* N-1-*naphthyl*-N-*tributylstannylcarbamate*, $\nu_{max.}$ 1550vs, 1590s, and 1610s cm.$^{-1}$ (Found: C, 54·95; H, 8·0; N, 2·0; Sn, 30·85. $C_{35}H_{61}NO_2Sn_2$ requires C, 54·9; H, 8·05; N, 1·85; S, 31·0%).

(*f*) Tripropyltin *N*-phenyl-*N*-tripropylstannylcarbamate. This compound was not analysed, but was used immediately in further reactions.

In every case, these carbamates decomposed when we tried to distil them.

Thermal Decomposition of Trialkyltin N-Trialkylstannylcarbamates.—Tributyltin *N*-phenyl-*N*-tributylstannylcarbamate was heated under reduced pressure. At 150° (bath) vigorous effervescence occurred, and the pressure in the system increased from 0·02 to 0·1 mm. The gas evolved was shown, by its infrared spectrum, to be carbon dioxide.

After 1·5 hr. at 150—160°, the reaction was complete. Distillation of the residue gave bistributyltin oxide, b. p. 118°/0·05 mm., and *bis*-NN′-*diphenyl*-NN′-*bistributylstannylurea*, as a pale yellow oil, b. p. *ca.* 130°/0·05 mm. (Found: C, 56·2; H, 8·3; N, 3·5; Sn, 30·0. $C_{37}H_{64}N_2OSn_2$ requires C, 56·3; H, 8·2; N, 3·6; Sn, 30·1%). The i.r. spectrum was identical with that of the adduct prepared from bistributyltin oxide and diphenylcarbodi-imide.

In the air, the compound was rapidly hydrolysed to *NN′*-diphenylurea and bistributyltin oxide.

Preparation of Bistrialkylstannylureas from Bistrialkyltin Oxides and Isocyanates.—A mixture of bistributyltin oxide (2·06 g.) in 1-naphthyl isocyanate (1 c.c., 2 mol.) was kept at 120—130°/15—20 mm. for 3 hr., and then at 100°/0·01 mm. for 0·75 hr. A small amount of white solid sublimed from the mixture. The residue of NN′-*di*-1-*naphthyl*-NN′-*bistributylstannylurea* was a viscous oil with an i.r. spectrum identical with that of the adduct from bistributyltin oxide and di-1-naphthylcarbodi-imide (Found: C, 59·9; H, 7·9; N, 3·3; Sn, 26·25. $C_{45}H_{68}N_2OSn_2$ requires C, 60·7; H, 7·7; N, 3·15; Sn, 26·65%). It reacted rapidly with atmospheric moisture to give *NN′*-di-1-naphthylurea [$\nu_{max.}$ 3175vs (NH), 1625 vs (C=O)].

Reaction of Trialkyltin N-*Trialkylstannylcarbamates with Acetic Anhydride.*—(i) Tributyltin *N*-phenyl-*N*-tributylstannylcarbamate and acetic anhydride (1 mol.) in carbon tetrachloride were enclosed in an n.m.r. sample tube sealed by a rubber serum cap (see Part I [1]). Spectra were recorded at periods of 6 min., 20 min., 2 hr., 6 hr., and 70 hr. after the reagents were mixed. During this time the singlet of the acetic anhydride (τ 7·89) slowly decreased, as that of tributyltin acetate (τ 8·05) appeared. This was accompanied by a complete change in the contour of the complex resonance of the phenyl group.

The i.r. spectrum of the solution, diluted with carbon tetrachloride, was consistent with that of a mixture consisting principally of tributyltin acetate and phenyl isocyanate, together with some triphenyl isocyanurate and acetic anhydride. Small unidentified peaks were also present at 1515, 1490, 1430, 1235, and 1125 cm.$^{-1}$.

(ii) This picture was confirmed by isolating the products from the reaction between tributyltin *N*-ethyl-*N*-tributylstannylcarbamate and a slight excess of acetic anhydride. The mixture was shaken from time to time because the reagents were not completely miscible. A white solid began to separate after 0·5 hr., giving a solid mass after 24 hr. This was separated by sublimation under reduced pressure, into a mixture of acetic anhydride and ethyl isocyanate (identified by i.r. spectra) in the trap, a white sublimate (m. p. 80—85°) of tributyltin acetate, and a liquid residue of unchanged carbamate.

This residue was treated again with acetic anhydride. After 24 hr. the i.r. spectrum was equivalent to that of a mixture of tributyltin acetate, acetic anhydride, and ethyl isocyanate.

Reaction of Tributyltin N-*Tributylstannylcarbamates with Protic Reagents.*—(i) Tributyltin *N*-ethyl-*N*-tributylstannylcarbamate (0·763 g.) in carbon tetrachloride (*ca.* 0·5 c.c.) was treated with methanol (0·0378 g.). The n.m.r. spectrum showed that the reaction was complete in less than 15 min., and showed a broad NH absorption (τ 4·15) and a methoxy-singlet (τ 6·46), consistent with the formation of tributyltin methoxide and tributyltin *N*-ethylcarbamate.

When water was added to the mixture, a gas (carbon dioxide?) was evolved, the smell of ethylamine was apparent, and the solution became viscous indicating the presence of bistributyltin carbonate. Volatile compounds were removed under reduced pressure, leaving the carbonate which was identified by its infrared spectrum.

(ii) Similar conclusions were reached from the reaction between tributyltin *N*-phenyl-*N*-tributylstannylcarbamate and methanol. A sharp singlet at τ 6·42 (OMe) and a broad peak at τ 1·64 (NH) were obtained, and the i.r. spectrum showed the absence of methyl *N*-phenylcarbamate.

(iii) Tributyltin *N*-phenyl-*N*-tributylstannylcarbamate (0·583 g., 0·816 mmole) in carbon tetrachloride (0·5 c.c.) was treated with t-butyl alcohol (0·0600 g., 0·810 mmole); the infrared and n.m.r. spectra indicated that tributyltin t-butoxide and tributyltin *N*-phenylcarbamate were rapidly formed. Treatment of the mixture with hydrochloric acid gave tributyltin chloride, carbon dioxide, and aniline hydrochloride.

Preparation of Trialkyltin Carbamates (III).—(i) *Tributyltin* N-*phenylcarbamate.* Tributyltin *N*-phenyl-*N*-tributylstannylcarbamate (8·55 mmoles) was prepared from bistributyltin oxide (5·051 g.) and phenyl isocyanate (1·023 g.), the excess of isocyanate being removed under reduced pressure. Carbon tetrachloride (*ca.* 5 c.c.) and aniline (0·797 g., 8·85 mmoles) were then added. After 30 min., dry carbon dioxide was passed through the mixture for 45 min., giving a slight evolution of heat.

The solvent was removed under reduced pressure, leaving *tributyltin* N-*phenylcarbamate* as a waxy crystalline solid, m. p. (sealed tube) 41—43°; τ 1·51 (NH); $\nu_{\text{max.}}$ 3450w, 3320m, 3210m (NH), 1650vs, and 1610vs (C=O?) (Found: C, 53·45; H, 7·9; N, 3·35; Sn, 27·45. $C_{19}H_{33}NO_2Sn$ requires C, 53·55; H, 7·8; N, 3·3; Sn, 27·85%). It reacted rapidly with water giving carbon dioxide and aniline.

(ii) *Tributyltin* N-*ethylcarbamate.* Bistributyltin oxide (4·264 g., 7·16 mmoles) and ethyl isocyanate (0·509 g., 7·16 mmoles) were mixed giving tributyltin *N*-ethyl-*N*-tributylstannylcarbamate. This was diluted with carbon tetrachloride (4 c.c.), then ethylamine (0·332 g., 7·38 mmoles) was added. After 1 hr., dry carbon dioxide saturated with carbon tetrachloride was passed through the solution, which became warm and viscous. The bulk of the solvent was removed under reduced pressure, yielding *tributyltin* N-*ethylcarbamate* as a crystalline solid, m. p. (sealed tube) 72—74°; τ 4·47 (broad, probably a triplet, NH) and 6·82 (a group of 5 or 6 peaks, CH_2); $\nu_{\text{max.}}$ 3500sh (NH) and 1590br (C=O) cm.$^{-1}$ (Found: C, 47·8; H, 8·6; N, 3·65; Sn, 31·5. $C_{15}H_{33}NO_2Sn$ requires C, 47·65; H, 8·8; N, 3·7; Sn, 31·4%). The carbamate was unchanged in appearance and m. p. after 1 month under dry nitrogen, but in the air it was slowly hydrolysed to bistributyltin carbonate.

Thermal Decomposition of Tributyltin Carbamates.—(i) *Tributyltin* N-*phenylcarbamate.* The carbamate was gently heated at a rotary pump. At 40—45° (bath) some gas was evolved and at 105° (bath), steady effervescence took place. The product was heated to reflux at 145° (bath)/0·05 mm. for 0·75 hr.; the i.r. spectrum then indicated that it was a mixture of *NN'*-diphenyl-*NN'*-bistributylstannylurea and bistributyltin oxide. A colourless oil was collected at −80°, and was identified by i.r. spectroscopy and g.l.c. as aniline.

(ii) *Tributyltin* N-*ethylcarbamate.* The carbamate was heated at a rotary pump. At 75—80° (bath) it melted with bubbling. After 30 min. at 80—85°, the product was allowed to cool whereupon it set to a gel with some supernatant liquid.

The weight of the product indicated 87% of reaction according to the equation

$$2EtNH{\cdot}CO_2{\cdot}SnBu_3 \longrightarrow EtNH_2 + CO_2 + Bu_3Sn{\cdot}NEt{\cdot}CO_2{\cdot}SnBu_3$$

The i.r. spectrum showed the absence of bistributyltin oxide and the presence of the tributyltin tributylstannylcarbamate, although the carbonyl peak was broad, probably because of the presence of residual tributyltin carbamate.

After a further 30 min. at 110° (bath)/0·05 mm., the product was a colourless oil with an infrared spectrum identical with that of tributyltin *N*-ethyl-*N*-tributylstannylcarbamate. From the trap, solid ethylammonium *N*-ethylcarbamate was recovered, with an n.m.r. spectrum (in D_2O) identical with that of the authentic material.

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