Organometallic Reactions. Part VII.¹ Further Addition Reactions of Tributyltin Methoxide and of Bistributyltin Oxide

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The addition of tributyltin methoxide and of bistributyltin oxide to the following acceptor molecules is described: isothiocyanates, trichloroacetonitrile, carbon disulphide, carbon dioxide, sulphur dioxide, and carbodi-imides. The corresponding phenoxide is generally less reactive than the methoxide. The initial product is always a 1:1 adduct, but in the reaction of bistributyltin oxide with isothiocyanates and with carbon disulphide, the nature of the ultimate product is determined by the elimination of bistributyltin sulphide. Many of the adducts dissociate when heated. Many react very readily with protic reagents, and consequently organotin compounds catalyse the addition of alcohols or of water to carbodi-imides.

PARTS I—IV² describe the addition of trialkyltin alkoxides and of bistrialkyltin oxides to isocyanates, and Part VI dealt with similar additions to carbonyl compounds.¹ This Paper is concerned with the reactions involving some of the other multiply bonded acceptor molecules which were referred to briefly in Part I.³ The reactants, reaction conditions, and products are summarised in the Table.

The alkyl and aryl isocyanates reacted exothermically with trialkyltin alkoxides to give carbamates which could be distilled under reduced pressure, and which were very sensitive to hydrolysis; only the adduct formed from The adducts (1A and 2A) were stable to moisture, and indeed methyl N-phenyl(tributylstannylthio)formimidate (1A) could be prepared by treating O-methyl N-phenylthiocarbamate with bistributyltin oxide [equation(1)]; Noltes has shown that O-ethyl N-phenylthiocarbamate undergoes a similar stannylation reaction with triethyltin methoxide.⁴

 $(Bu_3Sn)_2O + 2PhNH \cdot CS \cdot OMe \longrightarrow 2Bu_3Sn \cdot S \cdot C(:NPh) \cdot OMe + H_2O \quad (1)$

The structure of the adducts formed between isocyanates and trialkyltin alkoxides was open to argument,³

Products of the reaction of various acceptor molecules with tributyltin methoxide and bistributyltin oxide

	A. Reaction with Bu ₃ Sn•OMe		
Acceptor 1 PhNCS 2 C_3H_5NCS 3 $Cl_3C \cdot CN$ 4 CO_2 5 CS_2 6 SO_2 7 Np·N:C:N·Np 8 Tol·N:C:N·Tol	Product Bu ₃ Sn·S·C(:NPh)OMe ^a Bu ₃ Sn·S·C(:N·C ₃ H ₅)OMe ^a [Bu ₃ Sn·N:C(CCl ₃)OMe] ^b Bu ₃ Sn·O·CO·OMe ^a [Bu ₃ Sn·S·CS·OMe] ^c Bu ₃ Sn·O·SO·OMe ^a Bu ₃ Sn·N(Np)C(:N·Np)OMe ^a [Bu ₃ Sn·N(Tol)C(:N·Tol)OMe] ^d	B. p./mm. ^k 68°/0·2 ⁱ 84—85/0·02 Decomp. 80/0·05 Decomp. 100/0·1 Decomp. 125/0·08 Decomp. 140/0·02	$C_{3}H_{5} = allyl;$ Np = 1-naphthyl; Tol = p-tolyl; C ₆ H ₁₁ = cyclohexyl. Compounds enclosed in parentheses were not obtained analytically pure. Reaction conditions: ^a Rapid and ex- othermic. ^b 20 hr. ^c 15 min. ^d 24 hr.
1 PhNCS 2 C ₃ H ₅ ·NCS 3 Cl ₃ C·CN 4 CO ₂ 5 CS ₂ 6 SO ₂ 7 Np·N:C:N·Np 9 PhN:C:NPh 10 Pr ¹ N:C:NPr ¹ 11 C ₆ H ₁₁ ·N:C:N·C ₆ H ₁₁	B. Reaction with $(Bu_3Sn)_2O$ $Bu_3Sn\cdotNPh\cdotCO_2SnBu_3 \circ$ $[Bu_3Sn\cdotN(C_3H_5)CO_2SnBu_3] \circ$ $Bu_3Sn\cdotN:C(CCl_3)O\cdotSnBu_3 \circ$ $Bu_3Sn\cdotO\cdotCO\cdotOSnBu_3 \circ$ $Bu_3Sn\cdotO\cdotCO\cdotOSnBu_3 \circ$ $Bu_3Sn\cdotO\cdotSO\cdotO\cdotSnBu_3 \circ$ $Bu_3Sn\cdotN(Np)CO\cdotN(Np)SnBu_3 \circ$ $Bu_3Sn\cdotNPh\cdotCO\cdotNPh\cdotSnBu_3$ $Bu_3Sn\cdotNPh\cdotCO\cdotNPh\cdotSnBu_3 \circ$ $Bu_3Sn\cdotNPh^+CO\cdotNPh^+SnBu_3 \circ$	Decomp. $150^{\circ}/0.02$ Decomp. $115/0.05$ Decomp. $100/0.01$ Decomp. $120/0.01$ Decomp. $120/0.1$ > 210/0.1 ca. 200/0.1 150 bath/0.05 ^c Decomp. $155/0.01$	[•] 72 hr. [†] 21 hr.; all at room temper- ature. ^h Decomposition points refer to the bath temperature. ⁱ With partial decomposition.

tributyltin phenoxide and phenyl isocyanate dissociated when heated.³

The isothiocyanates are less powerful acceptor molecules for this type of addition. Phenyl isothiocyanate and allyl isothiocyanate reacted exothermically with tributyltin methoxide to give the formimidates (1A and 2A), but the adduct from allyl isothiocyanate dissociated during distillation, and tributyltin phenoxide did not react with phenyl isothiocyanate during 8 days at room temperature. but the physical and chemical properties could be reconciled with the alkyl *N*-trialkylstannylcarbamate structure (I).

R¹₃Sn•NR²•CO•OR³	R ² N:C(OR ³)S [.] SnR ¹ ₃	R ¹ 3Sn•NR ² •CS•OR ³
(I)	(II)	(III)

In the case of the isothiocyanate adducts, the evidence is in favour of the formimidate (II) rather than the thiocarbamate structure (III). The observed hydrolytic stability would be surprising for a compound in which nitrogen is bonded to 4-co-ordinate tin, but would

³ Part I, A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 1965, 5238.

⁴ J. G. Noltes, Rec. Trav. chim., 1965, 84, 799.

¹ Part VI, A. G. Davies and W. R. Symes, J. Chem. Soc. (C), 1967, 1009.

² Part IV, A. J. Bloodworth and A. G. Davies, J. Chem. Soc. (C), 1966, 299, and Papers cited therein.

be expected for a compound containing the Sn-S bond. The adducts show strong infrared absorption at 1625 cm.⁻¹, which may be assigned to the stretching frequency of the C=N bond in structure (II). Noltes assumed a similar structure for the product of triethylstannylation of O-ethyl N-phenylthiocarbamate.

This evidence, however, must be interpreted with caution, as both hydrolytic stability and infrared spectra would be modified if inter- or intra-molecular association were to occur.

The reaction between isothiocyanates and bistributyltin oxide is more complicated. Even at -10° , phenyl isothiocyanate and bistributyltin oxide in a 1:2 molar ratio reacted rapidly to give a mixture of bistributyltin sulphide and the adduct (1B) of phenyl isocyanate and bistributyltin oxide. A similar but slower reaction took place with allyl isothiocyanate.

$$(Bu_{g}Sn)_{g}O + S:C:NPh \longrightarrow \begin{bmatrix} Bu_{g}Sn \cdot O \\ Bu_{g}Sn \cdot S \end{bmatrix} (IV)$$

$$\downarrow (IV)$$

$$Bu_{g}Sn \cdot NPh \cdot CO \cdot OSnBu_{g} 4 O:C:NPh + (Bu_{g}Sn)_{g}S$$

We assume that the bistributyltin oxide, like the methoxide, adds to the C=S bond of the isothiocyanate to give a formimidate (IV), the would-be adduct of phenyl isocyanate and bistributyltin sulphide [equation (2)]. The evidence is against such adducts being stable; we could not observe any reaction between bistributyltin sulphide and phenyl isocyanate, phenyl isothiocyanate, or carbon disulphide. The compound (IV) thus probably eliminates bistributyltin sulphide leaving phenyl isocyanate, which reacts with more of the oxide to give the carbamate.

Simple nitriles such as propionitrile do not react with tributyltin methoxide or bistributyltin oxide, but, as with aldehydes, the introduction of α -halogeno-substituents enhances the acceptor power. Trichloroacetonitrile reacted with tributyltin methoxide to give methyl-(N-tributylstannyl)trichloroacetimidate (3A).

Bistributyltin oxide reacted more slowly to give the adduct (3B) which decomposed when heated to give a distillate which was largely tributyltin chloride but which gave a strong infrared band at 2220 cm.⁻¹. Subsequent work on the decomposition of the trichloro-acetaldehyde-bistributyltin oxide ⁵ adduct suggests that this absorption may be due to the presence of tributyltin isocyanate ² and that the tributyltin chloride arises, at least in part, by way of tributyl(trichloromethyl)tin [equation (3)].

Carbon dioxide reacted with tributyltin methoxide to give methyl tributyltin carbonate (4A) as a viscous oil;

its dissociation on heating has since been used in a new route to trialkyltin alkoxides.⁶ In air, it is rapidly converted into bistributyltin carbonate (4B) which could be obtained as a very viscous oil by treating bistributyltin oxide with carbon dioxide. During many days in the air, this oil was transformed into white needles the constitution of which has not yet been established.

Again, tributyltin phenoxide was less reactive than the methoxide, and did not give a carbonate with carbon dioxide.

Carbon disulphide is one of the less reactive acceptor molecules, and did not react with tributyltin phenoxide during 6 days. Simple addition apparently occurred with tributyltin methoxide to give *O*-methyl *S*-tributyltin dithiocarbonate (5A) but the pure adduct could not be isolated.

Carbon disulphide and bistributyltin oxide reacted to give a viscous oil consisting mainly of bistributyltin carbonate and bistributyltin sulphide. The reaction is probably analogous to that illustrated for phenyl isothiocyanate in equation (2); the addition-elimination sequence occurs twice to exchange both sulphur atoms with the oxygen of two bistributyltin oxide molecules, and the carbon dioxide which is formed reacts with a third molecule of the oxide to give bistributyltin carbonate.

$$3(Bu_3Sn)_2O + CS_2 \longrightarrow 2(Bu_3Sn)_2S + Bu_3Sn \cdot O \cdot CO \cdot OSnBu_3$$
 (4)

Reichle has shown that when bistributyltin oxide is heated with a large excess of carbon disulphide at 145° for 16 hr., bistributyltin sulphide is obtained in 99%yield. Under these conditions, bistributyltin carbonate is not stable, and only the sulphide and carbon dioxide (or carbonyl sulphide) are formed.

The reactions of sulphur dioxide were parallel to those of carbon dioxide. Tributyltin methoxide gave methyl tributyltin sulphite (6A) as a viscous oil, which was rapidly converted in air into bistributyltin sulphite (6B), also obtained by passing sulphur dioxide through a solution of bistributyltin oxide. Tributyltin phenoxide reacted only slowly with sulphur dioxide giving phenyl tributyltin sulphite.

Carbodi-imides are less reactive than isocyanates as acceptors for the Sn-O bond. The adducts formed between tributyltin methoxide and diarylcarbodi-imides (7A and 8A) dissociated during distillation, whereas the adducts of the aryl isocyanates did not, and di-isopropylcarbodi-imide did not react with tributyltin methoxide during 11 hr. at 80°, whereas the alkyl isocyanates exothermically gave the methyl N-tributylstannyl-N-alkylcarbamates at room temperature. Again tributyltin phenoxide did not react with 1-naphthylcarbodi-imide during 24 hr. at room temperature, whereas phenyl isocyanate exothermically gave the carbamate.

The O-alkyl-N-stannylisoureas react very rapidly with protic reagents to liberate the parent O-alkylisoureas; in particular, alcohols react in this sense

⁵ A. G. Davies and W. R. Symes, Chem. Comm., 1965, 25.

⁶ A. G. Davies, P. R. Palan, and S. C. Vasishtha, *Chem. and Ind.*, 1967, 229.

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[equation (6)] to regenerate the trialkyltin alkoxide, which then attacks another carbodi-imide molecule by the reaction (5). A small amount of an organotin compound will therefore catalyse the addition of an

 $Bu_3Sn OMe + ArN:C:NAr \longrightarrow Bu_3Sn NAr (:NAr)OMe$ (5)

Bu₃Sn·NAr·C(:NAr)OMe + MeOH \longrightarrow ArNH·C(:NAr)OMe + Bu₃Sn·OMe (6)

ArN:C:NAr + MeOH \longrightarrow ArNH·C(:NAr)OMe (7)

alcohol to a carbodi-imide by a combination of the reactions (5) and (6); di-1-naphthylcarbodi-imide does not react with methanol during 2 hr. at room temperature, but addition is complete in 100 min. in the presence of 15 mol. % of tributyltin methoxide. Tributyltin acetate similarly catalysed the addition of ethanol to di-1-naphthylcarbodi-imide. These reactions are parallel to the tin-catalysed addition of alcohols to isocyanates, giving urethanes, which we have discussed previously.³

Bistrialkyltin oxides are more reactive than trialkyltin alkoxides in adding to carbodi-imides to form distannylureas (7B, 9B, 10B, 11B) [equation (8)]

$$(Bu_{3}Sn)_{2}O + RN:C:NR \longrightarrow Bu_{3}Sn \cdot NR \cdot C(:NR)O \cdot SnBu_{3} (8)$$

$$(V)$$

$$(Bu_{3}Sn)_{2}O + 2RN:C:O - CO_{3}$$

$$Bu_{3}Sn \cdot NR \cdot CO \cdot NR \cdot SnBu_{3} (9)$$

$$-H_{2}O - (VI)$$

(Bu₃Sn)₂O + RNH·CO·NHR -

which have been obtained previously by the routes shown in equation (9).² The properties of these distannylureas appear to be compatible with either the *NO*- or the *NN'*-bonded structure [(V) or (VI), respectively]. These compounds indeed are probably cationotropic, and again the apparent difference between the extreme forms (V) and (VI) may be reduced by intermolecular association.

These distantly reading are hydrolysed very readily to the corresponding protic compounds, and, as would be expected, bistributyltin oxide catalysed the hydrolysis of NN'-disubstituted carbodi-imides to the corresponding NN'-disubstituted ureas.

EXPERIMENTAL

General methods are described in earlier Parts.

Reactions between Acceptor Molecules and Organotin Compounds.—(a) Phenyl isothiocyanate and tributyltin methoxide. Phenyl isothiocyanate (0.635 g., 4.70 mmoles) and tributyltin methoxide (1.510 g., 4.70 mmoles) reacted to give methyl N-phenyl(tributylstannylthio)formimidate (1A; 2.04 g., 95%), v_{max} . 1625 (C=N) cm.⁻¹ (Found: C, 52.7; H, 7.8; N, 3.15; S, 7.3. C₂₀H₃₅NOSSn requires C, 52.6; H, 7.7; N, 3.1; S, 7.0%). It was stable to moisture, and could also be obtained by shaking a mixture of O-methyl N-phenylthiocarbamate (0.753 g., 4.5 mmoles) with bistributyltin oxide (1.293 g., 2.18 mmoles) for 1 hr. The oily product was treated with light petroleum to precipitate a small amount of unreacted thiocarbamate, and distilled, b. p. 60°/0.01 mm.

(b) Allyl isothiocyanate and tributyltin methoxide. Methyl

N-allyl(tributylstannylthio)formimidate (2A) [τ 6·25 (OMe)], prepared similarly, underwent partial dissociation during distillation giving 38·5% of tributyltin methoxide [τ 6·40 (OMe)]. The impure formimidate (v_{max} 1625 cm.⁻¹) could be obtained by carrying out the reaction with a slight excess of the isothiocyanate, which was then removed under reduced pressure (Found: C, 48·3; H, 8·2; N, 4·25; S, 9·35. Calc. for C₁₇H₃₅NOSSn: C, 48·6; H, 8·4; N, 3·35; S, 7·6%).

(c) Phenyl isothiocyanate and bistributyltin oxide. The infrared spectrum of a mixture of the isothiocyanate (0.77 g., 5.71 mmoles) and oxide (3.393 g., 5.71 mmoles) showed that the product contained a mixture of tributyltin N-tributylstannyl-N-phenylcarbamate and unreacted isothiocyanate. The isothiocyanate was removed at $30-35^{\circ}/0.01$ mm., leaving the carbamate, which decarboxylated at $115^{\circ}/0.01$ mm. yielding a mixture containing bistributylstannyl-NN'-diphenylurea. A similar reaction took place when the reagents were mixed at -10° .

When the isothiocyanate and oxide were mixed in the molar ratio 1:2, the oxide band at 770 cm.⁻¹ disappeared. The infrared spectrum of the product was identical with that of tributyltin *N*-tributylstannyl-*N*-phenylcarbamate except that the relative intensities of bands due to the tributylstannyl group were increased (bistributyltin sulphide has no other characteristic bands in the region $2\cdot 5$ —15 μ). In subsequent reactions (e.g., methanolysis) the product behaved in the same way as the authentic carbamate.

(d) Allyl isothiocyanate and bistributyltin oxide. The isothiocyanate and oxide were mixed in a 1:2 molar ratio. The disappearance of the isothiocyanate band from the infrared spectrum was complete within 15 min., and the product showed bands at 1610, 1590, and 1550 cm.⁻¹, characteristic of tributyltin N-tributylstannyl-N-alkylcarbamates.

(e) Trichloroacetonitrile and tributyltin methoxide. Trichloroacetonitrile (0.757 g.) and tributyltin methoxide (1.577 g.) were mixed. During about 50 min., the weak absorption at 2270 cm.⁻¹ (C \equiv N) decayed, and new bands at 1720 and 1135 cm.⁻¹ appeared. After 20 hr. the reaction was complete. The slight excess of nitrile was removed under reduced pressure, leaving impure methyl (N-tributylstannyl)trichloroacetimidate (3A; 2.25 g., 96%) as a golden-yellow oil, ν_{max} 1720 (C=N), 1135 (C–O?), 800 (C–Cl) cm.⁻¹ (Found: C, 40.0; H, 6.7; Cl, 20.8; N, 2.65. Calc. for C₁₅H₃₀Cl₃NOSn: C, 38.7; H, 6.5; Cl, 22.8; N, 3.0. Calc. for Bu₃SnOMe,0.91Cl₃CCN: C, 39.7; H, 6.75; Cl, 20.8; N, 2.75%). This product was hydrolysed very readily by atmospheric moisture. Decomposition occurred during distillation to give impure tributyltin methoxide, trichloroacetonitrile, and some unidentified volatile products.

(f) Trichloroacetonitrile and bistributyltin oxide. Trichloroacetonitrile (0.438 g., 3.03 mmoles) and bistributyltin oxide (1.727 g., 2.91 mmoles) were mixed. No heat was evolved, but during 72 hr. the nitrile reacted, and a new infrared band at 1600 cm.⁻¹ appeared. The golden-yellow oil was kept at 0.01 mm. for 3 hr. to yield NO-bistributyltin trichloroacetimidate (3B), v_{max} 1600 (C=N), 825b (C-Cl) cm.⁻¹ (Found: C, 42.5; H, 7.75; Cl, 14.0. C₂₆H₅₄Cl₃NOSn₂ requires C, 42.2; H, 7.35; Cl, 14.3%).

Again, the product was very susceptible to hydrolysis. During distillation at 115° , effervescence occurred, the pressure rising from 0.05 to 0.1 mm. The distillate (*ca.* 50%) consisted largely of tributyltin chloride (b. p. 93.5°/0.1 mm.) (Found: C, 44.6; H, 8.35; Cl, 11.6; N, 0.0. Calc. for $\rm C_{12}H_{27}ClSn:$ C, 44·4; H, 8·3; Cl, 10·9%), although it showed a strong absorption at 2220 cm.⁻¹ (NCO?). The involatile residue showed this same band, but was not examined further. No reaction occurred between the oxide and propionitrile at room temperature during 10 days.

(g) Carbon dioxide and tributyltin methoxide. Dry carbon dioxide was passed through a solution of the methoxide (1.554 g.) in light petroleum (5 c.c.) for 1 hr. After 3 hr. volatile material was removed under reduced pressure, and the oil was kept at 0.01 mm. for 3 hr., to give methyl tributyltin carbonate (4A; 1.7 g.), v_{max} 1600vs (C=O), 1095s, 820m (Found: C, 46.4; H, 8.5. C₁₄H₃₀O₃Sn requires C, 46.0; H, 8.25%).

The sample was exposed to air for 3 min., and the infrared spectrum became identical with that of bistributyltin carbonate (4B) described below. The methyl tributyltin carbonate lost carbon dioxide at $60-80^{\circ}$ to yield tributyltin methoxide, b. p. $68-69^{\circ}/0.05$ mm.

Tributyltin phenoxide showed no reaction with carbon dioxide under similar conditions.

(h) Carbon dioxide and bistributyltin oxide. Carbon dioxide reacted exothermically with bistributyltin oxide in light petroleum, yielding bistributyltin carbonate as a viscous oil, v_{max} 1515 (C=O), 1360, and 835 cm.⁻¹ (Found: C, 46.8; H, 8.3. C₂₅H₅₄O₃Sn₂ requires C, 46.9; H, 8.5%). It dissociated at *ca.* 100° (bath)/0.01 mm. It was not affected by atmospheric moisture, but on prolonged exposure to air it formed white needles, m. p. 78-80°.

(i) Carbon disulphide and tributyltin methoxide. Tributyltin methoxide (0.904 g.) and carbon disulphide (0.222 g., 1 mol.) were mixed. The n.m.r. signal of the methoxygroup at τ 6.35 decayed, and was replaced by a new signal at τ 5.90, presumably due to O-methyl-S-tributyltin dithiocarbonate (5A). After 15 min. the reaction was complete; it could not be reversed at 0.1 mm. at room temperature, but at 0.1 mm. and 100°, carbon disulphide could be pumped off and the tributyltin methoxide was recovered.

Repeated attempts to isolate the pure dithiocarbonate were unsuccessful (Found: S, 3-6%. Calc. for $C_{14}H_{30}OS_2Sn$: S, $16\cdot2\%$).

(j) Carbon disulphide and bistributyltin oxide. Bistributyltin oxide (3.10 g., 6.62 mmoles) and carbon disulphide (0.503 g., 6.62 mmoles) were mixed at -10° . No reaction was apparent until the mixture was allowed to warm to room temperature, when it changed from a mobile to a viscous oil. Carbon disulphide was collected in a cold trap at 0.01 mm. The infrared spectrum of the residue showed all the bands present in bistributyltin carbonate. On distillation, carbon dioxide was evolved, giving an oil, b. p. ca. 140°/0.15 mm., which was shown by analysis to consist of bistributyltin sulphide together with 15—25% of bistributyltin oxide.

(k) Sulphur dioxide and tributyltin methoxide. Heat was evolved when sulphur dioxide was passed through a solution of tributyltin methoxide in light petroleum. After 50 min., the solvent was removed from the viscous solution, yielding methyl tributyltin sulphite (6A) as a viscous colourless oil, v_{max} 1050, 1000, and 960 cm.⁻¹ (all intense, broad and overlapping) (Found: C, 40.7; H, 8.2; S, 8.3. C₁₃H₃₀O₃SSn requires C, 40.6; H, 7.85; S, 8.35%). When the sample was exposed to air for 3 min., the infrared spectrum became identical with that of bistributyltin sulphite (6B), described later.

(1) Sulphur dioxide and tributyltin phenoxide. The phen-

oxide reacted less readily than the methoxide. Sulphur dioxide was passed through the light petroleum solution for 4.75 hr., yielding *phenyl tributyltin sulphite* (Found: S, 7.55. $C_{18}H_{32}O_3SSn$ requires S, 7.15%).

(m) Sulphur dioxide and bistributyltin oxide. An exothermic reaction took place when sulphur dioxide was bubbled through a solution of the oxide in benzene, to yield bistributyltin sulphite (6B) as a colourless viscous oil, v_{max} . 955vs, br, 850vs, br (Found: C, 43.9; H, 8.3; S, 5.3. $C_{24}H_{54}O_3SSn_2$ requires C, 43.7; H, 8.25; S, 4.85%). The sulphite dissociated at ca. 120°/0.1 mm.

(n) Tributyltin methoxide and di-1-naphthylcarbodi-imide. Equimolar amounts of the reagents were mixed in benzene, whereupon heat was evolved. The solvent was removed under reduced pressure leaving impure O-methyl-NN'-di-1-naphthyl-N-tributylstannylisourea (7A) as an oil (Found: C, 68.8; H, 7.2; N, 4.25. Calc. for $C_{34}H_{44}N_2OSn: C, 66.3; H, 7.2; N, 4.55\%$). It was very readily hydrolysed to O-methyl-NN'-di-1-naphthylisourea, m. p. 157—158°, ν_{max} . 3335 (NH), 1665 (C=N), and 775 cm.⁻¹ (Found: C, 80.3; H, 6.6. Calc. for $C_{22}H_{18}N_2O: C, 81.0;$ H, 5.5%). On attempted distillation, it dissociated to tributyltin methoxide, b. p. 75°/0.02 mm., and a residue of di-1-naphthylcarbodi-imide.

(o) Di-p-tolylcarbodi-imide and tributyltin methoxide. Equimolar amounts of the reagents were mixed in dry benzene. The reaction was not obviously exothermic, but, when the solvent was removed next day, the infrared spectrum showed that reaction was complete. O-Methyl-NN'di-p-tolyl-N-tributylstannylisourea (8A) was isolated as an oil (Found: C, 61.9; H, 8.15; N, 5.15. $C_{20}H_{44}N_2OSn$ requires C, 62.2; H, 8.0; N, 5.05%).

(p) Di-1-naphthylcarbodi-imide and bistributyltin oxide. Bistributyltin oxide (1·107 g., 1·86 mmoles) reacted exothermically with di-1-naphthylcarbodi-imide (0·547 g., 1·86 mmoles) in benzene (4 c.c.). The solvent was removed to yield NN'-di-1-naphthylbistributylstannylurea (7B) (Found: C, 60·4; H, 8·1; N, 3·1; Sn, 26·6. Calc. for C₄₅H₆₈N₂OSn₂: C, 60·7; H, 7·7; N, 3·15; Sn, 26·6%).

(q) Diphenylcarbodi-imide and bistributyltin oxide. These reagents similarly yielded NN'-diphenylbistributylstannylurea (9B) as a pale yellow oil (Found: C, 56.9; H, 8.15; N, 3.7; Sn, 29.6. Calc. for $C_{37}H_{62}N_2OSn$: C, 56.3; H, 8.15; N, 3.55; Sn, 30.1%).

(r) Di-isopropylcarbodi-imide and bistributyltin oxide. Equimolar amounts of the two reagents were heated at 80°, and the progress of the reaction was followed by the disappearance of the carbodi-imide infrared band at 2100 cm.⁻¹. After 21 hr., reaction was almost complete, and gave NN'-di-isopropylbistributylstannylurea (10B) which partially dissociated during distillation at 150°/0.05 mm. (Found: C, 50.4; H, 9.3. Calc. for $C_{31}H_{68}N_2OSn$: C, 49.7; H, 9.2%). It reacted with methanol to give the corresponding urea, which softened and turned brown at 270°, but did not melt below 360°.

(s) Dicyclohexylcarbodi-imide and bistributyltin oxide. Reaction was practically complete after 10 hr. at 80° and 10 hr. at 100°. The NN'-dicyclohexylbistributylstannylurea (11B) was an oil which dissociated on distillation at 155°/0.001 mm.; it was therefore analysed without distillation (Found: C, 55.2; H, 9.4; N, 3.4; Sn, 28.0. $C_{37}H_{76}N_2OSn_2$ requires C, 55.4; H, 9.55; N, 3.5; Sn, 29.6%). It was hydrolysed immediately by methanol to give NN'-dicyclohexylurea, m. p. 228—230°.

Catalysis of the Reaction Between Carbodi-imides and

Org.

Methanol or Water.—(a) Di-1-naphthylcarbodi-imide (2·28 g.) and methanol (0·5 ml., 1·6 mol.) were mixed in benzene at 25°. The infrared spectrum showed that no reaction occurred during 2·5 hr. Tributyltin methoxide (0·3 c.c., 0·15 mol.) was then added; the absorption band of the carbodi-imide at 2130 cm.⁻¹ diminished rapidly, and disappeared after 100 min. O-Methyl-NN'-dinaphthylisourea, m. p. 158°, was isolated (Found: C, 81·6; H, $5\cdot85\%$).

(b) A solution of di-1-naphthylcarbodi-imide (1.0 g.) in acetone (10 c.c.) was divided into two portions (A and

B) and to solution A 3 drops of bistributyltin oxide were added. Solution B remained clear, but within 10 min. a white solid began to separate from solution A. Next day, this solid was separated and identified as NN'-di-1-naphthylurea, m. p. 282—285°.

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7 W. T. Reichle, Inorg. Chem., 1962, 1, 650.