Organometallic Reactions. Part VIII.[1] Addition Reactions of Dibutyltin Dimethoxide and Related Compounds

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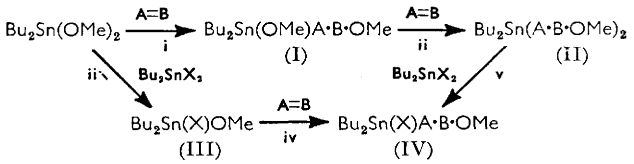
Dibutyltin dimethoxide reacts with a variety of multiply bonded acceptor molecules, A=B (isocyanates, isothiocyanates, aldehydes, carbon disulphide, sulphur dioxide, carbon dioxide, trichloroacetonitrile, and carbodiimides), to give, in most cases, both 1 : 1 [$Bu_2Sn(OMe)A{\cdot}B{\cdot}OMe$] and 1 : 2 adducts [$Bu_2Sn(A{\cdot}B{\cdot}OMe)_2$]. The 1 : 2 adducts react with compounds Bu_2SnX_2 to give the products of disproportionation, $Bu_2Sn(X)A{\cdot}B{\cdot}OMe$, which can also be obtained by adding the monomethoxides, $Bu_2Sn(X)OMe$ (X = Cl, Br, I, CNS, or O·COR) to the acceptors, A=B.

TRIALKYLTIN alkoxides react readily with a variety of multiply bonded reagents to give adducts which are useful intermediates in organic synthesis.[1] This Paper describes the behaviour of dibutyltin dimethoxide in similar systems.

Adducts Derived from Dibutyltin Dimethoxide.—An equimolar mixture of the dimethoxide and the acceptor molecule might, *a priori*, react in either a 1 : 1 or a 1 : 2 molar ratio to give, respectively, the adduct (I), or a mixture of the dimethoxide and the adduct (II). It has recently been shown, however, that a mixture of a dialkyltin dialkoxide, $R^1_2Sn(OR^2)_2$, and a compound $R^1_2SnX_2$ (X = F, Cl, Br, I CNS, O·COR, O·SO·OR) rapidly disproportionates to give the compound $R^1_2Sn(X)OR^2$.[2] Consistent with this, we find that both the 1 : 1 adducts (I) [reaction (i)] and the 1 : 2 adducts (II) [reactions (i) and (ii)] can usually be obtained by using the appropriate ratio of reagents, as shown in Table 1.



The course of the reactions can be followed by the proton magnetic resonance of the methoxy-groups. Dibutyltin dimethoxide in carbon tetrachloride shows a single signal at τ 6·42; the 1 : 1 adducts (I) usually show two separate signals for the two different methoxy-groups, and the 1 : 2 adducts (II) again show a single signal. These characteristic τ values are shown in Table 1.

The reactions of dibutyltin dimethoxide with the first and second molecular amounts of phenyl isocyanate were both very fast and exothermic, and the 1 : 2 adduct (IIa) (Table 1) was isolated. The same dicarbamate was formed when the dimethoxide was treated with phenyl isocyanate dimer, and, as in the reaction of tributyltin methoxide, there was no indication of the formation of an allophanate.[3] Both the 1 : 1 and the 1 : 2 adduct were hydrolysed rapidly in air to give methyl *N*-phenylcarbamate; the formation and alcoholysis of stannylcarbamate intermediates of these types are probably involved when catalysts such as dibutyltin dilaurate are used in preparing polyurethanes.[4]

N-Trialkylstannylcarbamates can be prepared by azeotropic dehydration of a mixture of the appropriate bistrialkyltin oxide and carbamate.[5] An attempt to prepare the dicarbamate (IIa) in a similar manner from dibutyltin oxide and methyl *N*-phenylcarbamate in xylene, however, gave *NN'*-diphenylurea as the main product.

The carbamates (Ib) and (IIb) were similarly formed exothermically from ethyl isocyanate. The n.m.r. spectrum of the 1 : 2 adduct (IIb) showed two methoxy-signals, perhaps implying restriction of rotation about

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[1] Part VII, A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, preceding Paper.

[2] A. G. Davies and P. G. Harrison, *J. Chem. Soc.* (*C*), 1967, 298.

[3] Part III, A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 1965, 6858.

[4] Part I, A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 1965, 5238.

[5] Part V, A. G. Davies, T. N. Mitchell, and W. R. Symes, *J. Chem. Soc.* (*C*), 1966, 1311.

the N–CO bond. If dibutyltin dimethoxide is treated with a large excess (7 mol.) of ethyl isocyanate, triethyl isocyanurate is formed in what we believe to be a repetitive insertion reaction.[3]

Both stages in the reaction of phenyl isothiocyanate were fast, but both the 1 : 1 and 1 : 2 adduct [(Ic) and (IIc)] dissociated when heated and neither could be purified. The 1 : 2 adduct with allyl isothiocyanate (IId), however, was isolated pure.

It is surprising that, whereas the adduct formed between tributyltin methoxide and phenyl isothiocyanate is stable to water,[1] that derived from dibutyltin dimethoxide and 2 mol. of phenyl isothiocyanate is very readily hydrolysed.

TABLE 1

Adducts formed from $\mathrm{Bu_2Sn(OMe)_2}$

A=B	$\mathrm{Bu_2Sn(OMe)A{\cdot}B{\cdot}OMe}$ (I)	$\mathrm{Bu_2Sn(A{\cdot}B{\cdot}OMe)_2}$ (II)
a, $\mathrm{PhN{:}C{:}O}$	$\mathrm{Bu_2Sn(OMe)NPh{\cdot}CO{\cdot}OMe}$ 6·42, 6·46	$\mathrm{Bu_2Sn(NPh{\cdot}CO{\cdot}OMe)_2}$ 6·45
b, $\mathrm{EtN{:}C{:}O}$	$\mathrm{Bu_2Sn(OMe)NEt{\cdot}CO{\cdot}OMe}$	$\mathrm{Bu_2Sn(NEt{\cdot}CO{\cdot}OMe)_2}$ 6·25, 6·30
c, $\mathrm{S{:}C{:}NPh}$	$\mathrm{Bu_2Sn(OMe)S{\cdot}C({:}NPh)OMe}$ 6·07, 6·49	$\mathrm{Bu_2Sn[S{\cdot}C({:}NPh)OMe]_2}$ 6·14
d, $\mathrm{S{:}C{:}N{\cdot}CH_2{\cdot}CH{:}CH_2}$	$\mathrm{Bu_2Sn(OMe)S{\cdot}C({:}N{\cdot}C_3H_5)OMe}$ 5·98, 6·37	$\mathrm{Bu_2Sn[S{\cdot}C({:}N{\cdot}C_3H_5)OMe]_2}$ 5·98
e, OCHMe	$\mathrm{Bu_2Sn(OMe)O{\cdot}CHMe{\cdot}OMe}$ 6·46, 6·68	$\mathrm{Bu_2Sn(O{\cdot}CHMe{\cdot}OMe)_2}$ 6·62
f, $\mathrm{OCH{\cdot}CCl_3}$	$\mathrm{Bu_2Sn(OMe)O{\cdot}CH(CCl_3)OMe}$ 6·27, 6·38	$\mathrm{Bu_2Sn[O{\cdot}CH(CCl_3)OMe]_2}$ 6·18
g, $\mathrm{S{:}C{:}S}$	$\mathrm{Bu_2Sn(OMe)S{\cdot}CS{\cdot}OMe}$ 5·89, 6·71	$\mathrm{Bu_2Sn(S{\cdot}CS{\cdot}OMe)_2}$ 6·73
h, $\mathrm{O{:}S{:}O}$	$\mathrm{Bu_2Sn(OMe)O{\cdot}SO{\cdot}OMe}$ 6·43br	
i, $\mathrm{O{:}C{:}O}$		$\mathrm{Bu_2Sn(O{\cdot}CO{\cdot}OMe)_2}$ 6·39
j, $\mathrm{N{:}C{\cdot}CCl_3}$	$\mathrm{Bu_2Sn(OMe)N{:}C(CCl_3)OMe}$	
k, $\mathrm{Np{\cdot}N{:}C{:}N{\cdot}Np}$	$\mathrm{Bu_2Sn(OMe)N(Np){\cdot}C({:}N{\cdot}Np){\cdot}OMe}$ 6·56, 6·76	$\mathrm{Bu_2Sn[N(Np){\cdot}C({:}N{\cdot}Np)OMe]_2}$ 6·76

τ Values for the methoxy-groups are given under the formulae. Np = 1-naphthyl.

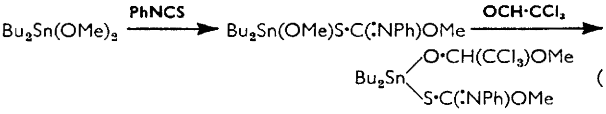
Acetaldehyde reacted exothermically; the infrared and n.m.r. spectra showed that both the 1 : 1 and 1 : 2 adducts [(Ie) and (IIe)] could be prepared, but the aldehyde could be removed under reduced pressure, to give the original dimethoxide. The chloral adducts [(If) and (IIf)] were more stable, and did not dissociate at room temperature.

The 1 : 1 adduct (Ig) formed from the dimethoxide and carbon disulphide was isolated as a pure solid. The 1 : 2 adduct (IIg) was stable to air, but the 1 : 1 adduct was rapidly transformed in air into a white oil, presumably by hydrolysis of the methoxytin group. In solution, this 1 : 1 adduct appeared, from the n.m.r. spectrum, to be in equilibrium with the parent dimethoxide and the 1 : 2 adduct (IIg).

When sulphur dioxide was passed through a solution of the dimethoxide in benzene, a crystalline solid separated in an exothermic reaction. The n.m.r. spectrum showed only a single rather broad methoxy-signal, but analysis showed that the compound was the 1 : 1 adduct (Ih). Conversely, carbon dioxide gave a very viscous liquid which appeared to be largely the 1 : 2 adduct (IIi).

Trichloroacetonitrile yielded the pure 1 : 1 adduct (Ij). Both the 1 : 1 and 1 : 2 adduct [(Ik) and (IIk)] from di-1-naphthylcarbodi-imide were characterised.

An experiment was carried out where the dimethoxide was treated successively with 1 mol. each of two different acceptor molecules, namely phenyl isothiocyanate and chloral; the product might in principle be either the single mixed adduct (V) or a mixture of the two simple 1 : 2 adducts (IIa) and (IIb).



$$\mathrm{Bu_2Sn(OMe)_2} \xrightarrow{\mathrm{PhNCS}} \mathrm{Bu_2Sn(OMe)S{\cdot}C({:}NPh)OMe} \xrightarrow{\mathrm{OCH{\cdot}CCl_3}} \mathrm{Bu_2Sn}\left\langle\begin{matrix}\mathrm{O{\cdot}CH(CCl_3)OMe}\\ \mathrm{S{\cdot}C({:}NPh)OMe}\end{matrix}\right. \quad (1)$$

(V)

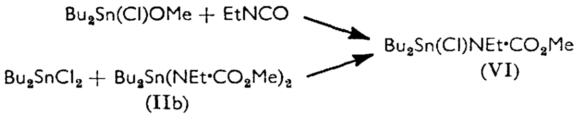
The n.m.r. signals of the methine and methoxy-groups were consistent with formation of the mixed adduct (V) and not the two simple adducts.

To summarise, the two Sn–O bonds in dibutyltin dimethoxide take part, stepwise, in the same types of addition reaction that were observed previously for the Sn–O bond in tributyltin methoxide.[1,4] The formation of the adducts, and their hydrolyses, are usually so fast that it is difficult to assess relative rates, but it appears that there is no large difference in the reactivity of the two reagents.

Adducts Derived from $\mathrm{Bu_2Sn(OMe)X}$.—The availability of the compounds $Bu_2Sn(X)OMe$ (III) * by the disproportionation reaction (iii) [2] makes it possible to study the effect of the ligand X on the reactivity of the Sn–OMe group as an addendum [reaction (iv)]. A number of these monomethoxides (III) were treated with selected acceptor molecules, to give the adducts (IV) shown in Table 2.

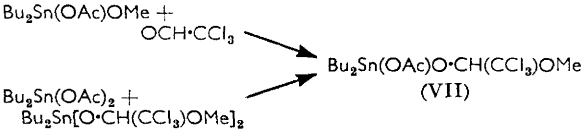
Dipropyltin fluoride methoxide did not react with ethyl isocyanate in 30 min. at room temperature. With that exception, the reactions between the compounds $R_2Sn(X)OMe$ (like the dimethoxide where X = OMe) and ethyl isocyanate were very fast and exothermic; the various groups X have no observable effect on the reactivity. If the reactions were carried out with a slight excess of the isocyanate, which was then removed under reduced pressure, the adducts could be isolated as pure oils which were light brown in colour when X was halide or carboxylate, but wine-red when X was thiocyanate. All these stannylcarbamates were readily hydrolysed regardless of the nature of the group X, to give methyl *N*-ethylcarbamate; the second product of hydrolysis could usually be identified by infrared spectroscopy as $R_4Sn_2X_2O$.

The compounds $Bu_2Sn(X)\cdot A\cdot B\cdot OMe$ (IV) could also be formed by disproportionation between Bu_2SnX_2 and $Bu_2Sn(A\cdot B\cdot OMe)_2$ [reaction (v)], which emphasises once again the readiness with which these disproportionations occur. Thus methyl *N*-chlorodibutylstannyl-*N*-ethylcarbamate (VI), which was prepared by adding dibutyltin chloride methoxide to ethyl isocyanate, was also formed immediately the dicarbamate (IIb) and the dichloride were mixed [equation (2)].



(2)

The additions to chloral were similarly very fast, and the adducts, like that derived from tributyltin methoxide, were very sensitive to moisture. Again, the adduct (VII) formed between dibutyltin acetate methoxide and chloral could also be obtained by disproportionation [equation (3)].



(3)

Phenyl isothiocyanate reacted relatively slowly, and not obviously exothermically; the reaction with dibutyltin chloride methoxide was 72% complete in 10 min., and complete after 2 hr., and the addition of dibutyltin acetate methoxide needed 15 min. for completion.

Carbon disulphide is a yet weaker acceptor and in this case the nature of the group X in $Bu_2Sn(X)OMe$ does have a significant affect on the reactivity of the Sn–OMe bond. Dibutyltin dimethoxide (X = OMe) gave the 1 : 1 adduct in about 5 min. at room temperature. With X = OAc, the adduct was formed in 0·5 hr. at 55°; with X = Cl, some reaction was apparent after 1 hr. at 55°, and with X = I no reaction could be detected.

These limited and qualitative observations on the reactivity of various methoxides, $R_2Sn(X)OMe$, must be interpreted with caution, but they do suggest that the nucleophilic attraction of the methoxy-group for

TABLE 2

Products of the reaction $Bu_2Sn(X)OMe \xrightarrow{A=B} Bu_2Sn(X)\cdot A\cdot B\cdot OMe$

		Found (%)				Required (%)				τ			ν_{max} (cm.$^{-1}$)		
A=B	$Bu_2Sn(X)\cdot A\cdot B\cdot OMe$ (IV)	C	H	N	X	C	H	N	X	OMe	NCH_2 [b]	OAc			
EtNCO	$Bu_2Sn(Cl)NEt\cdot CO\cdot OMe$ [a]	39·8	7·6	4·0	9·4	38·9	7·1	3·8	9·6	6·14	6·69		1680	1725	
	$Bu_2Sn(Br)NEt\cdot CO\cdot OMe$	35·7	6·5	3·6	19·1	34·8	6·3	3·4	19·3	6·16	6·69		1690	1725	
	$Bu_2Sn(I)NEt\cdot CO\cdot OMe$	31·9	5·6	3·5	27·4	31·2	5·7	3·0	27·5	6·18	6·80		1720		
	$Bu_2Sn(OAc)NEt\cdot CO\cdot OMe$			3·8	14·7			3·6	15·0	6·22	6·67	8·09	1615	1630	1715
	$Bu_2Sn(O\cdot COR)NEt\cdot CO\cdot OMe$ [c]	52·0	8·4	2·3	39·8	53·8	9·2	2·6	40·2	6·22	6·72		1615	1715	
	$Bu_2Sn(NCS)NEt\cdot CO\cdot OMe$				14·7				14·8	6·01 6·07			1680	1720	2050
PhNCO	$Bu_2Sn(Cl)NPh\cdot CO\cdot OMe$ [a]	46·5	6·6	4·0	8·6	45·9	6·3	3·4	8·5	6·18			1735		
SCN·Ph	$Bu_2Sn(Cl)SC(\vdots NPh)OMe$				8·7				8·2	6·08			1250	1560	
	$Bu_2Sn(OAc)S\cdot C(\vdots NPh)OMe$ [a]									6·01		8·13	1570	1580	1625
$OCH\cdot CCl_3$	$Bu_2Sn(OAc)O\cdot CH(CCl_3)OMe$	33·4	5·5		12·5	33·2	5·4		12·8	6·22 [d]		7·91	810	830	1610
	$Bu_2Sn(SCN)O\cdot CH(CCl_3)OMe$				12·1				12·4				800	830	1030 [e]
CS_2	$Bu_2Sn(OAc)S\cdot CS\cdot OMe$ [a]				14·0				14·4	5·79		7·99	1065	1610	
	$Bu_2Sn(Cl)S\cdot CS\cdot OMe$									5·76					
PhNCO	$Et_2Sn(ClNPh\cdot CO_2Me$ [a]				10·0				10·1	6·29			1725		
$OCH\cdot CCl_3$	$Et_2Sn(Br)O\cdot CH(CCl_3)OMe$				18·2				18·4	6·14 [f]			805	830	1020

[a] The compound $R_4Sn_2X_2O$ was identified in the hydrolysis products. [b] Centre of quartet of NCH_2CH_3, *J* = *ca.* 7 c./sec. [c] $R = C_{11}H_{23}$. [d] τ 4·88 (CH). [e] And 2070 (SCN) cm.$^{-1}$. [f] τ 4·83 (CH).

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* The constitution of these compounds has been discussed briefly (ref. 2). None of the available evidence appears to be inconsistent with the simple structure $R_2Sn(X)OMe$, but Kocheshkov and co-workers have pointed out that a dinuclear structure, $R_2Sn(OMe)_2,R_2SnX_2$, must also be considered.[6] We hope to report on this more fully.

[6] I. P. Gol'dshtein, N. N. Zemlyanskii, O. P. Shamagina, E. N. Gur'yanova, E. M. Panov, N. A. Slovokhotova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1965, **163**, 880.

the group B of the acceptor, rather than the electrophilic attraction of the tin for group A, usually dominates the reaction. The same inference may be drawn from the reactivity of various aldehydes and ketones towards Sn–O bonded addenda,[6] and from the diminished reactivity of tributyltin phenoxide compared with tributyltin methoxide towards different acceptor molecules.[1,6]

A more drastic structural change is apparently needed before its effect through the electrophilic power of the tin becomes apparent. The fact that dipropyltin fluoride methoxide does not react with ethyl isocyanate is probably an example of this; dimerisation of the addendum molecule,[2] presumably through fluorine bridging, renders the tin already 5-co-ordinate and resistant to nucleophilic attack by the nitrogen of the isocyanate.

EXPERIMENTAL

General methods have been described in earlier Parts of this Series.

The Addition of Dibutyltin Dimethoxide to Acceptor Molecules.—(a) *Phenyl isocyanate*. Phenyl isocyanate (0·848 g., 7·13 mmoles) and dibutyltin dimethoxide (2·105 g., 7·13 mmoles) were mixed; heat was evolved, and the mixture became viscous. The infrared spectrum showed the absence of the isocyanate band at 2275 cm.$^{-1}$ and of the dimethoxide bands at 1035 and 1070 cm.$^{-1}$, and the presence of a new carbonyl frequency at 1595 cm.$^{-1}$. Two overlapping singlets of approximately equal area (see Table 1), corresponding to two methoxy-groups, were present in the n.m.r. spectrum.

More phenyl isocyanate (0·860 g., 7·23 mmoles) was added. Much heat was evolved; distillation gave N-*dibutylstannylene di*(*methyl* N-*phenylcarbamate*) (IIa), b. p. 154°/0·2 mm. (82%) (Found: C, 53·0; H, 6·8; N, 5·4. $C_{24}H_{24}N_2O_4Sn$ requires C, 53·9; H, 6·45; N, 5·3%).

The reaction between the dimethoxide and phenyl isocyanate dimer (1 or 2 mol.) was carried out in acetone. After about 15 min., 1 mol. of the dimer had dissolved; any more dimer remained undissolved. In each case the product was identified as the dicarbamate described above.

(b) *Ethyl isocyanate*. Ethyl isocyanate similarly gave (exothermically) a 1 : 1 adduct (Ib) [$\nu_{\text{max.}}$ 1695 (C=O) cm.$^{-1}$] and then a 1 : 2 adduct (IIb) [$\nu_{\text{max.}}$ 1695 (C=O) cm.$^{-1}$]. The N-*dibutylstannylene di*(*methyl* N-*ethylcarbamate*) (IIb) underwent partial dissociation during distillation; it was prepared as a brown oil by using a slight excess of the isocyanate, which was later removed under reduced pressure (Found: C, 44·5; H, 7·95; N, 6·2. $C_{16}H_{34}N_2O_4Sn$ requires C, 43·9; H, 7·85; N, 6·4%).

A mixture of the dimethoxide (1 mol.) and ethyl isocyanate (7 mol.) gave, after 24 hr., crystals of triethyl isocyanurate (quantitative yield based on isocyanate), m. p. 93—94°, $\nu_{\text{max.}}$ 1680 cm.$^{-1}$, infrared and n.m.r. spectra identical with authentic material,[3] m. p. 94—95° (Found: C, 50·9; H, 7·0; N, 20·7. Calc. for $C_9H_{15}N_3O_3$: C, 50·7; H, 7·1; N, 19·7%).

(c) *Phenyl isothiocyanate*. Both stages in the addition were rapid and exothermic. The 1 : 2 adduct (IIc) showed a band in the infrared spectrum at 1630 cm.$^{-1}$, which can probably be ascribed to the C=N stretching frequency. Both adducts dissociated during distillation at 100°(bath)/0·25 mm. Both were hydrolysed immediately by water giving, quantitatively, dibutyltin oxide and *O*-methyl *N*-phenylthiocarbamate, m. p. 86—87° (lit.,[7] 92—93°), $\nu_{\text{max.}}$ 3180 (NH) cm.$^{-1}$ (Found: C, 57·8; H, 4·85; N, 8·5; S, 19·3. Calc. for C_8H_9NOS: C, 57·5; H, 5·45; N, 8·4; S, 19·2%). The infrared spectrum was identical with that of authentic material (m. p. 94—95°) prepared from methanol and phenyl isothiocyanate.

(d) *Allyl isothiocyanate*. The 1 : 1 adduct (Id) was formed exothermically within 5 min. [$\nu_{\text{max.}}$ 1625 (C=O) cm.$^{-1}$]. The second stage in the addition was not exothermic, but still rapid, giving the 1 : 2 *adduct* (IId) as a pale yellow oil, $\nu_{\text{max.}}$ 1630 (C=O) cm.$^{-1}$ (Found: Sn, 25·0. $C_{16}H_{30}N_2O_2S_2Sn$ requires Sn, 25·5%). Both adducts were very rapidly hydrolysed by water.

(e) *Acetaldehyde*. Both stages in the reaction were exothermic. The n.m.r. spectrum of the 1 : 2 adduct (IIe) showed the presence of a quartet due to an acetal proton, τ 4·87, $J = 4{\cdot}2$ c./sec. At 0·1 mm., however, all the aldehyde was removed, and the dimethoxide was recovered.

(f) *Chloral*. Both stages were exothermic, giving the 1 : 1 adduct, (If), τ 4·84 (CH), and the 1 : 2 adduct (IIf) as a very viscous oil, τ 4·81 (CH), $\nu_{\text{max.}}$ 1155, 1085 (C–O?), 805, and 830 (CCl_3) cm.$^{-1}$.

(g) *Carbon disulphide*. A mixture of carbon disulphide (13·52 mmoles) and the dimethoxide (13·21 mmoles) set to a crystalline mass within 5 min. The excess of carbon disulphide was removed under reduced pressure giving S-*dibutyl*(*methoxy*)*tin*-O-*methyldithiocarbonate* (Ig) (12·2 mmoles) as waxy crystals, m. p. 64—67°, $\nu_{\text{max.}}$ 1060, 1140, and 1200 cm.$^{-1}$ (Found: C, 36·0; H, 6·9; S, 16·8. $C_{11}H_{24}O_2S_2Sn$ requires C, 35·6; H, 6·5; S, 17·2%). It was rapidly hydrolysed in air to a white oily liquid.

The n.m.r. spectrum indicated that in carbon tetrachloride, the 1 : 1 adduct (Ig) [τ 5·79 (OMe)] was in equilibrium with the dimethoxide (τ 6·43) and the 1 : 2 adduct (IIg) (τ 6·72). In an excess of carbon disulphide, the dimethoxide showed a single methoxide signal at τ 6·73, presumably due to the bisdithiocarbonate (IIg).

(h) *Sulphur dioxide*. Dry sulphur dioxide was bubbled through a solution of dibutyltin dimethoxide (1·097 g.) in dry benzene. After 3 min. the flask became warm and crystals began to separate. After 10 min. more, the solvent and the excess of sulphur dioxide were removed, to yield *methyl dibutyl*(*methoxy*)*tin sulphite* (Ih) (0·95 g.) as crystals, m. p. 95·5—96·5°, $\nu_{\text{max.}}$ 970, 1025 cm.$^{-1}$ (Found: C, 33·4; H, 6·55; S, 8·1; SO_2, 18·8. $C_{10}H_{24}O_4SSn$ requires C, 33·4; H, 6·75; S, 8·9; SO_2, 18·1%).

(i) *Carbon dioxide*. Dry carbon dioxide was passed through dibutyltin dimethoxide. Heat was evolved, and a very viscous oil resulted, $\nu_{\text{max.}}$ 1620 (C=O), 1325 cm.$^{-1}$, which had the composition $Bu_2Sn(OMe)_2$, 1·84 CO_2 (by quantitative hydrolysis to Bu_2SnO).

(j) *Trichloroacetonitrile*. A mixture of trichloroacetonitrile (0·3838 g., 2·65 mmoles) and dibutyltin dimethoxide (0·7653 g., 2·59 mmoles) crystallised overnight; the same product was obtained when the reagents were taken in a molar ratio of 2 : 1. The white waxy crystals were separated, and washed several times with light petroleum to give *methyl* N-*dibutyl*(*methoxy*)*stannyltrichloroacetimidate* (Ij) (0·89 g.), m. p. 93—94°, $\nu_{\text{max.}}$ 1725 (C=N), 800 (CCl_3) cm.$^{-1}$. The product was analysed immediately, because it decomposes in about 1 day in a sealed tube with development of

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[7] D. Groeckentz and R. Pohlondek-Fabini, *Pharm. Zentralhalle*, **1963**, **102**, 685.

a red colour (Found: C, 32·8; H, 5·6. $C_{12}H_{24}Cl_3NO_2Sn$ requires C, 32·8; H, 5·5%).

(k) *Di*-1-*naphthylcarbodi-imide*. The infrared and n.m.r. spectra showed that dibutyltin dimethoxide and di-1-naphthylcarbodi-imide reacted in both a 1 : 1 and a 1 : 2 molar ratio. Both adducts were characterised by a strong infrared band at 1645 (C=N) cm.$^{-1}$. Both were very sensitive to moisture, and removal of the solvent left only a brown resinous material.

The Addition of Dibutyltin Dimethoxide to Phenyl Isothiocyanate and Chloral.—The acceptors (1 mol. each) were added, in the above order, to dibutyltin dimethoxide; both stages of the reaction were exothermic. The τ values of the significant signals in the product (V) were 6·02 and 6·63 (OMe), 5·24 (CH); 8·22 (down-field peak of Bu resonance). The corresponding values for the compound (IIc) are 6·14 (OMe), 4·82 (CH), and 8·30 (Bu).

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