Organometallic Reactions. Part XVI.[1,2] Trihalogenomethyltin Compounds: their Preparations, Properties, and Reactions

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Trialkyl(diethylamino)tin compounds react readily with halogenoforms to give the corresponding trialkyl(trihalogenomethyl)tins, $R_3Sn{\cdot}CX_3$; these can then be reduced by trialkyltin hydrides or by lithium aluminium hydride to give the di- and mono-halogenomethyltin compounds, $R_3Sn{\cdot}CHX_2$ and $R_3Sn{\cdot}CH_2X$, respectively. Some properties and reactions of these products have been investigated.

In Part XV[1] we reported the preparation of trialkyltrihalogenomethyltin compounds *via* the adducts formed between trialkyltin oxides or alkoxides and trihalogenomethyl aldehydes or ketones. This paper describes an easier and more versatile route to the same family of trihalogenomethyltins, which has made it possible to examine their physical properties and reactions more thoroughly.

The Reaction of Trialkyldialkylaminotin Compounds with Halogenoforms.—Dialkylaminotin compounds react with a wide variety of protic reagents to liberate the dialkylamine and provide a route to the appropriate functionally substituted organotin compound.[3] Abel[4] showed, by following the i.r. and n.m.r. spectra, that, if the protic reagent is chloroform and the aminotin compound is in large excess, the initial reaction is limited to a hydrogen-bonding interaction.

We find, however, that if more halogenoform is present (0·1 mol.) protolysis of the Sn–N bond occurs in a few minutes to give the corresponding trihalogenomethyltin compound [equation (1), R = Me, Et, Bu, or Ph,

$$R_3Sn{\cdot}NEt_2 + HCX_3 \longrightarrow R_3Sn{\cdot}CX_3 + HNEt_2 \quad (1)$$

X = Br or Cl]. When R = Ph, some complications occur, which will be discussed below. No reaction occurs when X = F or I, and the mixed halogenoform $HCFCl_2$ (when R = Me) gave trimethyltin fluoride as the main product.

When the aminotin compound and halogenoform (2—5 mol.) were mixed at room temperature they reacted rapidly and exothermically, except when R = Ph; with more than 1 g. of reactants, the presence of an inert solvent is advisable to moderate the reaction. Bromoform is more reactive than chloroform, and trimethyltin compounds than tributyltin compounds.

The trihalogenomethyltin compounds must not be left in contact with the diethylamine, or they react further as described below. The products were isolated by removing the diethylamine and excess of halogenoform under reduced pressure. Trimethyl-trichloromethyltin and -tribromomethyltin are solids which can readily be purified by recrystallisation from pentane at low temperature, but the corresponding triethyl- and tributyl-tin compounds are oils which could not be distilled or recrystallised. All the compounds prepared were sensitive to atmospheric moisture, and reacted with methanol to give the corresponding halogenoform and trialkyltin methoxide. The CCl_3 group in trichloromethyltin compounds is characterised by a strong i.r. band in the spectrum at 710 cm.$^{-1}$; a corresponding band occurs at 610 cm.$^{-1}$ in the spectra of tribromomethyltin compounds.

We were unable to prepare tributyltrichloromethyltin by treating tributyltin chloride with trichloromethyllithium,[1] but Seyferth[5] and his co-workers have since prepared trimethyltrichloromethyltin by an analogous route [equation (2)], and also isolated trimethylbromodichloromethyltin from the reaction between trimethyltin bromide and bromodichloromethylphenylmercury in boiling benzene [equation (3)].

$$Me_3SnCl + LiCCl_3 \xrightarrow{-110^\circ} Me_3Sn{\cdot}CCl_3 + LiCl \quad (2)$$

$$Me_3SnBr + PhHg{\cdot}CCl_2Br \xrightarrow{80^\circ} Me_3Sn{\cdot}CCl_2Br + PhHgBr \quad (3)$$

Seyferth's initial products contained tin halides, which were separated by distillation under high vacuum and by g.l.c. Our trimethyltrichloromethyltin melted at 65—68°, whereas Seyferth's sample melted just above room temperature, but otherwise the properties of the two products are in agreement. Chivers and David have repeated the preparation by our method[6] and report m.p. 43—45° for an unrecrystallised sample.

The reaction of diethylaminotriphenyltin with chloroform [equation (1) R = Ph, X = Cl or Br] and with bromoform was relatively slow, and, in benzene as solvent, needed 1 day at 65°, and 1 day at 33°, respectively, for completion. The products always contained considerable amounts of the corresponding triphenyltin halides, more of which were formed when the trihalogenomethytin compounds were recrystallised from carbon tetrachloride. We observed similar behaviour when we tried to purify trichloromethyltriphenyltin, prepared by a modification of Symes' method.[7]

Extension of the General Reaction.—Attempts were

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[1] Part XV, A. G. Davies and W. R. Symes, preceding paper.

[2] Preliminary report, A. G. Davies and T. N. Mitchell, *J. Organometallic Chem.*, 1966, **6**, 568.

[3] K. Jones and M. F. Lappert, *J. Organometallic Chem.*, 1965, **3**, 295.

[4] E. W. Abel, D. A. Armitage, and D. B. Brady, *Trans. Faraday Soc.*, 1966, **62**, 3459; E. W. Abel, D. A. Armitage, and S. P. Tyfield, *J. Chem. Soc.* (*A*), 1967, 554.

[5] D. Seyferth, F. M. Armbrecht, B. Prokai, and R. J. Cross, *J. Organometallic Chem.*, 1966, **6**, 573.

[6] T. Chivers and B. David, *J. Organometallic Chem.*, 1967, **10**, P35; 1968, **13**, 177.

[7] A. G. Davies and P. R. Palan, unpublished; P. R. Palan, Ph.D. Thesis, London, 1967.

first made to extend these reactions to bisdiethylaminotin compounds by reaction (4) ($R = Me$ or Et, $X = Cl$ or Br).

$$R_2Sn(NEt_2)_2 + 2HCX_3 \longrightarrow R_2Sn(CX_3)_2 + 2HNEt_2 \quad (4)$$

The n.m.r. spectra suggested that equilibria were established, which could not be displaced to the right. The products were highly coloured oils which apparently contained both trihalogenomethyl and carbonyl groups. For the case $R = Me$, $X = Cl$, the product decomposed spontaneously with a mild explosion; the corresponding product for the case $R = Me$, $X = Br$ was therefore not isolated. Zuckermann[8] reported that solutions of dimethylbis(dimethylamino)tin in chloroform (1 : 1 v/v) exploded during n.m.r. measurements.

Similar reactions between trialkyldialkylaminotins and dihalogenomethanes were also attempted, in the hope that dihalogenomethyltins could be obtained by equation (5) ($R = Me$, $X = Cl$ or Br).

$$R_3Sn\cdot NEt_2 + H_2CX_2 \longrightarrow R_3Sn\cdot CHX_2 + HNEt_2 \quad (5)$$

The n.m.r. spectra showed that the reactions were slow at room temperature, and the only products identified were the diethylammonium halides, which are also the major products when the dihalogenomethanes react with diethylamine. The spectra showed none of the characteristic signals of the compounds $R_3Sn\cdot CHX_2$ and $R_3Sn\cdot CH_2X$, which are described below. Tseng and his co-workers have reported that sodium trichloroacetate will insert the dichlorocarbene unit into the Sn–H bond of triethyl- and tributyl-tin hydride, to give triethyldichloromethyltin and tributyldichloromethyltin (b.p. 114—116°/1·3 mm.) respectively,[9] but from this type of reaction we could isolate only tributyltin dichloroacetate.

Some preliminary studies were also carried out with other compounds containing a weakly acidic CH group. Methyl and ethyl orthoformate were inert. Dichloro- and dibromo-acetonitrile, and 1,1,2,2-tetrachloro- and pentachloro-ethane did react, but their reactions were complicated by the fact that diethylamine reacts exothermically with these compounds giving diethylammonium halides. Chivers and David showed that trimethyldimethylaminotin reacted with pentachloroethane to give the dimethylamine adduct of trimethyltin chloride as a major product, but trichloroethylene reacted in 15 min. under reflux to give trimethyl(trichlorovinyl)tin in 80% yield in a straightforward acidolysis.[6]

Reactions of Trihalogenomethyltin Compounds.—(a) *With halogens*. Trimethyltrichloromethyltin reacted with chlorine and with bromine in carbon tetrachloride, to give the corresponding trimethyltin halide and dimethyltin dihalide according to equations (6) and (7) ($X = Cl$ or Br).

$$Me_3Sn\cdot CCl_3 + X_2 \longrightarrow Me_3SnX + CCl_3X \quad (6)$$

$$Me_3SnX + X_2 \longrightarrow Me_2SnX_2 + MeX \quad (7)$$

Chlorine reacted more rapidly than bromine, and iodine did not react during 3 days at 65°, although the trimethyltrichloromethyltin slowly decomposed under these conditions. Acetyl chloride similarly did not react.

In contrast, Clark and Willis[10] found that trimethyltrifluoromethyltin reacted with an equimolar amount of chlorine with cleavage of the methyl–tin rather than the trifluoromethyl–tin bond, by equation (8).

$$Me_3Sn\cdot CF_3 + Cl_2 \longrightarrow Me_2Sn(CF_3)Cl + MeCl \quad (8)$$

(b) *Thermal decomposition*. The trihalogenomethyl derivatives of several metals have been reported to decompose thermally to give the corresponding metal halide and dihalogenocarbene by equation (9) (see ref. 1).

$$MCX_3 \longrightarrow MX + {:}CX_2 \longrightarrow C_2X_4 + C_3X_6 \quad (9)$$

However, Symes found[1] that tributyltrichloromethyltin and tributyltribromomethyltin decomposed to give mainly the corresponding dibutyltin dihalides, which were identified as their bipyridyl adducts, and the trichloromethyl compound could not be caused to transfer a dichlorocarbene unit to *cis,cis*-cyclo-octa-1,5 diene at 110°. Seyferth, however, has reported[5] that trimethyltrichloromethyltin and trimethylbromodichloromethyltin do act as carbene transfer reagents towards olefins, though they are much less reactive than the corresponding phenylmercury compounds.

We found that trimethyltribromomethyltin decomposed in carbon tetrachloride in 50 days at 65°, giving trimethyltin bromide (95%) and dimethyltin dibromide (5%). The trichloromethyl compound decomposed much more slowly. A sample of triethyltribromomethyltin, the decomposition of which was probably catalysed by the impurities present, gave, after 5 days at 65°, triethyltin bromide (83%) and diethyltin dibromide (17%). It appears that there is a definite trend towards formation of the dihalide as the size of the alkyl group increases. It may be relevant that Seyferth reports that a dihalogenocarbene attacks the β- and γ-C–H bonds of a large alkyl group in preference to the α-C–H bonds of a methyl group.[11]

(c) *With stannic chloride*. The reactions of stannic chloride with trimethyltrichloromethyltin and with trimethyltribromomethyltin were followed by n.m.r. spectroscopy. Trimethyltrichloromethyltin reacted during 10 days at room temperature, giving methyltin trichloride as one major product. The n.m.r. spectrum of the second product corresponded to that reported[6] by Chivers and David for dimethyltrichloromethyltin chloride, which they obtained from the reaction between

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[8] E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 105.

[9] C.-L. Tseng, R.-X. Zhuo, and S.-T. Ma, *Kexue Tongbao*, 1966, **17**, 71.

[10] H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888.

[11] D. Seyferth, 3rd International Symposium on Organometallic Chemistry, Munich, August 1967.

trimethyltrichloromethyltin and boron trichloride at 25°. Our reaction therefore corresponds to that shown in equation (10).

$$\mathrm{Me_3Sn{\cdot}CCl_3 + SnCl_4 \longrightarrow MeSnCl_3 + Me_2Sn(CCl_3)Cl} \quad (10)$$

At 65°, the products entered into an equilibrium involving methyltin trichloride, dimethyltin dichloride, dimethyltrichloromethyltin chloride, and a fourth product which is presumably methyltrichloromethyltin dichloride [equation (11)].

$$\mathrm{Me_2Sn(CCl_3)Cl + MeSnCl_3 \rightleftharpoons MeSn(CCl_3)Cl_2 + Me_2SnCl_2} \quad (11)$$

Trimethyltribromomethyltin reacted only slowly with stannic chloride, perhaps because the reaction is controlled by steric factors. Reactions corresponding to those of equations (10) and (11) did not take place; the rate-controlling step appeared to be the decomposition of the trimethyltribromomethyltin into trimethyltin bromide, which then reacted with stannic chloride according to equation (12).

$$\mathrm{Me_3SnBr + SnCl_4 \longrightarrow Me_2SnBrCl + MeSnCl_3} \quad (12)$$

(d) *With diethylamine.* When n.m.r. tubes containing equimolar amounts of diethylamine and compounds $\mathrm{R_3Sn{\cdot}CX_3}$ in the corresponding halogenoform were set aside, a further reaction occurred and the solution became brown and more viscous. The methyl and methylene signals of the amine at τ 8·90 and 7·30 disappeared and were replaced by less well resolved systems at τ *ca.* 6·3 and 8·65, and an associated singlet signal appeared at 1·55 (X = Br) or 1·70 (X = Cl). Similar behaviour was observed when the products of the reaction between dibutylbis(diethylamino)tin and halogenoforms were set aside, but mixtures of the halogenoforms and diethylamine itself showed no reaction during similar periods.

Spectroscopic evidence suggests that the reaction we are observing is the insertion of a dihalogenocarbene unit into the NH bond of the amine to give the diethyldihalogenomethylamine (I; R = Et, X = Cl or Br).

$$\mathrm{R_2NH + [\colon CX_2] \longrightarrow R_2N{\cdot}CHX_2 \xrightarrow{H_2O} R_2N{\cdot}CHO} \quad (13)$$

Trimethyltrichloromethyltin and diethylamine were kept at room temperature for 2 days so that about 60% decomposition of the trimethyltrichloromethyltin had occurred, and the sample showed a new singlet at τ 1·70 and two methylene quartets at τ 7·26 and 6·3, for the reactant and product respectively. Diethylformamide was then added, giving rise to new signals at 1·75 (CHO) and 6·6 ($\mathrm{N{\cdot}CH_2}$). The addition of aqueous acetone then caused the peaks ascribed to the compound $\mathrm{Et_2N{\cdot}CHCl_2}$ to disappear almost at once, while the signals of diethylformamide increased in intensity. Apparently the dichloromethylamine (I) is very easily hydrolysed to the formamide (II). Analogous behaviour was shown by a mixture of trimethyltribromomethyltin and diethylamine, but in neither case were we able to isolate and characterise the dihalogenomethylamine (I).

Some previous work supports this interpretation. Saunders and Murray[12] studied the reaction between dichlorocarbene (generated from chloroform and potassium t-butoxide) and amines. With secondary amines, the only product which they could identify was the appropriate *NN*-dialkylformamide (II), and, despite many precautions, the intermediate dialkyldichloromethylamines (I) could not be isolated.

(e) *With trialkyltin hydrides and with lithium aluminium hydride.* The trihalogenomethyltin compounds are reduced by trimethyltin hydride or tributyltin hydride in a stepwise manner according to equations (14)—(16). Seyferth and his co-workers[13] have reported that phenyltrihalogenomethylmercury compounds are reduced by trialkyltin hydrides in a reaction analogous to that of equation (14).

$$\mathrm{R^1{}_3Sn{\cdot}CX_3 + R^2{}_3SnH \longrightarrow R^1{}_3Sn{\cdot}CHX_2 + R^1{}_3SnX} \quad (14)$$

$$\mathrm{R^1{}_3Sn{\cdot}CHX_2 + R^2{}_3SnH \longrightarrow R^1{}_3Sn{\cdot}CH_2X + R^2{}_3SnX} \quad (15)$$

$$\mathrm{R^1{}_3Sn{\cdot}CH_2X + R^2{}_3SnH \longrightarrow R^1{}_3Sn{\cdot}CH_3 + R^2{}_3SnX} \quad (16)$$

With X = Br, reaction (14) was always accompanied by reaction (15), and the reaction between trimethyltribromomethyltin and tributyltin hydride in a 1 : 3 molar ratio was extremely exothermic, giving tetramethyltin as a major product.

These reactions usually give mixtures of products which cannot readily be separated. For example, one particular reduction of trimethyltrichloromethyltin with tributyltin hydride (1 mol.) gave a mixture of $\mathrm{Me_3Sn{\cdot}CCl_3}$ (2·5%), $\mathrm{Me_3Sn{\cdot}CHCl_2}$ (63%), $\mathrm{Me_3Sn{\cdot}CH_2Cl}$ (8%), and $\mathrm{Me_3SnCl}$ (25%). Lithium aluminium hydride in ether, however, was no more selective: it reacted exothermically to give a mixture containing $\mathrm{Me_3Sn{\cdot}CCl_3}$ (6%), $\mathrm{Me_3Sn{\cdot}CHCl_2}$ (67%), $\mathrm{Me_3Sn{\cdot}CH_2Cl}$ (9%), $\mathrm{Me_3SnCl}$ (3%), and $\mathrm{Me_4Sn}$ (16%). Sodium borohydride did not react.

N.m.r. data for the various compounds $\mathrm{R_3SnCX_3}$, $\mathrm{R_3Sn{\cdot}CHX_2}$, and $\mathrm{R_3Sn{\cdot}CH_2X}$ are summarised in Tables 1 and 2. As the electronegativity of the functionally-substituted group is reduced in the sequence $\mathrm{R_3Sn{\cdot}CX_3 \longrightarrow R_3Sn{\cdot}CHX_2 \longrightarrow R_3Sn{\cdot}CH_2X \longrightarrow R_3Sn{\cdot}CH_3}$ (X = Cl or Br), the chemical shifts of the protons of the methyl groups (R = Me) and of the $\mathrm{CH}_n\mathrm{X}_{3-n}$ groups show the expected rise. In the same sequence, the magnitude of the coupling between $^{119}\mathrm{Sn}$ nuclei and the methyl groups shows little change, but $J(^{119}\mathrm{Sn{-}CH}_n\mathrm{X}_{3-n})$ increases slightly. Verdonck and

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[12] M. Saunders and R. W. Murray, *Tetrahedron*, 1960, **11**, 1.

[13] D. Seyferth, H. D. Simmons, and L. J. Todd, *J. Organometallic Chem.*, 1963, **4**, 284.

van der Kelen[14] have presented similar data for the compounds $(XCH_2)_xSnX_{4-n}$ (X = Cl or Br).

Attempts have been made to correlate coupling constants of this type with the percentage of *s* character in the tin–carbon bonds,[15] but this approach seems to be of doubtful validity.[14,16,17]

^{119}Sn N.m.r. chemical shifts for some of the compounds in Table 1 are discussed in ref. 18.

TABLE 1

Compounds $Me_3Sn{\cdot}CH_nX_{3-n}$ and $Me_2Sn(CH_nX_{3-n})Br$

	τ(Me)	$J(^{119}Sn-Me)$ (Hz)	$\tau(CH_nX_{3-n})$	$J(^{119}Sn-CH_nX_{3-n})$ (Hz)
$Me_3Sn{\cdot}CCl_3$	9·50	56·0		
$Me_3Sn{\cdot}CHCl_2$	9·66	57·0	4·30	15·0
$Me_3Sn{\cdot}CH_2Cl$	9·78	56·4	6·97	19·4
$Me_3Sn{\cdot}CH_3$	9·93	54·0	9·93	54·0
$Me_3Sn{\cdot}CBr_3$	9·50	57·2		
$Me_3Sn{\cdot}CHBr_2$	9·64	56·2	4·52	13·2
$Me_3Sn{\cdot}CH_2Br$	9·74	56·4	7·34	18·0
$Me_2Sn(CHCl_2)Br$	8·97	64·2	4·04	16·0
$Me_2Sn(CH_2Cl)Br$	9·10	63·0	6·54	23·0
$Me_2Sn(CH_2Br)Br$	9·07	60·7	6·82	19·8

TABLE 2

Compounds $Et_3Sn{\cdot}CH_nX_{3-n}$ and $Bu_3Sn{\cdot}CH_nX_{3-n}$

	X = Cl		X = Br	
	$\tau(CH_nX_{3-n})$	$J(^{119}Sn-CH_nX_{3-n})$ (Hz)	$\tau(CH_nX_{3-n})$	$J(^{119}Sn-CH_nX_{3-n})$ (Hz)
$Et_3Sn{\cdot}CHX_2$	4·21	13·0	4·48	10·0
$Et_3Sn{\cdot}CH_2X$	6·88	17·0	7·31	15·6
$Bu_3Sn{\cdot}CHX_2$	4·26	14·0	4·50	10·5
$Bu_3Sn{\cdot}CH_2X$	6·91	17·0	7·33	15·6

All values refer to solutions in carbon tetrachloride. Seyferth[5] reports the following values for solution in carbon disulphide: $Me_3Sn{\cdot}CCl_3$ τ(Me) 9·52, $J(^{119}Sn-Me)$ 55 Hz; $Me_3Sn{\cdot}CCl_2Br$ τ(Me) 9·51; $J(^{119}Sn-Me)$ 55 Hz.

The compounds $R_3Sn{\cdot}CHX_2$ and $R_3Sn{\cdot}CH_2X$ which were obtained from the reductions are not hydrolysed as thin films in the air, nor are they readily attacked by glacial acetic acid. Moreover, bromine cleaves a methyl–tin bond rather than a halogenomethyl–tin bond, according to equation (17). This is now similar to the behaviour observed by Clark and Willis in the reactions between trimethyltrifluoromethyltin and chlorine.[10]

$$Me_3Sn{\cdot}CH_nX_{3-n} + Br_2 \longrightarrow Me_2Sn(CH_nX_{3-n})Br + MeBr \qquad (17)$$

The reaction of bromine with $Me_3Sn{\cdot}CHCl_2$ in carbon tetrachloride was exothermic, whilst that with $Me_3Sn{\cdot}CH_2Cl$ and $Me_3Sn{\cdot}CH_2Br$ took place within a few minutes at room temperature. N.m.r. parameters of the products are given in Table 1; the values follow the same trends as those for the compounds $Me_3Sn{\cdot}CHX_2$ and $Me_3Sn{\cdot}CH_2X$.

EXPERIMENTAL

General methods are described in earlier Parts of this series. N.m.r. spectra were recorded at 33·4° with a Perkin-Elmer R10 instrument. Analyses for Cl and Br were carried out by the oxygen-flask method.[19]

Preparation of the Trialkyltrihalogenomethyltins.—(*a*) Trialkyltrichloromethyltins were prepared by adding an excess of the halogenoform to the appropriate aminotin compound with stirring. Volatile compounds were removed after 15 min. Most preparations were carried out on the scale of 1 g. or less; with methyl- or ethyl-tin compounds on a larger scale (2—5 g.), benzene was used as a diluent to avoid excessive heating of the mixture. The general method is exemplified by the preparation of *trimethyltrichloromethyltin*.

The n.m.r. spectrum of trimethyldiethylaminotin shows signals at τ 6·99 (q, CH_2), 9·01 (t, *J* 7·2 Hz, $CH_2{\cdot}CH_3$) and 9·82 [s, $SnCH_3$, *J*(Sn–H) 54·3 and 56·7 Hz]. When an excess (4—5 times v/v) of chloroform was added to a sample of the aminotin compound in an n.m.r. tube, some heat was evolved, and, after 5 min., the n.m.r. spectrum showed that the reaction was complete, with signals at 9·50 (s, $SnCH_3$), 7·30 (quintet) and 8·92 (t) [*cf.* Et_2NH, 7·30 (q) and 8·92 (t)].

Volatile compounds were removed under reduced pressure, leaving a white crystalline solid which sintered at 55—55·5°, m.p. 57·5—59·5°, $\nu_{max.}$ 710 (CCl_3) cm.$^{-1}$. It was recrystallised from pentane at −80° to give white needles, m.p. 65—68° (Found: C, 17·4; H, 3·5; Cl, 36·0. $C_4H_9Cl_3Sn$ requires C, 17·1; H, 3·2; Cl, 37·5%).

As a thin film in the air it was hydrolysed immediately to trimethyltin hydroxide, and it reacted with aqueous methanol in acetone to give chloroform in 98% yield (integrated n.m.r. spectrum).

By this method, triethyltrichloromethyltin was prepared as a colourless oil, $\nu_{max.}$ 705 (CCl_3) cm.$^{-1}$, which was readily hydrolysed as a thin film, and which could not be recrystallised from pentane at −80° [Found: Cl, 30·9 and 31·3% (by different methods). Calc. for $C_7H_{15}Cl_3Sn$; Cl, 32·8%, *i.e.* the sample was 95% pure].

Similarly tributyltrichloromethyltin was isolated as a colourless oil, $\nu_{max.}$ 705s (CCl_3) and 770br (SnOSn) cm.$^{-1}$, which was hydrolysed to the extent of 50% when a thin film was exposed to air for 2 min. The oil could neither be crystallised nor distilled without decomposition, and contained 70% $Bu_3Sn{\cdot}CCl_3$, the main impurity being bistributyltin oxide.

(*b*) Trialkyltribromomethyltins required the above method to be modified for R = Me or Et; in this case the aminotin compounds were treated with a 50% (v/v) solution of bromoform in benzene with stirring. For R = Bu, benzene was not required. Volatile compounds were removed under reduced pressure as before.

Trimethyltribromomethyltin was obtained as a white crystalline solid, m.p. 96·5—97°, $\nu_{max.}$ 610vs (CBr_3) cm.$^{-1}$, which when recrystallised from pentane at −80° had m.p. 100—102° (Found: C, 11·3; H, 2·5; Br, 56·2. $C_4H_9Br_3Sn$ requires C, 11·5; H, 2·2; Br, 57·7%). It was rapidly

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[14] L. Verdonck, G. P. van der Kelen, and Z. Eeckhaut, *J. Organometallic Chem.*, 1968, **11**, 487.

[15] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3906.

[16] L. Verdonck and G. P. van der Kelen, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 478.

[17] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 528.

[18] A. G. Davies, P. G. Harrison, J. D. Kennedy, W. McFarlane, T. N. Mitchell, and R. J. Puddephatt, *J. Chem. Soc.* (*A*), 1969, 1136.

[19] A. M. G. Macdonald, *Adv. Analyt. Chem. and Instrumentation*, 1965, **4**, 75.

hydrolysed as a thin film in air, and methanolysis gave bromoform in 95% yield (integrated n.m.r. spectrum).

Triethyltribromomethyltin was obtained as a pale yellow oil of 85—90% purity, which was readily hydrolysed as a thin film; $\nu_{max.}$ 605s (CBr_3) cm.$^{-1}$.

Tributyltribromomethyltin was isolated in *ca.* 80% purity as a pale yellow oil, $\nu_{max.}$ 610s (CBr_3) cm.$^{-1}$, slowly hydrolysed as a thin film.

Triphenyltribromomethyltin was prepared by treating triphenyldiethylaminotin with an excess of bromoform; the reaction was complete in 6 hr.; volatile compounds were then removed to leave a yellow solid, m.p. 70—75°, $\nu_{max.}$ 620s (CBr_3) and 780w (SnOSn) cm.$^{-1}$, which contained 71% $Ph_3Sn{\cdot}CBr_3$, 24% Ph_3SnBr, and 5% $(Ph_3Sn)_2O$. It was dissolved in carbon tetrachloride and recovered by evaporation of the solvent at room temperature, giving a pale yellow crystalline solid, m.p. 99—103°, with no C–Br stretch in the i.r., and containing triphenyltin bromide (43%) and bistriphenyltin oxide.

The Reactions of Dialkylbis(diethylamino)tins with Halogenoforms. (a) *Dibutylbis(diethylamino)tin.* (i) *With chloroform.* An excess of chloroform was added to the aminotin compound in an n.m.r. tube. After 15 min., the spectrum showed the $SnNCH_2$ quartet at τ 6·95, and the characteristic quintet of $HN(CH_2{\cdot}CH_3)_2$ at τ 7·30, in the ratio 1 : 1. The tube was kept at 33·4° and the spectrum recorded after a further 15, 45, and 75 min. The first two spectra showed no change, but when the third was being recorded, the sample began to heat up rapidly. When thermal equilibrium was restored, new signals were observed at τ 1·55 (singlet), and 6·4 (q, NCH_2). Volatile compounds were removed under reduced pressure, leaving a brown oil, $\nu_{max.}$ 1680vs (C=O) and 700 (C–Cl) cm.$^{-1}$.

(ii) *With bromoform.* The aminotin compound was treated with an excess of bromoform. The mixture was cooled to 0°, then evacuated with a rotary pump for 1 hr. at 0° and 2 hr. at room temperature, leaving a black oil, $\nu_{max.}$ 1680vs and 610m (C–Br) cm.$^{-1}$, τ 1·44 and 6·2 (q).

(b) *Dimethylbis(diethylamino)tin.* An excess of chloroform was added to the aminotin compound in an n.m.r. tube. After 10 min., the spectrum showed the $SnNCH_2$ quartet and the $HN(CH_2{\cdot}CH_3)_2$ quintet in the ratio 1 : 2. Removal of volatile materials under reduced pressure gave an orange oil, $\nu_{max.}$ 1680s and 705s (CCl_3) cm.$^{-1}$, which decomposed with a mild explosion after 20 min.

Reactions of Trimethyltrichloromethyltin.—(a) *With bromine.* A solution of trimethyltrichloromethyltin in carbon tetrachloride was treated with an excess of a solution of bromine in carbon tetrachloride. The n.m.r. spectrum was recorded at intervals; the bromine was slowly decolourised and the signal at τ 9·50 disappeared during 20 hr., being replaced by signals at 9·26 and 8·64 in a 1 : 1 ratio. Volatile components were removed at a water pump, leaving a crystalline solid which was identified as a mixture of trimethyltin bromide and dimethyltin dibromide.

(b) *With chlorine.* A rapid stream of dry chlorine was passed through a solution of trimethyltrichloromethyltin (1·7 g.) in carbon tetrachloride (10 c.c.). Initially, some heat was evolved. After 20 min., the n.m.r. spectrum showed peaks at τ 9·34 (Me_3SnCl) and 9·50 ($Me_3Sn{\cdot}CCl_3$) in the ratio 1 : 5. Chlorine was passed for a further 2·5 hr. Next day, volatile components were removed at a water pump, and the remaining suspension was treated with carbon tetrachloride, leaving a residue of dimethyltin dichloride (55·4%).

(c) *With iodine.* Iodine (0·18 g.) was added to the trimethyltrichloromethyltin (0·2 g.) in benzene (0·5 c.c.). When the flask was shaken, the iodine partially dissolved, but no more dissolved during 6 days at 65°, after which the n.m.r. spectrum showed a signal characteristic of trimethyltin chloride. Iodine was recovered in good yield.

(d) *With stannic chloride.* Stannic chloride (0·21 c.c., 0·47 g., 1 equiv.) was added to trimethyltrichloromethyltin (0·4 g.) in carbon tetrachloride (0·5 c.c.), and the n.m.r. spectrum was recorded at intervals. During 10 days, the peak at τ 9·50 disappeared and new peaks appeared at 8·25 [*J*(Sn–H) 97·8 and 102·1 Hz], 8·74, and 8·93 [*J*(Sn–H) 63·3 and 65·7 Hz] in the approximate ratio 3 : 1 : 6. A sample of methyltin trichloride (prepared by Dr. D. A. ARMITAGE) had τ 8·26 [*J*(Sn–H) 96·0 and 100·3 Hz] {lit.,[15,20,21] τ 8·35 [*J*(Sn–H) 95·7 and 100·0 Hz]}.

Carbon tetrachloride was removed under reduced pressure, leaving a white solid, $\nu_{max.}$ 810vs (CCl_3) cm.$^{-1}$. The solid was redissolved in carbon tetrachloride (0·5 c.c.), and the solution kept at 65° for 48 hr., when an equilibrium was established involving methyltin peaks as follows: τ, $J(^{117\text{ and }119}Sn{-}H)$, rel. area: 8·25, 97·8 and 102·1 Hz, 1; 8·45, 79·8 and 83·4 Hz, 4; 8·75, 68·4 and 71·4 Hz, 6; 8·95, 63·0 and 65·4 Hz, 5. A sample of dimethyltin dichloride had τ 8·80, *J*(Sn–H) 67·8 and 70·8 Hz.

Dimethyltin dichloride and methyltin trichloride were isolated from the mixture and identified as their bipyridyl derivatives.

Reduction of Trihalogenomethyltin Compounds with Tin Hydrides.—All reactions were carried out by mixing the trihalogenomethyltin compound, either neat or as a solution or suspension in benzene, with either tributyltin hydride or trimethyltin hydride in the desired molar ratio at room temperature. The mixtures were transferred to n.m.r. tubes, and the reactions followed spectroscopically. Some representative experiments are outlined below.

(*a*) Trimethyltrichloromethyltin (0·64 g.) was treated with tributyltin hydride (0·66 g., 1 mol.); it dissolved during 5 min. After 30 min., the n.m.r. spectrum showed that all the tin hydride had been consumed. The main methyltin signal was at τ 9·66 [*J*(Sn–CH_3) 56·2 and 58·8 Hz], and a singlet was present at τ 4·30 [*J*(Sn–H) 16·0 Hz]; the ratio of the areas of these peaks was 9·25 : 1. The oil showed $\nu_{max.}$ 690s (C–Cl) cm.$^{-1}$, and exposure of the plates of the i.r. cell to air for 2 min. produced no change in the spectrum. Potentiometric titration showed the presence of 5·9% ionizable Cl (Calc. for a 1 : 1 mixture of Bu_3SnCl and $Me_3Sn{\cdot}CHCl_2$, 6·2%), *i.e.* Bu_3SnCl is formed in 95% yield.

(*b*) Trimethyltribromomethyltin (0·61 g.) was suspended in benzene (0·5 c.c.), and tributyltin hydride (0·43 g., 1 mol.) was added with vigorous shaking, the tribromomethyltin compound dissolving at once. The benzene was removed under reduced pressure and the resulting oil diluted with carbon tetrachloride (0·5 c.c.). The n.m.r. spectrum showed peaks ascribed to $Me_3Sn{\cdot}CHBr_2$ at τ 4·52 [*J*(Sn–CH) 13·2 Hz] and 9·63 [*J*(Sn–Me) 56·6 and 59·2 Hz] and to $Me_3Sn{\cdot}CH_2Br$ at 7·34 [*J*(Sn–CH_2) 17·4 Hz] and 9·76; the ratio of the area of the two Me_3Sn peaks was 3 : 1. An excess of glacial acetic acid was added, and the mixture was kept for several hours at 55°; the chloromethyltin compounds were unaffected.

(*c*) Tributyltribromomethyltin (0·66 g.) was treated with

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[20] G. P. van der Kelen, *Nature*, 1962, **193**, 1069.

[21] M. P. Brown and D. E. Webster, *J. Phys. Chem.*, 1960, **64**, 698.

tributyltin hydride (0·39 g., 1 mol.). The hydride reacted during 3 hr., and the n.m.r. spectrum showed that the dibromomethyl- and bromomethyl-tin compounds were present in the ratio 2 : 1; small peaks due to bromoform and dibromomethane were also present.

Reduction of Trimethyltrichloromethyltin with Lithium Aluminium Hydride.—Lithium aluminium hydride (0·25 g., 0·007 mole) was added to trimethyltrichloromethyltin (4·0 g., 0·014 mole) in ether (15 c.c.). The mixture was stirred magnetically and cooled in water at 15°; a vigorous reaction occurred, causing the ether to reflux.

After 2 hr. a white solid which had been precipitated was filtered off. Volatile material was removed at the water pump, leaving a colourless oil (2·5 g.) which apparently contained some metal salts. The n.m.r. spectrum of the oil showed that it contained Me_4Sn 16%, Me_3SnCl 3%, Me_3SnCCl_3 6%, $Me_3Sn{\cdot}CH_2Cl$ 9%, and $Me_3Sn{\cdot}CHCl_2$ 67%.

When trimethyltrichloromethyltin (3·4 g.) was refluxed with sodium borohydride (0·3 g.) in ether (15 c.c.) for 6·5 hr., no reaction occurred, and the organotin compound was recovered.

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