Organometallic Reactions. Part XVII.[1] Some Exchange and Addition Reactions of Aminodimethyltin Compounds

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Dimethyltin bis(diethylamide) reacts with dimethyltin dihalides to produce the dimethyltin halide diethylamides; these are unstable, but can be characterised as their adducts with carbon disulphide.

NN'N''-Triethylhexamethylcyclotristannazane, $(Me_2Sn{\cdot}NEt)_3$, disproportionates when treated with organotin chorides, R_nSnCl_{4-n}, to give distannazanes of general formula $R_nSnCl_{3-n}{\cdot}NEt{\cdot}SnMe_2Cl$. Treatment of 1,1,3-trichloro-2-ethyl-1,3,3-trimethyldistannazane with 2,2'-bipyridyl gives Me_2SnCl_2,bipy and *sym*-trichloro-*NN'N''*-triethyltrimethylcyclotristannazane. A mixture of dimethyltin sulphide and the triethylhexamethylcyclotristannazane exists in equilibrium with the cyclotristannazadithiane and the cyclotristannadiazathiane.

DIALKYLTIN dimethoxides readily disproportionate with dialkyltin dihalides to give dialkyltin halide methoxides (I) [equation (1)].[2] The tin–oxygen bond of the product

$$R_2Sn(OMe)_2 + R_2SnX_2 \longrightarrow 2R_2Sn(X)OMe \ (I) \qquad (1)$$

readily undergoes addition reactions with suitable multiply-bonded acceptor molecules (A=B) [equation (2)], and the same adducts can be obtained by the reverse of this sequence of reactions, *i.e.* by initial addition of the doubly-bonded acceptor molecule (equation 3), and then disproportionation of the product with the dialkyltin dihalide [equation (4)].[3]

$$R_2Sn(X)OMe + A{=}B \longrightarrow R_2Sn(X)A{\cdot}B{\cdot}OMe \qquad (2)$$

$$R_2Sn(OMe)_2 + 2A{=}B \longrightarrow R_2Sn(A{\cdot}B{\cdot}OMe)_2 \qquad (3)$$

$$R_2Sn(A{\cdot}B{\cdot}OMe)_2 + R_2SnX_2 \longrightarrow 2R_2Sn(X)A{\cdot}B{\cdot}OMe \qquad (4)$$

Dialkyltin oxides[4] and sulphides[5] also readily disproportionate with alkyltin halides to give halogen-substituted organodistannoxanes and organodistannthianes. Thus dibutyltin dichloride reacts with dibutyltin oxide to give 1,1,3,3-tetrabutyl-1,3-dichlorodistannoxane [equation (5)], and dibutyltin sulphide reacts with phenyltin trichloride to give 1,1-dibutyl-3-phenyl-1,3,3-trichlorodistannthiane [equation (6)].

$$Bu_2SnO + Bu_2SnCl_2 \longrightarrow ClBu_2Sn{\cdot}O{\cdot}SnBu_2Cl \qquad (5)$$

$$1/3(Bu_2SnS)_3 + PhSnCl_3 \longrightarrow ClBu_2Sn{\cdot}S{\cdot}SnPhCl_2 \qquad (6)$$

This paper demonstrates that the types of reaction

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[1] Part XVI, A. G. Davies and T. N. Mitchell, *J. Chem. Soc.* (*C*), 1969, 1896.

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

[3] Part VIII, A. G. Davies and P. G. Harrison, *J. Chem. Soc.* (*C*), 1967, 1313.

[4] A. G. Davies and P. G. Harrison, *J. Organometallic Chem.*, 1967, **7**, P13.

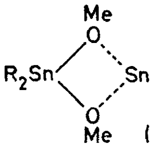
[5] A. G. Davies and P. G. Harrison, *J. Organometallic Chem.*, 1967, **8**, P19.

exemplified in equations (1)—(6), are also readily undergone by the equivalent aminotin species dimethyltin bis(diethylamide) [$\mathrm{Me_2Sn(NEt_2)_2}$] and *NN'N''*-triethylhexamethylcyclotristannazane [$\mathrm{(Me_2Sn{\cdot}NEt)_3}$].

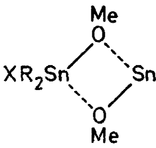
The Reactions of Dimethyltin Bis(diethylamide).—The diethylamide reacts immediately and exothermically with dimethyltin dichloride, dibromide, and di-iodide [equation (7)]. If the reaction is carried out in ether, and the solution is then rapidly concentrated under reduced pressure below 0°, the halide diethylamides (II) can be isolated (30—50%) as white crystalline solids with sharp m.p.s. As the bis(diethylamide) is prepared by treating a dihalide with 2 mol. of lithium diethylamide, the reaction between the appropriate dihalide and 1 mol. of lithium diethylamide would presumably provide an alternative route to the halide diethylamides.

$$\mathrm{Me_2Sn(NEt_2)_2 + Me_2SnX_2 \longrightarrow 2Me_2Sn(X)NEt_2 \quad (II)} \quad (7)$$

Kocheshkov[6] proposed that the corresponding methoxide halides did not have the simple structure (I), but were unsymmetrical binuclear complexes (III). More recent evidence, however,[7,8] suggests that the binuclear species which exists in concentrated solution in equilibrium with monomer, is the symmetrical dimer (IV). Analogous structures (V) and (VI) can be written for the halide amides, but we did not try to investigate this because the compounds are unstable.

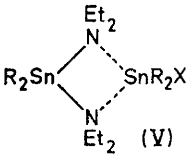


(III)

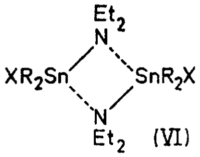


(IV)

Even in a sealed tube, under nitrogen, and in the dark, the solid chloride diethylamide decomposes within a few hours at room temperature (more quickly in solution) and the decomposition of the bromide and iodide is successively more rapid; because of this, only approximate analytical data were obtained.

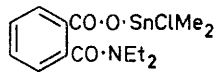


(V)



(VI)

(VII)



However, the dimethyltin halide diethylamides can be characterised by the adducts which they form with suitable reagents. The chloride diethylamide readily reacts with phthalic anhydride to give the air-stable phthalamide (VII); its ^{1}H n.m.r. spectrum indicates that rotation about the carbonyl–nitrogen bond is restricted, and that the two *N*-ethyl groups are in different magnetic environments.

The chloride diethylamide reacts exothermically with an equimolar amount of phenyl isothiocyanate [equation (8a)] to give an air-sensitive, low-melting solid, which on methanolysis gives dimethyltin chloride methoxide and *NN*-diethyl-*N'*-phenylthiourea [equation (8b)]. This sensitivity of the adduct to protolytic reagents suggests that the tin may be bonded to nitrogen, rather than to the sulphur as precedent might suggest.[9,10]

$$\mathrm{Me_2Sn(Cl)NEt_2 \xrightarrow[PhNCS]{a} ClMe_2Sn{\cdot}NPh{\cdot}CS{\cdot}NEt_2 \xrightarrow[MeOH]{b} Me_2Sn(Cl)OMe + PhNH{\cdot}CS{\cdot}NEt_2} \quad (8)$$

Carbon disulphide similarly reacts exothermically with the dimethyltin halide diethylamides, but in this case air-stable, highly crystalline compounds, the dimethylhalogenotin *NN*-diethyldithiocarbamates (VIII; X = Cl, Br, or I) [equation (9a)] are formed.

$$\begin{tikzcd} \mathrm{Me_2Sn(X)NEt_2} \arrow[r, "a", "\mathrm{CS_2}"'] & \mathrm{XMe_2Sn{\cdot}S{\cdot}CS{\cdot}NEt_2} \text{ (VIII)} \\ \mathrm{Me_2Sn(NEt_2)_2} \arrow[r, "b", "\mathrm{CS_2}"'] & \mathrm{Me_2Sn(S{\cdot}CS{\cdot}NEt_2)_2} \arrow[u, "c", "\mathrm{Me_2SnCl_2}"'] \end{tikzcd} \quad (9)$$

The reaction of dimethyltin bis(diethylamide) with carbon disulphide is similar, yielding the bis(dithiocarbamate) as a crystalline air-stable solid [reaction (9b)], which can be caused to disproportionate with dimethyltin dichloride [reaction (9c)], to produce the chloride dithiocarbamate (VIII; X = Cl) by an alternative route. When this work was carried out, the only previous example of a diorganohalogenotin dithiocarbamate was diphenylchlorotin *NN*-diphenyldithiocarbamate, which was prepared from diphenyltin dichloride and the sodium dithiocarbamate;[11a] subsequently the preparation of dimethylhalogenotin *NN*-dimethyldithiocarbamates by a similar route has been described.[11b]

The ^{1}H and ^{119}Sn (ref. 12) n.m.r. parameters are given in Table 1. The high-field ^{119}Sn chemical shifts

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[6] I. P. Gol'dshtein, N. N. Zemlyanskii, O. P. Shamagina, E. N. Gur'yanova, E. M. Panov, N. A. Slovokhtova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1965, **163**, 880; *Doklady Chem.*, 1965, **163**, 715; N. N. Zemlyanskii, I. P. Gol'dshtein, E. N. Gur'yanova, O. P. Syutkina, E. M. Panov, N. A. Shovokhotova, and K. A. Kocheshkov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 728; *Bull. Acad. Sci., U.S.S.R.*, 1967, 707; I. P. Gol'dshtein, E. N. Gur'yanova, N. N. Zemlyanskii, O. P. Syutkina, E. M. Panov, and K. A. Kocheshkov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 2201; *Bull. Acad. Sci. U.S.S.R.*, 1967, 2115.

[7] J. C. Pommier and J. Valade, *Compt. rend.*, 1968, **268**, 633.

[8] A. C. Chapman, A. G. Davies, P. G. Harrison, and W. McFarlane, *J. Chem. Soc.* (*C*), in the press.

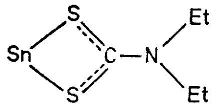
[9] A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc.* (*C*), 1967, 1309.

[10] T. A. George and M. F. Lappert, *J. Organometallic Chem.*, 1968, **14**, 327.

[11] (*a*) E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, 1965, **4**, 973; (*b*) M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, R. Okawara, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3231.

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

suggest that the dithiocarbamate group is chelating as in structure (IX), making the tin five-co-ordinate in the halogeno-dithiocarbamates, and perhaps six-co-ordinate in the bis(dithiocarbamate);[12] this agrees with the evidence of n.m.r.,[11b] i.r.,[11b,13] and Mössbauer spectra[14] on other tin dithiocarbamates.



(IX)

If the solvent is changed from carbon disulphide to benzene, the chemical shifts of the methylene protons of the *N*-ethyl group move upfield by about 0·4—0·6 p.p.m. A similar effect has been observed independently by Honda and others in the compounds $MeXSn(S{\cdot}CS{\cdot}NMe_2)_2$ and $Me_2XSn(S{\cdot}CS{\cdot}NMe_2)$ (X = Cl, Br, or I), and in $Me_2Sn(S{\cdot}CS{\cdot}NMe_2)_2$ and $Me_2Sn(S{\cdot}CS{\cdot}NEt_2)_2$;[11b,15] it was tentatively suggested that this effect might be caused by a stereospecific solvation of the planar dithiocarbamate group by benzene, which places the *N*-alkyl protons in the diamagnetic region of the benzene ring.

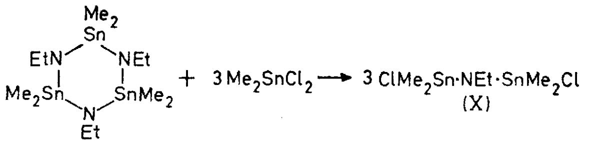
TABLE 1

N.m.r. spectra of the compounds $Me_2Sn(X)S{\cdot}CS{\cdot}N(CH_2{\cdot}CH_3)_2$

X	Solvent	τ Me	τ [a]	τ CH_2CH$_3$	Δτ [a]	τ CH$_2$$CH_3$	Δτ [a]	J (^{119}Sn–Me) (Hz)	δ(^{119}Sn) [b]
Cl	C_6H_6	8·83		6·76		9·12		75·9	+204
	CS_2	8·88		6·28		8·70		76·2	
			−0·05		+0·48		+0·42		
Br	C_6H_6	8·71		6·85		9·21			+233
	CS_2	8·68		6·26		8·74		74·1	
			+0·03		+0·59		+0·47		
I	C_6H_6	8·56		6·88		9·21		73·2	+292
	CS_2	8·55		6·25		8·67		73·5	
			+0·01		+0·63		+0·54		
S·CS·NEt$_2$	C_6H_6	8·25		6·55		9·08		86·4	+336
	CS_2	8·63		6·23		8·73		86·4	
			−0·38		+0·32		+0·35		

[a] τ (C_6H_6) − τ (CS_2). [b] In CH_2Cl_2; p.p.m. with respect to Me_4Sn.

Reactions of NN′N″-*Triethylhexamethylcyclotristannazane.*—Dimethyltin dichloride reacts spontaneously with the cyclotristannazane to give 1,3-trichloro-2-ethyl-1,1,3,3-tetramethyldistannazane (X). Diphenyltin dichloride reacts similarly, and methyltin trichloride more vigorously, to give 1,3-dichloro-2-ethyl-1,1-dimethyl-3,3-diphenyldistannazane (XI) and 1,3,3-trichloro-2-ethyl-1,1,3-trimethyldistannazane (XII), respectively.

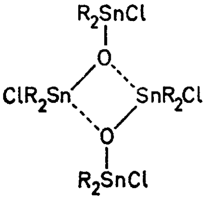


(10)

All three products (X)—(XII) are colourless crystalline solids, which are stable in the absence of air.

$ClPh_2Sn{\cdot}NEt{\cdot}SnMe_2Cl$ (XI) $\qquad$ $Cl_2MeSn{\cdot}NEt{\cdot}SnMe_2Cl$ (XII)

The tetra-alkyldichlorodistannazanes (X) and (XI) are analogous to the tetra-alkyldichlorodistannoxanes [*e.g.* equation (5)], which have been studied extensively, and for which there is evidence of association into dimers (XIII).[16] The corresponding distannthianes, however, are monomeric.[5]



(XIII)

The halogenodistannazanes (X), (XI), and (XII) react immediately with chloral to precipitate a distannoxane and leave *N*-(2,2,2-trichloroethylidene)ethylamine as the only soluble product. The reaction probably proceeds by addition of the Sn–N bond across the carbonyl group of the chloral [equation (11a)] to form an adduct (XIV), which then eliminates the weak acceptor, the chloral imine, leaving the distannoxane [equation (11b)]. These imine-forming eliminations

$$\begin{array}{l} \geqslant\!Sn{\cdot}NEt{\cdot}Sn\!\leqslant + O{=}CH{\cdot}CCl_3 \xrightarrow{a} \\ \qquad\qquad \geqslant\!Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}NEt{\cdot}Sn\!\leqslant \text{ (XIV)} \\ \qquad\qquad\qquad \Big\downarrow \text{b} \\ \qquad\qquad \geqslant\!Sn{\cdot}O{\cdot}Sn\!\leqslant + Cl_3C{\cdot}CH{=}NEt \qquad (11) \end{array}$$

will be discussed more fully in a subsequent paper.

Just as the chlorodistannoxanes, $ClR_2Sn{\cdot}O{\cdot}SnR_2Cl$, are less reactive than the distannoxanes, $R_3Sn{\cdot}O{\cdot}SnR_3$,

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[13] F. Bonati and R. Ugo, *J. Organometallic Chem.*, 1967, **10**, 257.

[14] B. W. Fitzsimmons, *Chem. Comm.*, 1968, 1485.

[15] M. Honda, Y. Kawasaki, and T. Tanaka, *Tetrahedron Letters*, 1967, 3313.

[16] D. L. Alleston, A. G. Davies, and M. Hancock, *J. Chem. Soc.*, 1964, 5744.

in addition reactions, so the chlorodistannazanes, $ClR_2Sn{\cdot}NEt{\cdot}SnR_2Cl$, are less reactive than the distannazanes, $R_3Sn{\cdot}NEt{\cdot}SnR_3$. Heptamethyldistannazane reacts rapidly with carbon disulphide to give trimethyltin sulphide and methyl isothiocyanate,[17] presumably by an addition–elimination sequence [equation (12)].

$$\geqslant Sn{\cdot}NR{\cdot}Sn\leqslant + CS_2 \longrightarrow \geqslant Sn{\cdot}S{\cdot}CS{\cdot}NR{\cdot}Sn\leqslant \longrightarrow \geqslant Sn{\cdot}S{\cdot}Sn\leqslant + SCNR \quad (12)$$

In contrast the trialkyltrichlorodistannazane (XII) reacts slowly with carbon disulphide; the reaction is not clean, but ethyl isocyanate was isolated as the only volatile hydrogen-containing product, indicating that the reaction of equation (12) is occurring, at least in part.

sym-Dichlorotetramethyl-*N*-ethyldistannazane (X) (like the corresponding dichlorodistannoxanes and dichlorodistannthianes) reacts immediately with 2,2′-bipyridyl, giving the dimethyltin dichloride bipyridyl complex and the hexamethylcyclotristannazane, thus effectively reversing the original disproportionation of equation (10). 2,2′-Bipyridyl also reacts immediately with the trichlorotrimethyldistannazane (XII), but in this case the formation of the distannazane is not reversed. The bipyridyl complex of dimethyltin dichloride rather than of methyltin trichloride is precipitated, leaving in solution a crystalline solid with analysis and n.m.r. spectrum corresponding to a cyclo-oligomer, presumably the trimer, *sym*-trichloro-*NN′N″*-triethyltrimethylcyclotristannazane (XIV) [equation (13)]. The high value of the ^{119}Sn chemical shift (+156 p.p.m. with respect to tetramethyltin) [12] suggests that the co-ordination number of the tin in compound (XIV) is raised above four by association.

$$Cl_2MeSn{\cdot}NEt{\cdot}SnMe_2Cl + bipy \longrightarrow Me_2SnCl_2{,}bipy + \underset{(XIV)}{(ClMeSn{-}NEt)_3} \quad (13)$$

Stannic chloride reacts exothermically with the hexamethylcyclotristannazane, but in this case the product of exchange, $Cl_3Sn{\cdot}NEt{\cdot}SnMe_2Cl$, is not formed; the compounds which are isolated are dimethyltin dichloride and an intractable white solid whose i.r. spectrum and elemental analysis suggest that it is probably a polymer of composition $(Cl_2Sn{\cdot}NEt)_n$ [equation (14)]. This is parallel to the reaction between

$$(Me_2Sn{\cdot}NEt)_3 + 3SnCl_4 \longrightarrow 3Me_2SnCl_2 + 3/n(Cl_2Sn{\cdot}NEt)_n \quad (14)$$

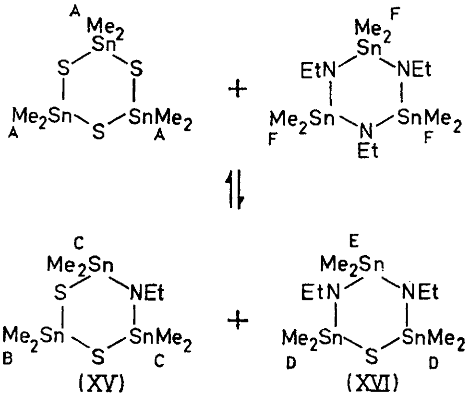
stannic chloride and dialkyltin oxides or dialkyltin sulphides, which give products of apparent composition $(Cl_2SnO)_n$[4] and $(Cl_2SnS)_n$.[5]

No products of exchange could be isolated from the reaction between the cyclotristannazane and trimethyltin chloride, but the n.m.r. spectrum showed a sharp singlet for the Me_3Sn group, whereas the signals for the protons of the cyclotristannazanes, especially those of the CH_2 group, are broad, suggesting perhaps that a rapid reversible exchange process is taking place.

The exchange involving Sn–N and Sn–S bonds in dialkylstannazanes and dialkylstannthianes was also investigated. No parallel studies involving the Sn–O bond appear to have been reported, perhaps because the dialkylstannoxanes are relatively intractable polymers, rather than cyclic trimers.

The ^1H and ^{119}Sn n.m.r. spectra show that *NN′N″*-triethylhexamethylcyclotristannazane and hexamethylcyclotristannthiane in benzene solution exist in equilibrium with the corresponding cyclotristannazadithiane (XV) and cyclotristanndiazathiane (XVI) [equation (15)].

The equivalent reaction is known to occur between the analogous silazanes and silthianes, though under much more vigorous conditions.[18]



(15)

In benzene the Me_2Sn groups of the trithiane show τ 9·30 (J_{Sn-H} 59·4 and 62·0 Hz), and of the triazane τ 9·65 (J_{Sn-H} 56·9 and 59·3 Hz). The ^1H n.m.r. spectrum of the mixture shows, apart from the absorptions of the *N*-ethyl groups, six sharp signals due to the six methyl species in the equilibrium, labelled A—F in equation (15). The relative intensities and average values of τ and of J (^{119}Sn–Me) for these six signals for benzene solutions of mixtures in which the initial ratio of trithiane to triazane was 2 : 1, 1 : 1, and 1 : 2, are given in Table 2. Coupling between $^{117/119}Sn$ and the methylene protons of the *N*-methyl group was also apparent, and is quoted in the Table as a mean value for the two isotopes.

The resonances of the various Me_2Sn groups were assigned on the basis that (*a*) the n.m.r. parameters for the azadithiane (XV) and diazathiane (XVI) should lie between those of the triazane and trithiane; (*b*) the intensity ratios of B to C and E to D are both 1 : 2; (*c*) the differences in chemical shift between A and B, C and D, and E and F, should be much smaller than those between B and C, and D and E, indicating that

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[17] K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 1967, 2667.

[18] K. Moedritzer and J. R. van Wazer, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 45; *J. Phys. Chem.*, 1966, **70**, 2033.

the members of the former pairs exist in similar environments.[12]

For the species A, C, D, and F, the side bands due to $^{119}\mathrm{Sn}$–$^{1}\mathrm{H}$ coupling were sufficiently well resolved to permit the $^{119}\mathrm{Sn}$ INDOR spectra to be recorded; these fully confirm the assignment made in Table 2. The spectra of the nucleus A in the triazane and of F in the trithiane, and D in the diazathiane are reproduced in refs. 19 and 12. The spectrum of nucleus C in the azadithiane is similar to the spectrum of nucleus D.

EXPERIMENTAL

Infrared spectra (neat liquids or Nujol mulls) were recorded with a Unicam SP 200 or a Perkin-Elmer 337 instrument. $^{1}\mathrm{H}$ N.m.r. spectra were measured for benzene solutions at 33·4° with a Perkin-Elmer R10 spectrometer, and $^{119}\mathrm{Sn}$ n.m.r. spectra with a modified JEOL C-60-H instrument, as described in ref. 12.

TABLE 2

N.m.r. spectra of $\mathrm{Me_2Sn}$ groups in equilibrium mixtures of $\mathrm{(Me_2Sn{\cdot}NEt)_3}$ and $\mathrm{(Me_2Sn{\cdot}S)_3}$ [equation (15)]

			Initial trithiane–triazane ratio					
			2 : 1		1 : 1		1 : 2	
Compound	$\mathrm{Me_2Sn}$ species	τ	Signal ratio	Compound ratio	Signal ratio	Compound ratio	Signal ratio	Compound ratio
Trithiane	A	9·32[a]	6·5	23·5	2·4	7		
Azadithiane (XV)	B	9·37[b]	5	54·5	5	43	3	19·5
	C	9·48[c,g]	10		10		6	
Diazathiane (XVI)	D	9·54[d,h]	4	22	10	43	20	65
	E	9·66[e]	2		5		10	
Triazane	F	9·69[f,i]			24	7	7	15·5

J ($^{117/119}\mathrm{Sn}$–Me) (Hz): [a] 59·5, 62·0; [b] 59·4, 62·0; [c] 59·4, 62·0; [d] 58·2, 60·6; [e] 56·2, 58·9; [f] 55·6, 58·2. J ($\mathrm{Sn{-}CH_2}$) (Hz) (mean): [g] 7·57; [h] 74·0; [i] 74·8.

Dimethyltin bis(diethylamide) and *NN′N″*-triethylhexamethylcyclotristannazane were prepared by Jones and Lappert's method.[20] All compounds containing an Sn–N bond were manipulated under dry nitrogen.

Dimethyltin Halide Diethylamides.—(*a*) Dimethyltin dichloride (1·88 g., 8·56 mmoles) in ether (35 c.c.) was added to dimethyltin bis(diethylamide) (2·48 g., 8·51 mmoles). The reaction was slightly exothermic. Ether was removed under reduced pressure until the volume was *ca.* 7 c.c.; dimethyltin chloride diethylamide (II; X = Cl) was then collected as white crystals (2·38 g., 55%), m.p. 53—55°, τ 8·94 (t, $\mathrm{CH_2{\cdot}C}H_3$), 6·79 (q, J 7·2 Hz, $\mathrm{C}H_2{\cdot}\mathrm{CH_3}$), and 9·56 ($J_{\mathrm{Sn-H}}$ 66·4 and 69·4 Hz, Me), $\nu_{\max.}$ 780vs, 1000, 1040, 1100, and 1125 cm.$^{-1}$ (Found: C, 24·9; H, 5·4; Cl, 14·7; N, 5·8. Calc. for $\mathrm{C_6H_{16}ClNSn}$: C, 28·1; H, 6·3; Cl, 13·8; N, 5·5%). The compound turned into a brown sticky solid, even in a sealed tube in the absence of light. When a Nujol mull was exposed to the air, the i.r. spectrum rapidly changed so that the principal band was at 790 cm.$^{-1}$ (Sn·O·Sn?).

(*b*) In a similar reaction, dimethyltin bromide diethylamide (II; X = Br) was isolated as white crystals (26%), m.p. 49—51°, τ 8·85 (t, $\mathrm{CH_2{\cdot}C}H_3$), 6·92 (q, J 7·2 Hz, $\mathrm{C}H_2{\cdot}\mathrm{CH_3}$), and 9·29 ($\mathrm{H}_{\mathrm{Sn-H}}$ 60·6 and 63·5 Hz, Me), $\nu_{\max.}$ 780vs, 1000, 1040, 1100, 1125, 1165, and 1190 cm.$^{-1}$.

(*c*) Similarly, dimethyltin iodide diethylamide was prepared as white crystals (35%), m.p. 28—34°, τ 8·84 (t, $\mathrm{CH_2{\cdot}C}H_3$), 7·0 (q, J 7·2 Hz, $\mathrm{C}H_2{\cdot}\mathrm{CH_3}$), and 9·29 ($J_{\mathrm{Sn-H}}$ 58·8 and 61·2 Hz, Me), $\nu_{\max.}$ 780vs, 1010, and 1165 cm.$^{-1}$. In 1 hr. at 21°, the compound decomposed to a sticky brown solid.

Reaction of Dimethyltin Chloride Diethylamide with Phthalic Anhydride.—Phthalic anhydride (0·592 g., 2·00 mmoles) was added to the chloride diethylamide (1·023 g., 2·00 mmoles) in ether (15 c.c.). Heat was evolved The mixture was heated under reflux for 40 min., and the solvent was removed under reduced pressure, leaving a white powder. This gave *chlorodimethyltin* o-(*diethylcarbamoyl*)-*benzoate* (VII) as hard prisms, m.p. 188—192° (from chloroform), τ ($\mathrm{CDCl_3}$) 1·75—2·10 and 2·25—2·85 ($\mathrm{C_6H_4}$), 6·44 and 6·81 (two quartets of equal intensity, $\mathrm{C}H_2{\cdot}\mathrm{CH_3}$), 8·74 and 8·99 (two triplets of equal intensity, J 7·2 Hz, $\mathrm{CH_2{\cdot}C}H_3$), and 8·90 ($J_{\mathrm{Sn-H}}$ 76·5 and 80·1 Hz, Me), $\nu_{\max.}$ 785, 1375, 1460, and 1605 cm.$^{-1}$ (Found: C, 41·2; H, 5·05; Cl, 9·5; N, 3·3. $\mathrm{C_{14}H_{20}ClNO_3Sn}$ requires C, 41·6; H, 5·0; Cl, 8·0; N, 3·4%).

Reaction of Dimethyltin Chloride Diethylamide with Phenyl Isothiocyanate.—Phenyl isothiocyanate (3·00 g., 22·2 mmoles) was added to the chloride diethylamide (5·69 g., 11·1 mmoles) in ether (50 c.c.). Volatile material was removed under reduced pressure, leaving pale yellow crystals, m.p. 18—26°, τ ($\mathrm{CCl_4}$) 2·52—3·33, 6·77 (q, $\mathrm{C}H_2{\cdot}\mathrm{CH_3}$), 8·92 (t, J 7·3 Hz, $\mathrm{CH_2{\cdot}C}H_3$), and 9·15 ($J_{\mathrm{Sn-H}}$ 71·8 and 74·8 Hz). Methanolysis precipitated dimethyltin chloride methoxide, m.p. 185—187° (Found: Cl, 17·3. Calc. for $\mathrm{C_3H_9ClOSn}$: Cl, 16·5%), and left an amber oil which crystallised from ethanol as a straw-coloured solid, m.p. 33°, identified as *NN*-diethyl-*N′*-phenylthiourea.

Reaction of Dimethyltin Halide Diethylamides with Carbon Disulphide.—An excess of a 25% solution of carbon disulphide in benzene was added to the halide diethylamide, whereupon a vigorous reaction took place. Volatile compounds were removed under reduced pressure leaving, in essentially quantitative yield, the dimethylhalogenotin *NN*-diethyldithiocarbamate as a yellow powder, which was recrystallised from a small volume of carbon disulphide. The n.m.r. data are given in Table 1; other properties were as follows:

Dimethylchlorotin NN-*diethyldithiocarbamate* (VIII; X = Cl), colourless prisms, m.p. 83·5—84·5°, $\nu_{\max.}$ 795s, 920,

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1075, 1150, 1205s, 1300, 1450, and 1525s cm.$^{-1}$ (Found: C, 24·3; H, 4·4; Cl, 9·7; N, 3·7. $C_7H_{16}ClNS_2Sn$ requires: C, 25·3; H, 4·8; Cl, 10·7; N, 4·2%).

Dimethylbromotin NN-*diethyldithiocarbamate* (VIII; X = Br), white prisms, m.p. 113—114°, i.r. spectrum similar to that of (VIII; X = Cl) (Found: C, 22·4; H, 4·4; Br, 21·2; N, 3·7. $C_7H_{16}BrNS_2Sn$ requires: C, 22·3; H, 4·25; Br, 21·2; N, 3·7%).

Dimethyliodotin NN-*diethyldithiocarbamate* (VIII; X = I) colourless prisms, m.p. 118—118·5°, i.r. spectrum similar to those of (VIII; X = Cl or Br) (Found: C, 19·5; H, 3·9; I, 30·8; N, 3·3. $C_7H_{16}NIS_2Sn$ requires C, 19·8; H, 3·8; I, 30·0; N, 3·4%).

Disproportionation of Dimethyltin Bis-(NN-*diethyldithiocarbamate*) *and Dimethyltin Dichloride*.—Carbon disulphide (3·0 c.c.) was added dropwise to dimethyltin bis(diethylamide) (3·86 g.) in benzene (10 c.c.); much heat was evolved. Volatile material was removed under reduced pressure, yielding *dimethyltin bis*(NN-*diethyldithiocarbamate*) (5·78 g.) which was recrystallised from carbon disulphide, then carbon tetrachloride; m.p. 134—135°, $\nu_{max.}$ 790s, 840, 920, 995, 1070, 1090, 1140, 1205, 1270vs, 1305, 1360, 1430, and 1495 cm.$^{-1}$; ^1H and ^{119}Sn n.m.r. data are given in Table 1 (Found: C, 32·3; H, 6·0; N, 6·3. $C_{10}H_{26}N_2S_4Sn$ requires C, 32·4; H, 5·8; N, 6·3%).

Dimethyltin dichloride (0·54 g., 2·47 mmoles) was added to the bis(dithiocarbamate) (1·10 g., 2·47 mmoles) in ether (17·5 c.c.). The solvent was removed, leaving a yellow solid which was recrystallised twice from carbon disulphide giving small prisms, m.p. 79—84°, which were identified by i.r. and n.m.r. spectroscopy as dimethylchlorotin *NN*-diethyldithiocarbamate (II; X = Cl) (Found: C, 24·0; H, 4·0; Cl, 10·1; N, 3·9. Calc. for $C_7H_{16}ClNS_2Sn$: C, 25·3; H, 4·8; Cl, 10·7; N, 4·2%).

Reaction of NN′N″-*Triethylhexamethylcyclotristannazane with Organotin Chlorides*.—(i) *Dimethyltin dichloride*. Dimethyltin dichloride (2·44 g., 11·3 mmoles) in ether (27 c.c.) was added to the tristannazane (2·14 g., 3·72 mmoles). Heat was evolved. The volatile components were removed under reduced pressure, leaving a white solid, which gave 1,3-*dichloro*-2-*ethyl*-1,1,3,3-*tetramethyldistannazane* (X) as fine prisms, m.p. 158—162° [from light petroleum (b.p. 60—80°)], τ 9·06 (J_{Sn-H} 71·5 and 74·8 Hz, $SnMe_2$), 6·53 (q, $C\mathit{H}_2{\cdot}CH_3$), and 8·91 (t, J 7·3 Hz, $CH_2{\cdot}C\mathit{H}_3$), $\nu_{max.}$ 795br,s, 865, 1025, and 1080 cm.$^{-1}$ (Found: Cl, 17·1; N, 2·9. $C_6H_{17}Cl_2NSn$ requires Cl, 17·2; N, 3·4%).

(ii) *Methyltin trichloride*. Methyltin trichloride (3·60 g., 15·0 mmoles) dissolved exothermically when added to the tristannazane (2·88 g., 4·99 mmoles) in benzene (6·0 c.c.). When the solution cooled, crystals were deposited, and were recrystallised from a small volume of benzene yielding 1,3,3-trichloro-2-ethyl-1,1,3-trimethyldistannazane (XII) as colourless prisms, m.p. 91—98°, τ 8·68 (J_{Sn-H} 92·4 and 94·8 Hz, SnMe), 9·36 (J_{Sn-H} 68·4 and 69·6 Hz, $SnMe_2$), 6·27 [q, J_{H-H} 7·0 Hz, J_{Sn-H} (mean) 45·5 Hz, $C\mathit{H}_2{\cdot}CH_3$], and 9·07 (t, $CH_2{\cdot}C\mathit{H}_3$) (Found: C, 13·6; H, 3·7; Cl, 22·8; N, 4·3. $C_5H_{14}Cl_3NSn_2$ requires C, 13·9; H, 3·25; Cl, 24·6; N, 3·25%).

(iii) *Diphenyltin dichloride*. Diphenyltin dichloride (2·57 g., 780 mmoles) dissolved exothermically when added to the tristannazane (1·43 g., 2·49 mmoles) in benzene (10 c.c.). The solvent was removed under reduced pressure, leaving a solid which was washed with pentane (3 × 5 c.c.) then recrystallised from a small volume of ether at −80°, yielding 1,3-*dichloro*-2-*ethyl*-1,1-*dimethyl*-3,3-*diphenyldistannazane* (XI) as a fine crystalline solid, m.p. 72—79°, τ 2·0—3·0 (Ph), 5·95 (q, $C\mathit{H}_2{\cdot}CH_3$), 8·70 (t, J 7·3 Hz, $CH_2{\cdot}C\mathit{H}_3$), and 8·98 (J_{Sn-H} 67·5 and 70·5 Hz), $\nu_{max.}$ 695, 735, 800, 1025, 1065, and 1435 cm.$^{-1}$ (Found: Cl, 13·7; N, 2·0. $C_{16}H_{21}Cl_2NSn$ requires: Cl, 13·3; N, 2·6%). When the sample was exposed to the air for 2 min., the only change in the i.r. spectrum was the appearance of a small band at 3400 cm.$^{-1}$.

(iv) *Tin tetrachloride*. Tin tetrachloride (1·78 g., 6·82 mmoles) in benzene (10 c.c.) was added to the tristannazane (1·28 g., 2·23 mmoles) in benzene (10 c.c.). Much heat was evolved, and a white solid separated. After 3 days, the supernatant liquid was decanted off, and the residual solid was triturated with benzene (20 c.c.), and dried; m.p. 180—185°, $\nu_{max.}$ 1025 and 1050 cm.$^{-1}$ (Found: C, 14·1; H, 2·8; Cl, 24·7; N, 5·1%). Dimethyltin dichloride, m.p. 103° (Found: Cl, 32·1. Calc. for $C_2H_6Cl_2Sn$: Cl, 32·3%), was recovered from the combined benzene solutions.

(v) *Trimethyltin chloride*. The tristannazane (3·20 g., 5·57 mmoles) and trimethyltin chloride (3·33 g., 16·7 mmoles) were mixed in benzene (5·0 c.c.); the n.m.r. spectrum then showed τ 9·63 (sharp) (J_{Sn-H} 54·6 and 57·6 Hz, Me_2Sn), 9·49br (Me_2Sn), 6·66br ($C\mathit{H}_2{\cdot}CH_3$), and 8·89br (J 7·2 Hz, $CH_2{\cdot}C\mathit{H}_3$).

After 1 month the solution deposited a solid which was not identified (Found: C, 18·1; H, 5·05; Cl. 13·0; N, 3·5. Calc. for Me_3SnCl,Me_2SnNEt: C, 21·5; H, 5·1; Cl, 9·2; N, 3·6%).

Reactions of Chlorodistannazanes.—(i) 1,3-*Dichloro*-2-*ethyl*-1,1,3,3-*tetramethyldistannazane and chloral*. Chloral (0·018 c.c., 0·18 mmole) was added to a suspension of the distannazane (X) (0·075 g., 0·18 mmole) in carbon tetrachloride (0·79 g.). When the mixture was shaken for 5 sec., heat was evolved and the suspension dissolved, then, after 15 sec., a white solid separated. The mixture was centrifuged; the n.m.r. spectrum of the supernatant liquid then showed only the signals of *N*-(2,2,2-trichloroethylidene)ethylamine: τ 2·34 (t, J 1·2 Hz, CH=N), 6·36 (qd, J 7·3 and 1·2 Hz, $N{\cdot}C\mathit{H}_2{\cdot}CH_3$), and 8·70 (t, $N{\cdot}CH_2{\cdot}C\mathit{H}_3$). The solid was washed with light petroleum and identified (i.r. spectrum) as 1,3-dichloro-1,1,3,3-tetramethyldistannoxane, m.p. >360° (Found: Cl, 19·3. Calc. for $C_4H_{12}Cl_2OSn$: Cl, 18·5%).

The other two distannazanes, (XI) and (XII), similarly gave the trichloroethylidene-ethylamine, but the distannoxane products were not investigated.

(ii) 1,3,3-*Trichloro*-2-*ethyl*-1,1,3-*trimethyldistannazane and carbon disulphide*. The distannazane (XII) (0·38 g., 0·67 mmoles) was dissolved in carbon disulphide (1·0 c.c.). The n.m.r. spectrum showed that a slow reaction took place, which was complete after 96 hr. at 33·4°, when the mixture showed a complex spectrum. Ethyl isothiocyanate, $\nu_{max.}$ 2100 and 1350 cm.$^{-1}$, τ 6·46 (q) and 8·62 (t), was isolated as the only volatile product.

(iii) 1,3-*Dichloro*-2-*ethyl*-1,1,3,3-*tetramethyldistannazane* and 2,2′-*bipyridyl*. 2′,2-Bipyridyl (0·99 g., 6·36 mmoles) in ether (10 c.c.) was added to the distannazane (X) (2·62 g., 6·36 mmoles) in ether (15 c.c.). The immediate white precipitate was collected and identified as Me_2SnCl_2,bipy, m.p. 206—210° (subl.), $\nu_{max.}$ 770, 1020, 1323, 1450, and 1598 cm.$^{-1}$. The volatile components were removed from the filtrate under reduced pressure, leaving an amber oil which was identified (i.r. and n.m.r. spectra) as the hexamethyltristannazane.

(iv) 1,3,3-*Trichloro*-2-*ethyl*-1,1,3-*trimethyldistannazane* *and 2,2′-bipyridyl.* 2,2′-Bipyridyl (1·51 g., 9·68 mmoles) in benzene (15 c.c.) was added to the distannazane (XII) (4·22 g., 9·69 mmoles) in benzene (21 c.c.). The precipitate was separated and identified as Me_2SnCl_2,bipy (3·48 g., 96%), m.p. 224—226° (decomp.), $\nu_{max.}$ 572 cm.$^{-1}$ (Found: C, 37·6; H, 3·8; Cl, 19·3; N, 7·3. Calc. for $C_{12}H_{14}Cl_2N_2Sn$: C, 38·3; H, 3·7; Cl, 18·9; N, 7·45%).

The filtrate was concentrated under reduced pressure, yielding sym-*trichloro*-NN′N″-*triethyltrimethylcyclotristannazane* (XIV) as fine white crystals. m.p. 163—168°, τ 6·29 (q, J_{H-H} 6·9 Hz, J_{Sn-H} 48·5 Hz, $CH_2{\cdot}CH_3$), 9·04 (t, $CH_2{\cdot}CH_3$), and 8·72 (s, J_{Sn-H} 92·1 and 96·6 Hz, SnMe), ^{119}Sn n.m.r.: +156 p.p.m. (Found: C, 17·0; H, 4·0; Cl, 16·8; N, 6·3. $C_6H_{24}Cl_3N_3Sn_3$ requires C, 16·9; H, 3·8; Cl, 16·7; N, 6·6%).

Reaction between NN′N″-*Triethylhexamethylcyclotristannazane and Hexamethylcyclotristannthiane*.—Three experiments were carried out, with the reactants in the molar ratios 2 : 1, 1 : 1, and 1 : 2. The general method is illustrated by the first of these.

The tristannazane (1·654 g., 2·875 mmoles) and the tristannthiane (0·778 g., 1·437 mmoles) were mixed in ether. After 2 days, the solvent was removed under reduced pressure, leaving a straw-coloured oil, which was dissolved in benzene: τ 6·74 (q, with complex ^{117,119}Sn–H side bands, $CH_2{\cdot}CH_3$), 8·99 (t, $CH_2{\cdot}CH_3$), and 9·04 (t, $CH_2{\cdot}CH_3$). Six different types of methyl group were apparent; their chemical shifts, and relative intensities, and the relative concentrations of the various species which these imply, are given in Table 2.

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