Organometallic Reactions. Part XIX.[1] Some Reactions of Aldehydes with Aminotin Compounds

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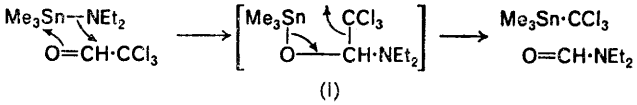
N-Phenylhexabutyldistannazane reacts with acetaldehyde to give bistributyltin oxide and ethylideneaniline. A similar reaction occurs between chloral and *N*-ethyl distannazanes to give 2,2,2-trichloroethylideneethylamine and the corresponding distannoxane. With *N*-aryl hexabutyldistannazanes, however, the reaction of chloral is more complicated; initially a 2:1 chloral–distannazane adduct is formed, and the decomposition products now include tributyltrichloromethyltin and the *N*-tributylstannylformarylamide.

Protolysis of the arylhexabutyldistannazanes gives the *N*-tributylstannylarylamines; these now react with chloral to give stable adducts, the 1,1,1-trichloro-2-arylamino-2-tributylstannyloxyethanes, which can also be obtained by the azeotropic dehydration of a mixture of bistributyltin oxide and the parent aminohydroxytrichloroethane. Azeotropic dehydration of the aminohydroxytrichloroethanes in the absence of an organotin compound gives the 2,2,2-trichloroethylidene arylamines, which do not take part in addition reactions with triorganotin oxygen and nitrogen compounds.

The reactions of triorganotin amines with the polar multiply bonded molecules carbon dioxide, carbon disulphide, isothiocyanates, isocyanates, carbodi-imides, ketens, sulphur dioxide, and *N*-sulphinylaniline have been thoroughly investigated by Jones and Lappert;[2] usually 1 : 1 adducts were formed. More recently, Itoh, Fukui, and Ishii[3] have reported that chloral reacts spontaneously and exothermically with trimethyltin diethylamide to give trimethyltrichloromethyltin and *NN*-diethylformamide [equation (1)] presumably *via* an intermediate 1 : 1 adduct (I). With trialkyltin oxides and alkoxides, the adduct can be isolated, and then observed to decompose;[4] with silylamines, the reaction stops at the stage of the adduct.



(I) (1)

Reports of investigations of the reactions of distannazanes with polar multiply bonded compounds are limited mainly to reactions with the sulphur-terminal heterocumulenes, carbon disulphide, and the isothiocyanates;[5–7] the distannthiane is usually eliminated [equation (2)].

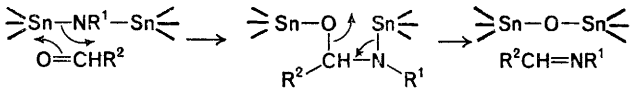
$$(R^1{}_3Sn)_2NR^2 + S{=}X{=}Y \longrightarrow (R^1{}_3Sn)_2S + R^2N{=}X{=}Y \quad (2)$$

Part VI of this series described the reactions of aldehydes with bistributyltin oxide and tributyltin alkoxides.[8] This paper describes some reactions of aldehydes with distannazanes and *N*-tributylstannylarylamines.

The Reactions of Distannazanes with Aldehydes.—No thermal or visual change is obvious when *N*-phenylhexabutyldistannazane is treated with acetaldehyde in 50% carbon tetrachloride solution, but the i.r. and n.m.r. spectra of the product indicate that immediate reaction has occurred to give bistributyltin oxide and ethylideneaniline [equation (3)]. In part XVII we have

$$(Bu_3Sn)_2NPh + MeCH{=}O \longrightarrow (Bu_3Sn)_2O + MeCH{=}NPh \quad (3)$$

reported the corresponding reaction between *Sn*-chloro-substituted *N*-ethylidistannazanes and chloral, which proceeded with the evolution of heat to give the 2,2,2-trichloroethylidene-ethylamine and the corresponding distannoxane.[9] Reaction (3) appears to be another example of the transfer of electronegative groups between a metallic addendum and organic acceptor, proceeding by an addition–elimination sequence [equation (4)], which we have previously shown can give rise, in the appropriate system, to distannazanes,[10] distannthianes,[5–7] and *N*-sulphonyldistannazanes.[1] Disilazanes have been shown to undergo a similar reaction with ketones and benzaldehydes, but under much more rigorous conditions.[11]

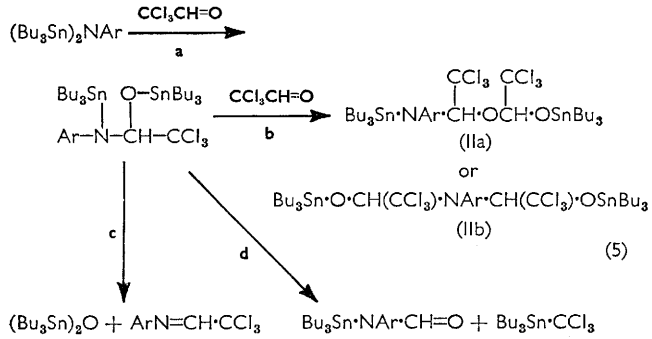


(4)

When *N*-arylhexabutyldistannazanes are treated with chloral, however, the reaction is more complicated. Firstly, the overall reaction occurs more slowly, being complete in *ca.* 1 day at room temperature, and the products comprise not only bistributyltin oxide and 2,2,2-trichloroethylidenearylamine, but also tributyltrichloromethyltin and *N*-tributylstannylformarylamide, all in approximately equimolar quantities [equations (5c) and (5d)]. Secondly, if the reaction between chloral and *N*-*p*-tolylhexabutyldistannazane is followed by

[1] Part XVIII, A. G. Davies and J. D. Kennedy, *J. Chem. Soc.* (*C*), 1970, 1570.
[2] T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 1965, 2157.
[3] K. Itoh, M. Fukui, and Y. Ishii, *Tetrahedron Letters*, 1968, 3867.
[4] Part XV, A. G. Davies and W. R. Symes, *J. Chem. Soc.* (*C*), 1969, 1892.
[5] Part XIV, A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc.* (*C*), 1968, 2640.
[6] K. Itoh, Y. Fukuoto, and Y. Ishii, *Tetrahedron Letters*, 1968, 3199 and 3203.
[7] K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 1967, 2667.
[8] Part VI, A. G. Davies and W. R. Symes, *J. Chem. Soc.* (*C*), 1967, 1009.
[9] Part XVII, A. G. Davies and J. D. Kennedy, *J. Chem. Soc.* (*C*), 1970, 759.
[10] Part XIII, A. G. Davies and J. D. Kennedy, *J. Chem. Soc.* (*C*), 1968, 2630.
[11] N. Duffaut and J-P. Dupin, *Bull. Soc. chim. France*, 1966, 3205.

n.m.r. spectroscopy, the signal due to the aldehydic proton is seen to diminish to zero intensity in 25 min. at 33·4 °C. During this period, the two doublets centred on τ 2·91 and 3·30, due to the protons of the *para*-substituted aromatic ring, diminish to half the original intensity; simultaneously growth of a second pair of aromatic doublets, centred on τ 2·72 and 3·12 is observed, together with two singlets of equal intensity in the acetal region at τ 4·45 and 4·63. The spectrum then slowly changes to be consistent with the final product mixture. This suggests that the initial reaction is a 2 : 1 addition between chloral and the distannazane, the second addition [reaction (5b)] proceeding much more readily than the first [reaction (5a)].



(5)

The 2 : 1 adduct might have the unsymmetrical structure (IIa), or the symmetrical structure (IIb) in which the two CH protons may be rendered magnetically inequivalent by co-ordinative cyclisation. Such cyclisation was postulated previously to account for the magnetic inequivalence of the CH protons in the 2 : 1 adduct between chloral and bistributyltin oxide, $Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}O{\cdot}CH(CCl_3){\cdot}OSnBu_3$, where the chemical shifts were τ (CH) 4·49 and 4·54.[8] In the case of the oxide, an equilibrium is established between chloral, the 1 : 1 adduct, and the 2 : 1 adduct; decomposition to give tributyltrichloromethyltin does not occur until the mixture is heated to 150°.

The *N*-phenyldistannazane undergoes the analogous reaction, except that, in this case, decomposition to give the ultimate products commences before formation of the 2 : 1 adduct is complete.

If the initial ratio of reactants was changed, or if the reaction was conducted at 0°, neither the course of the reaction, nor the ultimate ratio of products was significantly altered.

The simplest processes by which the ultimate products might be formed are the unimolecular elimination reactions of the 1 : 1-adduct, (5c) and (5d). However, it is shown below that 1,1,1-trichloro-2-arylamino-2-tributylstannyloxyethanes decompose only when an excess of chloral is present [equation (18)] and the possibility that the decompositions outlined in reaction (5) also involve a second molecule of chloral [*cf.* equation (19) of ref. 1] cannot be excluded.

The Reactions of N-*Tributylstannylaniline with Aldehydes.*—Protolysis of an *N*-arylhexabutyldistannazane leads to the *N*-tributylstannylarylamine. If a mixture of aniline and *N*-phenylhexabutyldistannazane, which are initially immiscible, is homogenized, the mono-organotin compound [equation (6)] is the only product, but it readily reverts to its factors if it is distilled.

$$(Bu_3Sn)_2NPh + PhNH_2 \longrightarrow 2Bu_3Sn{\cdot}NHPh \qquad (6)$$

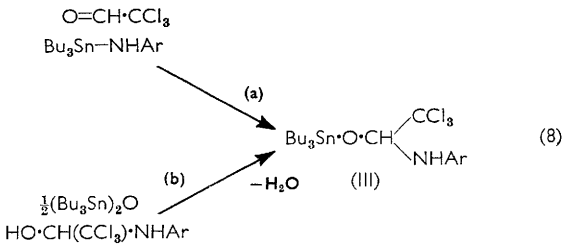
It is beyond doubt that the product is the mono-substituted amine, and not a mixture of the unsubstituted and di-substituted species. The i.r. spectrum shows only one N–H stretching band at 3380 cm.$^{-1}$, whereas aniline itself has two in this region. Again, the NH_2 bending mode of aniline at 1630 cm.$^{-1}$ is absent in the mixture; the C–N stretch (1280 cm.$^{-1}$) of aniline is displaced by 20 cm.$^{-1}$ in the mixture and the strong band at 1240 cm.$^{-1}$ (tentatively assigned to C–N) of *N*-phenylhexabutyldistannazane also disappears in the mixture. The band at 795 cm.$^{-1}$ (tentatively assigned to Sn–N–Sn) of the distannazane is also not observed. Addition of a two-fold excess of aniline to the distannazane results in a product mixture which exhibits two broadened absorptions in the ^{1}H n.m.r. spectrum at τ 6·58 and 7·11 (20% v/v carbon tetrachloride solution at 33·4°) due to the amino-protons of aniline and *N*-tributylstannylaniline respectively. This puts an upper limit on the rate of interchange of hydrogen and tributyltin under these conditions.

The reaction of *N*-tributylstannylaniline with acetaldehyde proceeds rapidly and with the stoicheiometry shown in equation (7). Aniline and acetaldehyde do not react to give the imine under these conditions. The products can be accounted for on the basis that either the monostannylated amine, or the distannazane with which it is in equilibrium [equation (6)] carries out the initial addition.

$$2\ Bu_3Sn{\cdot}NHPh + CH_3{\cdot}CH{:}O \longrightarrow (Bu_3Sn)_2O + PhNH_2 + CH_3{\cdot}CH{:}NPh \qquad (7)$$

The reaction of chloral, however, with both *N*-tributylstannylaniline and *N*-tributylstannyl-*p*-toluidine takes place exothermically, giving the 1 : 1 adducts, the 1,1,1-trichloro-2-arylamino-2-tributylstannyloxyethanes [(III; Ar = Ph or *p*-MeC_6H_4) equation (9)]. N.m.r. studies indicate that *N*-tributylstannylpentafluoroaniline also undergoes this reaction, but in this case the product was not isolated.

The products (III) are heavy oils, and are characterised, in their n.m.r. spectra by a pair of doublets at τ *ca.* 4·5 and 5·5 (*J ca.* 10 Hz) corresponding to the CH–NH system. These compounds are more conveniently prepared by the azeotropic dehydration of the adduct between chloral and the aromatic amine in the presence of bistributyltin oxide [equation (8b)]. By this method, the derivative of *p*-nitroaniline (III; Ar = *p*-$NO_2{\cdot}C_6H_4$) has also been made. This is an extension of the known method for preparing organotin alkoxides by the azeotropic dehydration of a mixture of the appropriate bistrialkyltin oxide and alcohol.



The trichloroarylaminotributylstannyloxyethanes, unlike the adducts of chloral with bistributylstannylamines described above, are quite stable at room temperature. Attempted distillation does not result in a clean decomposition, but i.r. and n.m.r. studies, together with the observed boiling points, of the complex mixture of decomposition products, suggest that these products include both 2,2,2-trichloroethylidenearylamine and the formarylamide which, in turn, suggests that the processes described in equations (1) and (4) both occur to a limited extent.

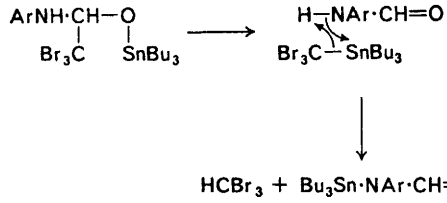
The pure adducts (III) were also not obtained by the addition reaction (8a), because it is so exothermic that some of the product is decomposed, but 1,1,1-trichloro-2-*p*-toluidine-2-triphenylstannyloxyethane was prepared as an analytically pure crystalline solid by the alternative route (8b).

Azeotropic dehydration of a 1,1,1-trichloro-2-arylamino-2-hydroxyethane in the absence of bistributyltin oxide gives the 2,2,2-trichloroethylidenearylamine [equation (9), Ar = Ph or *p*-Me·C_6H_4, but not *p*-NO_2·C_6H_4]; this provides a new and easy route to these compounds, which are usually prepared by a more difficult process.[12]

$$ArNH{\cdot}CH(OH){\cdot}CCl_3 \longrightarrow H_2O + ArN{=}CH{\cdot}CCl_3 \quad (9)$$

$$Bu_3Sn{\cdot}OMe + ArNH{\cdot}CH(OH){\cdot}CX_3 \longrightarrow MeOH + ArNH{\cdot}CH(OSnBu_3){\cdot}CX_3 \quad (10)$$

The hydroxylic proton of 1,1,1-trihalogeno-2-arylamino-2-hydroxyethanes is sufficiently acidic to undergo ready exchange with triorganotin methoxides at room temperature [equation (9)] which offers an alternative route to the tributylstannyloxy-compounds. Using this route we have prepared the 2-tributylstannyloxy- and 2-triphenylstannyloxy-1,1,1-tribromo-2-*p*-toluidinoethanes, which would be expected to be less thermally stable than the corresponding chloro compounds. The triphenylstannyloxy-compound was quite stable (in carbon tetrachloride solution), and showed little decomposition after 14 days at room temperature. The tributylstannyloxy-compound, however, under the same conditions, decomposed completely in 2 days to give bromoform and *N*-tributylstannyl-*N*-methylene-*p*-toluidine as the only products. The most likely mechanism appears to be an elimination reaction similar to that of reactions (1) and (5d), followed by acidolysis of the tributyltribromomethyltin[4] [equation (11)], the difference in behaviour between the trichloromethyl and tribromomethyl compounds being governed by the relative susceptibility of the two trihalogenomethyl groups towards electrophilic attack.



No alkylamino-analogues of the 1,1,1-trihalogeno-2-arylamino-2-hydroxyethanes (III) are known and hence it was not possible to prepare 1,1,1-trihalogeno-1-alkylamino-2-tributylstannyloxyethanes by reactions (8b) or (10). An attempt to prepare these latter compounds by reactions (12)—(15) proceeded smoothly until the final stage, when, simultaneously with the evolution of carbon dioxide, water was eliminated, and decomposition occurred with the stoicheiometry of equation (16). It therefore appears that 1,1,1-trichloro-2-ethylamino-2-tributylstannyloxyethane is unstable at ambient temperatures.

$$(Bu_3Sn)_2O + EtN{=}C{=}O \longrightarrow Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}OSnBu_3 \quad (12)\ [13,14]$$

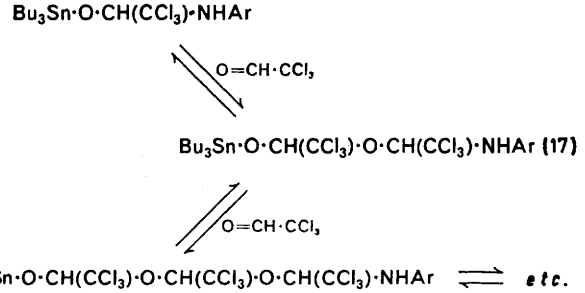
$$Bu_3Sn{\cdot}NEt{\cdot}CO{\cdot}OSnBu_3 + EtNH_2 \longrightarrow Bu_3SnNHEt + Bu_3Sn{\cdot}O{\cdot}CO{\cdot}NHEt \quad (13)\ [13,14]$$

$$Bu_3Sn{\cdot}NHEt + Cl_3C{\cdot}CH{=}O \longrightarrow Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}NHEt \quad (14)$$

$$Bu_3Sn{\cdot}O{\cdot}CO{\cdot}NHEt + Cl_3C{\cdot}CH{=}O \longrightarrow [Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}NHEt] + CO_2 \quad (15)\ [14]$$

$$2[Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}NHEt] \longrightarrow (Bu_3Sn)_2O + H_2O + 1{\cdot}6EtN{=}CH{\cdot}CCl_3 + 0{\cdot}4H{\cdot}CCl_3 + 0{\cdot}4EtN{\equiv}C \quad (16)$$

The tin–oxygen bond of the 1,1,1-trichloro-2-arylamino-2-tributylstannyloxyethanes itself will take part in addition reactions with chloral. Treatment of one of these compounds with an equimolar quantity of chloral results in an immediate reaction which is characterised by a complex series of peaks in the ^1H n.m.r. spectrum in the region τ 4·0—5·0 and 5·5—6·0, which can be interpreted as a series of several matched doublets with a coupling constant of *J ca.* 10 Hz, and, in the region τ 4·0—5·0, two or three isolated singlets. This behaviour can be rationalized in terms of a system in which chloral and the *N*-tributylstannylarylamine are in a series of equilibria with oligomers of increasing size [equation (17)].

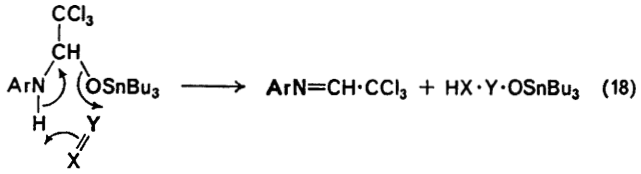


[12] G. Kresze and R. Albrecht, *Angew. Chem. Internat. Edn.*, 1967, **6**, 149.

[13] Part II, A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.* (*C*), 1965, 6245.

[14] A. G. Davies and S. C. Vasishtha, unpublished work. S. C. Vasishtha, Thesis, London, 1967.

Over a period of 7 days at 33·4°, however, decomposition of the monostannylarylamine–chloral system occurs to give 2,2,2-trichloroethylidenearylamine and 1,1,1-trichloro-2-hydroxy-2-tributylstannyloxyethane [equation (19); X=Y = O=CH·CCl_3)]. A similar decomposition occurs in less than 1 day at room temperature between 1,1,1-trichloro-2-arylamino-2-tributylstannyloxyethane and ethyl isocyanate, to give the imine and tributyltin *N*-ethylcarbamate [equation (18); X=Y = EtN=CO]. The 1,1,1-tribromo-compounds behave similarly. A reasonable mechanism by which the adduct could be decomposed by the acceptor is shown in equation (18).

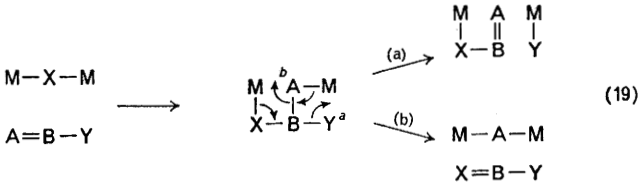


(18)

The alkylideneamines RN=CHR are not reactive towards addition reactions with triorganotin oxygen and nitrogen compounds, although benzylidene *p*-toluidine, *p*-MeC_6H_4N=CHPh, reacts with triorganotin hydrides to give *N*-triorganostannyl-*N*-benzyl *p*-toluidines.[15] No reaction occurred when 2,2,2-trichloroethylidene-*p*-toluidine was incubated with bistributyltin oxide for 1 week at 55 °C, indicating that there is no tendency for the reversal of reaction (5c), leading ultimately to the products of reaction (5d). No reaction occurs with tributyltin diethylamide under the same conditions. The relative rates of elimination of these imines from their effective adducts with organotin compounds described above suggests a sequence of acceptor power which can be interpreted in terms of the electrophilicity of the imino-carbon atom. In the 2,2,2-trichloroethylidene sulphonamides the imino-carbon is very highly activated towards nucleophilic attack, and ready reaction with triorganotin oxygen and nitrogen compounds takes place. These and related reactions are described in Part XVIII.[1]

CONCLUSION

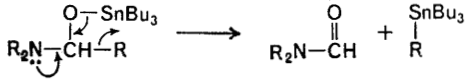
The formation of a 1 : 1-adduct between an organotin–nitrogen compound and an aldehyde may be followed by either or both of two types of reaction; these have been observed previously with organotin–oxygen compounds, and are written in the general form shown in equation (19).



(19)

The first reaction (19a)[1,5–7,10] results in overall exchange of the groups XM and Y (here NR^2·$SnBu_3$ and R^1) between the acceptor and addendum, *i.e.* the aldehyde R^1CH=O is converted into the stannylformamide Bu_3Sn·NR^2·CHO. The second reaction (19b)[4] brings about exchange of the groups X and A (here NR^2 and O) between acceptor and addendum, *i.e.* the aldehyde R^1CH=O is converted into the alkylideneamine R^1CH=NR^2.

The facility of the first process [equation (20)] is controlled by the reactivity of the aldehydic group R^1 towards electrophilic attack, and by mesomeric release by the nitrogen.*



(20)

In the reaction of triorganotin diethylamides with chloral, the combination of a good aldehydic leaving group (CCl_3), and of mesomeric electron-release by the amido-group, makes the adduct very reactive by the process (19a) [*e.g.* equation (1)], but if the leaving ability of the aldehydic group is reduced (as with acetaldehyde), the 1 : 1 adduct is stable.[14] Similarly, if the mesomeric effect of the NR^1_2 group is decreased (*e.g.* NR^1_2 = NHAr), a stable adduct is formed, even with chloral [equation (8a)], but the introduction of a more reactive leaving group with the aldehyde (CBr_3) again results in the formation of formamide [equation (11)].

The second process (19b) occurs when the alkylideneamine R^1CH=NR^1 is a weak acceptor, *i.e.* when its double bond is not activated towards nucleophilic attack by electronegative substituents. Thus *N*-phenylhexabutyldistannazane reacts with acetaldehyde exclusively by this process to give ethylideneaniline [equation (3). The reaction with chloral, however, shows both types of behaviour (19a) and (19b): the higher acceptor power of 2,2,2-trichloroethylideneaniline makes the elimination (5c) a more difficult process, and the alternative decomposition (5d) can compete.

EXPERIMENTAL

I.r. spectra were recorded on neat liquids or Nujol mulls of solids, with a Unicam SP 200 instrument. N.m.r. spectra were recorded on carbon tetrachloride solutions, with a Perkin-Elmer R10 spectrometer.

Many of the products could not be distilled without decomposition, or caused to crystallise, and were then identified by their spectral characteristics, in admixture with the authentic compounds whenever appropriate. The sources of data for uncommon reference compounds are quoted at the first mention of the particular compound. *N*-Phenylhexabutyldistannazane, b.p. 168°/0·03 mm., and *N*-*p*-tolylhexabutyldistannazane, b.p. 173°/0·5 mm., were prepared from the reaction between the appropriate diarylsulphodi-imide and bistributyltin oxide.[10]

Reaction between Distannazanes and Aldehydes.—(a) *N-Phenylhexabutyldistannazane and acetaldehyde.* The distannazane (0·384 g., 0·57 mmoles) and aldehyde (0·025 g., 0·57 mmoles) were mixed in carbon tetrachloride at room temperature. The n.m.r. and i.r. spectra showed that a

* Ishii has suggested that reactivities may be correlated with the σ^+ value of the group X.[3]

[15] W. P. Neumann and E. Heymann, *Annalen*, 1965, **683**, 24.

1 : 1 reaction occurred in 10 min. to give ethylideneaniline [τ 1·98 (q, =CH·CH_3), 7·87 (d, J 5·1 Hz, =CH·CH_3), 2·40—3·00 (Ph); $\nu_{max.}$ (N=C) 1640 cm.$^{-1}$], and bistributyltin oxide [τ 8·0—9·5; $\nu_{max.}$ 770 cm.$^{-1}$], the presence of which was confirmed by adding the authentic compounds.

(b) N-p-*Tolylhexabutyldistannazane and chloral.* The distannazane (0·258 g., 0·38 mmoles) and chloral (0·055 g., 0·38 mmoles) were mixed in carbon tetrachloride (0·41 g.) and kept at 33·4°. During 25 min. the signal at τ 0·78 (CHO) decayed to zero, and the doublets at τ 2·91 and 3·30 (J *ca.* 9 Hz, C_6H_4) decayed to half their original intensity. A new pair of doublets at τ 2·72 and 2·32 (J *ca.* 9 Hz) appeared, together with a pair of singlets of equal intensity at 4·45 and 4·63. During the next 24 hr. the spectrum slowly changed, to give the following final values: τ 1·52 and 1·87 [Bu_3Sn·NAr·C*H*O [16] and ArN=C*H*·CCl_3 (see below), ratio 44 : 56], 2·66 (s, MeC_6H_4N=CH·CCl_3), 2·84 and 3·14 (2d, J *ca.* 9 Hz, Bu_3Sn·N(C_6H_4Me)CHO), 7·59 and 7·63 (approx. equal intensity, $CH_3C_6H_4$), and 8·0—9·5 (three different Bu_3Sn species).

(c) N-*Phenylhexabutyldistannazane and chloral.* The distannazane (0·310 g., 0·46 mmoles) and chloral (0·068 g., 0·46 mmoles) were mixed in carbon tetrachloride (0·3 ml). The following changes in the spectrum were observed. The signal at τ 0·80 (Cl_3C·CHO) decayed and was lost after 30 min., and singlets at 1·51 and 1·89 (−C*H*=O and −C*H*=N) appeared. Singlets at 4·77 (small, 1 : 1 chloral adduct) and at 4·34 and 4·59 (equal intensity; 2 : 1 chloral adduct) appeared then diminished. After 24 hr., the ultimate spectrum showed τ 1·51 and 1·89 [Bu_3Sn·NAr·C*H*O [16] and ArN=C*H*·CCl_3 (see below); rel. intensity 44 : 56], 2·3—3·2 (Ar), and 8·0—9·5 (three different Bu_3Sn species).

Methanol (0·0375 ml., 0·924 mmoles) was then added; formanilide (τ 1·35, 1·57, from protolysis of Bu_3Sn·NPh·CHO), formed immediately, and chloroform (τ 2·15, from protolysis of Bu_3Sn·CCl_3), formed during 2 hr., were identified in the product by comparison with authentic samples. The relative intensities of the signals at τ 1·35, 1·57, 1·86 were 0·35 : 0·54 : 1·0 : 1·42; accurate integration was difficult because the peak at τ 2·15 overlapped with the signal for the aromatic ring, and because the peak at τ 1·35 was broadened.

Preparation of N-*Tributylstannylaniline.*—The distannazane (13·105 g., 19·55 mmoles) and aniline (1·819 g., 19·55 mmoles) were mixed, yielding *N*-tributylstannylaniline as an oil, $\nu_{max.}$ 3380, 2950, 1600, 1500, 1470, 1370, 1290, 1175, 1075, 995, 850, 750, and 690 cm.$^{-1}$; τ 2·6—3·6 (C_6H), 7·14br (NH), 8·0—9·5 (Bu). An attempt to distil the oil gave three approximately equal fractions of aniline, b.p. 30°/0·1 mm., impure *N*-tributylstannylaniline, b.p. 30—160°/0·1 mm., and *N*-phenylhexabutyldistannazane, b.p. 160—180°/0·1 mm. If 2 mol. of aniline were added to the distannazane, the identical n.m.r. spectrum was obtained but with an additional very broad signal at τ 6·58 (NH_2).

Reaction between N-*Tributylstannylarylamines and Aldehydes.*—(a) N-*Tributylstannylaniline and acetaldehyde.* *N*-Tributylstannylaniline (0·653 g., 1·71 mmoles) in carbon tetrachloride (0·5 ml.) was treated with acetaldehyde (0·069 ml., 1·20 mmoles) at 33·4°. After 4 min., the n.m.r. spectrum showed the following characteristics, which did not change during 18 hr: τ 0·42 (q, J 3·5 Hz, MeC*H*:O), 2·26 (q, J 5·4 Hz, MeC*H*:NPh), 2·4—2·6 (contour corresponding to that for a mixture of C_6H_5N:CH·CH_3 and $C_6H_5NH_2$), 5·65br (PhNH_2), 7·97 (d, J 5·4 Hz, CH_3·CH:NPh), 8·05 (d, J 3·5 Hz, CH_3·CH:O), and 8·0—9·5 [Bu_3Sn; same contour as for $(Bu_3Sn)_2O$]; the relative intensities of the signals at τ 0·42 and 2·26 was 29 : 71. No other products were apparent.

Volatile compounds were removed under reduced pressure, leaving an oil, $\nu_{max.}$ 770 (SnOSn) and 1640 (C=N) cm.$^{-1}$, which could not be distilled.

(b) N-*Tributylstannylaniline and chloral.* *N*-Tributylstannylaniline (0·1834 g., 0·48 mmoles) in an equal volume of carbon tetrachloride, was treated with chloral (0·047 ml., 0·48 mmoles). Heat was evolved; the n.m.r. spectrum and, after the volatile components were removed under reduced pressure, the infrared spectrum, were identical to those described below for 1,1,1-trichloro-2-anilino-2-tributylstannyloxyethane. No other products were apparent.

(c) N-*Tributylstannyl*-p-*toluidine and chloral.* The stannylamine [0·3357 g., 0·846 mmoles; from *N*-*p*-tolylhexabutyldistannazane (0·2903 g.) and *p*-toluidine (0·0454 g.)] in carbon tetrachloride (0·5 ml.) was treated with chloral (0·083 ml., 0·805 mmoles); heat was evolved. The product was an oil which could not be distilled, and was identified as 1,1,1-trichloro-2-*p*-toluidino-2-tributylstannyloxyethane (n.m.r. spectrum) which is described below.

Preparation of 1,1,1-*Trichloro*-2-p-*arylamino*-2-*triorganostannyloxyethanes.*—Satisfactory analyses could not be obtained for these compounds because the tributylstannyloxy-derivatives could not be distilled or caused to crystallise, even at low temperature, but their identities were confirmed by the n.m.r. and i.r. spectra.

(*a*) 1,1,1-Trichloro-2-hydroxy-2-*p*-toluidinoethane [17] (4·09 g., 20 mmoles) and bistributyltin oxide (5·96 g., 10 mmoles) were heated under reflux in toluene (20 ml.), under a Dean and Stark water separator. Water (0·2 ml.) quickly collected. After 1·5 hr., volatile compounds were removed under reduced pressure, leaving impure 1,1,1-trichloro-2-*p*-toluidino-2-tributylstannyloxyethane as an amber oil, $\nu_{max.}$ 825, 865, 1100, 1130, 1525, 1620, 2930, and 3400 cm.$^{-1}$ (unchanged when the sample was exposed to air for 2 min.); τ 2·86 and 3·24 (2d, J 9 Hz, C_6H_4), 4·57 and 5·81 (2d, J 10 Hz, N*H*·C*H*), 7·73 (CH_3·C_6H_4), and 8·0—9·5 (Bu_3Sn).

Distillation gave a fraction, b.p. 88°/0·2 mm.—100°/0·6 mm., with τ 1·3, 1·7, 1·9, and 2·58 (singlets); 2·3—3·4 (5d); 4·4—4·7 and 5·1—5·8br (multiplets); 5·32, 7·59, 7·76, and 7·83 (singlets), 8·0—9·4 (Bu_3Sn). The odour of phenyl isocyanide was apparent.

By a similar procedure, the following compounds were prepared.

(*b*) 1,1,1-Trichloro-2-anilino-2-tributylstannyloxyethane, amber oil, $\nu_{max.}$ 750, 830, 1100 (br.), 1505, 1600, 2930, and 3400 cm.$^{-1}$; τ 2·5—3·3 (C_6H), 4·53 and 5·68 (2d, J 9·6 Hz, N*H*C*H*), and 8·0—9·5 (Bu_3Sn).

(*c*) 1,1,1-Trichloro-2-*p*-nitroanilino-2-tributylstannyloxyethane, yellow oil, $\nu_{max.}$ 845, 1080, 1110, 1330, 1515, 1600, 2930, and 3400 cm.$^{-1}$; τ 1·68 and 2·97 (3d, J 9 Hz, C_6H_4), 4·34 and 4·56 (2d, J 9·6 Hz, C*H*N*H*), and 8·0—9·5 (Bu_3Sn).

(*d*) 1,1,1-Trichloro-2-*p*-toluidino-2-triphenylstannyloxyethane, colourless crystals (from light petroleum), m.p. 84°, $\nu_{max.}$ 700, 730, 830, 1080, 1115, 1440, 1510, and 3380 cm.$^{-1}$ (Nujol mull); τ 2·0—2·8 (Ph_3Sn), 3·02 and 3·57 (2d, J 8·4 Hz, C_6H_4), 4·48 and 5·58 (2d, J 9·8 Hz, C*H*N*H*), and 7·74 (MeC_6H_4) (Found: C, 51·6; H, 4·0; Cl, 17·8; N, 2·3. Calc. for $C_{27}H_{24}Cl_3NOSn$, C, 53·7; H, 4·0; Cl, 17·6; N, 2·3%).

[16] A. G. Davies and T. N. Mitchell, unpublished work.

Preparation of 2,2,2-*Trichloroethylidenearylamines*.—(*a*) 1,1,1-Trichloro-2-hydroxy-2-*p*-toluidinoethane [17] (4·0 g.) was subjected to azeotropic dehydration in benzene (25 ml.) in a Dean and Stark apparatus for 1·5 hr. The solvent was removed under reduced pressure leaving 2,2,2-*trichloroethylidene*-p-*toluidine* in essentially quantitative yield, m.p. 81° (from light petroleum), $\nu_{max.}$ 740, 830, 1330, 1510, and 1640 (C=N) cm.$^{-1}$; τ 1·88 (CH), 2·66 (s, C_6H_4), and 7·67 (MeC_6H_4) (Found: C, 46·0; H, 3·4; Cl, 45·2; N, 5·8. $C_9H_8Cl_3N$ requires C, 45·7; H, 3·4; Cl, 45·0; N, 5·9%).

(*b*) 2,2,2-Trichloroethylideneaniline, b.p. 94°/1·0 mm. was prepared in the same way from 1,1,1-trichloro-2-hydroxy-2-anilinoethane; it was identical with the compound obtained by treating the adduct of *N*-sulphinylaniline and bistributyltin oxide with chloral.[10]

Reaction between Triorganotin Methoxides and 1,1,1-*Trihalogeno*-2-*arylamino*-2-*hydroxyethanes*.—(a) *Tributyltin methoxide and* 1,1,1-*tribromo*-2-*hydroxy*-2-p-*toluidinoethane*. *p*-Toluidine (1·076 g., 0·01 mmoles) and bromal (0·96 ml., 0·01 mmoles) were mixed in carbon tetrachloride (25 ml.) yielding a suspension of a yellow solid. This dissolved when tributyltin methoxide (3·21 g., 0·01 mmoles) was added, giving a yellow solution. The volatile compounds were removed under reduced pressure, giving impure 1,1,1-tribromo-2-*p*-toluidino-2-tributylstannyloxyethane as an amber oil, τ 2·31 and 2·86 (2d, *J* 8·4 Hz, C_6H_4), 4·79 and 5·79 (2d, *J* 9·6 Hz, NH·CH), 7·72 (CH_3), and 8·0—9·5 (Bu_3Sn).

After the specimen had been stored for 24 hr. at room temperature, the spectrum showed signals at τ 1·51 (Bu_3Sn·NAr·C*H*O [16]), 2·71 and 3·02 (2d, *J* 8·4 Hz, C_6H_4), 7·61 (CH_3), and 8·0—9·5 (Bu_3Sn). Bromoform was removed under reduced pressure, and identified by its i.r. spectrum; the residual oil had $\nu_{max.}$ 1590 (C=O) cm.$^{-1}$.

(b) *Triphenyltin methoxide and* 1,1,1-*tribromo*-2-*hydroxy*-2-*toluidinoethane*. In an attempt to obtain a solid product which could be recrystallised, *p*-toluidine (0·177 g., 0·166 mmoles) in carbon tetrachloride (20 ml.) was treated with bromal (0·15 ml., 0·167 mmoles), and then with triphenyltin methoxide (0·722 g., 0·163 mmoles), to give a clear solution. Volatile components were removed under reduced pressure leaving a pasty solid. The n.m.r. spectrum indicated that it was impure 1,1,1-tribromo-2-*p*-toluidino-2-triphenylstannyloxyethane (60% yield), τ 3·04 and 3·58 (2d, *J* 8·4 Hz, C_6H_4), 4·67 and 5·53 (2d, *J* 9·7 Hz, NH·CH), and 7·76 (CH_3). The spectrum did not change significantly when the compound was kept in the solid state at room temperature for 14 days, but a pure specimen could not be obtained by recrystallisation.

Attempted Preparation of 1,1,1-*Trichloro*-2-*ethylamino*-2-*tributylstannyloxyethane*.—Ethyl isocyanate (4·09 g., 57·6 mmoles) was added to bistributyltin oxide (34·37 g., 57·6 mmoles). When the mixture had cooled, ethylamine (2·60 g., 57·5 mmoles) in carbon tetrachloride (40 ml.), then chloral (16·98 g., 115 mmoles) were added. The mixture became warm, a gas was evolved, the solution became cloudy, and an upper layer of water separated during 30 min. The organic layer showed n.m.r. signals at τ 2·09 (t, *J* 1·4 Hz, CH_3·CH_2·N:C*H*·CCl_3), and 2·42 (*H*CCl_3) (relative intensities 82 : 18), 4·71 (H_2O), 6·25 (q of d, *J* 7·3 and 1·4 Hz, CH_3·C*H*$_2$·N:CH·CCl_3), 8·78 (t, *J* 7·3 Hz, C*H*$_3$·CH_2), and 8·0—9·5 (Bu_3Sn). Distillation yielded two fractions, b.p. 72—105° (CCl_4 and $CHCl_3$), and 105—160° (impure Et N:CH·CCl_3); redistillation of this second fraction gave a liquid which was shown by n.m.r. to contain $CHCl_3$ and Et N:CH·CCl_3 in the ratio of 18 : 82, together with a second ethyl compound with τ 6·38 (CH_2); the smell of ethyl isocyanide was very noticeable.

Reaction of 1,1,1-*Trichloro*-2-*arylamino*-2-*tributylstannyloxyethanes with Chloral*.—Chloral (0·083 ml., 0·86 mmoles) was added to 1,1,1-trichloro-2-*p*-toluidino-2-tributylstannyloxyethane (0·58 g., 0·86 mmoles) in carbon tetrachloride. After 20 min., the n.m.r. spectrum showed τ 0·84 (Cl_3C·CHO), 2·6—3·4 ($\tau_{max.}$ 2·73, 2·79, 2·89, 2·93, 3·03, 3·17, and 3·30); 4·08, 4·39, 4·59, 5·59, 5·66, 5·74 (6d, *J ca.* 10 Hz), 7·72, and 8·0—9·5 (Bu_3Sn). During 7 days at 33·4°, the mixture decomposed to give a product which showed only the following n.m.r. signals: τ 1·87, 2·65, and 7·64 (Me·C_6H_4·N:CH·CCl_3 see above), 4·72br [Bu_3SnO·CH(OH)·CCl_3, and 8·0—9·5 [Bu_3Sn, identical in contour to the spectrum of the product obtained by treating bistributyltin oxide (0·431 g., 0·723 mmoles) with chloral (0·142 ml., 0·146 mmoles) and then with water (0·07 ml.)].

Equivalent results were obtained with 1,1,1-trichloro-2-anilino-2-tributylstannyloxyethane.

Reaction of 1,1,1-*Trihalogeno*-2-*arylamino*-2-*tributylstannyloxyethanes with Ethyl Isocyanate*.—All the reactions which were studied behaved similarly; that of the trichloro-*p*-toluidino-compound is typical.

Ethyl isocyanate (0·075 ml., 0·96 mmoles) was added to 1,1,1-trichloro-2-*p*-toluidino-2-tributylstannyloxyethane (0·514 g., 0·96 mmoles) in carbon tetrachloride (0·5 ml.). The initial n.m.r. spectrum was consistent with a mixture of these two components. The growth of the following signals then occurred, and was complete after 7·5 hr. at 33·4°; τ 190, 2·69, 7·61 (3s ratio 1 : 4 : 3, *p*-Me·C_6H_4·N:CH·CCl_3); 5·09br, 6·80br (q), and 8·0—9·5 (Bu_3Sn). A mixture of tributyltin *N*-ethylcarbamate [13] (1·99 g., 1·62 mmoles) and 2,2,2-trichloroethylidene *p*-toluidine (0·38 g., 1·62 mmoles) had an identical spectrum, which did not change when the mixture was kept at 33·4° for 3 days.

The tribromo-compounds reacted more quickly (3 hr. at 33·4°) and the trichloro-2-*p*-toluidino-2-triphenylstannyl compound more slowly (1·5 days at 33·4°). The reaction of 1,1,1-trichloro-2-*p*-nitroanilino-2-tributylstannylethane was complete in 2 hr. at 33·4°.

Reaction of N-*Tributylstannylpentafluoroaniline with Chloral and Ethyl Isocyanate*.—An excess of chloral was added to a 50% v/v) solution of *N*-tributylstannylpentafluoroaniline [16] in carbon tetrachloride. The mixture showed the expected n.m.r. spectrum for 1,1,1-trichloro-2-pentafluoroanilino-2-tributylstannyloxyethane: τ 4·36 (d, *J* 10·2 Hz, CH), 5·51 (d, *J* 10·2 Hz, broadened by unresolved coupling with ^{19}F; NH), and 8·0—9·5 (Bu_3Sn), together with small peaks in the region 3·8—5·8, due possibly to 2 : 1 addition, and a signal at 0·71 (Cl_3C·CHO). An excess of ethyl isocyanate was then added; during 12 hr., a colourless gas was evolved, and the spectrum changed to the following: τ 1·48br (C_6F_5·N:CH·CCl_3), 2·05 (t, *J* 1·4 Hz; Et N:CH·CCl_3), 5·51br and 4·37 [2d, *J* 10·2 Hz, C_6H_5·N*H*·C*H*(CCl_3)O·$SnBu_3$], 6·20 (q of d, *J* 7·3 and 1·4 Hz, CH_3·C*H*$_2$·N:CH·CCl_3), and 8·0—9·5 (Bu_3Sn and C*H*$_3$CH$_2$).

We are grateful to the Tin Research Institute for the award of a Research Studentship (to J. D. K.).

[0/183 *Received, February 4th,* 1970]

[17] A. Eibner, *Annalen*, 1898 **302**, 335.