385. *Amino-derivatives of Metals and Metalloids. Part II.*[1] *Aminostannylation of Unsaturated Substrates, and the Infrared Spectra and Structures of Carbamato- and Dithiocarbamato-trimethylstannanes and Related Compounds*

By T. A. GEORGE, K. JONES, and M. F. LAPPERT

The aminostannylation of carbon dioxide, keten, carbon disulphide, phenyl iso- and isothio-cyanate, benzonitrile, di-*p*-tolylcarbodi-imide, sulphur dioxide, and *N*-thionylaniline is reported. The infrared spectra of the novel carbamato-, homoamido- ($-CH_2CO\cdot NMe_2$), dithiocarbamato-, ureido-, thioureido-, amidino-, and thionyldiamido-organostannanes are described. It is concluded that only the first two compounds are polymeric in the solid state, with the ligand as a bridging group between neighbouring five-co-ordinate tin atoms. *NN*-Dimethyldithiocarbamatotrimethylstannane, $Me_3SnSCS\cdot NMe_2$, is monomeric, but may have five-co-ordinate tin, with the $-SCS-$ group as a bidentate ligand. This is consistent with tin(IV) being a class "*b*" acceptor, as is confirmed by a displacement reaction.

It is suggested that the mechanism of aminostannylation involves a low-energy 4-centre transition state, and that the reactions are thermodynamically controlled.

IN Part I,[1] we described the synthesis of aminostannanes, stannylamines, and stannazanes. In 1962, we briefly reported the discovery of a new type of reaction, that of aminometallation;[2] this was illustrated by citing numerous examples of insertion reactions of type (1), particularly of dimethylaminotrimethylstannane with unsaturated substrates A=B (see also ref. 3). The essential characteristic of the reagent AB appeared to be that it should be susceptible to attack by nucleophiles, but not by electrophiles. We now describe these and related experiments more fully, and comment on the infrared spectra and structures of some of the novel organotin products, and on the mechanism of these reactions.

$$Me_3Sn\cdot NMe_2 + A{=}B \longrightarrow Me_3Sn{-}A{-}B{-}NMe_2 \qquad (1)$$

At the time of our first Communication,[2] the only example of an aminometallation appeared to be that found in the reaction of diethylaminotrimethylsilane with either carbon dioxide or carbon disulphide.[4] Since then, there has been described the aminoboration of carbon dioxide and carbon disulphide,[5] and of phenyl iso- and isothio-cyanate [5,6] (also of sulphur dioxide [7]); the aminosilylation [8,9] (also of keten [10] and of sulphur trioxide [11]), aminophosphination,[8,12] aminoarsination,[8,13] and aminosulphenylation [8,14] of these unsaturated compounds have also been described.

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[1] Part I, K. Jones and M. F. Lappert, *J.*, 1965, 1944.

[2] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1962, 358.

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[4] H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 1126; 1962, **81**, 276.

[5] R. H. Cragg and M. F. Lappert, *Adv. Chem. Ser.*, 1964, No. 42, p. 220.

[6] (*a*) R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J.*, 1964, 2108; (*b*) J. L. Boone and G. W. Willcockson, Abstr. of Papers, 142nd National Meeting, Amer. Chem. Soc., Atlantic City, N.J., 1962, p. 6N; H. Beyer, J. W. Dawson, H. Jenne, and K. Niedenzu, *J.*, 1964, 2115; T. L. Heying and H. D. Smith, *Adv. Chem. Ser.*, 1964, No. 42, p. 201.

[7] H. Nöth and P. Schweizer, *Chem. Ber.*, 1964, **97**, 1464.

[8] G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891.

[9] G. Oertel, H. Malz, H. Holtschmidt, and E. Degener, Ger. Pat. 1,154,457/1963; G. Oertel, H. Holtschmidt, and H. Malz, Ger. Pat. 1,157,226/1963; W. Fink, *Chem. Ber.*, 1964, **97**, 1424, 1433.

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[11] M. Schmidt and H. Schmidbaur, *Angew. Chem.*, 1958, **70**, 657.

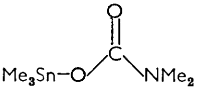
[12] G. Oertel, H. Malz, and H. Holtschmidt, Belg. Pat. 623,926/1963; H. J. Vetter and H. Nöth, *Chem. Ber.*, 1963, **96**, 1308.

[13] G. Oertel, H. Malz, H. Holtschmidt, and E. Degener, Belg. Pat. 624,614/1963; H. J. Vetter, H. Strametz, and H. Nöth, *Angew. Chem.*, 1963, **75**, 417.

[14] H. Malz, G. Oertel, and H. Holtschmidt, Belg. Pat. 624,818/1963, 628,173/1963; E. S. Blake, *J. Amer. Chem. Soc.*, 1943, **65**, 1267.

It is becoming evident (see also ref. 15) that aminometallation is merely an example taken from a wider class, in which derivatives of metals or metalloids act as 1,2-dipolarophiles with respect to unsaturated substrates. Among other reactions of this class, mention may be made of Grignard and other organometallation reactions, of halogenometallation (*e.g.*, of boron compounds [16]), of alkoxymetallation (*e.g.*, using alkoxides of tin(IV) [15] or boron [6a]), and of hydrometallation (*e.g.*, using diborane [17] or tin hydrides [18]); a review of this subject is in preparation.[19] Such reactions potentially have considerable applications, for instance, in the preparation of organometallics containing functional groups attached to the metal.

Aminostannylation of carbon dioxide and carbon disulphide, keten, phenyl iso- and isothio-cyanate, benzonitrile, di-*p*-tolylcarbodi-imide, sulphur dioxide, and *N*-thionylaniline (PhNSO) has been effected under mild conditions and in essentially quantitative yield. These reactions thus provide a route to several new classes of organotin compounds, namely, the carbamato-, dithiocarbamato-, homoamido- ($-CH_2CO{\cdot}NMe_2$), ureido-, thioureido-, amidino-, guanidino-, oxythionylamido- ($-OSONMe_2$), and thionyldiamido- ($-NPh{\cdot}SO{\cdot}NMe_2$) organostannanes. The particular examples of these which have been identified are shown in formulae (I)—(IX), respectively.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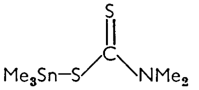
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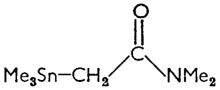
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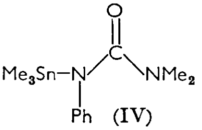
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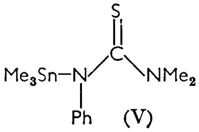
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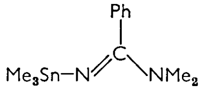
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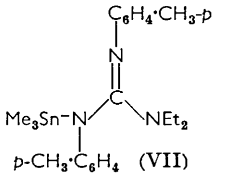
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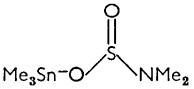
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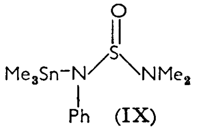
(IX)

Compounds (I)—(IX) were characterised by means of full elemental analyses. Evidence for their structures rests on analogy with products obtained by aminoboration of similar unsaturated substrates, and on their infrared spectra.

Infrared Spectra and Structures of Compounds (I)—(VI).—The assignments of the principal absorption bands in the spectra of compounds (I)—(VI) are indicated in Tables 1 and 2.

Our approach has been empirical. In the first instance, bands attributable to the Me_3Sn- and Me_2N- groups were picked out, on the basis of intensity as well as frequency, using available correlations on chlorotrimethylstannane [20] and dimethylaminotrimethylsilane; [21] a similar approach was employed for absorptions ascribable [22] to a monosubstituted phenyl group for compounds (IV)—(VI). This left a number of bands unassigned.

In the mull spectrum of solid *NN*-dimethylcarbamatotrimethylstannane, by far the

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[15] A. J. Bloodworthy and A. G. Davies, *Proc. Chem. Soc.*, 1963, 264, 315.

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[17] H. C. Brown, " Hydroboration," Benjamin, New York, 1962.

[18] G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.*, 1959, **9**, 106; W. P. Neumann, H. Niermann, and R. Sommer, *Annalen*, 1962, **659**, 27; D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, 1963, **28**, 1707; J. G. Noltes and M. J. Janssen, *Rev. Trav. chim.*, 1963, **82**, 1055; *J. Organometallic Chem.*, 1964, **1**, 346.

[19] M. F. Lappert and B. Prokai, in " Advances in Organometallic Chemistry," ed. F. G. A. Stone and R. West, Academic Press, New York, Vol. IV, in the press.

[20] H. Kriegsmann and S. Pischtschan, *Z. anorg. Chem.*, 1961, **308**, 212.

[21] J. Goubeau and J. Jimenez-Barbera, *Z. anorg. Chem.*, 1960, **303**, 217.

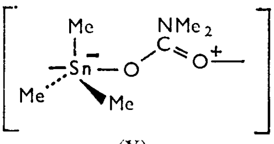
[22] D. H. Whiffen, *J.*, 1956, 1350.

TABLE 1

Frequencies (cm.$^{-1}$) and assignments of principal absorption bands in compounds (I)—(III)

$Me_3SnOCO{\cdot}NMe_2$	$Me_3SnSCS{\cdot}NMe_2$	$Me_3SnCH_2{\cdot}CO{\cdot}NMe_2$	Assignment
2994s	3077msh	2985s	CH str.
2924vs	3030msh	2959ssh	
2865vs	3003s	2898s	
	2899vs		
	2857msh		
2519w			Overtone of 1261 cm.$^{-1}$
1866w			
1733wsh			
1695m			C=O str. (4-co-ord. Sn)
1642ssh			
	1613w		Combination (?) of 1183 + 433 cm.$^{-1}$
	1538w		S_2C-N str.
1555s		1576vssh	C=O str. (5-co-ord. Sn)
		1558vs	
1490vs, b	1488vs	1497msh	$CH_3(N)$ deform.
1445ssh	1453msh	1437ssh	
		1456msh	CH_2 deform.
1393vs, b	1399msh	1418vs, b	$CH_3(Sn)$ deform.
1261vs, b	1370vs	1340s	
	1255s	1258s	
1186s	1183m	1200s	$CH_3(Sn)$ sym. deform. and $CH_3(N)$ rock
		1188s	
	1143s		CS_2 asym. str.
1055m		1077s	CNC asym. str.
1042m	1047m	1042s	
	1027m	1015s, b	
	995vs		CS_2 sym. str., masking CNC sym. str.
974m, b		939m	CNC sym. str.
915wsh, 792vs, b	882w		$CH_3(Sn)$ rock
770vs, b	772vs, b	775vs, b	
722vssh	735ssh	748vssh	
653s, b, 599s	575s	665vs	
		612s	
548vs	546s	553vs	SnC_3 asym. str.
	526s		SnC_3 sym. str.
	507s		SnS_2 asym. str.
	448s		SnS_2 sym. str.
438s, b	433s	495s	

strongest band in the 1500—1900 cm.$^{-1}$ region is that at 1555 cm.$^{-1}$. This is some 50—100 cm.$^{-1}$ lower than would be expected [23] from structure (I). A tertiary amide absorbs at *ca.* 1650 cm.$^{-1}$, and this might well be lowered, but only by about 30—40 cm.$^{-1}$, because of additional conjugation of the carbonyl group with the stannyl-oxygen lone-pair electrons. However, a further lowering of the C=O frequency, consistent with absorption at 1555 cm.$^{-1}$, would arise if the carbamato-group acted as a bidentate ligand, as shown in the single unit (X) from a polymeric structure. Here tin would be five-co-ordinate, using sp^3d hybrid orbitals, with the methyl groups in equatorial positions and the carbamato-groups in axial positions of a trigonal bipyramid. Consistent with this interpretation is the appearance of only one strong band in the 500—550 cm.$^{-1}$ region. This falls at 548 cm.$^{-1}$, and is assigned to the asymmetric SnC_3 stretching mode; structure (X) requires that the symmetric SnC_3 stretching vibration be infrared-forbidden. The medium-intensity absorption at 1695 cm.$^{-1}$, with a shoulder at 1642 cm.$^{-1}$, may well arise from the unco-ordinated, monomeric structure (I), present in relatively low abundance compared with (X). Such a situation would be an exact parallel to that of the carboxylatotrimethylstannanes [which have structures identical with (I) and (X), except that alkyl groups replace dimethylamino-groups].[24]



(X)

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[23] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, ch. 12.

[24] M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1963, **82**, 90.

TABLE 2

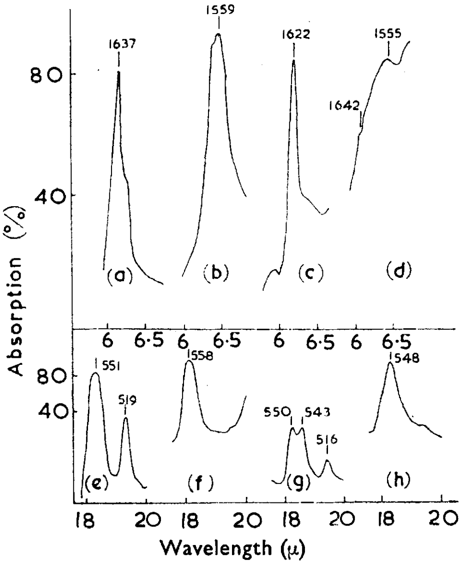
Frequencies (cm.$^{-1}$) and assignments of principal absorption bands in compounds (IV)—(VI)

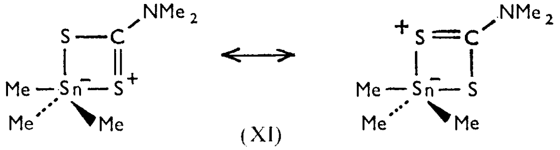
$Me_3SnN(Ph)CO{\cdot}NMe_2$	$Me_3SnN(Ph)CS{\cdot}NMe_2$	$Me_3SnN{=}CPh{\cdot}NMe_2$	Assignment
3086msh	3040msh	3077msh	CH str. (arom.)
3012msh	2985s	2997msh	
2933s	2857m	2907s	CH str. (aliph.)
2941msh	2801msh	2825msh	
		2778msh	
1942w	1992w	1961w	Arom. overtone and combination
1862w	1931w	1898w	
1802w	1859w	1818w	
	1779w	1695w	
1660s			C=O str. (4-co-ord. Sn)
		1582vs	C=N str.
1603vssh			C=O str. (5-co-ord. Sn)?
1592vs	1605vs	1605vs	CC str. (A_1)
1580vs	1587vs	1575vssh	CC str. (B_1)
1570vssh, 1550msh		1565ssh	CN_2 str.
	1538vssh		CN_2 (thioureide) str.
1490vs	1497vs	1488s	CC str. (A_1)
1456s	1479ssh	1477ssh	CC str. (B_1)
	1439s	1462s	CH_3(N) deform.
1408ssh	1403msh	1395s	CH(Sn) asym. deform. and CC str. (B_1)
1391vs	1383ssh	1355vs	
	1368vs		
	1328ssh		
1294s	1307vs		CH deform. (B_1)
	1279ssh		
1255m	1266vs	1259s	C_{ar}–N str.
	1242ssh		
1208vs	1205s	1214s	NCN asym. str.
1198ssh	1189s	1183s	Mass-dependent (A_1) CH_3(Sn) sym. deform., and CH_3(N) rock
1171m	1176msh		
	1170ms		
1156msh	1152ms	1138m	CH deform. (B_1)
	1136m		
	1101vs		C=S str.
1072m, b	1071m	1066vs	CH deform. (B_1) and CNC asym. str.
	1058msh		
1031m, 1022m	1026m, 1018msh	1027s	CH deform. (A_1)
999w	1000w, 985w, 976w	993w	Ring deform. (A_1)
929m	943m, 924w	927m	CNC sym. str.
899w	906w, b	907w	CH deform. (B_2)
818m, b	833m		CH deform (A_2)
777vssh	767vs, b	786vs	CH_3(Sn) rock
763vs	757ssh	764vs, b	
733m, b	730s, b		CH deform. (B_2)
699vs	697vs	700vs	Ring deform. (B_2)
690ssh	654w, b	689ssh	
625m	625w, b	672s	
614m	602w	617wsh	
		670m, 551msh	
545s	544vs	532vs	SnC_3 asym. str.
529s	510s	510s	SnC_3 sym. str.
510s			Sn–N str.?
477m	422m, b	484m	
		440m	

The above assignments are confirmed by examining the spectrum of a sample in dilute solution in benzene, the principal differences being (i) the diminution in intensity of the absorption at 1555 cm.$^{-1}$, (ii) the appearance of two additional strong bands in the 550—500 cm.$^{-1}$ region (at 543 and 516 cm.$^{-1}$), (iii) the presence of a new carbonyl stretching frequency at 1622 cm.$^{-1}$, and (iv) the development of a strong peak at 1232 cm.$^{-1}$ (which may largely be associated with CN stretching). These features are illustrated in the Figure. The two new low-frequency bands, (ii), in the solution spectrum are most plausibly accounted for by assigning them to Sn–O and symmetrical SnC_3 stretching vibrations. We conclude that the compound is largely depolymerised in solution, and this is confirmed by molecular-weight estimation.

In the spectrum of *NN*-dimethyldithiocarbamatotrimethylstannane, it is possible to account for all the absorption bands appearing at higher frequency than *ca.* 900 cm.$^{-1}$, on the basis of Me_3Sn– and Me_2N– groups, except for the strong bands at 1143 and 995 cm.$^{-1}$, the very weak bands at 1613 and 1538 cm.$^{-1}$, and the shoulder at 1626 cm.$^{-1}$. Partly, these are to be expected from structure (II). It has been pointed out [25] that compounds having the R $\underset{|}{\mathrm{N}}\text{–}\overset{|}{\mathrm{C}}\text{=S}$ structure have a strong band in the 1613—1471 cm.$^{-1}$ region, attributed to a CN vibration, this linkage being shortened from the normal length by association with the C=S group. In some planar chelate platinum(II) and related metal complexes, this vibration was located [26] at 1542—1480 cm.$^{-1}$. The C=S stretching frequency in thioamides and thioureas is generally found [27] as an intense band at 1234—1053 cm.$^{-1}$. A structure consistent with these data is the trigonal bipyramidal, monomeric chelate (XI). On this basis, the 1538-cm.$^{-1}$ band is assigned to the S_2C–N stretching mode, and those at 1143 and 995 cm.$^{-1}$ to the asymmetric and symmetric SnS_2 stretching vibrations. This leaves the 1613-cm.$^{-1}$ band unaccounted for, but it may possibly be a combination of others at 1183 and 433 cm.$^{-1}$. In agreement with (XI), we find strong bands attributable both to asymmetric (546 cm.$^{-1}$) and symmetric (526 cm.$^{-1}$) SnC_3 stretching frequencies, whilst the strong bands at 507 and 448 cm.$^{-1}$ are tentatively assigned to the similar modes of SnS_2.

Infrared spectra [(a)—d), carbonyl region; (e)—(f), SnC_3 region; maxima in cm.$^{-1}$] of: (a) and (e), $Me_3SnCH_2{\cdot}CO{\cdot}NMe_2$ in chloroform; (b) and (f), $Me_3SnCH_2{\cdot}CO{\cdot}NMe_2$ (mull); (c) and (g), $Me_3SnOCO{\cdot}NMe_2$ in benzene; and (d) and (h), $Me_3SnOCO{\cdot}NMe_2$ (mull)





(XI)

Acceptance of structures (X) and (XI) implies that the Sn–S bond is stronger than the Sn–O bond. This is confirmed by preliminary thermochemical studies,[28] which indicate that tin(IV) is certainly a class " *b* " acceptor. Furthermore, carbon disulphide readily displaces the dioxide from $Me_3SnOCO{\cdot}NMe_2$ to form the dithio-analogue. It is partly on this basis that the rather high values for the SnS_2 stretching frequencies are chosen.

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[25] H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, " Infra-red Determination of Organic Structures," Van Nostrand, New York, 1949.

[26] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kem.*, 1956, **29***B*, 75.

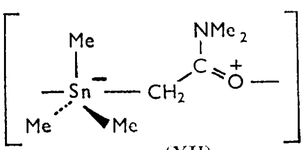
[27] Ref. 23, ch. 22.

[28] J. C. Baldwin, M. F. Lappert, and J. B. Pedley, unpublished work.

A further corollary is that substitution of two sulphur atoms for those of oxygen facilitates the formation of small rings. This is also in agreement with general experience; thus σ bonds from two-co-ordinate sulphur, in contrast to oxygen, are expected to have almost no *s* character.

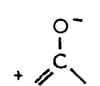
In agreement with the above assignment for $Me_3SnSCS{\cdot}NMe_2$, there is little difference between mull and solution spectra, and the compound is monomeric in solution. On the other hand, the spectrum of the silicon compound, $Me_3SiSCS{\cdot}NMe_2$,[4] has been examined for comparison, and above *ca.* 900 cm.$^{-1}$ the two spectra are very similar, and yet a five-co-ordinate structure for the silicon compound is unlikely. The three strongest bands in the 1300—900 cm.$^{-1}$ region are at 1235, 1099, and 962 cm.$^{-1}$ for the silicon compound, and at 1255, 1143, and 995 cm.$^{-1}$ for the tin analogue. A better interpretation of the spectra may, therefore, be in terms of the four-co-ordinate structure (II), with the three bands assigned to $\delta[CH_3(Sn)]$, $\nu(C{=}S)$, and $\nu(CNC)$, respectively.

In the mull spectrum of *NN*-dimethylamidohomotrimethylstannane, the band assigned to $\nu(C{=}O)$ is at 1558 cm.$^{-1}$, and other features are interpreted as shown in Table 1. It is suggested that the solid is polymeric, with the $-CH_2CO(NMe_2)-$ entity as a bridging group between neighbouring five-co-ordinate tin atoms, as shown for a single unit in (XII). In support of this, we find only the asymmetric mode (at 553 cm.$^{-1}$), and not the symmetric SnC_3 mode. On the other hand, the spectrum of a sample in dilute chloroform solution shows a shift of the carbonyl stretching frequency to 1637 cm.$^{-1}$, and the appearance of a new band [sym. $\nu(SnC_3)$] at 519 cm.$^{-1}$ These features are illustrated in the Figure. Molecular-weight determination shows that the compound is monomeric, and therefore properly described by structure (III), in solution.



(XII)

In the spectrum of *N'N'*-dimethyl-*N*-phenylureidotrimethylstannane, the strong bands appearing at frequencies higher than 1000 cm.$^{-1}$, which are unaccounted for after allocation of those arising from vibrations associated with Me_3Sn-, Me_2N-, and $Ph-$, are at 1660 cm.$^{-1}$, and shoulders at 1603, 1570, and 1550 cm.$^{-1}$. The band at 1660 cm.$^{-1}$ undoubtedly originates from a carbonyl stretching mode of a fully-substituted urea,[23] in accord with structure (IV). It is probable that this is the principal form present in the solid ureidostannane, although a polymer form of type (X) may be present, but to a smaller extent than for the carbamato-derivative, also because of the well-developed SnC_3 symmetric stretching mode at 529 cm.$^{-1}$. It is likely, furthermore, that, apart from absorption at 546 cm.$^{-1}$ (asymmetric SnC_3 stretching frequency), the other strong band in the 500-cm.$^{-1}$ region arises from the Sn–N vibration characteristic of a four-co-ordinate tin(IV) compound. As carbon and nitrogen are so close in mass, it is reasonable to expect Sn–C and Sn–N vibrations to lie close together. This, of course, assumes that bond-strengths are comparable, which is more likely to be the case for a four- rather than a five-co-ordinate Sn–N comcompound. While the Sn–N thermochemical bond-strength in an aminostannane is certainly [28] much lower than the Sn–C bond-strength, it is probable that the Sn–N bond-strength in a ureidostannane will be appreciably higher (see below). Implicit in our interpretation is also the conclusion that the carbonyl oxygen in (I) is a better donor than in (IV), which might be due to a significant contribution from structures such as (XIII). In keeping with this concept, it is found that the A_1 aromatic C–C stretching vibration at 1592 cm.$^{-1}$ is accompanied by a well-developed band at 1580 cm.$^{-1}$, which must be the B_1 stretching vibration; this is not normally distinguishable in the spectra of monosubstituted aromatic compounds, unless the aromatic ring has an unsaturated side-chain which allows for extended conjugation.[29]



(XIII)

Our interpretation of the spectrum of *N'N'*-dimethyl-*N*-phenylthioureidostannane is essentially similar to that of its oxygen analogue. Thus, we believe that the results are

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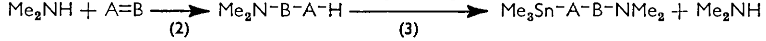
[29] Ref. 23, pp. 71 and 73.

consistent with an essentially monomeric unidentate structure [(IV) and (V)] for both compounds. On this basis, the very strong band at 1101 cm.$^{-1}$, in the spectrum of (V), is assigned to the C=S stretching mode.

Similarly, we regard structure (VI) for the amidinostannane to be verified by its infrared spectrum. The C=N stretching vibration is probably the origin of the very strong band at 1562 cm.$^{-1}$, since, during the course of reaction, this band gradually increased in intensity.

The spectra of compounds (VII)—(IX) (see Experimental section) are consistent with the suggested structures.

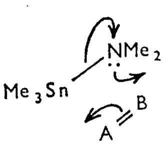
Mechanism of Aminostannylation.—It has been suggested [4] that the aminosilylation of carbon dioxide or carbon disulphide involves an ionic chain mechanism, requiring the presence of at least a trace of free amine. For the case of tin compounds, reaction (1) would thus involve the following sequence, with (2) and (3) as the propagation steps:



$$\mathrm{Me_2NH + A{=}B \xrightarrow[(2)]{} Me_2N{-}B{-}A{-}H \xrightarrow[(3)]{Me_3Sn{\cdot}NMe_2} Me_3Sn{-}A{-}B{-}NMe_2 + Me_2NH}$$

This mechanism is not likely to be valid for aminostannylations, since these proceeded readily even in the presence of a small amount of chlorotrimethylstannane (which reacts immediately with amine).

Aminostannylations were effected with great facility and under the mildest of conditions, as are aminometallations in general. This indicates that the associated activation energy is very small, and that the process is thermodynamically rather than kinetically controlled. Furthermore, as the reactions are not favoured by entropy considerations, it must follow that the products are significantly more stable than the reactants. There are not sufficient thermochemical data available at this time to permit even an approximate calculation. On the other hand, it is relevant that the $Sn-NMe_2$ thermochemical bond-energy is only about 40 kcal./mole, whilst the corresponding E ($Si-NMe_2$) is about 75 kcal./mole.[28] A low activation energy suggests that a cyclic transition state of the type (XIV) is plausible.



(XIV)

Reactions with other Unsaturated Substrates.—In contrast with the addition reactions observed with benzonitrile, it appears that aliphatic nitriles bearing an α-hydrogen atom undergo substitution reactions with aminostannanes, and corresponding nitro-compounds behave similarly. For example, dimethylamine was rapidly and quantitatively obtained when dimethylaminotrimethylstannane and acetonitrile were mixed, and the less-volatile products contained nitrile groups, as evident from their infrared spectra. Reactions with carbonyl compounds, including ketones and enol acetates, were also complex, and do not merely involve the formation of simple addition products. Further discussion of these systems is deferred until Part III, which will in the main deal with reactions of aminostannanes with protic reagents.

No reactions were realised between dimethylaminotrimethylstannane and olefins, including cyclohexene, norbornadiene, styrene, and α-methylstyrene.

EXPERIMENTAL

The analyses and the preparations of aminostannanes were carried out as previously described.[1]

In experiments (not detailed here) where we report lack of reaction, the reagents were invariably recovered almost quantitatively and were fully characterised.

Reaction of Dimethylaminotrimethylstannane with Carbon Dioxide.—Powdered carbon dioxide (*ca.* 2 g., excess of 1 mol.) was added rapidly to dimethylaminotrimethylstannane (3·60 g., 1 mol.) at 20°. After the vigorous reaction had ceased, a white powder (4·30 g., 98%) remained, and was dried at 20°/0·1 mm. The product was identified as NN-*dimethylcarbamatotrimethylstannane*, m. p. 165° (Found: C, 28·3; H, 5·9; N, 5·5. $C_6H_{15}NO_2Sn$ requires C, 28·6; H, 6·0; N, 5·6%). The molecular weight (ebullioscopically; 0·5% solution in benzene) was 508 ($C_6H_{15}NO_2Sn$ requires 252).

Reaction of Dimethylaminotrimethylstannane with Carbon Disulphide.—Carbon disulphide (1·06 g., 1 mol.) in light petroleum (b. p. 30—40°; 10 ml.) was added dropwise to dimethylaminotrimethylstannane (2·89 g., 1 mol.) in the same solvent (10 ml.). A vigorous reaction took place, and a white solid separated. The mixture was refluxed (½ hr.), and then most of the solvent was removed at 20°/15 mm. The solid was filtered off and dried at 20°/0·1 mm. The product was identified as NN-*dimethyldithiocarbamatotrimethylstannane* (3·75 g., 95%), m. p. 63° (Found: C, 25·2; H, 5·0; N, 5·1%; *M*, 287. $C_6H_{15}NS_2Sn$ requires C, 25·4; H, 5·3; N, 4·9%; *M*, 284).

Reaction of Dimethylaminotrimethylstannane with Phenyl Isocyanate.—Phenyl isocyanate (1·83 g., 1 mol.) was added dropwise to dimethylaminotrimethylstannane (3·20 g., 1 mol.) at 20°. An exothermic reaction took place, and, after cooling, the mixture showed no infrared absorption due to −NCO at 2200 cm.$^{-1}$. The product was distilled at reduced pressure to give a colourless, viscous liquid which was identified as NN-*dimethyl*-N-*phenylureidotrimethylstannane* (4·60 g., 94·5%), b. p. 103°/0·5 mm. (Found: C, 44·4; H, 6·0; N, 8·7%; *M*, 331. $C_{12}H_{20}N_2OSn$ requires C, 44·1; H, 6·1; N, 8·5%; *M*, 327).

Reaction of Dimethylaminotrimethylstannane with Phenyl Isothiocyanate.—Phenyl isothiocyanate (3·77 g., 1 mol.) was added dropwise to dimethylaminotrimethylstannane (5·80 g., 1 mol.) at 20°. An exothermic reaction took place, and the mixture showed only weak infrared absorption due to −NCS at 2100 cm.$^{-1}$. The product was a liquid, n_D^{22} 1·6024, which had the spectral characteristics reported in Table 2. Attempted distillation at 0·1 mm. led to decomposition.

Reaction of Dimethylaminotrimethylstannane with Benzonitrile.—Benzonitrile (2·09 g., 1 mol.) was added dropwise to dimethylaminotrimethylstannane (4·22 g., 1 mol.) at 20°. The mixture was refluxed for 1½ hr., and showed a progressive decrease in the intensity of infrared absorption due to $-C{\equiv}N$ at 2237 cm.$^{-1}$, and the appearance of a new band at 1582 cm.$^{-1}$, due to $>C{=}N-$. Distillation of the mixture gave a forerun of benzonitrile (0·30 g.), b. p. 30°/0·2 mm., n_D^{20} 1·5260, and the main fraction, a colourless viscous liquid, was identified as NN-*dimethyl*-N′-*trimethylstannylbenzamidine* (3·20 g., 60%), b. p. 79°/0·2 mm., n_D^{20} 1·5561 (Found: C, 46·8; H, 6·0; N, 9·3. $C_{12}H_{20}N_2Sn$ requires C, 46·3; H, 6·5; N, 9·0%).

Reaction of Diethylaminotrimethylstannane with Di-p-*tolylcarbodi-imide.*—Di-*p*-tolylcarbodi-imide (3·05 g., 1 mol.) was added to diethylaminotrimethylstannane (3·24 g., 1 mol.) at 20°. After the exothermic reaction had ceased, the mixture showed no infrared absorption due to $-N{=}C{=}N-$ at 2140 cm.$^{-1}$. The product (6·29 g., 100%) was distilled at reduced pressure to give a pale yellow viscous liquid which was identified as N-p-*tolyl*-N′N′-*diethyl*-N″-p-*tolyl*-N″-*trimethylstannylguanidine* (4·50 g., 71·6%), b. p. 168°/0·1 mm. (Found: N, 9·0. $C_{22}H_{33}N_3Sn$ requires N, 9·2%).

Reaction of Dimethylaminotrimethylstannane with Keten.—Keten was bubbled through the stannane (4·26 g.) in light petroleum (20 ml.) until no more yellow solid was deposited. The solvent was removed at 20°/16 mm., and subsequently at 20°/0·1 mm. The residual solid was identified as NN-*dimethylacetamidohomotrimethylstannane* (5·08 g., 99%), subliming above 160° (Found: C, 35·4; H, 7·2%; *M*, 270. $C_7H_{17}NO$ requires C, 35·6; H, 7·2%; *M*, 250).

Reaction of Dimethylaminotrimethylstannane with Sulphur Dioxide.—Sulphur dioxide was bubbled through the stannane (5·92 g.) in light petroleum (30 ml.). An immediate exothermal reaction was observed, and an orange, viscous liquid separated out. Removal of volatiles at 20°/15 mm. left a residue, believed to be *NN*-dimethyloxythionylamidotrimethylstannane (7·69 g., 98·6%), $\nu_{max.}$ 1000 cm.$^{-1}$ (S=O stretching vibration). Attempted distillation, even under reduced pressure, led to decomposition.

Reaction of Dimethylaminotrimethylstannane with N-*Thionylaniline.*—*N*-Thionylaniline (0·43 g., 1 mol.) in light petroleum (10 ml.) was added dropwise to the stannane (0·64 g., 1 mol.). An immediate exothermal reaction resulted. Removal of volatiles gave a quantitative yield of the 1 : 1 adduct, n_D^{22} 1·5642, believed to be *N*-phenyl-*N′N′*-dimethylthionyldiamidotrimethylstannane (Found: *M*, 355. $C_{11}H_{20}N_2OSSn$ requires *M*, 347). The asymmetric and symmetric $-N{=}S{=}O$ stretching frequencies at 1282 and 1166 cm.$^{-1}$ had virtually disappeared, and new strong bands at 1299 and 1068 cm.$^{-1}$ are assigned to vibrations essentially associated with $-\overset{|}{C}{=}N-$ and $>S{=}O$ stretching, respectively.

Reaction of NN-*Dimethylcarbamatotrimethylstannane with Carbon Disulphide.*—Carbon disulphide (0·50 g., 1 mol.) and the stannane (1·66 g., 1 mol.) in benzene (20 ml.) were heated (1 hr.) under reflux. Removal of solvent, at 20°/16 mm. and subsequently at 20°/0·1 mm., afforded *NN*-dimethyldithiocarbamatotrimethylstannane (1·87 g., 100%), m. p. 61·5° (infrared spectrum identical with that of an authentic sample).

Infrared Spectra.—These were measured with a Perkin-Elmer model 21 (2—15 μ) double-beam spectrophotometer fitted with sodium chloride optics, and with a Perkin-Elmer K14 instrument (15—25 μ) fitted with potassium bromide optics.

The instruments were calibrated throughout their ranges by means of accepted primary standards. Samples were examined as mulls in paraffin oil and hexachlorobutadiene [compounds (I)—(III)], as liquid capillary films [(IV)—(VI)], or as dilute solutions, as indicated. The results are recorded in Tables 1 and 2.

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