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# AMIDO DERIVATIVES OF METALS AND METALLOIDS VII*. CARBON–CARBON INSERTION REACTIONS INTO METAL–NITROGEN BONDS AND RELATED SYSTEMS

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## SUMMARY

The addition of aminostannanes to a variety of di-substituted acetylenes and ethylenes is reported; leading to a wide range of functionally-substituted organotin compounds. It has been demonstrated that $R_3SnNMe_2$ (where R = Me or Et) adds to diethyl acetylenedicarboxylate, 1-chloro-2-phenylacetylene, and substituted ethylenes of the type RCH=CR′R″ (where R and R′ = H and/or Me; and R″ = CN, CHO, or COOMe). Similarly, it is shown that the less reactive $Me_3SiNMe_2$ and $Me_3GeNMe_2$ will also add to diethyl acetylenedicarboxylate. The aminostannylation of nitrosobenzene, ethyl isothiocyanate, and tetracyanoethylene are also presented. Of particular interest is the formation of $p$-$CH_3C_6H_4N{=}C(SnMe_3)NMe_2$ from $Me_3SnNMe_2$ and $p$-$CH_3C_6H_4NC$; this represents the first example of a 1,1-insertion reaction of an unsaturated substrate outside transition metal chemistry.

An attempt is made to elucidate the structures by spectra and by comparison with similar systems.

## INTRODUCTION

The reactions of aminostannanes with 1,2-dipoles (eqn. 1) such as PhNCO, PhNCS, PhNSO, PhCN, $CO_2$, $CS_2$, $SO_2$, and di-$p$-tolylcarbodiimide were reported in Part II of this Series of Papers[2].

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

Attempts to insert acetylene and monosubstituted acetylenes into the Sn–N bond resulted in the formation of (organostannyl)acetylenes and amine, while no reaction occurred with diphenylacetylene[3]. Aminostannanes did not react with olefins, including cyclohexene, norbornadiene, styrene, and α-methylstyrene[2]. However, it is now found that the presence of powerfully electron-withdrawing groups, when conjugated with the acetylenic or ethylenic bond, encourages addition to occur (see ref. 4, for a preliminary communication).

Hydrometallation of olefins and acetylenes is well-known. By contrast, amido derivatives of metals and metalloids (*e.g.*, $LMNMe_2$, where L represents the

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sum of all ligands other than one $NMe_2$ group attached to the metal or metalloid M) had not previously (but see ref. 4) been observed to react in the sense of eqns. (1) and (2). The $R_3Sn$–X insertion reactions (other than X=H[5] and X=halide[6]) involving

$$LM{-}NMe_2 + RC{\equiv}CR' \rightarrow LM{-}C(R){=}C(R'){-}NMe_2 \quad (2)$$

$$LM{-}NMe_2 + RR'C{=}CR''R''' \rightarrow LM{-}C(R,R'){-}C(R'',R'''){-}NMe_2 \quad (3)$$

Sn–C bond-making that have been reported are the addition of $R_3SnOR'$ to $EtOOCC{\equiv}CCOOEt$[7], and $Ph_3SnPPh_2$ to $PhCH{=}CH_2$, $CH_2{=}CHCH_2Cl$, and $PhCH{\equiv}CH$[8]. The latter, however, differ from (4)–(13) in being free radical processes.

## DISCUSSION

The new 1,2-insertion reactions are summarised in eqns. (4)–(13).

$$Me_3Sn{-}NMe_2 + EtOOC{-}C{\equiv}C{-}COOEt \rightarrow Me_3Sn{-}\overset{EtOOC}{\underset{}{C}}{=}\overset{COOEt}{\underset{}{C}}{-}NMe_2 \quad (4)$$

$$Me_3Si{-}NMe_2 + EtOOC{-}C{\equiv}C{-}COOEt \rightarrow Me_3Si{-}\overset{EtOOC}{\underset{}{C}}{=}\overset{COOEt}{\underset{}{C}}{-}NMe_2 \quad (5)$$

$$Me_3Ge{-}NMe_2 + EtOOC{-}C{\equiv}C{-}COOEt \rightarrow Me_3Ge{-}\overset{EtOOC}{\underset{}{C}}{=}\overset{COOEt}{\underset{}{C}}{-}NMe_2 \quad (6)$$

$$Me_3Sn{-}NMe_2 + Ph{-}C{\equiv}C{-}Cl \rightarrow Me_3Sn{-}\overset{Cl}{\underset{}{C}}{=}\overset{Ph}{\underset{}{C}}{-}NMe_2 \quad (7)$$

$$Et_3Sn{-}NMe_2 + CH_2{=}CH{-}CN \rightarrow Me_2N{-}CH_2{-}\overset{SnEt_3}{\underset{}{C}}H{-}CN \quad (8)$$

$$Me_3Sn{-}NMe_2 + CH_2{=}C(CH_3){-}CN \rightarrow Me_2N{-}CH_2{-}\overset{SnMe_3}{\underset{}{C}}(CH_3){-}CN \quad (9)$$

$$Et_3Sn{-}NMe_2 + CH_2{=}CH{-}CHO \rightarrow Me_2N{-}CH_2{-}\overset{SnEt_3}{\underset{}{C}}H{-}CHO \quad (10)$$

$$Et_3Sn{-}NMe_2 + CH_3{-}CH{=}CH{-}CHO \rightarrow Me_2N{-}\overset{CH_3}{\underset{}{C}}H{-}\overset{SnEt_3}{\underset{}{C}}H{-}CHO \quad (11)$$

$$Et_3Sn{-}NMe_2 + Ph{-}CH{=}CH{-}CHO \rightarrow Me_2N{-}\overset{Ph}{\underset{}{C}}H{-}\overset{SnEt_3}{\underset{}{C}}H{-}CHO \quad (12)$$

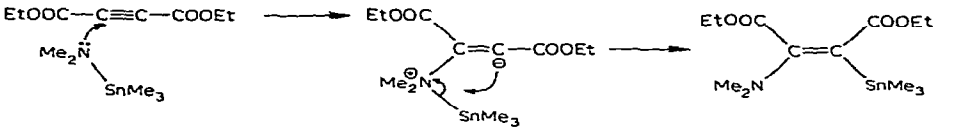
$$Et_3Sn{-}NMe_2 + CH_2{=}CH{-}COOMe \rightarrow Me_2N{-}CH_2{-}\overset{SnEt_3}{\underset{}{C}}H{-}COOMe \quad (13)$$

*Reactions* (4)–(7)

It has been shown[9] that benzylamine, aniline, mono-substituted anilines, and n-butylamine react with diesters of acetylenedicarboxylic acid to give, in each case, the *trans*-addendum. By contrast, the stereochemistry of the addition of secondary

aliphatic or alicyclic amines, or alcohols to dimethyl acetylenedicarboxylate is *cisoid*[10]. We propose, therefore, that addition of $Me_3SnNMe_2$, $Me_3GeNMe_2$, and $Me_3SiNMe_2$ to EtOOCC≡CCOOEt affords the *cis*-isomers exclusively (NMR and IR data show that a mixture of isomers is not obtained).

The most satisfactory mechanism to explain the mild reaction conditions is via a cyclic transition state. For example, the addition of $Me_3SnNMe_2$ to EtOOC-C≡CCOOEt is represented by eqn. (14), where the initial step involves nucleophilic attack at an acetylenic carbon followed by a concerted bond-making and bond-breaking step. This mechanism indicates initial *cis*-isomer formation, but subsequent isomerisation to a *trans*-isomer, if this is thermodynamically more stable, is not excluded.



(14)

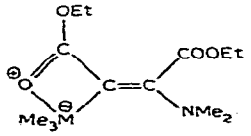
The products of eqns. (4)–(7) were further characterized by their infrared spectra (Table 1). These were not apparently informative as to the stereochemistry of the product, but an interesting feature is the presence of doublets in the C=O and C=C stretching regions.

TABLE 1

IR DATA ON ENAMINES

| Compound | ν(C=O) ($cm^{-1}$) | ν(C=C) ($cm^{-1}$) |
|---|---|---|
| $Me_3Si-\underset{EtOOC}{\overset{}{C}}=\underset{COOEt}{\overset{}{C}}-NMe_2$ | 1735, 1680 | 1570, 1550 |
| $Me_3Ge-\underset{EtOOC}{\overset{}{C}}=\underset{COOEt}{\overset{}{C}}-NMe_2$ | 1739, 1698 | 1590, 1555 |
| $Me_3Sn-\underset{EtOOC}{\overset{}{C}}=\underset{COOEt}{\overset{}{C}}-NMe_2$ | 1740, 1705 | 1625, 1590 |
| EtOOC–C≡C–COOEt | 1725 | |
| MeOOC–C≡C–COOMe | 1750 | |
| $H-\underset{MeOOC}{\overset{}{C}}=\underset{COOMe}{\overset{}{C}}-NEt_2$[10] | 1750, 1710 | 1590 |
| $H-\underset{MeOOC}{\overset{}{C}}=\underset{COOMe}{\overset{}{C}}-NC_5H_{10}$[10] | 1750, 1710 | 1590 |
| $H-\underset{MeOOC}{\overset{}{C}}=\underset{COOMe}{\overset{}{C}}-NC_2H_4$[10] | 1760, 1735 | 1635 |
| $Me_3Sn-\underset{Cl}{\overset{}{C}}=\underset{Ph}{\overset{}{C}}-NMe_2$ | | 1595, 1568 |

The splitting of the carbonyl stretching vibration is probably due to intramolecular coordination, so that the metal (Si, Ge, or Sn) is in a five-coordinate state (I). A similar suggestion has been made for carboxylatotrimethylstannanes[11].




I

Further support is provided by the IR spectra of the *cis*-addition products of $HNEt_2$, $HNC_5H_{10}$, and $HNC_2H_4$ with MeOOCC≡COOMe, (see Table 1), in which two C=O stretching vibrations occur due to hydrogen bonding.

The compounds under discussion are enamines and it is likely that the C=C–N system, due to conjugation, gives rise to an asymmetric and symmetric vibration in the C=C stretching range, as is observed with the related vinyl ethers[12].

*Reactions* (8)–(13)

The addition of aminostannanes to substituted ethylenes (eqns. 8–13), in which an electron-withdrawing group is conjugated to the double bond, can in principle give two possible isomers (II) and (III).

$$R_3Sn-CH_2-CH(NR'_2)-X \quad (II) \qquad R'_2N-CH_2-CH(SnR_3)-X \quad (III)$$

$$X = COOMe, CN, \text{ or } CHO; \quad R = Me \text{ or } Et; \quad R' = Me$$

The $^1H$ NMR spectrum of the product of eqn. (13), where R=Et, R′=Me, and X=COOMe, was studied. For isomer (II), all eight $CH_2$ protons would be expected to be masked by the main multiplet of the spectrum around τ 8.8 ppm. Analysis of the $^1H$ NMR spectrum of tetraethylstannane[13] shows that the methylene protons are located slightly upfield from the methyl triplet. The CH proton should appear as a triplet and the $N(CH_3)_2$ and $OCH_3$ protons as two separate singlets. Isomer (III), however, should exhibit two singlets due to $N(CH_3)_2$ and $OCH_3$ protons, a doublet due to $CH_2$ (not associated with Sn), and a triplet due to the CH proton. The essential difference between the two spectra would be the appearance of a downfield doublet (due to $CH_2$) in isomer (III). The $^1H$ NMR spectrum shows isomer (III) to be the product. The chief characteristics are shown in Table 2.

The suggested (see Table 2) lack of stereospecificity is consistent with a

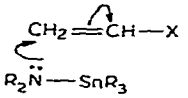
TABLE 2

$^1H$ NMR OF $(CH_3)_2N-CH_2-CH(COOCH_3)SnEt_3$

| τ (relative to $Me_4Si$) | Relative area | Assignment |
|---|---|---|
| 6.37 singlet | 3.1 | $OCH_3$ |
| 7.01 partially collapsed triplet | 1.0 | CH[a] |
| 7.25 non-equivalent doublet | 2.05 | $CH_2$[a] |
| 7.76 singlet | 6.1 | $N(CH_3)_2$ |

[a] Band multiplicity probably caused by hindered rotation about $CH_2$–CH.

mechanism for addition of aminostannanes to unsaturated substrates whereby the initial step is the nucleophilic attack of nitrogen at the most electropositive site (see IV).



IV

It is of interest to note that the aminosilane, $Me_3SiNMe_2$, does not react with methyl acrylate. The result is attributable to the greater Si–N bond strength and the higher basicity of the Sn- rather than the Si-amine.

*Reactions* (15)–(19)

A number of reactions (eqns. 15–19) were observed, which followed a different pattern. With vinyl acetate (eqn. 15), methyl methacrylate (eqn. 16), tetracarbethoxyethylene (eqn. 18), and chlorotrifluoroethylene (eqn. 19) the characteristic feature was substitution. The $OMe/NMe_2$ exchange reaction, as shown in (eqn. 16), has also been established by us in other systems[14]. The new problem is the preference for this particular mode of reaction rather then C=C addition. As for vinyl acetate, the $CH_3$–COO-group is presumably not sufficiently electron-drawing; and in any event, this substrate differs from the others in not being conjugated.

$$Me_3Sn{-}NMe_2 + CH_2{=}CHOOCMe \rightarrow Me_3SnOOC{-}Me + CH_2{=}CHNMe_2 \qquad (15)$$

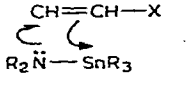
$$Me_3Sn{-}NMe_2 + CH_2{=}\overset{\displaystyle Me}{\overset{|}{C}}{-}COOMe \rightarrow Me_3SnOMe + CH_2{=}\overset{\displaystyle Me}{\overset{|}{C}}{-}CONMe_2 \qquad (16)$$

$$Et_3Sn{-}NMe_2 + n\,CH_2{=}CH{-}CHO \rightarrow Me_2N(-CH_2-\overset{\displaystyle CHO}{\overset{|}{C}}H-)_nSnEt_3 \quad (n=6\text{–}12) \qquad (17)$$

$$Bu_3Sn{-}NMe_2 + (EtOOC)_2C{=}C(COOEt)_2 \rightarrow Bu_3SnOEt + (Me_2NOC)\overset{\displaystyle EtOOC}{\overset{|}{C}}{=}C(COOEt)_2 \qquad (18)$$

$$Me_3SnNMe_2 + CF_2{=}CFCl \rightarrow Me_3SnF + CFCl{=}CFNMe_2 \qquad (19)$$

The methyl methacrylate experiment is surprising in view of the result with methyl acrylate. Clearly, $OMe/NMe_2$ exchange and C=C addition are potentially competing processes, and the opposite preference chosen by $CH_2$=CHCOOMe and $CH_2$=CMeCOOMe probably reflects a steric effect with respect to C=C addition in the latter case. This may imply that the transition state involves virtually synchronous bond-making and bond-breaking (see V), rather than a discretely separate bond-making process, as shown in eqn. (14).



V

Reaction with acrolein (eqn. 17) was shown to yield the telomers (VI) rather than (VII), because reaction with cold aqueous potassium permanganate rapidly

$Me_2N(-CH_2-\underset{\displaystyle CHO}{\underset{|}{CH}}-)_nSnEt_3$ (VI) $\quad Me_2N(-CH_2=\underset{\displaystyle H}{\underset{|}{CH}}-CO-)_nSnEt_3$ (VII)

precipitated manganese dioxide. Comparing reactions (10) and (17), the former represents the situation observed under milder conditions (0° against 25°). The mechanism of telomerization probably involves successive molecular insertion processes rather than an ionic chain mechanism. Elemental analysis of the telomer suggests that the value of $n$ lies between 6 and 12, in marked contrast[4] to the case of $Ti(NMe_2)_4$ where polymerization was observed at 0°.

The preference for $OEt/NMe_2$ exchange over C=C addition in reaction (18) is consistent with the steric hindrance interpretation invoked above for the methyl methacrylate result. Reactions (15), (16) and (18) will be further elaborated in Part X, in the context of the $LMNR_2/>C=O$ and $LMNMe_2/>S=O$ systems, and (19) in Part VIII with other aminations.

*Reactions* (20)–(25)

A wide range of addition reactions of aminostannanes to unsaturated substrates has been reported in Part II[2]. We now report a number of new reactions in this area (eqns. 20–23).

$$Me_3Sn-NMe_2 + (CN)_2C=C(CN)_2 \rightarrow Me_3Sn-N=C\begin{matrix}NMe_2\\ \diagup\\ NC\diagdown C=C(CN)_2\end{matrix} \quad (20)$$

$$Me_3Sn-NMe_2 + Et-NCS \rightarrow Me_3Sn-S-\underset{\displaystyle NMe_2}{\underset{|}{C}}=N-Et \quad (21)$$

$$Me_3Sn-NMe_2 + Ph-NO \rightarrow Me_3Sn-O-\underset{\displaystyle Ph}{\underset{|}{N}}-NMe_2 \quad (22)$$

$$Me_3Sn-NMe_2 + p\text{-}CH_3-C_6H_4-NC \rightarrow p\text{-}CH_3-C_6H_4-N=C\begin{matrix}SnMe_3\\ \diagdown\\ NMe_2\end{matrix} \quad (23)$$

Preliminary thermochemical studies of the Sn–S bond[15], and the fact that (alkylthio)stannanes can be prepared in aqueous alkaline solution[16], while alkoxystannanes react rapidly with water, suggest that Sn–S bonding is favoured over Sn–O. We have already reported the displacement of carbon dioxide from a carbamatostannane by carbon disulphide[2] to give the dithiocarbamato analogue (eqn. 24).

$$Me_3SnOCONMe_2 + CS_2 \rightarrow Me_3SnSCSNMe_2 + CO_2 \quad (24)$$

This reaction, however, could be explained in terms of the greater volatility of carbon dioxide. However, thioacetic acid readily liberates acetic acid from trimethyltin acetate (eqn. 25) and the former is the more volatile ($CH_3COOH$, b.p. 118°; $CH_3COSH$, b.p. 93°).

$$Me_3SnOCOMe + MeCOSH \rightarrow Me_3SnSCOMe + MeCOOH \quad (25)$$

Bloodworth and Davies[17] have studied the reaction of methoxytributylstannane with allyl and phenyl isothiocyanates and suggest that addition occurs across the C=S bond, because of the strong absorption at 1625 $cm^{-1}$ in the IR spectrum, which they assign to a C=N stretching mode. A similar conclusion has been arrived at by Noltes[18]. The IR spectrum of the phenyl isothiocyanate/aminostannane adduct shows a very strong band at 1605 $cm^{-1}$, formerly assigned to CC ($A_1$) ring stretch[2]. While this may well be correct, it no doubt could mask the C=N stretch. In order to study this region more clearly, (dimethylamino)trimethylstannane was reacted with ethyl isothiocyanate. A very strong band appeared at 1625 $cm^{-1}$ which is unambiguously assigned to the C=N stretching mode. Therefore, while addition of aminostannanes to isocyanates occurs across the C=N bond, addition to isothiocyanates is at the C=S bond.

Addition of an aminostannane to *p*-tolyl isocyanide (eqn. 23) can in principle be envisaged in two ways; either as a 1,1-addition to the carbon, or as a 1,2-addition across the C=N bond. The latter would result in an unsaturated carbon, while 1,1-addition would better satisfy the electron requirements of the carbon. The IR spectrum of the adduct shows a very strong band at 1640 $cm^{-1}$ which is assigned to $\nu$(C=N) (see Table 3) and this therefore supports a 1,1-addition product. The reaction re-

TABLE 3

$\nu$(C=N) ABSORPTION IN THE INFRARED SPECTRUM OF SOME ADDUCTS

| Compound | Frequency ($cm^{-1}$) |
|---|---|
| $Me_3Sn-S-C(NMe_2)=NEt$ | 1625[a] |
| $p\text{-}CH_3-C_6H_4-N=C(SnMe_3)(NMe_2)$ | 1640[b] |
| $Me_3Sn-N=C(NMe_2)(NC)C=C(CN)_2$ | 1600[b] |

[a] Liquid film. [b] "Nujol" mull.

presents the first instance of a 1,1-insertion of an unsaturated substrate in main group chemistry, although it is well-established in transition metal chemistry with CO[19]. It is also the first isocyanide insertion reaction[19].

The IR spectrum of the tetracyanothylene addition product (eqn. 20) indicates that addition occurs at –C≡N. The low value for $\nu$(C=N) is attributable to conjugation. The $\nu$(C=C) vibration was not observed. It may be masked by $\nu$(C=N); and is expected to be of low intensity due to the relatively high electrical symmetry about the double bond.

Reaction (22) undoubtedly involves nucleophilic attack at the nitrogen of nitrosobenzene with the resulting formation of a Sn–O bond. It represents the first example of insertion of a nitroso compound[19].

No reaction occurred between an aminostannane and severally benzylideneaniline, azobenzene, triphenylphosphine, ethylene oxide, nitrous oxide, or carbon monoxide. No reaction occurred with carbon monoxide under ambient conditions of temperature and pressure; in an autoclave, an unknown product was isolated which was not characterized.

## EXPERIMENTAL

### *General procedures*

Diethyl ether and hydrocarbon solvents were dried over sodium wire; dichloromethane was distilled from phosphorus pentoxide. All liquid starting materials were distilled before use. Nitrosobenzene was recrystallized from methanol and tetracyanoethylene was sublimed. The analyses of new compounds were carried out at the Bernhardt Microanalytical Laboratory, Hohenweg, West Germany; The Beller Microanalytical Laboratory, Göttingen, West Germany; and by Mr. B. Bona and his staff in the Microanalytical Laboratory, University of Sussex. The aminostannanes were prepared as previously described[20]. In experiments, not detailed here, where we report lack of reaction, the reagents were invariably recovered almost quantitatively and fully characterised. Molecular weights were determined isopiestically using a Mechrolab vapour pressure osmometer, melting points in sealed capillary tubes, refractive indices with an Abbé-type refractometer using sodium-D light, IR spectra on Perkin–Elmer 237 and 337 instruments, and NMR spectra on a Perkin–Elmer R-10. Further details of the spectra are to be found in ref. 21.

### *Reaction of (dimethylamino)trimethylstannane with diethyl acetylenedicarboxylate*

(Dimethylamino)trimethylstannane (1.51 g, 0.0725 mole) in light petroleum (b.p. 40–60°, 10 ml) was added to diethyl acetylenedicarboxylate (1.24 g, 0.0725 mole) in the same solvent (10 ml). An exothermic reaction occurred. Solvent was removed (20°/60 mm), and the green product was identified as *[1,2-dicarbethoxy-2-(dimethylamino)vinyl]trimethylstannane* (2.71 g, 98%), b.p. 100°/0.02 mm, $n_D^{25}$ 1.4700. (Found: C, 40.1; H, 6.6; N, 4.1. $C_{13}H_{25}NO_4Sn$ calcd.: C, 41.2; H, 6.6; N, 3.7%.)

### *Reaction of (dimethylamino)trimethylsilane with diethyl acetylenedicarboxylate*

(Dimethylamino)trimethylsilane (6.64 g, 0.06 mole) in diethyl ether (20 ml) was refluxed (6 h) with diethyl acetylenedicarboxylate (4.58 g, 0.03 mole). Solvent was removed, and (dimethylamino)trimethylsilane (3.0 g, 0.025 mole), b.p. 75°, was recovered on distillation. The orange residue was identified as *[1,2-dicarbethoxy-2-(dimethylamino)vinyl]trimethylsilane* (5.57 g, 72%), b.p. 100°/0.01 mm, $n_D^{25}$ 1.4866. (Found: C, 54.7; H, 8.9; N, 5.0. $C_{13}H_{25}NO_4Si$ calcd.: C, 54.3; H, 8.7; N, 4.9%.)

### *Reaction of (dimethylamino)trimethylgermane with diethyl acetylenedicarboxylate*

(Dimethylamino)trimethylgermane (1.76 g, 0.01 mole) in diethyl ether (10 ml) was added to diethyl acetylenedicarboxylate (1.85 g, 0.01 mole) in the same solvent (10 ml). An exothermic reaction ensued. Solvent was removed, and the green product identified as *[1,2-dicarbethoxy-2-(dimethylamino)vinyl]trimethylgermane* (2.80 g, 78%), b.p. 80°/0.02 mm, $n_D^{25}$ 1.4840. (Found: C, 47.9; H, 7.5; N, 4.5. $C_{13}H_{25}GeNO_4$ calcd.: C, 46.9; H, 7.5; N, 4.2%.)

*Reaction of (dimethylamino)trimethylstannane with 1-chloro-2-phenylacetylene*

(Dimethylamino)trimethylstannane (7.75 g, 0.03 mole) in light petroleum (b.p. 30–40°, 10 ml) was added slowly to 1-chloro-2-phenylacetylene (5.04 g, 0.03 mole). An exothermic reaction occurred. Volatiles were removed (25°/0.025 mm), from which unreacted 1-chloro-2-phenylacetylene (2.18 g) (Found: Cl, 24.9. $C_8H_5Cl$ calcd.: Cl, 26%.) was recovered. The remaining liquid was believed to be [*1-chloro-2-(dimethylamino)-2-phenylvinyl*]*trimethylstannane* (4.84 g, 40%). (Found: Cl, 10.1. $C_{13}H_2ClNOSn$ calcd.: Cl, 10.3%.) Attempted distillation, however, caused decomposition, yielding a yellow liquid (3.08 g), b.p. 60–80°/0.04 mm (Found: C, 65.41; H, 8.38; N, 10.72%.), and a viscous, red residue.

*Reaction of (dimethylamino)triethylstannane with acrylonitrile*

(Dimethylamino)triethylstannane (8.40 g, 0.03 mole) in light petroleum (b.p. 40–60°, 15 ml) was added dropwise to acrylonitrile (1.78 g, 0.03 mole) in the same solvent (10 ml) at 0°. Solvent was removed and the product identified as [*1-cyano-2-(dimethylamino)ethyl*]*triethylstannane* (7.00 g, 69%), b.p. 97°/0.02 mm, $n_D^{28}$ 1.5853. (Found: C, 42.7; H, 8.0; mol.wt., 320. $C_{11}H_{24}N_2Sn$ calcd.: C, 43.5; H, 7.9%; mol.wt., 303.)

*Reaction of (dimethylamino)trimethylstannane with methacrylonitrile*

(Dimethylamino)trimethylstannane (8.2 g, 0.04 mole) in light petroleum (b.p. 20–40°, 20 ml) was added dropwise to methacrylonitrile (2.64 g, 0.04 mole). Solvent was removed, and the colourless product was identified as [*1-cyano-2-(dimethylamino)-1-methylethyl*]*trimethylstannane* (5.8 g, 54%), b.p. 78–80°/0.02 mm, $n_D^{30}$ 1.5871. (Found: C, 39.2; H, 7.3; N, 10.0; mol.wt., 309. $C_9H_{20}N_2Sn$ calcd.: C, 39.2; H, 7.3; N, 10.1%; mol.wt., 275.)

*Reaction of (dimethylamino)triethylstannane with methyl acrylate*

(Dimethylamino)triethylstannane (6.26 g, 0.025 mole) in diethyl ether (5 ml) was added to methyl acrylate (2.15 g, 0.025 mole) in the same solvent (25 ml) at 0°. Solvent was removed, and the yellow product identified as [*1-acetoxy-2-(dimethylamino)ethyl*]*triethylstannane* (7.84 g, 93%), b.p. 88°/0.03 mm. $n_D^{25}$ 1.5836. (Found: C, 42.8; H, 7.9; N, 4.2; mol.wt., 318. $C_{12}H_{22}NO_2Sn$ calcd.: C, 42.8; H, 8.0; N, 4.1%; mol.wt., 336.)

*Reaction of (dimethylamino)triethylstannane with acrolein*

Acrolein (0.995 g, 0.02 mole) was added to (dimethylamino)triethylstannane (4.45 g, 0.02 mole) in light petroleum (b.p. 20–40°, 15 ml) at 0°. Solvent was removed, and the yellow liquid was identified as [*2-(dimethylamino)-1-formylethyl*]*triethylstannane* (5.24 g, 99%), b.p. 86°/0.025 mm. (Found: C, 43.2; H, 8.2; N, 4.5. $C_{11}H_{25}NOSn$ calcd.: C, 43.1; H, 8.2; N, 4.6%.)

*Reaction of (dimethylamino)triethylstannane with crotonaldehyde*

(Dimethylamino)triethylstannane (4.45 g, 0.018 mole) in light petroleum (b.p. 0–40°, 15 ml) was added to crotonaldehyde (1.272 g, 0.018 mole) in the same solvent (10 ml). Solvent was removed, and the orange-yellow liquid was identified as [*2-(dimethylamino)-1-formyl-2-methylethyl*]*triethylstannane* (5.57 g, 95%), b.p. 80°/0.01 mm,

$n_D^{25}$ 1.5840. (Found: C, 44.7; H, 8.1; N, 4.5; mol.wt., 319. $C_{12}H_{27}NOSn$ calcd.: C, 45.0; H, 8.41; N, 4.3%; mol.wt., 320.)

*Reaction of (dimethylamino)triethylstannane with cinnamaldehyde*

(Dimethylamino)triethylstannane (5.79 g, 0.023 mole) in light petroleum (b.p. 40–60°, 10 ml) was added to cinnamaldehyde (3.06 g, 0.023 mole) in the same solvent (10 ml). An exothermic reaction occurred. Solvent was removed, and the yellow residual liquid was identified as *[2-(dimethylamino)-1-formyl-2-phenylethyl]triethylstannane* (8.02 g, 88%), b.p. 69–71°/0.02 mm, $n_D^{28}$ 1.5881. (Found: C, 53.3; H, 7.1; N, 3.9; mol.wt., 324. $C_{17}H_{29}NOSn$ calcd.: C, 53.4; H, 7.1; N, 3.9%; mol.wt., 382.)

*Reaction of (dimethylamino)triethylstannane with acrolein; telomerisation*

(Dimethylamino)triethylstannane (12.38 g, 0.05 mole) in light petroleum (b.p. 20–40°, 10 ml) was added to acrolein (2.76 g, 0.05 mole) in the same solvent (10 ml). A yellow solid was formed. On filtration and removal of solvent, (dimethylamino)triethylstannane (10.5 g, 82%) was recovered, and a solid telomer, $Me_2N[-CH_2-CH(CHO)-]_nSnEt_3$, (2.75 g), m.p. >300° (sealed tube), (Found: C, 57.6; H, 7.3; N, 2.5; Sn, 18.0%.) obtained.

*Reaction of (dimethylamino)trimethylstannane with p-tolyl isocyanide*

(Dimethylamino)trimethylstannane (3.66 g, 0.02 mole) in diethyl ether (20 ml) was added to *p*-tolyl isocyanide (2.1 g, 0.02 mole), and the mixture was refluxed (4 h). Solvent was removed, and distillation gave two products: (*i*) a colourless liquid (unidentified, 1.1 g), b.p. 30°/0.01 mm (Found: C, 61.8; H, 6.2; N, 8.1%.), and (*ii*) *(N,N-dimethyl-N'-p-tolylamidino)trimethylstannane* (2.05 g, 37%), m.p. 40° (sealed tube), b.p. 100°/0.01 mm (Found: C, 48.4; H, 6.8; N, 8.7. $C_{13}H_{22}N_2Sn$ calcd.: C, 48.0; H, 6.8; N, 8.6%.)

*Reaction of (dimethylamino)triethylstannane with nitrosobenzene*

(Dimethylamino)triethylstannane (6.52 g, 0.03 mole) in diethyl ether (10 ml) was added dropwise to nitrosobenzene (2.79 g, 0.03 mole) in the same solvent (60 ml) at 0°, with vigorous stirring. Solvent was removed, and distillation gave *(N',N'-dimethyl-N-phenylhydrazinoxy)triethylstannane* (5.849 g, 63%), b.p. 98–99°/0.02 mm. (Found: C, 46.1; H, 7.3; N, 7.0. $C_{14}H_{26}N_2OSn$ calcd.: C, 47.1; H, 7.3; N, 7.8%.)

*Reaction of (dimethylamino)trimethylstannane with ethyl isothiocyanate*

Ethyl isothiocyanate (1.97 g, 0.02 mole) was added to (dimethylamino)trimethylstannane (4.71 g, 0.02 mole). An exothermic reaction ensued, and an IR spectrum of the mixture showed only a weak absorption at 2100 $cm^{-1}$ due to –NCS. Unreacted starting materials were removed (25°/0.01 mm), but the product, believed to be *[(N,N-dimethyl-N'-ethylamidino)thio]trimethylstannane* (6.49 g, 96%), decomposed on attempted distillation at 0.01 mm.

*Reaction of (dimethylamino)trimethylstannane with tetracyanoethylene*

(Dimethylamino)trimethylstannane (2.0 g, 0.095 mole) in dichloromethane (10 ml) was added slowly to tetracyanoethylene (1.24 g, 0.095 mole) in the same solvent (35 ml). An exothermic reaction occurred. Solvent (20 ml) was added, and the solution

stored (12 h) at −20°. The resulting red-brown solid (0.2 g) was filtered off and washed with dichloromethane (2 × 10 ml). (Found: C, 27.6; H, 5.0; N, 8.1%.) The combined filtrates were evaporated and the black-brown solid identified as {[2,3,3-*tricyano*-1-(*dimethylamino*)*allylidene*]*amino*}*trimethylstannane* (3.0 g, 93%), m.p. 110°–112° (sealed tube) (Found: C, 40.1; H, 4.3; N, 20.9. $C_{11}H_{15}N_5Sn$ calcd.: C, 39.8; H, 4.5; N, 21.0%.)

*Reaction of tributyltin acetate with thioacetic acid*

Thioacetic acid (0.46 g, 0.006 mole) in light petroleum (b.p. 40–60°, 5 ml) was added to tributyltin acetate (2.1 g, 0.006 mole) in the same solvent (30 ml). Solvent was removed, and distillation gave acetic acid (0.35 g, 98%), b.p. 117°, and tributyltin thioacetate (2.0 g, 94%), b.p. 86–88°/0.02 mm.

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