928. *Some Organotin Isocyanates and their Hydrolysis Products*

By A. S. Mufti and R. C. Poller

Tributyl-, dibutyl-, and triphenyl-tin isocyanates have been prepared; the isolation of diphenyltin di-isocyanate was accompanied by hydrolysis. The di-isocyanates are sensitive to moisture and hydrolysis products of the type $R_8Sn_4(NCO)_4O_2$ and $R_8Sn_4(NCO)_2(OH)_2O_2$ were isolated. An additional hydrolysis product of diphenyltin di-isocyanate, $Ph_4Sn_2(NCO)_2(OH)_2$, was obtained. The 2,2′-bipyridyl derivative of diphenyltin di-isocyanate was found to be a 1 : 2 adduct and it is concluded that this compound contains a bridging bipyridyl group.

Little is known about organotin isocyanates. Early workers [1] claimed to have isolated triethyltin isocyanate but the first detailed account of its preparation was reported by Anderson and Vasta.[2] An attempt [3] to prepare dimethyltin di-isocyanate under aqueous conditions gave what was described as a 1 : 1 mixture of the latter compound and dimethyltin oxide. For reasons which will become apparent it seems likely that this product was di-μ-(isocyanatodimethylstannyloxo)bis(isocyanatodimethyltin) (II; R = Me, X = NCO).

The heterogeneous reaction between the appropriate organotin chloride in ether or light petroleum and silver isocyanate gave triphenyltin isocyanate, tributyltin isocyanate, and dibutyltin di-isocyanate. Since this work was completed the preparation of triphenyltin isocyanate by a similar method has been briefly reported.[4] Treatment of

[1] (*a*) P. Kulmiz, *J. prakt. Chem.*, 1860, **80**, 60; (*b*) A. Cahours, *Annalen*, 1862, **122**, 48.
[2] H. H. Anderson and J. A. Vasta, *J. Org. Chem.*, 1954, **19**, 1300.
[3] E. G. Rochow, D. Seyferth, and A. C. Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 3099.
[4] T. N. Srivastava and S. K. Tandon, *Indian J. Appl. Chem.*, 1963, **26**, 171.

triphenyltin or tributyltin chloride with a suspension of sodium urethane in xylene also furnished the isocyanates in high yield by the following reaction:

$$R_3SnCl + NaNH{\cdot}CO_2Et \longrightarrow [R_3SnNH{\cdot}CO_2Et] \longrightarrow R_3SnNCO + EtOH$$

A similar method has been used to prepare the corresponding silicon compounds.[5]

The mono-isocyanates are stable in the atmosphere and are hydrolysed under basic conditions to the hydroxides R_3SnOH. Early experiments [1] in which a trialkyltin isocyanate treated with ethanolic ammonia (with no attempt to exclude moisture) was said to give the corresponding urea $R_3SnNH{\cdot}CONH_2$ could not be repeated. Under these conditions tributyltin isocyanate gave tributyltin hydroxide and urea, presumably by interaction of the cyanic acid liberated in the hydrolysis reaction, with ammonia. Lappert and Pyszora [6] have discussed the reaction of boron isocyanates with ammonia and amines and it is clear that, when an isocyanate group is attached to an electropositive metal such as tin, substitution rather than addition reactions are to be expected.

Triphenyltin isocyanate was recovered unchanged after 24 hours' refluxing in anhydrous butanol indicating that the alcohol is too weakly nucleophilic to effect substitution.

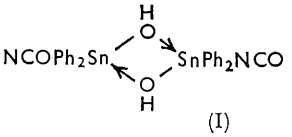
Dibutyltin di-isocyanate is very sensitive to moisture; exposure to the air or crystallisation from moist solvents lead to the isolation of the hydrolysis products in the sequence:

$$Bu_2Sn(NCO)_2 \longrightarrow Bu_8Sn_4(NCO)_4O_2 \longrightarrow Bu_8Sn_4(NCO)_2(OH)_2O_2 \longrightarrow Bu_2SnO$$

Diphenyltin di-isocyanate was so labile that, despite rigorous attempts to exclude moisture, we could not prepare a pure specimen. Instead a highly reactive intermediate, whose analysis and molecular weight indicated the formulation $Ph_4Sn_2(NCO)_2(OH)_2$, was obtained. Repeated crystallisation of this compound converted it successively into the products shown in the sequence:

$$[Ph_2Sn(NCO)_2] \longrightarrow Ph_4Sn_2(NCO)_2(OH)_2 \longrightarrow Ph_8Sn_4(NCO)_4O_2 \longrightarrow Ph_8Sn_4(NCO)_2(OH)_2O_2 \longrightarrow Ph_2SnO$$

The dimeric diphenyltin hydroxyisocyanate corresponds to the labile dibutyltin hydroxychloride formulated as a monomer by Gibbons *et al.*[7] The diphenyl compound has an O–H stretching band at 3530 cm.$^{-1}$ but no Sn–O band in the 900 cm.$^{-1}$ region, unlike triphenyltin hydroxide [8] and $Ph_8Sn_4(NCO)_2(OH)_2O$ which show similar doublet bands centred at 905 and 914 cm.$^{-1}$, respectively. The compound does not react as a hydroxytin compound with the Karl Fischer reagent [9] and this diminished reactivity, together with the absence of an infrared absorption band at 900 cm.$^{-1}$, is ascribed to co-ordination by the hydroxyl group and it is tentatively concluded that the structure is di-μ-hydroxybis(isocyanatodiphenyltin) (I).



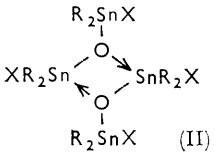
(I)

The structures of $Bu_8Sn_4(NCO)_4O_2$ and $Ph_8Sn_4(NCO)_4O_2$ follow from the work of Alleston *et al.*[10] on the corresponding intermediates obtained in the controlled basic hydrolysis of the organotin dihalides and they are, respectively, di-μ-(isocyanatodibutylstannyloxo)bis(isocyanatodibutyltin) (II; R = Bu, X = NCO) and di-μ-(isocyanatodiphenylstannyloxo)bis(isocyanatodiphenyltin) (II; R = Ph, X = NCO).

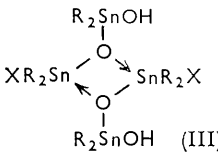
Hydrolysis of (II) gives either (III) or (IV) according to whether it is considered that the X groups attached to 4- or 5-co-ordinate tin will be replaced.[11] Tanaka *et al.*[12] stated

[5] H. Gilman, B. Hofferth, and H. W. Melvin, *J. Amer. Chem. Soc.*, 1950, **72**, 3045.
[6] M. F. Lappert and H. Pyszora, *J.*, 1963, 1744.
[7] A. J. Gibbons, A. K. Sawyer, and A. Ross, *J. Org. Chem.*, 1961, **26**, 2304.
[8] R. C. Poller, *J. Inorg. Nuclear Chem.*, 1962, **24**, 593.
[9] H. Gilman and L. S. Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 2367.
[10] D. L. Alleston, A. G. Davies, M. Hancock, and R. F. M. White, *J.*, 1963, 5469.
[11] D. L. Alleston, A. G. Davies, and M. Hancock, *J.*, 1964, 5744.
[12] T. Tanaka, M. Komura, Y. Kawasaki, and R. Okawara, *J. Organometallic Chem.*, 1964, **1**, 484.

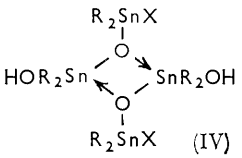
that substitution will take place more readily at the 5-co-ordinate tin atoms. However there is no basis for an unequivocal choice between the two alternatives though there are examples in other branches of organotin chemistry [13] where hydrolytically unstable compounds become stable when the co-ordination number of tin is raised from 4 to 5.



(II)



(III)



(IV)

Also it is shown below that when the co-ordination number of tin in diphenyltin di-iso-cyanate is raised from 4 to 5 by complex formation then the compound becomes stable to water. Accordingly the structures preferred for $Bu_8Sn_4(NCO)_2(OH)_2O_2$ and $Ph_8Sn_4(NCO)_2(OH)_2O_2$ are, respectively, di-μ-(hydroxydibutylstannyloxo)bis(isocyanatodibutyltin) (III; R = Bu, X = NCO) and di-μ-(hydroxydiphenylstannyloxo)bis(isocyanatodiphenyltin) (III; R = Ph, X = NCO).

Compound (I) was exposed to the atmosphere and its melting point and infrared spectrum measured at intervals; within 5 hr. it was converted into $Ph_8Sn_4(NCO)_4O_2$ and, after a further 24 hr. into $Ph_8Sn_4(NCO)_2(OH)_2O_2$. After 3 days the melting point was >360° and, except for a weak isocyanate band persising at 2200 cm.$^{-1}$, the infrared absorption spectrum was identical with that of diphenyltin oxide. Thus it is clearly demonstrated that these intermediates are necessary stages in the hydrolysis of diphenyltin di-isocyanate to diphenyltin oxide.

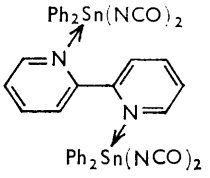
Addition of excess of 2,2′-bipyridyl to the reaction mixture containing crude diphenyltin di-isocyanate gave a stable adduct, m. p. 204—206°, which was found from repeated analysis to have the composition bipy,$[Ph_2Sn(NCO)_2]_2$.[14] This compound contrasts with the extensive series of bipyridyl derivatives of organotin dihalides reported by Alleston and Davies [15] which were all shown to be 1 : 1 adducts. The di-isocyanate adduct behaves as a non-electrolyte in nitromethane so that ionic structures are unlikely. It may be formulated with either a bridging bipyridyl group or bridging isocyanate groups and structures (V) and (VI) were considered. Structure (VI) was discounted since (*a*) no corresponding 1,10-phenanthroline derivative could be isolated and (*b*) the ν_{as}(NCO) band in the infrared spectrum of this compound was in the same position as that of the corresponding bands of the other organotin isocyanates. The ultraviolet absorption spectra of *cis*- and *trans*-bipyridyl derivatives are different [16] but measurements on solutions of the adduct in dioxan showed that the bipyridyl band was not split [17] and occurred as the same position ($\lambda_{max.}$ 284 mμ) as that of free bipyridyl in dioxan (2,2′-bipyridyldiphenyltin dibromide showed identical behaviour). It is therefore concluded that the adduct dissociates in solution; Tanaka [12] *et al.* have shown that bipy,Bu_2SnCl_2 is dissociated in a number of solvents.

Further support for structure (V) was obtained when the crude diphenyltin di-isocyanate was treated with excess of pyridine giving the monopyridine adduct py,$Ph_2Sn(NCO)_2$ which also contains 5-co-ordinate tin. The bipyridyl adduct appears to be the first example of a compound containing a bridging bipyridyl group.

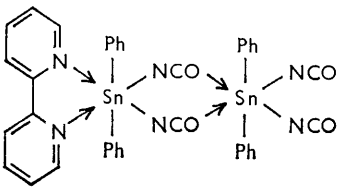
Interaction of phenyltin trichloride with silver isocyanate gave an extremely labile product which rapidly lost all isocyanate and no well defined product could be isolated. Attempts to substitute the halogens in 2,2′-bipyridylphenyltin trichloride and 2,2′-bipyridyldiphenyltin dibromide by isocyanate were unsuccessful.

[13] G. J. M. van der Kerk, J. G. A. Luijten, and M. J. Janssen, *Chimia*, 1962, **16**, 10.
[14] A. S. Mufti and R. C. Poller, *J. Organometallic Chem.*, 1965, **3**, 99.
[15] D. L. Alleston and A. G. Davies, *J.*, 1962, 2050.
[16] R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.*, 1961, **65**, 1196.
[17] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 212.

The evidence for formulating all these organotin pseudo-halides as isocyanates ($\rangle$Sn–N=C=O) rather than cyanates ($\rangle$Sn–O–C≡N) is largely circumstantial. In principle it should be possible to distinguish between these two possibilities by means of the infrared spectra. All the compounds showed a very strong intensity ν_{as}(NCO) band in the range 2200—2240 cm.$^{-1}$ and, although the position of this band is not diagnostic, it was anticipated that the position of the ν_s(NCO) band, expected to occur at ~1400 cm.$^{-1}$ for



(V)



(VI)

an isocyanate and at ~1200 cm.$^{-1}$ for a cyanate, would enable a choice to be made.[18] Careful examination of the solid state and solution spectra of the compounds failed to reveal any band which could be assigned to the ν_s(NCO) vibration and, for example, the spectra in the sodium chloride region of triphenyltin chloride and triphenyltin isocyanate are identical except for the intense ν_{as}(NCO) band shown by the latter at 2230 cm.$^{-1}$.

However, when covalent derivatives of cyanic acid are considered generally, it is only in the case of the carbon compounds that the existence of isocyanates and cyanates has been proved and the few cyanates which are known are much less stable than the corresponding iso-compounds.[19] The cyanic esters of boron,[20] silicon,[18,21] and germanium [18] are all known to be isocyanates and no cases of isomerism exist (earlier reports [22] of an isomeric form of silicon tetraisocyanate were shown to be in error [21,23]). Since the methods of synthesis of the organotin compounds are the same as those used for the silicon and germanium derivatives it seems reasonably certain that the organotin compounds are isocyanates. The ν_s(NCO) band must be weak and is probably masked in the phenyl compounds by the C–C stretching modes which occur at 1425 and 1475 cm.$^{-1}$,[8] and in the butyl compounds by the C–H deformation bands which occur in the 1400 cm.$^{-1}$ region.[24]

Experimental

Molecular weights were measured using a Mechrolab vapour pressure osmometer. Infrared spectra of the compounds as Nujol mulls and as carbon tetrachloride solutions were measured using a Perkin-Elmer 137 spectrometer.

Triphenyltin Isocyanate.—Method 1. A mixture of triphenyltin chloride (5·0 g., 0·013 mole), silver cyanate (1·9 g., 0·013 mole), and ether (50 ml.) was heated under reflux with stirring for 3 hr. The silver chloride was filtered off and the solvent evaporated to give the crude product (4·5 g., 89%), m. p. 96—98°. Crystallisation from light petroleum (b. p. 60—80°) gave pure triphenyltin isocyanate, m. p. 100—103° (Srivasta and Tandon [4] give m. p. 98—99°) (Found: C, 58·1; H, 4·1; N, 4·2; NCO, 10·9; Sn, 31·0%; *M*, 389. Calc. for $C_{19}H_{15}NOSn$: C, 58·2; H, 3·9; N, 3·6; NCO, 10·7; Sn, 30·3%; *M*, 392).

Method 2. Sodium (0·46 g., 0·02 g.-atom) was added to a boiling solution of urethane (1·78 g., 0·02 mole) in xylene (40 ml.). Sodium urethane was precipitated and the cooled suspension was stirred with triphenyltin chloride (7·70 g., 0·02 mole) for 3 hr. at room temperature. The sodium chloride was filtered off and the solvent removed by distillation (reduced pressure) to give the crude product (8·0 g.), m. p. 75—90°. Crystallisation from light petroleum (b. p. 60—80°) gave pure triphenyltin isocyanate (6·5 g., 83%), m. p. and mixed m. p. 101—102°.

[18] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 1961, **17**, 977.
[19] D. Martin, *Angew. Chem. Internat. Edn.*, 1964, **3**, 311.
[20] M. F. Lappert and H. Pyszora, *Proc. Chem. Soc.*, 1960, 350.
[21] J. Goubeau, E. Heubach, D. Paulin, and I. Widmaier, *Z. anorg. Chem.*, 1959, **300**, 194.
[22] G. S. Forbes and H. H. Anderson, *J. Amer. Chem. Soc.*, 1940, **62**, 761.
[23] G. S. Forbes and H. H. Anderson, *J. Amer. Chem. Soc.*, 1947, **69**, 3048.
[24] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., p. 20.

The presence of ethanol in the xylene distillate was shown by a positive iodoform test and by gas chromatography.

Tributyltin Isocyanate.—This was prepared from tributyltin chloride by procedures identical with those described above except that the crude product was purified by fractional distillation. Method 1 gave pure *tributyltin isocyanate* (63%), b. p. 144—147°/1·3 mm., n_D^{20} 1·4885 (Found: C, 47·3; H, 8·7; Sn, 35·3%; *M*, 324. $C_{13}H_{27}NOSn$ requires C, 47·0; H, 8·2; Sn, 35·75%; *M*, 332). The yield from Method 2 was 81%.

Reaction between Tributyltin Isocyanate and Ammonia.—A solution of tributyltin isocyanate (5·2 g.) in ethanol was saturated with ammonia and kept at room temperature for three days. The solvent was removed at 40° and the resulting gum boiled with light petroleum (b. p. 40—60°). Filtration gave urea (0·5 g.), m. p. and mixed m. p. 130—132°. Evaporation of the filtrate and distillation of the residue gave tributyltin hydroxide, b. p. 153—154°/1·0 mm. (lit.,[25] b. p. 186—190°/5 mm.), whose infrared spectrum was identical with that of an authentic specimen.

Dibutyltin Di-isocyanate.—This reaction was carried out under anhydrous conditions; the product was manipulated in a dry-box. A mixture of dibutyltin dichloride (6·0 g., 0·02 mole), silver cyanate (6·0 g., 0·04 mole), and anhydrous light petroleum (b. p. 60—80°, 100 ml.) was heated under reflux and stirred for 3 hr. The silver chloride was filtered off and the filtrate cooled to give crystals (5·9 g., 94%), m. p. 44—48°. Crystallisation from light petroleum (b. p. 60—80°) gave pure *dibutyltin di-isocyanate,* m. p. 48—51° (Found: C, 37·4; H, 5·9; NCO, 26·3; Sn, 37·0%; *M*, 339. $C_{10}H_{18}N_2O_2Sn$ requires C, 37·9; H, 5·7; NCO, 26·5; Sn, 37·4%; *M*, 317). Repeated crystallisation caused hydrolysis.

Di-μ-(isocyanatodibutylstannyloxo)bis(isocyanatodibutyltin).—When the above preparation was repeated using dry (Na) ether (100 ml.) as solvent the crude product, after repeated crystallisation from light petroleum (b. p. 40—60°), gave the *compound* (II; R = Bu, X = NCO) (4·6 g., 82%), m. p. 100—102° (Found: C, 38·2; H, 6·6; N, 4·05; Sn, 42·1. $C_{36}H_{72}N_4O_6Sn_4$ requires C, 38·2; H, 6·4; N, 5·0; Sn, 41·95%).

Di-μ-(hydroxydibutylstannyloxo)bis(isocyanatodibutyltin).—The preparation of dibutyltin di-isocyanate was repeated but no attempt was made to exclude atmospheric moisture and moist ether (100 ml.) was used as the reaction medium. The crude *product* had m. p. 120—135° and repeated crystallisation from light petroleum (b. p. 60—80°) gave (III; R = Bu, X = NCO) (3·5 g., 66%), m. p. 162—164° (Found: C, 38·2; H, 6·7; N, 3·3; Sn, 44·0. $C_{34}H_{74}N_2O_6Sn_4$ requires C, 37·75; H, 6·9; N, 2·6; Sn, 43·9%).

Di-μ-hydroxybis(isocyanatodiphenyltin).—This reaction was carried out under anhydrous conditions in a dry-box. A mixture of diphenyltin dibromide (8·6 g., 0·02 mole), silver cyanate (6·0 g., 0·04 mole), and anhydrous light petroleum (b. p. 60—80°, 70 ml.) was heated under reflux and stirred for 3 hr. After filtering the hot solution the product (6·4 g.), m. p. 97—99° crystallised from the cooled filtrate. One crystallisation from light petroleum (b. p. 60—80°) gave the *compound* (I) (5·9 g., 89%), m. p. 99—100° (Found: C, 46·1; H, 3·6; NCO, 11·9; Sn, 35·3%; *M* (in benzene), 679, 610. $C_{26}H_{22}N_2O_4Sn_2$ requires C, 47·0; H, 3·3; NCO, 12·7; Sn, 33·75%; *M*, 664). Further crystallisation caused hydrolysis.

Di-μ-(isocyanaiodiphenylstannyloxo)bis(isocyanatodiphenyltin).—*Method* 1. When the above preparation was repeated using dry (Na) tetrahydrofuran (70 ml.) as solvent, after filtering and evaporating the solvent (reduced pressure) the crude product had m. p. 120—148°. One crystallisation in the atmosphere from nitromethane gave the *compound* (II; R = Ph, X = NCO) (5·0 g., 78%), m. p. 158—160° (Found: C, 47·8; H, 3·3; NCO, 13·3. $C_{52}H_{40}N_4O_6Sn_4$ requires C, 48·35; H, 3·1; NCO, 13·0%). Further crystallisation caused hydrolysis.

Method 2. When compound (I) was exposed to the atmosphere for 5 hr. the resulting material had m. p. 148—152°, one crystallisation from nitromethane gave (II; R = Ph, X = NCO), m. p. 158—160°.

Di-μ-(hydroxydiphenylstannyloxo)bis(isocyanatodiphenyltin).—*Method* 1. The conditions for the preparation of (I) were modified by using moist tetrahydrofuran (60 ml.) as reaction medium and no attempt to exclude atmospheric moisture was made. Evaporation (reduced pressure) of the filtered reaction mixture gave the crude product, m. p. 190—260°. Crystallisation from nitromethane gave the *compound* (III; R = Ph, X = NCO) (5·6 g., 91%), m. p. 300—301° (Found: C, 48·3; H, 3·5; NCO, 6·9; Sn, 38·6. $C_{50}H_{42}N_2O_6Sn_4$ requires C, 48·4; H, 3·4; NCO, 6·8; Sn, 38·2%).

[25] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, **60**, 459.

Method 2. When di-μ-hydroxylbis(isocyanatodiphenyltin) was exposed to the atmosphere for 29 hr. the resulting material had m. p. 294—296°; one crystallisation from nitromethane gave di-μ-(hydroxydiphenylstannyloxo)bis(isocyanatodiphenyltin), m. p. 300—301°.

2,2′-*Bipyridylbis*(*diphenyltin di-isocyanate*).—A mixture of diphenyltin dibromide (4·33 g., 0·01 mole), silver cyanate (3·0 g., 0·02 mole), and dry (NaH) benzene (30 ml.) was heated under reflux and stirred for 3 hr. with exclusion of atmospheric moisture. The silver bromide was filtered off in a dry-box and 2,2′-bipyridyl (1·56 g., 0·01 mole) in dry benzene (20 ml.) was shaken with the filtrate. There was an immediate precipitation of a solid (3·85 g.), m. p. 202—204°, which, after crystallisation from nitromethane, gave 2,2′-*bipyridylbis*(*diphenyltin di-isocyanate*) (3·25 g., 75%), m. p. 204—206° (Found: C, 52·9; H, 3·6; N, 9·7; Sn, 27·0. $C_{38}H_{28}N_6O_4Sn_2$ requires C, 52·5; H, 3·2; N, 9·7; Sn, 27·3%).

Diphenylpyridinetin Di-isocyanate.—The above experiment was repeated using an excess of pyridine (3·0 g., 0·038 mole) in place of the 2,2′-bipyridyl. The crude product (3·65 g.), m. p. 120—125°, was crystallised from dry benzene giving *diphenylpyridinetin di-isocyanate* (2·0 g.), m. p. 129—130°. The infrared spectrum showed, besides the bands expected for a pyridine adduct of diphenyltin di-isocyanate, an additional strong band at 685 cm.$^{-1}$ characteristic of benzene.[26] This fact, together with the analysis, indicated that the compound contained benzene of crystallisation corresponding to the formulation py,$(C_6H_5)_2Sn(NCO)_2$,$(C_6H_6)_{1·5}$ (Found: C, 60·7; H, 4·7; N, 7·7; Sn, 21·8. $C_{28}H_{24}N_3O_2Sn$ requires C, 60·8; H, 4·4; N, 7·6; Sn, 21·5%).

2,2′-*Bipyridiyldiphenyltin Dibromide*.—Solutions of diphenyltin dibromide (4·33 g., 0·01 mole) and 2,2′-bipyridyl (1·56 g., 0·01 mole) were shaken together. The precipitate was crystallised from nitromethane to give 2,2′-*bipyridyldiphenyltin dibromide* (5·2 g., 88%), m. p. 245—248° (Found: C, 45·2; H, 3·3; N, 4·8; Br, 27·2. $C_{22}H_{18}Br_2N_2Sn$ requires C, 44·9; H, 3·1; N, 4·8; Br, 27·1%).

2,2′-*Bipyridylphenyltin Trichloride*.—When solutions of phenyltin trichloride (1·5 g., 0·005 mole) and 2,2′-bipyridyl (0·78 g., 0·005 mole) in benzene were mixed a crystalline precipitate was obtained of 2,2′-*bipyridylphenyltin trichloride* (2·2 g., 96%), m. p. 276—280° (Found: C, 41·7; H, 3·0; N, 6·0. $C_{16}H_{13}Cl_3N_2Sn$ requires C, 41·9; H, 2·9; N, 6·1%).

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[26] C. R. Bailey, J. B. Hale, C. K. Ingold, and J. W. Thompson, *J.*, 1936, 931.