267. *Organometallic Compounds Containing a Tin–Phosphorus Bond.*

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A series of organometallic compounds containing the Sn–P bond has been prepared and the properties of the phosphines, $R_3Sn{\cdot}PPh_3$ and $R_3Sn{\cdot}PPh{\cdot}SnR_3$, and the stannane, $Ph_2P{\cdot}SnPh_2{\cdot}PPh_2$, have been studied. Fission of the Sn–P bond occurs on reaction with water, methyl iodide, and sodium in liquid ammonia. Oxidation of $R_3Sn{\cdot}PPh_2$ gives the stannyl phosphinates, $R_3SnO{\cdot}P(O)Ph_2$, and these have been prepared (for comparison) by a variety of methods.

At the start of this work no organometallic compound containing a tin–phosphorus bond was known (those considered to be of this type[1] had been shown to have the Sn–O–P linkage[2]), but two authentic examples have been described recently. One of these, tris(trimethylstannyl)phosphine,[3] obtained from monosodium phosphide and trimethyltin bromide, was described as a liquid (b. p. 137°/3 mm.) which did not ignite in air, and the chemistry of the other diphenyl(triethylstannyl)phosphine,[4] obtained from diphenylphosphinosodium and triethyltin bromide, was not investigated in detail. Apart from its physical constants the only property mentioned was a sensitivity to air and moisture.

It is possible that the lone-pair of electrons of tervalent phosphorus might be used to strengthen a tin–phosphorus link through d_π–p_π bonding. We decided, therefore, to attempt the preparation of organometallic compounds containing the Sn–P bond and study their properties, and, if the bond proved sufficiently stable, to attempt the preparation of polymers containing more than one Sn–P link, either straight-chain polymers or cross-linked types.

Initially, we attempted to form the bond by the process shown in equation (1),

$$R_3SnM + Ph_2PCl \longrightarrow R_3Sn{\cdot}PPh_2 + MCl, \qquad (1)$$

where M was an alkali metal, and we prepared the sodium and potassium derivatives by reactions (2) and (3), using tetrahydrofuran or 1,2-dimethoxyethane as solvents.

$$2R_3SnCl + 2Na \longrightarrow R_3Sn{\cdot}SnR_3 + 2NaCl \qquad (2)$$

$$R_3Sn{\cdot}SnR_3 + 2Na \longrightarrow 2R_3SnNa \qquad (3)$$

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[1] Arbuzov and Pudovik, *Proc. Acad. Sci. U.S.S.R.*, 1947, **57**, 153; *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 2158; Arbuzov and Grechkin, *Proc. Acad. Sci. U.S.S.R.*, 1947, **57**, 353; *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 2166; *Zhur. obshchei. Khim.*, 1950, **20**, 107.

[2] Malatesta, *Gazzetta*, 1950, **80**, 527; Arbuzov and Grechkin, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel khim. Nauk*, 1956, 440.

[3] Bruker, Balashova, and Soborovskii, *Doklady Akad. Nauk S.S.S.R.*, 1960, **4**, 843.

[4] Kuchen and Buchwald, *Ber.*, 1959, **92**, 227.

This method was unsatisfactory. Reaction of an ethereal solution of triphenylstannylsodium, prepared from triphenyltin chloride, and sodium in liquid ammonia gave a product from which hexaphenyldistannane was isolated in 34% yield. The isolation of this product clearly suggests that a degree of halogen-metal interconversion occurs.

$$\mathrm{Ph_2PCl + Ph_3SnNa \longrightarrow Ph_3SnCl + Ph_2PNa} \tag{4}$$

$$\mathrm{Ph_3SnCl + Ph_3SnNa \longrightarrow Ph_3Sn{\cdot}SnPh_3} \tag{5}$$

Triphenylstannyl-lithium, made[5] according to scheme (6),

$$\mathrm{SnCl_2 + 3PhLi \longrightarrow Ph_3SnLi + 2LiCl,} \tag{6}$$

obviously reacted with diphenylphosphinous chloride and with phenylphosphonous dichloride in ether, but the coupled products could not be isolated pure.

The reverse process (7) was then tried.

$$\mathrm{R_3SnX + Ph_2PM \longrightarrow R_3Sn{\cdot}PPh_2 + MX} \tag{7}$$

Diphenylphosphinolithium, prepared by Chatt and Hart's method[6] (reaction 8), reacted readily with triphenyltin chloride but again a pure product could not be separated from the reaction mixture which also contained tetraphenyltin.

$$\mathrm{Ph_3P + 2Li \longrightarrow Ph_2PLi + PhLi} \tag{8}$$

The first successful synthesis of a compound containing the Sn–P bond was achieved by the reaction of diphenylphosphinomagnesium bromide[7] with triphenyltin chloride in ether–benzene, a moderate yield of diphenyl(triphenylstannyl)phosphine, m. p. 103—105° being obtained. A more satisfactory method for the preparation of the liquid trialkylstannyl compounds was that involving the interaction of trialkyltin bromide with diphenylphosphinosodium in liquid ammonia, because any unchanged trialkyltin bromide could be removed as the solid ammoniate, $\mathrm{R_3SnBr},x\mathrm{NH_3}$, before distillation. By this process a series of trialkylstannylphosphines was obtained in yields up to 70% (cf. Table 1).

Treatment of phenylphosphinosodium[8] with triethyltin bromide under similar conditions yielded phenylbis(triethylstannyl)phosphine rather than the expected hydride, $\mathrm{Et_3Sn{\cdot}PPhH}$; the latter evidently reacts further with the triethyltin bromide. Russian workers[3] have shown that phosphinosodium, $\mathrm{PH_2Na}$, reacts in the same way with trimethyltin bromide to produce tris(trimethylstannyl)phosphine, $\mathrm{(Me_3Sn)_3P}$.

Attempts to make compounds containing the P–Sn–P linkage were successful in only one case, that of the fully aromatic member $\mathrm{Ph_2Sn(PPh_2)_2}$, which was obtained as an orange powder, m. p. 144—147°. Bis(diphenylphosphino)diethylstannane, $\mathrm{Et_2Sn(PPh_2)_2}$, was almost certainly the initial product of the reaction of diphenylphosphinosodium with diethyldibromostannane, for immediate degradation gave compounds characteristic of the molecule, but distillation of the crude material caused disproportionation and the only pure compound isolated was diphenyl(trimethylstannyl)phosphine. The preparation of a polymeric species $\cdot[\mathrm{PPh{\cdot}SnR_2}]_n\cdot$ was also unsuccessful. A series of reactions coupling either phenylphosphinosodium or dilithiophenylphosphine with diethyltin dibromide gave liquids which, after distillation, had an indefinite composition and a molecular weight of not more than twice that of the constituents. That disproportionation had again occurred was shown by the isolation of derivatives not of dialkyl- but of trialkyl-tin.

The Sn–P bond is evidently quite strong since the organometallic compounds can be distilled under reduced pressure at almost 200° without decomposition. This stability is

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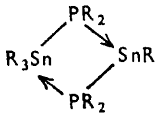
[5] Gilman and Rosenberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.

[6] Chatt and Hart, *J.*, 1960, 1385.

[7] Job and Dusoiller, *Compt. rend.*, 1927, **184**, 1454.

[8] Mann, Millar, and Watson, *J.*, 1958, 2516.



(A)

unlikely to arise through the formation of condensed species, *e.g.*, *A*, because the compounds are monomeric in benzene; whilst there still could be some association in the pure compound the linking forces must be quite weak if they break down in benzene. It is more likely that additional bonding may be present as a result of overlap of the phosphorous lone-pair (p_π) with a vacant *d* orbital of tin. Some evidence for the possibility of π bonding by tin has been presented recently by Hague and Prince,[9] who observed that a very intense band in the ultraviolet spectrum of hexaphenyldistannane masked the fine structure characteristic of the phenyl groups. It was thought that this arose because of intense interaction between phenyl groups on different tin atoms across the Sn–Sn bond, as a result of overlap of vacant *d* orbitals on the tin atoms. We have found a similar intense band (at 249 mμ) in the ultraviolet spectrum of diphenyl(triphenylstannyl)phosphine, which indicates a similar interaction through the Sn–P link.

Furthermore, whereas the compounds with a single Sn–P link are colourless, bis(diphenylphosphino)diphenylstannane, $(Ph_2P)_2SnPh_2$, is orange-red. It seems that the P–Sn–P skeleton provides a good basis for the delocalisation of the π electrons, the two diphenylphosphino-groups interacting through the linking tin atom. It is known that for a phosphorus atom forming three σ bonds interactions can occur between the π orbitals of attached phenyl groups [10] and between these orbitals and the phosphorus lone-pair.[11]

To avoid the complications of peaks from the phenyl groups we examined the ultraviolet spectrum of the ethyl compound $Et_3Sn\cdot PEt_2$, and observed a very intense band at 214 mμ. Neither tetraethyltin nor triethylphosphine showed any bands above 200 mμ, so the peak at 214 mμ must be associated with the tin–phosphorus link, and the intensity of the band suggests that it is caused by a $\pi^* \longleftarrow \pi$ transition. The description of the ground state as π implies that the phosphorus lone-pair (p_π) has overlapped with a vacant *d* orbital of tin to give a measure of π bonding, but there is no evidence as to the extent to which this pair is shared. The small dipole moments (~1·0 D) indicate that the phosphorus lone-pair has been shared partially with the tin atom, so reducing the expected moment. The slight lowering in moment (0·1 D) observed in going from the ethyl to the butyl compound suggests that the Sn–P bond is polarised in the expected sense, the tin atom being at the positive end of the dipole, and this is confirmed by the mode of attack of various reagents.

For example, fission of the tin–phosphorus bond in this series of compounds occurred with water at room temperature, except in the case of the fully aromatic member, $Ph_3Sn\cdot PPh_2$, which was unaffected, possibly because of its insolubility. The fully alkylated compound, $Et_3Sn\cdot PEt_2$, was particularly sensitive to moisture, but as phenyl groups were progressively introduced the compounds became less susceptible to hydrolysis.

The products, trialkyltin hydroxide and diphenylphosphine, are those expected for a nucleophilic attack on tin, the positive end of the dipole. The phosphorus moiety, which separated as diphenylphosphine, was not isolated as such but oxidised to the phosphinic acid for characterisation.

Methyl iodide reacted very vigorously, splitting the Sn–P bond in the same sense to give a trialkyltin iodide and dimethyldiphenylphosphonium iodide, both of which were isolated in good yield. Diphenylphosphinosodium and trialkylstannylsodium were evidently the products when the stannylphosphines reacted with solutions of sodium in liquid ammonia, for addition of methyl iodide again gave dimethyldiphenylphosphonium iodide; unfortunately the unsymmetrical tetra-alkylstannanes could not be isolated in pure condition.

The stannylphosphines are also sensitive to atmospheric oxygen, and at room temperature dry air cleaves the Sn–P bond and simultaneously converts phosphorus into the

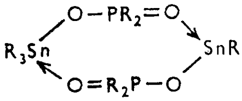
[9] Hague and Prince, *Proc. Chem. Soc.*, 1962, 300.

[10] Van Wazer, " Phosphorus and its Compounds," Interscience, 1958, **1**, 43.

[11] Jaffé and Orchin, " Theory and Applications of Ultraviolet Spectroscopy," Wiley, 1962, p. 497.

quinquevalent state; the phosphinic esters, $R_3SnO{\cdot}P(O)Ph_2$, are formed. These oxidation products were characterised by analysis and by comparison with compounds synthesised in excellent yield by condensation of diphenylphosphinic acid with the required trialkyltin hydroxide or, preferably, oxide. Interaction of sodium diphenylphosphinite, Ph_2PONa (obtained by reaction of sodium hydride and triphenylphosphine oxide in benzene), with a trialkyltin bromide also gave the stannyl phosphinates. The possible intermediate in this reaction, $R_3SnO{\cdot}PPh_2$, would certainly be oxidised rapidly, because the analogous arsenic and antimony siloxanes, *e.g.*, $R_3SiO{\cdot}AsR_2$, react explosively with oxygen between 40 and 60°.[12a] Silylphosphines and germylphosphines are oxidised similarly to systems containing $\cdot Si{\cdot}O{\cdot}P(O)\cdot$ and $\cdot Ge{\cdot}O{\cdot}P(O)\cdot$ groups.[12b]

All the stannyl phosphinates were dimeric in benzene, with the exception of the trimethylstannyl derivative which was tetrameric. Examination of the infrared spectra of these esters shows a lowering of the P=O stretching frequency, indicating that the dimers are formed by co-ordination of the phosphoryl oxygen to the tin which therefore becomes five-co-ordinate in the eight-membered ring (*B*). Five co-ordination for tin has been suggested recently for several trimethyltin compounds, including the acetate [13] and perchlorate.[14]



(B)

Since trialkyltin compounds are known [15] to have powerful fungicidal properties, samples of triethylstannyl diphenylphosphinate were tested with four standard moulds, *Botrytis allii*, *Penicillium italicum*, *Aspergillus niger*, and *Rhizopus nigricans*. The minimum concentrations (mg./l.) required to completely inhibit the mould growth after three days' incubation were, respectively, 0·5 (1), 10 (2), 5 (5), and 20 (2). Comparison with values reported [15] for triethyltin acetate (given in parentheses) show that the stannyl phosphinate has the same order of activity.

EXPERIMENTAL

Infrared Spectra.—Solids were measured as Nujol mulls; liquids were examined undiluted in 0·1-mm. cells, Unicam S.P. 200 or Infracord (KBr) spectrophotometers being used.

Ultraviolet Spectra.—These were measured in cyclohexane on a Unicam S.P. 700 spectrophotometer. The 1-cm. silica cells were filled and sealed on the vacuum line.

Molecular Weights.—These were measured on benzene solutions either ebullioscopically by using a Gallenkamp ebulliometer or cryoscopically in apparatus attached to the vacuum line.

Dipole Moments.—Because of the sensitivity of the compounds to hydrolysis and oxidation, elaborate precautions were taken to exclude moisture and air. The dipole moments were calculated from measurements at 25° of the dielectric constants and refractive indices of benzene solutions (0·014—0·114M). The dielectric constant was measured in a gold-plated 20-ml. DFL1 cell by means of a WTW (Wissenschaftlich-Technische Werkstatten) type DM01 dipolemeter. The dipolemeter operated on the superposition method by which the oscillations of two high-frequency oscillators were brought to superposition in a mixing section. Refractive indices were measured on a Abbé refractometer, suitably modified to enable measurements to be made in dry nitrogen. Dipole moments determined were: $Et_3Sn{\cdot}PPh_2$, 1·05 D and $Bu^n{}_3Sn{\cdot}PPh_2$, 0·96 D.

Preparations.—All the stannylphosphines (except $Ph_3Sn{\cdot}PPh_2$) were prepared on a vacuum line.

Diphenyl(trialkylstannyl)phosphines. Diphenylphosphine (4·83 g.) was pipetted under nitrogen into a three-necked flask. Dry liquid ammonia (30 ml.) was distilled into the flask under vacuum at −78° and sodium (0·6 g., 0·026 g.-atom) was added in small pieces. A clear

[12a] Schmidbaur and Schmidt, *Angew. Chem.*, 1961, **73**, 655.
[12b] Glockling and Hooton, *Proc. Chem. Soc.*, 1963, 146.
[13] Beattie and Gibson, *J.*, 1961, 2585.
[14] Okawara, Hathaway, and Webster, *Proc. Chem. Soc.*, 1963, 13.
[15] Van der Kerk and Luijten, *J. Appl. Chem.*, 1954, **4**, 314.

orange solution eventually resulted. The required trialkyltin bromide (0·026 mole) in dry ether (25 ml.) was added sufficiently rapidly to prevent formation of the solid trialkyltin bromide ammoniate but not so rapidly as to result in loss of vacuum. The mixture was stirred for 5 min. whereupon the orange colour was discharged with simultaneous separation of a white precipitate. Evaporation (reduced pressure) of the solvents left a sludge which was extracted with dry ether and filtered under nitrogen. The cloudy liquid remaining after evaporation of the ether was vacuum distilled through a 4 in. Vigreux column under nitrogen.

The yields, physical properties, and analysis data of the compounds are collected in Table 1.

TABLE 1.

Compd.	B. p.	Yield (%)	Formula	Reqd.				Found			
				C	H	Sn	*M*	C	H	Sn	*M*
1. $Me_3Sn{\cdot}PPh_2$ ...	141—142°/0·7 mm.	60	$C_{15}H_{19}PSn$	51·6	5·5	34·0	349	52·1	5·5	33·5	380
2. $Et_3Sn{\cdot}PPh_2$ ...	167—168°/0·7 mm.	55	$C_{18}H_{25}PSn$	55·3	6·4	30·4	—	54·7	6·3	29·9	—
3. $Pr^n_3Sn{\cdot}PPh_2$ ...	176—177°/0·6 mm.	67	$C_{21}H_{31}PSn$	58·2	7·2	27·4	—	58·0	6·9	27·3	—
4. $Bu^n_3Sn{\cdot}PPh_2$ ...	192°/0·6 mm.	72	$C_{24}H_{37}PSn$	60·7	7·8	25·0	474	60·7	7·6	24·6	480
5. $Et_3Sn{\cdot}PPhEt$...	99—100°/0·2 mm.	60	$C_{14}H_{25}PSn$	49·0	7·35	34·6	—	48·5	7·1	34·4	—
6. $Pr^n_3Sn{\cdot}PPhEt$	125—126°/0·3 mm.	27	$C_{17}H_{31}PSn$	53·0	8·1	30·8	—	52·6	8·4	30·6	—
7. $Et_3Sn{\cdot}PEt_2$ ...	70°/0·3 mm.	34	$C_{10}H_{25}PSn$	40·7	8·5	40·2	—	40·2	8·2	40·1	—

Ethylphenyl(triethylstannyl)phosphine, compound 5, was prepared from ethylphenylphosphine synthesised by Mann's method.[8] Ethylphenyl(tri-n-propylstannyl)phosphine, compound 6, was prepared from tri-n-propyltin bromide (3·95 g., 0·012 mole) and ethylphenylphosphinosodium, the latter resulting from reaction of sodium (0·755 g., 0·033 atom) with ethyldiphenylphosphine (3·51 g., 0·0164 mole) in liquid ammonia (25 ml.).

Diethyl(triethylstannyl)phosphine. In an atmosphere of nitrogen diethylphosphine (2·0 g., 0·022 mole) was treated with a filtered solution of phenyl-lithium prepared from bromobenzene (3·15 g., 0·02 mole) and lithium (0·31 g., 0·045 g.-atom) in dry ether (25 ml.). The solution of diethylphosphinolithium was heated under reflux for 0·5 hr. before removal of the solvent (reduced pressure), and the brown residue was stirred into a fine suspension in dry benzene (15 ml.). Triethyltin bromide (5·8 g., 0·02 mole) in benzene (15 ml.) was added dropwise. The immediate exothermic reaction produced a white precipitate and a considerable rise in temperature. Fractionation of the filtrate after removal of the precipitate gave *diethyl(triethylstannyl)phosphine* (compound 7, 2 g., 33·8%).

Diphenyl(triphenylstannyl)phosphine. Diphenylphosphine (4·1 g., 0·022 mole) was added under nitrogen to a solution of phenylmagnesium bromide, prepared from bromobenzene (3·9 g., 0·025 mole), magnesium (0·6 g., 0·025 g.-atom), and ether (20 ml.). The solution was heated under reflux for 0·5 hr. yielding a cream-coloured precipitate of diphenylphosphinomagnesium bromide. To this suspension triphenyltin chloride (8·45 g., 0·022 mole) in benzene (20 ml.) was added and the mixture heated under reflux for 2 hr. The resultant solution was concentrated to approximately two-thirds of the original volume and filtered. The filtrate after 5 days yielded *diphenyl(triphenylstannyl)phosphine* as large crystals, which after being crushed and washed with a small amount of ether and benzene had m. p. 103—105° (sealed tube) (yield 1·8 g., 15·3%) (Found: C, 67·2; H, 4·9; Sn, 22·3%; *M*, 566 (in benzene). $C_{30}H_{25}PSn$ requires C, 67·3; H, 4·7; Sn, 22·2%; *M*, 535). Diphenyl(triphenylstannyl)phosphine (0·5 g.) was shaken with distilled water at room temperature for 7 days. The compound appeared to be completely insoluble and when recovered was unchanged in melting point.

Bis(diphenylphosphino)diphenylstannane. A solution of diphenylphosphinosodium (3·0 g., (0·0144 mole) in liquid ammonia (30 ml.) was prepared as previously described. Diphenyltin dichloride (2·5 g., 0·0073 mole) in ether (20 ml.) was added, and the mixture stirred for 10 min. The orange colour was discharged with simultaneous separation of a white precipitate. Evaporation of solvents left an orange compound which was extracted with benzene (40 ml.) and filtered. Removal of the solvent (reduced pressure) left a yellow solid which was dried for 14 hr. at 70—80°/0·1 mm. (nitrogen), then powdered and washed with hot light petroleum (b. p. 60—80) (3 × 30 ml.). The orange powder (1·42 g., 30·4%) had m. p. 144—147° (sealed tube) (Found: C, 65·9; H, 4·5; Sn, 18·6%; *M*, 623. $C_{36}H_{30}P_2Sn$ requires C, 67·2; H, 4·7; Sn, 18·5%; *M*, 643).

Attempted preparation of bis(diphenylphosphino)diethylstannane. A solution of diphenylphosphinosodium was prepared from diphenylphosphine (4·26 g., 0·023 mole) and sodium

(0·53 g., 0·023 mole) in liquid ammonia (30 ml.). Diethyltin dibromide (3·86 g., 0·0115 mole) in ether (40 ml.) was added to the stirred solution. The solvents were removed, the residue extracted with ether (50 ml.), and the solution filtered. The low-melting solid which remained on evaporation of the ether was distilled through a 4 in. Vigreux column and gave a liquid (1·16 g.), b. p. 144—147°/0·18 mm. (Found: C, 55·5; H, 6·6; Sn, 29·6. Calc. for $C_{28}H_{30}P_2Sn$: C, 61·5; H, 5·5; Sn, 21·7%). The analysis and b. p. indicated that the initially-formed stannane had disproportionated on distillation to give diphenyl(triethylstannyl)phosphine. (Calc. for $C_{18}H_{25}PSn$: C, 55·3; H, 6·4; Sn, 30·4%). This was further characterised by oxidation to give triethylstannyl diphenylphosphinate, m. p. 246—247°, and by reaction with methyl iodide whereby dimethyldiphenylphosphonium iodide, m. p. 239°, was obtained along with triethyltin iodide isolated through formation of the ammoniate (Found: Sn, 36·2. Calc. for $C_6H_{15}ISn$: Sn, 35·7%).

When the product (0·44 g.) was treated with methyl iodide in ether *before* distillation, dimethyldiphenylphosphonium iodide, m. p. 240° (0·23 g.), and diethyltin di-iodide were obtained; the latter isolated as the bipyridyl complex (0·11 g.) Found: C, 28·9; H, 3·4; Sn, 20·4. $C_4H_{10}I_2Sn,C_{10}H_8N_2$ requires C, 28·7; H, 3·1; Sn, 20·2%). Oxidation before distillation produced a mixture from which is was impossible to isolate pure product.

Phenylbis(triethylstannyl)phosphine. A solution of phenylphosphinosodium (PhPHNa) (4·92 g., 0·037 mole) in liquid ammonia (25 ml.) and ether (15 ml.) was prepared by Mann's method.[8] Triethyltin bromide (10·5 g., 0·037 mole) in dry ether (20 ml.) was added and the mixture stirred for 5 min. Evaporation of solvents (reduced pressure) left a sludge which was extracted with dry ether and filtered under nitrogen. The liquid remaining after evaporation of the ether was vacuum-distilled through a 4 in. Vigreux column under nitrogen giving *phenylbis(triethylstannyl)phosphine* (6·9 g., 72·3% based on Et_3SnBr) b. p. 150—151°/0·3 mm. [Found: C, 41·6; H, 6·4; Sn, 45·7%; *M* (benzene), 554. $C_{18}H_{35}PSn_2$ requires C, 41·6; H, 6·8; Sn, 45·7%; *M*, 520].

Reaction of phenylphosphinosodium or dilithiophenylphosphine with diethyltin dibromide. A series of runs in which the sodium salt made from phenylphosphine (2 g., 0·018 mole) sodium (0·42 g., 0·018 g.-atom), and liquid ammonia (30 ml.) was treated with diethyltin dibromide (6·13 g., 0·018 mole) in ether (30 ml.) gave products, b. p. 149—152°/0·2 mm. (1—1·8 g.) which had molecular weights between 476 and 530 and analysis limits C, 42·2—43·8; H, 6·4—6·9; Sn, 40·5—43·1%.

Interaction of dilithiodiphenylphosphine, prepared from phenylphosphine (2 g., 0·018 mole) and phenyl-lithium [from bromobenzene (6·75 g., 0·043 mole) in ether (50 ml.)] with diethyltin dibromide (6·13 g., 0·018 mole) in ether (20 ml.) gave a similar product (1·4 g.), b. p. 152—155°/0·3 mm. (Found: C, 44·2; H, 6·6; Sn, 40·6%). The required polymer had obviously not been obtained and that disproportionation had occurred was shown by reaction with methyl iodide. None of the expected diethyltin di-iodide was isolated but triethyltin iodide was obtained in 50—60% yield, along with trimethylphenylphosphonium iodide, m. p. 227—228° (lit., 226—227°) (Found: C, 39·1; H, 5·1. Calc. for $C_9H_{14}IP$: C, 38·6; H, 5·0%).

Infrared spectra (in cm.$^{-1}$). (i) Ph_3SnPPh_2: 1585w, 1440s, 1305w, 1260w, 1155w, 1130m, 1075m, 1025m, 1005m, 750m, 730s, 700s, 680s, 500m, 455m, 445s. (ii) Et_3SnPEt_2: 2910—3000vs, 2750m, 2410w, 2160w, 1660w, 1600w, 1470vs, 1460vs, 1430s, 1260m, 1230s, 1180vs, 1145m, 1060m, 1045s, 1020vs, 965m, 950m, 820w, 760s, 745m, 705w, 680s, 660s, 495s, 480s. (iii) $(Et_2Sn)_2PPh$: 3080s, 2910—3000vs, 2740m, 2130w, 1865w, 1585s, 1465vs, 1435vs, 1380vs, 1295w, 1255w, 1235s, 1180vs, 1130w, 1065m, 1015vs, 960s, 945s, 845w, 735vs.

Fission of the Sn–P Bond.—(a) *Oxidation.* The required diphenyl(trialkylstannyl)-phosphine (1 g.) was pipetted under nitrogen into a small conical flask connected to a closed system containing dry air. The pressure in the system gradually dropped and after 6 hr. the trialkylstannyl diphenylphosphinate was obtained as a sticky solid which was recrystallised from ethanol. The yields, physical properties, and analysis data are listed in Table 2.

TABLE 2.

			Reqd.				Found				
Compd.	M. p.	Formula	C	H	Sn	*M*	C	H	Sn	*M*	Yield (%)
$Et_3SnO\cdot P(O)Ph_2$ ...	246—247°	$C_{18}H_{21}O_2PSn$	51·1	6·0	28·3	423	51·2	6·0	28·1	851	50
$Pr^n{}_3SnO\cdot P(O)Ph_2$ ...	226	$C_{21}H_{31}O_2PSn$	54·2	6·7	25·7	465	54·1	6·5	25·5	958	70
$Bu^n{}_3SnO\cdot P(O)Ph_2$...	215	$C_{24}H_{37}O_2PSn$	56·8	7·35	23·4	507	57·3	7·3	23·5	1140	65

(b) *Hydrolysis.* (i) Diphenyl(triethylstannyl)phosphine (1 g.) was shaken with distilled water (0·5 ml.) in an atmosphere of nitrogen for 1 hr. Glacial acetic acid (0·2 g.) was added and the reaction maintained at 100° for 0·5 hr. Excess of water was removed by distillation (reduced pressure) and the residue was kept at 90° for 0·5 hr.; distillation then gave triethyltin acetate (0·45 g.), m. p. 132° (Found: Sn, 44·6%. Calc. for $C_8H_{18}O_2Sn$: Sn, 44·8%).

(ii) The hydrolysis was repeated with a second 1-g. portion, but instead of acetic acid, hydrogen peroxide (20 vol.) was added to the mixture. The phosphorus moiety separated as diphenylphosphinic acid, m. p. 190° (lit., m. p. 190—192°). It should be noted that this acid would be formed if either diphenylphosphine or diphenylphosphinous acid was produced by hydrolysis, but the isolation of triethyltin acetate is, however, conclusive.

(c) *Methyl Iodide.* Diphenyl(tri-n-butylstannyl)phosphine (0·63 g., 0·00133 mole) was treated under nitrogen with methyl iodide (5 ml., 0·08 mole) added dropwise. The white precipitate was recrystallised from ethanol giving dimethyldiphenylphosphonium iodide (0·32 g., 70·5%), m. p. 243° (Found: C, 49·3; H, 5·0; I, 36·8. Calc. for $C_{14}H_{16}IP$: C, 49·1; H, 4·7; I, 37·1%).

The filtrate was evaporated (reduced pressure) leaving tri-n-butyltin iodide (0·38 g., 68·7%) (Found: I, 30·0; Sn, 28·0. Calc. for $C_{12}H_{27}ISn$: I, 30·4; S, 28·5%).

In a similar experiment phenylbis(triethylstannyl)phosphine (0·34 g.) gave a 53% yield of trimethylphenylphosphonium iodide, m. p. 236° (Found: I, 45·5. Calc. for $C_9H_{14}IP$: 45·3%), and triethyltin iodide (0·39 g., 89·6%) (Found: I, 35·4. Calc. for $C_6H_{15}ISn$: I, 35·7%).

(d) *Sodium in liquid ammonia.* Diphenyl(tri-n-butylstannyl)phosphine (1 g., 0·0021 mole) was pipetted under nitrogen into a two-necked flask. Dry liquid ammonia (10 ml.) was distilled into the flask under vacuum at −78° and sodium (0·096 g., 0·0042 g.-atom) was added in small portions. On addition of methyl iodide (4·5 g., 0·032 mole) the orange colour was discharged with simultaneous separation of a white precipitate. After removal of the solvent (reduced pressure) the residue was recrystallised from ethanol giving dimethyldiphenylphosphonium iodide, m. p. 244° (Found: I, 37·6. Calc. for $C_{14}H_{16}IP$: I, 37·1%).

Preparation of Trialkylstannyl Diphenylphosphinates.—Method 1. Triphenylphosphine oxide (4 g., 0·0144 mole) and sodium hydride [16] (0·5 g., 0·021 mole, used as 50% w/w dispersion in oil) were mixed under nitrogen, and the mixture was slowly heated to 180° and maintained at this temperature for 1 hr. to complete the conversion into sodium diphenylphosphinite. Triethyltin bromide (4·12 g., 0·0144 mole) in dry benzene (25 ml.) was added to the cooled product and the mixture was heated under reflux for 12 hr. The precipitate was filtered off and the solvent evaporated (reduced pressure). The remaining solid gave *triethylstannyl diphenylphosphinate* (21%), m. p. 248° (from ethanol) (Found: C, 51·3; H, 6·0; Sn, 28·4. $C_{18}H_{25}O_2PSn$ requires C, 51·1; H, 6·0; Sn, 28·3%).

A similar preparation with tri-n-butyltin bromide (5·33 g., 0·0144 mole) gave tri-n-butylstannyl diphenylphosphinate (25%), m. p. 216° (Found: C, 56·6; H, 6·9; Sn, 23·8. Calc. for $C_{24}H_{37}O_2PSn$: C, 56·8; H, 7·35; Sn, 23·4%).

Method 2. Tri-n-butyltin oxide (3·0 g., 0·005 mole) and a solution of diphenylphosphinic acid (2·2 g., 0·01 mole) in benzene (150 ml.) were heated under reflux for 12 hr.[17] The solution was frozen (salt–ice bath) and set aside overnight at room temperature. The precipitate, on crystallisation from ethanol, gave short needles of tri-n-butylstannyl diphenylphosphinate (4·3 g., 84%), m. p. 216—217° (Found: C, 56·7; H, 7·0; Sn, 23·6%; *M*, 1063 (in benzene). Calc. for $C_{24}H_{37}O_2PSn$: C, 56·8; H, 7·35; Sn, 23·4%, *M*, 507).

Similar treatment of an equimolecular mixture of diphenylphosphinic acid and the required tin hydroxide gave, after crystallisation from ethanol, the stannyl diphenylphosphinate: (i) *trimethylstannyl diphenylphosphinate* (72%), m. p. >360° (softening at 214—216° and again at 255—258°) (Found: C, 47·6; H, 5·0; Sn, 31·3%; *M*, 1471. $C_{15}H_{19}O_2PSn$ requires C, 47·3; H, 5·0; Sn, 31·2%; *M*, 380). (ii) *tri-n-propylstannyl diphenylphosphinate* (71%), m. p. 226° (Found: C, 54·0; H, 6·5; Sn, 25·7%; *M*, 930. $C_{21}H_{31}O_2PSn$ requires C, 54·2; H, 6·7; Sn, 25·7%); *M*, 465); (iii) *triphenylstannyl diphenylphosphinate* (86%), m. p. >360° (Found: C, 63·5; H, 4·5; Sn, 20·7. $C_{30}H_{25}O_2PSn$ requires C, 63·5; H, 4·4; Sn, 20·9%).

Preparation of Diethylstannyl Bisdiphenylphosphinate. Sodium diphenylphosphinite (3·23 g., 0·0144 mole, prepared as previously described, was heated with diethyltin dibromide (2·43 g., 0·0072 mole) in dry benzene (25 ml.) under reflux for 14 hr. The precipitate was filtered off

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[16] Horner, Beck, and Toscano, *Ber.*, 1961, **94**, 1323.

[17] Kubo, unpublished observations.

and the solvent evaporated (reduced pressure). The remaining sticky solid was extracted with ethanol (3 × 25 ml.) leaving a white solid, insoluble in benzene, ethanol, ether, light petroleum, and ethyl acetate. The compound appears to be *diethylstannyl bisdiphenylphosphinate* (1·06 g., 24%), m. p. 370—372° (Found: C, 54·7; H, 4·6; Sn, 19·4. $C_{28}H_{30}O_4P_2Sn$ requires C, 55·0; H, 4·95; Sn, 19·4%).

Attempted Reaction of Triethylstannyl Diphenylphosphine with Sulphur.—Triethylstannyl diphenylphosphine (1 g.), sulphur (0·1 g.), and benzene (15 ml.) were heated under reflux for 3 hr. No reaction appears to have taken place since the sulphur was recovered.

Analysis.—Existing procedures for the estimation of tin, involving the initial oxidative destruction of the organotin compound are very tedious and a determination takes at least 5 hr. A rapid (50 min.) method was accordingly developed which involved the wet oxidation of the organotin compound with hydrogen peroxide, reduction of tin to the bivalent state with antimony powder, and final titration with standard potassium iodate–potassium iodide solution. Details are as follows: To the organotin compound (sufficient to provide 4—20 mg. of Sn) was added concentrated sulphuric acid (6 ml.); the solution was gently heated, and 20-vol. hydrogen peroxide was added dropwise until the solution became perfectly clear. The solution was then heated until fumes of sulphur trioxide were evolved. If any brown coloration formed it was removed by the addition of a further drop of peroxide. The solution was diluted with boiled-out distilled water and (180 ml.) concentrated hydrochloric acid (80 ml.) and then heated to boiling, and the tin reduced to the +2 state by the addition of antimony metal powder (0·6 g.). The resulting solution was cooled and titrated in the usual way with standard potassium iodate–iodide solution, with starch as indicator, an atmosphere of carbon dioxide being used to prevent aerial oxidation.

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