Nuclear Magnetic Resonance and Mössbauer Spectra of some Organotin Anions

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^{1}H N.m.r. spectra of SnH_4, $[Me_{3-x}SnH_x]^-$, $[Ph_{3-x}SnH_x]^-$, and $[(PhCH_2)_2SnH]^-$ have been obtained in liquid ammonia and the nature of the species present in solution is discussed. Evidence to support the presence of 2− ions in solution has not been obtained. Mössbauer data on Na$[SnPh_3]$ confirm that both contact and solvent-separated ion pairs are present together in dimethoxyethane solutions and that their Mössbauer parameters are δ 1·20, Δ = 0·0 and δ = 2·14, Δ = 1·87 mm s^{-1}, respectively.

TIN anions have been used as intermediates in the synthesis of hydrides, mixed tetra-alkyltin compounds, and tin–transition metal complexes by reaction of $[R_3Sn]^-$ ions with the appropriate halide.[1-3] Stannyl ions have been prepared by the reaction of R_6Sn_2,[1] $[R_3SnCl]$,[2] or $[R_3SnH]$ [4] with sodium in liquid ammonia. Lithium and potassium salts of the trimethylstannyl ion have also been isolated from tetrahydrofuran (thf) [5] and dimethoxyethane [6] solutions and triphenylstannyl-lithium has been prepared by the reaction of tin(II) chloride with phenyl-lithium in thf.[7] However, relatively little spectroscopic data are available on these ions. Flitcroft and Kaesz [8] examined ^{1}H n.m.r. spectra of the ions formed by reaction of lithium with some methyltin chlorides in methylamine and the n.m.r. spectrum of Li$[SnPh_3]$ in thf has also been reported.[9] More recently, Mössbauer spectra of Li$[SnPh_3]$ and Na$[SnMe_3]$ have been recorded.[10,11]

Recently we reported the first spectroscopic evidence for the $[SnH_3]^-$ ion [12] and we now present n.m.r. data for a number of organo-substituted stannyl ions. In addition some preliminary Mössbauer data on solutions of M$[SnPh_3]$ in dimethoxyethane are also presented. Spectroscopic data are also reported for benzyltin chlorides and hydrides, some of which have not been prepared before.

EXPERIMENTAL

All the alkyltin halides were obtained from Alfa Inorganics and used without further purification. The phenyltin chlorides were prepared by reaction of $SnCl_4$ with Ph_4Sn in

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[1] C. A. Kraus and W. N. Greer, *J. Amer. Chem. Soc.*, 1922, **44**, 2629.

[2] C. A. Kraus and W. V. Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361, 2568.

[3] R. F. Chambers and P. C. Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1054.

[4] R. E. Dessey, W. Kitching, and T. Chivers, *J. Amer. Chem. Soc.*, 1966, **88**, 453.

[5] C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, 1963, **28**, 181.

[6] M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, 1958, 2811.

[7] H. Gilman and S. D. Rosenburg, *J. Org. Chem.*, 1953, **18**, 680.

[8] N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1963, **85**, 1377.

[9] W. L. Wells and T. L. Brown, *J. Organometallic Chem.*, 1968, **11**, 271.

[10] M. Cordey-Hayes, R. D. Peacock, and M. Vucelie, *J. Inorg. Nuclear Chem.*, 1963, **29**, 1177.

[11] K. A. Bilevich, V. I. Gol'danskii, V. Ya. Rockov, and V. V. Khrapov, *Akad. Nauk. S.S.S.R. Bull. Div. Chem. Sci.*, 1969, 1583.

[12] T. Birchall and A. Pereira, *J.C.S. Chem. Comm.*, 1972, 1150.

sealed tubes in accordance with literature methods.[13] Di- and tri-benzyltin chlorides were prepared according to the literature.[14] Attempts to prepare benzyltin trichloride from $[(PhCH_2)_3SnCl]$ and $SnCl_4$ were unsuccessful and yielded only $[(PhCH_2)_2SnCl_2]$ or starting material. The chlorides were generally converted to the corresponding hydrides by reduction with $Li[AlH_4]$ in ether solvents and purified by vacuum distillation. The benzyltin chlorides were reduced with $Li[AlH_4]$ in diethyl ether, and the ether layer separated, dried, and the ether removed *in vacuo*. The tribenzyltin hydride remained as a pale yellow solid, m.p. 51—52 °C, while the dibenzyltin hydride was obtained as a clear colourless liquid which turned brown on prolonged standing. Attempts to purify this latter compound by vacuum distillation were unsuccessful due to decomposition and rapid hydrogen evolution. Since the n.m.r. spectrum of the freshly prepared liquid showed only minor impurity peaks, it was used without further attempts to purify it. I.r. spectra showed bands for $[(PhCH_2)_3SnH]$ at: (in Nujol) 692, 731, 751, 796, 1 029, 1 049, 1 097, 1 205, 1 259, 1 595, and 1 823; (in benzene) 695, 736, 756, 797, 1 029, 1 049, 1 101, 1 206, 1 459, 1 491, 1 597, 1 819, 2 920, 3 026, and 3 065 cm^{-1}. For $[(PhCH_2)_2SnH_2]$ (neat liquid) bands occurred at 693, 730, 754, 796, 1 029, 1 050, 1 099, 1 206, 1 236, 1 452, 1 491, 1 601, 1 841, 2 927, 3 029, and 3 065 cm^{-1}. The Sn–H stretch occurred at 1 820 and 1 841 cm^{-1} in $[(PhCH_2)_3SnH]$ and $[(PhCH_2)_2SnH_2]$, respectively. Attempts to prepare $[(PhCH_2)SnH_3]$ by addition of $PhCH_2Br$ to a solution of $Na[SnH_3]$ in liquid NH_3 at −45 °C were unsuccessful and SnH_4 and $C_6H_5CH_3$ were the only identifiable products.

N.m.r. spectra were recorded on a Varian A-60 spectrometer in cases where the samples were stable. Spectra of the less stable materials and of all the solutions of the anions in liquid ammonia at a concentration of 0·5M were recorded on Varian DA-60 or HA-100 spectrometers at −60 °C.* Analysis of the spectra of the $M[SnPh_3]$ salts was accomplished using LAOCN3,[15] which had proved successful in the analysis of the corresponding germyl anions.[16] Mössbauer instrumentation and spectral analysis have been described.[17] Isomer shifts are quoted with respect to the resonance of SnO_2 at room temperature. All Mössbauer spectra were recorded with the absorber at liquid-nitrogen temperature and the source at room temperature. The samples contained 10—15 (mg Sn) cm^{-2} and the frozen solution samples were 0·25M in $Na[SnPh_3]$.

RESULTS AND DISCUSSION

Stannane reacts with sodium in liquid ammonia according to equation (1). The n.m.r. spectrum of the

$$SnH_4 + Na \xrightarrow{NH_3} [SnH_3]^- + Na^+ + \tfrac{1}{2}H_2 \qquad (1)$$

$[SnH_3]^-$ ion in this solution has been reported and an extremely small Sn–H spin–spin coupling constant was observed.[12] The dramatic increase in $J(^{117,119}Sn{-}^1H)$ for the series $[SnH_3]^-$, SnH_4, $[SnH_3]^+$ was interpreted in terms of the known and probable structures [18] of these species using the method of Pople and Santry.[19] It is clear that changes in geometry will alter the energy separation between the occupied and unoccupied molecular orbitals for the $[SnH_3]^-$ ion and hence effect the coupling constant. Such changes in geometry could arise because of changes in the position of equilibria in (2) between solvated separate ions, solvent-separated ion pairs, and contact ion pairs. Increasing the temperature

$$M^+(solv) + [SnH_3]^-(solv) \rightleftharpoons M^+(solv)[SnH_3]^- \rightleftharpoons M[SnH_3] \qquad (2)$$

resulted in a decrease in coupling constant (Table 1), and at 30° C we were unable to assign with certainty any value for $J(^{117,119}Sn{-}^1H)$. Weak peaks were observed at *ca.* 45 Hz to low field of the $[SnH_3]^-$ resonance but no corresponding resonance to high field could be observed because this region was obscured by the sharp triplet arising from the solvent. At lower temperatures the NH_3 triplet was broadened due to the slower tumbling rate of the solvent which allows a more effective interaction between the quadrupole moment of the ^{14}N and proton resonances. However, at all temperatures sharp $^{15}N{-}^1H$ satellites were visible and separate $[SnH_3]^-$ and NH_3 resonances observed. This indicates that these changes are not the result of proton exchange between $[SnH_3]^-$ and the solvent NH_3. The temperature variation in $J(^{117,119}Sn{-}^1H)$ is likely the result of an intramolecular exchange caused by shifts in the positions of the equilibria in (2): the contact ion pair would be expected to be less pyramidal about tin and have a higher J value than the solvent-separated ion pair or the free solvated ions.[12]

TABLE 1

N.m.r. parameters for solutions of stannyl ions in liquid ammonia

Salt	θ_c/°C	δ(Sn–H)/ p.p.m.	$J(^{117,119}Sn{-}^1H)$/ Hz		$\delta(NH_3)$/ p.p.m.
$Na[SnH_3]$	−60	−1·68	104·9	109·4	−0·75
	0	−1·54	99·4	103·8	−0·57
	30	−1·49			−0·49
$[NH_4][SnH_3]$	−78 (10 min) *	−1·82	127·8	133·7	−1·23
	−78 (6 h)	−1·86	204·3	213·6	−1·24
	−78 (18 h)	−1·94	320·3	334·4	−1·23
	−63 (2 h)	−2·04	502		−1·23

* The times refer to the interval between preparing the samples and recording their spectra.

Emeléus and Kettle [20] studied the reaction between SnH_4 and Na in liquid ammonia by monitoring the hydrogen evolved and measuring the conductivity. The breaks in the conductivity curve were interpreted in terms of formation of $Na_2[SnH_2]$ and $Na[SnH_3]$ according to (1) and (3). The n.m.r. spectrum of a solution

$$Na + Na[SnH_3] \longrightarrow Na_2[SnH_2] + \tfrac{1}{2}H_2 \qquad (3)$$

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* 1M = 1 mol dm^{-3}.

[13] H. Gilman and L. A. Gist, jun., *J. Org. Chem.*, 1957, **22**, 368.

[14] K. Sisido, Y. Taneda, and Z. Kinugawa, *J. Amer. Chem. Soc.*, 1961, **83**, 538.

[15] S. M. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

[16] T. Birchall and I. Drummond, *J. Chem. Soc. (A)*, 1970, 1401.

[17] T. Birchall, R. J. Bouchard, and R. D. Shannon, *Canad. J. Chem.*, 1973, **51**, 2077.

[18] J. R. Webster and W. L. Jolly, *Inorg. Chem.*, 1966, **10**, 877.

[19] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[20] H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 1958, 2444.

containing stannane and an excess of sodium showed only two absorptions, one due to the solvent and the other due to the $[SnH_3]^-$ ion. However, neither $[SnH_3]^-$ not NH_3 showed any spin–spin coupling indicating that both are involved in exchange processes, though not with each other. Addition of MeCl to this solution resulted in production of $[Me_2SnH_2]$ and $[MeSnH_3]$ and this would appear to be confirmatory evidence for the presence of $[Na_2SnH_2]$ and $Na[SnH_3]$. We were unable to detect any resonance which could be attributed to the $[SnH_2]^{2-}$ ion though this species, if it exists, may well be insoluble in liquid ammonia. It is well known that the electron reacts directly with ammonia to give sodium amide and hydrogen, that this reaction is catalysed by the presence of impurities and, once started, is autocatalytic.[21,22] Sodium amide, being only slightly soluble in liquid ammonia, would crystallise when formed and contribute virtually nothing to the conductivity in the earlier experiments.[20] Furthermore, since only small amounts of the amide ion are necessary to completely collapse the $^{14,15}N{-}^1H$ spin–spin coupling,[21,23] the production of $[NH_2]^-$ would explain the single sharp N–H resonance that we observe. The most likely explanation of the experimental facts is that reactions (1) and (4) occur, and that (5)—(7) explain the products

$$Na + NH_3 \longrightarrow Na[NH_2] + \tfrac{1}{2}H_2 \qquad (4)$$

$$Na[SnH_3] + MeCl \longrightarrow [MeSnH_3] + NaCl \qquad (5)$$

$$[MeSnH_3] + Na[NH_2] \longrightarrow Na[MeSnH_2] + NH_3 \qquad (6)$$

$$Na[MeSnH_2] + MeCl \longrightarrow [Me_2SnH_2] + NaCl \qquad (7)$$

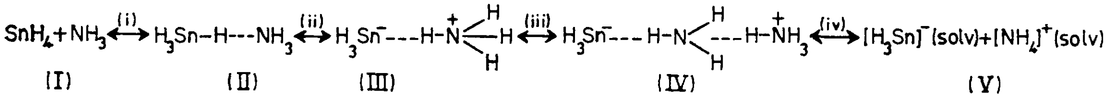
after addition of MeCl rather than (8). There remains as yet no direct spectroscopic evidence for $Na_2[SnH_2]$.

$$[H_2SnNa_2] + 2MeCl \longrightarrow [Me_2SnH_2] + 2NaCl \qquad (8)$$

When stannane was condensed into an n.m.r. tube containing liquid ammonia at −78 °C a pale yellow solution resulted. In addition a tin mirror was formed above the liquid-ammonia level and some grey-green solid was deposited at the bottom of the tube indicating that some decomposition had occurred. The n.m.r. spectrum (Table 1) showed peaks attributable to the $[SnH_3]^-$ ion, a sharp solvent peak with no $^{15}N{-}^1H$ coupling visible, and a resonance at −2·18 p.p.m. which had no satellite peaks visibly associated with it. Clearly there is an exchange process occurring involving solvent, in sharp contrast to the stoicheiometric reaction between SnH_4 and Na where no rapid proton exchange involving solvent occurs. These observations are consistent with the ionisation of stannane according to (9), and the collapse of the N–H

$$SnH_4 + NH_3 \xrightarrow{NH_3} [SnH_3]^- + [NH_4]^+ \qquad (9)$$

coupling in the solvent resonance is the result of rapid proton exchange with the ammonium ion produced.[24] Addition of MeCl to the solution resulted in formation of $[MeSnH_3]$ and confirms the self ionisation. It was also noted that in this solution $J(^{117,119}Sn{-}^1H)$ increased with time, slowly at temperatures close to the solvent freezing point but more rapidly at higher temperatures. This behaviour may be attributable to the uniqueness of the $[NH_4]^+$ cation, being the conjugate acid of the liquid ammonia solvent system. Ionisation of stannane in ammonia could be represented (10) and proceed after the initial solvation of stannane (II) *via* a series of proton transfers to (V), the solvated separate ions. Such a scheme provides a ready mechanism for proton exchange between the solvent and $[SnH_3]^-$ which was confirmed by carrying out the analogous experiment with ND_3 when an $ND_{3-x}H_x$ resonance increased in intensity at the expense of $[SnH_3]^-$. However, this exchange is slow on the n.m.r. time scale. At no time were we able to observe separate n.m.r. signals for SnH_4 and $[SnH_3]^-$ together in these solutions. This means either that there is rapid proton exchange between these two tin species or that ionisation is complete by the time the spectrum is recorded. The former possibility appears unlikely in view of the fact that $^{117,119}Sn{-}^1H$ coupling was observed throughout. The tin–hydrogen coupling will depend on the concentrations of the various species involved in equilibria (ii)—(iv) and on the positions of these equilibria. These will certainly be temperature dependent but are not obviously time dependent. The time dependence might be the result of a slow base-catalysed decomposition. Further studies on this system will be necessary before a full explanation of these changes can be given, though such studies will be experimentally difficult because side reactions do occur.



$$SnH_4 + NH_3 \overset{(i)}{\longleftrightarrow} H_3Sn{-}H{---}NH_3 \overset{(ii)}{\longleftrightarrow} H_3Sn^-{---}H{-}\overset{+}{N}H_3 \overset{(iii)}{\longleftrightarrow} H_3Sn^-{---}H{-}NH_2{---}H{-}\overset{+}{N}H_3 \overset{(iv)}{\longleftrightarrow} [H_3Sn]^-(solv) + [NH_4]^+(solv) \qquad (10)$$

(I) (II) (III) (IV) (V)

Alkylstannyl Compounds.—Substitution of only one hydrogen in SnH_4 by a methyl group reduces the acidity enough to prevent any detectable ionisation of methylstannane, and none of the methylstannanes undergo self ionisation in pure liquid ammonia. Like $[SnH_3]^-$, the methylstannyl ions can be produced in solution by reaction with alkali metals. Methylstannate gives a pale yellow solution when allowed to react with the stoicheiometric amount of sodium in liquid ammonia. The resulting n.m.r. spectrum is shown in Figure 1. The triplet at +0·44 p.p.m. and quartet at −2·78 p.p.m. confirms the presence of the $[MeSnH_2]^-$ ion and this

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[21] R. A. Ogg, jun., and J. D. Ray, *J. Chem. Phys.*, 1957, **26**, 1515.

[22] W. L. Jolly and E. J. Kirschke, *Inorg. Chem.*, 1967, **6**, 855.

[23] T. J. Swift, S. B. Marks, and W. G. Sayre, *J. Chem. Phys.*, 1966, **44**, 2797.

[24] T. Birchall and W. L. Jolly, *J. Amer. Chem. Soc.*, 1965, **87**, 3007.

spectrum clearly shows that proton exchange with the solvent does not occur. The spectral data are summarised in Table 2. Tin-117,119–hydrogen coupling was only observed after spin-decoupling experiments had been carried out. Addition of MeCl to this solution, followed by vacuum fractionation, gave only $[Me_2SnH_2]$ which was added confirmation of the presence of $[MeSnH_2]^-$ in solution. When excess of alkali metal was used red-brown solutions resulted again showing the triplet and quartet structure, but the NH_3 signal showed no $^{14,15}N-^1H$ coupling indicating that the solvent protons are involved in an exchange process most probably with amide ion. Both $[Me_2SnH_2]$ and $[Me_3SnH]$ were isolated from this reaction after adding MeCl and subsequent fractionation. While the isolation of $[Me_3SnH]$ could arise from reaction of MeCl with $[MeSnH]^{2-}$ there were no peaks in the n.m.r. spectrum which could be attributed to this ion. We believe that reactions analogous to (5)—(7) satisfactorily explain the products isolated.

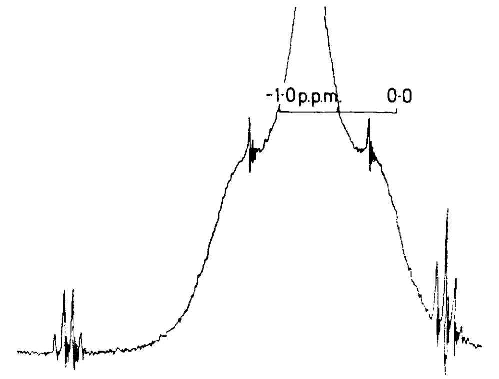

FIGURE 1 ^1H N.m.r. spectrum of the methylstannyl ion in liquid ammonia at −60 °C

TABLE 2

N.m.r. parameters for some organotin hydrides and their anions[a]

Compound	δ[b]/p.p.m.			J/Hz		
	C_6H_5[b]	Sn–*H*	SnC–*H*	$^{117,119}Sn-H$	$^{117,119}Sn-C-H$	H–Sn–C–H
SnH_4[c]		−3·85		1 846, 1 931		
$[SnH_3]^-$		−1·68		104·9, 109·4		
$[MeSnH_3]$[c]		−4·14	−0·27	1 770, 1 852	62	2·7
$[MeSnH_2]^-$		−2·78	+0·44	117·8, 122·1	27·7	4·6
$[Me_2SnH_2]$[c]		−4·76	−0·17	1 682, 1 758	55·5, 58·0	2·55
$[Me_2SnH]^-$		−3·59	+0·24		18·2	4·0
$[Me_3SnH]$[c]		−4·73	−0·18	1 664, 1 744	54·5, 56·5	2·37
$[Me_3Sn]^-$			+0·57		14·2	
$[(PhCH_2)_2SnH_2]$	−6·93	−5·21	−2·11	1 733, 1 814	63·1, 66·2	1·7
$[(PhCH_2)_2SnH]^-$	−6·89, −6·25	−4·22	−2·01			3·8
$[(PhCH_2)_3SnH]$	−6·86	−5·70	−2·19	1 697, 1 772	59·7, 62·7	1·5
$[PhSnH_3]$[d]		−4·93		1 836·7, 1 921·5		
$[PhSnH_2]^-$	−7·53, −6·78	−4·28				
$[Ph_2SnH_2]$[d]		−6·09		1 842·0, 1 927·8		
$[Ph_2SnH]^-$	−7·59, −6·88	−6·25		142·0, 148·5		
$[Ph_3SnH]$[d]	−7·83, −7·49	−6·83		1 850·7, 1 935·8		
$[Ph_3Sn]^-$[e]	−7·43, −6·8					
$[PhMeSnH_2]$	−7·23, −6·99	−5·10	−0·61	1 771, 1 835	57·5, 60·2	2·6
$[Ph_2MeSnH]$	−7·50, −7·13	−6·17	−0·34	1 788, 1 872	56·0, 58·5	2·2
$[Ph_4Sn_2Me_2]$	−7·50, −7·13		−0·65		47·8, 50·0	14·7 (*Sn*–Sn–C–*H*)

[a] With reference to external $SiMe_4$. [b] These chemical shifts refer to the most prominent peaks. [c] Ref. 8. [d] Ref. 26. [e] Analysis by LAOCN 3 [15] gave: δ_o −7·432, δ_m 6·846, and δ_p = −6·777 p.p.m.; $J(H^1H^2)$ 7·37, $J(H^1H^3)$ 1·34, $J(H^1H^4)$ 0·57, $J(H^2H^3)$ 7·55, $J(H^1H^5)$ 0·85, and $J(H^2H^4)$ 1·45 Hz.

Similar behaviour results from the reaction of $[Me_2SnH_2]$ and $[Me_3SnH]$ with sodium. No $^{117,119}Sn-^1H$ coupling could be observed for the $[Me_2SnH]^-$ ion even though decoupling experiments were tried. As with the other hydrides, side reactions occurred when an excess of sodium was used and, more particularly, if potassium rather than sodium was used. Potassium amide, which could be produced in these solutions, is very soluble in liquid ammonia whereas sodium amide is only sparingly soluble and high concentrations of $[NH_2]^-$ in these solutions are the most likely cause of the side reactions.

The only previous spectroscopic evidence for methylstannyl ions was that of Flitcroft and Kaesz [8] who reacted $[Me_3SnCl]$ and $[Me_2SnCl_2]$ with lithium in methylamine. Both gave methyl resonances at 0·4 p.p.m. from $SiMe_4$ with J(Sn–C–H) of 14·6 and 19·5 Hz for the trimethyl and dimethyl cases, respectively, and these parameters were attributed to $[Me_3Sn]^-$ and $[Me_2SnH]^-$. This latter ion was postulated to arise by solvolysis of $[Me_2Sn]^{2-}$ but with rapid proton exchange with the solvent. While these chemical shifts and Sn–C–H coupling constants are in reasonable agreement with our results, the absence of the hydride resonance in Flitcroft and Kaesz's spectrum is surprising since in no case do we find rapid proton exchange between Sn–H and N–H species.

Attempts to prepare the corresponding benzyltin hydrides and their anions were not altogether successful. We were unable to prepare $[(PhCH_2)SnH_3]$ and of the anions only $[(PhCH_2)_2SnH]^-$ could definitely be identified. Toluene was produced in the reactions with sodium indicating that cleavage of the C–Sn bond had occurred.

Phenylstannyl Compounds.—N.m.r. spectra of the phenylstannanes have been reported previously.[25] Like most monosubstituted benzenes, the aromatic region shows two groups of resonances, one at *ca.* −7·8 p.p.m. from $SiMe_4$ due to the *m*-protons and the other at *ca.* −7·5 p.p.m. attributable to the *o*- and *p*-protons. Reaction with alkali metals affords the corresponding anionic species with n.m.r. patterns similar to those of the parent hydrides but with the resonances shifted to higher field. The spectrum of $[PhSnH_2]^-$ is shown in Figure 2.

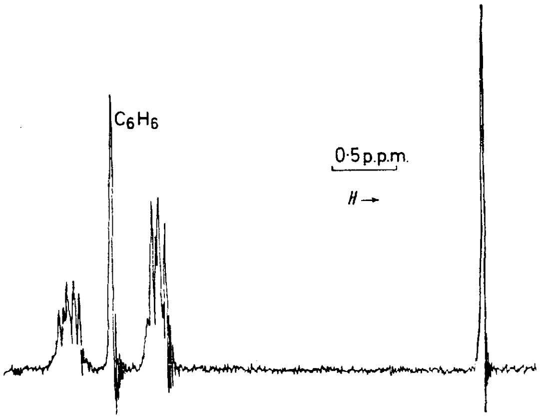

FIGURE 2 ¹H N.m.r. spectrum of the phenylstannyl ion in liquid ammonia at −60 °C

A complete analysis of the spectrum of $[Ph_3Sn]^-$ was carried out.[15] Good computer fits for these spectra could only be obtained by assigning the lowest-field multiplets to the *o*- rather than the *m*-protons so that the phenyl multiplets of area 2 : 3 arise from the *o*- and (*m* + *p*)-protons. The phenylstannyl ions are then exactly analogous to the corresponding germyl ions.[16] The negative charge on tin polarises the electron density in the ring towards the *m*- and *p*-protons at the expense of the *o*-protons with the result that there is virtually no shift to higher field, on ionisation, for the *o*-protons but a substantial shift for the *m*- and *p*-protons. This also means that there is no delocalisation of negative charge from tin into the phenyl rings since this would concentrate negative charge on the *o*- and *p*- at the expense of the *m*-positions as is observed for the triphenyl carbanions. The reduced acidity of stannanes which accompanies substitution of phenyl for hydrogen is then exactly analogous to the germane case.[16]

N.m.r. parameters for these phenylstannyl ions are summarised in Table 2. These data were obtained from solutions in which the reaction between the stannane and the alkali metal was essentially stoicheiometric. In these cases the reactions were clean with the only detectable side product in solution being benzene (see Figure 2) indicating that some C–Sn bonds are cleaved in this reaction. The presence of these anions was confirmed by the addition of an alkyl chloride to give the corresponding alkyl derivative and the n.m.r. data for some of these are also included in Table 2. If an excess of the phenylstannane was used side reactions occurred and more hydrogen was evolved than can be accounted for by (11).

$$[Ph_2SnH_2] + Na \longrightarrow [Ph_2SnH]^- + Na^+ + \tfrac{1}{2}H_2 \quad (11)$$

$$2[Ph_2SnH_2] + 2Na \longrightarrow [(Ph_2Sn)_2]^{2-} + 2Na^+ + 2H_2 \quad (12)$$

Addition of MeCl to these solutions gave the expected methylphenylstannane together with other alkylarylstannanes. In the case of $[Ph_2SnH_2]$ we were able to identify $[(Ph_2MeSn)_2]$ as one product suggesting that (12) also takes place in the initial reaction. Direct n.m.r. evidence for the dianion $[(Ph_2Sn)_2]^{2-}$ was not obtained although the phenyl : Sn–H proton signal areas were greater than 10 : 1. Dessey *et al.*[4] in a polarographic reduction of $[Ph_2SnCl_2]$ obtained evidence for $[(Ph_2Sn)_2]^{2-}$ which supports our n.m.r. results. Dessey *et al.*[4] were unable to obtain any evidence for the production of $[Ph_2Sn]^{2-}$ nor could we from our reactions with excess of alkali metal over phenyltin hydride. However, our results do not mean that this dianion is not produced, though we believe it unlikely, but only that it is not present in solution.

N.m.r. Parameters.—The trends in chemical shifts of the Sn–H protons for the stannyl anions follow those of the parent hydrides. Increasing alkyl or aryl substitution resulted in deshielding of the hydride proton and resonance occurred at lower magnetic fields. The shift to lower field is greater for phenyl substitution presumably because the Sn–H comes under the influence of the aromatic ring-current effect. These shifts were enhanced in the anions amounting to *ca.* 1 p.p.m. for successive methyl substitution and 2—2·5 p.p.m. for phenyl substitution.

The decrease in Sn–H coupling constant on successive methyl substitution has been interpreted in terms of a decrease in *s* character in the orbitals involved in the Sn–H bond,[8] since the Fermi-contact term is the dominant one in coupling involving ¹H.[19] In the case of phenyl substitution, *J*(Sn–H) increases implying an increase in *s* character in the tin–hydrogen bonds. Unfortunately we were unable to measure *J*(Sn–H) for all the substituted stannyl ions but, where observed, the same dramatic decrease already reported for $[SnH_3]^-$[12] was found. These decreases are consistent with the change in geometry from an essentially tetrahedral hydride to a pyramidal anion. The reasons why *J*(Sn–H) was not observed for $[Me_2SnH]^-$ or $[PhSnH_2]^-$ are not clear. Tin satellites for the former ion would be complex due to coupling with the two CH_3 groups and could result in a spectrum too broad to be observed, but proton-decoupling experiments to simplify the spectrum were of no help in locating the $^{117,119}Sn$ satellites. For the $[PhSnH_2]^-$ ion the satellites could be hidden by the resonances from the phenyl protons on the low-field side

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[25] E. Amberger, H. P. Fritz, C. G. Kreiter, and M. Kula, *Chem. Ber.*, 1963, **96**, 3270.

and by the solvent NH_3 on the high-field side. If this were the case, J(Sn–H) would be between 300 and 400 Hz and such a coupling was found for $[H_4N][SnH_3]$ (Table 1). Another possibility is that J(Sn–H) in these two cases is zero and this could be settled by observing the ^{117,119}Sn resonance directly. We found that the two bond ^{117,119}Sn–C–^{1}H couplings decreased on ionisation and are in agreement with the value previously reported by Flitcroft and Kaesz [8] for $[Me_3Sn]^-$. The three-bond coupling J(H–Sn–C–*H*) increased on ionisation and parallels that observed for the corresponding germanes,[26,27] though this may also be a decrease since the sign of this coupling could be negative.

Mössbauer Spectra.—Table 3 summarises the ^{119}Sn Mössbauer data obtained for the benzyltin compounds which have not previously been reported and for frozen solutions of the triphenylstannyl ion in dimethoxyethane. The data for the benzyl compounds are as expected for organotin halides and hydrides and do not warrant further discussion. The data reported for $Na[SnPh_3]$ in dimethoxyethane are, however, interesting. The trimethylstannylsodium salt was examined some years ago by Cordey-Hayes *et al.*[10] who found that the tin nucleus was in a symmetrical environment. In solution, however, a different situation may pertain because of the equilibria involving the separate ions with both contact and solvent-separated ion pairs as in (2). We attempted to obtain information on these equilibria from an analysis of the n.m.r. spectra of the $M[SnPh_3]$ system, but the proton chemical shifts and coupling constants were too insensitive to changes in either concentration or cation to allow any conclusions to be reached. A solution Mössbauer study was therefore attempted to obtain information on the nature of the ions in solution. Solvated stannyl anions, *i.e.* $[R_3SnS_x]^-$ where S is solvent, would almost certainly have different Mössbauer parameters to an unsolvated contact ion pair $M[SnR_3]$ because the co-ordination number about the tin nucleus would be different.

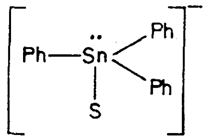
TABLE 3

Mössbauer parameters for some organotin hydrides and their anions

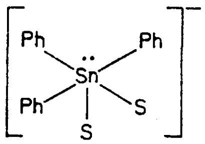
Compound	Medium	Isomer shift (δ/mm s^{-1})	Quadrupole splitting (Δ/mm s^{-1})
$[(PhCH_2)_2SnCl_2]$	Solid	1·63	3·0
$[(PhCH_2)_2SnH_2]$	Solid	1·42	0·0
$[(PhCH_2)_3SnCl]$	Solid	1·52	2·82
$[(PhCH_2)_3SnH]$	Solid	1·43	0·0
$Na[SnPh_3]$	Dimethoxy-ethane	1·20, 3·07 or 1·20, 2·14	0·0, 0·0, or 0·0, 1·87
$Li[SnPh_3]$ [a]		1·30, 3·35	0·0, 0·0
$Na[SnMe_3]$ [b]	Solid	1·38	0·0

[a] Ref. 11. [b] Ref. 10.

Solutions of triphenylstannylsodium in dimethoxyethane, when frozen to a glass, gave a Mössbauer spectrum which consisted of two resonances of unequal intensity. The more intense resonance occurred at 1·20 mm s^{-1} while the other was at 3·07 mm s^{-1} from the SnO_2 reference. Bilevich *et al.*[11] reported similar results (Table 3) and interpreted their data in terms of the presence in solution of both contact and solvent-separated ion pairs. They assigned the resonance at 3·35 mm s^{-1} to the contact ion pair and that at 1·30 mm s^{-1} was attributed to the solvent-separated ion pair. However, these workers appear to have disregarded the possibility that the resonance at 3·35 mm s^{-1} might be half a quadrupole-split doublet whose other component is under the resonance at 1·30 mm s^{-1}. We believe the latter assignment to be more likely for the following reasons. Isomer-shift values greater than *ca.* 2·1 mm s^{-1} have been taken as an indication of the presence of a Sn^{II} species and a value of 3·35 mm s^{-1} is clearly in this region. We were unable to obtain any evidence that triphenylstannylsodium dissociates into diphenyltin and phenylsodium, in agreement with previous workers.[7] One would expect a solvated triphenylstannyl ion to have structures similar to (VI) or (VII), both of which would be expected to exhibit quadrupole coupling though the magnitude would depend on the strength of the tin–solvent interaction. If the high-velocity absorption were half a quadrupole-split doublet the solvated species would have Mössbauer parameters of δ 2·14 and Δ 1·87 mm s^{-1} which are very reasonable for a Sn^{IV} species of this kind. Finally, the absorption at low velocity has an isomer-shift value close to that for $M[SnR_3]$ species in the solid state [10] and is most reasonably assigned to the contact ion pair. Obviously much remains to be done before our assignment can be confirmed and work in this regard is currently in progress.



(VI)



(VII)

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[26] T. Birchall and W. L. Jolly, *Inorg. Chem.*, 1966, **5**, 2177.
[27] T. Birchall and I. Drummond, *Inorg. Chem.*, 1972, **11**, 250.