The benzene was evaporated, and the residue was recrystallized from acetonitrile to give 0.64 g. (98%) of bis(triphenyltin) sulfide, m.p. 142–144°.[19]

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[19] NOTE ADDED IN PROOF.—W. T. Reichle, *Inorg. Chem.*, **1**, 650 (1962), has obtained bis(triphenyltin) sulfide in high yield by allowing bis(triphenyltin) oxide to react directly with carbon disulfide at 95° for 18 hr. in a stainless steel bomb. We have observed that bis(triphenyltin) oxide does not react appreciably with carbon disulfide alone at room temperature.

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Nuclear Magnetic Resonance Spectra of Tin Compounds. III. H^1 Magnetic Resonance Spectra of Some Alkyl Tin Compounds

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We have recently reported H^1 and F^{19} magnetic resonance spectra of some alkyl and fluoroalkyl tin compounds[1] and followed this by an extensive study of the H^1 and Sn^{119} spectrum of hexamethylditin.[2] In the present note we propose to communicate results for the H^1 resonance spectra in a series of alkyl tin compounds. Some of these compounds have been measured previously by other workers but are included since additional features of their spectra have become important. Trimethyltin hydride[3] and tetramethyltin[3,4] have been studied recently. Reeves and Wells[5] have noted that the reduced coupling constants involving group IV elements are linear with Z_x, the atomic number of the group IV element.

TABLE I

Compound	δ_{Sn-H}[a]	δ_{CH_3}[a]	$J_{C^{13}-H_3}$	$J_{Sn^{119}-H}$	$J_{Sn^{117}-H}$	$J_{Sn^{119}-CH_3}$	$J_{Sn^{117}-CH_3}$	$J_{H-Sn-CH}$
Tri-*n*-butyltin hydride	−4.78			1609 ± 2	1532 ± 2			1.8 ± 0.1[b]
Trimethyltin hydride	−4.61	−0.08	128.8 ± 0.3	1755 ± 2	1677 ± 2	56.9 ± 0.2	54.5 ± 0.2	2.4 ± 0.2
Dimethylethyltin hydride	−4.73	−0.08	126.4 ± 0.3	1706.6 ± 2	1630 ± 2	53.8 ± 0.2	52.1 ± 0.2	2.6 ± 0.2
Tetramethyltin		−0.01	127.4 ± 0.3			54.0 ± 0.2	52.0 ± 0.2	
Dimethyldiethyltin						49.8 ± 0.2	47.6 ± 0.2	
Trimethyltrifluoromethyltin		−0.30	131.7 ± 0.3			60.3 ± 0.2	57.6 ± 0.2	
Trimethyltin bromide		−0.74	132.6 ± 0.3			59.1 ± 0.2	56.6 ± 0.2	
Trimethyltriethylditin[c]		−0.315	130.2 ± 0.3			48.8 ± 0.2	46.5 ± 0.2	

[a] P.p.m. from TMS. [b] Coupling $J_{H-Sn-CH_2}$ from Sn–H to methylene protons adjacent to tin. [c] For this compound, $J_{Sn^{117,119}-SnCH_3}$ = 13.4 ± 0.3 c.p.s.

Results and Discussion

The spectra obtained on an A60 spectrometer were calibrated by audio side bands measured on a Hewlett Packard Model 522B frequency counter. In some cases the spectra were representative of many strongly coupled nuclear spins with small chemical shifts between them. Typical of these were tri-*n*-butyltin hydride, dimethylethyltin hydride, diethyldimethyltin, and trimethyltriethylditin. The alkyl side chains which are more complex than methyl were therefore not analyzed since the most interesting features are the coupling constants to C^{13} and Sn^{119}.[1–3,5] The data obtained from the spectra are listed in Table I together with the relevant compounds. It is evident from an examination of the table that an increase in the C^{13}–H coupling constant of a methyl group attached to tin is accompanied by a low-field shift of the same methyl group except in trimethyltriethylditin. This anomaly of compounds containing an "Sn–Sn" bond has been reported in our previous paper.[2] It is interesting to represent the unusual nature of the compounds with an "Sn–Sn" bond by plotting $J_{C^{13}-H}$ in the methyl groups against $J_{Sn^{119}-CH_3}$ from the tin to the methyl protons. This is indicated in Fig. 1, which

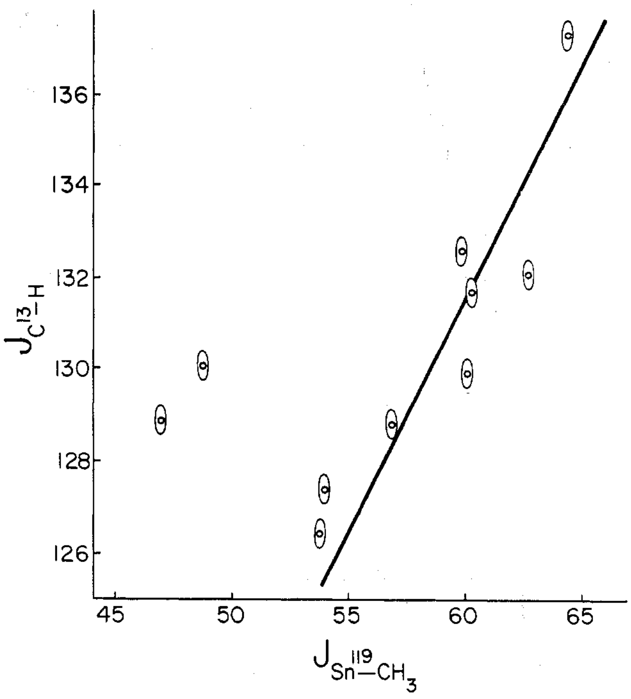

Figure 1.

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[1] H. C. Clark, J. T. Kwon, L. W. Reeves, and E. J. Wells, *Can. J. Chem.*, **41**, 3005 (1963).

[2] H. C. Clark, J. T. Kwon, L. W. Reeves, and E. J. Wells, *ibid.*, in press.

[3] N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

[4] G. W. Smith, *J. Chem. Phys.*, **39**, 2031 (1963).

[5] L. W. Reeves and E. J. Wells, *Can. J. Chem.*, **41**, 2698 (1963).

shows not only the results of the present work but also previous results.[1,2] The compounds containing one tin atom show an approximate linearity between $J_{C^{13}-H}$ and $J_{Sn^{119}-CH_3}$ which is indicated by a line in the figure. The substituent groups at the tin vary from simple alkyl to $-CH_3$ and $-Br$. Hexamethylditin[2] and triethyltrimethylditin are represented by the two points at the left of the figure, which are clearly anomalous. $J_{C^{13}-H}$ is representative of the product $|2s_C(0)|^2|1s_H(0)|^2$ where these symbols represent the s character probabilities at the respective nuclei.[6] The s character in the C–H bonds is thus seen to increase as the electronegativity of substituents at the tin increases. The highest value of $J_{C^{13}-H_3}$ is that obtained for $(CH_3)_2Sn(C_2F_4H)_2$.[1]

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(6) L. W. Reeves, *J. Chem. Phys.*, in press.

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The Interaction of Boron Trichloride with Diborane[1]

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Monochlorodiborane was identified by Stock[2] as a product resultant from the interaction of diborane and boron trichloride. Schlesinger and Burg[3] obtained monochlorodiborane by passing a mixture of boron trichloride and hydrogen through an electric arc. Monochlorodiborane was observed to decompose and form an equilibrium mixture containing diborane and boron trichloride. If the diborane were removed by distillation and the remaining material allowed to warm to 0°, a new equilibrium resultant from further decomposition was obtained. This could be continued until only a trace of monochlorodiborane remained. They observed that it was very difficult to get monochlorodiborane to decompose in the presence of a large excess of boron trichloride. Interaction of boron trichloride with diborane at 0°, followed by fractionation through a $-130°$ bath, showed that approximately one-eighth of the diborane had been consumed. On standing at 0°, the $-130°$ fraction had its vapor pressure increased from 58.0 to 685 mm. in 5 min., thus showing that equilibrium was attained very rapidly even at 0°. Hurd[4] prepared monochlorodiborane by passing mixtures of boron trichloride and hydrogen over active metals at elevated temperatures.

Urry, Wartik, Moore, and Schlesinger[5] suggest dichloroborane as a probable reaction intermediate formed in the reaction of diboron tetrachloride with hydrogen to form diborane. Lynds and Stern[6] obtained dichloroborane by passing a mixture of hydrogen and boron trichloride over magnesium at a temperature of 400–450°. They report that equimolar mixtures of boron trichloride and dichloroborane are relatively stable. Myers and Putnam[7] isolated monochlorodiborane using low temperature gas chromatography techniques. Contrary to previous reports they found the pure compound to be comparatively stable.

Experimental

Diborane was prepared by the reaction of boron trifluoride with sodium borohydride in diglyme (diethylene glycol dimethyl ether).

Boron trichloride, 99.8% pure (Stauffer Chemical Co.), was freed of phosgene by passage over boron carbide at 1000°.

The experiments were carried out in an all-glass high vacuum system using standard techniques.[8] Volumes of differing portions of the apparatus were determined using weighed quantities of carbon dioxide.

Measured portions of boron trichloride and diborane were mixed in differing portions of the apparatus at temperatures of 20.5 to 25.5°. If interaction did not take place an infrared spectrum of the gas mixture showed only the spectra of diborane and boron trichloride superimposed on each other.[9] If the gas mixture was fractionated through a $-131.5°$ trap into a $-196°$ trap, the starting quantity of diborane was obtained in the $-196°$ trap. When reaction occurred, an infrared spectrum such as that shown in Fig. 1 was obtained. When equimolar quantities of boron trichloride and diborane interacted approximately one-eighth of the diborane was consumed as shown by fractionation and by infrared analysis. Repeated observations of the infrared spectrum showed that equilibrium had been attained in the first observation.

The reaction product gases were measured and the number of moles of gas calculated. The results in Table I show that differing mole ratios of boron trichloride and diborane interact to form chloroboranes without any change in the number of moles of gas present. The results also show that change of pressure has little, if any, effect on the number of moles of gas present. This observation could be explained by equations such as

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_5Cl + BHCl_2 \quad (1)$$

$$BCl_3 + 2B_2H_6 \rightleftarrows 2B_2H_5Cl + BH_2Cl \quad (2)$$

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_4Cl_2 + BH_2Cl \quad (3)$$

$$3BCl_3 + 2B_2H_6 \rightleftarrows 3BH_2Cl + 2B_2H_3Cl_3 \quad (4)$$

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(1) The original concept and experimental work were supported by the research program of Stauffer Chemical Company, Richmond, Calif. Support for the completion of the work was provided by the Lockheed Independent Research Fund.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).

(4) D. T. Hurd, *ibid.*, **71**, 20 (1949).

(5) G. Urry, T. Wartik, R. Moore, and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

(6) L. Lynds and D. R. Stern, *ibid.*, **81**, 5006 (1959).

(7) H. W. Myers and R. F. Putnam, *Inorg. Chem.*, **2**, 655 (1963).

(8) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(9) This was only observed to happen when the reactants were mixed in a new, clean vacuum system. Possibly traces of a boron oxide are needed to catalyze the reaction.