too large to allow rapid exchange under the conditions of the present study.

Although no new precise numerical figures for either the rate or the equilibrium for the diborane dissociation have been added to the literature by the present study, future calculations of these will be more severely limited by the data reported here for studies over an extended temperature range.

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Some Convenient Methods for Preparing Bis(triphenyltin) Sulfide and Related Compounds

BY EUGENE J. KUPCHIK AND PETER J. CALABRETTA

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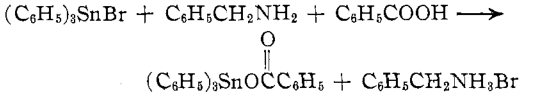
It was reported previously that triphenyltin bromide reacts with ammonia in anhydrous diethyl ether to give bis(triphenyltin) oxide and ammonium bromide.[1]

$$2(C_6H_5)_3SnBr + 2NH_3 + H_2O \longrightarrow (C_6H_5)_3SnOSn(C_6H_5)_3 + 2NH_4Br \quad (1)$$

The conversion of triphenyltin bromide to bis(triphenyltin) oxide (82% yield) can also be accomplished with benzylamine.

$$2(C_6H_5)_3SnBr + 2C_6H_5CH_2NH_2 + H_2O \longrightarrow (C_6H_5)_3SnOSn(C_6H_5)_3 + 2C_6H_5CH_2NH_3Br \quad (2)$$

In this reaction triphenyltin bromide and benzylamine probably form a complex which undergoes hydrolysis on exposure to the moisture in the air to give the observed products. The ability of organotin compounds to give complex addition compounds with ammonia or amines is well known.[2-6] The low hydrolytic stability of these complexes has been mentioned.[7] If benzoic acid is added to the reaction mixture before exposing it to the air the products are triphenyltin benzoate (80%) and benzylammonium bromide (87%).



$$(C_6H_5)_3SnBr + C_6H_5CH_2NH_2 + C_6H_5COOH \longrightarrow (C_6H_5)_3SnO\overset{O}{\overset{\|}{C}}C_6H_5 + C_6H_5CH_2NH_3Br \quad (3)$$

Equation 3 represents a convenient method for preparing triphenyltin esters of carboxylic acids in high yield. High yields have been obtained with bridgehead carboxylic acids.[8]

When carbon disulfide is used as a solvent in reaction 1, bis(triphenyltin) sulfide is formed in high yield. The other products are ammonium bromide and ammonium thiocyanate.

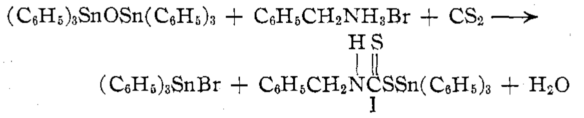
$$2(C_6H_5)_3SnBr + 4NH_3 + CS_2 \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + NH_4SCN + 2NH_4Br \quad (4)$$

The use of bis(triphenyltin) oxide in place of the triphenyltin bromide also results in a high yield of bis(triphenyltin) sulfide.

$$(C_6H_5)_3SnOSn(C_6H_5)_3 + 2NH_3 + CS_2 \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + NH_4SCN + H_2O \quad (5)$$

In reactions 4 and 5 hydrogen sulfide probably is formed by reaction between the ammonia and the carbon disulfide. Ammonia is known to react with carbon disulfide to give ammonium dithiocarbamate, which decomposes at room temperature to give hydrogen sulfide and ammonium thiocyanate.[9] In (4) hydrogen sulfide or ammonium sulfide reacts either directly with the triphenyltin bromide or with a possible complex formed between the triphenyltin bromide and ammonia. In (5) the hydrogen sulfide or ammonium sulfide reacts with the bis(triphenyltin) oxide to produce the observed products.

It has been found that bis(triphenyltin) oxide reacts with benzylammonium bromide in carbon disulfide to give triphenyltin bromide (70%) and triphenyltin N-benzyldithiocarbamate (I) (60%).



$$(C_6H_5)_3SnOSn(C_6H_5)_3 + C_6H_5CH_2NH_3Br + CS_2 \longrightarrow (C_6H_5)_3SnBr + \underset{\text{I}}{C_6H_5CH_2\overset{H}{\overset{|}{N}}\overset{S}{\overset{\|}{C}}SSn(C_6H_5)_3} + H_2O \quad (6)$$

I can also be obtained (94% yield) by allowing sodium N-benzyldithiocarbamate to react with triphenyltin bromide. Perhaps the most convenient method for preparing I (85% yield) involves adding benzylamine to a carbon disulfide solution of bis(triphenyltin) oxide.

$$(C_6H_5)_3SnOSn(C_6H_5)_3 + 2C_6H_5CH_2NH_2 + 2CS_2 \longrightarrow 2\text{I} + H_2O \quad (7)$$

In (7) N-benzyldithiocarbamic acid probably is formed by reaction between the benzylamine and the carbon disulfide. This compound then immediately reacts with the bis(triphenyltin) oxide to give I and water. In (6) the benzylammonium bromide probably first reacts with the bis(triphenyltin) oxide to give triphenyltin bromide, benzylamine, and either triphenyltin hydroxide or bis(triphenyltin) oxide. The triphenyltin hydroxide or bis(triphenyltin) oxide then reacts as in (7).

Bis(triphenyltin) oxide also reacts with ammonium bromide in carbon disulfide to give triphenyltin bromide (72%) and bis(triphenyltin) sulfide (90%).

I decomposes on heating to give bis(triphenyltin) sulfide in high yield. This decomposition can be conveniently carried out by refluxing an acetonitrile

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or benzene solution of I. Another product of the reaction is benzyl isothiocyanate, which was identified by conversion to 1-benzyl-2-thiobiurea.

$$2\text{I} \xrightarrow[\Delta]{} (C_6H_5)_3SnSSn(C_6H_5)_3 + H_2S + 2C_6H_5CH_2NCS \quad (8)$$

Equations 4, 5, and 8 represent new and convenient methods for preparing bis(triphenyltin) sulfide. Bis(triphenyltin) sulfide has been prepared previously by reaction of bis(triphenyltin) oxide with aqueous sodium sulfide,[10] by reaction of triphenyltin chloride with hydrogen sulfide and triethylamine in benzene,[10] and by reaction of lithium triphenyltin sulfide with triphenyltin chloride.[11] It has also been obtained from the reaction between triphenyltin hydride and allyl mercaptan.[12]

The possibility of using reactions 4 and 5 for the preparation of other group IVB and VB aryl metal sulfides is being investigated. Other organometallic derivatives of N-alkyl and N-aryldithiocarbamic acids are being prepared and their decompositions studied.

Experimental

Melting points were determined with a Mel-temp capillary melting point apparatus and are uncorrected.

Reaction of Triphenyltin Bromide with Ammonia in Carbon Disulfide.—Ammonia was passed for 2.5 hr. into a solution of 3.0 g. (0.007 mole) of triphenyltin bromide in 200 ml. of carbon disulfide.

The carbon disulfide was evaporated with a stream of nitrogen, and the residue was extracted with diethyl ether. Evaporation of the diethyl ether left a solid which gave, after recrystallization from acetonitrile, 2.1 g. (82%) of bis(triphenyltin) sulfide, m.p. 143–144° (lit.[10] 145.5–147°), no depression on admixture with authentic bis(triphenyltin) sulfide, infrared spectrum superimposable upon that of authentic bis(triphenyltin) sulfide.

The infrared spectrum of the residue from the ether extraction (3.0 g.) had characteristic bands for ammonium bromide at 3.1 and 7.15 μ and a characteristic band for ammonium thiocyanate at 4.85 μ.

Reaction of Bis(triphenyltin) Oxide with Ammonia in Carbon Disulfide.—Ammonia was passed for 2 hr. into a solution of 5.0 g. (0.00698 mole) of bis(triphenyltin) oxide in 250 ml. of carbon disulfide.

The mixture was filtered to give 0.2 g. of solid whose infrared spectrum was superimposable upon that of authentic ammonium thiocyanate.

Evaporation of the carbon disulfide from the filtrate left 4.9 g. of solid, m.p. 133–140°, which afforded after recrystallization from acetonitrile 4.7 g. (92%) of bis(triphenyltin) sulfide, m.p. 145–147°, no depression on admixture with authentic bis(triphenyltin) sulfide.

Reaction of the Triphenyltin Bromide–Benzylamine Complex with Benzoic Acid.—A solution of 2.5 g. (0.0234 mole) of benzylamine in 50 ml. of chloroform was added rapidly to a solution of 10 g. (0.0234 mole) of triphenyltin bromide in 200 ml. of chloroform, and the turbid solution was stirred at 25° for 2 hr. A solution of 2.9 g. (0.0234 mole) of benzoic acid in 75 ml. of chloroform was then added rapidly causing the formation of a white solid.

The white solid was collected on a filter and recrystallized from ethanol to give 3.8 g. (87%) of benzylammonium bromide, m.p. 225–228°, no depression on admixture with authentic benzylammonium bromide.

The chloroform was evaporated from the filtrate, and the gummy residue was slurried with petroleum ether (b.p. 30–60°). The solid which formed was collected on a filter, washed with petroleum ether, and then recrystallized from ethanol–water to give 9.5 g. (80%) of triphenyltin benzoate, m.p. 80–83° (lit.[13] 82.5–84°), no depression on admixture with authentic triphenyltin benzoate, infrared spectrum superimposable upon that of authentic triphenyltin benzoate.

Reaction of Bis(triphenyltin) Oxide with Benzylammonium Bromide in Carbon Disulfide.—Benzylammonium bromide (2.2 g., 0.0117 mole) was added to a solution of 8.4 g. (0.0117 mole) of bis(triphenyltin) oxide in 250 ml. of chloroform. The solution was stirred at 25° for 0.5 hr., 50 ml. of carbon disulfide was added, and the solution was stirred at 25° for 1 hr.

The solvent was evaporated, and the residue was recrystallized rapidly from acetonitrile to give 3.7 g. (60%) of triphenyltin N-benzyldithiocarbamate (I), m.p. 124–126°.

Anal.[14] Calcd. for $C_{26}H_{23}S_2NSn$: C, 58.66; H, 4.36; N, 2.63; Sn, 22.30; mol. wt., 532. Found: C, 58.50; H, 4.78; N, 2.30; Sn, 22.61; mol. wt.[15] (thermoelectric[16] in benzene at 40°), 528.

Triphenyltin N-Benzyldithiocarbamate (I). (A).—To a suspension of 6 g. (0.03 mole) of sodium N-benzyldithiocarbamate[17] in 200 ml. of benzene was added a solution of 12.9 g. (0.03 mole) of triphenyltin bromide in 200 ml. of benzene. The mixture was stirred at 25° for 1 hr. and then filtered to yield 4.4 g. of solid which did not melt up to 350° and which gave a positive test for bromide ion with silver nitrate solution.

The benzene was evaporated from the filtrate with a stream of air to give 16.0 g. of solid, m.p. 121–123°, which gave, after washing with acetonitrile, 15.0 g. (94%) of triphenyltin N-benzyldithiocarbamate, m.p. 124–126°. In two other runs the yields were 80 and 70%.

(B).—A solution of 2.2 g. (0.02 mole) of benzylamine in 10 ml. of chloroform was added to a solution of 7.2 g. (0.01 mole) of bis(triphenyltin) oxide in 100 ml. of carbon disulfide and 50 ml. of chloroform. The reaction mixture was stirred at 25° for 1 hr., after which the solvent was evaporated with a stream of air leaving a solid which gave, after washing with acetonitrile, 9.0 g. (85%) of triphenyltin N-benzyldithiocarbamate, m.p. 124–126°.

Decomposition of Triphenyltin N-Benzyldithiocarbamate (I)) (A).—Triphenyltin N-benzyldithiocarbamate (5.3 g., 0.01 mole. was heated at 130° for 3 hr. The residue was allowed to cool to 25°, and then 10 ml. of ethanol was added followed by a solution of 1.2 g. (0.01 mole) of semicarbazide hydrochloride and 0.53 g. (0.005 mole) of sodium carbonate in 3 ml. of water. The mixture was heated on a steam bath for 10 min. and then filtered to give 2.0 g. of solid material, m.p. 165–185°. Recrystallization from ethanol gave 1.6 g. (72%) of 1-benzyl-2-thiobiurea, m.p. 194–196°, no depression on admixture with authentic 1-benzyl-2-thiobiurea.[18]

The ethanol was evaporated from the filtrate, and the residue was recrystallized from acetonitrile to give 3.1 g. (86%) of bis(triphenyltin) sulfide, m.p. 143–145°, no depression on admixture with authentic bis(triphenyltin) sulfide.

(B).—A solution of 3 g. (0.0056 mole) of triphenyltin N-benzyldithiocarbamate in 50 ml. of acetonitrile was refluxed overnight at 81° and then concentrated to one-third the original volume. The crystals which formed on cooling were collected on a filter to give 1.9 g. (95%) of bis(triphenyltin) sulfide, m.p. 142–145°.

(C).—A solution of 1 g. (0.0018 mole) of triphenyltin N-benzyldithiocarbamate in 50 ml. of benzene was refluxed at 80° for 8 hr.

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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.

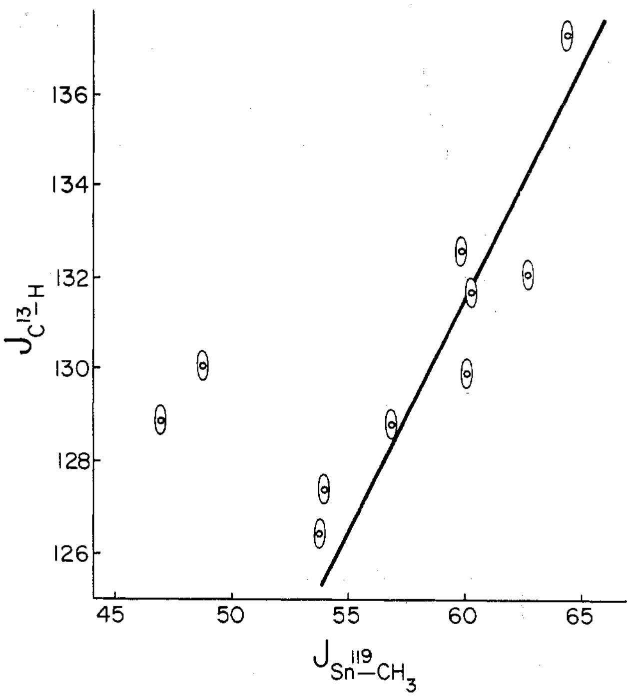

Figure 1.

TABLE I

Compound	δ_{Sn-H}[a]	δ_{CH_3}[a]	$J_{C^{13}-H}$	$J_{Sn^{119}-H}$	$J_{Sn^{117}-H}$	$J_{Sn^{119}-CH_3}$	$J_{Sn^{117}-CH_3}$	$J_{H-Sn-CH}$
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

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