heated at reflux temperature for 1 hr. The resulting isopropyl alcohol (2.59 g., 96%) was removed by distillation through a packed column. The residual reaction mixture was cooled to room temperature and the resulting solid separated by filtration and dried to give 3.45 g. (82.5%) of 2-phenyl-1,3,2-benzodiazaboroline. This compound and that described in the following paragraph did not depress the melting point of a sample of 2-phenyl-1,3,2-benzodiazaboroline prepared by a previously described method[5,6] and their infrared spectra were identical.

b. *From triphenylboroxine.* A solution of 5.0 g. (16.2 mmoles) of triphenylboroxine and 5.0 g. (46.3 mmoles) of *o*-phenylenediamine in 70 ml. of benzene was heated at reflux temperature for 2–3 hr. The resulting water (0.9 g., *ca.* 100% yield) was collected in a Dean-Stark water trap and the residual solution cooled to room temperature. The solid product was collected on a filter and dried to give 7.98 g. (81% yield) of 2-phenyl-1,3,2-benzodiazaboroline as fine colorless crystals.

2-Phenyl-1,3,2-benzooxaazaboroline. A solution of 26.8 g. (0.130 mole) of diisopropoxyphenylborane and 14.15 g. (0.130 mole) of *o*-aminophenol in 53 ml. of xylene was heated at reflux for 155 min. The resulting isopropyl alcohol (15.75 g., 100% yield) was removed by continuous distillation and the residual solution cooled to 0°. Successive filtrations and concentrations of the xylene solution gave 24.42 g. (94% yield) of crude product, m.p. 97.5–101°; recrystallization from toluene gave pure 2-phenyl-1,3,2-benzooxaazaboroline, m.p. 101–102° (lit. m.p., 99–101°[7]).

Anal. Calcd. for $C_{12}H_{10}NOB$: B, 5.55; mol. wt. 195. Found: B, 5.37; mol. wt., 200 (cryoscopic in benzene).

Reaction of triisopropoxyborane with o-phenylenediamine. A mixture of 40.09 g. (0.213 mole) of triisopropoxyborane and 23.05 g. (0.213 mole) of *o*-phenylenediamine was heated for 18 hr. in refluxing xylene. The reaction mixture temperature rose from 136° to 150° as isopropyl alcohol (35.05 g., 86%) was removed by slow fractional distillation through a packed column. After cooling to room temperature, the residual crude solid product was separated by filtration and recrystallized from acetone to give 19.96 g. (80.5%) of 5*H*,12*H*,19*H*-tris[1,3,2-benzodiazaborolo]-borazine, m.p., sealed capillary tube, 380–390° dec., after previous softening at 350–355°.

Anal. Calcd. for $C_{18}H_{15}N_6B_3$: C, 62.2; H, 4.32; N, 24.2; B, 9.33; mol. wt., 347. Found: C, 61.8; H, 3.96; N, 23.0; B, 9.33; mol. wt., 321 (cryoscopic in dioxane).

The borazine is insoluble in hexane, benzene, and ether but can be recrystallized from dioxane or cyclohexane as well as acetone. It is soluble in hot dimethylformamide, bis-2-ethoxyethyl ether and methanol (with reaction).

The reaction of one molar equivalent of *o*-phenylenediamine with 1.4 equivalents of triethoxyborane (the excess was necessary since the resulting ethanol-triethoxyborane azeotrope was removed continuously) gave the same borazine derivative.

Reaction of triisopropoxyborane with o-aminophenol. A mixture of 31.85 g. (0.169 mole) of triisopropoxyborane and 18.45 g. (0.169 mole) of *o*-aminophenol was heated for 16.5 hr. at 130–150° in 50 ml. of refluxing xylene. Isopropyl alcohol (94.8% yield) was removed by continuous fractional distillation. After cooling to room temperature, the reaction mixture was filtered to give 19.2 g. of crude product. Washing with dry diethyl ether yielded a residue of 15.7 g. (79%) of tris[1,3,2-benzooxaazaborolo]borazine, m.p. 210–280° dec. in a sealed capillary tube.

Anal. Calcd. for $C_{18}H_{15}N_3O_3B_3$: C, 61.5; H, 3.41; B, 9.25; mol. wt., 351. Found: C, 60.1; H, 3.52; B, 9.44; mol wt., 338 (cryoscopic in dioxane).

The borazine was soluble in ethyl acetate and ethylene glycol dimethyl ether, partially soluble in acetone, dioxane, and tetrahydrofuran and insoluble in most other organic solvents.

Attempted reaction of triisopropoxyborane with p-phenylenediamine. A refluxing equimolar mixture of triisopropoxyborane and *p*-phenylenediamine in xylene resulted in only trace amounts of isopropyl alcohol in 0.7 hr. When bis-2-ethoxyethyl ether was used as the solvent, 21.3% of the isopropyl alcohol was recovered in 7.3 hr.

Reaction of triisopropoxyborane with aniline. A solution of 32.38 g. (0.172 mole) of triisopropoxyborane and 47.99 g. (0.516 mole) of aniline was heated for 5.5 hr. in 50 ml. of refluxing xylene. Isopropyl alcohol (7.17 g., 23.2% yield) was removed by continuous distillation, and the final residue was cooled to room temperature. The resulting crude solid was collected on a filter and recrystallized from xylene to give 2.74 g. (5.6% yield) of tris(anilino)borane, m.p. 168–170° (lit. m.p., 166–169°[3]). The boron content of this product was 3.83% compared to 3.77% for tris(anilino)-borane and its infrared spectrum was identical with that of an authentic sample.

ANAHEIM, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNION CARBIDE PLASTICS COMPANY, A DIVISION OF UNION CARBIDE CORP.]

Nature of the Interaction of Aqueous Sulfide Ion with Organotin Oxides and Related Substances

WALTER T. REICHLE

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The mechanism of the interaction of aqueous sulfide ion with polydiphenyl-, -dimethyl-, -di-*n*-butyl-and -di-*n*-octyltin oxides has been investigated. This reaction is believed to proceed *via* a water-soluble hexacoordinate metal ion, which on acidification yields the known diaryl- or dialkyltin sulfide trimers quantitatively. The corresponding selenides and tellurides, similarly prepared, are unstable and decompose. Diphenylgermanium oxide trimer, polydiphenyllead oxide and bis(triphenyltin) oxide also undergo this reaction with sulfide ion followed by acidification, to yield the corresponding sulfides.

INTRODUCTION

The Group Va alkyl- and aryl metal oxides or hydroxides react with aqueous hydrogen sulfide or ammonium sulfide to yield the metal sulfides.[1] For example, phenylantimony oxide reacts with hydrogen sulfide in aqueous ammonia followed by acidification to yield the corresponding sulfide.

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[1] E. Krause and A. von Grosse, *Die Chemie der metallorganischen Verbindungen*, p. 483, 548, 613, 599, 605; Verlag Borntraeger, Berlin, 1937.

$$C_6H_5SbO + H_2S \xrightarrow[2)\ HCl]{1)\ NH_3\text{-}C_2H_5OH} C_6H_5SbS$$

Such a reaction, of aqueous sulfide ion with an oxygen-containing metal-organic compound, has also been observed between polydiphenyltin oxide and aqueous sulfide ion.[2a] The reaction of organotin

$$[(C_6H_5)_2SnO]n + Na_2S \xrightarrow[2)\ H^+]{1)\ H_2O} [(C_6H_5)_2SnS]_3$$

and organogermanium *halides* with hydrogen sulfide in aqueous media has been previously[2b] used to prepare the corresponding sulfides.

RESULTS

The reaction of these organotin oxides with aqueous sulfide ion, followed by acidification, results in high yields of the corresponding organotin sulfides. The stoichiometry of this reaction requires two moles of sulfide ion per mole of $[R_2SnO]$, followed by four equivalents of acid to precipitate all the organotin sulfide.

$$2S^{=} + [R_2SnO] + 4H^+ \xrightarrow{H_2O} [R_2SnS] + H_2O + H_2S$$

The following facts support this stoichiometry. (1) When less than two moles of aqueous sulfide ion is used (per "mole" of R_2SnO), then only incomplete solution results. When exactly two or more moles of sulfide ion is used, a complete solution process takes place sometimes very rapidly (the octyl derivative forms a slurry). (2) The addition of just two equivalents of acid to the sulfide solution produces a transient precipitate; the addition of another two equivalents of acid immediately precipitates the organotin sulfide quantitatively and in high purity. (3) The addition of sulfide ion and acid must occur consecutively and in the correct order; otherwise only an incomplete reaction will result.

The reaction of organotin oxides with sulfide ion appears to be of a very general nature. Both aqueous selenide and telluride (but not hydroxide) ions may be used to dissolve the organotin oxides. The products in these cases turn out to be unstable and could not be isolated. The red, elemental selenium,[3] and black, elemental tellurium[4] were in evidence on attempted isolation of the products. Compounds containing carbon-selenium-germanium bonds [$(p\text{-}ClC_6H_4Se)_4Ge$; m.p. 201.5°] appear to be quite stable.[5] Dimethyltin selenide trimer has been prepared[6] in anhydrous medium and found to be unstable to hydrolysis. Since the products are here being generated in aqueous solution an isolation of a tin-selenium-tin containing compound could not be expected. Diphenylgermanium oxide trimer and the polydiphenyllead oxide can also be treated with the sulfide ion to yield, after acidification, the corresponding sulfides.

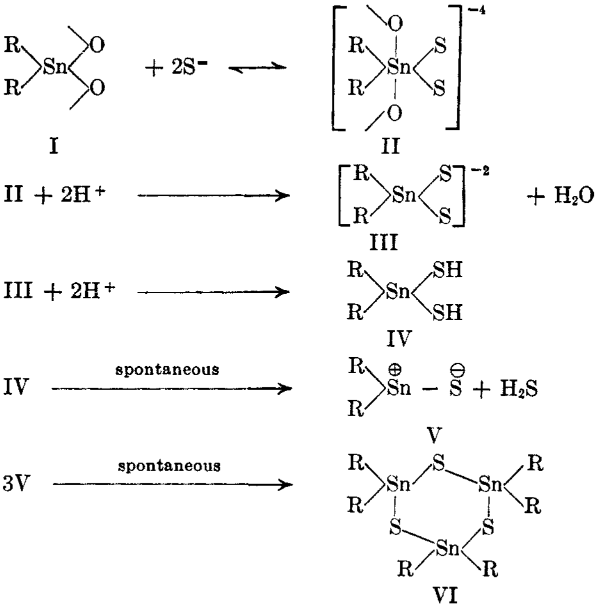
Other oxides of tin can be used in this reaction. The bis(triphenyltin) oxide, for example, yields bis-(triphenyltin) sulfide:

$$[(C_6H_5)_3Sn]_2O + 2Na_2S + 4H^+ \longrightarrow [(C_6H_5)_3Sn]_2S + H_2S + H_2O + 4Na^+$$

This reaction, therefore, appears to be a very general one in the Groups IVa and Va. The corresponding silicon compounds are not expected to yield sulfides in this aqueous medium since the silicon-sulfur bond hydrolyzes very readily.[7]

DISCUSSION

The mechanism of the reaction of organotin oxide with sulfide ion can be visualized as follows:



Tin has the known[8,9] tendency to accept ligands in order to become hexacoordinate. This hexacoordinate species is probably present as II. Experimentally, it has been demonstrated that no benzene solubles are extracted from a *solution* of polydiphenyltin oxide in aqueous sodium sulfide. The oxygen-tin bonds of II are probably very loose, since such solutions do not exhibit viscous behavior, nor is there the expected drop in solution viscosity on acidification with two equivalents of acid to

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(2) (a) W. T. Reichle, *J. Poly. Sci.*, **49**, 521 (1961). (b) E. G. Rochow, *J. Am. Chem. Soc.*, **70**, 1801 (1948). M. P. Brown, R. Okawara, and E. G. Rochow, *Spectrochimica Acta*, **16**, 595 (1960).

(3) T. Moeller, *Inorganic Chemistry*, p. 492; John Wiley and Sons, Inc., New York, 1952.

(4) L. Chugaeff and W. Chlopin, *Ber.*, **47**, 1269–75 (1914).

(5) H. J. Backer and J. B. G. Hurenkamp, *Rec. trav. chim.*, **61**, 802 (1942).

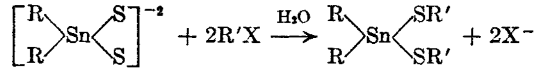
(6) M. Schmidt and H. Ruf, *Angew. Chem.*, **73**, 64 (1961).

(7) E. Rochow, *The Chemistry of the Silicones*, 2nd ed., p. 73, John Wiley and Sons, Inc., New York, 1951.

(8) E. E. Jelley, *J. Chem. Soc.*, 1580 (1933).

(9) R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 276 (1922).

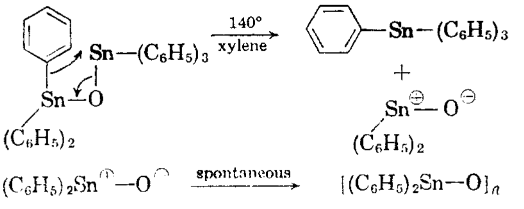
form "monomeric" species III. This intermediate (III) should, in principle, be capable of reacting with an alkyl halide, to form the dialkyltin bis(alkyl sulfide). Thus, benzyl chloride reacts with the intermediate III, of a reaction of polydimethyltin oxide with two moles of sulfide ion which had been acidified with *two* equivalents of acid, to give on distillation a 64% yield of dimethyltin bis(benzyl sulfide) plus some dimethyltin sulfide trimer. The reaction of unacidified intermediate II with benzyl chloride produces no dialkyltin bis(benzyl sulfide) but only dibenzyl sulfide.



$$\left[\begin{matrix}R\\R\end{matrix}>Sn<\begin{matrix}S\\S\end{matrix}\right]^{-2} + 2R'X \xrightarrow{H_2O} \begin{matrix}R\\R\end{matrix}>Sn<\begin{matrix}SR'\\SR'\end{matrix} + 2X^-$$

The intermediate III, when acidified with two equivalents of acid should yield the dialkyltin dithiol IV which is evidently not capable of existence since it polymerizes immediately to the trimeric and stable dialkyltin sulfide VI, probably *via* a species such as V.

The hydroxide analog of IV does not appear capable of existence, except in cases where the alkyl group prevents polymerization (with loss of water) to the polydialkyltin oxides (R = *t*-amyl, *t*-butyl[10]). No recorded observation could be found which demonstrated clearly the existence of the oxygen analog of species III. The hydrolysis of diaryltin dihalides, even in concentrated, aqueous caustic, always results in an immediate and quantitative yield of the polydiaryltin oxide. The thermal rearrangement of bis(triphenyltin) oxide, to yield tetraphenyltin and polydiphenyltin oxide,[11,12] could proceed *via* the oxygen analog of V.



So far attempts to capture this hypothetical intermediate [$(C_6H_5)_2Sn^{\oplus}—O^{\ominus}$] have been unsuccessful.[13]

Previously,[2a] it had been observed that the polydialkyl- and polydiphenyltin oxides were very high melting, largely insoluble, crystalline, brittle, high molecular weight substances. It was proposed that these properties could be readily explained on the basis of a highly ionic tin–oxygen bond. These polymers proved to be insoluble in even hot (130°), 50% aqueous sodium hydroxide solution. For this reason it was surprising to find that they dissolved readily in aqueous sodium sulfide at room temperature and yielded, after acidification, the organotin sulfides.

The properties of these sulfides are completely unlike those of the corresponding oxides. They are low molecular weight (trimers), are very soluble in organic solvents, relatively low melting, and probably have covalent tin-sulfur bonding.

EXPERIMENTAL

Chemicals. The preparation and properties of the tin polymers was discussed previously.[2a]

The polydiphenyllead oxide was prepared by hydrolysis of the corresponding nitrate.[14]

Anal. Calcd. for $C_{12}H_{10}PbO$: C, 38.2. Found· C, 38.21, 38.24.

The diphenylgermanium oxide trimer was prepared by aqueous caustic hydrolysis of the dibromide, m.p. 147.5–148.5°.

Anal. Calcd. for $[C_{12}H_{10}GeO]\cdot$ C, 59.40; H, 4.12; mol. wt., 729 (trimer). Found: C, 59.07; 59.31; H, 4.18, 4.29 mol. wt. (ebullioscopic in *o*-xylene), 750.

The bis(triphenyltin) oxide was prepared by hydrolysis of the chloride, m.p. 121–122°, lit. m.p. 123°.[11] The sodium selenide was purchased; the sodium telluride prepared under argon as an aqueous solution.[4] The infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer.

Preparation of diphenyltin sulfide trimer. The preparation of diphenyltin sulfide trimer from aqueous sodium sulfide and polydiphenyltin oxide has been described previously,[2a] m.p. 182–184°, lit. m.p. 183–184°.[15]

Preparation of dimethyltin sulfide trimer. Polydimethyltin oxide (8.25 g., 0.05 mole) and sodium sulfide nonahydrate (24.0 g., 0.10 mole) were placed into a flask with some distilled water (200 ml.) and a trace (~ 5 ml.) of ethanol. This was stirred for about 1 hr. and resulted in a clear solution. To this glacial acetic acid (6.0 g., 0.10 mole) was added producing only a transient precipitate. On addition of a like amount of glacial acetic acid (total of 12.0 g., 0.20 mole), a white precipitate appeared, and the odor of hydrogen sulfide became noticeable. No further precipitate resulted when additional acid was used. The white solid was filtered, washed twice with cold water, and dried; 8.92 g. was recovered, 98.7% yield of dimethyltin sulfide trimer.

The solid was dissolved in hot cyclohexane, treated with charcoal, filtered and cooled. Colorless crystals (6.8 g., 75% yield) m.p. 149.5–151.0° resulted; lit.[16] m.p. 149°. This is the known dimethyltin sulfide trimer.

Anal. Calcd. for C_2H_6SnS: Sn; 65.75; S, 17.7. Found: Sn, 65.1; S, 18.0.

Preparation of di-n-butyltin sulfide trimer. This material was prepared as outlined above from the corresponding oxide; sometimes it appeared as a powdery solid, at other times as an oil following the acidification step.

Anal. Calcd. for $C_8H_{18}SnS$: Sn, 44.9; S, 12.1; mol. wt., 795 (trimer). Found: Sn, 44.9; S, 15.0; mol. wt. (ebullioscopic in acetone), 780.

Attempted crystallization of the white solid sulfide, obtained from the acidification, from cold (20°) acetone, in which it was reasonably soluble, also resulted in an oil. On standing for several months, the material turned into a solid, m.p. 63–69°. Solution in solvent or heating yielded the liquid form again.

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(10) Ref. (1), p. 329–330.

(11) O. Schmitz-Dumont and H. Meyer, *Z. anorg. allgem. Chem.*, 284, 289 (1941).

(12) R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.*, 48, 1054 (1926).

(13) W. T. Reichle, unpublished observations.

(14) Ref. (1), p. 422.

(15) I. T. Eskin, A. N. Nesmeyanov, and A. K. Kocheshkov, *J. Gen. Chem.* (*U.S.S.R.*), 8, 35–41 (1938); *Chem. Abstr.*, 32, 5386–9 (1938).

(16) T. Harada, *Bull. Chem. Soc. Japan*, **17**, 283–286 (1942); *Chem. Abstr.*, **41**, 4444e (1947).

Preparation of di-n-octyltin sulfide trimer. Polydi-*n*-octyltin oxide was treated as above. Attempted crystallization from hot cyclohexane or cold benzene-acetone yielded a liquid polymer in both cases.

Anal. Calcd. for $C_{16}H_{34}SnS$: Sn, 31.55; S, 8.48; mol. wt., 1350 (trimer). Found: Sn, 29.8; S, 6.95; mol. wt. (ebullioscopic in acetone), 1130.

On standing for several months this material turned into a solid (m.p. about 25–30°); solution in solvent or heating yielded the liquid form again.

Reaction of aqueous sodium telluride with polydimethyltin oxide. Aqueous sodium telluride (0.1 mole) was prepared[4] and treated with 0.05 mole of polydimethyltin oxide to give a clear solution. Acidification yielded a jet-black precipitate which was evidently not the desired compound.

Reaction of aqueous sodium selenide with polydimethyltin oxide. A similar run as above, using 0.1 mole of aqueous sodium selenide and 0.05 mole of polydimethyltin oxide yielded a clear solution. Acidification yielded a curdy precipitate which decomposed to red selenium and other compounds on drying and extraction with ethanol.

Reaction of aqueous sodium sulfide with polydiphenyllead oxide. Five grams of polydiphenyllead oxide yielded 1.30 g. of dry solid on acidification, filtering and drying of the solid from the sulfide solution. Recrystallization from benzene-hexane (cold) gave light yellow crystals m.p. 112–115°.

Anal. Calcd. for $C_{12}H_{10}PbS$: C, 36.65; H, 2.54; S, 8.14. Found: C, 36.85, 36.95; H, 2.76, 2.74; S, 7.81, 8.00.

This material was unstable to even boiling benzene, and hence no molecular weight determination was carried out.

Reaction of diphenylgermanium oxide trimer with aqueous sodium sulfide. This oxide (0.27 g., 0.384 mmole) was dissolved in warm ethanol (50 ml.) and sodium sulfide nonahydrate added (0.56 g., 2.31 mmole) as a water solution (50 ml.). This was left standing for 1 hr. To the clear solution an excess of glacial acetic acid was added, producing a white precipitate. Filtration, washing, drying, and recrystallization from benzene-hexane yielded about 0.1 g. of colorless crystals; m.p. 198–200°.

Anal. Calcd. for $C_{12}H_{10}GeS$: C, 55.60; H, 3.87; S, 12.38. Found: C, 55.56; 55.27; H, 4.08, 4.15; S, 12.18, 12.35.

It was noted that this reaction would not proceed in an all-aqueous medium. No molecular weight measurement was carried out.

Reaction of bis(triphenyltin) oxide with aqueous sodium sulfide. This oxide (5.00 g., 0.00698 mole) was dissolved in ethanol (75 ml.) and aqueous sodium sulfide nonahydrate (6.71 g., 0.02795 mole, 50 ml. of water) was added producing a cloudy solution. Addition of more ethanol (100 ml.) resulted in a clear solution which was allowed to stand for 1 hr. Then glacial acetic acid (1.68 g., 0.02795 mole) was added producing only a transient precipitate. A like amount of this acid produced a yellowish precipitate. The liquors were evaporated under vacuum and the residue washed and dried, yielding 5.0 g. of a light, grey powder. Crystallization from hot acetonitrile (twice) yielded white crystals, m.p. 145.5–147.0°.

Anal. Calcd. for $C_{24}H_{20}Sn_2S$: Sn, 32.5; S, 4.37. Found: Sn, 30.3; S, 4.61, 4.55.

This material was identical with the reaction product of triphenyltin chloride with hydrogen sulfide and triethyl amine in benzene, m.p. 145.5–147.0°.

Anal. Calcd. for $C_{24}H_{20}Sn_2S$: Sn, 32.5; S, 4.37; mol. wt., 732. Found: Sn, 32.6; S, 3.64; mol. wt. (ebullioscopic in methyl ethyl ketone), 736.

Reaction of intermediate II *with benzyl chloride.* Polydimethyltin oxide (8.25 g., 0.05 mole) and sodium sulfide nonahydrate (24.0 g., 0.10 mole) were treated in water (200 ml.) containing some ethanol (5–10 ml.) at room temperature until a clear solution had been obtained (30 min.). Then benzyl chloride (12.6 g., 0.10 mole) was added and allowed to react with good stirring for 24 hr. Gel-like particles were observed in the reaction, a test for chloride ion was positive, no mercaptan odor was noticed. The solid was filtered off, washed three times with water, and dried at 25°; 9.90 g. (19.75 g. theory for dimethyltin bis(benzyl sulfide). This was recrystallized from *n*-pentane yielding colorless crystals (6.2 g.) m.p. 50–51° (dibenzyl sulfide m.p. 49°[17]).

Anal. Calcd. for $C_{14}H_{14}S$: C, 78.45; H, 6.58; S, 14.95. Found: C, 78.27, 78.11; H, 6.63, 6.59; S, 14.6.

Reaction of intermediate III *with benzyl chloride.* Polydimethyltin oxide (8.25 g., 0.05 mole) and sodium sulfide nonahydrate (24.0 g., 0.10 mole) were treated in water (200 ml.) containing some ethanol (5–10 ml.) at room temperature until a clear solution had been obtained (30 min.). Then hydrochloric acid (0.10 mole, 8.16 ml., 37.6% hydrogen chloride in 42 ml. of water) was slowly added producing a little cloudiness. Then benzyl chloride (12.6 g., 0.10 mole) was allowed to react, with good stirring and slight warming (about 40–50°), for 20 hr. A heavier-than-water phase was extracted with ether; this was dried with magnesium sulfate, and the solvent was removed leaving 17.0 g. of a clear liquid [19.75 gm.theory for dimethyltin bis(benzyl sulfide)]. Distillation yielded a clear distillate from which 2.9 g. of a crystalline solid (this was dimethyltin sulfide trimer) was removed by washing with cold pentane. Evaporation of the solvent left behind a slightly viscous liquid (12.7 g., 64.5%) whose infrared spectrum was essentially the same as that of dimethyltin bis(benzyl sulfide) prepared by a different route.

Preparation of dimethyltin bis(benzyl sulfide). Benzyl mercaptan (12.4 g., 0.10 mole) was added to a solution of sodium hydroxide (4.0 g., 0.10 mole) in ethanol-water (20 ml. and 60 ml.). After heating to reflux, dimethyltin dichloride (11.0 g., 0.05 mole) dissolved in dry ethanol (75 ml.) was added. After reacting for 24 hr. the solution was extracted with ether, dried with sodium sulfate, and the solvent removed leaving a viscous oil (17.8 g., 91%). This material could not be crystallized from pentane. Flash distillation yielded a viscous liquid (175–185°/0.25 mm., 15.2 g., 77% yield).

Anal. Calcd. for $C_{16}H_{20}S_2Sn$: C, 48.60; H, 5.07; Sn, 30.1; S, 16.2; mol. wt., 395. Found: C, 50.55, 50.35; H, 5.23, 5.29; Sn, 26.6; S, 16.3; mol. wt. (ebullioscopic in acetone, Geller Laboratories), 341.

The analytical results are only in fair agreement; it should be emphasized that the product was merely flash distilled and therefore contained some benzyl thiol (low mol. wt., high hydrogen, low tin).

Determination of the solution viscosities of a polydimethyltin oxide-sodium sulfide reaction product. The viscosities (effluent times) were measured in an Oswald viscometer at 25°. The experiment was carried out as follows. Distilled water (200 g., 100 sec.) was mixed with sodium sulfide nonahydrate (24.0 g., 0.10 mole) and 5.0 ml. of ethanol (solution 120 sec.). To this polydimethyltin oxide (8.25 g., 0.05 mole) was added and allowed to react for 1.5 hr., forming a clear solution (solution 130.5 sec.). The addition of glacial acetic acid (6.0 g., 0.10 mole) raised the viscosity of the clear solution slightly (136.5 sec.). The addition of the rest of the acid (6.0 g., 0.10 mole) precipitated out the dimethyltin sulfide and did not change the viscosity of the filtered liquors (136.5 sec.) from that of the previous reading. The dried solid weighed 8.80 g., 97.4% yield.

Acknowledgment. The author is indebted to the members of the Union Carbide Plastics Co. Analytical Group for numerous analyses and to Mr. J. J. Smith for critique and advice. The carbon-hydrogen determinations were carried out by Drs. Weiler and Strauss, Oxford, England, and by the Geller Laboratories, Bardonia, N. Y.

BOUND BROOK, N. J.

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(17) N. A. Lange, *Handbook of Chemistry*, 8th ed., p. 463, Handbook Publishers, Inc., Sandusky, Ohio, 1952.