the resulting solution was cooled in ice. White crystals of diphenyl disulfide separated almost immediately. These were washed with dilute alkali, filtered, and dried in a desiccator. The yield was 1.35 g. (73%), m.p. 60.4–60.9°, lit.[22] m.p. 61.5°. A mixture melting point was undepressed. In another experiment, the titration mixture was made alkaline and extracted with ether. Examination of the ether extract *via* v.p.c. indicated the presence of *t*-butyl alcohol in about 20% of the theoretical amount.

Reaction of Diphenyl Disulfide with Bromide–Bromate Reagent.—Diphenyl disulfide (0.3 g., 1.37 mmoles) was dissolved in a mixture of glacial acetic acid (50 ml.) and concentrated hydrochloric acid (2 ml.), and the solution was heated to 80°. With stirring, 13.8 ml. of 1.0 *N* bromide–bromate (13.8 mequiv.) was added to the hot solution. The reaction mixture was then quickly cooled to room temperature, diluted with 100 ml. of distilled water, and extracted twice with 20-ml. portions of benzene. Concentrated ammonia solution was then added to the benzene extract and the mixture was momentarily brought to reflux. After cooling, the aqueous phase was separated and allowed to evaporate at room temperature. Crystals of benzenesulfonamide (0.262 g. 61.6%) which separated overnight were filtered and dried in a desiccator, m.p. 151–152°, lit.[23] m.p. 150–151°. The infrared spectra of the product was identical with that of authentic benzenesulfonamide.

Reaction of Di(*t*-butyl) Sulfide with Bromide–Bromate Reagent.—A solution of di(*t*-butyl) sulfide (0.2390 g., 1.632 mmoles) in a mixture of glacial acetic acid (50 ml.) and concentrated hydrochloric acid (4 ml.) was treated with 116.5 ml. of 0.0995 *N* bromide–bromate reagent for 5 min. at room temperature. The pH of the reaction mixture was then adjusted to 6.5 with 25% sodium hydroxide solution.

An aqueous solution containing barium chloride (0.5 g.) was added to the reaction mixture and a white precipitate immediately appeared. The reaction mixture was digested for 0.5 hr. at about 60°. The precipitate was washed by decantation using distilled water. The precipitate was separated from the last traces of water by drying at 110°, after which it was heated to 1000° for 1 hr. in an open crucible suspended above a Fisher burner. The weight of the sample remained essentiallly constant during this latter treatment. The product, 0.2621 g. (1.12 mmoles), was identified as barium sulfate by its X-ray diffraction pattern.

Oxidation of 1,2-Bis(*t*-butylthio)ethane with Hydrogen Peroxide.—A solution of 1,2-bis(*t*-butylthio)ethane (1.006 g., 4.39 mmoles) in glacial acetic acid (50 ml.) was allowed to stand for 24 hr. The solution was then heated to 60° and a 10% excess of 30% hydrogen peroxide (2.5 ml.) was added dropwise. After the addition was complete, the mixture was heated an additional 0.5 hr. at 60°. The solution was then carefully evaporated to dryness at 40–60° and the residue was recrystallized from 95% ethanol to yield white crystals of 1,2-bis(*t*-butylsulfonyl)ethane, 0.8485 g. (64.6%), m.p. 228–230°, lit.[24] m.p. 230–231°.

Anal. Calcd. for $C_{10}H_{22}O_4S_2$: C, 44.42; H, 8.21; S, 23.70. Found: C, 44.72; H, 7.82; S, 22.96.

When this experiment was repeated in the presence of concentrated hydrochloric acid (6 ml.), the yield of recrystallized sulfone was 54.7%.

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The Reduction of Sulfur-Containing Functional Groups with Triphenyltin Hydride

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The reducing action of triphenyltin hydride on a variety of sulfur-containing functional groups has been studied. Aryl disulfides are cleaved at the S–S bond to give triphenyltin aryl sulfide, $(C_6H_5)_3SnSAr$. The allyl C–S bond in $(C_6H_5CH_2)_2S$, dibenzyl sulfide, and $(C_6H_5CH_2S)_2$, benzyl disulfide, is cleaved to give toluene. Thiophenols and methyl mercaptan evolve hydrogen and give the mixed sulfides. Thiobenzophenone is decolorized in the cold and on heating produces diphenylmethane. Benzenesulfonic acid gives hydrogen and triphenyltin benzenesulfonate. Benzenesulfinic acid and benzenesulfonyl chloride both give triphenyltin benzenesulfinate, hydrogen, and triphenyltin chloride, respectively. The aryl C–S bond is not reduced (Ph_2S, thianthrene) and diphenyl sulfone and diphenyl sulfoxide are not reduced. Catalytic effects of 2,2′-azobis(2-methylpropionitrile) and of triphenylborine were studied.

The purpose of this investigation is to report on the use of triphenyltin hydride as a reducing agent for sulfur functions. Only three previous reports in this area have been made: J. G. Noltes and G. J. M. van der Kerk have reported that allyl mercaptan is converted to propylene while triphenyltin hydride is converted to bis(triphenyltin) sulfide[5] and also that vinyl sulfone and sulfoxide[6] are reduced; Lorenz and Becker have reported that 1-naphthyl and phenyl isothiocyanates are converted to the corresponding aryl isocyanide and N-methylarylamine.[7] The reductions attempted here include aromatic and aliphatic mercaptans and related compounds, a sulfone and a sulfoxide, a sulfinic acid and a sulfonic acid and certain of their derivatives, and carbon disulfide and hydrogen sulfide.

The Aromatic C–S Bond.—No aromatic C–S bond was cleaved by triphenyltin hydride. Thus, neither diphenyl sulfide nor thianthrene reacted. Phenyl disulfide did react, but only to give triphenyltin phenyl sulfide, reduction having taken place only at the S–S bond (eq. 1). Thiophenol and 2-thionaphthol reacted,

$$C_6H_5SSC_6H_5 + 2(C_6H_5)_3SnH \longrightarrow 2(C_6H_5)_3SnSC_6H_5 + H_2 \quad (1)$$

but only at the S–H bond, producing the corresponding triphenyltin aryl sulfide and hydrogen (eq. 2).

$$ArSH + (C_6H_5)_3SnH \longrightarrow ArSSn(C_6H_5)_3 + H_2 \quad (2)$$

$$Ar = C_6H_5,\ \text{2-naphthyl}$$

Benzenesulfenyl chloride reacted spontaneously to give triphenyltin phenyl sulfide in yields as high as 95% (eq. 3).

$$C_6H_5SCl + 2(C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnCl + (C_6H_5)_3SnSC_6H_5 + H_2 \quad (3)$$

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[4] To whom inquiries should be directed.

[5] Reports of Tin Research Institute, "Functionally Substituted Organotin Compounds," 1958, pp. 73, 115.

[6] J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959). In this report the products of the reduction were not established.

[7] D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **28**, 1707 (1963).

In comparison with these results, lithium aluminum hydride ($LiAlH_4$) cleaves disulfides, but also does not hydrogenolyze the aromatic C–S bond.[8,9] In contrast to the reactions cited for thiophenol and 2-thionaphthol, lithium aluminum hydride does not react. *p*-Toluenesulfenyl chloride reacts with lithium aluminum hydride to give the disulfide in 89% yield.[10]

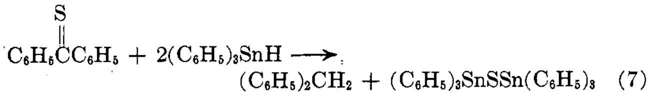
The Aliphatic C–S Bond.—Benzyl disulfide reacted with triphenyltin hydride to give bis(triphenyltin) sulfide, toluene, hydrogen sulfide, and benzyl mercaptan, thus demonstrating that the benzyl C–S bond was cleaved (eq. 4).

$$(C_6H_5CH_2S)_2 + (C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + C_6H_5CH_3 + \underset{\text{(trace)}}{C_6H_5CH_2SH} + H_2S \quad (4)$$

Benzyl mercaptan reacted to give toluene, hydrogen sulfide, and bis(triphenyltin) sulfide (eq. 5). The C–S bond of benzyl sulfide also was cleaved to give toluene and bis(triphenyltin) sulfide (eq. 6). Thiobenzophenone was decolorized at room temperature and then, after heating at 145° for 4 hr., was converted to diphenylmethane (eq. 7).

$$2C_6H_5CH_2SH + 2(C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + 2C_6H_5CH_3 + H_2S \quad (5)$$

$$C_6H_5CH_2SCH_2C_6H_5 + (C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + C_6H_5CH_3 \quad (6)$$



$$C_6H_5\overset{\overset{\displaystyle S}{\|}}{C}C_6H_5 + 2(C_6H_5)_3SnH \longrightarrow (C_6H_5)_2CH_2 + (C_6H_5)_3SnSSn(C_6H_5)_3 \quad (7)$$

Carbon disulfide reacted to give bis(triphenyltin) sulfide, but in poor yield (13%). Other products were not identified. The S–H bond of methyl mercaptan was not cleaved even at 160°.

$$CS_2 + (C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 \quad (8)$$

Acids and Their Derivatives.—The reaction of triphenyltin hydride and benzenesulfonic acid takes place rapidly to give triphenyltin benzenesulfonate (89%) and hydrogen (eq. 9). The product was characterized by saponification which produced hexaphenylstannoxane and sodium benzenesulfonate (eq. 10 and 11).

$$C_6H_5SO_3H + (C_6H_5)_3SnH \longrightarrow C_6H_5SO_3Sn(C_6H_5)_3 + H_2 \quad (9)$$

$$C_6H_5SO_3Sn(C_6H_5)_3 + NaOH \longrightarrow C_6H_5SO_3Na + (C_6H_5)_3SnOH \quad (10)$$

$$2(C_6H_5)_3SnOH \overset{\text{heat}}{\rightleftharpoons} (C_6H_5)_3SnOSn(C_6H_5)_3 + H_2O \quad (11)$$

With benzenesulfinic acid, triphenyltin hydride produced triphenyltin benzenesulfinate in a vigorous exothermic reaction when no solvent was employed; in benzene as solvent the cessation of effervescence (hydrogen) was used visually to mark the end of the reaction (eq. 12). The yield varied from 75–85%.

$$C_6H_5SO_2H + (C_6H_5)_3SnH \longrightarrow C_6H_5SO_2Sn(C_6H_5)_3 + H_2 \quad (12)$$

The same product was obtained in 85% yield from the reaction of triphenyltin hydride with benzenesulfonyl chloride (eq. 13). In the latter reaction hydrogen and triphenyltin chloride were obtained.

$$C_6H_5SO_2Cl + 2(C_6H_5)_3SnH \longrightarrow C_6H_5SO_2Sn(C_6H_5)_3 + (C_6H_5)_3SnCl + H_2 \quad (13)$$

The question whether the tin is attached to oxygen or to sulfur in triphenyltin benzenesulfinate arose. Spectral evidence was not satisfactory because of the absence of suitable models. The argument that it is formed from either benzenesulfinic acid or benzenesulfonyl chloride loses effectiveness since benzenesulfinic acid may be an intermediate in the reaction. However, sodium hydroxide saponifies the product producing hexaphenylstannoxane and sodium benzenesulfinate, which facts point to a Sn–O rather than a Sn–S bond (eq. 14).

$$2C_6H_5SO_2Sn(C_6H_5)_3 + 2NaOH \longrightarrow 2C_6H_5SO_2Na + [(C_6H_5)_3Sn]_2O + H_2O \quad (14)$$

For comparison, it is of interest that lithium aluminum hydride reduces sulfonyl halides to the corresponding sulfinic acids, or disulfides, or mercaptans depending upon the conditions of the reaction.[8,10]

Miscellaneous Compounds.—Diphenyl sulfone, diphenyl sulfoxide, and methyl *p*-toluenesulfonate were not reduced. In contrast, lithium aluminum hydride is known to convert sulfones and sulfoxides to the corresponding sulfides[11,12]; sulfonate esters are displaced on the alcohol C–O bond to give the hydrocarbon derived from the alcohol and the sulfonic acid.[8]

Recently Kuivila, Menapace, and Warner have reported that 2,2′-azobis(2-methylpropionitrile) catalyzes the hydrogenation of halides.[13] Lorenz, *et al.*,[14] have shown that dibenzoyl peroxide and triphenylborine can also catalyze the hydrogenolysis. A study of the effect of triphenylborine and of 2,2′-azobis(2-methylpropionitrile) was made here as well.

The results are summarized in Table I. With thiophenol, benzyl mercaptan, carbon disulfide, phenyl disulfide, and benzyl disulfide, the yields were appreciably improved using either 2,2′-azobis(2-methylpropionitrile) or triphenylborine. With benzyl disulfide, triphenylborine was more effective than with 2,2′-azobis(2-methylpropionitrile). With methyl mercaptan, reaction took place to give triphenyltin methyl sulfide and hydrogen. Neither catalyst caused the unreactive diphenyl sulfone, diphenyl sulfoxide, methyl *p*-toluenesulfonate, thianthrene, or diphenyl sulfide to react. In considering the positive results, it may again be inferred that, as for the halides,[13,14] the hydrogenolysis reaction with sulfur functions may be catalyzed by cationic or radical catalysts (see below).

Mechanism.—The mechanism of the hydrogenolysis reaction has been examined.[13,14] Kuivila, Menapace, and Warner have claimed a free-radical reaction for catalysis with 2,2′-azobis(2-methylpropionitrile) and have presented a mechanism. Recently,[14] benzoyl peroxide also was shown to catalyze the hydrogenolysis reaction. As an example of a Lewis acid catalyst, triphenylborine was shown to catalyze the reaction for

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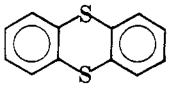
TABLE I

HYDROGENOLYSIS WITH TRIPHENYLTIN HYDRIDE

	Conditions				% yield		
Reactants	Temp., °C.	Time, hr.	Products	M.p. or B.p., °C.	No catalyst	AIBN[a] catalyst	(Ph)$_3$B[b] catalyst
C_6H_5SH	85	2	$(C_6H_5)_3SnSC_6H_5$, H_2	99.4–100.5	67.5	78.9	85.0
$C_6H_5SSC_6H_5$	90	1	$(C_6H_5)_3SnSC_6H_5$, H_2	. . .	88.0	83.5	91.0
$2C_{10}H_7SH$	120	3	$2C_{10}H_7SSn(C_6H_5)_3$, H_2	74.5–76.0	68.0	72.2	78.7
$C_6H_5CH_2SSCH_2C_6H_5$	130	2	$(C_6H_5)_3SnSSn(C_6H_5)_3$, H_2S, $C_6H_5CH_3$	144.0–144.6	11.6	16.8	78.8
CH_3SH	160	3	$(C_6H_5)_3SnSCH_3$, H_2	94.6–95.4	0	46.6	32.8
$C_6H_5CH_2SH$	85	5	$(C_6H_5)_3SnSSn(C_6H_5)_3$, H_2S, $C_6H_5CH_3$	144.0–144.6	0	54.7	60.0
$C_6H_5CH_2SCH_2C_6H_5$	130	3	$(C_6H_5)_3SnSSn(C_6H_5)_3$, $C_6H_5CH_3$	. . .	27.3	38.2	41.6
CS_2	155	6	$(C_6H_5)_3SnSSn(C_6H_5)_3$	. . .	13.0	45.6	54.0
$(C_6H_5)_2SO_2$	130	5			0	0	0
$(C_6H_5)_2SO$	130	5			0	0	0
	130	3			0	0	0
$C_6H_5SC_6H_5$	150	9			0	0	0
$C_6H_5CSC_6H_5$	145	4	$C_6H_5CH_2C_6H_5$	264.5	68.0		
			$(C_6H_5)_3SnSSn(C_6H_5)_2$	114.0–144.6	58.5		
H_2S	130	5	. . .	. . .	25.7		
	150	0.5					
$C_6H_5SO_3H$	Spontaneous		$(C_6H_5)_3SnOSO_2C_6H_5$, H_2	253.0–255.0	88.7		
$C_6H_5SO_2H$	. . .		$(C_6H_5)_3SnOSOC_6H_5$, H_2	228.5–230.5	99.6		
$C_6H_5SO_2Cl$	. . .		$(C_6H_5)_3SnCl$, H_2	103–104	100		
C_6H_5SCl	. . .		$(C_6H_5)_3SnCl$, H_2	. . .	78		
			$(C_6H_5)_3SnSC_6H_5$	99.4–100.5	60		

[a] 2,2′-Azobis(2-methylpropionitrile). [b] Triphenylborine.

halides[14] and, in the present work, for sulfur functions. However, certain new considerations make the assumption of Lewis acid catalysis suspect.

When triphenylborine was first prepared by Krause and Nitsche,[15] it was reported to react rapidly with oxygen. Recently, Kolesnikov,[16-18] Ashikari,[19-21] Welch,[22] Furukawa,[23,24] and Fordham and Sturm[25] have reported that triethylborine or tributylborine will polymerize vinyl monomers and that the reaction is most likely free radical. If the same considerations hold by analogy with triphenylborine, then the catalytic effect we have observed may indeed be simply another free-radical reaction to add to those reported by Kuivila[13] and also by Lorenz and Becker.[14] This point is under further investigation.

Experimental

Phenyl Sulfide.—A mixture of phenyl sulfide (1.8 g., 9.67 mmoles) and triphenyltin hydride (7.5 g., 0.0214 mole) in an ampoule which was sealed *in vacuo* was heated at 150° for 9 hr. Distillation of the reaction mixture afforded only phenyl sulfide, b.p. 296°.

Thianthrene.—Triphenyltin hydride (3.51 g., 0.0100 mole) and thianthrene (1.08 g., 5.00 mmoles) were allowed to react at 130° for 3 hr. with stirring and under nitrogen atmosphere. Thianthrene was isolated quantitatively.

Phenyl Disulfide.—A mixture of triphenyltin hydride (7.0 g., 0.0199 mole) and phenyl disulfide (2.0 g., 9.16 mmoles) was allowed to react in nitrogen atmosphere with stirring at 90° and 1 hr. The mixture solidified when cooled. After recrystallization from *n*-hexane, triphenyltin phenyl sulfide was isolated, m.p. 98.0–99.5°, 7.4 g. (0.0162 mole, 88%).

Thiophenol. 1.—Triphenyltin hydride (7.5 g., 0.0214 mole) and thiophenol (4.0 g., 0.0366 mole) were allowed to react under nitrogen at 85° for 6 hr. Hydrogen was given off during the reaction, and the reaction mixture solidified on cooling. Two recrystallizations from petroleum ether and one from a 1:1 mixture of dioxane–petroleum ether (b.p. 60–70°) gave colorless triphenyltin phenyl sulfide, melting at 92.2–93.0°. After drying *in vacuo* at 80°, it melted at 99.4–100.5° (8.0 g., 0.0174 mole, 81.3%).

Anal. Calcd. for $C_{24}H_{20}SSn$: C, 62.78; H, 4.39; S, 6.98; Sn, 25.85; mol. wt., 459.2. Found: C, 62.80; H, 4.41; S, 6.98; Sn, 25.8; mol. wt., 462 (cryoscopic in benzene).

Thiophenol. 2.—When the above reaction was run at 140° for 3 hr., beginning with triphenyltin hydride (14.0 g., 0.040 mole) and thiophenol (4.0 g., 0.0366 mole), triphenyltin phenyl sulfide was isolated, m.p. 99.4–100.5° (14.0 g., 0.0320 mole, 87%). When the reaction was run at 85° for 2 hr., the yield was 67.5% (12.40 g., 0.0270 mole).

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2-Naphthalenethiol.—Triphenyltin hydride (7.0 g., 0.0199 mole) and 2-naphthalenethiol (3.2 g., 0.020 mole) in 10 ml. of benzene were heated at 120° for 3 hr. Hydrogen was given off during the reaction. After 15 ml. of n-hexane was added to the cooled reaction mixture, triphenyltin 2-naphthyl sulfide precipitated. After recrystallization from n-hexane, it melted at 74.5–76.0° (6.92 g., 0.0136 mole, 68%).

Anal. Calcd. for $C_{28}H_{22}SSn$: C, 66.04; H, 4.36; S, 6.30; Sn, 23.3; mol. wt., 509.3. Found: C, 66.00; H, 4.47; S, 6.39; Sn, 23.2; mol. wt., 515 (ebullioscopic with benzene).

Benzenesulfenyl Chloride.—Benzenesulfenyl chloride[26] was prepared as reported. Triphenyltin hydride (3.2 g., 9.12 mmoles) was added dropwise to a stirred, ice-cooled solution of benzenesulfenyl chloride (1.25 g., 8.64 mmoles) in 10 ml. of n-hexane. Hydrogen was given off violently and the red color discharged. At this point there was no observable change when another drop of triphenyltin hydride was added. A small sample indicated thiophenol by vapor phase chromatography (v.p.c.). An infrared band at 2550 cm.$^{-1}$ also indicated the presence of thiophenol. Evaporation of another sample to dryness afforded triphenyltin chloride. Another portion of triphenyltin hydride (5.3 g., 0.0151 mole) was added to the above reaction mixture which was heated in an oil bath at 130° for 1 hr. Hydrogen was given off during the reaction. When the mixture cooled, a precipitate was formed. The filtered solid was extracted with ethanol and the residue recrystallized from n-hexane to give triphenyltin phenyl sulfide, m.p. 99.4–100.6° (3.1 g., 6.74 mmoles, 78%). Evaporation of the ethanolic extract *in vacuo* yielded triphenyltin chloride, m.p. 103–104° (2.0 g., 5.2 mmoles, 60%). Other runs gave up to 95% of the sulfide.

α-Tolyl Disulfide.—Triphenyltin hydride (15.0 g., 0.0427 mole) and α-tolyl disulfide (2.46 g., 0.0100 mole) were sealed into an evacuated ampoule and heated at 160° for 3 hr. The cooled product mixture was extracted with 5 ml. of n-hexane. Toluene and benzyl mercaptan were found in the hexane extract by infrared spectrum and v.p.c. analysis. Hydrogen sulfide odor was detected and confirmed by acidified lead acetate test. The residual solid, which remained after the hexane extraction, was dissolved in ethyl ether, then filtered by suction, and evaporated to dryness. A white crystalline material was obtained. After two recrystallizations from a 1:3 mixture of benzene–n-hexane, bis(triphenyltin) sulfide was obtained (6.0 g., 8.20 mmoles, 82%), m.p. 144.0–144.6°. When a similar reaction was run at 130° for 2 hr., the yield was 11.6%.

Benzyl Mercaptan.—At 85° triphenyltin hydride did not reduce benzyl mercaptan. When triphenyltin hydride (14.0 g., 0.0399 mole) and benzyl mercaptan (4.9 g., 0.394 mole) were held at 160° for 3 hr. with stirring, hydrogen sulfide was evolved. Toluene was identified by its vapor phase chromatogram from a sample of the reaction mixture injected into the v.p.c. unit and by its infrared spectrum. Upon cooling, the reaction mixture solidified and the solid was recrystallized three times from petroleum ether. Bis(triphenyltin) sulfide was isolated (3.0 g., 4.1 mmoles, 20.8%), m.p. 144.0–144.5° (lit.[27] m.p. 141.5–143°).

Benzyl Sulfide.—A mixture of benzyl sulfide (2.14 g., 0.0100 mole) and triphenyltin hydride (3.51 g., 0.0100 mole) was heated at 130° for 3 hr. n-Hexane was added and crystallization took place when cooled. Bis(triphenyltin) sulfide was isolated (1.00 g., 1.365 mmoles, 27.3%), m.p. 144.0–144.5°.

Thiobenzophenone.—A mixture of triphenyltin hydride (8.0 g., 0.0228 mole) and thiobenzophenone[28] (1.4 g., 7.0 mmoles) was heated at 145° for 4 hr. It was extracted with n-pentane which yielded diphenylmethane (0.80 g., 4.76 mmoles, 68%) on evaporation of the pentane *in vacuo*. Recrystallization of the residue afforded bis(triphenyltin) sulfide (3.0 g., 4.1 mmoles, 58.5%), m.p. 144.0–144.5°.

Carbon Disulfide.—A mixture of triphenyltin hydride (14.0 g., 0.0300 mole) and carbon disulfide (25.0 g., 0.3283 mole) was refluxed at 155° for 6 hr. The mixture turned brown. When cooled, it solidified after 15 ml. of n-hexane was added. Bis(triphenyltin) sulfide was isolated, and, after recrystallization with n-hexane, had m.p. 144.0–145.0° (2.85 g., 3.89 mmoles, 13%).

Methanethiol.—A mixture of triphenyltin hydride (3.5 g., 0.0100 mole) and methanethiol (1.28 g., 0.0400 mole) in an evacuated ampoule was heated at 160° for 3 hr. Methyl mercaptan was left unchanged.

Benzenesulfonic Acid.—Triphenyltin hydride (3.51 g., 0.0100 mole) in 10 ml. of benzene was added with stirring to benzenesulfonic acid (1.76 g., 0.0100 mole) in an ice bath. No apparent change was observed for 25 min. When the mixture was allowed to warm to room temperature, hydrogen bubbled out and a white curdy precipitate formed. A total of 30 ml. of benzene was added during the reaction in order to ease stirring. The product on filtration by suction afforded a solid, which, after recrystallization with dioxane, melted at 253.0–255.0° (4.52 g., 8.87 mmoles, 88.7%).

Anal. Calcd. for $C_{24}H_{20}O_3SSn$: C, 56.77; H, 3.97, S, 6.43; Sn, 23.38. Found: C, 56.68; H, 4.04; S, 6.54; Sn, 22.85.

Chemical Analysis.—Two grams (3.94 mmoles) of the above product was heated with stirring with 35 ml. of 25% sodium hydroxide at 100° for 2 hr. After the solution cooled, it was filtered by suction, and the hexaphenylstannoxane collected was recrystallized from ether, m.p. 120–122° dec. (1.3 g., 1.82 mmoles 92.4%). The alkaline filtrate was acidified with 1:1 aqueous sulfuric acid, then titrated with 25% sodium hydroxide until the solution was just basic, and evaporated to dryness *in vacuo*. The white solid, which remained, was extracted with ethanol. Evaporation of the ethanol gave a solid whose infrared spectrum was superimposable on that of sodium benzenesulfonate.

Benzenesulfinic Acid. 1.—Triphenyltin hydride (3.51 g., 0.0100 mole) and benzenesulfinic acid (1.42 g., 0.0100 mole) were mixed in a 25-ml. flask. A vigorous and exothermic reaction accompanied by hydrogen evolution was observed. The reaction mixture solidified and was recrystallized twice from 1:1 mixture of chloroform–ethanol to afford 3.9 g. (7.94 mmoles, 79.4%) of colorless product, m.p. 228.5–230.5°.

Benzenesulfinic Acid. 2.—Triphenyltin hydride (1.540 g., 4.490 mmoles) was injected through a syringe to a solution of benzenesulfinic acid (0.3280 g., 2.310 mmoles) in 20 ml. of benzene with stirring. Hydrogen, 53.4 ml. (cor.) (calcd.[29] 52.65 ml.) was collected. Triphenyltin benzenesulfinate (1.1296 g., 2.300 mmoles, 99.6%) was isolated.

Anal. Calcd. for $C_{24}H_{20}O_2SSn$: C, 58.69; H, 4.10; S, 6.53; Sn, 24.16. Found: C, 58.67; H, 4.04; S, 6.40; Sn, 24.50.

Degradation of Triphenyltin Benzenesulfinate.—Triphenyltin benzenesulfinate (3.0 g., 6.12 mmoles) of 30 ml. of 25% sodium hydroxide solution were allowed to stand with stirring at 100° in an open flask for 2 hr. Bis(triphenyltin) oxide was obtained on suction filtration of the reaction mixture. After recrystallization twice from ether, it melted at 120–122° dec. (lit.[30] m.p. 124° for hexaphenylstannoxane) (1.8 g., 2.51 mmoles, 82.3%). The filtrate from above was acidified with dilute (1:1) hydrochloric acid, and then extracted twice with ether. The ethereal extract, after being washed with water, was evaporated to dryness *in vacuo* giving benzenesulfinic acid, m.p. 79.5–81.7° (lit. m.p. 82.5° for benzenesulfinic acid) (0.210 g., 15 mmoles, 15%).

Benzenesulfonyl Chloride. 1.—Triphenyltin hydride (7.0 g., 0.0200 mole) was added dropwise to benzenesulfonyl chloride (1.76 g., 0.0100 mole). Within 2 min. after the addition, violent effervescence occurred and the temperature of the reaction mixture rose to 120°. The effluent gas did not redden wet litmus paper but gave a "pop" test. When it had cooled to room temperature, 1.02 g. (2.91 mmoles) of triphenyltin hydride was added, and no further reaction was noted. About 10 ml. of n-pentane was added and the mixture was filtered by suction to give, after washing the solid with 5 ml. of n-pentane, 8.1 g. of crystalline solid starting to melt at 95°. There was no observable solubility of the solid in hot water. The crystalline product was extracted with ether and evaporation of the extract to dryness yielded triphenyltin chloride (3.50 g., 9.10 mmoles, 91%), m.p. 103–104° (recrystallized with n-hexane). The residue after washing with ethanol afforded triphenyltin benzenesulfinate (4.20 g., 8.56 mmoles, 85%), m.p. 228.5–230.5° (recrystallized).

Benzenesulfonyl Chloride. 2.—Triphenyltin hydride (3.0800 g., 8.600 mmoles) was injected through a syringe to a solution of benzenesulfonyl chloride (0.5142 g., 2.900 mmoles) in 10 ml. of benzene with stirring. Hydrogen,[31] 66.8 ml. (cor.) (calcd.[32]

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[26] H. Lecher and F. Holschneider [*Ber.*, **57**, 757 (1924)] report b.p. 58–60° (3 mm.), n^{30}D1.6132, red liquid.

[27] J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959).

[28] F. H. Westheimer, R. H. Abeles, and R. F. Hutton, *J. Am. Chem. Soc.*, **79**, 712 (1957).

[29] This value is obtained by reaction 12.

[30] H. Gilman and L. A. Gist, Jr., *J. Org. Chem.*, **22**, 250 (1957).

[31] The absence of hydrogen chloride was tested by wet litmus paper.

[32] Value is based on reaction 13.

TABLE II

Phenyl sulfone		Triphenyltin hydride				
g.	mmoles	g.	mmoles	Temp., °C.	Time, hr.	Other conditions
2.0	9.16	5.0	14.2	135	3	Under nitrogen
...	...	6.5	18.5	160	2	...
...	...	...	...	130	1	...
1.5	6.87	4.8	13.7	130	5	*in vacuo*
1.48	6.78	11.9	34.0	130	1	*in vacuo*
				180	0.5	...

65.2 ml.) was collected. Triphenyltin chloride (1.120 g., 2.910 mmoles; theoretical, 1.118 g., 2.900 mmoles) and triphenyltin benzenesulfinate (1.412 g., 2.88 mmoles; theoretical, 1.424 g., 2.900 mmoles) were isolated separately.

Phenyl Sulfone.—A mixture of phenyl sulfone and triphenyltin hydride was heated in an evacuated ampoule as shown in Table II. To the cooled product, 25 ml. of ether was added and then filtered by suction. The filtrate on evaporation to dryness afforded a white solid which, after recrystallization with *n*-hexane, melted at 124.5–125.5° (lit. m.p. 125° for phenyl sulfone). The amount of phenyl sulfone reisolated was nearly 100% in all cases.

Phenyl Sulfoxide.—A mixture of triphenyltin hydride (7.0 g., 0.020 mole) and phenyl sulfoxide (2.0 g., 9.9 mmoles) was sealed in an evacuated ampoule and was heated at 130° for 5 hr. To the cooled product, 20 ml. of *n*-hexane was added and the mixture was filtered by suction immediately. The filtrate on standing yielded phenyl sulfoxide (2.0 g., 9.9 mmoles), m.p. 69.0–70.4°.

Methyl *p*-Toluenesulfonate.—The title compound was not reduced at 80° for 1 hr. using a ratio of 4:1 triphenyltin hydride–ester. When 11.6 g. (0.0330 mole) of triphenyltin hydride and 0.87 g. (4.72 mmoles) of methyl *p*-toluenesulfonate (7:1) were heated at 150° for 7 hr. and then at 180° for 0.5 hr. in a sealed evacuated ampoule, again there was no hydrogenation.

Reactions Catalyzed by 2,2′-Azobis(2-methylpropionitrile) or Triphenylborine Thiophenol.—Triphenyltin hydride (3.51 g., 0.0100 mole), thiophenol (1.10 g., 0.0100 mole), and 2,2′-azobis-(2-methylpropionitrile) (1.6 mg., 0.10 mmole) were mixed, then heated at 85° for 2 hr. under nitrogen. Triphenyltin phenyl sulfide (3.62 g., 7.89 mmoles, 78.9%) was isolated. When using triphenylborine as catalyst the above reaction under similar conditions yielded phenyl triphenyltin sulfide (3.90 g., 8.50 mmoles, 85.0%).

Benzyl Mercaptan.—A mixture of triphenyltin hydride (3.51 g., 0.0100 mole), benzyl mercaptan (1.24 g., 0.0100 mole), and 2,2′-azobis(2-methylpropionitrile) (1.6 mg., 0.100 mmole) was heated at 85° for 5 hr. under nitrogen. Bis(triphenyltin) sulfide (2.00 g., 2.733 mmoles, 54.7%) was isolated. When using triphenylborine as catalyst the above reaction under similar conditions yielded bis(triphenyltin) sulfide (2.20 g., 3.00 mmoles, 60%).

Benzyl Sulfide.—Triphenyltin hydride (3.51 g., 0.0100 mole), benzyl sulfide (2.14 g., 0.0100 mole), and 2,2′-azobis(2-methylpropionitrile) (1.6 mg., 0.100 mmole) were allowed to react at 130° for 3 hr. under nitrogen. Bis(triphenyltin) sulfide (1.40 g., 1.912 mmoles, 38.2%) was isolated. When using triphenylborine as catalyst the above reaction under similar conditions yielded bis(triphenyltin) sulfide (1.52 g., 2.078 mmoles, 41.6%).

Phenyl Disulfide.—A mixture of triphenyltin hydride (7.50 g., 0.0213 mole), phenyl disulfide (2.18 g., 0.0100 mole), and 2,2′-azobis(2-methylpropionitrile) (3.2 mg., 0.200 mmole) was heated at 90° for 1 hr. under nitrogen. Triphenyltin phenyl sulfide (7.66 g., 0.0167 mole, 83.5%) was isolated. When the above reaction was run under similar conditions using triphenylborine as catalyst, phenyl triphenyltin sulfide (8.38 g., 0.0182 mole, 91.0%) was isolated.

Carbon Disulfide.—A mixture of triphenyltin hydride (3.51 g., 0.0100 mole), carbon disulfide (7.60 g., 0.1000 mole), and 2,2′-azobis(2-methylpropionitrile) (1.6 mg., 0.100 mmole) was heated at 155° for 6 hr. Bis(triphenyltin) sulfide (1.67 g., 2.280 mmoles, 45.6%) was isolated. When the above reaction using triphenylborine as catalyst was run under similar conditions, bis(triphenyltin) sulfide (2.00 g., 2.730 mmoles, 54.6%) was obtained.

Benzyl Disulfide.—Triphenyltin hydride (7.01 g., 0.0200 mole), benzyl disulfide (1.23 g., 5.000 mmoles), and 2,2′-azobis-(2-methylpropionitrile) (2.3 mg., 0.2000 mmole) were heated at 130° for 2 hr. under nitrogen. Bis(triphenyltin) sulfide (1.20 g., 1.64 mmoles, 16.8%) was isolated. When the above reaction using triphenylborine as catalyst was run under similar conditions, bis(triphenyl) sulfide (5.62 g., 7.88 mmoles, 78.8%) was isolated.

Methyl Mercaptan.—A mixture of triphenyltin hydride (3.51 g., 0.0100 mole), methyl mercaptan (1.28 g., 0.0400 mole), and 2,2′-azobis(2-methylpropionitrile) (1.6 mg., 0.100 mmole) in a sealed evacuated Carius tube was heated at 160° for 3 hr. Triphenyltin methyl sulfide (1.85 g., 4.660 mmoles, 46.6%), m.p. 94.6–95.4° was isolated. When the above reaction was run using triphenylborine as catalyst under similar conditions triphenyltin methyl sulfide (1.30 g., 3.280 mmoles, 32.8%) was obtained.

Anal. Calcd. for $C_{19}H_{18}SSn$: C, 57.45; H, 4.58; S, 8.07; Sn, 29.90; mol. wt., 397.1. Found: C, 57.23; H, 4.77; S, 7.88; Sn, 30.03; mol. wt., 423 (ebullioscopic in CCl_4).

Diphenyl Sulfone, Diphenyl Sulfoxide, Methyl *p*-Toluenesulfonate, Thianthrene, and Diphenyl Sulfide.—Their reactions with triphenyltin hydride were repeated as described in the preceding reactions with the exception of using 2,2′-azobis(2-methylpropionitrile) or triphenylborine as catalyst. Neither catalyst had any effect on the reaction as described previously.