alkali. A copper-containing product was extracted from the residue with hot ammonia, and was analyzed for the content of copper and acetate groups. Found (%): Cu, 52.24; OAc, 46.68. CuOAc. Calculated (%): Cu, 52.03; OAc, 47.97. The remaining nonmelting precipitate contained (%): Bi, 74.59; OAc, 20.28. $C_2H_3O_3Bi$. Calculated (%): Bi, 73.59; OAc, 20.77.

The reactions of Bu_3Bi with other alcohols (see Table 1) and the reactions of $(PhCH_2)_3Bi$ with alcohols were carried out in a similar way.

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Reactions of hexamethylditin and trimethyltin sulfide with *N*-thio-derivatives of phthalimide

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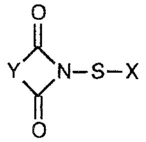
The initial formation of organotin derivatives with Sn—S—N bonds in heterolytic reactions of hexamethylditin or trimethyltin sulfide with *N*-(chlorothio)phthalimide is suggested. Subsequent interaction of these compounds with sulfenyl chloride affords *N,N'*-thio- or *N,N'*-dithiobisphthalimide. Homolytic reaction of hexamethylditin with *N,N'*-dithiobisphthalimide also occurs *via* an organotin intermediate, which, in the absence of a nucleophilic reagent, eliminates sulfur and converts into *N*-trimethylstannylphthalimide.

Key words: hexamethylditin; trimethyltin sulfide; *N*-(chlorothio)phthalimide; *N,N'*-dithiobisphthalimide; reactivity.

In a continuation of the investigations of the reactions of *N*-trialkylstannylimide[1—4] and organotin sulfides[5] containing labile Sn—N and Sn—S bonds we have studied the possibility of synthesizing novel organotin compounds with the Sn—S—N bond sequence of the following general structure:



X = R_3Sn; Y = CH_2CH_2, o-C_6H_4

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Table 1. Products of the reaction of organotin compounds with *N*-thiophthalimide derivatives

Run	Reagents	Reaction conditions (reagent ratios)	Yield (mole/mole of initial compound)							
			Me_6Sn_2	Me_3SnCl	$PhtNSnMe_3$	$(Me_3Sn)_2S$	$(PhtN)_2S_n$ $n = 1$	$n = 2$	$n = 3$	S
1	Me_6Sn_2, PhtNSCl	0°C, PhMe (1 : 1)	0.50	0.95	—	—	—	0.47	—	—
2	Me_6Sn_2, PhtNSCl	0°C, PhMe (1 : 2)	—	1.96	—	—	—	0.89	—	—
*3**	$(Me_3Sn)_2S$, PhtNSCl	20°C, PhMe (1 : 1)	—	1.30	0.64	—	—	0.16	0.17	1.25
4	Me_6Sn_2, $(PhtN)_2S_2$	130°C, in melt (1 : 1)	—	—	1.60	0.20	0.20	—	—	1.55
5	Me_6Sn_2, $(PhtN)_2S_2$	20°C, CH_2Cl_2 (1 : 1)	Not determined	—	—	0.45	0.48	0.48	—	—

* Product yields given as moles per 1 mole reacting **3**.

Organic analogs of these compounds (X = Alk, Ar) have been described previously,[6] some of them are used as insecticides and fungicides.[6,7]

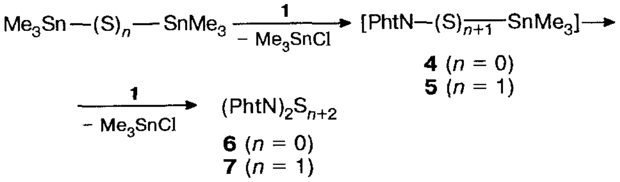
Results and Discussion

N-(Chlorothio)phthalimide (phthalimidosulfenyl chloride, PhtNSCl) (**1**), the chlorine atom in which is very active in nucleophilic substitution,[8] reacts readily with hexamethylditin, $(Me_3Sn)_2$ (**2**), and trimethyltin sulfide, $(Me_3Sn)_2S$ (**3**). The products of the reactions studied in this work are listed in Table 1.

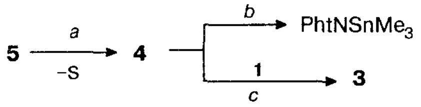
When equimolar amounts of **1** and **2** are used, sulfenyl chloride is consumed completely, while only half of the distannane **2** is consumed, irrespective of the order of mixing the reagents (see Table 1, run *1*). The complete conversion of **2** occurs with a twofold molar excess of sulfenyl chloride (run *2*). The composition and the ratio of the products of these reactions, in which the material balance is close to theoretical, correspond to a two-step process involving the initial formation of *N*-(trimethylstannylthio)phthalimide (**4**) followed by its reaction with the sulfenyl chloride added (Scheme 1, $n = 0$). Then, the only sulfur-containing product is *N*,*N'*-dithiobisphthalimide (**6**). A similar reaction has been observed as a side process in the synthesis of esters of sulfenic acids or sulfenamides.[9]

The reaction of compound **1** with compound **3** (see Table 1, run *3*) to give *N*,*N'*-trithiobisphthalimide (**7**) also proceeds according to Scheme 1 ($n = 1$) with the intermediate formation of **5**. In this case, sulfenyl chloride **1** is converted completely, while sufide **3** reacts only partly (75 %). This process is more complicated than that with distannane **2** as follows from the presence of *N*-trimethylstannylphthalimide, bisphthalimide **6**, and elemental sulfur in the reaction products. The formation of these products can be explained by competing transformations of intermediate **5** according to Scheme 2, which involve the exhaustive desulfurization of **5** (routes *a* and *b*) and the reaction of the resulting compound **4** with sulfenyl chloride **1** (routes *a* and *c*).

Scheme 1



Scheme 2

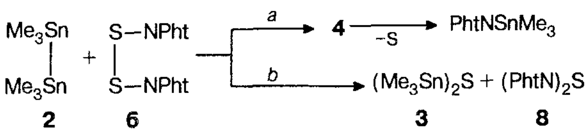


On the basis of the results obtained it may be concluded that the initially formed organotin compounds **4** or **5** containing the expected chain of N—S_n—Sn bonds are decomposed by the next portions of sulfenyl chloride **1** before the latter can react with the starting **2** or **3**. In order to preclude this process we carried out the reaction of compound **2** with bisphthalimide **6** under homolytic conditions, similar to those for the oxidation of distannanes or trialkyl- (or dialkyl)tin sulfides with acyl peroxides.[10]

Compounds **3** and **6** do not interact in toluene at 0 °C. Under more drastic conditions (without a solvent, in a melt (see Table 1, run *4*)), the reaction mixture melted at 125—130 °C and solidified after 1—2 min at the same temperature to form a crystalline mass. As can be seen from the data obtained, the yields of the two pairs of products (*N*-trimethylstannylphthalimide—sulfur and **3**—*N*,*N'*-thiobisphthalimide) are nearly equimolar.

We believe that these two pairs are formed by two possible pathways (*a* and *b*) for the reaction under study (Scheme 3). Route *a* is predominant (80 % of the overall process), however, the resulting compound **4** decomposes under the reaction conditions with the elimination of sulfur. Route *b*, the proportion of which is 20 %, is the sulfurization of $(Me_3Sn)_2$. In this case, compound **6** acts as the source of the sulfur atom.[11,12]

Scheme 3



In a methylene chloride solution, the degree of conversion of the starting compounds **2** and **6** was 50 % after 10 days (see Table 1, run *5*). The reaction mixture consisted of only two products, sulfide **3** and compound **8**, in equimolar amounts. The reaction under these conditions can obviously be described only by pathway *b* of Scheme 3.

Experimental

Synthesis and purification of compounds **1**, **2**, and also **6** and **8** were carried out according to the known procedures[13–15] in evacuated glass ampules using absolute solvents. IR spectra were recorded on a Perkin-Elmer-577 spectrophotometer (thin film in vaseline oil or KBr). Quantitative determination of sulfur was in all cases duplicated by combustion analysis according to Schoeniger.

The reaction of $(Me_3Sn)_2$ with *N*-(chlorothio)phthalimide. ***A.*** A solution of 3.27 g of distannane **2** in 5 mL of toluene was added dropwise at 0 °C to a stirred suspension of 2.14 g (10 mmol) of compound **1** in 25 mL of toluene. The reaction mixture decolorized, and a precipitate formed. The mixture was heated to 20 °C, stirred for 30 min, and filtered to give 1.63 g (4.5 mmol) of compound **6**, m.p. 208—215 °C (from chloroform) (m.p. of the mixture with an authentic sample was undepressed). Found: S, 17.63 %. $C_{16}H_8N_2O_4S_2$. Calculated: S, 17.98 %. Volatile products from the filtrate were evaporated *in vacuo* at 60 °C and recondensed into a trap cooled with liquid nitrogen. An additional 0.04 g (0.2 mmol) of compound **6** was obtained by extraction with chloroform. The condensate (38.77 g) contained trimethyltin chloride (determined by alkaline titration in the presence of phenolphthalein), yield 1.89 g (9.5 mmol). Determination of the unchanged compound **2** was performed as follows. Benzoyl peroxide (1.5 g) was dissolved in the condensate (29.7 g), and the solution was left overnight. Then the solvent was evaporated *in vacuo* at 30 °C, and the nonvolatile residue was treated with 20 mL of hot hexane and filtered. The filtrate was cooled to 5 °C, and the precipitated crystals were purified by vacuum sublimation at 60 °C (0.5 Torr) to give 2.21 g of trimethyltin benzoate, m.p. 125—127 °C (equal to m.p. of a mixture with an authentic sample). The overall yield of trimethyltin benzoate was 2.84 g (10 mmol), which corresponded to 1.63 g (5 mmol) of compound **2**.

B. A suspension of 2.74 g (12.8 mmol) of phthalimide **1** in 30 mL of toluene was added at 0 °C in small portions to a solution of 4.19 g (12.8 mmol) of compound **2** in 10 mL of toluene. Subsequent workup of the reaction mixture was carried out as described above to afford 2.27 g (6.4 mmol) of compound **6** (yield 100 %) and 2.5 g (12.6 mmol) of trimethyltin chloride (98 %).

The reaction of compound **2** with **1** was carried out at a 1 : 2 ratio between the reactants in a similar way.

The reaction of $(Me_3Sn)_2S$ with *N*-(chlorothio)phthalimide. A suspension of 2.95 g (13.8 mmol) of compound **1** in 45 mL of toluene was added portionwise to a vigorously shaken solution of 4.96 g (13.8 mmol) of sulfide **3** in 15 mL of toluene. The reaction mixture was shaken for a few minutes until it became completely homogeneous and left overnight. The precipitate (0.85 g) was separated by filtration, and extraction with hot heptane (40 mL, 60 °C) afforded 0.17 g of a mixture of *N*-trimethylstannylphthalimide (0.16 g), m.p. 148—152 °C (coincides with that of a mixture with an authentic sample), and elemental sulfur (0.01 g). The mixture was separated by extraction with cold acetone. The precipitate remaining undissolved was treated with cold acetone to separate elemental sulfur (0.02 g) from compound **7**, m.p. 156—170 °C. Found (%): C, 49.51; H, 2.50; S, 24.35. $C_{16}H_8N_2O_4S_3$. Calculated (%): C, 49.48; H, 2.06; S, 24.74. The filtrate was concentrated *in vacuo* at 50 °C, and the volatile products were recondensed into a trap cooled with liquid nitrogen. The nonvolatile residue was treated with boiling hexane (3×50 mL) and filtered; treatment with cold acetone separated the precipitate into compound **6** (0.58 g), m.p. 218—228 °C (from chloroform) and an unidentified nonmelting compound (0.31 g). The hexane solution was evaporated *in vacuo* at 50 °C into a trap cooled with liquid nitrogen. The nonvolatile residue was separated by treatment with cold acetone (30 mL) into elemental sulfur (0.38 g) and *N*-trimethylstannylphthalimide (1.88 g), m.p. 149—153 °C (the same as that of a mixture with an authentic sample). The liquids collected in the traps were combined. The resulting solution was analyzed for the content of trimethyltin chloride (by alkaline titration in the presence of phenolphthalein) and of compound **3** (by treating a weighed portion of the solution with conc. HCl and absorption of the hydrogen sulfide evolved by a solution of a mixture of cadmium and zinc acetates).[16] The yield of trimethyltin chloride was 2.67 g, that of compound **3** was 1.27 g.

The reaction of $(Me_3Sn)_2$ with compound 6. ***A.*** A mixture of 2.51 g (7.1 mmol) of compound **6** and 2.31 g (7.1 mmol) of distannane **2** was heated for several minutes at 130 °C until the molten mass solidified. The mixture was treated with 60 mL of cold acetone, 0.81 g of the undissolved precipitate was filtered off and dissolved in 30 mL of hot chloroform, and 0.35 g of elemental sulfur was isolated by slow evaporation. From the concentrated solution 0.43 g of compound **8**, which did not melt up to 300 °C (see Ref. 15), was obtained. The acetone solution was concentrated *in vacuo* at ~20 °C, and the nonvolatile residue was extracted with 80 mL of boiling hexane. Cooling the solution to 5 °C gave 3.53 g of *N*-trimethylstannylphthalimide, m.p. 148—151 °C (coincides with that of a mixture with an authentic sample). The hexane mother liquor contained sulfide **3** (0.48 g).

B. A solution of 1.37 g (4.2 mmol) of distannane **2** and 1.49 g (4.2 mmol) of compound **6** in 90 mL of dichloromethane was allowed to stand for 10 days at ~20 °C. The solvent was evaporated *in vacuo* at ~20 °C into a trap cooled with liquid nitrogen. The nonvolatile residue was treated with

50 mL of cold acetone. Elemental sulfur insoluble in acetone was absent. Acetone was evaporated *in vacuo* into a trap and combined with the distilled dichloromethane. In this mixture, the content of compound **3** (0.68 g) was determined by the above procedure. The residue after removing acetone (1.37 g) was a mixture of the starting reactant **6** and product **8** melting at a temperature between 180 and 274 °C. Judging by the content of sulfur, the mixture consisted of 47 % compound **8** and 53 % compound **6**. The calculated yield of compound **8** was 0.65 g; the degree of conversion of the starting compounds was estimated from the amount of compound **6** recovered.

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Visualization of solid-state reactions of anisylmercury and triphenylphosphinegold derivatives of phthaleins with bromides

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The visualization of solid-state reactions of bis-*O*-metallated phenolphthaleins and xylenolphthaleins (M = HgC_6H_4OMe, $AuPPh_3$) with bromides, which has been discovered for the first time, was studied by IR and electronic reflectance spectroscopy. The appearance of intense coloration (purple, violet, or blue) after short-term grinding of colorless or faintly colored solid samples with salts is due to their ionization with the formation of ion pairs or dianions depending on the nature of the counterion. The reaction affects only a small fraction of the molecules in the surface layers of the metallocomplexes.

Key words: phthaleins; electronic reflectance spectroscopy; IR spectroscopy.

The present work describes for the first time the visualization phenomenon of reactions of a new class of metal-containing indicators (ligandochromes) with solid bromides, which was established by us and named solid ligandochromism.[1,2]

Bis-*O*-metallated phthaleins, *p*-anisylmercury and

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