Reaction of Organic Tin(II) Compound with Phenyl Isothiocyanate and Carbon Disulfide

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(Received December 22, 1977)

Reaction of organic tin(II) compounds, $Sn(OR)_2$[R=C_2H_5, $CH_2CH_2N(CH_3)_2$, C_6H_5, *o*-$CH_3C_6H_4$], with phenyl isothiocyanate and carbon disulfide have been investigated. The reaction of di(ethoxo)tin(II) with phenyl isothiocyanate in benzene at room temperature gave the corresponding addition product. The reaction at 80—81 °C however gave diethyl *N*-phenylcarbonimidate. Phenyl isothiocyanate reacted exothermically with bis[2-(dimethylamino)ethoxo]tin(II) to yield the 1:1 addition product. In the reaction with bis(2-methylphenoxo)-tin(II), a compound containing one molecule of phenyl isothiocyanate per two molecules of the tin(II) compound was isolated, but the reaction with di(phenoxo)tin(II) did not occur. Di(ethoxo)tin(II) reacted with carbon disulfide to give diethyl thiocarbonate, diethyl carbonate, and tetraethyl orthocarbonate. Bis(*o*-methylphenoxo)-tin(II) and di(phenoxo)tin(II) however did not react with carbon disulfide.

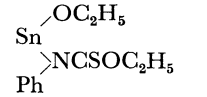
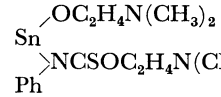
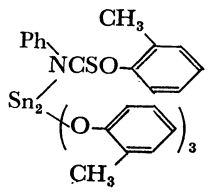
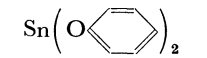
Since P. G. Harrison and J. J. Zuckerman reported the reaction between di(methoxo)tin(II) and multiple-bond compounds,[1] there have been many investigations concerning the reactivity of organic and organotin(II) compounds.[2-6] The reaction of alkylalkoxotin(IV) with phenyl isothiocyanate led to the corresponding *S*-stannyl derivatives[7-8] and di(methoxo)tin(II) reacted with phenyl isothiocyanate to give the corresponding *N*-stannyl derivative.[1] In the reaction of alkylalkoxotin-(IV) and di(ethoxo)tin(II) with carbon disulfide, S. Sakai and coworkers reported that alkylalkoxotin(IV) reacted with carbon disulfide to give the corresponding orthocarbonate, dithiocarbonate or carbonate. However di(ethoxo)tin(II) did not react.[9]

In this paper, the reaction of organic tin(II) compounds, $Sn(OR)_2$[R=C_2H_5, $CH_2CH_2N(CH_3)_2$, C_6H_5, *o*-$CH_3C_6H_4$], with phenyl isothiocyanate and carbon disulfide will be described.

Results and Discussion

Reaction of Organic Tin(II) Compound with Phenyl Isothiocyanate. The reaction of di(ethoxo)tin(II) (**1**), bis[2-(dimethylamino)ethoxo]tin(II) (**2**), bis(*o*-methyl-phenoxo)tin(II) (**3**), and di(phenoxo)tin(II) (**4**) with phenyl isothiocyanate (PhNCS) were conducted in

Table 1. Reactions of $Sn(OR)_2$ with PhNCS

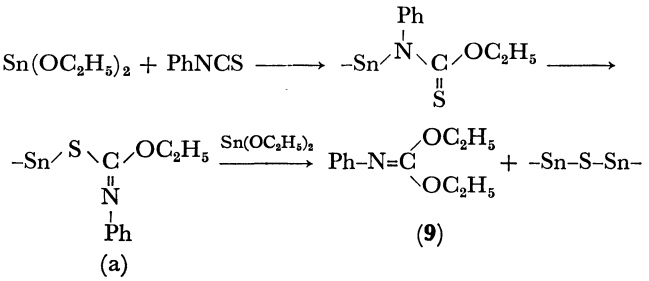
$Sn(OR)_2$	Reaction conditions: [PhNCS]/[$Sn(OR)_2$]	Temp (°C)	Time(h)	Products[a]: Yield (%)	Mp(°C) (Dec)	Sn(%) (Calcd)	$\nu_{c=s}$ (cm^{-1})	Ref.	
1	1	48—50	10[b]	66	69	33.6[c] (34.6)	1225		(**5**)
1	2	30—32	3	96	53	24.9 (24.8)	1225		(**6**)
2	1	17—19	3	92	110	27.1 (27.6)	1148		(**7**)
2	2	19—20	3	89	110	27.1 (27.6)	1148		(**7**)
3	1	32—33	3	61	90	29.8 (29.8)	1150		(**8**)[d]
3	2	30—34	15	23	90	29.8 (29.8)	1150		(**8**)
4	1	30—31	3	85	171	38.1 (38.9)			(**4**)

a) All compounds are white powders. b) In min. c) Although the existence of 1:2 addition product **6** is estimated, it was impossible to separate compound **6** from compound **5**. d) N (%); 1.74 (Calcd for $C_{35}H_{33}NO_4SSn_2$, 1.76%).

benzene and the results are summarized in Table 1.

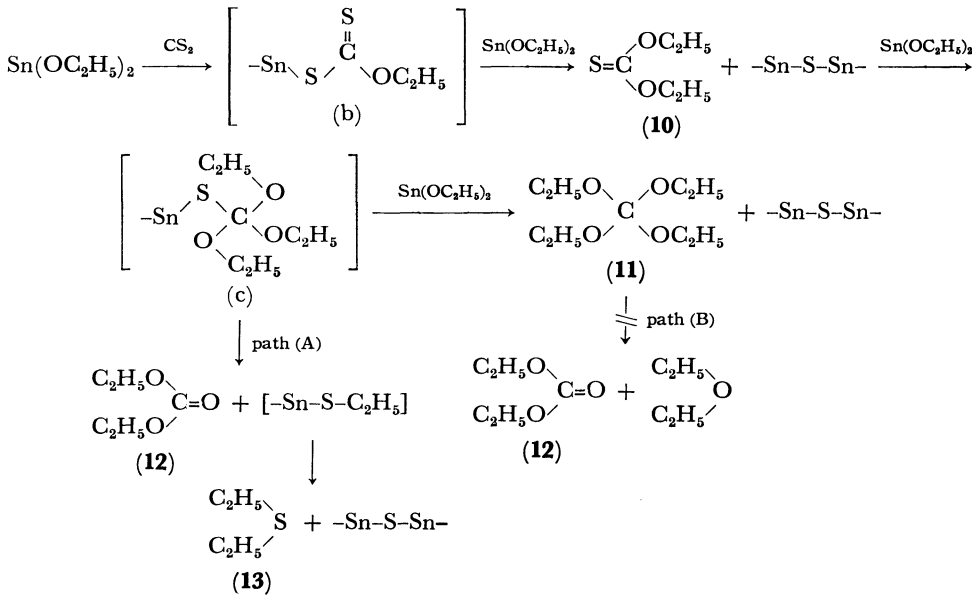
Compound **1** reacted with two equivalents of PhNCS in benzene at 30—32 °C to give the 1 : 2 addition product (**6**) in good yield. However, in the case of 1 : 1 molar ratio, the reaction was sluggish and brought to completion by heating at 48—50 °C. The reaction between compound **2** and one or two equivalents of PhNCS was exothermic and proceeded smoothly below 20 °C to afford only the 1 : 1 addition product (**7**). In the case of compound **3** with PhNCS, the resulting product was found to be a compound containing one molecule of PhNCS per two molecules of compound **3**. Compound **4** did not react. All of the isolated products **5**—**8** were sensitive to atmospheric moisture, exhibiting a new characteristic absorption band assigned to $\nu_{C=S}$ at 1148—1225 cm^{-1}. These results suggest the formation of an Sn–N bond. In addition, the *N*-phenylthiocarbamate derivatives were isolated as the hydrolysis products of compounds **5**—**8**. On the basis of these results, the aryloxotin(II) compounds **3** and **4** may be considered less reactive than the alkoxotin(II) compounds **1** and **2**. This difference may be attributed to the decrease in nucleophilicity of oxygen by the R-effect of the aryl group on the Sn–O–Ar bond.

When compound **1** was treated with PhNCS under reflux in benzene, a transparent liquid and black-brown solid were formed. The liquid was assinged as diethyl *N*-phenylcarbonimidate (**9**) according to elemental analysis, IR and NMR spectra. The carbonimidate was also obtained by heating the addition product **5** in benzene at 80—81 °C. Therefore, it is thought that the intermediate **a** results from a rearrangement of the tin atom from nitrogen to sulfur which further reacts with $Sn(OC_2H_5)_2$ to give the elimination products as shown in Scheme 1.



Scheme 1.

Reaction of Organic Tin(II) Compounds with Carbon Disulfide. The reaction of the compound **1** with carbon disulfide (CS_2) in benzene afforded diethyl thiocarbonate (**10**) ($\nu_{C=S}$ 1235 cm^{-1}), tetraethyl orthocarbonate (**11**) (ν_{C-O} 1185, 1115 cm^{-1}), and diethyl carbonate (**12**) ($\nu_{C=O}$ 1750 cm^{-1}). The yields depended on the reaction temperatures; the reaction at 69—71 °C for 20 h afforded compounds **10**, **11**, and **12** in 8, 16, and 48% yields, respectively, whereas the reaction at room temperature (below 22 °C) for one month lead to the formation of compound **10**, **11**, and **12** in 3, 42, and 4% yields, respectively. In each reaction, the NMR spectra of the benzene removed indicated the presence



Scheme 2.

TABLE 2. REACTION OF $Sn(OR)_2$ WITH CS_2

$Sn(OR)_2$	Reaction conditions		Products and yields (%)[c]		
	Temp (°C),	Time (h)	Compound **10**,	Compound **11**,	Compound **12**
1	69—71[a]	20	8	16	46
	r.t.(<22°C)[a]	one month	3	42	4
3	68—71[a]	20		no reaction	
4	60—65[b]	8		no reaction	

a) Benzene solution. b) Hexane solution. c) Based on the proton ratio of NMR spectra.

of a slight amount of diethyl sulfide (**13**).

Scheme 2 suggests the following reaction route; first, the nucleophilic attack of compound **1** on carbon disulfide produces the intermediate **b**. Subsequently, the attack of compound **1** on the carbon atom of >C=S group on the intermediate **b** results in the formation of compound **10** and tin sulfide. Furthermore, the attack of $Sn(OC_2H_5)_2$ on compound **10** gives the intermediate **c** which may undergo either the nucleophilic attack of compound **1** with the formation of compound **11** or intramolecular elimination followed by the formation of compound **12** (path A). This path is supported from the proton NMR spectra data; CH_3 8.76 (t) and CH_2 7.50 (q) ppm.[10] Assuming path B is a possible route, then diethyl ether should be derived from compound **11** (path B). However, no direct evidence for the presence of diethyl ether has been obtained.

The reaction of compounds **3** and **4** with CS_2 at 69—71 °C in benzene, showed no appreciable change occured. These results are summarized in Table 2.

Experimental

Experiments were carried out in a nitrogen atmosphere dried with liquid nitrogen. The melting and boiling points are uncorrected. IR spectra were recorded with a Hitachi EPI-2S spectrometer and ^{1} NMR spectra on a Hitachi R-24 (60 MHz) using TMS as an internal standard. The elemental analysis were carried out with a Yanagimoto MT-2 CHN corder. Liquid chromatographic determinations were performed on a Nippon Bunseki LC-08, using a polystyrene–divinylbenzene copolymer GPC column.

PhNCS was dried with the azeotropic distillation method using benzene which was freshly distilled before use. Carbon disulfide was purified according to the method of Pestermer[11] and distilled after dehydration over P_2O_5.

Reaction of Compound 1 with PhNCS in a 1: 1 Molar Ratio. In a flask equipped with a mechanical stirrer, a condenser, and a dropping funnel, were placed compound **1** (11.6 g, 56 mmol) and benzene (28 ml). PhNCS (7.5 g, 55 mmol) was slowly added so that the temperature did not exceed 24—24.5 °C. After stirring at room temperature for 2 h, the flask was allowed to stand overnight, followed by heating at 48—50 °C for 10 min with stirring. During this time, the heterogeneous solution became almost clear together with a small amount of black solid. After suction filtration, the filtrate was concentrated *in vacuo* to about one-half of the volume, and hexane (30 ml) was added to the residue. The resulting white precipitates were collected by filtration, washed with benzene, and dried to give 12.8 g (66%) of product **5**. Analytical and physical data are summarized in Table 1.

Reaction of Compound 1 with PhNCS in a 1: 2 Molar Ratio. In a similar procedure, PhNCS (21.2 g, 157 mmol) was slowly added to the suspension of compound **1** (16.2 g, 78 mmol) in benzene and heated at 29—30 °C for 3 h. During this time, the heterogeneous solution became clear without any formation of the black solid. After concentration to one-half volume, hexane (30 ml) was added to the residue. The white powdery precipitates were isolated in a 96% yield (25.9 g).

Reaction between Compound 4 and PhNCS. After compound **4** was treated with PhNCS under the conditions described in Table 1, the unreacted compound **4** was recovered in a 85% yield.

Reaction of Compound 1 with PhNCS in Boiling Benzene. Compound **1** (12.5 g, 60 mmol) was refluxed in benzene for 5 h. After separation of the resultant black solid, ditillation of the filtrate under reduced pressure gave diethyl *N*-phenylcarbonimidate (**9**) in 50% yield (5.8 g): bp 117 °C at 8 mmHg (lit,[12] 122 °C at 12 mmHg); IR (liquid film), $\nu_{C=N}$ 1660cm^{-1}; NMR (CCl_4, τ), 8,85 (t, CH_3), 5.89 (q, CH_3), and 2.7—3.3 (m, C_6H_5) ppm; Found, C, 68.51; H, 7.91; N, 7.28%, Calcd for $C_{11}H_{15}NO_2$, C, 68.37; H, 7.82; N, 7.25%. The treatment of compound **9** with 2 M-HCl ethanolic solution lead to the formation of a compound having a characteristic band at 1745 cm^{-1}.

Reaction of Compound 1 with CS_2. CS_2 (10.2 g, 34 mmol) was added dropwise to a suspension of compound **1** (13.3 g, 63 mmol) in benzene (31 ml) with stirring, and the mixture refluxed for 20 h. The heterogeneous reaction mixture changed gradually from a semi-transparent mixture to yellowish transparent solution with the formation of a black suspension. After the insoluble solids were removed by filtration, the benzene solution was distilled to afford two fractions; bp 35—50 °C at 28 mmHg, bp 50—75 °C at 28 mmHg. Each fraction was subjected to liquid chromatography (eluant, $CHCl_3$): the former gave compound **12** and the latter a mixture of **10**, **11**, and **12**.

Compound **10**: IR (CCl_4 soln); 1235 cm^{-1} (C=S). NMR (τ); 8.57 (CH_3), 5.67 (CH_2) ppm.

Compound **11**: IR (liquid film); 1185, 1115 cm^{-1} (C–O), NMR (τ); 8.85 (CH_3), 6.48 (CH_2) ppm.

Compound **12**: IR (liquid film); 1750 cm^{-1} (C=O), 1260 cm^{-1} (C–O), NMR (τ); 8.75 (CH_3), 5.99 (CH_2) ppm.

Compound **3** and **4** were treated with CS_2 according to a similar procedure, and the unreacted tin(II) compounds were recovered in quantitative yields.

General Procedure of Hydrolysis. Compound **5**—**8** were hydrolyzed with a solution of water (5—6 ml) and acetone (100 ml) at room temperature. After separation of inorganic tin with a centrifugal separator, the organic layer was concentrated under reduced pressure and cooled with an ice bath. The resulting white crystals were filtered off and dried. Physical and analytical data were as follows:

PhNHC(S)OC_2H_5: Mp 68—70 °C (lit,[13] 71—72 °C), IR; 1205 cm^{-1} ($\nu_{C=S}$), Found, C, 59.4; H, 6.10; N, 7.60%. Calcd for $C_9H_{11}NOS$, C, 59.6; H, 6.12; N, 7.73%.

PhNHC(S)$OCH_2CH_2N(CH_3)_2$: A pale yellow viscous liquid, IR; 1115 cm^{-1} ($\nu_{C=S}$), Found, C, 58.1; H, 7.22; N, 12.2%. Calcd for $C_{11}H_{16}N_2OS$, C, 58.9; H, 7.14; N, 12.5%.

PhNHC(S)O-*o*-$CH_3C_6H_4$: Mp 146—148 °C, IR; 1150 cm^{-1} ($\nu_{C=S}$) Found, C, 69.2; H, 5.34; N, 5.86%, Calcd for $C_{14}H_{13}$-NOS, C, 69.1; H, 5.35; N, 5.67%.

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