PREPARATION AND PROPERTIES OF DIALKYLTIN ISOTHIOCYANATE DERIVATIVES

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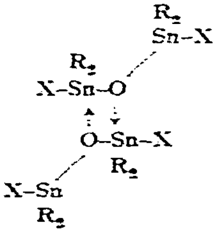
Although organotin (iso)[*]thiocyanate derivatives have been described previously, no systematic studies of such compounds have been reported. Seyferth and Rochow[1] described dimethyltin di(iso)thiocyanate and dibutyltin di(iso)thiocyanate obtained from the corresponding dialkyltin dichloride and sodium thiocyanate. Divinyltin di(iso)thiocyanate was prepared by this procedure[2]. Dibutyltin diisothiocyanate was also prepared by Green *et al.*[3] by the reaction of ammonium thiocyanate and dibutyltin dichloride in acetonitrile, and it was proposed from the result of the infrared spectra that the thiocyanate group was bound through the nitrogen atom to the tin atom, giving isothiocyanate. Alleston *et al.*[4] reported quite recently di-μ-[(iso)thiocyanatodibutylstannyloxo]-bis[(iso)thiocyanatodibutyltin] by the reaction of dibutyltin di(iso)thiocyanate and dibutyltin oxide, which might be called dimeric tetrabutyl-1,3-diisothiocyanatodistannoxane in our current nomenclature[5]. As was mentioned in the above two references[4,5], this type of compound is unique in that it contains tetra- and penta-coordinated tin atoms in the same molecule and provides an example of oxygen donation to tin bound to two organic groups, giving the dimeric distannoxane, as shown below.



Dimeric tetraalkyl-1,3-disubstituted distannoxane

This paper will report the preparation and properties of some dialkyltin isothiocyanate derivatives: (I), (II), (III), (IV) and (V) given in the reaction scheme as shown below.

Dialkyltin diisothiocyanates (I) were prepared according to the procedure of Seyferth *et al.*[1,2]. The solution of dialkyltin dichloride in alcohol became tinted pink on addition of sodium thiocyanate, but the crystals of dialkyltin diisothiocyanates were colorless after recrystallization. These compounds also were prepared by the reaction of dialkyltin dibromide with silver thiocyanate.

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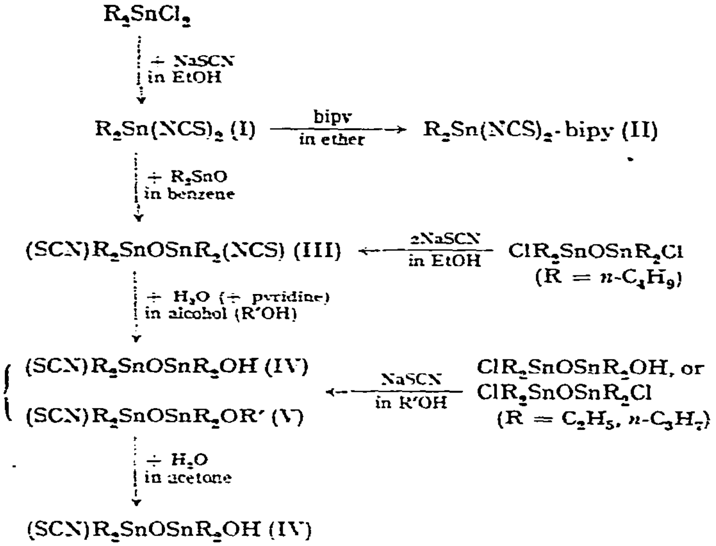
[*] The compounds with a parenthesized "iso" were originally reported as "thiocyanate".

When a diethyl ether solution of bipyridine was added to the dialkyltin diisocyanate in ether, white precipitates of dialkyl(2,2′-bipyridine)tin diisothiocyanates (II) were obtained. This procedure is analogous to that used to obtain dialkyl(2,2′-bipyridine)tin dichlorides[6]. The addition of a small amount of methanol sometimes was necessary, because of a poor solubility of the starting compounds in ether.



Tetraalkyl-1,3-diisothiocyanatodistannoxanes (III) were obtained either by the reaction of dialkyltin diisothiocyanates and dialkyltin oxide in an inert solvent such as benzene, or by the reaction of tetraalkyl-1,3-dichlorodistannoxanes[5] and sodium thiocyanate in alcohol. The former route gave the butyl, propyl and ethyl compounds in good yield, but the latter was successful only for the butyl compound. In the case of ethyl and propyl compounds it gave a mixture of tetraalkyl-1-isothiocyanato-3-hydroxydistannoxane (IV) and tetraalkyl-1-isothiocyanato-3-alkoxydistannoxane (V). However, when this mixture was recrystallized from aqueous acetone, only the compound (IV) was isolated. It was confirmed that (III) ($R = C_2H_5$, $n\text{-}C_3H_7$) suffered easy hydrolysis to (IV). The compounds (IV) were most conveniently obtained from the corresponding tetraalkyl-1-chloro-3-hydroxydistannoxanes and sodium thiocyanate. Experiments to obtain the compounds (III) by partial hydrolysis of (I) were carried out in alcohol, but were successful only for the butyl compound. In the case of other alkyl compounds mixtures of (IV) and (V) were obtained.

A molecular weight determination was carried out for (III) ($R = n\text{-}C_3H_7$) by the cryoscopic method in benzene. The compound was dimeric, as expected from our knowledge of other distannoxane derivatives[5]. The infrared spectra of (I), (II), (IV) and (V) in the solid states showed the N=C stretching band in the region 2080–2010 cm^{-1}, and that of (III) showed two strong bands near 2040 and 1960 cm^{-1}. The appearance of C=S stretching absorption for these compounds in the region 820–850 cm^{-1} indicates[7] that the nitrogen atom of the thiocyanate group is directly bound to the tin atom. The detailed discussion of the infrared spectra will be given in the following paper[8].

EXPERIMENTAL

Materials

Dialkyltin dichlorides (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9) were supplied by Nitto Kasei Company, and purified by sublimation or recrystallization. Dialkyltin dibromides, tetraalkyl-1,3-dichlorodistannoxanes and tetraalkyl-1-chloro-3-hydroxydistannoxanes (R = C_2H_5, n-C_3H_7, n-C_4H_9) were prepared according to the procedure described elsewhere[5]. Sodium thiocyanate, silver thiocyanate and 2,2'-bipyridine were of commercial grade.

Preparation of dialkyltin diisothiocyanates (I)

To a solution of di-n-propyltin dichloride (2.8 g) in 6 ml of ethanol was added sodium thiocyanate (1.6 g) in 13 ml of ethanol (mole ratio 1 : 2). Sodium chloride precipitated immediately. From the filtrate 2.9 g of colorless crystals were obtained by evaporating ethanol under reduced pressure. Recrystallization from benzene gave silky white crystals of melting point 135–136°. Dimethyl, diethyl and di-n-butyl derivatives were similarly synthesized.

Dimethyltin dibromide (1.0 g) in the mixed solvent of 9 ml of benzene and 1 ml of methanol over silver thiocyanate (2.0 g) was refluxed for four hours. From the filtrate 0.4 g of crystals which melted at 184–185° was obtained by evaporating the solvent. Recrystallization from benzene containing a small amount of methanol gave needle crystals of melting point 194–196°.

These compounds are generally soluble in polar solvents, less soluble in non-polar solvents, and the solubility decreases with decreasing size of the alkyl group bound to the tin atom. The dimethyltin derivative is exceptionally soluble in water. The melting points and the results of analysis are summarized in Table 1.

TABLE 1

DIALKYLTIN DIISOTHIOCYANATES, (I), $R_2Sn(NCS)_2$

R	*M.p. °C (reported)*	*Yield (%)*	*% Sn Found (Calcd.)*	*% C Found (Calcd.)*	*% H Found (Calcd.)*
CH_3	194–196 (198.6–199.4)[*]	84	44.83 (44.80)	17.98 (18.14)	2.39 (2.28)
C_2H_5	188.5–190	95	40.64 (40.51)	24.72 (24.60)	3.55 (3.44)
n-C_3H_7	135–136	95	37.00 (36.97)	30.10 (29.93)	4.74 (4.40)
n-C_4H_9	142–142.5 (144–145)[**]	86	33.98 (34.00)	35.02 (34.41)	5.11 (5.20)

[*] Ref. 1.
[**] Refs. 1 and 3.

Preparation of dialkyl(2,2'-bipyridine)tin diisothiocyanates (II)

A solution of 2,2'-bipyridine (0.2 g) in ether and an ethereal solution of di-n-propyltin diisothiocyanate (0.3 g) (mole ratio *ca.* 1 : 1) were mixed; a white precipitate appeared immediately, which was washed with ether and analyzed. In the case of dimethyltin or diethyltin diisothiocyanate, a small amount of methanol was added to increase the solubility in ether. Properties of the product are summarized in Table 2. The *n*-butyl compound is slightly soluble in benzene, but it was not enough to determine the molecular weight with the cryoscopic method.

TABLE 2

DIALKYL(2,2'-BIPYRIDINE)TIN DIISOTHIOCYANATES, (II), $R_2Sn(NCS)_2 \cdot bipy$

R	*M.p. °C*	*Yield* (%)	*%Sn Found* (*Calcd.*)	*%C Found* (*Calcd.*)	*%H Found* (*Calcd.*)
CH_3	219–220.5	95	28.16 (28.19)	40.11 (39.93)	3.64 (3.35)
C_2H_5	220–222	92	26.40 (26.42)	43.02 (42.79)	4.10 (4.04)
n-C_3H_7	158–159	80	24.92 (24.87)	45.70 (45.30)	4.34 (4.65)
n-C_4H_9	150–150.5	88	23.51 (23.51)	47.36 (47.54)	4.77 (5.19)

Preparation of tetraalkyl-1,3-diisothiocyanatodistannoxanes (III)

Diethyltin diisothiocyanate (2.9 g) and diethyltin oxide (1.9 g) (mole ratio *ca.* 1:1) were refluxed in benzene until an almost clear solution was obtained. The large crystals which formed were recrystallized from a mixture of benzene and petroleum ether. The *n*-propyl and *n*-butyl derivatives also were obtained by this method. The compounds given in Table 3 are more soluble in inert organic solvents than any other compounds reported in this paper.

TABLE 3

TETRAALKYL-1,3-DIISOTHIOCYANATODISTANNOXANES, (III), $(SCN)R_2SnOSnR_2(NCS)$

R	*M.p. °C* (*reported*)	*Yield* (%)	*%Sn Found* (*Calcd.*)	*%C Found* (*Calcd.*)	*%H Found* (*Calcd.*)
C_2H_5	178–179	99	48.99 (48.87)	24.66 (24.73)	4.16 (4.15)
n-C_3H_7	108–108.5	93	43.68 (43.80)	30.86 (31.05)	5.24 (5.21)
n-C_4H_9	83.5–84.5 (84)*	88	39.67 (39.70)	36.31 (36.15)	6.19 (6.08)

* Ref. 4.

To the solution of tetra-*n*-butyl-1,3-dichlorodistannoxane (1.1 g) in hot ethanol, sodium thiocyanate (0.3 g) in ethanol was added. Sodium chloride precipitated slowly. A large amount of water was added to the filtrate; the soft solid obtained was dried in vacuum, yielding 0.8 g, and recrystallized from petroleum ether. The melting point and the infrared spectrum of the crystals agreed well with (III) (R = *n*-C_4H_9) shown in Table 3. In the case of the *n*-propyl and ethyl compounds, this procedure gave a mixture of (IV) and (V).

Preparation of tetraalkyl-1-isothiocyanato-3-hydroxydistannoxanes (IV)

An ethanol solution of tetraethyl-1-chloro-3-hydroxydistannoxane (1 g) and sodium thiocyanate (0.5 g) (in excess) in ethanol were mixed. After removing sodium chloride, cubic crystals (0.6 g) were obtained from the solution, which were recrystallized from aqueous acetone. The results of analysis showed that it was the compound (IV) (R = C_2H_5) as shown in Table 4. Similarly, *n*-propyl and *n*-butyl derivatives were also obtained in this manner. In the case of ethyl or propyl derivatives, (IV) was obtained by soaking crushed crystals of (III) in water.

TABLE 4

TETRAALKYL-1-ISOTHIOCYANATE-3-HYDROXYDISTANNOXANES, (IV), $(SCN)R_2SnOSnR_2(OH)$

R	*M.p. °C*	*Yield (%)*	*%Sn Found (Calcd.)*	*%C Found (Calcd.)*	*%H Found (Calcd.)*
C_2H_5	170–176*	60	53.47 (53.38)	24.25 (24.33)	4.86 (4.76)
n-C_3H_7	162–167*	55	47.60 (47.40)	31.08 (31.18)	5.88 (5.84)
n-C_4H_9	123–134*	70	42.78 (42.62)	36.66 (36.66)	6.63 (6.70)

* Decomposition.

Determination of molecular weight

The molecular weight was determined cryoscopically in benzene. Calcd. for $[(SCN)(n\text{-}C_3H_7)_2SnOSn(n\text{-}C_3H_7)_2(NCS)]_2$: mol. wt., 1084; found: mol. wt., 998, 1000 at concentrations [*w*(sample)/*W*(solvent)], 0.021 and 0.041, respectively.

Analyses

The tin analysis for all these compounds were carried out by the acid digestion method[9]. In contrast to dialkyltin(2,2′-bipyridine) dichlorides[6], the method is quite applicable even for dialkyltin(2,2′-bipyridine) diisothiocyanate. The analysis for NCS was successfully carried out by precipitimetry with silver nitrate for dimethyltin diisothiocyanate (which is soluble in water). (Found: NCS, 43.89. $C_4H_6N_2S_2Sn$ calcd.: NCS, 43.85 %.)

SUMMARY

Several series of dialkyltin (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$) isothiocyanate derivatives: dialkyltin diisothiocyanates (I), dialkyl(2,2′-bipyridine)tin diisothiocyanates (II), tetraalkyl-1,3-diisothiocyanatodistannoxanes (III) and tetraalkyl-1-isothiocyanato-3-hydroxydistannoxanes (IV) were prepared according to the reactions: $R_2SnCl_2 + 2NaSCN \rightarrow (I)$; $(I) + \text{bipy} \rightarrow (II)$; $(I) + R_2SnO \rightarrow (III)$; $ClR_2SnOSnR_2Cl + 2NaSCN \rightarrow (III)$ or (IV); $ClR_2SnOSnR_2OH + NaSCN \rightarrow (IV)$. There are included eleven new compounds.

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