

NOTE

PREPARATION AND PROPERTIES OF TRIMETHYLANTIMONY HALIDE THIOCARBOXYLATES

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INTRODUCTION

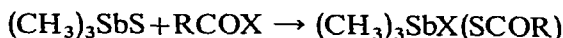
In our previous paper¹, we have reported that trimethylstibine sulfide reacts with alkyl halides to give trimethylstibine, trimethylantimony dihalides and dialkyl disulfides. It was suggested that trimethylantimony halide thioalkoxides are formed as unstable intermediates in these reactions. Only a few compounds of the type R_3SbXY have been reported²⁻⁵, and little has been studied concerning their physicochemical properties. Here we wish to report the isolation of trimethylantimony halide thio-carboxylates and their characterizations on the basis of X-ray powder patterns, IR and PMR spectra.

EXPERIMENTAL

The preparation of organoantimony compounds employed has already been described^{6,7}. All acyl halides were of reagent-grade quality and were purified by distillation.

The X-ray powder patterns and PMR spectra were measured using a Geigerflex made by Rigaku-Denki Co. Ltd. and a Japan Electron Optics Model JNM-3H-60 spectrometer, respectively. The IR spectral measurements were carried out with Hitachi EPI-2G and Hitachi EPI-L spectrometers, both equipped with gratings.

Preparation of trimethylantimony halide thiocarboxylates $(CH_3)_3SbX(SCOR)$ (I)

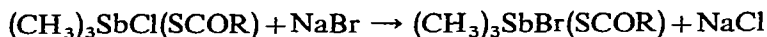


To a chloroform solution of trimethylstibine sulfide was added an equimolar amount of acyl halide. An exothermic reaction occurred immediately. After the mixture had been stirred for 15 min at room temperature, chloroform was removed *in vacuo*. Recrystallization of the residue from benzene/ligroin gave (I) in quantitative yield. The halide thiocarboxylates also were obtained as follows:



A mixture of equimolar amounts of trimethylantimony dihalide and bis(thiocarboxylate) in chloroform was stirred for 30 min at room temperature. Evaporation of the solvent *in vacuo* yielded (I) quantitatively.

In addition to the above procedures, the bromides were prepared from the chlorides:



An equimolar mixture of the chloride and sodium bromide in methanol was heated under reflux for 30 min. After removing methanol *in vacuo*, the bromide was extracted by benzene from the reaction products. Melting points and analytical data of (I) are summarized in Table 1.

TABLE I
PROPERTIES OF $(\text{CH}_3)_3\text{SbX}(\text{SCOR})$, (I)

R	X	M.p. (°C)	Analysis found (calcd.) (%)		
			X	C	H
C_6H_5	Cl	134–135	10.28	34.97	4.21
			(10.44)	(35.38)	(4.16)
C_6H_5	Br	141–142	20.85	31.02	3.61
			(20.81)	(31.28)	(3.67)
CH_3	Cl	93–95	12.91	20.94	4.51
			(12.78)	(21.65)	(4.36)
CH_3	Br	ca. 110 ^a	24.69	18.48	3.82
			(24.83)	(18.66)	(3.76)

^a Decomposed.

RESULTS AND DISCUSSION

In the reactions of trimethylstibine sulfide with alkyl halides¹, we could not isolate the supposed intermediate trimethylantimony halide thioalkoxides. However, our present study shows that trimethylantimony halide thiocarboxylates (I) are readily obtained in the reactions of trimethylstibine sulfide with acyl halides. This difference in behavior may be attributed to a less reactive Sb–S bond in (I) and is consistent with the greater stability of trimethylantimony bis(thiocarboxylates) as compared with the bis(thioalkoxides)⁷.

From Fig. 1 and the IR spectrum in nujol mull (Table 2), it is concluded that trimethylantimony chloride thiobenzoate in the solid state is not an equimolar mixture of the dichloride and the bis(thiobenzoate). The IR data given in Table 2 indicate that the other halide thiocarboxylates are also distinct compounds in the solid state.

All our compounds (I) show a strong $\nu(\text{C}=\text{O})$ band at $1626\text{--}1644\text{ cm}^{-1}$, which indicates that the thiocarboxylate group is bonded to antimony *via* sulfur, as has been proposed for trimethylantimony bis(thiocarboxylates)⁷. Accordingly, a new band at $359\text{--}381\text{ cm}^{-1}$ may be assigned to $\nu(\text{Sb}\text{--}\text{S})$. Appearance of this band at higher frequency than $\nu(\text{Sb}\text{--}\text{O})$ (at 280 cm^{-1}) in trimethylantimony diacetate suggests that the Sb–S bond has more covalent character than the Sb–O bond. In addition to ν_{asym}

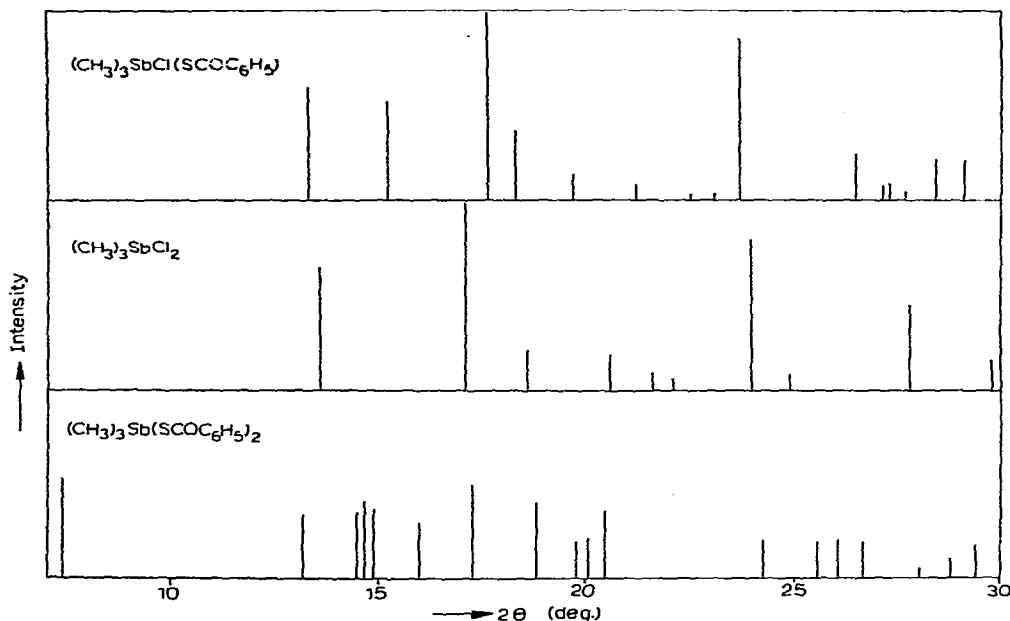


Fig. 1. X-ray powder patterns of $(\text{CH}_3)_3\text{SbCl}(\text{SCOC}_6\text{H}_5)$, $(\text{CH}_3)_3\text{SbCl}_2$ and $(\text{CH}_3)_3\text{Sb}(\text{SCOC}_6\text{H}_5)_2$.

(Sb-C) at $568\text{--}572\text{ cm}^{-1}$, $\nu_{\text{sym}}(\text{Sb-C})$ is observed at $518\text{--}526\text{ cm}^{-1}$, showing that the SbC_3 moiety has a lower local symmetry (probably C_{3v}) than D_{3h} to which most of the SbC_3 moieties of trimethylantimony(V) derivatives belong.

The PMR spectra of the trimethylantimony halide thiobenzoates in dichloromethane solution (Table 3) show, in the methyl proton region, two small signals with equal intensities on both sides of the main signal at 7.73 or 7.59 ppm, this main signal being assigned to the methyl protons of the trimethylantimony halide thiobenzoate. The weak signals at 7.68 and 7.39 ppm are quite consistent with the methyl protons of trimethylantimony dichloride and dibromide, respectively, and that at 7.75 ppm with the bis(thiobenzoate). The relative intensity of the total of these three methyl resonan-

TABLE 3

METHYL PROTON CHEMICAL SHIFTS^a OF $(\text{CH}_3)_3\text{SbX}(\text{SCOR})$, (I), IN CH_2Cl_2

R = C_6H_5		R = CH_3		Assignment
X = Cl	X = Br	X = Cl	X = Br	
7.74	7.76 (1)	7.95	7.95 (1)	$(\text{CH}_3)_3\text{Sb}$ of $(\text{CH}_3)_3\text{Sb}(\text{SCOR})_2$
7.73	7.59 (12.5)	7.83	7.70 (11.5)	$(\text{CH}_3)_3\text{Sb}$ of $(\text{CH}_3)_3\text{SbX}(\text{SCOR})$
7.68 (1)	7.39 (1)	7.68	7.39 (1)	$(\text{CH}_3)_3\text{Sb}$ of $(\text{CH}_3)_3\text{SbX}_2$
		7.65	7.66	SCOCH_3 of $(\text{CH}_3)_3\text{SbX}(\text{SCOCH}_3)$
		7.63	7.63	

^a τ values with reference to internal tetramethylsilane (10.00 ppm); relative intensity between brackets.

ces with that of phenyl protons (9/5) suggests that the halide thiobenzoate in solution is involved in the following equilibrium:



Although the relative intensities of these three methyl signals are not noticeably dependent on temperature variation (from -50° to 50°), this equilibrium is confirmed by addition of the dihalide [or the bis(thiobenzoate)] to this system, which results in disappearance of the bis(thiobenzoate) (or the dihalide) signal. In the spectrum of trimethylantimony chloride thioacetate, some of the signals overlap each other, and therefore it is difficult to estimate reliable relative intensities. However, the partial conversion of this compound to the dichloride and the bis(thioacetate) in solution appears probable, since if excess dichloride is added, the signal at 7.95 ppm attributed to the bis(thioacetate) disappears. In the case of the bromide thioacetate, the partial conversion is evident from the relative intensities shown in Table 3.

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