

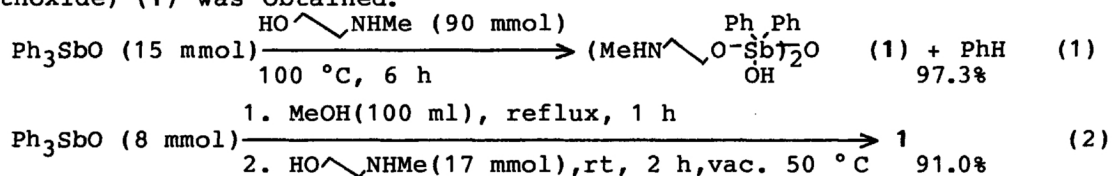
PREPARATION AND REACTIONS OF NOVEL  $\mu$ -OXO-BISANTIMONY  
AMINOALKOXIDE

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Novel  $\mu$ -oxo-bis(diphenylhydroxyantimony) di[2-(methylamino)-ethoxide] (**1**) was obtained in the reaction of triphenylstibine oxide and 2-(methylamino)ethanol. Cyclic urethane derivatives were obtained by the reaction of **1** with  $\text{CO}_2$  or  $\text{CS}_2$  in good yields.

Recently, we have found that the 2-aminoethanols were easily cyclocondensed with  $\text{CO}_2$  catalyzed by triphenylstibine oxide ( $\text{Ph}_3\text{SbO}$ ) via antimony(V) 2-aminoethoxides as an intermediate.<sup>1)</sup> Therefore, we attempted to isolate the antimony(V) 2-aminoethoxide. Meanwhile, it has been reported that  $\text{Ph}_3\text{SbO}$  readily reacted with simple alcohols to give triphenylantimony dialkoxides.<sup>2)</sup> We expected that  $\text{Ph}_3\text{SbO}$  and 2-(methylamino)ethanol should give triphenylantimony di[2-(methylamino)-ethoxide], however, unexpected  $\mu$ -oxo-bis(diphenylhydroxyantimony) di(2-aminoethoxide) (**1**) was obtained.



Thus,  $\text{Ph}_3\text{SbO}$  was suspended in 2-(methylamino)ethanol, and heated at  $100 \text{ }^\circ\text{C}$  (Eq.1). Generation of benzene was observed and white crystals were obtained. The crystals were filtered and washed several times with cold ethanol, and dried *in vacuo*. Mp.  $286\text{--}287 \text{ }^\circ\text{C}$ ; IR(KBr)  $3440(\text{OH})$ ,  $3280(\text{NH})$ ,  $3050(\text{Ph})$ ,  $2980\text{--}2830(\text{alkyl})$  and  $747 \text{ cm}^{-1}(\text{Sb-O})^3$ ;  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta=1.42(6\text{H}, \text{s}, \text{NCH}_3)$ ,  $2.30\text{--}2.80(8\text{H}, \text{bd}, \text{NCH}_2, \text{NH}, \text{OH})$ , simplified to  $4\text{H}, \text{t}, \text{J}=6.0 \text{ Hz}$ , with addition of  $\text{D}_2\text{O}$ ,  $4.08(4\text{H}, \text{t}, \text{J}=6.0 \text{ Hz}, \text{OCH}_2)$ ,  $7.2\text{--}7.4$  and  $7.8\text{--}8.0(20\text{H}, \text{m}, \text{Ph})$ : Found: C, 48.72; H, 4.94; N, 3.85 %; Molecular weight (VPO,  $\text{CHCl}_3$ ), 765: Calcd for  $\text{C}_{30}\text{H}_{38}\text{N}_2\text{O}_5\text{Sb}_2$ : C, 48.03; H, 5.11; N, 3.73%; Mw, 750.4. Appearance of  $\nu_{\text{NH}}$  bands in IR shows that **1** has free amino group bearing no chelation ( $\text{Sb}-\text{O}-\text{N}$ ). These analytical results satisfied the proposed  $\mu$ -oxo bridged structure. Similar  $\mu$ -oxo-bisantimony(V) alkoxides have been synthesized only by pyrolysis of triphenylantimony glycolates.<sup>4)</sup> In addition, **1** could also be synthesized by triphenylantimony dimethoxide prepared *in situ* (Eq.2). Further, **1** was soluble in  $\text{CHCl}_3$ , hot alcohols and hot benzene but insoluble in  $\text{CCl}_4$  and hexane. A benzene solution of **1** was autoclaved under  $\text{CO}_2$  pressure ( $50 \text{ kg/cm}^2$ ) at  $160 \text{ }^\circ\text{C}$  and 3-methyl-2-oxazolidinone (**2**) was given in good yield. No reaction occurred below  $160 \text{ }^\circ\text{C}$  (Table 1). Neither exotherm nor spectral change which would suggest the insertion of  $\text{CO}_2$  into Sb-O bond was observed when  $\text{CO}_2$  was bubbled into a solution of **1**.

Table 1. Reactions with CO<sub>2</sub><sup>a)</sup>

No.	1 (mmol)	T/°C	t/h	Yield of 2 <sup>b)</sup>
1	1	100	6	0
2	1	130	6	trace
3	2	160	6	73.4

a) In a stainless steel autoclave(50 ml), CO<sub>2</sub> 50 kg/cm<sup>2</sup>. Benzene(5 ml) was used as solvent. b) Based on 1.

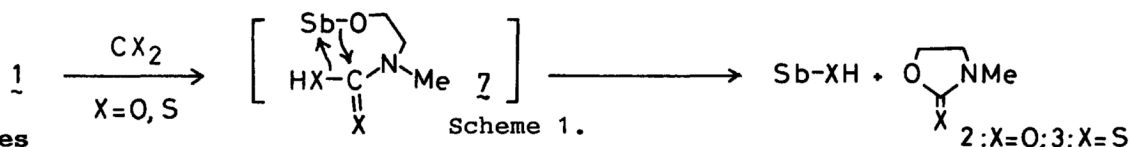
Table 2. Reactions with CS<sub>2</sub>

No.	Sb compds (mmol)	HO\NHMe (mmol)	CS <sub>2</sub> (mmol)	T/°C	t/h	Yield/%	
						3	4
4	1 (0.47) <sup>a)</sup>	-	1.0	rt	1	79.1	0.91 <sup>b)</sup>
5	Ph <sub>3</sub> SbO (1) <sup>c)</sup>	2	2.0	rt	1	93.2	2.7
6	1 (0.5) <sup>d)</sup>	10	10	100	6	3.4	34.0
7	Sb <sub>2</sub> O <sub>3</sub> (10) <sup>e)</sup>	60	-	rt	6	nr	
				reflux	6		
8	Sb <sub>2</sub> O <sub>3</sub> (12) <sup>e)</sup>	72	72	rt	2	5	(91.3)
9	Sb(S <sub>2</sub> CNMe OH) <sub>3</sub> <sup>f)</sup> (2)	-	-	reflux	6	80.0	14.0
10	Ph <sub>3</sub> SbO (6.25) <sup>g)</sup>	Et <sub>2</sub> NH (19)	19	rt	24	6	(99.0)

a) Benzene 1ml. b) Ph<sub>2</sub>SbO<sub>2</sub>H was recovered quantitatively. c) MeOH 20ml. d) Benzene 5ml in the autoclave. e) MeOH 20ml. f) Xylene 20ml. g) Acetonitrile 5ml.

While, the reaction of 1 and CS<sub>2</sub> proceeded even at rt to afford cyclocondensed products. The reaction between 1 and an equivalent amount of CS<sub>2</sub> selectively gave 3-methyl-oxazolidin-2-thione (3) in high yields. Catalytic amounts of 1 and CS<sub>2</sub>, however, produced mainly 3-methylthiazolidin-2-thione (4). Thus, 1 or its precursor Ph<sub>3</sub>SbO will be one of useful reagents for the syntheses of such cyclic compounds.

Although antimony trioxide, Sb<sub>2</sub>O<sub>3</sub>, did not react with the aminoalcohol under the similar conditions, when CS<sub>2</sub> was added into the mixture, antimony tris[(2-hydroxyethyl)methylthiocarbamate] (5) was immediately obtained in quantitative yields without any cyclo-condensed product (3 or 4) at rt. In order to obtain 3 pyrolysis of 5 in refluxed xylene was necessary. On the other hands, Ph<sub>3</sub>SbO played as an oxidant to give *N,N,N',N'*-tetraethylthiuram disulfide(6) when Ph<sub>3</sub>SbO was mixed with Et<sub>2</sub>NH and CS<sub>2</sub>. In addition, the oxidation could proceed with a catalytic amount of Ph<sub>3</sub>SbO. Because 6 was not detected in the reaction of 2-(methylamino)ethanol and CS<sub>2</sub> in the presence of Ph<sub>3</sub>SbO, the cyclocondensation did not proceed *via* 6. Based on the above mentioned results, the reaction between 1 and CO<sub>2</sub> or CS<sub>2</sub> proceeded *via* intermediate 7 shown in the Scheme. The formation of 7 might be supported with the disappearance of the absorption of ν<sub>NH</sub> of 1 by addition of CS<sub>2</sub> into the chloroform solution of 1. The cyclization was considered to occur *via* four centered transition state. The resulted Sb-S species may afford 4 in the catalytic reaction (No.5).



## References

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(Received February 8, 1985)