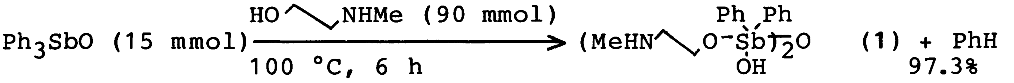
CHEMISTRY LETTERS, pp. 579-580, 1985.

PREPARATION AND REACTIONS OF NOVEL μ-OXO-BISANTIMONY AMINOALKOXIDE

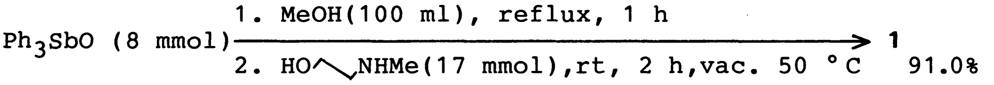
Ryoki NOMURA,* Masakuni KORI, and Haruo MATSUDA
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamada-Oka, Suita, Osaka 565

Novel μ-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 CO_2 or CS_2 in good yields.

Recently, we have found that the 2-aminoethanols were easily cyclocondensed with CO_2 catalyzed by triphenylstibine oxide (Ph_3SbO) *via* antimony(V) 2-aminoethoxides as an intermediate.[1)] Therefore, we attempted to isolate the antimony(V) 2-aminoethoxide. Meanwhile, it has been reported that Ph_3SbO readily reacted with simple alcohols to give triphenylantimony dialkoxides.[2)] We expected that Ph_3SbO and 2-(methylamino)ethanol should give triphenylantimony di[2-(methylamino)-ethoxide], however, unexpected μ-oxo-bis(diphenylhydroxyantimony) di(2-aminoethoxide) (**1**) was obtained.



$$\mathrm{Ph_3SbO}\ (15\ \mathrm{mmol}) \xrightarrow[100\ ^\circ\mathrm{C},\ 6\ \mathrm{h}]{\mathrm{HO{\sim}NHMe}\ (90\ \mathrm{mmol})} (\mathrm{MeHN{\sim}O{-}}\overset{\mathrm{Ph\ Ph}}{\underset{\mathrm{OH}}{\mathrm{Sb}}}{)_2}\mathrm{O}\quad (\mathbf{1}) + \underset{97.3\%}{\mathrm{PhH}} \qquad (1)$$



$$\mathrm{Ph_3SbO}\ (8\ \mathrm{mmol}) \xrightarrow[2.\ \mathrm{HO{\sim}NHMe}(17\ \mathrm{mmol}),\mathrm{rt},\ 2\ \mathrm{h},\mathrm{vac.}\ 50\ ^\circ\mathrm{C}]{1.\ \mathrm{MeOH}(100\ \mathrm{ml}),\ \mathrm{reflux},\ 1\ \mathrm{h}} \underset{91.0\%}{\mathbf{1}} \qquad (2)$$

Thus, Ph_3SbO was suspended in 2-(methylamino)ethanol, and heated at 100 °C (Eq.1). Generation of benzene was observed and white crystalls were obtained. The crystalls were filtered and washed several times with cold ethanol, and dried *in vacuo*. Mp. 286-287 °C;IR(KBr) 3440(OH), 3280(NH), 3050(Ph), 2980-2830(alkyl) and 747 cm^{-1}(Sb-O)[3)];^1H NMR($CDCl_3$) δ=1.42(6H,s,$NC\underline{H}_3$), 2.30-2.80(8H,bd,$NC\underline{H}_2$,$N\underline{H}$,$O\underline{H}$, simplified to 4H,t,J=6.0 Hz, with addition of D_2O), 4.08(4H,t,J=6.0 Hz,$OC\underline{H}_2$), 7.2-7.4 and 7.8-8.0(20H,m,Ph): Found:C, 48.72;H, 4.94;N, 3.85 %;Molecular weight (VPO, $CHCl_3$), 765:Calcd for $C_{30}H_{38}N_2O_5Sb_2$:C, 48.03;H, 5.11; N,3.73%; Mw, 750.4. Appearance of $^{\nu}NH$ bands in IR shows that **1** has free amino group bearing no chelation ($\mathrm{Sb}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{N}}$). These analytical results satisfied the proposed μ-oxo bridged structure. Similar μ-oxo-bisantimony(V) alkoxides have been synthesized only by pyrolysis of triphenylantimony glycolates.[4)] In addition, **1** could also be synthesized by triphenylantimony dimethoxide prepared *in situ* (Eq.2). Further, **1** was soluble in $CHCl_3$, hot alcohols and hot benzene but insoluble in CCl_4 and hexane. A benzene solution of **1** was autoclaved under CO_2 pressure (50 kg/cm^2) at 160 °C and 3-methyl-2-oxazolidinone (**2**) was given in good yield. No reaction occurred below 160 °C (Table 1). Neither exotherm nor spectral change which would suggest the insertion of CO_2 into Sb-O bond was observed when CO_2 was bubbled into a solution of **1**.

Table 1. Reactions with CO_2[a)]

No.	**1**(mmol)	T/°C	t/h	Yield of **2**[b)]
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_2 50 kg/cm^2. Benzene(5 ml) was used as solvent. b) Based on **1**.

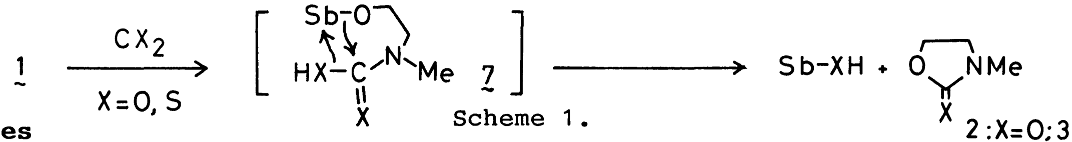
Table 2. Reactions with CS_2

No.	Sb compds (mmol)	 (mmol)	CS_2 (mmol)	T/°C	t/h	Yield/% **3**	Yield/% **4**
4	**1** (0.47)[a)]	-	1.0	rt	1	79.1	0.91[b)]
5	Ph_3SbO (1)[c)]	2	2.0	rt	1	93.2	2.7
6	**1** (0.5)[d)]	10	10	100	6	3.4	34.0
7	Sb_2O_3 (10)[e)]	60	-	rt reflux	6 6	nr	
8	Sb_2O_3 (12)[e)]	72	72	rt	2	**5**	(91.3)
9	$Sb(S_2C\overline{NMe\ OH})_3$[f)] (2)	-	-	reflux	6	80.0	14.0
10	Ph_3SbO (6.25)[g)]	Et_2NH (19)	19	rt	24	**6**	(99.0)

a) Benzene 1ml. b) Ph_2SbO_2H 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_2 proceeded even at rt to afford cyclocondensed products. The reaction between **1** and an equivalent amount of CS_2 selectively gave 3-methyl-oxazolidin-2-thione (**3**) in high yields. Catalytic amounts of **1** and CS_2, however, produced mainly 3-methylthiazolidin—2-thione (**4**). Thus, **1** or its precursor Ph_3SbO will be one of useful reagents for the syntheses of such cyclic compounds.

Although antimony trioxide, Sb_2O_3, did not react with the aminoalcohol under the similar conditions, when CS_2 was added into the mixture, antimony tris[(2-hydroxyethyl)methyldithiocarbamate] (**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_3SbO played as an oxidant to give *N,N,N',N'*-tetraethylthiuram disulfide(**6**) when Ph_3SbO was mixed with Et_2NH and CS_2. In addition, the oxidation could proceed with a catalytic amount of Ph_3SbO. Because **6** was not detected in the reaction of 2-(methylamino)ethanol and CS_2 in the presence of Ph_3SbO, the cyclocondensation did not proceed *via* **6**. Based on the above mentioned results, the reaction between **1** and CO_2 or CS_2 proceeded *via* intermediate **7** shown in the Scheme. The formation of **7** might be supported with the disapperance of the absorption of ν_{NH} of **1** by addition of CS_2 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).



Scheme 1.

2:X=O;3:X=S

References

1) H. Matsuda, A. Baba, R. Nomura, and M. Kori, The 47th Spring Meeting of the Chemical Society of Japan, Kyoto, April 1983, Abstr., No. 3G44.
2) R. G. Goel and D. R. Ridley, J. Organomet. Chem. 182, 207 (1979).
3) E. Maslowsky, Jr., "Vibrational Spectra of Organometallic Compounds," Wiley Interscience, New York (1977), pp.119-128.
4) F. Nerdel, J. Buddrus, and K. Hoeher, Chem. Ber., 97, 124 (1964).

(Received February 8, 1985)