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Alkoxysilanes. I. Preparation of Alkoxysiloxy Derivatives of Antimony

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Much work has been done concerning the preparation of alkyl or arylsiloxy derivatives of metals $(R_3SiO)_nM$ (M=Si,1) Al,2) Sn,3) Ti,4) Zr,4)). Although the preparation of tris(triethylsilyl) antimonite by Andrianov5) and the preparation of (trimethylsiloxy)(alkyl)antimony derivatives of the $(Me_3SiO)_nSbR_{m-n}$ ($m=3$ or 5, $n=1$ or 2, R=Me or Ph) type by Schmidbaur6) have been reported, no other derivatives of antimony are known. Moreover, none of the alkoxysiloxyderivative of metals have been investigated.

We, therefore, attempted to prepare antimony derivatives containing a relatively stable trialkoxysiloxy group and tris(trimethyl or triphenylsilyl) antimonite.7) The results of measurements of the relative hydrolytic stability and the infrared absorption spectra of these new compounds will also be indicated.

The preparation of tris(triorganosilyl) antimonite was carried out according to two procedures. One was a reaction between antimony trialkoxide and silanols; the other was a reaction of antimony trichloride with silanols in the presence of amine. Tris(tri-*t*-butoxysilyl) antimonite was distilled out as a white crystalline solid; it was very soluble in common organic solvents. Tris(triphenylsilyl)

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7) Methyl- and phenylsiloxy derivatives have been recently reported by Orlov and Volonkov before our work, but their details have not been fully described. N. F. Orlov and M. G. Voronkov, *J. General Chem.*, **36**, 357 (1966).

antimonite was obtained from recrystallization; it was also distilled at about 180—182°C/2 mmHg. It was soluble in THF, chloroform and hot benzene, but insoluble in ether and *n*-hexane.

The IR spectra of stibiosiloxane have been reported by Schmidbaur,[6,8] who assigned the absorption at 940—980 cm^{-1} to ν_{as}Si–O–Sb. He also observed that the absorption peaks of the Si–O–X (X=Si, Ge, Sn, Pb) bond in the structural unit of the heterosiloxanes shift systematically to lower wave numbers in the sequence; Si, Ge, Sn, Pb (1055, 990, 980, 959 cm^{-1}). Therefore, it is reasonable to assume the absorption related to ν_{as}Si–O–Sb is in the region between Ge and Sn. The absorption peaks of phenyl and methyl derivatives were observed in this region (at 990 and 995 cm^{-1} respectively), but in tris(tri-*t*-butoxysilyl) antimonite the characteristic absorption band in the vicinity of 990 cm^{-1} was not observed. It seems that the band shifts to a higher wave number (1025 cm^{-1}).

The relative hydrolytic stability of these compounds was determined by measuring the antimonous ion, Sb^{3+}, formed by hydrolysis in an acidic medium. The results are shown in Fig. 1. The results indicate that the relative stability decreases in the order; tris(triphenylsilyl) antimonite, tris(tri-*t*-butoxysilyl) antimonite, tris(trimethylsilyl) antimonite (Sb% × 10). On the other hand, when the hydrolysis was carried out using a basic solvent (THF) at 50°C, the stability decreased as follows; tris(triphenylsilyl) antimonite, tris(trimethylsilyl) antimonite, tris(tri-*t*-butoxysilyl) antimonite. The first was remarkably stable.

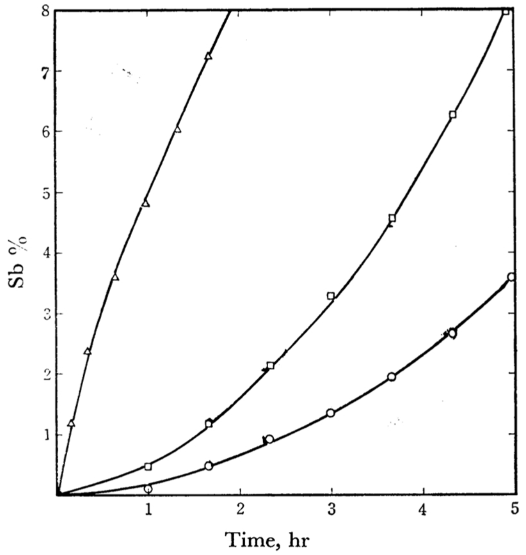

Fig. 1. The relative hydrolytic stability.
○: tris(triphenylsilyl) antimonite
□: tris(tri-*t*-butoxysilyl) antimonite
△: tris(trimethylsilyl) antimonite (Sb % × 10)

Experimental[9]

Materials. Antimony tri-*i*-propoxide was prepared by the reaction of antimony trichloride with *i*-propyl alcohol in the presence of ammonia,[10] bp 62—63°C/1 mmHg. Trimethylsilanol was prepared by Sauer's method,[11] 99—100°C. Triphenylsilanol was prepared by the hydrolysis of triphenylchlorosilane in the presence of triethylamine, mp 149—150°C. Tri-*s*-butoxysilanol was obtained by Wright's method,[12] bp 89.5°C/1 mmHg, n_D^{20} 1.4135. Tri-*t*-butoxysilanol was first prepared by Backer and Klasens through the hydrolysis of sodium tri-*t*-butoxysilanolate.[13] Wright *et al.*[12] described how the silanol was obtained by the hydrolysis of tri-*t*-butoxychlorosilane in boilling water, but its details have not been documented. In the present work, the silanol was prepared by a modification of the procedure of Wright; tri-*t*-butoxychlorosilane[14] was hydrolyzed in the presence of pyridine, yield 69.5% mp 65—66°C (Found: Si, 10.60%; mol wt, 268).

Preparation of Tris(tri-*t*-butoxysilyl) Antimonite. *Method A.* A solution of 9.8 g (0.033 mol) of antimony tri-*i*-propoxide in 50 m*l* of *n*-hexane was added to a solution of 26.0 g (0.099 mol) of tri-*t*-butoxysilanol in 50 m*l* of *n*-hexane. Then the combined solution was refluxed for 1.5 hr, and the alcohol formed was distilled with the solvent. The residue was distilled under reduced pressure to give 22.3 g (74.5%) of a white crystalline solid, bp 200.5—201.0°C/1 mmHg, mp 102—104°C. Found: C, 47.35; H, 9.79; Si, 9.22; Sb, 13.20%; mol wt, 900. Calcd for $C_{36}H_{81}O_{12}Si_3Sb$: C, 47.41; H, 8.94; Si, 9.24; Sb, 13.35%; mol wt, 912.

Method B. Into a solution of 26.0 g (0.099 mol) of tri-*t*-butoxysilanol, 10.0 g (0.099 mol) of triethylamine in 130 m*l* of benzene was stirred, drop by drop, at 0—5°C. At the end of the addition, the mixture was refluxed for 2.5 hr. The triethylamine hydrochloride was filtered out, and the benzene was removed. The residue was distilled under reduced pressure to give 20.0 g (66.7%) of a pale yellow solid, bp 197.0—198°C/0.5 mmHg. IR: 2975 (m), 1474(w), 1390(m), 1365(m), 1240(m), 1215(shoulder), 1190(m), 1060(s), 1025(m), 915(s), 830(m), 850(w), 705(m) cm^{-1}.

Preparation of Tris(tri-*s*-butoxysilyl) Antimonite. *Method A.* The reaction of 9.8 g of antimony tri-*i*-propoxide with 26.0 g of tri-*s*-butoxysilanol in *n*-hexane gave 10.3 g (34.4%) of a colorless liquid, bp 204—207°C/1 mmHg. Found: C, 46.80; H, 9.82; Si, 9.21; Sb, 13.79%; mol wt, 889. Calcd for $C_{36}H_{81}O_{12}$-

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8) H. Schmidbaur, *Angew. Chem.*, **77**, 206 (1965); H. Schmidbaur, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

9) All experiments were carried out in dry atmosphere or nitrogen purge. Melting points and boilling points were uncorrected.

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Si_3Sb: C, 47.41; H, 8.94; Si, 9.24, Sb, 13.35%; mol wt, 912.

Method B. The reaction with the same molar ratio of reactants as the case of the tri-*t*-butoxysiloxy derivative gave 5.6 g (18.7%) of a pale yellow liquid, bp 202—204°C/0.5 mmHg.

Preparation of Tris(trimethylsilyl) Antimonite. *Method A.* The reaction of 33.3 g (0.111 mol) of antimony tri-*i*-propoxide with 34.6 g (0.388 mol) of trimethylsilanol in *n*-hexane gave 28.0 g (65.0%) of a colorless liquid, bp 108—108.2°C/21.5 mmHg, n_D^{20} 1.4368. Found: Si, 21.52; Sb, 31.24%; mol wt, 382. Calcd for $C_9H_{27}O_3Si_3Sb$: Si, 21.66 Sb, 31.28%; mol wt, 389.

Method B. The reaction of 9.0 g (0.0393 mol) of antimony trichloride with 14.0 g (0.157 mol) of trimethylsilanol in the presence of 15.9 g (0.157 mol) of triethylamine gave 8.4 g (55.0%) of a colorless liquid, bp 118—119°C/33.5 mmHg, n_D^{20} 1.4363. IR: 2900(s), 1247(s), 995(m), 900(s), 840(s), 752(m) cm^{-1}.

Preparation of Tris(triphenylsilyl) Antimonite. A solution of 6.5 g (0.0221 mol) of antimony tri-*i*-propoxide in 50 m*l* of benzene was added to a dispersed solution of 19.0 g (0.0687 mol) of triphenylsilanol in 50 m*l* of benzene. Then the clear solution was refluxed for 1.5 hr. When the solvent was removed along with the alcohol formed, a pale yellow solid appeared. After the solvent had been removed completely, the solid was recrystallized from a mixed solvent of benzene and ether(2 : 1), giving 9.7 g (94.0%) of a white, crystalline matter, mp 202—205°C. Found: C, 69.62; H, 4.75; Si, 8.41; Sb, 12.58%; mol wt, 920. Calcd for $C_{64}H_{45}O_3Si_3Sb$: C, 68.42; H, 4.78; Si, 8.98; Sb, 12.84%; mol wt, 948. IR: 3050(m), 2990(shoulder), 1585(w), 1564 (shoulder), 1480(w), 1425(m), 1380(vs), 1330(vw), 1256(vw), 1183(vw), 1155(vw), 1114(s), 1103(shoulder), 1060(vw), 1025(vw), 990(m), 905(s), 740(m), 710 and 700(s), 680(m) cm^{-1}.

Measurement of Relative Hydrolytic Stability. Weighed samples (0.5—0.8 g) of tris(triorganosilyl) antimonite were vigorously stirred at 23°C, into a mixture of 100 m*l* of a 5% aqueous hydrochloric acid solution, 30 m*l* of acetone, and 1 g of sodium potassium tartrate. After twenty minutes, 5 m*l* of the solution was neutralized with a saturated sodium bicarbonate solution and then titrated with an iodine solution, using a starch indicator. The results are shown in Fig. 1. On the other hand, samples (0.4—0.2 g) in 10 m*l* of THF were added to a solution of 1 g of sodium potassium tartrate in 20 m*l* of a 5% aqueous hydrochloric acid solution, they were titrated after having been stirred at 50°C. The results were as follows; tris(triphenylsilyl) antimonite; Sb, 72.5% (after 5 minutes), 77.0(10), 99.0(20): tris(trimethylsilyl) antimonite; 90.2(5), 100 (10): tris(tri-*t*-butoxysilyl) antimonite; 100(5).

Analysis. The antimony was determined by iodometry after a weighed sample had been hydrolyzed with a 20% alcohol solution, a few drops of concentrated hydrochloric acid, and 1 g of sodium potassium tartrate. The silicon was determined as silicon dioxide after a sample had been decomposed by concentrated sulfuric acid and a mixture of ammonium nitrate and sulfate.