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A REDOX REACTION INVOLVING $(CH_3)_3Sb$ MOIETY

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IN the course of our study on organoantimony compounds[1]. the following interesting reactions were found. Redox reactions of thiols and trimethylantimonydiethoxide or -oxide gave trimethylstibine and disulfides; the former reaction proceeds particularly smooth as shown in (I).

$$(CH_3)_3Sb(OC_2H_5)_2 + 2RSH \longrightarrow (CH_3)_3Sb + RSSR + 2C_2H_5OH \quad (I)$$

Also, a similar reaction of sodiumdialkyldithiocarbamates with $(CH_3)_3SbBr_2$ was found to occur as has been reported with $(C_6H_5)_3SbBr_2$[2]. In this paper we will describe informations on the redox reaction involving trimethylantimonydiethoxide and thiols, thioacetic acid and thiobenzoic acid.

Although possible intermediates $(CH_3)_3Sb(SR)_2$ could not be isolated in the reaction (I) even at 0°, the reaction with thioacetic acid at 5° and thiobenzoic acid at room temperature gave a thermally unstable $(CH_3)_3Sb(SCOCH_3)_2$ and a fairly stable $(CH_3)_3Sb(SCOC_6H_5)_2$, respectively. The results of the IR spectra suggest that these two thiocarboxylates have Sb-S linkages in the solid and in solution.

By refluxing in benzene, trimethylantimonybisthiobenzoate decomposed into trimethylstibine and dibenzoyldisulfide as shown in (II), and interestingly, the reverse reaction was found to occur in this case.

$$(CH_3)_3Sb(SCOC_6H_5)_2 \rightleftharpoons (CH_3)_3Sb + C_6H_5\overset{\overset{O}{\|}}{C}SS\overset{\overset{O}{\|}}{C}C_6H_5 \quad (II)$$

Experimental

All reactions were carried out under nitrogen atmosphere. Trimethylstibine was distilled off with benzene from the reaction mixture under reduced pressure. The distillate was brominated and the solid insoluble in benzene was weighed as $(CH_3)_3SbBr_2$ and identified by the melting point.

Preparation of $(CH_3)_3Sb(OC_2H_5)_2$

Trimethylantimonydibromide (100 g.) was added slowly to sodium ethoxide (sodium 14 g. in 300 ml ethanol). The mixture was stirred for 30 min. at room temperature, and 50 ml of benzene was added. The supernatant liquid was separated and the solvent was removed under reduced pressure to give 45 g. (59 %) of colorless hygroscopic trimethylantimonydiethoxide, $(CH_3)_3Sb(OC_2H_5)_2$. B.p. 66-67°/5 mm. (Found: C, 32.91; H, 7.18. $C_7H_{19}O_2Sb$ calcd.: C, 32.70; H, 7.40 %.)

Reaction of $(CH_3)_3Sb(OC_2H_5)_2$ with thiols

To a solution of 2.48 g. (0.04 mol) of ethanethiol in benzene (50 ml), 5.1 g. (0.02 mol) of $(CH_3)_3Sb(OC_2H_5)_2$ was added. The mixture was stirred for 15 min. at room temperature. Bromination of the distillate gave 6.3 g. (91 %) of $(CH_3)_3SbBr_2$. m.p. 198° decomp.. The residue was distilled under reduced pressure to give 2.2 g. (92 %) of diethyldisulfide, $(C_2H_5S)_2$, b.p. 52°/20 mm. (Found: C, 39.07; H, 8.46. $C_4H_{10}S_2$ calcd.: C, 39.28; H, 8.25 %.) In a similar way, reactions of $(CH_3)_3Sb(OC_2H_5)_2$ with propanethiol, butanethiol, 2-hydroxyethanethiol and thiophenol were carried out. Yield: disulfide;

85-92 %, $(CH_3)_3Sb$; 90-91 %.

Reaction of $(CH_3)_3Sb(OC_2H_5)_2$ with CH_3COSH and C_6H_5COSH

A reaction of $(CH_3)_3Sb(OC_2H_5)_2$ and thioacetic acid, CH_3COSH, was carried out as described above under 5°. A small amount of $(CH_3)_3Sb$ and colorless needle-like crystals of trimethylantimonybisthioacetate, $(CH_3)_3Sb(SCOCH_3)_2$, m.p. 51-52°, were obtained. Yield: 71 % (Found: C, 26.82; H, 4.80. $C_7H_{15}O_2S_2Sb$ calcd.: C, 26.50; H, 4.77 %.) Mol. wt. found by vapor pressure osmometer in $CHCl_3$ at 25°, 337 and 344 at concentrations 0.46 and 0.88 % w(sample)/W(solvent) respectively; calcd. for monomer, 317.

From the reaction with thiobenzoic acid at room temperature, colorless scale-like crystals of trimethylantimonybisthiobenzoate, $(CH_3)_3Sb(SCOC_6H_5)_2$, m.p. 108° was obtained. Yield: 92 % (Found: C, 46.33; H, 4.38. $C_{17}H_{19}O_2S_2Sb$ calcd.: C, 46.28; H, 4.33 %.) Mol. wt. by vapor pressure osmometer in $CHCl_3$ at 25°, 419 at concentration 0.57 % w(sample)/W(solvent); calcd. for monomer, 441.

IR frequency associated with C=O : $(CH_3)_3Sb(SCOCH_3)_2$: 1639, 1634 cm^{-1} in the solid; 1645 cm^{-1} in CCl_4 solution. $(CH_3)_3Sb(SCOC_6H_5)_2$: 1621 cm^{-1} in the solid and in CCl_4 solution. These results suggested that both compounds have Sb-S linkages both in the solid and in solution.

Decomposition of $(CH_3)_3Sb(SCOC_6H_5)_2$

A solution of 4.41 g. of trimethylantimonybisthiobenzoate, $(CH_3)_3Sb(SCOC_6H_5)_2$, in 50 ml of benzene was refluxed for 7 hrs. From the distillate 1.0 g. (30 %) of $(CH_3)_3SbBr_2$ was obtained. The residue was fractionally recrystallized from ethanol to give

0.7 g. (27 %) of dibenzoyldisulfide, m.p. 127° decomp. (reported[3] 127-128° decomp.).

Reaction of $(CH_3)_3Sb$ with $(C_6H_5COS)_2$

1.7 g. (0.01 mol) of $(CH_3)_3Sb$ was added to a solution of 2.7 g. (0.01 mol) of dibenzoyldisulfide, $(C_6H_5COS)_2$, in benzene and the mixture was refluxed for 7 hrs.. From the distillate, 0.8 g. of $(CH_3)_3SbBr_2$ (24 %) was obtained. The residue was recrystallized from ethanol to give 2.7 g. (61 %) of $(CH_3)_3Sb(SCOC_6H_5)_2$, m.p. 108°.

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