Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

REACTION OF TRIMETHYLSTIBINE SULFIDE WITH ALKYL HALIDES

JUNZO OTERA AND ROKURO OKAWARA
Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka (Japan)
(Received November 1st, 1968)

INTRODUCTION

The Sb–S bond of triorganostibine sulfides has been found to be reactive in sulfur–halogen exchange reactions with organotin halides[1] and mercuric halides[2]. In this paper, further studies of the reactions of trimethylstibine sulfide with some alkyl halides are described and the results are discussed in terms of the nature of the Sb–S bond as determined in UV spectral investigations.

EXPERIMENTAL

Materials

The preparation of organoantimony compounds employed has been described[1]. All the solvents were purified according to literature directions[3]. Benzyl iodide was prepared from benzyl chloride and sodium iodide and purified by distillation under reduced pressure. All other alkyl halides were commercial products and distilled before use.

Determination of reaction products

In the case of the reaction with benzyl bromide, trimethylstibine and trimethylantimony dibromide were determined separately by azeotropic distillation of the former from the reaction mixture. In the reactions with alkyl iodides, the trimethylstibine formed was allowed to be oxidized by air in the chloroform solution to form insoluble oxybis(trimethylantimony) diiodide in the presence of the trimethylantimony diiodide formed in equimolar quantity as described below, since trimethylantimony diiodide is not stable enough to isolate quantitatively.

$$(CH_3)_3Sb + 1/2\,O_2 + (CH_3)_3SbI_2 \rightarrow [I(CH_3)_3Sb]_2O \qquad (1)$$

Quantitative determination of dimethyl and diethyl disulfides was carried out using PMR spectroscopy with reference to the known amount of dichloromethane as an internal standard.

Reactions of trimethylstibine sulfide

(*a*) *With benzyl bromide.* Trimethylstibine sulfide (4 g, 0.02 mole) and benzyl bromide (3.4 g, 0.02 mole) were dissolved in 50 ml of chloroform through which nitrogen had been bubbled to remove oxygen. After the mixture had been heated at reflux for 15 minutes under a nitrogen atmosphere, trimethylstibine was removed by azeotropic distillation with chloroform under reduced pressure (5 mm Hg) and identified as trimethylantimony dibromide by the reaction with bromine[4]; m.p. 198°, (reported[5], 198°), yield 2.9 g (89%). To the undistillable residue was added 100 ml of a 1/1 ether–water mixture. Recrystallization of the white precipitates obtained from the ethereal layer from ethanol and carbon tetrachloride gave 2.0 g (81%) of dibenzyl disulfide; m.p. 69–70° (undepressed mixed m.p.). From the aqueous layer, 2.9 g (89%) of trimethylantimony dibromide, m.p. 199°, was obtained.

(*b*) *With benzyl iodide.* Ten ml of a chloroform solution of trimethylstibine sulfide (1.0 g, 0.005 mole) and benzyl iodide (1.1 g, 0.005 mole) was kept in air in the dark at room temperature for 7 days in order to complete reaction (1)*. Recrystallization of the precipitate from water–acetone yielded 0.9 g (60%) of oxybis(trimethylantimony) diiodide which was identified by its IR spectrum. From the chloroform solution, 0.5 g (82%) of dibenzyl disulfide, m.p. 70°, was obtained.

(*c*) *With methyl iodide.* An analogous procedure was employed. Oxybis(trimethylantimony) diiodide was recrystallized from water–acetone to yield 1.3 g (87%). From the PMR spectrum of the chloroform solution, the amount of dimethyl disulfide was found to be 0.00228 mole (91%).

(*d*) *With ethyl iodide.* The same operation as in the case of the reaction with methyl iodide gave 1.1 g (73%) of oxybis(trimethylantimony) diiodide. The PMR spectrum of the chloroform solution showed the amount of diethyl disulfide to be 0.00188 mole (75%); small amounts of unreacted trimethylstibine sulfide and ethyl iodide also were present.

Physical measurements

The PMR and IR spectra were measured using a Japan Electron Optics Model JNM-3H-60 spectrometer and a Hitachi EPI-2G grating spectrometer, respectively. The UV spectra measurements were carried out with a Hitachi EPS-3 spectrometer equipped with 1 cm quartz cells.

RESULTS AND DISCUSSION

Among various organometallic sulfides, only the reactions of methylsilthianes with alkyl halides have been reported[6] to give dialkyl sulfides and methylhalosilanes under drastic conditions (at 160–180° for 100 h–2 weeks). It is remarkable that our reactions proceed so smoothly under mild conditions to give dialkyl disulfides and organoantimony compounds in quantitative yields as shown in eqn. (2).

$$2(CH_3)_3SbS + 2\,RX \rightarrow (CH_3)_3Sb + (CH_3)_3SbX_2 + R_2S_2 \qquad (2)$$

($RX = CH_3I, C_2H_5I, C_6H_5CH_2I$ and $C_6H_5CH_2Br$)

An IR study has suggested that the Sb–S bond in trimethylstibine sulfide has

---

* The PMR spectrum of the reaction mixture showed no signal due to trimethylstibine sulfide after 24 h.

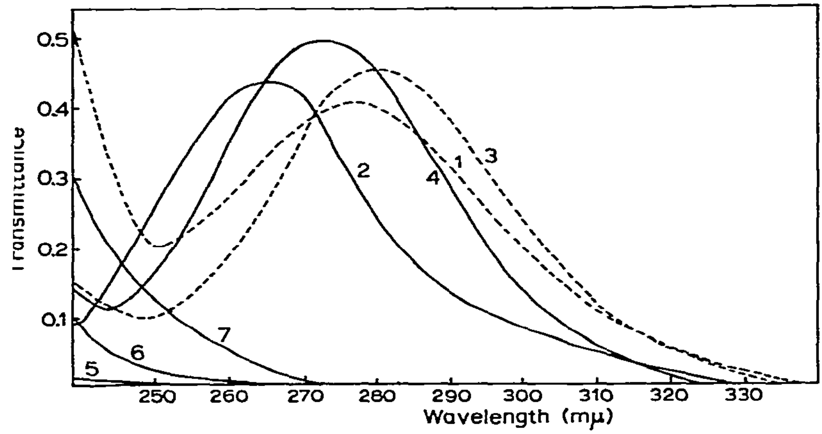


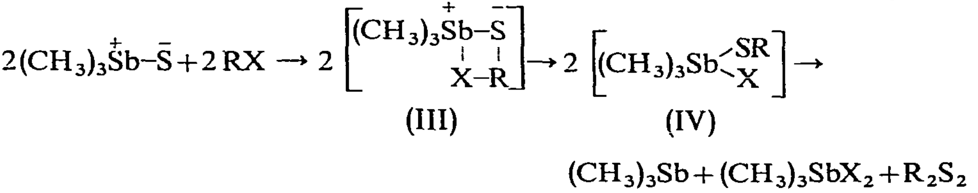
Fig. 1. UV spectra of R_3SbS and R_3SbX_2. – – –, in n-hexane; ——, in acetonitrile; (1) $(CH_3)_3SbS$; [λ_{max} 279 mμ] (On account of its poor solubility, the supernatant solution obtained after shaking for 30 minutes was used); (2) $(CH_3)_3SbS$; $1.10 \cdot 10^{-4}$ [λ_{max} 267 mμ, log ε 3.6]; (3) $(C_6H_{11})_3SbS$; $0.893 \cdot 10^{-4}$ [λ_{max} 282 mμ, log ε 3.7]; (4) $(C_6H_{11})_3SbS$; $0.839 \cdot 10^{-4}$ [λ_{max} 274 mμ, log ε 3.8]; (5) $(CH_3)_3SbCl_2$; $1.27 \cdot 10^{-4}$; (6) $(CH_3)_3SbBr_2$; $1.06 \cdot 10^{-4}$; (7) $(C_6H_{11})_3SbBr_2$; $1.01 \cdot 10^{-4}$ mole/l.

partial π-bond character[1]. Hoping to obtain further information concerning this bond and a better understanding of these reactions, we measured UV spectra of triorganostibine sulfides in various solvents. As shown in Fig. 1, trimethyl- and tricyclohexylstibine sulfide have absorption maxima at *ca.* 280 mμ in n-hexane and show a blue shift in acetonitrile. These characteristic bands seem to be derived from the Sb–S bond, because such absorption was not observed in the spectra of triorganoantimony dihalides in this region. These bands may be assigned to intramolecular charge transfer from the semi-polar structure (I) to the double bond structure (II). It may be noted that the absorption bands at 270–300 mμ (log ε≃

$$\underset{\text{(I)}}{(CH_3)_3\overset{+}{Sb}-\overset{-}{S}} \qquad \underset{\text{(II)}}{(CH_3)_3Sb=S}$$

4.0–4.5) in cyclopentadienylidene-dimethylsulforane and -tri-n-propylphosphorane show a similar solvent effect and were assigned to intramolecular charge transfer bands from the ylide structure to the ylene structure[7]. This suggests that the semi-polar structure makes a major contribution to the resonance hybrid of the sulfide in its ground state.

In the reactions of trimethylstibine sulfide with alkyl halides, therefore, the semi-polar character of the Sb–S bond may easily allow formation of trimethylanti-



$$2(CH_3)_3\overset{+}{Sb}-\overset{-}{S}+2\,RX \rightarrow 2\left[\begin{array}{c}(CH_3)_3\overset{+}{Sb}-\overset{-}{S}\\ \quad\ \ X-R\end{array}\right] \rightarrow 2\left[(CH_3)_3Sb{<}^{SR}_{X}\right] \rightarrow$$
$$\text{(III)} \qquad\qquad \text{(IV)}$$
$$(CH_3)_3Sb+(CH_3)_3SbX_2+R_2S_2$$

mony halide thioalkoxide (IV) via a four-centered intermediate (III). Since trimethylantimony bis(thioalkoxide) is unstable and decomposes to trimethylstibine and dialkyl disulfide[4], probably the Sb–S bond of compound (IV) is also unstable, and thus (IV) would be expected to give the final reaction products immediately.

REFERENCES

1 M. SHINDO, Y. MATSUMURA AND R. OKAWARA, *J. Organometal. Chem.*, 11 (1968) 299.
2 T. SAITO AND R. OKAWARA, unpublished data.
3 J. A. RIDDICK AND E. E. TOOPS, JR., *Organic Solvents*, Interscience, New York, 1955.
4 Y. MATSUMURA, M. SHINDO AND R. OKAWARA, *Inorg. Nucl. Chem. Letters*, 3 (1967) 219.
5 M. SHINDO AND R. OKAWARA, *J. Organometal. Chem.*, 5 (1966) 537.
6 E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1964) 2455.
7 Z. YOSHIDA AND K. IWATA, *Abstr. 19th Ann. Meeting Japan Chem. Soc.*, 1 (1966) 189.