Journal of Organometallic Chemistry, 131 (1977) 31—34

REACTION OF TRIMETHYL- AND TRIPHENYL-ANTIMONY DIBROMIDE WITH PHOSPHINIC ACIDS EXHIBITING P—H BONDING

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(Received September 21st, 1976)

Summary

Treatment of $(CH_3)_3SbBr_2$ with $C_6H_5P(O)(H)OH$ or $C_6H_5CH{=}CHP(O)(H)OH$ gave $(CH_3)_3Sb[OP(O)(H)C_6H_5]_2$, and $(CH_3)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$, respectively. Similarly, treatment of $(C_6H_5)_3SbBr_2$ with the same phosphinic acids gave $(C_6H_5)_3Sb[OP(O)(H)C_6H_5]_2$, and $(C_6H_5)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$. These compounds were found to have Sb—O—P linkages rather than Sb—P bonds.

Introduction

Numerous publications deal with reactions of antimony(III) and antimony(V) halides and their derivatives. Several of these reactions involve interaction with compounds containing labile hydrogens in which a condensation occurs with the concurrent splitting off of a hydrogen halide, e.g. (X = halogen):

$$\text{Sb—X} + \text{HY} \rightarrow \text{Sb—Y} + \text{HX}, \text{ and } \underset{|}{\text{Sb}}\text{—X} + \text{HY} \rightarrow \underset{|}{\text{Sb}}\text{—Y} + \text{HX}$$

The hydrogen halide is usually removed by the action of a reagent such as triethylamine to form a triethylammonium halide complex. A diverse series of reactants have included sulfuric acid [1], mercaptans [2], silanols [3], and peroxides [4].

The present study examines the interaction of monosubstituted phosphinic acids with trimethyl- and triphenyl-antimony dibromides. These acids exist essentially completely in the "keto" form of the tautomeric pair: $RP(OH)_2 \rightarrow RPH(O)OH$. As such, the acids are monobasic [5] and can undergo reaction at either the P—O—H bond or the P—H bond. The purpose of this research is to elucidate which type of interaction occurs between the antimony(V) dihalides and these phosphinic acids.

Experimental

Trimethylantimony dibromide was prepared according to the literature [6], while triphenylantimony dibromide was prepared in a similar manner by the

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF SOME PHOSPHINIC ACID DERIVATIVES OF TRIMETHYL- AND TRIPHENYL-ANTIMONY DIBROMIDES

Compound	Analyses Calcd. (found) (%)				Mol. wt. [a]	Yield (%)	M.p. (°C)
	C	H	P	Sb			
$(CH_3)_3Sb[OP(O)(H)C_6H_5]_2$	40.12	4.71	13.80	27.11	449	75	86–89
	(40.30)	(4.80)	(13.96)	(26.91)	(460)		
$(CH_3)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$ [b]							
$(C_6H_5)_3Sb[OP(O)(H)C_6H_5]_2$	56.72	4.28	9.75	19.17	635	61	142–144
	(56.94)	(4.12)	(9.70)	(19.40)	(619)		
$(C_6H_5)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$	59.42	4.55	9.01	17.71	687	19	158–160
	(59.16)	(4.63)	(8.83)	(17.89)	(680)		

[a] By vapor-pressure osmometry in $CHCl_3$. [b] Slightly impure oil.

TABLE 2

NMR DATA OF ANTIMONY(V) DERIVATIVES AND RELATED COMPOUNDS

Compound	^1H NMR [a]					^{31}P [b]
	$\delta(CH_3)$	$\delta(C_6H_5)$	$\delta(OH)$	$\delta(P{-}H)$	$\delta(CH{=}CH)$	
$(CH_3)_3Sb[OP(O)(H)C_6H_5]_2$	2.08(s)	7.46(m)		7.52(d, 547)		−15.49
		7.74(m)				
$(C_6H_5)_3Sb[OP(O)(H)C_6H_5]_2$		7.20(m)		7.26(d, 547)		−13.56
		7.55(m)				
		8.13(m)				
$(CH_3)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$	2.17(s)	7.41(m)		7.31(d, 548)	6.57(m)	−15.45
$(C_6H_5)_3Sb]OP(O)(H)CH{=}CHC_6H_5]_2$		8.23(m)		7.11(d, 546)	5.99(m)	−13.73
		7.67(m)				
		7.31(m)				
$(CH_3)_3SbBr_2$	2.66(s)					
$(C_6H_5)_3SbBr_2$		7.53(m)				
		8.19(m)				
$C_6H_5P(O)(H)OH$		7.63(m)	13.59(s)	7.71(d, 580)		−21.74
		7.89(m)				
$C_6H_5CH{=}CHP(O)(H)OH$		7.38(m)	12.27(s)	7.36(d, 570)	6.38(m)	−22.89

[a] In $CDCl_3$; in ppm measured downfield from internal TMS. [b] In $CDCl_3$; in ppm relative to 85% H_3PO_4 as the external standard. All signals are singlets.

bromination of triphenylantimony. Phenylphosphinic acid was purchased from Eastman and used as received. β-Styrylphosphinic acid was prepared as previously reported [7].

Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

The ^1H nuclear magnetic resonance (NMR) spectra were run on a JEOLCO JNM-MH-100 spectrometer in $CDCl_3$ and are referenced to tetramethylsilane as an internal standard, with positive shifts being downfield. The ^{31}P NMR measurements were carried out using a Varian XL-100-15 spectrometer equipped with Fourier-transform accessories supplied by Nicolet Technology Corporation. The spectra were run in $CDCl_3$ with broad-band proton decoupling. The chemical shifts were referenced by the tube-interchange method to 85% H_3PO_4, with negative shifts being downfield.

The compounds were prepared in a similar manner and are white solids except for $(CH_3)_3Sb[OP(O)(H)CH{=}CHC_6H_5]_2$, which was an oil that defied all attempts at crystallization. A typical preparation was as follows:

Synthesis of $(CH_3)_3Sb[OP(O)(H)C_6H_5]_2$. Phenylphosphinic acid (0.471 g, 3.41 mmol) and triethylamine (0.548 g, 5.43 mmol) were dissolved in 35 ml of deaerated benzene and placed in a 100 ml round-bottom flask fitted with a nitrogen-inlet tube and dropping funnel. Trimethylantimony dibromide (0.55 g, 1.68 mmol) was dissolved in 50 ml of deaerated benzene, placed in the dropping funnel and was added to the reaction flask at room temperature with stirring over a period of 15 minutes. During the addition a white precipitate formed. The reaction mixture was stirred for an additional hour. At the end of this time, the white solid ($(C_2H_5)_3N \cdot HBr$, 0.608 g) was removed by filtration. Stripping off the solvent by a water aspirator left the product (0.567 g, 1.26 mmol), which was recrystallized twice from a benzene–heptane mixture. Physical properties for the new compounds are presented in Table 1, while the NMR spectral properties are listed in Table 2.

Results and discussion

The reaction of trimethyl- or triphenyl-antimony dibromides with two molar equivalents of either of the two phosphinic acids resulted in the elimination of hydrogen bromide and the formation of several new antimony(V) derivatives.

$$R_3SbBr_2 + 2\,R'PO_2H_2 \xrightarrow{2(C_2H_5)_3N} R_3Sb(PO_2R'H)_2 + 2\,(C_2H_5)_3N \cdot HBr \qquad (1)$$

where R = CH_3, C_6H_5 and R′ = C_6H_5, $C_6H_5CH{=}CH$

An essentially quantitative yield of $(C_2H_5)_3N \cdot HBr$ was recovered from each reaction and identified by its ^1H NMR spectrum. A hydrogen bromide acceptor was necessary in the reaction. With no acceptor, heating the starting materials together in a sealed tube at 100°C for 20 hours resulted in no reaction. Using pyridine and refluxing in benzene for 20 hours led to the reaction of about 2/3 of the starting materials to give a practically equimolar mixture of $R_3SbBr(PO_2R'H)$ and $R_3Sb(PO_2R'H)_2$. Triethylamine as the acceptor yielded the $R_3Sb(PO_2R'H)_2$ exclusively.

The reaction of the antimony(V) dihalide and the phosphinic acid in 1/1 molar ratio gave an equimolar mixture of the starting material, the mono-, and the di-substituted product, as determined by integration of the ^1H NMR spectrum. The monosubstituted product, $R_3SbBr(PO_2R'H)$, was not isolated but was identified by ^1H NMR, with the Sb—CH_3 signal (at 2.40 ppm) appearing midway between that of the starting material and the disubstituted product.

$$3\,R_3SbBr_2 + 3\,R'PO_2H_2 \xrightarrow{3(C_2H_5)_3N} R_3SbBr_2 + R_3SbBr(PO_2R'H) +$$

$$R_3Sb(PO_2R'H)_2 + 3(C_2H_5)_3N \cdot HBr \qquad (2)$$

Proton NMR clearly establishes that the products contain a Sb—O—P linkage rather than Sb—P bond. The parent phosphinic acids exhibit an OH signal around 12—13 ppm downfield from TMS, while none of the products showed this. Furthermore, in all of the products the P—H proton signal remained, but with a small reduction (4—6%) in the phosphorus—hydrogen coupling constant. Under broad-band proton decoupling, the ^{31}P NMR of the new compounds shows a single sharp resonance. The products all exhibited ^{31}P signals which appeared 5—9 ppm upfield of the parent acids. From the finding reported here, we conclude that the new compounds made by this procedure exhibit the following structural formulas: $R_3Sb(Br)[OP(O)(H)R']$ and $R_3Sb[OP(O)(H)R']_2$, with the three R groups presumably lying in the equatorial positions of the trigonal bipyramid of substituents surrounding the antimony atom.

Acknowledgment

We wish to thank the National Science Foundation for supporting this work under Research Grant CHE76-04287.

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