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METHYL GROUP REPLACEMENT ON PENTAMETHYLANTIMONY WITH ORGANOPHOSPHORUS SUBSTITUENTS

GUY E. GRAVES and JOHN R. VAN WAZER *
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235 (U.S.A.)
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Summary

Phosphinic and phosphonic acids were treated with pentamethylantimony to replace one of its methyl groups (with formation of methane) to give the following new compounds: $(CH_3)_4SbOP(O)(C_6H_5)_2$, $(CH_3)_4SbOP(O)(OH)CH_3$, and $(CH_3)_4SbOP(O)(OH)C_6H_5$. The latter two compounds are associated, presumably through hydrogen bonding.

Introduction

The chemistry of trivalent organoantimony compounds is much more extensive than the chemistry of the pentavalent organoantimony compounds containing five antimony—carbon bonds [1]. Wittig and co-workers first reported the latter type of compound with the preparation of pentaphenylantimony [2,3] and pentamethylantimony [4]. Additional derivatives include pentaalkyl compounds containing unsaturated organic groups [5—10], pentaethylantimony [11], and various mixed methylethyl organoantimony compounds [2].

The chemistry of pentamethylantimony has received virtually no attention except for the series of papers by Schmidbaur and co-workers [13—19]. The present article describes the results of our work in replacing methyl groups on pentamethylantimony with organophosphorus substituents. In this presentation we have not speculated about the reaction mechanisms; however mechanisms of somewhat related reactions of pentaphenylantimony have been reported [20—23].

Experimental

Pentamethylantimony [4] and methylphosphonic acid [24] were prepared according to the literature. Phenylphosphonic and diphenylphosphinic acids were obtained from Aldrich. Chlorodiphenylphosphine was purchased from Alfa Ventron.

TABLE 1

ELEMENTAL ANALYSES AND PHYSICAL CONSTANTS

Compound	Analysis (Found (calcd.) (%))				Mol wt [a] (Found calcd.)	Yield (%)	M.p. (°C)
	C	H	P	Sb			
$(CH_3)_4SbOP(O)(C_6H_5)_2$	48.33 (48.16)	5.70 (5.56)	7.69 (7.76)	30.54 (30.51)	398 (399)	83	150—156
$(CH_3)_4SbOP(O)(OH)CH_3$	21.92 (21.69)	5.90 (5.82)	11.16 (11.19)	43.80 (43.97)	668 (276)	74	145—148
$(CH_3)_4SbOP(O)(OH)C_6H_5$	35.29 (35.43)	5.51 (5.35)	9.07 (9.14)	35.80 (35.92)	720 (338)	94	204—205

[a] Run by osmometry in $CHCl_3$.

Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected.

The ^1H nuclear magnetic resonance (NMR) spectra were run on a JEOLCO JNM-MH-100 spectrometer in $CDCl_3$ and are referenced to tetramethylsilane (τ 10 ppm) as an internal standard. 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 CH_2Cl_2 with broad-band proton decoupling. The chemical shifts were referenced to 85% H_3PO_4 by the tube-interchange method, with negative shifts being downfield.

The compounds were prepared in a similar manner and are white solids. A typical preparation was as follows.

Synthesis of $(CH_3)_4SbOP(O)(C_6H_5)_2$

Pentamethylantimony (0.239 g, 1.17 mmol) was weighed into a nitrogen-filled flask. The flask was then cooled to —78°C in a dry-ice/acetone bath. Di-

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA [a] (τ, ppm)

Compound	^1H			$\delta(^{31}P)$
	$\tau(Sb—CH_3)$	$\tau(P—CH_3)$	$\tau(C_6H_5)$	
$(CH_3)_4SbOP(O)(C_6H_5)_2$	8.55 (s) 12 H	—	2.32 (m) 2.78 (m)	—13.48
$(CH_3)_4SbOP(O)(OH)CH_3$	8.51 (s) 12 H	8.82 (d, J 16 Hz) 3H	—	—18.92
$(CH_3)_4SbOP(O)(OH)C_5H_5$	8.55 (s) 12 H	—	2.30 (m) 2.58 (m) 5H	—8.87

[a] Abbreviations: s = singlet, d = doublet, m = multiplet. H = relative number of hydrogens found by integration. Negative ^{31}P shifts are downfield from 85% H_3PO_4.

phenylphosphinic acid (0.250 g, 1.15 mmol) was added to the flask along with about two ml of dried dichloromethane. The reaction flask was allowed to warm slowly under a nitrogen atmosphere. Upon reaching room temperature, gas evolution was noted by the presence of bubbles rising through the solution. After allowing the reaction mixture to remain at room temperature overnight, the solvent was stripped from the clear, colorless solution to give a white solid identified as $(CH_3)_4SbOP(O)(C_6H_5)_2$ (yield 0.383 g, 83%). Physical properties for the new compounds are listed in Table 1, while spectral properties are given in Table 2.

Results and discussion

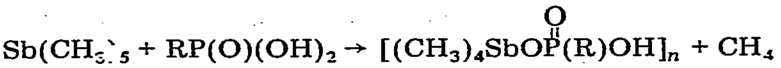
The room-temperature reaction of diphenylphosphinic acid with pentamethylantimony went as shown in eq. 1 with no evidence for any higher substituted

$$Sb(CH_3)_5 + (C_6H_5)_2P(O)OH \rightarrow (CH_3)_4SbOP(O)(C_6H_5)_2 + CH_4 \qquad (1)$$

products. Heating a 5/1 ratio of diphenylphosphinic acid to pentamethylantimony in a sealed tube at 100°C for 72 h again resulted in the monosubstituted product only as evidenced by ^1H NMR.

The proton NMR of the product showed a single peak in the methyl region downfield from the resonance for $Sb(CH_3)_5$. Although one might expect more than one peak due to the methyl groups being in different environments, this is not the case. Even at —100°C, $Sb(CH_3)_5$ is reported to have only a single peak in CS_2 [25], while the previously described tetramethylantimony derivatives also exhibited just a single peak [13—19]. This equivalence of the four methyl groups was attributed to ligand reorganization (pseudorotation) processes, an argument that probably applies to the new compound also.

The interaction of methyl- and phenyl-phosphonic acids with pentamethylantimony gave white crystalline solids. According to elemental analyses and cryoscopic molecular weight determinations, a product of type I was obtained (eq. 2) with n being 2.1 to 2.5. The ^1H NMR spectrum exhibited a single peak



$$Sb(CH_3)_5 + RP(O)(OH)_2 \rightarrow [(CH_3)_4SbO\overset{O}{\overset{\|}{P}}(R)OH]_n + CH_4 \qquad (2)$$

(I)

$(R = C_6H_5, CH_3)$

for the antimony methyl groups, while integration established a ratio of four antimony methyls to one phosphorus phenyl or methyl group. In all phosphorus compounds containing $>P(O)(OH)$ and $-P(O)(OH)_2$ groups, association through H bonding is almost certain to occur in organic solvents not exhibiting hydrogen bonding [26]. This association has been reported for trifluoromethylphosphonous acid (dimer) [27] and phenylphosphonic acid (high order of association) [28] and is almost certainly present in our new compounds.

The ^{31}P NMR spectra for the three new compounds discussed above exhibited a single sharp peak upfield from the parent acid. The upfield shift increases from the parent phosphoric acids ranged from 1.47 to 5.83 ppm.

The reaction of pentamethylantimony with chlorodiphenylphosphine was expected to proceed with the elimination of methyl chloride (eq. 3), as previously found in the case of methyl phosphorus [28,29] and arsenic compounds [31].

$$Sb(CH_3)_5 + (C_6H_5)_2PCl \rightarrow (CH_3)_4SbP(C_6H_5)_2 + CH_3Cl \tag{3}$$

However, it appears that the following reaction took place in methylene chloride with precipitation of the tetramethylstibonium chloride (eq. 4).

$$Sb(CH_3)_5 + (C_6H_5)_2PCl \rightarrow (CH_3)_4Sb^+Cl^- + (C_6H_5)_2PCH_3 \tag{4}$$

The ^1H NMR spectrum of the reaction product gave a doublet (J 5 Hz) at τ 1.62 ppm corresponding to τ 1.51 ppm (J 6 Hz), as reported for $(C_6H_5)_2PCH_3$ [32]; and the ^{31}P measurements yielded a single peak at +26.2 ppm, as compared to a literature value of +28 ppm [33]. The tetramethylstibonium chloride was identified by elemental analysis.

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