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

ALKOXYTETRAPHENYLANTIMONY COMPOUNDS

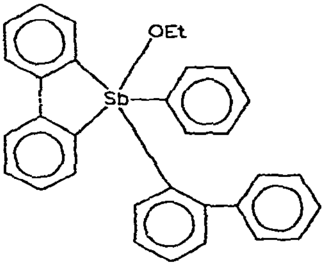
G. O. DOAK, G. G. LONG AND LEON D. FREEDMAN
North Carolina State University, Raleigh, North Carolina, 27607 (U.S.A.)

(Received December 5th, 1967)

SUMMARY

Several alkoxytetraphenylantimony compounds have been prepared by the reaction between tetraphenylstibonium bromide (or chloride) and the appropriate sodium alkoxides. The alkoxy compounds are unstable and decompose rapidly at about 130°. The PMR and infrared spectra of the alkoxy compounds are consistent with the assumed pentacovalent structures. The ultraviolet absorption spectra of the alkoxy compounds are virtually identical with one another and with the spectrum of tetraphenylstibonium hydroxide. These spectra differ markedly, however, from the spectra of other compounds in which several phenyl groups are bonded to a single central atom. It is suggested that the phenyl groups in the alkoxy compounds and in the hydroxide are able to interact.

Wittig and Hellwinkel[1] obtained 5-(2-biphenylyl)-5-ethoxy-5,5-dihydro-5-phenyldibenzostibole (I) by treating 5-phenyl-5,5′-spirobis(dibenzostibole) with ethanol. Schmidbaur, Arnold and Beinhofer[2] prepared tetramethyl- and tetraphenyl-(trimethylsiloxy)antimony, $(CH_3)_4SbOSi(CH_3)_3$ and $(C_6H_5)_4SbOSi(CH_3)_3$, by the reaction between the sodium salt of trimethylsilanol and tetramethylstibonium chloride or tetraphenylstibonium bromide, respectively. With the possible exception of tetraphenylstibonium hydroxide[3] these represented, until quite recently, the only pentacovalent antimony compounds of the type R_4SbOY. We have suggested[4] that this class of compound might be of value in studies leading to the preparation of isomers of trigonal bipyramids. The present paper describes the synthesis and properties of compounds of the type $(C_6H_5)_4SbOR$. During the course of this work Dr.



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W. E. McEwen kindly informed us that methoxytetraphenylantimony had been prepared in his laboratory; a preliminary communication on this subject has now appeared[5].

Briles and McEwen[5] obtained methoxytetraphenylantimony by the reaction between sodium methoxide and tetraphenylstibonium bromide in absolute methanol. Although no details of their isolation procedure were given, the compound was isolated under anhydrous conditions[6]. We prepared methoxytetraphenylantimony by the addition of water to a solution of tetraphenylstibonium bromide and sodium methoxide in methanol. The compound, which precipitates almost quantitatively from solution, can be recrystallized from either methanol or aqueous methanol. The recrystallized material is identical, as judged by its PMR spectrum, with the compound prepared by Briles and McEwen.

We have also prepared pure samples of the corresponding ethoxy-, n-propoxy- and isopropoxytetraphenylantimony compounds. The n-butoxy, sec-butoxy, and tert-butoxy compounds were also isolated, but no methods for their purification could be devised. An attempt to prepare ethoxytetraphenylantimony by the procedure we used for the preparation of the methoxy compound gave tetraphenylstibonium hydroxide. In the case of the two propoxy and the three butoxy compounds, moisture was rigidly excluded by the use of a modified Schlenk apparatus. The difference between the methoxy compound and the other alkoxy compounds is surprising. It seems possible that methoxytetraphenylantimony is in equilibrium with the hydroxide in aqueous methanol, but precipitates on the addition of water because of its lower solubility. The methyl group is lost, however, when the compound is refluxed with water for three hours.

The ethoxy, n-propoxy and isopropoxy compounds were readily recrystallized from ethyl, n-propyl, and isopropyl alcohols, respectively. These same alcohols were used as solvents in the preparation of the compounds. The n-butoxy and sec-butoxy compounds separated as oils from n-butyl and sec-butyl alcohols, respectively, after partial removal of the solvents *in vacuo*. These oils did not crystallize on prolonged standing in the refrigerator or in the deep-freeze. They boiled in the range 180–200° at 0.1 mm with extensive decomposition. The analyses and properties given, therefore, are for the crude products obtained by removal of the solvent alcohols at $< 100°$ *in vacuo*. The tert-butoxy compound was obtained, in low yield, as a solid by removal of the solvent, tert-butyl alcohol, in the same manner. Attempts to recrystallize this solid from chloroform or toluene resulted in partial or complete loss of the butyl groups (revealed by PMR studies). Analyses and properties for this compound are also given for the crude product.

PMR spectra

The PMR spectra of freshly prepared samples of the alkoxytetraphenylantimony compounds are consistent with the presence of the expected alkyl groups. Methoxytetraphenylantimony gave a sharp singlet at $\delta = 2.78$ ppm (referred to TMS) and an aromatic/aliphatic proton ratio of 20/2.9 (calcd. 20/3). These results are in almost perfect agreement with the data reported by Briles and McEwen[5]. The ethoxy compound gave a triplet centered at $\delta = 0.85$ due to the methyl group and a quartet centered at $\delta = 2.86$ due to the methylene group. The n-propoxy compound gave a triplet centered at $\delta = 0.64$ due to the methyl group, a complex multiplet centered at $\delta = 1.26$ due to the center methylene group and a triplet at $\delta = 2.78$ due to the methylene group attached to the oxygen. The isopropoxy compound gave a doublet centered at $\delta = 1.15$ due to the methyl protons; the expected multiplet for the methinyl proton was not observed. The tert-butoxy compound gave a sharp singlet at $\delta = 1.26$ due to the three equivalent methyl groups and an aryl/alkyl ratio of 20/9 (calcd. 20/9). The n-butoxy and sec-butoxy compounds gave PMR spectra in $CDCl_3$ which indicated the presence of both aryl and alkyl protons in approximately the ratio of 20/9. The peaks were also in approximately the positions expected for the n-butyl and sec-butyl groups, but no attempt was made to further interpret the complex spectra obtained with the crude products.

Infrared spectra

We have reported in a previous paper the IR frequencies associated with the phenyl groups in $(C_6H_5)_3Sb$ and $(C_6H_5)_3SbY_2$ (where Y is a halogen, nitrate, sulfate or other negative group)[7]. With a few exceptions the phenyl frequencies found for the alkoxytetraphenylantimony compounds did not differ significantly from those we reported previously. The results are also in essential agreement with the phenyl frequencies reported by Deacon *et al.*[8] for tetraphenylphosphonium compounds and by Cullen *et al.*[9] for several arsonium compounds. We have also determined the spectrum of tetraphenylstibonium perchlorate (as an example of a typical ionic stibonium salt) and found, with a few exceptions, that the frequencies associated with the phenyl group are essentially the same as those found for the alkoxytetraphenylantimony compounds. The differences found are all in the X-sensitive bands, $q(a_1)$, $r(a_1)$ and $y(b_1)$[9]. In the perchlorate these bands are found at 1068, 668 and a doublet at 438 and 451 cm^{-1}, respectively. In the alkoxytetraphenylantimony compounds, $q(a_1)$ is split into several bands centered closely about 1068 cm^{-1}, $r(a_1)$ is split into 3 or 4 bands which occur 8 to 28 cm^{-1} below the single frequency observed in the perchlorate, and $y(b_1)$ occurs as three bands which appear between 465 and 441 cm^{-1}.

All the spectra of the alkoxytetraphenylstibonium compounds contain rather weak C–H stretching frequencies; the C–H bending frequencies were usually not observed. They also exhibit a band of weak to medium intensity which does not occur in the spectrum of tetraphenylstibonium perchlorate. This band, which occurs between 335 and 320 cm^{-1}, is also found in the spectrum of tetraphenylstibonium hydroxide and is probably the Sb–O stretching vibration*.

Ultraviolet spectra

Table 1 lists the molar absorptivities found at the maxima and inflections of the ultraviolet absorption spectra of the recrystallized alkoxytetraphenylantimony compounds as well as tetraphenylstibonium hydroxide and chloride. Since the butoxy compounds could not be purified, their spectra are not included. We were unable to follow the customary practice of using the same solvent for all the compounds. Some of our compounds are not soluble enough in non-polar solvents such as hexane or cyclohexane; and it was considered inadvisable to use a single alcohol for all the

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* Bands at 360 and 315 cm^{-1} have previously been observed in the spectrum of triphenylantimony diformate and have been assigned to Sb–O vibrations; *cf.* ref. 7. Okawara and Yasuda[10] have assigned a band at 370 cm^{-1} to the Sn–O stretching vibration in trimethyltin hydroxide in the solid state.

TABLE 1

ULTRAVIOLET ABSORPTION MAXIMA[a]

Compound	λ_{max} (mμ)	ε_{max}	Compound	λ_{max} (mμ)	ε_{max}
$(C_6H_5)_4SbOCH_3$	220[b]	43,000	$(C_6H_5)_4SbOCH(CH_3)_2$	220[b]	43,100
	250[b]	3,410		250[b]	5,230
	256.5[b]	2,890		256.5[b]	4,300
	262[b]	2,500		262.5[b]	3,450
	269.5	1,610		269.5[b]	2,120
$(C_6H_5)_4SbOC_2H_5$	220[b]	42,200	$(C_6H_5)_4SbOH$	220[b]	43,000
	251[b]	3,800		252[b]	3,770
	256.5[b]	3,200		256[b]	3,180
	262.5[b]	2,620		263[b]	2,410
	269.5[b]	1,610		269[b]	1,440
$(C_6H_5)_4SbO(CH_2)_2CH_3$	220[b]	40,800	$(C_6H_5)_4SbCl$[c]	220[b]	40,900
	251[b]	3,460		254[b]	1,820
	256.5[b]	3,170		258	2,210
	262.5[b]	2,770		263.5	2,540
	269.5[b]	1,780		270	1,910

[a] The spectrum of each alkoxide was determined in the corresponding alcohol. The spectra of tetraphenylstibonium hydroxide and chloride were determined in 95% ethanol. [b] Shoulder or inflection. [c] The ultraviolet absorption spectrum of tetraphenylstibonium bromide has been determined by Rao *et al.*[12], but absorptivity data were not given. These workers reported peaks at 252, 258, 263, and 270 mμ.

alkoxides because of the probability of exchange between the alkoxy group and the alcohol*. Accordingly, the spectrum of each alkoxide was determined in its corresponding dry alcohol. The spectra of tetraphenylstibonium hydroxide and chloride were determined in 95% ethanol.

As illustrated in Fig. 1, the spectrum of tetraphenylstibonium chloride shows the group of well-defined medium-intensity bands characteristic of unperturbed or weakly perturbed benzene rings. It is thus typical of a considerable number of compounds in which several phenyl groups are attached to a central atom lacking an unshared pair of electrons. Jaffé[11] has concluded that there is little or no resonance interaction between the phenyl groups in this type of compound. The intense absorption at about 220 mμ is presumably comparable to the 203.5 mμ band of benzene, and the peak at 263.5 mμ is comparable to the 254.5 mμ benzene band; *i.e.*, the spectrum of tetraphenylstibonium chloride exhibits a rather small bathochromic shift compared to benzene.

The spectra of tetraphenylstibonium hydroxide and the alkoxy compounds are virtually identical to one another. There are no clearly defined maxima or minima in the accessible region of the ultraviolet. The spectra exhibit a very broad, intense shoulder near 220 mμ and several inflection points in the benzenoid fine-structure region. It is not easy to interpret these spectra, since they are quite different from the spectra of other compounds in which several phenyl groups are bonded to a single central atom. Since it is obvious, however, that there is considerable perturbation of

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* Briles and McEwen[5] have observed a rapid exchange of the methoxy group between methoxytetraphenylantimony and methyl alcohol.

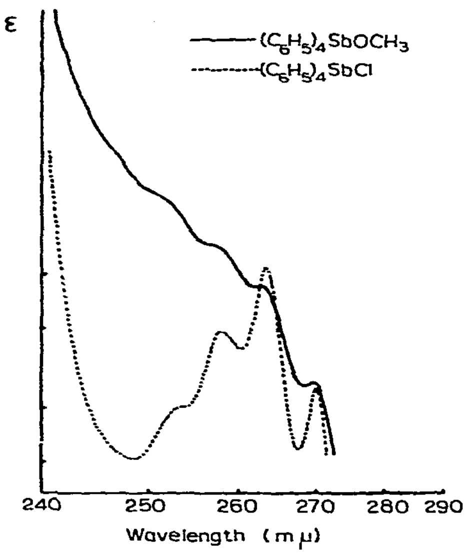

Fig. 1. The ultraviolet absorption spectra of methoxytetraphenylantimony and tetraphenylstibonium chloride.

the benzene spectrum, it is tempting to suggest that the phenyl groups in the hydroxide and the alkoxy compounds are able to interact with one another.

EXPERIMENTAL

Determination of spectra

Infrared spectra were determined between 4000 and 250 cm^{-1} on a Perkin–Elmer 521 infrared spectrophotometer. Solid samples were run as Nujol or Fluorolube mulls which were prepared and sealed between 0.004" polyethylene sheets in a dry box; liquid samples were run as films between cesium bromide plates. The PMR spectra were determined on a Varian HA-100 high resolution spectrophotometer. The solvent used was $CDCl_3$ or CCl_4. Ultraviolet absorption spectra were determined on a Beckman DK-2 spectrophotometer.

Analyses

Elemental analyses were done either by Galbraith Laboratories, Inc., Knoxville, Tennessee, or by Mr. R. L. Johnston, Department of Chemistry, North Carolina State University.

Preparation of compounds

Tetraphenylstibonium bromide and tetraphenylstibonium chloride. At first we used tetraphenylstibonium bromide prepared by the method of Chatt and Mann[13]. In a number of separate preparations of this compound we noted that analytical values for carbon and hydrogen showed considerable variation and were always higher than theoretical. Repeated recrystallization failed to improve the analytical figures. If, however, the material was treated with aqueous ammonia to form tetraphenylstibonium hydroxide, and this in turn was reconverted to the bromide with hydrobromic acid, the analytical values now agreed with the theoretical. Since in the procedure used by Chatt and Mann both chloride and bromide ions must be present in solution, we believe that a mixture of tetraphenylstibonium bromide and chloride is obtained. We suggest that the failure of Chatt and Mann to obtain satisfactory analyses on their tetraphenylstibonium bromide when recrystallized from water may be accounted for by this mixture of bromide and chloride. In a typical preparation of tetraphenylstibonium bromide by Chatt and Mann's procedure, we obtained carbon and hydrogen values of 58.09% and 3.85%, respectively, on a recrystallized sample. This would correspond to a mixture of 29% tetraphenylstibonium chloride and 71% tetraphenylstibonium bromide (based on the carbon analyses). The above difficulty can be avoided by using chlorobenzene rather than bromobenzene in the procedure of Chatt and Mann and precipitating tetraphenylstibonium chloride by the addition of sodium chloride. The resulting compound, after recrystallization from water, gave analytical figures in excellent agreement with the theoretical. The only change in reaction conditions necessitated by the use of chlorobenzene was a longer reaction time (24 h rather than the 1.5 h used by Chatt and Mann).

In a typical experiment, 30 g of triphenylstibine, 30 g of anhydrous aluminum chloride, and 9.6 g of freshly distilled chlorobenzene were refluxed gently for 24 h in a reflux apparatus protected from atmospheric moisture by a drying tube. The hot solution was poured into 1 l of water and the mixture boiled for 0.5 h to effect solution of the product. The solution was treated with charcoal and filtered. To the hot filtrate 250 ml of a saturated solution of sodium chloride were added, and the mixture cooled in the refrigerator overnight. The crystalline material which separated (46%) was recrystallized from water. (Found: C, 61.86; H, 4.29. $C_{24}H_{20}ClSb$ calcd.: C, 61.91; H, 4.33%.)

Methoxytetraphenylantimony. Tetraphenylstibonium bromide (5.1 g, 0.01 mole) and 0.54 g of sodium methoxide were dissolved in 100 ml of absolute methanol and warmed for 1 h. The clear solution was treated with 150 ml of water. The precipitate which formed on standing was removed by filtration and dried *in vacuo.* It weighed 4.23 g (90%). The crude product was readily recrystallized from aqueous methanol; m.p. (dec.) 218–220*; yield, 66%. (Found: C, 65.16; H, 4.59. $C_{25}H_{23}OSb$ calcd.: C, 65.11; H, 5.03%.)

n-Propoxytetraphenylantimony. All glass apparatus was dried in the oven at 110° and assembled while hot. A 250 ml 1-neck flask was equipped with an addition funnel (Ace Glass Catalog Number 5275) and reflux condenser to which a drying tube was attached. Sodium hydride (0.41 g of material which assayed 51.5% NaH) and 4.65 g of tetraphenylstibonium chloride, previously dried at 110°, were placed in the flask

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* Briles and McEwen[5] record a m.p. of 130–132° for methoxytetraphenylantimony. We have observed partial melting in the range 120–140° on a Fisher–Johns m.p. block. The liquid rapidly disappears, however, and the remaining solid melts with decomposition at 218–220°. Partial melting occurs with several other alkoxytetraphenylantimony compounds, but final melting with decomposition is always observed in the range 215–235°. The partial melting at low temperatures is not reproducible but depends upon the rate of heating. Briles and McEwen[14] have noted that tetraphenylstibonium hydroxide decomposes on heating at 80° in xylene to give benzene and triphenylstibine oxide, m.p. 221.5–222°, approximately the same melting point we have observed with all of the alkoxytetraphenylantimony compounds. We have found that methoxytetraphenylantimony also decomposes to triphenylstibine oxide at 80° in xylene.

and 25 ml of n-propyl alcohol, previously dried over molecular sieves, were added. The mixture was refluxed for 24 h. While the solution was still boiling, the addition funnel and condenser were removed and replaced by a short connecting tube with a fine sintered-glass disk in the center of the tube. The fine disk was found necessary to remove the sodium chloride which separated from the alcohol in a finely divided state. To the other end of the connecting tube a 250 ml 2-neck flask was attached. The other opening of the 2-neck flask was protected by a drying tube. The apparatus was inverted and the hot liquid filtered by suction. The filtrate, on cooling in the deep-freeze, deposited crystals. They were removed by filtration on a sintered disk with minimum exposure to atmospheric moisture and dried *in vacuo* at 0.2 mm. The crystals were then recrystallized from anhydrous n-propyl alcohol in a Schlenk apparatus. The yield of recrystallized material was 45%. (Found: C, 65.52; H, 5.43. $C_{27}H_{27}OSb$ calcd.: C, 66.28; H, 5.56%.)

Isopropoxytetraphenylantimony. This was prepared in essentially the same manner as the n-propoxy compound and recrystallized from anhydrous isopropyl alcohol; yield, 29% (Found: C, 66.10; H, 4.92. $C_{27}H_{27}OSb$ calcd.: C, 66.28; H, 5.56%.)

Ethoxytetraphenylantimony was prepared in a similar manner to the two compounds described above. The solvent was removed *in vacuo* and the crystals recrystallized from absolute ethyl alcohol; yield 51%. (Found: C, 65.52; H, 5.11. $C_{26}H_{25}OSb$ calcd.: C, 65.71; H, 5.30%.)

n-Butoxytetraphenylantimony. This was prepared in a similar manner to the previous compounds. The filtrate, after removal of the sodium chloride, was cooled in the deep-freeze, but no crystals separated. The solvent was then partially removed *in vacuo* and again cooled in the deep-freeze. The oil, which separated, had not solidified after several weeks in the deep-freeze. Accordingly, all the solvent alcohol was removed *in vacuo* at 0.1 mm and $< 100°$. The resulting oil could not be distilled without decomposition. (Found: C, 66.98; H, 5.40. $C_{28}H_{29}OSb$ calcd.: C, 66.82; H, 5.81%.)

sec-Butoxytetraphenylantimony. This was prepared in exactly the same manner as the n-butoxy compound, but the analyses on the crude oil were less satisfactory. (Found: C, 63.84; H, 5.51. $C_{28}H_{29}OSb$ calcd.: C, 66.82; H, 5.81%.)

tert-Butoxytetraphenylantimony. This was prepared in a similar manner to the two butoxy compounds described above. After refluxing for 24 h the connecting tube and 2-neck flask were attached. The reaction mixture was then allowed to stand for 24 h so that the precipitate could settle. The apparatus was then carefully inverted, and the clear liquid was filtered through the sintered glass disk. If this precaution is not observed, it is almost impossible to remove the sodium chloride without clogging the filter. The tert-butyl alcohol in the filtrate was then removed *in vacuo* at 0.1 mm and $< 100°$. The yield of solid remaining in the flask was 0.71 g, 14%. (Found: C, 64.64; H, 6.10. $C_{28}H_{29}OSb$ calcd.: C, 66.82; H, 5.81%.)

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. GEORGE E. PARRIS, who prepared some of the compounds, and of Mrs. DELORES E. KNIGHT, who determined the infrared and ultraviolet spectra.

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