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ORGANOANTIMONY COMPOUNDS

VIII *. CLEAVAGE OF Sb—O—Sb BONDS IN μ—OXYBIS(TRIPHENYLCHLOROANTIMONY) AND TRIPHENYLANTIMONY OXIDE BY METHANOL AND ACETYLACETONE

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Summary

Sb—O—Sb bonds in $(Ph_3ClSb)_2O$ and PH_3SbO are cleaved readily by methanol and acetylacetone. The reactions provide convenient synthetic routes for $Ph_3Sb(OMe)Cl$, $Ph_3Sb(OMe)_2$, $Ph_3Sb(acac)Cl$, and $Ph_3Sb(acac)OH$. Characterization of these compounds by infrared, Raman, and ^1H NMR spectral measurements is reported.

Several triphenylantimony(V) derivatives of the type $(Ph_3XSb)_2O$, where X = an anionic group, have been prepared [1—4] in this laboratory. Their structural features have been elucidated by vibrational spectral studies [1—4] as well as by a crystallographic study [5] of $[Ph_3(N_3)Sb]_2O$. The Sb—O distances in $Ph_3(N_3)Sb—O—Sb(N_3)Ph_3$ are significantly shorter than the Sb—O single bond lengths found for $Ph_3Sb(OMe)_2$ [6], $Ph_4Sb(OMe)$ [6] and $Ph_4Sb(OH)$ [7]. The polymeric form of Ph_3SbO is also indicated [8] to contain strong Sb—O—Sb bonds. Reactions involving facile cleavage of the Sb—O—Sb bonds in $(Ph_3ClSb)_2O$ and polymeric Ph_3SbO are reported herein.

Results and discussion

The Sb—O—Sb bonds in $(Ph_3ClSb)_2O$ and Ph_3SbO *** are readily cleaved by MeOH and acacH (acetylacetone). The reactions can be represented by the

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[***] Ph_3SbO used in this work melted at 290°C and its infrared spectrum was identical to that reported for polymeric Ph_3SbO [8].

following equations:

$$(Ph_3ClSb)_2) + 2\,MeOH \rightarrow 2\,Ph_3Sb(OMe)Cl + H_2O \tag{1a}$$

$$(Ph_3ClSb)_2O + 2\,acacH \rightleftharpoons 2\,Ph_3Sb(acac)Cl + H_2O \tag{1b}$$

$$Ph_3SbO + 2\,MeOH \rightleftharpoons Ph_3Sb(OMe)_2 + H_2O \tag{2a}$$

$$Ph_3SbO + acacH \rightleftharpoons Ph_3Sb(acac)OH + H_2O \tag{2b}$$

These reactions proceed at ambient temperature, providing convenient synthetic routes for the previously reported compounds $Ph_3Sb(OMe)Cl$ [9], $Ph_3Sb(OMe)_2$ [6,10], and hitherto inaccessible compounds, $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)(OH)$. The four compounds isolated in the present work were characterized by elemental analyses, molecular weights measurements and by ^1H NMR, infrared and Raman spectral measurements.

Characterization of $Ph_3Sb(OMe)_2$ and $Ph_3Sb(OMe)Cl$

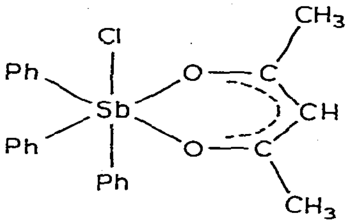
^1H NMR data for $Ph_3Sb(OMe)_2$ have been reported but neither ^1H NMR nor vibrational spectroscopic data for $Ph_3Sb(OMe)Cl$ are available. The ^1H NMR spectrum for $Ph_3Sb(OMe)_2$ was identical to that reported by previous workers [10]. The ^1H NMR spectrum of $Ph_3Sb(OMe)Cl$ in $CDCl_3$ showed a single sharp peak (δ 3.08 ppm) due to the methoxy protons, a quartet (δ 8.25 ppm) due to the *ortho* protons of three equivalent phenyl groups and a triplet (δ 7.51 ppm) due to the *meta* and *para* protons of the phenyl groups. The infrared spectra of both $Ph_3Sb(OMe)_2$ and $Ph_2Sb(OMe)Cl$ showed a very strong band at 1050 cm^{-1} due to the O—CH_3 stretching frequency. In accordance with the D_{3h} skeletal symmetry of $Ph_3Sb(OMe)_2$ [6], its infrared spectrum showed an intense band at 479 cm^{-1} due to the antisymmetric Sb—OCH_3 stretching mode. This frequency was not present in the Raman spectrum which showed a medium intensity band at 468 cm^{-1} attributable to the symmetric Sb—OCH_3 stretching mode. Strong infrared bands at 494 and 264 cm^{-1} which can be assigned to the Sb—OCH_3 and Sb—Cl [11] stretching modes, respectively, were observed for $Ph_3Sb(OMe)Cl$; a medium band at 492 cm^{-1} and a strong band at 265 cm^{-1} were observed in the Raman spectrum. The infrared and Raman bands due to the Ph_3Sb moiety for both compounds were similar to those reported for several Ph_3SbX_2 derivatives [11].

Characterization of $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)OH$

^1H NMR and infrared spectral data for analytically and spectroscopically impure samples of $Ph_3Sb(acac)Cl$ have been reported by Meinema and co-workers [12]. The preparative routes used by these workers included reaction of $Ph_3(OMe)Cl$ with acacH and the reaction of Ph_3SbCl_2 with Na(acac) and the failure to isolate pure $Ph_3Sb(acac)Cl$ was attributed to the instability of the compound. Analytically and spectroscopically pure samples of $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)OH$ were isolated in the present work from the reaction of acacH with $(Ph_3SbCl)_2O$ and Ph_3SbO, respectively, at ambient temperature. Samples of both compounds were found to be unchanged for at least six months and no spectral changes were observed upon exposing the compounds to air for a week. However, reaction of Ph_3SbO in refluxing acacH afforded

$Ph_3Sb(O_2CCH_3)_2$ as the sole antimony containing species. $Ph_3Sb(O_2CCH_3)_2$ was also formed upon refluxing a solution of Ph_3Sb(acac)OH in acacH. Similar remarkable decomposition reactions of $Zn(acac)_2H_2O$ [13] and Et_3Sn(acac) [14] to give the acetato complexes have been observed by other workers.

The observed chemical shifts for the acac protons for Ph_3Sb(acac)Cl and Ph_3Sb(acac)OH are listed in Table 1 and the pertinent infrared and Raman data are listed in Table 2. The chemical shifts for the acac protons for Ph_3Sb(acac)Cl and Ph_3Sb(acac)OH are consistent with those for other acetylacetonatoorganoantimony(V) compounds [12] as well as acetylacetonate complexes [15] of other metals, all of which are known to contain chelated O-bonded acac ligands. The two possible structures (I and II) for octahedral Ph_3Sb(acac)X are shown below. Isomer I will give rise to a single resonance due to the CH_3 protons whereas two CH_3 resonances are expected for isomer II. The ^1H NMR data for Ph_3Sb(acac)Cl reported by Meinema and co-workers [12] indicate the presence of only one isomer (II). Contrary to their results, the ^1H NMR data for Ph_3Sb(acac)Cl obtained in the present work clearly show the presence of both isomers. As shown in Table 1, the ^1H NMR spectrum of Ph_3Sb(acac)Cl in $CDCl_3$ as well as in C_6D_6 showed two resonances due to the γ-CH proton and two resonances due to the CH_3 protons. Low temperature NMR measurements in $CDCl_3$ showed that the highfield CH_3 peak is resolved into two peaks at —10°C. On the basis of the integrated intensities of the NMR peaks, the two isomers are indicated to be present in approximately 1/1 ratio in both $CDCl_3$ and C_6D_6 solutions at ambient temperature. Variable temperature NMR mea-



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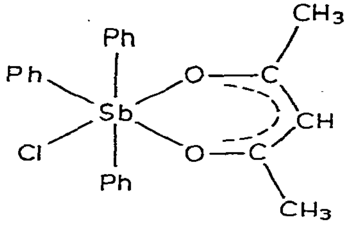

(II)

TABLE 1

CHEMICAL SHIFTS (PPM DOWNFIELD FROM INTERNAL TMS) FOR acac PROTONS OF Ph_3Sb(acac)Cl AND Ph_3Sb(acac)OH

Compound	In C_6D_6 Ambient temp.		In $CdCl_3$			
			Ambient temp.		—10°C	
	δ(CH)	δ(CH_3)	δ(CH)	δ(CH_3)	δ(CH)	(CH_3)
Ph_3Sb(acac)Cl	5.00	1.61	5.50	2.04	5.53	2.07
	4.86	1.51	5.32	1.91	5.37	1.97
						1.93
Ph_3Sb(acac)OH	5.05	1.60	5.51	2.03	5.55	2.07
			5.15	1.76	5.16	1.94
						1.80

TABLE 2

INFRARED AND RAMAN DATA FOR $Ph_3Sb(acac)Cl$ AND $Ph_3Sb(acac)OH$

Compound	Stretching frequencies (cm^{-1})							
	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$		$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$		ν(Sb—O)		ν(Sb—Cl)	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman
$Ph_3Sb(acac)Cl$	1583s 1575s 1378s(br)	— — 1375m	1520s	1521s	405m	408m	—	286s
$Ph_3Sb(acac)OH$	1598s 1579s 1379s(br)	— — 1374m	1521s	1521s	400s	399m	—	—

surements showed that neither isomer is preferred extensively in the 40 to —20°C temperature range. The resonances of the phenyl groups appeared as a quartet (due to *ortho* protons) and a triplet (due to *meta* and *para* protons) similar to those observed for $Ph_3Sb(OMe)_2$ and $Ph_3Sb(OMe)Cl$. The integration ratios indicated the presence of one acac group for three phenyl groups.

The ^1H NMR spectrum of $Ph_3Sb(acac)OH$ in C_6D_6, at ambient temperature, showed a quartet and a triplet due to the phenyl protons, a single peak due to the γ-CH proton, and another single peak due to the CH_3 protons. Integrated intensities due to the ortho phenyl protons, methine proton and the methyl protons were in 6/1/7 ratio suggesting an overlap of the resonance signals due to the methyl and OH protons. In $CDCl_3$, the ^1H NMR signals due to the acac protons for $Ph_3Sb(acac)OH$ are similar to those observed for $Ph_3Sb(acac)Cl$ and clearly indicate the presence of two isomeric forms (I and II). At ambient temperature, the isomers I and II are present in an approximately 2/1 ratio. Variable temperature NMR measurements showed that the ratio of the two isomers is not changed significantly in the 40 to 20°C temperature range. A broad peak at 1.70 ppm was observed for $Ph_3Sb(acac)OH$ in $CDCl_3$ which can be assigned to the OH proton. Integration of this peak was not possible due to its close proximity to the strong CH_3 peak but it disappeared upon addition of D_2O.

The infrared and Raman spectra of both $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)OH$ are consistent with their proposed formulations. As shown in Table 2, the infrared spectra of both compounds showed strong bands in the 1600—1375 cm^{-1} region which can be attributed to the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretching modes [14,16] of the chelated O-bonded acac group. The Raman spectra of both compounds, in this region, showed a strong band at ca. 1520 cm^{-1} and a medium or a weak band at ca. 1375 cm^{-1} which can be assigned to the symmetric $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ and the symmetric $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretching modes, respectively. In the low frequency region, a band at ca. 400 cm^{-1} is observed in the infrared as well as the Raman spectra for both compounds. This can be assigned to the Sb—O stretching by comparison with the infrared and Raman data for $Me_2Sn(acac)_2$

[17,18]. The Raman spectrum of $Ph_3Sb(acac)Cl$ also showed a strong band at 286 cm^{-1} which was not observed for $Ph_3Sb(acac)OH$. By comparison with the Raman data for Ph_3SbCl_2 [11], this band is assigned to the Sb—Cl stretching frequency. This frequency is masked in the infrared due to the presence of a very strong band at 300 cm^{-1}. Like the ^{1}H NMR data, the C┅O, C┅O, Sb—O and Sb—Cl stretching frequencies for $Ph_3Sb(acac)Cl$ reported by Meinema and co-workers [12] are different than those found in the present work.

Experimental

Materials and Solvents

$(Ph_3ClSb)_2O$ was prepared as reported previously [1,4]. Ph_3SbO was supplied by Research Organic/Inorganic Chemical Corporation. Methanol was dried by refluxing over magnesium and subsequent distillation. Benzene, ether, diethyl ether and petroleum ether were dried by treatment with sodium wire and subsequent distillation. Acetylacetone was reagent grade.

Physical Measurements

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were determined in benzene with a Hitachi Perkin—Elmer 115 vapour osmometer. ^{1}H NMR spectra were recorded on $CDCl_3$ and C_6D_6 solutions with a Varian A 60 spectrometer using TMS as internal reference. Infrared spectra (4000—200 cm^{-1}) were recorded in the solid state with a Beckman IR12 spectrophotometer. Samples were prepared as mulls in Nujol or halocarbon oil. Raman spectra were measured on powdered samples with a Cary 82 spectrophotometer using the 5145 Å exciting line of an argon ion laser.

Reactions of $(Ph_3ClSb)_2O$ and Ph_3SbO with MeOH

(a) $(Ph_3ClSb)_2O$ (~1.0 g) was dissolved in hot methanol and the hot solution was stirred for 2 h and then filtered. Colourless needle-shaped crystals of $Ph_3Sb(OMe)Cl$ were obtained in almost quantitative yield upon cooling the filtrate to 0°C. Yield, 90%; m.p. 122°C. Analysis. Found: C, 54.32; H, 4.27; Cl, 8.50. $C_{19}H_{18}ClOSb$ calcd.: C, 54.50; H, 4.30; Cl, 8.45%. Molecular weight: Found, 417; calcd., 420.

(b) Under an atmosphere of dry nitrogen, Ph_3SbO (0.5 g) was added to 30 ml methanol containing molecular sieves (4 Å effective pore size) and the mixture was stirred overnight. The solution was filtered in a dry-box and the solvent was removed in vacuo. The resulting white solid was sublimed at 110—130°C at a pressure of 0.1 mmHg to give white crystals of $Ph_3Sb(OMe)_2$. Yield, 25%; m.p. 100°C. Analysis. Found: C, 58.20; H, 5.17. $C_{20}H_{21}O_2Sb$ calcd.: C, 57.87; H, 5.10%.

Reactions of $(Ph_3ClSb)_2O$ and Ph_3SbO with acacH

(a) Under an atmosphere of dry nitrogen, $(Ph_3ClSb)_2O$ (0.5 g), was added to a mixture containing 20 ml benzene, 5 ml acacH and some molecular sieves (4 Å effective pore size). After stirring the mixture overnight at room temperature it was filtered in an atmosphere of dry nitrogen and the filtrate was concentrated in vacuo to give white crystals of $Ph_3Sb(acac)Cl$ which were washed with anhydrous ether. Yield: 25%. Analysis. Found: C, 56.84; H, 4.34, Cl, 7.30%. $C_{23}H_{22}ClO_2$ calcd.: C, 56.64; H, 4.54, Cl, 7.27. Molecular weight: Found, 480; calcd., 488.

(b) Ph_3SbO (~0.80 g) was stirred overnight in 15 ml acacH at room temperature in a dry-box. The solution was filtered, the filtrate was concentrated under vacuum and petroleum ether (30—60° C boiling range) was added to the concentrated solution to give a white precipitate which was recrystallized from benzene. Yield: 85%. Analysis. $Ph_3Sb(acac)OH$: calcd.: C, 59.00; H, 4.88%. Found: C, 59.24; H, 4.68. Molecular weight: Found, 470; calcd., 469.

(c) Ph_3SbO (~1.00 g) or $Ph_3Sb(acac)OH$ (0.50 g) was refluxed in 30 ml acacH for 1 h and the solution was filtered. The filtrate was concentrated in vacuo and petroleum ether (30—60° C boiling range) was added to give a white solid which was recrystallized from benzene. The infrared and ^1H NMR spectra of the product were identical to those for $Ph_3Sb(O_2CCH_3)_2$ [19].

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References

1 R.G. Goel, P.N. Joshi, D.R. Ridley and R.E. Beamont, Can. J. Chem., 47 (1969) 1423.
2 R.G. Goel and D.R. Ridley, Inorg. Nucl. Chem. Lett., 7 (1971) 21.
3 G. Ferguson, R.G. Goel, F.C. March, D.R. Ridley and H.S. Prasad, Chem. Commun., (1971) 1549.
4 R.G. Goel and H.S. Prasad, Inorg. Chem., 11 (1972) 2141.
5 G. Ferguson and D.R. Ridley, Acta. Cryst. B, 29 (1973) 2221.
6 K. Shen, W.E. McEwen, S.J. La Placa, W.C. Hamilton and A.P. Wolf, J. Amer. Chem. Soc., 90 (1968) 1718.
7 A.L. Beauchamp, M.J. Bennett, and F.A. Cotton, J. Amer. Chem. Soc., 91 (1969) 267.
8 D.L. Venezky, C.W. Sink, B.A. Nevett, and W.F. Fortescue, J. Organometal. Chem., 35 (1972) 131.
9 L. Kolditz, M. Gitter and E. Rosel, Z. Anorg. Allg. Chem., 316 (1962) 270..
10 W.E. McEwen, G.H. Briles, and B.E. Giddings, J. Amer. Chem. Soc., 91 (1969) 7079.
11 R.G. Goel, E. Maslowsky, Jr., and C.V. Senoff, Inorg. Chem., 10 (1971) 2572.
12 H.A. Meinema, A. Mackor, and J.G. Noltes, J. Organometal. Chem., 37 (1972) 285, and ref. cited therein.
13 G. Rudolph and M.C. Henry, Inorg. Chem., 3 (1964) 1317.
14 F. Bonati, Organometal. Chem. Rev., 1 (1966) 379.
15 J.A.S. Smith and E.J. Wilkins, J. Chem. Soc. A, (1966) 1749.
16 G.T. Behnke and K. Nakamoto, Inorg. Chem., 6 (1967) 433, and ref. cited therein.
17 M.M. McGrady and R.S. Tobias, J. Amer. Chem. Soc., 87 (1965) 1909.
18 V.B. Ramos and R.S. Tobias, Spectrochim. Acta. A, 29 (1973) 953.
19 R.G. Goel and D.R. Ridley, J. Organometal. Chem., 38 (1972) 83.
20 R.G. Goel and H.S. Prasad, J. Organometal. Chem., 59 (1973) 253.