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

STUDY OF ORGANOANTIMONY COMPOUNDS CONTAINING THE $SbCH_2Sb$ MOIETY

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(Received June 22nd, 1970)

SUMMARY

A series of organoantimony compounds which contain the novel $SbCH_2Sb$ moiety was prepared. Among these, only compounds of the type $[X(CH_3)_3Sb]_2CH_2$ were easily cleaved by a base to give $(CH_3)_4Sb^+$ and $(CH_3)_3Sb^{2+}$ species. Three infrared bands in the KBr region $\rho(CH_2)$, $\nu_{asym}(Sb-C-Sb)$ and $\nu_{sym}(Sb-C-Sb)$, were found to be characteristic of the $SbCH_2Sb$ moiety. A relationship obtained between $\rho(CH_2)$ and $\nu_{av}(Sb-C-Sb)$ was interpreted by considering changes in the *s*-character of the orbitals of the antimony atom used for the Sb–C bonds.

INTRODUCTION

Compounds containing the PCH_2P or $AsCH_2As$ moiety, such as bis(diphenylphosphino)methane or bis(diphenylarsino)methane, are well known. However, analogous organoantimony compounds have been prepared only recently. We have reported[1] that $[Br(CH_3)_3Sb]_2CH_2 \cdot 2\,H_2O$ was obtained unexpectedly from the reaction of trimethylstibine with iodoform, followed by treatment with hydrobromic acid. Later, we described[2] a method for the preparation of bis(dimethylstibino)methane and its pentavalent derivatives, such as $[I(CH_3)_3Sb]_2CH_2 \cdot 2\,H_2O$ and $[Cl_2(CH_3)_2Sb]_2CH_2$.

Here, we wish to report on a cleavage reaction and an infrared spectroscopic investigation of this type of organoantimony compound. Several new compounds have been included in this study.

EXPERIMENTAL

General comments

The preparations and reactions of stibinomethanes were carried out under a nitrogen atmosphere, and nitrogen was bubbled into solvents before use.

Preparation of bis(diorganostibino)methane, $(R_2Sb)_2CH_2$

$[(CH_3)_2Sb]_2CH_2$ (I) from $[Cl_2(CH_3)_2Sb]_2CH_2$ (IX). Compound (IX)[2] (6.0 g) was mixed with zinc dust (2.0 g). Water (50 ml) was added dropwise, and the mixture was stirred for 3 h. Then ether (30 ml) was added, and stirring was continued for an additional 15 min. The ether layer was separated with a syringe and was distilled

under reduced pressure to give 2 g of a colorless liquid* (b.p. 67–68°/4 mm). PMR τ (neat liquid, TMS as an internal standard): (CH_3–Sb), 9.20; (Sb–CH_2–Sb), 8.80 ppm.

$[(C_6H_5)_2Sb]_2CH_2$ (XI). Triphenylstibine (19.5 g; 55.2 mmole) was dissolved in 300 ml of liquid ammonia at −78°, followed by addition of sodium (2.5 g; 110 mmole) with stirring for 5 h. At the end-point of the reaction the solution became dark red[3]. After treatment of the reaction mixture with ammonium chloride (2.95 g; 55.2 mmole) to consume the phenylsodium, dichloromethane (2.35 g; 27.6 mmole) was added dropwise until the color of the solution disappeared. Ammonia was allowed to boil off, and water (100 ml), ether (200 ml) and benzene (50 ml) were added to dissolve the residue. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure, and the residual solid was recrystallized from acetone to give 11.6 g (74%) of colorless crystals of (XI). This compound is stable to air in the solid state but oxidizes slowly in solution.

Preparation of $(X_2R_2Sb)_2CH_2$

$[X_2(C_6H_5)_2Sb]_2CH_2$ [X=Cl (XII); X=Br (XIII)]. These halides were prepared from the reactions of $[(C_6H_5)_2Sb]_2CH_2$ (XI) with SO_2Cl_2 or Br_2, which are similar to the preparation of $[Cl_2(CH_3)_2Sb]_2CH_2$ (IX)[2].

$[(SCN)_2(CH_3)_2Sb]_2CH_2$ (X) and $[(SCN)_2(C_6H_5)_2Sb]_2CH_2$ (XIV). Compound (IX) was treated with NaNCS in a mixture of acetone and chloroform with stirring for 2 h. The filtrate was evaporated and the solid was recrystallized from acetone/chloroform to give colorless crystals of (X). Similarly, (XIV) was prepared.

$[F_2(CH_3)_2Sb]_2CH_2$ (VIII). Compound (IX) was mixed with silver fluoride in methanol, and the mixture was stirred for 3 h. The solid obtained by evaporating the filtrate was recrystallized from acetone to give colorless crystals of (VIII).

$O[NO_3(CH_3)_2Sb]_2CH_2$ (VII). Compound (IX) was mixed with silver nitrate in methanol. The solid obtained by evaporating the filtrate was thought to be $[(NO_3)_2(CH_3)_2Sb]_2CH_2$; however recrystallization from moist acetone gave colorless crystals of (VII). An infrared band at 775 cm^{-1} which is characteristic of the SbOSb moiety was observed for this compound.

Preparation of $[Y(CH_3)_3Sb]_2CH_2$ [Y=ClO_4, NCS or 0.5 ($SO_4 \cdot 3\ H_2O$)]

These onium salts were prepared in a manner similar to that reported[1,2] for $[NO_3(CH_3)_3Sb]_2CH_2$ (VI), which was prepared from the reaction of $[X(CH_3)_3Sb]_2CH_2 \cdot 2\ H_2O$ (X=Br or I) with $AgNO_3$.

Properties and analytical data of new compounds thus obtained are given in Table 1.

Cleavage reaction of $[Br(CH_3)_3Sb]_2CH_2 \cdot 2\ H_2O$ (IV)

With Ag_2O. Compound (IV) (1.3 g; 2.4 mmole) was treated with silver oxide (0.7 g; 3.0 mmole) in water. To the filtrate**, hydrochloric acid was added dropwise. The resulting white precipitate was recrystallized from acetone to give 0.50 g (88%)

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* We reported[2] that bis(dimethylstibino)methane (I) prepared from dimethylchlorostibine, sodium and dichloromethane, was a yellow liquid, since the yellow color did not disappear even after several distillations. The PMR spectra of these yellow liquids always show, in addition to the two main peaks, a small singlet peak at 9.03 ppm. In the present preparation the yellow color may be attributed to an impurity.

** At this stage, the PMR spectrum (dioxane as an internal standard) in D_2O showed two peaks due to $(CH_3)_4Sb^+$ (+2.13 ppm) and $(CH_3)_3Sb^{2+}$ (+2.19 ppm).

of $(CH_3)_3SbCl_2$, m.p. 224° decomp. (reported[4], m.p. 224° decomp.). Evaporation of the filtrate gave a solid, which was recrystallized from moist acetone to give 0.50 g (96%) of $(CH_3)_4SbCl$. This was converted to $(CH_3)_4SbNO_3$ by $AgNO_3$ and identified by comparison of its IR spectrum with that of an authentic sample[5].

With NaOH. Compound (IV) and sodium hydroxide were mixed in D_2O in a PMR tube. The PMR spectrum (dioxane as an internal standard) showed that the peaks ($SbCH_2Sb$, +1.30 ppm; $SbCH_3$, +1.97 ppm) due to the $(CH_3)_3SbCH_2Sb(CH_3)_3$ group disappeared and were replaced by those attributed to $(CH_3)_4Sb^+$ (+2.13 ppm) and $(CH_3)_3Sb^{2+}$ (+2.19 ppm) groups.

Physical measurements

The PMR spectra were measured using Japan Electron Optics JNM-3H-60 or HNM-MH-60 spectrometers. The IR spectra were measured using Hitachi EPI-2G or 225 spectrophotometers, both equipped with gratings.

Relevant infrared frequencies of the compounds containing the $SbCH_2Sb$ moiety are shown in Table 2.

DISCUSSION

From the reactions of the halides, $(X_2R_2Sb)_2CH_2$ ($R=CH_3$ or C_6H_5; $X=Cl$ or Br), with sodium or silver salts, various derivatives were obtained without cleavage of the Sb–C–Sb linkage.

In the case of $[X(CH_3)_3Sb]_2CH_2$, similar reactions were observed only with sodium or silver salts of strong acids. Separation of the reaction products was successful with the silver salts.

$$[X(CH_3)_3Sb]_2CH_2 + 2\,AgY \rightarrow [Y(CH_3)_3Sb]_2CH_2 + 2\,AgX$$
$$(X = Br \text{ or } I;\ Y = NO_3, ClO_4, NCS \text{ or } 0.5\,SO_4)$$

The $[X(CH_3)_3Sb]_2CH_2$ compounds undergo cleavage of the Sb–C–Sb linkage with either sodium hydroxide or silver oxide in water to give the tetramethylstibonium and trimethylantimony species, and derivatives were successfully prepared in the latter case as shown below.

$$[Br(CH_3)_3Sb]_2CH_2 \xrightarrow{Ag_2O} (CH_3)_4Sb^+ + (CH_3)_3Sb^{2+}$$
$$\xrightarrow{HCl} (CH_3)_4SbCl + (CH_3)_3SbCl_2$$

This cleavage reaction is thought to proceed by the nucleophilic attack of the base (such as OH^-) on the antimony atom, analogous to the reaction of $[(C_6H_5)_3PCH_2Si(CH_3)_3]Br$ with sodium hydroxide, which has been reported[6] to give $CH_3(C_6H_5)_3POH$ and $(CH_3)_3SiOSi(CH_3)_3$.

Among the infrared bands characteristic of the methyl compounds shown in Table 2, a linear relationship between $\rho(CH_2)$ and the average stretching frequency $\nu_{av}=0.5(\nu_{asym}+\nu_{sym})$ of Sb–C–Sb was obtained, as shown in Fig. 1. On the other hand, the bands due to $\rho(CH_3)$ or $\nu(Sb\text{–}CH_3)$ are complicated, and it is difficult to obtain a relationship between these two vibrations.

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TABLE 1

PROPERTIES OF NEW COMPOUNDS CONTAINING THE $SbCH_2Sb$ MOIETY

Compounds	M.p. (°C)	Analysis found (calcd.) (%)			PMR data[a] (ppm)		
		C	H	Br, Cl, N or Sb	τ(CH_2)	τ(CH_3)	τ(C_6H_5)
(VIII) $[F_2(CH_3)_2Sb]_2CH_2$	190.5–191.5	15.51 (15.26)	3.60 (3.58)		7.17[b]	8.15[c]	
(X) $[(SCN)_2(CH_3)_2Sb]_2CH_2$	147–148	19.28 (19.65)	2.65 (2.57)	10.75 (N) (10.19)	6.61	7.60[d]	
(VII) $O[NO_3(CH_3)_2Sb]_2CH_2$	213–216	12.82 (13.12)	3.36 (3.08)	5.96 (N) (6.12)	6.30	8.08[e]	
$[ClO_4(CH_3)_3Sb]_2CH_2$	265 (decomp.)			44.13 (Sb) (44.55)	+1.32	+2.04[f]	
$[(SO_4)_{0.5}(CH_3)_3Sb]_2CH_2 \cdot 3\,H_2O$	243 (decomp.)	17.04 (17.08)	5.28 (5.26)		+1.31	+2.05[f]	
$[SCN(CH_3)_3Sb]_2CH_2$	186 (decomp.)	23.30 (23.30)	4.62 (4.35)	5.90 (N) (6.04)	7.74	8.35[g]	
(XI) $[(C_6H_5)_2Sb]_2CH_2$	82–83.5	53.26 (53.06)	3.85 (3.89)		7.96		2.74[h]
(XII) $[Cl_2(C_6H_5)_2Sb]_2CH_2$	208–209	42.53 (42.43)	3.05 (3.13)	20.15 (Cl) (20.04)	5.24		1.85[h] 2.54[h]
(XIII) $[Br_2(C_6H_5)_2Sb]_2CH_2$	182–183	34.04 (33.91)	2.70 (2.50)	36.10 (Br) (36.09)	4.41		1.85[h] 2.55[h]
(XIV) $[(SCN)_2(C_6H_5)_2Sb]_2CH_2$	158–159.5	43.92 (43.63)	2.96 (2.78)	7.12 (N) (7.02)	6.40		2.08[h] 2.41[h]

[a] Measured in $CDCl_3$, using TMS as an internal standard unless otherwise stated. [b] Quintet. [c] Triplet. [d] In CD_3CN. [e] In CD_3OD. [f] In D_2O, δ value from dioxane as an internal standard. [g] In $(CD_3)_2SO$. [h] Multiplet.

TABLE 2. RELEVANT INFRARED FREQUENCIES (IN cm^{-1}) OF COMPOUNDS CONTAINING THE $SbCH_2Sb$ MOIETY MEASURED IN NUJOL MULLS

Compounds	$\rho(CH_2)$	$\nu_{asym}(SbCSb)$	$\nu_{sym}(SbCSb)$	$\rho(CH_3)$	$\nu_{asym}(SbCH_3)$	$\nu_{sym}(SbCH_3)$	Additional bands around $\nu(SbCH_3)$
(I) $[(CH_3)_2Sb]_2CH_2$[a]	595 (sh)	588 s	479 w	808 vs 778 vs	511 s	465 w	
(II) $PdCl_2[(CH_3)_2Sb]_2CH_2$[a]	633 s	616 s	498 m	844 vs 820 vs	549 m 543 (sh)	484 w	
(III) $PtCl_2[(CH_3)_2Sb]_2CH_2$[a]	635 m	611 m	494 w	833 s	547 (sh) 538 m		
(IV) $[Br(CH_3)_3Sb]_2CH_2 \cdot 2\,H_2O$[b]	673 s	668 (sh)		862 vs 816 s	568 m 563 (sh)	538 w	
(V) $[I(CH_3)_3Sb]_2CH_2 \cdot 2\,H_2O$[a]	666 s	654 m	474 vw	858 vs 814 s	563 m 559 (sh)	530 w	
(VI) $[NO_3(CH_3)_3Sb]_2CH_2$[a,b,c]	670 s	654 s	490 w	876 vs 858 vs 816 m	576 m 570 m	545 vw	550 vw
(VII) $O[NO_3(CH_3)_2Sb]_2CH_2$	667 s	643 s	500 m	858 (sh) 848 m	581 m 576 m	537 w	551 w
(VIII) $[F_2(CH_3)_2Sb]_2CH_2$	681 s	662 s		852 vs 805 m	593 (sh) 589 s	535 m	555 m
(IX) $[Cl_2(CH_3)_2Sb]_2CH_2$[a]	678 m	664 s	493 w	860 vs 816 (sh)	568 m	534 vw	546 w
(X) $[(SCN)_2(CH_3)_2Sb]_2CH_2$	683 s	644 s	510 m	858 (sh) 850 vs 811 m	578 m		552 m
(XI) $[(C_6H_5)_2Sb]_2CH_2$	618 m[d] 614 m	594 s	498 w				
(XII) $[Cl_2(C_6H_5)_2Sb]_2CH_2$	[e]	620 s	505 m				
(XIII) $[Br_2(C_6H_5)_2Sb]_2CH_2$	[e]	606 m	485 m				
(XIV) $[(SCN)_2(C_6H_5)_2Sb]_2CH_2$	[e]	628 m	512 m				

[a] See ref. 2. [b] See ref. 1. [c] IR frequencies (in cm^{-1}) of NO_3 groups: 1379 s, 1316 s (NO_3 deg. stretch); 1042 w (NO_3 sym. stretch); 831 w (NO_3 def.); 709 vw (NO_3 def.). [d] Only one band at 618 cm^{-1} is observed in $CHCl_3$ solution. [e] Masked by the strong C–H out-of-plane bending vibration of phenyl groups.

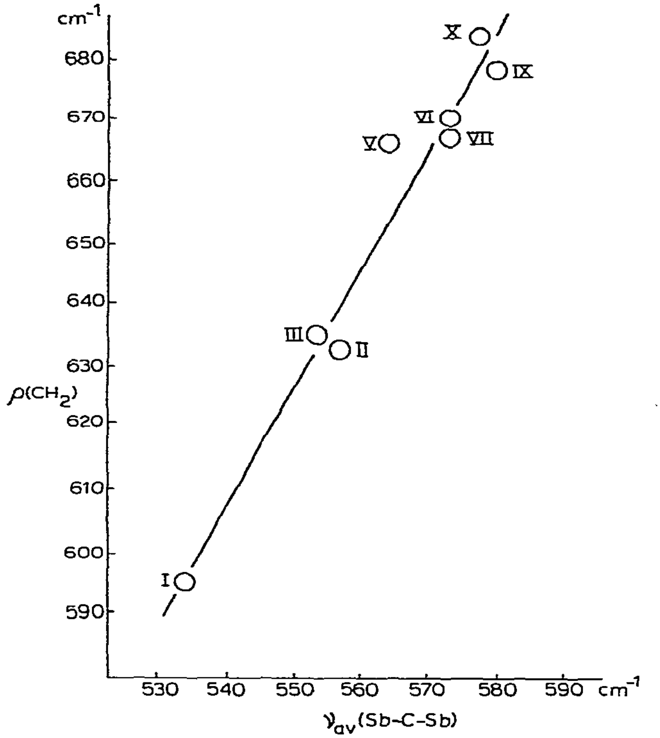

Fig. 1. Relationship between $\rho(CH_2)$ and ν_{av}(Sb–C–Sb) in methyl derivatives containing the $SbCH_2Sb$ moiety.

The relationship between $\rho(CH_2)$ and ν_{av}(Sb–C–Sb) may be interpreted by considering the variations in the *s*-character of the orbitals of the antimony atom used for the Sb–C bonds. In trimethylstibine, and perhaps in bis(dimethylstibino)methane (I), the antimony atom is thought to use mainly *p* orbitals. This follows from a consideration of the bond angle*.

Incorporation of the ligand (I) into the coordination compounds, (II) and (III), probably increases the C–Sb–C angles as a result of the coordination involving the lone-pair electrons of the antimony. In $[NO_3(CH_3)_3Sb]_2CH_2$ (VI), the infrared frequencies of the NO_3 groups (see footnote c of Table 2) are similar to those of $(CH_3)_4Sb^+NO_3^-$ with a $(CH_3)_4Sb^+$ group of T_d symmetry[5]. Thus, the compound is more correctly represented as $[(CH_3)_3SbCH_2Sb(CH_3)_3]^{2+}2(NO_3)^-$, and the antimony atoms in this cation are considered to use sp^3 hybrid orbitals. The nature** of the Sb–Cl bond in $[Cl_2(CH_3)_2Sb]_2CH_2$ (IX) is similar to that in $(CH_3)_3SbCl_2$, which has a trigonal bipyramidal structure with a trigonal C_3Sb plane and the chlorine atoms at the apices[10,11]. Thus, the antimony atoms in (IX) are thought to use mainly sp^2

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* The bond angles in the pyramidal compounds $N(CH_3)_3$, $P(CH_3)_3$ and $As(CH_3)_3$, were reported to be 108.7° [7], 99.1° [7] and 96° [7], respectively. The angle of $Sb(CH_3)_3$ has not been measured, but it is reasonable to assume it to be 96° or less (see refs. 8 and 9).

** In the solid, $[Cl_2(CH_3)_2Sb]_2CH_2$ and $(CH_3)_3SbCl_2$ showed the ν(Sb–Cl) infrared frequency at 285 and 283 cm^{-1}, respectively.

hybrid orbitals for the Sb–C bonds. From these considerations, the *s*-character of the orbitals of the antimony used for the Sb–C bonds in our compounds would appear to increase in order from (I) to (X). As seen in Fig. 1, this order closely parallels that of the increase in the frequencies of $\rho(CH_2)$ and ν_{av}(Sb–C–Sb). A similar relationship between $\rho(CH_3)$ and ν_{asym}(Tl–C) or ν_{sym}(Tl–C) in compounds of the type $(CH_3)_2TlX$ was explained[12] also by considering the variations in the *s*-character of the orbitals of the thallium atom in the TlC_2^+ moiety.

ACKNOWLEDGEMENTS

Thanks are due to Prof. D. G. White of The George Washington University for his help in improving our manuscript.

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