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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XVI *. PREPARATION AND PROPERTIES OF HETEROCYCLIC TRICHLORO-*cis*-DIORGANOANTIMONY(V) COMPOUNDS AND OF THE CORRESPONDING TETRAMETHYLAMMONIUM TETRACHLORODIORGANOANTIMONATES

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Summary

Trichlorodiorganoantimony(V) compounds, R_2SbCl_3, in which the antimony atom is part of a heterocyclic ring have been synthesized. They have been converted into the corresponding tetramethylammonium tetrachlorodiorganoantimonates, $[R_2SbCl_4]^-$ $[Me_4N]^+$, which are hexacoordinate diorganoantimony(V) species in which the antimony—carbon bonds are forced into a *cis*-position.

5,5,5-Trichlorodibenzostibole, 10,10,10-trichlorophenoxantimonin, 5,5,5-trichloro-5,10-dihydrodibenz[*b*, *e*]antimonin and 5,5,5-trichloro-10,11-dihydro-5*H*-dibenzo[*b*, *f*]stibepin have been prepared by chlorination of the corresponding heterocyclic chlorodiarylstibines. Heterocyclic trichlorodialkylantimony(V) compounds have been prepared by a reaction sequence involving the chlorination of the corresponding heterocyclic distibines. Treatment of 1-methylstibolane (1-methylstibacyclopentane) or 1-methylantimonane (1-methylstibacyclohexane) with sodium in liquid ammonia results in the almost exclusive cleavage of the antimony—methyl carbon bond to give sodium antimonides, which on treatment with 1,2-dichloroethane give the corresponding heterocyclic distibines, 1,1′-bistibolane and 1,1′-biantimonane. Upon treatment with sulphuryl chloride in a 1/3 molar ratio these heterocyclic distibines give 1,1,1-trichlorostibolane and 1,1,1-trichloroantimonane, respectively. The trivalent heterocyclic monochlorostibines 1-chlorostibolane and 1-chloroantimonane have been prepared analogously by reaction of the corresponding distibines with sulphuryl chloride in a 1/1 molar ratio.

* For Part XV see ref. 1.

Complexes of the types $[cis\text{-}R_2SbCl_4]^-$ $[Me_4N]^+$ were readily obtained from the 1/1 reaction of compounds $cis\text{-}R_2SbCl_3$ with tetramethylammonium chloride, but the seven-membered heterocyclic antimony compound 5,5,5-trichloro-10,11-dihydro-5*H*-dibenzo[*b*, *f*]stibepin is unreactive because of steric hindrance around the antimony atom. The complexes $[(CH_2)_nSbCl_4]^-$ $[Me_4N]^+$ (n = 4, 5) decompose slowly in methanol with formation of $[Sb_2Cl_9]^{3-}$ $[Me_4N]_3^+$.

IR data of the various compounds are reported.

Introduction

Among the various types of organoantimony(V) compounds, R_nSbX_{5-n} (n = 1—5), those of the type R_3SbX_2 have received most attention. Until recently little was known about the chemistry of diorganoantimony(V) compounds R_2SbX_3, and only the synthesis of a few diarylantimony(V) derivatives had been reported [2,3]. Dialkylantimony(V) compounds were considered to be thermally unstable. Me_2SbCl_3 and Me_2SbBr_3, the only compounds which had been isolated, were found to undergo a gradual decomposition at room temperature into halodimethylstibine and methyl halide [4].

Recently, the study of the coordination chemistry of diorganoantimony(V) compounds has opened a new and fertile field of organoantimony(V) chemistry (see refs. 5 and 6 and references cited therein). A synthetic sequence which makes the trihalodialkylantimony(V) starting materials more easily accessible has recently been reported [7]. As a result of the presence of three electronegative halogen atoms the antimony atom in trihalodiorgancantimony(V) compounds exhibits significant electron-acceptor properties. In the presence of Lewis bases [6] and of anionic mono-, bi- and tri-dentate ligands [5,6,8—11] thermally stable hexacoordinate diorganoantimony(V) complexes are easily formed. The stereochemistry and bonding in such compounds has been intensively studied. The results clearly indicate that the organic groups R in general occupy *trans*-positions.

So far, it has been generally accepted that trihalodiorganoantimony compounds themselves possess a trigonal bipyramidal geometry, in which the two organic groups R together with one halogen atom occupy the equatorial positions [12]. Beattie et al. [13], however, recently suggested that in trichlorodimethylantimony, Me_2SbCl_3, the acceptor activity of the antimony atom might be sufficient to induce hexacoordination through the formation of a dimeric species containing bridging chlorine atoms. A redetermination of the molecular structure of trichlorodiphenylantimony, Ph_2SbCl_3, recently revealed that dimeric units containing bridging chlorine atoms are present in the crystalline state [14]. The antimony atoms are hexacoordinated in a *trans*-diphenyl tetrachloro configuration. In view of these data the presence of dimeric units of trichlorodimethylantimony in the crystalline state is regarded to be quite likely, although in solution (benzene and other solvents) the compound appears to be monomeric [15,16]. As part of a series of ^{121}Sb Mössbauer studies on diorganoantimony(V) compounds Bertazzi et al. [17,18] have studied the Mössbauer spectrum of trichlorodimethylantimony. The data point to a hexacoor-

dinate structure with *trans*-dimethyl groups and bridging chlorine atoms. In a recent ^{121}Sb Mössbauer study on hexacoordinate antimony(V) compounds Pebler et al. [19] have reached the same conclusion.

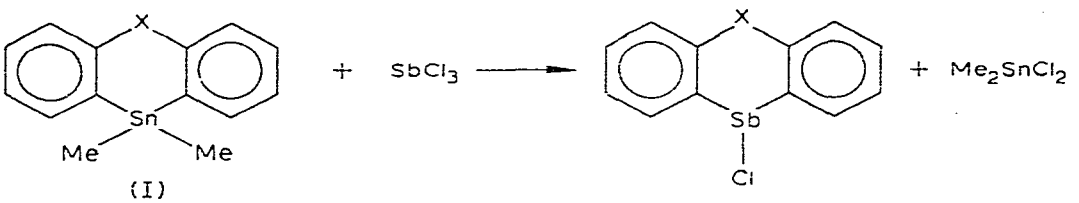
Little information is available concerning hexacoordinate diorganoantimony(V) compounds in which the organic groups R occupy *cis*-positions. Although dihalodiarylantimony(V) β-diketonate complexes have a *trans*-diaryl structure in the solid state, *cis—trans*-isomerism is observed in solution [5,6,20]. Recently, we reported on a few compounds of this type in which as a result of geometric constraints the aryl groups are forced into a *cis*-configuration [5,21]. UV, IR and PMR spectroscopic measurements did not allow a definite assignment of the structure of dichlorodiphenylantimony oxinate in solution to be made [22]. Ruddick and Sams [23] have recently assigned a *cis*-configuration to this compound in the solid state on the basis of ^{121}Sb Mössbauer spectroscopy.

The paucity of data for *cis*-diorganoantimony(V) compounds has led to the present work. A series of heterocyclic trichlorodiorganoantimony(V) compounds has been synthesized in which the antimony—carbon bonds are forced into a *cis*-position. The corresponding tetrachloro-*cis*-diorganoantimonate salts $[cis\text{-}R_2SbCl_4]^-[Me_4N]^+$ have also been prepared. The various compounds have been investigated by infrared spectroscopy in the solid state and by PMR spectroscopy in solution. A ^{121}Sb Mössbauer spectroscopy study of these compounds will be reported separately [24].

Results and discussions

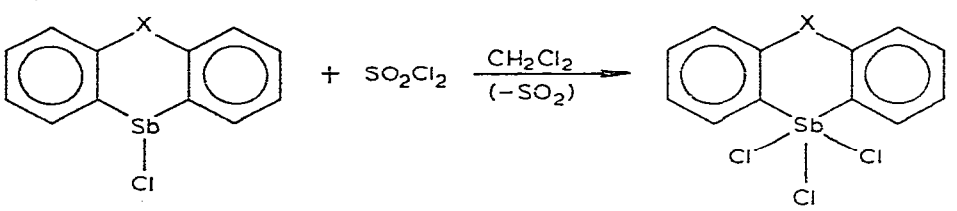
cis-Diarylantimony(V) compounds

We previously described the synthesis of a series of heterocyclic chlorodiarylstibines by the treatment of the corresponding heterocyclic dimethyltin(IV)



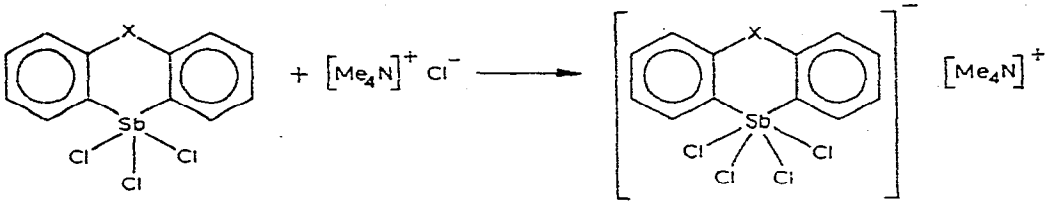
(X = O, S, SO_2, CH_2 or CH_2CH_2)

compounds with antimony trichloride [25]. A number of these chlorostibines have now been converted into the corresponding trichloro *cis*-diarylantimony(V) compounds by treatment with sulphuryl chloride in dichloromethane.



(X = O, CH_2, CH_2CH_2)

The complex tetramethylammonium salts of these compounds as well as of the previously reported 5,5,5-trichlorodibenzostibole(III, X = —) [26] were obtained with one exception (III, X = CH_2CH_2) upon addition of stoichiometric amounts of tetramethylammonium chloride in methanol to a solution of the heterocyclic trichloro-*cis*-diarylantimony(V) compounds in dichloromethane, which leads to immediate precipitation. The seven-membered heterocyclic trichloro-*cis*-diarylantimony compound (III, X = CH_2CH_2) appeared to be unreactive. Steric hindrance around the antimony atom inhibits complex forma-



(III) (IV)

(X = —, O or CH_2)

tion. The compounds were isolated as colourless solids. Melting points and analytical data are given in Table 1.

cis-Dialkylantimony(V) compounds

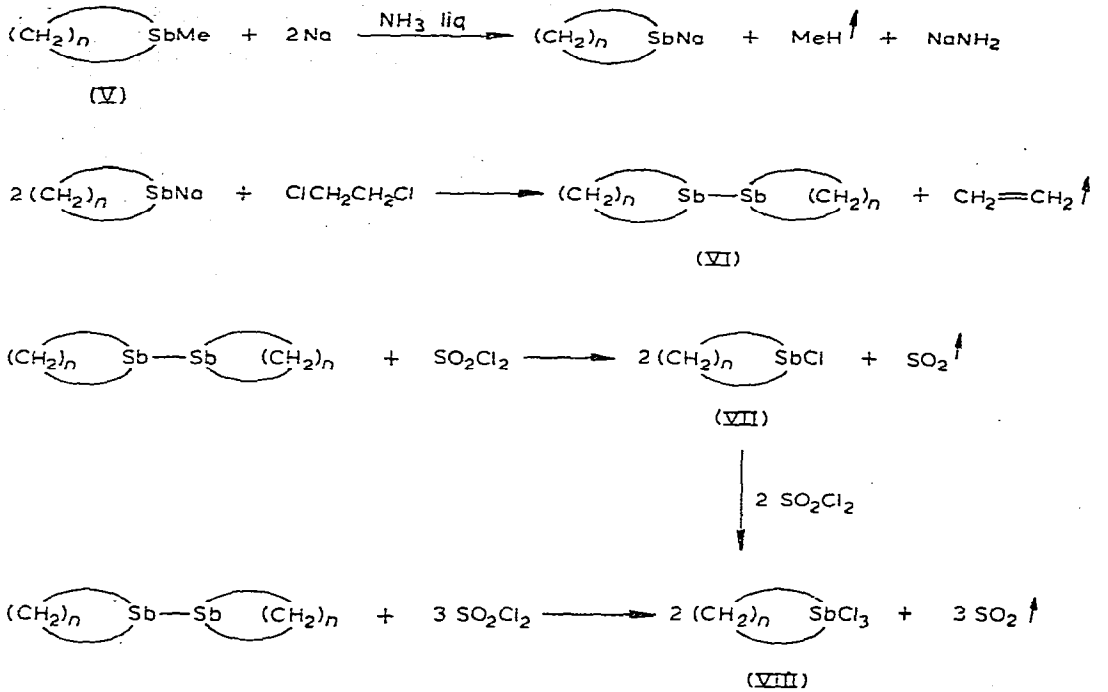
Earlier we described a convenient route to the synthesis of trichlorodialkylantimony(V) compounds which involves the chlorination of tetraalkyldistibines with sulphuryl chloride [7]. The tetraalkyldistibine starting materials are easily made by sodium cleavage of trialkylstibines in liquid ammonia followed by reaction with dichloroethane [7]. The same reaction has now been successfully applied to the synthesis of heterocyclic trichloro-*cis*-dialkylantimony(V) compounds.

Upon addition of 1-methylstibolane (1-methylstibacyclopentane) (Va, $n = 4$)

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR SOME HETEROCYCLIC TRICHLORO-*cis*-DIARYL ANTIMONY(V) COMPOUNDS AND CORRESPONDING TETRAMETHYLAMMONIUM TETRACHLOROANTIMONATES

Compound	X	M.p. (°C)	Analyses found (calcd.) (%)		
			C	H	Cl
IIIa	—	140—142 (dec.)	37.84 (37.90)	2.21 (2.12)	28.24 (27.97)
IIIc	CH_2	>135 (dec.)	39.31 (39.59)	2.78 (2.55)	26.78 (26.97)
IIId	CH_2CH_2	>270 (dec.)	41.27 (41.18)	3.27 (2.96)	25.65 (26.04)
IVa	—	>270 (dec.)	39.39 (39.24)	4.15 (4.08)	28.49 (28.96)
IVb	O	200 (dec.)	37.39 (37.99)	4.07 (3.98)	28.19 (28.03)
IVc	CH_2	250 (dec.)	40.82 (40.52)	4.63 (4.40)	27.81 (28.14)



(n = 4 or 5)

or 1-methylantimonane (1-methylstibacyclohexane) (Vb, $n = 5$) (cf. ref. 1) to a solution of sodium in liquid ammonia in a 1/2 molar ratio, almost exclusive cleavage of the antimony—methyl carbon bond occurs to give the corresponding sodium antimonides. Reaction with 1,2-dichloroethane affords the corresponding distibines, 1,1′-bistibolane (VIa) and 1,1′-biantimonane (VIb). The PMR spectra of benzene solutions of the crude reaction products show the presence of traces of contaminants which contain methyl groups bound to antimony. Obviously, these products have been formed as a result of a side reaction in which antimony—carbon ring cleavage has taken place to a minor extent in the formation of the sodium antimonides. Distillation at reduced pressure affords 1,1-bistibolane as a yellow high-boiling liquid which solidifies to an orange-red solid, m.p. 46—47° C, and 1,1-biantimonane as a yellow high-boiling liquid which solidifies to a yellow solid, m.p. 31—32° C. Upon reaction in dichloromethane solution with sulphuryl chloride in 1/1 and 1/3 molar ratios these heterocyclic distibines are converted into 1-chlorostibolane (VIIa), 1,1,1-trichlorostibolane (VIIIa), 1-chloroantimonane (VIIb) and 1,1,1-trichloroantimonane (VIIIb), respectively.

The trivalent monochlorostibines, 1-chlorostibolane and 1-chloroantimonane appear to be air-sensitive, thermally stable, high boiling, pale-yellow liquids which solidify at room temperature to low-melting yellow solids. The pentavalent trichloro derivatives appear to be colourless solids. The five-membered heterocyclic compound 1,1,1-trichlorostibolane gradually becomes dark-brown at room temperature. The six-membered heterocyclic compound 1,1,1-trichloroantimonane, on the other hand, appears to be remarkably stable at room temper-

TABLE 2

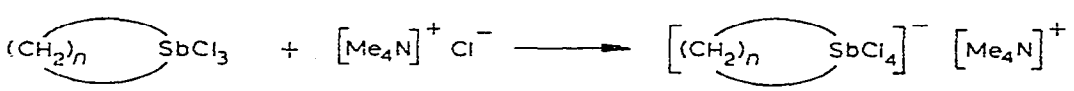
PHYSICAL AND ANALYTICAL DATA FOR SOME HETEROCYCLIC *cis*-DIALKYLANTIMONY COMPOUNDS

Compound	B.p. (°C/mm)	M.p. (°C)	Analyses found (calcd.) (%)				
			C	H	Cl	N	Sb
VIa	93—97/0.04	46—47					68.36
$n = 4$							(68.46)
VIb	120—124/0.06	31—32					62.47
$n = 5$							(63.45)
VIIa	55/0.08	33—34			16.45		57.36
$n = 4$					(16.61)		(57.08)
VIIb	58—59/0.1	35			15.32		52.97
$n = 5$					(15.60)		(53.56)
VIIIa		[a]	16.90	2.98	35.55		42.52
$n = 4$			(16.89)	(2.81)	(37.47)		(42.85)
VIIIb		103—115	20.46	3.59	35.15		40.78
$n = 5$		(dec.)	(20.14)	(3.38)	(35.66)		(40.82)
IXa		120	24.50	5.26	35.93	3.49	30.85
$n = 4$		(dec.)	(24.40)	(5.12)	(36.01)	(3.56)	(30.91)
IXb		130	26.53	5.59	34.54	3.29	30.39
$n = 5$		(dec.)	(26.50)	(5.44)	(34.77)	(3.43)	(29.85)

[a] Decomposes gradually at room temperature.

ature. A pure sample is obtained by recrystallization from petroleum ether (60—80°C). However, prolonged heating in refluxing petroleum ether (60—80°C) produces an unidentified purple-brown solid.

Treatment of freshly prepared 1,1,1-trichlorostibolane and 1,1,1-trichloroantimonane in methylene chloride with tetramethylammonium chloride in methanol results in precipitation of the corresponding tetrachloroantimonates (IX).



(VIII) (IX)

At room temperature these complex salts are fairly stable in contact with air, but slowly decompose on storage. Interestingly, after several weeks hexagonal colourless crystals were deposited in very low yield from the methanol solution. These were characterized by X-ray analysis * as the complex salt $[Me_4N]_3^+ [Sb_2Cl_9]^{3-}$. This compound has previously been obtained from the reaction of tetramethylammonium chloride with antimony trichloride [27].

Physical constants and analytical data of the stibolane and antimonane derivatives (VI—IX) are presented in Table 2.

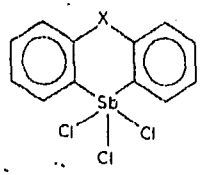
IR spectra

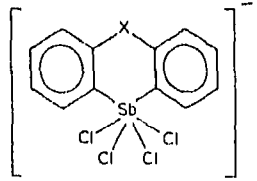
IR spectra of the *cis*-diorganoantimony(V) compounds described in this paper have been recorded in the 4000—200 cm^{-1} region. Antimony—carbon and antimony—chlorine stretching vibrations, which may provide information about the

* We thank Dr. H.J. Haupt, University of Dortmund, BRD, for carrying out the X-ray structure analyses.

TABLE 3

RELEVANT INFRARED STRETCHING FREQUENCIES FOR SOME HETEROCYCLIC TRICHLORO *cis*-DIARYLANTIMONY(V) COMPOUNDS AND CORRESPONDING TETRAMETHYLAMMONIUM TETRACHLOROANTIMONATES IN THE 600–200 cm^{-1} REGION [a]





$[Me_4N]^+$

IIIa X = —	IIIc X = CH_2	IIId X = CH_2CH_2	IVa X = —	IVb X = O	IVc X = CH_2	Assignments
	585mw		560vw (br)	560vw (br)	585mw	—
			515vw (br)	520vw (br)		
480m	485m		480s		490s	
470m		465s	470w			
	440s		455vw	455s	440s	aryl
420m	432m	405 (sh)	420m			
	385s (br)	395s		388m	390m (br)	
			360w (br)			
	345vs (br)					
	320vs (br)	310s	315s	310vs		
360–200 [b] vs (br)		290s	290 (sh)	290vs (br)	310–275vs	ν(Sb—Cl), ν(Sb—aryl)
	275vs (br)		275vs (br)			
				260m	260 (sh)	
					240m	aryl, δ(SbCl)
	215s		215s		220m	

[a] s = strong, m = medium, w = weak, br = broad, sh = shoulder, v = very; spectra refer to Nujol mulls, unless otherwise stated.
[b] Peaks at 360m, 330s in KBr pellets.

TABLE 4

RELEVANT INFRARED STRETCHING FREQUENCIES FOR SOME HETEROCYCLIC *cis*-DIALKYL-ANTIMONY(V) COMPOUNDS IN THE 600—200 cm^{-1} REGION [a]

$(CH_2)_n$ $SbCl_3$	$[(CH_2)_n$ $SbCl_4]^-$	$[Me_4N]^+$		Assignments
VIII b [b]	IXa	IXb		
$n = 5$	$n = 4$	$n = 5$		
575m				
550m	550vs	548vs	}	ν(Sb—C)
460m	460mw	462m		
	440ms	435w (sh)	}	ν(Sb—C); heterocyclic ring vibr.?
370s				
310 (sh)	325vs	355w		
295vs	285 (sh)	300—250vs (br)	}	ν(Sb—Cl)
280 (sh)	265vs			
250 (sh) ?				
	225s	220s		
	210s	210s	}	δ(Sb—Cl)

[a] Spectra refer to Nujol mulls, unless otherwise stated. [b] KBr pellets.

mutual positions of the various atoms bound to antimony, are expected to occur in the 600—200 cm^{-1} region. The absorption bands in this region are listed in Tables 3 and 4. Tentative assignments have been made on the basis of a comparative study of the IR spectral data of a series of diorganoantimony(V) compounds (see refs. 1,8,11—13,16,20,22,28).

Comparison of the IR data of the heterocyclic trichloro-*cis*-diarylantimony-(V) compounds (*cis*-R_2SbCl_3, IIIa, IIIc) with those of the corresponding complexes with tetramethylammonium chloride ([*cis*-$R_2SbCl_4]^-$ $[Me_4N]^+$, IVa, IVc) does not reveal the frequency decrease of $\nu(SbCl_n)$ modes which is expected to occur upon expansion of the coordination number of antimony from five to six (see Table 3). This effect is observed in the corresponding heterocyclic *cis*-dialkylantimony(V) compounds (VIIIb and IXb, see Table 4). The IR spectrum of 1,1,1-trichloroantimonane (VIIIb) shows strong adsorption bands centered at 370 and 295 cm^{-1}, which may be assigned to ν(Sb—Cl) equatorial and $\nu(Sb—Cl_2)$ apical, respectively. However, definite choice between a five-coordinate trigonal bipyramidal species in which the antimony—carbon bonds together with one antimony—chlorine bond occupy the equatorial positions and a hexacoordinate dimeric species containing bridging chlorine atoms can not be made.

Experimental

All reactions were carried out under dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. IR spectra, in the 4000—200 cm^{-1} region, were run by a Perkin—Elmer Mod. 577 instrument, in Nujol mulls (KBr and/or polyethylene windows) or in KBr pellets, PMR spectra were recorded using a

Varian Associates HA 100 NMR spectrometer.

Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO under the supervision of Mr. W.J. Buis. Compounds have been numbered as indicated in Tables 1—4.

Preparation of 5,5,5-trichlorodibenzostibole (IIIa, X = —) and tetramethylammonium 5,5,5,5-tetrachlorodibenzostibolate (IVa, X = —)

Orange-yellow 5,5,5-trichlorodibenzostibole (0.60 g), prepared as described by Hellwinkel and Bach [26], was dissolved in 25 ml of methanol acidified with a few drops of 4 *N* HCl, and a solution of 0.25 g of tetramethylammonium chloride in 25 ml of methanol was added dropwise. A colourless solid precipitated immediately. Recrystallization from methanol afforded 0.35 g of tetramethylammonium 5,5,5,5-tetrachlorodibenzostibolate (m.p. 270—275°C, dec.; yield 45%).

Preparation of 10,10,10-trichlorophenoxantimonin (IIIb, X = 0) and tetramethylammonium 10,10,10,10-tetrachlorophenoxantimonate (IVb, X = 0)

A solution of 0.2 g of 10-chlorophenoxantimonin [22] in chloroform (20 ml) cooled at 0°C was chlorinated by the dropwise addition of an equimolar amount of sulphuryl chloride. Evaporation of the solvent afforded 10,10,10-trichlorophenoxantimonin as a yellow-greenish oil which was converted into the corresponding tetramethylammonium 10,10,10,10-tetrachlorophenoxantimonate by treatment of a chloroform solution (15 ml) of this product with an equimolar amount of tetramethylammonium chloride in methanol (10 ml); 0.18 g of the colourless tetramethylammonium salt separated immediately (m.p. 200°C, dec., yield 64% based on 10-chlorophenoxantimonin).

Preparation of 5,5,5-trichloro-5,10-dihydrodibenz[b, e]antimonin (IIIc, X = CH_2) and tetramethylammonium 5,5,5,5-tetrachloro-5,10-dihydrodibenz[b, e]antimoninate (IVc, X = CH_2)

A solution of 0.8 g of 5-chloro-5,10-dihydrodibenz[*b*, *e*]antimonin (ref. 22) in chloroform (25 ml) cooled at 0°C was chlorinated by dropwise addition of an equimolar amount of sulphuryl chloride. Evaporation of the solvent afforded a crude sample of 5,5,5-trichloro-5,10-dihydrodibenz[*b*, *e*]antimonin, which was purified by recrystallization from chloroform/petroleum ether (40—60°C) to give 0.5 g of a yellow crystalline solid (m.p. 135—165°C, dec., yield 52%).

Dropwise addition of a solution of tetramethylammonium chloride (0.17 g, 1.55 mmol) in 15 ml of methanol to a chloroform solution of 0.72 g of 5,5,5-trichloro-5,10-dihydrodibenz[*b*, *e*]antimonin led to immediate precipitation of a colourless solid (0.61 g). Recrystallization from methanol afforded 0.42 g of tetramethylammonium 5,5,5,5-tetrachloro-5,10-dihydrodibenz[*b*, *e*]antimonate (m.p. 250°C, dec., yield 54%).

Preparation of 5,5,5-trichloro-10,11-dihydro-5H-dibenzo[b, f]stibepin (IIId, X = CH_2CH_2). Attempted preparation of tetramethylammonium 5,5,5,5-tetrachloro-10,11-dihydro-5H-dibenzo[b, f]stibepinate

To 0.5 g of 5-chloro-10,11-dihydro-5*H*-dibenzo[*b*, *f*]stibepin (ref. 22) in chloroform (25 ml) was added an equimolar amount of sulfuryl chloride.

Evaporation of the solvent and recrystallization of the crude product from chloroform/petroleum ether (40—60°C) afforded 0.4 g of 5,5,5-trichloro-10,11-dihydro-5*H*-dibenzo[*b*, *f*]stibepin as a colourless crystalline solid (m.p. >275°C, dec., yield 66%). This compound appeared to be inert towards complex salt formation with tetramethylammonium chloride in methanol.

Preparation of 1,1'-bistibolane (VIa) and 1,1'-biantimonane (VIb)

1-Methylstibolane (ref. 1) (16.6 g, 86 mmol) was added to a solution of sodium (4.0 g, 172 mmol) in liquid ammonia (300 ml). The colour gradually changed from dark-blue to red. After 1.5 h stirring, 1,2-dichloroethane (8.6 g, 87 mmol) in diethyl ether (150 ml) was added dropwise, and the colour disappeared. Ammonia was allowed to evaporate off, and diethyl ether (100 ml) and water (100 ml) were added to the residue. The mixture became black as a result of the deposition of a small amount of antimony. The diethyl ether layer was separated, dried on Molecular sieve 4A, filtered, and evaporated to leave an orange-coloured solid. Distillation at reduced pressure afforded 12.6 g of 1,1'-bistibolane as a yellow-coloured liquid, b.p. 93—97°C/0.04 mmHg, which solidified to an orange-red solid (m.p. 46—47°C, yield 82.3%). The PMR spectrum in benzene shows a complex pattern of proton resonance signals at δ 1.50—2.30 ppm downfield from TMS.

1,1'-Biantimonane (9.1 g), a yellow liquid, b.p. 120—124°C/0.06 mmHg which solidifies to a yellow solid (m.p. 31°C), was prepared analogously from 12.5 g (60 mmol) of 1-methylantimonane [1] (yield 78.5%). The PMR spectrum in benzene shows a complex pattern of proton resonance signals at δ 1.00—2.40 ppm.

Preparation of 1-chlorostibolane (VIIa), 1,1,1-trichlorostibolane (VIIIa) and tetramethylammonium 1,1,1,1-tetrachlorostibolanate (IXa)

A solution of 1,1'-bistibolane (6.9 g, 19.4 mmol) in methylene chloride (80 ml) was cooled to —78°C to give an orange suspension, to which was added dropwise an equimolar amount of sulphuryl chloride. Evaporation of the solvent and distillation of the residue gave 8.0 g of pale-yellow 1-chlorostibolane, b.p. 55°C/0.08 mmHg which solidified to a yellow solid (m.p. 33—34°C, yield 96.6%). The PMR spectrum in benzene showed two sets of resonance signals at δ 1.70—2.00 ppm ($\underline{CH_2}$—Sb) and δ 1.40—1.70 ppm ($\underline{CH_2}$—CH_2—Sb), respectively.

Treatment of a methylene chloride solution (20 ml) of 0.9 g (2.6 mmol) of 1,1'-bistibolane with 7.8 mmoles of sulphuryl chloride at 0°C gave a clear solution. Evaporation of the solvent afforded 1.48 g of 1,1,1-trichlorostibolane as a colourless solid, which appeared to be thermally unstable at room temperature (yield 100%). The PMR spectrum in benzene solution showed two sets of resonance signals at δ 1.60—2.30 ppm ($\underline{CH_2}$—Sb) and δ 1.20—1.60 ppm ($\underline{CH_2}$—CH_2—Sb), respectively.

Addition of 0.6 g (5.4 mmol) of tetramethylammonium chloride in 15 ml of methanol to a freshly prepared solution of 1.5 g (5.2 mmol) of 1,1,1-trichlorostibolane in 20 ml of methylene chloride gave 1.6 g of a pale-yellow precipitate (m.p. 120°C, dec.), which analysed perfectly for the complex salt, tetramethylammonium 1,1,1,1-tetrachlorostibolanate (yield 79%). The PMR spectrum in

acetone-d_6 showed a singlet at δ 3.45 ppm $[Me_4N]^+$ and a complex pattern of ring proton resonances at δ 1.60—2.00 ppm.

Preparation of 1-chloroantimonane (VIIb), 1,1,1-trichloroantimonane (VIIIb) and tetramethylammonium 1,1,1,1-tetrachloroantimonanate (IXb)

These six-membered ring systems were prepared from 1,1'-biantimonane by the procedures as used for the synthesis of the corresponding five-membered ring systems from 1,1'-bistibolane.

1-Chloroantimonane (6.4 g) (pale-yellow liquid, b.p. 58—59°C/0.1 mmHg; pale-yellow solid, m.p. 35°C) was prepared in 76% yield from 7.1 g of 1,1'-biantimonane. The PMR spectrum in deuterochloroform solution showed two sets of resonance signals at δ 1.90—2.30 ppm (CH_2—Sb) and δ 1.40—1.90 ppm ($\underline{CH_2}$—CH_2—CH_2Sb), respectively.

1,1,1-Trichloroantimonane (1.4 g) was obtained quantitatively as a colourless solid with m.p. 103—105°C(dec.) from 0.9 g of 1,1'-biantimonane. The compound could be recrystallized from petroleum ether (60—80°C). Cryometric mol.wt. determinations showed 1,1,1-trichloroantimonane to be monomeric in freezing benzene. The PMR spectrum in deuterochloroform solution showed three sets of resonance signals at δ 3.30—3.55 ppm (CH_2—Sb), δ 2.40—2.60 ppm ($\underline{CH_2}$—CH_2—Sb) and δ 1.80—2.15 ppm ($\underline{CH_2}$—CH_2—CH_2—Sb).

Addition of 0.77 g (7.0 mmol) of tetramethylammonium chloride in 10 ml of methanol to a solution of 2.1 g (7.0 mmol) of 1,1,1-trichloroantimonane in 20 ml of methylene chloride gave a precipitate of 1.9 g of a pale-yellow solid (m.p. 130°C, dec.) which analysed correctly for the complex salt, tetramethylammonium 1,1,1,1-tetrachloroantimonanate (yield 66%). The PMR spectrum in acetone-d_6 solution showed a singlet at δ 3.45 ppm $[Me_4N]^+$ and complex patterns of ring proton signals at δ 2.80—3.00 ppm ($\underline{CH_2}$—Sb), 2.15—2.45 ppm ($\underline{CH_2}$—CH_2—Sb) and 1.40—1.70 ppm ($\underline{CH_2}$—CH_2—CH_2—Sb).

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