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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XV *. THE SYNTHESIS OF HETEROCYCLIC ANTIMONY COMPOUNDS VIA THERMOLYSIS OF α,ω-BIS(DIMETHYLSTIBINO)ALKANES. A NEW ROUTE TO THE SYNTHESIS OF 1-METHYLSTIBACYCLOALKANES

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Summary

The intramolecular disproportionation of α,ω-bis(dimethylstibino)alkanes provides a new route to small-ring stibacycloalkanes. 1-Methylstibacyclopentane and 1-methylstibacyclohexane have been prepared in good yield via thermolysis of 1,4-bis(dimethylstibino)butane and 1,5-bis(dimethylstibino)pentane. Attempts to prepare 1-methylstibacyclobutane and 1-methylstibacycloheptane via thermolysis of 1,3-bis(dimethylstibino)propane and 1,6-bis(dimethylstibino)hexane instead resulted in intermolecular disproportionation leading to the formation of polymeric material.

The α,ω-bis(dimethylstibino)alkanes used as starting materials were prepared by the reaction of dimethylstibylsodium with α,ω-dichloro- or α,ω-dibromoalkanes in liquid ammonia. Upon reaction of dimethylstibylsodium with 1,4-dibromobutane and 1,5-dibromopentane in a 2/1 ratio, 1-methylstibacyclopentane and 1-methylstibacyclohexane were formed probably via intramolecular quaternization of intermediate α-methylstibino-ω-bromoalkanes.

All antimony(III) compounds prepared have been converted into the corresponding dichloroantimony(V) derivatives. Quaternization with methyl iodide leads to the formation of 1,1-dimethylstibacyclopentane and 1,1-dimethylstibacyclohexane iodides.

IR spectra of the stibacycloalkanes show a characteristic absorption in the region 460—470 cm^{-1}. Moreover, the stibacyclohexane derivatives show two characteristic bands in the region 900—920 and 980—1010 cm^{-1}, which are not observed in the spectra of the stibacyclopentanes.

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Introduction

Heterocyclic compounds containing a carbon—antimony—carbon sequence in the ring are rare [2]. In most of the compounds known so far the antimony atom bridges two aromatic ring systems. In a recent paper we reported on the preparation of a number of heterocyclic chlorostibines of this type [3]. Stibacycloalkanes, saturated ring systems containing only carbon and antimony atoms, have received little attention.

In 1915 Grüttner and Wiernik [4] reported on the synthesis of 1-phenylstibacyclohexane by the reaction of dichlorophenylstibine with the di-Grignard reagent of 1,5-dibromopentane. In 1916 1-phenylstibacyclopentane was prepared [5] by essentially the same procedure using the di-Grignard reagent of 1,4-dibromobutane as the alkylating reagent. Both compounds appeared to be high-boiling liquids which upon reaction with chlorine were easily converted into colourless, crystalline 1,1-dichloro derivatives. The only other study on stibacycloalkanes reported is that of Steinkopf et al. [6] who described in 1932 the synthesis of 1-methylstibacyclohexane and the 1,1-dichloro derivative by the Grignard procedure. The method used in the preparation of these compounds is not very attractive as the dihaloorganostibine starting materials are not easily accessible.

Recently, at our Institute Bulten and Budding [7,8] have obtained small-ring stannacycloalkanes via thermolysis of α,ω-bis(trialkylstannyl)alkanes. In the present paper we report on the preparation of α,ω-bis(dimethylstibino)alkanes and their conversion into 1-methylstibacycloalkanes via a similar thermolysis pathway. Reaction of these compounds with sulphuryl chloride or with methyl iodide results in the formation of 1,1-dichloro-1-methylstibacycloalkanes and 1,1-dimethylstibacycloalkane iodides, respectively.

Results and discussion

Preparation of α,ω-bis(dimethylstibino)alkanes

α,ω-Bis(diorganostibino)alkanes have been synthesized by Issleib and Hamann in the course of their study on the reactivity of diorganostibyllithium derivatives R_2SbLi. Diorganostibyllithium derivatives were found to react with α,ω-dichloroalkanes to give α,ω-bis(diorganostibino)alkanes, $R_2Sb(CH_2)_nSbR_2$ (R = Et [9], t-Bu [10], cyclohexyl [11], phenyl [12] and n = 3—6, in good yield. However, the fact that diorganostibines R_2SbH, used as starting materials for the synthesis of R_2SbLi are not readily available, makes this procedure less attractive.

Recently, we have reported on a convenient synthesis of diorganostibylsodium derivatives R_2SbNa (R = Me, Et, Pr, Ph) involving antimony—carbon bond cleavage in triorganostibines by sodium in liquid ammonia. Also dichlorotrialkylantimony compounds were found to be suitable starting materials for the synthesis of dialkylstibylsodium [13]. For instance, the reaction in liquid ammonia of dichlorotrimethylantimony with sodium in a 1/4 molar ratio appeared to result in the formation of dimethylstibylsodium in over 80% yield. α,ω-Bis(dimethylstibino)alkanes can now be conveniently prepared from dichlorotrimethylantimony by the following reaction sequence:

$$2Me_3SbCl_2 + 8\ Na \xrightarrow{NH_3} 2\ Me_2SbNa + 2\ NaNH_2 + 2\ MeH + 4\ NaCl$$

$$2\ Me_2SbNa + Cl(CH_2)_nCl \xrightarrow{NH_3} Me_2Sb(CH_2)_nSbMe_2 + 2\ NaCl$$

The reaction of dimethylstibylsodium with dichloromethane (n = 1) and with 1,2-dichloroethane (n = 2), resulting in the formation of bis(dimethylstibino)methane and tetramethyldistibine, respectively, has been described previously [13,14]. The reaction with longer-chain α,ω-dichloroalkanes (n = 3—6) readily affords the α,ω-bis(dimethylstibino)alkanes $Me_2Sb(CH_2)_nSbMe_2$ (n = 3—6) as air-sensitive, high-boiling, colourless liquids. The instability of these products at elevated temperatures posed difficulties for the isolation of completely pure samples. PMR spectra of the α,ω-bis(dimethylstibino)alkanes after distillation at reduced pressure showed the presence of traces (less than 5%) of decomposition products, such as trimethylstibine, 1-methylstibacycloalkanes (n = 4, 5) and unidentified products containing methylantimony groups. Boiling points and PMR data in benzene-d_6 solution are given in Table 1.

α,ω-Bis(dimethylstibino)alkanes have not been analysed as such, but were converted into the corresponding α,ω-bis(dichlorodimethylstibino)alkanes by treatment with sulphuryl chloride in dichloromethane solution:

$$Me_2Sb(CH_2)_nSbMe_2 + 2\ SO_2Cl_2 \xrightarrow[[-SO_2]]{CH_2Cl_2} Cl_2Me_2Sb(CH_2)_nSbMe_2Cl_2$$

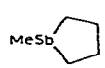
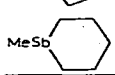
(n = 1, 3—6)

These compounds are colourless solids, inert towards oxidation by air oxygen. Melting points, analyses and PMR data are presented in Table 2.

In the reaction with dimethylstibylsodium, replacement of α,ω-dichloroalkanes by the corresponding dibromo derivatives gave a nearly quantitative

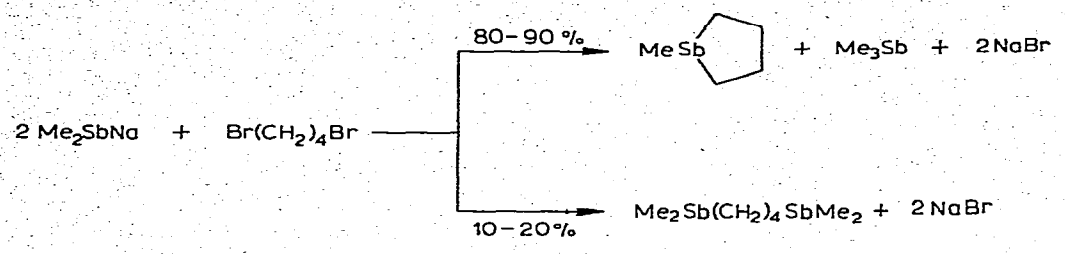
TABLE 1

BOILING POINTS AND PMR DATA OF α,ω-BIS(DIMETHYLSTIBINO)ALKANES, $Me_2Sb(CH_2)_nSbMe_2$ (n = 1, 3—6), TRIMETHYLSTIBINE, 1-METHYLSTIBACYCLOPENTANE AND 1-METHYLSTIBACYCLOHEXANE

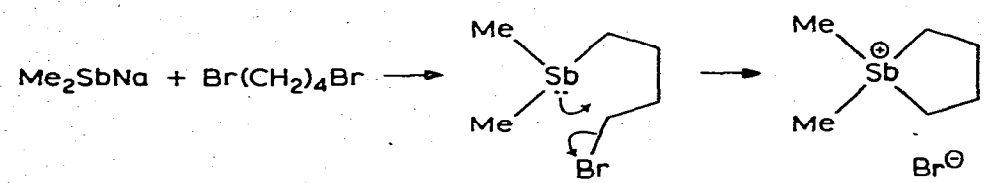
Compound	B.p. (°C/mm Hg)	Chemical shifts, δ (ppm) in C_6D_6	
		δ(CH_3—Sb)	δ(Sb(CH_2)$_n$Sb)
$Me_2SbCH_2SbMe_2$ [a]	59—61/3	0.68	0.97
$Me_2Sb(CH_2)_3SbMe_2$	67/0.5	0.65	1.1—2.0 [b]
$Me_2Sb(CH_2)_4SbMe_2$	79—80(0.5)	0.65	1.1—1.8 [b]
$Me_2Sb(CH_2)_5SbMe_2$	87—95/0.25	0.65	1.0—1.8 [b]
$Me_2Sb(CH_2)_6SbMe_2$	109/0.16	0.67	1.2—1.6 [b]
Me_3Sb	80/760	0.62	
	67—68/30	0.52	1.0—1.8 [b]
	77—79/19	0.66	1.0—1.8 [b]

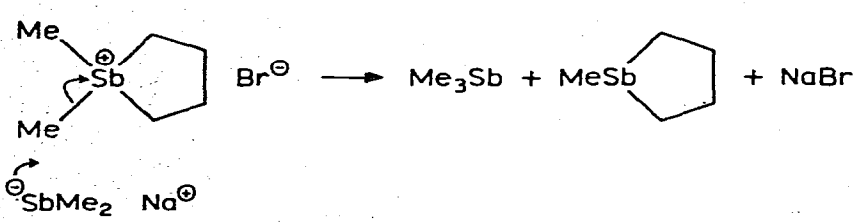
[a] Ref. [14], b.p. 56—57°C/2.5 mm Hg. [b] Multiplets.

yield of α,ω-bis(dimethylstibino)alkanes, $Me_2Sb(CH_2)_nSbMe_2$, for $n = 1$, 3 or 6. However, for $n = 4$, PMR spectroscopy revealed that the reaction had taken a different course leading to the formation of 1-methylstibacyclopentane and trimethylstibine as the main reaction products:



As regards the mechanism for the formation of 1-methylstibacyclopentane in this reaction, we suggest that upon addition of 1,4-dibromobutane to a solution of dimethylstibylsodium in liquid ammonia, the 1/1-reaction product 1-methylstibino-4-bromobutane quaternizes rapidly to the cyclic tetraorganostibonium bromide which then undergoes nucleophilic attack at a methyl carbon by a second dimethylstibyl anion.





Similar intramolecular quaternization reactions leading to the formation of 5- and 6-membered heterocyclic phosphines [2, 15, 16] and arsines [2, 17] have been reported to occur for ω-bromoalkyl phosphines and arsines.

The occurrence of intramolecular quaternization reactions for α-dimethylstibino-ω-bromoalkanes, $Me_2Sb(CH_2)_nBr$, will, of course, be favoured for steric reasons if $n = 4$ or 5.

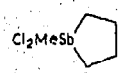
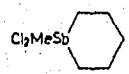
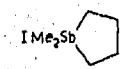
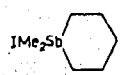
Reaction of dimethylstibylsodium in liquid ammonia with 1,5-dibromopentane affords both the linear and the cyclic reaction product. However, as observed by PMR spectroscopy, the non-cyclic product is preferrred (1,5-bis(dimethylstibine)pentane, yield 60—70%; 1-methylstibacyclohexane and trimethylstibine, yield 30—40%).

Preparation of 1-methylstibacycloalkanes, 1,1-dichloro-1-methylstibacycloalkanes and 1,1-dimethylstibacycloalkane iodides

We have observed that upon heating α,ω-bis(dimethylstibino)alkanes at temperatures above 200°C a redistribution reaction takes place resulting in the

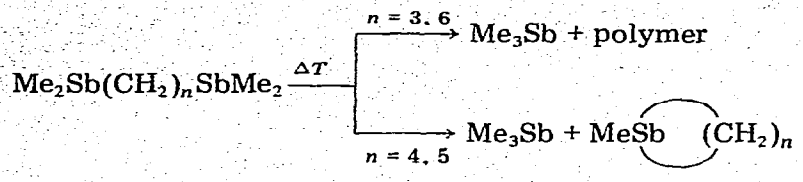
TABLE 2

MELTING POINTS, ANALYTICAL AND PMR DATA OF α,ω-BIS(DICHLORODIMETHYLANTIMONY)ALKANES, 1,1-DICHLORO-1-METHYLSTIBACYCLOALKANES AND 1,1-DIMETHYLSTIBACYCLOALKANE IODIDES

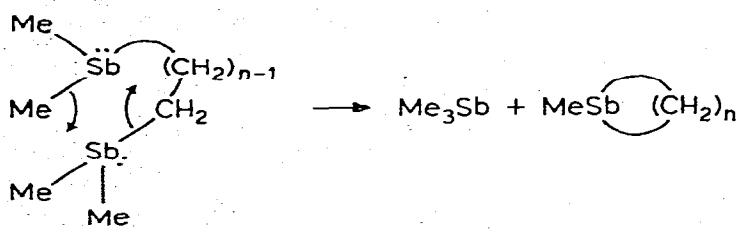
Compound	M.p. (°C)	Analysis found (calcd.) (%)				Chemical shifts, δ (ppm) in $CDCl_3$		
		Sb	Cl, I	C	H	δ(CH_3–Sb)	δ(CH_2–Sb)	δ($SbCH_2(CH_2)_nCH_2Sb$)
$Cl_2Me_2SbCH_2SbMe_2Cl_2$ [a]	170 (dec.)	52.83 (52.99)	30.66 (30.86)	13.41 (13.07)	3.12 (3.07)	2.56	3.92	
$Cl_2Me_2Sb(CH_2)_3SbMe_2Cl_2$	265 (dec.)	49.80 (49.95)	29.20 (29.09)	17.45 (17.24)	3.83 (3.72)	2.33		
$Cl_2Me_2Sb(CH_2)_4SbMe_2Cl_2$	190 (dec.)	48.47 (48.55)	28.15 (28.28)	18.85 (19.16)	3.97 (4.02)	2.30	2.82	2.40
$Cl_2Me_2Sb(CH_2)_5SbMe_2Cl_2$	198 (dec.)	46.53 (47.23)	27.06 (27.50)	21.18 (20.96)	4.37 (4.30)	2.30	2.80	1.5–2.3
$Cl_2Me_2Sb(CH_2)_6SbMe_2Cl_2$	126	44.99 (45.98)	27.88 (26.78)	23.16 (22.68)	4.68 (4.56)	2.27	2.72	1.2–2.3
	105–130 (dec.)	45.87 (46.15)	26.86 (26.88)	22.97 (22.77)	4.34 (4.20)	2.75	2.60	2.30
	120–140 (dec.)	43.60 (43.82)	25.41 (25.52)	25.93 (25.94)	4.72 (4.71)	2.45	2.92	2.82, 1.83
	220 (dec.)	36.04 (36.36)	37.52 (37.90)	21.57 (21.52)	4.40 (4.21)	1.79 [b]		
	220 (dec.)	34.68 (34.90)	36.38 (36.38)	24.22 (24.10)	4.75 (4.62)	1.69 [b]		

[a] Ref. [14], m.p. 190–191°C. [b] In D_2O with $Me_3SiCD_2CD_2COONa$ as an internal standard.

formation of trimethylstibine and dependent on the chain length of the α,ω-substituted alkane either polymeric decomposition products or 1-methylstibacycloalkane.

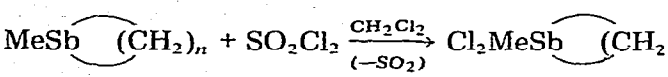


For n = 3 or 6, apparently at elevated temperature an intermolecular electrophilic substitution reaction occurs, resulting in the formation of trimethylstibine and unidentified polymeric products which, according to the PMR spectrum, contain methyl groups bound to antimony. For n = 4 or 5, we propose that concerted intramolecular electrophilic attack of antimony at carbon in the manner depicted below leads to the formation of trimethylstibine in addition to 1-methylstibacyclopentane or 1-methylstibacyclohexane, respectively.



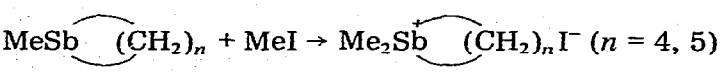
Boiling points and PMR data in benzene-d_6 solution are given in Table 1.

The 1-methylstibacycloalkanes obtained are colourless liquids, sensitive towards oxidation by air oxygen. These compounds have not been analysed as such, but were converted into the corresponding 1,1-dichloro-1-methylstibacycloalkanes by treatment with sulphuryl chloride in dichloromethane solution:



(n = 4, 5)

or into the tetraorganoantimony iodides, 1,1-dimethylstibacycloalkane iodide, by quaternization with methyl iodide:



The latter compounds which are salt-like in nature display a good solubility in water.

Melting points, analyses and PMR data are presented in Table 2.

IR spectra

IR spectra of 1-methylstibacycloalkanes, α,ω-bis(dichlorodimethylstibino)-alkanes, 1,1-dichloro-1-methylstibacycloalkanes and 1,1-dimethylstibacycloalkane iodides were run in the 4000—200 cm^{-1} region either on the pure liquids

or on solids in KBr pellets. Absorption frequencies are listed in the Experimental Part.

So far the study of the infrared spectra of heterocyclic metallocycloalkanes has dealt mainly with the study of Group IVB metal derivatives. Results have recently been reviewed by Topart and Gielen [18, 19 and ref. cited therein]. Nametkin et al. [20] have marked three absorption bands as characteristic for silacyclopentanes, an intense band at 1075 and a doublet with maxima of approximately equal intensity at 1030 and 1020 cm^{-1}. Topart et al. consider absorption bands at 1040, 1020 and 1015 cm^{-1} to be characteristic for the corresponding tin compounds. Sila- and stanna-cyclohexanes show two characteristic adsorption bands situated at 970 and 905 cm^{-1} [18, 19, 21, 22]. An adsorption band observed at 1175—1190 in stannacycloalkanes [18] has also been observed by Oshesky [21] in the IR spectra of silacyclohexanes. Such a band is also present in the infrared spectra of the stibacyclopentane and stibacyclohexane derivatives described in this paper. Examination of the spectra of stibacyclopentane derivatives revealed that different from the spectra of sila- and stanna-cyclopentanes no ring-characteristic bands are present in the 1000—1100 cm^{-1} region. On the other hand, stibacyclohexanes like sila- and stanna-cyclohexanes do show two characteristic absorption bands at 980—1010 and 900—920 cm^{-1}, respectively. Furthermore, a characteristic absorption band assigned to ring skeletal vibrations is observed at 460—470 cm^{-1} both in the spectra of stibacyclopentane and of stibacyclohexane derivatives.

All compounds show absorption bands in the region 500—600 cm^{-1}, related to asymmetric and symmetric antimony—carbon stretching vibrations. Similar to Me_3SbCl_2 [23] a broad absorption band situated at 270—280 cm^{-1} is assigned to ν_{asym}(Sb—Cl), pointing to a *trans* position of the two chloride atoms.

Experimental

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Liquids were handled by the syringe technique. PMR spectra were recorded using a Varian Associates HA 100 NMR spectrometer. IR spectra were run by a Perkin—Elmer Mod. 577 instrument. Elemental analyses were carried out by the Element Analytical Section of this Institute under the supervision of Mr. W.J. Buis.

α,ω-Bis(dimethylstibino)alkanes

Sodium (13.8 g, 0.6 g-atom), cut in small pieces, was slowly added to a suspension of dichlorotrimethylantimony (35.7 g, 0.15 mol) in liquid ammonia (300 ml). A reaction took place instantaneously and a greenish oil separated. When 0.3 g-atom of sodium had been consumed a colourless suspension was obtained. Further addition of sodium (0.3 g-atom) resulted in the formation of a dark-red solution of dimethylstibylsodium in liquid ammonia. Dropwise addition of α,ω-dichloroalkane, $Cl(CH_2)_nCl$ (n = 3—6) (75 mmol) in diethyl ether (250 ml) resulted in an instantaneous reaction to give a pale-yellow suspension. Ammonia was allowed to evaporate and water (150 ml) was added to the residue. The diethyl ether layer was separated, dried on Mol. sieve 4A and subsequently evaporated. According to the PMR spectrum, run in benzene solu-

tion, the residual liquid consisted of fairly pure α,ω-bis(dimethylstibino)alkane, $Me_2Sb(CH_2)_nSbMe_2$ (n = 3—6) in an almost quantitative yield. The residual liquid was distilled at reduced pressure to give 14.3 g of 1,3-bis(dimethylstibino)propane, b.p. 67°C/0.5 mm Hg (yield 55%) and 15.1 g of 1,6-bis(dimethylstibino)hexane, b.p. 109°C/0.2 mm Hg (yield 52%) as colourless air-oxygen sensitive liquids. Distillation of samples of crude 1,4-bis(dimethylstibino)-butane and 1,5-bis(dimethylstibino)pentane appeared to be accompanied by an intramolecular disproportionation reaction resulting in a contamination of these products by trimethylstibine and 1-methylstibacyclopentane or 1-methylstibacyclohexane, respectively.

The α,ω-bis(dimethylstibino)alkanes were converted into the corresponding bis(dichlorodimethylantimony) derivatives by treatment with 2 equivalents of sulphuryl chloride in dichloromethane.

α,ω-Bis(dichlorodimethylantimony)alkanes

A solution of α,ω-bis(dimethylstibino)alkane (0.05 mol crude reaction product) in dichloromethane (20 ml) cooled to —78°C, was chlorinated by the dropwise addition of sulphuryl chloride (0.1 mol). Evaporation of the solvent afforded crude samples of α,ω-bis(dichlorodimethylstibino)alkanes which were purified by recrystallization to give:

1,1-Bis(dichlorodimethylstibino)methane [13]; m.p. 170°C (dec.) (after recrystallization from ethanol); IR data: ν_{max} 2999m, 2924s, 1398s, 1333vw, 1230m, 1217vw, 1038w, 861vvs(br), 820(sh), 675m-s, 661s, 577m, 554vw, 541vw, 500w, 270vvs(br) (cf. ref. 24).

1,3-Bis(dichlorodimethylstibino)propane, m.p. 265°C (dec.) (after recrystallization from tetrahydrofuran); IR data: ν_{max} 3010m(br), 2930w, 1455w, 1415m, 1400(sh), 1223m, 1196m, 1147vw, 995w, 935s, 870vs, 820(sh), 703m, 661vw, 585m, 572w, 275vs.

1,4-Bis(dichlorodimethylstibino)butane, m.p. 190—192°C (dec.) (after recrystallization from ethanol); IR data: ν_{max} 3000w(br), 2940w, 2972w, 1460m, 1407m, 1308w, 1250w, 1224w, 1147m, 1067m, 999w, 861vs(br), 715m, 582m, 545mw, 280vs.

1,5-Bis(dichlorodimethylstibino)pentane, m.p. 198°C (dec.) (after recrystallization from ethanol): IR data: ν_{max} 3000w, 2925s, 2897(sh), 2850m, 1462m, 1403m, 1355w, 1345w, 1270w, 1255w, 1240w, 1230w, 1225w, 1215w, 1200m, 1180s, 1155w, 1043w, 1030w, 995s, 862vs(br), 770(sh), 713s, 610w, 582s, 547m, 270vs(br).

1,6-Bis(dichlorodimethylstibino)hexane, m.p. 125—126°C (after recrystallization from petroleum ether 60—80° C); IR data: ν_{max} 2950s, 2930s, 2860m, 1460s, 1402s, 1350w, 1312w, 1254m, 1223m, 1160s, 1070s, 980m, 925s, 850vvs, 800(sh), 712s, 638w, 580m, 543m, 388w, 270vvs(br).

Yields after recrystallization: 60—70%.

1-Methylstibacycloalkanes via thermolysis of the corresponding α,ω-bis(dimethylstibino)alkanes

Attempted synthesis of 1-methylstibacyclobutane and 1-methylstibacycloheptane. An attempt to prepare 1-methylstibacyclobutane via thermolysis of 1,3-bis(dimethylstibino)propane failed. Upon heating a sample of 5.2 g of 1,3-

dimethylstibinopropane up to 250°C a colourless liquid distilled, in the b.p. range 80—90°C (2.9 g), which according to the PMR spectrum in benzene solution consisted in over 90% of trimethylstibine. In the distilling flask a black tarry residue was present.

Similarly, an attempt to prepare 1-methylstibacycloheptane failed. Upon heating a sample of 4.4 g of 1,6-bis(dimethylstibino)hexane, trimethylstibine was formed (1.6 g) leaving in the distilling flask a solid, grey decomposition product.

Synthesis of 1-methylstibacyclopentane and 1-methylstibacyclohexane. A sample of crude 1,4-bis(dimethylstibino)butane (27.0 g, 7.5 mmol) was heated for 2 h at 230°C at atmospheric pressure. Trimethylstibine (b.p. 80°C/760 mm Hg) distilled from the sample, followed by a mixture of trimethylstibine and 1-methylstibacyclopentane (max. b.p. of the distillate, 160°C). Redistillation of this mixture at reduced pressure afforded 9.1 g of 1-methylstibacyclopentane with b.p. 67—68°C/30 mmHg, which according to its PMR spectrum was pure. IR data: ν_{max} 2960s, 2920vs, 2840s, 1440s, 1404s, 1324m, 1307m, 1243s, 1235m, 1185s, 1120m, 1064s, 1040w, 1021w, 946s, 929m, 862w, 850m, 790s(br), 770(sh), 728w, 690w, 557m, 535m, 516s(br), 467m. Yield 63%.

Thermolysis of a sample of crude 1,5-bis(dimethylstibino)pentane by essentially the same procedure, afforded 1-methylstibacyclohexane, b.p. 77—79°C/19 mm Hg, in over 90% purity. IR data: ν_{max} 2980(sh), 2900vs, 2840s, 2800(sh), 2660m, 1452(sh), 1442s, 1410s, 1344s, 1337(sh), 1280m, 1238m, 1229(sh), 1191m, 1180w, 1167w, 1104w, 1085w, 1025w(br), 985s, 913s, 870s, 792(sh), 773s, 725m, 517s, 507(sh), 470w. Yield 60—70%.

1-Methylstibacyclopentane and 1-methylstibacyclohexane were not analysed as such, but were converted into the corresponding dichloroantimony derivatives by treatment with sulphuryl chloride in dichloromethane.

Direct synthesis of 1-methylstibacycloalkanes by reaction of dimethylstibylsodium with α,ω-dibromoalkanes

1-Methylstibacyclopentane. Dropwise addition of 1,4-dibromobutane to a solution of dimethylstibylsodium (15 mmol) in liquid ammonia (300 ml) resulted in an instantaneous reaction to give a pale yellow suspension. Work-up of this reaction mixture by the usual procedure resulted in the isolation of a crude reaction product (15.7 g), which according to its PMR spectrum (benzene solution) consisted of a mixture of 1-methylstibacyclopentane and 1,4-bis(dimethylstibino)butane in a 4 : 1 molar ratio. The volatile fraction collected upon evaporation into a cold trap (—78°C), was brominated to give 11.1 g of Me_3SbBr_2.

Distillation of the reaction product afforded 9.0 g of 1-methylstibacyclopentane, b.p. 65°C/27 mm Hg. Yield 63%.

1-Methylstibacyclohexane. Reaction of 1,5-dibromopentane (7.5 mmol) with dimethylstibylsodium (15 mmol) in liquid ammonia (300 ml) resulted in the isolation of 3.7 g Me_3SbBr_2 (from the diethyl ether condensate collected in a cold trap) and of 20.8 g of a crude reaction product consisting of a mixture of 1-methylstibacyclohexane and 1,5-bis(dimethylstibino)pentane in a molar ratio of approximately 1 : 4. Thermolysis of this product at 240°C gave 9.7 g of 1-methylstibacyclohexane, b.p. 77—79°C/17 mm Hg in over 90% purity. Yield 62%.

1,1-Dichloro-1-methylstibacycloalkanes

A solution of 1-methylstibacyclopentane or 1-methylstibacyclohexane (5 mmol) in dichloromethane (20 ml) was cooled to —78°C and subsequently chlorinated by the dropwise addition of sulphuryl chloride (5 mmol) in dichloromethane (10 ml). Evaporation of the solvent afforded 1,1-dichloro-1-methylstibacyclopentane with m.p. 105—130°C (dec.) (recrystallization from carbon tetrachloride/hexane 2 : 1) and 1,1-dichloro-1-methylstibacyclohexane, m.p. 120—140°C (dec.) (recrystallization from hexane) as colourless crystalline solids. Yields 60—70%.

IR data: 1,1-dichloro-1-methylstibacyclopentane, ν_{max} 2960m, 2940m, 2920m, 2860w, 1440s, 1400s, 1312m, 1251w, 1238m, 1214w, 1182s, 1130s, 1080m, 1038s, 950m, 937w, 867(sh, br), 832s(br), 810(sh), 741s, 577s, 544m, 458s, 310m, 275vs.

IR data: 1,1-dichloro-1-methylstibacyclohexane, ν_{max} 3000w, 2960s, 2920(sh), 2860m, 1444s, 1400s, 1345m, 1335m, 1284m, 1238s, 1213w, 1187s, 1172m, 1053w, 944s, 924s, 877(sh), 848vs(br), 780(sh), 769s, 572m, 539m, 463m, 272vs.

1,1-Dimethylstibacycloalkane iodides

1-Methylstibacyclopentane or 1-methylstibacyclohexane (10 mmol) was added to an excess of freshly distilled, iodinefree, methyl iodide (5—10 ml). This solution was stirred for 2—3 h and meanwhile a colourless solid deposited which after recrystallization from a 2:1 carbon tetrachloride/ethanol mixture analysed for 1,1-dimethylstibacyclopentane iodide, m.p. 120°C (dec.) or 1,1-dimethylstibacyclohexane iodide, m.p. 220°C (dec.), respectively. Both compounds appeared to be soluble in water. Yields 60—70%.

IR data: 1,1-dimethylstibacyclopentane iodide, ν_{max} 2985m, 2920m, 2859m, 2850m, 1450w, 1395s, 1334w, 1320w, 1245m, 1222w, 1210w, 1181m, 1127m, 1079s, 1030w, 945w, 872vs, 847vs, 820vs, 710w, 572s, 550m, 460m, 310m.

IR data: 1,1-dimethylstibacyclohexane iodide, ν_{max} 2985w, 2945m, 2910m, 2850m, 1460(sh), 1450m, 1405m, 1350m, 1335m, 1289w, 1248m, 1226w, 1190s, 1170s, 1053m, 1005s, 927s, 878vs, 850vs, 816vs, 760m, 586m, 574s, 562s, 540m, 470m.

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