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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS
X*. PREPARATION OF SOME HETEROCYCLIC CHLOROSTIBINES

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SUMMARY

Some new heterocyclic chlorostibines have been prepared by treatment of the corresponding dimethyltin(IV) heterocycles with antimony trichloride.

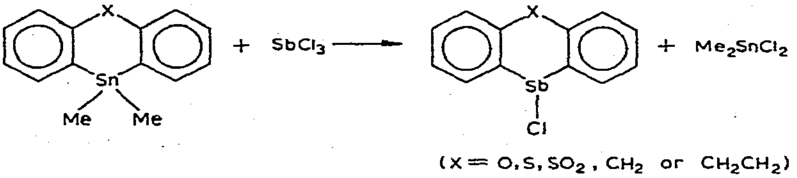
INTRODUCTION

Heterocyclic compounds containing a carbon–antimony–carbon linkage in the ring are rare[2]. Morgan and Davies were the first to prepare heterocyclic chlorostibines, *i.e.* 5-chlorodibenzostibole[3] and 5-chloro-5,10-dihydrodibenz[*b*, *e*]antimonin[4] by a rather tedious reaction procedure. Hellwinkel and Bach[5] have reported an improved synthesis of 5-chlorodibenzostibole involving the reaction of antimony trichloride with 2,2′-biphenylylenecadmium. Recently, the reaction of organotin heterocycles with metal or organometal halides has been found to be especially useful for the synthesis of organometallic heterocycles. This reaction which was first applied by Leusink *et al.*[6] and independently by Sheehan[7] for the synthesis of boron heterocycles, has been used by Jutzi[8] among others for the synthesis of 5-chloro-5,10-dihydrodibenz[*b*, *e*]antimonin, starting from 5,5-dimethyl-5,10-dihydrodibenzo-[*b*, *e*]stannin. Ashe[9] has obtained 1-chloro-1,4-dihydroantimonin from the reaction of 1,1-dibutyl-1,4-dihydrostannin with antimony trichloride.

In this paper we report the preparation of some new heterocyclic chlorostibines.

RESULTS AND DISCUSSION

Treatment of a series of heterocyclic dimethyltin(IV) compounds with antimony trichloride affords the corresponding heterocyclic chlorostibines in 50–70% yield:



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[*] For Part IX see ref. 1.

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TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SOME HETEROCYCLIC CHLOROSTIBINES

	X	*M.p.* (°C)	*Analyses found (calcd.) (%)*				*Mol. wt. found (calcd.)*
			C	*H*	*Cl*	*S*	
(I)	O	150–151	44.40	2.58	10.73		334
			(44.29)	(2.49)	(10.96)		(325.2)
(II)	S	130	42.14	2.54	10.49	9.33	349
			(42.21)	(2.36)	(10.38)	(9.39)	(341.2)
(III)	SO_2	199–200	38.70	2.24	9.23	8.51	381
			(38.59)	(2.16)	(9.49)	(8.59)	(373.2)
(IV)	CH_2	102[a]	48.35	3.27	11.40		333
			(48.28)	(3.12)	(10.96)		(323.2)
(V)	CH_2–CH_2	138	49.83	3.58	10.50		344
			(49.80)	(3.76)	(10.63)		(337.2)

[a] Ref. 4: m.p. 105°; Ref. 8: m.p. 89°.

The compounds were isolated as colourless crystalline solids, which were found to be monomeric in benzene. Analytical, melting point and molecular weight data are given in Table 1.

The PMR spectra of compounds (IV) and (V) in $CDCl_3$ solution show the methylene and ethylene proton resonances as a broadened singlet at δ 4.32 and δ 3.24 ppm, respectively. In CCl_4, CS_2 and benzene solution, the ethylene proton resonances in compound (V) appear as a well resolved AA'BB' type spectrum. This spectrum is the subject of a more detailed study.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Elemental analyses were carried out by Mr. W. J. Buis of this Institute. Molecular weights were determined by Miss M. E. Kurth on 2–5 % solutions in benzene using a Mechrolab dynamic vapour pressure osmometer.

10-*Chlorophenoxantimonin (I)*

Upon bringing together equimolar amounts of 10,10-dimethylphenoxastannin[10] (0.63 g) and antimony trichloride (0.45 g) in the absence of a solvent an instantaneous reaction occurred, and the two solids melted to a liquid, which after 10 min solidified to a colourless solid. Thereupon the reaction mixture was heated to 150° and during 1 h at 15 mmHg, dimethyltin dichloride sublimed out of the reaction vessel leaving a crude reaction product which upon recrystallization from carbon tetrachloride afforded 0.4 g of 10-chlorophenoxantimonin (I). Yield ≈ 60 %.

10-*Chlorophenothiantimonin (II)*; 10-*Chlorophenothiantimonin 5,5-dioxide (III)*; 5-*chloro*-5,10-*dihydrodibenz[b, e]antimonin (IV) and* 5-*chloro*-10,11-*dihydro*-5*H*-*dibenzo*-*[b, f]stibepin (V)*

Compounds (II)–(V) were prepared by the procedure described for (I). Equimolar amounts of 10,10-dimethylphenothiastannin[10], 10,10-dimethylphenothiastannin 5,5-dioxide[10,11], 5,5-dimethyl-5,10-dihydrodibenzo[*b*, *e*]stannin[8] or 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*, *f*]stannepin[12] and antimony trichloride are brought together. The reaction mixture is heated to 150° and during 1 h at 15 mmHg, dimethyltin dichloride sublimes out of the reaction vessel, leaving a crude reaction product which upon recrystallization from carbon tetrachloride affords either (II), (III), (IV) or (V) as colourless needles. Yield 50–70%.

ACKNOWLEDGEMENT

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