

## INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS III\*. ALKYLGROUP EXCHANGE IN THE PREPARATION OF MIXED METHYLETHYL PENTAALKYLANTIMONY COMPOUNDS

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### SUMMARY

The compounds series  $\text{Me}_n\text{SbEt}_{(5-n)}$  with  $n=0-5$  have been prepared. PMR spectroscopic measurements have shown that some experiments directed towards the preparation of  $\text{MeSbEt}_4$ ,  $\text{Me}_2\text{SbEt}_3$ ,  $\text{Me}_3\text{SbEt}_2$  and  $\text{Me}_4\text{SbEt}$  result in the formation of mixtures of these compounds because of alkyl group exchange between the initially formed pentaorganoantimony compound and the alkylating agent. Low-temperature PMR experiments on all the compounds  $\text{Me}_n\text{SbEt}_{(5-n)}$  with  $n=1-5$  have shown that rapid intramolecular exchanges occur even at  $-80^\circ$ .

The ready occurrence of exchange reactions during the preparation of mixed pentaorganoantimony compounds is further illustrated by the formation of a mixture of methylvinylantimony(V) compounds in the reaction of trivinyl dibromoantimony with methyllithium.

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### INTRODUCTION

The chemistry of pentavalent organoantimony compounds containing five antimony-carbon bonds has received increasing attention in recent years. Following the isolation by Wittig *et al.* of  $\text{Ph}_5\text{Sb}^{2,3}$  and  $\text{Me}_5\text{Sb}^4$ , Russian workers reported the preparation of a series of pentaalkenyl<sup>5</sup> and diethyltrialkenylantimony<sup>6</sup> compounds. In 1967 the preparation of  $\text{Et}_5\text{Sb}$  was reported by Takashi<sup>7</sup>. Very recently Hellwinkel and Bach<sup>8,9</sup> have extended the earlier work<sup>3</sup> on spirocyclic pentaorganoantimony compounds.

In this paper we describe a study of the preparation of the mixed methyl/ethyl pentaalkylantimony compounds,  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=1-4$ ).

### RESULTS AND DISCUSSION

In an attempt to prepare  $\text{Me}_2\text{SbEt}_3$  and  $\text{Me}_3\text{SbEt}_2$  the chlorides  $\text{Et}_3\text{SbCl}_2$ <sup>10</sup> and  $\text{Me}_3\text{SbCl}_2$ <sup>10</sup> were treated with  $\text{MeLi}$  and  $\text{Et}_2\text{Mg}$  respectively, in diethyl ether

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\* For Part II see ref. 1.

solution. However, both reactions resulted in the isolation of a slightly yellow liquid with a wide boiling range [ $\sim 50$ – $100^\circ$  (16 mm)]. PMR spectra of each of these products in benzene showed one broad ethyl proton resonance signal and a series of singlets due to methyl proton resonances, indicating the presence of a mixture of methyl/ethyl pentaalkylantimony compounds. Distillation of the  $\text{Me}_3\text{SbCl}_2/\text{Et}_2\text{Mg}$  reaction product using a spinning band distilling column afforded three essentially pure products, which were identified from their PMR spectra as  $\text{Me}_4\text{SbEt}$ ,  $\text{Me}_3\text{SbEt}_2$ , and  $\text{Me}_2\text{SbEt}_3$ , respectively.

Similarly, the reaction of  $\text{Et}_4\text{SbI}^{11}$  with  $\text{MeLi}$  in diethyl ether resulted in the isolation of a yellow liquid. The PMR spectrum of this product, recorded in benzene solution indicated that  $\text{MeSbEt}_4$  contaminated with  $\sim 20\%$  of  $\text{Me}_2\text{SbEt}_3$  and a trace of  $\text{Me}_3\text{SbEt}_2$  had been formed. Distillation of the reaction product *in vacuo* did not give an effective separation of  $\text{Me}_2\text{SbEt}_3$  and  $\text{MeSbEt}_4$ .

These studies complete the preparation of all compounds of the series  $\text{Me}_n\text{SbEt}_{(5-n)}$ . Their boiling points as well as PMR chemical shift data are given in Table 1.

TABLE 1  
BOILING POINTS AND PMR DATA OF  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=0-5$ )

Compound	B.p. [ $^\circ\text{C}$ (mm)]	$\delta$ [ $\text{CH}_3(\text{Sb})$ ] (ppm) <sup>a,b</sup>
$\text{SbEt}_5$	64(0.4) <sup>c</sup>	
$\text{MeSbEt}_4$	55(0.4) <sup>c</sup>	0.45
$\text{Me}_2\text{SbEt}_3$	42(0.03)	0.46
$\text{Me}_3\text{SbEt}_2$	71–74(16)	0.50
$\text{Me}_4\text{SbEt}$	53–54(16)	0.54
$\text{Me}_5\text{Sb}$	130–131(760) <sup>c</sup>	0.58 <sup>f</sup>

<sup>a</sup> Downfield from TMS at  $27^\circ$  in  $\text{C}_6\text{H}_6$ . <sup>b</sup>  $\delta$ [ $\text{CH}_3\text{CH}_2(\text{Sb})$ ] for all compounds: 1.1–1.2 ppm. <sup>c</sup> Ref. 7, no b.p. determined. <sup>d</sup> Contaminated with  $\sim 20\%$   $\text{Me}_2\text{SbEt}_3$ . <sup>e</sup> Ref. 4, b.p. 126–127 $^\circ$ . <sup>f</sup> Ref. 12,  $\delta$  0.7 ppm in  $\text{CS}_2$  solution.

The PMR spectra of  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=1-5$ ) recorded in toluene- $d_8$  solution display only one singlet due to methylproton resonances even at  $-80^\circ$ . The spectroscopic equivalence of all methyl groups which has also been observed for  $\text{Me}_5\text{Sb}$  in  $\text{CS}_2$  solution at  $-100^\circ$  (ref. 12), points to rapid intramolecular exchange of non-equivalent axial and equatorial methyl groups. (In the case of the compounds with  $n=1-3$  it is theoretically possible for all the methyl groups to be either equatorial or axial, but the absence of rapid pseudorotation for these compounds seems very unlikely.)

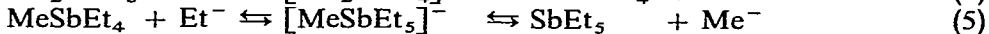
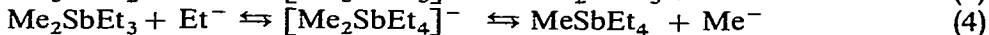
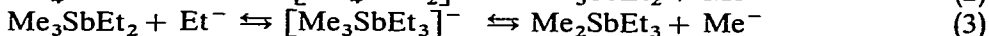
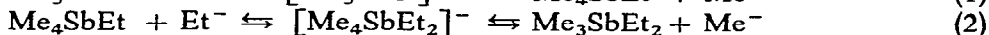
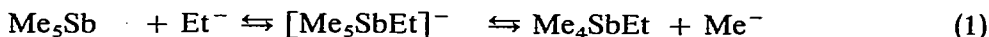
The differences in the chemical shifts of the methyl protons in  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=1-5$ ) make PMR spectroscopy an outstanding method for determining the composition of mixtures containing such compounds. *E.g.* integration of the PMR spectrum of the  $\text{Et}_3\text{SbCl}_2/2\text{MeLi}$  reaction product revealed the presence of  $\text{MeSbEt}_4$ ,  $\text{Me}_2\text{SbEt}_3$ ,  $\text{Me}_3\text{SbEt}_2$  and  $\text{Me}_4\text{SbEt}$  in a  $\sim 2/10/6/1$  molar ratio and a trace of  $\text{Me}_5\text{Sb}$ .

The formation of mixtures in these reactions is attributed to nucleophilic substitution of alkyl groups on antimony by alkyllithium or alkylmagnesium compounds. Whether a real ate-complex or a four-centre transition state is involved is not clear. However, both mechanisms are essentially similar in that the intermediate

contains a hexacoordinate antimony atom. This type of reactions has been extensively studied, especially the reactions of tri- and pentaarylphosphor, -arsenic, -antimony and -bismuth compounds with aryllithium (*cf.* refs. 13, 14 and references cited therein). Nucleophilic substitution by methyllithium has been observed in the attempted preparation of  $\text{Ph}_4\text{SbMe}$  in which a mixture of  $\text{Ph}_3\text{SbMe}_2$  and  $\text{Ph}_5\text{Sb}$  was formed<sup>4</sup>.

We have investigated the susceptibility of methyl/ethyl pentaalkylantimony compounds,  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=0-5$ ) towards nucleophilic attack by methyl- and ethyllithium or -magnesium compounds. Addition of  $\text{Me}_5\text{Sb}$  to a solution of methyllithium in diethyl ether results in a relatively slow methyl group exchange as demonstrated by PMR spectroscopy. At the magnet temperature ( $27^\circ$ ) the spectrum shows broadened methyl resonances for  $\text{Me}_5\text{Sb}$  and  $\text{MeLi}$  at  $\delta$  0.63 and  $-1.75$  respectively. The addition of  $\text{Me}_5\text{Sb}$  to a solution of  $\text{Et}_2\text{Mg}$  in diethyl ether results in the formation of a mixture of  $\text{Me}_n\text{SbEt}_{(5-n)}$  ( $n=2-5$ ), whereas a similar addition of  $\text{Et}_5\text{Sb}$  to  $\text{MeLi}$  results in the recovery of  $\text{Et}_5\text{Sb}$  contaminated with only a trace of  $\text{MeSbEt}_4$ . Likewise, experiments directed towards the preparation of  $\text{Me}_4\text{SbEt}$  gave mixtures of  $\text{Me}_5\text{Sb}$ ,  $\text{Me}_4\text{SbEt}$  and  $\text{Me}_3\text{SbEt}_2$ , whereas  $\text{MeSbEt}_4$  appears to be less sensitive towards nucleophilic attack by  $\text{MeLi}$ .

These results point to the occurrence of alkyl group exchanges due to a combination of equilibria 1-5. The exchange must be slow, with the rate gradually decreasing upon replacing methyl by the more electron-donating ethyl groups.



Our results suggest that the possibility of exchange reactions must always be taken into account in the preparation of pentaorganoantimony compounds by alkylation of organoantimony halides. Thus the PMR spectrum of the crude reaction product obtained from trivinyl dibromoantimony and methyllithium in diethyl ether shows the presence of  $\text{Me}_5\text{Sb}$ , but in addition three sets of methyl and vinyl proton resonances are present which can be tentatively assigned to  $\text{Me}_4\text{SbVi}$ ,  $\text{Me}_3\text{SbVi}_2$ ,  $\text{Me}_2\text{SbVi}_3$ . Therefore, we consider it likely that the earlier reported reactions of trialkenyldibromoantimony compounds with ethylmagnesium bromide resulted in the formation of a mixture of compounds  $\text{Et}_n\text{Sb}(\text{alkenyl})_{5-n}$  rather than of pure diethyl-trialkenylantimony<sup>6</sup>.

## EXPERIMENTAL PART

### General

All reactions were carried out in an atmosphere of dry nitrogen. The organoantimony compounds  $\text{Me}_4\text{SbI}^{15}$ ,  $\text{Me}_3\text{SbCl}_2^{10}$ ,  $\text{Et}_4\text{SbI}^{11}$ ,  $\text{Et}_3\text{SbCl}_2^{10}$ ,  $(\text{Vinyl})_3\text{SbBr}_2^5$ ,  $\text{Me}_5\text{Sb}^4$  and  $\text{Et}_5\text{Sb}^7$  were prepared as previously described.

The composition of the reaction mixtures was established by PMR spectroscopy. Spectra of 5-10% solutions in benzene, were run on precalibrated chart paper at either 250 or 100 cps sweepwidth, using a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal standard.

*Attempted preparation of trimethyldiethylantimony*

Trimethyldichloroantimony (19.0 g, 0.08 mole) was slowly added to a stirred solution of 0.1 mole of diethylmagnesium in diethyl ether (100 ml). After 3 h of refluxing, the solvent was removed by distillation at atmospheric pressure using a 20 cm Vigreux column. Pentane (100 ml) was added to the reaction residue and after filtration and subsequent evaporation of the pentane a slightly yellow oil was obtained. Distillation in a spinning band column gave 2.5 g of tetramethylethylantimony, b.p. 53–54° (16 mm) and 3.4 g of trimethyldiethylantimony, b.p. 71–74° (16 mm). The residue appeared to consist of 3.5 g of dimethyltriethylantimony, b.p. 42° (0.03), decomposing at temperatures above 100°. The purity of these compounds was established by PMR spectroscopy. Yields based on antimony 15%, 19%, and 18% respectively.

*Attempted preparation of dimethyltriethylantimony*

By the procedure described above, methylolithium (34 mmoles) in diethyl ether (60 ml) was treated with 5.0 g (17 mmoles) of triethyldichloroantimony in diethyl ether (40 ml). The slightly yellow crude reaction product (2.2 g) appeared to consist of a mixture of  $\text{MeSbEt}_4$ ,  $\text{Me}_2\text{SbEt}_3$ ,  $\text{Me}_3\text{SbEt}_2$  and  $\text{Me}_4\text{SbEt}$  (molar ratio 2/10/6/1).

*Preparation of methyltetraethylantimony*

Methylolithium (14.6 mmoles) in diethyl ether (20 ml) was added dropwise to a suspension of 5.3 g (14.5 mmoles) of tetraethyliodoantimony in diethyl ether (20 ml). After stirring for 30 min the solvent was evaporated and 2.05 g of a yellow liquid [b.p. 55°/(0.4 mm)] was distilled from the reaction residue. PMR spectroscopy revealed that methyltetraethylantimony contaminated with ~20% dimethyltriethylantimony had been formed. (Yield based on antimony  $\approx$  60%.)

*Attempted preparation of tetramethylethylantimony*

Reaction of tetramethyliodoantimony with ethylmagnesiumbromide in diethyl ether in a 1/1 molar ratio, resulted in the formation of a mixture of  $\text{Me}_5\text{Sb}$ ,  $\text{Me}_4\text{SbEt}$  and  $\text{Me}_3\text{SbEt}_2$  (molar ratio 4/6/3) and a trace of  $\text{Me}_2\text{SbEt}_3$ .

*Attempted preparation of dimethyltrivinylantimony*

Methylolithium (20 mmoles) in diethyl ether (20 ml) was added dropwise to 3.6 g (10 mmoles) of trivinyl dibromoantimony in ether (20 ml). After stirring for 30 min the solvent was evaporated at  $-20^\circ$  and pentane was added to the reaction residue. The precipitate of magnesium salts was removed by filtration. The filtrate afforded after evaporation of the pentane at  $-20^\circ$ , 1.1 g of a pale yellow oil, which at a bath temperature of  $100^\circ$  was distilled (0.1 mm) into a  $-78^\circ$  trap. The PMR spectrum of this reaction product in benzene- $d_6$  indicated the presence of  $\text{Me}_4\text{SbCH}=\text{CH}_2$ ,  $\text{Me}_3\text{Sb}(\text{CH}=\text{CH}_2)_2$  and  $\text{Me}_2\text{Sb}(\text{CH}=\text{CH}_2)_3$ . [ $\delta$   $\text{CH}_3(\text{Sb})$  at 0.62, 0.64 and 0.68 ppm respectively]. A singlet at 0.58 ppm revealed the additional presence of a considerable amount of  $\text{Me}_5\text{Sb}$ .

*Warning*

In one experiment a serious detonation which completely destroyed the apparatus occurred during distillation of a 25 g sample of  $\text{Me}_5\text{Sb}$  at atmospheric pressure

(temperature of the heating bath  $\approx 160^\circ$ ). It is thus advisable to distil  $\text{Me}_5\text{Sb}$  and other pentaalkylantimony compounds at reduced pressure.

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