

### Preliminary communication

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## THE PREPARATION OF PHENYL SUBSTITUTED ANTIMONY(III) AND ANTIMONY(V) CHLORIDES AND BROMIDES

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### Summary

In the absence of solvent, the redistribution of 2/1 and 1/2 molar mixtures of  $\text{Ph}_3\text{Sb}$  and  $\text{SbX}_3$ , where  $\text{X} = \text{Cl}$  or  $\text{Br}$ , is rapid giving quantitative yields of  $\text{Ph}_2\text{SbX}$  and  $\text{PhSbX}_2$ , respectively.

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Of the organo-substituted antimony(III) halides, those containing phenyl substituents, i.e.  $\text{Ph}_n\text{SbX}_{3-n}$  where  $\text{X} = \text{Cl}$  or  $\text{Br}$  and  $n = 1$  or  $2$ , can be handled with only minor precautions against oxidation. In contrast, the corresponding alkyl-substituted compounds react rapidly with oxygen in the atmosphere. The phenyl compounds are thus useful intermediates, but their preparation, summarised by Doak and Freedman [1], is not easy, nor do the reactions in general proceed in high yield.

Recently, by successive bromination and thermolysis reactions, triphenylantimony has been converted into both  $\text{Ph}_2\text{SbBr}$  and  $\text{PhSbBr}_2$ , but the procedure is time consuming and the yields are not good [2]. An attractive alternative is the redistribution of  $\text{Ph}_3\text{Sb}$  with either  $\text{SbCl}_3$  or  $\text{SbBr}_3$  but these reactions are reported to give mixtures which can only be separated with difficulty [1]. The four phenylantimony(III) halides are, however, claimed to result after long periods of reflux from mixtures of  $\text{Ph}_3\text{Sb}$  and  $\text{SbX}_3$  in dichloromethane [3]; in our hands this method has been non-reproducible. In view of our interests in this area, we have reinvestigated the  $\text{Ph}_3\text{Sb}/\text{SbCl}_3$  and  $\text{Ph}_3\text{Sb}/\text{SbBr}_3$  redistribution reactions.

In the absence of solvent, a 2/1 molar mixture of  $\text{Ph}_3\text{Sb}$  and  $\text{SbCl}_3$  rapidly liquefies and at  $25^\circ\text{C}$ , redistribution is complete in ca. 3 h. The resulting  $\text{Ph}_2\text{SbCl}$  is a pale-yellow viscous oil, which usually solidifies on standing. It is possible to crystallise the product from either dichloromethane or warm glacial acetic acid but the initial redistribution product is sufficiently pure for further reactions.

For example, in dichloromethane solution, it can be chlorinated to  $\text{Ph}_2\text{SbCl}_3$  or brominated to  $\text{Ph}_2\text{SbClBr}_2$  [4]. A 1/2 molar mixture of  $\text{Ph}_3\text{Sb}$  and  $\text{SbCl}_3$  reorganises similarly and solid  $\text{PhSbCl}_2$  can be isolated in high yield from the resulting viscous liquid.

Antimony tribromide redistributions appear to be faster but because of the higher melting point of  $\text{SbBr}_3$ , initial reaction mixtures were warmed to 35–40°C. On completion of reorganisation, the product usually solidified and, as in the chloride systems, crystalline samples of  $\text{Ph}_2\text{SbBr}$  and  $\text{PhSbBr}_2$  could be obtained from dichloromethane or acetic acid solutions. Unrecrystallised products are however sufficiently pure for further reactions, and  $\text{Ph}_2\text{SbBr}_3$  can be obtained in high yield by directly brominating the product from reorganisation of a 2/1 mixture of  $\text{Ph}_3\text{Sb}$  and  $\text{SbBr}_3$ .

We have carried out a similar series of reorganisation reactions between  $\text{SbCl}_3$  or  $\text{SbBr}_3$  and a range of substituted triphenylstibines, including the 4-Me, 4-F, 4-Br and 3-Cl derivatives. The reactions leading to  $(\text{YC}_6\text{H}_4)_2\text{SbX}$  and  $(\text{YC}_6\text{H}_4)\text{SbX}_2$  are all rapid, but to ensure completion they were allowed to proceed overnight at ca. 35°C. All products gave satisfactory analyses and infrared spectra.

This observation of fast and complete reorganisation provides the basis for the rapid synthesis, from readily available starting materials, of large quantities of pure  $\text{Ph}_2\text{SbCl}$ ,  $\text{PhSbCl}_2$ ,  $\text{Ph}_2\text{SbCl}_3$  and  $\text{PhSbCl}_4$ , together with bromine analogues of the first three. The speed of reorganisation is surprising in view of data on the related arsenic chloride system [5], for which the reactions require both high temperatures and long times, and the product is a mixture of all four possible compounds.

## References

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