

Preliminary communication

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 Ph_3Sb and SbX_3 , where $\text{X} = \text{Cl}$ or Br , is rapid giving quantitative yields of Ph_2SbX and PhSbX_2 , respectively.

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 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, triphenyl-antimony has been converted into both Ph_2SbBr and PhSbBr_2 , but the procedure is time consuming and the yields are not good [2]. An attractive alternative is the redistribution of Ph_3Sb with either SbCl_3 or 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 Ph_3Sb and 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 Ph_3Sb and SbCl_3 rapidly liquefies and at 25°C , redistribution is complete in ca. 3 h. The resulting Ph_2SbCl 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 Ph_2SbCl_3 or brominated to $\text{Ph}_2\text{SbClBr}_2$ [4]. A 1/2 molar mixture of Ph_3Sb and SbCl_3 reorganises similarly and solid 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 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 Ph_2SbBr and PhSbBr_2 could be obtained from dichloromethane or acetic acid solutions. Unrecrystallised products are however sufficiently pure for further reactions, and Ph_2SbBr_3 can be obtained in high yield by directly brominating the product from reorganisation of a 2/1 mixture of Ph_3Sb and SbBr_3 .

We have carried out a similar series of reorganisation reactions between SbCl_3 or 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 Ph_2SbCl , PhSbCl_2 , Ph_2SbCl_3 and 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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