

## Preliminary communication

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### The formation of bismuth–carbon bonds by sulphur dioxide elimination

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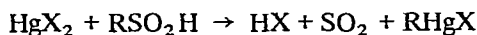
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Sulphinato complexes of several transition metals, *viz.* iridium<sup>1,2</sup>, rhodium<sup>2</sup>, platinum<sup>3</sup>, iron<sup>4</sup>, and molybdenum<sup>5</sup>, undergo thermal decomposition with the formation of sulphur dioxide and the corresponding organometallics.

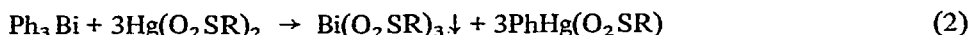


Amongst the main group elements, the reaction has been used for the preparation of diarylmercurials<sup>6,7</sup>, and the related reaction<sup>8</sup>,

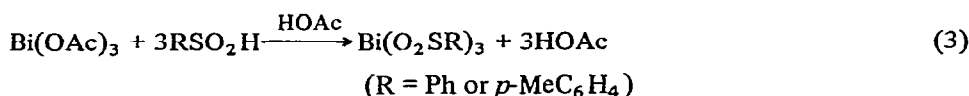


which may involve an intermediate sulphinatomercury(II) complex<sup>7</sup>, is well-known for the preparation of mono-organomercurials. However, extensions to other main group elements appear limited to a single organoarsenic compound<sup>9</sup>. All sulphinato complexes known to undergo reaction (1) are *S*-sulphinates<sup>1-6</sup>, with the exception of a few arylmercuric arenesulphinates, which have unidentate *O*-sulphinato coordination<sup>7</sup>. We now report that some arenesulphinatobismuth(III) compounds with *O*-sulphinato coordination give tri-arylbismuth compounds and sulphur dioxide on thermal decomposition.

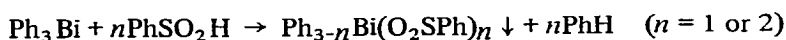
Bismuth triarenesulphinates,  $Bi(O_2SR)_3$  ( $R = Ph$  or  $p\text{-MeC}_6\text{H}_4$ ), were initially prepared by the reaction,



in chloroform ( $R = Ph$ ) or methanol ( $R = p\text{-MeC}_6\text{H}_4$ ) at room temperature, but the *p*-toluenesulphinato could not be obtained analytically pure, and it was difficult to obtain products free of the insoluble mercuric arenesulphinates. Subsequently, reaction (3) was

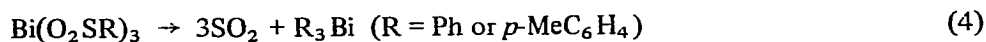


used and analytically pure products (C, H and S) were obtained; Although the infrared spectrum of  $\text{Bi}(\text{O}_2\text{SPh})_3$  prepared by reaction (2) was similar to that of the product from (3), X-ray powder photographs showed that two different crystalline forms were obtained. However,  $\text{Bi}(\text{O}_2\text{S-}i>p\text{-MeC}_6\text{H}_4)_3$  was obtained in the same form by either route. Phenylbismuth dibenzenesulphinate and diphenylbismuth benzenesulphinate were obtained by reaction of equimolar amounts of triphenylbismuth and benzenesulphinic acid in boiling benzene/chloroform (1/1, v/v), and in ether at room temperature respectively:



The former was obtained analytically pure, but the X-ray powder photograph and analyses of the latter showed a little dibenzenesulphinate to be present. The infrared spectrum of each arenesulphinatobismuth(III) complex showed very broad absorption attributable to  $\nu(\text{SO}_2)$  at  $970\text{--}890\text{ cm}^{-1}$ . This is indicative of *O*-sulphinate coordination and suggests the presence of bidentate or bridging bidentate *O*-sulphinate groups<sup>7</sup>. The latter arrangement would give a polymeric structure, which is consistent with the very low solubility of the complexes.

On heating the bismuth triarenesulphinates obtained by either route ( $200^\circ$ ; 5 h),  $\text{PhBi}(\text{O}_2\text{SPh})_2$  ( $190^\circ$ ; 5 h), or  $\text{Ph}_2\text{Bi}(\text{O}_2\text{SPh})$  ( $216^\circ$ ; 4 h), under vacuum ( $10^{-2}\text{--}10^{-3}$  mm), sulphur dioxide was evolved together with a little benzene or toluene, and the corresponding triaryl bismuth compound sublimed from the reaction mixture in 68–85% yield:



The products were identified by their infrared spectra, which were identical with those of authentic samples prepared by the Grignard method<sup>10</sup>, and melting points. The arenesulphinatobismuth(III) complexes are susceptible to oxidation on heating. Thus, with a slight air-leak during the decomposition of  $\text{Bi}(\text{O}_2\text{SPh})_3$ , diphenyl sulphone was obtained. The possibility of obtaining other organobismuth compounds via reactions (3) and (4) is being investigated.

This study suggests that the ability of main group element sulphinate complexes to form metal–carbon bonds by sulphur dioxide elimination may be more widespread than has been demonstrated so far.

#### ACKNOWLEDGEMENTS

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