

LXXXIX.—*Arsenic Di-iodide.*

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SOME twenty-six years ago E. Bamberger and J. Philipp discovered that arsenic and iodine, besides uniting to form the ordinary triiodide, can also combine in the proportion of one atom of arsenic to two atoms of iodine (*Ber.*, 1881, **14**, 2643). Having established the composition and studied the solubilities and some reactions, they assigned to this substance the simplest possible formula,  $\text{AsI}_2$ , and stated their intention of applying it to the synthesis of organo-arsenic compounds. No further work has appeared, and the substance has not apparently been examined by other chemists.

The present authors decided on a determination of the molecular weight with the intention, should the substance have the double formula  $\text{As}_2\text{I}_4$ , to use it, if possible, in conjunction with Grignard reagents in the synthesis of aromatic analogues of cacodyl. The formula  $\text{As}_2\text{I}_4$  proved correct, but the substance is valueless as a synthetic agent, arsenic being liberated, and organic derivatives of arsine being produced.

*Preparation and Formula.*

The directions given by Bamberger and Philipp to heat arsenic with twice its weight of iodine in sealed tubes to  $230^\circ$  were usually followed, although we have obtained more certain results in preparing a product free from tri-iodide by employing a temperature of  $260^\circ$ . Recrystallisation from carbon disulphide was effected in an atmosphere of dry carbon dioxide, and the solution was driven from one vessel to another by a stream of the same gas. These conditions are essential, as the substance is very sensitive to moisture and

oxygen, and the specimen used for analysis was dried in a current of carbon dioxide, the tubes in which it was preserved being also filled with the gas. In carrying out the analysis the substance was transferred from the weighing tube into a dilute solution of sodium carbonate, the free arsenic which separated was filtered off, the solution acidified with hydrochloric acid, and the remaining arsenic precipitated as sulphide. Iodine was estimated in a separate portion, the solution having been acidified with sulphuric acid:

0·8044 gave 0·0347 As. As = 4·3.  
and 0·2385 As<sub>2</sub>S<sub>3</sub>. As = 18·2. } Total 22·5.

0·5704 gave 0·8099 AgI. I = 76·8.

As<sub>2</sub>I<sub>4</sub> requires As = 22·8; I = 77·2 per cent.

The molecular weight was determined by the Landsberger boiling point method in carbon disulphide ( $\Delta t = 23\cdot7$ ) solution:

0·5256 raised the boiling point of 13·83 CS<sub>2</sub> by 0·15°. M.W. = 601.

0·5768 " " 19·07 CS<sub>2</sub> by 0·125°. M.W. = 574.

As<sub>2</sub>I<sub>4</sub> requires M.W. = 658 (AsI<sub>2</sub> = 329 and AsI<sub>3</sub> 456).

The results, although not good, owing to the sensitiveness of the substance, leave no doubt as to the molecular weight.

#### Reactions.

Bamberger and Philipp already noted that when the substance was decomposed by water, the amount of arsenic liberated was less than that required by the equation



The results obtained in our analysis of the compound confirm this observation.

Cold concentrated sulphuric acid is apparently without action, but some iodine is eliminated when the acid is raised to near its boiling point. Cold fuming nitric acid has apparently little immediate action, but, on heating, oxides of nitrogen and iodine vapour are given off, whilst eventually arsenic and iodic acids are produced.

Pyridine decomposes the substance immediately, arsenic is liberated, and arsenic tri-iodide passes into solution. The substance dissolves in boiling acetic anhydride; the material which separates on cooling is mostly yellow, but evidently not homogeneous. It is very probable that the greater portion of the product is a derivative of arsenic tri-iodide, since the solution of this substance in boiling acetic anhydride deposits beautiful orange crystals on cooling.

On adding one molecular proportion of finely-powdered arsenic di-iodide to an ethereal solution of four molecules of magnesium

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phenyl bromide, an oily substance, insoluble or sparingly soluble in ether, separated; as this was qualitatively shown to contain arsenic, halogen, and magnesium, it was probably an additive product. On decomposition with ice and dilute sulphuric acid, the ether dissolved an organic arsenic compound, which was deposited at first as an oil, on evaporating the ether. The oil having solidified, the product was crystallised from dilute alcohol, and colourless needles melting at  $60^{\circ}$  were obtained. The suspicion that the substance was merely triphenylarsine was confirmed by a mixed melting point with a specimen prepared by P. Pfeiffer and H. Pietsch's method (*Ber.*, 1904, **37**, 4621) from arsenic trichloride and magnesium phenyl bromide, the purity of which had been controlled by analysis:

0.2996 gave 0.1193  $\text{As}_2\text{S}_3$ . As = 24.3.

$\text{As}(\text{C}_6\text{H}_5)_3$  requires As = 24.5 per cent.

It is evident that arsenic di-iodide can be of little use as a synthetic agent, the ease with which it furnishes the tri-iodide or its derivatives being prohibitive.

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