# XXVIII.—*Organo-derivatives of Bismuth (Supplementary Note).*

By FREDERICK CHALLENGER.

SINCE the publication of Parts I. and II. of this research (T., 1914, **105**, 2210; 1915, **107**, 16) further results have been obtained, the publication of which, in ordinary circumstances, would have been postponed. Owing to the pressure of other work, this research is temporarily suspended, but will be resumed at a later date. The recent papers of Grüttner and Wiernik (*Ber.*, 1915, **48**, 1473, 1749, 1759) also render desirable the publication of this note.

Contrary to the statement of Marquardt (*Ber.*, 1887, **20**, 1516), bismuth trichloride is readily soluble in ether, and can be employed in preparing tertiary aromatic bismuthines. *Tri*-p-*tolylbismuthine* (Michaelis and Marquardt, *Annalen*, 1889, **251**, 331) is obtained in a 60 per cent. yield from *p*-bromotoluene, magnesium and bismuth bromide in ether. *Di*-p-*tolylchlorobismuthine* (m. p. 181·5°) is obtained by mixing ethereal solutions of bismuth trichloride (1 mol.) and tri-*p*-tolylbismuthine (2 mols.). The reaction of this substance and that of the corresponding bromo-derivative with magnesium phenyl bromide has been investigated. Triphenylbismuthine (2 mols.) and bismuth bromide (1 mol.) in ether give rise to both diphenylbromobismuthine and phenyldibromobismuthine, the latter only in small quantity (compare, however, Michaelis and Marquardt, *ibid.*, 328).

This result is similar to those obtained by Grüttner and Wiernik (*ibid.*, 1749) with the corresponding stibine derivatives. When heated with sodium and toluene, phenyldibromobismuthine yields triphenylbismuthine, metallic bismuth and sodium bromide.

The instability noticed in connexion with diphenylethylbismuthine (T., 1914, **105**, 2216) seems to be characteristic of mixed aromatic aliphatic bismuthines, at least in the presence of air, since when diphenylbromobismuthine and magnesium *iso*butyl bromide interact the principal product is triphenylbismuthine.

Grüttner (*Ber.*, 1914, **47**, 3257) has prepared tri*cyclo*hexylbismuthine, and states that it is decomposed by air. This was also observed by the author in 1913. From magnesium *cyclo*hexyl bromide and bismuth bromide in the presence of air no organo-derivative can be isolated on treating with water, bismuth oxybromide being the main product. Magnesium *iso*butyl bromide behaves similarly.

Dr. C. K. Tinkler and the author have observed that triphenylbismuthine gives colorations with certain nitro-derivatives.

### *Attempts to Prepare Acidic and Basic Derivatives of Quinquevalent Bismuth.*

When triphenylbismuthine is dissolved in cold concentrated sulphuric acid, or when its chloroform solution is treated with chlorosulphonic acid, the phenyl groups are eliminated. The quinquevalent derivatives are much more stable under these conditions. With cold sulphuric acid, the dichloride evolves hydrogen chloride and forms a substance,* probably $Ph_3BiSO_4$, which reacts with ammonium hydroxide, giving a solution identical with that similarly obtained from the dichloride. With picric, tartaric or acetic acid, the solution of the dihydroxide or oxide gives crystalline salts; the acetate melts at 148—150°. The action of cold concentrated hydrochloric acid is less simple than might be expected, the dichloride not being directly regenerated.

In dilute chloroform solution, triphenylbismuthine dichloride reacts only slowly with chlorosulphonic acid, but with excess of this reagent hydrogen chloride is evolved, and yellow crystals containing bismuth, sulphur and chlorine are deposited. These decompose on heating, giving phenol and sulphur dioxide and, under other conditions, chlorobenzene.

Triphenylbismuthine and sulphuryl chloride in light petroleum give sulphur dioxide and triphenylbismuthine dichloride. Sulphur monochloride and thionyl chloride also produce the same substance, accompanied in the latter case by sulphur dioxide, organic sulphur compounds and probably diphenylchlorobismuthine.

Bismuth bromide reacts easily with a solution of the magnesium derivative of ethyl bromoacetate, giving a yellowish-white product insoluble in ether.

My thanks are due to Mr. N. A. Nicholls, B.Sc., for assistance in the early stages of this work, and to the Research Fund of the Chemical Society for a grant which has defrayed the expenses.

THE UNIVERSITY, BIRMINGHAM. [*Received, February 28th,* 1916.]

---

* As in the case of triphenylbismuthine dihaloids, ammonium sulphide converts this product into triphenylbismuthine.