LXXXII.—*Organo-derivatives of Bismuth. Part III. The Preparation of Derivatives of Quinquevalent Bismuth.*

By Frederick Challenger and Archibald Edwin Goddard.

With the object of preparing salts of the unknown compounds Ph_3BiO or $Ph_3Bi(OH)_2$, the action of aqueous potassium hydroxide and moist silver oxide on triphenylbismuthine dichloride has been investigated under various conditions. In all cases, triphenylbismuthine is regenerated. The same result is obtained if the dibromide is treated with alcoholic sodium hydroxide. Triphenylstibine dibromide when similarly treated yields triphenylstibine dihydroxide (Michaelis and Reese, *Annalen*, 1886, **233**, 50). If the solution obtained from triphenylbismuthine dichloride and aqueous alkali is treated with acetic, tartaric, or a similar organic acid, mixtures are obtained which contain dichloride and basic chloride, and very little, if any, acetate or tartrate. Better results were obtained with the carbonate described, but not analysed, by Michaelis and Marquardt (*Annalen*, 1889, **251**, 330). This compound with acetic acid gives *triphenylbismuthine acetate*, $Ph_3Bi(OAc)_2$. The corresponding camphorsulphonate and lactate appear to be formed, and are now under investigation. With hydriodic acid, the carbonate reacts at the ordinary temperature, with the formation of a red compound, which is probably the one already described by Challenger and Allpress (T., 1915, **107**, 21). Similar results were obtained by triturating the carbonate with water and iodine. This is further evidence of the instability of triphenylbismuthine di-iodide, which cannot be prepared from triphenylbismuthine and iodine. Triphenylbismuthine dichloride dissolves in cold concentrated sulphuric acid, giving *triphenylbismuthine sulphate*, which does not melt at 284°. Very little bismuth sulphate is produced in this reaction if rise of temperature is avoided, but the amount increases if the solution in sulphuric acid is left for several hours before pouring into water. Solution in ammonia and treatment with hydrochloric acid converts the sulphate into the *basic chloride*, which, on warming with concentrated hydrochloric acid, gives the dichloride. The basic chloride, $Ph_3Bi(OH)Cl$ (m. p. 160—161°), is formed in various reactions, for example, (*a*) by the action of moist ammonia gas on triphenylbismuthine dichloride in chloroform solution (a method by which the *basic bromide*, m. p. 150—151°, has also been prepared);

(*b*) from sodium and the dichloride in ether containing a trace of moisture; (*c*) by the action of aqueous ammonia on the dichloride. Up to the present, however, this compound has not been obtained from the dichloride by means of water or aqueous alcohol, according to which method Stilp * (*Diss.*, Rostock, 1910) prepared the basic bromides of tri-*p*-tolyl- and trixylyl-bismuthines.

When warmed with concentrated hydrochloric acid, it gives the dichloride. The action of acetic acid on the basic chloride gives rise to the dichloride and a compound, which is probably the acetate, in which case the reaction may be represented thus:

$$2(C_6H_5)_3Bi(OH)Cl = (C_6H_5)_3BiCl_2 + (C_6H_5)_3Bi(OH)_2,$$
$$(C_6H_5)_3Bi(OH)_2 + 2CH_3\cdot CO_2H = (C_6H_5)_3Bi(O\cdot CO\cdot CH_3)_2 + 2H_2O.$$

This is analogous to the action of acetic acid on the basic bromide of diphenyltelluride, $Ph_2Te(OH)Br$, which gives rise to the dibromide, and probably the diacetate (Lederer, *Annalen*, 1912, **391**, 335).

With magnesium methyl iodide, the basic chloride does not give triphenylmethylbismuthonium hydroxide, $Ph_3Bi(OH)CH_3$, but the dichloride and triphenylbismuthine, which points to the instability of the hydroxide. Triphenylmethylarsonium hydroxide, however, is a crystalline compound melting at 125—126°, prepared by the action of moist silver oxide on the iodide (Michaelis, *Annalen*, 1902, **321**, 166).

The action of copper bronze on triphenylbismuthine dichloride leads to the production of diphenylchlorobismuthine, probably owing to the prolonged action of heat, and not to contact with the copper. No compound of the type $Ph_3Bi\colon BiPh_3$ was isolated.

In this connexion, it is worthy of note that triphenyl- and tri-*p*-tolyl-bismuthines and arsines, and also tri-*a*-naphthylbismuthine and triphenylbismuthine dichloride, have the normal molecular weight in benzene solution. Complexes of the type $R_3M\colon MR_3$, which might possibly arise owing to the unsaturated nature of these organo-metallic or metalloidal compounds, do not appear to be formed.

The abnormal behaviour of the halogen derivatives of the bismuthines towards the Grignard reagent has been referred to in previous papers.† It is further exemplified by the fact that triphenylbismuthine is the principal product obtained when

---

* The results described in this dissertation do not appear to have been published elsewhere.

† Better results may possibly be obtained by modifying the conditions of reaction with the Grignard reagent, or by the use of organo-zinc or mercury derivatives. Experiments in this direction are in progress.

magnesium *p*-tolyl bromide reacts with triphenylbismuthine dichloride and diphenylbromobismuthine, and in the reaction between triphenylbismuthine dichloride and magnesium α-naphthyl bromide. Lederer (*Ber.*, 1911, **44**, 2287) has shown that triphenyltelluronium chloride yields diphenyltelluride and diphenyl when treated with magnesium phenyl bromide, whilst di-*o*-anisyltelluride dibromide is reduced to di-*o*-anisyltelluride on treatment with magnesium methyl iodide [(*Ber.*, 1920, **53**, 713). Compare also the remarkable instability of the mixed mercury diaryls (Hilpert and Grüttner, *Ber.*, 1915, **48**, 406)].

Iodine trichloride reacts with triphenylbismuthine, producing the dichloride and iodobenzene.

Tri-α-naphthylbismuthine dichloride was prepared by the action of chlorine on the bismuthine; Stilp (*loc. cit.*) was unable to obtain this compound. Like triphenylbismuthine dichloride, it is more stable than the corresponding dibromide.

The action of moist silver oxide in acetone is similar to that observed with triphenylbismuthine dichloride, and gives rise to tri-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine has been previously described (T., 1914, **105**, 2216). Since attempts to obtain other mixed bismuthines have failed, the reaction between diphenylbromobismuthine and magnesium α-naphthyl bromide has been further studied. Whilst the mixed bismuthine has again been obtained and diphenyl-α-naphthylbismuthine dibromide analysed, the main product of the reaction consists of triphenylbismuthine.

Michaelis and Marquardt (*Annalen*, 1889, **251**, 320) observed that excess of ammonium sulphide decomposed triphenylbismuthine dibromide according to the equations:

$$(1)\ (C_6H_5)_3BiBr_2 + (NH_4)_2S = (C_6H_5)_3Bi + 2NH_4Br + S;\ ^*$$
$$(2)\ 2(C_6H_5)_3Bi + 3H_2S = 6C_6H_6 + Bi_2S_3.$$

We have found that this reaction can be made the basis for the estimation of bismuth in substances of an analogous composition which, unlike the tertiary bismuthines, do not yield bismuth chloride with hydrochloric acid.

Triphenylstibine dihaloids do not react thus with hydrogen sulphide in alcoholic ammonia, but yield triphenylstibine sulphide. The bismuthine is therefore less stable than the corresponding stibine.

---

* In the absence of excess of hydrogen sulphide the bismuthine only is obtained.

EXPERIMENTAL.

Action of Moist Silver Oxide on Triphenylbismuthine Dichloride.

(*a*) *In the Cold.*—Two grams of triphenylbismuthine dichloride, about 30 c.c. of acetone, 0·93 gram of silver oxide, and 1 c.c. of water were shaken on a machine for sixteen hours, when 1·1 grams of triphenylbismuthine (m. p. 78°) were obtained from the acetone solution. The residue consisted of silver oxide, silver chloride, and a trace of bismuthine.

(*b*) *At about* 60°.—Five grams of triphenylbismuthine dichloride and 2·3 grams of silver oxide were heated in moist acetone on a water-bath for one hour. After removing the silver chloride and unchanged silver oxide, 3·2 grams of triphenylbismuthine were obtained.

Action of Alcoholic Potassium Hydroxide on Triphenylbismuthine Dichloride.

(*a*) *In the Cold.*—Three grams of triphenylbismuthine dichloride and 0·7 gram of potassium hydroxide in absolute alcohol were shaken for five and a-half hours.

Two kinds of crystals separated on keeping, (*a*) stout needles, and (*b*) small, fine needles mixed with a heavy powder, which were extracted with absolute alcohol, leaving potassium chloride. The alcoholic extract yielded triphenylbismuthine (m. p. 78—80°). The crystals (*a*) were found to be triphenylbismuthine dichloride.

The main bulk of the mixture was evaporated, when more triphenylbismuthine was obtained.

(*b*) *At the Boiling Point.*—Five grams of triphenylbismuthine dichloride in absolute alcohol were boiled for three hours with 1·2 grams of potassium hydroxide, and the solution filtered. From the filtrate, three deposits, (*a*), (*b*), and (*c*), were obtained. The crystals (*a*) melted at 138°, contained halogen, and most probably consisted of a mixture of triphenylbismuthine, triphenylbismuthine dichloride, and the basic chloride (see p. 768).

Deposit (*b*) was shaken with cold light petroleum; the extract deposited triphenylbismuthine, the insoluble portion yielding unchanged dichloride (m. p. 120—121°).

Deposit (*c*) was heated with water, the soluble portion yielding triphenylbismuthine (m. p. 78°); the insoluble residue consisted chiefly of potassium chloride.

Action of Aqueous Potassium Hydroxide on Triphenylbismuthine Dichloride.

Three grams of triphenylbismuthine dichloride, 0·7 gram of potassium hydroxide, and 30 c.c. of water were shaken in the cold for five and a-half hours, and the mixture was filtered. The residue was triphenylbismuthine dichloride. The filtrate was evaporated to dryness and treated with absolute alcohol, which removed potassium chloride. The solution was evaporated, and the residue, after crystallisation from light petroleum, melted at 77—78°, and did not depress the melting point of triphenylbismuthine.

Attempts to Isolate Triphenylbismuthine Dihydroxide or Triphenylbismuthine Oxide.

(1) Triphenylbismuthine dichloride was treated with aqueous potassium hydroxide in the cold as before, and the solution extracted three times with ether. The extract became cloudy on keeping, possibly owing to the absorption of atmospheric carbon dioxide. A solid finally separated which, on crystallisation from petroleum, melted at 74°. This was shown to be impure triphenylbismuthine. The aqueous portion also became cloudy and deposited triphenylbismuthine, which melted at 78—79° after crystallisation from alcohol. No compound corresponding with a dihydroxide or oxide was isolated.

(2) Triphenylbismuthine dibromide was dissolved in alcoholic sodium hydroxide, and the precipitate of sodium bromide filtered off. No further deposit was noticed after the solution had remained for a week. Part of the alcohol was therefore evaporated, when long needles of triphenylbismuthine were deposited.

Preparation of Michaelis's so-called Basic Carbonate.

Triphenylbismuthine dibromide (m. p. 122—124°) was suspended in alcohol and treated with excess of solid sodium hydroxide. Carbon dioxide was passed through the solution, the voluminous, white precipitate collected, and the operation repeated until no further deposit was formed. The solid was washed with much cold water, and appeared to be free from halogen. In order to free it from adhering alkali carbonate, it was boiled with water, but even after continued boiling it gave the flame reaction for sodium. This trace of impurity probably accounts for the low percentages of carbon obtained in the analyses. It did not melt at 220° (Found: C=44·40, 44·16; H=3·01, 3·07; Bi=41·87, 41·45. $C_{19}H_{15}O_3Bi$ requires C=45·68; H=3·03; Bi=41·67 per cent.).

It is evident from these results that the compound which Michaelis described as a basic carbonate, $Ph_3BiO + CO_2$, is in reality the normal carbonate, Ph_3BiCO_3.

Triphenylbismuthine carbonate is insoluble in ordinary organic solvents; different preparations varied in colour from pure white to pale yellow. With concentrated hydrochloric acid, effervescence took place, and triphenylbismuthine dichloride (m. p. 126°) was obtained.

Action of Glacial Acetic Acid on Triphenylbismuthine Carbonate.

Three grams of triphenylbismuthine carbonate were dissolved in a small quantity of glacial acetic acid by the aid of heat. Carbon dioxide was evolved, and, on cooling and adding a small quantity of water, a white precipitate was obtained, which was collected and washed with light petroleum, air being drawn through until the solid no longer had the odour of acetic acid. The substance melted sharply at 162°, and on crystallisation from water and acetic acid had the same melting point. The yield was 3·3 grams (Found: C=47·06, 47·58; H=3·86, 3·72; Bi=37·31, 37·13. $C_{22}H_{21}O_4Bi$ requires C=47·39; H=3·79; Bi=37·32 per cent.).

Triphenylbismuthine acetate is a white powder completely soluble in glacial acetic acid or ethyl acetate on warming. It is readily soluble in cold chloroform or nitrobenzene and in xylene on warming, moderately so in warm benzene, acetone, carbon tetrachloride, or alcohol, and insoluble in water or light petroleum.

If the acetic acid solution of the acetate is allowed to remain for several days without addition of water, long, transparent needles separate, which soften at 130° and melt at 136—137° (Found: Bi=35·16, 35·36. $C_{22}H_{21}O_4Bi,\frac{1}{2}C_2H_4O_2$ requires Bi=35·43 per cent.).

If this substance is triturated with water, the acetate (m. p. 162°) is obtained, which, if dissolved in acetic acid and allowed to crystallise, again yields the acid acetate.

Action of Hydriodic Acid and Iodine on Triphenylbismuthine Carbonate.

Hydriodic acid, containing as usual a little free iodine, was added to the carbonate; a red compound was immediately formed and an odour of iodobenzene noticed. The red product appeared to be a mixture.

The same result was obtained when the carbonate was triturated with an aqueous solution of iodine.

Action of Sulphuric Acid on Triphenylbismuthine Dichloride.

Triphenylbismuthine dichloride (6 grams) was added during fifteen minutes, with constant shaking, to 20 c.c. of sulphuric acid maintained at about 10° Hydrogen chloride was evolved, and a clear solution obtained, through which air was drawn for three hours to remove dissolved hydrogen chloride, after which the mixture was poured on ice. The precipitated solid (5·3 grams) was well washed with water, dried, extracted twice with boiling chloroform, and washed with ether. The acid wash waters contained inorganic bismuth, from which, however, the solid was free (Found: Bi = 38·60; S = 6·10. $C_{18}H_{15}O_4SBi$ requires Bi = 38·80; S = 5·98 per cent.).

Triphenylbismuthine sulphate is a white solid not melting below 280°, and is very sparingly soluble in the usual organic solvents.

Action of Moist Ammonia Gas on Triphenylbismuthine Dichloride.

Nine grams of triphenylbismuthine dichloride were dissolved in chloroform containing a little light petroleum. Moist ammonia gas was passed in, the solution became cloudy, and soon deposited a white solid. This was collected, and the operation repeated until no more solid separated. The deposit was washed with cold water until all ammonium chloride was removed. Washing was then continued with boiling water. This produced violent frothing of the solid, and chloroform was evolved, the latter probably being present as chloroform of crystallisation. When no further effervescence was noticed, the residue was dried on porous porcelain, and then in the air. It melted at 156—158°, and, after crystallisation at 160—161°, the latter figure being unaltered after repeated recrystallisation. Two separate preparations were analysed (Found: Cl = 7·25, 7·20; Bi = 42·34, 42·54. $C_{18}H_{16}OClBi$ requires Cl = 7·21; Bi = 42·31 per cent.).

Triphenylbismuthine hydroxychloride is a white powder insoluble in water or light petroleum, moderately soluble in ether, acetone, benzene, or xylene, completely so in alcohol or nitrobenzene on heating, and readily so in cold chloroform.

The derivative containing chloroform was not analysed, since the combined solvent was liberated on keeping in air or drying in a vacuum.

Action of Sodium on Triphenylbismuthine Dichloride in Ether.

Five grams of triphenylbismuthine dichloride and 1 gram of sodium were suspended in ether and heated on a water-bath for nine hours, and the product was filtered. The filtrate, on keeping, deposited crystals melting at 160—162°, which did not depress the melting point of triphenylbismuthine hydroxychloride. The sodium in the residue was destroyed by alcohol, and the remaining solid extracted with acetone, when sodium chloride was left, and the solution gave a further quantity of hydroxychloride. The production of this compound was probably due to a trace of moisture in the ether.

Action of Water on Triphenylbismuthine Dichloride.

Two grams of triphenylbismuthine dichloride were dissolved in alcohol, the solution was poured into a large excess of water, and evaporated slowly to dryness. The residue was evaporated with water several times, and the melting point of the product was unchanged. No hydroxychloride, hydroxide, or oxide had thus been formed.

Action of Glacial Acetic Acid on Triphenylbismuthine Hydroxychloride.

Two grams of triphenylbismuthine hydroxychloride were dissolved in glacial acetic acid by the aid of heat. On cooling, a solid was deposited, which melted sharply at 142°. This was boiled with acetone and filtered. On cooling the filtrate, crystals appeared (m. p. 152—153°), containing bismuth and organic matter, but no halogen. Recrystallisation from chloroform and then alcohol gave products melting at 146—148° and 152—153°, probably impure triphenylbismuthine acetate (m. p. 162°).

The acetone mother liquors deposited well-defined crystals melting at 128—130° after recrystallisation from alcohol. Further crystallisation gave long needles (m. p. 126°), which did not depress the melting point of triphenylbismuthine dichloride.

The residue left from the acetone extraction of the product, melting at 142°, fused at 136—138°, and was shaken with cold chloroform, in which it was completely soluble. This solution was carefully investigated, but only unchanged basic chloride (m. p. 160—161°) and a small amount of a viscid residue could be isolated.

Action of Magnesium Methyl Iodide on Triphenylbismuthine Hydroxychloride.

Triphenylbismuthine hydroxychloride (1·2 grams) was added to a solution of 0·05 gram of magnesium and 0·3 gram of methyl iodide in dry ether; an orange coloration appeared, which persisted for some time. Next day the mixture was heated on a water-bath for five hours and filtered. The residue contained practically no organic matter. The main ethereal solution was evaporated, when two distinct types of crystals separated, together with a trace of oil. The crystals were washed with warm alcohol; the residue contained halogen, melted at 125—126°, and did not depress the melting point of triphenylbismuthine dichloride. The alcoholic solution yielded triphenylbismuthine. Since no trace of the iodine was discovered, it was probably contained in the oil, which was too small in quantity for further investigation.

Action of Moist Ammonia Gas on Triphenylbismuthine Dibromide.

The preparation was carried out as in the case of the basic chloride, the crude product apparently containing chloroform of crystallisation, as before. After washing with hot water, it melted at 150—151°, and, after four recrystallisations, had a constant melting point of 147—148° (Found: Br = 15·44, 15·41; Bi = 38·43, 39·13. $C_{18}H_{16}OBrBi$ requires Br = 14·91; Bi = 38·79 per cent.).

The two preparations were made at an interval of several months, and the somewhat high halogen content seems to point to the presence of a trace of unchanged dibromide.

Triphenylbismuthine hydroxybromide is a yellow powder, insoluble in water, light petroleum, or ether, sparingly soluble in boiling acetone or benzene, moderately so in boiling toluene or xylene, and readily so in boiling alcohol or nitrobenzene and in cold chloroform.

Action of Copper Bronze on Triphenylbismuthine Dichloride.

Five grams of triphenylbismuthine dichloride and 0·6 gram of copper bronze were heated for eleven hours with dry acetone on a water-bath, and the solid was separated. On treatment of the concentrated acetone solution with light petroleum, triphenylbismuthine, a small amount of copper chloride, and diphenylchlorobismuthine (2·4 grams: m. p. 184—186°) were obtained, whilst the final residues had a strong odour of chlorobenzene.

The last two substances were probably formed from the dichloride by the prolonged heating, and not owing to the action of the copper.

Molecular Weights of some Bismuth and Arsenic Derivatives.

These determinations were carried out by the cryoscopic method in benzene solution.

Triphenylbismuthine.—0·2845 gave $\Delta = -0{\cdot}153°$. M.W. 427. $(C_6H_5)_3Bi$ requires 439.

Triphenylarsine.—0·2370 gave $\Delta = -0{\cdot}179°$. M.W. 298·9. $(C_6H_5)_3As$ requires 306·1.

Tri-p-*tolylbismuthine.*—0·2304 gave $\Delta = -0{\cdot}115°$. M.W. 458·3. $(C_7H_7)_3Bi$ requires 481.

Tri-p-*tolylarsine.*—0·3605 gave $\Delta = -0{\cdot}241°$. M.W. 342·8. $(C_7H_7)_3As$ requires 348.

Triphenylbismuthine Dichloride.—0·8847 gave $\Delta = -0{\cdot}470°$. M.W. 498·5. $(C_6H_5)_3BiCl_2$ requires 509·5.

Tri-α-naphthylbismuthine.—0·1588 gave $\Delta = -0{\cdot}122°$. M.W. 577. $(C_{10}H_7)_3Bi$ requires 589.

All the above show normal values.

Action of Magnesium p-*Tolyl Bromide on Triphenylbismuthine Dichloride.*

The Grignard solution (1·1 mols.) was added to triphenylbismuthine dichloride suspended in ether, and the usual transient violet coloration observed. The whole was heated on a water-bath for three to four hours, when a granular precipitate settled out. After twelve hours, the ether was evaporated and the residue distilled in a current of steam. The product remaining in the distillation flask solidified (m. p. 72—73°), and was recrystallised four times from alcohol, giving crops melting at 76°, 78°, 78°, the last fraction being melted with triphenylbismuthine. The mother liquors were fractionally crystallised, but no product other than triphenylbismuthine could be isolated.

Action of Magnesium p-*Tolyl Bromide on Diphenylbromobismuthine.*

The reaction was carried out as above, and the mixture distilled in a current of steam; the residue melted at 70°, and was recrystallised three times from acetone, but in each case the crystals melted at 78° and gave the reactions of triphenylbismuthine. The mother liquors yielded a further quantity of triphenylbismuthine.

Action of Iodine Trichloride on Triphenylbismuthine.

Five grams of the bismuthine were dissolved in dry ether and 2·7 grams of iodine trichloride in the same solvent gradually added. A momentary red coloration appeared on mixing, and a pale brown oil separated out and soon solidified. The ethereal solution was evaporated, yielding an oil, which with chlorine in chloroform solution gave 0·4 gram of iodobenzene dichloride. The solid, after crystallisation from acetone and light petroleum, melted at 120° and did not depress the melting point of triphenylbismuthine dichloride.

Tri-α-naphthylbismuthine Dichloride.

Five grams of the bismuthine were dissolved in dry chloroform and treated with chlorine. The addition of light petroleum gave a yellow precipitate (4·6 grams: m. p. 158—159°), and the mother liquors yielded a further 0·7 gram. Recrystallisation twice from chloroform–petroleum solution gave a product melting sharply on both occasions at 166° (Found: Cl = 10·68, 10·66; Bi = 30·67, 30·84. $C_{30}H_{21}Cl_2Bi$ requires Cl = 10·74; Bi = 31·51 per cent.).

Tri-α-naphthylbismuthine dichloride is a yellow, crystalline powder readily soluble in chloroform, moderately so in acetone or benzene, and insoluble in light petroleum. On heating for several hours at 100°, it did not smell of chloronaphthalene, was stable to hydrochloric acid, and melted at 167—169°.

Action of Moist Silver Oxide on Tri-α-naphthylbismuthine Dichloride.

The dichloride (2 grams) and silver oxide (0·7 gram) were suspended in moist acetone and well shaken. Reaction occurred almost at once, and, after two days, the mixture was filtered and the residue extracted with chloroform, which yielded two deposits of tri-α-naphthylbismuthine, 0·5 gram (m. p. 230°) and 0·2 gram (m. p. 232° on one crystallisation). Spontaneous evaporation of the acetone solution yielded a small amount of a brown solid, which became very viscid on warming with alcohol, had a strong odour of naphthalene, and was not further examined.

Diphenyl-α-naphthylbismuthine Dibromide.

Diphenyl-α-naphthylbismuthine (0·8 gram) was treated in dry chloroform–ether solution with a slight excess of bromine in chloroform. On addition of light petroleum, 0·81 gram of dibromide was precipitated (Found: Br = 24·83; Bi = 31·87. $C_{22}H_{17}Br_2Bi$ requires Br = 24·59; Bi = 31·99 per cent.).

Determination of the Metal in Derivatives of Quinquevalent Bismuth.

The substance (0·2—0·3 gram) was treated with about 10 c.c. of an ammoniacal solution of hydrogen sulphide, and the mixture evaporated to dryness in an air-bath at 115—125°, the benzene formed during the decomposition driven off, and the residue of bismuth sulphide and sulphur boiled for a few minutes with 10 c.c. of concentrated hydrochloric acid. The solution was filtered, diluted with water, hydrogen sulphide passed, and the precipitated bismuth sulphide filtered on a Gooch crucible, washed with carbon disulphide, dried, and weighed.

The method was first tested on two well-known compounds, namely, triphenylbismuthine dichloride (Found: Bi = 40·44. $C_{18}H_{15}Cl_2Bi$ requires Bi = 40·78 per cent.) and dibromide (Found: Bi = 34·92. $C_{18}H_{15}Br_2Bi$ requires Bi = 34·73 per cent.).

Our thanks are due to the Research Fund of the Chemical Society for a grant which has defrayed the expenses of this investigation.

THE UNIVERSITY,
EDGBASTON, BIRMINGHAM.

[*Received, June 3rd,* 1920.]