CII.—*Organo-derivatives of Bismuth. Part IV. The Interaction of the Halogen derivatives of Tertiary Aromatic Bismuthines with Organo-derivatives of Magnesium and Mercury.*

By FREDERICK CHALLENGER and CHARLES FREDERICK ALLPRESS.

IN consequence of the failures which accompanied many attempts to prepare mixed aromatic bismuthines of the type $BiR'R_2''$ and bismuthonium haloids $BiR_3'R''X$, the action of the Grignard reagent on halogen derivatives of the types BiR_2X, $BiRX_2$, and BiR_3X_2 has been carefully studied. For this purpose several new halogen derivatives have been prepared. Bismuth chloride (1 mol.) and tri-*p*-tolylbismuthine (2 mols.) yield chiefly *di*-p-*tolylchlorobismuthine*, m. p. 181°, a small amount of p-*tolyldichlorobismuthine*, m. p. 207°, being also produced, as frequently happens in reactions of this type. *Di-α-naphthylchlorobismuthine*, m. p. 168°, is similarly formed, although with some difficulty, from bismuth chloride and tri-α-naphthylbismuthine. In whatever proportion this bismuthine and bismuth bromide are mixed, however, the product is α-naphthyldibromobismuthine, m. p. 208°. This is also produced together with α-bromonaphthalene and tri-α-naphthylbismuthine when tri-α-naphthylbismuthine dibromide is heated at 100°. The production of the dibromobismuthine seems of interest, since in boiling benzene triphenylbismuthine dichloride and dibromide yield diphenylchlorobismuthine and the corresponding bromo-compound.

α-Naphthyldibromobismuthine is also formed when iodine bromide (1 mol.) and tri-α-naphthylbismuthine interact. some bismuthine remaining unchanged. In these cases a special tendency appears to exist for the formation of the dibromo- in preference to the monobromo-derivative.

Phenyldibromobismuthine (T., 1914, **105**, 2215; 1916, **109**, 250) is the main product obtained from two mols. of bismuth bromide and one mol. of triphenylbismuthine.

Tri-m-*tolylbismuthine*, m. p. 65°, has been prepared from bismuth chloride and magnesium *m*-tolyl bromide.

The use of sulphuryl chloride in chloroform solution at the ordinary temperature (T., 1916, **109**, 251) appears to be a general method for the preparation of bismuthine dichlorides; traces of organic sulphur compounds are, however, simultaneously produced. The dichlorides of tri-*p*-tolyl- and tri-α-naphthyl-bismuthines have been prepared in this manner.

With the magnesium derivative of *p*-iodo-*m*-xylene, diphenylchlorobismuthine and di-*p*-tolylchlorobismuthine gave triphenyl- and tri-*p*-tolyl-bismuthines respectively. Magnesium phenyl bromide (1 or 2 mols., as required by theory) gave with di-α-naphthylchlorobismuthine and α-naphthyldibromobismuthine the tri-α-naphthylbismuthine and in the latter instance a trace of diphenyl-α-naphthylbismuthine. With 1·2 mols. of magnesium α-naphthyl bromide, di-*p*-tolylchlorobismuthine similarly gave tri-*p*-tolylbismuthine. In most of these experiments a certain amount of bismuth oxide or oxyhaloid was produced on addition of water.

The constant production in these reactions of the bismuthine from which the original halogen compound was derived would appear to indicate that BiR_2X or $BiRX_2$ might react as a mixture of BiR_3 and BiX_3, but then the simultaneous production of a tertiary bismuthine containing only the radicle of the Grignard reagent would be expected.

Except in the aliphatic series, where the odour of an alkylbismuthine was detected (T., 1914, **105**, 2216; 1916, **109**, 250), and in cases where large excess of the Grignard reagent was employed, this has not been observed. It appeared possible that in the absence of a large excess of the Grignard solution * much of the halogen bismuthine might remain unattacked,† although in almost every instance it completely dissolved. On decomposition with water, reaction with the magnesia might then occur thus:

$$6BiPh_2Br+3Mg(OH)_2=4BiPh_3+2Bi(OH)_3+3MgBr_2.$$

This type of reaction has been shown to occur with phenyl- and α-naphthyl-dibromobismuthines and diphenylbromobismuthine in

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* Compare the necessity for such excess in the preparation of the tetra-derivatives of tin and lead (Grüttner and Krause, *Ber.*, 1919, **52**, [*B*], 2159; Krause and Becker, *ibid.*, 1920, **53**, [*B*], 17) and the organo-derivatives of mercury (Hilpert and Grüttner, *Ber.*, 1915, **48**, 906).

† This appears to be the case, for example, when 2½ mols. of magnesium α-naphthyl bromide interact with phenyldibromobismuthine. See also p. 922.

presence of aqueous ammonia, sodium hydroxide, or magnesium oxide. With water or alcohol alone, however, only hydrocarbon and bismuth oxyhaloid are produced. (An account of these and other properties of the halogen derivatives of the bismuthines will shortly be communicated to the Society in conjunction with Mr. J. F. Wilkinson.)

This hypothesis, although probably correct in some cases, does not explain the production of triphenylbismuthine from diphenylbromobismuthine and magnesium α-naphthyl bromide or magnesium ethyl bromide when the reaction mixture is worked up in the absence of water.

The complex nature of some of the changes involved is shown by the production of triphenylbismuthine and diphenyl-α-naphthylbismuthine by the action of six molecules of magnesium phenyl bromide on α-naphthyldibromobismuthine. The interchange of groups observed when mercury diphenyl is employed (p. 923) may be analogous. Similarly, with 5½ mols. of magnesium α-naphthyl bromide, phenyldibromobismuthine gives rise to much tri-α-naphthylbismuthine.

The action of magnesium phenyl bromide and magnesium methyl iodide on tri-α-naphthylbismuthine dibromide yields tri-α-naphthylbismuthine, in the second case, without the addition of water. In the first case the reaction proceeds thus :

$$(C_{10}H_7)_3BiBr_2+MgPhBr=(C_{10}H_7)_3Bi+PhBr+MgBr_2.$$

Diphenyl does not appear to be formed in quantity much greater than that already present in the Grignard solution.

It was of interest to determine whether this reducing action of the Grignard reagent,* which is so frequently noticed in connexion with the dihaloids of the tellurides (Lederer, *Ber.*, 1916, **49**, 1615; 1920, **53**, [*B*], 713, 1674) and bismuthines, is also exerted on the corresponding arsenic and antimony compounds. We find that triphenylarsine is produced from its dichloride and magnesium phenyl bromide or magnesium methyl iodide. Triphenylstibine dichloride is reduced to the stibine when treated with magnesium methyl iodide, possibly by way of $SbPh_3I_2$, since iodobenzene is also produced.

The yield of triphenylbismuthine from mercury diphenyl and bismuth bromide is nearly quantitative and better than that obtained with the Grignard reagent (60 per cent.). The reaction

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* The metal or a lower haloid is also produced by the action of the Grignard reagent on salts of lead, copper, mercury(ous), thallium and chromium, whilst Hepworth (T., 1921, **119**, 253) has shown that nitric esters similarly give rise to traces of dialkylamines.

of mercury diphenyl with α-naphthyldibromobismuthine is, however, most unexpected, mercury phenyl bromide, triphenylbismuthine, and mercury di-α-naphthyl being obtained. This recalls the ease with which mercury phenyl bromide yields mercury diethyl and mercury dibenzyl with the appropriate Grignard reagent (Hilpert and Grüttner, *loc. cit.*).

In marked distinction to the behaviour of α-naphthyldibromobismuthine, tri-α-naphthylbismuthine dibromide does not react with mercury diphenyl at room temperature. In boiling benzene, however, a somewhat complicated reaction occurs analogous with that of magnesium phenyl bromide, tri-α-naphthylbismuthine, mercury phenyl bromide, and bromobenzene being obtained, as also triphenylbismuthine and mercury di-α-naphthyl in much smaller quantities. The last two compounds probably arise from the action of mercury diphenyl on traces of α-naphthylbromobismuthines arising from the decomposition of the dibromide (see p. 919). In agreement with this is the fact that only traces of α-bromonaphthalene seem to be produced. Preliminary experiments have been made on the interaction of the aromatic bismuthines with the salts of other metals. With alcoholic silver nitrate, fine yellow or orange-yellow, crystalline precipitates are produced, which are probably similar to or identical with the $AgNO_3,2AgC_6H_5$ described by Krause and Schmitz (*Ber.*, 1919, **52**, [*B*], 2150).

As these authors desire to continue the investigation of these products, we do not propose further to examine the silver compounds we have obtained. It appears, however, that in this case triphenylbismuthine can act as a phenylating agent, as has already been observed with mercuric chloride (Gillmeister, *Ber.*, 1897, **30**, 2844). Other reactions of this type are being investigated in conjunction with Mr. L. R. Ridgway.

Bismuth chloride combines with benzenediazonium chloride to form a stable, well-crystallised additive product. Its behaviour with sodium hydroxide and similar reagents is under examination with a view to the possible production of the bismuth analogues of the arsinic and stibinic acids.

EXPERIMENTAL.

Action of Iodine Monochloride on Diphenyl-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine (0·8 gram) was treated with 0·26 gram of iodine monochloride, both in chloroform–ether solution. A brown turbidity was produced, which disappeared on shaking, and, on standing, a colourless solid separated. On crystallisation from chloroform–ether, this melted at 182° (diphenylchlorobismuthine melts at 184—185°).

The mother-liquor and washings were evaporated, separated from a further small deposit with light petroleum, glacial acetic acid was added and the cooled solution treated with chlorine, when 0·15 gram of α-iodonaphthalene dichloride was obtained.

Action of Cyanogen Iodide on Tri-α-naphthylbismuthine.

Three grams of tri-α-naphthylbismuthine and 0·76 gram (1 mol.) of cyanogen iodide were boiled in 30 c.c. of dry chloroform for four hours. On adding ether, 1·2 grams of unchanged bismuthine were recovered. The mother-liquors, still smelling of cyanogen iodide, gave a brownish-yellow deposit, which on extraction with light petroleum and treatment with chlorine gave a very small quantity (less than 0·05 gram) of α-iodonaphthalene dichloride. The reaction occurs less readily than with triphenylbismuthine.

*Di-*p*-tolylchlorobismuthine and* p*-Tolyldichlorobismuthine.*

On mixing dry ethereal solutions of bismuth chloride and tri-*p*-tolylbismuthine, a turbidity was produced, and crystals gradually deposited. These were separated, washed with ether, dried, and recrystallised from chloroform–ether (free from alcohol and specially dried), leaving a yellow substance (m. p. 207°) almost insoluble in chloroform. After four crystallisations, the main bulk melted constantly at 180°, and no further yellow product was obtained (Found: Cl=8·43; Bi=49·16. $C_{14}H_{14}ClBi$ requires Cl=8·34; Bi=48·89 per cent.).

*Di-*p*-tolylchlorobismuthine* forms colourless needles, m. p. 181°, moderately soluble in hot benzene and chloroform, and almost insoluble in ether and light petroleum.

The yellow substance was crystallised from dry benzene (Found: Cl=18·80. $C_7H_7Cl_2Bi$ requires Cl=19·19 per cent.). p*-Tolyldichlorobismuthine* forms yellow needles, m. p. 206—207°, difficultly soluble in hot benzene and almost insoluble in other solvents.

Both these compounds are decomposed by alcohol and moist solvents, and with hydrochloric acid give toluene and bismuth chloride.

Action of Sodium on Diphenylbromobismuthine and α-Bromonaphthalene.

Diphenylbromobismuthine (m. p. 157°) (6·63 grams), α-bromonaphthalene (3·1 grams) and sodium (0·35 gram) were heated with benzene for about twenty hours, filtered hot, and the solvent evaporated. The residue solidified on cooling (m. p. 74—76°), and, on recrystallisation from alcohol, was shown to consist of triphenylbismuthine.

When diphenylchlorobismuthine, α-bromonaphthalene and sodium were heated in benzene, triphenylbismuthine was produced, as also a greyish-black solid insoluble in benzene, which contained bismuth but no organic matter, some of the bismuth being probably present as the metal (Challenger, T., 1916, **109**, 250). The method appears quite unsuitable for the preparation of a mixed bismuthine.

Action of Copper Bronze on Phenyldibromobismuthine.

A small quantity of phenyldibromobismuthine was boiled with dry benzene and copper bronze for three hours, the reaction commencing at the ordinary temperature. The black solution on concentration and treatment with alcohol deposited triphenylbismuthine, which after one crystallisation melted at 79°. The black colour was due to metallic bismuth, which was isolated from the residue, and not to the presence of organic compounds containing a high percentage of bismuth, analogous to the arsenic derivatives described by Fargher (T., 1920, **117**, 865) or by Ehrlich and Karrer (*Ber.*, 1913, **46**, 3564). Linkage of the bismuth atoms appears not to occur.

Di-α-naphthylchlorobismuthine.

Tri-α-naphthylbismuthine (3·54 grams) in the minimum quantity of cold dry chloroform (free from alcohol), was treated with 0·96 gram of bismuth chloride in ether–chloroform solution. After standing a few minutes, some bismuth oxychloride was precipitated and filtered off. The solution, on addition of more ether, gradually deposited a grey powder and a flocculent mass of yellow needles. These, after one crystallisation from chloroform–ether, had a constant melting point of 168°. The mother-liquor from the original deposit yielded bismuth chloride and naphthalene (Found Bi=41·34; Cl=7·56. $C_{20}H_{14}ClBi$ requires Bi=41·81; Cl=7·14 per cent.).

Other preparations similarly gave deposits of bismuth oxychloride, although every care was taken to have absolutely dry flasks and solvents, and in two cases unchanged tri-α-naphthylbismuthine and bismuth chloride were isolated, showing the comparative difficulty with which the reaction occurs.

Di-α-naphthylchlorobismuthine forms fine, yellow needles, moderately soluble in dry benzene and chloroform, much less so in ether and light petroleum. It is extremely susceptible to traces of moisture, and even after keeping a short time in a closed vessel loses its yellow colour, and smells of naphthalene.*

α-Naphthyldibromobismuthine.

Bismuth bromide (1·5 grams; 1 mol.) in dry ether was added to 3·9 grams (2 mols.) of tri-α-naphthylbismuthine in dry chloroform. After keeping, the mother-liquor was poured off, and the orange-coloured solid washed with ether. On crystallisation from benzene it melted at 208° (Found: Br=32·74. $C_{10}H_7Br_2Bi$ requires Br=32·32 per cent.).

The mother-liquor, on concentration, gave 1·95 grams of unchanged tri-α-naphthylbismuthine, further proof of the non-formation of di-α-naphthylbromobismuthine.

Tri-α-naphthylbismuthine (2·95 grams; 1 mol.) in chloroform and 4·1 grams of bismuth bromide (2 mols.) in ether gave a deep orange, crystalline deposit, which was recrystallised from benzene (Found: Br=32·44; Bi=41·06. $C_{10}H_7Br_2Bi$ requires Br=32·32; Bi=42·00 per cent.).

α-Naphthyldibromobismuthine is a deep orange, crystalline solid melting and decomposing at 208°. It is difficultly soluble in benzene and almost insoluble in other solvents.

Formation of α-Naphthyldibromobismuthine from Tri-α-naphthylbismuthine Dibromide.

A quantity of dry tri-α-naphthylbismuthine dibromide was heated for half an hour at 100° in the absence of moisture, when it melted in the course of a few minutes. The pasty mass, after being washed with dry ether to remove α-bromonaphthalene, was extracted with chloroform-ether, yielding tri-α-naphthylbismuthine, m. p. 230°. The residue was extracted with benzene, giving orange crystals, melting at 208°, and consisting of α-naphthyldibromobismuthine. The final residue was bismuth oxybromide.

Preparation of Phenyldibromobismuthine.

On adding 1·5 grams of triphenylbismuthine in ethereal solution to 3·0 grams of bismuth bromide in the same solvent, yellow crystals, m. p. 201°, were deposited, which on recrystallisation from dry

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* Phenyldichlorostibine and phenyldi-iodostibine also decompose on keeping (Schmidt, *Annalen*, 1920, **421**, 219).

benzene melted at 202° (T., 1914, **105,** 2216) (Found: Br=36·33. $C_6H_5Br_2Bi$ requires Br=35·93 per cent.).

Tri-m-*tolylbismuthine.*

Bismuth chloride (23 grams) in ether was slowly added with frequent shaking to a solution prepared from magnesium (6 grams; 3·3 atoms) and *m*-bromotoluene (39 grams; 3 mols.) in dry ether. On the next day the solvent was removed, ice added, toluene removed in steam, and the filtered residue extracted with acetone. The solution deposited 9 grams of white needles, m. p. 56°, mixed with some oil which soon solidified. On crystallisation from acetone and finally from alcohol, these melted at 65° (Found: Bi=43·40, 43·35. $C_{21}H_{21}Bi$ requires Bi=43·25 per cent.).

Action of Magnesium α-Naphthyl Bromide on Di-p-*tolylchlorobismuthine and of Magnesium Phenyl Bromide on Di-α-naphthylchlorobismuthine.*

(*a*) Di-*p*-tolylchlorobismuthine (1·7 grams) and the Grignard reagent (1·2 mols.) gave only tri-*p*-tolylbismuthine.

(*b*) Di-α-naphthylchlorobismuthine (2·5 grams) and the Grignard reagent gave 1·6 grams of tri-α-naphthylbismuthine.

In (*a*) the Grignard reagent was added to the halogen bismuthine, in (*b*) the reverse method was adopted, with no apparent reaction at the ordinary temperature in either case. After five hours on the water-bath the reaction seemed complete in (*a*) and almost so in (*b*). The ether was evaporated, water added, and the filtered residues extracted with in (*a*) alcohol and (*b*) chloroform. The products obtained from these extracts did not depress the melting points of the respective bismuthines.

Action of the Magnesium Derivative of p-*Iodo*-m-*xylene on Diphenylchlorobismuthine and Di*-p-*tolylchlorobismuthine.*

(*a*) Diphenylchlorobismuthine (4 grams), magnesium (0·3 gram), and iodoxylene (2·8 grams) gave triphenylbismuthine.

(*b*) Di-*p*-tolylchlorobismuthine (11 grams), magnesium (0·75 gram), and iodoxylene (7·1 grams) gave tri-*p*-tolylbismuthine.

The Grignard reagent was added to the halogen bismuthine. After three hours on the water-bath in (*a*) and twelve hours at room temperature in (*b*), the ether was removed, water added and the filtered residue containing much bismuth oxyhaloid (seemingly from unchanged halogen bismuthine) extracted with benzene or alcohol.

Action of Magnesium Phenyl Bromide and Magnesium p-*Tolyl Bromide on α-Naphthyldibromobismuthine.*

(1) The dibromobismuthine (13 grams; 1 mol.) was added to 2·5 mols. of magnesium phenyl bromide (1·59 grams of magnesium; 10·3 grams of bromobenzene). A vigorous reaction took place. The solid immediately disappeared and was gradually replaced by a yellow oil. The ether was evaporated, the residue decomposed by water, filtered, and extracted with benzene. Alcohol was added to the solution so obtained, giving a yellow oil, which slowly became semi-solid, and on washing with light petroleum gave crystals, m. p. 212—220° (1·3 grams). After three recrystallisations, these melted at 232°, and did not depress the melting point of tri-α-naphthylbismuthine. The alcohol–benzene solution deposited traces of an oily solid, which on washing with light petroleum and recrystallising from alcohol melted at 115—116°, and did not depress the m. p. of diphenyl-α-naphthylbismuthine.

(II) When a mixture of 25 grams of α-naphthyldibromobismuthine (free from bismuth bromide) with magnesium phenyl bromide (6 mols.) was kept at room temperature for two weeks, the ether removed, and the residue, without further heating, distilled in steam, more satisfactory results were obtained. Extraction with acetone and alternate crystallisation from chloroform–alcohol and aqueous alcohol gave triphenylbismuthine and diphenyl-α-naphthylbismuthine in almost equal amounts, about 4 grams. No tri-α-naphthylbismuthine or phenyldinaphthylbismuthine was isolated in this case. This seems to be the best method for preparing the mixed bismuthine. When the mixture was heated instead of remaining at room temperature, the yield of this product was much smaller.

(III) α-Naphthyldibromobismuthine (4 grams) and magnesium *p*-tolyl bromide (about 3·5 mols.) were heated during four hours on the water-bath. The decanted ether yielded crystals, m. p. 222°, which on recrystallisation melted at 234—235°, and did not depress the m. p. of tri-α-naphthylbismuthine. A further quantity was obtained from the insoluble residue.

Action of Magnesium α-Naphthyl Bromide on Diphenylbromobismuthine.

Diphenylbromobismuthine (10 grams) and the Grignard reagent * (1·2 mols.) were heated under reflux for some hours, the ether

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* Concentrated solutions of magnesium α-naphthyl bromide on keeping frequently deposit magnificent crystals, presumably of the etherate. These redissolve on warming.

was decanted, and without addition of water the residue extracted with light petroleum and then with chloroform. From these solutions triphenylbismuthine, bismuth oxybromide, and some unchanged diphenylbromobismuthine were obtained. The mixed bismuthine was probably present, but in this case was not isolated from the viscous mass.

Action of Magnesium Ethyl Bromide on Diphenylbromobismuthine.

This was carried out as previously (T., 1914, **105**, 2216), but after removal of the ether the residue was extracted with light petroleum without addition of water. Triphenylbismuthine and the odour of an alkylbismuthine were produced and the extract deposited a yellow powder, which took fire explosively on heating in air, and was probably an oxidation product of triethylbismuthine.

Action of Magnesium Phenyl Bromide on Tri-α-naphthylbismuthine Dibromide.

(I) The dibromide (23 grams) was treated with the Grignard reagent (2 mols.; 9·5 grams of bromobenzene, 1·5 grams of magnesium, and 70 c.c. of ether), when a vigorous reaction occurred, the yellow solid being replaced by a grey, granular precipitate. Ether (30 c.c.) was then added, the mixture heated on the water-bath for five hours, the ether removed, ice added, and the mixture distilled with steam. The volatile product (6·5 grams) was twice fractionated, yielding 2·7 grams of bromobenzene,* which boiled at 150—160° on redistillation and was converted into *p*-bromonitrobenzene. Only traces of diphenyl were isolated. The residue (16·5 grams) after steam distillation was extracted with benzene, leaving 1 gram of inorganic matter and yielding 12 grams of almost pure tri-α-naphthylbismuthine. The benzene mother-liquor finally gave a friable solid, which melted at about 95° and on extraction with alcohol appeared to contain traces of diphenyl-α-naphthylbismuthine.

(II) The dibromide (3·75 grams) and 1 mol. of the Grignard reagent showed no apparent reaction in the cold. After six hours on the water-bath the product was extracted twice with benzene. The first extract yielded yellow crystals containing halogen, m. p. 210°, after recrystallisation from chloroform–ether (α-naphthyldibromobismuthine). Unchanged dibromide was obtained from the second extraction. Similarly from the interaction of triphenyl-

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* The absence of free bromobenzene in the standard Grignard solution employed was established by a blank experiment.

bismuthine dichloride and magnesium phenyl bromide (1 mol.) some dichloride was recovered unchanged.

Action of Magnesium Methyl Iodide on Tri-α-naphthylbismuthine Dibromide.

With 3·2 grams of the dibromide and 1·5 mols. of the Grignard reagent the ether boiled rapidly and a deep red product was formed. After an hour on the water-bath and removal of the ether, it was extracted with dry chloroform. The yellow solution on addition of light petroleum gave tri-α-naphthylbismuthine.

Preparation of Triphenylbismuthine from Bismuth Bromide and Mercury Diphenyl.

On mixing mercury diphenyl (3·5 grams; 3 mols.), bismuth bromide (1·5 grams), and dry ether (25 c.c.), reaction was immediate and a flocculent, white precipitate was produced. After twelve hours the mixture was heated on the water-bath and filtered. The residue, mercury phenyl bromide, m. p. 273° (3·3 grams), was free from mercuric bromide. The ethereal solution yielded 1·6 grams of an oil, which quickly crystallised and was almost pure triphenylbismuthine. The yield was quantitative.

Interaction of α-Naphthyldibromobismuthine and Mercury Diphenyl.

The dibromobismuthine (18·5 grams, free from bismuth bromide) and mercury diphenyl (27·4 grams; 2 mols.) reacted very quickly when suspended in cold dry ether (60 c.c.), the yellow colour disappearing. On the next day dry benzene was added, the precipitate (28 grams) separated, and extracted twice with benzene. The residue (23 grams) was mercury phenyl bromide. The united extracts and filtrate gave an oil from which benzene and light petroleum separated a solid (*A*), m. p. 125—128°. The evaporated filtrate slowly solidified (10 grams). On solution in chloroform-alcohol a crystalline deposit (*B*), m. p. 67°, was obtained, from which similar treatment removed a white solid, m. p. 240°, which was free from bismuth and halogen, and gave naphthalene and mercuric chloride with hot hydrochloric acid. After recrystallisation from chloroform, it did not depress the m. p. of mercury di-α-naphthyl (241°). Further quantities were obtained from the intermediate fractions, which also contained some naphthalene and probably a certain amount of unchanged mercury diphenyl.

On concentration of the mother-liquor from *B*, and repeated fractionation of the residue from dilute alcohol, a few grams of pure triphenylbismuthine were obtained and also about 0·2 gram of a crystalline bismuth compound, m. p. 95—100°, which was possibly crude diphenyl-α-naphthylbismuthine. A repetition of this reaction gave similar results.

Interaction of Tri-α-naphthylbismuthine Dibromide and Mercury Diphenyl.

The dibromide (22·1 grams), mercury diphenyl (20·8 grams; 2 mols.), and dry ether (50 c.c.) were well shaken, but after a week the mixture was still unchanged. This is in marked contrast with the behaviour of α-naphthyldibromobismuthine. The ether was then evaporated, dry benzene added, and the mixture boiled for two and a half hours. The yellow solid disappeared and 7·7 grams of mercury phenyl bromide (m. p. 275°) were deposited. The filtrate yielded 9·4 grams of a solid, m. p. about 200° (not sharp). After two extractions with acetone, to remove mercury diphenyl, and recrystallisation from benzene, this had m. p. 233—234° and did not depress the m. p. of tri-α-naphthylbismuthine.

The main benzene filtrate was evaporated, diluted with light petroleum, the deposit (m. p. 115—180°) extracted with acetone and recrystallised from benzene, yielding mercury di-α-naphthyl, m. p. 243°. The intermediate fractions contained mercury phenyl bromide. Concentration of the mother-liquors and treatment with light petroleum gave a solid (*A*) and an oil (*B*), from which by steam distillation about a gram of bromobenzene was isolated and converted into *p*-bromonitrobenzene. The non-volatile residue smelled very faintly of α-bromonaphthalene and on repeated fractionation from alcohol yielded 0·4 gram of pure triphenylbismuthine. The deposit *A*, after laborious treatment with various solvents, gave about 0·5 gram of impure diphenyl-α-naphthylbismuthine.

Action of Magnesium Methyl Iodide and Magnesium Phenyl Bromide on Triphenylarsine Dichloride.

(I) With the dichloride (3 grams) and magnesium methyl iodide (2 mols.) a red oil was deposited. After some hours the ether was evaporated, water added (which destroyed the red colour), and the mixture filtered. The residue (1·2 grams) on crystallisation from alcohol melted at 60° and was triphenylarsine. The aqueous liquor deposited colourless plates free from halogen, m. p. about 116° on rapid heating, but 200°, sintering from 113°, on slow heating;

these are the properties of triphenylarsine dihydroxide (Phillips, *Ber.*, 1886, **19**, 1032).

(II) With magnesium phenyl bromide (2·5 mols.) and the dichloride (13 grams) suspended in dry ether, a vigorous reaction occurred and a granular precipitate was formed. After four hours on the water-bath the mixture was distilled with steam, the residue filtered, and extracted with alcohol, whereby 6·6 grams of triphenylarsine, m. p. 57—59°, were obtained.

The use of 1·5 mols. of the Grignard reagent also gave triphenylarsine.

Action of Magnesium Methyl Iodide and Magnesium Phenyl Bromide on Triphenylstibine Dichloride.

Twelve grams of the dichloride were covered with dry ether and magnesium methyl iodide (2·5 mols.) was slowly added. A violent effervescence occurred and a light brown, pasty mass separated, which with more Grignard reagent became white and almost disappeared. After four hours on a water-bath, distillation with steam yielded iodobenzene, from which at least two grams of the iodo-dichloride were isolated. Extraction of the non-volatile residue with alcohol yielded 4·4 grams of triphenylstibine (m. p. 51—52°), which was characterised by conversion into the dibromide. The alcoholic mother-liquor gave about 0·1 gram of a pink, viscous residue, which crystallised from water or aqueous alcohol in colourless needles, m. p. 205—210°, decomposing at about 225°, giving a red sublimate. The production of this substance, possibly a stibonium derivative, is of interest, and the reaction is being investigated further.

With 1·5 mols. of the Grignard reagent in the cold no stibine could be isolated on addition of water, the product consisting of hydroxyhaloids of triphenylstibine, yielding the dichloride with concentrated hydrochloric acid.

Estimation of Halogen in Derivatives of the Types $BiRX_2$ *and* BiR_2X.

0·2 to 0·3 Gram of the substance is decomposed by warming with alcoholic ammonia for half an hour. The halogen is then precipitated by silver nitrate solution acidified with nitric acid. The method was tested on diphenylchlorobismuthine (Found: Cl=8·97, 8·88. Calc., Cl=8·97 per cent.).

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THE UNIVERSITY,
EDGBASTON,
BIRMINGHAM.

THE LEVINSTEIN LABORATORY,
THE UNIVERSITY,
MANCHESTER.

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