XVII.—*Organo-derivatives of Bismuth. Part VI. The Preparation and Properties of Tertiary Aromatic Bismuthines and their Interaction with Organic and Inorganic Halogen Compounds.*

By FREDERICK CHALLENGER and LESLIE RANDAL RIDGWAY.

IN order to determine whether any abnormality of reaction was associated with the halogen-substituted bismuthines, *tri*-p-*chlorophenylbismuthine* and *tri*-p-*bromophenylbismuthine* have been prepared from bismuth chloride and the magnesium derivatives of *p*-chlorobromobenzene and *p*-dibromobenzene respectively.

The halogen atoms of tri-*p*-chlorophenylbismuthine do not react with magnesium phenyl bromide or with ammonia at 160°, and both bismuthines behave normally with chlorine and bromine, giving *dichlorides* and *dibromides*.

As was to be expected, tri-*p*-chlorophenylbismuthine does not give a di-iodide, *di*-p-*chlorophenyliodobismuthine*, *p*-chloroiodobenzene, and a red powder containing organic matter and tervalent bismuth being produced (compare Challenger and Allpress, T., 1915, **107**, 21, 23; Michaelis, *Annalen*, 1902, **321**, 164).

The m. p.'s of the dibromides and to a smaller extent the m. p. of tri-*p*-bromophenylbismuthine dichloride vary with the rate of

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* When diphenyl-α-naphthylbismuthine is prepared, and the naphthalene removed by steam distillation, the last portions of the distillate have a strong odour of α-naphthol.

heating. It is interesting to note that almost all bismuthine dibromides melt at about 100—115°.

With moist silver oxide, tri-*p*-chlorophenylbismuthine dichloride and tri-*p*-bromophenylbismuthine dibromide yield the corresponding bismuthines. This is also the case with triphenylbismuthine dibromide and hydroxychloride, and with tri-*p*-tolylbismuthine dibromide (Challenger and Goddard, unpublished observation).

Di-p-*chlorophenylbromobismuthine* was prepared from the corresponding bismuthine and bismuth bromide. With alcoholic ammonia, the bismuthine and bismuth hydroxide are produced, a reaction which is given by all compounds of the types $BiRX_2$ and BiR_2X in presence of bases.

In boiling benzene, di-*p*-chlorophenylbromobismuthine yields the unstable p-*chlorophenyldibromobismuthine*, which is also produced in small quantity from the bismuthine and bismuth bromide, thus :—

$$(C_6H_4Cl)_3Bi + BiBr_3 = (C_6H_4Cl)_2BiBr + C_6H_4Cl{\cdot}BiBr_2$$
$$2(C_6H_4Cl)_2BiBr = C_6H_4Cl{\cdot}BiBr_2 + Bi(C_6H_4Cl)_3.$$

Instances of this type of reaction are numerous (Challenger and Allpress, T., 1921, **119**, 917; Challenger, T., 1916, **109**, 250; Grüttner and Wiernik, *Ber.*, 1915, **48**, 1749).

Bismuth chloride and magnesium benzyl chloride in presence of air give bismuth oxychloride and benzaldehyde. A similar reaction is frequently observed with analogous benzyl derivatives; thus tribenzylarsine, when recrystallised from ether, gives benzaldehyde and finally benzoic and arsenic acids (Michaelis and Paetow, *Annalen*, 1886, **233**, 62), whilst from benzyldichloroarsine and water, benzylarsine oxide, arsenious acid, and benzaldehyde are obtained (*ibid.*, p. 91). Tribenzylamine yields toluene and benzaldehyde on distillation or oxidation with bromine water (Limpricht, *Annalen*, 1867, **144**, 307). Benzaldehyde is also formed when tribenzylamine dibromide is decomposed with steam (Wallach, *Annalen*, 1890, **259**, 306. Compare also Smith and Kipping, T., 1912, **101**, 2560).

An attempt to prepare tri-*p*-aminophenylbismuthine by the action of boiling aniline on bismuth chloride was not successful, aniline hydrochloride and diphenylamine being produced (compare Vanino and Hauser, *Ber.*, 1900, **33**, 2271; 1901, **34**, 416).

It has not yet been possible to prepare additive compounds of tertiary bismuthines with alkyl haloids, although the corresponding arsine and stibine derivatives are well defined.

The action of benzyl chloride on triphenylbismuthine was first investigated by Michaelis and Marquardt (*Annalen*, 1889, **251**, 323), who isolated no definite product. The authors find that at room temperature the mixture reacts vigorously on standing, hydrogen chloride and diphenylmethane being produced. Tri-α-naphthylbismuthine also reacts violently with benzyl chloride, yielding hydrogen chloride, bismuth chloride, a trace of stilbene, and fluorescent products of high b. p., which have not been identified.

It was of interest to determine whether additive compounds were produced from tertiary bismuthines and acid chlorides, but in all instances examined the production of compounds of the types BiR_2X and $BiRX_2$ and a ketone was observed.

	Acid chloride.	Products.
Triphenylbismuthine.	Acetyl chloride.	Acetophenone and diphenylchlorobismuthine.
,,	Benzoyl ,,	Benzophenone and diphenylchlorobismuthine.
Tri-*p*-tolylbismuthine.	Acetyl ,,	*p*-Tolyldichlorobismuthine (Challenger and Allpress, T., 1921, **119**, 917). Ketone not isolated in sufficient quantity.
Triphenylstibine.	Benzoyl ,,	No action.

These results are in close agreement with those of Waga (*Annalen*, 1894, **282**, 323), who treated magnesium diphenyl with acid chlorides.

Triphenylbismuthine and alcoholic mercuric chloride give mercury phenyl chloride (Gillmeister, *Ber.*, 1897, **30**, 2844). It seemed probable that the bismuth oxychloride also isolated arose from diphenylchlorobismuthine produced and decomposed thus :

$$BiPh_3 + HgCl_2 = BiPh_2Cl + HgPhCl;$$
$$BiPh_2Cl + H_2O = BiOCl + 2C_6H_6.$$

This has now been proved to be the case, diphenylchlorobismuthine and mercury phenyl chloride being produced in dry ethereal solution. It was not possible to decide with certainty whether an additive product, $Ph_3Bi,HgCl_2$, was primarily formed.

Triphenylstibine and alcoholic mercuric chloride give no additive product, but form mercury phenyl chloride, antimony trichloride, mercurous chloride, and triphenylstibine dichloride. The three tritolylstibines form additive products, of which the *o*-derivative is stable, whilst with alcohol the *m*- and *p*-isomerides give the corresponding mercuric tolyl chlorides (Michaelis and Genzken, *Annalen*, 1887, **242**, 164 *et seq*.).

This phenylating action of triphenylbismuthine seems further exemplified by its behaviour with silver nitrate (Challenger and Allpress, T., 1921, **119**, 916). These results led to a study of the reactions between triphenylbismuthine and the chlorides of tervalent arsenic, antimony, and phosphorus, and this has shown that double decomposition occurs to a certain extent in all cases, the phenyl radicle passing from bismuth to arsenic, antimony, and phosphorus, the halogen travelling in the opposite direction. These results and some others having a bearing on the question may conveniently be summarised.

*Interaction of Organo-metallic Compounds with Inorganic Halogen Derivatives.**

			Products.
1	Ph_3Bi	PCl_3	Ph_2BiCl; $PhPCl_2$; Ph_2PCl.
2	,,	$AsCl_3$	Ph_2BiCl; $PhAsCl_2$; Ph_2AsCl.
3	,,	$SbCl_3$	Ph_2BiCl; Ph_3SbCl_2.
4	,,	$BiCl_3$	Ph_2BiCl.
5	,,	$HgCl_2$	Ph_2BiCl; $HgPhCl$.
6	,,	$TlCl_3$	Ph_2BiCl; Ph_2TlCl.†
7	,,	$CuCl_2$	Ph_2BiCl; Cu_2Cl_2. No Ph_3BiCl_2.
8	,,	$AgNO_3$	Probably $AgNO_3,2AgPh$.
9	$(C_{10}H_7)_3Bi$	$AsCl_3$	$(C_{10}H_7)_2AsCl$; $BiOCl$ and $C_{10}H_8$ (from $C_{10}H_7{\cdot}BiCl_2$?).
10	$SbPh_3$	$BiCl_3$	$SbPh_3Cl_2$; Bi_2Cl_4 (?).
11	,,	$TlCl_3$	$SbPh_3Cl_2$; $TlCl$.†
12	,,	$CuCl_2$	$SbPh_3Cl_2$; Cu_2Cl_2 (Michaelis and Reese, *Annalen*, 1886, **233**, 49).
13	$AsPh_3$	$BiCl_3$	Probably forms additive product. No Ph_2BiCl isolated. Odour of phenyl halogen arsines. None isolated.
14	NPh_3	$BiBr_3$	Green solid. Water regenerates NPh_3 and forms $BiOCl$. No other action.
15	$HgPh_2$	$BiBr_3$	$HgPhBr$; $BiPh_3$.
16	,,	$SbCl_3$	$HgPhCl$; $SbPh_3Cl_2$; $SbPh_2Cl_3$ (Hasenbäumer, *Ber.*, 1898, **31**, 2911).

* These reactions were usually carried out at room temperature in ethereal solution, but occasionally other solvents were employed.

† Private communication from Mr. A. E. Goddard.

The tendency of antimony to pass into the quinquevalent condition (compare Michaelis and Reese, *Annalen*, 1886, **233**, 45) is illustrated by reactions 3, 10, 11, 12, and 16. It is possible that reaction 10 is analogous to 12, giving bismuth dichloride, Bi_2Cl_4 (Schneider, *Pogg. Ann.*, 1855, **96**, 130; Weber, *ibid.*, 1859, **107**, 596). The contrast between reactions 2 and 3 is very striking. Reaction 14 is probably analogous to the production of dark green or blue compounds from tertiary aromatic amines and the pentachlorides of phosphorus and antimony (Wieland, *Ber.*, 1907, **40**, 4279).

Whilst the transfer of a phenyl group from nitrogen to bismuth seems impossible, only slightly better results were obtained with bismuth chloride and triphenylarsine, from which it would appear that the course of reactions of this type is not solely determined by considerations of solubility. This conclusion is strengthened by the fact that whilst the phenyl group can be easily transferred from mercury to phosphorus, arsenic, antimony, or bismuth, triphenylphosphine and triphenylarsine have little or no tendency to convert mercuric chloride to mercury phenyl chloride, although the analogous stibine and bismuthine readily do so.

In the reactions here described the migration of phenyl groups from one element to another occurs in the presence of a halogen atom. Schlenk and Holtz (*Ber.*, 1917, **50**, 262) describe the production of the sparingly soluble lithium methyl by interaction of lithium ethyl and mercury dimethyl in benzene–light petroleum at the ordinary temperature. Lithium phenyl was similarly prepared by the use of mercury diphenyl in benzene solution.

So far as the authors are aware, no other reactions of this type have been recorded among organo-metallic compounds.* Accordingly, mercury diphenyl and tri-α-naphthylbismuthine were heated in benzene solution, but mercury di-α-naphthyl was not detected. At 200°, however, in the absence of a solvent, an interchange of groups was found to occur, mercury di-α-naphthyl, triphenylbismuthine, and diphenyl-α-naphthylbismuthine being obtained.

Tri-*p*-tolylbismuthine and mercury diphenyl at 180° similarly gave rise to mercury di-*p*-tolyl, but under the same conditions tri-*p*-tolylbismuthine and mercury di-α-naphthyl were unchanged. It would thus appear that the α-naphthyl group has a greater affinity for mercury than the phenyl or *p*-tolyl group. This is confirmed by our observation that mercury di-α-naphthyl is produced by the action of magnesium α-naphthyl bromide on mercury phenyl bromide, presumably according to the equation $2C_{10}H_7{\cdot}MgBr + HgPhBr = Hg(C_{10}H_7)_2 + MgPhBr + MgBr_2$, and not by the decomposition of the unknown mercury α-naphthylphenyl, $2C_{10}H_7{\cdot}HgPh = Hg(C_{10}H_7)_2 + HgPh_2$, since only traces of mercury diphenyl could be detected (compare Hilpert and Grüttner, *loc. cit.*).

A most interesting example of this type of reaction is afforded by the ready production of diphenyl-α-naphthylbismuthine by the fusion of tri-α-naphthylbismuthine and triphenylbismuthine at 190°. The extension of this method to the preparation of other mixed bismuthines is under investigation. A preliminary experiment appeared to indicate that this reaction is reversible. No interaction was observed between tri-α-naphthylbismuthine and tri-*p*-tolylarsine at 200°.

EXPERIMENTAL.

Tri-p-*chlorophenylbismuthine.*

An ethereal solution of magnesium *p*-chlorophenyl bromide prepared from *p*-chlorobromobenzene (50 grams), magnesium

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* Apart from the work of Frankland on the methyl and ethyl derivatives of zinc and mercury (*Annalen*, 1859, **111**, 57. Compare Hilpert and Grüttner, *Ber.*, 1915, **48**, 906)

(6·3 grams), and iodine (0·5 gram) was treated with 24·6 grams of bismuth chloride in dry ether. A vigorous reaction took place, a yellow solid being deposited. The ether was removed, the mixture heated at 100° for four hours, treated with water, halogenobenzenes and any diphenyl derivatives were removed in steam, and the filtered residue was extracted with acetone. The solution deposited a colourless solid, which, on crystallisation from a mixture of ethyl acetate and acetone, melted at 116° (Found: Bi = 38·21, 38·19; Cl = 19·79, 19·78. $C_{18}H_{12}Cl_3Bi$ requires Bi = 38·34; Cl = 19·61 per cent.).

Tri-*p*-chlorophenylbismuthine is easily soluble in most organic solvents, but sparingly so in alcohol or light petroleum. With hydrochloric acid, chlorobenzene is produced.

When heated for several hours with 1 mol. of magnesium phenyl bromide, the ether distilled, and the residue, after three hours at 100°, decomposed with water, only unchanged bismuthine, diphenyl and bismuth oxybromide (0·1 gram) were isolated.

When the bismuthine (2 grams) was heated with concentrated alcoholic aqueous ammonia for five hours at 100° or at 160° in a sealed tube for four hours, 1·9 grams were recovered unchanged and no ammonium chloride was formed.

Tri-*p*-chlorophenylbismuthine dichloride was prepared from the bismuthine and chlorine in chloroform–light petroleum solution, and on crystallisation from the same solvents formed a colourless solid, m. p. 141°, readily soluble in chloroform or benzene, but sparingly so in light petroleum. The yield was almost quantitative (Found: Bi = 33·39; Cl = 28·68. $C_{18}H_{12}Cl_5Bi$ requires Bi = 33·91; Cl = 28·90 per cent.). After one hour at 100° the dichloride did not smell of chlorobenzene and melted at 138°.

Two grams of the dichloride and 0·75 gram of silver oxide were suspended in moist acetone, after two days the mixture was filtered, and the residue extracted with ethyl acetate, yielding 1·2 grams of tri-*p*-chlorophenylbismuthine (m. p. 115°).

Tri-*p*-chlorophenylbismuthine dibromide was similarly prepared and crystallised from chloroform–light petroleum; m. p. 105° (Found: Bi = 29·33 per cent.; AgCl + AgBr = 0·2063 gram. $C_{18}H_{12}Cl_3Br_2Bi$ requires Bi = 29·61 per cent.; AgCl + AgBr = 0·2053 gram). It forms colourless crystals, the m. p. varying with the rate of heating. After a few minutes at 100°, the odour of a dihalogenated benzene is apparent.

*Action of Iodine on Tri-*p*-chlorophenylbismuthine.*

When 1 gram of the bismuthine was gradually treated with 0·47 gram of iodine, both in ether–chloroform solution, a red precipitate

(0·2 gram) was produced and the temperature rose slightly. After filtration in absence of moisture and evaporation to a small bulk, light petroleum precipitated a yellow solid (0·5 gram), m. p. 113° (Found : AgCl + AgI = 0·2159. $C_{12}H_8Cl_2IBi$ requires AgCl + AgI = 0·2164 gram).

Di-*p*-chlorophenyliodobismuthine dissolves easily in chloroform or ether. On recrystallisation from chloroform–light petroleum, dry solvents (free from alcohol) being used, a red solid containing organic matter and readily soluble in most solvents was deposited with the yellow crystals, which then melted at 139°.

When the mother-liquors and washings were evaporated, the solidified residue, on treatment with hot water, gave bismuth oxyiodide and an oil which, with light petroleum, yielded *p*-chloroiodobenzene (m. p. 56°). This was treated with chlorine in chloroform solution, giving *p*-chloroiodobenzene dichloride (m. p. 110° [decomp.]).

The original red precipitate contained organic matter and turned black at 150°, but did not melt. With hydrochloric acid, halogenobenzene was liberated.

Di-p-*chlorophenylbromobismuthine and* p-*Chlorophenyldibromobismuthine.*

Tri-*p*-chlorophenylbismuthine (3 grams; 2 mols.) in dry ether was treated with a similar solution of bismuth bromide (1·24 grams; 1 mol.), when some bismuth oxybromide was precipitated and removed. On concentration in a vacuum, colourless crystals and a trace of yellow solid separated.

The colourless substance, when crystallised from ether, melted at 159° (Found : Br = 15·95, 15·84 ;* Bi = 40·52, 40·61. $C_{12}H_8Cl_2BrBi$ requires Br = 15·64 ; Bi = 40·70 per cent.).

Di-*p*-chlorophenylbromobismuthine is easily decomposed by water and moist solvents. When warmed with alcoholic ammonia, the bismuthine is regenerated. Its solution in hot dry benzene deposits a yellow solid, m. p. 244° (Found : Br = 33·26, 33·11 ;* Bi = 43·41, 43·36 per cent. ; AgCl + AgBr = 0·1797 gram. $C_6H_4ClBr_2Bi$ requires Br = 33·35 ; Bi = 43·39 per cent. ; AgCl + AgBr = 0·1809 gram).

p-Chlorophenyldibromobismuthine is only slightly soluble in hot benzene or hot chloroform, and almost insoluble in all other solvents. It decomposes on standing for a few hours.

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* Reactive bromine estimated volumetrically by means of silver nitrate solution.

Tri-p-*bromophenylbismuthine.*

The solution of magnesium *p*-bromophenyl bromide (3 mols.) prepared from 60 grams of *p*-dibromobenzene, 6·1 grams of magnesium, 200 c.c. of dry ether, and 0·5 gram of iodine, which had an intense blue colour, was vigorously stirred and slowly treated with an ethereal solution of 26·6 grams (1 mol.) of bismuth chloride. A green solid was deposited, the ether removed, the residue heated at 100° for four hours, decomposed with water, and distilled with steam to remove bromobenzene and any dibromodiphenyl. The filtered residue was extracted three times with acetone, which on concentration deposited a viscous, brown oil. After prolonged treatment with acetone, chloroform, and alcohol, this became solid and was crystallised from a mixture of acetone and ethyl acetate, when it formed a white, granular powder, m. p. 149° (Found: Bi = 30·67, 30·73; Br = 35·23, 35·34. $C_{18}H_{12}Br_3Bi$ requires Bi = 30·77; Br = 35·49 per cent.).

Tri-*p*-bromophenylbismuthine is very soluble in ether, chloroform, acetone, or ethyl acetate, less so in light petroleum or alcohol, and with hydrochloric acid yields bromobenzene.

An experiment performed with 4·5 molecules of the Grignard reagent yielded, in addition to the bismuthine, a small quantity of white solid, m. p. 220° on recrystallisation from ethyl acetate. This awaits investigation (compare Lederer, *Ber.*, 1916, **49**, 2004).

Tri-*p*-bromophenylbismuthine dichloride was prepared as usual (see p. 109) and on crystallisation from dry chloroform–light petroleum melted at 155° (Found: Bi = 27·79 per cent.; AgCl + AgBr = 0·1984 gram. $C_{18}H_{12}Cl_2Br_3Bi$ requires Bi = 27·85 per cent.; AgCl + AgBr = 0·1982 gram). It forms white, matted crystals readily soluble in chloroform, benzene, or acetone, insoluble in light petroleum. The m. p. varied slightly, the same specimen melting at 151°, 153°, and 155° when the rate of heating was altered.

Tri-*p*-bromophenylbismuthine dibromide was obtained from the bismuthine and bromine in chloroform–light petroleum solution, and on crystallisation from dry benzene–light petroleum formed a faintly yellow solid, m. p. 107° (decomp.). When heated at 100°, the odour of dibromobenzene was very pronounced (Found: Bi = 24·86; Br = 48·09. $C_{18}H_{12}Br_5Bi$ requires Br = 47·81; Bi = 24·88 per cent.).

On shaking 2 grams of the dibromide, 0·56 gram of silver oxide, and 15 c.c. of acetone, a reaction quickly occurred. The acetone filtrate had a very pungent and lachrymatory odour, and was concentrated in a current of air. This removed the irritant, and tri-

p-bromophenylbismuthine was deposited together with a trace of unchanged dibromide (m. p. 98°).

Interaction of Bismuth Chloride and Magnesium Benzyl Chloride.

On addition of 11·2 grams of bismuth chloride (1 mol.) in dry ether to an ethereal solution of 3 mols. of magnesium benzyl chloride (2·8 grams of magnesium; 15·0 grams of benzyl chloride), a yellow precipitate was deposited. Water was added and the ether separated and distilled, yielding only dibenzyl. The precipitate, on extraction with alcohol, gave a yellow solution, which decomposed in air, bismuth oxychloride and benzaldehyde being produced. The latter was removed in steam, and converted into its semicarbazone, which melted at 212° and did not depress the m. p. of pure benzaldehydesemicarbazone.

The residue from the steam distillation, on extraction with alcohol, yielded an oil which contained no bismuth and did not decolorise a solution of bromine in chloroform.

Action of Aniline on Bismuth Chloride.

Ten grams (1 mol.) of bismuth chloride and 18 grams (6 mols.) of aniline were heated for thirty-five hours at 190°, forming a viscous mass. Hot water removed 6 grams of aniline as hydrochloride, and a blue solid remained which dissolved readily in alcohol, leaving bismuth oxychloride. From the alcohol, by evaporation and extraction with light petroleum, a small quantity of diphenylamine (m. p. 52°) was isolated, together with unchanged aniline. The residue contained all the colouring matter, melted above 200°, and was free from bismuth. On treatment with solvents, nothing further was isolated.

Action of Acetyl Chloride on Triphenylbismuthine.

When the bismuthine (8·5 grams) was treated with 1·52 grams of acetyl chloride in carbon tetrachloride, a vigorous reaction took place, but no hydrogen chloride was liberated. The solution was boiled for four hours, when it became yellow and deposited a brown precipitate. The liquid, still containing acetyl chloride, was decanted and the precipitate (m. p. 175°) washed with light petroleum and extracted with dry benzene, which removed some inorganic matter. The filtrate, on addition of light petroleum, deposited diphenylchlorobismuthine.

The mother-liquor and washings yielded a yellow oil which solidified at 0°. This was treated with hot, dilute hydrochloric acid to remove bismuth compounds, washed with water, and poured into a hot aqueous solution of semicarbazide hydrochloride and sodium acetate, when acetophenonesemicarbazone (m. p. 195°) was deposited on cooling; the pure product melted at 198°.

Action of Benzoyl Chloride on Triphenylbismuthine.

The bismuthine (5·5 grams; 1 mol.), benzoyl chloride (1·77 grams; 1 mol.), and carbon tetrachloride (15 c.c.) were heated for six hours, until the odour of benzoyl chloride disappeared. Extraction with chloroform and light petroleum gave a grey solid, which was recrystallised from dry benzene–light petroleum, colourless crystals (m. p. 183°) being obtained. These did not depress the m. p. of diphenylchlorobismuthine and with ammonia formed triphenylbismuthine (see p. 105).

The chloroform–petroleum extracts yielded an oil which on treatment with dilute hydrochloric acid gave a viscous solid. This, when dried and washed with light petroleum, formed pale yellow crystals (m. p. 47°) resembling benzophenone in odour. With hydroxylamine hydrochloride these yielded crystals, m. p. 140°, not depressing the m. p. of benzophenoneoxime.

*Action of Acetyl Chloride on Tri-*p*-tolylbismuthine.*

No reaction took place in the cold when the bismuthine (2 grams; 1 mol.) and acetyl chloride (0·5 gram; 2 mols.) were mixed in carbon tetrachloride solution. After four hours on the water-bath, the cold solution deposited a white solid (1·4 grams; m. p. 179°) and a small quantity of a yellow substance (m. p. 200°). The deposit was recrystallised from cold dry chloroform–light petroleum, giving di-*p*-tolylchlorobismuthine (m. p. 180°) (Found: Bi = 48·75; Cl = 8·30. $C_{14}H_{14}ClBi$ requires Bi = 48·88; Cl = 8·33 per cent.).

The mother-liquors and washings were united and heated for five hours, yellow crystals (m. p. 206°), which were almost certainly *p*-tolyldichlorobismuthine (m. p. 206°), being deposited.

The supernatant liquid was decanted and distilled in steam, giving traces of a colourless oil which had a strong, aromatic odour, but did not react with semicarbazide hydrochloride.

Benzoyl Chloride and Triphenylstibine.

The stibine (3 grams) and benzoyl chloride (1·2 grams) were boiled with carbon tetrachloride for four hours. No reaction occurred even after removing the solvent and heating for four hours at 100°. Much benzoyl chloride remained unchanged, and on treatment with chlorine 2·5 grams of stibine were recovered as dichloride (3 grams).

Phosphorus Trichloride and Triphenylbismuthine.

The bismuthine (5 grams) was treated with phosphorus trichloride (1·6 grams), both in dry ether, colourless crystals being immediately deposited, which, on crystallisation, melted at 183° and did not depress the m. p. of diphenylchlorobismuthine.

The ether yielded a yellow, viscid oil (*A*) containing halogen but no bismuth. A portion solidified on treatment with chlorine in a freezing mixture; the product, m. p. 64°, fumed in air, rapidly changing to a viscous liquid and was in all probability crude phosphenyl tetrachloride (m. p. 73°). The oil (*A*) similarly gave an unstable solid when treated with bromine at 0°. The presence of phenyldichlorophosphine (phosphenyl chloride) was further shown by conversion of (*A*) into phenylphosphinous acid, $PhP(OH)_2$. The oil was dropped slowly into ice-water, immediate reaction taking place. The mixture was boiled and rapidly filtered. The solution, on concentration in a stream of carbon dioxide, deposited a white solid, m. p. 68°. Phenylphosphinous acid melts at 70°.

A boiling aqueous solution of the acid reduced mercuric chloride to mercurous chloride. The phenylphosphinic acid, $PhPO(OH)_2$, formed in this way was not isolated.

Arsenic Trichloride and Triphenylbismuthine.

To 8 grams (1 mol.) of the bismuthine in dry ether 3·3 grams of arsenic trichloride in the same solvent were slowly added. In the course of ten minutes 7·2 grams of colourless crystals were deposited which, washed with dry ether and recrystallised from dry benzene–light petroleum, melted at 183°, contained halogen, but no arsenic, and did not depress the m. p. of diphenylchlorobismuthine (Found : Bi = 52·55. $C_{12}H_{10}ClBi$ requires Bi = 52·32 per cent.). From the ethereal solution a pale yellow, viscid oil (containing halogen but no bismuth) was isolated. This had a very pungent odour and a destructive action on the skin. It was fluid below 0° and stable to water, but with dry chlorine at 0° gave a yellow solid, m. p. 40° (not sharp). This was probably phenylarsenic chloride, $C_6H_5{\cdot}AsCl_4$, m. p. 45° (La Coste and Michaelis, *Annalen*, 1880, **201**, 191).

The bulk of the oil, in aqueous suspension, was treated with chlorine for some hours, boiled, and filtered. The solution deposited white crystals, which decomposed at 157°, gave silver and copper salts, and were doubtless phenylarsinic acid. The yellow oil must therefore have contained phenyldichloroarsine.

In a second experiment, the mixture remained for twelve hours after the deposition of diphenylchlorobismuthine (m. p. 184°), when a yellow, unstable solid, sparingly soluble in hot benzene, was precipitated. It contained organic matter and melted above 185°, but could not be purified.

The ethereal solution was decanted and evaporated. The residual oil was suspended in water, treated with chlorine, boiled, and cooled, when diphenylarsinic acid, m. p. 174°, was deposited. The barium salt was analysed (Found: Ba = 20·86. $C_{24}H_{20}O_4As_2Ba$ requires Ba = 20·83 per cent.). The yellow oil therefore contained diphenylchloroarsine. Probably both experiments gave a mixture of the chloroarsines.

Antimony Trichloride and Triphenylbismuthine.

One gram (1 mol.) of antimony trichloride in dry ether was added to 2 grams (1 mol.) of the bismuthine in the same solvent, when a white precipitate consisting largely of inorganic compounds of bismuth and antimony was produced. The decanted ether deposited bismuth oxychloride, but on concentration gave a solid, m. p. 140°, containing chlorine and antimony, but no bismuth. This on crystallisation from chloroform–light petroleum did not depress the m. p. of triphenylstibine dichloride. When evaporated with aqueous alcohol and crystallised from benzene, triphenylstibine hydroxychloride (m. p. and mixed m. p. 217°) was obtained.*

A chloroform extract of the first deposit yielded more triphenylstibine dichloride and also diphenylchlorobismuthine (m. p. 184°), which was further characterised by conversion to triphenylbismuthine with ammonia.

Bismuth Trichloride and Triphenylstibine.

Bismuth trichloride (7·7 grams; 1 mol.) was slowly added to the stibine (8·6 grams; 1 mol.), both in dry ether. The first few drops produced a transient, brown coloration and a permanent, yellow precipitate, containing inorganic compounds of bismuth and antimony.

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* It is interesting that the m. p. of a mixture of triphenylstibine dichloride and triphenylbismuthine dichloride is only four degrees lower than that of the pure triphenylstibine dichloride (m. p. 143°). The m. p.'s taken simultaneously were: Triphenylstibine dichloride = 143°. Mixture = 139°. Triphenylbismuthine dichloride = 139°.

On the next day, the ether was decanted, evaporated in absence of moisture, and the yellow, semi-solid residue extracted with light petroleum, which discharged the colour. The extract deposited triphenylstibine dichloride, m. p. 142°, which was converted to the hydroxychloride (m. p. 217°; mixed, 217°).

The mother-liquors and the original solution gave no trace of any organic bismuth compound.

Arsenic Trichloride and Tri-α-naphthylbismuthine.

Three grams of the bismuthine in a mixture of dry benzene and dry chloroform were treated with 0·93 gram of arsenic trichloride in dry ether. During fifteen hours, a dark solid free from organic matter and containing arsenic was deposited and the yellow solution became green. The decanted mother-liquor was evaporated spontaneously in absence of moisture, yielding di-α-naphthylchloroarsine, m. p. 167° (Matsumiya, *J. Tōkyō Chem. Soc.*, 1920, **41**, 868) (Found: Cl = 9·57; As = 20·49. $C_{20}H_{14}ClAs$ requires Cl = 9·72; As = 20·56 per cent.).

Bismuth oxychloride and naphthalene (m. p. 80°; picrate, m. p. 148°) were produced at the same time, probably as decomposition products of α-naphthyldichlorobismuthine.

The dark solid was insoluble in chloroform or benzene. Dry ether extracted bismuth chloride.

Bismuth Tribromide and Triphenylamine.

With bismuth bromide (5·5 grams; 1 mol.) and triphenylamine (3·0 grams; 1 mol.), both in dry ether, a dark green solid was deposited. On the next day, some of the solvent was removed, when triphenylamine (m. p. 125°; mixed, 125°) was recovered. The whole of the ether was then evaporated and water added. This discharged the colour, only bismuth oxybromide and triphenylamine (m. p. 126°) being isolated.

Bismuth Trichloride and Triphenylarsine.

(*a*) Bismuth trichloride (7 grams; 1 mol.) in dry ether was slowly added to an ethereal solution of the arsine (6·8 grams; 1 mol.). No precipitate was formed, but the solution on evaporation deposited a yellow, viscous solid. This with cold light petroleum and with benzene yielded triphenylarsine, m. p. 59° on recrystallisation. The crude arsine contained traces of a halogen compound (copper-wire test) and had the odour of a phenylchloroarsine, but no such substance was isolated. A portion of the yellow residue was treated with water, when all colour was discharged. Extraction with chloroform then gave bismuth oxychloride and triphenylarsine (m. p. 58°) containing traces of halogen. The remainder of the oil was decomposed with ammonia, and extracted with alcohol, triphenylarsine (m. p. 53°; recrystallised, 58°) being obtained. Treatment of the crude arsine with hydrochloric acid and hydrogen sulphide yielded a trace of bismuth sulphide, indicating the probable presence of traces of triphenylbismuthine, arising from diphenylchlorobismuthine and ammonia (see p. 105).

(*b*) Bismuth chloride (5·1 grams) and the arsine (5 grams) were boiled with toluene. After six hours the solution became yellow and, on cooling, deposited colourless, hygroscopic crystals (m. p. 80—90°), becoming yellow in air. These were probably a double compound of the arsine and bismuth chloride, since with water only triphenylarsine and bismuth oxychloride were obtained.

The mother-liquor was evaporated and treated with ammonia; careful fractionation yielded only triphenylarsine (m. p. 59°). A slight odour of a phenylchloroarsine was observed, but no such compound or any triphenylbismuthine was isolated.

The Action of Hydrated Cupric Chloride on Triphenylbismuthine.

The bismuthine (2 grams), cupric chloride (1·55 grams; 2 mols.), and alcohol (20 c.c.) were vigorously shaken together. The solution was decolorised in fifteen minutes and the theoretical quantity (0·9 gram) of cuprous chloride precipitated. The filtered solution, when evaporated at room temperature, gave three deposits of diphenylchlorobismuthine (m. p. 183°, 183°, 179°). The last was washed with chloroform, but the extract contained no triphenylbismuthine dichloride. Similar results were obtained in chloroform solution. This reaction is being further investigated with a view to the isolation of an organo-copper compound.

Interaction of Mercuric Chloride and Triphenylbismuthine.

Mercuric chloride (1·85 grams; 1 mol.) was added to triphenylbismuthine (3 grams; 1 mol.), both in dry ether. A solid, m. p. 164°, was at once precipitated, which was dissolved in a large volume of cold dry benzene. Addition of light petroleum gave mercury phenyl chloride, m. p. 250°. The mother-liquor yielded diphenylchlorobismuthine (m. p. 183°), which with alcoholic ammonia gave triphenylbismuthine.

A portion of the original ethereal filtrate was concentrated, when more solid (m. p. 166°) separated. This and the mother-liquor yielded the same products as before. The original precipitate (m. p. 166°),* when treated with hot glacial acetic acid or with water, gave mercury phenyl chloride and inorganic bismuth compounds. The aqueous solution was free from metallic radicles, but contained hydrochloric acid.

Interaction of Triphenylbismuthine and Benzyl Chloride.

The bismuthine was treated with excess of benzyl chloride in dry ether and, after eight weeks at room temperature, a trace of bismuth oxychloride was deposited. On removing the ether, most of the triphenylbismuthine was recovered.

Spontaneous reaction took place when the mixture, free from ether, was left in a desiccator, hydrogen chloride and a brown, oily mass being produced. On extraction with chloroform and light petroleum, bismuth oxychloride remained. The solvent was then evaporated and the residue distilled, when a viscous liquid (b. p. 255—265°) was obtained. This was probably diphenylmethane, since oxidation with chromic acid gave benzophenone, which was isolated as the oxime (m. p. 140°).

Interaction of Tri-α-naphthylbismuthine and Mercury Diphenyl.

The bismuthine (5 grams; 1 mol.) and mercury diphenyl (3 grams; 1 mol.) were boiled for two hours in benzene–chloroform solution, but on fractional crystallisation were recovered unchanged.

The same quantities of the bismuthine and mercury diphenyl were then heated in an oil-bath at 200°. The mixture softened at 180° and melted at 200°. After two and a half hours, it was cooled and extracted with acetone. Practically no inorganic matter remained. The residue was crystallised from benzene, yielding mercury di-α-naphthyl (m. p. 245°; mixed, 243°), which was characterised by conversion to mercury α-naphthyl bromide (m. p. 198°).

The acetone extract yielded an oil, a portion of which was distilled with steam, yielding naphthalene (m. p. 82°). The residue could not be crystallised from any solvent and appeared to be a mixture of triphenylbismuthine and diphenyl-α-naphthylbismuthine. The whole of the acetone-soluble products were therefore dissolved

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* Although three deposits, m. p. 164°, 166°, 166°, were obtained, analysis appeared to indicate that the product was not $Bi(C_6H_5)_3,HgCl_2$ nor even an equimolecular mixture of $(C_6H_5)_2BiCl$ and $C_6H_5{\cdot}HgCl$. Production and partial separation of these last-named substances probably occur even in dry ethereal solution.

in chloroform–light petroleum and treated with chlorine (Challenger and Wilkinson, this vol., p. 95), whereby a viscous solid (*A*) was precipitated. The mother-liquors deposited diphenyl-α-naphthylbismuthine dichloride (m. p. 140°; mixed, 139°). This was decomposed with ammonium sulphide (Challenger and Wilkinson, *loc. cit.*) and the product recrystallised from alcohol, giving crude diphenyl-α-naphthylbismuthine (m. p. 113°). The quantity was too small for further purification.

The solid (*A*), on treatment with chloroform and ether, yielded (*a*) a small quantity of mercury phenyl chloride (m. p. 249°), resulting from the action of chlorine on unchanged mercury diphenyl, and (*b*) crude triphenylbismuthine dichloride (m. p. 120°), which with moist silver oxide in acetone yielded triphenylbismuthine (m. p. 76°; mixed, 77°), thereby confirming the presence of this substance in the original fused mixture.

Interaction of Triphenylbismuthine and Tri-α-naphthylbismuthine.

Triphenylbismuthine (5 grams; 2 mols.) and tri-α-naphthylbismuthine (3·4 grams; 1 mol.) were heated at 190° for two hours, cooled, extracted with acetone, and filtered. The residue contained some inorganic bismuth compound together with a little unchanged tri-α-naphthylbismuthine (m. p. 235°). The acetone extract deposited diphenyl-α-naphthylbismuthine (m. p. 112°), which, after several crystallisations from chloroform-alcohol, melted at 118° and was characterised by conversion to the dichloride (m. p. 140°; mixed, 140°). The acetone liquors were evaporated and distilled with steam, whereby naphthalene (m. p. 87°) was removed. The residue was unchanged triphenylbismuthine (m. p. 76°).

*Tri-*p*-tolylbismuthine and Mercury Diphenyl.*

On heating the bismuthine (5 grams; 1 mol.) and mercury diphenyl (3·7 grams; 1 mol.), complete fusion took place at 120°. After one hour the mass became quite solid again at this temperature and only partly melted when kept at 180° for one hour. The cold mixture was extracted with acetone, filtered, and the residue crystallised from benzene, when mercury di-*p*-tolyl (3 grams) was obtained (m. p. 237°). This was converted by bromine in chloroform to mercury *p*-tolyl bromide (m. p. 226°) and *p*-bromotoluene. The acetone mother-liquors deposited a solid (m. p. 88°), which, when recrystallised from acetone, yielded tri-*p*-tolylbismuthine (m. p. 120°; mixed, 120°).

The mother-liquors gave an oil which could not be crystallised.

With chlorine in chloroform–light petroleum solution it yielded mercury phenyl chloride (m. p. 249°), indicating the presence of unchanged mercury diphenyl. The final mother-liquors deposited crystals (m. p. 119—124°), which were probably a mixture of triphenylbismuthine dichloride and tri-*p*-tolylbismuthine dichloride.

Action of Magnesium α-Naphthyl Bromide on Mercury Phenyl Bromide.

Mercury phenyl bromide (8 grams) was gradually added to the Grignard reagent (4 mols.) in benzene–ether solution. Rapid solution occurred, and after half an hour at room temperature the mixture was cooled in ice, decomposed with excess of 1 per cent. sulphuric acid, and filtered. A portion of the benzene solution was evaporated at room temperature, the residue yielding about 3 grams of mercury di-α-naphthyl (m. p. 245°). Since all rise of temperature had been avoided, it appeared very unlikely that this could have been formed by decomposition of mercury α-naphthylphenyl. The remainder of the benzene solution was therefore distilled with steam to remove naphthalene, and crystallised from benzene as before. The mother-liquors finally yielded a small amount of a solid, which on treatment with bromine in chloroform–light petroleum solution gave a trace of mercury phenyl bromide. Another experiment gave similar results.

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THE "LEVINSTEIN" RESEARCH LABORATORY,
THE UNIVERSITY, MANCHESTER. [*Received, November* 17*th*, 1921.]
