IV.—*Organo-derivatives of Bismuth. Part II. The Stability of Derivatives of Quinquevalent Bismuth.*

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In a previous communication (T., 1914, **105**, 2211) it was stated that certain derivatives of quinquevalent bismuth are characterised by the ease with which they can be degraded to compounds in which bismuth functions as a triad. For example, it was not found possible to prepare tetraphenylbismuthonium bromide or triphenylethylbismuthonium bromide; moreover, triphenylbismuthine dibromide and tri-α-naphthylbismuthine dibromide readily eliminate aryl bromide under the influence of heat.

This led to an investigation of the stability of tertiary bismuthine dihaloids containing dissimilar halogen atoms, since the question as to which of these halogens would be eliminated in union with an aryl radicle seemed to be of interest.

Attempts were therefore made to prepare additive products of triphenyl- and tri-α-naphthyl-bismuthine, with iodine, iodine chloride, and iodine bromide, and also of triphenylbismuthine with cyanogen, cyanogen iodide, cyanogen bromide, and cyanamide.

When triphenylbismuthine and iodine monobromide or iodine monochloride interact, no additive product can be isolated, but iodobenzene and either diphenylbromobismuthine or diphenylchlorobismuthine (see p. 19) are produced in yields which approach closely to those demanded by the equation:

$$BiPh_3 + IX = BiPh_2X + PhI.$$

Chlorobenzene or bromobenzene could not be detected. Similarly, cyanogen iodide gives iodobenzene and *diphenylcyanobismuthine*, which decomposes at about 210°.

The reaction of triphenylbismuthine with iodine is somewhat complicated, and certain points in this connexion yet remain to be elucidated, but owing to the inability of one of us to continue the investigation the results obtained up to the present may briefly be summarised.

In ether or light petroleum solution no di-iodide appears to be formed (compare Gillmeister, *Ber.*, 1897, **30**, 2843), the products of the reaction being diphenyliodobismuthine, iodobenzene, and a red powder containing much organic matter and more than 50 per cent. of iodine.

The red compound is also obtained when iodine is added to a solution of diphenyliodobismuthine, so is probably a product of a secondary reaction. It cannot be triphenylbismuthine di-iodide, since this contains only about 26 per cent. of iodine.

Moreover, the fact of the formation of diphenyliodobismuthine and iodobenzene points to the extreme instability of such a substance. The results obtained with iodine and tri-α-naphthylbismuthine also support this conclusion. The evidence obtained up to the present points strongly in one direction, but owing to the existence of such compounds as triphenylarsine tetraiodide, Ph_3AsI_4, and tri-*p*-tolylarsine tetraiodide, $(C_7H_7)_3AsI_4$ (Michaelis, *Annalen*, 1902, **321**, 203), further discussion is undesirable until these compounds have been prepared for the purposes of comparison.

Gillmeister mentions that iodobenzene, bismuth oxyiodide, and diphenyliodobismuthine are obtained when triphenylbismuthine dichloride and potassium iodide interact and the mixture is poured into water. We have confirmed these results, but find that the red compound referred to above is also a product of the reaction.

The action of iodine monochloride and monobromide on tri-α-naphthylbismuthine is similar to that on the triphenyl compound. No additive product was isolated, but α-iodonaphthalene in yields somewhat below the theoretical was obtained.

With iodine and tri-α-naphthylbismuthine the products are bismuth iodide, α-iodonaphthalene (isolated as dichloride), unchanged bismuthine, and (probably) di-α-naphthyliodobismuthine.

The results so far described, excluding those with iodine, show that when two dissimilar halogen atoms, and, in the case of triphenylbismuthine, cyanogen iodide, enter into reaction with a tertiary aromatic bismuthine the more negative atom or group remains attached to bismuth, whilst iodine is eliminated as aryl iodide. In the case of tri-α-naphthylbismuthine, since the yields of α-iodonaphthalene are not quite quantitative, the formation of some α-bromo- or α-chloro-naphthalene is not absolutely excluded, but seems improbable.

The action of iodine haloids on unsymmetrical (or mixed) bismuthines is being investigated. It might be expected that iodine, being a comparatively positive element, would be eliminated in union with the most strongly negative or unsaturated hydrocarbon radicle present.

In a preliminary experiment diphenyl-α-naphthylbismuthine was treated with iodine monobromide, and α-iodonaphthalene was detected in the solution.

The interaction of diphenylbromobismuthine and iodine chloride is also instructive, a yield of iodobenzene 77 per cent. of that required by the equation $Ph_2BiBr + ICl = PhBiClBr + PhI$ being obtained.

As regards the experiments with cyanogen and its derivatives it might be expected that the unknown compound $Ph_3Bi(CN)_2$ would be very stable owing to the strongly negative nature of both the cyano- and the phenyl group. Under the conditions employed up to the present, however, cyanogen does not react with triphenylbismuthine; moreover, under conditions in which the iodide readily reacts with triphenylbismuthine, cyanogen bromide has no action.

Von Braun (*Ber.*, 1900, **33**, 1438, 2728; 1902, **35**, 1279; 1903, **36**, 1196; 1907, **40**, 3914, 3933) has shown that cyanogen bromide is without action on triphenylamine even when heated in sealed tubes, although it reacts with tribenzylamine. With aliphatic or aliphatic-aromatic amines an unstable additive product is obtained, which decomposes so as to yield alkyl or aryl bromide and a substituted cyanamide.

Unsaturated radicles such as allyl are particularly easily eliminated as bromide.

Cyanamide, which might have been expected to yield aniline and diphenylcyanobismuthine when heated with triphenylbismuthine, polymerised to dicyanodiamide without otherwise reacting.

EXPERIMENTAL.

Diphenylchlorobismuthine.

Marquardt (*Annalen*, 1889, **251**, 326) states that diphenylchlorobismuthine, $BiPh_2Cl$, appears to be formed by the interaction of triphenylbismuthine and bismuth chloride in glacial acetic acid or ethyl acetate, but that he was unable to crystallise it.

Since one of us has observed that triphenylbismuthine is decomposed by glacial acetic acid, and since diphenylchlorobismuthine is decomposed by water or alcohol (both frequently present in ordinary ethyl acetate) the reason for this non-success may not be far to seek. An ethereal solution of 2·5 grams of triphenylbismuthine (2 mols.) was treated with 1·3 grams of bismuth chloride, likewise dissolved in anhydrous ether. Three grams of colourless crystals, melting at 184—185°, were deposited, and on recrystallisation from benzene the melting point was unchanged.

The results of analysis indicate the presence of traces of phenyldichlorobismuthine:

0·3727 gave 0·2202 Bi_2O_3. Bi=52·94.*

$C_{12}H_{10}ClBi$ requires Bi=52·33 per cent.

$C_6H_5Cl_2Bi$,, Bi=58·43 ,, ,,

Diphenylchlorobismuthine forms colourless crystals fairly readily soluble in dry benzene, toluene, or chloroform, but much less so in ether or light petroleum.

Alcohol and moist solvents cause decomposition as with all compounds of the type BiR_2X and $BiRX_2$. On keeping in a sealed tube gradual decomposition occurs, and benzene is produced. Concentrated hydrochloric acid readily liberates benzene.

Action of Iodine Monochloride on Triphenylbismuthine.

Five grams of triphenylbismuthine in dry ether were treated with 1·85 grams of iodine chloride (1 mol.) in the same solvent. A brownish-yellow turbidity was produced, which quickly disappeared, pale yellow crystals (A, 3·35 grams) separating simultaneously. These melted at 182—183° after being recrystallised, and did not depress the melting point of diphenylchlorobismuthine. On evaporating the decanted ether and treating the oily residue with light petroleum, a further quantity of the crystals was obtained (B, 0·8 gram). The theoretical yield of diphenylchlorobismuthine is 4·5 grams. Deposits A and B contained traces of iodine.

On removal of the light petroleum the residual oil, when treated with chlorine in chloroform solution, gave 2·65 grams of iodobenzene dichloride, whereas the theoretical yield is 3·1 grams.

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* A second estimation gave = 52·91.

In another experiment 5 grams of triphenylbismuthine were treated with slightly more than 2·3 grams (1·3 mols.) of iodine chloride. Deposits A_1 (3·25 grams) and B_1 (1·2 grams) were obtained as before, and the yield of iodobenzene dichloride was 3·9 grams. Deposit A_1 contained practically no iodine, but B_1 contained relatively large amounts in comparison with B.

Action of Iodine Monobromide on Triphenylbismuthine.

Iodine bromide (2·35 grams; 1 mol.) dissolved in anhydrous ether was gradually added to triphenylbismuthine (5 grams) in the same solvent. A brownish-yellow turbidity, disappearing on shaking, was produced, and yellow crystals were deposited. These melted at 154°, and after recrystallisation from chloroform, sharply at 157°. The total quantity obtained was 4·6 grams, the theoretical yield of diphenylbromobismuthine being 5 grams.

Fractional extraction of the crystals with hot benzene gave deposits melting at 156—157°, 156—157°, 148°, and 157°. The third deposit after one recrystallisation melted at 155—157°. Further recrystallisation of these deposits produced no change in melting point, so that the presence of compounds other than diphenylbromobismuthine (m. p. 157—158°), except in traces, is excluded.

The ethereal solution was distilled, and a further deposit of diphenylbromobismuthine removed by means of cold chloroform or ether. The iodobenzene remaining in the chloroform was converted into the iododichloride. The yield was 2·95 grams.

Action of Cyanogen Iodide on Triphenylbismuthine.

When 5 grams of triphenylbismuthine and 2·2 grams of cyanogen iodide ($1\frac{1}{4}$ mols.) were heated with benzene under a reflux condenser, 3·2 grams of a yellow solid separated. On distilling off the benzene and treating the oily residue with light petroleum, 0·7 gram of the yellow solid remained.*

On removing the petroleum, adding chloroform, and passing chlorine, 2·95 grams of iodobenzene dichloride were obtained.

The solid substance was recrystallised from hot alcohol, only a very small, insoluble residue remaining:

0·2396 + 10·1 c.c. 0·13N-$AgNO_3$ required 7·3 c.c. $N/10$-NH_4CNS. CN = 6·29.

$C_{13}H_{10}NBi$ requires CN = 6·71 per cent.

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* This deposit contained a certain amount of an iodine compound. On crystallising from benzene, however, a very small quantity of yellow solid remained undissolved, whilst the solution deposited white crystals identical with the main product. The formation of the yellow insoluble substance containing iodine is probably due to the excess of cyanogen iodide.

Diphenylcyanobismuthine forms colourless needles, resembling glass-wool, and smelling faintly of hydrocyanic acid. These melt and decompose at about 210°, and are sparingly soluble in hot alcohol or benzene, still less so in ether or light petroleum. On concentrating the alcoholic solution, hydrocyanic acid is evolved (recognised by conversion into ammonium thiocyanate), and on cooling, triphenylbismuthine is deposited. Warm concentrated hydrochloric acid liberates benzene and hydrocyanic acid; warm sodium hydroxide forms sodium cyanide and a yellow, insoluble substance, which is being further investigated. With silver nitrate solution diphenylcyanobismuthine readily gives silver cyanide.

Action of Iodine on Triphenylbismuthine.

A. *In Dry Ethereal Solution.*—When 10 grams of triphenylbismuthine were treated with 5·8 grams of iodine (1 mol.) a red precipitate was produced. The ether containing a yellow solid in suspension was poured off, and the red precipitate (3·5 grams) washed with dry ether.

(The yellow solid in ethereal suspension melted at 134°. Diphenyliodobismuthine forms yellow needles, melting at 133°.) After distilling about half of the ether a solid separated, which melted at 131°; this was removed, and the ether completely evaporated. The residual oil still contained bismuth. Its chloroform solution was treated with a very slight excess of bromine, in the hope of removing any triphenylbismuthine as triphenylbismuthine dibromide (m. p. 122°). The crystals which separated, however, melted after one recrystallisation at 201—202°, and did not depress the melting point of a specimen of phenyldibromobismuthine.

Their formation was obviously due to the action of bromine on diphenyliodobismuthine thus: $BiPh_2I + Br_2 = BiPhBr_2 + PhI$.

The chloroform mother liquor gave rise to 5·5 grams of iodobenzene dichloride, corresponding with 4·1 grams of iodobenzene. The theoretical yield to be expected from the equation

$$BiPh_3 + I_2 = BiPh_2I + PhI$$

is 4·65 grams. Since much iodobenzene was probably produced through the agency of the bromine, the quantity directly obtained by the action of iodine on the bismuthine is seen to be far below the theoretical.

The red precipitate, melting at about 194°, contained much iodine and organic matter, and evolved benzene on treatment with hydrochloric acid. When heated with benzene or chloroform a purplish-black residue, still containing organic matter, and a yellow solution were obtained, which on addition of light petroleum deposited a red solid.

B. *In Ether–Light Petroleum Solution.*—Five grams of triphenylbismuthine were treated with 2·9 grams of iodine. The usual brown turbidity, followed by the deposition of crystals melting at 131—134°, was produced, and the red precipitate, which this time melted at 131°, was also deposited (4·5 grams). A further quantity of yellow crystals melting at 133° was obtained by distilling off the petroleum, after which the solution contained only a trace of solid matter, and gave rise, in the usual way, to 2·4 grams of iodobenzene dichloride, corresponding with 1·8 grams of iodobenzene. The theoretical yield is 2·33 grams.

The red powder was heated with dry benzene, the yellow solution filtered, and allowed to deposit five separate crops of crystals:

Original substance red, m. p. 131°.
1st deposit. Deep red crystals, m. p. 194—198°.
2nd deposit. Paler red crystals, m. p. 130°.
3rd deposit. Orange crystals, m. p. 125°.
4th deposit. Pale yellow crystals, m. p. 127°.
5th deposit. Brown solid, m. p. above 210°.

The substance therefore decomposes on contact with hot benzene and other solvents. If it is extracted with hot dry carbon tetrachloride until the extract is no longer coloured, the residue is brownish-black, and consists principally of bismuth iodide.

Action of Iodine Monochloride on Tri-α-naphthylbismuthine.

Five grams of tri-α-naphthylbismuthine were gradually treated with 1·95 grams (1·4 mols.) of iodine monochloride, both being dissolved in a mixture of ether and chloroform.

The solvent was then partly distilled off, and the yellow deposit collected. It decomposed at about 240°, and probably consisted largely of di-α-naphthylchlorobismuthine, $Bi(C_{10}H_7)_2Cl$. The chloroform–ether filtrate was distilled to dryness, the residual oil removed from a small quantity of dark-coloured solid by means of light petroleum, and the solution diluted with glacial acetic acid, cooled, and treated with chlorine. The weight of iodonaphthalene dichloride (m. p. 55°) obtained was 2·75 grams, the theoretical yield being 3·90 grams.

Action of Iodine Monobromide on Tri-α-naphthylbismuthine.

Tri-α-naphthylbismuthine (2·5 grams) was treated with 0·85 gram (1 mol.) of iodine monobromide, both in chloroform solution. The reaction mixture was worked up in the usual way, and found to yield in addition to 1·1 grams of α-iodonaphthalene dichloride (theoretical yield 1·4 grams) a certain amount of unchanged bismuthine. The principal solid product, although containing traces of iodine, probably consisted largely of di-α-naphthylbromobismuthine. It was only superficially examined, and is reserved for further investigation.

Action of Iodine on Tri-α-naphthylbismuthine.

One gram of tri-α-naphthylbismuthine in dry benzene was slowly treated with a similar solution of 0·43 gram of iodine, and the brown precipitate was collected. It was free from organic matter, and indistinguishable as regards the action of heat, water, sulphuric acid, or nitric acid, from bismuth iodide.

The benzene was removed from the filtered reaction mixture, and the reddish-yellow residue extracted with cold light petroleum. On evaporation of the extract, and removal of a small quantity of tri-α-naphthylbismuthine, the oily residue was treated with light petroleum and glacial acetic acid, boiled in order to decompose any traces of bismuthine, cooled, and treated with chlorine, when α-iodonaphthalene dichloride (0·45 gram) was obtained.

The residue insoluble in light petroleum weighed 0·5 gram, and contained iodine. It almost certainly consisted of tri-α-naphthylbismuthine and di-α-naphthyliodobismuthine, since on allowing it to remain in the air it developed a strong odour of naphthalene.* On then extracting with cold benzene, tri-α-naphthylbismuthine was obtained, and the residue was bright red, free from organic matter, and indistinguishable from bismuth oxyiodide.

If the substance, when freshly obtained, was extracted with hot benzene and the extract treated with alcohol, pure tri-α-naphthylbismuthine crystallised out. The colourless mother liquors gradually deposited bismuth oxyiodide, indicating the decomposition by alcohol of di-α-naphthyliodobismuthine.

Action of Iodine Monobromide on Diphenyl-α-naphthylbismuthine.

Diphenyl-α-naphthylbismuthine (0·3 gram) was treated with iodine monobromide (0·13 gram) in chloroform-ether solution. Instant decolorisation took place, and the solvent was distilled off. The residue was treated with light petroleum, the extract filtered, diluted with glacial acetic acid, and treated with chlorine, when about 0·05 gram of α-iodonaphthalene dichloride (m. p. 65—70°) was obtained.

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* Compounds of the type BiR_2X decompose on keeping even in closed vessels, or in the presence of alcohol and moist solvents, giving a hydrocarbon and bismuth oxyhaloid (see page 19 and Gillmeister, *Ber.*, 1897, **30**, 2844).

Action of Iodine Monochloride on Diphenylbromobismuthine.

Four grams of diphenylbromobismuthine were covered with dry ether and slowly treated with an ethereal solution of 1·5 grams (1 mol.) of iodine monochloride. A brown turbidity was produced, which on vigorous shaking slowly disappeared.

The insoluble residue (2·60 grams), which contained iodine, melted very indefinitely at about 190°, and was not further examined, since from its method of preparation it seemed very probable that it might contain phenylchlorobromobismuthine, $BiPhClBr$, bismuth dichlorobromide, $BiCl_2Br$, and similar substances.

The oily residue from the ethereal solution and washings was extracted with cold chloroform, and the solution yielded 1·95 grams of iodobenzene dichloride, the theoretical amount (removal of one phenyl group) being 2·5 grams. The small residue insoluble in chloroform contained no organic matter.

Cyanogen and Triphenylbismuthine.

Cyanogen was passed into 0·9 gram of triphenylbismuthine dissolved in about 10 c.c. of benzene, but no reaction appeared to occur. The liquid was diluted with an equal volume of ether, and the gas again passed, but with the same result. On spontaneous evaporation of the solvent the bismuthine was recovered unchanged. Similar results were obtained in boiling benzene.

Cyanogen Bromide and Triphenylbismuthine.

Five grams of triphenylbismuthine and 1·5 grams of cyanogen bromide (1¼ mol.) were heated in benzene solution for four hours without any separation of the sparingly soluble diphenylcyanobismuthine taking place. In ether there was no action, either on boiling or on allowing to remain for three weeks.

Cyanamide and Triphenylbismuthine.

When 5 grams of triphenylbismuthine and 0·9 gram of cyanamide were heated with benzene a white solid separated, which was free from bismuth. It melted at about 203°, and after recrystallisation from alcohol and light petroleum, at 205—207°. It was obviously dicyanodiamide, and was also obtained when cyanamide alone was heated in benzene.

Since the cyanamide employed was deliquescent and contained traces of dicyanodiamide (quite insufficient, however, to account for the large amount obtained as above), a portion was treated with ether, in which dicyanodiamide is insoluble, and with phosphoric oxide, filtered, the ether removed, and the dry cyanamide heated with benzene and triphenylbismuthine, but with the same result. No change occurred when cyanamide and triphenylbismuthine were heated in dry ether.

Relative Stabilities of the Triphenylbismuthine Dihaloids.

Owing to the comparatively positive nature of the iodine atom, triphenylbismuthine di-iodide seems to be an extremely unstable substance, which decomposes as soon as formed, eliminating iodobenzene, whereas the corresponding dibromide is much more stable.

The question naturally suggested itself, whether, on account of the stronger negative nature of chlorine, the dichloride would be found to be more stable than the dibromide.

On heating in a sealed tube at 100° the dichloride was unaltered, but on boiling its solution in dry benzene partial decomposition occurred, diphenylchlorobismuthine (see p. 19) separating. The mother liquors yielded unchanged dichloride. The difference in stability is therefore only slight.

Nevertheless, it seemed possible that although the action of magnesium phenyl bromide on triphenylbismuthine dibromide does not give rise to tetraphenylbismuthonium bromide, the corresponding bismuthonium chloride might be obtained from triphenylbismuthine dichloride.

The action of magnesium phenyl bromide on the dichloride led, however, to the formation of derivatives of tervalent bismuth.

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