CCVII.—Organo-derivatives of Bismuth. Part I. The Preparation and Properties of some Tertiary Aromatic Bismuthines and their Halogen Derivatives.

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THE object with which the present research was commenced was primarily the synthesis of an asymmetric organo-bismuth compound, which could be resolved into optically active components (P., 1913, **29**, 76).

Such a result, however, could hardly be expected until a considerable amount of further information had been obtained regarding the properties of organo-bismuth compounds. The comparatively large number of publications dealing with this subject * have confined themselves to a very superficial examination of the compounds described, their reactions having been very little investigated. Experiments were therefore made with the object of discovering (1) the extent to which the Grignard reagent could be used in the synthesis of bismuthines, and (2) the nature of its reaction with various types of halogen bismuthines, for example, BiR_1R_2X , and bismuthine dihaloids of the type $BiR_1R_2R_3X_2$. It was then found that the properties of these halogen compounds were extremely interesting, and worthy of a closer investigation.

Especially interesting and important from a theoretical point of view is the question of the stability of compounds of the type

^{*} Löwig, Annalen, 1850, 75, 355; Breed, *ibid.*, 1852, 82, 106; Dunhaupt, *ibid.*; 1854, 92, 371; Michaelis and Polis, Ber., 1887, 20, 52, 54; Marquardt, Ber., 1887, 20, 1516; 1888, 21, 2035; Michaelis and Marquardt, Annalen, 1889, 251, 323; Gillmeister, Ber., 1897, 30, 2843; Pfeiffer and Pietsch, *ibid.*, 1904, 37, 4620; Hilpert and Grüttner, *ibid.*, 1913, 46, 1685; Hilpert and Ditmar, *ibid.*, 3741; Ehrlich and Karrer, *ibid.*, 3564.

 $BiR_1R_2R_3R_4X$ and $BiR_1R_2R_3XY$, where X and Y are similar or dissimilar halogen atoms.*

From the work of Pope and Peachey (T., 1899, 75, 1127) and Meisenheimer (*Ber.*, 1908, 41, 3966; 1911, 44, 356), it might be expected that compounds of the types (1) $BiR_1R_2R_3R_4X$ or (2) $O:BiR_1R_2R_3$ would be capable of resolution into enantiomorphously related optically active forms.

A compound of the type (1) might conceivably be synthesised in at least two ways, namely, (a) by the addition of an alkyl or aryl haloid to an unsymmetrical bismuthine, and (b) by the action of the Grignard reagent on the dihalogen additive products of an unsymmetrical bismuthine.

As regards substances of the bismuthine oxide type, certain methods of preparation will immediately suggest themselves. Investigations in these directions are in progress.

The author has found that when triphenylbismuthine is warmed for a short time with *iso*butyl bromide, small quantities of diphenylbromobismuthine, BiPh₂Br, are obtained. It is just possible, although rendered still more doubtful by results now to be described, that the conditions requisite for the production in this manner of bismuthonium haloids have not yet been obtained. Further experiments in this direction are in progress.

In order to gain some idea as to the course which the reaction between an unsymmetrical compound of the type $BiR_1R_2R_3Br_2$ and the Grignard reagent might be expected to take, the behaviour of triphenylbismuthine dibromide, $BiPh_3Br_2$, with magnesium ethyl bromide and magnesium phenyl bromide has been investigated.

Neither of these reactions appears to take a normal course. With magnesium phenyl bromide the products obtained consisted of triphenylbismuthine, diphenylbromobismuthine (Michaelis and Marquardt, *Annalen*, 1889, **251**, 328), and phenyldibromobismuthine, BiPhBr₂ (see p. 2215). It is very probable that tetraphenylbismuthonium bromide is first formed, but undergoes decomposition into triphenylbismuthine and bromobenzene.

The formation of diphenylbromobismuthine is possibly due to the decomposition of the triphenylbismuthine dibromide, since the pure compound is by no means stable, and when boiled with dry benzene gives a good yield of diphenylbromobismuthine. Moreover, if pure, colourless triphenylbismuthine dibromide is heated for a few minutes at 100°, it decomposes, forming a yellow, viscid mass, which has a powerful odour of bromobenzene.

The interaction of magnesium ethyl bromide and triphenyl-

^{*} An account of experiments with compounds of the latter type will shortly be communicated to the Society in conjunction with Mr. C. F. Allpress.

bismuthine dibromide led to results which were very similar to those just described. Triphenylbismuthine and diphenylbromobismuthine were obtained, whilst the reaction mixture had a strong odour of bromobenzene.

The formation of the first-named substance may be due to the decomposition of the unstable triphenylethylbismuthonium bromide, BiPh₃EtBr, which may first be formed, ethyl bromide being eliminated. The decomposition of phenyltrimethylarsonium iodide, which, on being heated, gives rise to methyl iodide and phenyldimethylarsine, is a somewhat similar reaction (Winmill, T., 1912, **101**, 719): AsPhMe₃I = AsPhMe₂ + MeI.

Owing to the undoubted formation of bromobenzene, it is possible that the diphenylbromobismuthine resulted from the decomposition \cdot of the triphenylbismuthine dibromide under the influence of the Grignard reagent.

An attempt was then made to remove one of the phenyl groups in diphenylbromobismuthine by means of bromine in chloroform solution, in the hope that the resulting compound might be of use in the synthesis of the so-called mixed or unsymmetrical tertiary bismuthines. *Phenyldibromobismuthine*, crystallising in goldenyellow needles, melting at $205-206^{\circ}$, was thus obtained. The chloroform solution was found to contain bromobenzene (which was identified by its conversion into *p*-bromonitrobenzene) and a certain amount of bismuth bromide. The formation of phenyldibromobismuthine in the above reaction is not analogous to the behaviour of the corresponding diphenylchlorostibine, SbPh₂Cl, which was found by Morgan and Micklethwait to yield Ph₂SbCl₃ on treatment with chlorine (T., 1911, **99**, 2295).

In consequence of the instability of the derivatives of quinquevalent bismuth, to which reference has already been made, and of numerous other compounds of the type R_3BiClI and R_3BiBrI , which are being investigated in conjunction with Mr. C. F. Allpress, the formation of a stable compound, $BiPh_2Br_3$, was hardly to be expected.

The action of magnesium ethyl bromide on diphenylbromobismuthine was next investigated in the hope that diphenylethylbismuthine, $BiPh_2Et$, would be produced. The reaction, however, took a somewhat unexpected course, the only product which could be isolated being triphenylbismuthine.

Triethylbismuthine was also formed (see p. 2216), but was not isolated. The course of the reaction is possibly represented by the equation $3BiPh_2Br + 3MgEtBr = 2BiPh_8 + BiEt_8 + 3MgBr_2$.

By the action of magnesium a-naphthyl bromide on diphenylbromobismuthine, better results were obtained, diphenyl-a-naphthyl-

bismuthine, $BiPh_2 \cdot C_{10}H_7$ (m. p. 118—119°), being readily isolated from the reaction mixture. This seems to be the first compound of the type BiR_2R' to be described. With bromine it gives rise to diphenyl-a-naphthylbismuthine dibromide, $BiPh_2 \cdot C_{10}H_7$, Br_2 (m. p. 140°). This decomposes when heated for a short time at 100°.

Tri-a-naphthylbismuthine (m. p. 234—235°) is readily obtained by the interaction of bismuth bromide and magnesium a-naphthyl bromide. It forms a yellow, crystalline *dibromide* (m. p. 122°), which decomposes when kept for a short time at 100°. An account of the properties of the dibromide of this and the preceding tertiary bismuthine, and of the decompositions they may be made to undergo, will shortly be communicated to the Society.

EXPERIMENTAL.

Stability of Triphenylbismuthine Dibromide.

This substance was prepared by Michaelis and Marquardt (*loc. cit.*), who state that it melts at 122°.

Triphenylbismuthine dibromide, when twice recrystallised from cold benzene and light petroleum, separates in needles, which melt at 118° when placed in a sulphuric-acid bath (previously warmed to 80°) and heated at the usual rate. If, however, the initial temperature of the bath was 80°, and the subsequent heating carried out much more quickly, the specimen melted at 123—124°, and on another occasion at 121°.

The melting point was also found to depend to a certain extent on the size of the crystals used in the determination. This was verified several times, the powdered crystals melting from three to five degrees lower than those which had not been powdered. The melting points were determined simultaneously.

Some of the recrystallised substance (m. p. 118° on fairly slow heating) was heated with dry benzene under a reflux condenser for two hours, every trace of moisture being carefully excluded. On cooling, crystals of diphenylbromobismuthine were deposited; these melted at 152° , and after one recrystallisation at $154-156^{\circ}$.

On heating a specimen of the dibromide in a small sealed tube at 100° for about twenty minutes, it was found to have become yellow and pasty, and a strong odour of bromobenzene was observed.

On attempting to concentrate the mother liquor obtained in the recrystallisation of triphenylbismuthine dibromide, a deposit of diphenylbromobismuthine was obtained.

Action of Magnesium Phenyl Bromide on Triphenylbismuthine Dibromide.

Nine grams of the pure dibromide were covered with dry ether and gradually treated with a solution of magnesium phenyl bromide (1 mol.) prepared from 0.5 gram of magnesium and 2.8 grams of bromobenzene in ether. After each addition of the Grignard reagent a transient but intense purple coloration was produced, and the ether boiled. Most of the dibromide dissolved, and its place was taken by an oily solid. After about forty hours the ether was decanted from the now almost solid, insoluble residue, which was then well washed with dry ether.

(1) Ethereal Extract and Washings.—On evaporation, a yellow oil was left, which had an odour of bromobenzene, and partly solidified on cooling. By extraction with a mixture of ether and light petroleum, 3 grams of triphenylbismuthine were removed from this residue.

(2) Original Residue Insoluble in Ether.—A small portion was shaken with cold benzene, the solution filtered, and treated with light petroleum. Fine yellow crystals of diphenylbromobismuthine (m. p. 155—156°) were deposited.

The bulk of the residue was heated for about five minutes with benzene, and filtered. Yellow crystals were deposited, which sintered at 143—150°, and melted to an opaque fluid; their whole behaviour indicated that the substance was a mixture. A further deposit was obtained on addition of light petroleum; this contained some magnesium compounds.

The yellow deposits were united, and twice extracted with boiling chloroform, which removed diphenylbromobismuthine. The residue was treated with boiling benzene. The filtered extract deposited yellow needles (m. p. 206°), which did not depress the melting point of a specimen of phenyldibromobismuthine (see p. 2215).

Exactly similar results were obtained when triphenylbismuthine dibromide was heated with the Grignard reagent.

Action of Magnesium Ethyl Bromide on Triphenylbismuthine Dibromide.

Eight grams of the pure dibromide were suspended in dry ether, and a solution of magnesium ethyl bromide, prepared from 0.45 gram of magnesium and 1.9 grams of ethyl bromide, was added. The reaction became vigorous, most of the insoluble dibromide disappeared, and an oily deposit was produced. The mixture was not heated, but was kept for some days, moisture being excluded.

Similar results were, however, obtained when the reaction mixture was heated on the water-bath.

The ethereal liquid (A) was finally poured off from the now crystalline deposit (B), which was washed with ether. On evaporation of the ether from A, an oil was left which had a strong odour of bromobenzene, and quickly solidified. From this, 2.5 grams of pure triphenylbismuthine were extracted by means of light petroleum. The small amount of insoluble matter which remained contained compounds of magnesium and bismuth, and was not further examined.

The residue B, after washing with cold chloroform, weighed 2 grams. On treatment with water, about 1.5 grams remained undissolved. This was quickly separated and dried. By recrystallisation from chloroform and light petroleum, yellow crystals were deposited, which melted at 156°, and did not depress the melting point of a specimen of diphenylbromobismuthine.

Action of Bromine on Diphenylbromobismuthine.

Diphenylbromobismuthine was dissolved in dry chloroform, and treated with one molecular proportion of bromine in chloroform solution. The red colour was discharged, and a yellow precipitate formed. When collected and washed with dry chloroform, this melted at about 190°, but on recrystallisation from hot benzene fine yellow needles were obtained, melting at $205-206^{\circ}$, and consisting of *phenyldibromobismuthine*:

0.1510 gave 0.1266 AgBr. Br = 35.68.

 $C_6H_5Br_2Bi$ requires Br = 35.95 per cent.

On distilling off the chloroform from the reaction mixture, an oil remained which had a strong odour of bromobenzene, along with a certain amount of a grey, crystalline substance. The oil was removed by repeated extractions with warm light petroleum, and found to be free from bismuth. On treatment with fuming nitric acid and addition of water to the solution, a solid was precipitated, which, after recrystallisation from alcohol, melted at $125-126^{\circ}$. A recrystallised specimen of *p*-bromonitrobenzene melted at $126-127^{\circ}$, and a mixture of the two melted at the same temperature.

The grey, crystalline solid was heated with toluene, and the filtered extract deposited crystals on cooling. These were free from organic matter, melted at about 200°, and distilled on heating strongly. The action on water and its solubility in ether showed the substance to be bismuth bromide. If the addition of bromine to diphenylbromobismuthine is continued until a per-

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manent red coloration is imparted to the chloroform, the precipitate contains almost no organic matter.

Attempted Preparation of Diphenylethylbismuthine.

Five grams of diphenylbromobismuthine were treated with a solution of 0.45 gram of magnesium and 1.9 grams of ethyl bromide in dry ether. A vigorous reaction took place, most of the yellow bromide disappeared, and a dark-coloured oil was precipitated. The mixture was heated on the water-bath under reflux for about After forty-eight hours the ether was distilled off, an hour. the residue treated with water, and the insoluble matter was collected and extracted three times with alcohol. The alcoholic extract deposited large quantities of triphenylbismuthine, and the mother liquors from these deposits possessed an unbearable odour, resembling that of the alkyl compounds of tin. The alcohol which was distilled from these mother liquors also possessed the same This was probably due to the presence of triethylodour. bismuthine, which is described by Breed (loc. cit.) as a volatile liquid which oxidises readily in air, and possesses a disgusting odour.

Diphenyl-a-naphthylbismuthine.

A solution of magnesium α -naphthyl bromide, prepared from 17 grams of α -bromonaphthalene and 2 grams of magnesium, was treated with 26.5 grams of diphenylbromobismuthine. A fairly vigorous reaction occurred, and an almost clear solution was obtained. The mixture was then heated under refux for two and a-half hours, and allowed to remain overnight. The ether was poured off, and the white, insoluble deposit washed with ether. On removal of the solvent, an oil was left which, after treatment with water, very slowly solidified. It probably contains a certain amount of phenyldi- α -naphthylbismuthine (arising from traces of phenyldibromobismuthine in the diphenylbromobismuthine), in addition to naphthalene and diphenyl- α -naphthylbismuthine, and is being reserved for further investigation.

The crystalline deposit, which was insoluble in ether, was warmed with water to remove magnesium salts, dried, and dissolved in chloroform. The solution deposited a crystalline substance when it was diluted with alcohol. This melted at 115—117°, and, after a few recrystallisations, at 118—119°:

 $C_{92}H_{17}Bi$ requires C = 53.97; H = 3.50; Bi = 42.53 per cent.

Diphenyl-a-naphthylbismuthine is readily soluble in chloroform, benzene, or toluene, but less readily so in alcohol or ether. Warm, concentrated hydrochloric acid immediately decomposes it, yielding benzene and naphthalene.

When treated in ethereal solution with one molecular proportion of bromine, likewise dissolved in ether, the solution was immediately decolorised, and a yellow, crystalline precipitate deposited. On recrystallisation from a mixture of benzene and light petroleum, this was obtained in yellow, prismatic needles, which, when pure, melted at 140° .

As in the case of other bismuthine dibromides described in this paper, the substance melts when heated for a few minutes in a sealed tube at 100° . On cooling, it remains pasty, and an odour resembling that of α -bromonaphthalene is very apparent. Towards hot concentrated hydrochloric acid the dibromide is relatively stable.

Tri-a-naphthylbismuthine.

Magnesium a-naphthyl bromide (3 mols.), prepared from 1.6 grams of magnesium and 13.7 grams of a-bromonaphthalene, was treated with 11 grams of anhydrous bismuth bromide, dissolved in the minimum quantity of dry ether. A vigorous reaction occurred, and a yellow precipitate was formed, which disappeared on shaking; simultaneously, a large quantity of solid matter was deposited. The mixture, after remaining overnight, was heated for one and a-half hours on the water-bath, after which the ether was distilled off, and the residue treated with water. The solid matter which remained was collected and dried. This product was repeatedly extracted with chloroform, the extracts united, concentrated somewhat, and treated with alcohol, when a slightly vellow, crystalline deposit was obtained. On recrystallisation from a mixture of chloroform and alcohol the substance was finally obtained in almost colourless needles, melting at 235°:

0.2152 gave 0.4803 CO₂ and 0.0728 H₂O. C=60.87; H=3.76. 0.3150 , 0.1253 Bi₂O₃. Bi=35.66.

 $C_{30}H_{21}Bi$ requires C = 61.10; H = 3.60; Bi = 35.30 per cent.

Tri-a-naphthylbismuthine is fairly readily soluble in chloroform, carbon tetrachloride, benzene, or toluene, sparingly so in hot alcohol, and almost insoluble in ether or light petroleum. Hot concentrated hydrochloric acid decomposes it quantitatively, bismuth chloride and naphthalene being produced.

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Tri-a-naphthylbismuthine Dibromide.

1.4 Grams of tri- α -naphthylbismuthine in chloroform were slowly treated with a solution of 0.3 gram of bromine in the same solvent. Decolorisation took place immediately, and on adding light petroleum, a yellow, crystalline substance was obtained in almost theoretical yield (1.65 grams). On recrystallisation, the melting point was found to depend on the rate of heating, and was usually about 119—121°, although when very slowly heated, readings as low as 110° were obtained. The cause of this lies in the instability of the pure substance, since, when heated in a small sealed tube at 100°, decomposition set in. After ten minutes the whole was found to be pasty, and the odour of α -bromonaphthalene was very noticeable.

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