XVI.—*Organo-derivatives of Bismuth.   Part V.   The Stability of Halogen, Cyano-, and Thiocyano-derivatives of Tertiary Aromatic Bismuthines.*

By FREDERICK CHALLENGER and JOHN FREDERICK WILKINSON.

THE dihaloids of triphenylbismuthine show diminished stability with increase in the positive character of the halogen until, with iodine, the di-iodide, Ph_3BiI_2, has not been isolated but immediately decomposes, giving iodobenzene and diphenyliodobismuthine (Challenger and Allpress, T., 1915, **107**, 21; Gillmeister, *Ber.*, 1897, **30**, 2843). As a result of work described in this and in previous communications, the relations existing between the dihaloids and similar derivatives may be summarised thus—

	M. p.	Temp. of Decomposition.
Difluoride	159°	190—200°
Dichloride	141°	150°, and slowly in boiling benzene.
Dibromide	122°	100°, and easily in boiling benzene.

Di-iodide, not isolated, unstable, yielding Ph_2BiI and PhI.
Dicyanide, not isolated, unstable, yielding $Ph_2Bi \cdot CN$ and $Ph \cdot CN$.
Dithiocyanate, not isolated, unstable, yielding $Ph_2Bi \cdot SCN$ and $Ph \cdot SCN$.

The decomposition of the dihaloids may be represented by the equations—

$$\text{(i) } Ph_3BiX_2 = Ph_2BiX + PhX$$
or $$\text{(ii) } 2Ph_3BiX_2 = Ph_3Bi + PhBiX_2 + 2PhX$$
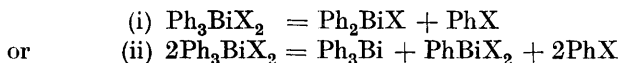
and at a higher temperature,

$$\text{(iii) } 2Ph_3Bi = 3Ph_2 + 2Bi.$$

When triphenylbismuthine dichloride is treated with potassium fluoride in aqueous-alcoholic solution, *triphenylbismuthine difluoride*, m. p. 159°, is produced. This decomposes when heated, giving fluorobenzene, triphenylbismuthine, diphenyl, and probably bismuth fluoride. Although no tetraphenylbismuthonium haloids have so far been obtained, the stability of the difluoride led us to hope that, by interaction with magnesium phenyl bromide, tetraphenylbismuthonium fluoride might possibly be formed, but only triphenylbismuthine was isolated.

The action of potassium hydrogen fluoride on triphenylbismuthine dichloride differs from that of the normal fluoride, triphenylbismuthine being obtained. The production of this substance from potassium fluoride and diphenylbromobismuthine (p. 101) appears to

be analogous, and is possibly due to the production of potassium hydroxide by hydrolysis (see p. 94; and Challenger and Goddard, T., 1920, **117**, 766).

The course of the reaction between diphenylbromobismuthine and silver nitrate depends on the temperature and possibly on the time of interaction. In boiling alcohol, silver bromide, bismuth oxynitrate, and sometimes triphenylbismuthine are produced, whilst reaction in the cold yields the bismuthine, bismuth salts, diphenyl, silver bromide, and metallic silver. Probably the first product is diphenylbismuthine nitrate, Ph_2BiNO_3, which may react with water, forming benzene and bismuth oxynitrate. It may also be hydrolysed to nitric acid and diphenylhydroxybismuthine, $Ph_2Bi \cdot OH$, which would then yield triphenylbismuthine and bismuth hydroxide (Michaelis and Marquardt, *Annalen*, 1889, **251**, 323). Challenger and Allpress (T., 1921, **119**, 916) have shown that triphenylbismuthine and silver nitrate give a yellow, crystalline precipitate, probably having the composition $AgNO_3,2AgPh$, a compound which has been described by Krause and Schmidt (*Ber.*, 1919, **52**, 2150). This compound would probably decompose, giving metallic silver and diphenyl *—

$$AgNO_3,2AgPh = AgNO_3 + 2Ag + Ph_2.$$
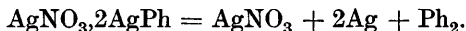
This would be analogous to the behaviour of alkyl and aryl plumbanes, which also reduce silver nitrate to the metal, giving organo-silver compounds as intermediate products (Krause and Schmidt, *loc. cit.*).

From lead thiocyanate and diphenylbromobismuthine in alcoholic solution, triphenylbismuthine and *diphenylthiocyanobismuthine*, $Ph_2Bi \cdot SCN$, were obtained. The production of triphenylbismuthine is due to decomposition of the diphenylthiocyanobismuthine in alcoholic solution, a reaction which has been observed during the purification of this substance, and which is analogous to the behaviour of diphenylcyanobismuthine (T., 1915, **107**, 20)—

$$3Ph_2Bi \cdot SCN = 2Ph_3Bi + Bi(SCN)_3.$$

Diphenylcyanobismuthine was also obtained from diphenyl-bromobismuthine and potassium cyanide in aqueous-alcoholic solution.

In an attempt to obtain the unknown dicyanide, $Ph_3Bi(CN)_2$, from the dichloride and alcoholic potassium cyanide, diphenyl-

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* Mr. A. L. Smith has shown that diphenylbromobismuthine and silver fluoride in the cold give silver bromide, bismuth fluoride, diphenyl, and metallic silver.

cyanobismuthine was isolated, which may be explained by the elimination of benzonitrile from the dicyanide. When the dry dichloride and silver cyanide are gently heated, the odour of benzonitrile is apparent at 75°. It was hoped that the unknown triphenylbismuthine dithiocyanate, $Ph_3Bi(SCN)_2$, might be obtained by treating the dichloride with silver thiocyanate in cold alcohol, but no reaction occurred.

When lead thiocyanate and triphenylbismuthine dichloride were heated to about 85°, phenyl thiocyanate was produced.

From lead thiocyanate and an alcoholic solution of triphenylbismuthine dichloride, diphenylthiocyanobismuthine, phenyl thiocyanate, and polymerised thiocyanogen, $(SCN)_x$ (Söderbäck, *Annalen*, 1919, **419**, 217) were isolated.
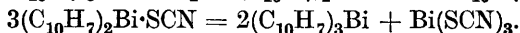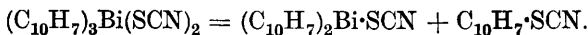
An attempt to obtain triphenylbismuthine dithiocyanate by the addition of free thiocyanogen, $(SCN)_2$, prepared according to the method of Söderbäck (*loc. cit.*), to triphenylbismuthine in ethereal solution was also unsuccessful, the products being bismuth thiocyanate (Bender, *Ber.*, 1887, **20**, 723), phenyl thiocyanate, and diphenylthiocyanobismuthine, which has therefore been prepared by three different methods. This is analogous to the action of thiocyanogen on mercury diphenyl, giving mercury phenyl thiocyanate and phenyl thiocyanate (Söderbäck, *loc. cit.*). The production of the small quantity of bismuth thiocyanate might be caused by further substitution, or decomposition of the diphenylthiocyanobismuthine as above.

From these results, it is obvious that triphenylbismuthine dicyanide and dithiocyanate—as well as the di-iodide—are extremely unstable compounds, a property which is shared by the corresponding salts of copper.

This being the case, it was of interest to determine whether the cyano- or the thiocyano-radicle possesses the greater affinity for bismuth. For this purpose, cyanogen sulphide, $(CN)_2S$ (Schneider, *J. pr. Chem.*, 1885, [ii], **32**, 187), and triphenylbismuthine were shaken with dry ether for eleven hours, yielding bismuth thiocyanate, unchanged triphenylbismuthine, diphenylthiocyanobismuthine, and phenyl thiocyanate. No diphenylcyanobismuthine was isolated. Other experiments confirmed these results, and the reaction is being further investigated.

A similar lack of success attended our efforts to prepare the dicyanide and dithiocyanate of tri-α-naphthylbismuthine. Lead thiocyanate and tri-α-naphthylbismuthine dichloride in boiling alcohol gave *α-naphthyl thiocyanate*, and tri-α-naphthylbismuthine. No α-naphthylthiocyanobismuthines were detected, due probably to their instability.

The hypothetical dithiocyanate probably breaks down thus :—

$$(C_{10}H_7)_3Bi(SCN)_2 = (C_{10}H_7)_2Bi{\cdot}SCN + C_{10}H_7{\cdot}SCN.$$
$$3(C_{10}H_7)_2Bi{\cdot}SCN = 2(C_{10}H_7)_3Bi + Bi(SCN)_3.$$

α-Naphthyl thiocyanate does not appear to have been described.* It was also obtained from tri-α-naphthylbismuthine and thiocyanogen, together with bismuth thiocyanate, thus :—

$$(C_{10}H_7)_3Bi + 3(SCN)_2 = 3C_{10}H_7{\cdot}SCN + Bi(SCN)_3.$$
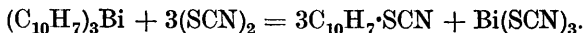
With potassium cyanide in boiling alcohol, tri-α-naphthylbismuthine dichloride gave the bismuthine. This may be due to the action of alkali, arising from the hydrolysis of potassium cyanide, on di-α-naphthylcyanobismuthine (compare p. 92; and Challenger and Allpress, T., 1921, **119**, 914).

Triphenylbismuthine dichloride was prepared by Michaelis and Marquardt (*loc. cit.*) by the action of chlorine on the bismuthine in chloroform, but no mention is made of the simultaneous production of a small quantity of diphenylchlorobismuthine, which may be isolated on crystallisation from acetone, in which it is sparingly soluble. This probably explains the low m. p. of the dichloride, when recrystallised from chloroform–light petroleum. The m. p. of the pure dichloride has, however, been shown to depend on the rate of heating, being somewhat higher when rapidly heated, and in the case of large crystals.

Potassium cyanate and triphenylbismuthine dichloride, when heated with alcohol, regenerated the free bismuthine, this being probably due to hydrolysis of the potassium cyanate. No reaction occurred in the cold.

Kipping and Sands (T., 1921, **119**, 842) have shown that with *s*-tetrachloroethane, certain silico-hydrocarbons give dichloro-additive products. Its action on tertiary bismuthines has been investigated, triphenylbismuthine yielding diphenylchlorobismuthine. No dichloride was isolated, even on heating for only a few seconds, although this compound is probably formed in the first instance. No reaction occurred in the case of tri-α-naphthylbismuthine, even on boiling for several hours.

Michaelis and Marquardt (*loc. cit.*) state that chloroform and triphenylbismuthine in a sealed tube at 150° give a charred mass and hydrogen chloride, the production of triphenylmethane being assumed. At 150—160°, contrary to the statement of these authors,

* Gattermann and Haussknecht (*Ber.*, 1890, **23**, 738) state that it is obtained by way of the diazo-reaction and cuprous thiocyanate, but give no details. We have prepared α-naphthyl thiocyanate by this method, but in very poor yield, and find it to be identical with the product obtained from tri-α-naphthylbismuthine dichloride.

the mixture did not char, but consisted of hydrogen chloride, bismuth chloride, and triphenylmethane in very small quantity. This would appear analogous to the action of chloroform on magnesium diphenyl (Waga, *Annalen*, 1894, **282**, 320). On attempting to increase the amount of triphenylmethane by heating at 130—140° for ten hours, none was detected, but an odour of ethyl benzoate was observed, and diphenylchlorobismuthine produced. The reaction probably proceeds in stages, the first being—

$$Ph_3Bi + CHCl_3 = Ph_2BiCl + PhCHCl_2.$$
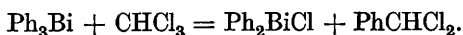
The production of ethyl benzoate was probably due to the action of air and impurities in the chloroform on benzal chloride.

Magnesium benzyl chloride (6 mols.) and diphenylbromobismuthine yielded triphenylbismuthine and inorganic compounds of bismuth. Neither diphenylbenzylbismuthine nor tribenzylbismuthine was isolated, and this is in agreement with the failure to obtain arylalkylbismuthines, such as diphenylethylbismuthine and diphenyl*iso*butylbismuthine (Challenger, T., 1914, **105**, 2216; 1916, **109**, 250).

The absence of tribenzylbismuthine is not surprising, since it is readily oxidised to benzaldehyde in the presence of air and moisture (Challenger and Ridgway, this vol., p. 112).

Diphenyl-α-naphthylbismuthine forms a crystalline dibromide, decomposing at 100° (T., 1914, **105**, 2217). As would be expected, the dichloride is a much more stable compound and is unchanged at 100°. It is almost insoluble in acetone, and can therefore readily be separated from triphenylbismuthine dichloride. The separation of triphenylbismuthine and diphenyl-α-naphthylbismuthine (T., 1921, **119**, 921) by crystallisation from chloroform–alcohol is extremely tedious, and much better results are obtained by treating the mixture with chlorine and separating the two dichlorides, from which the bismuthines may be regenerated by treatment with ammonium sulphide (Michaelis and Marquardt, *loc. cit.*). This is of interest, since it shows that, at the moment of liberation from its dichloride, diphenyl-α-naphthylbismuthine has no tendency to break down to triphenylbismuthine and tri-α-naphthylbismuthine.

Although bismuth trichloride forms crystalline and moderately stable compounds with diazonium chlorides, they do not appear to be strictly analogous to the antimony compounds described by May (T., 1912, **103**, 1037), analyses not agreeing very closely with any simple formulæ. The product obtained from bismuth trichloride and benzenediazonium chloride appears to be represented by the formula $BiCl_3,2PhN_2Cl$ with between 1 and 3 mols. of water of crystallisation. The compounds obtained from *p*-toluene-, and

α- and β-naphthalene-diazonium chlorides are rather more stable at 100° than the phenyl derivative. The behaviour of these compounds towards alkalis is under investigation.

EXPERIMENTAL.

Triphenylbismuthine Difluoride.

Triphenylbismuthine dichloride * (10 grams) and potassium fluoride (3·4 grams) were boiled with 150 c.c. of alcohol and a trace of water. After one and a half hours, the solvent was removed and the residue extracted with hot water. The product thus obtained contained unchanged dichloride. The treatment with potassium fluoride (3 grams) and alcohol was therefore repeated, yielding a solid, which gave no precipitate with alcoholic silver nitrate and, on crystallisation from chloroform–light petroleum and from acetone, melted at 158·5—159° (Found : Bi = 43·26, 43·41 ; F = 7·77, 7·84. $C_{18}H_{15}F_2Bi$ requires Bi = 43·52 ; F = 7·95 per cent. $C_{18}H_{16}OFBi$ requires Bi = 43·87 ; F = 4·01 per cent.).

Estimation of Fluorine in the Difluoride.—The substance was heated for half an hour with excess of calcium oxide and water, containing a little alcohol. (The addition of a small quantity of sodium or calcium carbonate facilitates the subsequent filtration.) The precipitate was washed with alcohol to remove triphenyl-bismuthine, and ignited. The residue was covered with dilute acetic acid, evaporated to dryness, washed with dilute acetic acid, and the calcium fluoride weighed.

Triphenylbismuthine difluoride is readily soluble in acetone, chloroform, and ether, less so in light petroleum.

The crystals obtained from acetone solution belong to the monoclinic system (class—holohedral, type—digonal equatorial). Measurements of three crystals give the axial ratios $a : b : c =$ 2·0201 : 1 : 1·1163 and the axial angle $\beta = 85° 42'$.†

When boiled with barium or calcium oxide in aqueous suspension, the difluoride gives triphenylbismuthine. With sulphuric acid, hydrogen fluoride is liberated.

On boiling the difluoride with 50 per cent. aqueous alcohol for fourteen hours, it was recovered unchanged. A trace of an insoluble powder (0·02 gram), containing bismuth and fluorine, was also obtained.

* When the dichloride was evaporated to dryness three times with aqueous hydrofluoric acid, almost the whole was recovered unchanged.

† We are much indebted to Sir Henry A. Miers, F.R.S., for his kind interest in these preliminary measurements.

Action of Magnesium Phenyl Bromide on Triphenylbismuthine Difluoride.

An ethereal solution containing 3·7 grams (2·6 mols.) of the Grignard reagent was added to 3·7 grams of the difluoride. A vigorous reaction ensued and a brilliant violet colour,* which slowly changed to yellow, was produced. The mixture was heated for one and a half hours and the clear solution decanted. The residue, after magnesium salts had been removed with ammonium chloride, contained bismuth and halogen.

The ether washings and solution were rapidly distilled, and the distillate again evaporated, when one drop of a colourless liquid remained. Judging from the colour produced on treatment with nitric acid, d 1·485, this was probably fluorobenzene.

The residue, from the first distillation, on crystallisation from light petroleum and from alcohol, gave 0·9 gram of triphenylbismuthine.

Distillation of Triphenylbismuthine Difluoride.

Twenty grams of the difluoride were distilled in two portions from a small flask, immersed in an oil-bath. The fused mass became turbid at about 200°, and at 226° a white solid was deposited. At 250°, the decomposition became faster and a colourless liquid distilled, whilst at 260° the contents of the flask became black, and rapid distillation of diphenyl was observed. The distillate was separated into three main portions—

(a) B. p. 84—88°. 2·6 Grams of fluorobenzene.
(b) B. p. 88—110°. A few drops of fluorobenzene.
(c) B. p. 235—245°. A few drops of diphenyl, m. p. 70°.

The fluorobenzene fraction was redistilled, b. p. 84—85° (uncorr.). The residue in the flask was repeatedly extracted with hot acetone, leaving a dark mass, containing bismuth and fluorine. The acetone gave an oily solid, from which equal quantities (1 gram) of triphenylbismuthine and diphenyl were isolated.

Action of Potassium Hydrogen Fluoride on Triphenylbismuthine Dichloride.

The dichloride (5·1 grams) and potassium hydrogen fluoride (2 grams) were boiled with aqueous alcohol for three and a half

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* This colour is almost always produced when the Grignard reagent interacts with a derivative of quinquevalent bismuth. The possibility of the momentary production of compounds of the type R_5Bi, analogous to the coloured triphenylmethyltetramethylammonium and benzyltetramethylammonium described by Schlenk (Ber., 1916, **49**, 603; 1917, **50**, 274), is not excluded.

hours, and filtered. The residue, on washing with water, gave
0·75 gram of inorganic matter, containing bismuth and fluorine.
The alcohol was strongly acid, and deposited a solid which, on
extraction with cold light petroleum, gave 2·1 grams of unchanged
dichloride and 1·5 grams of triphenylbismuthine.

Action of Potassium Cyanide on Triphenylbismuthine Dichloride.

The dichloride (5·1 grams) and 2·6 grams of potassium cyanide
were heated with aqueous alcohol. Some hydrocyanic acid was
evolved and, after an hour, the alcohol was evaporated, and warm
water added to remove potassium salts. No benzoic acid or benzo-
nitrile was detected in the washings, or in the recovered alcohol.
The residue was crystallised from alcohol and then from hot chloro-
form, giving diphenylcyanobismuthine, m. p. 208°, becoming black
at 210° * (Found : CN = 6·55.† $C_{13}H_{10}NBi$ requires CN = 6·70
per cent.).

Action of Potassium Cyanate on Triphenylbismuthine Dichloride.

A. The dichloride (5·1 grams) and 3·2 grams of potassium cyanate
were boiled with alcohol for one hour, filtered, and extracted with
hot water, when one gram of a solid remained, containing bismuth
but no organic matter. The alcohol gave 2·7 grams of triphenyl-
bismuthine.

B. When 2 grams of the dichloride and 0·7 gram of potassium
cyanate were shaken for eight and a half hours with 70 c.c. of dry
benzene, no reaction occurred.

Diphenylthiocyanobismuthine.

Triphenylbismuthine dichloride (5·1 grams) and lead thiocyanate
(6 grams) were boiled with 200 c.c. of alcohol. The mixture became
bright yellow, and, after half an hour, the solution was decanted
and the solid heated for a further half-hour with more alcohol.
The alcoholic extracts had an odour of phenyl thiocyanate. On
concentration, a yellow, amorphous powder was obtained resembling
the yellow polymerised thiocyanogen, $(SCN)_x$, described by Söder-
bäck (loc. cit.). The filtered solution deposited a solid which, on
crystallisation from alcohol and acetone, melted at 122—122·5°
(uncorr.) and was quite odourless (Found : S = 7·99, 7·61 ; Bi =

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* In another experiment, triphenylbismuthine was also obtained, prob-
ably owing to decomposition of some of the cyano-derivative.

† By treatment with excess of standard silver nitrate solution.

49·98; SCN = 13·67.* $C_{13}H_{10}NSBi$ requires S = 7·62; Bi = 49·44; SCN = 13·81 per cent.). The evaporated mother-liquors were distilled in steam. The oily distillate smelled strongly of phenyl thiocyanate, and, with alcoholic potassium hydrosulphide, gave phenyl mercaptan, which was converted to the mercaptides of mercury, lead, and copper. Potassium thiocyanate was recognised in the alkaline solution by the addition of zinc sulphate and ferric chloride.

Diphenylthiocyanobismuthine forms pale yellow crystals, moderately soluble in alcohol and most organic solvents, except light petroleum. It is quite stable when dry, but gradually decomposes in solution, particularly on warming, yielding triphenylbismuthine and a yellow solid, possibly $(SCN)_x$. The yield is therefore low.

The crystals obtained from alcohol belong to the monoclinic system (class—holohedral, type—digonal equatorial). Measurements of three crystals gave the axial ratios $a : b : c = 2·4969 : 1 : 3·0590$, and the axial angle $\beta = 75°54'$.

Action of Potassium Cyanide on Tri-α-naphthylbismuthine Dichloride.

The dichloride † (1·1 gram), potassium cyanide (1 gram), and alcohol were boiled for two hours, the alcohol evaporated, and the potassium salts removed with water.

The insoluble residue had an odour of naphthalene and, on extraction with chloroform, gave a pale yellow, crystalline solid, m. p. 232°, which did not depress the m. p. of tri-α-naphthylbismuthine. No other organic compounds were isolated.

Action of Potassium Thiocyanate on Tri-α-naphthylbismuthine Dichloride.

The dichloride (1 gram) and potassium thiocyanate (0·4 gram), suspended in benzene, were shaken for eleven hours. The dichloride slowly dissolved, the insoluble matter becoming yellow. The solid was filtered, washed with water and dried, giving 0·45 gram of bismuth salts. The yellow filtrate gave bismuth oxychloride, and

* The thiocyanogen radicle was estimated by dissolving the substance in cold alcohol and diluting to 100 c.c.; 25 c.c. were treated with excess of standard silver nitrate solution, well shaken, heated for a few minutes at 100°, and titrated with ammonium thiocyanate.

† Mixtures of 15, 30, and 60 per cent. of tri-α-naphthylbismuthine, m. p. 235°, and the dichloride, m. p. 167°, melted at 168°, 176°, and 186—205° respectively.

crystals melting at 230—231° and not depressing the m. p. of tri-α-naphthylbismuthine.

Action of Lead Thiocyanate on Tri-α-naphthylbismuthine Dichloride.

Equal weights (5 grams) of these substances were heated with alcohol for eighty minutes, the yellow solid (*a*) separated, heated with more alcohol and filtered, when tri-α-naphthylbismuthine was deposited. The alcoholic mother-liquor deposited a red oily mass which, on extraction with light petroleum, yielded α-*naphthyl thiocyanate*, m. p. 55°.

The residue (*a*) was extracted three times with benzene, yielding 2·6 grams of tri-α-naphthylbismuthine, leaving 4·9 grams of a yellow solid, containing bismuth and lead salts, and polymerised thiocyanogen.

No mono- or di-α-naphthylthiocyanobismuthines were isolated.

Action of Thiocyanogen on Tri-α-naphthylbismuthine.

Lead thiocyanate (7·5 grams) was added to a solution of 1 c.c. of bromine in 40 c.c. of dry, alcohol-free ether, the mixture cooled in ice, and shaken for thirty-three minutes, when decolorisation was complete. It was then filtered, and the residue washed with dry ether (60 c.c.), when the solution contained 0·02 gram-mol. of thiocyanogen, $(SCN)_2$. On boiling, or allowing to stand, a yellow polymeride was obtained.

Thirty-four c.c. of the solution were added to 3·93 grams of the bismuthine in dry ether, cooled in ice. The mixture was shaken for five hours, the colour deepening, and, after four hours, the odour of thiocyanogen disappeared. The mixture was filtered and the yellow residue washed with ether. Extraction with boiling benzene removed 2·65 grams of unchanged tri-α-naphthylbismuthine, m. p. 230°; the residue (0·9 gram) appeared to be bismuth thiocyanate.

The ethereal filtrate and washings were evaporated in a vacuum giving an oily, yellow mass which, after two recrystallisations from light petroleum, formed a colourless solid, m. p. 54°. Analysis showed it to be α-naphthyl thiocyanate (Found : $S = 17·49, 17·38$; $C = 71·00$; $H = 3·82$. $C_{11}H_7NS$ requires $S = 17·32$; $C = 71·30$; $H = 3·81$ per cent.).

This, on treatment with alcoholic potassium hydrosulphide and acidification with hydrochloric acid, gave an oil, having the odour of a mercaptan, which gave the respective mercaptides with lead, silver, mercury, and copper salts. Potassium thiocyanate was also detected.

Action of Thiocyanogen on Triphenylbismuthine.

Thirty-four c.c. of the thiocyanogen solution were added to 2·93 grams of the bismuthine in ice-cold ether. Yellow crystals slowly formed on the sides of the vessel but, on shaking for four and a half hours, became oily and were extracted with cold alcohol, yielding 1·7 grams of diphenylthiocyanobismuthine, m. p. 121—122°. The ether was evaporated in a vacuum, the oily residue extracted with cold, dry light petroleum and filtered from 0·8 gram of bismuth thiocyanate and polymerised thiocyanogen. The solution yielded phenyl thiocyanate, which was identified as above.

Action of Potassium Cyanide on Diphenylbromobismuthine.

Diphenylbromobismuthine (2·2 grams) was shaken with 0·6 gram of potassium cyanide in alcohol, containing a small quantity of water, and boiled for a quarter of an hour, when a white, crystalline precipitate was obtained. This was separated, washed with water, dried, and extracted with hot alcohol, leaving a residue of less than 0·05 gram, whilst the alcoholic solutions deposited 1·2 grams of diphenylcyanobismuthine, m. p. 210° (mixed, 210°).

Action of Potassium Fluoride on Diphenylbromobismuthine.

Diphenylbromobismuthine (2·2 grams) was shaken with a cold alcoholic solution of 0·58 gram of potassium fluoride and a few drops of water for five minutes, the solid separated (1·8 grams) and washed with water. Extraction with alcohol yielded 1·9 grams of triphenyl-bismuthine. The insoluble residue (0·1 gram) contained bismuth and fluorine.

Action of Lead Thiocyanate on Diphenylbromobismuthine.

With diphenylbromobismuthine (1·2 grams) and lead thiocyanate (1·6 grams) in cold alcohol, no reaction was observed. On the next day, the mixture was boiled for one hour, cooled, and filtered. The residue consisted of lead thiocyanate and bromide (probably the double salt, $PbBr_2,Pb(SCN)_2$; Grissom and Thorp, *J. Amer. Chem. Soc.*, 1888, **10**, 229) and bismuth oxybromide. The filtrate gave two deposits—

(*a*) Colourless crystals, m. p. 74—94°.

(*b*) A mixture of colourless, radiating crystals and yellow prisms. These, on fractional crystallisation from cold alcohol, yielded tri-phenylbismuthine, and diphenylthiocyanobismuthine, m. p. 122° (mixed, 122°).

Action of Silver Nitrate on Diphenylbromobismuthine.

A. Diphenylbromobismuthine (2·2 grams) was shaken with a cold alcoholic solution of silver nitrate (1·5 grams). The white precipitate gradually darkened. After filtering from the residue (probably containing metallic silver) the solution deposited triphenyl-bismuthine, m. p. 77—78°, on crystallisation from alcohol.

B. Diphenylbromobismuthine (2·2 grams) was added to a boiling alcoholic solution of silver nitrate (0·8 gram). After boiling for an hour, the white precipitate was filtered, and consisted of 0·7 gram of silver bromide and 0·7 gram of bismuth subnitrate.

The evaporated mother-liquor, on successive extractions with hot light petroleum and hot water, yielded 0·3 gram of triphenylbis-muthine, m. p. 78°, and unchanged silver nitrate.* The residue was bismuth oxybromide (0·4 gram).

Diphenyl-α-naphthylbismuthine Dichloride.

The bismuthine (2·3 grams), in dry alcohol-free chloroform, was treated with 0·33 gram of chlorine in 6 c.c. of the same solvent, the solution remaining clear. Dry light petroleum was then added until the liquid was turbid, when pale yellow crystals were deposited, m. p. 141—142° (Found : Cl = 12·76, 12·60; Bi = 36·71. $C_{22}H_{17}Cl_2Bi$ requires Cl = 12·64; Bi = 37·07 per cent.).

Diphenyl-α-naphthylbismuthine dichloride is soluble in chloroform, but insoluble in acetone. Moist silver oxide in acetone suspension removes the chlorine atoms, regenerating the bismuthine.

Interaction of Benzenediazonium Chloride and Bismuth Trichloride.

Bismuth trichloride (15 grams) was dissolved in the minimum quantity of hydrochloric acid, and water added until a slight turbidity was produced. A solution of benzenediazonium chloride, prepared from 5 grams of aniline, 30 c.c. of hydrochloric acid, and 75 c.c. of water, was then added and, after a few moments, an orange-yellow, crystalline precipitate was deposited. (No precipitate was obtained on addition of the diazonium solution to bismuth chloride in concentrated hydrochloric acid.) This was filtered, washed quickly with a little of the diazonium solution, and then with a very small quantity of 25 per cent. hydrochloric acid, dried on tile for fifteen to twenty minutes, and washed with

* When 1·5 grams of silver nitrate were used, some diphenyl was also produced.

dry ether (Found : by Carius's method, Cl = 28·50, 28·34, 28·34 ; by precipitation, Cl = 27·26, 27·67 ; Bi * = 31·56, 31·43. $BiCl_3,2PhN_2Cl,1\frac{1}{2}H_2O$ requires Cl = 28·47 ; Bi = 33·39 per cent. $BiCl_3,2PhN_2Cl,3\frac{1}{2}H_2O$ requires Cl = 26·90 ; Bi = 31·56 per cent.).

This orange-yellow compound is insoluble in organic solvents and in the diazonium solution, but is easily soluble in water or hydrochloric acid, and readily reacts with aqueous silver nitrate solution. It shows no melting point, but decomposes vigorously at 100°, giving a powerful odour of phenol, which would indicate the presence of water of crystallisation.

The substance gradually decomposes on standing, especially in the presence of light, but not completely after ten days.

Interaction of p-Toluenediazonium Chloride and Bismuth Trichloride.

A solution of 15 grams of bismuth trichloride in dilute hydrochloric acid was treated with a solution of toluenediazonium chloride, prepared from 5·3 grams of p-toluidine, 15 c.c. of hydrochloric acid, and 50 c.c. of water. The white, crystalline precipitate was filtered and washed as in the last experiment (Found : by Carius's method, Cl = 26·16, 26·08 ; by precipitation, Cl = 24·72, 24·92 ; Bi = 22·88, 22·50. $BiCl_3,3C_7H_7N_2Cl,2H_2O$ requires Cl = 26·13 ; Bi = 25·56 per cent. $BiCl_3,3C_7H_7N_2Cl,8H_2O$ requires Cl = 23·02 ; Bi = 22·53 per cent.).

Production of a Blue Colouring Matter by the Action of Air and Ammonia on Magnesium Phenyl Bromide.

In preparing triphenylbismuthine from bismuth chloride and magnesium phenyl bromide, the authors have occasionally treated the solid residue, after removal of the ether, with dilute ammonia, with a view to the conversion of diphenylchloro(or -bromo-)-bismuthine (Challenger and Allpress, loc. cit.) to triphenylbismuthine. On standing for some days and then distilling in steam to remove diphenyl,† the distillate occasionally had a blue colour, the intensity of which depended on the time the reaction mixture was allowed to stand. The colouring matter was removed by organic solvents, giving a red solution, which on evaporation had a slight odour of p-benzoquinone. Porter and Steele (J. Amer. Chem. Soc., 1920, **42**,

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* Determined as sulphide by precipitation in dilute hydrochloric acid solution.

† The bismuthine is more quickly obtained in a pure condition if the distillation with steam is omitted.

2650) have shown that p-benzoquinone and phenol are among the oxidation products of magnesium phenyl bromide, phenol being almost invariably present in any solution of this reagent.* It was then found that similar colorations could be produced by warming a mixture of p-benzoquinone, phenol, and aqueous ammonia.

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