94. *Organo-derivatives of Bismuth and Thallium.*

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THIS communication contains an account of certain organo-derivatives of bismuth the preparation of which presented difficulties in earlier work. For comparison, certain analogous thallium compounds have been prepared from arylboric acids (see J., 1931, 1462). This has afforded opportunity for recording further examples of the mobility of aryl groups attached not only to boron, but also to thallium, bismuth, or silver.

Triphenylbismuthine dihydroxide has now been prepared (compare Challenger and Goddard, J., 1920, **117**, 762; Challenger and Ridgway, J., 1922, **121**, 109) from the dichloride and aqueous silver oxide. It decomposes readily above 100° and more slowly in cold solvents, giving bismuth hydroxide and triphenylbismuthine. Oxidation apparently takes place, since with ethyl, *n*- and *iso*-propyl alcohols, acetaldehyde, propaldehyde, and acetone and, in each case, an odour of benzene can be detected. The reactions (*a*) $Ph_3Bi(OH)_2 = Ph_2Bi{\cdot}OH + PhOH$, (*b*) $3Ph_2Bi{\cdot}OH = 2BiPh_3 + Bi(OH)_3$ cannot represent the decomposition, since phenol is not detectable (it is formed, however, from hydrogen peroxide and the aqueous dihydroxide). The decomposition probably occurs thus: (*c*) $Ph_3Bi(OH)_2 = PhH + Ph_2BiO{\cdot}OH$, (*d*) $Ph_2BiO{\cdot}OH = Ph_2Bi{\cdot}OH + O$. Reaction (*b*) then occurs. The diphenylbismuthic acid postulated in (*d*) has not been detected, but two analogous reactions are met with in the antimony series (Schmidt, *Annalen*, 1922, **429**, 125, 139, 141), yielding diphenylstibonic acid and its di-*p*-acetamido-derivative. The well-known oxidising properties of sodium bismuthate may here be cited.

With potassium cyanide and sodium azide the dihydroxide or the dichloride gives *triphenylbismuthine hydroxycyanide* and *diazide*, which, unlike the stable hydroxychloride and dichloride, readily lose benzonitrile or phenylazoimide in boiling water and are partly hydrolysed by warm water. The hydroxycyanide in hot alcohol gives triphenylbismuthine, diphenylcyanobismuthine, benzonitrile, and inorganic matter. The dry diazide at 95° similarly yields the bismuthine, *diphenylazidobismuthine*, $(C_6H_5)_2BiN_3$, and phenylazoimide. For other reactions of this type see J., 1922, **121**, 91.

The thermal instability of the azido-derivative was to be expected in view of the position of this radical in the electrochemical series for the halogens and pseudo-halogens deduced by Birckenbach and Kellermann from a study of the decomposition potentials of the potassium salts in water (F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN). In earlier papers (for references, see J., 1927, 209) it was shown that the relative stability of the compounds Ph_3BiX_2, where X is a halogen or pseudo-halogen, is almost exactly the same as the order of the groups X in this series.

As the dicyanide of triphenylbismuthine is unknown, the behaviour to heat of a dry mixture of the dichloride with two molecular proportions of potassium cyanide was examined. Benzonitrile was hardly to be recognised before 130° and the odour did not become strong until 190°, whereas the pure diazide loses phenylazoimide at 95°. From the above series benzonitrile would be expected to be the more readily eliminated.

Phenylthallium dichloride (Challenger and Parker, J., 1931, 1462) with 4 mols. of potassium cyanide gives *potassium phenylthallicyanide*, which on boiling breaks down thus, $2K[PhTl(CN)_3] = 2KCN + Ph_2TlCN + Tl(CN)_3$, giving *diphenylthallium cyanide.* With 2 mols. of sodium hydroxide, sodium azide, potassium cyanide, and potassium thiocyanate, the dichloride gives *phenylthallium dihydroxide, diazide* (stable at 200°), *dicyanide*, and *dithiocyanate* respectively. The last two compounds lose benzonitrile and phenylthiocyanate at 228° and 120° respectively. Phenylthallium dichloride is more stable than the dibromide, which rather easily loses bromobenzene. The corresponding di-iodide is unknown, iodobenzene being immediately liberated (J., 1931, 1463). The order of stability of compounds of the type $PhTlX_2$ is therefore roughly parallel to that of Ph_3BiX_2, though the temperatures of decomposition are higher.

The use of arylboric acids in the preparation of organothallium derivatives (Challenger and Parker, *loc. cit.*) has been further exemplified in the case of *mono-* and *di-*p-*tolyl-* and p-*bromophenyl-thallium chlorides* and of *phenyl-*p-*tolylthallium chloride.* With mercuric oxide and water, arylboric acids give excellent yields of mercury diaryls (compare Nesmejanow and co-workers, *Ber.*, 1933, **66**, 199; 1934, **67**, 319, who obtained arylmercury hydroxides from aryl iodoxy-compounds, mercuric oxide, and silver oxide).

A striking difference in reactivity is exhibited by *n*-propylboric acid. This is unaffected by water or by thallic chloride at 140°; mercuric chloride has little action in the cold and at 100° the (incomplete) reaction (*a*) $Pr^{\alpha}B(OH)_2 + HgCl_2 + H_2O = Pr^{\alpha}HgCl + B(OH)_3 + HCl$ is accompanied by a secondary one, (*b*) $Pr^{\alpha}HgCl + HgCl_2 = Hg_2Cl_2 + Pr^{\alpha}Cl$. Reaction (*b*) is more pronounced at 140°, and its absence in the aryl series may be attributed to the lower temperature employed and the insolubility of arylmercury chlorides. The occurrence of reaction (*b*) was indicated by the production of mercurous chloride from *n*-propylmercury chloride and mercuric chloride under similar conditions.

Phenyl- and *p*-bromophenyl-thallium dichlorides with mercuric chloride transfer their aryl group, giving phenyl- and *p*-bromophenyl-mercury chlorides, and eliminating thallic chloride, $ArTlCl_2 + HgCl_2 = ArHgCl + TlCl_3$. Pyridine compounds of the type $C_6H_5{\cdot}TlX_2,C_5H_5N$ (X = Cl or Br) have been prepared and their behaviour to halogen acid studied. The diarylthallium halides so far examined do not combine with pyridine.

With ethyl- and *cyclo*hexyl-magnesium bromides, phenylthallium dichloride gives a mixture of diphenyl- and dialkyl-thallium halide, but a mixed halide, PhTlAlkX, could not be isolated. This recalls the behaviour of aryl halogen bismuthines (J., 1921, **119**, 920) and in certain circumstances of aryl- and alkyl-mercury chlorides (Hilpert and Grüttner, *Ber.*, 1915, **48**, 906; Kharasch and Marker, *J. Amer. Chem. Soc.*, 1926, **48**, 3130). Phenyl-*p*-tolylthallium chloride, however, appears to be formed from phenyl- or *p*-tolylthallium dichloride and *p*-tolyl- or phenyl-boric acid respectively.

Triphenylbismuthine and silver nitrate give a yellow unstable compound apparently identical with the product, $AgNO_3,2AgPh$, described by Krause and Schmitz (*Ber.*, 1919, **52**, 2150). This, as would be expected, has a mobile phenyl group which is easily transferred to mercury, thallium, and to the cyanogen and thiocyanogen radicals.

EXPERIMENTAL.

Triphenylbismuthine Dichloride and Silver Oxide.—The dichloride (20·45 g.; 1 mol.) was shaken with silver oxide (from 27·2 g., 1 mol., of silver nitrate) in cold boiled water (260 c.c.)

for 8 hours. Next day the precipitate was separated and washed, considerable frothing occurring. The clear, slightly alkaline filtrate (A) (400 c.c.) gradually became turbid, especially in light, depositing triphenylbismuthine and bismuth hydroxide.

With excess of aqueous sodium chloride, (A) gave a flocculent precipitate, sintering at 123°. Crystallisation separately from alcohol and from benzene yielded triphenylbismuthine dichloride and the corresponding hydroxychloride (mixed m. p. 158—161°; J., 1920, **117**, 764). Sodium bromide similarly gave the dibromide and hydroxybromide. Hydrochloric acid gave the dichloride. With potassium iodide or hydriodic acid, iodobenzene and phenyldi-iodobismuthine were obtained (see J., 1924, **125**, 854).

On exposure to air (A) rapidly acquired a surface film. Air freed from carbon dioxide had no such effect. Carbon dioxide precipitated triphenylbismuthine carbonate.

Triphenylbismuthine dihydroxide. A portion of (A), when evaporated at 100°, left a yellow residue containing the bismuthine and bismuth hydroxide (compare J., 1920, **117**, 765). Concentration in a vacuum over calcium chloride or sulphuric acid gave a glass, which with ether formed a nearly white, amorphous powder. It was found preferable to drop (A) slowly into a large evacuated flask at 35—40°. The residue, which could not be crystallised from organic solvents without decomposition (see below), decomposed vigorously at 100—120° and deflagrated when heated in a flame. A sample, of which a small test portion on washing with (a) light petroleum and (b) dilute hydrochloric acid was found to be practically free from bismuthine and inorganic bismuth, was analysed without recrystallisation, after admixture with ignited sand prior to combustion [Found : C, 45·5; H, 3·5; Bi, 44·65. $C_{18}H_{15}Bi(OH)_2$ requires C, 45·6; H, 3·6; Bi, 44·1%. $C_{18}H_{15}BiO$ requires C, 47·4; H, 3·3; Bi, 45·8%]. The residue appears, therefore, to be the *dihydroxide* and not the oxide. Further small quantities were usually obtained on extraction of the silver chloride with cold chloroform (yield of AgCl, 11·2 g.; theo., 11·45 g.).

Triphenylbismuthine dihydroxide does not readily redissolve in water and is sparingly soluble in light petroleum or ether, moderately in acetone, and easily in chloroform or alcohol. It decomposes in all these solutions, giving bismuth oxide and triphenylbismuthine; the latter is also formed when the dry solid is heated at 100°, the odour of diphenyl being produced.

Decomposition of Triphenylbismuthine Dihydroxide in Different Solvents.—(a) *In ethyl alcohol* (30 c.c.). The dihydroxide (2·4 g.) after 12 hours gradually deposited the bismuthine and bismuth oxide. After 7 days the liquid was filtered and 2—3 c.c. were distilled into cold water, which acquired a strong odour of acetaldehyde. The odour of benzene was also recognised here and in experiments (b) and (c). Schiff's test was positive and 2 : 4-dinitrophenylhydrazine hydrochloride gave acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. (after crystallisation from alcohol) and mixed m. p. 162—164°. 1·4 G. of triphenylbismuthine were recovered from the alcohol. Steam-distillation of the residue gave no phenol or diphenyl.

(b) *In* iso*propyl alcohol* (50 c.c.). The dihydroxide (1·5 g.) decomposed in 1—2 days. Treatment as before yielded the bismuthine and acetone-2 : 4-dinitrophenylhydrazone, m. p. (after recrystallisation) and mixed m. p. 127°.

(c) *In* n-*propyl alcohol* (15 c.c.). The dihydroxide (1 g.) gave propaldehyde-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154°.

In all three cases a blank distillation of the alcohol gave neither aldehyde nor ketone.

Triphenylbismuthine hydroxychloride is best obtained by repeated extraction of the dichloride with hot aqueous ammonia till almost all has dissolved. Saturated ammonium chloride solution then gives a solid which, recrystallised from benzene, melts at 157—159°, turning red (see J., 1920, **117**, 764).

Triphenylbismuthine Hydroxycyanide.—The dichloride (5·1 g.; 1 mol.) was shaken for 5 hours with potassium cyanide (2·6 g.; 4 mols.) in water (20 c.c.). The product (m. p. 115—130°) was fractionally precipitated from chloroform by light petroleum and after two crystallisations from this mixture was halogen-free and had m. p. 136°, turning ruby-red (Found : C, 46·6; H, 3·1; CN, 5·1; Bi, 43·0. $C_{19}H_{16}ONBi$ requires C, 47·1; H, 3·3; CN, 5·4; Bi, 43·25%). The *hydroxycyanide* forms colourless matted needles smelling of hydrogen cyanide and is readily soluble in cold chloroform or warm alcohol, and moderately so in benzene.

Concentrated aqueous potassium cyanide and a solution of the dihydroxide gave a solid, m. p. 112—115°, which was practically free from triphenylbismuthine and inorganic bismuth. After four crystallisations from chloroform–light petroleum, this melted at 132—133° and at 134—135° in admixture with the pure hydroxycyanide (m. p. 136°). Distillation with steam gave benzonitrile, which was hydrolysed to benzoic acid, m. p. and mixed m. p. 120°.

Triphenylbismuthine Dichloride and Sodium Azide.—The dichloride (5·1 g.; 1 mol.), sodium azide (1·3 g.; 2 mols.), and water (10 c.c.) were gently warmed. Phenylazoimide was not detected below 60—65°, but after 10 minutes at this temperature its odour was intense. Steam-distillation gave an oil, which with zinc dust and sulphuric acid yielded aniline, identified as acetanilide, m. p. and mixed m. p. 114°, thus confirming the presence of phenylazoimide. The aqueous distillate gave a red colour with ferric chloride due to hydrazoic acid (see below). The non-volatile portion of the original reaction mixture yielded triphenylbismuthine (2·44 g.) and 0·94 g. of inorganic matter.

Triphenylbismuthine Diazide.—The dichloride (10·22 g.; 1 mol.), sodium azide (5·2 g.; 4 mols.), and water (25 c.c.) were shaken for 8 hours. The solid product, after four crystallisations from chloroform–light petroleum, gave the *diazide* in short thick needles, m. p. 95°, which exploded violently when suddenly heated (Found : C, 41·2, 41·2; H, 3·0, 3·0; N, 15·9, 15·9; Bi, 40·1. $C_{18}H_{15}N_6Bi$ requires C, 41·2; H, 2·9; N, 16·0; Bi, 39·9%). From excess of sodium azide and aqueous triphenylbismuthine dihydroxide, the resulting solid, m. p. 85—92°, recrystallised as before, had m. p. and mixed m. p. 94—95°. When 2 g. of the diazide were gradually warmed to 100°, a pasty mass and a strong odour of phenylazoimide were formed. Extraction with cold light petroleum yielded triphenylbismuthine (0·8 g.); the residue with hot alcohol gave microscopic crystals of *diphenylazidobismuthine*, m. p. 168° on recrystallisation, which with hot water gave a slight odour of hydrazoic acid (Found : C, 36·3; H, 2·7; Bi, 51·7. $C_{12}H_{10}N_3Bi$ requires C, 35·55; H, 2·5; Bi, 51·6%). This compound is also deposited from hot solutions of the hydroxyazide in organic solvents. Hydrochloric acid gives hydrazoic acid, benzene, and bismuth chloride.

Triphenylbismuthine Hydroxychloride and Hydrobromic Acid.—The hydroxychloride (4·92 g.) was shaken with 100 c.c. of *N*/10-hydrobromic acid (1 mol.) for 3 hours. There was no odour of bromobenzene and the filtrate was free from inorganic bismuth. The solid product appeared to be an equimolecular mixture of triphenylbismuthine dichloride and dibromide. No chlorobromide could be isolated (compare J., 1920, **117**, 769).

Phenylthallium Dichloride and Potassium Cyanide.—The dichloride (17·5 g.; 1 mol.) and potassium cyanide (13 g.; 4 mols.) in warm water (75 c.c.) gave colourless plates of *potassium phenylthallicyanide*, m. p. 265·5° (decomp.), on recrystallisation from water (Found : Tl, 51·4; CN, 19·4. $C_9H_5N_3KTl$ requires Tl, 51·3; CN, 19·6%). A clear solution on boiling gave hydrocyanic acid and a bulky precipitate of *diphenylthallium cyanide*, which was washed with hot alcohol and acetone; m. p. 318° (decomp.) (Found : Tl, 52·9. $C_{13}H_{10}NTl$ requires Tl, 53·1%). It is sparingly soluble in water (slight hydrolysis) and most solvents, including pyridine. Hydrochloric acid gives hydrocyanic acid and diphenylthallium chloride.

The original aqueous filtrate contained a thallic salt produced thus : $2RTlX_2 = R_2TlX + TlX_3$. Sodium hydroxide gave a precipitate of thallic hydroxide and phenylthallium dihydroxide.

Addition of more potassium cyanide to the solution of potassium phenylthallicyanide lessens its decomposition on boiling with sodium hydroxide or potassium iodide.

Phenylthallium Dicyanide.—The dichloride (10·5 g.; 1 mol.) was shaken with potassium cyanide (3·9 g.; 2 mols.) in water (50 c.c.) for 5 hours. There was no odour of benzonitrile. The separated solid on recrystallisation from water gave unchanged dichloride and colourless needles of the *dicyanide*, m. p. 228° (turning black) (Found : Tl, 61·0; CN, 15·8. $C_8H_5N_2Tl$ requires Tl, 61·3; CN, 15·6%).

Phenylthallium Dichloride and Potassium Thiocyanate.—The aqueous dichloride gave with normal thiocyanate solution a 92% yield of a white, halogen-free solid, but no odour of phenyl thiocyanate. Crystallisation from hot water gave needles, which turned red and liberated phenyl thiocyanate at 100—120° (Found : Tl, 51·5; S, 15·9. $C_8H_5N_2S_2Tl$ requires Tl, 51·4; S, 16·1%). *Phenylthallium dithiocyanate* is almost insoluble in cold water, but readily soluble in potassium thiocyanate solution. Treated with potassium iodide, it gives iodobenzene.

Phenylthallium Dichloride and Sodium Azide.—The aqueous solutions gave a halogen-free precipitate, which was extracted with hot water, leaving the insoluble dihydroxide; this decomposed at 280—290°, giving an odour of diphenyl. The aqueous extract smelled of hydrazoic acid and deposited glittering leaflets, which had no m. p. but were stable below 200°. When suddenly heated, the *diazide* exploded and gave an odour of phenylazoimide (Found : Tl, 55·6; N, 23·3. $C_6H_5N_6Tl$ requires Tl, 55·9; N, 23·0%). It is hydrolysed in hot water. Hydrochloric acid gives the dichloride, and potassium iodide, iodobenzene.

Phenylthallium Dichloride and Sodium Hydroxide.—The aqueous dichloride (3·5 g.) was treated with *N*/5-sodium hydroxide. Precipitation ceased and the liquid was alkaline when 95 c.c. (calc., 100 c.c.) had been added. The gelatinous solid could not be crystallised (Found :

Tl, 64·7; C, 21·6; H, 2·0. $C_6H_7O_2Tl$ requires Tl, 64·8; C, 22·8; H, 2·2%. C_6H_5OTl requires Tl, 68·7; C, 24·2; H, 1·7%). *Phenylthallium dihydroxide* decomposes without melting at 280—285°. It is almost insoluble in most organic solvents, but slightly soluble in hot pyridine.

p-*Tolylboric Acid and Thallic Chloride.*—The boric acid (7 g.; 1 mol.) and thallic chloride (40 g.; 3 mols.) in the minimum quantity of boiling water gave a precipitate, m. p. 217°, and 223—224° after two crystallisations from water (Found: Tl, 56·0. $C_7H_7Cl_2Tl$ requires Tl, 55·8%). p-*Tolylthallium dichloride* is less stable than the corresponding phenyl compound. Boiling water converts it into thallic chloride and di-*p*-tolylthallium chloride, which is easily prepared from thallic chloride and 2 mols. of *p*-tolylboric acid at 100° and crystallisation of the precipitate from pyridine (Found: Tl, 48·5. Calc.: Tl, 48·4%). Goddard and Goddard (J., 1922, **121**, 260) prepared this compound by means of tri-*p*-tolylbismuthine.

p-*Bromophenylboric Acid and Thallic Chloride.*—The arylboric acid, m. p. 266°, was prepared from the Grignard reagent and methyl borate (König and Scharrnbeck, *J. pr. Chem.*, 1930, **128**, 153, give 266°; Krause, D.R.-P. 371467, gives 191°).

The arylboric acid (6 g.; 2 mols.) and thallic chloride (4·65 g.; 1 mol.) were heated for 4 hours in the minimum quantity of water; crystals separated (7·36 g. Calc., 8·28 g.), which were washed with acetone and recrystallised from pyridine (Found: Tl, 36·8. $C_{12}H_8ClBr_2Tl$ requires Tl, 37·0%). *Di-*p*-bromophenylthallium chloride* decomposes above 300°, giving thallous chloride and an odour of *pp'*-dibromodiphenyl.

When thallic chloride (23·2 g.; 3 mols.) and the arylboric acid (5 g.; 1 mol.) were boiled in water (75 c.c.) for a few minutes, 11·2 g. of p-*bromophenylthallium dichloride*, m. p. 262—263°, were obtained (Found: Tl, 47·6. $C_6H_4Cl_2BrTl$ requires Tl, 47·4%). Potassium iodide gave a yellow solid, turning black. Addition of alkali and steam-distillation yielded *p*-bromoiodobenzene, m. p. 90°, giving an iodo-dichloride, decomp. 119°, the recorded values for these compounds. The non-volatile residue on extraction with pyridine left thallous iodide; the extract deposited colourless needles, m. p. above 300°, doubtless di-*p*-bromophenylthallium iodide.

p-*Bromophenylboric Acid and Mercuric Chloride.*—The arylboric acid (1 g.) and excess of boiling aqueous mercury salt gave about 2 g. of *p*-bromophenylmercuric chloride, crystals, m. p. 253°, from alcohol–benzene (Found: Hg, 51·35. Calc.: Hg, 51·2%). This compound was also obtained from aqueous mercuric chloride and *p*-bromophenylthallium dichloride; m. p. and mixed m. p. 253°. König and Scharrnbeck (*loc. cit.*), who used the former method, give m. p. 235°, doubtless a misprint.

Phenylthallium Dichloride and Mercuric Chloride.—The dichloride (1·76 g.) and excess of boiling aqueous mercury salt gave a solid (1·52 g. Calc., 1·56 g.), m. p. 248—250°, and, after crystallisation from alcohol, m. p. and mixed m. p. 251° with phenylmercury chloride. The filtrate contained thallic chloride, detected as hydroxide with ammonia.

Phenylthallium Dihalides and Pyridine.—(a) The dichloride (3 g.) in pyridine (50 c.c.) was slowly treated with light petroleum, giving a viscous deposit, which solidified when rubbed with petrol and then, after two crystallisations from alcohol, formed colourless needles, m. p. 172° (decomp.) (Found: Tl, 47·4; Cl, 16·5. $C_6H_5{\cdot}TlCl_2,C_5H_5N$ requires Tl, 47·4; Cl, 16·45%). The *compound* gives iodobenzene with potassium iodide. Cold dilute hydrochloric acid gives the dichloride, m. p. 235°; on boiling, diphenylthallium chloride is formed, and the acid solution deposits the compound $2TlCl_3,3(C_5H_5N,HCl)$, m. p. and mixed m. p. 130° (Renz, *Ber.*, 1902, **35**, 1110).

(b) The dibromide gave with pyridine a compound, m. p. 75—78°, which after solution in cold alcohol and addition of light petroleum (some diphenylthallium bromide first separated) formed glistening leaflets, m. p. 85° on recrystallisation from warm alcohol (Found: Tl, 39·0; Br, 30·9. Calc. for $C_{11}H_{10}NBr_2Tl$: Tl, 39·3; Br, 30·7%). A crude specimen was prepared by Challenger and Parker (*loc. cit.*). With hydrobromic acid, diphenylthallium bromide and the compound $2TlBr_3,3(C_5H_5N,HBr)$, m. p. and mixed m. p. 178° (Renz, *loc. cit.*, p. 2768), were obtained.

Experiments on the Preparation of Mixed Organo-thallium Halides, R_1R_2TlX.—(1) *Ethylmagnesium bromide and phenylthallium dihalide.* A solution of magnesium (0·24 g.) and ethyl bromide (1·1 g.; 1 mol.) in dry ether was slowly added to the dichloride (3·52 g.; 1 mol.) suspended in ether. When reaction ceased, aqueous ammonium chloride was added, the solid (D, 2·7 g.) removed, and the two layers separately evaporated. The residues were mostly inorganic, but hot aqueous ammonia removed small amounts of an organo-thallium halide. (D) was similarly treated. The three united extracts were concentrated and the deposit was twice crystallised from hot dilute ammoniacal ammonium bromide, giving diethylthallium bromide (Found: Tl, 59·95. Calc.: Tl, 59·7%). That portion of (D) which was insoluble in aqueous ammonia was crystallised from pyridine, giving a mixture of diphenylthallium chloride and bromide (Found: Tl, 49·9. Calc. for $C_{12}H_{10}BrTl$: Tl, 46·6%. Calc. for $C_{12}H_{10}ClTl$: Tl, 51·9%).

Addition of the dihalide (3·52 g.; 1 mol.) to 2 mols. of the Grignard solution gave identical results. There was no evidence of the formation of a completely alkylated derivative.

(2) cyclo*Hexylmagnesium bromide and phenylthallium dichloride.* The dichloride (3·52 g.) was added to the Grignard compound (2 mols.), the ether removed, water added, and the separated solid extracted with hot alcohol, giving white leaflets, m. p. above 300°. Hot potassium iodide solution gave equally infusible crystals of *di*cyclo*hexylthallium iodide* (Found: I, 25·4. $C_{12}H_{22}ITl$ requires I, 25·5%). For the chloride, see Krause and Grosse (*Ber.*, 1925, **58**, 1933). The residue insoluble in alcohol was crystallised from pyridine (Found: Tl, 49·6%). It was clearly a mixture of diphenylthallium halides similar to that obtained in the last experiment.

(3) *Phenylboric acid and phenylthallium dichloride.* Equimolecular proportions in the minimum of hot water gave in 10 minutes an 85% yield of diphenylthallium chloride (Found: Tl, 51·8. Calc.: Tl, 51·9%).

(4) p-*Tolylboric acid and phenylthallium dichloride.* Concentrated aqueous solutions of the dichloride (5·28 g.; 1 mol.) and the arylboric acid (2·1 g.; 1 mol.) gave, after 15 minutes at 100°, 5·34 g. of a crystalline precipitate (calc., 6·0 g.), m. p. above 300°. The filtrate contained unchanged reactants but no thallic ions, indicating the probable non-occurrence of the reaction $2RTlX_2 = TlX_3 + R_2TlX$. The precipitate was washed with acetone and crystallised from hot pyridine, giving a deposit (A) and leaving 50% in solution. Dilution with water gave (B), which was recrystallised from the minimum of pyridine (C) [Found for (A): Tl, 50·05. Found for (C): Tl, 50·0. $C_6H_5{\cdot}Tl(C_7H_7)Cl$ requires Tl, 50·1%].

(5) *Phenylboric acid and* p-*tolylthallium dichloride.* These in molecular proportion (0·6 g. and 1·83 g.) gave in 10 minutes 1·65 g. of solid, which was treated as in the last experiment, giving deposits A′ (Tl, 50·13%) and C′ (Tl, 50·09%). (A) and (A′) were united and crystallised twice from pyridine, giving deposits of thallium content 50·35 and 50·21% respectively. The product from each experiment would appear to be homogeneous, a conclusion borne out by the behaviour of an equimolecular mixture of diphenyl- and di-*p*-tolyl-thallium chlorides (Tl, 51·9 and 48·4% respectively), which when crystallised exactly as in the two preceding cases was easily recognised as a mixture. (A″) gave Tl, 51·33% and (C″) gave Tl, 48·9%.

Properties of Arylboric Acids.

Action of Water.—*p*-Bromophenylboric and *p*-tolylboric acids were recovered almost quantitatively after 40 and 28 hours' heating, respectively, at 100°. After 6 hours, at 140—150° and 130—140° respectively, decomposition to bromobenzene and toluene was complete. Boric acid was detected in each case (compare J., 1930, 2175).

Arylboric Acids and Mercuric Oxide.—(1) Phenylboric acid (1·22 g.; 1 mol.) and the yellow oxide (2·16 g.; 1 mol.) in water (25 c.c.) were boiled for 1 hour. The hot filtrate deposited a solid of no definite m. p., which gave phenylmercury chloride (m. p. and mixed m. p. 250°) with hydrochloric acid and was therefore phenylmercury hydroxide. An acetone extract gave a small quantity of diphenylmercury, m. p. and mixed m. p. 124° after crystallisation from alcohol. When 2·44 g. of phenylboric acid were used, filtration after 30 minutes gave 3·45 g. (98% yield) of diphenylmercury.

(2) *p*-Tolylboric acid (2·72 g.), mercuric oxide (2·16 g.), and water (50 c.c.) at 100° gave di-*p*-tolylmercury (2·7 g.), m. p. and mixed m. p. 236° after crystallisation from benzene.

(3) *p*-Bromophenylboric acid similarly gave di-*p*-bromophenylmercury, m. p. 240° after crystallisation from benzene (Nesmejanow, *Ber.*, 1929, **62**, 1020, gives m. p. 244°). With mercuric chloride in alcohol–benzene, this gave *p*-bromophenylmercury chloride, m. p. 250—253° (see p. 409).

(4) *m*-Nitrophenylboric acid and mercuric oxide in water gave *di*-m-*nitrophenylmercury*, m. p. 286—287° after recrystallisation from xylene (Found: C, 32·8; H, 2·0. $C_{12}H_8O_4N_2Hg$ requires C, 32·4; H, 1·8%).

Reactions of n-*Propylboric Acid.*—The acid has m. p. 112°. Khotinsky and Melamed (*Ber.*, 1909, **32**, 3090) give 74—75° and Krause (*Ber.*, 1921, **54**, 2784) records 107°.

With water. n-Propylboric acid (0·4 g.), after 7 hours' heating with water (5 c.c.) at

140°, was completely recovered by extraction with ether and evaporation in a vacuum. The water contained no boric acid.

With thallic chloride. *n*-Propylboric acid (0·4 g.; 2 mols.) was heated with thallic chloride (0·7 g.; 1 mol.) and water (3·5 c.c.) for 4 hours at 100°. On cooling, yellow plates of the double chloride, $Tl[TlCl_4]$, separated along with unchanged *n*-propylboric acid (m. p. and mixed m. p. 112°). The same result was obtained after 6½ hours at 140—160°, the alkylboric acid being quantitatively recovered.

With mercuric chloride. The alkylboric acid (2 g.), mercuric chloride (8 g.), and water (10 c.c.) were heated at 140—150° for 20 hours. Extraction with ether left mercurous chloride (0·5 g.). The ether was fractionated; the later distillates gave silver chloride with alcoholic silver nitrate, indicating the presence of *n*-propyl chloride. The non-volatile residue was shaken with excess of aqueous sodium carbonate, the mercuric oxide separated, and the filtrate extracted with ether, yielding *n*-propylmercury chloride (3·5 g.), m. p. and mixed m. p. 143—144°, in 55% yield. No propylboric acid was recovered.

Phenylation of Silver Nitrate. Reactions of Phenylsilver–Silver Nitrate.—Triphenylbismuthine was shaken with an excess of saturated alcoholic silver nitrate in a black bottle for 30 minutes. A yellow solid (S) which quickly formed was separated and washed with alcohol and with ether. The filtrate on standing or on concentration deposited basic bismuth nitrate and silver and had an odour of benzene. Steam-distillation gave diphenyl, m. p. and mixed m. p. 69—70°. (S) was insoluble in organic solvents, quickly decomposed at the ordinary temperature, but less rapidly in the dark, and could be kept for some hours at − 15°. Above 80° it decomposed explosively, giving diphenyl, silver, and silver nitrate. Distillation of 1·12 g. in steam gave 0·28 g. of diphenyl and 0·47 g. of silver. The filtrate gave 0·27 g. of silver chloride with hydrochloric acid. The amounts calculated from the equation $AgNO_3,2AgPh = AgNO_3 + 2Ag + Ph{\cdot}Ph$ are 0·32, 0·44, and 0·30 g. respectively. There was a slight odour of benzene, due to simultaneous hydrolysis to silver oxide.

Cold hydrochloric acid gave only silver chloride and benzene; the warm dilute acid gave in addition some diphenyl. With aqueous sodium chloride, benzene, silver chloride, sodium hydroxide, and a trace of diphenyl resulted. Aqueous mercuric chloride produced a white solid. Separation after 30 minutes and extraction with acetone gave silver chloride, a little metallic silver, phenylmercury chloride (m. p. and mixed m. p. 250°), and traces of diphenyl. The grey solid obtained from aqueous thallic chloride and (S) after 30 minutes was extracted with hot water, giving phenylthallium dichloride, m. p. and mixed m. p. 233—234°. Hydrated cupric chloride (1·53 g.; 4·5 mols.) in 20 c.c. of water and (S) (1·08 g.; 1 mol.) quickly gave cuprous and silver chlorides. Steam distillation gave diphenyl (m. p. 70°) and chlorobenzene, recognised by conversion into *p*-chloronitrobenzene, m. p. and mixed m. p. 85°. (S), mixed with aqueous copper sulphate, was separately treated with potassium cyanide and potassium thiocyanate. Benzonitrile and phenyl thiocyanate were at once produced. Bromine water and iodine in potassium iodide immediately gave halogenobenzene.

Triphenylbismuthine and Cupric Chloride and Bromide.—The bismuthine (4 g.) in dry ether (40 c.c.) was treated with the anhydrous chloride (2·44 g.; 2 mols.). A yellowish solid (A) gradually separated; next day the ether was decanted and evaporated, and the residue extracted with light petroleum, yielding chlorobenzene (b. p. 132°; 2 : 4-dinitrochlorobenzene, m. p. and mixed m. p. 52°). The solid (A) on extraction with hot benzene left 1·8 g. of cuprous chloride (calc., 1·8 g.) and gave diphenylchlorobismuthine in 72% yield (m. p. 184°).

With cupric bromide an analogous experiment gave bromobenzene (b. p. 156°; 2 : 4-dinitro-derivative, m. p. and mixed m. p. 72°), cuprous bromide, and diphenylbromobismuthine, m. p. 158°.

Diphenylmercury and Cupric Bromide.—5 G. and 6·3 g. (2 mols.) respectively in 90 c.c. of dry ether were shaken for 5 hours and the liquid was filtered next day and treated as in the two previous experiments. Bromobenzene (characterised as before), cuprous bromide, phenylmercury bromide (m. p. 276—277°), and 1·6 g. of unchanged diphenylmercury were isolated. No evidence of the formation of a stable organo-derivative of copper was obtained.

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