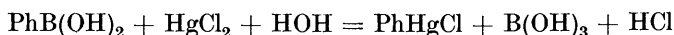


CXCIX.—*A Method for the Preparation of Some New Organo-thallium Halides.*

By FREDERICK CHALLENGER and BERTHA PARKER.

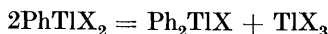
IT was shown by Michaelis and Becker (*Ber.*, 1882, **15**, 182) that phenylboric acid and mercuric chloride react in hot aqueous solution, giving insoluble phenylmercury chloride :



In the course of a study of the mobility of alkyl and aryl radicals when attached to boron (Ainley and Challenger, *J.*, 1930, 2171), the behaviour of phenylboric acid to the thallic halides has been investigated. The close relation of thallium to mercury and the great insolubility and stability to water of diphenylthallium halides (Goddard and co-workers, *J.*, 1922, **121**, 40, 257) suggested that the reaction in question might proceed similarly. In the analogous reaction with cadmium and zinc halides, only benzene was obtained, probably owing to the instability of the organo-halides of cadmium and zinc in presence of water.

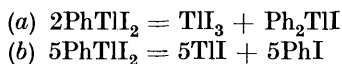
Thallic chloride and bromide react at once in hot aqueous solution with phenylboric acid, giving, according to the proportion of phenylboric acid employed, diphenylthallium halides (Goddard, *loc. cit.*), *phenylthallium dichloride*, m. p. 235°, and *phenylthallium dibromide*, m. p. 153° (decomp.). The mono- and di-chlorides are readily separated and purified owing to their widely differing solubility in water. This is also true of the monobromide, but the isolation of the dibromide presents more difficulty. The dihalides, which do

not appear to have been described, are decomposed by heating with water, the dibromide very readily, giving thallic halide and diphenylthallium halide :



Numerous aryl mercury chlorides and acetates have been prepared by the use of arylboric acids (Michaelis and Richter, *Annalen*, 1901, **315**, 26; König and Scharnbeck, *J. pr. Chem.*, 1930, **128**, 153) and doubtless the reaction with thallium salts is capable of a similar extension. With *p*-tolylboric acid (2 mols.), di-*p*-tolylthallium bromide (Goddard and Goddard, *loc. cit.*, p. 258) is readily obtained. It gives *p*-iodotoluene with iodine, but is unaffected by potassium iodide (see below). If *p*-tolylboric acid is boiled with a large excess of thallic bromide, *p*-bromotoluene is evolved and thallic bromide deposited. This recalls the decomposition of phenylboric acid with bromine water (Ainley and Challenger, *loc. cit.*). *p*-Tolylthallium dibromide (m. p. 160—165° decomp.) is obtained along with some *p*-bromotoluene from 2 mols. of thallic bromide and one of *p*-tolylboric acid.

Phenylthallium dichloride or dibromide gives an immediate yellow precipitate with potassium iodide which quickly turns black, eliminating iodobenzene. The corresponding iodide appears to decompose spontaneously according to the equations

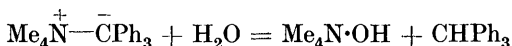


The black precipitate is the double salt 5 TlI, TlI₃ (Jørgensen, *J. pr. Chem.*, 1872, **6**, 82). With excess of potassium iodide it loses iodine, giving thallic iodide. Phenyl thiocyanate and selenocyanate are similarly obtained with the corresponding potassium salts. Potassium bromide gives no bromobenzene, thus recalling the stability of the dichloride and dibromide of triphenylbismuthine at the ordinary temperature, whereas the di-iodide, dithiocyanate and diselenocyanate immediately eliminate aryl halide or pseudo-halide (Challenger, Peters, and Halévy, *J.*, 1926, 1648; Challenger and Wilson, *J.*, 1927, 209).

It was remarked by Berry, Lowry, and Gilbert (*J.*, 1928, 1757) and by Krause and Dittmar (*Ber.*, 1930, **63**, 1953) that organo-thallium derivatives of the types RTlX₂ and R₃Tl were unknown. Krause and v. Grosse (*Ber.*, 1926, **59**, 1712) attempted to prepare alkylthallium dibromides by using bromine and a pyridine solution of dialkylthallium halide, but obtained a compound of thallic bromide with alkylpyridinium bromide. Mendeléeff (*Annalen*, 1872, Spl. **8**, 152) regarded the existence of triethylthallium as

required by analogy with the other odd series elements in Group III. According to v. Grosse (*Z. anorg. Chem.*, 1926, **152**, 133) both these types should be capable of existence, since all three valency electrons of the thallium atom are contained in the same electron shell.

Groll (*J. Amer. Chem. Soc.*, 1930, **52**, 2999) has prepared triethylthallium as a yellow liquid, the colour of which deepens with rise of temperature, but fades in liquid air. Sodium benzyl, tetramethylammonium triphenylmethyl, and tetramethylammonium benzyl (Schlenk and co-workers, *Ber.*, 1917, **50**, 262, 274; 1916, **49**, 603) are coloured and the first two form conducting solutions and are doubtless ionised. With water decomposition occurs:—



Triethylthallium and diethylthallium triphenylmethyl are similarly decomposed, giving diethylthallium hydroxide, and it appears probable that triethylthallium will exhibit electrical conductivity.

Berry, Lowry, and Gilbert (*loc. cit.*) state that "the dialkyl (thallium) halides and the bases from which they are derived, as well as the corresponding trihalides and their bases . . . yield non-conducting molecules. . . . Spectroscopic evidence indicates that the non-conducting forms of these salts may be ionic doublets rather than covalent molecules. The existence of systems in which the thallium nucleus is surrounded by 84 electrons in . . . Me_2TlBr and TlBr_3 is therefore less well established than in the case of mercury. . . . The doubt as to the real existence of the 84 electron system . . . may furnish a clue to the reason why it has not been found possible to prepare the trialkyl derivatives of thallium since these could not be expected to exist in a form corresponding with the ionised molecules of Me_2TlI and could, therefore, only be produced if the 84 electron system were stable."

In view of Groll's work (*loc. cit.*) these remarks are of much interest, since, although Berry, Lowry, and Gilbert seem to regard it as improbable that any ionised structure could be associated with TlEt_3 , they cannot envisage the compound apart from the structure $[\text{TlEt}_2]^+\text{Et}^-$, which has an 82 electron system (see also *Chemistry and Industry*, 1931, 180).

EXPERIMENTAL.

The Action of Thallic Halides on Phenylboric Acid.—Phenylthallium dichloride. Excess of thallic chloride was used to prevent formation of diphenylthallium chloride. Thallic chloride (4.5 g.; 3 mols.) in water (6—8 c.c.) was boiled with phenylboric acid (0.6 g.; 1 mol.) for 1 minute, giving a precipitate (A, 1.6 g.; calc., 1.76 g.),

m. p. 234° (decomp.). On heating with water, all but a trace dissolved, but on long boiling a solid (B) separated while still hot. The filtrate from (A) contained no phenylboric acid (mercury chloride test) (see p. 1462). After precipitation of the excess of thallium as the trihydroxide, the filtrate was shown to contain a borate.

Recrystallisation from water yielded white needles, m. p. 235° (decomp.) (Found : Cl, 19.85; Tl, 58.9. $C_6H_5Cl_2Tl$ requires Cl, 20.2; Tl, 57.95%).

Phenylthallium dichloride is much more soluble in water and in most organic solvents than the diphenyl derivative. Its aqueous solution gives silver chloride with silver nitrate and a white precipitate with potassium hydroxide, indicating the absence of thallic chloride.

On cautious evaporation of an aqueous solution of phenylthallium dichloride on the steam-bath, it is unchanged, but on boiling it is slowly converted into diphenylthallium chloride (B, above) and thallic chloride (sodium hydroxide test). Diphenylthallium chloride is stable to potassium iodide, but not to iodine.

Diphenylthallium chloride. Thallic chloride (1.5 g.; 1 mol.) in water (6 c.c.) was boiled with phenylboric acid (1.2 g.; 2 mols.), giving after 1 minute a white solid (C, 1.4 g.). This was mostly insoluble in hot water, the filtrate giving only a yellow turbidity and a faint odour of iodobenzene with potassium iodide. C was again boiled with water, recrystallised twice from pyridine, and washed with alcohol and ether. It was unmelted at 310° (Found : Cl, 8.7. $C_{12}H_{10}ClTl$ requires Cl, 9.1%).

Diphenylthallium bromide. Thallic bromide (1.9 g.; 1 mol.) and phenylboric acid (1.2 g.; 2 mols.) were heated in water for 20 minutes on the steam-bath, and the solid (0.70 g.) separated; after 4 hours at 100°, the filtrate gave a further 0.85 g. (calc., 1.84 g.). The solid was crystallised from pyridine (Found : Br, 17.8. Calc. : Br, 18.25%).

Phenylthallium dibromide. Phenylboric acid (1.2 g.; 1 mol.) in water (10 c.c.) was added to 10 c.c. of a thallic bromide solution obtained from thallic bromide (8.5 g.; 3 mols.) After 2 minutes' boiling, a lemon-yellow solid (D, 2.4 g.) was deposited, m. p. 149°. On attempted recrystallisation of D from hot water, only a trace remained insoluble, but the clear filtrate on cooling deposited diphenylthallium bromide, which was unmelted at 320°.

By washing D with very little ether to remove any thallic bromide, extracting the residue with much cold ether, and evaporating the solution in an air stream, a white solid, m. p. 152° (decomp.), was obtained, and found to be free from inorganic thallium. It was

not purified, being much more unstable than the corresponding chloride (Found: Br, 35.2; Tl, 46.0. $C_6H_5Br_2Tl$ requires Br, 36.3; Tl, 46.3%).

Phenylthallium dibromide gradually decomposes to the monobromide on standing. It reacts with potassium iodide like the dichloride, giving iodobenzene and a black solid (see p. 1463). On heating, bromobenzene and thallic bromide are obtained, whereas diphenylthallium bromide gives an odour of diphenyl. The original filtrate from D was concentrated, giving yellow crystals (E). With water these became red (F). E and F were identical with the compounds $TlBr, TlBr_3$, and $3TlBr, TlBr_3$ obtained by Willm (*Ann. Chim. Phys.*, 1865, 5, 4) and Cushman (*Amer. Chem. J.*, 1900, 24, 231).

Formation of Phenylthallium Dibromide from Phenylmagnesium Bromide and Thallic Chloride.—Diphenylthallium bromide was prepared by the method of Goddard and Goddard (J., 1922, 121, 257) by adding ethereal thallic chloride (107 g.; 0.3 mol.) to a solution of magnesium (29.4 g.; 1.2 atom.) and bromobenzene (186 g.; 1.2 mols.) in ether. After removal of solvent and addition of dilute acetic acid the separated solid was extracted with pyridine, giving crude diphenylthallium bromide (Found, after crystallisation from pyridine: Tl, 45.95. Calc.: Tl, 46.6%). The pyridine mother-liquor on dilution with water gave two deposits, G, m. p. 70–76°, and H, m. p. below 100°. These were not described by Goddard and were therefore examined after being freed from adhering pyridine. When G was heated, a mixture of pyridine and bromobenzene distilled. With potassium iodide, G became yellow and, when warmed, gave iodobenzene, the presence of a phenylthallium dihalide thus being indicated.

G was heated with 10% hydrobromic acid, giving an infusible solid which, on crystallisation from pyridine, was shown to be diphenylthallium bromide (M) (Found: Br, 18.5. Calc.: Br, 18.25%). The main acid filtrate deposited pale yellow crystals, m. p. 172°.

The pyridine mother-liquor from (M) was diluted with water, giving two deposits, K and L, m. p.'s 92° and 90°. These gave iodobenzene with potassium iodide. With hot dilute hydrobromic acid, K and L gave more insoluble diphenylthallium bromide, and a further deposit of yellow needles, m. p. 176°, was obtained from the acid filtrate. These and the product of m. p. 172° both gave pyridine and thallic hydroxide with potassium hydroxide. The compound $2TlBr_3, 3(C_5H_5N, HBr)$ melts at 174° (Renz, *Ber.*, 1902, 35, 2768) (Found: Tl, 30.0; Br, 52.7. Calc.: Tl, 29.9; Br, 52.6%).

The decomposition of G was at first incomplete, doubtless owing

to formation of a layer of diphenylthallium bromide round the unattacked inner portion.

A portion of G was washed with light petroleum to remove diphenyl. The residue had m. p. 82—84°. Volumetric analysis in dilute acid solution with silver nitrate gave Br = 21.0%.

K and L were mixed and analysed by Goddard's method (J., 1922, **121**, 488) (Found: Br, 21.5. $C_6H_5Br_2Tl, 3C_5H_5N$ requires Br, 23.6. $C_6H_5Br_2Tl, 4C_5H_5N$ requires Br, 21.1%). Both substances were probably slightly impure, but there is no doubt as to their nature. Further evidence was obtained by dissolving phenylthallium dibromide in pyridine and diluting the solution with water. A solid, m. p. 92°, was deposited, which was decomposed by hot dilute hydrobromic acid in a similar manner to G.

The presence of phenylthallium dibromide (m. p. 152°) was also detected in (H). Diphenyl was removed by light petroleum. The residue was fluid at 151°, and decomposed at 155°. It gave iodobenzene with potassium iodide and after some months it had decomposed and was unmelted at 300°.

p-Tolylthallium Halides.—Thallic bromide (7.5 g.; 2 mols.) in water (27 c.c.) was added in one portion to a hot solution of *p*-tolylboric acid (1.2 g.; 1 mol.) in water (55 c.c.). After cooling, the solid was separated and dried. Its m. p. depends on the rate of heating, but when it is placed in a bath at 160—165°, immediate fusion occurs; at 150° fusion is incomplete. On attempted crystallisation from acetone—light petroleum decomposition occurs, thallic bromide is produced (sodium hydroxide test), and di-*p*-tolylthallium bromide separates (Found: Br, 17.1. Calc.: Br, 17.2%). This was also obtained directly by using 2 mols. of *p*-tolylboric acid and thallic bromide.

The crude *p-tolylthallium dibromide* was analysed without recrystallisation (Found: Tl, 44.5; Br, 34.3. $C_7H_7Br_2Tl$ requires Tl, 44.9; Br, 35.1%). When kept, it becomes brown on the surface, the odour of *p*-bromotoluene is noticed, and a portion becomes insoluble in acetone. Potassium iodide and *p*-tolylthallium dibromide give *p*-iodotoluene; with pyridine an additive compound is formed, as with the corresponding phenyl derivative.

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