

Chemistry of Arylboric Acids IX. Reaction of Arylboric and Alkylboric Acids with Mercuric Halides *

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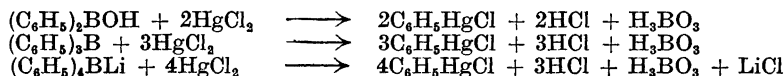
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The reaction between mercuric salts and arylboric acids is an electrophilic displacement reaction. Electron attracting substituents hamper the boron-mercury exchange whereas electron releasing substituents facilitate the reaction. Most arylboric acids react readily in aqueous solution; unreactive arylboric acids are rapidly converted in excellent yield to the corresponding mercury compound in glacial acetic acid medium with perchloric acid as catalyst. Alkylboric acids are converted in acetic acid medium to alkylmercuric salts without any catalyst.

According to Michaelis¹ phenylboric acid is converted to phenylmercuric chloride by aqueous mercuric chloride:

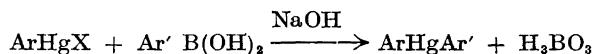


The mercuration reaction has been proved to proceed quantitatively and has been used for analytical purposes^{2,3}. Diarylboric acids,^{4,5} triphenylboron² and lithium tetraphenylboron² react in the same manner:



From lithium bis(*o,o'*-diphenyl)-boron Wittig and Herwig⁶ obtained *o,o'*-bis(chloromercuri) diphenyl in a yield of 51 %. Alkylboric acids react slowly⁷ or not at all⁸ with mercuric halides.

In alkaline solution diphenylmercury is obtained⁷ and according to Nesmejanow *et al.*⁹ asymmetrical diarylmercurials can be prepared by reacting arylmercuric halides with arylboric acid containing a different arylgroup:



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Table 1. Conversion of arylboric acids into arylmercuric halides by treatment with mercuric halides in aqueous solution. PhBA = Phenylboric acid.

Arylboric Acid	Arylmercuric halide		Yield, crude product, %	M.p., °C	M. p. Lit., °C	Analysis			
	ArHgX	Mol. wt.				Calc C %	Found C %	Calc H %	Found H %
1 PhBA	PhHgCl	313.2	74	257-8	258 a	—	—	—	—
2 PhBA	PhHgBr	357.6	42	282-3	280 b	—	—	—	—
3 4-OCH ₃ -PhBA	4-OCH ₃ -PhHgCl	343.2	93	249-50	239 c	24.50	24.38	2.06	1.97
4 4-OCH ₃ -PhBA	4-OCH ₃ -PhHgBr	387.7	62	255-6	243-4 d	21.69	22.13	1.82	1.74
5 α -NaphthylBA	α -NaphthylHgCl	363.3	95	190-1	191 a	—	—	—	—
6 α -NaphthylBA	α -NaphthylHgBr	407.7	50	203-4	202 b	—	—	—	—
7 2-CH ₃ -OH-PhBA	2-CH ₃ -OH-PhHgCl	343.2	59	135-6	—	24.50	24.16	2.06	1.83
8 2-CHO-PhBA	2-CHO-PhHgCl	341.2	88	176-7	—	24.64	24.81	1.48	1.46
9 2-CH ₃ -3,5-diNO ₂ -PhBA	2-CH ₃ -3,5-diNO ₂ -PhHgCl	417.2	32 e	253-4, d.	—	20.15	19.88	1.21	1.00
10 3-COOH-PhBA	3-COOH-PhHgCl	357.2	—	268-9, d.	—	23.53	23.82	1.41	1.63
11 2-NO ₂ -4-NH ₂ -PhBA	2-NO ₂ -4-NH ₂ -PhHgCl	373.2	88	255-6, d.	—	19.31	19.69	1.35	1.16
12 3-NO ₂ -5-NH ₂ -PhBA	3-NO ₂ -5-NH ₂ -PhHgCl	373.2	40	273-5, d.	—	—	—	—	—
13 2-NO ₂ -4-COOCH ₃ -PhBA	2-NO ₂ -4-COOCH ₃ -PhHgCl	416.2	0	—	—	—	—	—	—
14 3-NO ₂ -5-COOCH ₃ -PhBA	3-NO ₂ -5-COOCH ₃ -PhHgCl	416.2	trace	—	—	—	—	—	—
15 <i>iso</i> -Butylboric acid	<i>iso</i> -butyl-HgBr	337.6	0	—	—	—	—	—	—
16 2-NO ₂ -4-COOCH ₃ -PhBA ^f	2-NO ₂ -4-COOCH ₃ -PhHgCl	416.2	97	172-3	—	23.09	23.00	1.45	1.40
17 3-NO ₂ -5-COOCH ₃ -PhBA ^f	3-NO ₂ -5-COOCH ₃ -PhHgCl	416.2	92	247-9	—	23.09	23.17	1.45	1.53
18 <i>iso</i> -Butylboric acid ^g	<i>iso</i> -butyl-HgBr	337.6	50	54-5	55.5 h	—	—	—	—
19 <i>n</i> -Octylboric acid ^g	<i>n</i> -octyl-HgCl	349.3	81	115-6	115-5.5 i	—	—	—	—

a. Nesmejanov, A. N. *Ber.* **62** (1929) 1011. b. Slotta, K. H. and Jakobi, K. R. *J. prakt. Chem.* (2) **120** (1929) 249.
c. Michaelis, A. and Rabinerson, F. *Ber.* **23** (1890) 2342. d. Challenger, F. and Miller, S. A. *J. Chem. Soc.* **1938** 894.
e. 56% of the starting material recovered. f. The reaction was carried out in glacial acetic acid with perchloric acid as catalyst. g. The reaction was carried out in glacial acetic acid without catalyst. h. Marvel, C. S., Ganerke, C. G. and Hill, E. L. *J. Am. Chem. Soc.* **47** (1925) 3009. i. Whitmore, F. C. and Bernstein, H. *Ibid.* **60** (1938) 2626.

Johnson *et al.*^{10,11} have used the reaction between arylboric acids and mercuric chloride for the structural determination of nitroderivatives obtained by nitration of arylboric acids. The corresponding mercury derivatives were formed in good yields.

In a series of papers, Torrsell *et al.*¹²⁻¹⁵ have shown that a number of reactions and rearrangements can be performed with arylboric acids, even under drastic conditions, without splitting off the dihydroxyboron group (borono group). The availability of new arylboric acids and their apparent ready conversion to mercury compounds by simple treatment with an aqueous mercury halide might therefore render this mercuration reaction of value as a preparative method.

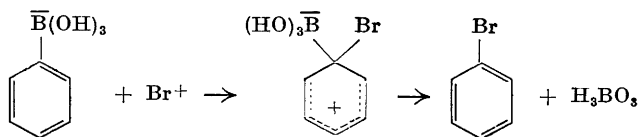
There seems to be one limitation. Arylboric acids containing many electron attracting substituents *e.g.* $-\text{NO}_2$, $-\text{COOR}$, react very slowly or not at all in aqueous solution. The unreactivity of certain compounds can, however, be easily overcome by using glacial acetic acid as medium and perchloric acid as catalyst. Klapproth and Westheimer¹⁶ had found previously that the rate of mercuration of aromatic compounds increases with the acid concentration.

When, *e.g.*, 2-nitro-4-carbomethoxy-phenylboric acid, which is unaffected by aqueous mercuric chloride, is reacted with the mercuric halide in glacial acetic acid to which a small amount of perchloric acid is added, the corresponding mercuric organic compound is formed practically instantaneously in good yield. (Table 1, numbers 16 and 17.)

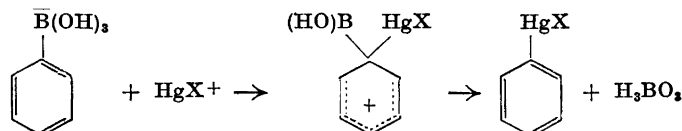
Mercuration of the aromatic nucleus is recognized as an electrophilic attack by positively charged mercuric ions¹⁶. Substituents increasing the electron density of the nucleus therefore facilitate the reaction, whereas substituents withdrawing electrons from the nucleus have the opposite effect.

The mercury-boron exchange seems to follow the same scheme. If mercuric chloride is added to a cold aqueous phenylboric acid solution, the mercury compound will be formed and precipitate immediately whereas a *m*-nitrophenylboric acid solution must be heated for a short time before precipitation occurs. From Table 1 it can be seen that 2-nitro-4-carbomethoxyphenylboric acid does not react and 3-nitro-5-carbomethoxyphenylboric acid gives only traces of the mercury compound. When 2-methyl-3,5-dinitrophenylboric acid is reacted with mercuric chloride for 20 min, only a part of the boron compound yields the mercury derivative and another part can be recovered as unreacted material. The ring carbon atom, to which the boron atom is attached, is electron deficient in these compounds. The mononitro¹⁰ and monocarboxy derivatives⁴, however, give the corresponding mercury compounds in good yield, which is also the case with all the other compounds tested in the present study.

Kuivila and Hendrickson¹⁷ have shown that the bromolysis of arylboric acids is an electrophilic substitution:



The mercuration can be formulated in the same way:



The unreactivity of alkylboric acids towards mercuric salts has been reconfirmed. When *iso*-butylboric acid, for example, is heated with mercuric chloride in aqueous solution for 30 min no mercury organic compound can be detected. Part of the *iso*-butylboric acid decomposes into boric acid and butanol during the heating, a reaction that also takes place when no mercuric salt is present.

However, the corresponding alkylmercuric halide is formed in good yields when the reaction is carried out in acetic acid medium. No catalyst is necessary. Prolonged heating or presence of perchloric acid causes formation of yellow colored products difficultly soluble in ordinary solvents (M.p. > 260°).

EXPERIMENTAL

General procedure for converting an arylboric acid into the corresponding arylmercuric halide compound. The arylboric acid is dissolved in hot water. For compounds difficultly soluble in water a mixture of ethyl alcohol and water, 1:1, is employed. A sufficient amount of solvent is thereby used to ensure that no arylboric acid precipitates when the aqueous mercuric chloride is added. Mercuric chloride (25 % excess) is dissolved in warm water and added to the arylboric acid solution. Usually the arylmercuric halide precipitates after a few minutes or less. In order to ensure complete conversion, the mixture is boiled for ca. 15 min and left standing overnight in a refrigerator. The precipitate is filtered, washed with water and dried.

Conversion of less reactive arylboric acids into arylmercuric halide in glacial acetic acid medium with perchloric acid as catalyst. 3-Nitro-5-carbomethoxy-phenylboric acid, 0.1 g, is dissolved in 3 ml of glacial acetic acid at 80–90°; mercuric acetate, 0.16 g, is added and then 60 % perchloric acid, 0.05 ml. After 2 min at this temperature, the solution is poured into 15 ml of water containing potassium chloride, 0.2 g. A white precipitate of 3-nitro-5-carbomethoxyphenylmercuric chloride is formed immediately. Yield 97 %, m. p. 247–249°, from ethyl alcohol.

Conversion of alkylboric acids into alkylmercuric halides. *n*-Octylboric acid,¹⁸ 0.10 g, is dissolved in 2 ml of cold glacial acetic acid. Mercuric acetate, 0.26 g, is added and the solution is warmed to 90–100° for 4–5 min whereafter it is poured into 12 ml water containing sodium chloride, 0.1 g. *n*-Octylmercuric chloride precipitates immediately, 0.18 g or 81 %, m. p. 115–116°.

iso-Butylmercuric bromide is prepared in the same way. Yield 50 %, m. p. 54–5°.

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