297. *Advances in the Preparation of Arylboron Dihalides, Cyclic 2-Arylboroles, and* B-*Triarylborazoles.*

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The novel method of preparing an arylboron halide from the arylmercury halide, $ArHgX + BX_3 \longrightarrow ArBX_2 + HgX_2$ (X = Cl or Br), has in general considerable advantages over the previous methods. Phenylmercury chloride and boron tribromide have afforded the first reported mixed halide, RBClBr. Interaction of phenylmercury nitrate and boron trichloride is described.

From the arylboron dichloride and pyrocatechol, certain 2-arylbenzo-1,3-dioxa-2-boroles, and from 2,3-dihydroxynaphthalene certain 2-arylnaphtho-1,3-dioxa-2-boroles were prepared. The relevant preparation of *B*-tritolylborazoles, $(MeC_6H_4{\cdot}BNY)_3$ (Y = H or Me) is described.

Mercury diaryls were the first reagents to be used for the attachment of aryl to boron, giving directly the arylboron dihalide,[1,2] *e.g.*, $HgPh_2 + 2BCl_3 \longrightarrow 2PhBCl_2 + HgCl_2$. A sealed-tube technique was used. Apart from a recent study[3] this system has been discarded in favour of the multi-step procedure involving halogenation of the arylboronic anhydride or ester;[2] techniques involving tetraphenyltin,[4] or aluminium powder with an aromatic hydrocarbon,[5] are also being developed.

[1] Michaelis and Becker, *Ber.*, 1880, **13**, 58; 1882, **15**, 180.

[2] Gerrard, "The Organic Chemistry of Boron," Academic Press, Inc., New York, 1961, p. 58.

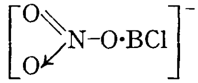
[3] Gilman and Moore, *J. Amer. Chem. Soc.*, 1958, **80**, 3609.

[4] Burch, Gerrard, Howarth, and Mooney, *J.*, 1960, 4916; Brinckmann and Stone, *Chem. and Ind.*, 1959, 254; Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223.

[5] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 4163.

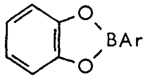
We have now prepared a number of arylboron dihalides (Table 1) by a novel reaction of boron trihalide in benzene with an arylmercury halide prepared by established procedures from mercuric dihalide and either the Grignard reagent or the aryldiazonium chloride (reaction 1).

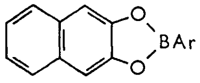
$$\mathrm{ArHgX} + \mathrm{BX_3} \longrightarrow \mathrm{ArBX_2} + \mathrm{HgX_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Phenylmercury chloride and boron tribromide gave the first reported example of a mixed dihalide (reaction 2), and this supports our postulate that the mechanism could be as shown in (3). A lower yield of *p*-tolylboron dibromide, and evolution of hydrogen bromide, in the *p*-tolylmercury bromide–boron tribromide system are attributed to the formation of the tetrabromoborate ion $[\mathrm{BBr_4}]^-$, which brominates the methyl group; for it has been observed that, whereas a tetrachloroborate will not, a tetrabromoborate will form benzyl halide when heated with toluene.[6] Phenylmercury nitrate and boron trichloride in benzene gave mercuric chloride, phenylboron dichloride, and nitrobenzene; this is not in discord with mechanism (3); for it is plausible that the ion  $\left[\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\!\!>\!\mathrm{N{-}O{\cdot}BCl}\right]^-$ would be prone to a more complicated sequence of reactions.

$$\mathrm{PhHgCl} + \mathrm{BBr_3} \longrightarrow \mathrm{PhBClBr} + \mathrm{HgBr_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{ArHgX} + \mathrm{BY_3} \longrightarrow [\mathrm{ArHg}]^+[\mathrm{XBY_3}]^- \longrightarrow \mathrm{Ar}^+ + \mathrm{HgY_2} + [\mathrm{BXY}]^- \longrightarrow \mathrm{ArBXY} + \mathrm{HgY_2} \quad . \quad (3)$$


(I)


(II)

The arylboron dichlorides, in benzene solution, afforded the boroles[7] (I) (from pyrocatechol) (Table 2) and (II) (from naphthalene-2,3-diol) (Table 3) in excellent yields. *B*-Tritolylborazoles and *B*-tritolyl-*N*-trimethylborazoles (Table 4) were prepared from the tolylboron dichloride and ammonia or methylamine, as previously described for the corresponding phenyl compounds.[2,8,9]

EXPERIMENTAL

Arylmercury Compounds.—The halides were prepared by addition of mercuric chloride to either the Grignard reagent or the aryldiazonium chloride solution, in accordance with established techniques. The phenylmercury chloride and nitrate were supplied by F. W. Berk and Co.

Preparation of Arylboron Dihalides.—The arylmercury halide (~70 g., 1·0 mol.) and the corresponding boron trihalide (1·0 mol.) were heated under reflux in benzene (250 ml.) for 4 hr.; the insoluble mercury halide was filtered off, and the filtrate afforded arylboron dihalide (Table 1). In some cases, *e.g.*, with phenylmercury chloride, the reactants need only be shaken in benzene for 1 hr. 1-Naphthylboron dichloride could not be obtained pure; it was characterised by conversion into the boroles (I) and (II) (Tables 2 and 3).

Interaction of Phenylmercury Chloride and Boron Tribromide.—The chloride (71·85 g., 1·0 mol. and boron tribromide (57·36 g., 1·0 mol.) were heated under reflux in benzene (250 ml.); the mercuric bromide (80·67 g., 97·6%) (Found: Hg, 55·3. Calc. for $\mathrm{HgBr_2}$: Hg, 55·6%) was filtered off, and the filtrate afforded *phenylboron bromide chloride* (25·30 g., 54·3%) (Found: C, 35·6; H, 2·7; B, 5·5; Br, 39·0; Cl, 17·6. $\mathrm{C_6H_5BBrCl}$ requires C, 35·5; H, 2·5; B, 5·3; Br, 39·3; Cl, 17·4%), b. p. 68—70°/10 mm.

Interaction of Phenylmercury Nitrate with Boron Trichloride.—Phenylmercury nitrate (67·52 g., 1·0 mol.) and boron trichloride (1 mol.) were heated under reflux in benzene (250 ml.)

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[6] Butcher, Gerrard, and Mooney, unpublished work.
[7] Dewar, Kubba, and Pettit, *J.*, 1958, 3076.
[8] Ruigh *et al.*, W.A.D.C. Technical Report 55-26, Parts II—IV.
[9] Burch, Gerrard, and Mooney, *J.*, 1962, 2200.

TABLE 1.

Preparation of arylboron dihalides from arylmercury halides.

ArHgX			BX_3	Yield				Found (%)			Calc. (%)	
Ar	X	g.	X	(%)	B. p./mm.	d_4^{20}	n_D^{20}	B	X	Formula	B	X
Ph	Cl	66·20	Cl	76	70—72°/10			6·9	44·4	$C_6H_5BCl_2$	6·8	44·65
Ph	Br	65·3	Br	43	94—104°/15 §			4·3	64·1	$C_6H_5BBr_2$	4·4	64·5
p-Me·C_6H_4	Cl	44·38	Cl	74	92°/10 §	1·179*	1·5390*	6·2	41·2	$C_7H_7BCl_2$	6·2	41·0
p-Me·C_6H_4	Br	72·60	Br	26	64°/10 §			4·0	59·8	$C_7H_7BBr_2$	4·1	61·1
o-Me·C_6H_4	Cl	97·66	Cl	67	88—92°/12	1·204	1·5499	6·2	40·4	$C_7H_7BCl_2$	6·2	41·0
m-Me·C_6H_4	Cl	70·8	Cl	57	86—88°/15	1·188	1·5430	6·2	40·3	$C_7H_7BCl_2$	6·2	41·0
p-Cl·C_6H_4	Cl	40·5	Cl	67	70°/0·4	1·357	1·5689	5·6	36·6 †	$C_6H_4BCl_3$	5·6	36·7 †
p-Br·C_6H_4	Cl	94·7	Cl	59	54—60°/0·4 §			4·6	29·6 †	$C_6H_4BBrCl_2$	4·6	29·8 †

* Both at 35°. † Easily hydrolysable halogen. § Low-melting solids.

TABLE 2.

Preparation of 2-arylbenzo-1,3-dioxa-2-boroles (I).

$ArBCl_2$		Yield		Found (%)					Required (%)			
Ar	g.	(%)	M. p.	C	H	B	X	Formula	C	H	B	X
p-Me·C_6H_4 ...	20·84	92·1	140—141·5°	74·1	5·3	5·2	—	$C_{13}H_{11}O_2B$	74·4	5·3	5·2	—
o-Me·C_6H_4 ...	20·3	82·8	88—89	74·2	5·3	5·1	—	$C_{13}H_{11}O_2B$	,,	,,	,,	—
m-Me·C_6H_4 ...	12·58	78·2	94—95	74·4	5·4	5·1	—	$C_{13}H_{11}O_2B$	,,	,,	,,	—
p-Cl·C_6H_4 ...	24·68	92·8	148—149	62·4	3·4	4·8	15·2	$C_{12}H_8O_2BCl$	62·5	3·5	4·7	15·4
p-Br·C_6H_4 ...	12·41	84·7	157—159	51·9	2·9	3·9	27·7	$C_{12}H_8O_2BBr$	52·4	2·9	3·9	29·1
1-$C_{10}H_7$	3·12	44·3	112—114	78·1	4·4	4·3	—	$C_{16}H_{11}O_2B$	78·1	4·5	4·4	—

TABLE 3.

Preparation of 2-arylnaphtho[2,3-*d*]-1,3-dioxa-2-boroles (II).

$ArBCl_2$		Yield		Found (%)					Required (%)			
Ar	g.	(%)	M. p.	C	H	B	X	Formula	C	H	B	X
Ph	22·1	90·2	234—236°	78·2	4·7	4·4	—	$C_{16}H_{11}O_2B$	78·1	4·5	4·4	—
p-Me·C_6H_4 ...	13·1	98·7	285—287	78·6	5·3	4·2	—	$C_{17}H_{13}O_2B$	78·5	5·0	4·2	—
o-Me·C_6H_4 ...	9·0	81·2	199—201	78·4	5·0	4·2	—	$C_{17}H_{13}O_2B$	,,	,,	,,	—
m-Me·C_6H_4 ...	10·98	93·9	214—216	78·7	5·2	4·2	—	$C_{17}H_{13}O_2B$	,,	,,	,,	—
p-Cl·C_6H_4 ...	17·89	91·5	294—295	68·5	3·7	3·8	12·4	$C_{16}H_{10}O_2BCl$	68·5	3·6	3·9	12·6
p-Br·C_6H_4 ...	13·12	88·5	293—295	61·1	3·3	3·3	23·7	$C_{16}H_{10}O_2BBr$	59·1	3·1	3·3	24·6
1-$C_{10}H_7$	4·52	87·4	221—224	81·1	4·4	3·65	—	$C_{20}H_{13}O_2B$	81·1	4·4	3·65	—

TABLE 4.

Preparation of *B*-tritolylborazole (Me·C_6H_4·BNY)$_3$.

Tolyl group	Y	Yield (%)	M. p.	Found (%) C	H	N	B	Formula	Required (%) C	H	N	B
p-	H	80	186—189°	71·6	6·6	12·1	9·3	$C_{21}H_{24}B_3N_3$	71·9	6·9	12·0	9·3
m-	H	97	140	72·6	7·3	12·0	9·2	$C_{21}H_{24}B_3N_3$	,,	,,	,,	,,
o-	H	85	89—92	71·6	7·0	11·9	9·3	$C_{21}H_{24}B_3N_3$	,,	,,	,,	,,
p-	Me	16	196—199	73·4	7·9	10·7	8·2	$C_{24}H_{30}B_3N_3$	73·35	7·7	10·7	8·3
m-	Me	54	192	73·0	7·8	10·7	8·2	$C_{24}H_{30}B_3N_3$	,,	,,	,,	,,
o-	Me	100	217—222	73·3	7·9	10·8	8·2	$C_{24}H_{30}B_3N_3$	,,	,,	,,	,,

for 12 hr.; mercuric chloride (54·80 g.) (Found: Hg, 73·0. Calc. for $HgCl_2$: Hg, 73·8%) was filtered off, and the filtrate afforded a mixture (12·34 g.) of nitrobenzene and phenylboron dichloride (Found: Cl, 30·4%), which on alkaline hydrolysis and ether-extraction gave nitrobenzene (1·85 g.), b. p. 206°. Acidification of the aqueous hydrolysate and filtration gave phenylboronic acid (3·62 g.) (Found: B, 8·7. Calc. for $C_6H_7BO_2$: B, 8·9%). There was a distillation residue (32·69 g.) (containing neither mercury nor chlorine) of phenylboronic anhydride and boric oxide (Found: B, 10·3%).

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