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Investiya Akademii Nauk
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ORGANOBORON COMPOUNDS. VIII.
SYNTHESIS AND PROPERTIES OF DIARYLBORIC ACIDS

Mikhailov, B. M. and Vaver, V. A.

In one of the authors' previous communications, a method of preparation of diphenylboric acid and its derivatives has been described (1). The properties of these derivatives and the desire to further establish (confirm) the existing in the literature data pertaining to other diarylboric acids have prompted the authors to undertake the synthesis of additional members of this class of chemical compounds.

The following preparations were undertaken with success: di-naphthyl, di-p-bromophenyl and di-p-chlorophenyl boric acids. Isobutyl esters of the above named acids were obtained in 40-53% of theoretical yield, as well as the diisobutyl esters of the corresponding monoaryl boric acids, from the products of the interaction of two equivalents of aryl magnesium bromides with one equivalent of triisobutyl borate. These reactions were carried out under conditions similar to the synthesis of isobutyl ester of diphenyl boric acid (1):



The characteristic property of these synthesized esters of diarylboric acids is their stability with respect to water and dilute mineral acid hydrolysis. Their second characteristic is their high solubility in alkaline solutions, with the consequent formation of the salts of diarylisobutoxy boric acids



Heating the water solutions of such salts, obtained from the action of esters of diarylboric acids with aqueous alkali metal and alkali earth hydroxides, results in saponification of the alkoxy group in the anion with the consequent formation of salts of diarylboric acids



Thus the barium salts of diarylboric acids are easily obtained with direct treatment of diarylboric acid with saturated water solution of barium hydroxide.

In this case, apparently, the same anion saponification reaction first forms the salt of diarylisobutoxy boric acid, but the reaction proceeds faster due to low solubility of barium salts of diarylboric acids.

The esters of di-naphthyl and di-p-bromophenyl boric acids also react easily with aqueous ammonia, forming ammonium salts of corresponding diarylboric acids. The ester of di-p-chlorophenyl boric acid is in this case an exception:

it is not affected by aqueous ammonia even upon heating.

The diarylboric acid salts of the general formula



where Me = K, Na, Ba, NH₄, Ar = *o*-C₁₀H₇, *p*-BrC₆H₄, *p*-ClC₆H₄, —
on acidification are transformed into acids:



The salts of the di-*o*-naphthyl and di-*p*-bromophenyl boric acids yield the corresponding diarylboric acids, while the salt of di-*p*-chlorophenyl boric acid yields an acid which corresponds, from analysis, to the monohydrate of di-*p*-chlorophenyl boric acid, as was already reported (1) in the case of phenyl boric acid.

In contrast to diphenylboric acid, the other diaryl boric acids, obtained by the authors, do not form anhydrides on heating in vacuum, instead monoaryl boric acids are formed upon loss of one aryl radical. The anhydrides may be obtained by treatment with thionyl chloride as shown in an example with di-*o*-naphthylboric acid:



In conclusion it is well to pause and consider the data, available in the literature, pertaining to the diarylboric acids. The di-*o*-naphthyl boric acid was recently obtained by Letsinger (2) and his co-workers from the acid hydrolysis of its aminocethyl ester. As to the di-*p*-bromophenyl and the di-*p*-chlorophenyl boric acids, described by Kdaig and Scharinbeck (3) and by Malnikoff (4) the examination of the methods of their preparation, as used by these authors, leads one to doubt if the above mentioned acids were actually obtained. Kdaig and Scharinbeck and later Malnikoff used the reaction of equimolar quantities of aryl magnesium bromide and tributyl borate for preparation of the organoboron compounds. After working up the reaction product with dilute mineral acid and isolation of the monoaryl boric acid by-products the residue, under these conditions, could at best contain the unsaponified ester of the diarylboric acid and not the free acid itself.

Kdaig and Scharinbeck determined the melting point of di-*p*-bromophenyl acid to be 113°C, while in reality it melts at 91°C. The data of Malnikoff, et al show the di-*p*-chlorophenyl boric acid to have the following composition (ClC₆H₄)₂B(OH)₂, while in reality its composition is (ClC₆H₄)₂B(OH)₂.H₂O.

Moreover, Malnikoff, et al erroneously shows that the reaction of equimolar quantities of *p*-chlorophenyl magnesium bromide with tributyl borate yields the di-*p*-chlorophenyl boric acid with a 17% yield together with a smaller yield (15% of theoretical) of the mono-*p*-chlorophenyl boric acid. Repeating Malnikoff's work, we found that under the above stated conditions only the mono-*p*-chlorophenyl boric acid is obtained and that no ester of di-*p*-chlorophenyl boric acid is obtained.

EXPERIMENTAL

Isobutyl ester of di- α -naphthylboric acid.

To a 1 molar ether-benzene solution of 0.5 mole of α -naphthylmagnesium bromide maintained in the -20 to -30°C temperature range, 0.225 moles (52 grams) of triisobutyl borate, dissolved in 50 ml of dry ether, are added with intensive mechanical agitation in a period of 15 minutes. Upon completion of addition of borate ester, the reaction temperature is lowered to the -70 to -75°C temperature range and the agitation of the reaction mass is continued for a period of 6 - 7 hrs. The next day the reaction products are treated with 350 ml of 5% hydrochloric acid. The ether-benzene layer is separated out, the water solution is extracted with ether. The combined ether-benzene extracts are dried over anhydrous sodium sulfate. The ether-benzene is then removed by distillation. The resulting viscous, slightly yellowish residue upon dilution with 50 ml of isopentane set up as a crystalline mass. The reaction residue was then filtered and sucked dry, carefully washed with isopentane and then dried under vacuum. Yield 47.5 grams (6% of theoretical) of isobutyl ester of di- α -naphthyl boric acid, melting point $104-5^{\circ}\text{C}$ (after recrystallization from *n*-hexane).

Found	% C 85.20, 85.14	H 6.73, 6.77	B 3.17, 3.24
Calc. for $\text{C}_{24}\text{H}_{22}\text{BO}$	% C 85.22	H 6.85	B 3.19

The isopentane filtrate, after removal of the isopentane solvent by distillation is esterified with isobutyl alcohol. Ten grams (1% of theoretical) of diisobutyl ester of α -naphthyl boric acid are obtained, m.p. $166-168^{\circ}\text{C}$ at 6 mm Hg, d_4^{20} 0.9777

Found	% C ₁₀ H ₇ 45.70, 45.84	B 3.60, 3.67
Calc. for $(\text{C}_{10}\text{H}_7)_2(\text{OC}_4\text{H}_9)_2$	% C ₁₀ H ₇ 44.42, 45.70	B 3.70

The isobutyl ester of di- α -naphthyl boric acid is a colorless crystalline substance, easily soluble in benzene and chloroform, very slightly soluble in petroleum ether and methyl alcohol, and insoluble in isopentane. Diisobutyl ester of α -naphthyl boric acid is a colorless liquid. Upon action of atmospheric moisture, it is easily hydrolyzed, liberating the α -naphthyl boric acid.

Ammonium Salt of di- α -naphthyl boric acid.

Ten grams of isobutyl ester of di- α -naphthyl boric acid are mixed with 20 ml of methyl alcohol. 15 ml of 30% aqueous ammonia are added with high agitation. A clear solution is produced momentarily, after which colorless crystalline substance is formed. After half hour agitation, the crystals are filtered and sucked dry, washed with methyl alcohol and dried under vacuum until constant weight. Yield 8.85 grams of the ammonium salt of di- α -naphthyl boric acid, representing 97.5% theoretical, m.p. $105-107^{\circ}\text{C}$. After recrystallization from methyl alcohol, the salt melts at $107-108^{\circ}\text{C}$.

Found	% C ₁₀ H ₇ 79.44, 79.84	H 3.24, 3.20	N 4.12, 4.09
Calc. for $[(\text{C}_{10}\text{H}_7)_2\text{B}(\text{OH})_2] \text{NH}_4$	% C ₁₀ H ₇ 80.17, 80.17	H 3.41	N 4.41

The ammonium salt of di- α -naphthylboric acid is a colorless crystalline compound, quite soluble in benzene and in hot methyl alcohol, only slightly soluble in cold methyl alcohol, and insoluble in water. In the air it is rapidly hydrolyzed with liberation of ammonia and naphthalene and forms the α -naphthyl

boric acid.

Di- α -naphthyl boric acid.

4.24 grams of the ammonium salt of di- α -naphthyl boric acid are mixed in 30 ml of diethyl ether. To the mixture 5 ml of 6N hydrochloric acid are added with intensive agitation with the resulting reaction mixture being acid to Congo red. The ether layer is separated out, while the water layer is extracted further with diethyl ether. The combined ether extracts are then vacuum distilled to remove ether, after which the residue is heated to 70°C for 10-15 minutes. The reaction product (the residue) is then dissolved in a minimum amount of dry benzene and then precipitated out by addition of 10 ml of isopentane. 3.15 grams of di- α -naphthyl boric acid are obtained, representing 71.7% of theoretical yield; melting point 113-114°C. After recrystallization from petroleum ether, the pure di- α -naphthyl boric acid was found to melt at 114.3-115°C.

Found %:	C 84.83, 84.90;	H 3.26, 3.38	B 3.91, 3.97
Calc. for $C_{20}H_{12}BO$:	% C 85.13	H 3.35	B 3.85

The di- α -naphthyl boric acid is a colorless, crystalline substance, readily soluble in benzene, very slightly soluble in ether, insoluble in isopentane. Upon heat treatment in vacuum, above melting point, no anhydride is formed. Instead, one of the naphthyl groups is split off as naphthalene, and the α -naphthyl boric acid is obtained.

Di- α -naphthyl boric acid anhydride.

Five grams of di- α -naphthyl boric acid are dissolved in 5 ml of thionyl chloride and the solution refluxed for 2 hours. The thionyl chloride is then removed in vacuum, the residue is recrystallized from the benzene-petroleum ether mixture. 1.9 grams (38 percent of theoretical yield) of the di- α -naphthyl boric acid anhydride are obtained; melting point 190-192°C.

Found %:	$C_{10}H_7$ 91.80, 91.96;	B 4.24, 4.20
Calc. for $(C_{10}H_7)_2BO_2$:	% $C_{10}H_7$ 92.98	B 4.34

This anhydride is a colorless, crystalline substance, only slightly soluble in benzene and insoluble in either petroleum ether or isopentane.

Isobutyl ester of di-p-bromophenyl boric acid.

To a 1 molar ether solution of 0.65 moles of p-bromophenyl magnesium bromide, prepared by the method described by Pink (5), 0.25 moles of triisobutyl borate, dissolved in 100 ml of absolute ether, are added with intensive mechanical agitation in the -30 to -60°C temperature range within a period of one half hour. The resulting reaction mass is then further agitated for 3 hours in the -70 to -75°C temperature range. The reaction products are then treated with 50 ml of 5% hydrochloric acid. The residue, after ether removal, is esterified with 25 ml of isobutyl alcohol and fractionated in vacuum from a Claisen flask in atmosphere of dry nitrogen. The distillate is obtained as two fractions, first in the 102-150°C temperature range, the second in the 158-164°C range, both at 1 mm Hg pressure. Upon further fractionation, 38 grams (59% of theoretical yield) of isobutyl ester of di-p-bromophenyl boric acid, m.p. 161-163°C at 1 mm Hg, and 30 grams (57% of theoretical yield) of diisobutyl ester of p-bromophenyl boric acid, m.p. 109-110°C at 1 mm Hg (lit. 1.158) are obtained.

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	Found	%	BrC ₆ H ₄	78.73, 78.60;	B	2.69, 2.75
Calc. for	(BrC ₆ H ₄) ₂ B(OC ₄ H ₉) ₂	%	BrC ₆ H ₄	78.80	B	2.73
	Found	%	BrC ₆ H ₄	49.72, 49.81;	B	3.27, 3.34
Calc. for	(BrC ₆ H ₄) ₂ B(OC ₄ H ₉) ₂	%	BrC ₆ H ₄	49.83	B	3.46

The isobutyl ester of di-p-bromophenyl boric acid is a colorless, very viscous liquid substance that slowly "sets" upon standing at room temperature. It is soluble in most of organic solvents and is slowly decomposed in the air. The diisobutyl ester of p-bromophenyl boric acid is a colorless liquid which is rapidly saponified in the air forming p-bromophenyl boric acid.

Ammonium salt of di-p-bromophenyl boric acid.

2.25 grams of isobutyl ester of di-p-bromophenyl boric acid are mixed with 5 ml of 30% water solution of ammonia. The resulting crystalline precipitated is filtered, sucked dry, washed with water and dried in vacuum to constant weight. 1.85 grams of the ammonium salt of di-p-bromophenyl boric acid are obtained (m.p. 133-135°C). This represents 87.3% of theoretical yield. After recrystallization from benzene, the m.p. was found to be 134-135°C.

	Found	%	BrC ₆ H ₄	83.59, 83.42;	B	2.90, 2.91;	N	3.64, 3.65
Calc. for	[(BrC ₆ H ₄) ₂ B(OH) ₂] NH ₄	%	BrC ₆ H ₄	83.23,	B	2.89,	N	3.74

The ammonium salt of di-p-bromophenyl boric acid is a colorless, odorless, crystalline substance, soluble in ethyl and methyl alcohols, slightly soluble in benzene, insoluble in isopentane.

Potassium salt of di-p-bromophenyl boric acid.

1.23 grams of isobutyl ester of di-p-bromophenyl boric acid are dissolved in the equivalent quantity of a water solution of potassium hydroxide (3.69 ml of 0.8N) after which the water is slowly removed under vacuum in the 60-70°C temperature range, in the small sweep of nitrogen. The resulting residue consists of colorless crystals. After recrystallization from benzene-methanol mixture, 0.8 grams of product are obtained.

	Found	%	BrC ₆ H ₄	78.56, 78.67;	B	2.71, 2.73	K	9.81, 9.84
Calc. for	[(BrC ₆ H ₄) ₂ BOH] ₂ K	%	BrC ₆ H ₄	78.70	B	2.73	K	9.87

The potassium salt of di-p-bromophenyl boric acid is very soluble in water and alcohols, insoluble in benzene, petroleum ether or isopentane. Upon treatment with dilute mineral acids, the di-p-bromophenyl boric acid is regenerated quantitatively.

Di-p-bromophenyl boric acid.

1.63 grams of the ammonium salt of di-p-bromophenyl boric acid are treated with diluted hydrochloric acid. The reaction product is then extracted with ether, after which ether is removed by vacuum evaporation. The residue is dissolved in a small quantity of isopentane. 1.30 grams (86% of theoretical yield) of di-p-bromophenyl boric acid are obtained. After recrystallization from petroleum ether, the melting point was found to be 90-91°C.

	Found	%	C	42.61, 42.69;	H	2.83, 2.66;	B	35.18, 3.17	Br	47.39, 47.10
Calc. for	C ₁₂ H ₁₀ BOBr ₂	%	C	42.41	H	2.67	B	35.18	Br	47.03

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The di-*p*-bromophenyl boric acid is a colorless crystalline substance, readily soluble in alcohols and in benzene, slightly soluble in petroleum ether, insoluble in isopentane. It may also be obtained upon acidification of the potassium salt, as mentioned previously. 0.889 grams of potassium salt yield 0.760 grams of acid upon acidification with dilute hydrochloric.

Isobutyl ester of di-*p*-chlorophenyl boric acid.

To a 1 molar ether solution of 0.6 moles of *p*-chlorophenyl magnesium bromide, maintained in the -30° to -60°C temperature range, 0.25 moles of tri-isobutyl borate, dissolved in 100 ml of dry ether, are added within a period of one half hour with intensive mechanical agitation. The reaction mixture is then further cooled to -70 to -75°C and agitated for a period of 8.9 hours. On the next day the reaction products are treated with 450 ml of 5 percent hydrochloric acid. The residue, after removal of ether is esterified with 25 ml of isobutyl alcohol and after removal of excess alcohol by distillation, is distilled rapidly from the Claysen flask in a stream of dry nitrogen. The reaction products are obtained as two separate fractions: The 70-145°C fraction (at 2 mm Hg) and the 145-155°C fraction (at 2 mm Hg). Upon further fractionation with the aid of a Hempel column in a stream of dry nitrogen 31 gms. of isobutyl ester of di-*p*-chlorophenyl boric acid are obtained at 134-135°C (1 mm Hg), d_4^{20} 1.1414. This represents 40 percent of theoretical yield. Also 17 grams of diisobutyl ester of *p*-chlorophenyl boric acid are obtained at 93-95°C (1 mm Hg), d_4^{20} 1.0091, representing 25% of theoretical yield.

Found	%: ClC ₆ H ₄	72.56, 72.23	B 3.55, 3.53	Cl 23.27, 23.31
Calc. for (ClC ₆ H ₄) ₂ B(OC ₄ H ₉) ₂	%: ClC ₆ H ₄	72.66	B 3.52	Cl 22.80
Found	%: ClC ₆ H ₄	41.34, 41.09	B 3.90, 4.09	
Calc. for (ClC ₆ H ₄) ₂ B(OC ₄ H ₉) ₂	%: ClC ₆ H ₄	41.53	B 4.03	

Isobutyl ester of di-*p*-chlorophenyl boric acid is a colorless, highly viscous liquid. It is immiscible with water, miscible with a majority of organic solvents. It is rapidly decomposed in the air. The diisobutyl ester of *p*-chlorophenyl boric acid is a colorless, mobile liquid, miscible with a majority of organic solvents. It is instantly hydrolyzed in the air, forming the *p*-chlorophenyl boric acid.

Barium salt of di-*p*-chlorophenyl boric acid.

1.73 grams of isobutyl ester of di-*p*-chlorophenyl boric acid are shaken for 5-10 minutes with 15 ml of a saturated solution (at room temperature) of barium hydroxide. The voluminous, flocculent precipitate, which forms after a few minutes, is filtered off, sucked dry, washed with water and dried to constant weight under vacuum. 1.7 grams of dry product are obtained, which represents 89.5 percent of theoretical yield. For determination of barium, known weights of the product were heated with a known amount of 1 N hydrochloric acid. The excess acid is then titrated with standard 1 N alkali.

Found	%: Ba	20.24, 20.26	ClC ₆ H ₄	65.38, 65.95	B 3.14, 3.09
Calc. for (ClC ₆ H ₄) ₂ B(OH) ₂ ·Ba	%: Ba	20.40	ClC ₆ H ₄	66.28	3.21

The barium salt of di-*p*-chlorophenyl boric acid is a colorless, crystalline substance. The salt is not soluble in water, benzene, isopentane, it is quite soluble in methyl and ethyl alcohols. Action of dilute hydrochloric acid yield free di-*p*-chlorophenyl boric acid.

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Di-p-chlorophenyl boric acid.

2.0 grams of the barium salt of di-p-chlorophenyl boric acid are shaken with 10 ml of 1:4 diluted hydrochloric acid. The momentarily formed emulsion changes to a colorless crystalline substance, which is filtered off, sucked dry, washed with water and dried over anhydrous calcium chloride. 1.1 grams of dry product, which melts at 76-78°C, is obtained. By analysis it corresponds to a monohydrate of di-p-chlorophenyl boric acid. Vacuum drying decomposes it into chlorobenzene and p-chlorophenyl boric acid.

Found %: C 54.53, 54.29; H 4.49, 4.28; B 4.08, 3.83 Cl 26.36, 26.66
Calc. for $C_{12}H_{11}BO_2Cl_2$ %: C 53.58 H 4.12 B 4.02 Cl 26.36

The monohydrate of di-p-chlorophenyl boric acid is soluble in benzene, methyl and ethyl alcohol, insoluble in water.

Sodium salt of di-p-chlorophenyl boric acid.

2.84 grams of isobutyl ester of di-p-chlorophenyl boric acid are dissolved in an equivalent amount of sodium hydroxide (8.4 ml of 1.09 N NaOH). The resulting solution is heated to about 60-70°C and then water is slowly removed by distillation under a reduced pressure. The residue is washed with benzene and dried in vacuum. Yield 2.2 grams of dry product.

Found %: Na 7.42, 7.56 B 3.55, 3.60
Calc. for $C_{12}H_{10}BO_2Cl_2Na$ %: Na 7.90 B 3.72

The sodium salt is quite soluble in alcohols and water, insoluble in benzene, petroleum ether and isopentane. Upon acidification the monohydrate of di-p-chlorophenyl boric acid is obtained.

All boron and aryl group analyses were carried out by the method described by Wittig (6).

CONCLUSIONS

1. Isobutyl esters of di-*o*-naphthyl, di-p-bromophenyl and di-p-chlorophenyl boric acids were obtained.
2. It was shown that the isobutyl esters of di-*o*-naphthyl, di-p-bromophenyl and di-p-chlorophenyl boric acids upon heating with potassium or sodium hydroxides, as well as upon action of ammonium or barium hydroxides, form the corresponding metal salts of the above mentioned acids.
3. Acidification of the above mentioned metal salts produces free di-*o*-naphthyl, di-p-bromophenyl and di-p-chlorophenyl boric acids.
4. Some of the data, previously reported, pertaining to di-p-bromophenyl and di-p-chlorophenyl boric acids were shown to be erroneous.

LITERATURE

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