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## Synthesis of some halogenated tetraarylborates

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**Abstract**—The reactions of 3,4-dichlorophenylmagnesium bromide and 3,5-dichlorophenylmagnesium bromide with B(OEt)<sub>3</sub> and NaBF<sub>4</sub> were studied The corresponding tetraarylborates  $[(3,4-Cl_2C_6H_3)_4B]NH_4$  and  $[(3,5-Cl_2C_6H_3)_4B]Na$  were obtained and characterized. The significant influence of the substituents inductive effect on the reaction course was revealed. NaBF<sub>4</sub> was found to be a valuable boron reagent in the synthesis of tetraarylborates containing highly electronegative substituents. The molecular structure of  $[(3-CF_3C_6H_4)_4B]NH_4$  obtained from the reaction of 3-trifluoromethylbromobenzene with NaBF<sub>4</sub> and Mg was determined using X-ray analysis.

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Tetraarylborates contain four aryl rings bonded to one boron atom. They form ionic salts of the formula [BAr<sub>4</sub>]M. Since their discovery, they have found many interesting applications in various areas of chemistry, for example, as analytical reagents in estimation of alkaloids and as co-catalysts in the polymerization of olefins.<sup>1-4</sup> A number of tetraarylborates have been obtained up to now.<sup>5-10</sup> The most extensively explored methods of their synthesis are the reactions of arylmagnesium compounds with trialkoxyboranes or NaBF<sub>4</sub> (Scheme 1).

In spite of many examples of the synthesis of tetraarylborates using both methods (I) and (II) there is no explanation regarding the influence of the boron no data concerning the influence of substituents in the phenyl ring on these reactions. Earlier, we studied the mechanism of the reaction (I) and we found that the reaction is complex and consists of several steps.<sup>11</sup> We have detected spectroscopically some intermediates of this reaction of the formula  $[ArB(OEt)_3]MgBr$  and  $[Ar_2B(OEt)_2]MgBr$  and we found that electron with-drawing substituents increase the stability of these compounds.

reagent on the reaction course. Furthermore, there are

For example we isolated and fully characterized (including X-ray analysis)  $[(C_6F_5)_2B(OEt)_2]MgBr \times OEt_2$ , the unusually stable intermediate formed in the reaction

4 ArMgBr + B(OR) <sub>3</sub>	Ether	$[Ar_4B]MgBr + 3 ROMgBr (I)$	
		1: Ar = $3 - ClC_6H_4$ -	
		<b>2:</b> $Ar = 4 - ClC_6H_4 - $	
		<b>3:</b> Ar = $3,4-Cl_2C_6H_3-$	
4 ArBr + Mg + NaBF <sub>4</sub>	Ether	[Ar <sub>4</sub> B]Na + 4 MgBrF	(II)
		4: Ar = $3,5-Cl_2C_6H_3$ -	
		<b>5:</b> $Ar = 3-CF_3C_6H_4-$	

Scheme 1.

Keywords: Grignard reagents; tetraarylborates; trialkoxyboranes.

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of  $C_6F_5MgBr$  with  $B(OEt)_3$ .<sup>12</sup> Our experiments also revealed that  $[(3-CF_3C_6H_4)_4B]MgBr$  and  $[(C_6F_5)_4B]MgBr$  cannot be obtained in reaction (I) due to the formation of stable intermediates of the formula  $[Ar_2B(OEt)_2]MgBr$ .

The present work is a continuation of our previous studies on the synthesis of tetraarylborates containing highly electronegative substituents. Both methods I and II for the synthesis of 3, 4, 5 and  $[(C_6F_5)_4B]$ Na were applied to show the influence of the substituents on the reaction course. It is known that 1 and 2 can be easily obtained using procedure (I). Following this procedure we obtained **3** from the reaction of 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr with  $B(OEt)_3$ . The yield of the reaction was quite good (75%). However, in contrast to this we failed to synthesize  $[(3,5-Cl_2C_6H_3)_4B]MgBr$  using the same procedure. Considering the fact that there is very little difference in the structures of the aryl moieties in these dichloroderivatives, the results obtained are surprising. In order to explain this discrepancy we measured the <sup>11</sup>B NMR spectra of the corresponding reaction mixtures. The spectrum of the reaction mixture of 3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr+  $B(OEt)_3$  revealed two signals: the main tetraarylborate signal at -6 ppm and the small signal of [(3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B(OEt)<sub>2</sub>]MgBr at 8 ppm. However, in the case of 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr we observed only one signal for [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B(OEt)<sub>2</sub>]MgBr at 8 ppm. After hydrolysis of this reaction mixture we obtained (3,5- $Cl_2C_6H_3)_2$ B-OH and 1,3-dichlorobenzene. On the basis of these data we can suggest that 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr reacts with  $B(OEt)_3$ to give [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B(OEt)<sub>2</sub>]MgBr and 2 equivalents of 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr remain unreacted. The stabilization of the intermediate  $[(3,5-Cl_2C_6H_3)_2B(OEt)_2]MgBr$  by the negative inductive substituent effect is a possible explanation for this result. This effect depends on the distance between two interacting atoms (Cl-B) and it should be greater in  $[(3,5-Cl_2C_6H_3)_2B(OEt)_2]MgBr$  than in  $[(3,4-Cl_2C_6H_3)_2B(OEt)_2]MgBr$ . For the same reason our approach to obtain [(3-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>B]MgBr and  $[(C_6F_5)_4B]MgBr$  in reaction (I) remained unsuccessful.

To be able to synthesize both dichloro and fluoro tetraarylborates in reasonable yields we applied procedure (II) involving the use of NaBF<sub>4</sub> as the boron source. The syntheses of  $[(3,4-Cl_2C_6H_3)_4B]$ Na and  $[(3,5-Cl_2C_6H_3)_4B]$ Na and [(3,5-Cl\_2C\_6H\_3)\_4B]Na and [(3,5-Cl\_2C  $Cl_2C_6H_3_4B$ ]Na were carried out at 35°C and gave both products in very good yields. In the case of 5 we obtained the product quantitatively by decreasing the temperature to 8°C. Unfortunately, we encountered considerable difficulties with the synthesis of  $[(C_6F_5)_4B]$ Na. The <sup>11</sup>B NMR spectrum of the reaction mixture revealed only the signal characteristic of  $[(C_6F_5)_2BF_2]$ Na which indicates that 2 equivalents of  $C_6F_5MgBr$  remained unreacted.<sup>13</sup> The compounds [Ar<sub>2</sub>BF<sub>2</sub>]MgBr undergo the reaction more easily with ArMgBr than the analogous [Ar<sub>2</sub>B(OEt)<sub>2</sub>]MgBr which are formed in the reaction (I) (fluoride is the better nucleofuge than the -OEt group). However, it should be noted that the substituent on the phenyl ring can modify the strength of the B-F bond as in the case of

the  $C_6F_5$ - ring making the complex  $[(C_6F_5)_2BF_2]Na$  resistant towards reaction with  $C_6F_5MgBr$ .

Compound 5 was characterized as the ammonium salt using X-ray analysis which revealed the pseudotetrahedral structure around the boron atom. The B–C bond distance is similar to the B–C distance in other known tetraarylborates (Fig. 1).

We conclude that the reactions (I) and (II) are very sensitive towards electronic factors which influence the stability of the intermediates  $[Ar_2B(OEt)_2]MgBr$  and  $[(C_6F_5)_2BF_2]MgBr$ . The choice of the boron reagent depends on the type of substituent bonded to the phenyl ring. The more electronegative the substituent the lower the yield of reaction (I). In such cases NaBF<sub>4</sub> instead of B(OR)<sub>3</sub> should be used as the boron source (reaction II). Moreover, if the phenyl ring contains extremely electronegative substituents (e.g.  $C_6F_5$ -) the corresponding tetraarylborate cannot be obtained even from the reaction (II).

Synthesis of  $[(3,4-Cl_2C_6H_3)_4B]NH_4$ : 2.43 g (0.1 mol) of magnesium were placed in a 500 mL reaction flask and 5 mL of diethyl ether was added. 22.6 g (0.1 mol) of 3,4-dichlorobromobenzene, dissolved in 65 mL of diethyl ether, was added slowly from a dropping funnel. After addition of 5 mL of the solution, the reaction started. The remaining 3,4-dichlorobromobenzene solution was added over 30 min to maintain gentle reflux. The reaction mixture was left for 30 min and then 3.7 g (0.025 mol) of B(OEt)<sub>3</sub> was added slowly causing the temperature to increase to 35°C. The reaction mixture was left to stand overnight and then poured slowly into 300 mL of water containing 20 g of Na<sub>2</sub>CO<sub>3</sub> to form a yellow ethereal solution and a white slurry of MgCO<sub>3</sub>.



**Figure 1.** The X-ray structure of  $[(3-CF_3C_6H_4)_4B]NH_4$ , (The NH<sub>4</sub> group and Cl atoms are omitted for clarity) B–C(1) 1.624(3), C(1)–B–C(1) # 113.3(3). Crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 212438.

The ethereal phase was removed and the water slurry was extracted twice using 50 mL portions of diethyl ether. The extracts were added to the previously separated ether solution and 200 mL of water was added. The ether was evaporated using a water pump and the remaining aqueous phase was filtered. NH<sub>4</sub>Cl (5.5 g) dissolved in 50 mL of water was added and resulting thick white precipitate was filtered off, washed with water, dried, washed with toluene and dried to give 6.9 g (45%) of [(3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>B]NH<sub>4</sub>. Analysis: <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  7.29–7.24 (m, 4H), 7.26–7.19 (m, 4H), 7.12–7.02 (m, 4H); <sup>11</sup>B NMR (acetone- $d_6$ ) –6.8. Anal. calcd for C<sub>24</sub>H<sub>16</sub>BCl<sub>8</sub>N: C, 47.00, H, 2.61, N, 2.28. Found: C, 47.08, H, 2.58, N, 2.18.

Synthesis of [(3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>B]Na: 2.74 g (0.025 mol) of NaBF<sub>4</sub> and 2.43 g (0.1 mol) of Mg were placed in a reaction flask, and 10 mL of diethyl ether was added. 22.6 g (0.1 mol) of 3,5-dichlorobromobenzene dissolved in 30 mL of diethyl ether was added slowly via a dropping funnel. After addition of 5 mL of the solution the reaction started. The remaining 3,5-dichlorobromobenzene was added over 2 h to maintain gentle reflux. The reaction mixture was left to stand for 12 h and then slowly poured into 300 mL of water containing 20 g of  $Na_2CO_3$  to form a yellow etheral solution and a white slurry of MgCO<sub>3</sub>. The ethereal phase was removed and the aqueous slurry was extracted twice using 50 mL portions of diethyl ether. The extracts were added to the previously separated ether solution and 200 ml of water was added. The ether was evaporated using a water pump to give a white precipitate which was filtered off, washed with water and hexane and dried to give 14 g (90%) of  $[(3,5-Cl_2C_6H_3)_4B]Na$ .

Analysis: <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  7.06–7.04 (m, 12H); <sup>11</sup>B NMR (acetone- $d_6$ ) –6.7. Anal. calcd for C<sub>24</sub>H<sub>12</sub>BCl<sub>8</sub>Na: C, 46.62, H, 1.94. Found: C, 46.12, H, 1.90.

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