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## Abstract

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# ON THE MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT THE BORON ATOM IN ORGANOBORON COMPOUNDS

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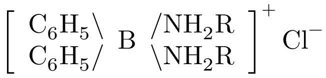
In a number of papers we have shown that the course of reactions between diarylboron chlorides and amines depends on the nature of the radicals at the boron and nitrogen atoms. In the interaction of diphenylboron chloride with diethylamine ([1a]) or aromatic amines (both primary ([1b]) and secondary ([1v])), replacement of the chlorine atom occurs with formation of N-substituted aminodiphenylboron compounds. The reaction of di-$\alpha$-naphthylboron chloride with ammonia ([1b]), primary ([1b]), or secondary amines ([1v]), both of the aliphatic and aromatic series, proceeds analogously.

At the same time, under the action of ammonia ([1b]) or primary aliphatic amines ([1g,1d,2]) on diphenylboron chloride, boronium salts (I) are formed, containing boron as the central atom of a complex cation



$$\left[\begin{matrix} C_6H_5\backslash \\ C_6H_5/ \end{matrix}\ B\ \begin{matrix} /NH_2R \\ \backslash NH_2R \end{matrix}\right]^+ Cl^- \qquad (I)$$

$$R = H,\ CH_3,\ C_2H_5,\ \text{iso-}C_4H_9.$$

In order to clarify in greater detail the influence of the nature of hydrocarbon radicals on the course of the reaction under consideration, we have now studied the action of ammonia and primary amines on di-*o*-tolylboron chloride and di-*p*-tolylboron chloride.

The reactions were carried out at room temperature in ether or benzene medium by adding two moles of amine to one mole of the chloride.

It turned out that, in contrast to diphenylboron chloride, di-*o*-tolylboron chloride forms with ammonia or primary amines not boronium salts, but substitution products—aminoditolylboron or its N-alkyl-substituted derivatives (II).

$$(o\text{-}CH_3C_6H_4)_2BCl + 2NH_2R \rightarrow (o\text{-}CH_3C_6H_4)_2BNHR + NH_3RCl \qquad (II)$$

$$R = H,\ CH_3,\ C_2H_5,\ \text{iso-}C_4H_9$$

Amino-di-*o*-tolylboron (II, $R = H$): b.p. 105-106° at 1.5 mm, $d_4^{20}1.0081$, $n_D^{20}1.5816$ (yield 80%). Methylamino-di-*o*-tolylboron (II, $R = CH_3$): b.p. 102-103° at 1.5 mm, $d_4^{20}0.9985$; $n_D^{20}1.5765$ (yield 96%). Ethylamino-di-*o*-tolylboron (II, $R = C_2H_5$): b.p. 110-111° at 1.5 mm, $d_4^{20}0.9750$, $n_D^{20}1.5641$ (yield 81%). Isobutylamino-di-*o*-tolylboron (II, $R = \text{iso-}C_4H_9$): b.p. 121-122° at 1.5 mm, $d_4^{20}0.9637$; $n_D^{20}1.5531$ (yield 81%). The reaction with dimethylamine proceeds analogously. Dimethylamino-di-*o*-tolylboron has b.p. 155-157° at 9 mm, m.p. 76-77° (yield 83%).

Very interesting and instructive was the study of the behavior of di-*p*-tolylboron chloride toward primary amines. In this case the process proceeds in two directions: a boronium salt (III) and a substitution product—alkylamino-di-*p*-tolylboron (IV)—are formed, the quantitative ratio of compounds (III) and (IV) depending on the nature of the amine

$$(p\text{-}CH_3C_6H_4)_2BCl + 2NH_2R \rightarrow [(p\text{-}CH_3C_6H_4)_2B(NH_2R)_2]^+Cl^- + \qquad \text{(III)}$$

$$+(p\text{-}CH_3C_6H_4)_2BNHR + NH_3RCl. \qquad \text{(IV)}$$

When ethylamine acts on di-*p*-tolylboron chloride in benzene solution, di-*p*-tolyl-bis-(ethylamine)-boronium chloride (m.p. 138-139°) and ethylammonium chloride are obtained in 86% yield (the salts were separated with the aid of chloroform), and ethylamino-di-*p*-tolylboron is also obtained in 7.5% yield (an oily liquid, b.p. 148-155° at 4 mm).

In the interaction of di-*p*-tolylboron chloride and isobutylamine, only 42% of the boronium salt is formed—di-*p*-tolyl-bis-(isobutylamine)-boronium chloride (m.p. 163-165°), while the yield of the substitution product—isobutylamino-di-*p*-tolylboron (b.p. 136-138° at 2 mm)—reaches 55% (calculated on the isolated isobutylammonium chloride).

The mechanism of formation of boronium salts upon the action of amines on diarylboron chlorides is not in doubt. It evidently comes down to the formation, in the first stage of the reaction, of a neutral 1 : 1 complex (V),

$$Ar_2BCl + NH_2R \longrightarrow Ar_2B^{Cl}\leftarrow NH_2R, \qquad V \qquad (1)$$

which then is converted into a cationic boron complex (VI) through incorporation of a second amine molecule and displacement of chlorine into the outer sphere

$$^{Cl}Ar_2B \leftarrow NH_2R + NH_2R \longrightarrow [Ar_2B(NH_2R)_2]^+Cl^-. \qquad VI \qquad (2)$$

As for the substitution product, it may be formed in two different ways. First, by capture of a proton by an amine molecule from the neutral complex (V) and formation of an alkylammonium salt (VII) (equation 3), which then rearranges into alkylaminodiarylboron (II) and alkylammonium chloride (equation 4).

$$\mathrm{Ar_2BCl\cdot NH_2R + NH_2R \longrightarrow \left[Ar_2B\begin{matrix}Cl\\ NHR\end{matrix}\right]^- [NH_3R]^+}, \qquad \mathrm{VII} \tag{3}$$

$$\mathrm{\left[Ar_2B\begin{matrix}Cl\\ NHR\end{matrix}\right]^- [NH_3R]^+ \longrightarrow Ar_2BNHR + NH_3RCl}. \qquad \mathrm{II} \tag{4}$$

The second possible pathway for formation of alkylaminodiarylboron consists in the interaction of free amine and the boronium salt formed in the course of the reaction. In this case, in the first stage of the reaction, migration of a proton occurs from the cationic boron complex to the amine molecule, with formation of alkylammonium chloride and the neutral amine complex of alkylaminodiarylboron (VIII) (equation 5), which then dissociates into its component parts (equation 6).

$$\mathrm{[Ar_2B(NH_2R)_2]^+Cl^- + NH_2R \longrightarrow Ar_2B^{NHR}\!\leftarrow NH_2R + NH_3RCl}, \qquad \mathrm{VIII} \tag{5}$$

$$\mathrm{Ar_2B^{NHR}\!\leftarrow NH_2R \longrightarrow Ar_2BNHR + NH_2R}. \tag{6}$$

As is seen (equations 3, 4 and 5, 6), according to the first mechanism the 1 : 1 complex (V) is converted into the substitution product under the action of one amine molecule, whereas according to the second mechanism this requires the participation of two amine molecules.

To elucidate the mechanism of formation of the substitution product, we carried out the following experiments. First, the action of isobutylamine on chlorodi-*p*-tolyl-bis-(isobutyl)-boronium was investigated. It was found that, under the influence of the amine, the boronium salt is capable of decomposing smoothly and rapidly into isobutylamino-di-*p*-tolylamine and isobutylammonium chloride (equations 5 and 6). Second, the interaction of di-*p*-tolylboron chloride and isobutylamine was investigated under conditions ensuring an excess of amine in the initial period of the reaction; namely, experiments were carried out with very slow addition of the diarylboron chloride to two moles of amine. It was found that with this order of mixing the reagents the yield of the substitution product increases from 55 to 75%, while the yield of the boronium salt decreases from 42 to 20%. If the substitution product were formed only from the neutral complex (V) (equations 3, 4), then the order of mixing of the reagents would not affect the ratio of the substances formed. Thus, the participation of the cationic boron complex in the process of substitution of the halide at the boron atom by the alkylamino group was demonstrated. It is very probable that some other reactions of nucleophilic substitution at the boron atom also proceed by this mechanism.

The influence of the nature of the aryl groups on the course of the reaction between diarylboron chlorides and amines is determined by their electronegativity. Cleavage of a proton from the cation $(Ar_2B(NH_2R)_2)^+$ (equation 5) should occur the more readily, the higher the electronegativity of the aryl radical. The manifestation of an inductive effect by the aryl radicals is explained by a change in the hybridization of the bonding orbitals of the boron and nitrogen atoms. In more electronegative radicals (on the Hara scale), the $S$-character of the carbon orbital directed toward the boron atom is greater than in less electronegative ones. Since the boron atom increases the $S$-character of orbitals directed toward the more electronegative aryl radicals, the $S$-character of the two other boron orbitals consequently decreases. As a result, the unshared pair of nitrogen electrons enters into a weaker donor–acceptor interaction with the boron atom; in other words, the $S$-character of its orbital toward boron decreases, which entails an increase in the $S$-character of the orbitals directed toward the other substituents at the nitrogen atom, including the hydrogen atoms. Ultimately, the proton will be more readily cleaved from the complex cation, since protonation of the N—H bond occurs the more readily, the greater the $S$-character of the orbital of the nitrogen atom binding it to the hydrogen atom.

The presence in diarylboron chlorides of *p*-tolyl radicals, which in their electronegativity occupy an intermediate position between phenyl and *o*-tolyl radicals, causes the reaction to proceed in both directions, i.e., leads to the formation of both alkylaminodiarylborane and the boronium salt.

The influence of the nature of the amine on the course of the reaction is more complex, since the ease of cleavage of a proton from the cationic boron complex must depend both on the basicity of the initial amine with respect to the proton and on its tendency to form a coordination bond with the boron atom.

The higher the basicity of the amine with respect to the proton, the more readily the cationic boron complex should be converted into the substitution product; conversely, with stronger donor–acceptor interaction, cleavage of a proton from the complex-bound amine molecule is hindered, and the complex cation proves to be more stable.

Since diethylamine ($K_b = 8.52 \cdot 10^{-4}$) is a stronger base with respect to the proton than dimethylamine ($K_b = 5.9 \cdot 10^{-4}$), one should expect that, in the reaction of the latter with an organoboron chloride, less substitution product will be obtained. On the other hand, the greater basicity of dimethylamine with respect to the organoboron compound [3] will act in the same direction, i.e., stabilize the boronium salt. These general considerations agree with experiment. Diphenylboron chloride gives with diethylamine only the substitution product

—ethylamino-

diphenylboron, whereas under the action of dimethylamine, along with the substitution product, a boronium salt is also formed.

As regards the influence of the nature of the primary amines on the course of the reaction, then, according to basicity with respect to the proton, ethylamine should have somewhat exceeded isobutylamine in its tendency to form the substitution product. In reality, however, the opposite picture is observed: isobutylamine, which is the weaker base ($K_b = 2.6 \cdot 10^{-4}$) than ethylamine ($K_b = 4.3 \cdot 10^{-4}$), gives more substitution product than the latter. This is explained by the fact that ethylamine, being a somewhat stronger base with respect to the proton than isobutylamine, considerably surpasses the latter in its ability to form cationic boron complexes.

According to data obtained in our laboratory by T. A. Shchegoleva and V. D. Sheludyakov, bis-(ethylamine)-boronium chloride is considerably more resistant toward hydrolyzing agents (in 50% ethyl alcohol the hydrolysis rate constant is 0.088) than bis-(isobutylamine)-boronium chloride ($K = 0.523$).

Thus, the factor determining the course of the reaction between di-*p*-tolylboron chloride and the indicated primary amines is the relative basicity of the amine with respect to the boron atom. It should be noted that di-*p*-tolyl-bis-(ethylamine)-boronium chloride and di-*p*-tolyl-bis-(isobutylamine)-boronium chloride are thermally less stable than the corresponding boronium salts obtained from diphenylboron chloride (1 ). At 150—170° they are smoothly converted into alkylamino-di-*p*-tolylboron and alkylammonium chloride.

$$[(n\text{-}CH_3C_6H_4)_2B(NH_2R)_2]^+Cl^- \rightarrow (n\text{-}CH_3C_6H_4)_2BNHR + NH_3RCl.$$

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*Note: Figure translations are in progress. See original paper for figures.*