CHEMISTRY

B. M. MIKHAILOV and L. S. VASIL’ EV

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

B. M. MIKHAILOV and L. S. VASIL' EV

REACTIONS OF DIBORANE AND ALKYLDIBORANES WITH ESTERS OF BORIC AND ALKYLBORONIC ACIDS AND THEIR THIO ANALOGUES

(Presented by Academician B. A. Kazanskii, 28 III 1961)

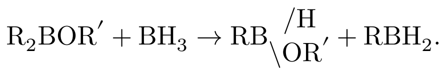
One of us and Dorokhov (^{1}) found that, when diborane acts on esters of diarylboronic acids, diaryldiboranes and orthoborates are formed.

Continuing the study of the reactions of diborane with organoboron compounds, we found that, on interaction of diborane and esters of dialkylborinic acids at room temperature, instead of the expected tetraalkyldiboranes and esters of boric acid, esters of alkylboronic acids and tetraalkyldiboranes are formed in good yields, according to the following equation:

$$8R_2BOR' + B_2H_6 \rightarrow 4RB(OR')_2 + 3(R_2BH)_2. \quad (1)$$

The mechanism of this reaction consists of a series of consecutive and parallel transformations, involving replacement of the hydrogen atom in diborane or its derivatives by alkoxyl or alkyl radicals.

The first direction of the initial stage of the reaction consists in exchange of a hydrogen atom in diborane for an alkyl group, as a result of which an alkylalkoxyborane and an alkylborane are formed:



$$R_2BOR' + BH_3 \rightarrow RB\begin{matrix}/H\\ \backslash OR'\end{matrix} + RBH_2. \quad (2)$$

The alkylalkoxyborane formed according to (2) then disproportionates into an ester of an alkylboronic acid and an alkylborane

$$2RB\begin{matrix}/H\\ \backslash OR'\end{matrix} \rightarrow RB(OR')_2 + RBH_2. \quad (3)$$

Equations (2) and (3) are schematic representations of the processes. In reality, these and all the reactions considered below proceed with the participation of reaction scheme

Figure 1: reaction scheme

dimeric molecules with three-center bonds formed by boron and hydrogen atoms, as well as by alkyl and alkoxyl groups. Thus, equations (2) and (3) should be depicted in the following way:

Alkylborane (3), as a compound containing a B—H bond, can in turn react with esters of dialkylborinic acids, exchanging a hydrogen atom for an alkyl group:

$$R_2BOR' + RBH_2 \rightarrow RB\begin{array}{l}/H\\ \backslash OR'\end{array} + R_2BH. \tag{4}$$

Thus, as a result of reaction (4), a dialkylborane is obtained, which dimerizes to a tetraalkyldiborane, and an alkylalkoxyborane, which according to (3) is converted into an ester of an alkylboronic acid and an alkylborane.

The second direction of the primary reaction consists in the exchange of an alkoxy group in an ester of a dialkylborinic acid for a hydrogen atom, as a result of which a dialkylborane and an alkoxyborane are obtained:

$$R_2BOR' + BH_3 \rightarrow R_2BH + R'OBH_2. \tag{5}$$

Alkoxyborane can undergo various transformations. Thus, reacting with esters of dialkylborinic acids, it is converted into alkylalkoxyborane

$$R_2BOR' + R'OBH_2 \rightarrow 2RB\begin{array}{l}/H\\ \backslash OR',\end{array} \tag{6}$$

and its reaction with dialkylborane leads to alkylborane and alkylalkoxyborane

$$R_2BH + R'OBH_2 \rightarrow RBH_2 + RB\begin{array}{l}/H\\ \backslash OR'.\end{array} \tag{7}$$

In addition, alkoxyboranes can decompose into orthoborates and diborane (through the stage of formation of dialkoxyborane) (2) according to the following equation:

$$R'OBH_2 \rightarrow {}^1/_3(R'O)_3B + {}^2/_3BH_3. \tag{8}$$

And indeed, in some experiments, during distillation of the reaction products it was possible to isolate small amounts of orthoborates.

Consequently, even with this initial direction of reaction (5), the process ultimately ends with the formation of the same final products, since alkylboranes and alkylalkoxyboranes are subsequently converted according to equations (3) and (4) into an ester of an alkylboronic acid and a tetraalkyldiborane.

We then investigated the reactions of orthoborates with alkylboranes. It was found that tetraalkyldiboranes, previously obtained by us from diborane and trialkylborons (3), react with orthoborates slowly at room temperature and rapidly upon moderate heating (60–100°), with the formation of esters of alkylboronic acids in yields of about 80% according to the following equation:

$$(R_2BH)_2 + 2\,(R'O)_3B \rightarrow 3RB(OR')_2 + {}^1/_2(RBH_2)_2. \qquad (9)$$

The initial stage of this reaction consists in the exchange of a hydrogen atom in tetraalkyldiborane for an alkoxy group:

$$R_2BH + (R'O)_3B \rightarrow R_2BOR' + (R'O)_2BH. \qquad (10)$$

The second theoretically possible reaction—the exchange of an alkyl group for an alkoxy group—is unlikely, since such a transformation, as is known from studies of reactions between trialkylborons and orthoborates (4,5), requires a higher temperature ($\sim 200°$).

Further transformations of esters of dialkylborinic acids and dialkoxyboranes (10) are analogous to the transformations described by equations (6)–

(8), (3)–(5), as a result of which an alkylboronic acid ester and an alkylborane are formed. All the reactions given above are reversible. Reaction (1), for example, can be shifted toward formation of a dialkylboronic acid ester if diborane is removed from the reaction mixture. Thus, on boiling tetra-*n*-propyldiborane and the dimethyl ester of *n*-propylboronic acid for 4 h, ~50% of diborane was evolved, and on distillation of the reaction products, previously treated with aniline, the methyl ester of di-*n*-propylboronic acid was obtained in the same yield:

$$3(R_2BH)_2 + 4RB(OR')_2 \rightleftarrows 8R_2BOR' + B_2H_6, \qquad (11)$$

$$R = n\text{-}C_3H_7; \quad R' = CH_3.$$

The conversion of dialkyldiborane into diborane and tetraalkyldiborane is also reversible

$$2R_2B_2H_4 \rightleftarrows R_4B_2H_2 + B_2H_6. \qquad (12)$$

Therefore, if tetraalkyldiborane and orthoborate are heated at reflux, the reaction will proceed not according to (9), but according to the following equation:

$$3(R_2BH)_2 + 8(R'O)_3B \rightarrow 12RB(OR')_2 + B_2H_6. \qquad (13)$$

Thus, on boiling tetra-*n*-propyldiborane and methyl borate for 2 h, 100% diborane was evolved, calculated according to equation (13), and on distillation of the reaction products dimethyl *n*-propylboronate was obtained in 80% yield.

We also found that dialkyldiboranes react with trialkylboranes to form tetraalkyldiboranes. This enabled us to carry out several interesting reactions in the presence of catalytic amounts of tetraalkyldiboranes between trialkylboranes, orthoborates, or alkylboronic acid esters, one of which had already been noted by us in a preliminary communication (6).

As we have already stated earlier, trialkylboranes react slowly with orthoborates at a temperature of about 200°, and, depending on the nature of the alkyl group in the trialkylborane, esters of alkyl- or dialkylboronic acids are formed. Carrying out this reaction in the presence of a catalytic amount of tetraalkyldiborane makes it possible, on moderate heating (60–100°), rapidly to obtain alkylboronic acid esters in high yields (70–90%):

$$R_3B + 2(R'O)_3B \xrightarrow{(R_2BH)_2} 3RB(OR')_2, \qquad (14)$$

The reaction is reduced to the interaction of tetraalkyldiborane and orthoborate (9) and the subsequent conversion of the dialkyldiborane formed and the initial trialkylborane into tetraalkyldiborane. In this way the tetraalkyldiborane, catalyzing process (14), is regenerated continuously. In the same way, dialkylboronic acid esters can be converted in high yields (70–90%) into alkylboronic acid esters if they are heated with orthoborates in the presence of a catalytic amount of tetraalkyldiborane:

$$R_2BOR' + (R'O)_3B \xrightarrow{(R_2BH)_2} 2RB(OR')_2. \qquad (15)$$

Here also, from tetraalkyldiborane and orthoborate there is first formed a dialkoxyborane, which either directly (analogously to (6) and (3)) or through the stage of decomposition into diborane and orthoborate converts dialkylboronic acid esters into alkylboronic acid esters (analogously to equations (8) and (1)), with regeneration of tetraalkyldiborane.

Finally, under the influence of a small amount of tetraalkyldiborane it is possible to convert an equimolar mixture of a trialkylborane and an alkylboronic acid ester into a dialkylboronic acid ester:

$$R_3B + RB(OR')_2 \xrightarrow{(R_2BH)_2} 2R_2BOR' \qquad (16)$$

(the yield of dialkylboronic acid esters is 50–70%).

It should be noted that reactions (15) and (16) (as well as (1)) are thus far the only methods for converting esters of dialkylboric acids into esters of alkylboric acids and vice versa. Thus, it has now become possible easily and simply, starting from olefins, diborane, and alcohols, to obtain esters of alkyl- and dialkylboric acids and to convert them mutually into one another.

Like orthoborates and esters of alkyl- and dialkylboric acids, their thio analogs behave similarly. Thus, on heating tri-*n*-butyl thioborate and tri-*n*-butylboron in the presence of catalytic amounts of tetra-*n*-butyldiborane at 130–140° for 2 hr, we obtained, in 73% yield, the di-*n*-butyl ester of *n*-butylthioboric acid (17). As a side product of the reaction, a small amount of the *n*-butyl ester of di-*n*-butylthioboric acid was isolated.

$$2(\mathrm{RS})_3\mathrm{B} + \mathrm{R}_3\mathrm{B} \overset{(\mathrm{R}_2\mathrm{BH})_2}{\longrightarrow} 3\mathrm{RB}(\mathrm{SR})_2, \tag{17}$$

$$\mathrm{R} = n\text{-}\mathrm{C}_4\mathrm{H}_9.$$

It should be noted that this reaction requires more severe conditions than in the case of orthoborates. This is apparently connected with the fact that the hydrogen atom in tetraalkylmercaptodiborane, formed in the first stage of the process (see (10), where $(\mathrm{R'O})_3\mathrm{B}$ is replaced by $(\mathrm{RS})_3\mathrm{B}$), reacts with various reagents only at a temperature of about 100° [7]. Consequently, the exchange of the hydrogen atom in tetraalkylmercaptodiborane for an alkyl group probably proceeds fairly rapidly at temperatures of about 100° and above. It is possible that dialkoxyborane, at room temperature or under moderate heating (60–100°), also only slowly exchanges its hydrogen atom for an alkyl group. However, in contrast to tetraalkylmercaptodiborane, dialkoxyborane is an unstable compound, readily decomposing into diborane and orthoborate (analogously to [8]); thus, in reactions involving dialkoxyboranes at low temperatures, when it exchanges its hydrogen atom for an alkyl group, it is in fact not the dialkoxyborane itself but diborane that participates.

It should be noted that all the reactions cited above involving tetraalkyldiborane are very convenient and simple from the preparative standpoint. To carry out the reaction, the mixture of reagents is heated with stirring for 1.5–2 hr on a boiling water bath (with the exception of reactions with thio derivatives, which proceed at the same rate at 130–140°) in the presence of 1% (molar) tetraalkyldiborane. Then the reaction mixture is treated with alcohol or aniline to remove traces of alkylboranes, and by simple distillation the esters of alkyl- or dialkylboric acids are obtained in high yields.

Since the reactions are reversible, after isolation of the main reaction product the process again shifts toward its formation. Thus, from the intermediate fractions and side products obtained during fractionation, when the process is repeated, the desired ester is again obtained, as a result of which the yield of the ester approaches the theoretical value.

The catalytic effect on reactions (14), (15), and (16) is exerted not only by tetraalkyldiborane, but also by diborane and its alkyl, alkoxy, and alkylmercapto derivatives.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
22 III 1961

CITED LITERATURE

1. B. M. Mikhailov, V. A. Dorokhov, DAN, **130**, 782 (1960).
2. A. B. Burg, H. J. Schlesinger, J. Am. Chem. Soc., **55**, 4020 (1933).
3. B. M. Mikhailov, A. A. Akhnazaryan, L. S. Vasil' ev, DAN, **136**, 828 (1961).
4. U. Buls, R. Thomas, Am. pat. 2835693 (1958); Chem. Abstr., **52**, 18216 (1958).
5. R. Köster, Angew. Chem., **71**, 31 (1959).
6. B. M. Mikhailov, L. S. Vasil' ev, Izv. AN SSSR, OKhN, 1961, No. 3, 531.
7. B. M. Mikhailov, T. A. Shchegoleva, DAN, **131**, 843 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.