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According to the reports of Topchiev, Paushkin, et al. [1, 2], triallylboron reacts with aldehydes, forming propylene, cyclohexadiene, and esters of diallylboric (I) or allylboric (II) acids according to the following equations

$$2(C_3H_5)_3B + 2RCHO \longrightarrow (C_3H_5)_2BOCH_2R + C_6H_8$$
(I)

$$(C_3II_5)_3B + 2RCHO \longrightarrow C_3H_5B(OCH_2R)_2 + C_6H_8 + C_3H_6$$
(II)

This scheme is analogous to the reaction of triethylboron with aldehydes, when the unsaturated hydrocarbon (ethylene) is eliminated, and the carbonyl group is reduced to an alcohol

$$(C_2H_5)_3B + RCHO \longrightarrow (C_2H_5)_2BOCH_2R + C_2H_4$$

In the reaction of triallylboron with aldehydes according to this scheme, we should have expected the formation of an allene rather than propylene and cyclohexadiene. Doubting the correctness of the work of Topchiev et al., we undertook an investigation of the reaction of triallylboron with carbonyl compounds and found that their data are erroneous*. It was found that the reaction of triallylboron with aldehydes takes place according to a scheme of organometallic synthesis: by the addition of allyl groups to the carbon atom and BR_2 groups to the oxygen atom of the carbonyl. Moreover, if pure aldehydes are used, no isolation of propylene is observed at all. The latter is formed to one degree or another only when insufficiently dry aldehydes are used. The formation of cyclohexadiene does not occur in this reaction.

Triallylboron reacts with aldehydes with heating, and, depending on the ratios of the initial reagents, esters of diallylboric acid (III), allylboric (IV), or borates (V) are obtained

$$(C_{3}H_{5})_{3} \xrightarrow{B} \xrightarrow{\text{RCHO}} (C_{3}H_{5})_{2} \xrightarrow{\text{BOCHC}}_{3}H_{5} \xrightarrow{\text{RCHO}} \xrightarrow{\text{RCHO}} C_{3}H_{5} \xrightarrow{B} (OCHC_{3}H_{5})_{2} \xrightarrow{\text{RCHO}} \xrightarrow{H} B (OCHC_{3}H_{5})_{3} \xrightarrow{(1)} (1)$$

 $R = C_2H_5, C_6H_5$

The reaction of $(C_3H_5)_3B$ with aldehydes takes place in steps. Under the action of C_2H_5CHO on triallyboron (1:1), we succeeded in obtaining the 1-allylpropyl ester of diallylboric acid (III, $R = C_2H_5$). Under the action of two equivalents of propionaldehyde or benzaldehyde, the corresponding esters of allylboric acid (IV, $R = C_2H_5$ and C_6H_5) are obtained (~ 70% yield). It should be mentioned that esters of allylboric (III) and diallylboric (IV) acids are readily symmetrized even at room temperature, and hence at a ratio (C_3H_5)_3B:RCHO equal to 1:1 or 1:2, a mixture of

^{*}When our investigation was completed, an author's abstract of the dissertation of A. A. Prokhorova appeared, in which she, in contrast to the published data, cites the correct reaction scheme.

esters (III)-(V) and triallylboron is obtained. Triallylboron is completely added to aldehydes at a 1:3 ratio of the reagents, forming the corresponding borates (V), the yields of which comprise 70-90%. Since alkyl borates are readily hydrolyzed and transesterified by amino alcohols, reaction (2) can serve as a method of synthesizing unsaturated alcohols of the type (VI)

$$(C_{3}H_{5})_{3} \xrightarrow{B} \xrightarrow{\text{RCHO}} \xrightarrow{B} (OCHCH_{2}CH = CH_{2})_{3} \xrightarrow{\text{N}(CH_{2}CH_{2}OH)_{3}} \xrightarrow{\text{R}} CH_{2} = CHCH_{2}CHOH$$
(2)
(V) (VI)

With ketones, triallylboron also reacts according to a scheme of organometallic synthesis. However, in contrast to aldehydes, when it reacts with acetone at a 1:3 ratio of the reagents, even with heating $(80^\circ, 2 h)$, no cleavage of the third boron-carbon bond occurs, and the reaction stops at the step of formation of the corresponding ester of allylboric acid (VII)

$$(C_{3}H_{5})_{3}B + 2 (CH_{3})_{2}CO \rightarrow C_{3}H_{5}B \begin{pmatrix} CH_{3} \\ OC \\ -CH_{2}CH = CH_{2} \end{pmatrix} \xrightarrow{N(CH_{2}CH_{2}OH)_{3}} CH_{2} = CHCH_{2}C - OH \begin{pmatrix} CH_{3} \\ -CH_{2}CH - CH_{2}CH \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{2}CH_{2}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{2}CH - CH_{2}CH \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}CH_{2}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}OH)_{3}} CH_{2} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \\ -CH_{3} \\ -CH_{3} \end{pmatrix} \xrightarrow{V(CH_{3}OH)_{3}} CH_{3} = CHCH_{2}C + OH \begin{pmatrix} CH_{3} \\ -CH_{3} \\$$

EXPERIMENTAL SECTION

<u>Reaction of Triallylboron with Propionaldehyde.</u> Reaction at a 1:3 ratio. In a two-necked flask, equipped with a reflux condenser and dropping funnel and connected to a gas pipette through the condenser, we placed 7.7 g of triallylboron and added 12.5 ml (10 g) of propionaldehyde at -70° . The reaction takes place with vigorous spontaneous heating, without the evolution of gas. The reaction mass was heated 130°. Upon fractionation under vacuum, we obtained 12.5 g (71%) of tri-1-allylpropyl borate (V, R = C₂H₅), b. p. 79.5-80° (1 mm); n_D²⁰ 1.4328; d₄²⁰ 0.8673. Found: C 69.94; H 10.75; B 3.68%. C₁₈H₃₃BO₃. Calculated: C 70.13; H 10.79; B 3.51%.

To 6.1 g (V, R = C₂H₅) we added 4 ml of triethanolamine and distilled off 5.89 g (99%) of 1-allylpropanol(VI, R = C₂H₅) under vacuum; b. p. 33-35° (7 mm); n_D^{20} 1.4307. Literature data [3]: b. p. 129-131°, n_D^{25} 1.4302.

Reaction at a 1:2 ratio. From 7.9 g of triallylboron and 8.6 of propionaldehyde we obtained 10.83 g (73.5%) of the di-1-allylpropyl ester of allylboric acid (IV, $R = C_2H_5$), b. p. 67.5-68° (1 mm); n_D^{20} 1.4382; d_4^{20} 0.8510. Found: C 71.88; H 10.68; B 4.38%. $C_{18}H_{27}BO_2$. Calculated: C 72.01; H 10.88; B 4.32%. In the experiment we also obtained 1.7 g of tri-1-allylpropyl borate, b. p. 80-83° (1 mm); n_D^{20} 1.4331.

<u>Reaction at a 1:1 ratio.</u> To a solution of 7.7 g of triallylboron in 20 ml of isopentane we gradually added a solution of 4.1 ml of propionaldehyde in 10 ml in isopentane at 5-15°; boiling of the mixture was observed. Upon fractionation we obtained: 1) 1 g of triallylboron, b. p. 42-45° (7 mm); 2) 4.18 g (38%) of the 1-allylpropyl ester of diallylboric acid (III, $R = C_2H_5$), with b. p. 75-79 (7 mm), n_D^{20} 1.4432; d_4^{20} 0.8212. Found: C 74.52; H 11.00; B 5.61%. C₁₂H₂₁BO. Calculated: C 75.02; H 11.02; B 5.63%; 3) 1.09 g of the di-1-allylpropyl ester of allylboric acid with b. p. 66-69° (1 mm); n_2^{20} 1.4405.

<u>Reaction of Triallylboron with Benzaldehyde.</u> Reaction at a 1:3 ratio. Benzaldehyde (19.3 g) was added to 8.15 g of triallylboron; distillation under vacuum produced 24.35 g (89%) of tri- α -allylbenzyl borate (V, R = C₆H₅) with b. p. 160-162° (0.05 mm); n_D²⁰ 1.5351; d₄²⁰ 1.0270. Found: C 79.49; H 7.34; B 2.28%. C₃₀H₃₃BO₃. Calculated: C 79.65; H 7.35; B 3.9%.

<u>Reaction at a 1:2 ratio.</u> To 7.9 g of triallylboron we added 12 ml of benzaldehyde over a period of 1.5 h, at a rate such that the temperature of the mixture did not rise above 70°. We obtained 10.6 g of the di- α -allylbenzyl ester of allylboric acid (IV, R = C₆H₅), b. p. 150-151° (0.35 mm); n_D²⁰ 1.5245; d₄²⁰ 0.9648. Found: C 80.15; H 7.55; B 3.15%. C₂₃H₂₇BO₂. Calculated: C 79.77; H 7.86; B 3.12%.

In the experiment we also obtained 3.71 g of tri- α -allylbenzyl borate with b. p. 185-187° (0.27 mm); n_D^{20} 1.5349 and ~1 g of triallylboron.

<u>Reaction of Triallylboron with Acetone</u>. To 7.7 g of triallylboron we added 10 g of absolute acetone at a rate such that the temperature of the reaction mass did not rise above 60°. The mixture was boiled for 2 h at 80°. Distillation produced 3 g of acetone and 11.3 g (79%) of the di-(dimethylallylmethyl) ester of allylboric acid (VII), b. p. 59-59.5° (1 mm); n_D^{20} 1;4420; d_4^{20} 0.8548. Found: C 72.09; H 10.76; B 4.58%. C₁₅H₂₇BO₂. Calculated: C 72.01; H 10.88; B 4.32%.

Upon heating of a mixture of 6.9 g of the compounds (VII) and 4 ml of triethanolamine on a boiling water bath under vacuum, we obtained 5.22 g (95.2%) of dimethallylcarbinol (VIII) with b. p. 26° (8 mm); n_D^{20} 1.4260. Literature data [4]: b. p. 117-119°; 32-36° (12 mm); n_D^{11} 1.4277. Gas-liquid chromatographic analysis showed that the content of impurities in the substance (VIII) is less than 0.3% (0.15% allyl alcohol).

CONCLUSIONS

Triallylboron reacts with carbonyl compounds according to the scheme of organometallic synthesis.

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.