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REACTIONS OF THE STEREOISOMERIC 2,4,5- AND 2,4,6-SUBSTITUTED 1,3,2-DIOXABORINANES WITH ALDEHYDES

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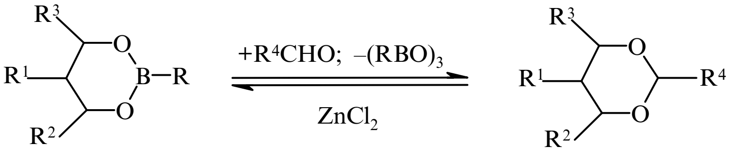
The reaction of six-membered cyclic esters of boric acids with aldehydes gives 1,3-dioxanes [1-3]. The present work is concerned with the study of the stereochemical rules of this process using as examples the reaction of individual 2,4,5- and 2,4,6-substituted 1,3,2-dioxaborinanes with aldehydes.

It has been shown by GLC and configurational comparisons that the reaction mentioned leads to the corresponding 2,4,5- or 2,4,6-substituted 1,3-dioxanes:



1–3 **4–8**

1, **4**, **5** R = C_3H_7, $R^1 = R^2 = CH_3$, R^3 = H, $R^4 = CH_3$ (**4**), C_2H_5 (**5**); **2**, **6**, **7** R = R^1 = *i*-C_3H_7, $R^2 = CH_3$, R^3 = H, $R^4 = CH_3$ (**6**), C_2H_5 (**7**); **3**, **8** R = *i*-C_3H_7, R^1 = H, $R^2 = R^3 = CH_3$, $R^4 = CH_3$

The reaction occurs only in the presence of catalytic amounts of anhydrous $ZnCl_2$. The maximum conversion of the cyclic borate esters was 70%. 1,3-Dioxanes **4-8** were identified by samples prepared by independent syntheses [6]. No matter which aldehyde is used the stereoisomeric composition of the 1,3,2-dioxoborinanes underwent considerable changes during the course of the reaction (compound, reaction time, *cis-trans* ratio by GLC): **1**, beginning of reaction, 57:43; 4 h, 48:52; 24 h, 44:56; 1 month, 40:60; **2**, beginning of reaction, 76:24; 4 h, 87:13; 1 month, 92:8; **3**, beginning of reaction, 60:40; 5 h, 60:40; 1 month, 79:21. Thus the content of the *cis* isomer decreased with time in the case of ester **1**, whereas the content increased for esters **2** and **3**. Control experiments showed that compounds **1-3** are configurationally stable and did not undergo isomerization under the influence of $ZnCl_2$ under the conditions of the reaction with aldehydes. Consequently the dynamic changes in the stereoisomeric composition of the 1,3,2-dioxaborinanes shows that, within the limits of the GLC method (± 3%) [7], the rates of reaction of the *trans* isomers of esters **2** and **3** are greater than those of the *cis* isomers, whereas for compound **1** the *trans* isomer reacts more slowly with aldehydes than the *cis* isomer. This is reflected in the stereoisomeric composition of the cyclic acetals formed.

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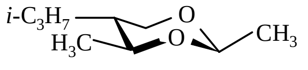
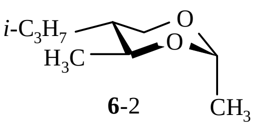
For example, for 5-isopropyl-2,4-dimethyl-1,3-dioxane **6** the ratio of the isomers, corresponding to the *threo*-form of the diol, i.e., obtained from *trans*-**3** (**6**-1 and **6**-2), and the *erythro* form of the initial diol, obtained from *cis*-3 (**6**-3 and **6**-4) a month after the start of the reaction was 53:47 in comparison with 35:65 for a sample of the same dioxane obtained by direct synthesis. Hence the greater rate of reaction of *trans*-**3** lead to an increase in the content of isomers **6**-1 and **6**-2 with *trans* position of the substituents at $C_{(4)}$ and $C_{(5)}$.



6-1



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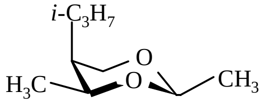

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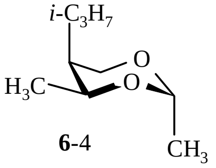

6-4

The principles observed is probably explained by the mechanism of the reaction under discussion [8] and indicates the defining influence of the configuration of molecules on the reactivity of cyclic boron esters in reactions which occur with breaking of the B–O bonds. Note that, contrary to previous data [3], the reaction of 1,3,2-dioxaborinans with aldehydes occurs stereospecifically, since it is not associated with the breaking of a bond at the chiral centers of the molecules.

Synthesis of compounds **1-3** is described elsewhere [1]. GLC analysis was carried out with a Tsvet-126 chromatograph with a flame ionization detector, a 3000 × 4 mm column, stationary phase 5% OV-17 on Chromaton N-Super, argon carrier gas, and a LKhM-80 chromatograph with a catharometer detector, a 2000 × 4 mm column, stationary phase 5% DC-550 on Chromaton N-AW-HDMS, helium carrier gas. The qualitative ratios of the 1,3,2-dioxaborinanes and 1,3-dioxanes were determined by internal normalization with calibration coefficients, established according to known data [7].

Interaction of 1,3,2-Dioxaborinanes 1-3 with Aldehydes. A mixture of a cyclic boric ester (0.01 mol), acetaldehyde or propionaldehyde (0.1 mol), and $ZnCl_2$ (0.5 g) was kept in a sealed weighing bottle at room temperature with periodic removal of a sample for GLC.

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