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STEREOCHEMICAL FEATURES OF REACTIONS OF ESTERS OF ALKYLBORONIC ACIDS WITH PENTANE-2,4-DIOL

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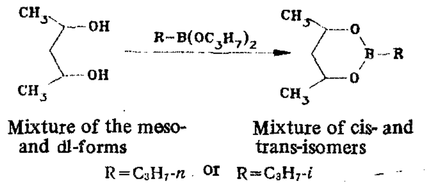
UDC 547.879'244'424.32:541.634

It has been shown for the first time that the transesterification of esters of alkylboronic acids with pentane-2,4-diol leads to 2,4,6-substituted 1,3,2-dioxaborinanes differing in their stereoisomeric composition from the initial 1,3-diol.



The ratio of the cis and trans isomers of the 2,4,6-substituted 1,3,2-dioxaborinanes amounts to 46:54 (GLC) in both cases, while the ratio of the meso and racemic forms of pentane-2,4-diol determined from the isomeric composition of the 4,6-dimethyl-1,3-dioxane obtained from this diol is 57:43. It is known that the reaction of 1,3-diols with carbonyl compounds takes place stereospecifically, and therefore the ratio of the meso–dl (erythro–threo) forms of the initial diol corresponds to the ratio of the cis and trans isomers of the 1,3-dioxane obtained from it [1]. This is not observed in the reaction of pentane-2,4-diol with esters of alkylboronic acids: the amounts of the cis isomers of the 2,4,6-substituted 1,3,2-dioxaborinanes were less, and those of the trans isomers were more than expected.

The noncorrespondence of the stereosiomeric composition of a 2-alkyl-4,6-dimethyl-1,3,2-dioxaborinane and the initial pentane-2,4-diol observed cannot be explained only by a difference in the reactivities of the meso and dl forms of the diol in relation to the boronic ester, since, as was shown by the GLC analysis of samples taken during the synthesis, the figures for the isomeric composition were obtained under the conditions of thermodynamic control. It follows from what has been said that the formation of an additional amount of the trans isomer of 1,3,2-dioxaborinane is due to a stereoselective reaction of the meso form of pentane-2,4-diol with the alkylboronic ester by a mechanism including the cleavage of the C–O bond of the chiral α-carbon atom of the diol.

The situation found, supplementing the previously established fact of the noncorrespondence of the stereoisomeric composition of 2-alkylbutane-1,3-diols and the 2,4,5-substituted 1,3,2-dioxaborinanes synthesized from them [2] indicates a qualitative stereochemical peculiarity of the reaction forming the 1,3,2-dioxaborinane ring.

The configurational assignment of the individual stereoisomers of the 2-alkyl-4,6-dimethyl-1,3,2-dioxaborinanes was made by us previously for the case of the 2-isopropyl analog [3].

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0009-3122/85/2105-0603$09.50