CONFIGURATIONAL ISOMERIZATION OF 2-ISOPROPYL-4,5-DIMETHYL-1,3,2-DIOXABORINANE

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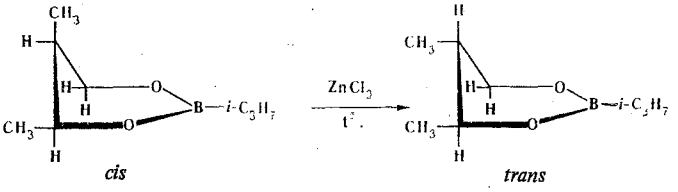
Irreversible conversion of the cis isomer to the trans isomer is observed [by gas–liquid chromatography (GLC)] when a mixture of the cis and trans isomers of 2-isopropyl-4,5-dimethyl-1,3,2-dioxaborinane in a ratio of 56:44 is heated to 150-170°C in the presence of $ZnCl_2$ (3-10%) as the catalyst. The rate of the process depends substantially on the concentration of the catalyst: When the amount of the latter is decreased from 10% to 3%, the time required for complete conversion of the cis isomer to the trans isomer increases from 7 h to 50 h. The reaction does not take place in the absence of the catalyst.



The existing concepts regarding the mechanism of the configurational isomerization of the thoroughly studied 1,3-dioxanes allow for only equilibrium transformations of the cis and trans isomers that proceed with successive cleavage and the formation of a $C_{(2)}$–O bond [1]. In contrast to this, the isomerization of 2,4,5-trisubstituted 1,3,2-dioxaborinane is accompanied by cleavage of the $C_{(4)}$–O bond at the asymmetric center and by rotation about the $C_{(4)}$–$C_{(5)}$ bond with the subsequent formation of a ring and is not characteristic for 4,5-disubstituted 1,3-dioxanes: prolonged heating at 170°C of a mixture of stereoisomers of 4,5-dimethyl-1,3-dioxane in the presence of $ZnCl_2$ did not lead to appreciable changes in their ratio.

Analysis by GLC was carried out with an LKhM-72 chromatograph with a catharometer as the detector; the column was 4 m long, the temperature was 75°C, the packings were 5% SE-30 on Chromaton N-AW and 3% OV-17 on Chromaton N-Super, and the carrier gas was helium. The synthesis of 2-isopropyl-4,5-dimethyl-1,3,2-dioxaborinane and the assignment of the configurations of the individual isomers were described in [2]. The model 4,5-dimethyl-1,3-dioxane was synthesized by the method in [3].

LITERATURE CITED

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