

SHORT
COMMUNICATIONS

Reaction of Stereoisomeric 2,4,5-Substituted 1,3,2-Dioxaborinanes with Paraformaldehyde

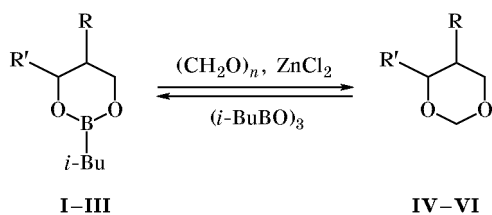
V. V. Kuznetsov

Ufa State Petroleum Technical University, ul. Kosmonavtov 1, Ufa, 450062 Bashkortostan, Russia
e-mail: physics@oil.rb.ru

Bogatskii Physicochemical Institute, Ukrainian National Academy of Sciences,
Lyustdorfskaya doroga 86, Odessa, 270080 Ukraine

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Reactions of six-membered cyclic boronic acid esters with aldehydes are known to result in formation of the corresponding 1,3-dioxanes [1, 2]. The present communication reports on the stereochemical features of reactions of a series of 2,4,5-substituted 1,3,2-dioxaborinanes **I–III** with paraformaldehyde. According to the GLC data, these reactions lead to formation of 4,5-disubstituted 1,3-dioxanes **IV–VI**:



I, IV, R = *i*-Pr, R' = Me; **II, V**, R = PhCH₂, R' = Me;
III, VI, R = Me, R' = Ph.

Two samples of compound **I** with *cis–trans* isomer ratios of 77:33 and 35:65 were used. The reaction occurs only in the presence of a catalytic amount of anhydrous ZnCl₂. Dioxanes **IV–VI** were identified by comparing with authentic samples which were prepared as described in [3]. The highest conversion of ester **I** was 25%, of **II**, 20%, and of **III**, no greater than 1% (according to the GLC data). The stereochemical compositions of the initial and equilibrium mixtures are given in table (for 1,3-dioxanes, given is the isomer ratio of samples prepared by independent method from the corresponding 1,3-diols and paraformaldehyde). It is seen that equilibrium mixtures are characterized by increased fraction of the *cis* isomers, as compared to the initial isomer ratio. By contrast, the fraction of *trans*-1,3-dioxanes in the

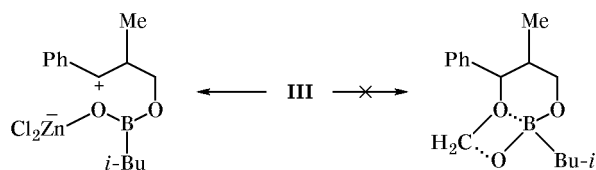
equilibrium mixture is greater than the expected value. Taking into account the accuracy of the GLC determination ($\pm 3\%$ [4]), the reaction of *trans*-esters **I** and **II** with paraformaldehyde is somewhat faster than the reaction of their *cis* isomers. As a result, increased fraction of *trans-IV* and *trans-V* is observed in the equilibrium mixture. Such a difference in the reaction rates is typical of configurationally stable 1,3,2-dioxaborinanes **I** and **II**. By special experiments we showed that no isomerization of **I** and **II** occurs by the action of ZnCl₂ in the reaction with paraformaldehyde. Obviously, the reason lies in the specificity of the reaction mechanism which involves initial coordination of the carbonyl oxygen atom to boron or of the carbonyl carbon atom to the ring oxygen atom with subsequent rupture of the B–O bond and formation of new C–O bond [5]. However, the ability of boronic ester **III** to

Stereoisomeric composition of cyclic boronic acid esters **I** and **II** and products of their reaction with paraformaldehyde (1,3-dioxanes **IV** and **V**)

Compound no.	<i>cis–trans</i> Isomer ratio	
	initial ^a	equilibrium
I	77:23	88:12
IV	67:33	62:38
I	35:65	48:52
IV	39:61	33:67
II	66:34	68:32
V	66:34	57:43

^a Given is the isomer ratio of samples of **IV** and **V** prepared by independent method.

undergo isomerization with cleavage of the C–O bond in the presence of $ZnCl_2$ [6], considerably reduces its reactivity toward paraformaldehyde.



Our results indicate some influence of the substituent and configuration on the reactivity of cyclic boronic esters in processes involving cleavage of the B–O bond. On the other hand, in contrast to earlier data [7], the reaction of 1,3,2-dioxaborinanes with aldehydes is stereospecific, for it does not involve rupture of bonds at chiral centers.

Compounds **I–III** were synthesized as described in [2, 6]. A sample of **I** containing 77% of the *cis* isomer and 23% of the *trans* isomer was prepared from 2-isopropyl-1,3-butanediol which was in turn synthesized by reduction of ethyl isopropylacetate with lithium aluminum hydride according to the procedure reported in [8]; a sample of **I** with a *cis–trans*-isomer ratio of 35:65 was obtained from the same diol with increased fraction of the *threo*-isomer; it was synthesized in 45% yield by reduction of 0.1 mol of ethyl isopropylacetate with $NaAlH_4$ (equimolar amount) in THF in the presence of 0.2 mol of dibenzo-18-crown-6 [9]. The configurational stabilities and stereoisomeric compositions of compounds **II** and **III** were determined in [6]; the isomer ratios of samples of ester **I** were determined in this work. 1H NMR spectrum, δ , ppm (J , Hz): *cis*-**Ia**: 3.69 m (1H, 6- H_A), 3.94 m (1H, 6- H_B), 4.17 m (1H, 4-H), 1.11 d (3H, 4- CH_3), 1.31 m (1H, 5-H, $^3J_{AX} = 11.5$, $^3J_{BX} = 5.0$); *trans*-**I**: 3.75 m (1H, 6- H_A), 3.92 m (1H, 6- H_B), 3.97 m (1H, 4-H), 1.21 d (3H, 4- CH_3), 1.31 m (1H, 5-H, $^3J_{AX} = 8.6$, $^3J_{BX} = 4.1$).

Reaction of 1,3,2-dioxaborinanes I–III with paraformaldehyde. A mixture of 0.01 mol of ester **I–III**, 0.05 mol of paraformaldehyde, and 0.5 g of

$ZnCl_2$ was placed in an ampule and was heated for 8 h at 130°C; samples were withdrawn intermittently and were analyzed by GLC.

The 1H NMR spectra were obtained on a Bruker AM-300 instrument from 10% solutions in $CDCl_3$ containing TMS as reference. GLC analysis was performed on a Tsvet-126 chromatograph equipped with a flame-ionization detector; 3000 \times 4-mm column packed with 5% of OV-17 on Chromaton N-Super; carrier gas argon. The components were quantitated by the internal normalization technique using calibration coefficients determined according to [4].

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