12. G. Vasiliu and A. Gioaba, Rev. Chim., 19, 253 (1968).
13. G. Vasiliu and A. Gioaba, Rev. Chim., 20, 357 (1969).
14. A. Gioaba, O. Maior, and M. Mitran, Rev. Roum. Chim., 21, 733 (1976).
15. A. Gioaba, M. Nedea, and O. Maior, Rev. Roum. Chim., 21, 739 (1976).
16. H. D. K. Drew, J. Chem. Soc., No. 1, 511 (1928).
17. N. J. Dance and C. H. W. Jones, Can. J. Chem., 56, 1746 (1978).
18. M. T. Bogert and B. Naiman, J. Am. Chem. Soc., 57, 1529 (1935).

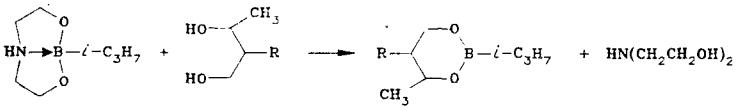
STEREOCHEMICAL FEATURES OF TRANSESTERIFICATION (N–B)-PERHYDRO-2-ISOPROPYL-1,3-DIOXA-6-AZA-2-BORACINE BY 2-ALKYL-1,3-BUTANEDIOLS

V. V. Kuznetsov and A. I. Gren'

UDC 547.895'879.07:541.634:543.544

The stereoisomeric composition of 2,4,5-substituted 1,3,2-dioxaborinanes, products of transesterification of the diethanolamine ester of isopropylboric acid by 2-alkyl-1,3-butanediols, are shown by GLC not to correspond to the ratio of erythro-threo-forms of the starting diols. The fraction of trans-isomer of 2,4,5-substituted 1,3,2-dioxaborinane which is elevated by comparison with that expected is explained by stereoselective reaction of the erythro-form of the 1,3-diol with diethalnolamino-borate.

Reaction of the erythro-isomer of 2-alkyl-1,3-butanediol with esters of monosubstituted boric acids was shown earlier [1-3] to occur stereoselectively and to lead not only to cis- but also to trans-isomers of the corresponding 2,4,5-substituted 1,3,2-dioxaborinanes. Reaction of alkylborondichlorides with 4,5-substituted 1,3-dioxanes [4], interaction of 2,4,5-substituted 1,3,2-dioxaborinanes with aldehydes [5], and hydrolysis of 2,4,5-substituted 1,3,2-dioxaborinanes [6] also obey similar principles. In order to expand studies of stereochemical features of formation of the 1,3,2-dioxaborinane ring, we investigated transesterification of (N–B)-perhydro-2-isopropyl-1,3-dioxa-6-aza-2-boracine (I) by 2-alkyl-1,3-butanediols (IIa-d).



I IIa-d IIIa-d

As a result of the reaction, 2-isopropyl-4-methyl-5-alkyl-1,3,2-dioxaborinanes IIIa-d are formed. The stereoisomeric composition of the starting diols II was established from the corresponding 4,5-dialkyl-1,3-dioxanes [7, 8]. The composition of the reaction products III was monitored by GLC taking into account the configurational references which were found earlier [9, 10]. The data obtained (Table 1) indicate a sharp discrepancy between the stereoisomeric composition of the starting (IIa-d) and final (IIIa-d) compounds with an increase of 1,3,2-dioxaborinane trans-isomer which was evident in all cases. The stereoisomeric composition of the III compounds does not depend on the reaction yield (see Experimental). The ratio of cis- and trans-isomers of the III compounds, which are prepared by reaction of diols II and boracine I, are in excellent agreement with the stereochemical result of the reaction of diols II with acyclic boric esters [1-3]. Thus, both of these processes obey the same stereochemical principles. Hence it follows that reaction of threo- and erythro-isomers II

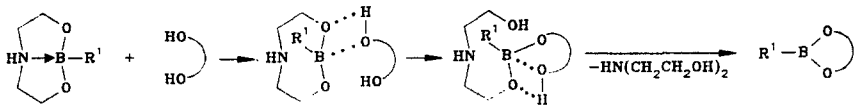
A. V. Bogatskii Physical Chemistry Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 994-996, July, 1989. Original article submitted September 29, 1987; revision submitted September 5, 1988.

TABLE 1. Stereoisomeric Composition of Compounds II and III from GLC Data

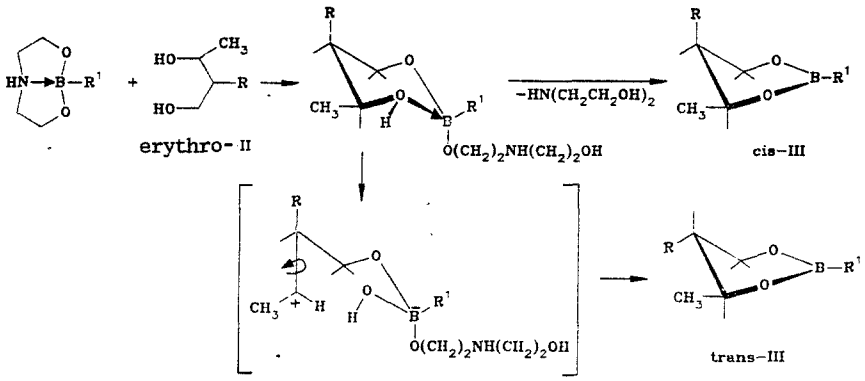
R	Compound	erythro-II:threo-II, mass %	Compound	cis-III:trans-III, mass %*	
				A	B
CH_3	IIa	90 : 10	IIIa	58 : 42	55 : 45
C_2H_5	IIb	70 : 30	IIIb	55 : 45	57 : 43
i-C_3H_7	IIc	67 : 33	IIIc	14 : 86	21 : 79
n-C_4H_9	IId	69 : 31	IIId	30 : 70	27 : 73

*A, reaction with diol I; B, reaction with i-$C_3H_7B(OC_3H_7)_2$ according to [1-3].

with ester I occurs by a different mechanism. The threo-form of diol II reacts with ester I according to the scheme which is known from the literature, initial rupture and subsequent formation of two B–O bonds [11-14]:



However, part of the erythro-isomer II reacts by an alternative mechanism which should include a step in which rupture of the C–O bond of the chiral center, inversion of configuration, and subsequent ring closure occurs [3]:



Thus, a given fraction of erythro-isomer II reacts with ester I nonstereospecifically, although stereoselectively, as a result of which an additional quantity of trans-isomer III is formed.

Stereoselective inversion of the erythro-form II is caused, according to all indications, by energetic nonequivalency of the cis- and trans-isomers of III due to strain which is imposed on the axial alkyl group at atom $C(_5)$ of the ring in the cis-isomer [15, 16]. The main reason for such strain is related to the presence of strong nonbonded interactions of this group with the heteroatomic part of the molecule due to electronic features of the structure of the O–B–O fragment [10], i.e., closure of the 1,3,2-dioxaborinane ring in the cis-isomer less favorably than in the trans-form. In this case, the effect of the R substituent on the stereochemical result of the reaction under study becomes clear. The fraction of the trans-isomer of III increases regularly with an increase of the conformational volume of R (Table 1) due to an increase of the spatial deformations noted above in the cis-isomer. The presence of the intramolecular N → B coordination bond in the ester molecule I [17], as the results obtained show, does not have a substantial effect on the stereochemistry of the studied process.

Thus, the ratio of erythro- and threo-forms of the 1,3-diols must be determined from the ratio of cis- and trans-isomers of the cyclic boric esters obtained from them. The attempts undertaken [18] can lead to a distorted result as a result of the stereoselective character of the reaction with participation of the erythro-isomer of the 1,3-diol.

The data obtained logically expand the formation features of stereoisomeric 1,3,2-dioxaborinanes which were found earlier. These are explained by the unique structure and conformational properties of these molecules.

EXPERIMENTAL

GLC analysis was done on a LKhM-80 instrument with a catarometer detector, 2 m × 4 mm column, temperature of 80°C, 5% DC-550 phase on Chromaton H-AW-HMDS carrier, and helium carrier gas. Determination of the qualitative stereoisomeric composition of 2,4,5-substituted 1,3,2-dioxaborinanes was done using markers obtained in agreement with [19] as well as using experimental configurational relations [9, 10]. The accuracy of determination of the quantitative ratios of GLC, established by the method of [20], was ±3%. Ester I, obtained by reaction of the dipropylester of isopropylboric acid with diethanolamine, had constants which corresponded with data of [21]. The 2-alkyl-1,3-butanediols which were required were synthesized according to [7, 22].

Transesterification Reaction. A mixture of 0.01 mole compound I and 0.01 mole diol II in 100 ml acetone was boiled for 3 h with mixing, the acetone was removed on a water bath, and the residue was fractionated in vacuum. Yield of IIIa, 50%; IIIb, 46%; IIIc, 37%; IIId, 30%. Use of excess ester I (0.016 mole I: 0.01 mole II) increased the yield of esters IIIa-d to 71-75% without changing the stereoisomeric composition of these.

LITERATURE CITED

1. V. V. Kuznetsov, Synthesis and Study of the Stereochemistry of Substituted 1,3,2-Dioxaborinanes, Author's abstract of dissertation for the degree of Candidate of Chemical Sciences, Odessa (1983).
2. V. V. Kuznetsov and A. I. Gren', Zh. Org. Khim., 19, 1987 (1983).
3. V. V. Kuznetsov and A. I. Gren', Zh. Obshch. Khim., 56, 613 (1986).
4. V. V. Kuznetsov and A. I. Gren', Zh. Org. Khim., 22, 2237 (1986).
5. V. V. Kuznetsov and A. I. Gren', Zh. Org. Khim., 21, 2016 (1985).
6. V. V. Kuznetsov and A. I. Gren', Ukr. Khim. Zh., 52, 882 (1986).
7. A. V. Bogatskii, Yu. Yu. Samitov, A. I. Gren', and S. G. Soboleva, Khim. Geterotsikl. Soedin., No. 7, 893 (1971).
8. V. V. Kuznetsov and A. I. Gren', Ukr. Khim. Zh., 49, 774 (1983).
9. V. V. Kuznetsov, A. I. Gren', I. V. Petrovskii, and V. A. Antonovich, Dep. in VINITI, No. 89-93 (1983), R. Zh. Kh., 8B 365 Dep. (1983).
10. V. V. Kuznetsov and A. I. Gren', Zh. Obshch. Khim., 54, 2263 (1984).
11. V. V. Gertsev and Ya. Ya. Makarov-Zemlyanskii, Vysokomol. Soedin., 6, 1458 (1964).
12. J. Lockhart, J. Chem. Soc. A, No. 4, 869 (1968).
13. K. Kustin and R. Pizer, J. Am. Chem. Soc., 91, 317 (1969).
14. A. E. Kamars and E. M. Shvarts, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 3, 299 (1984).
15. V. V. Kuznetsov and A. I. Gren', Khim. Geterotsikl. Soedin., No. 7, 993 (1983).
16. V. V. Kuznetsov and A. I. Gren', Ukr. Khim. Zh., 51, 535 (1985).
17. R. Contreras, C. Garcia, T. Macilla, and B. Wrackmeyer, J. Organomet. Chem., 246, 213 (1983).
18. G. McGarvey and S. B. Joginder, Tetrahedron Lett., 26, 6297 (1985).
19. V. V. Kuznetsov, Dep. in VINITI, No.5646-83 (1983), R. Zh. Kh. 5Zh 343 Dep. (1984).
20. K. A. Gol'bert and M. S. Vigdergauz, Course in Gas Chromatography [Russian translation], Khimiya, Moscow (1974), p. 224.
21. S.-O. Lawesson, Ark. Kemi, 10, 171 (1956).
22. V. V. Kuznetsov, Reactants and High Purity Substances [in Russian], NIITEKhim, Moscow (1982), No. 1, p. 18.