STEREOCHEMICAL PECULIARITIES OF THE FORMATION OF 2,4,6- AND 2,3,4,6-SUBSTITUTED 1,3,2-OXAZABORINANES

A. R. Kalyuskii, V. V. Kuznetsov, and A. I. Gren'

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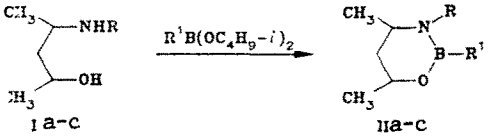
We have observed that the transesterification of alkylboric acid esters with 4-amino-2-pentanol (Ia), N-methyl-4-amino-2-pentanol (Ib), and N-phenyl-4-amino-2-pentanol (Ic) with ratios of the erythro to threo isomers of 70:30 [1], 70:30 [2], and 65:35 [3], respectively, leads to stereoisomeric 2,4,6- (IIa) and 2,3,4,6-substituted (IIb, c) 1,3,2-oxazaborinanes with increased percentages of the trans isomers.



I a-c IIa-c

I, II a R = H; b R = CH_3; c R = C_6H_5

Ia-c mixture of erythro and threo isomers; IIa-c mixture of cis and trans isomers

The ratios of the cis and trans forms of IIa-c established by GLC were as follows: for IIa, 61:39 ($R^1 = C_2H_5$), 59:41 (R^1 = iso-C_4H_9); for IIb, 45:55 ($R^1 = C_2H_5$), 48:52 (R^1 = iso-C_3H_7), 44:56 (R^1 = iso-C_4H_9); for IIc, 49:51 ($R^1 = C_2H_5$). The overall yields of IIa-c in all cases ranged from 70 to 80%.

It is known that the reaction of carbonyl compounds with 1,3-amino alcohols proceeds stereospecifically and is characterized by conformity of the stereoisomeric compositions of the starting compounds and the final products [4]. The nonconformity observed in our case cannot be explained by the different reactivities of the erythro and threo forms of Ia-c with respect to the boric acid esters, since the data on the isomeric compositions, as demonstrated by GLC analysis of samples taken during the synthesis, were obtained under conditions of thermodynamic control. Consequently, the formation of additional amounts of the trans isomers of IIa-c is due to a stereoselective reaction of the erythro forms of the starting 1,3-amino alcohols with the boric acid esters via a mechanism that includes cleavage of the C–N bond at the chiral α-carbon atom of the amino alcohol. This process is evidently due to a nonbonded interaction of the substituent attached to the nitrogen atom with the methyl group attached to the $C_{(4)}$ atom, which affects the relative stabilities of the cis and trans forms of IIa-c. The noted interaction is intensified with an increase in the effective volume of the N–R group, which leads to appreciable preponderance of trans-IIb, c in the mixtures. The observed principle is probably quite general for organoboron heterocycles that contain B–O and B–N bonds: the formation of 2,4,6-substituted 1,3,2-dioxaborinanes also takes place stereoselectively [5].

The configurations of the individual stereoisomers of IIa isolated from the mixture by preparative GLC [6] were established by means of PMR spectroscopy. In the case of IIb, c all of the configurational assignments were made for mixtures of the isomers.

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A. V. Bogatskii Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 854-855, June, 1990. Original article submitted July 31, 1989.

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RECYCLIZATION REACTIONS. SYNTHESIS OF 3-(2,3-EPITHIOPROPYL)-BENZOTHIAZOL-2-ONE FROM 2-(ALLYLTHIO)BENZOTHIAZOLE

N. I. Korotkikh, A. F. Aslanov, and O. P. Shvaika

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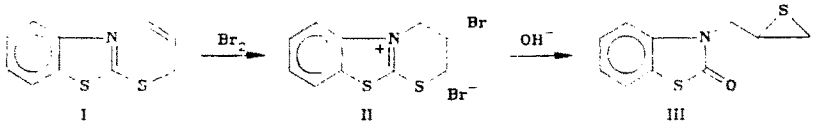
We have established that 3-(2,3-epithiopropyl)benzothiazol-2-one (III) is obtained in satisfactory yield by bromination of 2-(allylthio)benzothiazole (I) and subsequent alkaline treatment of reaction product II.



I II III

The formation of salt II, which ensures the success of this method for the synthesis of thiiranes, is not predetermined unambiguously by the known analogies [1, 2], according to which the product of the corresponding bromomethylthiazolidinium salt was most likely. However, the recyclization of salt II to thiirane III apparently takes place in the ion pair of the initially formed pseudobase.

The cyclization of I was accomplished by the action of bromine on a solution of allylthio derivative I in dioxane or in acetic acid at 20°C. To complete the process, the reaction mixture was then refluxed for 3-4 h. The recyclization of salt II was carried out by the action of sodium hydroxide on a solution of the salt in epichlorohydrin or in the two-phase ether–water system at room temperature.

2-(Allylthio)benzothiazole (I, $C_{10}H_{15}NS_2$). This compound was obtained by the action of allyl bromide on the triethylammonium salt of benzothiazole-2-thione in DMF at 20°C. The product was obtained in 96% yield and had R_f 0.97 [here and subsequently, on Silufol with elution with chloroform–methanol (10:1)]. IR spectrum (thin layer): 1640 (m, C=C), 2860 (w), 2980 (w, CH_2), 2922 (m, CH), 3015 (w), 3080 (m, $CH=CH_2$), 3030 (w), 3065 cm^{-1} (m, CH_{arom}). PMR spectrum ($CDCl_3$): 3.80 (2H, d, CH_2), 4.90-5.30 (2H, m, CH_2=C), 5.50-6.30 (m, 1H, CH=C), 7.13-7.80 ppm (4H, m, H_{arom}).

3-Bromo-3,4-dihydro-2H-benzothiazolo(2,3-b)(1,3)thiazinium Bromide (II, $C_{10}H_9Br_2NS_2$). This compound was obtained in 52% yield and had mp 221-222°C (from acetic acid) and R_f 0.03. IR spectrum (in Nujol): 770 (m, C–Br), 1500 cm^{-1} (sh, aromatic). PMR spectrum (d_6-DMSO): 3.96 (2H, m, CH_2–S), 5.06 (2H, m, CH_2–N), 5.36 (1H, m, CH–Br), 7.76 (2H, m, H_{arom}), 8.26 ppm (2H, m, H_{arom}).

3-(2,3-Epithiopropyl)benzothiazol-2-one (III). This compound was obtained in 92% yield and had mp 50-51°C (from hexane) and R_f 0.95. IR spectrum (thin layer): 3070 (w, CH_2–S), 1682 cm^{-1} (s, C=O). PMR spectrum ($CDCl_3$): 2.53 (2H, d, CH_2–S), 3.30 (1H, m, CH–S), 4.17 (2H, d, CH_2–N), 7.10 ppm (4H, m, H_{arom}). No melting-point depression was noted for a mixture of this product with III obtained in accordance with [3].

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