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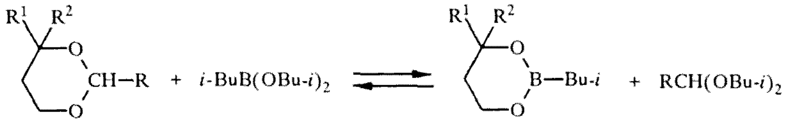
# REACTION OF SUBSTITUTED 1,3-DIOXANES WITH THE DIISOBUTYL ESTER OF ISOBUTYLBORIC ACID

**V. V. Kuznetsov, A. V. Tereshchenko, and A. I. Gren'**

*The reaction of substituted 1,3-dioxanes with the diisobutyl ester of isobutylboric acid leads to the corresponding 1,3,2-dioxaborinanes. The determining factor in the reactivity of the 1,3-dioxanes is the degree of substitution of the acetal atom.*

It has been demonstrated in [1-5] that the reaction of boric acid and of the esters of substituted boric acid with 1,3-dioxanes leads to the corresponding 1,3,2-dioxaborinanes. The reactivity of the 1,3-dioxanes is determined mainly by the degree of substitution of the acetal carbon atom; it also depends to a certain degree on the character of the alkyl substituent at the $C_{(5)}$ carbon atom [2, 3] and on the degree of substitution of the $C_{(4)}$ and $C_{(6)}$ atoms [4, 5].

The objective of the present work was to continue these investigations on the reaction of the cyclic formals and acetals of 1,3-butanediol, 1-phenyl-1,3-propanediol, and 3-methyl-1,3-butanediol (compounds Ia-d, f, g) with the diisobutyl ester of isobutylboric acid; 2-phenyl-1-1,3-dioxane (Ie) was used as reference compound.



Ia-g IIa-d

Ia, d, f) R = H; Ib, g) R = $C_3H_7$; Ic, e) R = $C_6H_5$; Ia-c, f, g) $R^1$ = $CH_3$; Id) $R^1$ = $C_6H_5$; Ie) $R^1$ = H; Ia-e) $R^2$ = H; If, g) $R^2$ = $CH_3$. IIa, d) $R^1$ = $CH_3$; IIb) $R^1$ = $CH_6H_5$; IIc) $R^1$ = H; IIa-c) $R^2$ = H; IId) $R^2$ = $CH_3$

The ratios of the initial and final compounds in the reaction mixtures were determined by GLC. Having kept the reaction mixtures for 24 h at room temperature, all the investigated substances Ia-d, f, g (except the reference compound Ie, which fully reacted at these conditions) remained unchanged. The reaction starts only after addition of the catalyst zinc chloride (Table 1).

The table shows that the formals Ia, d, f are the most interesting in the reaction discussed. Noticeable amounts of the 1,3,2-dioxaborinanes IIa-d are formed only when the reaction mixture is heated in the presence of catalytic amounts of $ZnCl_2$. We did not succeed to achieve a full conversion of the formals to the corresponding compounds II. A comparison with unsubstituted 1,3-dioxane (the equilibrium ratio of the concentrations is 30:70 in favor of the 1,3,2-dioxaborinane [4, 5]) indicates that the presence of one or two substituents at the $C_{(4)}$ carbon atom noticeably lowers the degree of conversion. 4,4-Dimethyl-1,3-dioxane (If) is the most passive, the 4-phenyl derivative (Id) is the most reactive and gives the deepest degree of conversion. A comparison of the 4-alkyl- or 4-phenyl-1,3-dioxanes with the 5-alkyl-substituted analogs [3] indicates that their reactivity toward the boric ester is approximately the same.

When changing to the acetals Ib, c, g, the reactivity of the 1,3-dioxanes increases significantly. An increase in the degree of conversion is observed at the same time. The 2-phenyl derivatives possess the highest conversion rate. This becomes particularly noticeable when comparing the course of the reaction with compounds Ic and Id, which differ in the position of the phenyl substituent. The most inert in this series is the 4,4-dimethyl derivative (Ig).

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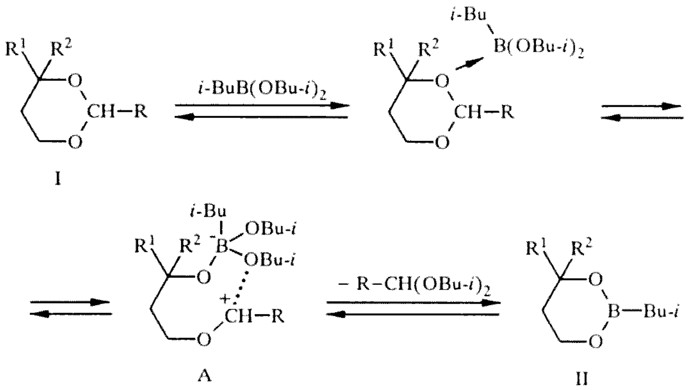
A. V. Bogatskii Physicochemical Institute, National Academy of Sciences of the Ukraine, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 160-162, February, 1995. Original article submitted February 27, 1995.

TABLE 1. Ratio of 1,3-Dioxanes Ia-d, f, g and 1,3,2-Dioxaborinanes IIa, b, d (mole %, by GLC) in the Reaction Mixture in the Presence of $ZnCl_2$

| Initial compound | Reaction product | Ratio I:II | | |
|---|---|---|---|---|
| | | 20 °C, 2 h | 130 °C | |
| | | | 5 min | 30 min |
| Ia | IIa | 100 : 0 | 80 : 20 | 47 : 53 |
| Ib | IIa | 40 : 60 | 0 : 100 | — |
| Ic | IIa | 0 : 100 | — | — |
| Id | IIb | 92 : 8 | 60 : 40 | 21 : 79 |
| If | IId | 100 : 0 | 100 : 0 | 100 : 0 |
| Ig | IId | 50 : 50 | 50 : 50 | 0 : 100 |

The results obtained confirm the earlier conclusions with respect to the mechanism of the investigated conversion: coordination of the acetal oxygen via the boron atom, followed by the formation of the bipolar structure A [3].



Its stability is related primarily with the electron donor character of the substituent R. Besides this, it is known that the alkyl groups at the $C_{(2)}$ atom most strongly increase the basicity of the oxygen atoms of cyclic acetals [6]. The proposed scheme explains satisfactorily the increased reactivity of the acetals. Based on the data given in [7] for 4-methyl and particularly for 4,4-dimethyl derivatives it can be postulated that the oxygen atoms $O_{(1)}$ and $O_{(3)}$ participate to an equal degree in the coordination with the acceptor of the electron pair. The steric stresses, occurring in the latter instance in the complex A lower its stability; this manifests itself on the reactivity of compounds If, g.

It must also be pointed out that at the conditions of thermodynamic control the degree of conversion of 1,3-dioxanes must be determined by the stability of the initial and final compounds. Finally, the preferred formation of the cyclic boric esters II in most instances is probably related to a stronger stabilizing effect of the reverse conjugation via the B−O bond in the ring, as compared to the acyclic boric ester [8]. The investigated reaction expands the range of the chemical conversions of 1,3-dioxanes and opens a new route for the synthesis of substituted 1,3,2-dioxaborinanes via the accessible cyclic formals and acetals (e.g. by the Prince reaction).

## EXPERIMENTAL

The analysis by GLC was carried out on LKhM-80 chromatographs with a catharometer detector; the column was 2 m × 4 mm, packed with 5% DC-550 on Chromaton-N-AW-HMDS as the stationary phase; helium served as the carrier gas; on a Tsvet-126 chromatograph with a flame ionization detector: the column was 3 m × 4 mm, packed with 5% OV-17 on Chromaton N-Super as the stationary phase; helium served as the carrier gas. Quantitative GLC data were obtained by the internal-standard method according to [9]. The qualitative composition of the reaction mixture was established with the use of reference compounds for the corresponding 1,3,2-dioxaborinanes, obtained by direct synthesis [10]. The initial 1,3-dioxanes were synthesized according to [11] and the diisobutyl ester of isobutylboric acid according to [12].

**Reaction of 1,3-Dioxanes Ia-g with the Boric Ester.** A mixture of 1 mmole 1,3-dioxane and 1 mmole of the diisobutyl ester of isobutylboric acid is kept in a weighing bottle (ampul) for 24 h at 20°C. A catalyst is added (~ 1 mass %), the mixture kept at 20°C for further 2 h; is then heated to 130°C, analyzing the reaction mixture periodically by GLC.

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