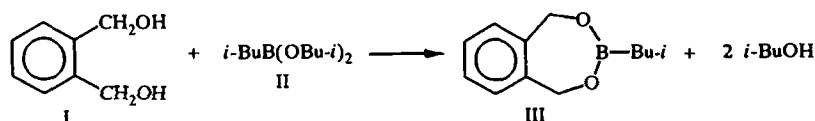


AUTOOXIDATION OF 2-ISOBUTYL-5,6-BENZO-1,3,2-DIOXABOREPANE

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Using PMR, IR, and mass spectrometric methods it was shown that the main autooxidation product upon prolonged storage of 2-isobutyl-5,6-benzo-1,3,2-dioxaborepane is 2,2'-oxybis(5,6-benzo-1,3,2-doxaborepane).

In contrast to their six-membered analogs, the formation of seven-membered cyclic boron esters is complicated by polymerization processes and is possible only for 1,4-diols containing a planar (e.g., aromatic) fragment [1, 2]. Features of the conformational and chemical behavior of this class of compound remain almost unexplored until now. In order to investigate the structure and properties of individual examples of these materials, we have treated 1,2-dihydroxymethylbenzene (I) with the diisobutyl ester of isobutylboronic acid (II) to give 2-isobutyl-5,6-benzo-1,3,2-dioxaborepane (III).

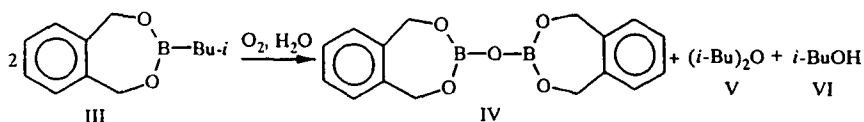


Ester III was prepared in 68% yield as a viscous, colorless liquid whose PMR spectral data are presented in Table 1 (CDCl₃ solution). The signal for the ring methylene protons is seen as a narrow singlet and it retains this character in the spectra measured in C₆D₆ and CD₂Cl₂. When the sample in CD₂Cl₂ is cooled to -110°C, a broadening of all signals is observed but the character of the spectrum is not changed and this suggests that the investigated molecule continues to exist as an equilibrium mixture of two inverting forms with quite a low energetic barrier.

When a sample of ester III is kept in a closed vessel in an air atmosphere for three years it is gradually converted to an amorphous solid product with a yellow-orange coloration. The PMR spectrum of the product (CDCl₃ solution) shows additional signals when compared with the spectra of the ester III. These are aromatic and aliphatic protons, typical doublets for two gem-dimethyl groups and multiplets for CH protons signals, two doublets for alicyclic CH₂O methylene protons, and two new signals near 7.3 ppm with integrated intensity approximately equal to the signals for the aromatic protons of ester III. Along with the signal for the methylene protons of the ring of ester III there is observed a further singlet of approximately equal intensity at 5.03 ppm. In addition, the signal for the CH₂B at 0.56 ppm in the spectrum of compound III is absent.

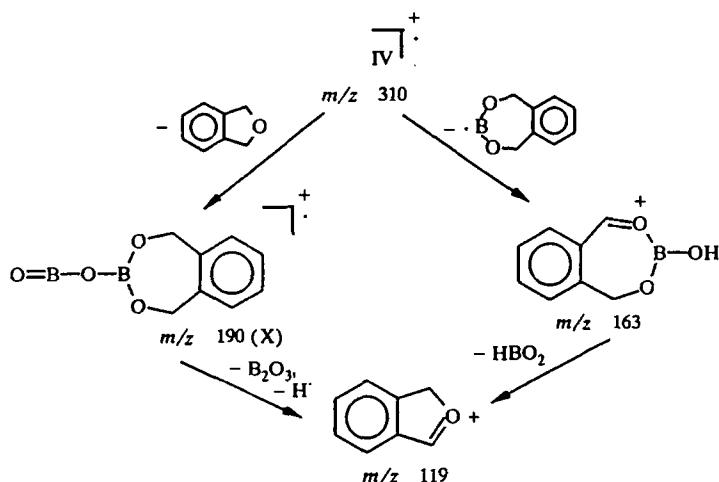
The mass spectrum of the obtained product shows a molecular ion peak for ester III (m/z 204) along with a rather intense signal with m/z 310 and the IR spectrum (after drying of the sample) shows an OH stretching absorption band at 3200 cm⁻¹.

The data above lead to our proposal that storage of ester III leads to partial oxidation by atmospheric oxygen to give 2,2'-oxybis(5,6-benzo-1,3,2-dioxaborepane) (IV) as well as diisobutyl ether (V) and, very likely through participation of atmospheric moisture, isobutyl alcohol (VI).



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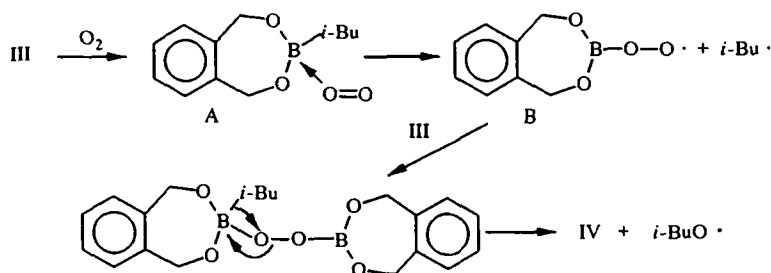
According to the integrated intensity data for the methylene proton signals, the content of compounds III, IV, V, and VI in the mixture is 38, 39, 7, and 16% respectively. The structure of the bis derivative IV is confirmed by the nature of the PMR spectrum (ring methylene proton singlet, the presence of aromatic proton signals, and the absence of proton signals for a substituent on the boron atom). The mass spectral ratio observed



for the $[M]^+$, $[M-1]^+$, and $[M-2]^+$ ions is 1:0.5:0.09 and this corresponds approximately with that expected for a molecule with two boron atoms (without calculation of the contributions for the ^{13}C , 2H , ^{17}O , and ^{18}O isotopes). The presence of the bisether IV is confirmed by the nature of the fragmentation of its molecular ion.

The ion intensity ratio for $[X]^+:[X-1]^+:[X-2]^+$ also confirms the presence of two boron atoms in its composition. The existence of compounds V and VI is indicated by the signals for the methylene chain protons at 3.42 and 3.49 ppm and the gem dimethyl groups at 0.86 and 0.93 ppm.

Based on the case of the known autooxidation mechanism for organoboron compounds [3-7], it might be expected that the reaction investigated includes an initial formation of a donor-acceptor type adduct A which decomposes further to free radicals. The subsequent progress of the process then probably occurs via a radical mechanism. Reaction of a molecule of ester III with the peroxide radical B then leads to formation of the dimer IV.



Formation of the other products of the studied reaction occurs similarly.

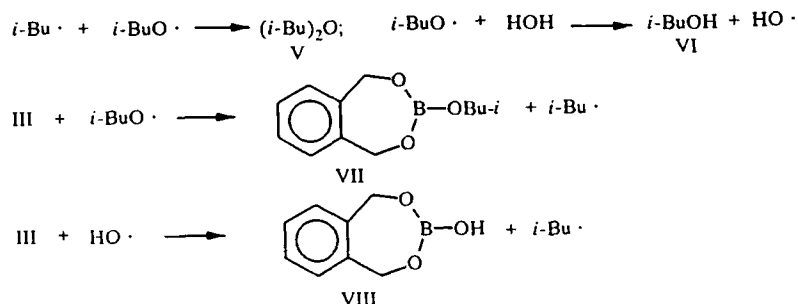


TABLE 1. PMR Spectra of Compound III and Its Autooxidation Products, δ , ppm

Compound	Ring methylene protons, s, 4H	Aromatic protons, s, 4H	=B — iBu	Additional signals
III	5,08	7,31, 7,32	0,56 d, 2H; 0,85 d, 6H; 1,75 m, 1H	—
Autooxidation products	5,03	7,33, 7,34	—	0,86 d 0,93 d 1,77 m 3,42 d 3,49 d

Esters VII and VIII are present in trace amounts (not seen in the PMR spectrum but identified in the mass spectrum by low intensity signals for $[M]^+$ in VII and VIII of 220 and 164 respectively). Evidently the product composition under these conditions is determined by thermodynamic control and this results in formation of the more stable bis derivative IV.

EXPERIMENTAL

PMR spectra for 10% solutions of the compounds examined (in $CDCl_3$, CD_2Cl_2 , and C_6D_6) were recorded on Bruker AM-250 and AM-300 spectrometers with TMS internal standard. IR spectra were measured on a Specord IR-75 spectrophotometer (Vaseline oil) and mass spectra on an MX-1321 (ionization energy 70 eV).

2-Isobutyl-5,6-benzo-1,3,2-dioxaborepane III was prepared by a standard method [1]. An equimolar mixture of diol I and ester II (0.018 mole) was refluxed in benzene (70 ml) for 2 h, the solvent evaporated, and the residue fractionated *in vacuo*. Yield 2.5 g (68%). Bp 84-87°C (0.5 mm Hg). Found, %: C 71.05; H 8.58; B 5.24. $C_{21}H_{17}BO_2$. Calculated, %: C 70.59; H 8.33; B 5.39.

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