Product (VII)-(XII) were obtained by analogy.

Reaction of Diethyl Ester of 1-Methoxy-2.3-alkadiene-2-phosphoric Acid with 2-(Isobutylamino)pyridine. A mixture of 2.48 g (0.01 mole) (I) and 1.50 g (0.01 mole) 2-(isobutylamino)pyridine was maintained for 72 h at 35-40°C. Two-fold column chromatography on silica gel with 1:3 hexane-ether as the eluent gave 0.87 g (XVI) and 0.36 g (XIV) with about 15% (XVI).

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BORYLATION OF o-HYDROXYPHENYL PHOSPHORUS DERIVATIVES

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The reactions of isobutyl diphenylborate with 0,0-diethyl o-hydroxyphenylphosphonate and o-hydroxyphenylphosphine gave 5,6-benzo-2-phenyl-4-ethoxy-4-oxo-1,3,2,4-dioxaboraphosphorinane and o-diphenylboryloxyphenylphosphine, respectively. The borylation only at the α -hydroxyalkyl fragments of bis $(\beta, \beta, \beta$ trichloro- α -hydroxyethyl)(o-hydroxyphenyl)phosphine and the conversion of the o-boryloxyphenyl phosphorus derivative to an α -boryloxyalkyl derivative upon the action of chloral indicates the greater stability of compounds with the P-C-O-B fragment than that for compounds with the P-C-C-O-B fragment.

The reaction of boric acids and their derivatives with α -hydroxyalkyl phosphorus derivatives is a convenient and promising method for the synthesis of compounds containing the P-C-O-B fragment [1]. The use of other phosphorus-containing hydroxy compounds in these reactions should lead to new types of phosphorus-boron compounds. We may use o-phosphory-lated phenols as such starting compounds, for which convenient syntheses have been developed [2-4]. The borylation of such compounds is interesting since it should lead to compounds with the P-C-C-O-B fragment, in which the arrangement of the phosphorus and boron groups is favorable for the formation of coordination bonds.

In contrast to α -hydroxyalkylphosphines, o-hydroxyphenyl phosphorus derivatives are borylated only under vigorous conditions. 0,0-Diethyl o-hydroxyphenylphosphonate [2] reacts with isobutyl diphenylborate only upon heating a mixture of the starting reagents without solvent at reflux. This reaction would be expected to lead to the formation of 0,0-diethyl o-diphenylboryloxyphenylphosphonate but the elemental analysis data of the stable crystalline product (II) do not correspond to the chemical formula of this compound. The ³¹P NMR chemical shift of (II) is 13.77 ppm. The IR spectrum for the crystalline (II) lacks hydroxyl group bands and absorption at 1300-1350 cm⁻¹ corresponding to B^{III}-O bond vibrations. The PMR spectrum has signals for protons of phenyl, methylene, and methyl groups in 9:2:3 integral intensity ratio. The structure of (II) was established by an x-ray diffraction structural analysis,* which showed that this compound in the crystalline state is a dimer of 5,6-benzo-2-phenyl-4-ethoxy-4-oxo-1,3,2,4-dioxaboraphosphorinane. The mass spectrum of (II) prior to recrystallization shows a molecular ion peak for monomeric 5,6-benzo-2-phenyl-4-

*The data of the x-ray diffraction structural analysis will be published later.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 477-482, February, 1991. Original article submitted May 11, 1989. ethoxy-4-oxo-1,3,2,4-dioxaboraphosphorinane with m/z 288 (43%) and a strong peak with m/z 260 ($M^{+-} - C_2H_4$). Product (II) is most likely formed by the participation of isobutyl alcohol produced in the first reaction step in further transformations according to the following scheme.



Judging from the chemical shift characteristic for phosphonates and the dipole moment of (II) in benzene at 25°C (2.41 D), the dimer predominates over the monomer in solution.

o-Hydroxyphenylphosphine (III) [2] is borylated by isobutyl diphenylborate also under vigorous conditions upon heating a mixture of the reagents at reflux in an argon atmosphere. The reaction course was monitored by ³¹P NMR spectroscopy. After 30 min the signal for starting phosphine (III) at -145 ppm disappeared in the ³¹P NMR spectrum of the reaction mixture and a signal at -142 ppm with ¹J_{PH} = 210 Hz appeared, corresponding to o-diphenylboryloxyphenylphosphine (IV).



Product (IV) was isolated from the reaction mixture by distillation. Crystalline (IV) was found to be extremely sensitive to oxidation and hydrolysis. This compound has mp 85-95°C and bp 181-190°C (0.07 mm). Its IR spectrum lacks hydroxyl group absorption. An only slight change in the ³¹P NMR chemical shift upon going from (III) to (IV) indicates the absence of a P+B bond.

Product (III) reacts vigorously with chloral to give $bis(\beta,\beta,\beta)$ -trichloro- α -hydroxy-ethyl)(o-hydroxyphenyl)phosphine (V).



Product (V) reacts with pyridine to give the corresponding pyridinium phenolate (VI).

Upon heating in benzene with azeotropic distillation of water for 3 h, (V) esterifies phenylboric acid to give 2-phenyl-4,6-bis(trichloromethyl)-5-o-hydroxyphenyl-1,3,2,5-dioxa-boraphosphorinane (VII), which is also formed upon the reaction of (V) with isobutyl diphenylborate.



The IR spectrum of (VII) has bands at 3230 and 3550 cm⁻¹ related to the hydroxyl group and at 1300-1350 cm⁻¹ related to the B^{III}-O bonds. The ³¹P NMR chemical shift of (VII) is -39 ppm, which is similar to the chemical shift of 4,6-bis(trichloromethyl)-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [5]. The PMR spectrum of (VII) has two groups of signals: a multiplet at 6.67-8 ppm, corresponding to the protons of the phenyl and hydroxyl group protons, and a symmetrical doublet at 5.7 ppm with ${}^{2}J_{PH} = 3$ Hz related to the methine protons. The equivalence of the methine protons indicates a diequatorial orientation of the trichloromethyl groups and that the esterification does not affect the phenolic hydroxyl group. The similarity of the ${}^{2}J_{PH}$ constants for (VII) and 4,6-bis(trichloromethyl)-2,5-diphenyl-1,3,2,5dioxaboraphosphorinane [5] indicates identical conformation of the 1,3,2,5-dioxaboraphosphorinane ring, while the magnitude of the coupling constants indicates equatorial orientation of the o-hydroxyphenyl group at the phosphorus atom.

Bases facilitate the borylation of α -hydroxyalkyl phosphorus derivatives [6,7] and involvement of the phenolic groups in this reaction [8]. Thus, we might have assumed that the action of pyridine on (VII) would lead to the formation of a bicyclic structure similar to that described in our previous work [8]. However, even when the (VII):pyridine ratio was 1:1, the complex of pyridinium o-(2,6-bis(trichloromethyl)-4-phenyl-3,5,4-dioxaboraphosphorinanyl)phenolate with pyridine (VIII) is formed.



The IR spectrum of (VIII) in the crystalline state lacks absorption for the hydroxyl group and B^{III}-O bonds but has a band for the N⁺-H bond at 2500-2800 cm⁻¹. The ratio of the integral intensities of the phenyl and pyridine group protons and methine protons in the PMR spectrum is 19:2. The methine protons give two symmetrical doublets with $^{2}J_{PH}$ 3 and 9 Hz, indicating their lack of equivalence. Thus, (VIII) exists predominantly as a single stereoisomer with the heterocyclic fragment in chair conformation with axial and equatorial trichloromethyl groups or in twist conformation. The ³¹P NMR spectrum of (VIII) has only one signal (-36 ppm).



Borylation of (VI) in order to obtain a heterocyclic compound with one pyridine fragment proved impossible using isobutyl diphenylborate or phenylboric acid.

An attempt was made to obtain boron-containing heterocycles with the participation of the phenyl hydroxy group by the reaction of o-diphenylboryloxyphenylphosphine (IV) and chloral with and without pyridine. The addition of two aldehyde molecules proceeded in the absence of amine and the ³¹P NMR spectrum initially showed a signal at -24 ppm, which differs from the chemical shift of (V), which served as a model for a cyclic phosphine (1 ppm), and (VII), which has a six-membered ring (-39 ppm), suggesting that the reaction is accompanied by the loss of benzene from the diphenylboryl group and formation of a seven-membered cyclic compound. However, a signal appeared at -39 ppm after 2 h, corresponding to (VII). The intensity of this signal increased over time. The addition of pyridine led to the crystallization of (VIII).



Thus, the intramolecular transesterification of phenyl ester of phenylboric acid proceeds by means of the α -hydroxyalkylphosphine. This finding indicates greater stability of the compound with the P-C-O-B fragment than for the compound with the P-C-O-B fragment due to stabilizing interactions between the phosphorus and boron atoms through the bond system.

EXPERIMENTAL

The 31 P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz with proton noise suppression (25.2 MHz) and on a Bruker WM-250 spectrometer using 85% H₃PO₄ as the external standard.^{*} The PMR spectra were taken on a Varian T-60 spectrometer at 34.5°C using TMS as an internal standard. The IR spectra were taken for vaseline mulls on a UR-20 spectrometer. The electron impact mass spectra were taken on an MKh-1310 mass spectrometer. The dipole moment of (II) was determined by a standard method (2.41 D in benzene at 25°C). All the operations with o-hydroxy- and o-diphenylboryloxyphenylphosphines were carried out in an argon atmosphere, while the operations with isobutyl diphenylborate were carried out with the exclusion of atmospheric moisture in dried solvents.

<u>Dimer of 5,6-Benzo-2-phenyl-4-ethoxy-4-oxo-1,3,2,4-dioxaboraphosphorinane (II)</u>. A mixture of 1.2 g (5 mmoles) 0,0-diethyl o-hydroxyphenylphosphonate and 1.24 g (5 mmoles) isobutyl diphenylborate was heated at reflux for 40 min. After cooling, the precipitate formed was filtered off and washed with ether. The yield of (II) was 0.7 g (49%), mp 165-168°C, $\delta_{\rm P}$ 13.77 ppm (in C₆H₆). Found: C, 58.45; H, 4.46; P, 10.06%. Calculated for C₁₄H₁₄BPO₄: C, 58.33: H 4.86; P, 10.76%.

<u>Bis(β , β , β -trichloro- α -hydroxyethyl)(o-hydroxyphenyl)phosphine (V)</u>. A sample of 4.28 g (29 mmoles) chloral in 15 ml ether was added to 1.83 g (14.5 mmoles) o-hydroxyphenylphosphine (III). After 1 h, the solvent was removed in vacuum. The residue crystallized upon standing. The yield of (V) was 5.81 g (95%), mp 108-111°C, δ_p 1 ppm (acetone). Found: C, 28.31; H, 2.38; P, 7.01%. Calculated for $C_{10}H_9PCl_6O_3$: C, 28.50; H, 2.14; P, 7.36%.

<u>Pyridinium o-(Bis(β,β,β -trichloro- α -hydroxyethyl)phosphino)phenolate (VI)</u>. A sample of 2.99 g (20 mmoles) chloral and 0.8 g (10 mmoles) pyridine in 10 ml ether were added consecutively to 1.28 g (10 mmoles) (III). After 1 h, the solvent was removed in vacuum and the residue was crystallized from acetone to give 2.44 g (49%) (VI), mp 103-105°C, δ_p 3 ppm (in acetonitrile). IR spectrum (ν , cm⁻¹): 2400-2700 br (N⁺-H), 3370 (OH) (oil). Found: C, 36.08; H, 2.83; N, 3.03; P, 6.29%. Calculated for C₁₅H₁₄PNCl₆O₃: C, 36.00; H, 2.80; N, 2.80; P, 6.20%.

<u>2-Phenyl-4,6-bis(trichloromethyl)-5-o-hydroxyphenyl-1,3,2,5-dioxabora)phosphorinane</u> (VII). A mixture of 2.39 g (6 mmoles) (V) and 0.7 g (6 mmoles) phenylboric acid was heated at reflux for 3 h in 25 ml benzene with azeotropic distillation of water. The solvent was removed in vacuum. The precipitate formed was filtered off and washed with benzene to give 1.25 g (43%) (VII), mp 170-173°C, $\delta_{\rm p}$ -39 ppm (in benzene). IR spectrum (ν , cm⁻¹): 1350 (B^{III}-O), 3230 br, 3550 (OH) (oil). Found: C, 36.98; H, 2.37; P, 6.38%. Calculated for C₁₆H₁₂PBCl₆O₃: C, 37.87; H, 2.36; P, 6.11%.

A mixture of 0.67 g (1.5 mmoles) (V) and 0.38 g (1.5 mmoles) isobutyl diphenylborate in 25 ml benzene was heated at reflux for 1 h. The solvent was removed in vacuum and the

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residue was crystallized from benzene to give 0.25 g (30%) (VII). The physical indices of this product were identical to those given above.

<u>Complex of Pyridinium o-(2.6-Bis(trichloromethyl)-4-phenyl-3.5,4-dioxaboraphosphor-anyl)phenolate with Pyridine (VIII)</u>. A sample of 0.3 g (4 mmoles) pyridine was added to 0.96 g (2 mmoles) (VII) in 5 ml ether. After 2 h, the solvent was removed in vacuum and the residue was crystallized from benzene to give 0.73 g (58%) (VIII), mp 137-140°C, δ_p -36 ppm (in benzene). IR spectrum (ν , cm⁻¹): 2500-2800 (N⁺-H) (oil). Found: C, 46.51; H, 3.12; N, 4.11; P, 4.10; Cl, 32.53%. Calculated for $C_{26}H_{22}BPN_2Cl_6O_3$: C, 46.92: H, 3.31; N, 4.31; P, 4.66; Cl, 32.03%.

A sample of 0.83 g (6 mmoles) chloral was added to 0.81 g (3 mmoles) o-diphenylboryloxyphenylphosphine (IV) in 5 ml ether. On the following day, ether was removed in vacuum and 0.22 g (3 mmoles) pyridine in 5 ml benzene was added to the reaction mixture. After standing overnight, the reaction mixture was concentrated in vacuum. The precipitate was filtered and washed with benzene to give 0.5 g (27%) (VIII). The physical indices coincide with those given above.

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