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SYNTHESIS OF CYCLIC BORYLOXYALKYLPHOSPHINES WITH ELECTRON-ACCEPTOR SUBSTITUENTS

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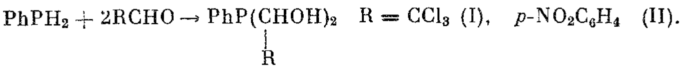
UDC 542.91:547.1'127'118

Boryloxyalkylphosphines are used in the synthesis of boroxyalkyl derivatives of phosphorus with the phosphorus and boron atoms in various valence states. One of the methods for synthesizing them may be the reaction of hydroxyalkylphosphines with esters or anhydrides of boric acids. For example, the reaction of methyl(hydroxymethyl)phenylphosphine with isobutyl diphenylborate gives diphenylboryloxymethylmethylphenylphosphine [1], and the reaction of bis(α-hydroxylalkyl)phenylphosphines with esters or the anhydride of phenylboric acid results in the formation of 4,6-disubstituted 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinanes [2, 3]. In the present work we attempted to introduce hydroxyalkylphosphines with electron-acceptor substituents on the carbon atoms attached to the phosphorus atom into the reaction under consideration.

Bis(α-hydroxy-β,β,β-trichloroethyl)phenylphosphine (I) and bis(α-hydroxy-p-nitrobenzyl)-phenylphosphine (II) are smoothly obtained by reacting phenylphosphine, respectively, with chloral hydrate and p-nitrobenzaldehyde:



$$PhPH_2 + 2RCHO \rightarrow PhP(\underset{\displaystyle R}{\underset{|}{C}}HOH)_2 \quad R = CCl_3\ (I),\ p\text{-}NO_2C_6H_4\ \ (II).$$

The ^{31}P NMR spectra of the reaction mixtures contained signals only for diastereoisomers of I and II at 0 and −10 ppm and at 14 and 2 ppm, respectively. A comparison of the spectra of I and of bis(α-hydroxyethyl)phenylphosphine (2 and −12 ppm [4]), as well as of II and bis-(hydroxybenzyl)phenylphosphine (10 and −6 ppm [5]) reveals the closeness of the parameters in the former case and the significant disparity in the latter case. The synthesis of tris(α-hydroxy-β,β,β-trichloroethyl)phosphine was described in [6]; its signal in the ^{31}P NMR spectrum has a downfield position at 18 ppm.

The reactions of I and II with phenylboric anhydride in benzene or MeCN with heating was quantitatively concluded by the formation of 2,5-diphenyl-4,6-di(trichloromethyl)-1,3,2,5-dioxaboraphosphorinane (III) and 2,5-diphenyl-4,6-di-p-nitrophenyl-1,3,2,5-dioxaboraphosphorinane (IV). The ^{31}P NMR spectra of the reaction mixtures contained signals only for stereoisomers of III and IV at −32 ppm and at −12, −19, and −24 ppm, respectively:

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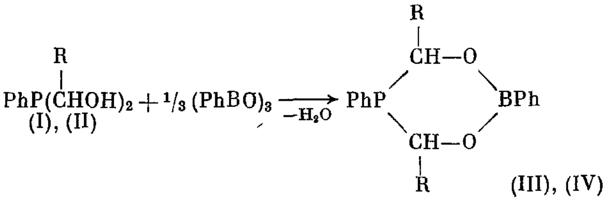
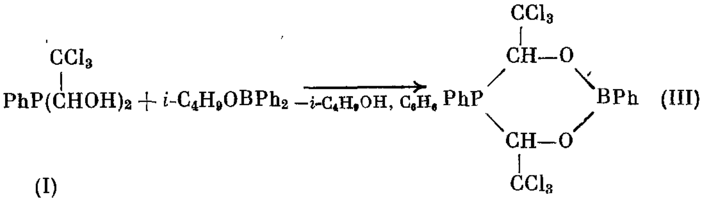


$R = CCl_3$ (III), $p\text{-}NO_2C_6H_4$ (IV).

An individual stereoisomer of III with a chemical shift equal to −32 ppm and a mixture of stereoisomers of IV with chemical shifts equal to −12 and −24 ppm were isolated. In the PMR spectrum of III, the ratio between the integrated intensities of the phenyl and methine protons is equal to 5:1, and the spin–spin coupling constant $^2J_{PH}$ equals 4 Hz.

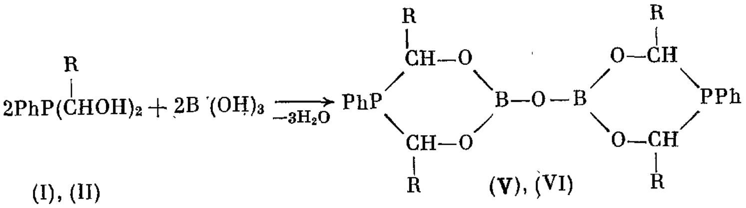
A comparison of the reactions of I and II and of bis(α-hydroxyalkyl)phenylphosphines [3] with phenylboric anhydride does not reveal any influence of the substituents on the conditions for the occurrence of these reactions. Both in the case of donor substituents and in the case of acceptor substituents, 1,3,2,5-dioxaboraphosphorinanes are obtained. Our attention is attracted by the fit between the chemical shifts of the signals of the stereoisomers of III and IV and of 4,6-dimethyl- and 4,6-diphenyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [3, 7], which may be utilized for establishing the spatial configuration of the stereoisomers.

The reaction of I with isobutyl diphenylborate did not stop at the stage of the boryloxyalkylphosphine, and the elimination of benzene with the formation of III occurred even at ∿20°C. The ^{31}P NMR spectrum of the reaction mixture did not contain signals of the original compounds or any products besides III.



Bis(hydroxymethyl)phenylphosphine and isobutyl diphenylborate give an ester-interchange product, which disproportionates to 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5-dioxaborataphosphoniarinane. The latter eliminates benzene only when it is heated above the melting point [8]. The easy elimination of benzene in the reaction of I is a consequence of the influence of the electron-acceptor substituent.

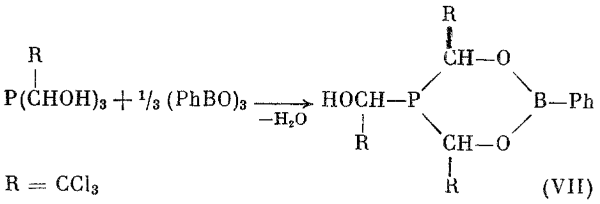
The reactions of hydroxyalkylphosphines with H_3BO_3 was not previously studied. It turned out that the reactions of I and II with H_3BO_3 under conditions for the azeotropic volatization of water give products, whose ^{31}P NMR spectra have signals at −32 and −12 ppm, respectively, which allow us to assign the 1,3,2,5-dioxaboraphosphorinane structure to them. The absence of the absorption of OH groups in the IR spectra leads to the conclusion that the molecules contain two dioxaboraphosphorinane rings joined at the boron atoms by an oxygen atom:



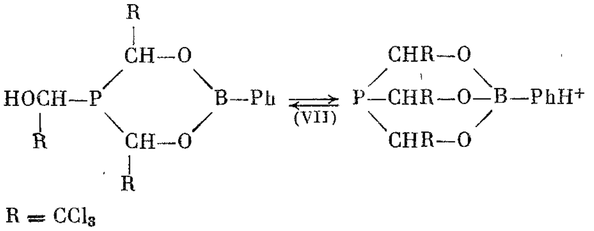
$R = CCl_3$ (V), $p\text{-}NO_2C_6H_4$ (VI).

The PMR spectra confirm the structure of V and VI: The phenyl and methine protons are manifested, their positions and splitting in the case of V being similar to those observed for III. The inequivalence of the methine protons in the spectrum of VI may be caused by the axial and equatorial orientations of the substituents at the carbon atoms attached to the phosphorus atom in the chair conformation, as was observed in the case of 2,4,5,6-tetraphenyl-1,3-2,5-dioxaboraphosphorinane in [7].

Tris(α-hydroxyalkyl)phosphines were not subjected to the reaction under consideration, although a number of cyclic products based on them have been obtained [6, 9]. The reaction of tris(α-hydroxy-β,β,β-trichloroethyl)phosphine with phenylboric anhydride took place under the same conditions as the reactions of I and II and gave a product, which had a signal at −10 ppm (C_6H_6) in the ^{31}P NMR spectrum and a band at 3480 cm^{-1} in the IR spectrum. The upfield displacement of the signal in such reactions (18 ppm in the case of the original triol) is usually associated with cyclization [3]. Therefore, it was concluded that 5-α-hydroxy-β,β,β-trichloroethyl-2-phenyl-4,6-ditrichloromethyl-1,3,2,5-dioxaboraphosphorinane (VII) was obtained:

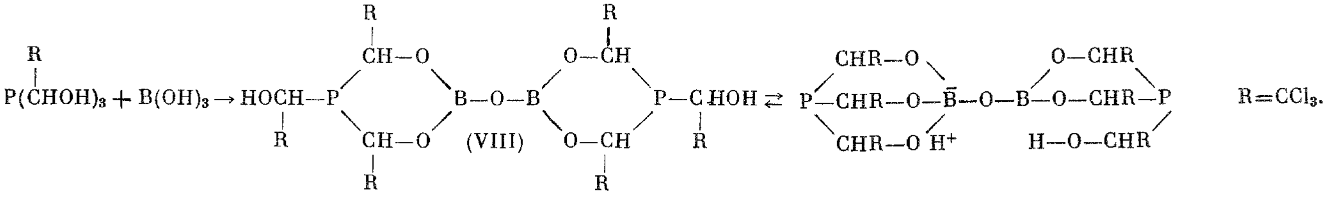


The IR spectrum of VII in CCl_4 also contained a band at 3480 cm^{-1} caused by the absorption of the OH group. However, the PMR spectrum demonstrated the equivalence of all three methine protons, which corresponds to a bicyclic form with a proton at B^{IV}. This contradiction is easily eliminated, if we postulate the occurrence of ring—chain tautomerism with interconversion of the forms which is rapid on the NMR time scale:



The tautomerism is also indicated by the significant influence of the nature of the solvent on the position of the signal in the ^{31}P NMR spectrum: −4 ppm in DMFA and −10 ppm in benzene. The chemical shifts of the bicyclic phosphines in which the site of the B atom is occupied by P, P(O), P(S), As, and SiPh atoms lie in the range from −14 to −23 ppm [6].

It was expected that the aforementioned features of the reactions involving H_3BO_3 and tris(α-hydroxy-β,β,β-trichloroethyl)phosphine will be manifested when they are reacted with one another and will result in the formation of compounds, which are similar to V and VI and have tautomerism, as does VII:



The structure of the product obtained is consistent with VIII. In the IR spectrum of VIII there is a band at 3225 cm^{-1} for a hydroxyl group. The methine protons are equivalent in the PMR spectrum. The signal in the ^{31}P NMR spectrum lies at −4 ppm in DMFA, which is close to the signal observed for VII. The results presented above show that the reaction of hydroxyalkylphosphines with esters or anhydrides of boric acids is a general method for obtaining boryloxyalkylphosphines, and it can be carried out with hydroxyalkyl derivatives of phosphine, primary and secondary phosphines with both donor and acceptor substituents on the carbon atoms attached to the phosphorus atom, and all types of boric acids.

EXPERIMENTAL

The PMR spectra were recorded on a Varian T-60 instrument (60 MHz, 34.5°) with TMS as an internal reference, and the ^{31}P NMR spectra were recorded on a KGU-4 NMR spectrometer (10.2 MHz) with noise decoupling from the protons at a frequency of 25.2 MHz. The IR spectra were recorded on a UR-20 spectrometer.

Bis(α-hydroxy-β,β,β-trichloroethyl)phenylphosphine (I). A solution of 1.5 g (9 mmoles) of chloral hydrate in 25 ml of absolute ether in an Ar atmosphere was given an addition of 0.5 g (4.5 mmoles) of phenylphosphine. The precipitate was filtered on the next day, washed with ether, and dried in a vacuum. The yield of I was 1.8 g (90%), and the mp was 123°C. $\delta^{31}P$: 0, −10 ppm (C_6H_6). Found: C 29.59; H 2.16; P 7.90%. Calculated for $C_{10}H_9PO_2Cl_6$: C 29.62; H 2.22; P 7.65%.

Bis(α-hydroxy-p-nitrobenzyl)phenylphosphine (II). A solution of 3 g (20 mmoles) of p-nitrobenzaldehyde in 50 ml of absolute ether in an Ar atmosphere was given an addition of 1.1 g (10 mmoles) of phenylphosphine, and the mixture was heated until the aldehyde dissolved and left to stand for 24 h at 20°C. The solvent was removed, and the residue was washed with benzene and ether. The yield of II was 3.4 g (82%), and the mp was 112°C. $\delta^{31}P$: 14 and 2 ppm (C_6H_6). Found: C 57.79; H 4.35; P 7.46; N 6.80%. Calculated for $C_{20}H_{17}PO_6N_2$: C 58.25; H 4.12; P 7.52; N 6.79%.

Tris(α-hydroxy-β,β,β-trichloroethyl)phosphine was obtained according to the method in [6].

2,5-Diphenyl-4,6-di(trichloromethyl)-1,3,2,5-dioxaboraphosphorinane (III). A. A solution of 2 g (4.8 mmoles) of I and 0.5 g (4.8 mmoles) of phenylboric anhydride in 20 ml of benzene was heated to boiling for 30 min. The benzene was driven off in a vaccum, and the solid residue, was washed with MeOH and ether. The yield of III was 2 g (82%), and the mp was 181°C. $\delta^{31}P$: −32 ppm (C_6H_6). Found: C 39.02; H 2.62; P 6.27%. Calculated for $C_{14}H_{12}O_2PBCl_6$: C 39.10; H 2.44; P 6.31%. PMR spectrum (δ, ppm in CCl_4): 5.15 d (CH), $^{2}J_{P-CH}$ = 4 Hz.

B. A solution of 2 g (5 mmoles) of I in 20 ml of ether was given an addition of 1.2 g (5 mmoles) of isobutyl diphenylborate. After 28 h the precipitate was filtered and washed with ether. The yield of III was 2.2 g (90%), and the mp was 181°C. $\delta^{31}P$: −32 ppm (C_6H_6).

2,5-Diphenyl-4,6-di-p-nitrophenyl-1,3,2,5-dioxaboraphosphorinane (IV). A mixture of 1 g (2.4 mmoles) of II and 0.25 g (2.4 mmoles) of phenylboric anhydride in 20 ml of benzene was heated for 30 min to dissolution. On the next day, the benzene was driven off in a vacuum, and the residue was recrystallized from MeCN. The yield of IV was 1 g (83%), and the mp was 194°C. $\delta^{31}P$: −12, −24 ppm (DMFA). Found: C 62.64; H 4.22; P 6.48; N 5.62%. Calculated for $C_{26}H_{20}PO_6N_2B$: C 62.65; H 4.02; P 6.22; N 5.62%.

Bis[4,6-bis(trichloromethyl)-5-phenyl-1,3-dioxa-5-phospha-2-boran-2-yl] Oxide (V). A mixture of 2 g (2.4 mmoles) of I and 0.15 g (2.4 mmoles) of H_3BO_3 in 100 ml of benzene was boiled with a Dean–Stark trap, the solution was filtered, the benzene was driven off in a vacuum, and the residue was washed with ether. The yield of V was 3.1g (85%), and the mp was 130°C. $\delta^{31}P$: −32 ppm (C_6H_6). Found: C 29.04; H 2.06; P 6.88%. Calculated for $C_{20}H_{17}P_2O_5B_2Cl_{12}$: C 28.36; H 2.07; P 7.32%. PMR spectrum (δ, ppm in CCl_4): 5.12 d (CH), $^{2}H_{P-CH}$ = 4 Hz.

Bis[4,6-bis(p-nitrophenyl)-5-phenyl-1,3-dioxa-5-phospha-2-boran-2-yl] Oxide (VI). This compound was obtained in analogy to V. The yield was 1.2 g (53%), and the mp was >280°C (with decomposition). $\delta^{31}P$: −12 ppm (C_6H_6). Found: C 55.87; H 3.44; P 7.31; N 6.13%. Calculated for $C_{40}H_{30}P_2N_4O_{13}B_2$: C 55.94; H 3.49; P 7.22; N 6.52%.

5-(α-Hydroxytrichloroethyl)-2-phenyl-4,6-ditrichloromethyl-1,3,2,5-dioxaboraphosphorinane (VII). A mixture of 1 g (1.8 mmoles) of tris(α-hydroxy-β,β,β-trichloroethyl)phosphine and 0.19 g (0.6 mmoles) of phenylboric anhydride in 15 ml of benzene was heated to dissolution, the benzene was driven off in a vacuum, and the residue was washed with MeCN. The yield of VII was 0.9 g (76%), and the mp was 177°C. $\delta^{31}P$: −10 ppm (CH_3CN). Found: C 25.99; H 1.8; P 5.49%. Calculated for $C_{12}H_9PO_3BCl_9$: C 25.60; H 1.6; P 5.51%. PMR spectrum (δ, ppm in CCl_4): 3.33 s (OH), 5.48 q (CH), $^{2}J_{P-CH}$ = 6, $^{3}J_{CH-CH}$ = 2 Hz.

Bis[4,6-bis(trichloromethyl)-5-(α-hydroxytrichloroethyl)-1,3-dioxa-5-phospha-2-boran-2-yl] Oxide (VIII). This compound was obtained in analogy to V from tris(α-hydroxy-β,β,β-trichloroethyl)phosphine and H_3BO_3. The product was washed with benzene and acetone. The yield was 1.6 g (69%), and the mp was >320°C. $\delta^{31}P$: −4 ppm (DMFA). Found: C 14.79; H 1.42; P 6.56%. Calculated for $C_{12}H_8P_2O_7BCl_{18}$: C 14.58; H 0.81; P 6.28%. PMR spectrum [δ, ppm in $(CD_3)_2CO$]: 5.47 d (CH), 7.41 s (OH), $^{2}J_{P-CH}$ = 4 Hz.

CONCLUSIONS

The reaction of hydroxyalkylphosphines containing electron-acceptor substituents with esters and anhydrides of boric acids and boric acid itself results in the formation of substituted 1,3-dioxa-5-phospha-2-boran-2-yl oxides.

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REACTION OF OXOCHLOROALKENES WITH PHOSPHOROUS ACID ESTERS

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An important aspect of investigations related to the solution of the problem of aging and stabilization of chlorine-containing polymers and, in particular, vinyl chloride polymers [1-4] is the study of reactions of low-molecular-weight compounds as models of structural defects in polymer chains. In particular, chloroalkanes $R^1CR^2ClCH_2(CHClCH_2)_nR^3$, chloroalkenes $R^1CH{=}CH{-}CR^2Cl{-}R^3$, and chloroalkadienes $R^1{-}CH{=}CHCH{=}CHCHCl{-}CH_2R^2$, where R^1, R^2, R^3 = H, Alk; $n \geqslant 1$ [5-7] have been synthesized and studied in some specific reactions with stabilizers of chlorine-containing polymeric products (phosphorous acid esters [1], epoxy compounds [2], carboxylates of coordination-unsaturated metals [3, 4], etc.).

Because of the development of the concept of the predominant role of oxygen-containing fragments including $C{=}C$ bonds, in particular $\sim C(O)CH{=}CHCHCl\sim$, as basic labile groups, determining the rate of elimination of HCl from vinyl chloride polymers [8], low-molecular-weight models of these structures are of great interest.

Oxochloroalkenes are structurally adequate reagents for study of the reactivity of carbonylallyl chloride groups $\sim C(O)CH{=}CHCHCl\sim$ and proof of the possibility of carrying out polymer-like reactions at one or several reaction centers of this group ($C{=}O$, $C{=}C$, CCl). In the present paper, we synthesized 2-oxo-5-chloro-3-heptene (I) and 2-oxo-3-methyl-5-chloro-3-hexene (II) and studied their reactions with tributyl phosphite, a stabilizer of chlorine-containing polymers (3-120 h, 20-80°C).

When $(BuO)_3P$ was stirred with an equimolar amount of (I) or (II) at 20°C, the ^{31}P NMR spectra contained only the signal of the starting phosphite (138 ppm from the external standard of 85% H_3PO_4), which was retained for 72 h. After heating (3 h, 40°C), in the case of (I) a signal appeared at −34 ppm, characteristic of cyclic phosphoranes [9], corresponding in this case to 1-oxa-3-(α-chloropropyl)-5-methyl-2,2,2-tris(butyloxy)phosphol-4-ene. Subsequent heating of the mixture (10 h, 60°C) led to the appearance of signals of three phosphonate structures at 21, 24, and 31 ppm.

The signal at 31 ppm corresponded to O,O-dibutyl butylphosphonate, formed according to the following scheme:

$$(BuO)_3P + BuCl \xrightarrow{\Delta} (BuO)_2P(O)Bu$$

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