Preparation of Complex of α-Diphenylboryloxyethyl(α-hydroxyethyl)phenylphosphine Sulfide

with Triethylamine (V) was carried out in analogy with (VI), but using MeCHO instead of Me<sub>2</sub>-CHCHO. Crystals were obtained from the reaction mixture, and were recrystallized from MeCN. The yield of (V) was 80%, mp 118°C,  $\delta^{31}$ P 33 ppm (MeCN). IR spectrum: 3100 cm<sup>-1</sup> (oil). Found: C 69.31; H 8.34; P 6.02; N 2.87%. C<sub>30</sub>H<sub>43</sub>PO<sub>2</sub>BNS. Calculated: C 68.83; H 8.22; P 5.93; N 2.68%.

Recrystallization of (V) from benzene gave crystals mp 132°C,  $\delta^{31}$ P 33 ppm (DMFA). IR spectrum: 2500, 2700 cm<sup>-1</sup>. Found: C 69.25; H 8.24; P 5.87; N 2.90; S 6.55%.

#### CONCLUSIONS

A ring-chain tautomerism of complexes of diphenylboryloxymethyl(hydroxymethyl)phenylphosphine selenides with amines has been discovered. At the equilibria of the pyridine and triethylamine complexes, the open and cyclic forms, respectively, predominate.

### LITERATURE CITED

- 1. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 2089 (1984).
- B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, I. P. Romanova, R. P. Arshinova, and O. V. Ovodova, Izv. Akad. Nauk SSSR, Ser. Khim., 2535 (1983).
- 3. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11 (1985).
- 4. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 954 (1980).
- 5. B. A. Arbuzov, O. A. Erastov, and S. Sh. Khetagurova, Izv. Akad. Nauk SSSR, Ser. Khim., 866 (1979).

### SYNTHESIS OF AMMONIUM 5-OXO-1,3,2,5-DIOXABORATAPHOSPHORINANES

B. A. Arbuzov, G. N. Nikonov, and O. A. Erastov

Under mild conditions, hydroxyalkylphosphines readily react with phenylboric acid anhydride and isobutyl ester of diphenylboric acid to form 1,3,2,5-dioxaboraphosphorinanes [1], diphenylboryloxymethyl(methyl)phenylphosphine [2], imidoylphosphines [3], and 1,3,2,5-dioxaborataphosphoniarinanes [2, 4]. Hydroalkylphosphine oxides react with phenylboric acid anhydride only in azeotropic distillation of water to form 5-oxo-1,3,2,5-dioxaboraphosphorinanes [1]. There was no reaction with i-BuOBPh<sub>2</sub>, but addition of sodium alcoholate catalyzes the reaction, which proceeds at ~20°C and leads to the Na salt of phenylisobutoxyboryloxymethyl(hydroxymethyl)phenylphosphine oxide [5].

UDC 542.91:547.1'118

The discovery of a basic catalysis for the reaction of hydroxyalkylphosphine oxides with boric acid esters opens up new possibilities for synthesizing boroxyalkyl derivatives of phosphorus. In particular, the introduction of amines into the reaction is interesting, since in this case, in the presence of a free hydroxyalkyl grouping in the product, complex—salt tautomerism is possible, causing varied reactivity of the compounds. Ring—chain complex—salt tautomerism was found in the ammonium 5-thio-1,3,2,5-dioxaborataphosphorinanes [6], which in the crystalline state are present in a cyclic salt form, and the open complex form predominates in concentrated solutions of some of them. This complex form can be isolated in the individual state. The compounds were isolated by the reaction of 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5dioxaborataphosphoniarinane with sulfur and amines.

In the present work it was shown that the reaction of  $bis(\alpha-hydroxyalkyl)$  phenylphosphine oxides (I)-(IV) with i-BuOBPh<sub>2</sub> in the presence of amines led to the formation of ammonium 5-oxo-1,3,2,5-dioxaborataphosphorinanes (V)-(IX). Phenylphosphine oxides (I)-(IV), obtained by the oxidation of  $bis(\alpha-hydroxyalkyl)$  phenylphosphines, are stable crystalline compounds

A. B. Arbuzov Institute of Organic and Physical Chemistry. Kazan' Division, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2369-2372, October, 1985. Original article submitted June 5, 1984.

2194

 $\begin{array}{c} R & O R \\ PhP(CHOH)_2 \xrightarrow{H_2O_2} PhP(CHOH)_2 \end{array}$ 

# $\mathbf{R} = Ph$ (I), $C_6H_4Cl_p$ (II), $C_6H_4NO_2p$ (III), $CCl_3$ (IV).

The reaction of oxides (I)-(IV) with  $i-BuOBPh_2$  begins after the addition of amines, and under mild conditions leads to crystalline compounds (V)-(IX)



The structure of (V)-(IX) was established from the data of elemental analysis and IR spectra. In the IR spectra of the compounds the absorption of the OH groups is missing in the  $3100-3600 \text{ cm}^{-1}$  region and there is an absorption of the N-H bond. There is also no absorption of the B-O bond of boric acid esters in the  $1300-1350 \text{ cm}^{-1}$  region in the spectra. The IR spectral data show that the structure of salts can be ascribed to the compounds, where 5-oxo-1,3,2,5-dioxaborataphosphorinane with a negative charge on the boron atom is the anion, and a protonated amine is the cation. It should be noted that, as in the case of ammonium 5-thio-1,3,2,5-dioxaborataphosphorinanes [6], absorption due to the vibrations of the N-H bond is more characteristic of a protonated triethylamine than of a protonated pyridine. In the first case, two intense bands are observed with maxima in the  $2500-2700 \text{ cm}^{-1}$  region. In the Second case, the absorption is observed as a broad band without a sharp maximum in the  $2000-2700 \text{ cm}^{-1}$  region. In the IR spectra of the compounds in benzene, not only absorption of the N-H bonds, but also absorption in the  $3100-3700 \text{ cm}^{-1}$  region is observed, which belongs to the OH groups. This indicates the existence of complex-salt tautomerism in the solutions.

A study of the reactions of (I)-(IV) with i-BuOBPh<sub>2</sub> in the presence of amines revealed the influence of a substitutent at the C atom and the basicity of the amine. It was found that (I) does not react with i-BuOBPh<sub>2</sub> in the presence of pyridine, while if the reaction is carried in the presence of Et<sub>3</sub>N, compound (V) is obtained. In the presence of pyridine, (IV) gave (VIII), but if this reaction is carried out using Et<sub>3</sub>N, there is resinification of the reaction mixture, while (II) reacts in the presence of both Et<sub>3</sub>N and pyridine. The above results show that the reactions are favored by increase in the electron-acceptor character of the substituent at the C atom and the basicity of the amine. The electron-acceptor character of the substituents increases in the series: Ph < C<sub>6</sub>H<sub>4</sub>Cl-p < C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-p < CCl<sub>3</sub>.

### EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer. The <sup>31</sup>P NMR spectra were run on a KGU-4 NMR spectrometer at 10.2 MHz with proton decoupling at a frequency of 25.2 MHz. The concentration of the solutions was 30-50%. The chemical shifts are given with reference to 85% H<sub>3</sub>PO<sub>4</sub>, the positive values refer to lower fields.

Bis(a-hydroxybenzyl)phenylphosphine oxide (I) was obtained in analogy with [7].

<u>Bis(p-chloro- $\alpha$ -hydroxybenzyl)phenylphosphine Oxide (II).</u> A solution of H<sub>2</sub>O<sub>2</sub> in 5 ml of acetone was added to 5 g of bis(p-chloro- $\alpha$ -hydroxybenzyl)phenylphosphine in 10 ml of acetone. The crystals that precipitated were washed with acetone; yield, 4.8 g (92%), mp 178°C,  $\delta^{31}$ P 39 ppm (DMFA). Found: C 59.13; H 4.44; P 7.73; Cl 17.91%. C<sub>20</sub>H<sub>17</sub>PO<sub>3</sub>Cl<sub>2</sub>. Calculated: C 58.96; H 4.18; P 7.62; Cl 17.44%.

 $\frac{\text{Bis}(p-nitro-\alpha-hydroxybenzyl)\text{phenylphosphine oxide (III)}}{(II), yield 75\%, mp 155°C, <math>\delta^{31}$ P 34 ppm (DMFA). Found: C 56.30; H 4.05; P 7.33; N 6.41\%. C<sub>20</sub>-H<sub>17</sub>PO<sub>7</sub>N<sub>2</sub>. Calculated: C 56.07; H 3.97; P 7.24; N 6.54\%.

Bis( $\alpha$ -hydroxy- $\beta$ , $\beta$ , $\beta$ -trichloroethyl)phenylphosphine oxide (IV) was obtained in the same way as (II) in a yield of 83%, mp 152°C,  $\delta^{31}$ P 17 ppm (methanol). Found: C 28.80; H 2.10; P 7.30. C<sub>10</sub>H<sub>2</sub>PO<sub>3</sub>Cl<sub>6</sub>. Calculated: C 28.50; H 2.13; P 7.36%.

Triethylammonium 2,2,4,5,6-Pentaphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane (V). A 1.4-g portion (6 mmoles) of i-BuOBPh<sub>2</sub> and 2 ml of Et<sub>3</sub>N were added to 2 g (6 mmoles) of (I) in 5 ml of MeCN. The mixture was heated to dissolution of the reagents, and after 3 h the solvents were evaporated in vacuo, and the residue was crystallized from acetone. The yield of (V) was 1.6 g (46%), mp 141°C,  $\delta^{31}P$  43 ppm (DMFA). IR spectrum (v, cm<sup>-1</sup>): 2500, 2700 (oil). Found: C 75.06; H 6.80; P 5.24; N 2.47%. C<sub>38</sub>H<sub>43</sub>PO<sub>3</sub>BN. Calculated: C 75.62; H 7.13; H 5.14; N 2.32%.

 $\frac{\text{Triethylammonium 2,2,5-Triphenyl-4,6-di(p-chlorophenyl)-5-oxo-1,3,2,5-dioxaborataphos-phorinane (VI) was obtained in the same way as (V) in a yield of 87%, mp 159°C, <math>\delta^{31}P$  35 ppm (DMFA). IR spectrum (v, cm<sup>-1</sup>): 2500, 2650 (oil). Found: C 67.37; H 6.06; P 4.57; N 2.67%. C<sub>38H41</sub>PO<sub>3</sub>NBCl<sub>2</sub>. Calculated: C 67.86; H 6.10; P 4.61; N 2.08%.

<u>Triethylammonium 2,2,5-triphenyl-4,6-di(p-nitrophenyl)-5-oxo-1,3,2,5-dioxaborataphosphor-inane (VII)</u> was obtained in the same way as (V). One hour after the reagents were mixed, excess solvent was evaporated, and the residue was dissolved in 1 ml of acetone. After ether was added to the solution, yellow crystals precipitated, which were washed on the filter by an acetone-ether (1:1) mixture. The yield of (VII) was 0.4 g (88%), mp 140°C,  $\delta^{31}P$  53 ppm (DMFA). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2500, 2700 (oil). Found: C 65.44; H 5.62; P 4.42; N 5.66%. C<sub>38</sub>H<sub>41</sub>PO<sub>3</sub>N<sub>3</sub>B. Calculated: C 65.80; H 5.92; P 4.47; N 6.06%.

<u>Pyridinium 2,2,5-triphenyl-4,6-bis(trichloromethyl)-5-oxo-1,3,2,5-dioxaborataphosphorinane (VIII)</u> was obtained in the same way as (V) in a yield of 90%, mp 125°C,  $\delta^{31}P$  23 ppm (acetone). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2030, 2140 (oil). Found: C 48.88; H 3.76; P 5.32; N 3.63%. C<sub>37</sub>H<sub>23</sub>PO<sub>3</sub>NBCl<sub>6</sub>. Calculated: C 48.80; H 3.46; P 4.67; N 2.11%.

Pyridinium 2,2,5-Triphenyl-4,6-di(p-chlorophenyl)-5-oxo-1,3,2,5-dioxaborataphosphorinane (IX). A 0.5-ml portion of pyridine and 0.2 g (9 mmoles) of i-BuOBPh<sub>2</sub> were added to a solution of 0.36 g (9 mmoles) of (II) in 2 ml of MeCN. After 4 h the crystals that precipitated were filtered and recrystallized from MeCN. The yield of (IX) was 0.55 g (95%), mp 142°C,  $\delta^{31}P$  42 ppm (DMFA). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2000, 2130 (oil). Found: C 68.11; H 4.93; P 4.68; N 2.48%. C<sub>37</sub>H<sub>31</sub>PO<sub>3</sub>NBCl<sub>2</sub>. Calculated: C 68.31; H 4.77; P 4.77; N 2.15%.

## CONCLUSIONS

In the reaction of  $bis(\alpha-hydroxyalkyl)$  phenylphosphine oxides with isobutyl ester of diphenylboric acid in the presence of amines, ammonium 5-oxo-2,2,5-triphenyl-4,6-di-R-1,3,2,5-dioxaborataphosphorinanes were obtained.

### LITERATURE CITED

- 1. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, I. P. Romanova, R. P. Arshinova, and R. A. Kadyrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1374 (1983).
- 2. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 2541 (1983).
- B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, T. A. Zyablikova, Yu. Ya. Efremov, and R. Z. Musin, Izv. Akad. Nauk SSSR, Ser. Khim., 676 (1982).
- 4. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, A. A. Espenbetov, A. I. Yanovskii, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1545 (1981).
- 5. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, Izv. Akad. Nauk SSSR, Ser. Khim., 954 (1980).
- 6. B. A. Arbuzov, G. N. Nikonov, and O. A. Erastov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, (1985).
- 7. B. A. Arbuzov, O. A. Erastov, S. Sh. Khetagurova, and T. A. Zyablikova, Izv. Akad. Nauk SSSR, Ser.Khim., 2136 (1979).