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

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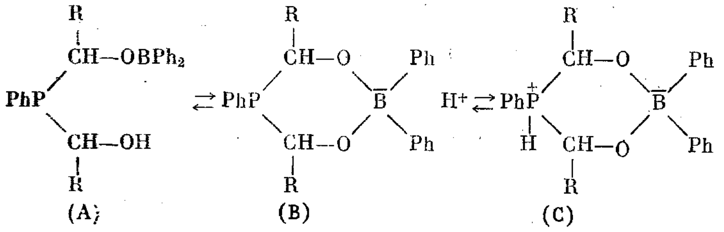
In [1] the existence of interaction between the P and B atoms in the P—C—O—B system was established. Thus, the reaction rate and stability of the products of reaction at one center depend on the state of the other. In particular, the strong influence of P atom coordination on the addition of pyridine to the B atom was discovered. For example, 5-thio- and 5-seleno-1,3,2,5-dioxaboraphosphorinanes form stable crystalline complexes with pyridine, while complexes of 1,3,2,5-dioxaboraphosphorinanes were not obtained. It was of interest to find more examples of the influence of P atom coordination on the reactivity of the B atom.

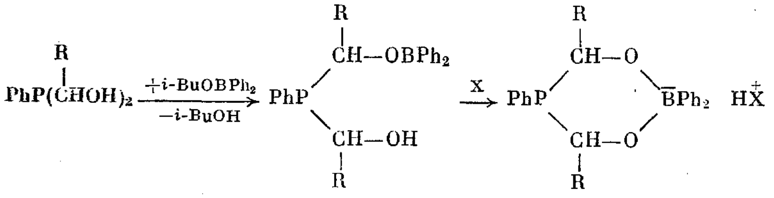
Upon interaction of bis(α-hydroxyalkyl)phenylphosphine with the isobutyl ester of diphenylborinic acid in the presence of dipolar reagents, diphenylboryloxyalkyl (hydroxyalkyl)phenylphosphines are formed as intermediates. These compounds have a mobile H atom and can exist in three tautomeric forms, one of which has acidic character (B).



Earlier we studied the reaction of bis(α-hydroxyalkyl)phenylphosphines with the isobutyl ester of diphenylborinic acid in the presence of S or Se and amines [2]. Triethylammonium and pyridinium 5-thio(seleno)-1,3,2,5-dioxaborataphosphorinanes are formed, which by their structure are derivatives of form (B). They were shown to undergo complex—salt tautomerism in solution with predominance of the salt form in the case of triethylamine and the complex for pyridine.

It was of interest to evaluate the acidity of form (B) for the case of tricoordinated P and the influence of radicals on the structure of the products.

Upon reaction of bis(α-hydroxyalkyl)phenylphosphines with the isobutyl ester of diphenylborinic acid in the presence of triethylamine or methylmorpholine, products were obtained which were crystallized from acetone. According to elemental analysis, the composition of the products corresponded to addition of 1 mole of amine to α-diphenylboryl oxyalkyl(α-hydroxyalkyl)phenylphosphine. In the IR spectra in the crystalline state absorption at 3100-3700 cm^{-1} was absent and absorption at 2500-2700 cm^{-1}, characteristic of protonated nitrogen atom, was observed. The ^{31}P NMR signals were in the negative region. On the basis of these data the products in the crystalline state exist as ammonium salts of 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinanes.



(I)—(IV)

R = Me(I), *i*-Pr(II), Ph(III), X = Et_3N; R = H, X = $MeN(CH_2CH_2)O$(IV).

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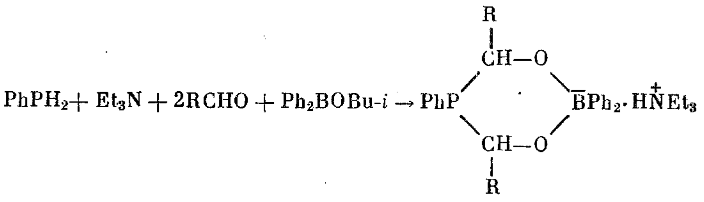
Upon reaction of bis(α-hydroxyalkyl)phenylphosphines with isobutyl diphenylborinate in the presence of pyridine and dimethylaniline a different picture was observed. Pyridine stabilized the initial bis(hydroxymethyl)phenylphosphine, and in the ^{31}P NMR spectrum of the reaction mixture only starting material was observed. Dimethylaniline did not participate in the reaction which formed 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5-dioxaborataphosphorinane due to disproportionation of diphenylboryloxymethyl(hydroxymethyl)phenylphosphine [3].

The formation of trimethylammonium and methylmorpholinium 1,3,2,5-dioxaborataphosphorinanes shows the high acidity of the tricoordinated P atom in form (B). At the same time, the absence of salt products with the weaker bases pyridine and dimethylaniline shows the acidity to be lower than in the case of tetracoordinated P which did yield salts.

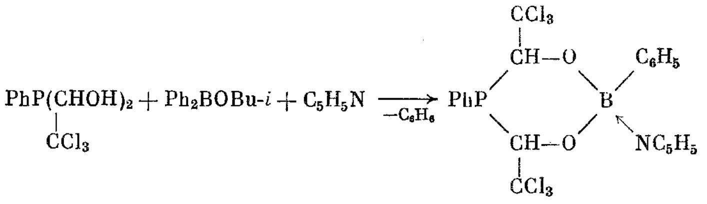
Ammonium 1,3,2,5-dioxaborataphosphorinanes can be synthesized starting from phenylphosphine. This is due to the fact that formation of bis(α-hydroxyalkyl)phenylphosphines from phenylphosphine and aldehydes proceeds under the same conditions as reaction of diol with isobutyl diphenylborinate in the presence of amines. Accordingly, a mixture of isobutyl ester and aldehyde was added to a solution of phenylphosphine and excess amine. The exothermic reaction produced ammonium 1,3,2,5-dioxaborataphosphorinane in good yield.



R = Et(V), *n*-Pr(VI), *i*-Bu(VII), C_6H_4Cl-*p*(VIII), $C_6H_4NO_2$-*o*(IX).

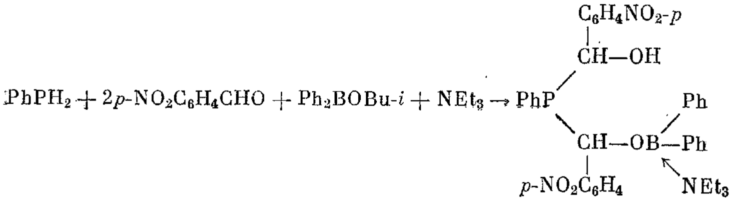
The use of phosphine as starting material reduces the number of steps and simplifies the synthesis of ammonium 1,3,2,5-dioxaborataphosphorinanes since the formation of highly reactive bis(α-hydroxyalkyl)phenylphosphines is avoided.

In the reaction of form (B) with tertiary amines the formation of ammonium salts competes with intramolecular cleavage of benzene. The direction of the reaction depends on the nature of the substituent. Cleavage of benzene was observed during the reaction of bis(α-hydroxy-β,β,β-trichloroethyl)phenylphosphine, which contains strong electron-accepting substituents, with isobutyl diphenylborinate in the presence of pyridine.



Earlier, cleavage of benzene was observed upon thermal decomposition of 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5-dioxaborataphosphorinane and during reaction of bis(α-hydroxy-β,β,β-trichloroethyl)phenylphosphine with isobutyl diphenylborinate [4, 5]. In the case of bis(α-hydroxyalkyl)phenylphosphines with electron-donating or weakly accepting substituents salt products are formed.

Upon reaction of 2 moles of p-nitrobenzaldehyde with isobutyl diphenylborinate in the presence of triethylamine a crystalline product was obtained which has a chemical shift of −20 ppm in the ^{31}P NMR spectrum. In the IR spectrum absorption in the region of 2500-2700 cm^{-1} (characteristic for NH) was absent and absorption with a maximum at 3170 cm^{-1} (HO group) was observed. The same absorption is found in 2,2,5-triphenyl-5-hydroxymethyl-1,3,2,5-dioxaborataphosphorinane [3]. On the basis of these data and the results of elemental analysis, which showed the presence of nitrogen, the compound appears to be a complex of α-diphenylboryloxy-α-p-nitrobenzyl(α-hydroxy-p-nitrobenzyl)phenylphosphine with triethylamine.



(X)

The formation of three types of products in the reaction of bis(α-hydroxyalkyl)phenylphosphines with isobutyl diphenylborinate and tertiary amines indicates the influence of the substituent on the reaction direction and the structure of the products. With strong electron-accepting substituents cleavage of benzene takes place or the product is stabilized by complex formation. With donor substituents the salt is formed.

4,6-Disubstituted ammonium 5-phenyl-1,3,2,5-dioxaborataphosphorinanes have asymmetric C and P atoms and can exist as several stereoisomers. The latter is confirmed by the presence of several signals in the ^{31}P NMR spectra of a series of compounds.

EXPERIMENTAL

The ^{31}P NMR spectra were obtained on a KGU-4 NMR spectrometer at 10.2 MHz with proton decoupling at 25.2 MHz, and without decoupling. The IR spectra were taken on a UR-20 spectrometer as oil mulls.

Triethylammonium 2,2,5-Triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane (I). To 10.4 g (53 mmoles) of bis(α-hydroxyethyl)phenylphosphine in 25 ml Et_3N was added 12.5 g (53 mmoles) of i-$BuOBPh_2$. Emission of heat occurred, and a solid precipitated which was recrystallized from acetone yielding 12 g of (I) (50%), with mp 76-77°C, δ^{31}P −12, −26 ppm (DMF). IR spectra (ν, cm^{-1}): 2500, 2600 (oil). Found: C 73.03; H 8.51; P 6.50; N 3.01%. $C_{28}H_{39}PO_2BN$. Calculated: C 72.57; H 8.42; P 6.70; N 3.02%.

Triethylammonium 2,2,5-Triphenyl-4,6-diisopropyl-1,3,2,5-dioxaborataphosphorinane (II). This compound was obtained analogously to (I). The yield was 75%, mp 77°C, ^{31}P: −3, −30, −46 ppm (DMF). IR spectra (ν, cm^{-1}): 2500, 2700 (oil). Found: C 73.92; H 9.00; P 5.45; N 2.87%. $C_{32}H_{47}PO_2BN$. Calculated: C 73.99; H 9.06; P 5.97; N 2.70%.

Triethylammonium 2,2,4,5,6-Pentaphenyl-1,3,2,5-dioxaborataphosphorinane (III). Compound (III) was obtained analogously to (I) and crystallized from a mixture of MeCN and acetone (1:1). The yield was 94%, mp 98-99.5°C, δ^{31}P: −2, −25 ppm (DMF). IR spectra (ν, cm^{-1}): 2500, 2680 (oil). Found: C 77.67; H 7.48; P 5.15; N 2.45; B 1.80%. $C_{38}H_{48}PO_2BN$. Calculated: C 77.68; H 7.33; P 5.28; N 2.39; B 1.87%.

Methylmorpholinium 2,2,5-Triphenyl-1,3,2,5- dioxaborataphosphorinane (IV). Compound (IV) was obtained analogously to (I). The yield was 58%, mp 108-116°C, δ^{31}P: 4, −33 ppm (DMF). IR spectra (ν, cm^{-1}): 2600 (oil). Found: C 68.85; H 7.36; P. 7.50; N 3.61%. $C_{25}H_{31}PO_2BN$. Calculated: C 68.97; H 7.13; P 7.13; N 3.22%.

Triethylammonium 2,2,5-Triphenyl-4,6-diethyl-1,3,2,5-dioxaborataphosphorinane (V). To a mixture of 1.2 g (11 mmoles) phenylphosphine and 3 ml Et_3N a mixture of 1.3 g (22 mmoles) EtCHO and 2.6 g (11 moles) i-$BuOBPh_2$ was added with water cooling. The reaction mixture was cooled to 20°C. On the next day the precipitate was recrystallized from acetone, yielding 4 g (75%) of (V) with mp 78°C, δ^{31}P: −38 ppm (DMF). IR spectra (ν, cm^{-1}): 2500, 2690 (oil). Found: C 73.37; H 8.90; P 6.25; N 3.28%. $C_{30}H_{43}PO_2BN$. Calculated: C 73.32; H 8.76; P 6.31; N 2.85%.

Triethylammonium 2,2,5-Triphenyl-4,6-dipropyl-1,3,2,5-dioxaborataphosphorinane (VI). Compound (VI) was obtained analogously to (V). The yield was 65%, mp 70°C, δ^{31}P: −34 ppm, (DMF). IR spectra (ν, cm^{-1}) 2500, 2700 (oil). Found: C 73.85; H 8.88; P 5.7; N 26.87%. $C_{31}H_{47}PO_2BN$. Calculated: C 73.99; H 9.06; P 5.97; N 2.70%.

Triethylammonium 2,2,5-Triphenyl-4,6-diisobutyl-1,3,2,5-dioxaborataphosphorinane (VII). This compound was obtained analogously to (V). The yield was 62%, mp 72°C, δ^{31}P: −32 ppm (DMF). IR spectra (ν, cm^{-1}): 2500, 2650 (oil). Found: C 74.08; H 9.14; P 5.98; N 2.66%. $C_{34}H_{51}PO_2BN$. Calculated: C 74.59; H 9.32; P 5.67; N 2.56%.

Triethylammonium 2,2,5-Triphenyl-4,6-di-p-chlorophenyl-1,3,2,5-dioxaborataphosphorinane (VIII). Compound (VIII) was obtained analogously to (V). The yield was 70%, mp 91°C, $\delta^{31}P$: −21, −40 ppm (DMSO). IR spectra (ν, cm^{-1}): 2500, 2700 (oil). Found: C 69.76; H 6.55; P 4.87; N 2.42%. $C_{38}H_{41}PO_2BN$. Calculated: C 69.51; H 6.25; P 4.72; N 2.13%.

Triethylammonium 2,2,5-Triphenyl-4,6-di-o-nitrophenyl-1,3,2,5-dioxaborataphosphorinane (IX). Compound (IX) was obtained analogously to (V). After mixing the reagents, the reaction mixture was dissolved in acetone. To the solution a small amount of sulfuric acid was added. On the next day the yellow crystals were recrystallized from acetone, yielding 40% of (IX) with mp 152°C, $\delta^{31}P$: +18 ppm (acetone). IR spectra (ν, cm^{-1}): 2500, 2650 (oil). Found: C 66.98; H 6.28; P 4.54; N 6.56%. $C_{38}H_{38}PO_6BN_3$. Calculated: C 67.36; H 6.06; P 4.58; N 6.20%.

Complex of α-Diphenylboryloxy-α-p-nitrobenzyl(α-hydroxy-p-nitrobenzyl)phenylphosphine with Triethylamine (X). Conditions of the reaction and method of separation are the same as for (IX). The yield of (X) was 70%, mp 101°C, $\delta^{31}P$: −20 ppm (acetone). IR spectra (ν, cm^{-1}): 3180 (oil). Found: C 67.62; H 6.41; P 4.37; N 6.46%. $C_{38}H_{38}PO_6BN_3$. Calculated: C 67.36; H 6.06; P 4.58; N 6.20%. Compounds (I)-(III) were obtained starting from phenylphosphine under the same conditions as for (V)-(VIII). The constants of the compounds obtained by various methods are identical.

Upon the reaction of bis(α-hydroxy-β,β,β-trichloroethyl)phenylphosphine with i-$BuOBPh_2$ in the presence of pyridine a cystalline product was obtained whose constants correspond to the complex of 2,5-diphenyl-4,6-di(trichloromethyl)-1,3,2,5-dioxaborataphosphorinane with pyridine. The yield was 43%, mp 182°C, $\delta^{31}P$: −30 ppm (pyridine) [6].

CONCLUSIONS

By reaction of bis(α-hydroxyalkyl)phenylphosphines with isobutyl diphenylborinate in the presence of tertiary amines ammonium 2,2,5-triphenyl-4,6-p-1,3,2,5-dioxaborataphosphorinanes were obtained.

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