REACTIONS OF BIS(α-HYDROXYALKYL)PHOSPHINES WITH IMINOBORANES

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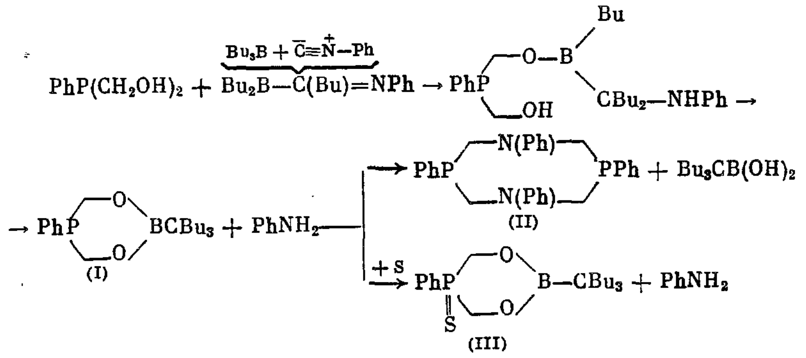
Complexes of trialkylboranes and isonitriles isomerize to give dialkyliminoboranes, which gradually convert to dimers. Heating the dimers to 180°C leads to migration of the second alkyl group from the boron atom to the adjacent carbon atom and the formation of 1,4-diaza-2,5-diborinanes [1]. Alcohols, thiols, and amines catalyze the migration of the second alkyl group and lead to hydroxymethyl(α-aminoalkyl)boranes. Stronger proton donors such as PhOH and HCl lead to migration of the third alkyl group with formation of esters or acid chloride of the corresponding alkylboric acids and aniline [2]. In contrast to proton donors, aromatic aldehydes lead to the loss of alkylboric acids after migration of the second alkyl group and formation of reduction products, namely, 1,3-oxazalidines [3].

α-Hydroxyalkylphosphines are phosphorus-containing alcohols but may act as cryptoaldehydes. In particular, the disproportionation of diphenylboryloxymethyl(hydroxymethyl)phenylphosphine has been described [4]. Thus, we undertook the study of the reactions of these compounds with iminoboranes.

α-Hydroxyalkylphosphines react with tributylborane and phenylisonitrile under mild conditions. The direction of this reaction depends on the substituent at the α-carbon atom of the α-hydroxyalkylphosphine. Bis(hydroxymethyl)phenylphosphine reacts as a proton donor with the migration of a butyl group of the iminoborane to the adjacent carbon atom. However, the reaction does not stop at the formation of boryloxymethyl(hydroxymethyl)phenylphosphine and is accompanied by the migration of the third butyl group. The signal for the starting diol at 20 ppm [5] disappears in the ^{31}P NMR spectra of the reaction mixture and a product signal arises at −40 ppm. This product was identified as 5-phenyl-2-(1',1'-dibutylamyl)-1,3,2,5-dioxaboraphosphorinane (I) on the basis of a comparison with the chemical shifts of signals of model compounds (this shift for 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane is −40 ppm [6]).



Phosphorinane (I) is stable in concentrated solution but reacts upon isolation with aniline present in the reaction mixture with the formation of 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane (II). This is in accord with the literature data on the properties of 1,3,2,5-dioxaboraphosphorinanes [7]. The structure of phosphorinane (I) was supported by its quantitative conversion to sulfide (III) as indicated by ^{31}P NMR spectroscopy.

Phosphorinane (I) is the first reported 1,3,2,5-dioxaboraphosphorinane with a branched alkyl substituent at the boron atom, while the reaction examined is a method for the synthesis of such compounds. The presence of a branched substituent imparts specific properties of (I) and (III). Sulfides and selenides of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinanes readily form complexes with pyridine. On the other hand, (III) dissolves in excess pyridine without change.

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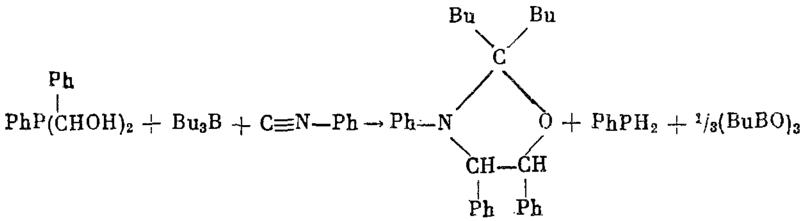
The reaction of bis(α-hydroxybenzyl)phenylphosphine with tributylborane and phenylisonitrile proceeds in a different direction. 2,2-Dibutyl-3,4,5-triphenyl-1,3-oxazalidine (IV) was obtained instead of 4,5,6-triphenyl-2-(1',1'-dibutylamine)-1,3,2,5-dioxaboraphosphirinane, while phenylphosphine was identified in the reaction mixture by ^{31}P NMR spectroscopy. The structure of (IV) was established by PMR and IR spectroscopy; the melting point of this compound corresponds to that given by Hesse et al. [3].



(IV)

The substituted phosphorus-containing diol reacts as a cryptoaldehyde. This is rather unexpected since the reactions of bis(α-hydroxybenzyl)phenylphosphine with boric acid derivatives give 2,4,5,6-tetraphenyl-1,3,2,5-dioxaboraphosphorinane [8] and triethylammonium-2,2,4,5,6-pentaphenyl-1,3,2,5-dioxaborataphosphorinane [9].

Thus, bis(α-hydroxyalkyl)phosphines may react with iminoboranes as either proton donors or cryptoaldehydes. In this case, both hydroxyl groups participate with migration of all the butyl groups to give 1,3,2,5-dioxaboraphosphorinanes with a branched group at the boron atom.

EXPERIMENTAL

Reaction of Bis(α-hydroxymethyl)phenylphosphine with (α-N-Phenyliminoamyl)dibutylborane. A sample of 1.46 ml (14 mmoles) phenylisonitrile in 2 ml ether was added to a solution of 2.52 g (14 mmoles) tributyl borane in 5 ml ether at −70°C. Needle crystals were formed. A solution of 2.38 g (14 mmoles) bis(hydroxymethyl)phenylphosphine in 5 ml THF was added at −70°C. Cooling was terminated and an exothermal reaction took place accompanied by a change in solution color from green to red. Evaporation in vacuum gave (I) with $\delta^{31}P = -40$ ppm and an equimolar amount of aniline (ν 3200 and 3300 cm^{-1}).

a. A yield of 2.22 g (70%) (II) was obtained after dissolving the mixture of (I) and aniline in acetone, $\delta^{31}P = -50$ ppm, mp 190°C [10].

b. A sample of 0.5 g (16 mmoles) sulfur was added to the mixture of (I) and aniline in 20 ml benzene and heated for 3 h. ^{31}P NMR spectroscopy shows replacement of the signal at −40 ppm by a signal at 17 ppm. The product was extracted by petroleum ether (40-70°C). The extract was evaporated and left to crystallize from 1:1 ether–acetone. The yield of 2-(1',1'-dibutylamyl)-5-phenyl-5-thio-1,3,2,5-dioxaboraphosphorinane (III) was 1.1 g (20%), mp 105°C, $\delta^{31}P$ 17 ppm (from acetonitrile). The rate of the integral intensities of the protons in the PMR spectrum $C_6H_5:CH_2:C_4H_9 = 5:4:27$. Found: C 64.06; H 9.25; S 7.90; P 7.00%. Calculated for $C_{21}H_{36}PSO_2B$: C 63.96; H 9.14; S 8.12; P 7.87%.

Reaction of Bis(α-hydroxybenzyl)phenylphosphine with (α-N-Phenyliminoamyl)dibutylborane. A sample of 1.7 ml (16 mmoles) phenylisonitrile was added to a solution of 5.09 g (16 mmoles) bis(α-hydroxybenzyl)phenylphosphine and 2.88 g (16 mmoles) tributylborane in 20 ml THF. At the end of the exothermal reaction, the solvent was evaporated in vacuum to give a yellow tarry residue with $\delta^{31}P = -127$ ppm (phenylphosphine). Crystallization of the residue from ether gave 4.62 g (70%) (IV), mp 99°C [3]. The ratio of the integral intensities in the PMR spectrum: $C_6H_5:CH:C_4H_9 = 15:2:18$.

CONCLUSIONS

Bis(α-hydroxyalkyl)phosphines react with iminoboranes as either proton donors or cryptoaldehydes depending on the substituents at the carbon atom.

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SUBSTITUTION OF THE CHR—O FRAGMENT IN 1,3,2,5-DIOXABORAPHOSPHORINANES

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Due to the presence of a tricoordinated boron atom, boryloxyalkylphosphines are Lewis acids, which indicates an analogy between these compounds and hydroxyalkylphosphines, which have a labile hydrogen atom. Hydroxyalkylphosphines are characterized by exchange of the hydroxyalkyl groups and replacement of these groups by the action of dipolar reagents, proceeding through the intermediate formation of unstable betaines [1]. On the basis of the analogy mentioned above, and the tendency of the tricoordinated boron atom to convert to a tetracoordinated state, we might expect that boryloxyalkylphosphines should form stable betaines and display a tendency to exchange of the boryloxyalkyl groups and to the replacement of these compounds by the action of dipolar reagents.

In previous work [2], we showed that diphenylboryloxymethyl(methyl)phenylphosphine adds formaldehyde and isobutyraldehyde with the formation of crystalline betaines. Upon heating to 150°C these betaines lose the added aldehyde. The reversibility of this reaction indicates exchange of the boryloxyalkyl groups at high temperatures. However, it was not possible to effect replacement of the formaldehyde fragment of diphenylboryloxymethyl(methyl)phenylphosphine (P^{III}—C—OB^{III} system) by isobutyraldehyde by an addition—dissociation mechanism since isobutyraldehyde is lost upon heating. On the other hand, the possibility of such a reaction is indicated by the replacement of the aldehyde fragment upon the action of chloral on diphenylboryloxyalkyl(imidoyl)phenylphosphines [3], chloral and butyraldehyde on 1,3,2,5-dioxaborataphosphoniarinanes [4], and p-nitro-, p-chloro-, and m-bromobenzaldehydes on ammonium-1,3,2,5-dioxaborataphosphorinanes [4] (the P^{III}—C—O—B^{III}—N, P^{IV}—C—O—B^{IV}, and P^{III}—C—O—B^{IV} systems, respectively).

In the present work, we studied the reaction of 4,6-dialkyl-2,5-diphenyl- and 2,4,5,6-tetraphenyl-1,3,2,5-dioxaboraphosphorinanes (the P^{III}—C—O—B^{III} system) with chloral and p-nitrobenzaldehyde at about 20°C in excess aldehyde or acetone. After 1-3 h, the volatile components were removed in vacuum to give crystalline 4,6-di(trichloromethyl)- and 4,6-di-p-nitrophenyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinanes in 60-76% yield after purification. In the case of insufficient aldehyde, the yield is reduced to 38%. A reaction mechanism (following page) is proposed.

Asymmetrically substituted intermediate 1,3,2,5-dioxaboraphosphorinanes were detected in the reaction mixture by ^{31}P NMR spectroscopy when the reaction is carried out in a solvent with 1:1 reagent ratio.

Thus, cyclic boryloxyalkylphosphines replace the aldehyde fragment upon the action of aldehydes by analogy to bis- and tris(hydroxymethyl)phosphines [5, 6].

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