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REACTIONS OF BORYLOXYMETHYL- AND HYDROXYMETHYLPHOSPHINES

WITH AMINES

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Previously it was shown that boryloxymethylphosphines react with primary amines with the formation of aminomethylphosphines. In the reaction of aromatic amines and benzylamine with 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane, 5-(hydroxymethyl)-2,2,5-triphenyl-1,3,2,5dioxaborataphosphoniarinane, and ammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane, the corresponding 1,3,5-diazaphosphorinanes, 1,5,3,7-diazadiphosphacyclooctanes, and bis-(aminomethyl)phosphines are obtained, depending on the reagent ratios [1-3]. The reaction of primary amines and bis(hydroxymethyl) phenylphosphine affords the same compounds [4]. No differences were observed in the reactivity of boroxymethyl- and hydroxymethylphosphines. Even in the case of 5-(hydroxymethyl)-1,3,2,5-dioxaborataphosphoniarinane, where the fourcoordinate boron atom stabilizes the molecule, it was not possible to carry out the reaction only with participation of the hydroxymethyl group.

The number of amines used in [1-4] is rather limited; therefore, we could expect that its expansion with weakly basic amines would make it possible to elucidate the characteristics of the reactions of boryloxymethyl- and hydroxymethylphosphines. For this purpose, we studied the reactions of boryloxy- and hydroxymethylphosphines with diphenylamine and o-, m-, and p-aminobenzoic acids.

In the reaction of diphenylamine with 5-(hydroxymethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinane (I) with reagent ratio 1:1, we recovered a crystalline product not having absorption of hydroxyl groups in the IR spectra and with chemical shift of the P-atom signal in the ³¹P NMR spectrum equal to 5 ppm. The data of elemental analysis indicated that the molecule contained nitrogen atoms and corresponded to 5-(diphenylaminomethyl)-2,2,5triphenyl-1,3,2,5-dioxaborataphosphoniarinane (II)



^{*}Deceased.

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During boiling of (II) in ethanol with an equivalent of diphenylamine, the reaction proceeded further, and bis(diphenylaminomethyl)phenylphosphine (III) was recovered

 $(II) + Ph_2NH \xrightarrow[(Ph_2BOH)]{-H_2O, -CH_2O} PhP(CH_2NPh_2)_2$ (III) (III)

o-Aminobenzoic acid reacts with (I) like diphenylamine, giving 5-(o-carboxyphenylaminomethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinane (IV)



It should be noted that unlike in the case of (II), further amination with substitution of boroxymethyl fragments does not occur in the presence of o-aminobenzoic acid. 2,5-Diphenyl-1,3,2,5-dioxaboraphosphorinane also does not react with o-aminobenzoic acid. Diphenylamine and o-aminobenzoic acid are weak nucleophiles, but the presence of the phosphonium fragment in (I) increases the electrophilicity of the carbon atom of the hydroxymethyl group. At the same time, the carbon atoms of the cyclic fragment in (I) have lower electrophilicity because of the effect of the borate anion, which terminates the reaction in the stage of formation of (II) and (IV).

Under analogous conditions, the reactions of m- and p-aminobenzoic acids do not terminate in the stage of formation of compounds analogous to (IV). 1,5,3,7-Diammoniadiphosphacyclooctanes, consisting of cyclic double betaines (V) and (VI), were recovered in yields close to quantitative. They were also obtained by reverse synthesis from bis(hydroxymethyl)phenylphosphine



Salts (V) and (VI) are high-melting, sparingly soluble crystalline substances having absorption in IR spectra in the region of 2550-2700 cm⁻¹, characteristics of the ammonium cation with N⁺-H bonding, and absorption of the carbonyl group in the region of 1680 cm⁻¹.

With bis(hydroxymethyl)phenylphosphine, o-aminobenzoic acid does not give 1,5,3,7-diammoniadiphosphacyclooctane even with prolonged boiling in ethanol with reagent ratio 1:1. Instead of it, bis(o-carobxyphenylaminomethyl)phenylphosphine (VII) is formed, which has a chemical shift of the P-atom signal in the ³¹P NMR spectrum of -33 ppm (cf. bis(anilinomethyl)phenylphosphine [4]) and absorption in the IR spectra at 3370 cm⁻¹, corresponding to the N-H group. The impossibility of formation of 1,5,3,7-diammoniadiphosphacyclooctane from o-aminobenzoic acid is probably explained either by steric hindrances or by strong hydrogen bonds in the ortho arrangement of the carboxyl and amino groups

$$\frac{PhP(CH_2OH)_2 + 2 o-H_2NC_6H_4COOH}{-2H_4O} \xrightarrow{PhP(CH_2NHC_6H_4COOH-o)_2} (VII)$$

The reaction of o-aminobenzoic acid with tris(hydroxymethyl)phosphine and tetrakis-(hydroxymethyl)phosphonium chloride occurs with quantitative yields, giving tris(o-carboxyphenylaminomethyl)phosphine (VIII) and tetrakis(o-carboxyphenylaminomethyl)phosphonium chloride (IX), respectively

 $P(CH_2OH)_3 + 3 \text{ o-}H_2NC_6H_4COOH \xrightarrow[-3H_2O]{} P(CH_2NHC_6H_4COOH-o)_3$ (VIII)

$\dot{P}(CH_2OH)_4C\bar{I} + 4 \ o-H_2NC_6H_4COOH \xrightarrow{-4H_4O} \dot{P}(CH_2NHC_6H_4COOH-o)_4C\bar{I}$ (IX)

The reaction occurs identically facilely both in the case of the phosphine and in the case of the phosphonium salt. Thus, the use of weakly basic amines makes it possible to observe a difference in the reactivity of the P-C-O-H and P-C-O-B fragments in boryloxy-methyl- and hydroxymethylphosphines.

EXPERIMENTAL

The synthesis of (I) is given in [5].

<u>Bis(diphenylaminomethyl)phenylphosphine (III)</u>. To 1 g of (II) in 20 ml of ethanol was added 0.5 g of diphenylamine. The mixture was kept at 40°C for 4 days. The precipitated crystals were filtered and washed with ethanol. The yield of (III) was 0.4 g (49%), mp 130-132°C. Phosphorus-31 NMR spectrum (δ , ppm): -34 (DMF). Found, %: C 81.03; H 6.60; P 6.97; N 6.12. C₃₂H₃₃PN₂. Calculated, %: C 80.67; H 6.93; P 6.51; N 5.88.

 $\frac{1,5-\text{Bis}(p-\text{carboxypheny1})-3,7-\text{dipheny1}-1,5,3,7-\text{diammoniadiphosphacyclooctane (VI)}{\text{Compound was obtained similarly to (V)}}.$ The yield of (VI) was 79%, mp 250°C, IR spectrum (v, cm⁻¹): 1680 (C=O), 2550, 2700 (H-N). Found, %: C 66.10; H 5.15; P 11.29; N 5.44.

Synthesis of (V) from Bis(hydroxymethyl)phenylphosphine. To 17 g (0.1 mole) of bis-(hydroxymethyl)phenylphosphine in 50 ml of ethanol was added 13.7 g (0.1 mole) of m-aminobenzoic acid. The mixture was boiled for 2 h with a reflux condenser, and the precipitate was filtered. The yield of (V) was 22.4 g (89%). The constants of (V) agreed with those given above.

Compound (VI) was obtained similarly from bis(hydroxymethyl)phenylphosphine. The yield was 90%.

<u>Bis(o-carboxyphenylaminomethyl)phenylphosphine (VII)</u>. To 8.5 g (0.05 mole) of bis-(hydroxymethyl)phenylphosphine was added 13.7 g (0.1 mole) of o-aminobenzoic acid. Release of water and heating of the reaction mixture were observed. The precipitate was filtered and washed with ethanol. The yield of (VII) was 17.3 g (85%), mp 178-180°C. Phosphorus-31 NMR spectrum (δ , ppm): -33 (DMF). Found, %: C 64.38; H 5.02; P 8.13; N 6.68. C₂₂H₂₁-PO₂N₂. Calculated, %: C 64.71; H 5.15; P 7.60; N 6.86.

 $\frac{\text{Tris}(\text{o-carboxyphenylaminomethyl})\text{phosphine (VIII)}}{\text{from tris}(\text{hydroxymethyl})\text{phosphine. The yield was 83%, mp 226°C. Phosphorus-31 NMR spectrum (δ, ppm): -35 (DMF), IR spectrum ($\u03c6$, cm^{-1}): 1680 (C=0), 23,370 (N-H). Found, %: C 59.69; H 4.90; P 6.54; N 8.56. C_{24}H_{24}PO_6N_3. Calculated, %: C 59.88; H 4.99; P 6.44; N 8.73.}$

 $\underline{\text{Tetrakis}(\text{o-carboxyphenylaminomethyl})\text{phosphonium Chloride (IX)}}_{\text{tained similarly to (VII) from tetrakis(hydroxymethyl)phosphonium chloride. The yield of (IX) was 97%, mp >300°C. Phosphorus-31 NMR spectrum (<math>\delta$, ppm): 25 (DMF). Found, %: C 57.50; H 5.11; P 4.43; N 8.66. $C_{32}H_{32}PO_8N_4C1$. Calculated, %: C 57.61; H 4.80; P 4.65; N 8.40.

CONCLUSIONS

5-(Hydroxymethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinane reacts with diphenylamine and o-aminobenzoic acid with the formation of 5-(aminomethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinanes, whereas 1,5,3,7-diammoniadiphosphacyclooctanes are formed with m- and p-aminobenzoic acids. With o-aminobenzoic acid, hydroxymethylphosphines and hydroxymethylphosphonium salts give the corresponding aminomethylphosphines and aminomethylphosphonium salts.

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ISOPRENYLATION OF CARBONYL COMPOUNDS, ESTERS, AND ALKOXYACETYLENES WITH 2-DIPROPYLBORYLMETHYL-1,3-BUTADIENE AND THE SYNTHESIS OF IPSENOL AND IPSDIENOL

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Allyl derivatives of boron are used extensively for obtaining, modifying, and functionalizing different classes of organic compounds [1]. In their properties, chemical activity, and uses, these compounds differ significantly from other organoboranes; this is due to their ability to react with allyl rearrangement [1]. The properties of allyl (I, R = H), methallyl (I, R = Me), crotyl (II, R = H), and prenyl (II, R = Me) organoboranes [1, 2], as well as several 3-substituted organoboranes (III) (RX = RO, RS, R_3Si) [3], have been studied in detail.



The present communication presents the synthesis of the first representative of a new type of allylborane - 2-dipropylborylmethyl-1,3-butadiene (IV) - and its use in the isoprenylation of carbonyl compounds, esters, and alkoxyacetylenes.*

Reagent (IV) was obtained in a yield of 75-80% by the reaction of 2-bromomethyl-1,3butadiene, alkoxydipropylborane, and aluminum activated with mercuric chloride in a small amount of ether.

*For previous communication, see [4].

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