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BORYLATION OF α-HYDROXYALKYLPHOSPHINE OXIDES IN THE PRESENCE OF STRONG BASES

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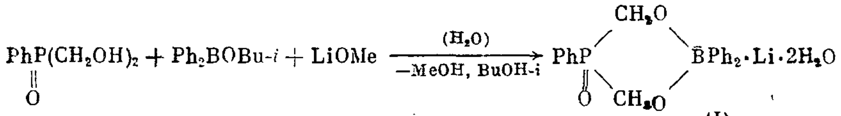
Lithium (sodium) 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinanes, forming crystals with two molecules of water, are produced when bis(hydroxymethyl)phenylphosphine oxide is reacted with isobutyl diphenylborate in the presence of metallic sodium or lithium (sodium) alcoholate.

The reaction of bis(α-hydroxyalkyl)phosphine oxides (sulfides) with isobutyl diphenylborate has been accomplished only in the presence of amines [1-3]. It was therefore suggested that amines act catalytically in the borylation reaction of α-hydroxyalkyl derivatives of tetracoordinated phosphorus. The catalytic action of organic bases was demonstrated using the example of primary, secondary, tertiary, functionally substituted amines and ammonia [4]. Amines subsequently undergo reaction with the borylation product, giving the corresponding ammonium oxaborataphosphorinanes.

In the present work, alkali metal alcoholates were used as the reagents catalyzing the borylation of α-hydroxyalkyl derivatives of tetracoordinated phosphorus.

The reaction of bis(hydroxymethyl)phenylphosphine oxide with i-BuOBPh$_2$ in the presence of LiOMe in acetone proceeds at ~20°C, leading to the formation of lithium 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane (I) in 67% yield. It should be emphasized that bis(hydroxymethyl)phenylphosphine oxide does not react with boric ester in the presence of an alcoholate of amine, even on heating. Since the reactions were not carried out in anhydrous solvents, and the reaction mixtures were processed without protection from atmospheric moisture, compound (I) and also (II)-(IV) described below crystallize with two molecules of water.



(I)

The structure of (I) was confirmed by IR and PMR spectroscopy. There are signals in the PMR spectra of the phenyl and methylene protons only, and also signals of protons of water, with the integral intensity of all the signals corresponding to the ascribed structure. In the IR spectra, absorption of the water of crystallization is observed in the region of 1600-1700 cm^{-1}, while the absorption of hydroxyl (3100-3600 cm^{-1}) and B^{III}O (1300-1350 cm^{-1}) groups is absent. The ^{31}P NMR spectra also conform with structure (I).

In this reaction, not only an alcoholate can be used, but also for example metallic Na or NaOH. Thus a Na-salt of boratophosphorinane (II) is formed.

Boratophosphorinane (II) was also obtained by the action of MeONa in acetone on dipropylammonium 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane, which confirms the structure of (II)

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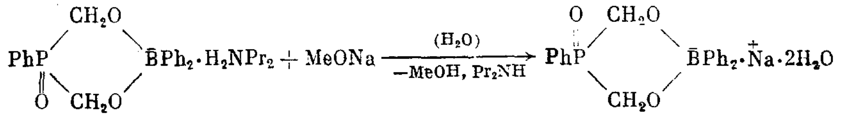
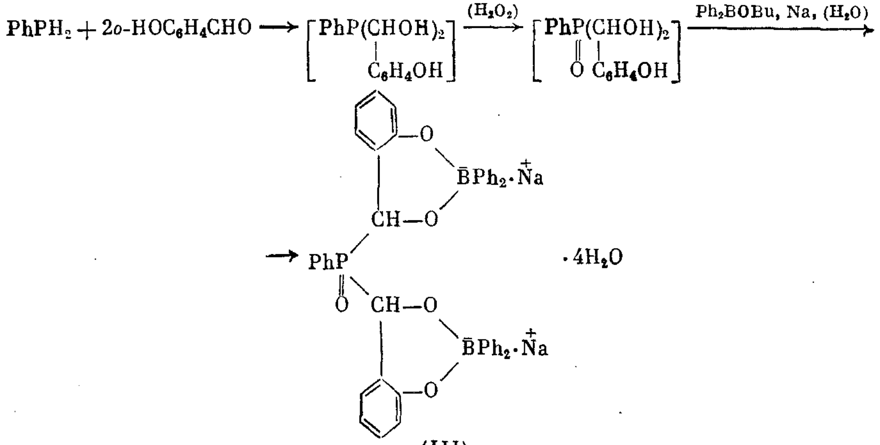


(II)

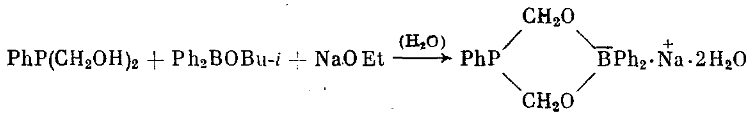
Compound (II) has spectral parameters similar to those of (I). The borylation of bis(α-hydroxyalkyl)phosphine oxides in the presence of strong bases was used to prepare the diborylated double salt (III). A diborylated product obtained from phenylphosphine and salicylaldehyde was described by us in [5].



(III)

The ratio of the phenyl and phenylene, methine protons and the water protons in the PMR spectra, is (25 + 8):2:8. In the IR spectra there is no absorption of the hydroxyl groups. Compounds (I)-(III) are white crystalline substances, mp > 300°C, which are sparingly soluble in organic solvents.

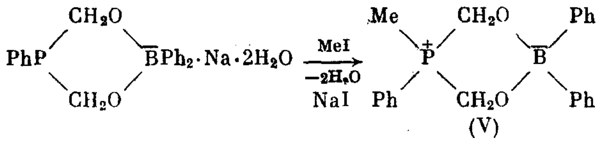
In the case of bis(hydroxymethyl)phenylphosphine, the borylation reactions proceed in the presence of sodium alcoholate, similarly to the case of bis(hydroxymethyl)phenylphosphine oxide, giving sodium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane (IV)



(IV)

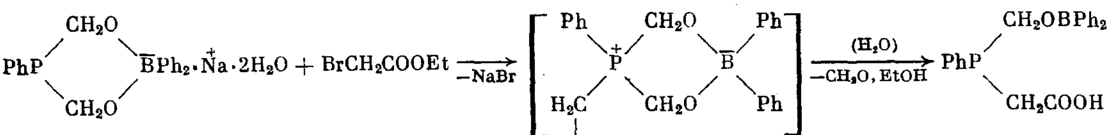
Compound (IV) shows a chemical shift of −30 ppm (DMF) in the ^{31}P NMR spectra, characteristic for cyclic phosphines with a tricoordinated phosphorus atom. The PMR and IR spectra confirm the structure of (IV).

It was shown in [6] that reactions with electrophilic reagents are characteristic for ammonium 1,3,2,5-dioxaborataphosphorinane in particular, with alkyl halides, this being due to the presence of an ammonium cation, which binds the halide anion. Compound (IV) reacts with MeI in a similar way.



(V)

The presence of functional groups in the electrophilic reagent may lead to further transformations. Thus, the presence of water in the composition of the molecule of (IV), and also the possibility of the occurrence of an acid–base hydrolysis of the ester fragment results in the formation of diphenylboryloxymethyl(α-carboxyethyl)phenylphosphine (VI) in the reaction of (IV) with ethyl bromoacetate



(VI)

In the IR spectra of (VI) in the solid state, the absorption of the C=O and O=H groups is observed (1730 cm^{-1}, 3230 cm^{-1}). The PMR spectra show a symmetric doublet of the $-CH_2-OB<$ fragment (δ 4.18 ppm, $^2J_{PH}$ = 4 Hz) and a multiplet of the $-CH_2COO-$ fragment (δ 4.81 ppm), and the ratio of the phenyl, methylene (CH_2OB) and methylene (CH_2COO) protons is equal to 15:2:2 while the ethyl group signals are absent.

EXPERIMENTAL

The PMR spectra were recorded on a Varian T-60 spectrometer (60 MHz) at 34.5°C, using TMS as internal standard and DMF-d_7 as a solvent; the ^{31}P NMR spectra were run on a KGU-4 NMR spectrometer (10.2 MHz with a noise uncoupling from protons at a frequency of 25.2 MHz), and the IR spectra on the UR-20 spectrophotometer in mineral oil.

Lithium 2,2,5-Triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane (I). A 2 g portion (11 mmoles) of bis(hydroxymethyl)phenylphosphine oxide and 2.56 g (11 mmoles) of i-$BuOBPh_2$ were added to dry MeOLi, obtained from 0.07 g (11 mmoles) of lithium and MeOH, in 30 ml of acetone. The alcoholate and bis(hydroxymethyl)phenylphosphine oxide dissolved. On the following day, the crystals that separated out were filtered off and washed with acetone. The yield of (I) was 2.8 g (67%), mp > 340°C, δ ^{31}P + 30 ppm (DMF), the ratio of the integral intensities of protons in the PMR spectra ws $C_6H_4:CH_2:H_2O$ = 15:4:4. Found: C 61.53; H 6.00; P 7.47; B 2.57; Li 1.63%. $C_{20}H_{23}PBO_5Li$. Calculated: C 61.22; H 5.86; P 7.90; B 2.80; Li 1.78%.

Sodium 2,2,5-Triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane (II). A 0.22 g portion (10 mmoles) of sodium was added to 1.8 g (10 mmoles) of bis(hydroxymethyl)phenylphosphine oxide in 40 ml of acetone. On the following day, i-$BuOBPh_2$ was added to the solution obtained and crystallization took place. The precipitate was filtered off and wshed with acetone. The yield of (II) was 3.6 g (91%), mp > 300°C, δ ^{31}P +30 ppm (DMF), the ratio of the integral intensities of protons in the PMR spectra was $C_6H_5:CH_2:H_2O$ = 15:4:4. Found: C 58.48; H 5.57; P 7.39; B 2.61; Na 5.48%. $C_{20}H_{19}PBO_3Na \cdot 2H_2O$. Calculated: C 58.92; H 5.64; P 7.60; B 2.61; Na 5.64%.

Reaction of Dipropylammonium 2,2,5-Triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane with Sodium Methylate. An 80 ml portion of acetone and 2.26 g (5 mmoles) of ammonium dioxaborataphosphorinane [4] was added to dry MeONa, obtained from 0.115 g (5 mmoles) of sodium and MeOH. The mixture was heated to the dissolution of the compounds, the warm solution was filtered, and crystals of (II) separated out from the filtrate on cooling; yield 0.3 g (15%), mp > 300°C, δ ^{31}P +30 ppm (DMF), IR spectrum – the absorption of the $H-\overset{+}{N}$ group is absent.

Bis(sodium 2,2-diphenyl-5,6-phenylene-1,3,2-dioxaboratarinyl-4)phenylphosphine Oxide (III). An 8.2 g portion (68 mmoles) of salicylaldehyde was added in an argon atmosphere to 3.7 g (34 mmoles) of phenyl phosphine. After 1 h, 50 ml of acetone was added to the mixture obtained, and after cooling to 10°C, a solution of H_2O_2 in acetone (a slight excess) was added to the above solution. After 3 h, the mixture was evacuated at 0.01 mm at 40-50°C for 1 h. The residue, a viscous, vitreous mass (δ ^{31}P +44 ppm), was dissolved in acetone. A 1.54 g portion (68 mmoles) of sodium was added to this solution, and then 16 g (68 mmoles) of i-$BuOBPh_2$ was added. Sodium rapidly dissolved with evolution of heat. An hour after the end of the reaction, diethyl ether was added to the mixture. The crystals that separated out were filtered off and washed with diethyl ether. The yield of (III) was 17 g (62%), mp > 300°C. The ratio of the integral intensities of protons in the PMR spectra was (C_6H_5 + C_6H_4):CH:H_2O = (25 + 8):2:8. In the IR spectra the absorption of the hydroxyl groups in the 3100-3600 cm^{-1} region was absent. Found: C 64.53; H 5.16; P 3.60%. $C_{44}H_{35}PBO_5Na \cdot 4H_2O$. Calculated: C 64.86; H 5.28; P 3.81%.

Sodium 2,2,5-Triphenyl-1,3,2,5-dioxaborataphosphorinane (IV). A 6 g portion (35 mmoles) of bis(hydroxymethyl)phenylphosphine and 8.4 g (35 mmoles) of i-$BuOBPH_2$ were added to dry EtONa, obtained from 0.81 g (35 mmoles) of sodium and EtOH, in 30 ml of acetone. After 3 h, the solvent was partially removed under vacuum, and crystals separated out, which were filtered off and crystallized from acetone. The yield of compound (IV) was 9.7 g (70%), mp 168°C, δ ^{31}P −34 ppm (DMF). The ratio of the integral intensities of protons in the PMR spectra was $C_6H_4:CH_2:H_2O$ = 15:4:4. In the IR spectra the absorption of the hydroxyl groups in the 3100-3600 cm^{-1} region was absent. Found: C 60.84; H 5.65; P 7.50%; $C_{20}H_{19}PBO_2Na \cdot 2H_2O$. Calculated: C 61.22; H 5.87; P 7.91%.

5-methyl-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinane (V). A 3ml portion of MeF was added to 1.3 g of (IV) in 30 ml of acetone. Compound (IV) dissolved and a precipitate separated out, which was recrystallized from acetone. The yield of (V) was 0.5 g (43%), mp 151°C, δ ^{31}P +1 ppm (pyridine), cf. [6].

Diphenylboryloxymethyl(α-carboxyethyl)phenylphosphine (VI). A 0.93 g portion (5.6 mmoles) of $BrCH_2COOEt$ was added to 2 g (5.6 mmoles) of (IV) in 30 ml of acetone. The reaction was accompanied by a slight evolution of heat. After 3 h, the crystals were filtered off. The yield of (VI) was 1.3 g (65%), mp 104°C. PMR spectrum: δ 4.18 ppm, $^2J_{PH}$ = 4 Hz $(CH_2{-}OB\langle)$, a multiplet with a maximum at δ 4.81 ppm (CH_2COO). The ratio of the integral intensities of protons in the PMR spectra was $C_6H_5:CH_2:CH_2 = 15:2:2$. The absorption of the C=O (1730 cm^{-1}) and hydroxyl groups (O–H, 3230 cm^{-1}) was observed in the IR spectra of the crystals. Found: C 69.38; H 5.81; P 8.58%. $C_{21}H_{20}PBO_3$. Calculated: C 69.61; H 5.52; P 8.56%.

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REACTIONS OF PHOSPHORYLATED ALLENES WITH DITHIOCARBAMATES

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The addition of morpholino-, piperidino-, and N,N-diethyldithiocarbamate anions to 1,2-propadiene- and 1,2-butadienephosphonates proceeds on the electrophilic 1,2-double bond of the allene system with the formation of linear dithioesters. 1-Vinylallenylphosphonates add dithiocarbamate anions on the 1,3-conjugated system of multiple bonds, forming a mixture of stereoisomeric dithioesters with a diene structure.

The reaction between dithioate anions with unsaturated electrophilic systems can proceed in two ways: by an anionic [3 + 2]-cycloaddition [1-3] and by Michael-type reactions with the formation of acyclic compounds [3-5]. The nature of the multiple bond activation of the unsaturated substrate and that of the radical attached to the central atom of the 1,3-dithiaallylic system has a decisive effect on the structure of the products that form. The reactions of the derivative dithiocarboxylic and dithiocarbamic acids with compounds containing cumulative multiple bonds have hardly been studied. Only the reaction of methyl and allyl esters of dithiobenzoic acid with diphenylketene is described. This reaction proceeds by [2 + 2]-cycloaddition with the formation of 4-alkylthio-2-thietanes [6]. There is evidence [7] that it is not possible for heterocumulenes like phenyl isocyanate, phenyl isothiocyanate, and phenyl ketene to add some dithioate anions on the double bond. We have established that the addition of the dithiobenzoate anion to esters of allenylphosphonic acids follows a nucleophilic pattern with the formation of products with a linear structure [8, 9]. In this work we carry this research further, studying the reaction of phosphorylallenes

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