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SYNTHESIS AND SEVERAL PROPERTIES OF 1,3,2,5-DIOXABORAPHOSPHORINANES WITH A BRANCHED SUBSTITUENT AT THE BORON ATOM

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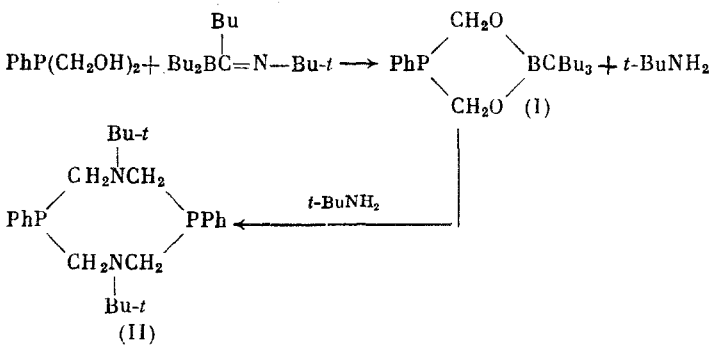
UDC 542.91:547.1'127'118

Bis(α-hydroxyalkyl)phenylphosphines react with α-iminoboranes in protic solvents such as dihydric alcohols to give 2-(1',1'-dibutylamyl)-4,6-di-R-5-phenyl-1,3,2,5-dioxaboraphosphorinanes, which react with CuI in pyridine to form [LCuI(Py)] complexes. PMR spectroscopy showed that the phosphorus-containing ligands exist as a single stereoisomer.

In previous work [1], we showed that bis(α-hydroxyalkyl)phosphines react with iminoboranes either as cryptoaldehydes or as proton donors. In the latter case, both hydroxyl groups participate in the reaction and all the butyl groups migrate, resulting in the formation of 1,3,2,5-dioxaboraphosphorinanes with a branched substituent at the boron atom, which were isolated as sulfides [1]. Not only the substituents at the carbon atoms of the α-hydroxyalkylphosphines but also the temperature and solvent may affect the course of the reaction.

The reaction of bis(hydroxymethyl)phenylphosphine with the α-iminoborane obtained in situ from tert-butyl isocyanide and tributylborane led to the formation of 2-(1',1'-dibutylamyl)-5-phenyl-1,3,2,5-dioxaboraphosphorinane (I), which gave rise to a signal at −40 ppm in the ^{31}P NMR spectrum [1]. However, (I) could not be isolated since dioxaboraphosphorinane may react with tert-butylamine formed during the reaction. Furthermore, tert-butylamine may aminate the starting reagent, bis(hydroxymethyl)phenylphosphine, to give 1,5-diaza-3,7-diphosphacyclooctane (II).



Products (I) and (II) are viscous, nondistilling liquids with ^{31}P NMR chemical shifts of −40 and −30 ppm, respectively [1]. Product (II) was obtained by convergent synthesis and

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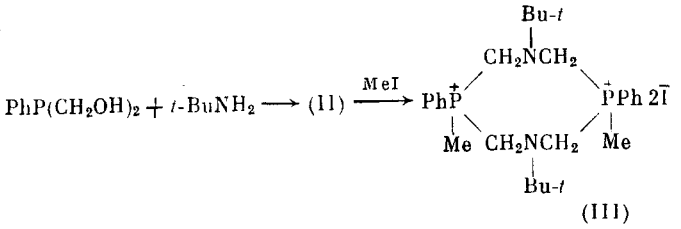
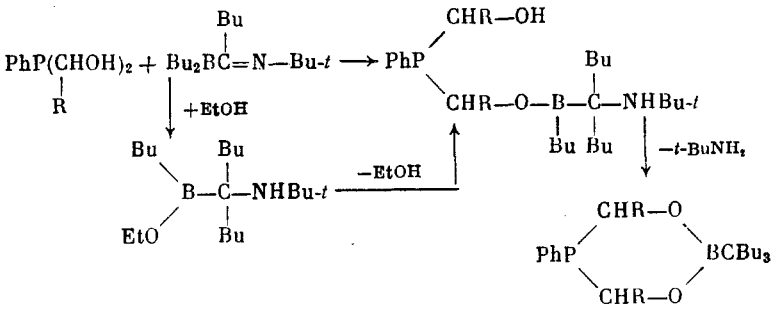
isolated as the bis(iodomethylate) (III), whose structure is analogous to the structure of the compounds presented in our earlier work [2].



(III)

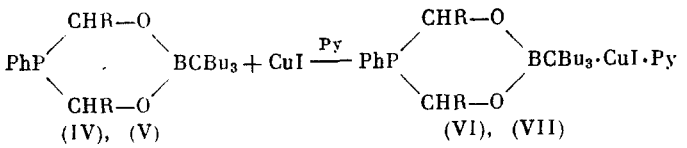
In order to stop the reaction at the step involving formation of 1,3,2,5-dioxaboraphosphorinanes and avoid amination, the mixing of bis(α-hydroxyalkyl)phenylphosphines and the iminoborane was carried out at −78°C. The temperature was gradually raised to 20°C. In order to remove the tert-butylamine formed during the reaction, the reaction was carried out at reduced pressure. Bis(α-hydroxyalkyl)phenylphosphines in solution are capable of dissociation with the formation of aldehydes [3]. In order to avoid formation of oxazolidines due to the reaction of the aldehyde and iminoborane, the reactions were carried out in ethanol. Iminoboranes react with proton donors, in particular, with alcohols, to form α-aminoalkylborate esters with migration of the second alkyl group from the boron atom. The reaction of α-aminoalkylborate esters with aldehydes has not been described. The reaction with aliphatic alcohols stops at this step and the third alkyl group does not migrate. However, in the case of α-hydroxyalkylphosphines, the reaction proceeds further.



(IV), (V)

Vacuum distillation of the reaction mixture (R = Me) gave 4,6-dimethyl-2-(1′,1′-dibutylamyl)-5-phenyl-1,3,2,5-dioxaboraphosphorinane (IV) in 30% yield with bp 140-150°C (0.02 mm). The ^{31}P NMR spectra of (IV) show signals at −27, −28, and −32 ppm, which virtually coincide with the chemical shifts for 4,6-dimethyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (−25, −28, and −32 ppm) [4] and correspond to three stereoisomers. Comparison of the intensity of the signals taking account of the assignments for 4,6-dimethyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane shows that the content of the stereoisomer of (IV) with an equatorial phenyl group at the phosphorus atom ($\delta^{31}P$ = −32 ppm) is greater than for 4,6-dimethyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [4]. Phosphorinane (IV) distills as an equilibrium mixture of stereoisomers, whose ratio in the reaction mixture remains unchanged upon distillation [4]. The ratio of the integral intensities of the C_6H_5:CH:(CH_3 + C_4H_9) groups in the PMR spectra is 5:2:33. The signals of the methine protons give a multiplet, corresponding to a mixture of stereoisomers. Product (V) decomposes upon distillation. The ^{31}P NMR spectra of the reaction mixture show signals at −14, −17, and −25 ppm, which is also similar to the chemical shifts observed for 2,4,5,6-tetraphenyl-1,3,2,5-dioxaboraphosphorinane (−13, −18, and −25 ppm) [4].

In order to identify (IV) and (V) in the crystalline state, their complexes with cuprous iodide were obtained.



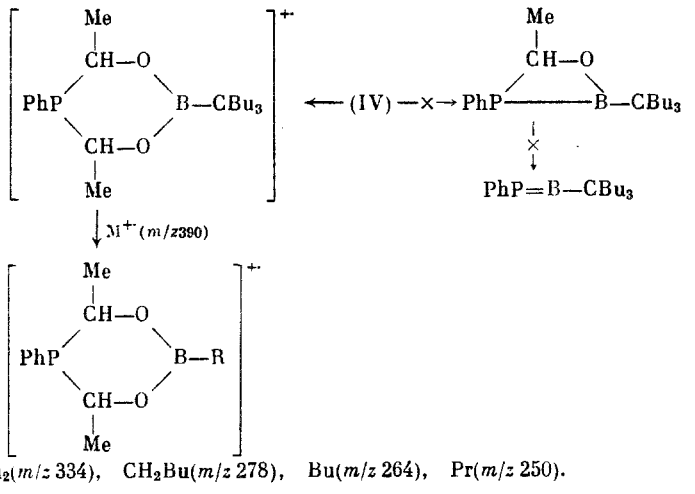
(IV), (V) (VI), (VII)

Complexes (VI) and (VII) are white, crystalline compounds, which give quantitative tests for iodide and cuprous ions. The ligand/metal ratio was established by elemental analysis.

The PMR data indicate that the heterocyclic fragments in (VI) and (VII) are in one predominant conformation. Thus, the PMR spectra of (VI) in $CDCl_3$ shows a symmetrical doublet of quartets with $^2J_{PH}$ close to 0 Hz, which indicates R*S* configuration of the heterocyclic carbon atoms. In other words, the heterocyclic fragment exists in a chair conformation with two equatorial methyl groups at the carbon atoms. The small coupling constant corresponds to an equatorial phenyl group at the phosphorus atom [5]. The PMR spectra of (VII) in $CDCl_3$ show two groups of signals for protons of the CH groups of the heterocycle. The ratio of the integral intensities of these groups is 1:1. These signals appear as a singlet ($^2J_{PH}$ = 0 Hz) and doublet ($^2J_{PH}$ = 9 Hz). All these findings indicate R*,R* configuration of the heterocyclic carbon atoms and, thus, an asymmetrical conformation of the heterocycle [5].

In earlier work [6], we showed that the stereoisomer with an axial phenyl group at the phosphorus atom is the most stable form for 1,3,2,5-dioxaboraphosphorinanes and their derivatives. The data on the three-dimensional structure of the 1,3,2,5-dioxaboraphosphorinane fragment in (VI) and (VII) show that CuI forms complexes with the less stable forms, namely, stereoisomers with an equatorial phenyl group at the phosphorus atom and the stereoisomer in an asymmetrical conformation.

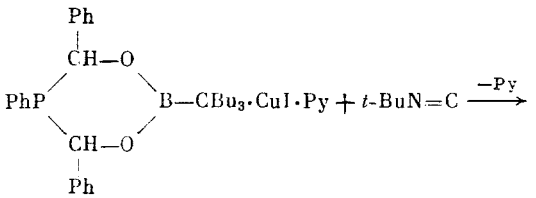
The fragments between the phosphorus and boron atoms in boryloxyalkylphosphines are found to have high lability. In particular, elimination by excess high-boiling aldehyde proceeds readily [7]. Dissociative ionization upon electron impact (EI) and thermal decomposition of diphenylboryloxyalkyl(acetimidoyl)phenylphosphine are accompanied by the loss of an aldehyde or nitrile molecule [8]. On the other hand, it is well known that substituents capable of shielding stabilize compounds with low coordination such as compounds with a -P=B- fragment. Thus, we may expect that upon EI, the heterocyclic fragment of (IV) will decompose with the loss of an aldehyde to form fragmentation ions with dicoordinated phosphorus and boron atoms. However, the mass spectrum of (IV) displays a molecular ion peak ($M^{+\cdot}$) and the fragmentation ions formed upon its decomposition; largely those related to decomposition of the 1′,1′-dibutylamyl group at the boron atom. This probably results from the good shielding provided by the branched substituent:

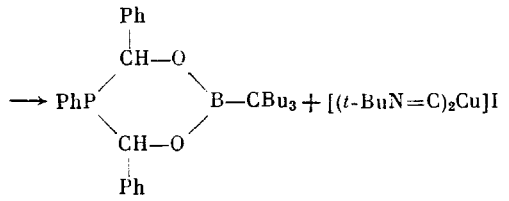


R = $CHBu_2$(*m/z* 334), CH_2Bu(*m/z* 278), Bu(*m/z* 264), Pr(*m/z* 250).

The formation of the cuprous iodide complex does not have a significant effect on the pathways for decomposition of the heterocyclic fragment in (VI) upon EI.

Isonitriles form strong ionic complexes with CuI with poor solubility in organic solvents. This permitted us to separate (V) as a pure stereoisomer from (VII) upon its treatment with tert-butyl isonitrile.





The ^{31}P NMR spectrum of a solution of the pure stereoisomer of (V) shows a single signal at −15 ppm, while its PMR spectrum has two equally intense doublets for CH protons of the heterocycle with $^{2}J_{PH}$ = 5 and 14 Hz. This finding indicates different orientation of the protons of the heterocyclic fragment and, thus, an asymmetrical conformation of the heterocycle. This conformation is identical to the conformation of the heterocycle in complex (VII).

EXPERIMENTAL

The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz at 34.5°C with TMS as the internal standard. The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz with noise proton decoupling at 25.2 MHz. The IR spectra were taken on a UR-20 spectrometer.

The electron impact mass spectra were taken on an MKh-1310 mass spectrometer connected to an SM-4 computer. The exact mass values were determined automatically relative to perfluorokerosene reference peaks. The relative error in determination of the ions masses was $5 \cdot 10^{-6}$ a.m.u. The energy of the ionizing electrons was 50 eV. The emission current was 30 μA. The temperature of the inlet system was 50°C.

1,5-Di(tert-butyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (II). A sample of 3.4 g (0.02 mole) bis(hydroxymethyl)phenylphosphine was added to a solution of 3.64 g (0.02 mole) tributylborane and 1.66 g (0.02 mole) tert-butyl isocyanide in 30 ml THF at −78°C. The reaction mixture was slowly brought to 20°C. The solvent was removed in vacuum. The ^{31}P NMR spectra shows signals at −31 and −40 ppm, corresponding to (II) and 2-(1′,1′-dibutylamyl)-5-phenyl-1,3,2,5-dioxaboraphosphorinane (I) [1]. Upon heating the mixture in acetone, (I) is quantitatively converted to (II) as monitored by ^{31}P NMR spectroscopy, $\delta^{31}P$ = −31 ppm.

A sample of 1.39 g (0.019 mole) tert-butylamine was added to 3.25 g (0.019 mole) bis(hydroxymethyl)phenylphosphine in 30 ml ethanol. At the end of the exothermal reaction, the solvent was removed in vacuum to give (II) in ~100% yield as a viscous, nondistilling liquid, $\delta^{31}P$ = −31 ppm. Found: P, 15.03%. Calculated for $C_{24}H_{36}N_2P_2$: P, 14.98%.

1,5-Di(tert-butyl)-3,7-dimethyl-3,7-diphenyl-1,5-diaza-3,7-diphosphoniocyclooctane diiodide (III). An excess of methyl iodide was added to a solution of 1.57 g (0.004 mole) (II) in ether. Crystallization was observed at the end of the exothermal reaction. The crystals were filtered off and washed with acetone to give 1.77 g (70%) (III), $\delta^{31}P$ 22 ppm (DMSO), mp 175°C. Found: C, 44.07; H, 6.05; N, 4.12; P, 8.87%. Calculated for $C_{26}H_{42}I_2N_2P_2$: C, 44.69; H, 6.02; N, 4.01; P, 8.88%.

2-(1′,1′-Dibutylamyl)-4,6-dimethyl-5-phenyl-1,3,2,5-dioxaboraphosphorinane (IV). A sample of 2.55 g (0.03 mole) tert-butyl isocyanide was added to a solution of 5.6 g (0.03 mole) tributylborane in 10 ml absolute ethanol at −78°C. Then, a solution of 6.09 g (0.03 mole) bis(α-hydroxyethyl)phenylphosphine was added at this temperature. The temperature was raised to ~20°C at about 15 mm Hg. The solvent was removed in vacuum. Distillation gave 4 g (30%) (IV), bp 146-151°C (0.025 mm Hg), $\delta^{31}P$, ppm (intensity): −27 (1.4), −28 (1), −32 (1). The C_6H_5:CH:(CH_3 + C_4H_9) intensity ratio in the PMR spectra is 5:2:33 ($CDCl_3$). Electron impact mass spectrum (relative intensity, %): 391 (3.1), 390 (13.44), 389 (2.92) $C_{23}H_{40}PO_2B$; 335 (1.69), 334 (6.54), 333 (2.76) $C_{19}H_{32}BO_2P$; 279 (0.82), 278 (3.19), 277 (1.71) $C_{15}H_{24}BO_2P$; 265 (1.71), 264 (12.24), 263 (5.11) $C_{14}H_{22}BO_2P$; 251 (1.66), 250 (6.57), 249 (4.00) $C_{13}H_{20}BO_2P$; 223 (1.83), 222 (6.82), 221 (4.07) $C_{11}H_{16}BO_2P$; 208 (6.99), 207 (6.87), 206 (1.35) $C_{10}H_{13}BO_2P$; 136 (100) C_8H_9P; 108 (77.3) C_6H_5P; 77 (9.55) C_6H_5; 57 (19.7) C_4H_9. Found: C, 69.69; H, 10.56; P, 8.02%. Calculated for $C_{23}H_{40}BO_2P$: C, 70.77; H, 10.25; P, 7.95%.

2-(1′,1′-Dibutylamyl)-4,5,6-triphenyl-1,3,2,5-dioxaboraphosphorinane (V). A sample of 1.74 g (0.021 mole) tert-butyl isocyanide and a solution of 6.73 g (0.021 mole) bis(α-hydroxybenzyl)phenylphosphine in 10 ml THF were added to a solution of 3.81 g (0.021 mole) tributylborane in 30 ml THF and 5 ml absolute ethanol at −78°C. The temperature was raised to about

20°C at ~15 mm Hg. The solvents were removed in vacuum to give (V) in quantitative yield as a colorless, nondistilling liquid, $\delta^{31}P$ = −14, −17, and −25 ppm. The intensity ratio was 2.6:1:4.

[{2-(1′,1′-Dibutylamyl)-4,6-dimethyl-5-phenyl-1,3,2,5-dioxaboraphosphorinane}pyridine Cuprous Iodide] (VI). A sample of 0.49 g (0.0025 mole) CuI was added to a solution of 1 g (0.0025 mole) (IV) in 3 ml pyridine. An exothermal reaction was noted. After 24 h, the solvent was removed in vacuum. The residue was crystallized from acetone to give 0.98 g (60%) (VI), mp 93-95°C. The $(C_6H_5 + C_5H_5N):CH:(CH_3 + C_4H_9)$ integral intensity ratio was 10:2:33 ($CDCl_3$). Found: C, 49.69; H, 7.08; N, 2.11; P, 4.95%. Calculated for $C_{28}H_{45}BCuINO_2P$: C, 50.94; H, 6.82; N, 2.12; P, 4.70%. Electron impact mass spectrum, m/z (relative intensity, %): 391 (12.08), 390 (44.62), 389 (10.50) $C_{23}H_{40}BO_2P$; 335 (4.81), 334 (23.61), 333 (8.74) $C_{19}H_{32}BO_2P$; 265 (0.8), 264 (5.49), 263 (4.26) $C_{14}H_{22}BO_2P$; 251 (2.07), 250 (13.05), 249 (8.29) $C_{13}H_{20}BO_2P$; 237 (1.17), 236 (9.52), 235 (4.53) $C_{12}H_{18}BO_2P$; 223 (0.4), 222 (2.89), 221 (1.01) $C_{11}H_{16}BO_2P$; 208 (1.16), 207 (1.04) $C_{10}H_{13}BO_2P$; 136 (100) C_8H_9P; 108 (40.38) C_6H_5P; 79 (56.88) C_5H_5N; 57 (9.15) C_4H_9.

[{2-(1′,1′-Dibutylamyl)-4,5,6-triphenyl-1,3,2,5-dioxaboraphosphorinane}pyridine Cuprous Iodide] (VII). By analogy to (VI), 10.7 g (V) gave 5 g (31%) (VII), mp 129-133°C. The $(C_6H_5 + C_5H_5N):CH:C_4H_9$ integral intensity ratio was 20:2:27. Found: C, 58.41; H, 6.48; N, 1.77; P, 4.05%. Calculated for $C_{38}H_{49}BCuINO_2P$: C, 58.20; H, 6.25; N, 1.79; P, 3.96%.

Reaction of (VII) with tert-Butyl Isocyanide. A sample of 0.5 ml tert-butyl isocyanide was added to a solution of 0.5 g (VII) in 3 ml THF. At the end of the exothermal reaction, the precipitate was filtered off to give 0.3 g (100%) [tetra(tert-butyl isocyanide)cuprous] iodide. The filtrate was evaporated. The residue contained (V) as a transparent liquid. The yield of (V) was quantitative, $\delta^{31}P$ = −15 ppm. The $C_6H_5:CH:C_4H_9$ integral intensity ratio was 15:2:27 ($CDCl_3$).

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