SYNTHESIS OF 3,4,6-BORATAOXAPHOSPHONIACYCLOHEXENES

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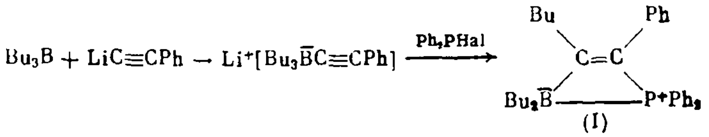
Methods of obtaining P and B containing cyclic compounds are not numerous [1]. From phenylphosphine and diethylaminobis(alkylnyl)boranes one obtains 3,4-boraphosphacyclohexadienes [2]. By reaction of bis(α-hydroxyalkyl)phosphines with esters or anhydrides of boric acids, 1,3,2,5-dioxaboraphosphorinanes are obtained [3], which add to S, Se, and pyridine to form the corresponding sulfides, selenides, and pyridine complexes [4, 5]. By reaction of bis(α-hydroxyalkyl)phosphines and their derivatives with the isobutyl ester of diphenylboric acid in the presence of amines ammonium 1,3,2,5-dioxaborataphosphorinanes and their derivatives are obtained and in the presence of aldehydes 1,3,2,5-dioxaborataphosphoniarinanes are formed [6, 7]. The latter also result from aldehyde addition to diphenylborylhydroxymethyl-(methyl)phenylphosphine [8].

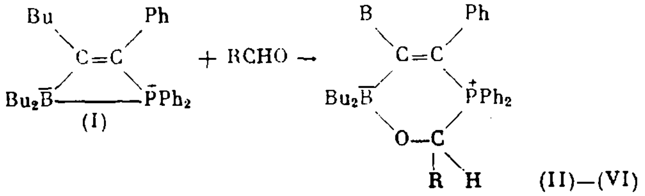
Earlier we showed [9] that 1,1,2-tributyl-3,4,4-triphenyl-1-borata-4-phosphoniacyclobut-2-ene (I) adds to salicylaldehyde with formation of 5-o-hydroxyphenyl-2,3,3-tributyl-1,6,6-triphenyl-3,4,6-borataoxaphosphoniacyclohexene, which represents a new type of P,B-containing cyclic compound.

In this work the reaction of (I) with various aldehydes has been studied. Compound (I) was obtained by reaction of lithium tributyl(1-phenylethynyl)borate with diphenylchlorophosphine, while for the synthesis of 1-boryl-2-phosphinoethylenes sodium trimethyl(or triethyl) (1-methylalkynyl)borates and diphenyl (or dicyclohexyl)chlorophosphines were used [10]



In the ^{31}P NMR spectrum of the reaction mixture signals of (I) (10 ppm) and (1-phenylethynyl)-diphenylphosphine (−34 ppm) were present with relative intensity of 8:2. The positive chemical shift for (I) indicates the presence of a coordinative bond between the P and B atoms, in agreement with ^{1}H and ^{11}B NMR spectral data in [10].

Reaction of (I) with chloral, MeCHO, i-PrCHO, PhCHO, and p-chlorobenzaldehyde proceeds at 20°C giving the corresponding 5-substituted 2,3,3-tributyl-1,6,6-triphenyl-3,4,6-borataoxaphosphoniacyclohexenes (II)-(VI). In the ^{31}P NMR spectrum of the reaction mixture the signal for (I) at 10 ppm disappears and signals with chemical shifts of −1 and −8 ppm for (II)-(VI) appear. The phosphonium character of the P atom and the cyclic structure of (II)-(VI) is confirmed by the coincidence of the ^{31}P chemical shifts of these compounds and those of 1,3,2,5-dioxaborataphosphoniarinanes [7, 8]



R = CCl_3(II), Me(III), *i*-Pr(IV), Ph(V), *p*-ClC_6H_4(VI).

Compounds (II)-(VI) are stable during storage in an Ar atmosphere. According to IR spectral data they dissociate in dilute solution with evolution of aldehydes and (I). Dissocia-

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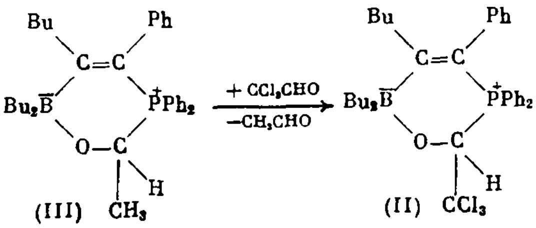
tion is also confirmed by the fact that substitution of the aldehyde fragment of 3,4,6-borataoxaphosphoniacylohexenes is possible under the action of dipolar reagents. Thus, from a solution of (III) in chloral crystals of (II) precipitate



EXPERIMENTAL

^{31}P NMR spectra were recorded on a KGU-4 NMR spectrometer at 10.2 MHz with broadband decoupling of the proton spectrum (25.2 MHz). The external standard was 85% H_3PO_4. PMR spectra were recorded on a Varian T-60 spectrometer at 34.5°C with TMS as internal standard.

1,2,2-Tributyl-3,4,4-triphenyl-1-borata-4-phosphoniacyclobutene-2 (I). To 3.87 g (0.038 mole) phenylacetylene at 0°C with stirring a solution of 3.3 g (0.038 mole) phenyllithium in 30 ml abs. ether was added. The mixture was heated to 20°C for 30 min and cooled to 0°C, then with stirring a solution of 6.92 g (0.038 mole) tributylborane in 10 ml abs. ether was added. The mixture was heated to 20°C and over 1 h a solution of 8.37 g (0.038 mole) diphenylchlorophosphine in 10 ml abs. ether was added. Then the mixture was refluxed for 3 h, evaporated under vacuum, and the precipitate was filtered. Upon standing crystals precipitated from the filtrate which were washed with acetone. The yield of (I) was 3.8 g (21%), mp 66-68°C, $\delta^{31}P$ + 10 ppm (DMF). Found: C 82.15; H 8.91; P 6.56%. $C_{32}H_{42}PB$. Calculated: C 82.05; H 8.97; P 6.62%.

2,3,3-Tributyl-1,6,6-triphenyl-5-trichloromethyl-3,4,6-borataoxaphosphoniacyclohexene(II). To 7.67 g (0.016 mole) of (I) 3 ml chloral was added. In 30 min the mixture was evaporated under vacuum and the residue was crystallized from acetone. The yield of (II) was 2.04 g (20%), mp 114-118°C, $\delta^{31}P$ −8 ppm (acetone). After recrystallization from MeCN compound (II) had a mp of 118-120°C. Found: C 66.53; H 6.82; P 4.58; B 1.57; Cl 17.48%. $C_{34}H_{43}PBOCl_3$. Calculated: C 66.28; H 6.98; P 5.04; B 1.78; Cl 17.30%.

5-Methyl-2,3,3-tributyl-1,6,6-triphenyl-3,4,6-borataoxaphosphoniacyclohexene (III). To 1.04 g (0.22 mole) of (I) in 5 ml dry acetone 2 ml MeCHO was added. Over 20 min the mixture was evaporated under vacuum. The residue was a viscous oil. The yield of (III) was 1.12 g (98%), $\delta^{31}P$ −4 ppm. The ratio of integral intensities of the protons in the PMR spectrum $[(C_6\underline{H}_5 + C\underline{H}):C_4\underline{H}_9]$ was 16:27.

Reaction of (III) with Chloral. Compound (III) (0.51 g, 0.001 mole) was dissolved in 3 ml chloral. After 3 days the mixture was evaporated under vacuum and the residue was crystallized from acetone. The yield of (II) was 0.18 g (30%), mp 114-116°C, $\delta^{31}P$ −8 ppm (acetone).

5-Isopropyl-2,3,3-tributyl-1,6,6-triphenyl-3,4,6-borataoxaphosphoniacyclohexene (IV). To 0.96 g (0.002 mole) of (I) in 5 ml dry acetone 0.15 g (0.002 mole) i-PrCHO was added. On the next day the precipitate was filtered and recrystallized from MeCN. The yield of (IV) was 0.5 g (45%). $\delta^{31}P$ −7 ppm (DMF), mp 72-75°C. Found: C 80.78; H 8.85; P 5.00%. $C_{36}H_{50}PBO$. Calculated: C 80.00; H 9.26; P 5.74%.

2,3,3-Tributyl-1,5,6,6-tetraphenyl-3,4,6-borataoxaphosphoniacyclohexene (V). To 1.16 g (0.0025 mole) of (I) in 5 ml dry acetone 0.27 g (0.0025 mole) of PhCHO was added. On the following day the mixture was evaporated under vacuum and the residue crystallized from acetone. The yield of (V) was 0.2 g (14%), mp 84-86°C, $\delta^{31}P$ −3 ppm (DMF). Found: C 80.85; H 8.44; P 5.38%. $C_{39}H_{48}PBO$. Calculated: C 81.53; H 8.36; P 5.40%.

2,3,3-Tributyl-1,6,6-triphenyl-5-p-chlorophenyl-3,4,6-borataoxaphosphoniacyclohexene (VI). To 0.96 g (0.002 mole) of (I) in 5 ml dry acetone 0.28 g (0.002 mole) of p-chlorobenzaldehyde was added. On the following day the acetone was evaporated under vacuum. The residue was a viscous oil. The yield of (VI) was 1.19 g (96%), $\delta^{31}P$ −1 ppm. The ratio of integral intensities of the protons in the PMR spectrum $[(C_6\underline{H}_5 + C\underline{H}):C_4\underline{H}_9]$ was 20:27.

CONCLUSIONS

1,1,2-Tributyl-3,4,4-triphenyl-1-borata-4-phosphoniacyclobutene-2 adds to aldehydes with formation of P and B containing heterocyclic compounds of a new type, 3,4,6-borataoxaphosphoniacyclohexenes.

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ARYLBIS(TRIPHENYLPHOSPHINYL)NICKEL CARBOXYLATES

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σ-Aryl nickel compounds $NiX(Ar)(PPh_3)_2$ (X = Cl, Br, I) were first reported in [1] and have been well studied [2]. However, only two examples are known for pentachlorophenyl compounds of Ni with the Ni—O bond stabilized by various tertiary phosphines via: $Ni(OCOCH_3)(C_6Cl_5)(PR_3)_2$ [3, 4] and $Ni(OC_6Cl_5)(C_6Cl_5)(PR_3)_2$ [4, 5]. At the same time such compounds (in particular arylbis(triphenylphosphinyl)nickel carboxylates) are suitable models for determining the relative polarity of the Ni—O bond. Thus ^{19}F NMR has been used to investigate the comparative polarity in a series of organometallic p-fluorobenzoates containing monovalent organometallic groups with a key heavy nontransition metal atom [6].

This study concerns methods of synthesizing σ-aryl Ni compounds, stabilized by triphenylphosphine, containing a Ni—OCOR bond.

The o-tolyl complex $NiCl(C_6H_4CH_3\text{-}o)(PR_3)_2$ (I) was chosen as starting material because of its stability towards atmospheric O_2. It was obtained by the oxidative addition of o-chlorotoluene to $Ni(PPh_3)_4$ [7].

In order to prepare o-tolylbis(triphenylphosphinyl)nickel carboxylates we carried out a halogen exchange in (I) with the corresponding carboxylate anion. It was found that treatment of (I) with silver p-fluorobenzoate caused the σ-aryl Ni compound to decompose to $AgCl(PPh_3)$ (II) and $Ni(OCOC_6H_4F\text{-}p)_2$. Treatment of (I) with excess MeCOOK gave only recovered (I). Hence the desired compound was synthesized from cationic Ni complexes and carboxylate anions. We have previously used this method with $AgClO_4$ to give only the carboxylate σ-aryl complex $Ni(OCOCH_3)(C_6Cl_5)(PR_3)_2$ [3, 4].

A particular problem arose in the synthesis of the cationic o-tolyl Ni complex. Thus (I) in the following scheme gave (II) (49%) along with (III)

$$(I) \xrightarrow[CH_3CN]{AgBF_4} \underset{(II)}{AgCl(PPh_3)} + \underset{(III)}{[Ni(C_6H_4CH_3\text{-}o)(CH_3CN)(PPh_3)_2]BF_4}$$

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