Russian Chemical Bulletin, International Edition, Vol. 50, No. 8, pp. 1461—1464, August, 2001

10-(3-Hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride: synthesis and molecular structure

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The reaction of 2-(3,4-dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine with *C*,*N*-diphenylnitrilimine yields 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride. Its structure was determined by X-ray diffraction analysis.

Key words: 2-(3,4-dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine, *C*,*N*-diphenylnitrilimine, 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride, X-ray diffraction analysis.

Tricyclic spirophosphoranes are of considerable interest as potential physiologically active compounds[1] and as objects of investigation into the spatial structures of phosphorus-containing heterocycles.[2] Such compounds can be obtained, for example, by the reactions of nitrilimines that are the Huisgen 1,3-dipoles with phosphorus(III) derivatives, in which the phosphorus atom is included in the heterocycle and simultaneously bound to the other heterocycle.[3] However, while studying the reaction of 2-(4,5-dihydrofuran-3-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine with *C*,*N*-diphenylnitrilimine, we found[3] that the closure of a new 1,2,4-diazaphosphorine ring in the multi-step process is accompanied by the opening of the both rings in the starting organophosphorus compound. We assumed that the formation of the final 5-(2-chloroethyl)-4-(*N*,*N'*-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2,4λ^5-diazaphosphorine can occur *via* a bicyclic spiro compound with a nodal quaternized phosphorus atom. In the present work, we found that the compound with this structure is the final product in the reaction of *C*,*N*-diphenylnitrilimine with 2-(3,4-dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine (**1**), which differs from the aforementioned 2-(4,5-dihydrofuran-3-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine in the size of the oxygen-containing heterocycle bound to the phosphorus atom.

The goal of the present work was to study the reaction of 2-(3,4-dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine (**1**) with *C*,*N*-diphenylnitril imine as a possible method for the synthesis of a new P,N-containing compound of bi- or tricyclic structure.

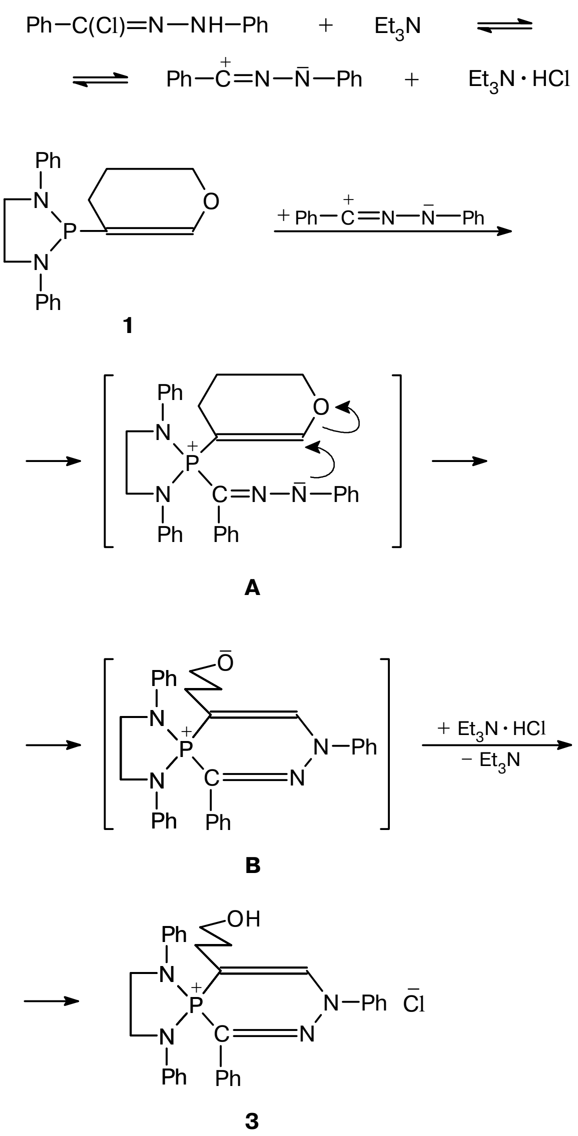
Results and Discussion

Compound **1** was obtained from 5-dibromophosphino-3,4-dihydro-2*H*-pyran (**2**) and *N*,*N'*-diphenylethylenediamine in the presence of triethylamine. 1,3-Diaza-2λ^3-phospholidine (**1**) reacts with *C*,*N*-diphenylnitril imine (generated *in situ* from *N*-phenylbenzohydrazonoyl chloride under the action of an excess of triethylamine) under mild conditions (benzene, 20 °C). As for a dihydrofuryl analog, the reaction seems to occur stepwise. Apparently, the initial nucleophilic attack of the phosphorus atom on the carbonium atom of nitril imine gives bipolar ion **A** (Scheme 1). Then the negatively charged N atom of the P^+CNN^- betaine fragment attacks the dihydropyran ring at position 6 activated by the phosphonium group. This results in the C—O bond cleavage and in the formation of a six-membered P,N-containing heterocycle **B** with the P^+CCCCO^- betaine fragment. Subsequent protonation of the alkoxide ion of betaine **B** with triethylamine hydrochloride yields the final 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (**3**).

Thus, unlike an analogous reaction of 2-(4,5-dihydrofuran-3-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine, the alcoholic OH group in spirophosphonium salt **3** does not interact with the quaternized phosphorus atom to give the oxaphosphorinane ring, which could result, in turn, in the opening of the diazaphospholidine ring followed by the decomposition of the phosphonium salt. Apparently, the six-membered 1,2-oxaphosphorinane ring is less stable thermodynamically than the five-membered 1,2-oxaphospholane one.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1390—1393, August, 2001.

Scheme 1



Chloride **3** is an uncommon example of bicyclic spirophosphonium compounds. It is a colorless crystalline substance moderately soluble in chloroform and acetone and insoluble in benzene and THF. The ^{31}P NMR spectrum of compound **3** shows a signal at δ_P 4.1 characteristic of cyclic phosphonium salts, and its IR spectrum contains an absorption band from the OH group (3260 cm^{-1}). In the ^{1}H NMR spectrum of spirophosphonium compound **3**, the doublet of the alkenyl proton is significantly shifted downfield (δ 9.17, $^3J_{P,H}$ = 27.2 Hz) compared to the spectra of analogous diazaphosphorine rings with the phosphoryl P atom,[4] which also confirms the quaternization of phosphorus. The protons of all the five methylene groups ($CH_2\underline{CH_2}CH_2$, $=CCH_2$, OCH_2 and two NCH_2) manifest themselves by the corresponding multiplets (δ 1.70, 2.88, 3.56, 3.99, 4.74).

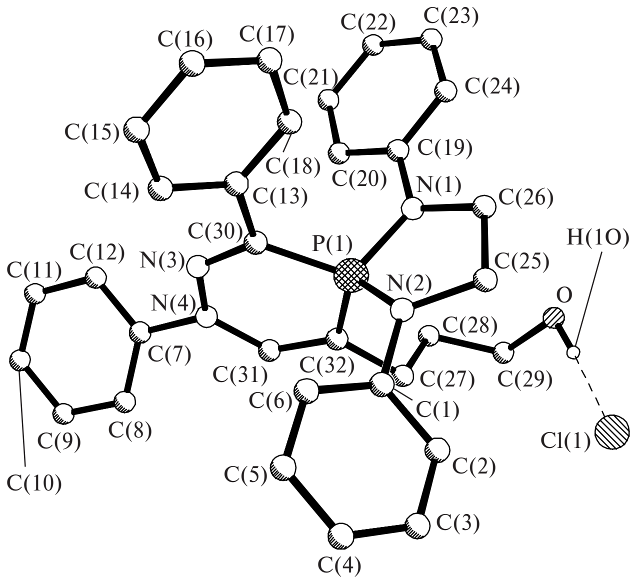


Fig. 1. General view of 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (**3**) (solvate with a $CHCl_3$ molecule).

The structure of compound **3** (in the form of its solvate with a chloroform molecule) was proved by X-ray diffraction analysis (Figs. 1, 2; Tables 1, 2). The six-membered ring in the bicyclic spiro system is planar with an accuracy of 0.020 Å, while the five-membered heterocycle has an envelope conformation, in which the atoms are coplanar within 0.015 Å, except for the C(25)

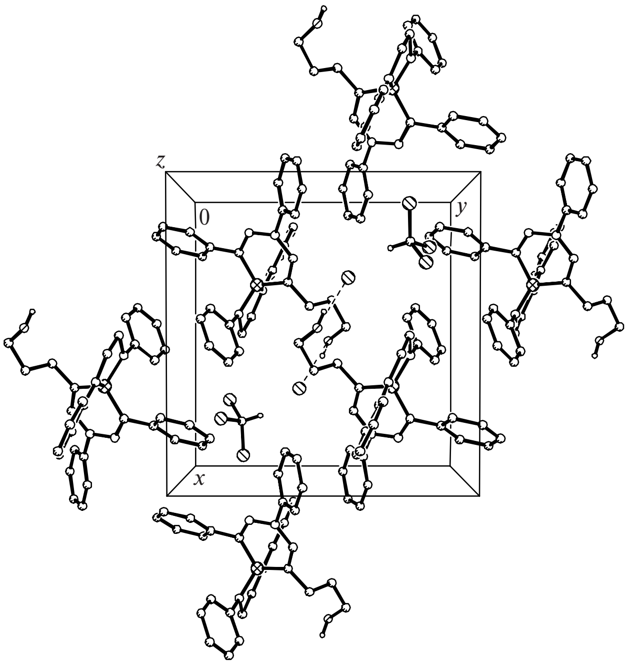


Fig. 2. Crystal structure of 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (**3**) (solvate with a $CHCl_3$ molecule).

Table 1. Selected bond lengths (*d*) in 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (**3**) (solvate with a $CHCl_3$ molecule)

Bond	*d*/Å	Bond	*d*/Å
P(1)—N(2)	1.648(2)	N(3)—N(4)	1.349(3)
P(1)—N(1)	1.649(2)	N(4)—C(31)	1.366(3)
P(1)—C(32)	1.733(2)	N(4)—C(7)	1.452(3)
P(1)—C(30)	1.780(2)	C(13)—C(30)	1.498(3)
O—C(29)	1.415(5)	C(25)—C(26)	1.501(5)
N(1)—C(19)	1.431(3)	C(27)—C(32)	1.514(3)
N(1)—C(26)	1.472(3)	C(27)—C(28)	1.532(4)
N(2)—C(1)	1.444(3)	C(28)—C(29)	1.518(4)
N(2)—C(25)	1.469(3)	C(31)—C(32)	1.359(3)
N(3)—C(30)	1.306(3)		

Table 2. Selected bond angles (ω) in 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (**3**) (solvate with a $CHCl_3$ molecule)

Angle	ω/deg	Angle	ω/deg
N(2)—P(1)—N(1)	95.02(10)	C(8)—C(7)—N(4)	119.4(2)
N(2)—P(1)—C(32)	114.09(11)	C(12)—C(7)—N(4)	119.1(2)
N(1)—P(1)—C(32)	114.70(11)	C(18)—C(13)—C(30)	122.0(2)
N(2)—P(1)—C(30)	116.22(11)	C(14)—C(13)—C(30)	119.3(2)
N(1)—P(1)—C(30)	115.09(11)	C(20)—C(19)—N(1)	122.0(2)
C(32)—P(1)—C(30)	102.43(11)	C(24)—C(19)—N(1)	119.7(3)
C(19)—N(1)—C(26)	120.3(2)	N(2)—C(25)—C(26)	107.5(2)
C(19)—N(1)—P(1)	125.46(16)	N(1)—C(26)—C(25)	107.8(2)
C(26)—N(1)—P(1)	113.34(19)	C(32)—C(27)—C(28)	112.5(2)
C(1)—N(2)—C(25)	120.4(2)	C(29)—C(28)—C(27)	112.9(3)
C(1)—N(2)—P(1)	123.39(17)	O—C(29)—C(28)	111.1(3)
C(25)—N(2)—P(1)	112.62(18)	N(3)—C(30)—C(13)	115.4(2)
C(30)—N(3)—N(4)	122.44(19)	N(3)—C(30)—P(1)	123.80(17)
N(3)—N(4)—C(31)	125.94(19)	C(13)—C(30)—P(1)	120.74(17)
N(3)—N(4)—C(7)	113.87(18)	C(32)—C(31)—N(4)	125.3(2)
C(31)—N(4)—C(7)	120.16(19)	C(31)—C(32)—C(27)	121.9(2)
C(6)—C(1)—N(2)	119.5(2)	C(31)—C(32)—P(1)	120.00(18)
C(2)—C(1)—N(2)	120.0(3)	C(27)—C(32)—P(1)	118.06(17)

atom deviating from their plane by 0.283 Å. The angle between the mean planes of these rings is 89.4°, *i.e.*, they make a near-right angle.

The configuration of the phosphorus atom is a strongly distorted tetrahedron (the XPY angles vary from 95.02° to 116.22°). The C(7)—C(12) benzene ring is rotated relative to the six-membered heterocycle plane by 43.0°, while the C(13)—C(18) ring makes a torsion angle of 34.6°. The C(1)—C(6) and C(19)—C(24) benzene rings are rotated relative to the five-membered heterocycle plane by 50.9° and 12.8°, respectively. The intermolecular hydrogen bond involving the OH group and the chlorine atom has the following parameters:

Bond	*d*/Å	Angle	ω/deg
O—H	0.90	O—H...Cl	168.0
H...Cl	2.22		
O...Cl	3.104		

Experimental

The IR spectra of compounds **1—3** were recorded on an IKS-29 instrument (in KBr pellets). ^1H NMR spectra were recorded on a Bruker AM-500 instrument (500.1 MHz, inner stabilization relative to the ^2H resonance line). ^{31}P NMR spectra were recorded on a Bruker AC-200 instrument (81.4 MHz) with 85% H_3PO_4 as the standard.

N,N'-Diphenylethylenediamine (Aldrich), 3,4-dihydro-2*H*-pyran (Merck) were used without additional purification. PBr_3 (Ural PO Galogen, technical specifications 6-09-30-79-88) was preliminarily distilled at reduced pressure (10 Torr) in a flow of argon. *N*-Phenylbenzohydrazonoyl chloride (m.p. 130—131 °C) was prepared as described earlier.[5] Diethyl ether, THF, and triethylamine were dried over NaOH and distilled over sodium. Benzene was dried with azeotropic removal of water and distilled over sodium.

Compounds **1** and **2** were synthesized and the reaction of phospholidine **1** with *C,N*-diphenylnitrilimine was carried out in an atmosphere of argon with dried solvents and triethylamine.

2-(3,4-Dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ^3-phospholidine (1). A solution of 5-dibromophosphino-3,4-dihydro-2*H*-pyran (**2**) (13.6 g, 50 mmol) in 20 mL of THF was added dropwise with stirring at 0—5 °C to a solution of *N,N'*-diphenylethylenediamine (10.6 g, 50 mmol) and triethylamine (10.1 g, 100 mmol) in 150 mL of THF. The reaction mixture was stirred at 0—5 °C for 0.5 h and at 20 °C for 0.5 h. Triethylamine hydrobromide was filtered off and washed with 50 mL of THF. The filtrate was concentrated at reduced pressure. The solid residue was recrystallized from benzene to give compound **1** (11.4 g, 70%), m.p. 182—184 °C. Found (%): C, 70.51; H, 6.29; P, 9.73. $C_{19}H_{21}N_2OP$. Calculated (%): C, 70.36; H, 6.53; P, 9.55. IR, ν/cm^{-1}: 1595 (C=C). ^1H NMR (C_6D_6), δ: 1.07 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 1.57 (m, 2 H, $=CCH_2$); 3.19, 3.27 (both m, each 2 H, CH_2N); 3.33 (m, 2 H, OCH_2); 7.12 (d, 1 H, =CH, $^3J_{P,H}$ = 10.4 Hz); 6.80—7.25 (m, 10 H, Ph). ^{31}P NMR ($CDCl_3$), δ: 90.4.

5-Dibromophosphino-3,4-dihydro-2*H*-pyran (2). 3,4-Dihydro-2*H*-pyran (18.5 g, 220 mmol) in 25 mL of ether was added dropwise at 20 °C to a solution of PBr_3 (59.5 g, 220 mmol) in 100 mL of ether. The reaction mixture was stirred at the same temperature for 12 h. Then triethylamine (24.3 g, 240 mmol) was added, and stirring was continued at 20 °C for 3 h. Triethylamine hydrobromide was filtered off, and the ether was removed at reduced pressure. The residue was fractionated *in vacuo* to give compound **2** (32.3 g, 54%), b.p. 80—82 °C (0.7 Torr), n_D^{18} 1.6362. Found (%): C, 21.71; H, 2.44; P, 11.17. $C_5H_7Br_2OP$. Calculated (%): C, 21.93; H, 2.58; P, 11.31. IR, ν/cm^{-1}: 1590 (C=C). ^1H NMR ($CDCl_3$), δ: 2.02 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.54 (m, 2 H, $=CCH_2$); 4.12 (m, 2 H, OCH_2); 7.25 (d, 1 H, =CH, $^3J_{P,H}$ = 12.7 Hz). ^{31}P NMR ($CDCl_3$), δ: 159.2.

10-(3-Hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]deca-6,9-diene chloride (3). A solution of 1,3-diaza-2λ^3-phospholidine (**1**) (1.62 g, 5 mmol), *N*-phenylbenzohydrazonoyl chloride (1.15 g, 5 mmol), and triethylamine (2 mL) in 20 mL of benzene was kept at 20 °C for 24 h. The precipitate (2.64 g) was filtered off, washed with benzene (5 mL), and recrystallized from $CHCl_3$. The yield was 2.53 g (75% from crystal solvate **3** · $CHCl_3$), m.p. 151—153 °C. Found (%): C, 58.70; H, 5.43; P, 4.36. $C_{33}H_{35}Cl_4N_4OP$. Calculated (%): C, 58.59; H, 5.22; P, 4.58. IR, ν/cm^{-1}: 3260 (OH), 1570 (C=C). ^1H NMR ($CDCl_3$), δ: 1.70 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.88 (m, 2 H, $=CCH_2$); 3.56 (m, 2 H, OCH_2);

3.99, 4.74 (both m, each 2 H, CH_2N); 5.28 (s, 1 H, OH); 6.90—7.65 (m, 20 H, Ph); 9.17 (d, 1 H, =CH, $^3J_{P,H}$ = 27.2 Hz). ^{31}P NMR ($CHCl_3$), δ: 4.1.

X-ray diffraction analysis of the solvate crystals of (**3**)$\cdot$$CHCl_3$ was carried out on a CAD-4 diffractometer (Mo-Kα radiation, θ/2θ scan mode). The crystals are monoclinic, $C_{33}H_{33}Cl_4N_4OP$, a = 13.523(3) Å, b = 13.008(4) Å, c = 18.908(5) Å, β = 91.954(8)°, V = 3324.2(15) Å^3; space group $P\,2_1/c$, Z = 4, d_{calcd} = 1.348 g cm^{-3}. The structure was solved by the direct method; R = 0.0545, R_w = 0.1395 (from 22 116 reflections with $I > 2\sigma(I)$). The atomic coordinates and complete tables of bond lengths and angles were deposited with the Cambridge Crystallographic Database (No. CCDC 161181).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32797).

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Received December 22, 2000;
in revised form April 30, 2001