# Reactions of 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine with nitrile imines

*Yu. G. Trishin,[a]* V. I. Namestnikov,[a] and V. K. Belsky[b]*

*[a]St.-Petersburg State Technological University of Plant Polymers,*
*4 ul. Ivana Chernykh, 198095 St.-Petersburg, Russian Federation.*
*Fax: +7 (812) 186 8600. E-mail: trish@YT4470.spb.edu*
*[b]State Research Center of Russian Federation "L. Ya. Karpov Research Physico-Chemical Institute,"*
*10 ul. Vorontsovo Pole, 103064 Moscow, Russian Federation.*
*Fax: +7 (095) 975 2450*

The multistep reactions of 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine with nitrile imines afforded phosphorus-containing spiro compounds of a new type, *viz.*, 6,8-disubstituted 9-oxo-10-(2-chloroethyl)-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-dienes.

**Key words:** 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine, nitrile imines, 6,8-disubstituted 10-(2-chloroethyl)-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-dienes, X-ray diffraction analysis.

The reactions of *C*,*N*-diphenylnitrile imine with 1,3-diaza-2λ$^3$-phospholidine derivatives in which the P atom is bound to the 4,5-dihydro-3-furyl or 3,4-dihydro-2*H*-pyran-5-yl heterocyclic fragment are multistep processes as evidenced by the structures of the resulting compounds.[1,2] The key step of these reactions involves the formation of the six-membered 1,2,4-diazaphosphorine ring with the simultaneous opening of the dihydrofuran or dihydropyran ring due to the nucleophilic attack of the anionic N atom of the intermediate bipolar ion on the sp$^2$-hybridized C atom of the oxygen-containing heterocycle. The reaction of 2-(4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine with *C*,*N*-diphenylnitrile imine was also accompanied by the diazaphospholidine-ring opening giving rise to a monocyclic compound, *viz.*, substituted 1,4-dihydro-1,2,4λ$^5$-diazaphosphorine, as the final product.[1] In the analogous reaction with 2-(3,4-dihydro-2*H*-pyran-5-yl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine, the diazaphospholidine ring was retained, and the bicyclic spiro compound with the quaternized P atom at the spiro position, *viz.*, 10-(3-hydroxypropyl)-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphoniaspiro[4.5]-deca-6,9-diene chloride, was obtained as the final product.[2]

As part of continuing studies aimed at developing new procedures for the synthesis of polycyclic phosphorus-containing compounds, we examined the reactions of nitrile imines with 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine (**1**). Taking into account the fact that this compound contains the Cl atom at position 2 of the dihydrofuran ring, one would expect another possible pathway of the transformation of the 1,2,4-diazaphosphorine cylcoadduct generated in the course of the reaction. This assumption is based on the results obtained in our previous investigations[3,4] on the reactions of nitrile imines with 3-dialkoxyphosphino-4,5-dihydrofurans, which either contain the Cl atom at position 2 of the dihydrofuran ring or are deprived of this atom. Thus in the reactions of nitrile imines with 3-dialkoxyphosphino-4,5-dihydrofuran, the 1,2,4-diazaphosphorine ring-closure was accompanied by the dihydrofuran ring-opening to yield finally bicyclic compounds containing the pentacoordinated spiro P atom.[3] By contrast, the 1,2,4-diazaphosphorine-ring closure in the reaction of 2-chloro-3-dialkoxyphosphino-4,5-dihydrofuran with *C*-*p*-nitrophenyl-*N*-phenylnitrile imine was accompanied by the replacement of the Cl atom, while the dihydrofuran ring was retained. In the latter case, a bicyclic compound in which the tetracoordinated P atom is not located at the spiro position was obtained as the final product.[4] In the present study, we examined the reactions of 1,3-diaza-2λ$^3$-phospholidine **1** with nitrile imines bearing different electron-withdrawing substituents at the carbenium atom.

## Results and Discussion

1,3-Diaza-2λ$^3$-phospholidine **1** was prepared as a colorless crystalline compound from 2-chloro-3-dichlorophosphino-4,5-dihydrofuran and *N*,*N*′-diphenylethylenediamine in the presence of triethylamine. The $^{31}$P NMR spectrum of compound **1** has a signal at $\delta_P$ 70.4, which is

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 960—964, June, 2002.

1066-5285/02/5106-1045 $27.00 

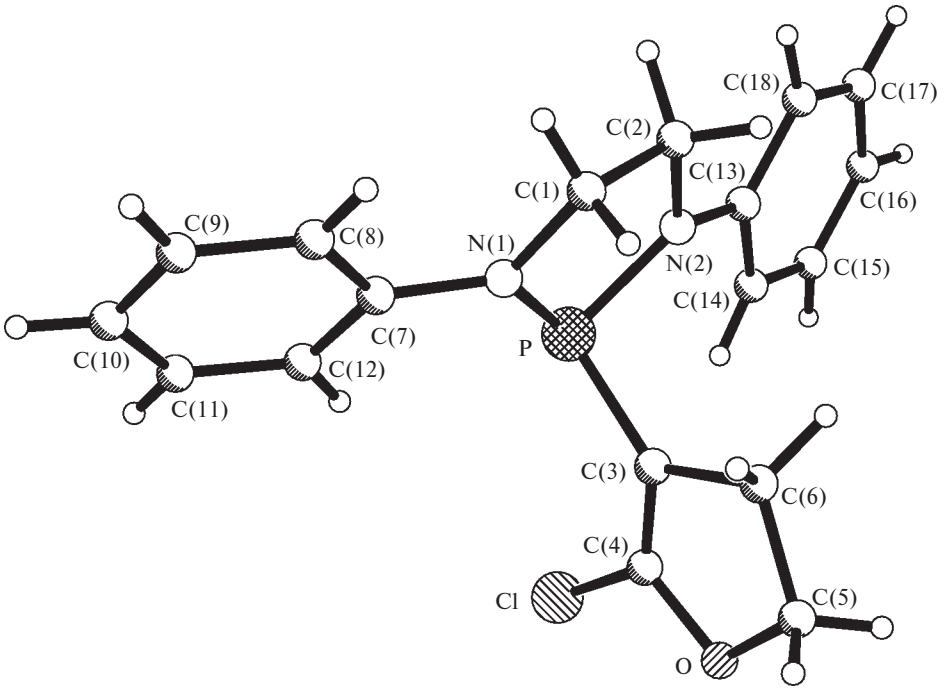



**Fig. 1.** Overall view of the molecule of 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine (**1**).

characteristic of compounds containing the trivalent tricoordinated P atom and is similar in the chemical shift to the signal for the P atom in analogous 2-(4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine.[1] The $^1$H NMR spectrum shows signals for the methylene protons of the $=CH_2$ and $OCH_2$ groups (δ 2.60 and 4.33) as triplets with $^3J_{H,H}$ = 9.3 Hz (the spin-spin coupling constant $^3J_{P,H}$ for the protons of the $=CH_2$ group is, apparently, close to zero). The protons of both $NCH_2$ groups are manifested as multiplets (δ 3.73 and 3.82).

According to the data from X-ray diffraction analysis, the 1,2,3-diazaphospholidine ring in crystalline compound **1** (Fig. 1, Tables 1 and 2) adopts an envelope conformation. The C(1) atom deviates from the plane of the heterocycle by 0.34 Å, and the remaining atoms are coplanar to within 0.01 Å. The 2-chloro-4,5-dihydrofuran ring is planar to within 0.02 Å. The angle between the planes of two heterocycles is 86.6°. The planes of the C(7)—C(12) and C(13)—C(18) benzene rings form angles of 26.5 and 19.0°, respectively, with the plane of the diazaphospholidine ring. The angle between the planes of the benzene rings is 44.1°. The P atom has a distorted pyramidal configuration (the X—P—Y angles are 90.46—103.63°).

The reactions of 1,3-diaza-2λ$^3$-phospholidine **1** with nitrile imines proceeded under mild conditions (benzene or THF, 20 °C) upon the *in situ* generation of nitrile imines from the corresponding hydrazonoyl halides under the action of triethylamine. As in the case of the dihydrofuryl analog, the reaction is, evidently, a multistep process. Apparently, the nucleophilic attack of the P atom on the carbonium atom of nitrile imine initially

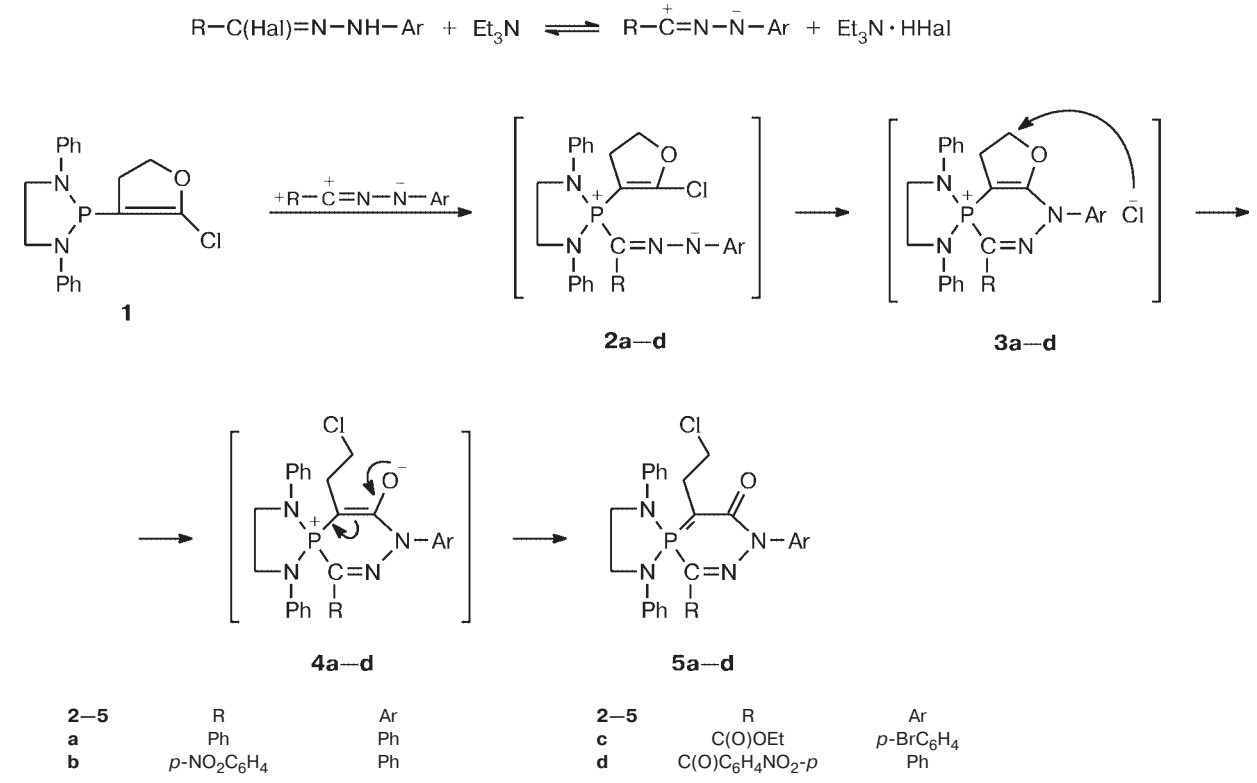
**Table 1.** Selected bond lengths (*d*) in molecule **1**

| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| Cl—C(4) | 1.699(4) | N(1)—C(1) | 1.459(5) |
| P—N(1) | 1.705(3) | N(2)—C(13) | 1.400(4) |
| P—N(2) | 1.712(3) | N(2)—C(2) | 1.454(5) |
| P—C(3) | 1.806(3) | C(1)—C(2) | 1.495(6) |
| O—C(4) | 1.345(4) | C(3)—C(4) | 1.313(4) |
| O—C(5) | 1.455(5) | C(3)—C(6) | 1.514(5) |
| N(1)—C(7) | 1.395(4) | C(5)—C(6) | 1.502(6) |

**Table 2.** Selected bond angles (ω) in molecule **1**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| N(2)—P—N(1) | 90.46(14) | C(4)—C(3)—C(6) | 106.4(3) |
| N(1)—P—C(3) | 103.63(15) | C(4)—C(3)—P | 123.2(3) |
| N(2)—P—C(3) | 100.74(14) | C(6)—C(3)—P | 130.0(3) |
| C(4)—O—C(5) | 104.9(3) | C(3)—C(4)—O | 118.2(3) |
| C(7)—N(1)—C(1) | 122.2(3) | C(3)—C(4)—Cl | 129.1(3) |
| C(7)—N(1)—P | 123.3(2) | O—C(4)—Cl | 112.8(3) |
| C(1)—N(1)—P | 113.0(9) | O—C(5)—C(6) | 107.9(3) |
| C(13)—N(2)—C(2) | 121.2(3) | C(5)—C(6)—C(3) | 102.5(4) |
| C(13)—N(2)—P | 121.9(2) | C(8)—C(7)—N(1) | 121.2(3) |
| C(2)—N(2)—P | 115.3(2) | C(12)—C(7)—N(1) | 121.1(3) |
| N(1)—C(1)—C(2) | 107.3(3) | C(14)—C(13)—N(2) | 119.9(3) |
| N(2)—C(2)—C(1) | 107.4(3) | C(18)—C(13)—N(2) | 121.3(3) |

**Scheme 1**




| 2—5 | R | Ar | 2—5 | R | Ar |
|---|---|---|---|---|---|
| **a** | Ph | Ph | **c** | C(O)OEt | *p*-BrC$_6$H$_4$ |
| **b** | *p*-NO$_2$C$_6$H$_4$ | Ph | **d** | C(O)C$_6$H$_4$NO$_2$-*p* | Ph |

affords bipolar ion **2a—d** (Scheme 1). Then, the N atom of the betaine P$^+$CNN$^-$ fragment bearing a negative charge attacks position 2 of dihydrofuran activated with the phosphonium group. This step is accompanied by the nucleophilic vinyl substitution of the Cl atom bound to the dihydrofuran ring and the closure of the six-membered phosphorus-containing nitrogen heterocycle to form the tricyclic phosphonium salt (**3a—d**). Then, the attack of the chloride ion on the C atom of the methylene group bound to the O atom of the heterocycle leads to the dihydrofuran-ring opening. The resulting spirocyclic bipolar ion (**4a—d**) is stabilized through the formation of the conjugated system of the P=C—C=O bonds giving rise to the final products, *viz.*, 6,8-disubstituted 10-(2-chloroethyl)-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-dienes (**5a—d**). It should be noted that the reaction follows this pathway regardless of the nature of the substituent at the carbenium atom of nitrile imine. Hence, unlike the analogous reaction involving 2-(4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine, the diazaphosphorine-ring closure in the latter reactions is accompanied by the replacement of the Cl atom rather than by the dihydrofuran-ring opening to yield finally products with essentially different structures.

10-(2-Chloroethyl)-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-dienes **5a—d** belong to rare bicyclic phosphorus-containing spiro compounds with the ylide P atom at the spiro position. These compounds occur as white (compound **5a**), yellow (compound **5c**), or yellowish-brown (compounds **5b,d**) crystals, which are readily soluble in chloroform and THF, moderately soluble in benzene and acetone, poorly soluble in ether, and insoluble in hexane.

The $^{31}$P NMR spectra of spiro compounds **5a—d** have a signal at $\delta_P$ 17.8—18.4, which differs substantially from the chemical shift of the P atom in the analogous spirophosphonium compound ($\delta_P$ 4.1).[2] In the IR spectra of spiro compounds **5a—d**, the absorption band of the carbonyl group of the ring is substantially shifted to the long-wavelength region (1575—1605 cm$^{-1}$), which is indicative of the involvement of this group into the conjugated O=C—C=P system. In the $^1$H NMR spectra of spiro compounds **5a—d**, the signals for the protons of the =CH$_2$ group are observed as doublets of triplets ($\delta$ 2.64—2.75, $^3J_{H,H}$ = 7.5—7.9 Hz, $^3J_{P,H}$ = 15.3—15.6 Hz), the signals for the protons of the CH$_2$Cl group are observed as triplets ($\delta$ 3.26—3.36, $^3J_{H,H}$ = 7.5—7.9 Hz), and the signals for the protons of two CH$_2$N groups are manifested as multiplets ($\delta$ 3.73—4.05 and 4.00—4.24).

The structures of spiro compounds **5a—d** were unambiguously established based on the results of X-ray diffraction analysis of 8-*p*-bromophenyl-10-(2-chloro-

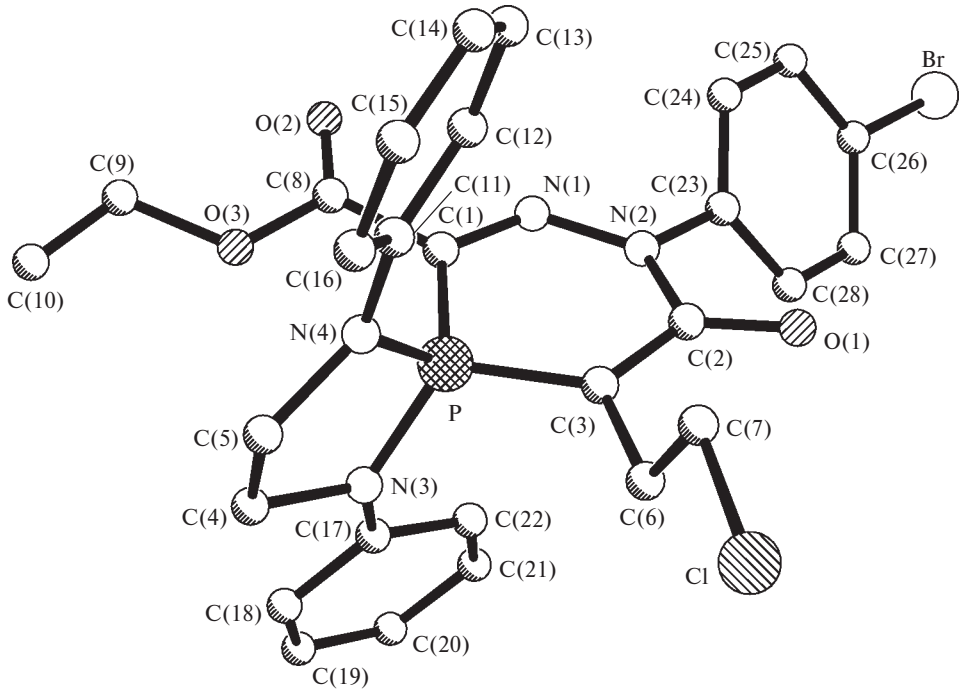



**Fig. 2.** Overall view of the molecule of 8-*p*-bromophenyl-10-(2-chloroethyl)-6-ethoxycarbonyl-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (**5c**).

ethyl)-6-ethoxycarbonyl-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (**5c**) (Fig. 2, Tables 3 and 4). The six-membered ring involved in the bicyclic spirane system adopts a half-boat conformation in which the P, N(2), C(2), and C(3) atoms are coplanar to within 0.03 Å, whereas the N(1) and C(1) atoms deviate from this plane in the same direction by 0.15 and 0.23 Å, respectively. The five-membered heterocycle, like that in the molecule of the starting 1,3-diaza-2$\lambda^3$-phospholidine **1**, adopts an envelope conformation in which with the C(4) atom deviates from the plane passing through the remaining atoms (which are coplanar to within 0.03 Å) by 0.29 Å. The angle between the mean planes of the heterocycles is 83.3°, *i.e.*, these heterocycles are approximately perpendicular to each other. The P atom has a strongly distorted tetrahedral configuration (the X—P—Y angles are 94.5—117.2°). The C(23)—C(28) benzene ring is twisted with respect to the plane of the six-membered heterocycle by 52.7°. The C(17)—C(22) and C(11)—C(16) benzene rings are twisted relative to the plane of the five-

**Table 3.** Selected bond lengths (*d*) in molecule **5c**

| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| Br—C(26) | 1.893(8) | N(2)—C(23) | 1.437(9) |
| Cl—C(7) | 1.789(9) | N(2)—C(2) | 1.463(9) |
| P—N(3) | 1.657(6) | N(3)—C(17) | 1.403(10) |
| P—N(4) | 1.664(7) | N(3)—C(4) | 1.469(9) |
| P—C(3) | 1.696(7) | N(4)—C(11) | 1.412(10) |
| P—C(1) | 1.762(8) | N(4)—C(5) | 1.462(10) |
| O(1)—C(2) | 1.216(8) | C(1)—C(8) | 1.480(10) |
| O(2)—C(8) | 1.201(9) | C(2)—C(3) | 1.403(10) |
| O(3)—C(8) | 1.316(9) | C(3)—C(6) | 1.482(11) |
| O(3)—C(9) | 1.453(10) | C(4)—C(5) | 1.498(12) |
| N(1)—C(1) | 1.299(9) | C(6)—C(7) | 1.525(11) |
| N(1)—N(2) | 1.334(8) | C(9)—C(10) | 1.471(19) |

**Table 4.** Selected bond angles (ω) in molecule **5c**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| N(3)—P—N(4) | 94.5(3) | O(1)—C(2)—C(3) | 126.7(7) |
| N(3)—P—C(3) | 117.2(3) | O(1)—C(2)—N(2) | 115.3(6) |
| N(4)—P—C(3) | 114.4(3) | C(3)—C(2)—N(2) | 117.9(6) |
| N(3)—P—C(1) | 113.2(3) | C(2)—C(3)—C(6) | 118.4(6) |
| N(4)—P—C(1) | 115.1(3) | C(2)—C(3)—P | 123.5(6) |
| C(3)—P—C(1) | 103.1(3) | C(6)—C(3)—P | 118.2(5) |
| C(8)—O(3)—C(9) | 118.0(7) | N(3)—C(4)—C(5) | 107.3(6) |
| C(1)—N(1)—N(2) | 122.8(6) | N(4)—C(5)—C(4) | 107.8(7) |
| N(1)—N(2)—C(23) | 114.4(6) | C(3)—C(6)—C(7) | 114.5(6) |
| N(1)—N(2)—C(2) | 126.9(6) | C(6)—C(7)—Cl | 110.2(6) |
| C(23)—N(2)—C(2) | 118.7(5) | O(2)—C(8)—O(3) | 123.0(7) |
| C(17)—N(3)—C(4) | 119.8(6) | O(2)—C(8)—C(1) | 126.1(7) |
| C(17)—N(3)—P | 124.0(5) | O(3)—C(8)—C(1) | 110.8(7) |
| C(4)—N(3)—P | 113.0(5) | C(10)—C(9)—O(3) | 112.5(10) |
| C(11)—N(4)—C(5) | 121.4(7) | C(16)—C(11)—N(4) | 119.9(8) |
| C(11)—N(4)—P | 124.1(5) | C(12)—C(11)—N(4) | 121.1(7) |
| C(5)—N(4)—P | 113.1(5) | C(22)—C(17)—N(3) | 121.9(6) |
| N(1)—C(1)—C(8) | 113.2(6) | N(3)—C(17)—C(18) | 120.9(7) |
| N(1)—C(1)—P | 124.1(5) | C(24)—C(23)—N(2) | 119.3(7) |
| C(8)—C(1)—P | 122.7(5) | C(28)—C(23)—N(2) | 120.0(7) |

membered heterocycle by 14.1 and 24.5°, respectively. The ethoxycarbonyl group is planar to within 0.05 Å. The C(3)—C(6)—C(7)—Cl chain is also planar to within 0.02 Å. The P—C(3) and C(3)—C(2) bond lengths are indicative of the conjugation in the P=C—C=O system. Thus, the P—C(3) bond (1.696 Å) in the six-membered heterocycle is shortened as compared to the corresponding bonds in the analogous spirophosphonium compound (1.733 Å)[2] and the monocyclic 1,2,4-diazaphosphorine compound (1.745 Å).[1] At the same time, the C(3)—C(2) bond (1.403 Å) is substantially elongated as compared to the corresponding bonds in the spirophosphonium compound (1.359 Å)[2] and the monocyclic 1,2,4-diazaphosphorine compound (1.338 Å).[1] Apparently, this conjugation, which eliminates the ylide character of the P=C bond, is responsible for high hydrolytic stability of spiro compounds **5a—d**. These compounds can be stored under normal conditions over a long period and are not hydrolyzed to a noticeable degree upon heating with water.

## Experimental

The IR spectra of compounds **1** and **5a—d** were recorded on an IKS-29 instrument in KBr pellets. The $^1$H NMR spectra of solutions in $CDCl_3$ were measured on a Bruker AM-500 spectrometer (500.1 MHz) in the mode of internal stabilization at the $^2$H resonance line. The $^{31}$P NMR spectra of solutions in $CDCl_3$ were recorded on a Bruker AC-200 instrument (81.4 MHz); the chemical shifts were measured relative to a 85% aqueous $H_3PO_4$ solution.

The reactions were carried out with the use of *N*,*N*′-diphenylethylenediamine (Aldrich), γ-butyrolactone (Novocherkassk Plant of Synthetic Products, TU 6-09-3610-79), phosphorus pentachloride (Plant G-4904, TU 609-3179-78), and tetraethylammonium iodide (Voikov Plant, TU 6-09-05-485-76). 2-Chloro-3-dichlorophosphino-4,5-dihydrofuran (b.p. 60—63 °C (0.5 Torr), $\delta_P$ 150.5) was prepared by the reaction of phosphorus pentachloride with γ-butyrolactone by analogy with a known procedure[5] followed by reduction of the resulting complex with tetraethylammonium iodide. *N*-Phenylbenzohydrazonoyl chloride (m.p. 130—131 °C), *p*-nitro-*N*-phenylbenzohydrazonoyl chloride (m.p. 158—159 °C), and *p*-bromophenylhydrazone of ethoxycarbonylformyl chloride (m.p. 164—165 °C) were synthesized according to procedures reported previously.[6] Phenylhydrazone of *p*-nitrobenzoylformyl bromide (m.p. 208—210 °C) was prepared analogously to the corresponding chlorides according to a known procedure.[7] Diethyl ether, THF, and triethylamine were dried over NaOH followed by distillation over sodium. Benzene was dried by azeotropic distillation with water and then distilled over sodium.

The synthesis of 2-(2-chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine (**1**) and its reactions with nitrile imines were carried out under argon with the use of anhydrous solvents and triethylamine.

**2-(2-Chloro-4,5-dihydro-3-furyl)-1,3-diphenyl-1,3-diaza-2λ$^3$-phospholidine (1).** A solution of 2-chloro-3-dichlorophosphino-4,5-dihydrofuran (6.2 g, 30 mmol) in benzene (20 mL) was added dropwise with stirring to a solution of *N*,*N*′-diphenylethylenediamine (6.4 g, 30 mmol) and triethylamine (6.6 g, 65 mmol) in benzene (150 mL) at 0—5 °C. The reaction mixture was stirred at 0—5 °C for 0.5 h and then at 20 °C for 0.5 h. Triethylamine hydrochloride was filtered off and washed with benzene (30 mL). The filtrate was concentrated under reduced pressure. The residue was treated with warm diethyl ether (100 mL), the solution was decanted from a small amount of the precipitate, and the ether was concentrated to 30% of the initial volume. The solution was kept at 0 °C for several days and then the precipitate of compound **1** that formed was filtered off. Compound **1** was obtained in a yield of 7.0 g (68%), m.p. 93—95 °C. Found (%): C, 62.51; H, 5.39; P, 8.73. $C_{18}H_{18}ClN_2OP$. Calculated (%): C, 62.71; H, 5.26; P, 8.98. IR, ν/cm$^{-1}$: 1035, 1259 (C—O—C); 1640 (C=C). $^1$H NMR, δ: 2.60 (t, 2 H, =CCH$_2$, $^3J_{H,H}$ = 9.3 Hz); 3.73 and 3.82 (both m, 2 H each, CH$_2$N); 4.33 (t, 2 H, OCH$_2$, $^3J_{H,H}$ = 9.3 Hz); 6.82—7.31 (m, 10 H, Ph). $^{31}$P NMR, δ: 70.4.

**6,8-Disubstituted 10-(2-chloroethyl)-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-dienes (5a—d) (general procedure).** A solution of 1,3-diaza-2λ$^3$-phospholidine **1** (5 mmol), the corresponding hydrazonoyl halide (5 mmol), and triethylamine (2 mL) in 20 mL of benzene (in the reaction with the use of *N*-phenylbenzohydrazonoyl chloride) or THF (in the reactions with the use of other hydrazonoyl halides) was kept at 20 °C for 3 days. Triethylamine hydrohalide (~100%) was filtered off and washed with the solvent (5 mL) in which the reaction was conducted. The solvent was distilled off under reduced pressure and the virtually crystalline residue was triturated with a 2 : 1 benzene—diethyl ether mixture (5 mL). Compounds **5a—d** were filtered off and recrystallized.

**10-(2-Chloroethyl)-9-oxo-1,4,6,8-tetraphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (5a)**, the yield was 86%, m.p. 210—212 °C (benzene). Found (%): C, 68.90; H, 5.43; P, 5.56. $C_{31}H_{28}ClN_4OP$. Calculated (%): C, 69.08; H, 5.24; P, 5.75. IR, ν/cm$^{-1}$: 1590 (C=O). $^1$H NMR, δ: 2.64 (dt, 2 H, =CCH$_2$, $^3J_{H,H}$ = 7.7 Hz, $^3J_{P,H}$ = 15.4 Hz); 3.31 (t, 2 H, CH$_2$Cl, $^3J_{H,H}$ = 7.7 Hz); 3.73 and 4.00 (both m, 2 H each, CH$_2$N); 6.92—7.51 (m, 20 H, Ph).$^{31}$P NMR, δ: 17.8.

**10-(2-Chloroethyl)-6-*p*-nitrophenyl-9-oxo-1,4,8-triphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (5b)**, the yield was 75%, m.p. 230—232 °C (acetone). Found (%): C, 63.90; H, 4.43; P, 5.52. $C_{31}H_{27}ClN_5O_3P$. Calculated (%): C, 63.75; H, 4.66; P, 5.30. IR, ν/cm$^{-1}$: 1550 (NO$_2$); 1575 (C=O). $^1$H NMR, δ: 2.64 (dt, 2 H, =CCH$_2$, $^3J_{H,H}$ = 7.5 Hz, $^3J_{P,H}$ = 15.4 Hz); 3.34 (t, 2 H, CH$_2$Cl, $^3J_{H,H}$ = 7.5 Hz); 3.82 and 4.08 (both m, 2 H each, CH$_2$N); 6.90—8.13 (m, 19 H, Ar). $^{31}$P NMR, δ: 17.8.

**8-*p*-Bromophenyl-10-(2-chloroethyl)-6-ethoxycarbonyl-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (5c)**, the yield was 82%, m.p. 201—202 °C (benzene). Found (%): C, 54.90; H, 4.33; P, 5.22. $C_{28}H_{27}BrClN_4O_3P$. Calculated (%): C, 54.78; H, 4.43; P, 5.05. IR, ν/cm$^{-1}$: 1030, 1190 (C—O—C); 1580, 1605 (C=O in the ring); 1695, 1720 (C=O in COOEt). $^1$H NMR, δ: 1.24 (t, 3 H, Me, $^3J_{H,H}$ = 7.2 Hz); 2.68 (dt, 2 H, =CCH$_2$, $^3J_{H,H}$ = 7.9 Hz, $^3J_{P,H}$ = 15.6 Hz); 3.26 (t, 2 H, CH$_2$Cl, $^3J_{H,H}$ = 7.9 Hz); 4.00 and 4.11 (both m, 2 H each, CH$_2$N); 4.17 (q, 2 H, CH$_2$O, $^3J_{H,H}$ = 7.2 Hz); 6.92—7.56 (m, 14 H, Ar). $^{31}$P NMR, δ: 18.4.

**10-(2-Chloroethyl)-6-*p*-nitrobenzoyl-9-oxo-1,4,8-triphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (5d)**, the

yield was 68%, m.p. 188—190 °C (acetone). Found (%): C, 62.90; H, 4.33; P, 5.22. $C_{32}H_{27}ClN_5O_4P$. Calculated (%): C, 62.80; H, 4.45; P, 5.06. IR, $\nu/cm^{-1}$: 1555 ($NO_2$); 1575, 1600 (C=O). $^1H$ NMR, δ: 2.75 (dt, 2 H, $=CCH_2$, $^3J_{H,H}$ = 7.9 Hz, $^3J_{P,H}$ = 15.3 Hz); 3.36 (t, 2 H, $CH_2Cl$, $^3J_{H,H}$ = 7.9 Hz); 4.05 and 4.24 (both m, 2 H each, $CH_2N$); 6.98—8.15 (m, 19 H, Ar). $^{31}P$ NMR, δ: 18.7.

**X-ray crystallography study** of crystals of 1,3-diaza-2λ$^3$-phospholidine **1** and 10-(2-chloroethyl)-6-ethoxycarbonyl-9-oxo-1,4-diphenyl-1,4,7,8-tetraaza-5-phosphaspiro[4.5]-deca-6,10-diene (**5c**) was carried out on a CAD-4 diffractometer (Mo-Kα radiation, θ/2θ scan technique). The crystals of compound **1** are monoclinic, $C_{18}H_{18}ClN_2OP$, $a$ = 10.518(2) Å, $b$ = 18.066(4) Å, $c$ = 9.828(2) Å, β = 113.25(3)°, $V$ = 1715.8(6) Å$^3$; space group $P2_1/c$, $Z$ = 4, $d_{calc}$ = 1.335 g cm$^{-3}$. The structure of **1** was solved by direct methods, $R$ = 0.0373, $R_w$ = 0.1395 (3410 reflections with $I > 2\sigma(I)$). The selected bond lengths and bond angles in molecule **1** are given in Tables 1 and 2, respectively. The crystals of compound **5c** are monoclinic, $C_{28}H_{27}BrClN_4O_3P$, $a$ = 16.422(3) Å, $b$ = 10.113(2) Å, $c$ = 18.676(4) Å, β = 113.76(3)°, $V$ = 2838.7(10) Å$^3$; space group $P2_1/c$, $Z$ = 4, $d_{calc}$ = 1.436 g cm$^{-3}$. The structure of **5c** was solved by direct methods, $R$ = 0.0437, $R_w$ = 0.1429 (2226 reflections with $I > 2\sigma(I)$). The selected bond lengths and bond angles in molecule **5c** are given in Tables 3 and 4, respectively. The atomic coordinates and the complete tables of the bond lengths and bond angles for compounds **1** and **5c** were deposited with the Cambridge Structural Database (CCDC 177905 and CCDC 177904, respectively).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32797) and by the Ministry of Education of the Russian Federation (Project No. E 00-5-317).

## References

1. Yu. G. Trishin, V. I. Namestnikov, and V. K. Belsky, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 125 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 129].
2. Yu. G. Trishin, V. I. Namestnikov, and V. K. Belsky, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1390 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1461].
3. V. I. Namestnikov, Yu. G. Trishin, and V. K. Belsky, *Zh. Obshch. Khim.*, 1996, **66**, 1404 [*Russ. J. Gen. Chem.*, 1996, **66** (Engl. Transl.)]; Yu. G. Trishin, V. I. Namestnikov, and V. K. Belsky, *Zh. Obshch. Khim.*, 1999, **69**, 767 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
4. V. I. Namestnikov and Yu. G. Trishin, *Zh. Obshch. Khim.*, 1997, **67**, 1923 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
5. S. V. Fridland, A. I. Efremov, and R. A. Salakhutdinov, *Zh. Obshch. Khim.*, 1978, **48**, 319 [*J. Gen. Chem. USSR*, 1978, **48** (Engl. Transl.)].
6. R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, 1962, **17**, 3; R. G. Dubenko and E. F. Gorbenko, *Zh. Org. Khim.*, 1968, **4**, 634 [*J. Org. Chem. USSR*, 1968, **4** (Engl. Transl.)].
7. R. G. Dubenko and P. S. Pel´kis, *Zh. Obshch. Khim.*, 1963, **33**, 3917 [*J. Gen. Chem. USSR*, 1963, **33** (Engl. Transl.)].

*Received February 15, 2002*