Reaction of 2-(4,5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza- $2\lambda^3$ -phospholidine with C,N-diphenylnitrilimine

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The reaction of 2-(4.5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza- $2\lambda^3$ -phospholidine with C.N-diphenylnitrilimine is a multistage process, in the course of which the 1,2,4-diaza-phosphorine ring is formed and both rings of the initial organophosphorus compound are cleaved. 5-(2-Chloroethyl)-4-(N,N'-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2,4\lambda^3-diazaphosphorine was obtained as the final product.

Key words: 2-(4,5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza- $2\lambda^3$ -phospholidine, C,N-diphenylnitrilimine. 5-(2-chloroethyl)-4-(N,N'-diphenylethylenediamino)-1,3-diphenyl-1,4dihydro-1,2,4 λ^5 -diazaphosphorine, IR spectra, NMR spectra, X-ray diffraction analysis.

Recently, we have found^{1.2} that the reactions of nitrilimines with 3-dialkoxyphosphino-4,5-dihydrofurans afford stable bicyclic products with a bridgehead fivecoordinate phosphorus atom adopting a trigonal-bipyramidal configuration. The route of their formation involves two stages, viz., the closure of the 1,2,4-diazaphosphorine ring simultaneously with the opening of the dihydrofuran ring in the initial P^{III} compound and the closure of the new O,P-containing ring. One would expect that the analogous reactions of nitrilimines with 3-phosphorylated 4,5-dihydrofuran containing the 1,3-diaza- $2\lambda^3$ -phospholidine residue instead of the dialkoxyphosphine group would afford tricyclic spirophosphoranes. The latter are of interest in structural chemistry of organophosphorus compounds. The assumption that these compounds can be formed is based on the fact that the reactions of substituted 1,3-diaza- $2\lambda^3$ phospholidines with a number of electrophilic reagents (hexafluoroacetone, α, α, α -trifluoroacetophenone, or phenanthrenequinone) yielded rather stable spirophosphoranes.3

We found that under mild conditions (THF, 20 °C), 2-(4,5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza- $2\lambda^{3-}$ phospholidine (1) reacted with *C*,*N*-diphenylnitrilimine, which was generated *in situ* from *N*-phenylbenzhydrazonoyl chloride under the action of triethylamine, to form 5-(2-chloroethyl)-4-(*N*,*N*'-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2,4 λ^{5} -diazaphosphorine (2) as the final product. Apparently, this reaction is a multistage process. Evidently, the reaction begins with nucleophilic attack of the phosphorus atom on the carbonium atom of the nitrilimine resulting in bipolar ion A (Scheme 1). Then the negatively charged nitrogen atom of the P⁺CNN⁻ betaine fragment attacks

position 2 of the dihydrofuran ring, which is activated with the phosphonium group. In this case, the dihydrofuran ring is cleaved at the C-O bond to form sixmembered phosphorus, nitrogen-containing heterocycle **B** with the P^+CCCO^- betaine fragment. Subsequent conversions of intermediate **B** can take two pathways. According to the first pathway (a), the O,P-heterocycle is closed with simultaneous cleavage of the P-N bond followed by protonation of betaine C with triethylamine hydrochloride (formation of salt E). The second pathway (b) involves initial protonation of the alkoxide ion of betaine **B** with triethylamine hydrochloride (formation of heterocyclic phosphonium salt **D**) followed by opening of the diazaphospholidine ring as a result of intramolecular nucleophilic attack of the alcoholic OH group on the quaternized phosphorus atom (formation of salt E). In both cases, the final stage of the reaction involves cleavage of the oxaphospholane ring of salt E under the action of a chloride ion analogously to dealkylation of phosphonium salts in the second stage of the Arbuzov reaction.

Substituted 1.4-dihydro- $1,2,4\lambda^5$ -diazaphosphorine 2 is a colorless crystalline compound, which is readily soluble in THF, acetone, chloroform, and benzene and poorly soluble in hexane and diethyl ether. The ³¹P NMR spectrum of compound 2 has a signal with the $\delta(^{31}P)$ chemical shift of -2.3 characteristic of 1,4-dihydro- $1,2,4\lambda^5$ -diazaphosphorine derivatives.⁴ The 1R spectrum of 2 has absorption bands of the NH (3375 cm⁻¹) and P=O (1195 cm⁻¹) groups. The structure of compound 2 is also confirmed by the fact that the ¹H NMR spectrum has a doublet of the alkenyl proton (δ 7.52) with a spin-spin coupling constant ³J_{PH} = 23.3 Hz, which is typical of substituted

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Ph-C(CI)=N-NH



Scheme 1

Et₃N

1,4-dihydro-1,2,4 λ^5 -diazaphosphorines.⁴ The methylene protons (=CCH₂, CH₂Cl, PNCH₂, and NHCH₂) are anisochronous and are observed as pairs of multiplets. The structure of 5-(2-chloroethyl)-4-(N, N'-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2.4λ⁵-diazaphosphorine (2) was unambiguously established by X-ray diffraction analysis (Fig. 1, Tables 1 and 2). The heterocycle adopts a strongly flattened sofa conformation. The phosphorus atom deviates from the plane of the heterocycle by 0.145 Å. The remaining atoms are coplanar to within 0.030 Å. The bond lengths in the heterocycle differ only slightly from the corresponding bond lengths in other 1.4-dihydro-1.2,4 λ^5 -diazaphosphorine derivatives. The angles between the plane of the heterocycle and the planes of the C(8)-C(13) and C(14)-C(19) benzene rings are 37.3° and 7.9°, respectively. The CH2CH2Cl chain has a trans conformation. The C(1)-C(4)-C(5)-Cl torsion angle is 178.3°.

Therefore, under mild conditions, the reaction of $2-(4,5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza-2\lambda^3-phospholidine (1) with C.N-diphenylnitrilimine yielded$

Table 1. Principal bond lengths (d) in the molecule of $5-(2-\text{chloroethyl})-4-(N,N'-\text{diphenylethylenediamino})-1,3-diphenyl-1,4-dihydro-1,2,4\lambda^5-diazaphosphorine (2)$

Et₃N · HCI,

Bond	d/A	Bond	d/Å
$\overline{CI-C(5)}$	1.801(8)	N(4) - C(8)	1.438(8)
P-0	1.474(4)	C(1) - C(2)	1.338(8)
P-N(1)	1.653(5)	C(1) - C(4)	1.521(9)
P-C(1)	1.745(6)	C(3) - C(14)	1.486(9)
P-C(3)	1.801(7)	C(4) - C(5)	1.491(10)
N(1) - C(20)	1.440(7)	C(6) - C(7)	1.506(9)
N(1)-C(6)	1.472(7)	C(8)-C(9)	1.364(11)
N(2) - C(26)	1.378(8)	C(8) - C(13)	1.372(10)
N(2) - C(7)	1.439(8)	C(9) - C(10)	1.367(15)
N(3) - C(3)	1.299(8)	C(10) - C(11)	1.35(2)
N(3) - N(4)	1.353(6)	C(11) - C(12)	1.356(19)
N(4) - C(2)	1.369(8)	C(12)-C(13)	1.375(12)

functionally substituted 1,4-dihydro-1,2,4 λ^5 -diazaphosphorine 2 instead of the expected spirophosphorane. Compound 2 may be of interest as a potential biologically active compound.

Angle	ത/deg	Angle	ω/deg
$\overline{O-P-N(1)}$	109.3(2)	C(14) - C(3) - P	120.3(6)
O - P - C(1)	115.1(3)	C(5) - C(4) - C(1)	111.3(6)
N(1) - P - C(1)	108.2(3)	C(4) - C(5) - CI	109.6(6)
0 - P - C(3)	116.9(3)	N(1) - C(6) - C(7)	112.7(6)
N(1) - P - C(3)	106.4(3)	N(2) - C(7) - C(6)	111.0(6)
C(1) - P - C(3)	100.1(3)	C(9)-C(8)-C(13)	121.2(8)
C(20) - N(1) - C(6)	116.6(5)	C(9) - C(8) - N(4)	119.5(7)
C(20) - N(1) - P	120.1(3)	C(13) - C(8) - N(4)	119.3(7)
C(6) - N(1) - P	122.6(4)	C(10) - C(9) - C(8)	119.0(12)
C(26) - N(2) - C(7)	123.6(6)	C(11) - C(10) - C(9)	120.5(14)
C(3) - N(3) - N(4)	122.0(5)	C(10)-C(11)-C(12)	120.5(12)
N(3) - N(4) - C(2)	124.8(5)	C(11)-C(12)-C(13)	120.5(13)
N(3) - N(4) - C(8)	114.2(4)	C(12) - C(13) - C(8)	118.3(10)
C(2) - N(4) - C(8)	121.0(5)	C(19) - C(14) - C(3)	122.1(6)
C(2) - C(1) - C(4)	119.3(6)	C(15)-C(14)-C(3)	120.7(6)
C(2) - C(1) - P	120.9(5)	C(21) - C(20) - N(1)	120.5(6)
C(4)C(1)-P	119.8(5)	C(25)-C(20)-N(1)	119.9(5)
C(1) - C(2) - N(4)	126.3(6)	C(31)-C(26)-N(2)	120.2(6)
N(3) - C(3) - C(14)	114.4(6)	N(2) - C(26) - C(27)	121.8(6)
N(3) - C(3) - P	125.2(6)		

Table 2. Principal bond angles (ω) in the molecule of 5-(2-chloroethyl)-4-(N,N'-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2,4 λ^{5} -diazaphosphorine (2)



Fig. 1. Overall view of the molecule of 5-(2-chloroethyl)-4-(N, N'-diphenylethylenediamino)-1,3-diphenyl-1,4-dihydro-1,2,4 λ^{5} -diazaphosphorine (2).

Experimental

The IR spectra of compounds 1 and 2 were recorded on an IKS-29 instrument in KBr pellets. The ¹H NMR spectra were measured on a Bruker AM-500 instrument (500.1 MHz) in the mode of internal stabilization at the ²H resonance line. The ³¹P NMR spectra were obtained on a Bruker instrument operating at 16.2 MHz relative to 85% H_3PO_4 .

The synthesis of $2-(4,5-dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza-2\lambda^3-phospholidine (1) and its reaction with <math>C,N$ -diphenylnitrilimine were performed under an argon atmosphere using dried solvents and triethylamine.

2-(4,5-Dihydrofur-3-yl)-1,3-diphenyl-1,3-diaza- $2\lambda^3$ -phospholidine (1). A solution of 3-dichlorophosphino-4,5-dihydrofuran² (0.05 mol) in THF (20 mL) was added dropwise with stirring to a solution of N,N'-diphenylethylenediamine (0.05 mol) and triethylamine (0.1 mol) in THF (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 THF (50 mL). The filtrate was concentrated under reduced pressure and the solid residue was recrystallized from a 1 : 2 benzene-diethyl ether mixture. The yield was 70%, m.p. 153–155 °C. Found (%): C. 69.51; H. 6.29; P. 9.83. C₁₈H₁₉N₂OP. Calculated (%): C, 69.67; H, 6.17; P, 9.98. IR, v/cm⁻¹: 1605 (Ph. C=C); 1100 (COC). ¹H NMR (C₆b₁), 8: 2.00 (td. 2 H. =CCH₂. ³J_{HH} = 9.6 Hz, ⁴J_{HH} = 2.1 Hz, ³J_{PH} ≈ 0 Hz); 3.21 (m. 4 H. NCH₂); 3.69 (t. 2 H. OCH₂. ³J_{HH} = 9.6 Hz); 6.67 (dt, 1 H, =CH, ³J_{PH} = 2.8 Hz, ⁴J_{HH} = 2.1 Hz); 6.50–7.30 (m, 10 H, Ph). ³¹P NMR (THF), 8: 70.3.

5-(2-Chloroethyl)-4-(N,N'-diphenylethylenediamino)-1,3diphenyl-1,4-dihydro-1,2, $4\lambda^5$ -diazaphosphorine (2). A solution of 1,3-diaza- $2\lambda^3$ -phospholidine 1 (0.005 mol), N-phenylbenzhydrazonoyl chloride (0.005 mol), and triethylamine (2 mL) in THF (20 mL) was kept at 20 °C for 24 h. An insignificant amount of triethylamine hydrochloride (15%) was filtered off. The filtrate was concentrated under reduced pressure and the crystalline precipitate was triturated with diethyl ether (5 mL), filtered off, and recrystallized from a 1 : 1 benzene-diethyl ether mixture. The yield was 67%, m.p. 148-150 °C. Found (%): C, 68.70; H, 5.73; P, 5.88. C₃₁H₃₀ClN₄OP. Calculated (%): C, 68.82; H, 5.59; P, 5.72. IR, v/cm⁻¹: 3370 (NH); 1195 (P=O). ¹H NMR (CDCl₃), δ: 2.57, 3.20 (both m, 1 H, =CCH₂); 2.99, 3.16 (both m, 1 H. CH2NHPh): 3.78, 3.94 (both m. 1 H, CH2Cl): 3.52, 4.04 (both m, 1 H, CH₂NP): 7.52 (d. 1 H, =CH, ${}^{3}J_{PH} = 23.3$ Hz); 6.40-8.20 (m, 20 H, Ph). ³¹P NMR (CHCl₃), δ: -2.6.

X-ray diffraction study of crystals of 2 was performed on a CAD-4 diffractometer (Mo-K α radiation, 0/20 scanning technique). The crystals of 2, C₃₁H₃₀ClN₄OP, belong to the monoclinic system, a = 11.668(2) Å, b = 28.295(6) Å, c = 8.644(2) Å, $\beta = 98.01(3)^\circ$, V = 2825.9(10) Å³; space group P_{21}/c , Z = 4, $d_{calc} = 1.272$ g cm⁻³. The structure was solved by the direct method. The *R* factor was 0.0255, $R_w = 0.0655$ (2010 reflections with $l > 2\sigma(\Lambda)$). The atomic coordinates and the complete list of the bond lengths and bond angles were deposited with the Cambridge Structural Database.

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