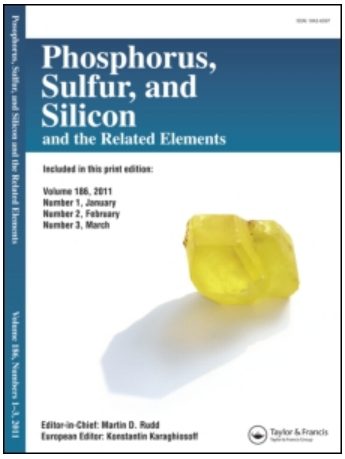

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THE SYNTHESIS AND STRUCTURE OF P(III)-PHOSPHORYLATED 2-AMINOPYRROLINES

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THE SYNTHESIS AND STRUCTURE OF P(III)-PHOSPHORYLATED 2-AMINOPYRROLINES

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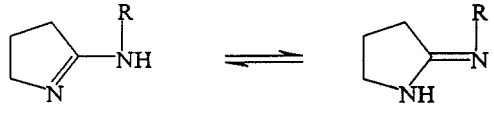
A series of derivatives of 2-aminopyrroline (2-iminopyrrolidine) and neopentylene-, pyrocatechol-phosphorous and diisopropylphosphinous acids 5, 11–13, 17, 19 has been synthesized. It was established that P(III)-phosphorylated 2-aminopyrrolines have different structures depending on nature of substituent at the exocyclic N atom: with R=Me phosphite 11 is preferably in aminopyrroline form A, with R=Ph phosphite 17 is in the iminopyrrolidine form B. The structure of the obtained compounds was studied by means of ^{1}H, ^{13}C, ^{15}N and ^{31}P NMR spectroscopy.

Key words: 2-Aminopyrroline; 2-iminopyrrolidine; tautomeric equilibrium; phosphorylation; exocyclic; endocyclic.

INTRODUCTION

In order to find new phosphorylating systems in the series of diaza derivatives of phosphorus(III) compounds we studied earlier the synthesis and structure of phosphorylated 2-aminopyridines, for which proto- and phosphorotropic tautomerism could be expected. It was established that these compounds exist preferably in phospha(III)-aminopyridine form.[1] Their alkylation and protonation did not lead to the expected shift of equilibrium to a phospha(III)iminopyridone form.[2] We connected this fact with the known stability of the aminopyridine fragment in relation to the disturbance of its aromatic nature at possible transition from aminopyridine to iminopyridone form. That is why in the present paper we paid our attention to P(III)-phosphorylated cyclic amidines of non-aromatic character. For these compounds higher tendency to prototropic processes and thus increased ability to phosphorylation of proton donor nucleophiles can be expected.[3] For our studies we chose derivatives of 2-aminopyrroline A which, as it is known,[4] can exist also in 2-iminopyrrolidine form B or as tautomeric equilibrium (A⇌B) depending on the nature of substituent R.



A B

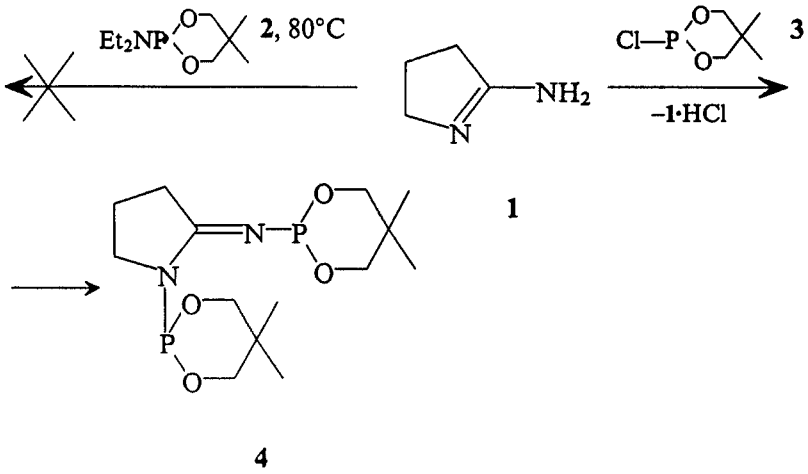
SCHEME 1

†To whom correspondence should be addressed.

Note that though structure and tautomerism of the simplest cyclic amidines have been studied in detail (e.g., see References 4 and 5), the dynamics of phosphorylated derivatives of this class was studied only in fragments, mostly for pentavalent phosphorus.[6]

RESULTS AND DISCUSSION

We started with the study of phosphorylation of unsubstituted 2-aminopyrroline 1 by 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane 2 (C_6H_6, reagent concentration 1 mol·l^{-1}). We found that transamination does not take place at heating up to 80°C for 10 hrs even in the presence of a catalyst (hydrochloride of amidine 1, 5 mol.% of initial reagents). Under more severe conditions destructive processes were observed. Note that phosphorylation of 2-aminopyridine by amide 2 occurs rather easily and produces the expected product of monophosphorylation of the primary aminogroup with good yield (75.0%).[2] Phosphorylation of amidine 1 by means of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane 3 also led to unexpected results. Thus interaction of equimolar amounts of reagents in the presence of triethylamine, led to the formation of diphosphorylated product 4, contaminated with chlorophosphite 3. However, when the ratio of reagents 1 and 3 was 3:2 practically only the diphosphorylated derivative 4 is formed, isolated with 80% yield:

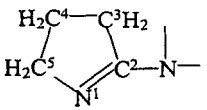


SCHEME 2

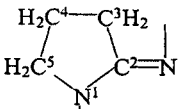
Unlike diphosphorylated 2-aminopyridine[2] diphosphorylation of amidine 1 leads to the compound 4 which contains phosphorus substituent at different nitrogen atoms. Such structure is proved by nonequivalence of protons and carbon atoms of two dioxaphosphorinane fragments in ^{1}H and ^{13}C NMR spectra (see Tables I and II). ^{31}P NMR spectrum of the obtained compound contains two singlet signals of equal intensity with chemical shifts δ = 114 and 124, which refer to the phosphorus atoms on exocyclic and endocyclic nitrogen atoms respectively. The imi-

TABLE I

The parameters of ^1H NMR spectra of compounds 1, 4, 5, 8, 11–24 (c 0.5 mol·l^{-1}) (δ)



A
1, 8, 11–13, 14A



B
4, 5, 14B, 15–24

Compound	Solvent	H^3 ($^3J_{H^3H^4}$, Hz)	H^4 ($^3J_{H^4H^3}$, $^3J_{H^4H^5}$, Hz)	H^5 ($^3J_{H^5H^4}$, Hz)	Other signals
1	$CDCl_3$	2.34 (8.1) (a)	1.89 (8.1, 7.0)	3.51 (7.0)	4.5 (br.s., 2H, NH_2)
4	C_6D_6	2.31 (7.9)	1.35 (7.9, 6.9)	2.79 (6.9)	0.40, 0.52 (2s, 6H, CH_3eq), 1.05, 1.36 (2s, 6H, CH_3ax), 2.40, 3.01 (2m, 4H, OCHeq), 3.30, 3.57 (2m, 4H, OCHax)
5	C_6D_6	2.32 (8.0)	1.35 (8.0, 7.1)	2.83 (7.1)	0.39 (s, 3H, CH_3eq), 1.31 (s, 3H, CH_3ax), 3.25 (m, 2H, OCHeq), 4.36 (m, 2H, OCHax), 8.17 (br.s., 1H, NH)
8	$CDCl_3$	2.31 (8.1) (a)	1.86 (8.1, 7.0)	3.57 (7.0)	2.78 (s, 3H, CH_3), 4.5 (br.s., 1H, NH)
11	$CDCl_3$	2.63 (8.0)	1.92 (8.0, 7.1)	3.60 (7.1)	0.81 (s, 3H, CH_3eq), 1.14 (s, 3H, CH_3ax), 3.05 (d, 3H, NCH_3, $^3J_{HCNP}$ 2.3Hz), 3.70 (m, 2H, OCHeq) 3.80 (m, 2H, OCHax)
	C_6D_6	2.52 (8.1)	1.59 (8.1, 7.0)	3.63 (7.0)	0.4 (s, 3H, CH_3eq), 0.94 (s, 3H, CH_3ax), 3.39 (s, 3H, NCH_3), 3.46 (m, 2H, OCHeq), 3.58 (m, 2H, OCHax)
12	C_6D_6	2.26 (8.2) (b)	1.46 (8.2, 7.0)	3.51 (7.0) (c)	2.77 (d, 3H, CH_3, $^3J_{HCNP}$ 1.9Hz), 6.67 (m, 2H, OCCHCH), 6.86 (m, 2H, OCCH)

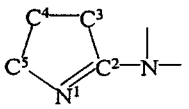
Compound	Solvent	H^3 ($^3J_H3_H4$, Hz)	H^4 ($^3J_H4_H3$, $^3J_H4_H5$, Hz)	H^5 ($^3J_H5_H4$, Hz)	Other signals
13	$CDCl_3$	2.58 (8.0)	1.80 (8.0, 7.0)	3.52 (7.0)	0.86–0.95 (m, 12H, $CHC\underline{H}_3$), 1.85 (m, 2H, $C\underline{H}CH_3$), 2.79 (s, 3H, NCH_3)
	C_6D_6	2.79 (8.0)	1.78 (8.0, 7.0)	3.85 (7.0)	0.92–0.98 (m, 12H, $CHC\underline{H}_3$), 1.71 (m, 2H, $C\underline{H}CH_3$), 3.01 (s, 3H, NCH_3)
14A (d)	C_6D_6	2.18 (8.1) (e)	1.69 (8.1, 7.1)	3.75 (7.1)	0.29 (s, 9H, $SiCH_3$), 2.73 (s, 3H, NCH_3)
14B (d)	C_6D_6	1.98 (7.9)	1.54 (7.9, 7.1)	2.98 (7.1)	0.39 (s, 9H, $SiCH_3$), 3.03 (s, 3H, NCH_3)
15	C_6D_6	2.10 (8.0)	1.39 (8.0, 7.0)	3.03 (7.0)	6.98 (m, 2H, CHortho), 7.24 (m, 4H, CHmetha, para, NH)
16 (d)	C_6D_6	2.05 (8.0)	1.48 (8.0, 6.9)	2.98 (6.9)	0.34 (s, 9H, $SiCH_3$), 6.77 (m, 2H, CHortho), 6.87 (m, 1H, CHpara), 7.16 (m, 2H, CHmetha)
17	C_6D_6	2.06 (8.1) (f)	1.37 (8.1, 7.0)	3.24 (7.0) (g)	0.51 (s, 3H, CH_3eq), 0.93 (s, 3H, CH_3ax), 3.38 (m, 2H, OCHeq), 3.70 (m, 2H, OCHax), 6.90 (d, 2H, CHortho), 6.92 (t, 1H, CHpara), 7.18 (t, 2H, CHmetha)
18	$CDCl_3$	2.31 (8.2)	1.86 (8.2, 7.0)	3.57 (7.0)	2.78 (s, 3H, CH_3)
19	C_6D_6	2.40 (8.0) (h)	1.23 (8.0, 7.2)	2.63 (7.2) (i)	0.47 (s, 3H, CCH_3eq), 1.32 (s, 3H, CCH_3ax), 2.65 (m, 3H, NCH_3, $^5J_{(H_3C)H}3$ 0.8Hz, $^5J_{(H_3C)P}$ 0.8 Hz), 3.29 (m, 2H, OCHeq), 4.70 (m 2H, OCHax)
20	$CDCl_3$	2.91 (7.8)	2.08 (7.8, 7.1)	3.78 (7.1)	0.85, 0.99 (2s, 6H, CH_3eq), 1.02, 1.30 (2s, 6H, CH_3ax), 3.80–4.00 (2m, 4H, OCHeq), 4.09, 4.17 (2m, 4H, OCHax)

21	$CDCl_3$	3.10 (8.1) (j)	2.11 (8.1, 6.9)	3.72 (6.9) (k)	0.89, 0.92 (2s, 6H, CH_3eq) 1.13, 1.30 (2s, 6H, CH_3ax), 3.89–4.02 (2m, 4H, OCHeq), 4.16, 4.29 (2m, 4H, OCHax)
22	$CDCl_3$	2.69 (8.1) (l)	2.04 (8.1, 7.1)	3.51 (7.1) (m)	0.95 (s, 3H, CH_3eq), 1.06 (s, 3H, CH_3ax), 3.86 (m, 2H, OCHeq), 4.15 (m, 2H, OCHax)
23	$CDCl_3$	2.43 (7.8)	1.92 (7.8, 7.0)	3.80 (7.0) (n)	0.98 (s, 3H, CH_3eq), 1.16 (s, 3H, CH_3ax) 4.12 (m, 2H, OCHeq), 4.33 (m, 2H, OCHax), 6.77 (d, 2H, CHortho), 6.98 (t, 1H, CHpara), 7.22 (t, 2H, CHmetha)
24	$CDCl_3$	3.04 (8.2)	2.01 (8.2, 7.3)	3.44 (7.3)	0.96 (s, 3H, CCH_3eq), 1.06 (s, 3H, CCH_3ax), 2.94 (t, 3H, NCH_3, $^5J_{(H_3C)H}$3 1.0 Hz)

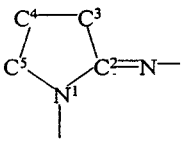
a) $^4J_H3_H5$ 1.0 Hz; b) $^4J_H3_H5$ 1.4 Hz, $^4J_H3_P$ 2.6 Hz; c) $^5J_H5_P$ 1.4 Hz; d) the data from ref. 7; e) $^4J_H3_H5$ 1.4 Hz; f) $^4J_H3_P$ 1.0 Hz; g) $^3J_H5_P$ 0.4 Hz; h) $^4J_H3_H5$ 0.8 Hz; i) $^5J_H5_P$ 1.3 Hz; j) $^4J_H3_P$ 2.0 Hz; k) $^3J_H5_P$ 0.5 Hz, $^5J_H5_P$ 1.4 Hz; l) $^4J_H3_P$ 2.1 Hz; m) $^5J_H5_P$ 0.3 Hz; n) $^3J_H5_P$ 1.9 Hz.

TABLE II

The parameters of ^{13}C NMR spectra of compounds 1, 4, 5, 8, 11–24 (c 1.0 mol·l^{-1}) (δ)



A
1, 8, 11–13, 14A

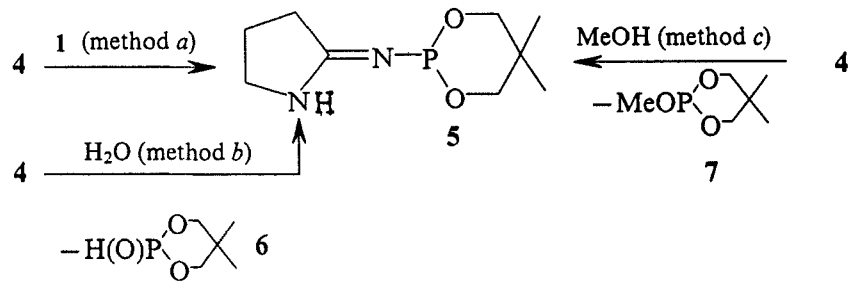


B
4, 5, 14B, 15–24

Compound	Solvent	C^2 (J_{CP}, Hz)	C^3 (J_{CP}, Hz)	C^4 (J_{CP}, Hz)	C^5 (J_{CP}, Hz)	Other signals
1	$CDCl_3$	167.3	32.5	23.6	55.4	
4	C_6D_6	172.1 (33.6, 12.3)	30.5 (18.5)	21.9 (3.3)	45.7 (2.4)	22.2, 22.6 (CH_3eq), 23.0, 23.5 (CH_3ax), 32.4 ($\underline{C}CH_3$, $^3J_{CP}$ 4.8 Hz), 33.5 ($\underline{C}CH_3$, $^3J_{CP}$ 4.7 Hz), 68.5 (OCH_2, $^2J_{CP}$ 2.5 Hz), 71.9 (OCH_2, $^2J_{CP}$ 1.6 Hz)
5	C_6D_6	171.1 (24.4)	30.5 (18.1)	22.0 (3.3)	43.5 (≤0.5)	22.7 (CH_3eq), 23.0 (CH_3ax), 33.2 ($\underline{C}CH_3$, $^3J_{CP}$ 4.5 Hz), 68.6 (OCH_2, $^2J_{CP}$ 1.0 Hz)
8	$CDCl_3$	167.3	32.5 (a)	23.5 (b)	56.2 (c)	29.4 (CH_3, $^1J_{CH}$ 136.3 Hz)
11	$CDCl_3$	167.2 (31.6)	33.1 (24.8)	23.9 (6.1)	55.7 (≤0.5)	21.8 (CH_3eq), 23.1 (CH_3ax, $^3J_{CP}$1.7 Hz), 29.4 (NCH_3, $^2J_{CP}$3.0 Hz), 32.8 ($\underline{C}CH_3$, $^3J_{CP}$8.7 Hz), 73.9 (OCH_2, $^2J_{CP}$4.9 Hz)
12	C_6D_6	164.3 (33.5)	32.9 (27.9)	24.0 (7.3)	55.9 (≤1.0)	28.9 (NCH_3, $^2J_{CP}$3.7 Hz), 111.8 (OCC$\underline{C}$arom), 122.8 (OC$\underline{C}$arom), 146.7 (O$\underline{C}$arom, $^2J_{CP}$8.1 Hz)
13	C_6D_6	171.4 (26.9)	35.1 (22.0)	25.0 (7.3)	57.8 (≤1.0)	19.5, 19.8, 20.0, 20.1 ($\underline{C}CH_3$), 26.7 (NCH_3, $^2J_{CP}$17.1 Hz), 33.6 ($\underline{C}CH_3$, $^1J_{CP}$7.3 Hz)
14A (d)	C_6D_6	169.8	32.8	24.0	56.7	0.71 (SiC), 33.4 (NCH_3)
14B (d)	C_6D_6	168.6	25.9	23.4	46.5	0.41 (SiC), 38.6 (NCH_3)

15	$CDCl_3$	163.9	30.4	22.2	47.2	121.2 (Cortho), 122 (Cpara), 129.0 (Cmetha), 149.0 (Cipso)
16 (d)	C_6D_6	167.4	28.2	23.6	47.2	−0.46 (SiC), 121.6 (Cpara), 122.3 (Cortho), 128.8 (Cmetha), 153.3 (Cipso)
17	C_6D_6	164.8 (10.3)	28.2 (1.3) (e)	22.8 (2.1) (f)	45.9 (≤0.5) (g)	22.2 (CH_3eq, $^4J_{CP} \leq 0.5$ Hz), 22.7 (CH_3ax, $^4J_{CP}$1.7 Hz), 32.5 ($\underline{C}CH_3$, $^3J_{CP}$5.4 Hz), 72.5 (OCH_2), 122.2 (Cortho), 122.3 (Cpara), 128.9 (Cmetha), 152.5 (Cipso)
18	$CDCl_3$	169.0	32.1 (h)	19.1 (i)	51.8 (j)	30.4 (CH_3, $^1J_{CH}$136.5 Hz)
19	C_6D_6	167.5 (33.4)	29.8 (21.1)	19.2 (4.7)	49.6 (≤0.5)	23.0 ($C\underline{C}H_3$eq, $^4J_{CP}$1.5 Hz), 23.4 ($C\underline{C}H_3$ax), 30.4 (NCH_3, $^2J_{CP} \leq 0.5$ Hz), 33.4 ($\underline{C}CH_3$, $^3J_{CP}$4.5 Hz), 67.8 (OCH_2, $^2J_{CP}$2.3 Hz)
20	$CDCl_3$	176.6 (12.5)	33.4 (5.7, 9.3)	21.5 (8.3)	49.7 (5.0)	20.2, 21.2 (CH_3eq), 21.8, 22.5 (CH_3ax), 32.1 ($\underline{C}CH_3$, $^3J_{CP}$9.7 Hz), 32.3 ($\underline{C}CH_3$, $^3J_{CP}$5.2 Hz), 75.0 (OCH_2, $^2J_{CP}$6.3 Hz), 79.6 (OCH_2, $^2J_{CP}$5.4 Hz)
21	$CDCl_3$	173.7 (13.0, 13.5)	32.4 (7.0, 7.0)	21.1 (8.2)	49.5 (4.5, 1.5)	20.7, 21.4 (CH_3eq), 21.8, 22.6 (CH_3ax), 32.1 ($\underline{C}CH_3$, $^3J_{CP}$7.6 Hz), 32.5 ($\underline{C}CH_3$, $^3J_{CP}$7.0 Hz), 76.0 (OCH_2, $^2J_{CP}$6.0 Hz), 78.7 (OCH_2, $^2J_{CP}$9.1 Hz)
22	$CDCl_3$	174.5 (≤1.0)	33.7 (16.7)	20.3 (≤0.5)	45.9 (≤0.5)	21.4 (CH_3eq), 22.2 (CH_3ax), 32.8 ($\underline{C}CH_3$, $^3J_{CP}$6.7 Hz), 78.6 (OCH_2, $^2J_{CP}$8.4 Hz)
23	$CDCl_3$	161.1 (1.9)	29.0 (7.7)	21.8 (9.9)	50.6 (7.7)	21.6 (CH_3eq), 22.7 (CH_3ax), 32.3 ($\underline{C}CH_3$, $^3J_{CP}$8.0 Hz), 78.8 (OCH_2, $^2J_{CP}$8.7 Hz), 120.9 (Cortho), 122.9 (Cpara), 128.9 (Cmetha), 150.3 (Cipso)
24	$CDCl_3$	171.1 (16.7)	31.2 (6.4)	18.7 (≤0.5)	51.4 (≤0.5)	21.3 (CH_3eq), 22.1 (CH_3ax), 31.4 (NCH_3, $^4J_{CP} \leq 0.5$ Hz), 32.6 ($\underline{C}CH_3$, $^3J_{CP}$5.5 Hz), 75.2 (OCH_2, $^2J_{CP}$6.1 Hz)

a) $^1J_C3_H$ 130.2 Hz; b) $^1J_C4_H$ 130.8 Hz; c) $^1J_C5_H$ 138.8 Hz; d) the data from ref. 7; e) $^1J_C3_H$ 133.0 Hz, $^2J_C3_H4$ 3.6 Hz, $^3J_C3_H5$ 3.6 Hz; f) $^1J_C4_H$ 131.6 Hz, $^2J_C4_H3$ 3.2 Hz; g) $^1J_C5_H$ 141.5 Hz, $^2J_C5_H4$ 3.2 Hz, $^3J_C5_H4$ 3.2 Hz; h) $^1J_C3_H$ 132.3 Hz; i) $^1J_C4_H$ 133.1 Hz; j) $^1J_C5_H$ 140.1 Hz



SCHEME 3

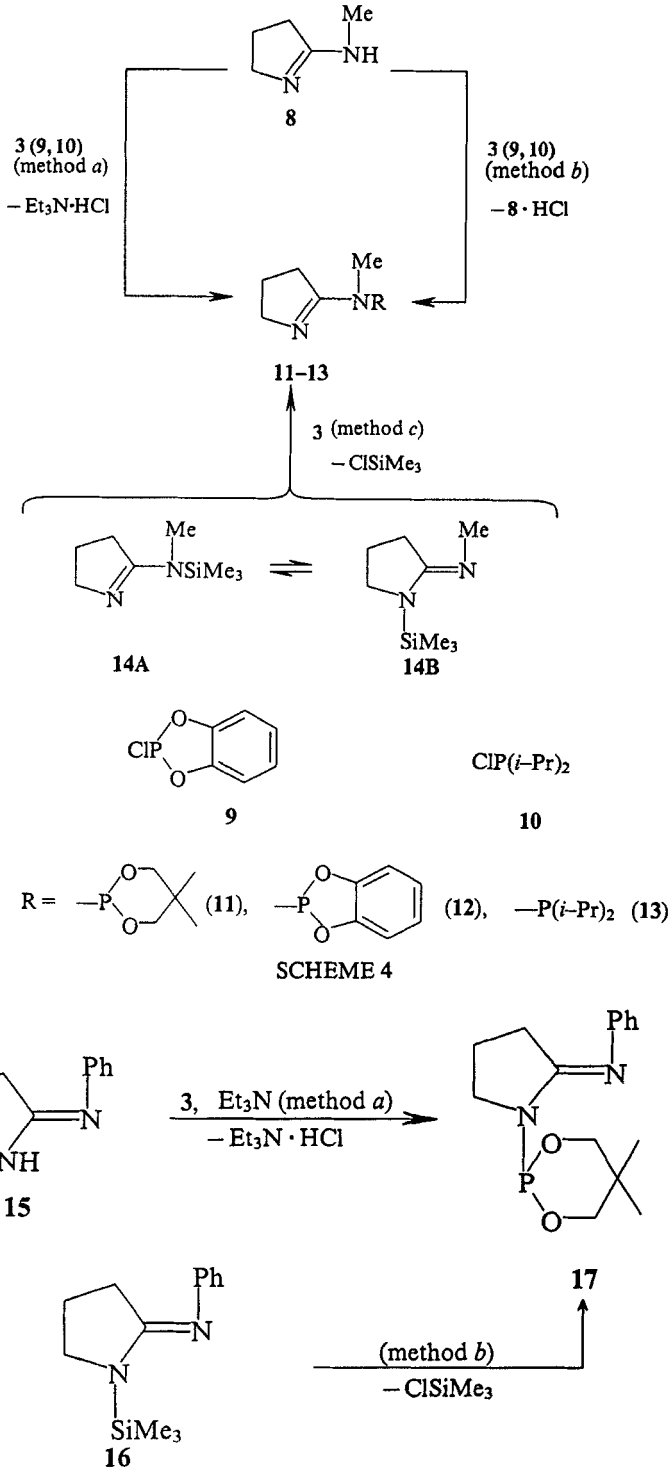
nostructure of compound 4 is also proved by ^{13}C NMR data (for the discussion see below).

The above mentioned fact of diphosphorylation is connected with the higher basicity of amidine 1 in comparison with that of triethylamine. Besides, we can propose that the intermediate product of monophosphorylation 5 can be phosphorylated more easily than amidine 1. We could isolate the monophosphoamidine 5 it with 60.0% yield by means of aminolysis of diphosphorylated product 4 by amidine 1 (method a). Moreover, this compound is also formed by hydrolysis (method b) and methanolysis (method c) of the diphosphorylated product 4 together with a derivative of phosphorous acid 6 and phosphite 7, respectively (see Experimental).

Unlike amidine 1 phosphorylation of 2-methylaminopyrroline 8 by chlorophosphite 3, pyrocatecholchlorophosphite 9 or diisopropylchlorophosphine 10 in the presence of triethylamine (method a) or a second equivalent of amidine 8 (method b) occurs with a good yield (70–85%) and leads to the formation of the corresponding aminophosphites 11, 12 and amino phosphine 13, containing the phosphorus residue at the exocyclic nitrogen atom. Aminophosphite 11 was obtained also from chlorophosphite 3 and the trimethylsilyl derivative 14 (method c) which, as it was determined earlier,[7] exists as a tautomeric mixture 1:4 of aminopyrroline form A and iminopyrrolidine form B, respectively. As well as in the case of aminophosphite 5, we could not obtain aminophosphite 11 by means of transamination of aminophosphite 2 by amidine 8 (80°C, 10 hrs).

At the same time phosphorylation of the 2-phenylimine analogue 15 (method a) and its trimethylsilyl derivative 16 (method b), which exist in the iminopyrrolidine form B,[4,7] by chlorophosphite 3 leads to the formation of aminophosphite 17 containing the phosphorus fragment at the endocyclic nitrogen atom.

Thus, unlike P(III)-phosphorylated 2-aminopyridines[1,2] the corresponding derivatives of 2-aminopyrrolines of non-aromatic nature can have different structure depending on the nature of the substituent at the exocyclic nitrogen atom. Meanwhile, according to ^1H NMR data heating of solutions of aminophosphites 11, 17 ($CDCl_3$, 1 mol/l^{-1}) in sealed ampoules (80°C, 2 hrs) even in the presence of a catalyst (hydrochloride of amidine 8 or 15, 5 mol.% of the initial amino-phosphites 11 or 17, respectively) does not lead to any observed phosphorotropic shift to another form (A or B), as it was found for some derivatives of phosphorous(V) and amidine 8.[6]



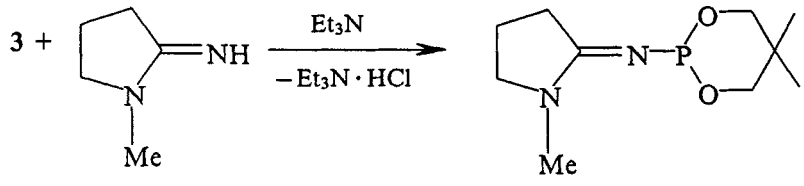
SCHEME 4

SCHEME 5

In order to make easier spectral identification of the A and B forms, derivative 19, existing in the fixed iminoform B, was prepared by interaction of chlorophosphite 3 and 1-methyl-2-imino-pyrrolidine 18.

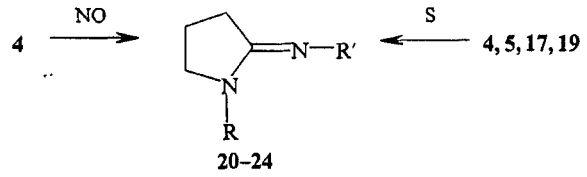
The obtained phosphorylated derivatives of pyrrolines 1, 8, 15 and 18 display the usual properties of trivalent phosphorus compounds. Thus they can be easily oxidized by nitrogen oxides and they add sulphur with the formation of corresponding phosphates and thionphosphates, respectively.

The structure of the synthesized compounds 4, 5, 11–14, 16–24, with the exception of 18, 19, 24 can exist in one or simultaneously in two tautomeric amino- (A) and imino- (B) forms, as clearly indicated by the ^{1}H, ^{13}C, ^{31}P and ^{15}N NMR spectra. Earlier it was shown, for example for derivatives of 2-aminopyrrolines[4] and their P(V) derivatives,[6] that in ^{1}H and ^{13}C NMR spectra signals for the protons and carbon atoms at positions 3 and 5 of the diazaheterocycle in aminopyrroline form A are at a lower field than signals of these nuclei in iminopyrrolidine form B. Though for a large group of the presented compounds ^{1}H NMR spectra (Table I) confirm in the whole this tendency, differences in ^{13}C NMR spectra of the two tautomeric forms are more definite and can serve as a reliable criterion for their



18 **19**

SCHEME 6



20–24

R = R′ = —(O)P (**20**); R = R′ = —(S)P (**21**);

R = H, R′ = —(S)P (**22**); R = —(S)P, R′ = Ph (**23**);

R = Me, R′ = —(S)P (**24**)

SCHEME 7

identification (Table II). Thus chemical shifts of C^3 signals of the compounds existing in A form (1, 8, 11–13, 14A) are in the area of δ = 32.5–35.1, while for the compounds in B form (4, 5, 14B, 15–24) they are correspondingly in the range of δ = 25.9–33.7. This difference becomes even more distinct for chemical shifts of C^5: δ = 55.4–57.8 and 43.7–51.8 for A and B forms, respectively. To make correct signal reference in ^1H and ^{13}C NMR spectra of the compounds 20, 21, 24, especially in the case of equilibrium mixture of tautomeric forms 14A⇌14B, the technique of 2D spectroscopy was used (COSY, HETCOR).

As it follows from ^1H NMR spectra, $^3J_{H}4_{H}5$ constant is smaller than $^3J_{H}3_{H}4$ constant. This fact can be used as the criterion for the identification of H^3 and H^5 signals. Besides, in ^1H NMR spectra obtained with high resolution we observed long range constants $^4J_{H}3_{H}5$ (only for form A – 1, 8, 12, 14A) as well as long range constants $^4J_{H}3_{P}$, $^5J_{H}5_{P}$ (for 12, 17, 19, 21–23) and $^5J_{CH_3P}$ (for 19, 24).

^{13}C NMR spectra of heterocycles phosphorylated at the exocyclic N-atom existing in both amino- and iminoforms are characterized by large values of the constants $^2J_{C}2_{P}$ and $^3J_{C}3_{P}$ (see Table II). According to the stereospecificity of these constants for trivalent phosphorus,[8] it follows that in compounds 11, 12 and 13 the amino-group and the unshared electron pair of phosphorus are situated in the plane of the diazaheterocycle. The difference in constants $^2J_{C}2_{P}$ and $^3J_{C}3_{P}$ for the compounds 22 and 24 is likely due to the changes of orientation of the thiophosphoryl group relative to the double C=N bond (Z,E-isomerisation).

The existence of compounds 11, 12 and 13 preferably in amino-form A is confirmed by the calculation of the minimal energies of both tautomeric forms by means of the molecular mechanics.[9] The minimal energy of the aminoform A is more than 10 kcal mol^{-1} lower than the energy of iminoform B.

Earlier for establishing the structure of P(III) phosphorylated 2-aminopyridine the ^{15}N NMR spectroscopy has proved to be the most efficient.[2] In our case this method, as it was shown for compounds 11, 17 (see Experimental) does not allow to identify reliably tautomeric forms because chemical shifts of nitrogen atoms in amino- and iminoforms are close together and do not depend on their endo- or exo-position. In both cases the highfield doublet ($^1J15_{NP}$ 71–75 Hz) indicates only that phosphorus is at the amino-nitrogen (not imino-) atom in endo- or exo-position. Nevertheless in the case of compound 5 the downfield doublet signal with constant $^1J15_{NH}$ 65 Hz indicates that this compound exists preferably in iminoform B with the phosphorus atom at the exocyclic imino-nitrogen atom. This result is in agreement with ^1H and ^{13}C NMR data (see above).

EXPERIMENTAL

All the experiments with the P(III)-derivatives are performed in an atmosphere of dry nitrogen and in dried solvents.[10] 2-Aminopyrroline 1, 2-methylaminopyrroline 8, 2-phenyliminopyrrolidine 15 and 1-methyl-2-iminopyrrolidine 18, were obtained as described,[11,12] respectively. The preparations of the tautomeric mixture of 2-trimethylsilylmethylaminopyrrolidine 14A and 1-trimethylsilyl-2-methyliminopyrroline 14B (1:4), as well as 1-trimethylsilyl-2-phenyliminopyrrolidine 16 were described previously.[7]

^1H, ^{13}C and ^{15}N NMR spectra were obtained on Bruker AM-400 spectrometer and ^{31}P spectra—on Bruker WP-80 spectrometer at frequencies 400.0, 100.5, 40.5 and 32.4 MHz respectively. The spectra of 2D-spectroscopy H,H-COSY and H,C-HETCOR were registered on a Varian XL-400 spectrometer according to the standard programs. External TMS standard for ^1H and ^{13}C NMR spectra and external NH_3 and 85% H_3PO_4 standards for ^{15}N and ^{31}P NMR spectra were used, respectively.

1-(5,5-Dimethyl-1,3,2-dioxaphosphorinane-2-yl)-2-(5,5-dimethyl-1,3,2-dioxaphosphorinane-2-yl) iminopyrrolidine 4. Chlorophosphite 3 (3.39 g, 20.0 mmol) was added dropwise with stirring to a solution of 2-aminopyrroline 1 (2.52 g, 30.0 mmol) in benzene (40 ml) at +5°C. The suspension was stirred at 20°C for 4 hrs. The precipitate was filtered off, the solution was evaporated under reduced pressure and the residue was washed with hexane (3 3 ml) to obtain diphosphorylated pyrrolidine 4 (2.96 g, 85.0% yield), m.p. 84–85°C. Found, %: C 48.45, H 7.69, P 17.58. Calcd. for $C_{14}H_{26}N_2O_4P_2$, %: C 48.27, H 7.54, P 17.78. ^{31}P NMR (C_6H_6): δ = 114 and 124 (ratio of intensities 1:1).

2-(2-Pyrrolidineimino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 5.

(a) 2-Aminopyrroline 1 (0.84 g, 10.0 mmol) was dissolved in a solution of diphosphorylated pyrrolidine 4 (3.48 g, 10.0 mmol) in benzene (20 ml) at 60°C for 1.5 hrs. The solvent was evaporated under reduced pressure and the residue was recrystallized from benzene (5 ml) to give 5 (3.20 g, 74.0% yield), m.p. 104–105°C. Found, %: C 50.15, H 7.71, P 14.05. Calcd. for $C_9H_{17}N_2O_2P$, %: C 49.98, H 7.94, P 14.33. ^{15}N NMR (C_6H_6): δ = 114 (N_{endo}, $^3J15_{NP}$ 4 Hz), 199 (N_{exo}, $^1J15_{NP}$ 65 Hz). ^{31}P NMR (C_6H_6): δ = 127.

(b) Water (0.09 g, 5.0 mmol) was added with stirring to a solution of diphosphorylated pyrrolidine 4 (1.74 g, 5.0 mmol) in benzene (8 ml). The emulsion was stirred at 80°C for 0.5 hr and the solvent was evaporated under reduced pressure. The residue was dissolved in benzene (2 ml) and the solution was kept in a cold place (10°C). The precipitate was filtered off and washed with cold benzene (1 ml) to obtain amide 5 (0.61 g, 56.0% yield), m.p. 104–105°C. ^{31}P NMR (C_6H_6): δ = 127.

(c) Methanol (0.16 g, 5.0 mmol) was added with stirring to a solution of diphosphorylated pyrrolidine 4 (1.74 g, 5.0 mmol) in benzene (8 ml). The solution was stirred at 60°C for 1.5 hrs and treated as described in method b to obtain amide 5 (0.54 g, 50.0% yield), m.p. 104–105°C. ^{31}P NMR (C H): δ = 127.

2-(2-Pyrrolinemethylamino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 11.

(a) Chlorophosphite 3 (5.26 g, 31.0 mmol) was added dropwise with stirring to a solution of 2-methylaminopyrroline 8 (3.04 g, 31.0 mmol) and triethylamine (3.44 g, 34.0 mmol) in benzene (30 ml) at 20°C. The suspension was stirred at 20°C for 2 hrs. The precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was distilled in vacuum to give 11 (5.71 g, 80.0% yield), b.p. 106–107°C at 1 mm Hg, m.p. 56–57°C. Found, %: C 52.05, H 8.51, P 13.63. Calcd. for $C_{10}H_{19}N_2O_2P$, %: C 52.15, H 8.33, P 13.45. ^{31}P NMR (C_6H_6): δ = 139.

(b) By analogy with method a, from chlorophosphite 3 (5.26 g, 31.0 mmol) and 2-methylaminopyrroline 8 (6.09 g, 62.0 mmol) in benzene (30 ml) the amide 11 (6.07 g, 85.0% yield) was obtained, b.p. 106–107°C at 1 mm Hg, m.p. 56–57°C. ^{31}P NMR (C_6H_6): δ = 139.

(c) A solution of chlorophosphite 3 (5.09 g, 30.0 mmol) and tautomeric mixture of 14A and 14B (1:4) (5.11 g, 30.0 mmol) in benzene (10 ml) was kept for 4 hrs at 20°C. Trimethylchlorosilane was distilled off under reduced pressure, the residue was distilled in vacuum to give the amide 11 (4.84 g, 70.0% yield), b.p. 106–108°C at 1 mm Hg, m.p. 56–57°C. ^{15}N NMR (C_6H_6): δ = 97 (N_{endo}, $^1J15_{NP}$ 71 Hz), 238 (N_{exo}, $^3J15_{NP}$ 2 Hz). ^{31}P NMR (C_6H_6): δ = 139.

2-(2-Pyrrolinemethylamino)-3,4-benzo-1,3,2-dioxaphospholane 12. 2-Chloro-4,5-benzo-1,3,2-dioxaphospholane 9 (1.95 g, 11.2 mmol) was added dropwise with stirring to a solution of 2-methylaminopyrroline 8 (1.10 g, 11.2 mmol) and triethylamine (1.21 g, 12.0 mmol) in benzene (10 ml) at 20°C. The suspension was stirred at 20°C for 2 hrs. The precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was washed with hexane to obtain 12 (2.20 g, 83.0% yield), a viscous pale yellow substance. Found, %: C 54.78, H 5.73, P 13.31. Calcd. for $C_{11}H_{13}N_2O_2P$, %: C 55.92, H 5.56, P 13.11. ^{31}P NMR (C_6H_6): δ = 146.

2-Pyrrolinemethylaminodiisopropylphosphine 13. By analogy with amide 11 (method a), from diisopropylchlorophosphine (3.66 g, 24.0 mmol), 2-methylaminopyrroline 8 (2.36 g, 24.0 mmol) and triethylamine (2.63 g, 26.0 mmol) in benzene (20 ml) 13 (3.86 g, 75.0% yield) was obtained, b.p. 83–84°C at 1 mm Hg. Found, %: C 61.78, H 7.41, P 10.45. Calcd. for $C_{11}H_{23}N_2P$, %: C 61.64, H 7.25, P 10.60. ^{31}P NMR (C_6H_6): δ = 75.

2-(2-Phenyliminopyrrolidine-1-yl)-5,5-dimethyl-1,3,2-dioxaphosphoinane 17.

(a) Chlorophosphite 3 (5.26 g, 31.0 mmol) was added dropwise with stirring to a solution of 2-phenyliminopyrrolidine 15 (5.00 g, 31.0 mmol) and triethylamine (3.44 g, 34.0 mmol) in benzene (30 ml) at 20°C. The suspension was stirred at 20°C for 2 hrs. The precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was recrystallized from hexane to obtain 17 (7.70 g, 85.0% yield), m.p. 78–79°C. Found, %: C 61.51, H 7.15, P 10.68. Calcd. for $C_{15}H_{21}N_2O_2P$, %: C

61.62, H 7.25, P 10.60. ^{15}N NMR (C_6H_6): δ = 114 (N_{endo}, $^1J15_{NP}$ 75 Hz), 233 (N_{exo}, $^3J15_{NP}$ 12 Hz). ^{31}P NMR (C_6H_6): δ = 118.

(b) A solution of chlorophosphite 3 (5.60 g, 33.0 mmol) and 1-trimethylsilyl-2-phenyliminopyrrolidine 16 (7.67 g, 33.0 mmol) in benzene (12 ml) was treated as described for amide 11 (method c). The residue was recrystallized from hexane to obtain amide 17 (6.75 g, 70.0% yield), m.p. 78–79°C. ^{31}P NMR (C_6H_6): δ = 118.

2-(1-Methyl-2-pyrrolidineimino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 19. By analogy with amide 11 (method a), from chlorophosphite 3 (3.73 g, 22.0 mmol), 1-methyl-2-iminopyrrolidine 18 (2.16 g, 22.0 mmol) and triethylamine (2.53 g, 25.0 mmol) in benzene (20 ml) 19 (4.05 g, 80.0% yield) was obtained, b.p. 112–113°C at 1 mm Hg. Found, %: C 52.00, H 8.45, P 13.61. Calcd. for $C_{10}H_{19}N_2O_2P$, %: C 52.15, H 8.33, P 13.45. ^{31}P NMR (C_6H_6): δ = 129.

1-(2-Oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-yl)-2-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-yl) iminopyrrolidine 20. A weak stream of NO was bubbled under stirring through a solution of diphosphorylated pyrrolidine 4 (3.48 g, 10.0 mmol) in benzene (10 ml) at 20°C for 1 hr. The solvent was evaporated under reduced pressure and the residue was recrystallized from hexane to give 20 (2.97 g, 78.0% yield), m.p. 205–206°C. Found, %: C 44.50, H 7.17, P 16.03. Calcd. for $C_{14}H_{26}N_2O_6P_2$, %: C 44.21, H 6.90, P 16.29. ^{31}P NMR ($CHCl_3$): δ = 6 and −10 (ratio of intensities 1:1).

1-(2-Thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-yl)-2-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-yl) iminopyrrolidine 21. Powdered sulfur (0.67 g, 20.9 mmol) was added under stirring to a solution of diphosphorylated pyrrolidine 4 (3.48 g, 10.0 mmol) in benzene (20 ml) and suspension was stirred at 20°C for 1 hr. The unreacted sulfur was filtered off, the solvent was evaporated under reduced pressure and the residue was recrystallized from cold (+10°C) benzene (7 ml) to give 21 (3.71 g, 90.0% yield), m.p. 220–221°C. Found, %: C 40.92, H 6.21, P 15.28. Calcd. for $C_{14}H_{26}N_2O_4P_2S_2$, %: C 40.76, H 6.37, P 15.02. ^{31}P NMR ($CHCl_3$): δ = 55 and 63 (ratio of intensities 1:1).

2-Thiono-2-(2-pyrrolidineimino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 22. By analogy with amide 21, from sulfur (0.67 g, 20.9 mmol) and amide 5 (4.33 g, 20.0 mmol) in benzene (25 ml) 22 (4.27 g, 86.0% yield) was obtained, m.p. 144–145°C. Found, %: C 43.72, H 7.09, P 12.25. Calcd. for $C_9H_{17}N_2O_2PS$, %: C 43.53, H 6.91, P 12.48. ^{31}P NMR ($CHCl_3$): δ = 63.

2-Thiono-2-(2-phenyliminopyrrolidine-1-yl)-5,5-dimethyl-1,3,2-dioxaphosphorinane 23. By analogy with amide 21, from sulfur (0.67 g, 20.9 mmol) and amide 17 (5.85 g, 20.0 mmol) in benzene (25 ml) 23 (5.39 g, 83.0% yield) was obtained, m.p. 124–125°C. Found, %: C 55.72, H 6.36, P 9.63. Calcd. for $C_{15}H_{21}N_2O_2PS$, %: C 55.53, H 6.54, P 9.55. ^{31}P NMR ($CHCl_3$): δ = 58.

2-Thiono-2-(1-methyl-2-pyrrolidineimino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 24. By analogy with amide 21, from sulfur (0.58 g, 18.1 mmol) and amide 19 (3.91 g, 17.0 mmol) in benzene (20 ml) 24 (3.57 g, 80.0% yield) was obtained, m.p. 127–128°C. Found, %: C 45.88, H 7.47, P 11.75. Calcd. for $C_{10}H_{19}N_2O_2PS$, %: C 45.78, H 7.31, P 11.81. ^{31}P NMR ($CHCl_3$): δ = 67.

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