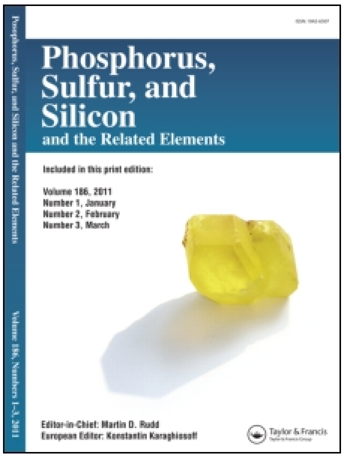


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

HIGHER 1,3,2-DIAZAPHOSPHOCYCLANES. V. 4,5; 6,7-DIBENZO-1,3,2-DIAZAPHOSPHEPANES

E. E. Nifantiev[a]; A. I. Zavalishina[a]; E. I. Orzhekovskaya[a]; N. N. Nurkulov[a]; L. K. Vasyanina[a]; A. R. Bekker[a]; V. K. Belskii[a]; A. I. Stash[a]
[a] Faculty of Chemistry, Moscow Pedagogical State University, Moscow, RUSSIA

To cite this Article Nifantiev, E. E. , Zavalishina, A. I. , Orzhekovskaya, E. I. , Nurkulov, N. N. , Vasyanina, L. K. , Bekker, A. R. , Belskii, V. K. and Stash, A. I.(1997) 'HIGHER 1,3,2-DIAZAPHOSPHOCYCLANES. V. 4,5; 6,7-DIBENZO-1,3,2-DIAZAPHOSPHEPANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 123: 1, 89 — 110

To link to this Article: DOI: 10.1080/10426509708044200

URL: http://dx.doi.org/10.1080/10426509708044200

Phosphorus, Sulfur, and Silicon, 1997, Vol. 123, pp. 89-110
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

HIGHER 1,3,2-DIAZAPHOSPHOCYCLANES. V. 4,5;6,7-DIBENZO-1,3,2-DIAZAPHOSPHEPANES

E. E. NIFANTIEV, A. I. ZAVALISHINA, E. I. ORZHEKOVSKAYA,
N. N. NURKULOV, L. K. VASYANINA, A. R. BEKKER, V. K. BELSKII
and A. I. STASH

Faculty of Chemistry, Moscow Pedagogical State University, Nesvizhskii per. 3, Moscow, 119021 RUSSIA ; L. Karpov Institute of Physical Chemistry, Moscow 103064 RUSSIA.

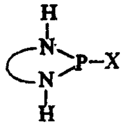
(Received 1 October1996; In final form 26 November 1996)

The synthesis, structure and chemical features of a new class of tricyclic phosphorus-containing heterocycles are reported. Special attention is paid to the dynamics of molecules and their tendency to enter into elimination reactions. A possibility to synthesize relatively stable dibenzo-1,3,2-diazaphosphepene containing a two-coordinated phosphorus atom is considered.

Keywords: Synthesis; chemical behavior; dibenzo-1,3,2-diazaphosphepanes; diazaphosphepene; athropisomery

INTRODUCTION

It was revealed previously that benzo-1,3,2-diazaphosphocyclanes (phospholanes, phosphorinanes and phosphepanes) are distinguished for their peculiar chemical behavior[1-8]. This is manifested primarily in the existence of benzene derivatives with the following fragment (where X is an electron-deficient substituent):



SCHEME 1

stable under normal conditions.

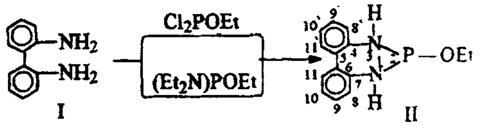
We note that such stability is not characteristic for most of monocyclic systems entering into elimination processes or intermolecular condensations. Meanwhile, the condensed compounds under consideration often differ in chemical properties, which is likely to be determined by both the size of the phosphocycle and other structural parameters[2,7,8].

In view of the aforesaid, it is of interest to expand the studies of benzophosphocyclanes and to synthesize new, more complex condensed systems.

In this paper, we present the results of the synthesis and chemical transformations of tricyclic heterocycles 4,5;6,7-dibenzo-1,3,2-diazaphosphepanes (preliminary communication[9]).

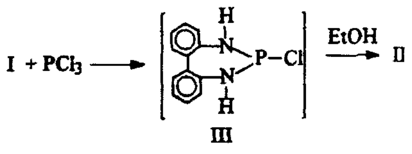
RESULTS AND DISCUSSION

We used o,o'-diaminodiphenyl, which easily undergoes cyclization on interaction with ethyl phosphorodichloridite and -diamidite, as the initial compound for the synthesis of diazaphosphepanes.



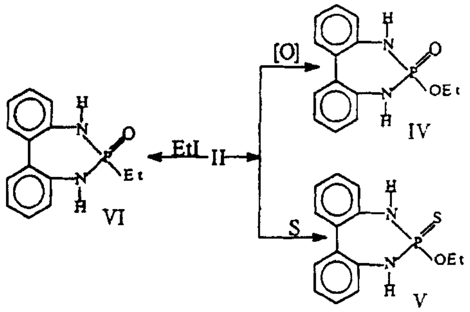
SCHEME 2

The obtained diamidoester (**II**) containing two secondary amido groups in positions 1 and 3 of phosphocycle is a stable compound, which is isolated by high-vacuum distillation. We also phosphorylated diaminodiphenyl (**I**) by phosphorus trichloride and found that, in this case, a cyclic acid chloride (**III**) was formed containing a bifunctional unit H–N–P–Cl. This compound is decomposed on vacuum distillation, therefore we worked with a crude product characterized by a ^{31}P NMR spectrum. The spectrum exhibits a singlet at 195 ppm, which corresponds to the structure presented.



SCHEME 3

Acid chloride (**III**) interacts with ethanol (the experiment was performed in the NMR tube), and corresponding diamidoester (**II**) is readily oxidized, adds sulfur and undergoes the Arbuzov alkylation.



SCHEME 4

The identity and structure of, compounds and (**II, IV–VI**) were proved by TLC, elemental analysis, as well as IR, mass- and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Tables I and II).

The IR spectra of all products exhibit absorption bands corresponding to stretching Vibrations of an N–H bond in the 3180–3120 cm^{-1} range, and absorption bands at 950-910 cm^{-1}correspond to stretching vibrations of a P–N bond (Table II). In the ^{31}P NMR spectra, singlets characteristic of three- and four-coordinated phosphorus atom are found (Table II). The resonance signals δp of the heterocycles examined are shifted downfield compared to bicyclic 1,3,2-diazaphosphepanes[7,8]. Such a shift is likely to be related to the effect of the electron-deficient biphenyl fragment. On recording spectra without deshielding on protons, doublet signals because of geminal spin–spin interaction of P–N–H bond were observed for most of the compounds obtained.

The PMR spectra of compounds obtained proved that their chemical shifts and integral intensities of the proton signals correspond to the structures suggested. Nevertheless, it should be noted that the PMR spectra present little information for the conformational analysis of the seven-membered heterocycle considered.

The ^{13}C NMR spectra of systems under study exhibit the signals of all carbon atoms. The signals of $C^{4,7,8,8'}$ atoms are split into doublets because of spin–spin interaction with the phosphorus atom.

Taking into account the dependence of vicinal intercyclic coupling constants ($^3J_{CP}$), we can suggest that the diazaphosphepane cycle can exist in two different forms : either pseudo-chair or twist-boat (Table II).

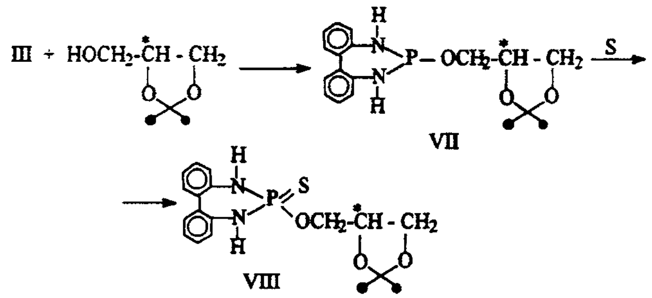
TABLE I Yields, constants and data of elemental analysis of 2-X-2-Y-4,5;6,7-dibenzo-1,2,3-diazaphosphepanes (**II, IV—VI, X—XVI**)

Compounds	*M.p. (°C)*	*Yield (%)*	*Rf (toluene: dioxane 1:1)*	*Found (%)*				*Formula*	*Calculated (%)*			
				C	*H*	*N*	*P*		*C*	*H*	*N*	*P*
II	190–200 (10^{-4} mm Hg, bath)	57.10	0.55	64.90	5.40	10.20	11.88	$C_{14}H_{15}N_2OP$	65.11	5.81	10.85	12.02
IV	228–229	74.40	0.16	61.80	5.13	10.56	10.82	$C_{14}H_{15}N_2O_2P$	61.30	5.47	10.21	11.31
V	95–96	64.10	0.82	57.20	5.30	9.95	10.05	$C_{14}H_{15}N_2OPS$	57.93	5.17	9.65	10.68
VI	210–212	78.50	0.10	65.80	5.10	10.62	11.73	$C_{14}H_{15}N_2OP$	65.11	5.81	10.85	12.02
XIII	134–135	75.10	0.30	62.11	4.48	12.38	13.60	$C_{12}H_{11}N_2OP$	62.61	4.78	12.17	13.47
XIV	160–161	80.10	0.70	64.50	6.42	13.18	9.44	$C_{17}H_{22}N_3OP$	64.76	6.98	13.33	9.84
XV	216–218	82.10	0.20	63.40	6.12	13.42	10.09	$C_{16}H_{20}N_3OP$	63.78	6.64	13.64	10.30

TABLE II Parameters of IR, ^1H, ^{13}C and ^{31}P NMR and mass spectra of 2-X-2-Y-4,5;6,7-dibenzo-1,3,2-diazaphosphepanes (**II, IV—VI,XIII**)

Compounds	*IR spectrum* (ν, cm^{-1})				δ_{NH}, *ppm* ($^2J_{HNP}$ *Hz*)	δ_c, *ppm (J, Hz)*						δ_P *ppm*	M^+
	N–H	*P–N*	*P=O or P=S*	*C–N*		$C^{4,7}$	$C^{5,6}$	$C^{8,8'}$	$C^{9,9}$	$C^{10,10'}$	$C^{11,11'}$		
II	3120	–	–	–	4.08 (26.5)	144.84 (6.63)	131.39	118.92	125.07	124.56	129.18	148.46	–
IV	3120	920	1170	1190	3.49	139.82 (3.18)	135.02	125.0	129.04	125.39	130.67	20.15	–
V	3120	920	720	1250	4.25 (9.8)	138.98 (4.90)	135.96	125.43	129.02	125.68	130.68	79.83	290
VI	3160	910	1100	1160	3.49 (30.2)	140.29 (4.01)	134.86	124.64	128.79	124.80	135.58	45.59	–
XIII	–	–	–	–	–	142.61 (2.50)	134.31	122.33	130.69	124.91	131.70	17.47 ($^1J_{PH}$ 599 Hz)	230

At the same time, account must be taken of the possibility of conformational transitions in phosphepane solutions because of the intermolecular rotation of the diphenyl system relative to the central σ–bond, which represents the axis of chirality. To study this problem, ester (**VII**) was synthesized from acid chloride (**III**) and 1,2-isopropylidene glycerol (**VII**) in the S-configuration and converted into the sulfide (**VIII**) for convenience.



SCHEME 5

It was shown that the ^{31}P NMR spectrum of thiophosphate (**VIII**) at room temperature does not demonstrate the formation of two diastereomers, as might be expected for the hampered rotation of the diphenyl system relative to the above σ–bond : the spectrum contains the single signal δ_P 84.9 ppm. However, on cooling the solution to –72°C (ethyl acetate), we observe the splitting of this signal into a doublet with $\Delta\delta^{31}{}_P$ 0.45 ppm (85.3 and 84.85 ppm) and the 1 : 1 ratio of integral intensities.

This suggests that dibenzophosphepane (**VIII**) undergoes conformational transitions because of intermolecular rotation under normal conditions. Only below –70°C, the freezing of several diastereomers is observed.

The X-ray diffraction study of compound (**VIII**) revealed that the seven-membered heterocycle is in the boat conformation : the C^7, C^8, P, and N^1 atoms lie in the same plane ; C^1, C^2, and N^2 atoms are located over this plane (Fig. 1). The four-coordinated phosphorus atom with different substituents, as it usually is, has a distorted tetrahedral structure. The interatomic P–N distances differ from each other, and all bonds of the phosphorus atoms slightly exceed their standard values (P–S 1.9365 and P–O 1.586 Å[10]). The angles at the phosphorus atom N_1–P–N_2 (102.69°) and S–P–O (113.14°) are considerably increased as compared with the endocyclic angles O–P–O and N–P–N in six- and seven-membered Rings[4,11,12], which suggests a noticeable flattening of the phosphorus tetrahedron. The angle of the tilting of two biphenyl rings relative to each other is 46.1°. Intermolecular N–H···O hydrogen bonds like $N^2H\cdots O^2$ are formed in the structure ; thereby, two diastereomeric forms linked only by hydrogen bonds occur in the same elementary cell (Fig.2). This suggests that anthropisomery can take place for such compounds.

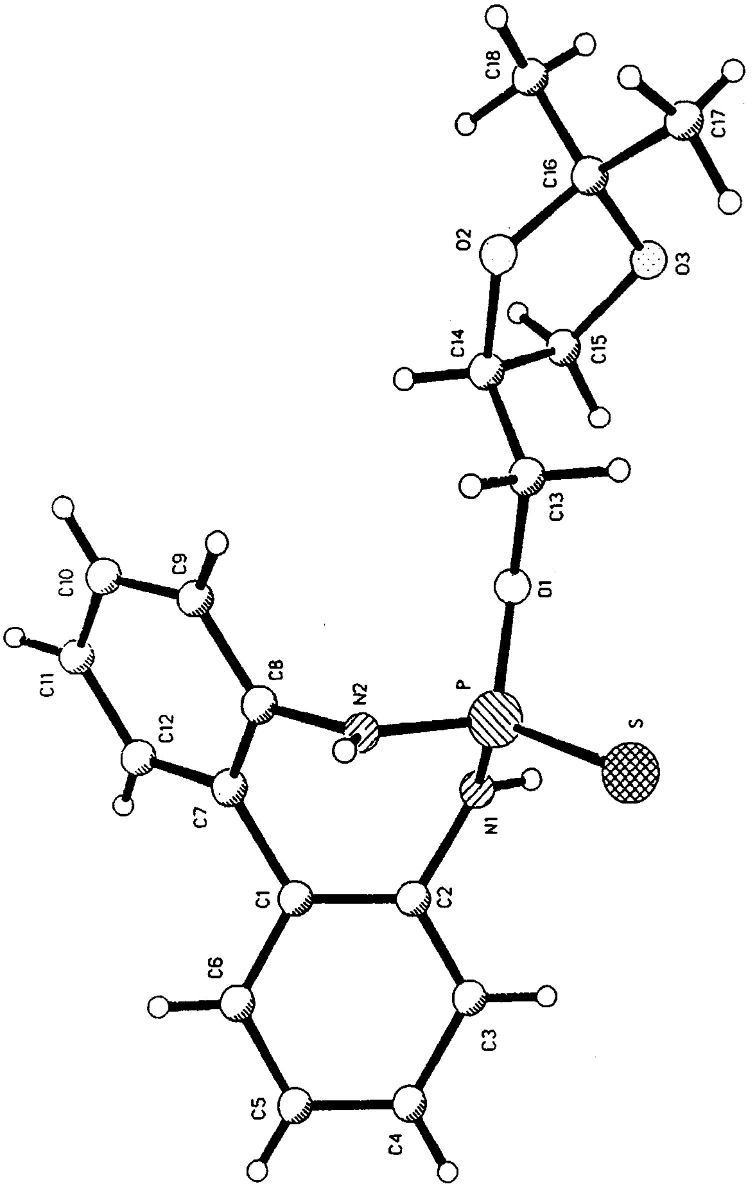


FIGURE 1

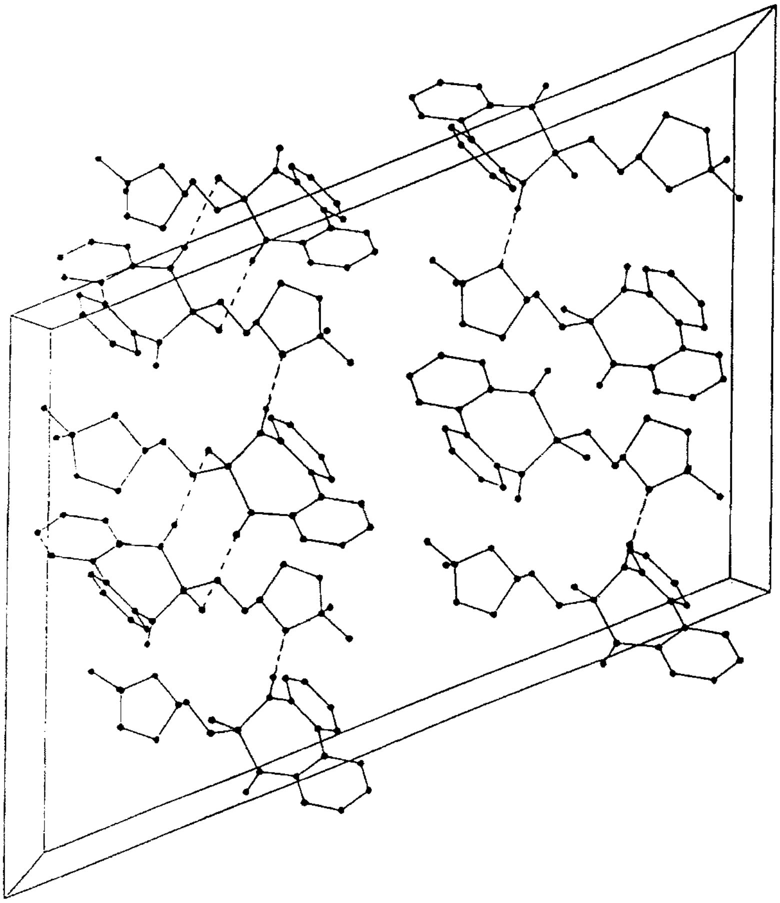
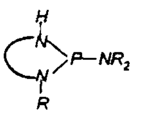


FIGURE 2

The second part of this work deals with 2-amido-4,5;6,7-dibenzo-1,3,2-diazaphosphepanes. It is known that the cyclic triamides of phosphorous acid are readily formed on the basis of secondary diamines[1,4,13-20]. At the same time, information is available in the literature on the synthesis of diazaphosphepanes on the basis of primary-secondary diamines[2,5,6], i.e., the systems of type



SCHEME 6

TABLE III Crystal data and structure refinement for **VIII**

Identification code	*ps73*
Empirical formula	C18 H21 N2 O3 P S
Formula weight	376.40
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 26.812(5) A alpha = 90 deg. b = 8.135(2) A beta = 111.31(3) deg c = 18.400(4) A gamma = 90 deg.
Volume	3738.9(14) A^3
Z	8
Diffractometer	Syntex P-1
Collection method	theta/2theta
Radiation type	CuK\a
Standards number	3
Standards interval count	100
Standards decay	4.7 %
Density (calculated)	1.337 Mg/m^3
Absorption coefficient	2.512 mm^-1
F(000)	1584
Crystal size	.42 x .24 x .20 mm
Theta range for data collection	3.54 to 57.45 deg.
Index ranges	-29<=h<=27, 0<=k<=8, 0<=l<=20
Reflections collected	2586
Independent reflections	2421 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2342 / 0 / 311
Goodness-of-fit on F^2	1.039
Final R indices [I>3sigma(I)]	R1 = 0.0416, wR2 = 0.1125
R indices (all data)	R1 = 0.0416, wR2 = 0.1125
Extinction coefficient	0.00050 (8)
Largest diff. peak and hole	0.310 and -0.261 e.A^-3

TABLE IV Atomic coordinates (× 10 ^ 4) and equivalent isotropic displacement parameters (A^2 × 10^3) for **VIII** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	*y*	*z*	*U (eq)*
S	2497 (1)	1627 (1)	6383 (1)	54 (1)
P	2178 (1)	3695 (1)	5923 (1)	41 (1)
O (1)	2607 (1)	5099 (2)	6011 (1)	51 (1)
O (2)	3515 (1)	7722 (3)	7493 (1)	64 (1)
O (3)	4011 (1)	7252 (3)	6747 (1)	63 (1)
N (1)	1858 (1)	3825 (3)	4972 (1)	45 (1)
N (2)	1736 (1)	4351 (3)	6266 (1)	47 (1)
C (1)	913 (1)	4298 (3)	4737 (2)	46 (1)
C (2)	1309 (1)	3344 (3)	4619 (1)	44 (1)
C (3)	1177 (1)	1999 (4)	4131 (2)	53 (1)
C (4)	646 (1)	1568 (4)	3743 (2)	67 (1)
C (5)	251 (1)	2487 (5)	3857 (2)	68 (1)
C (6)	380 (1)	3832 (4)	4343 (2)	58 (1)
C (7)	1036 (1)	5806 (3)	5230 (2)	44 (1)
C (8)	1438 (1)	5824 (3)	5970 (1)	45 (1)
C (9)	1550 (1)	7252 (4)	6412 (2)	56 (1)
C (10)	1272 (1)	8660 (4)	6136 (2)	64 (1)
C (11)	867 (1)	8666 (4)	5404 (2)	62 (1)
C (12)	756 (1)	7256 (4)	4963 (2)	55 (1)
C (13)	2980 (1)	5534 (4)	6781 (2)	52 (1)
C (14)	3149 (1)	7275 (4)	6726 (2)	56 (1)
C (15)	3478 (1)	7479 (5)	6222 (2)	63 (1)
C (16)	4035 (1)	7974 (4)	7454 (2)	58 (1)
C (17)	4442 (2)	7040 (9)	8107 (3)	99 (2)
C (18)	4140 (2)	9795 (6)	7455 (3)	87 (1)

TABLE V Bond lengths [A] and angles [deg] for **VIII**

S-P	1.9365 (10)
P-O (1)	1.586 (2)
P-N (2)	1.622 (2)
P-N (1)	1.650 (2)
O (1) -C (13)	1.451 (3)
O (2)-C (16)	1.435 (3)
O (2)-C (14)	1.443 (3)
O (3)-C (16)	1.407 (4)
O (3)-C (15)	1.415 (4)
N (1)-C (2)	1.430 (3)
N (2)-C (8)	1.434 (3)
C (1)-C (2)	1.395 (4)
C (1) -C (6)	1.400 (4)
C (1)-C (7)	1.489 (4)
C (2)-C (3)	1.377 (4)
C (3)-C (4)	1.386 (5)
C (4)-C (5)	1.372 (5)
C (5)-C (6)	1.375 (5)
C (7)-C (12)	1.388 (4)
C (7)-C (8)	1.397 (4)
C (8) -C (9)	1.387 (4)
C (9)-C (10)	1.360 (5)
C (10)-C (11)	1.389 (5)
C (11) -C (12)	1.374 (4)
C (13)-C (14)	1.502 (4)
C (14)-C (15)	1.503 (5)
C (16)-C (17)	1.503 (5)
C (16)-C (18)	1.509 (5)
O (1)-P-N (2)	109.16 (12)
O (1)-P-N (1)	98.03 (11)
N (2)-P-N (1)	102.69 (12)
O (1)-P-S	113.14 (8)
N (2)-P-S	112.63 (10)
N (1)-P-S	119.74 (9)
C (13)-O (1)-P	119.5 (2)
C (16)-O (2)-C (14)	108.3 (2)
C (16)-O(3)-C (15)	105.8 (2)
C (2)-N (1)-P	121.1 (2)
C (8)-N (2)-P	120.9 (2)
C (2)-C (1)-C (6)	117.4 (3)
C (2)-C (1)-C (7)	122.8 (2)
C (6)-C (1)-C (7)	119.8 (2)

C (3)-C (2)-C (1)	120.8 (2)
C (3)-C (2)-N (1)	119.5 (2)
C (1)-C (2)-N (1)	119.5 (2)
C (2)-C (3)-C (4)	120.7 (3)
C (5)-C (4)-C (3)	119.2 (3)
C (5)-C (4)-C (3)	119.2 (3)
C (4)-C (5)-C (6)	120.5 (3)
C (5)-C (6)-C (1)	121.4 (3)
C (12)-C (7)-C (8)	117.5 (3)
C (12)-C (7)-C (1)	120.9 (2)
C (8)-C (7)-C (1)	121.6 (2)
C (9)-C (8)-C (7)	120.5 (3)
C (9)-C (8)-N (2)	120.3 (2)
C (9)-C (8)-N (2)	119.2 (2)
C (7)-C (8)-N (2)	119.2 (2)
C (10)-C (9)-C (8)	120.9 (3)
C (9)-C (10)-C (11)	119.6 (3)
C (12)-C (11)-C (10)	119.7 (3)
C (11)-C (12)-C (7)	121.8 (3)
O (1)-C (13)-C (14)	106.4 (2)
O (2)-C (14)-C (15)	103.5 (2)
O (2)-C (14)-C (13)	106.7 (2)
C (15)-C (14)-C (13)	113.9 (3)
O (3)-C (15)-C (14)	103.7 (2)
O (3)-C (16)-O (2)	105.6 (2)
O (3)-C (16)-C (17)	107.7 (3)
O (2)-C (16)-C (17)	108.9 (3)
O (3)-C (16)-C (18)	110.9 (3)
O (2)-C (16)-C (18)	109.0 (3)
C (17)-C (16)-C (18)	114.5 (4)

Symmetry transformations used to generate equivalent atoms :

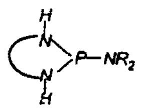
TABLE VI Anisotropic displacement parameters (A^2 x 10^3) for **VIII** The anisotropic displacement factor exponent takes the form : -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
S	56 (1)	50 (1)	53 (1)	9 (1)	17 (1)	9 (1)
P	38 (1)	46 (1)	34 (1)	2 (1)	9 (1)	1 (1)
O (1)	52 (1)	56 (1)	39 (1)	1 (1)	9 (1)	-11 (1)
O (2)	52 (1)	84 (2)	59 (1)	-27 (1)	24 (1)	-20 (1)
O (3)	62 (1)	73 (1)	60 (1)	-4 (1)	28 (1)	0 (1)
N (1)	41 (1)	59 (1)	34 (1)	0 (1)	12 (1)	4 (1)
N (2)	51 (1)	56 (1)	36 (1)	7 (1)	16 (1)	9 (1)
C (1)	42 (1)	54 (2)	38 (1)	1 (1)	12 (1)	2 (1)
C (2)	43 (2)	50 (2)	34 (1)	1 (1)	9 (1)	0 (1)
C (3)	52 (2)	51 (2)	52 (2)	-5 (1)	14 (1)	4 (1)
C (4)	69 (2)	57 (2)	64 (2)	-15 (2)	12 (2)	-8 (2)
C (5)	49 (2)	75 (2)	67 (2)	-9 (2)	6 (2)	-13 (2)
C (6)	43 (2)	69 (2)	58 (2)	-8 (2)	12 (1)	2 (2)
C (7)	40 (1)	52 (2)	40 (1)	0 (1)	14 (1)	3 (1)
C (8)	45 (1)	52 (2)	38 (1)	1 (1)	16 (1)	5 (1)
C (9)	56 (2)	63 (2)	44 (2)	-9 (2)	12 (1)	3 (2)
C (10)	70 (2)	54 (2)	65 (2)	-15 (2)	21 (2)	3 (2)
C (11)	69 (2)	53 (2)	65 (2)	4 (2)	25 (2)	16 (2)
C (12)	50 (2)	66 (2)	45 (2)	0 (2)	11 (1)	12 (2)
C (13)	51 (2)	59 (2)	43 (2)	-4 (1)	12 (1)	-7 (1)
C (14)	51 (2)	49 (2)	63 (2)	-9 (1)	14 (1)	-2 (1)
C (15)	72 (2)	60 (2)	56 (2)	-1 (2)	24 (2)	-9 (2)
C (16)	51 (2)	68 (2)	57 (2)	-8 (2)	24 (1)	-7 (2)
C (17)	70 (3)	142 (5)	74 (3)	22 (3)	14 (2)	0 (3)
C (18)	88 (3)	80 (3)	100 (3)	-23 (2)	44 (3)	-33 (2)

TABLE VII Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **VIII**

	x	*y*	*z*	*U (eq)*
H (3)	1444 (12)	1353 (36)	4104 (17)	52 (8)
H (4)	553 (14)	657 (48)	3393 (22)	87 (11)
H (5)	-84 (13)	2229 (42)	3620 (18)	65 (9)
H (6)	113 (12)	4410 (37)	4433 (17)	54 (8)
H (9)	1816 (13)	7207 (40)	6903 (19)	68 (9)
H (10)	1345 (13)	9604 (46)	6395 (21)	75 (10)
H (11)	673 (14)	9723 (48)	5218 (21)	86 (11)
H (12)	510 (13)	7273 (39)	4485 (19)	61 (9)
H (131)	3291 (12)	4702 (40)	6925 (18)	65 (9)
H (132)	2787 (11)	5510 (37)	7138 (18)	58 (8)
H (14)	2849 (14)	8004 (45)	6631 (19)	74 (10)
H (151)	3389 (13)	6673 (42)	5815 (21)	67 (9)
H (152)	3429 (16)	8629 (50)	5990 (24)	92 (12)
H (171)	4366 (15)	7399 (48)	8580 (24)	91 (12)
H (172)	4743 (22)	7284 (69)	8084 (31)	132 (20)
H (173)	4346 (22)	5779 (79)	8031 (33)	154 (23)
H (181)	4182 (16)	10176 (53)	7955 (28)	102 (14)
H (182)	4430 (17)	9874 (52)	7363 (24)	97 (14)
H (183)	3804 (22)	10298 (69)	7053 (35)	152 (22)
H (1N)	2047 (12)	3698 (35)	4692 (18)	51 (9)
H (2N)	1679 (10)	3933 (35)	6646 (18)	46 (8)

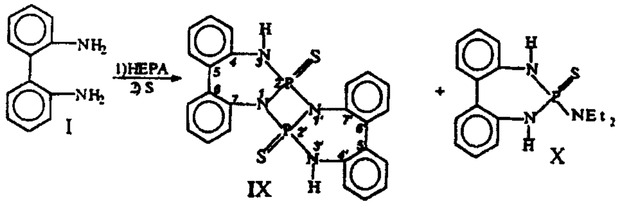
Such compounds are unstable and prone to the elimination of amines[2,6] and secondary phosphorylation[5]. The cyclic triamides of phosphorous acid, whose molecules contain two secondary amido groups, are not described in the literature



SCHEME 7

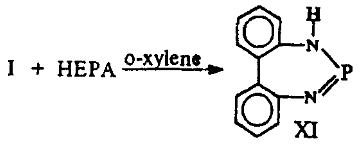
In view of aforesaid, we considered it expedient to perform the synthesis of a cyclic triamide of phosphorous acid on the basis of o,o'-diphenyldiamine, whose molecule contains two N–H groups directly bonded to the benzene ring.

It should be noted that the reaction of o,o'-diphenyldiamine (I) with the hexaethyltriamide of phosphorous acid (HEPA) is nonselective, and its result depends on the reaction conditions. So, the heating of the initial compounds to 90-100°C without solvent for one hour results in a mixture of phosphorus-containing compounds, as evidenced by NMR spectroscopy. After sulfurization of the reaction mixture, thiophosphamide (X) and dimer (IX) containing a diazadiphosphetidine cycle were isolated and identified.



SCHEME 8

An unusual result was obtained on heating diamine (I) with hexaethyltriamide of phosphorous acid to 120–130°C in an *o*-xylene solution. A white crystalline substance with δp 242.2 ppm and $^{2}J_{PH}$ 26.16 Hz is precipitated on cooling the reaction mixture. The appearance of such a downfield signal is related with the formation of a two-coordinated phosphorus compound (XI).

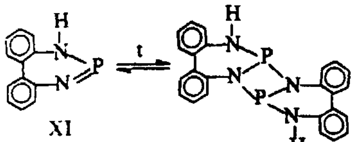


SCHEME 9

The structure of 1,3,2-diazaphosphepene (XI) was proved by IR and NMR spectroscopy.

A strong absorption band corresponding to the stretching vibrations of an N–H bond is observed in the 3320 cm^{-1} range of the IR spectrum of 4,5;6,7-dibenzo-1,3,2-diazaphosphepene (XI). The absorption bands at 1270 and 1220 cm^{-1} are assigned to the stretching vibrations of –C–N= and –C–N– groups, and those at 1100 and 920 cm^{-1} are assigned to –P=N– and –P–N–, respectively.

A peculiar feature of compounds containing low-coordinated atoms of trivalent phosphorus is their tendency to oligomerization[3]. 1,3,2-Diazaphosphepene (XI) also has a tendency to dimerization. So, the ^{31}P NMR spectrum of its dioxane solution, along with the signal with δ_P 242.2 ppm, develops a singlet with δ_P 158 ppm corresponding to diazadiphosphetidine (**XII**) within 30–40 min at room temperature. The peak ratio is 80 : 20. The subsequent heating to 50-60°C results in an increasing proportion of dimer product, and an equilibrium is established at the 60 : 40 ratio



XI

XII

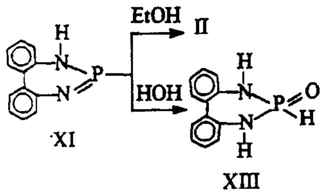
SCHEME 10

It should be noted that the equilibrium XI = XII under ordinary conditions is displaced toward the formation of the two-coordinated form (**XI**) without adding any stabilizing compounds like BF_3[2]. The stability of the obtained compound (**XI**) is likely to be dependent on geometric peculiarities of the arylenamide fragment of the phosphocycle and sufficient for its isolation as a monomer. At the same time, 1,3,2-diazaphosphepene (**XI**) is readily soluble in pyridine, and no dimerization is observed at room temperature within several days. However, the heating of the solution obtained to 150°C in a sealed ampoule for 1.5 h leads to the formation of dimer (**XII**). Thus, in our case, a dimerization typical to a greater extent for acyclic systems[21,22] is observed.

The molecular structure of diazaphosphetidine dimers containing three- (**XII**) and four-coordinated (**IX**) phosphorus atom was proved by X-ray diffraction analysis. (Complete data of X-ray diffraction analysis will be reported later.) In both cases, the molecules are symmetrical relative to the ideally flat four-membered ring.

In seven-membered heterocycles, the N^1, P^2, C^4, and C^5 atoms lie in the same plane ; the N^3, C^6, and C^7 atoms are deflected from this plane to one side but by different distances, i.e., the seven-membered ring takes the conformation of distorted asymmetrical boat. the nitrogen atoms of the heterocycle are planar–trigonal, and the phosphorus atoms have a pyramidal coordination. In the biphenyl fragment, the planes of the two aromatic rings are tilted to each other at an angle of 41.4° for compound (**XII**) and 45.5° for compound (**IX**).

To prove the structure of compound (**XI**) containing a coordinated unsaturated trivalent phosphorus atom, several chemical transformations were performed. It is known that compounds with a –P=N– π- bond manifest high reactivity in relation to proton-donating nucleophilic reagents. It was shown that dibenzo-1,3,2-diazaphosphepene (**XI**) easily adds ethanol within several minutes at room temperature With formation of 2-ethoxy-4,5;6,7-dibenzo- 1,3 2-diazaphosphepane (**II**) obtained previously (the experiment was performed in the ampoule of the spectrometer).



SCHEME 11

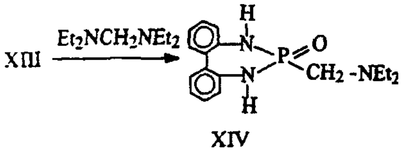
We also performed the hydration of the –P=N– bond of diazaphosphepene (**XI**). With formation of hydrophosphoryl compound (**XIII**).

$$\text{III} + H_2O \xrightarrow{NEt_3} \text{XIII}$$

SCHEME 12

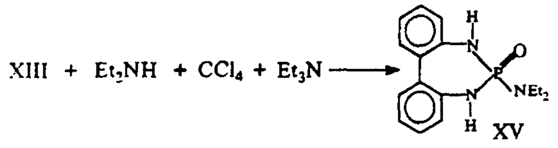
Incomplete cyclic diamide of phosphorous acid (**XIII**) was also synthesized by monitored hydrolysis of acid chloride (**III**). The ^{31}P NMR spectrum of obtained 2-H-2-oxo-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**XIII**) exhibits a doublet with δ_P 17.47 ppm, $^1J_{PH}$ 599 Hz, the position and splitting of which are characteristic for the hydrophosphoryl fragment.

2-H-2-Oxo-1,3,2-diazaphosphepane (**XIII**) can be used as the initial substance for the synthesis of phosphonates and phosphates; for example, diamide (**XIII**) readily reacts with tetraethyldiaminomethylene with formation of corresponding cyclic aminomethyl-phosphonate (**XIV**).



SCHEME 13

1,3,2-Diazaphosphepane (**XIII**) was also entered into the Todd-Atherton reaction with diethylamine



SCHEME 14

All synthesized 4,5;6,7-dibenzo-1,3,2-diazaphosphepanes (**XIII-XV**) were characterized by TLC, elemental analysis, as well as by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Tables I and II).

EXPERIMENTAL

All syntheses of the compounds of trivalent phosphorus were performed under an atmosphere of dry argon or nitrogen. The ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer at 32.4 MHz with 85 % H_3PO_4 as an external reference. The ^{1}H and ^{13}C NMR spectra were run on a Bruker AM–400 instrument at 400.13 and 100.627 MHz, respectively. Chemical shifts are downfield from internal Me_4Si. IR spectra were recorded on a Specord UR-75 spectrometer in petrolatum or KBr. Mass-spectrometric studies were performed by the field desorption method on a Varian MAT–731. The compounds were chromatographed on Silufol plates in the systems (A) benzene–dioxane (3 : 1) and (B) benzene-dioxane (1 : 1).

2-Ethoxy-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**II**). (a) A solution of 0.4 g (0.0027 mol) of ethylphosphodichloridite in 3 ml of dry benzene was progressively added to a solution of 0.5 g (0.0027 mol) of o,o'-diaminobiphenyl (**I**)[23] and 0.54 g (0.0053 mol) of triethylamine in 7 ml of dry benzene under stirring and cooling to 0–5°C. The reaction mixture was stirred at room temperature for 1.5 h ; then the precipitate of triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was vacuum distilled. Yield and other parameters are listed in Table I. (b) A mixture of 1 g (0.0054 mol) of o,o'-diaminobiphenyl (**I**), 1.2 g (0.0054 mol) of ethyl ester of tetraethyldiamide of phosphorous acid and a catalytic amount of triethylamine hydrochloride was heated to 100-110°C for 1.5 h until the release of diethylamine ceased. The residue was distilled under vacuum; yield was 0.8 g (57 %).

2-Chloro-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**III**). A solution of 0.74 g (0.0054 mol) of phosphorus trichloride in 5 ml of dry dioxane was progressively added to a solution of 1.0 g (0.0054 mol) of diamine (**I**) and 1.1 g (0.01 mol) of triethylamine in 10 ml of dry dioxane under stirring and cooling to 0–5°C. The reaction mixture was stirred at room temperature for 1.5 h ; then the precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed. The residue was mobile yellow oil. The yield of crude product (**III**) was 1.2 g (92.3 %) : δ_P 195 ppm.

2-Ethoxy-2-oxo-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**IV**). NO was passed through a solution of 2.8 g (0.011 mol) of diamidoester (**II**) in 30 ml of dry benzene for 4 h. Then the solvent was removed, and the residue was crystallized from dioxane. Yield and other parameters are listed in Table I.

2-Ethoxy-2-thio-4,5;6,7-dibenzo-1.3.2-diazaphosphepane (**V**). Finely dispersed sulfur 0.35 g, (0.011 mol) was progressively added to a solution of 2.8 g (0.011 mol) of diamidoester (**II**) in 15 ml of dry benzene under stirring. The reaction mixture was stirred at 50°C for 30 min. The reaction was monitored by TLC. Then the solvent was removed, and the residue was crystallized from the benzene-dioxane (3 : 1) moisture.

2-Ethoxy-2-ethyl-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**VI**). A mixture of 1.4 g (0.0054 mol) of diamidoester (**II**) and 0.84 g (0.0054 mol) of ethyl iodide in 20 ml of dry benzene was heated to 50°C for 10 h ; then the solvent was removed by evaporation, and the residue was crystallized from dioxane.

2 (β,γ-isopropylidene-glyceroxy)-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**VII**). A mixture of 0.71 g (0.0054 mol) of 1,2(+)-isopropylideneglycerol and 0.55 g (0.0054 mol) of triethylamine in 5 ml of dioxane was progressively added to a solution of 1.35 g (0.0054 mol) of chlorophosphite (**III**) in 7 ml of dry dioxane under stirring and cooling to 0–5°C. The reaction mixture was stirred at room temperature for 1.5 h ; then the precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed. The yield of crude product was 0.96 g (55 %) ; δ_P (dioxane) 157.7 ppm ; R_f 0.73 (A).

2 (β,γ-isopropylideneglyceroxy)-2-thio-4;5;6,7-dibenzo-1,3,2-diazaphosphepane (**VIII**). Finely dispersed sulfur 0.09 g (0.0028 mol) was progressively added to a solution of 0.96 g (0.0028 mol) of diamidoester (**VII**) in dioxane under stirring. The reaction mixture was kept at 40–50°C for 30 min ; then solvent was removed, and the residue was purified on a column packed with silica gel in the system (B). On removal of eluent, the substance was obtained as crystals which were washed with benzene and dried in a vacuum-desiccator. The yield was 0.27 g (25 %) ; m.p. 181-182°C ; δ_P 81.9 ppm ; R_f 0.67 (B). Anal. Calcd. for $C_{18}H_{23}N_2O_3PS$: C, 62.42 ; H, 6.64 ; N, 8.09 ; P, 8.96. Found : C, 62.31 ; H, 6.43; N, 8.15 ; P, 9.02.

Interaction of o,o'-diphenyldiamine with phosphorous hexamethyltriamide followed by sulfurization. A mixture of 1 g (0.0054 mol) of diamine (**I**) with 1.34 g (0.0054 mol) of phosphorous hexaethyltriamide was heated to 90–100°C until the release of diethylamine ceased. The reaction mixture was dissolved in 15 ml of dry benzene, and 0.17 g (0.0054 mol) of finely dispersed sulfur was added progressively ; then the mixture was stirred at 40°C for 0.5 h, and the precipitation of white crystalline substance was observed.

The crystals precipitated were filtered off, washed With hexane, and dried. The yield of dimer (**IX**) was 0.47 g (28 %) ; m.p. 253–254°C, δ_P (dioxane) 66.0 ppm. ^{13}C NMR (DMSO-*d*, δ, ppm) : 139.13 s ($C^{4,7}$), 135.9 s ($C^{5,6}$), 130.67 s ($C^{11,11'}$, 129.90 s (C$^{9,9'}$, 128.72 s (C$^{10,10'}$), 125.78 s (C$^{8,8'}$). Mass-spectrum m/e 488. Anal. Calcd. for $C_{24}H_{18}N_4P_2S_2$: C, 59.00 ; H, 3.68 ; N, 11.47 ; P, 12.70. Found : C, 59.12 ; H, 3.40 ; N, 11.31 ; P, 12.63.

2-Diethylamido-2-thio-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**X**) was isolated from the mixture by the chromatography on a column packed with silica gel L 40/100 in the system (A). Yield was 1.2 g (40 %) ; m.p. 198-199°C, δ_P (dioxane) 79.1 ppm. ^{1}H NMR (DMSO-*d*, δ, ppm) : 1.08 m (6H, 2CH$_3$) ; 3.24 q (4H, 2CH$_2$) ; 4.51 d ; $^2J_{PNH}$ 6.9 Hz (2H, 2NH). ^{13}C NMR (DMSO-*d*, δ, ppm) : 13.98 s (CH$_3$), 140.00 d (^{C4,7}, $^2J_{P\text{-}C}$ 9.8 Hz), 133.41 s (C^{5,6}), 119.39 s (C$^{11,11'}$), 127.90 s (C$^{9,9'}$), 124.15 s (C$^{10,10'}$), 123.78 s (C$^{8,8'}$). Mass-spectrum m/e 317. Anal. Calcd. for $C_{16}H_{20}N_3PS$: C, 60.56 ; H, 6.31 ; N, 13.25 ; P, 9.78. Found : C, 60.38; H, 6.13; N, 13.40; P, 9.78.

4,5;6,7-Dibenzo-1,3,2-diazaphosphepene (**XI**). A mixture of 1 g (0.0054 mol) of diamine (**I**) with 1.34 g (0.0054 mol) of phosphorous hexaethyltriamide in dry *o*-xylene was heated to 120–130°C for 1.5 h, until the release of diethylamine ceased. On cooling the reaction mixture, white crystalline substance was precipitated which was filtered off, washed with dry benzene under an argon atmosphere, and dried under vacuum. The yield of dibenzo-1,3,2-diazaphosphepene (**XI**) was 0.6 g (40 %) ; m.p. 180–182°C with decomposition (in a sealed capillary), δ_P (dioxane) 242.2 ppm, $^2J_{PNH}$ 26.16 Hz, δ_P (C_6H_5N) 241.1 PPM. ^{1}H NMR (dioxane-*d*, δ, ppm) : 3.52 m (NH, $^2J_{PNH}$ 25 Hz), 7.11–7.44 m (HN). IR spectrum (under an argon atmosphere): $\nu_{N\text{-}H}$ 3320 cm^{-1}, $\nu_{\text{-}C\text{-}N}$= 1270 cm^{-1}, $\nu_{\text{-}C\text{-}N\text{-}}$ 1220 cm^{-1} $\nu_{N=P}$ 1100 cm^{-1}, $\nu_{P\text{-}N}$ 920 cm^{-1}. Anal. Calcd. for $C_{12}H_9N_2P$: C, 67.42 ; H, 4.68 ; N, 13.01 ; P, 14.81. Found : C, 67.92 ; H, 4.24 ; N, 13.21 ; P, 14.62.

2-H-2-Oxo-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**XIII**). (a) Water (0.84 g) in 5 ml of dioxane was progressively added to 1.0 g of diazaphosphepene (**XI**) in 10 ml of dioxane at 0–5°C. The reaction mixture was stirred at room temperature for 1 h ; then the solvent was removed, and the residue was crystallized from a mixture of dioxane-hexane (3 : 1). Yield was 0.9 g (82 %) ; m.p. 134–135°C.

(b) A mixture of 0.094 g (0.0054 mol) of water and 0.52 g (0.0054 mol) of triethylamine in 5 ml of dioxane was progressively added to a solution of 1.3 g (0.0054 mol) of acid chloride (**III**) in 15 ml of dioxane under cooling to 0-5°C. The reaction mixture was stirred at room temperature for 1 h ; then the precipitate of triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was crystallized from a mixture dioxane–hexane (3 : 1).

2-Oxo-2-diethylaminomethyl-4.5;6,7-dibenzo-1,3,1-diazaphosphepane (**XIV**). A mixture of 0.4 g (0.0017 mol) of acid diamine (**XIII**) with 0.27 g (0.0017 mol) of tetraethyldiaminomethylene was heated to 120–130°C until the release of diethylamine ceased. The residue was crystallized from a mixture dioxane-DMFA (3 : 1).

2-Diethylamido-2-oxo-4,5;6,7-dibenzo-1,3,2-diazaphosphepane (**XV**). Diethylamine 0.15 g (0.0022 mol) and triethylamine 0.21 g (0.0022 mol) in 5 ml of benzene were progressively added to a mixture of 0.5 g (0.0022 mol) of 1,3,2-diazaphosphepane (**XIII**) and 0.33 g (0.0022 mol) of tetrachloromethane in 20 ml of dry benzene. The reaction mixture was stirred at room temperature for 2 h ; then the precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed. The residue was stiff oil. Triamidophosphate (**XV**) was purified chromatographically on a column packed with silica gel L 40/100. Yield was 0.6 g (36.4 %) ; m.p. 216–218°C ; δ_P 23.93 ppm. ^1H NMR (CD_3CN, *d*, δ, ppm) : 1.05 t (6H, $3CH_3$), 3.02 m. $^2J_{HP}$ 11.0 Hz, (4H, $2CH_2$), 5.51 s (2H, 2NH). ^{13}C NMR (DMFA-*d*, δ, ppm) : 141.44 d (^{C4,7}, $^2J_{P\text{-}C}$ 4.88 Hz), 134.61 s ($C^{5,6}$), 130.52 s ($C^{11,11'}$), 128.78 s ($C^{9,9'}$), 124.79 d ($C^{8,8'}$, $^3J_{P\text{-}C}$ 2.4 Hz), 124.26 s ($C^{10,10'}$), 40.34 d (CH_2, $^2J_{P\text{-}C}$ 5.88 Hz), 14.47 d (CH_3, $^3J_{P\text{-}C}$ 2.4 Hz). Mass-spectrum m/e 301. Anal. Calcd. for $C_{16}H_{20}N_3PO$: C, 63.78 ; H, 6.64 ; N, 13.95 : P, 10.30. Found : C, 63.54; H, 6.72; N, 13.85; P, 10.30.

References

[1] M. A. Pudovik, V. V. Ovchinnikov, R. A. Cherkasov and A. N. Pudovik, *Usp. Khim.* **52**, 640-668 (1983).

[2] Ch. Malavand, Th. MPondo and J. Barrans, *Can. J. Chem.*, **62**, 43-50 (1984).

[3] Y. Charbonnel and J. Barrans, *C. R. Acad. Sci., Ser. C*, **278**, 355-358 (1974).

[4] E. E. Nifant'ev, A. I. Zavalishina, S. S. Dorogotovtsev, E. I. Orzhekovskaya, A. R. Bekker, N. S. Magomedova, A. N. Sobolev and V. K. Bel'skii, *Zh. Obshch. Khim.*, **62** 289-302 (1992).

[5] E. E. Nifant'ev, A. I. Zavalishina, S. S. Dorogotovtsev, E. I. Orzhekovskaya, N. N. Nurzhulov, A. R. Bekker and L. K. Vasyanina, *Zh. Obshch. Khim.*, **62**, 1994-2005 (1992).

[6] E. E. Nifant'ev, A. I. Zavalishina, S. S. Dorogotovtsev, E. I. Orzhekovskaya, A. R. Bekker, S. P. Sirotinkin and N. N. Nevskii, *Dokl. Akad. Nauk SSSR*, **312**, 372-376 (1990).

[7] E. E. Nifant'ev, A. I. Zavalishina, N. N. Nurgulov, E. I. Orzhekovskaya, A.R. Bekker, N. S. Magomedova and V. K. Bel'skii, *Zh. Obshch. Khim.*, **63**, 1739-1747 (1993).

[8] E. E. Nifant'ev, A. I. Zavalishina, N. N. Nurgulov, E. I. Orzhekovskaya, A. R. Bekker, N. S. Magomedova and V. K. Bel'skii, *Zh. Obshch. Khim.*, **63**, 1726-1738 (1993).

[9] A. I. Zavalishina, N. N. Nurgulov, E. I. Orzhekovskaya, A. R. Bekker, L. K. Vasyanina, I. V. Bespalova and E. E. Nifant'ev, *Zh. Obshch. Khim.*, **65**, 777-781 (1995).

[10] F. N. Allen, O. Kennard, D. Y. Weston, Z. Breinmer, O. Y. Oppen and R. Taylor, *J. Chem. Soc. Perkin Trans.*, **51** (1987).

[11] B. F. Grand and J. B. Robert, *Acts Cryst.*, **34**, 199-204 (1978).

[12] N. S. Magomedova, A. N. Sobolev, V. K. Bel'skii, M. P. Koroteev, N. M. Pugashova and E. E. Nifant'ev, *Phosph. Sulfur*, **57**, 261-271 (1991).

[13] E. I. Smirnova, A. I. Zavalishina, A. A. Borisenko, M. N. Rybina and E. E. Nifant'ev, *Zh. Obshch, Khim.*, **51**, 1956-1962 (1981).

[14] J. A. Mosbo, *Tetrahedron Lett.*, **52**, 4789-4792 (1976).

[15] E. E. Nifant'ev, A. I. Zavalishina, S. O. Sorokina, A. A. Borisenko, E. I. Smirnova and I. V. Gustova, *Zh. Obshch. Khim.*, **47**, 1960-1970 (1977).

[16] E. E. Nifant'ev, A. I. Zavalishina, S. O. Sorokina, E. I. Smirnova, V. V. Kurochkin and L. I. Moiseeva, *Zh. Obshch, Khim.*, **49**, 64-74 (1979).

[17] E. E. Nifant'ev, A. I. Zavalishina and E. I. Smirnova, *Phosph. Sulfur*, **3**, 261-266 (1981).

[18] L. A. Vorob'eva, S. O. Sorokina, A. I. Zavalishina, E. I. Smirnova and E. E. Nifant'ev, *Zh. Obshch, Khim.*, **54**, 1212-1220 (1984).

[19] E. E. Nifant'ev, A. I. Zavalishina, E. I. Orzhekovskaya and L. K. Vasyanina, *Zh. Obshch, Khim.*, **59**, 816-820 (1989).

[20] V. V. Kurochkin, A. I. Zavalishina, E. I. Orzhekovskaya, A. R. Bekker, A. G. Agranovich and E. E. Nifant'ev, *Zh. Obshch, Khim.*, **57**, 311-321 (1987).

[21] O. J. Scherer and W. Jassel, *Chem. Ber.*, **110**, 3874-3880 (1977).

[22] A. F. Granov, L. V. Razvodovskaya and N. N. Mel'nikov, *Usp. Khim.*, **50**, 606-638 (1981).

[23] W. Z. Mosby, *J. Org. Chem.*, **22**, 671-673 (1957).