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INTRAMOLECULAR P=S AND P=N ALKYLATION. GENERAL METHOD FOR SYNTHESIZING 1,2-HETERAPHOSPHACYCLANES*

I. M. Aladzheva, O. V. Bykhovskaya, D. I. Lobanov, P. V. Petrovskii, K. A. Lysenko, and T. A. Mastryukova

Results have been generalized for investigations on the synthesis of 1,2-thiaphosphacyclanes by intramolecular P=S alkylation of ω-haloalkyl substituted compounds of four-coordinated phosphorus with a P=S bond. The method has been extended to nitrogen-containing analogs with a P=N bond. A new general method is proposed for the synthesis of 1,2-thia- and 1,2-azaphosphacyclanes.

Keywords: 1,2-azaphosphacyclanes, 1,2-thiaphosphacyclanes, intramolecular alkylation, ring–chain halotropic tautomerism.

Interest in the chemistry of phosphorus-containing heterocyclic compounds is linked with their participation in many biochemical processes, with their use as therapeutic preparations and agents for plant protection, with use in organic synthesis, metal-complex catalysis, and other areas. Unlike the 1,3,2-diheteraphosphacyclanes, which have been well investigated, the 1,2-heteraphosphacyclanes have been little studied due to their lower availability. A most part of them were obtained by multistage syntheses, frequently under rigid conditions [1-4].

In recent years we have developed a new general approach to the synthesis of 1,2-heteraphosphacyclanes based on the intramolecular alkylation of ω-haloalkyl substituted compounds of four-coordinated phosphorus with a P=E bond (E = S, N). The aim of the present work was to correlate our investigations on the synthesis and study of the properties of 1,2-thiaphosphacyclanes [5-10] and to supplement them with new data on the development of methods of synthesizing 1,2-azaphosphacyclanes.

Intramolecular P=E alkylation (E=S) was used for the first time for the synthesis of 2,2-diphenyl-1,2λ^4-thiaphospholanium iodide and 2,2-diphenyl-1,2λ^4-thiaphosphorinanium iodide (**1**), which were obtained on refluxing ω-chloroalkyldiphenylphosphine sulfides **2** with NaI in acetone [5] (Scheme 1). Reaction occurs through the intermediate formation of the ω-iodoalkyl-substituted derivatives **3**, revealed on the base of ^{31}P and ^{1}H NMR spectra. The ω-bromoalkyl-substituted phosphine sulfides **4** are smoothly converted on short-term heating at 100°C in the absence of solvent into the cyclic bromides **5** [6,8], from which the perchlorates **6** and tetrafluoroborate **7b** are obtained by anion exchange reaction [7].

* Dear Mikhail Grigorievich! Accept our congratulations on your anniversary. We acknowledge profoundly your enormous creative powers.

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 119991; e-mail: fos@ineos.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 105-116, January, 2002. Original article submitted June 8, 2001.

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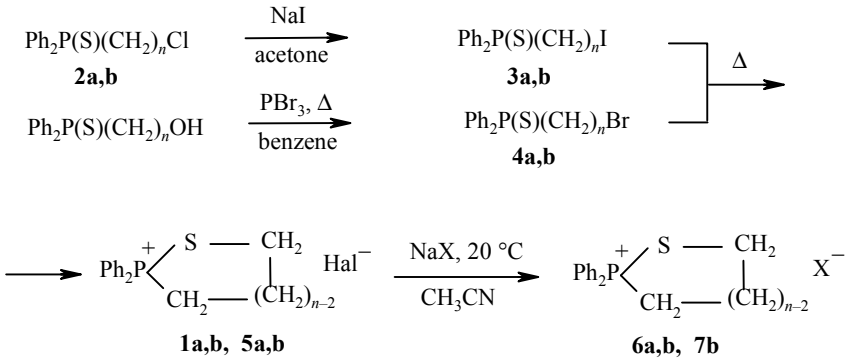
Scheme 1



1 Hal = I, **5** Hal = Br, **6** X = ClO_4, **7** X = BF_4, **a** n = 3, **b** n = 4

The 1,2-thiaphosphacyclanium salts **1**, **5-7** are stable crystalline compounds, which structures were confirmed by data of IR, and ^{31}P and ^{1}H NMR spectra (Table 1), and also by data of X-ray structural investigations for iodides **1a,b**, bromides **5a,b**, and for perchlorate **6a**. An intense absorption band was observed in the IR spectra of the cyclic salts at 570 cm^{-1}, assigned to the vibrations of the P–S–CH_2 ring fragment. The position of the δ_P signal in the ^{31}P NMR spectra depends on the ring size. It was shifted by 35 ppm towards low field in 1,2-thiaphospholanium salts compared with 1,2-thiaphosphorinanium salts, which is in agreement with the data of [11].

According to the data of X-ray structural investigations [5-7] the five-membered phosphorus-containing rings in compounds **1a**, **5a**, and **6a** are characterized by an envelope conformation with the average deviation of one of the carbon atoms from the plane of the remaining coplanar atoms by 0.6 Å. The six-membered phosphorus-containing rings in 1,2-thiaphosphorinanium salts **1b** and **5b** have the conformation of a slightly distorted chair. In all the structures investigated the phosphorus atom is characterized by a slightly distorted tetrahedral configuration with a reduction in the endocyclic angle to 100.3(2)° and 108.1(2)° in the 1,2-thiaphospholanium and 1,2-thiaphosphorinanium rings respectively. Unexpectedly shortened $P^{+}S\cdots Hal^{-}$ interionic contacts were detected for the halide salts. 1,2-Thiaphosphacyclanes have not been investigated by X-ray structural analysis previously.

TABLE 1. Physicochemical and Spectral Characteristics of Compounds **1, 5-7**

Com-pound	mp, °C (solvent)	IR spectrum (KBr), ν, (P–S–CH_2), cm^{-1}	^{31}P NMR spectrum (in CH_2Cl_2), δ, ppm	Yield, %	Ref.
1a	203-204 (CH_3CN–EtOAc)	572	72.2	77	[5]
1b	204-205 (CH_3CN–EtOAc)	565	37.6	65	[5]
5a	163-164 ($CHCl_3$–EtOAc)	572	72.6	77	[6]
5b	161-162 ($CHCl_3$–EtOAc)	567	38.0	78	[8]
6a	152-153.5 ($CHCl_3$–ether)	570	72.6	81	[7]
6b	182-184 (CH_2Cl_2–ether)	570	37.6	67	[7]
7b	186-188 (CH_2Cl_2–ether)	572	37.4	Quant.	[7]

The behavior of 1,2-thiaphosphacyclanium salts **1** and **5** and ω-haloalkylphosphine sulfides **2** and **4** in solution proved to be very interesting. It was found that a tautomeric equilibrium was established in solution between the cyclic and linear forms, which belongs to a new type of ring–chain anionotropic tautomerism, comparatively rarely met in organic chemistry and little investigated [12]. We studied the ring–chain tautomerism of 1,2-thiaphosphacyclanium salts using bromides as an example, for which both the linear **4a,b** and cyclic **5a,b** isomers were successfully isolated as individual compounds [6,8]. The equilibrium for bromide **5a** and its linear isomer **4a** in CH_2Cl_2 was established after 1 day. In the case of bromide **5b** with a six-membered ring (or its linear isomer **4b**) about 25 days were required to establish equilibrium in CH_2Cl_2 at 20°C. The dependence of the position of tautomeric equilibrium on temperature was studied using bromide **4a** as example by ^{31}P NMR spectroscopy. On increasing the temperature the content of the linear form in the equilibrium mixture increased, i.e. the conversion of the cyclic into the linear form, as in other ring–chain tautomeric systems, is an endothermal process. Certain thermodynamic parameters of the equilibrium have been calculated [6].

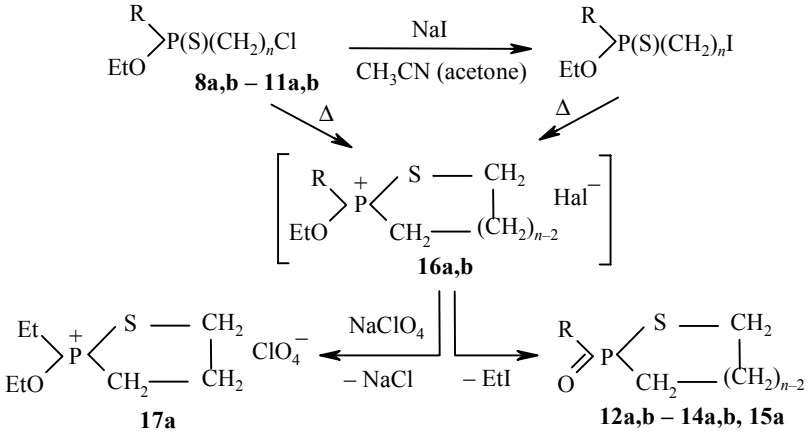
Kinetic investigations of the tautomeric interconversions **5a**⇄**4a** and **5b**⇄**4b** were carried out by ^{31}P NMR spectroscopy in CH_2Cl_2 at 20°C. Both the cyclic and linear isomers were used as starting materials. The rate constants k_1 and k_2 for the mutual interconversion of isomers were calculated [7].

A study of the various factors on the position of equilibrium in solutions of the cyclic salts and their linear isomers showed (Table 2) [7] that the content of the cyclic form in the equilibrium mixture increased on going from the 1,2-thiaphospholane ring to the 1,2-thiaphosphorinane, from chlorides to bromides, and further to iodides and salts with complex anions. The content of the cyclic form is also increased on reducing the temperature and increasing the polarity of the solvent.

The intramolecular P=S alkylation reaction was also investigated for other classes of ω-haloalkyl-substituted compounds with a P=S group to synthesize new types of 1,2-thiaphosphacyclanes [10].

It was established that esters of ω-chloroalkylphosphonic and thiophosphinic acids (**8-11**), with an alkoxy substituent at the phosphorus atom, undergo an intramolecular thione–thiol rearrangement on refluxing with an excess of NaI in acetone or acetonitrile with the formation of 2-substituted 2-oxo-1,2-thiaphosphacyclanes (so-called thiolphostones) **12-15**.

Scheme 2



8, 12 R = EtO, **9, 13** R = Ph, **10, 14** R = Et, **11, 15** R = Et_2N, Hal = Cl, I, **a** n = 3, **b** n = 4

The compounds synthesized (with the exception of the crystalline thiolphostones **13a,b**) were undistillable oily liquids, which were purified by column chromatography. The structures of the compounds obtained were confirmed by IR, ^{31}P NMR (Table 3) and ^{1}H NMR spectra, and for compounds **13a,b** by data of ^{13}C NMR spectra as well [10].

TABLE 2. Content of the Cyclic Form (%) in Solutions of Compounds **1**, **2**, and **4-6** (according to ^{31}P NMR spectra) [7]

Solvent	Chlorides		Bromides		Iodides		Perchlorates	
	n = 3	*n* = 4	*n* = 3	*n* = 4	*n* = 3	*n* = 4	*n* = 3	*n* = 4
CH_2Cl_2	0	0	38	48	70	85	100	100
$CHCl_3$	0	0	65	85	87	92	100	100
CH_3CN	9*	3*[2]	82	82	100	100	—	—

*After 6 months.
*[2] System did not achieve an equilibrium state.

TABLE 3. Physicochemical and Spectral Characteristics of Compounds **12-15** and **17** [7, 10]

Compound	mp, °C (solvent)	IR spectrum (KBr), ν, cm^{-1}		^{31}P NMR spectrum (in CH_2Cl_2), δ, ppm	Yield*, %
		P–S–CH_2	P=O		
12a	Oil*[2]	555	1212, 1232	83.0	90
12b	Oil*[2]	543	1218, 1248	46.8	65
13a	102-103 (hexane)	555	1190	73.4	95
13b	77-78.5 (hexane)	548	1190	39.5	96
14a·0.4NaI	Oil*[2]	555	1190	92.9 br. s	82
14b·0.5NaI	Oil*[2]	553	1190	56.5 br. s	86
15a	Oil*[2]	535	1200, 1230	76.4	83
17a	93-95 (MeCN–EtOAc)	565	—	138.8	27

* From ^{31}P NMR spectra of the reaction mixture.
*[2] Purified by column chromatography.

The structure of the 2-phenyl substituted thiaphosphorinane **13b** was investigated by X-ray structural analysis. It was found that the 1,2-thiaphosphorinane ring has a slightly distorted chair conformation with the oxygen atom of the P=O group in the axial position. The bond lengths were close to the corresponding values for the 1,2-thiaphosphacyclanium salts investigated previously [7].

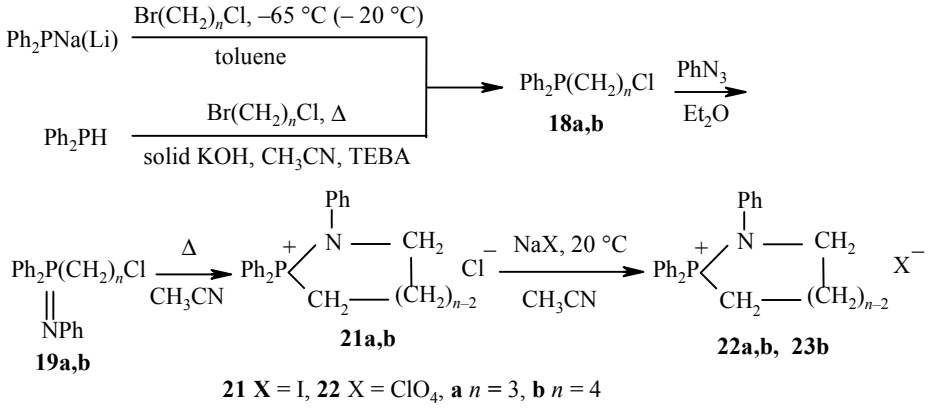
It was estimated that the rate of rearrangement of esters of ω-haloalkyl substituted phosphorus thioacids was influenced by the length of the alkyl chain in the ω-haloalkyl residue (1,2-thiaphospholane cycles are formed more readily), the polarity of the solvent, the temperature, and the nature of the substituent R at the phosphorus atom. Reaction occurs through the intermediate formation of products of P=S alkylation, the quasiphosphonium salts **16** (Scheme 2), the dealkylation of which under the reaction conditions leads to the final thiolphostones **12-15**. We succeeded, by substituting the nucleophilic halogen anion by perchlorate anion in the case of **16a** (R = Et), in obtaining the crystalline perchlorate **17a** (Scheme 2, Table 3), the first isolated intermediate of the thiol-thiol rearrangement of esters of phosphorus thioacids proceeding under the action of alkyl halides.

The intramolecular P=E alkylation method has been further extended to ω-haloalkyl-substituted iminophosphoryl compounds. It is known that the P=N group exceeds significantly the P=S group in relative reactivity in nucleophilic substitution reactions. Consequently it might have been expected that alkylation of iminophosphoryl compounds will take place under milder conditions. To synthesize ω-haloalkyl-substituted iminophosphoryl compounds by the interaction of ω-chloroalkyldiphenylphosphines **18a,b** with phenyl azide the iminophosphoranes **19a,b** were synthesized.

Two methods were used to obtain phosphines **18a,b**. These were the alkylation of $Ph_2PNa(Li)$ with α,ω-bromochloroalkanes in toluene (classical method) [13-15], and the alkylation of Ph_2PH with α,ω-bromochloroalkanes under phase-transfer catalysis (PTC) conditions in the two-phase system of solid KOH/CH_3CN in the presence of triethylbenzylammonium chloride (TEBA) as catalyst. The latter method was significantly more simple experimentally.

Phosphine **18b** was obtained in low yield, which is explained by its partial cyclization under the conditions of the reaction leading to 1,1-diphenylphospholanium chloride. The latter is hydrolyzed under PTC conditions with the formation of 1-oxo-1-phenylphospholane **20** (see Experimental).

Scheme 3



21 X = I, **22** X = ClO_4, **a** n = 3, **b** n = 4

TABLE 4. Physicochemical Characteristics of Compounds **19**, **21-23**

Compound	Empirical formula	Found, % / Calculated, %					mp, °C (solvent)	Yield, %
		C	H	Hal	N	P		
19a	$C_{21}H_{21}ClNP$	71.20 / 71.28	6.17 / 5.98	—	3.84 / 3.96	—	—*	15.0 (86)*[2]
19b	$C_{22}H_{23}ClNP$	71.81 / 71.84	6.35 / 6.26	—	3.70 / 3.81	8.42 / 8.44	81-83 (hexane)	30.0 (87)*[2]
21a*[3]	$C_{21}H_{21}ClNP{\cdot}H_2O$	67.63 / 67.87	6.36 / 6.23	—	3.53 / 3.77	—	—*[4]	85 (70)*[5]
21b	$C_{22}H_{23}ClNP$	72.09 / 71.84	6.23 / 6.26	9.60 / 9.66	3.71 / 3.81	8.30 / 8.44	226-230 (decomp.) (CH_2Cl_2–EtOAc)	quant. (96)*[5]
22a	$C_{21}H_{21}INP$	57.00 / 56.64	4.97 / 4.75	29.15 / 28.50	—	6.86 / 6.96	232-234 (decomp.) (CH_2Cl_2–EtOAc)	92
22b	$C_{22}H_{23}INP$	57.60 / 57.53	5.18 / 5.05	27.81 / 27.63	—	6.71 / 6.74	191-193 (decomp.) (CH_2Cl_2–EtOAc)	80
23b	$C_{22}H_{23}ClNO_4P$	61.20 / 61.19	5.38 / 5.37	8.97 / 8.21	3.24 / 3.22	7.34 / 7.17	213-215 (decomp.) (CH_2Cl_2–EtOAc)	82

* Undergoes cyclization on determining mp.

*[2] According to data of ^{31}P NMR spectra of the reaction mixture.

*[3] Crystallizes with a molecule of water.

*[4] Decomposes on determining mp.

*[5] Yield from phosphine **18**.

TABLE 5. Spectral Characteristics of Compounds **19** (in C_6D_6) and **21-23** (in $CDCl_3$)

Com-pound*	^{31}P NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ, ppm, coupling constant *J* (Hz)*[2]	^{1}H NMR spectrum, δ, ppm, coupling constant *J* (Hz)
19a	2.78		1.84-1.94 (2H, m, C<u>H</u>$_2$CH$_2$P); 2.34-2.44 (2H, m, CH$_2$P); 3.08 (2H, t, $^3J_{HH}$ = 6.2, CH$_2$Cl); 6.87-7.78 (15H, m, H$_{arom}$)
19b	3.77	19.47 (<u>C</u>H$_2$CH$_2$P, d, $^2J_{PC}$ = 3.2); 27.17 (CH$_2$P, d, $^1J_{PC}$ = 69.5); 33.33 (<u>C</u>H$_2$CH$_2$Cl, d, $^3J_{PC}$ = 13.5); 43.97 (CH$_2$Cl, br. s)	1.41 (2H, dt, $^3J_{HH}$ = 7.2, C<u>H</u>$_2$CH$_2$Cl); 1.55-1.66 (2H, m, C<u>H</u>$_2$CH$_2$P); 2.06-2.15 (2H, m, CH$_2$P); 2.90 (2H, t, $^3J_{HH}$ = 6.8, CH$_2$Cl); 6.87-7.82 (15H, m, H$_{arom}$)
22a	54.6	21.68 (<u>C</u>H$_2$CH$_2$P, s); 28.27 (CH$_2$P, d, $^1J_{PC}$ = 63.4); 52.99 (CH$_2$N, d, $^2J_{PC}$ = 16.5)	2.46 (2H, s, H$_2$O); 2.49-2.54 (2H, m, C<u>H</u>$_2$CH$_2$P); 3.68 (2H, dt, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 7.2, CH$_2$N); 4.32 (2H, dt, $^3J_{HH}$ = 6.0, $^2J_{PH}$ = 8.4, CH$_2$P); 6.76-8.00 (15H, m, H$_{arom}$)
22b	42.5	19.44 (<u>C</u>H$_2$CH$_2$P, s); 22.48 (CH$_2$P, d, $^1J_{PC}$ = 61.0); 25.04 (<u>C</u>H$_2$CH$_2$N, d, $^3J_{PC}$ = 5.4); 54.11 (CH$_2$N, d, $^2J_{PC}$ = 1.7)	2.11-2.28 (4H, m, <u>C</u>H$_2$<u>C</u>H$_2$CH$_2$P); 3.37-3.45 (2H, m, CH$_2$N); 3.78-3.88 (2H, m, CH$_2$P); 6.93-7.85 (15H, m, H$_{arom}$)
23a	53.9	21.31 (<u>C</u>H$_2$CH$_2$P, s); 28.45 (CH$_2$P, d, $^1J_{PC}$ = 64.5); 52.87 (CH$_2$N, d, $^2J_{PC}$ = 16.5)	2.66 (2H, m, <u>C</u>H$_2$CH$_2$P); 3.64 (2H, dt, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 7.6, CH$_2$N); 4.38 (2H, dt, $^3J_{HH}$ = 6.4, $^2J_{PH}$ = 8.4, CH$_2$P); 6.89-8.04 (15H, m, H$_{arom}$)
23b	42.0	19.38 (<u>C</u>H$_2$CH$_2$P, d, $^2J_{PC}$ = 7.1); 23.06 (CH$_2$P, d, $^1J_{PC}$ = 61.9); 25.07 (<u>C</u>H$_2$CH$_2$N, d, $^3J_{PC}$ = 5.3); 54.17 (CH$_2$N, br. s)	2.13-2.32 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$P); 3.23-3.31(2H, m, CH$_2$N); 3.85-3.93 (2H, m, CH$_2$P); 7.04-7.84 (15H, m, H$_{arom}$)
24	41.7	19.38 (<u>C</u>H$_2$CH$_2$P, d, $^2J_{PC}$ = 7.1); 22.42 (CH$_2$P, d, $^1J_{PC}$ = 62.6); 25.09 (<u>C</u>H$_2$CH$_2$N, d, $^3J_{PC}$ = 4.3); 54.16 (CH$_2$N, br. s)	2.14-2.28 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CH$_2$P); 2.98-3.07 (2H, m, CH$_2$N); 3.91 (2H, dt, $^3J_{HH}$ = 5.6, $^3J_{PH}$ = 8.8, CH$_2$P); 7.00-7.78 (15H, m, H$_{arom}$)

* IR spectrum (KBr): $\nu_{P=N}$ 1346 (**19a**) and 1340 cm^{-1} (**19b**).

*[2] Chemical shifts of benzene ring carbon atoms are not given.

The interaction of phosphines **18a,b** with phenyl azide in ether solution proceeds to iminophosphoranes **19a,b** in high yield, according to data of ^{31}P NMR spectra of the reaction mixture. However isolation of the crystalline readily hydrolysable compounds **19a,b** succeeded with significantly lower yields (see [16]). This is attributed preferably to iminophosphorane **19a**, for which an intramolecular P=N alkylation partially occurs during its isolation with the formation of 1,2,2-triphenyl-1,2λ^4-azaphospholanium chloride (**21a**). The composition and structure of iminophosphoranes **19a,b** were confirmed by data of elemental analysis, IR spectra, and ^1H, ^{31}P, and ^{13}C NMR spectra (Tables 4, 5).

An intense absorption band was present in the IR spectra of the compounds at 1300 cm^{-1} for the stretching vibrations of the P=N group. The chemical shift of the δ_P signal in the ^{31}P NMR spectra was found in the region of iminophosphorane signals (about 0 ppm) [11]. In the ^1H NMR spectra a characteristic triplet signal was observed near 3.0 ppm for the protons of the $(CH_2)CH_2Cl$ group with a coupling constant of about 6 Hz in addition to multiplet signals for the protons of the CH_2 groups and the phenyl rings.

Further investigations showed that iminophosphoranes **19a,b** readily entered into an intramolecular alkylation reaction with the formation of 1,2,2-triphenyl-1,2λ^4-azaphospholanium salt **21a** and azaphosphorinanium salt **21b**. The rate of cyclization depended significantly on the length of the alkyl chain. In benzene iminophosphorane **19a** was completely converted into chloride **21a** on heating for 40 min at 50°C, while iminophosphorane **19b** was cyclized to only 30% on refluxing in benzene for 3 h. In the more polar CH_3CN the cyclization of iminophosphorane **19b** was completed after 2 h at 80°C. To increase the yield, chlorides **21a,b** were also obtained directly from phosphines **18a,b** without isolating the intermediate iminophosphoranes **19a,b**. The yields in this case were 70 and 96% calculated on the initial phosphine. It was established [7] that in difference to the iminophosphoranes **19a,b**, the phosphine sulfides **2a,b** with an ω-chloroalkyl substituent on the phosphorus atom did not participate in the intramolecular alkylation reaction even under rigid conditions.

The synthesized compounds **21a,b** are high-melting crystalline substances. The iodides **22a,b** and a perchlorate **23b** were obtained by anion exchange from the chlorides (Table 4). The structures of compounds **21-23** were confirmed by data of NMR spectra (^1H, ^{31}P, ^{13}C) (Table 5). The δ_P signal low-field shift was observed in the ^{31}P NMR spectra of the 1,2-azaphospholanium salts **21a, 22a** compared with the 1,2-azaphosphorinanium salts **21b, 22b** ($\Delta\delta$ 12 ppm).

The structures of iodides **22a,b** were investigated by X-ray structural analysis (Figs. 1 and 2).

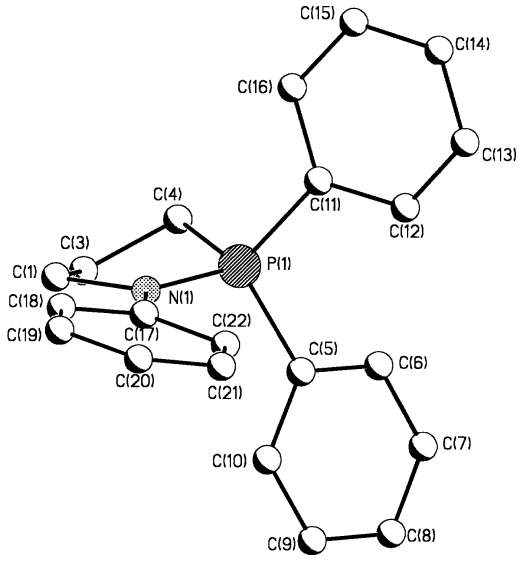


Fig. 1. General view and numbering of atoms in the cation of iodide **22a**.

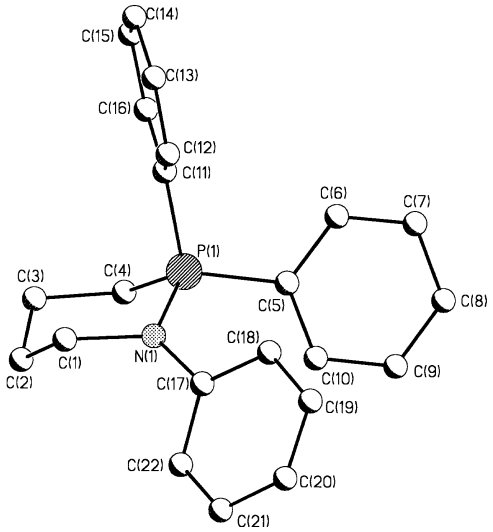


Fig. 2. General view and numbering of atoms in the cation of iodide **22b**.

The main geometric parameters, with the exception of the endocyclic angle $N_{(1)}P_{(1)}C_{(4)}$ do not in fact depend on the size of the ring (Table 6). The 1,2-azaphospholane ring is characterized by an envelope conformation with deviation of the $C_{(3)}$ atom from the plane of $C_{(1)}N_{(1)}P_{(1)}C_{(4)}$ by 0.54 Å, but the 1,2-azaphosphorinane ring has the conformation of a slightly distorted chair. The bonds at the nitrogen atom in both structures lie in a plane (sum of valence angles at $N_{(1)}$ is 359.6° on average). The mutual dispositions of the $N_{(1)}$–$P_{(1)}$ bond and the phenyl group at the nitrogen atom in cations **22a** and **22b** are different. In **22a** the torsion angle $N_{(1)}$–$P_{(1)}$–$C_{(17)}$–$C_{(22)}$ is equal to 13° while in **22b** it is 45°, which probably causes the differences in the $N_{(1)}$–$C_{(11)}$ distance. The iodine anions in both structures participate in the formation of weak C–H···I contacts (the H···I distances are in the range 2.9-3.1 Å).

Unlike the 1,2-thiaphosphacyclanium salts **1, 5** no ring–chain halotropic tautomerism was detected in solutions of 1,2-azaphosphacyclanium chlorides and iodides **21** and **22** according to data of ^{31}P NMR spectra. In this case due to the higher nucleophilicity of the nitrogen atom of the P=N group the equilibrium is completely displaced to the cyclic isomer.

TABLE 6. Bond Lengths and Valence Angles in Compounds **22a,b**

Bond	*d*, Å		Angle	ω, deg	
	22a*	**22b**		**22a***	**22b**
$P_{(1)}$–$N_{(1)}$	1.644(4)	1.641(5)	$N_{(1)}$–$P_{(1)}$–$C_{(4)}$	96.8(2)	105.3(3)
$P_{(1)}$–$C_{(4)}$	1.788(5)	1.794(6)	$N_{(1)}$–$P_{(1)}$–$C_{(5)}$	111.3(2)	112.0(2)
$P_{(1)}$–$C_{(5)}$	1.787(5)	1.779(5)	$N_{(1)}$–$P_{(1)}$–$C_{(11)}$	113.3(2)	109.2(3)
$P_{(1)}$–$C_{(11)}$	1.796(4)	1.793(5)	$C_{(4)}$–$P_{(1)}$–$C_{(5)}$	110.9(3)	110.7(3)
$N_{(1)}$–$C_{(1)}$	1.492(6)	1.494(7)	$C_{(4)}$–$P_{(1)}$–$C_{(11)}$	112.5(2)	109.3(3)
$N_{(1)}$–$C_{(17)}$	1.421(6)	1.437(7)	$C_{(5)}$–$P_{(1)}$–$C_{(11)}$	111.3(2)	110.1(2)
			$P_{(1)}$–$N_{(1)}$–$C_{(17)}$	126.2(3)	127.7(4)
			$P_{(1)}$–$N_{(1)}$–$C_{(1)}$	112.0(3)	113.9(4)
			$C_{(1)}$–$N_{(1)}$–$C_{(17)}$	121.4(4)	118.4(4)

* Mean values for the two independent molecules are given for compound **22a**.

TABLE 7. Main Crystallographic Parameters and Refinement Characteristics of Compounds **22a** and **22b**

Parameter	$C_{21}H_{21}INP$ (**23a**)	$C_{22}H_{23}INP$ (**23b**)
M	445.26	459.28
F(000)	1776	460
μ (Mo*K*α), cm^{-1}	17.33	16.83
d_{calc}, $g \cdot cm^{-3}$	1.522	1.523
Space group	$P2_1/c$	$P2_1$
Diffractometer	Siemens P3/PC	Smart 1K CCD
Scanning type	θ/2θ	ω with 0.3° step in ω and 10 sec exposure for each frame
T, K	298	110
a, Å	13.570(2)	8.1818(4)
b, Å	14.285(2)	10.3687(6)
c, Å	20.554(2)	12.1005(7)
β, deg	102.82(1)	102.755(1)
V, $Å^3$	3885.0(7)	1001.2(1)
Z	8	2
$2\theta_{max}$, deg	50	55
Reflections measured	6464	6860
Independent reflections	6157 (R_{int} = 0.0232)	3576 (R_{int} = 0.0235)
wR_2 calculated on F^2 for each reflection	0.0856	0.0932
R_1 calculated on *F* for reflections with I > 2 σ(*I*)	0.0378 (4554 ref.)	0.0376 (3335 ref.)
GOF	0.989	1.020

In conclusion it must be said that the P=E intramolecular alkylation method may also be used for the synthesis of 1,2-heteraphosphacyclanes containing various functional substituents in the ring. For example the method was successfully applied to the synthesis of 3-cyano-substituted 1,2-thiaphosphacyclanes [17,18].

EXPERIMENTAL

Reactions were carried out in an atmosphere of argon using absolute solvents. The IR spectra were taken on a UR 20 instrument (KBr). The NMR spectra were recorded on Bruker WP 200SY (operating frequency 200.13 MHz for ^1H and 81.01 MHz for ^{31}P) and Bruker AMX 400 (operating frequency 400.13 MHz for ^1H, 161.98 MHz for ^{31}P, and 100.61 MHz for ^{13}C) instruments. Internal standard was TMS (^1H, ^{13}C), external standard was 85% H_3PO_4 (^{31}P).

(3-Chloropropyl)diphenylphosphine (18a). Powdered KOH (1.12 g, 20 mmol) was added at 20°C with vigorous stirring to a solution of Ph_2PH (1.50 g, 8.0 mmol), 1,3-bromochloropropane (1.88 g, 12 mmol), and TEBA (0.20 g, 0.9 mmol) in CH_3CN (10 ml). The reaction mixture was heated at 70°C for 1.5 h, then benzene (20 ml) and ice-water (20 ml) were added on cooling. The benzene layer was separated, washed with water (2 × 10 ml), and dried over Na_2SO_4. The benzene was removed in vacuum, the residue was extracted with boiling hexane, and the extract left for 1 day in the refrigerator. The hexane solution was decanted from the crystalline residue, the solvent and the excess of 1,3-bromochloropropane were removed by heating in vacuum. Phosphine **18a** was obtained as a viscous oil. Yield 1.56 g (74%). ^{31}P NMR (hexane): -16.9 ppm (lit. [13]: δ_P -17.5 ppm).

(4-Chlorobutyl)diphenylphosphine (18b) was obtained analogously to **18a** from Ph_2PH (2.0 g, 11 mmol), 1,4-bromochlorobutane (3.77 g, 22 mmol), KOH (1.50 g, 26 mmol), and TEBA (0.24 g, 1.1 mmol) in CH_3CN (15 ml). The mixture was heated at 55-60°C for 1.5 h, then treated as in the previous experiment at a

temperature below 40°C. Compound **18b** (1.30 g, 43%) was obtained as a viscous oil. ^{31}P NMR spectrum (hexane): -16.4 ppm {lit. [14]: δ_P -17.1 ppm ($CHCl_3$)}.

(3-Chloropropyl)diphenylphenyliminophosphorane (19a). Phenyl azide (0.78 g, 6.5 mmol) in ether (9 ml) was added dropwise to a solution of compound **18a** (1.56 g, 5.9 mmol) in ether (10 ml). Evolution of nitrogen was observed and the reaction mixture warmed to 26°C. The reaction mixture was stirred for 1 h at 20°C and then for 1 h on refluxing. The ether was removed, the residue was maintained in vacuum (1 mm Hg) at a temperature no greater than 40°C, and then extracted with hot hexane. The crystalline solid precipitated from the hexane solution was filtered off, and iminophosphorane **19a** (0.31 g, 15%) was obtained (Tables 4, 5).

(4-Dhlorobutyl)diphenylphenyliminophosphorane (19b) was obtained analogously to compound **19a** from phosphine **18b** (1.3 g, 4.7 mmol) and PhN_3 (0.8 g, 6.7 mmol) in ether. The yield of compound **19b** 0.5 g (30%) (Tables 4, 5).

1,2,2-Triphenyl-1,2λ^4-azaphospholanium Chloride (21a). A. Synthesis from iminophosphorane **19a**. A solution of compound **19a** (0.12 g, 0.34 mmol) in benzene (2 ml) was heated at 50°C for 40 min, the precipitated solid was filtered off, washed with benzene, and chloride **21a** (0.10 g, 85%) was isolated (Tables 4, 5).

B. Synthesis from phosphine **18a**. Phenyl azide (0.76 g, 6.4 mmol) in benzene (5 ml) was added dropwise with stirring to a solution of compound **18a** (1.41 g, 5.4 mmol) in benzene (10 ml). The reaction mixture was maintained at 20°C for 1 h, then at 50°C for 40 min, and processed as in method A. Yield 1.34 g (70%).

1,2,2-Triphenyl-1,2λ^4-azaphosphorinanium Chloride (21b). A. Synthesis from iminophosphorane **19b**. A solution of compound **19b** (0.30 g, 0.82 mmol) in CH_3CN (8 ml) was refluxed for 2 h, and the solvent removed in vacuum. Benzene (10 ml) was added to the residue, the mixture refluxed for 10 min, the precipitated solid was filtered off, and washed with benzene. Chloride **21b** (0.30 g, quantitative yield) was obtained (Tables 4, 5).

B. Synthesis from phosphine **18b**. Phenyl azide (0.50 g, 4.0 mmol) in ether (5 ml) was added to a solution of compound **18b** (1.41 g, 5.4 mmol) in ether (5 ml) at 20°C. The reaction mixture was refluxed for 1 h, then CH_3CN (10 ml) added, the mixture refluxed for 2.5 h, and processed as in method A. Yield 0.95 g (96%).

1,2,2-Triphenyl-1,2λ^4-azaphospholanium Iodide (22a). A solution of NaI (0.13 g, 0.87 mmol) in CH_3CN (2 ml) was added at 20°C to a solution of chloride **21a** (0.20 g, 0.56 mmol) in CH_3CN (2 ml). After 1 h the precipitate of NaCl was filtered off, the solvent removed in vacuum, and the residue dissolved in $CHCl_3$ with heating. The excess of NaI was filtered off, and after removing the solvent, the residue was crystallized from CH_2Cl_2–EtOAc. Yield 0.26 g (92%) (Tables 4, 5).

1,2,2-Triphenyl-1,2λ^4-azaphosphorinanium Iodide (22b) was obtained analogously to compound **22a** from chloride **21b** (0.12 g, 0.33 mmol) and NaI (0.15 g, 1.0 mmol) in CH_3CN (7 ml). Yield 0.12 g (80%) (Tables 4, 5).

1,2,2-Triphenyl-1,2λ^4-azaphosphorinanium Perchlorate (23b) was obtained analogously to compound **23a** from chloride **21b** (0.20 g, 0.54 mmol) and $NaClO_4$ (0.20 g, 1.63 mmol) in CH_3CN (15 ml). Yield 0.19 g (82%) (Tables 4, 5).

1-Oxo-1-phenylphospholane (20). The aqueous solution obtained in the synthesis of phosphine **18b** (see above) was evaporated to dryness in vacuum. The residue was extracted with benzene. After removing the benzene the waxy product **20** (0.4 g) was obtained. IR spectrum ($CHCl_3$): $\nu_{P=O}$ 1175 cm^{-1} (lit. [19]: $\nu_{P=O}$ 1180 cm^{-1}). ^{31}P NMR spectrum ($CDCl_3$): δ_P 60.8 ppm. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.77-2.15 [8H, m, $(CH_2CH_2)_2P$]; 7.35-7.68 (5H, m, C_6H_5) {lit. [20]: ^{1}H NMR spectrum, δ, ppm: 1.95 (8H, m); 7.71 (5H, m)}.

X-ray Structural Investigation. The main crystallographic data and refinement characteristics of compounds **22a** and **22b** are given in Table 7. Estimation of the absorption was carried out from azimuthal scanning for (**22a**) and empirically as the equivalent for (**22b**). The structures were solved by the direct method and refined with an anisotropic–isotropic full matrix approach on F^2. The hydrogen atoms were revealed

in difference syntheses of electron density and inserted in the final refinement in an isotropic approach. The absolute configuration of structure **22b** was determined based on the Flack parameter [0.02(3)]. All calculations were carried out using the SHELXTL PLUS Ver. 5.0 set of programs on a personal computer.

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