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Pishchimuka's Intramolecular Rearrangement. The General Method for the Synthesis of 2-Oxo-1,2λ^5-thiaphoapholanes and Thiaphosphorinanes

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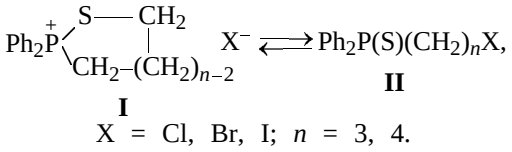
Abstract — A new method is developed for the synthesis of 2-substituted 2-oxo-1,2λ^5-thiaphospholanes and thiaphosphorinanes (thiolphostones) on the basis of intramolecular Pishchimuka rearrangement of thiophosphonic and thiophosphinic esters with ω-chloroalkyl substituentsat the phosphorus atom. Intermediate compound in the Pishchimuka rearrangement, 2-ethyl-2-ethoxy-1,2λ^4-thiaphospholanium perchlorate, was isolated.

Unlike 1,3,2-diheterophosphacyclanes, 1,2-monoheterophosphacyclanes were much less studied. Most of the synthesized compounds belonging to this class are 1,2-oxaphospholanes and 1,2-oxaphosphorinanes. Related sulfur-containing compounds, 1,2-thiaphospholanes and 1,2-thiaphosphorinanes are poorly investigated and there are no convenient methods for their synthesis. Hovever, such compounds are undoubtedly interesting as cyclic analogs of the phosphorus thioacids *S*-alkyl estersr which play important role in the pesticide ichemistry. Besides, phosphorus acids thioesters are widely used in biochemical investigations as sulfur analogs of nucleotides [1, 2]. Recently [3–5] we developed a new general approach to the synthesis of 1,2-thiaphosphacyclanes based on the reaction of haloalkyl-substituted organothiophosphorus compounds possessing a P=S bond. We prepared a series of 2,2-diphenyl-1,2λ^4-thiaphosphacyclanium salts (**I**). That showed in solution a rare type of ring-chain halotropic tautomerism **I** ⇄ **II** (scheme 1).

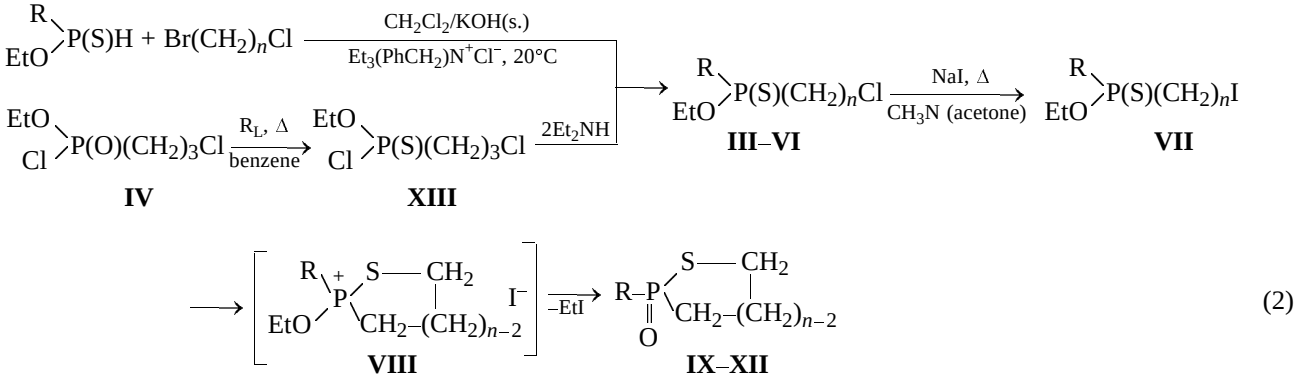


(1)

I

X = Cl, Br, I; *n* = 3, 4.

We found that in the case of *O*,*O*'-diethyl ω-cloroalkylthiophosphonates (**IIIa, IIIb**) this reaction not stops in the step of formation of phosphonium salt **VIII** (scheme 2) but 2-oxo-2-ethoxy-1,2λ^5-thiaphospholane (**IXa**) and 2-oxo-2-ethoxy-1,2λ^5-thiaphosphrinane (**IXb**) are formed, as a result of Pishchimuka rearrangement.



(2)

R = EtO (**III, IX**), Ph (**IV, X**), Et (**V, XI**), Et$_2$N (**VI, XII**); *n* = 3 (**a**), 4 (**b**); R_L is Lawesson reagent.

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Table 1. Yields, physical constants and IR and NMR spectral data of ω-chloroalkyl-substituted thiophosphonates and thiophosphinates **III**–**VI**

Comp. no.	Yield, %[a]	bp, °C (*p*, mm)	n_D^{20}	d_4^{20}	IR spectrum (KBr), ν(P=S), cm^{-1}	^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm
IIIa[b]	86	103–105 (1)	1.4859	1.1488	610	97.6
IIIb[b]	82	120–122 (3)	1.4869	1.1377	610	98.5
IVa	80	[c]	1.5639	1.1858	618, 625	92.1
IVb	81	163–165 (2)	1.5586	1.1629	618, 625	92.6
Va	77	116–119 (3)	1.5075	1.1226	590	104.0
Vb	77	123–124 (2)	1.5041	1.1210	590	104.3
VIa	90	130–132 (1)	1.5127	1.1229	605	91.5

[a] The yield from the ^{31}P NMR spectrum of reaction mixture. [b] From data of [5]. [c] Exerts rearrangement at the vacuum distillation.

In this work we expanded intramolecular *S*-alkylation over a series of new ω-chloroalkyl-substituted thiophosphinates and thiophosphonates. On the ground of the obtained results we propose the general method for the synthesis of 2-substituted 2-oxo-1,2λ^5-thiaphospholanes and thiaphosphorinanes (thiolphostones). Only two compounds of such type obtained by much more complicated route has been described before our investigations [6].

We prepared initial compounds, ω-chloroalkylthiophosphonate esters **IV**, **V**, by the action of α,ω-bromochloroalkanes on the incomplete thiophosphorus acid esters under the conditions of phase transfer catalysis (Scheme 2). Thiophosphonate **VIa** containing dimethylamino group was synthesized by reaction of acyl chloride **XIII** with diethylamine. The Acyl chloride **XIII** in turn was prepared by reaction of its oxygenic analog **XIV** with Lawesson reagent.

Compounds **IV**–**VI** that we first prepared are capable of distillation liquids, except 3-chloropropylthiophosphinate **IVa** containing phenyl group attached to phosphorus (Attempted distillation of this compound in 2 mm Hg vacuum at 160–170°C resulted in Pishchimuka rearrangement). Analytically pure samples of thiophosphonates **IV**–**VI** were prepared by column chromatography (Table 1).

IR spectra of the initial compounds **III**–**VI** (Table 1) contain absorption band of P=S group in the region of 590–625 cm^{-1} [5]. 31P NMR spectra contain a singlet in the region typical of thionophosphinic and thionophosphonic esters [7]. ^1H NMR spectra of each compound (solutions in CDCl3) besides other signals contain triplet or multiplet signal in the region of 3.40–3.60 ppm ($^3J_{HH}$ 6.0–6.4 Hz) related to the protons of CH_2CH_2Cl group (cf. Experimental).

In the course of this investigation we found that boiling of ω-chloroalkylsubstituted thiophosphinates and thiophosphonates **IV**–**VI** with excess sodium iodide in acetone or acetyonitrile leads to intramolecular Pishchimuka's rearrangement (Scheme 2). As a result, corresponding 2-substituted 2-oxo-1,2λ5-thiaphosphacyclanes **X**–**XII** are formed (Table 2). Like the case with thiophosphonates **III**, these reaction obviously proceed via formation of ω-iodoalkyl-substituted intermediates **VII**. The process of rearrangement was monitored by ^{31}P NMR spectroscopy. We established that the rearrangement rate is affected by the size of alkylene chain in the ω-chloroalkyl group and by the nature of the solvent used. Thus, 3-chloropropyl-substituted thiophosphorus acid esters **IVa** and **Va** enter this reaction with twice higher rate than corresponding 4-chlorobutyl-substituted compounds **IVb** and **Vb**. In acetone, the rearrangement is twice slower than in acetonitrile, probably not only due to higher polarity, but also due to higher boiling temperature of the later. Nature of substituent R at the phosphorus atom affects less the reaction rate. It follows from the results obtained that the higher reaction rate of intramolecular Pishchimuka's rearrangement occurs in the case of thiophosphinates Va and **Vb** possessing ethyl group at phosphorus atom (cf. Experimental). Ethoxy derivatives **IIIa** and **IIIb** requires the most prolonged heating [5].

All the synthesized 2-substituted 2-oxo-1,2λ5-thiaphosphacyclanes **X**–**XII** (except crystalline 2-phenyl derivatives **Xa** and **Xb**) are oily liquid that cannot be distilled, and they were purified by column chromatography. Compounds **Xa** and **Xb** were recrystallized from hexane. Note that 2-ethyl-2-oxo-1,2λ5-thiaphosphacyclanes **XIa** and **XIb** were isolated as complexes wit sodium iodide. Treatment of the complexes with water did not give nonbonded thiolphostones, but resulted in cleavage of the rings. Structures of all synthesized 2-oxo-1,2λ5-thiaphosphacyclanes were confirmed by the data of IR spectroscopy and ^{31}P and

^{1}H NMR spectroscopy, and for compounds **Xa** and **Xb** also by ^{13}C NMR spectroscopy (Table 2, see Experimental).

In the IR spectra of compounds **IX**–**XII** instead of the absorption band of P=S group occurred in the spectra of parent thiophosphontates and thiophosphinates, appears absorption band of P–S–CH_2 group [5, 8] in the region of 550 cm^{-1} (from 535 till 555 cm^{-1} for certain compounds) and strong band of P=O group at 1190–1250 cm^{-1}. Position of the signal in ^{31}P NMR spectra depends on the size of the ring: for the fivemembered ring compound occurs 33–36 ppm downfield shift compared to thiolphostones with sixmembered ring. Structure of 2-phenylsubstituted thiophosphorinane **Xb** in crystal was studied by X-ray crystallography.

The X-ray diffraction study of compound **Xb** showed that 1,2-thiaphoaphorinane ring has slightly destroyed chair conformation, like the earlier studied similar compounds [5, 9]. The phosphoryl oxygen atom and phenyl group occupy axial and equatorial positions, respectively (Fig. 1). Phosphorus atom is characterized by slightly destroyed tetrahedral coordination, with the endocyclic angle diminished to 103.4(1)°. Bond lengths in compound **Xb** (Fig. 1) are close to those in earlier studied 1,2-thiaphosphacyclanium salts [5] and 2-oxo-3-cyano-1,2-tiaphosphorinanes [9]. Note that P^1=S^1 bond [2.082(1) Å] in **Xb** is sligtly longer, while P^1=O^1 [1.272(2) Å] shorter than in 2-methyl-2-oxo-3-cyano-1,2-tiaphosphorinane [2.062(1) ans 1.488(2) Å, respectively] [9]. Taking into account that P=O group is antiperiplanar to one of sulfur lone pairs and following this difference we can assume that n–σ^* interaction in **Xb** is weaker than in the corresponding cyano derivative.

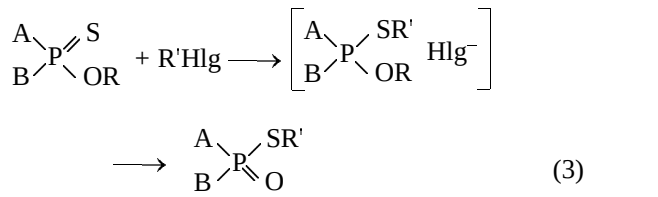
In crystal, **Xb** molecules are joined as chains along crystallographic *b* axis due to strong C–H···O contacts, namely, $C^4H^{4A}\cdots O^{1'}$(*x*, *y* + 1, *z*), $C^4\cdots O^{1'}$ 3.243(3) Å, $H^{4A}\cdots O^{1'}$ 2.21 Å, and $C^4H^4AO^{1'}$ 162°. These chains in turn are bonded by weak C–H···O interactions to form double chains, $C^4H^{4B}\cdots O^{1''}$ (–*x*, 3/2 + *y*, 3/2 – *z*), $C^4\cdots O''$ 3.243(3) Å, $H^{4B}\cdots O''$ 2.52 Å, $C^4H^{4B}O^{1''}$ 154° (Fig. 2).

Now let us consider shortly mechainsm of the studied rearrangement. Earlier for the reaction of thiophosphoric acids *O*-alkyl esters with haloalkyls leading to formation of corresponding *S*-alkyl esters, which has been known in literature as Pishchimuka's rearrangement, was proposed [10, 11] a two-step mechanism with formation of intermediate phosphonium salt where alkyl group of the haloalkyl bonds to sulfur, followed by dealkylation (Scheme 3).

Table 2. Yields, physical constants and IR and ^{31}P NMR spectral data for 2-substituted 2-oxo-1,2λ^5-thiaphospholanes and thiaphosphorinanes **IX**–**XII**

Comp. no.	Yield, %[a]	IR spectra (KBr), ν, cm^{-1}		^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm
		P–S–CH_2	P=O	
IXa[b]	90	555	1212, 1232	83.0
IXb[b]	65	543	1218, 1248	46.8
Xa[c]	95	555	1190	73.4
Xb[d]	96	548	1190	39.5
XIa · 0.4 NaI	82	555	1190	92.9 br.s
XIb · 0.5 NaI	86	553	1190	56.5 br.s
XIIa	83	535	1200, 1230	76.4

[a] The yield from the ^{31}P NMR spectrum of reaction mixture. [b] From data of [5]. [c] mp 102–103°C {mp 102–103.5°C, ν(P=O) 1190 cm^{-1}, δ_P 71.7 ppm [6]}. [d] mp 77–78.5°C {mp 74–75°C, ν(P=O) 1190 cm^{-1}, δ_P 39.0 ppm [6]}.



(3)

However, in no case of the thion-thiol rearrangement under the action of haloalkyls such intermediates were isolated or their formation was confirmed by spectroscopy. Teichman and Hilgetag [12] did not succeed in obtaining alkylphosphonium intermediates in the reaction of *O*,*O*',*O*''-trimethyl thiophosphate

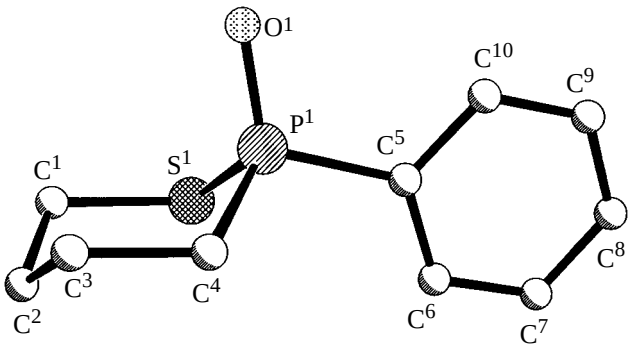


Fig. 1. General view of the molecule of compound **Xb**. Principal bond lengths, Å: P^1–O^1 1.474(2), P^1–C^4 1.790(3), P^1–S^1 2.082(1), S^1–C^1 1.828(3). Bond angles, deg: $O^1P^1C^4$ 113.9(1), $O^1P^1C^5$ 113.0(1), $C^4P^1C^5$ 108.5(1), $O^1P^1S^1$ 115.3(9), $C^4P^1S^1$ 103.4(1), $C^5P^1S^1$ 101.66(9), $C^1S^1P^1$ 96.8(1), $C^2C^1S^1$ 113.6(2).

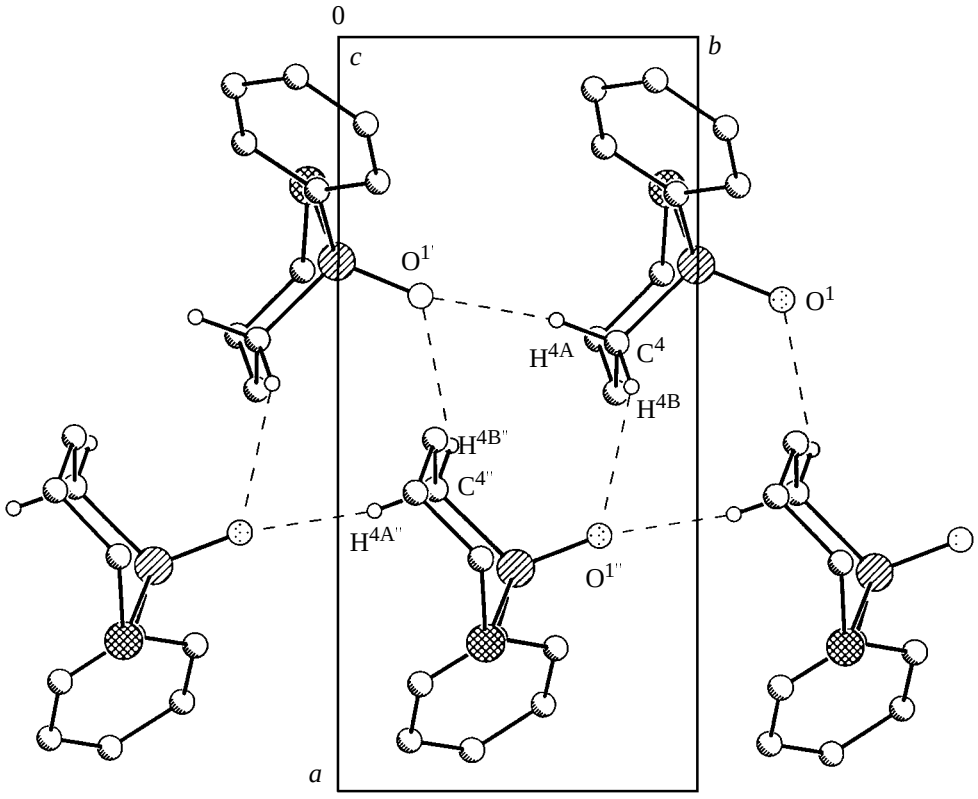
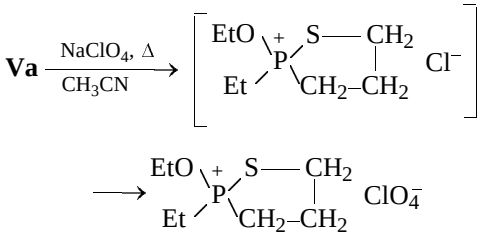


Fig. 2. Formation of C–H···O contacts in a crystal of **Xb** (in the projection orthogonal to the crystallographic *c* axis).

with haloalkyls in the presence of silver tetrafluoroborate. However, they isolated and characterized phosphonium salt $[(MeO)3P^{+}SMe]SbCl_6^{-}$ at the thiol-thion rearrangement of te same thiophosphate in the presence of the Lewis acid antimonium pentachloride. More recently [13], Bruzik and Stec confirmed formation of phosphonium salt intermediates also in the case of thiolthion rearrangement catalyzed by protic acids.

For the studied earlier by us intramolecular Pishchimuka's rearrangement [5] on the example of *O,O'*-diethyl ω-chloroalkylthiophosphonates **IIIa** and **IIIb** was found that in the presence of NaI this reaction proceeds with intermediate formation of ω-iodoalkyl-substituted thiophosphonates **VII** (R = EtO), which were registered by ^{31}P NMR spectroscopy (see Scheme 2 above). It was assumed that thiophosphonates **VII** enter to intramolecular *S*-alkylation forming quasiphosphonium salts **VIII** (R = EtO), but we were unable to register them by ^{31}P NMR spectroscopy due to their instant conversion into thiaphosphacyclanes **IX** under the reaction conditions.

In this work we attempted to stop the reaction in the step of formation of intermediate salt **VIII** by introducing perchlorate anion instead of nucleophilic cloride anion. For this purpose, thiophosphinate **Va** possessing 3-cholropropyl and ethyl groups at phosphorus was refluxed in acetonitrile in the presence of sodium perchlorate. In 1.5 h, in its ^{31}P NMR spectrum, besides the signal of the parent thiophosphinate (δ_P 104 ppm), appeared a signal with chemical shift δ_P 138 ppm growing upon the boiling. However, as it might be expected, in the absence of NaI the intramolecular alkylation of 3-chloropropyl-substituted thiophosphinate **Va** proceeds much slower, and further prolonged heating results in formation of decomposition products in a noticeable amounts. Treatment of reaction mixture after 5-h refluxing we isolated in 20% yield perchlorate **XV**, the intermediate of intramolecular Pishchimuka's rearrangement (Scheme 4).



XV

(4)

Quasiphosphonium salt **XV** is a stable crystalline compound. Its structure and composition were confirmed by elemental analysis, IR spectra and ^{1}H and ^{13}C NMR spectroscopy. IR spectrum of **XV** instead of absorption band of P=S group at 590 cm^{-1} observed in the spectrum of the parent compound **Va** appears strong absorption band at 565 cm^{-1} related to P–SCH_2 vibrations. In ^{1}H NMR spectrum disappears triplet of the protons of CH_2 group bounded to chlorine atom, but appear two multiplets of the protons of (S)–CH_2 group in the ring. In ^{13}C NMR spectrum besides other signals appears doublet δ_C 38.97 ppm ($^2J_{PC}$ 6.0 Hz) assigned to the carbon atom of the methylene group CH_2S in the ring.

Thus, in the performed investigation based on the intramolecular Pishchimuka's rearrangement of ω-chloro-substituted alkylthiophosphonic and -thiophosphinic acids we elaborated convenient general method for the synthesis of 2-substituted 2-oxo-1,2λ5-thiaphosphacyclanes (thiolphostones) which makes available this class of organofphosphorus heterocycles that was practically unknown earlier.

EXPERIMENTAL

All reactions were conducted under argon atmosphere, absolute solvents were used. IR spectra were taken up on a UR-20 instrument (KBr). ^{1}H and ^{31}P–{^{1}H} spectra were recorded on WP-200SY [operating frequency 200.13 (^{1}H) and 81.01 (^{31}P) MHz] and Bruker AMX-400 [operating frequency 400.13 (^{1}H), 161.98 (^{31}P) and 100.1 (^{13}C) MHz]. The solvent concentration was 0.1 mol l^{-1}. Silica gel Aldrich 130–270 mesh was used for column chromatography, elution in the system of hexane–acetone.

X-ray diffraction investigation of 2-oxo-2-phenyl-1,2λ^5-thiaphosphorinane ($C_{10}H_{13}OPS$) Xb was performed at room temperature on a 4-circle difractometer Siemens P3/PC [MoK_α (λ = 0.71073 Å), graphite monochromator, τ/2τ scan]. The crystals at room temperature are monoclinic, *a* 12.031(6), *b* 5.807(3), *c* 15.358 Å, β 96.58(4)°, *V* 1066(1) Å^3, *Z* 4, steric group $P2_1/c$, *M* 212.23, *F*(000) 448, μ 4.12 cm^{-1}, ρ_{calc} 1.322 g cm^{-3}. Among the 3325 measured reflections (τ_{max} 62°), 3186 independent reflections were taken for further calculations.

The structure was decoded by direct synthesis and refined in full matrix anisotropic-isotropic approximation on F^2. All hydrogen atoms were elucidated in the differential synthasis of electron density and included in the final refinement in isotropic approximation. Final divergence factors are: wR_2 0.1348, *GOF* 0.852 on 3186 independent reflections, R_1 0.0534 (calculated on F^2_{hki} with 1713 reflections with $I > 2\sigma(I)$. All calculations were performed with the program package SHELXTL PLUS 5.0. Coordinates of non-hydrogen atoms and their thermal parameters for the **Xb** structure were deposited in Cambridge Base of Structural Data.

***O*-Ethyl Ethylthiophosphonite** was prepared according to procedure in [14] from 4.5 g of *O*-ethyl ethylphosphonite and 7.9 g of Lawesson reagent. Yield 3.1 g (61%), bp 69–72°C (7 mm), n_D^{20} 1.4905. ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 78.7 ($^1J_{PH}$ 564 Hz). Published bp 84°C (19 mm), n_D^{20} 1.4894 [15].

***O*-Ethyl (3-chloropropyl)chlorothiophosphonate (XIII).** To 11.0 g of Laweson reagent suspended in 100 ml of benzene was added 11.0 g of acyl chloride **XIV** [16] and the mixture was refluxed for 13 h. A not dissolved precipitate was filtered off, benzene was removed and residue was distilled in a vacuum. 7.2 g (61%) of acyl chloride **XIII** was isolated, bp 95–98°C (1 mm), n_D^{20} 1.5127, d_4^{20} 1.2749. IR spectrum: ν(P=S) 645 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 t (3H, Me, $^3J_{HH}$ 7.2 Hz), 2.15–2.26 m, 2.48–2.56 m (4H, PCH_2CH_2), 3.62 t (2H, CH_2Cl, $^3J_{HH}$ 6.4 Hz), 4.12–4.23 m (H_A), 4.27–4.38 m (H_B) (2H, OCH_AH_B). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 102.3 s. Found, %: C 27.70; H 5.00; Cl 32.32; P 14.20. $C_5H_{11}Cl_2OPS$. Calculated, %: C 27.15; H 4.98; Cl 32.13; P 14.03.

***O*-Ethyl phenyl(3-chloropropyl)thiophosphinate (IVb).** To a mixture of 9.0 g of *O*-ethyl phenylthiophosphonite [14], 7.7 g of 1,3-bromochloropropane and 2.0 g of tetraethylbenzylammonium chloride in 60 ml of CH_2Cl_2 was added with stirring 5.5 g of powdered KOH. The mixture heated to 40°C. It was kept for 3 h at 20°C, twice washed with ice water, the organic layer was dried over Na_2SO_4. After removing of the solvent 11.8 g of crude compound was isolated. Atempted distillation at 2 mm Hg at 160–170°C the compound exerted rearrangement. The crude compound was purified by the column chromatography, the yield from the column was 60%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.25 t (3H, Me, $^3J_{HH}$ 7.0 Hz), 1.96–2.38 m (4H, PCH_2CH_2), 3.51–3.56 m (2H, CH_2Cl, $^3J_{HH}$ 6.0 Hz), 3.72–3.85 m (H_A), 4.05–4.14 m (H_B) (2H, OCH_AH_B), 7.44–7.93 m (5H, Ph). Found, %: C 50.09; H 5.88; Cl 13.27; P 11.89. $C_{11}H_{16}ClOPS$. Calculated, %: C 50.29; H 6.14; Cl 13.49; P 11.79.

ω-Chloroalkyl-substituted thiophosphinates **IVb**, **Va**, and **Vb** were synthesized by the similar procedure.

***O*-Ethylphenyl(4-chlorobutyl)thiophosphinate (IVb)** was prepared from 8.6 g of *O*-ethyl phenylthiophosphonite and 8.0 g of 1,4-bromochlorobutane. After removing of solvent, 11.4 g of crude compound

was isolated and purified by vacuum distillation. The analytically pure sample was obtained by column chromatography, yield from the column was 75%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 t (3H, Me, $^3J_{HH}$ 7.1 Hz), 1.56–2.23 m (6H, $PCH_2CH_2CH_2$), 3.46 t (2H, CH_2Cl, $^3J_{HH}$ 6.4 Hz), 3.70–3.80 m (H_A), 4.04–4.13 m (H_B) (2H, OCH_AH_B), 7.42–7.90 m (5H, Ph). Found, %: C 52.15; H 6.55; Cl 12.86; P 11.21. $C_{12}H_{18}ClOPS$. Calculated, %: C 52.09; H 6.56; Cl 12.81; P 11.19.

***O*-Ethyl (3-chloropropyl)ethylthiophosphinate (Va)** was prepared by similar procedure from 4.6 g of *O*-ethyl ethylthiophosphonite and 5.3 g of 1,3-bromochloropropane. After removing of the solvent, 6.1 g of crude compound was isolated and purified by vacuum distillation and column chromatography; yield from the column was 57%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 d.t (3H, CH_3CH_2P, $^3J_{HH}$ 7.6, $^3J_{PH}$ 20.0 Hz), 1.17 t (3H, CH_3CH_2O, $^3J_{HH}$ 7.2 Hz), 1.81–2.06 m (6H, $CH_2CH_2P + CH_3CH_2P$), 3.53 t (2H, CH_2Cl, $^3J_{HH}$ 6.0 Hz), 3.86–4.02 m (2H, OCH_2). Found, %: C 38.74; H 7.37; Cl 16.98; P 14.60; S 15.05. $C_7H_{16}ClOPS$. Calculated, %: C 39.20; H 7.46; Cl 16.55; P 14.45; S 14.92.

***O*-Ethyl (4-chlorobutyl)ethylthiophosphinate (Vb)** vas prepared from 4.0 g of *O*-ethyl ethylthiophosphonite and 5.0 g of 1,4-bromochlorobutane. Yield of crude compound was 5.7 g, it was purified by vacuum distillation and column chromatography; yield from the column was 68%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 d.t (3H, CH_3CH_2P, $^3J_{HH}$ 7.6, $^3J_{PH}$ 19.8 Hz), 1.21 t (3H, CH_3CH_2O, $^3J_{HH}$ 7.0 Hz), 1.67–1.92 m (8H, $CH_2CH_2CH_2P + CH_3CH_2P$), 3.49 t (2H, CH_2Cl, $^3J_{HH}$ 6.2 Hz), 3.90– 4.03 m (2H, OCH_2). Found, %: C 41.72; H 7.88; Cl 15.97; P 13.46. $C_8H_{18}ClOPS$. Calculated, %: C 42.01; H 7.87; Cl 15.53; P 13.57.

***N,N*-Diethyl *O*-ethyl (3-chloropropyl)thiophosponic *N,N*-diethylamide (VIa).** To a solution of 8.5 g of diethylamine in 30 ml of benzene and 50 ml of petroleum ether was added dropwise at 3°C a solution of 6.0 g of acyl chloride **XIII** in 20 ml of benzene. The reaction mixture was kept for 1 h at 20°C and then for 3 h at 40–45°C. The diethylamine hydrochloride precipitate was filtered off, the solution was twice washed with ice water and dried over Na_2SO_4. The solvent was then removed and the residue was distilled in a vacuum. 5.4 g (81%) thiophosphonate **VIa** was isolated. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (6H, CH_3CH_2N, $^3J_{HH}$ 7.2 Hz), 1.06 t (3H, CH_3CH_2O, $^3J_{HH}$ 6.8 Hz), 1.75–1.96 m (4H, CH_2CH_2P), 2.94–3.07 m (4H, CH_2N), 3.35–3.59 m (3H, $CH_2Cl + OCH_A$), 3.78–3.90 m (1H, OCH_B). Found, %: C 42.31; H 8.14; Cl 13.79; P 12.09. $C_9H_{21}ClNOPS$. Calculated, %: C 41.94; H 8.15; Cl 13.79; P 12.04.

2-Oxo-2-phenyl-1,2λ^5-thiaphospholane (Xa). 0.7 g of thiophosphinate **IVa** mixed with 1.2 g of NaI was refluxed in 15 ml of CH_3CN for 8 h. According to the data of ^{31}P NMR spectroscopy, the reaction was complete. The precipitate of NaCl was filtered off, the solvent was removed and the residue vas treated with boiling $CHCl_3$. The excess of NaI was filtered off, the solvent was removed and the residue was left to crystallization. After recrystallization from hexane, 0.35 g (67%) of thiaphospholane **Xa** was obtained. For complete reaction at refluxing in acetone 15.5 h was necessary. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10–2.57 m (4H, CH_2CH_2P), 3.28 m (H_A), 3.50 m (H_B) (2H, SCH_AH_B), 7.43–7.94 m (5H, Ph). ^{13}C ($CDCl_3$), δ_C,[1] ppm: 27.35 d (CH_2CH_2P, $^2J_{PC}$ 2.4 Hz), 36.13 d (CH_2P, $^1J_{PC}$ 61.7 Hz), 36.47 d (CH_2SP, $^2J_{PC}$ 1.4 Hz).

Thiapjhospholanes **XIa** and **XIIa** and thiaphosphorinanes **Xb** and **XIb** were synthesized by similar procedure.

2-Oxo-2-phenyl-1,2λ^5-thiaphosphorinane (Xb) was prepared from 0.66 g of thiophosphinate **IVb** and 1.1 g of NaI in 15 ml of CH_3CN under reflux for 16 h. After crystallization from hexane, 0.32 g (64%) of thiaphosphorinane **Xc** was obtained. In acetone, completing of the reaction requires refluxing for 35 h. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.78–2.40 m (6H, $CH_2CH_2CH_2P$), 2.83 m (H_A), 3.32 m (H_B) (2H, SCH_AH_B), 7.41–7.90 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C,[1] ppm: 21.87 d ($CH_2CH_2CH_2P$, $^3J_{PC}$ 7.3 Hz), 27.30 d (CH_2CH_2P, $^2J_{PC}$ 4.5 Hz), 27.56 d (CH_2SP, $^2J_{PC}$ 2.1 Hz), 31.64 d (CH_2P, $^1J_{PC}$ 71.8 Hz).

Complex of 2-oxo-2-ethyl-1,2λ^5-thiaphospholane with NaI (XIa·0.4NaI) was obtained from 3 g thiophosphinate **Va** and 6.3 g of NaI in 50 ml of acetone at 10 h reflux. The complex was purified by column chromatography, yield from the column was 65%. The product was elued by anhydrous acetone. Refluxing with CH_3CN requires 4 h for completeness of the reaction. Found, %: C 28.87; H 5.47; P 14.60. $C_5H_{11}OPS \cdot 0.4$ NaI. Calculated, %: C 28.57; H 5.24; P 14.76.

Complex of 2-oxo-2-ethyl-1,2λ^5-thiaphosphorinane with NaI (XIb·0.4NaI) was obtained similarly from 2.9 g thiophosphinate (Vb) and 5.2 g of NaI in acetone at 14.5 h reflux. Like with Xia, the product was elued by anhydrous acetone, yield 55%. Found,

[1] The chemical shifts of benzene ring carbon atoms are not listed.

%: C 29.86; H 5.61; P 12.73; S 13.34. $C_6P_{13}OPS \cdot 0.5NaI$. Calculated, %: C 30.12; H 5.45; P 12.97; S 13.38.

2-Diethylamino-2-oxo-1,2λ^5-thiaphospholane (XIIa) was prepared 4.4 g of thiophosphonate **VIa** and 3.8 g NaI at 8 h reflux in 10 ml of CH_3CN. The reaction mixture was treated as in above experiments, NaI was removed by twice washing with ice water. The product was purified by column chromatography, yield from the column was 71%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.63 t (6H, Me, $^3J_{HH}$ 7.2 Hz), 1.37–1.81 m (4H, PCH_2CH_2), 2.59–2.81 m (6H, $2CH_2N + CH_2S$). Found, %: C 43.96; H 8.81; P 16.02; S 16.13. $C_7H_{16}NOPS$. Calculated, %: C 43.52; H 8.29; P 16.06; S 16.58.

2-Ethyl-2-ethoxy-1,2λ^4-thiaphospholanium perchlorate (XV). 0.8 g of thiophosphinate **Va** and 0.55 g of $NaClO_4$ in 20 ml of CH_3CN was refluxed for 5 h. The heating was stopped when the reaction mixture contained 27% of final compound (according to the data of ^{31}P NMR). The NaCl precipitate was filtered off, the solvent was removed and to the residue was added 20 ml of CH_2Cl_2, and the $NaClO_4$ excess was filtered off. From the mother liquor the solvent was removed and ether was added, and the residue crystallized. 0.2 g (20%) of perchlorate **XV** was isolated and recrystallized from a CH_3CN–ethyl acetate mixture; mp 93–95°C. IR spectrum (KBr), ν, cm^{-1}: 565 (P–S–CH_2), 1100 br (ClO_4^-). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 d.t (3H, C*H*$_3$CH$_2$P, $^3J_{HH}$ 7.2, $^2J_{PH}$ 23.2 Hz), 1.39 t (3H, C*H*$_3$CH$_2$O, $^3J_{HH}$ 7.2 Hz), 2.44–2.59 m, 2.68–2.79 m, 2.87–3.03 m (6H, CH_2CH_2P +CH_3CH_2P), 3.47–3.56 m (H_A), 3.67–3.75 m (H_B) (2H, SCH_AH_B), 4.27–4.34 m (2H, CH_2O). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 6.39 d (*C*H$_3$·CH$_2$O, $^3J_{PC}$ 6.0 Hz), 15.60 d (*C*H$_3$CH$_2$P, $^2J_{PC}$ 7.2 Hz), 22.17 d (CH_3CH_2, $^1J_{PC}$ 67.9 Hz), 28.02 s (*C*H$_2$CH$_2$P), 28.27 d (CH_2CH_2P), $^1J_{PC}$ 45.8 Hz), 38.97 d (CH_2SP, $^2J_{PC}$ 6.0 Hz), 67.68 d (CH_2OP, $^2J_{PC}$ 9.2 Hz). ^{31}P NMR spectrum ($CHCl_3$), δ_P, ppm: 138.8 s. Found, %: C 30.44; H 5.74; P 10.83; S 11.30. $C_7H_{16}ClO_5PS$. Calculated, %: C 30.16; H 5.75; P 11.13; S 11.49.

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