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Phosphorylation of Trihydroxybenzenes with the Trivalent Phosphorus Derivatives

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Abstract—Phosphorylation of the simplest trihydroxybenzenes and their acylated derivatives with the trivalent phosphorus reagents of cyclic and acyclic structure was discussed. A possibility of the selective phosphorylation of acylated trihydroxybenzene derivatives was demonstrated. A dismutation was detected, leading to dimers of the linear structure containing a variety of phosphorus-containing fragments of different nature.

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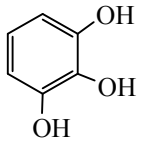
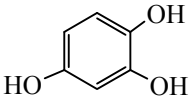
Polyatomic phenols are widely used in fine organic synthesis. On their basis macrocyclic systems are created such as cryptands, spherands and calixarenes used in various branches of science, medicine and technology [1, 2]. It is essential that the introduction into such systems of the phosphorus atom can significantly extend the range of their functional application. On the basis of the phosphorus-containing polyols unusual supramolecular systems [3] and polydentate ligands were synthesized used for the creation of transition metal complexes [4, 5].

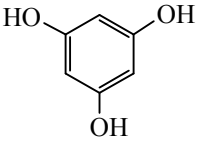
Continuing our research on the phosphorylation of phenols [6–8], we planned the synthesis of a series of acyclic ligands containing in their composition alongside the aromatic rings three or more phosphorus-containing fragments of different structure and degree of oxidation of the phosphorus atom. As the initial compounds for the design of the ligands of this type we selected the geometrically simplest rigid system of trihydroxybenzenes, with the hydroxy groups located in different positions.



Pyrogallol
1,2,3-trihydroxybenzene



Oxyhydroquinone
1,2,4-trihydroxybenzene



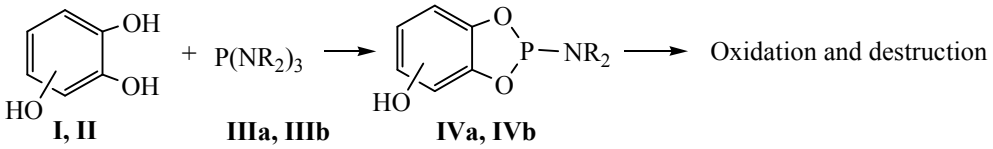
Phloroglucinol
1,3,5-trihydroxybenzene

The first stage of the synthesis of the above multifunctional ligands consisted in the study of phosphorylation of the initial aromatic triols since these processes were not practically described. It is known that phosphorylation of oligohydroxy compounds, both of the aromatic [9–11] and aliphatic [12–14] type, leads mostly either to perphosphorylated products, or to the formation of phosphocyclic systems (in the presence of closely spaced hydroxy groups). If the ratio of reagents does not match the number of hydroxy groups in the original molecule, a mixture of products is formed [15].

The present research was initiated to study the phosphorylation of trihydroxybenzenes with the *ortho*-located hydroxy groups, pyrogallol (**I**) and oxyhydroquinone (**II**), which are similar chemically to pyrocatechol. From the literature it is known that

phosphorylation of the last compound even with an excess of phosphorous di- or triamide leads to the formation of 1,3,2-dioxybenzophospholane [16, 17], and the phosphorylation with the cyclochlorophosphites of phosphorinane type, to the formation of relatively stable dicyclophosphites. However, their distillation in a high vacuum, or storage in air leads to decomposition [18]. On the other hand, it was shown that phosphorylation of pyrocatechol and pyrogallol with 2-diethylamido-5,5-dimethyl-1,3,2-dioxaphosphorinane at room temperature at the equimolar ratio of reagents led to the formation of hexacoordinated phosphorus derivatives [19].

We regarded as interesting to carry out phosphorylation of trihydroxybenzenes **I** and **II** with one mole of phosphorous triamide. We expected to get a cyclic system containing mutually unbound hydroxy and amide fragments. Then it was anticipated to use the third hydroxy group for the prophosphorylation with another phosphorylating reagent. As the initial phosphorylating reagents we used phosphorous hexamethyl- (**IIIa**) and hexaethyltriamides (**IIIb**). As a result of this reaction formed 1,3,2-dioxaphospholanes (**IVa, IVb**) that produce in ^{31}P NMR spectrum a singlet signal at 151 ppm characteristic of the amidophospholane ring. However, they are extremely unstable at keeping in solution, and the attempted isolation leads to decomposition of the phosphorus-containing fragment. We suggest that this is due to the intermolecular interaction of free hydroxy groups to form a ring.



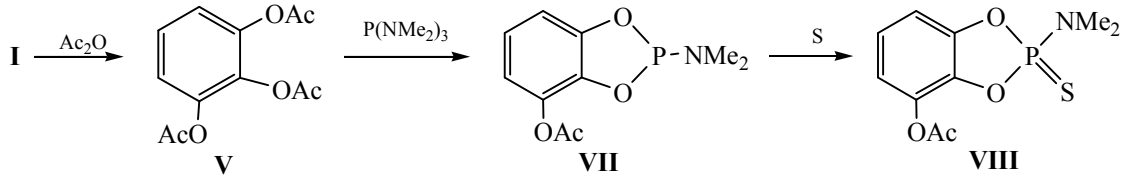
I, II **IIIa, IIIb** **IVa, IVb**

R = Me (**a**), Et (**b**).

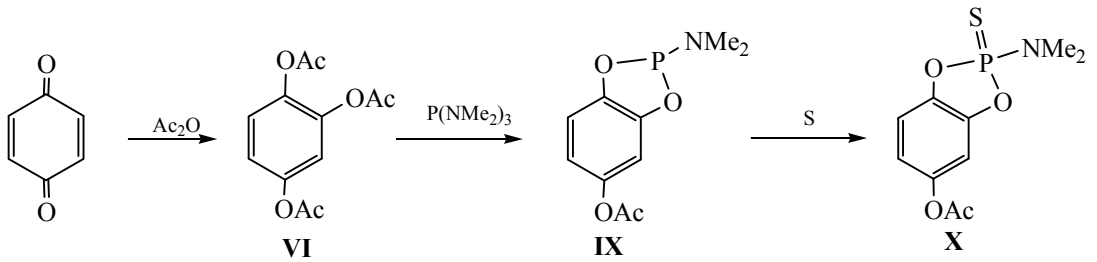
In order to prevent such reactions, we decided to protect the hydroxy groups remaining in the parent molecule, but in a way not preventing phosphorylation. For such protection the acyl derivatives are suitable, which can be phosphorylated with phosphorous amides but at a lower rate [20].

The phosphorylation of pyrogallol triacetate (**V**) and oxyhydroquinone triacetate (**VI**) was carried out with phosphorous hexamethyltriamide or phosphorous hexaethyltriamide at a ratio of reagents 1:1. Note that phosphorylation with phosphorous hexaethyltriamide in different solvents and at different temperatures did not lead to positive results.

The reaction with phosphorous hexamethyltriamide in dioxane completed in 2 days at room temperature. The ^{31}P NMR spectrum of the reaction solution showed the signal at 150 ppm typical of the phospholane ring with amide substituents at the phosphorus atom.



V **VII** **VIII**

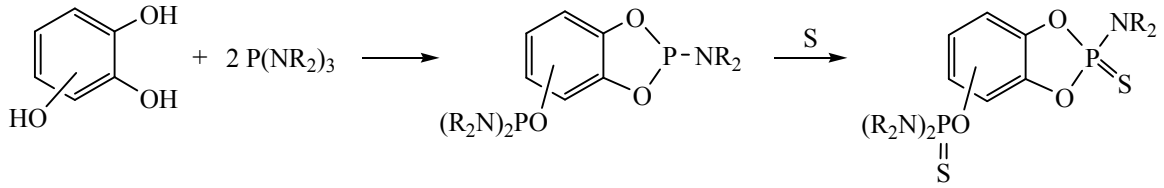


VI **IX** **X**

The structure of the compounds obtained was confirmed after the the sulfurization of the reaction mixture and chromatographic separation of thionophosphates **VIII** and **X**. In the ^{31}P NMR spectra two singlet signals were observed at 87–89 ppm. In the ^{1}H NMR spectrum of compound **X** there are singlet signals of methyl protons of acyl groups (δ 2.88 ppm), a doublet signal of methyl protons of amide group (δ 2.87 ppm) as well as two doublets and a singlet of the protons of aromatic fragment (δ 6.71, 6.86, 7.03 ppm, respectively), while for the protons H^3 and H^5 the *meta*-coupling constants $^{4}J_{HH}$ 2.4 Hz were observed. Integral curve corresponded to this distribution of protons.

The obtained compounds **VIII** and **X** are stable and can be used in future for the introduction of other phosphorus substituents and produce structures with mixed phosphorus functions.

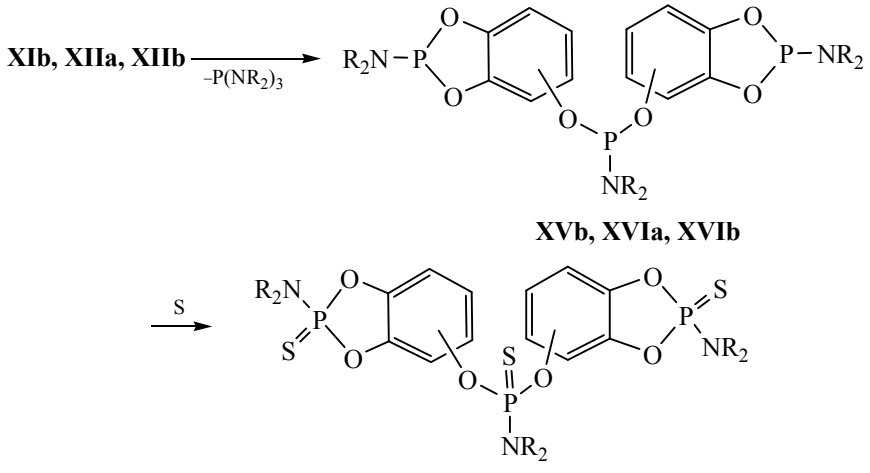
At the phosphorylation of trihydroxybenzenes **I** and **II** with two moles of phosphorous triamide (**IIIa** or **IIIb**) in acetonitrile or dioxane the reaction ends in 2 days at room temperature. In the ^{31}P NMR spectrum of the reaction solution three signals appeared simultaneously: at 151 and 144 ppm, typical of monoamidoester, and at 137 ppm, characteristic of phosphorous diamidoester.



I, II **IIIa, IIIb** **XIb, XIIa, XIIb** **XIIIb, XIVa, XIVb**

For a more reliable identification of the compounds obtained they were brought into the sulfurization. The reaction was carried out at room temperature over 2 days. The products **XIIIb**, **XIVa**, and **XIVb** were isolated by column chromatography as oily substances. Yields were quite small, not exceeding 22%. In their ^{31}P NMR spectra two singlet signals were observed at 89–90 and 74–79 ppm, with a ratio of integral intensities 1:1. In the ^{1}H NMR spectrum the signals of all groups of protons were registered with an estimated ratio of the integral intensities, but all the protons were nonequivalent.

Upon storage the reaction solution of compounds **XIb** and **XIIa, XIIb,** the signal at 144 ppm in the ^{31}P NMR spectra increased. After keeping them for 3 days (methyl derivative **XIIa**) or 10 days (ethyl derivatives **XIb, XIIb**) at room temperature we performed the sulfurization of the reaction mixture. The thio derivatives **XVIIb**, **XVIIIa**, and **XVIIb** were isolated by column chromatography and identified as dimer compounds with two benzamidophospholane rings in their composition (δ_P 89–90 ppm) and one acyclic monoamide fragment (δ_P 74–79 ppm), integral intensities ratio was 2: 1.



XVb, XVIa, XVIb

XVIIb, XVIIIa, XVIIIb

In the ^{1}H NMR spectrum of compounds **XVIIb, XVIIIa,** and **XVIIIb** there were the signals of all groups of protons. Integration of the signals showed that four alkyl groups belong to the cyclic molecular fragments, and two to acyclic. In addition, in the MALDI–TOF mass spectrum of compound **XVIIb** there was a peak at *m/z* 651 corresponding to the calculated one, which also indicated that these systems are dimeric.

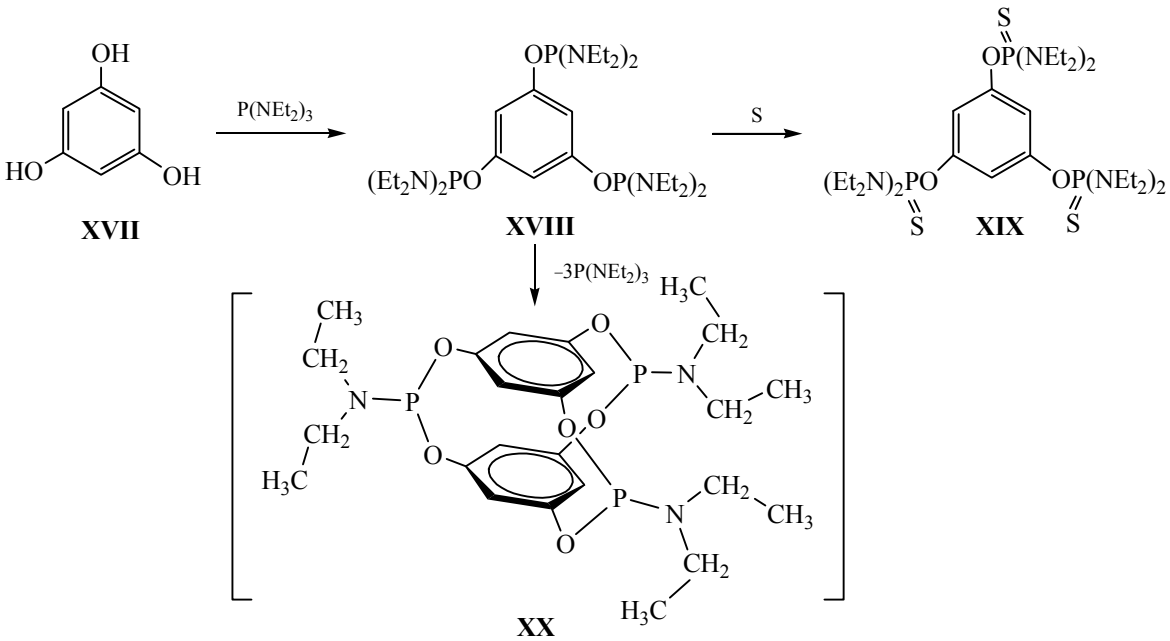
Thus, it was shown that in this case the dismutation [21] of two molecules of compounds **XIb, XIIa**, and **XIIb** proceeds with the formation of dimeric products containing three phosphoric centers of different structures. This provides a possibility to use the compounds of this type in the future as three-centered ligands for the synthesis of metal complexes.

1,3,5-Trihydroxybenzene, or phloroglucinol (**XVII**), is an interesting object for the creation of not only three-centered ligands, but of the phosphomacrocyclic systems, because it has three distant in space hydroxy groups. Data on its phosphorylation were not found in the literature.

The study was started with the perphosphorylation of phloroglucinol with phosphorous hexaethyltriamide, hoping to use the resulting product for further synthesis of "double-decked" system. The reaction was carried out in acetonitrile at room temperature.

After 45 min the reaction completed, and in the ^{31}P NMR spectrum one singlet signal was observed with δ_P 132.2 ppm (**XVIII**), typical of diamidophosphites. After the sulfurization of the reaction mass and chromatographic purification product **XIX** was isolated, which was an oily substance containing in its ^{31}P NMR spectrum one singlet signal at 74.2 ppm, typical of thionodiamidophosphates. In its ^{1}H NMR spectrum a triplet of methyl groups in the region of 1.13 ppm, a multiplet of methylene protons at 3.20 ppm, and a singlet of aromatic protons in the region of 6.51 ppm were detected. Some nonequivalence of methylene protons of ethyl groups should be noted, leading to the presence of two doublet signals elucidated by the method of double magnetic resonance ($^3J_{PH}$ 12.6 and 11.6 ppm).

At the storage of acetonitrile solution of compound **XVIII** over 45 min, in its ^{31}P NMR spectrum a signal appeared at 140.4 ppm indicating the dismutation of the formed perphosphorylated **XVIII**.



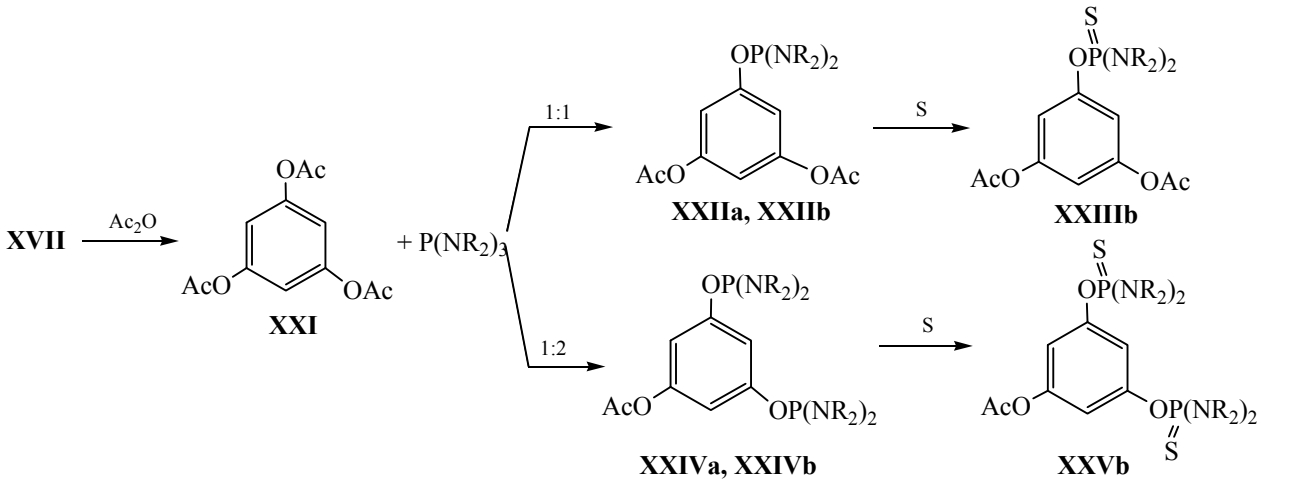
XVII **XVIII** **XIX** **XX**

Upon the reaction completion, an oily substance precipitated insoluble in common organic solvents, but swelling in DMF indicating the formation of a cyclic dimeric product **XX**, or a cross-linked oligomer. The phosphorylation of phloroglucinol with one or two moles of phosphorous triamide resulted in similar oligomeric products.

The preparation of the mono- and diphosphorylated systems based on phloroglucinol was performed on

1,3,5-triacetoxybenzene (**XXI**) obtained by the usual method. The phosphorylation with the phosphorous triamides was carried out at the ratio of reagents 1:1 and 1:2.

At the mono- and diphosphorylation of compound **XXI** with phosphorous hexamethyltriamide the appearance in the ^{31}P NMR spectrum of a signal at 140.3 ppm is observed, indicating either a very rapid dismutation of the formed compounds **XXIIa** and **XXIVa**, or the interaction of these diamides with acyl groups of adjacent molecules, but we have not yet studied this reaction. In the course of the reaction the formation of precipitates occurred insoluble in organic solvents, which makes them inappropriate for identification.



R = CH_3 (**a**), C_2H_5 (**b**).

At the use of phosphorous hexaethyltriamide mono- (**XXIIIb**) and diphosphorylated (**XXVb**) products were isolated by column chromatography after the sulfurization. In the ^{31}P NMR spectrum of compound **XXIIIb** a singlet signal appeared at δ_P 74.1 ppm. In the ^{1}H NMR spectrum a triplet signal was observed of methyl protons of ethyl group (1.15 ppm) and a singlet signal of methyl protons of acyl groups (2.30 ppm), a multiplet of methylene protons of ethyl group (3.22 ppm), and two singlets of the protons of aromatic rings (6.72 ppm and 6.87 ppm). Integral intensities of the signals of methyl protons corresponded to six protons of acyl groups and twelve protons of amide groups. Apart from that, the ^{13}C NMR spectra were obtained and the molecular weight was measured by MALDI-TOF mass spectrometry, which confirmed the formation of the monophosphorylated product.

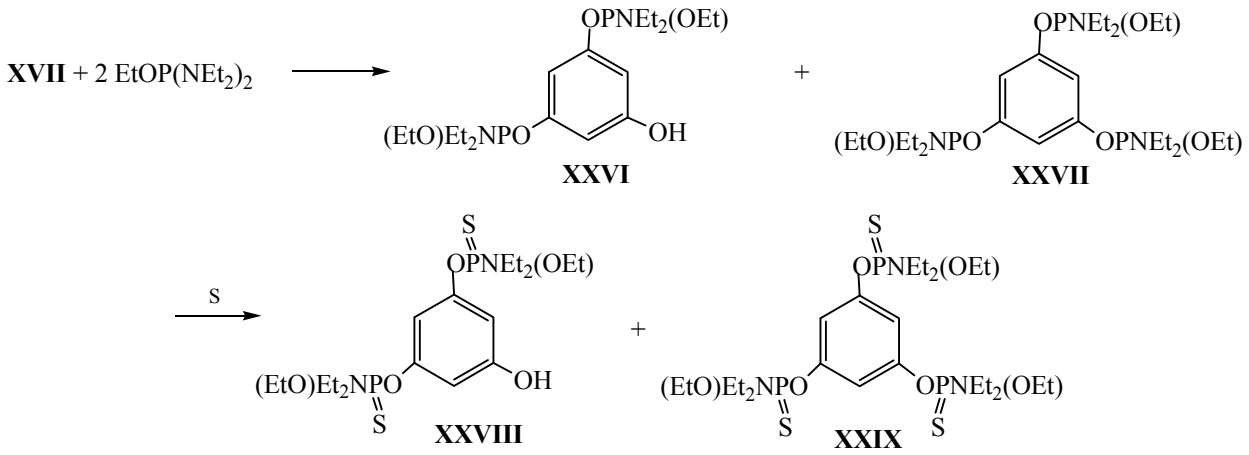
Similar methods were used for the identification of compound **XXVb**. It was proved that this compound was diphosphorylated and contained two phosphamide fragment and one acyl group.

Thus, the presence in compounds **XXIIb–XXVb** of acyl groups makes it possible to introduce into the molecule the other phosphoric centers.

To avoid dismutation which leads to the formation of oligomeric systems, we carried out phosphorylation of trihydroxybenzenes **I, II,** and **XVII** with ethyl tetraethyldiamidoethylphosphite $EtOP(NEt_2)_2$. This reaction should lead to the formation of monoamides that at room temperature do not enter in further transformations. However, we succeeded to perform this reaction only with phloroglucinol **XVII**. The phosphorylation of pyrogallol **I** and oxyhydroquinone **II** resulted in the formation of bright-colored insoluble precipitates, inappropriate for identification.

The phosphorylation of phloroglucinol **XVII** was carried out in dioxane at a ratio of reagents 1: 2 over 1 day. From the reaction a mixture of products was obtained consisting of di- and triphosphorylated phloroglucinol **XXVI** and **XXVII**, while according to the ^{31}P NMR spectrum of the reaction mixture, the mixture contained 85% only of the desired product **XXVI**.

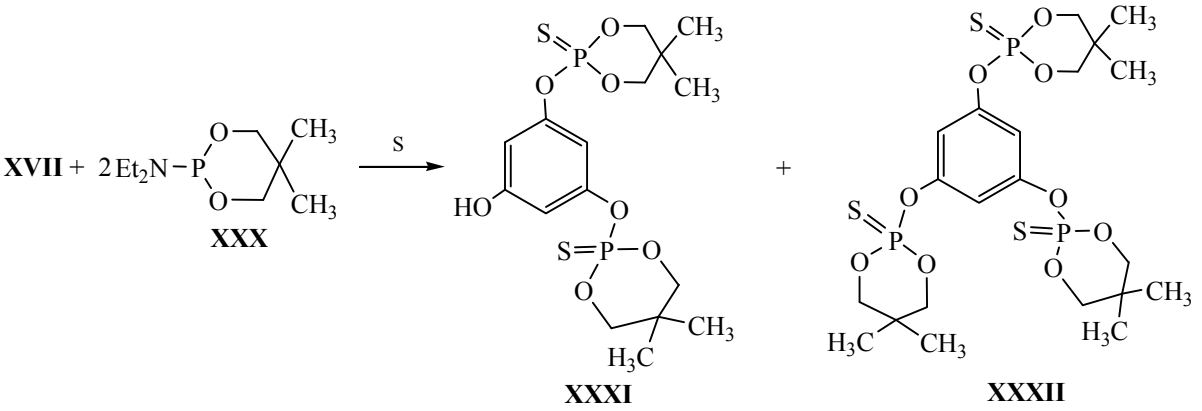
After the the sulfurization, the thionphosphates **XXVIII** and **XXIX** were isolated by column chromatography. These compounds are oily substances. In their ^{31}P NMR spectra a signal at 72 ppm was observed characteristic of thionophosphoric monoamidoesters.



They were also were characterized by ^{1}H and ^{13}C NMR spectroscopy.

For the same purpose, at the the phosphorylation of phloroglucinol **XVII** we used alkylenephosphorous amides and chlorides like neopentylene tetraethylamidophosphite (**XXX**), propylene and neopentylene chlorophosphites (**XXXIII**) and (**XXXIV**).

The reaction with amidophosphite **XXX** was carried out in dioxane at 50°C, at the reagent ratio 1: 2 for 15 days. In the ^{31}P NMR spectrum of the reaction solution the slow accumulation was observed of the signal of cyclic phosphorous triester (δ_P 115.4 ppm). The sulfurization of the compounds formed was carried out for 7 days at room temperature. After the reaction completion, in the ^{31}P NMR spectrum of the reaction mixture a singlet signal at 53 ppm was detected, but the chromatography indicated the presence of two products.

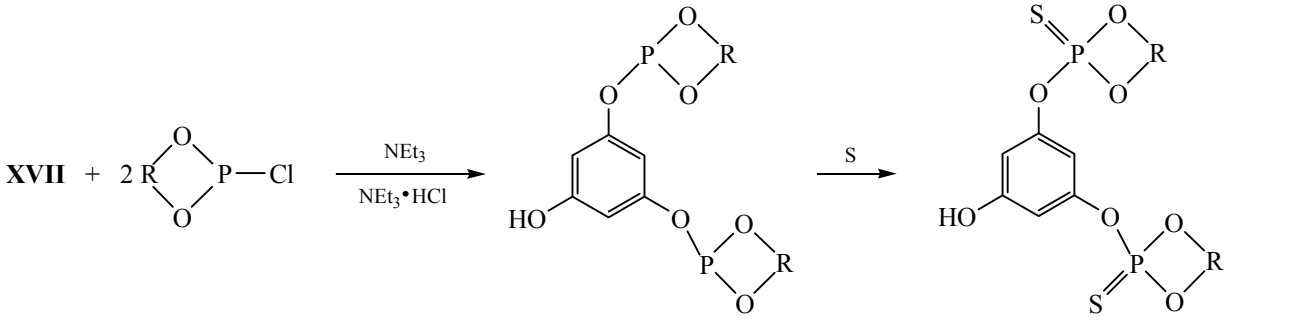


Compounds **XXXI** and **XXXII** were isolated chromatographically and characterized by NMR spectroscopy as di- (**XXXI**) and triphosphorylated (**XXXII**) oily and powdery substances, respectively. To the desired compound **XXXI** in ^{1}H NMR spectrum corresponded the signals of axial and equatorial protons of methyl groups at 1.08 and 1.32 ppm, respectively, and the signals of axial and equatorial protons of methylene groups in the region of 4.04, 4.32 ppm with the respective spin–spin coupling constants $^{2}J_{HH}$ and $^{3}J_{PH}$.

With the phosphorylating reagent propylene (**XXXIII**) and neopentylene chlorophosphites (**XXXIV**) at the ratio of reactants 1:1 in the presence of triethylamine as an acceptor of hydrogen chloride only a trisphosphorylated product formed, but a part of the original trihydroxybenzene (**XVII**) remained in solution unused. Moreover, such a direction of the reaction does not depend on the order of mixing the reagents. This is due, we think, to the high rate of the the phosphorylation with the chlorophosphites.

At introducing two moles of a chlorophosphite **XXXIII** or **XXXIV** bisphosphorylated product **XXXV** or **XXXVI** formed, respectively. The products were isolated after the sulfurization and were characterized

by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. Bisthionophosphate **XXXI** according to its physicochemical characteristics was identical to that obtained previously by the reaction with amide, but the yield of the desired product in the case of the chloride method was higher.

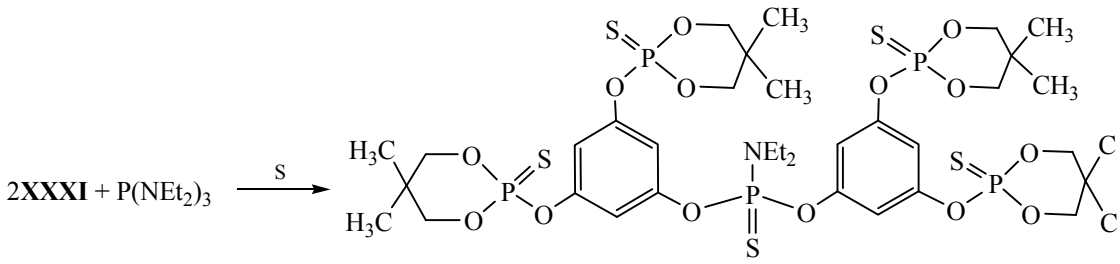


XXXIII, XXXIV **XXXV, XXXVI** **XXXI, XXXVII**

R = (**XXXIII, XXXV, XXXVII**); (**XXXI, XXXIV, XXXV**).

Thionophosphate **XXXVII** was also obtained as an oily substance. In its ^{31}P NMR spectrum a singlet was observed at 55.7 ppm, characteristic of cyclic thionophosphates. In the ^{1}H NMR spectrum multiplets were observed of equatorial and axial methylene protons in the fifth position of the ring, at 1.85 and 2.23 ppm, respectively, of the equatorial and axial methylene protons in 4 and 6 positions of the ring in the region of 4.51 ppm, of the aromatic protons, with the ratio of integral intensities 1:2, and the signal of the proton of hydroxy group.

The isolated thionophosphates **XXXI** and **XXXVII** can be entered in the phosphorylation with equimolar amount of phosphorous hexaethyltriamide at room temperature, as was illustrated by an example of thionophosphate **XXXI**.



After stirring for 15 days in dioxane sulfur was added to the solution and the resulting product **XXXVIII** was isolated. In its ^{31}P NMR spectrum two singlet signal were observed with δ_P 53.2 and 65.3 ppm, with the ratio of integral intensities 4:1. The formation of dimeric product **XXXVIII** was confirmed by the ^{1}H NMR spectrum.

Thus, we can conclude that the most successful in the synthesis of initial compounds for the molecular assembling is the phosphorylation of 1,2,3- and 1,2,4-trihydroxybenzenes with phosphorous amides at a ratio of reagents 1:2. However, another amide center in this case cannot be involved into the reaction. On the other hand, using acyl derivatives of trihydroxybenzenes, in particular, of phloroglucinol, free acyl group can be further replaced by other phosphorous sites.

EXPERIMENTAL

The ^{1}H, ^{13}C ($CDCl_3$) and ^{31}P NMR spectra were obtained on a JEOL ECX-400 instrument (400 MHz), the ^{1}H and ^{13}C chemical shifts are given relative to TMS, the ^{31}P shifts, relative to 85% phosphoric acid.

Mass-spectral studies were performed on a Bruker Ultra Flex instrument with a time-on-flight (TOF)

detector by the method of matrix-activated laser desorption and ionization (MALDI) (λ 337 nm) using trihydroxyanthracene as a matrix.

All syntheses involving compounds of trivalent phosphorus were carried out in an atmosphere of dry argon. The adsorption column chromatography was carried out on silica gel L 100–250 mm; R_f values were determined by TLC on the Silufol UV-254 plates using the systems: hexane–dioxane 3:1 (A), hexane–dioxane 5:1 (B), benzene–dioxane 3:1 (C). The substances were detected by iodine vapor and calcination.

Phosphorous hexamethyl- (**IIIa**) and hexaethyltriamides (**IIIb**) were obtained by the method [22]. Pyrogallol (**V**) and phloroglucinol (**XVII**) triacetates were obtained by the method [23], oxyhydroquinone triacetate (**VI**) by [24]. Ethyl phosphorous tetraethyldiamide was obtained by the method [25], 5,5-dimethyl-2-diethylamide-1,3,2-dioxaphosphorinane (**XXX**), by the method [26], 2-chloro-1,3,2-dioxaphosphorinane (**XXXIII**) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (**XXXIV**), by the method [27].

2-Thiono-2-(dimethylamino)benzo[*d*][1,3,2]dioxaphosphol)-4- or -5-yl acetates (VIII, X). To 0.79 mmol of 1,2,3- or 1,2,4-triacetoxybenzene (**V, VI**) dissolved in 5 ml of dioxane was added 0.79 mmol of phosphorous hexamethyltriamide while continuous stirring at room temperature. After 2 days 0.79 mmol of sulfur was added to the solution. After another day the solvent was evaporated, and the residue was chromatographed on a column, eluting compounds **VIII, X** with hexane. The isolated products were dried in a vacuum (1 mm Hg, 70ºC).

2-Thiono-2-(dimethylamino)benzo[*d*][1,3,2]dioxaphosphol)-4-yl acetate (VIII), yield 80%, mp. 63–64ºC, R_f 0.54 (A). ^{1}H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 2.81 d (6H, CH_3–N, $^3J_{PH}$ 12.4 Hz), 6.63 d (1H, CH, $^3J_{HH}$ 8.4 Hz), 6.78 dd (1H, CH, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 2.6 Hz), 6.94 m (1H, CH, $^3J_{HH}$ 8.4 Hz). ^{31}P NMR spectrum, δ_P, ppm: 90.0 ($CHCl_3$). Found, %: C 43.82, H 4.42; N 5.13; P 11.35. $C_{10}H_{12}NO_4PS$. Calculated, %: C 43.96; H 4.43; N 5.13; P 11.34.

2-Thiono-2-(dimethylamino)benzo[*d*][1,3,2]dioxaphosphol)-5-yl acetate (X), yield 71%, oily substance, R_f 0.27 (B). ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 2.87 d (6H, CH_3, $^3J_{PH}$ 12.5 Hz), 6.71 d.d (1H, CH, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 2.4 Hz), 6.86 d (1H, CH, $^4J_{HH}$ 2.4 Hz), 7.03 d (1H, CH, $^3J_{HH}$ 8.6 Hz). ^{31}P NMR spectrum, δ_P, MD: 87.5 ($CHCl_3$). Found, %: C 43.91, H 4.39; N 5.07; P 11.36. $C_{10}H_{12}NO_4PS$. Calculated, %: C 43.96; H 4.43; N 5.13; P 11.34.

2-Thiono-2-(dialkylamino)benzo[*d*][1,3,2]dioxaphosphol)-4- or 5-yl *N,N,N′,N′*-tetraalkyldiaminothionophosphates (XIIIb, XIVa, XIVb) To 1.6 mmol of 1,2,3- or 1,2,4-trihydroxybenzene (**I, II**) dissolved in 5 ml of acetonitrile or dioxane, was added 3.2 mmol of phosphorous hexamethyltriamide or phosphorous hexaethyltriamide at room temperature at continuous stirring. After two days to the reaction mixture 3.2 mmol of sulfur was added and the mixture was stirred for another two days. Then the solvent was evaporated and the residue was chromatographed on a column, the products **XIIIb, XIVa, XIVb** were eluted with benzene. The obtained products were dried in a vacuum (1 mm Hg, 70ºC).

2-Thiono-2-(diethylamino)benzo[*d*][1,3,2]dioxaphosphol)-4-yl *N,N,N′,N′*-tetraethyldiaminothionophosphate (XIIIb), yield 42%, oily substance, R_f 0.65 (C). ^{1}H NMR spectrum, δ, ppm: 1.15 m (12H, CH_3, $^3J_{HH}$ 7.3 Hz), 1.18 m (6H, CH_3, $^3J_{HH}$ 5.8 Hz), 3.17 m (8H, CH_2, $^3J_{PH}$ 12.4 Hz), 3.30 m (4H, CH_2, $^3J_{PH}$ 13.2 Hz), 6.84–6.90 m (3H, CH). ^{31}P NMR spectrum, δ_P, ppm: 88.0, 78.7 (C_6H_6). Found, %: C 46.44, H 7.14; N 9.03; P 13.31. $C_{18}H_{33}N_3O_3P_2S_2$. Calculated, %: C 46.48; H 7.13; N 9.00; P 13.34.

2-Thiono-2-(dimethylamino)benzo[*d*][1,3,2]dioxaphosphol)-5-yl *N,N,N′,N′*-tetramethyldiaminothionophosphate (XIVa), yield 22%, oily substance, R_f 0.40 (A). ^{1}H NMR spectrum, δ, ppm: 2.72 d.d (12H, CH_3, $^3J_{PH}$ 11.9, 12.2 Hz, $^4J_{HH}$ 1.5, 1.2 Hz), 2.76 d (6H, CH_3, $^3J_{PH}$ 12.5 Hz), 6.70 d.d (1H, CH, $^3J_{HH}$ 8.6 Hz, $^4J_{HH}$ 1.6 Hz), 6.85 d (1H, CH, $^4J_{HH}$ 1.5 Hz), 6.98 d (1H, CH, $^3J_{HH}$ 8.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 89.8, 81.9 (C_6H_6). Found, %: C 37.79; H 5.55; N 11.02; P, 16.24. $C_{13}H_{21}N_3O_3P_2S_2$. Calculated, %: C 37.71; H 5.53; N 11.07; P 16.30.

2-Thiono-2-(diethylamino)benzo[*d*][1,3,2]dioxaphosphol)-5-yl *N,N,N′,N′*- tetraethyldiaminothionophosphate (XIVb), yield 21%, oily substance, R_f 0.58 (A). ^{1}H NMR spectrum, δ, ppm: 1.11 m (12H, CH_3), 1.14 m (6H, CH_3, $^3J_{HH}$ 7.8 Hz), 3.18 m (8H, CH_2), 3.40 m (4H, CH_2, $^3J_{PH}$ 11.7 Hz), 6.87–6.93 m (3H, CH). ^{31}P NMR spectrum, δ_P, ppm: 88.0, 78.6 (C_6H_6). Found, %: C 46.44, H 7.14; N 9.03; P 13.31. $C_{18}H_{33}N_3O_3P_2S_2$. Calculated, %: C 46.48; H 7.13; N 9.00; P 13.34.

Bis(2-thiono-2-(dialkylamino)benzo[*d*][1,3,2]dioxaphosphol-4- or 5-yl) dialkylaminothionophos-

phates (XVIIb, XVIIIa, XVIIIb). After keeping the reactive solution of the compound **XIIa** for 3 days, or compounds **XIb, XIIb** for 10 days at room temperature, to the reaction mixture was added 5 mmol of sulfur and the mixture was kept at room temperature for 3 days. The compounds formed were isolated by column chromatography, eluting the products **XVIIb, XVIIIa, and XVIIIb** with benzene. The obtained products were dried in a vacuum (1 mm Hg, 70ºC).

Bis(2-thiono-2-(diethylamino)benzo[*d*][1,3,2]dioxaphosphol-4-yl) diethylaminothionophosphate (XVIIb), yield 26%, oily substance, R_f 0.37 (A). ^{1}H NMR spectrum, δ, ppm: 1.09 m, 1.17 m, 1.21 m (18H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.20 m (4H, CH_2, $^3J_{PH}$ 11.9 Hz), 3.26 m (4H, CH_2, $^3J_{PH}$ 14.9 Hz), 3.50 m (4H, CH_2, $^3J_{PH}$ 15.8 Hz), 6.85–6.94 m (4H, CH), 7.10 d (1H, CH), 7.12 d (1H, CH). ^{31}P NMR spectrum, δ_P, ppm: 89.6, 70.2 (C_6H_6). Found, %: C 44.20; H 5.54; N 6.46; P 14.25. $C_{24}H_{36}N_3O_6P_3S_3$. *M* (*m/z*): 651.12 Calculated, %: C 44.23; H 5.57; N 6.45; P 14.26. *M* 651.

Bis{2-thiono-2-(dimethylamino)benzo[*d*][1,3,2]dioxaphosphol-5-yl}} dimethylaminothionophosphate (XVIIIa), yield 19%, oily substance, R_f 0.27 (A). ^{1}H NMR spectrum, δ, ppm: 2.86 g (12H, CH_3, $^3J_{PH}$ 12.5 Hz), 2.96 d (6H, CH_3, $^3J_{PH}$ 11.9 Hz), 6.80 d.d (1H, CH, $^3J_{HH}$ 8.9 Hz, $^4J_{HH}$ 1.8 Hz), 6.84 d.d (1H, CH, $^3J_{HH}$ 7.9 Hz, $^4J_{HH}$ 1.2 Hz), 6.88–6.93 m (5H, CH), 7.00 d (1H, CH, $^3J_{HH}$ 8.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 89.8, 68.5 (C_6H_6). Found, %: C 38.09; H 4.26; N, 7.40; P 16.37. $C_{18}H_{24}N_3O_6P_3S_3$. Calculated, %: C 38.12; H 4.29; N 7.38; P 16.35.

Bis{2-thiono-2-(diethylamino)benzo[*d*][1,3,2]dioxaphosphol-5-yl}} diethylaminothionophosphate (XVIIIb), yield 17%, oily substance, R_f 0.53 (A). ^{1}H NMR spectrum, δ, ppm: 0.86 m (6H, CH_3), 1.17 m (12H, CH_3, $^3J_{HH}$ 6.1 Hz), 3.23 m (8H, CH_2, $^3J_{PH}$ 15.6 Hz), 3.41 m (4H, CH_2, $^3J_{PH}$ 14.3 Hz), 6.62 d (1H, CH), 6.83–6.91 m (3H, CH), 6.97 d (1H, CH, $^3J_{HH}$ 8.9 Hz), 7.00 d (1H, CH, $^3J_{HH}$ 8.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 88.4, 67.0 (C_6H_6). Found, %: C 44.21; H 5.50; N 6.43; P 14.24. $C_{24}H_{36}N_3O_6P_3S_3$. Calculated, %: C 44.23; H 5.57; N 6.45; P 14.26.

1,3,5-Tris(tetraethyldiamidothionophosphoryloxy)benzene (XIX). To 0.2 g of phloroglucinol **XVII** dissolved in 5 ml of acetonitrile was added 1.2 g of phosphorous hexaethyltriamide at continuous stirring and room temperature. After 45 min to the reaction solution was added 0.05 g of sulfur, the stirring was continued for another day, the solvent was evaporated, and product **XIX** was isolated chromatographically, eluent benzene. The obtained product was dried in a vacuum (1 mm Hg, 70ºC). Yield 86%, oily substance. R_f 0.80 (C). ^{1}H NMR spectrum, δ, ppm: 1.13 m (36H, CH_3, $^3J_{HH}$ 7.2 Hz), 3.21 m (24H, CH_2, $^3J_{PH}$ 11.7, 12.7 Hz), 6.84 s (3H, Ar). ^{31}P NMR spectrum, δ_P, ppm: 74.1 (C_6H_6). Found, %: C 48.35; H 8.50; N 11.30; P 12.47. *M* (*m/z*): 744.99. $C_{30}H_{63}N_6O_3P_3S_3$. Calculated, %: C 48.37; H 8.52; N 11.28; P 12.47. *M* 744.

1-(Tetraethyldiamidothionophosphoryloxy)-3,5-diacetoxybenzene (XXIIIb). To 0.2 g of 1,3,5-triacetoxybenzene **XXI** dissolved in 5 ml of acetonitrile was added 0.2 g of phosphorous hexaethyltriamide at continuous stirring, at room temperature. After 2 days 0.025 g of sulfur was added and the stirring was continued for another 2 days, the solvent was evaporated, and compound **XXIIIb** was isolated by column chromatography, eluent benzene. The obtained product was dried in a vacuum (1 mm Hg, 70ºC). Yield 63%, oily substance. R_f 0.75 (C). ^{1}H NMR spectrum, δ, ppm: 1.11 m (6H, CH_3, $^3J_{HH}$ 6.9 Hz), 2.25 s (6H, CH_3CO), 3.20 m (8H, CH_2, $^3J_{PH}$ 12.4 Hz), 6.72 d (1H, CH, $^4J_{HH}$ 1.2 Hz), 6.87 q (2H, CH, $^4J_{HH}$ 1.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.7 s (CH_3), 21.0 s (CH_3–C), 40.1 d (CH_2), 111.0 s (1), 112.4 s ($C^{3,5}$), 150.1 s ($C^{2,6}$), 151.7 s (C^4), 169.0 s [C (O)]. ^{31}P NMR spectrum, δ_P, ppm: 75.7 ($CHCl_3$). Found, %: C 51.93; H 7.11; N 6.58; P 7.45. $C_{18}H_{29}N_2O_5PS$. *M* (*m/z*): 416.76. Calculated, %: C 51.91; H 7.02; N 6.73; P 7.44. *M* 416.

1,3-Bis(tetraethyldiamidothionophosphoryloxy)-5-acetoxybenzene (XXVb). To 0.2 g of compound **XXI** dissolved in 5 ml of acetonitrile was added 0.4 g of phosphorous hexaethyltriamide at continuous stirring at room temperature. After 2 days was added 0.05 g of sulfur, and the stirring was continued for another 2 days, the solvent was evaporated and compound **XXVb** was isolated by column chromatography, eluent benzene. The obtained product was dried in a vacuum (1 mm Hg, 70ºC). Yield 57%, oily substance. R_f 0.64 (C). ^{1}H NMR spectrum, δ, ppm: 1.12 m (24H, CH_3, $^3J_{HH}$ 7.0 Hz), 2.26 s (3H, CH_3CO), 3.20 m (16H, CH_2, $^3J_{PH}$ 12.4 Hz), 6.76 q (2H, CH, $^4J_{HH}$ 1.1 Hz), 6.95 d (1H, CH, $^4J_{HH}$ 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8 s (CH_3), 21.2 s (CH_3–C), 40.2 d (CH_2), 110.9 s ($C^{1,3}$), 112.2 s (C^5), 152.0 s (C^6), 154.1 s ($C^{2,4}$), 169.0 s [C(O)]. ^{31}P NMR spectrum, δ_P, ppm: 76.5. ($CHCl_3$). Found, %: C 49.67; H 7.95; N 9.63; P 10.60. $C_{24}H_{46}N_4O_4P_2S_2$. *M* (*m/z*): 580.24. Calculated, %: C 49.64; H 7.98; N 9.65; P 10.67. *M* 580.

1,3-Bis[ethoxy(diethylamido)thionophosphoryloxy]-5-hydroxybenzene (XXVIII) and 1,3,5-tris[ethoxy(diethylamido)thionophosphatoxy]benzene (XXIX). To 0,2 g of phloroglucinol **XVII** dissolved in 5 ml of dioxane at room temperature at continuous stirring was added 0.88 g of ethyl diethylamidophosphite. A day latter to the reaction mixture 0.1 g of sulfur was added, and the mixture was stirred for another 4 days, the solvent was evaporated and the residue was chromatographed on a column eluting the obtained product **XXVIII** or **XXIX** with benzene. The obtained products were dried in a vacuum (1 mm Hg, 70ºC).

1,3-Bis[ethoxy(diethylamido)thionophosphoryl]-5-hydroxybenzene (XXVIII). Yield 85%, oily substance. R_f 0.55 (C). ^{1}H NMR spectrum, δ, ppm: 1.12 m (12H, CH_3, $^3J_{HH}$ 6.8 Hz), 1.32 m (6H, CH_3–O, $^3J_{HH}$ 6.0 Hz), 3.28 m (8H, CH_2–N, $^3J_{PH}$ 13.7 Hz), 4.11 m (4H, CH_2–O, $^3J_{PH}$ 18.8 Hz), 5.42 br.s (1H, OH), 6.15 s (1H, CH), 6.29 s (2H, CH). ^{31}P NMR spectrum, δ_P, ppm: 71.6 (C_6H_6). Found, %: C 44.60; H 7.00; N 5.77; P 12.70. $C_{18}H_{34}N_2O_5P_2S_2$. Calculated, %: C 44.62; H 7.07; N 5.78; P 12.78.

1,3,5-Tris[ethoxy(diethylamido)thionophosphoryl]benzene (XXIX). Yield 12%, mp 115–116ºC, R_f 0.72 (C). ^{1}H NMR spectrum, δ, ppm: 1.08 m (18H, CH_3, $^3J_{HH}$ 7.3 Hz), 1.32 m (9H, CH_3, $^3J_{HH}$ 7.4 Hz), 3.27 m (12H, CH_2–N, $^3J_{PH}$ 13.3 Hz), 4.07 m (9N, CH_2–O, $^3J_{PH}$ 13.3 Hz, $^3J_{HH}$ 9.6 Hz), 6.53 s (3H, CH). ^{13}C NMR spectrum, δ_C, ppm: 14.2 d (6C, CH_3, $^3J_{PC}$ 8.7 Hz), 15.9 dd (3C, CH_3, $^3J_{PC}$ 14.4 Hz), 40.4 g (6C, CH_2–N, $^2J_{PC}$ 3.9 Hz), 63.3 dd (2C, CH_2–O, $^2J_{PC}$ 15.3 Hz), 105.3 s (3C, CH), 151.7 d (3C, C–O, $^2J_{PC}$ 6.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 71.5 (C_6H_6). Found, %: C 43.39; H 7.69; N 6.43; P 14.2. $C_{24}H_{48}N_3O_6P_3S_3$. Calculated, %: C 43.43; H 7.29; N 6.33; P 14.00.

3,5-Bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yloxy)phenol (XXXI) and 1,3,5-tris(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yloxy)benzene (XXXII). To 1.5 mmol of compound **XVII** dissolved in 5 ml of dioxane was added 3.2 mmol of compound **XXX**. The reaction was carried out at 50ºC at continuous stirring. After 15 days to the reaction mixture3.2 mmol of sulfur was added, and the mixture was further stirred for 7 days and the products **XXXI, XXXII** were isolated by column chromatography, eluent benzene. The obtained products were dried in a vacuum (1 mm Hg, 70ºC).

3,5-Bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yloxy)phenol (XXXI), yield 65%, oily substance. R_f 0.80 (C). ^{1}NMR spectrum, δ, ppm: 0.91 s (6H, CH_3^e), 1.31 s (6H, CH_3^a), 3.98 d.d (4H, CH_2^e, $^3J_{PH}$ 21.8 Hz, $^2J_{HH}$ 11.1 Hz), 4.27 d.d (4H, CH_2^a, $^3J_{PH}$ 21.1 Hz, $^2J_{HH}$ 11.1 Hz), 5.88 br.s (1H, OH), 6.63 s (2H, CH), 6.69 s (1H, CH). ^{31}P NMR spectrum, δ_P, ppm: 53.8 ($CHCl_3$). Found, %: C 42.31; H 5.30; P 13.64. $C_{16}H_{24}O_7P_2S_2$. Calculated, %: C 42.29; H 5.32; P 13.63.

1,3,5-Tris(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yloxy)benzene (XXXII), yield 20%, mp 190–120ºC, R_f 0.54 (C). ^{1}H NMR spectrum, δ, ppm: 0.92 s (9H, CH_3^e), 1.32 s (9H, CH_3^a), 3.99 d.d (6H, CH_2^e, $^3J_{PH}$ 21.8 Hz, $^2J_{HH}$ 11.1 Hz), 4.28 d.d (6H, CH_2^a, $^3J_{PH}$ 22.3 Hz, $^2J_{HH}$ 11.1 Hz), 7.02 s (3H, CH). ^{31}P NMR spectrum, δ_P, ppm: 52.7 ($CHCl_3$). Found, %: C 40.72; H 5.35; P 15.05. $C_{21}O_9H_{33}P_3S_3$. Calculated, %: C 40.77; H 5.38; P 15.02.

3,5-Bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yloxy)phenol (XXXI) and 3,5-bis(2-thiono-1,3,2-dioxaphospharinan-2-yloxy)phenol (XXXVII). To 1.6 mmol of compound **XVII** dissolved in 5 ml of dioxane was added 0.32 g of triethylamine. The resulting solution at cooling and continuous stirrng was added dropwise to 1.6 mmol of 2-chloro-1,3,2-dioxaphosphorinane **XXXIII** or 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **XXXIV** dissolved in 3 ml of dioxane. The reaction mixture was kept at room temperature for 1 h, then triethylamine hydrochloride was filtered off and to the solution was added 3.2 mmol of sulfur. After 15 days the solvent was evaporated and the residue was chromatographed on a column eluting the products **XXXI, XXXVII** with benzene. The obtained products were dried in vacuum (1 mm Hg, 70ºC).

3,5-Bis(2-thiono-1,3,2-dioxaphospharinan-2-yloxy)phenol (XXXVII), yield 75%, oily substance. R_f 0.31 (C). ^{1}H NMR spectrum, δ, ppm: 1.86 d.d (2H, CH_2^a, $^2J_{HH}$ 15.1 Hz), 2.24 d.d (2H, CH_2^a, $^2J_{HH}$ 15.1 Hz), 4.48 m (4H, OCH_2^e, $^2J_{HH}$ 12.9 Hz), 4.51 m (4H, OCH_2^a, $^2J_{HH}$ 12.9 Hz), 6.06 s (2H, CH), 6.12 s (1H, CH), 8.23 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 26.1 s (2C, CH_2), 69.9 s (4C, OCH_2), 99.2 s (3C, CH), 152.1 s (1C, C–OH), 159.5 s (2C, C–OR). ^{31}P NMR spectrum, δ_P, ppm: 54.9 (DMSO). Found, %: C 43.50; H 6.18; P 14.14. $C_{16}H_{27}O_6P_2S_2$. Calculated, %: C 43.53; H 6.16; P 14.03.

Bis[3,5-bis(5,5-dimethyl-2-thiono-1,3,2-dioxaphospharinan-2-yl)phenyl] diethylamidophosphate (XXXVIII). To 0.1 g of compound **XXXI** dissolved in

5 ml of dioxane was added 0.064 ml of phosphorous hexaethyltriamide at continuous constant stirring, at room temperature. After keeping the solution for 15 days 0.0082 g of sulfur was added and the mixture was stirred for 1 day. Then the solvent was evaporated and the residue was chromatographed on a column eluting compound **XXXVIII** with benzene. The obtained product was dried in a vacuum (1 mm Hg, 70ºC). Yield 68%, oily substance, R_f 0.81 (C). ^{1}H NMR spectrum, δ, ppm: 1.18 m (6H, CH_3CH$_2$, $^3J_{HH}$ 9.2 Hz), 1.20 s (12H, CH_3^e), 1.31 s (12H, CH_3^a) 3.44 m (4H, CH_3CH_2, $^3J_{PH}$ 14.2 Hz), 3.98 d.d (8H, CH_2^a, $^3J_{PH}$ 22.0 Hz, $^2J_{HH}$ 12.0 Hz), 4.28 d.d (8H, CH_2^a, $^2J_{HH}$ 11.1 Hz), 6.95 s (4H, CH), 7.06 s (2H, CH). ^{31}P NMR spectrum, δ_P, ppm: 53.2, 65.9 ($CHCl_3$). Found, %: C 41.52; H 5.43; N 1.32; P 14.80. $C_{36}H_{56}NO_{14}P_5S_5$. Calculated, %: C 41.49; H 5.42; N 1.34; P 14.86.

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