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Synthesis of New Phosphines and P-Heterocycles from Phosphonates Containing Allyl Group

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Abstract — Addition of phenylphosphine to allylphosphonate followed by reduction of the resulting diphosphonate gives a new branched phosphine, bis(3-phosphinopropyl)phenylphosphine. Its reaction with paraform and *p*-toluidine yields oligomeric 3-[3-(propylenophenylphosphino)propyl]-1,5-di-*p*-tolyl-1,5,3,7-diazadiphosphacyclooctane. Diethyl (5-allyl-2-ethoxybenzyl)phosphonate was obtained. Its reduction gives unsaturated (5-allyl-2-ethoxybenzyl)phosphine. This product adds two moles of formaldehyde to give bis(hydroxymethyl)(5-allyl-2-ethoxybenzyl)phosphine. The reaction of this compound with *p*-toluidine yielded, depending on the conditions, the corresponding bis(aminomethyl)phosphine, 1,3,5-diazaphosphorinane, and 1,5,3,7-diazadiphosphacyclooctane, and also their derivatives containing allyl substituents.

The interest in the preparation of new phosphonates with unsaturated substituents is due to their considerable synthetic potential. In particular, these compounds can be readily converted into unsaturated primary phosphines and then into functionalized tertiary phosphines capable of copolymerization with organic oligomers, which is of interest for preparing new polymeric materials. Also, starting from vinylphosphonate, dendrimers containing up to 15 phosphine fragments were synthesized [1].

In this connection, our goal was to prepare polyphosphines from phosphonates containing allyl groups. As starting compounds we used diethyl allylphosphonate and previously unknown diethyl 5-allyl-2-ethoxybenzylphosphonate.

Addition of phenylphosphine to two molecules of diethyl allylphosphonate under homolytic conditions [80°C, 2,2'-azobis(isobutyronitrile)] was virtually quantitative. The reaction progress was monitored by ^{31}P NMR spectroscopy. After 8 h, only the signals of the bridging phosphorus atom at –26 ppm and terminal phosphonate groups at 26 ppm in a 1 : 2 ratio were observed. The resulting bis(3-diethoxyphosphorylpropyl)phenylphosphine **A**, without further purification, was reduced with an excess of lithium aluminum hydride to bis(3-phosphinopropyl)phenylphosphine **I**, whose ^{31}P NMR spectrum contained two signals with the chemical shifts of –26 and –137 ppm in a 1 : 2 ratio, belonging to the bridging tertiary and terminal primary phosphorus atoms.

$$PhPH_2 + 2(EtO)_2P(O)Al \xrightarrow{????,\ 80^\circ C} PhP[(CH_2)_3P(O)(OEt)_2]_2 \ \mathbf{A} \xrightarrow{LiAlH_4} PhP[(CH_2)_3PH_2]_2 \ \mathbf{I}$$

Trisphosphine **I** took up four molecules of formaldehyde on heating to 100°C to give bis[3-(dihydroxymethylphosphino)propyl]phenylphosphine **B**, which further reacted with 2 mol of *p*-toluidine in ethanol to give a mixture of oligomers of 3-[3'-(propylenophenylphosphino)propyl]-1,5-di-*p*-tolyl-1,5,3,7-diazadiphosphacyclooctanes **II**. Similar oligo(diazadiphosphacyclooctanes) were recently prepared under the similar conditions by the reactions of bis(dihydroxymethylphosphino)xylylene with primary aromatic amines [2]. The IR spectrum of **II** contained the weak bands of stretching vibrations of the terminal amino and hydroxy groups, and the ^{31}P NMR spectrum contained the signal at δ_P –26.88 ppm belonging to the phosphino groups of the bridging fragments and a group of closely located signals at –48.3 ppm belonging to the phosphorus atoms of diazadiphosphacyclooctane fragments. The characteristic phosphorus chemical shifts in 1,5,3,7-diazadiphosphacyclooctanes range from –48 to –52 ppm [2, 3].

To prepare diethyl (5-allyl-2-ethoxybenzyl)phosphonate **III**, we developed a multistage scheme including the preparation of *p*-allylphenol and formation of

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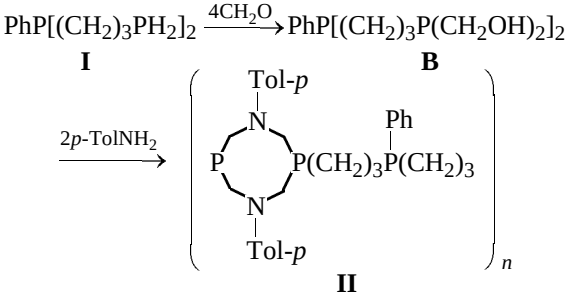
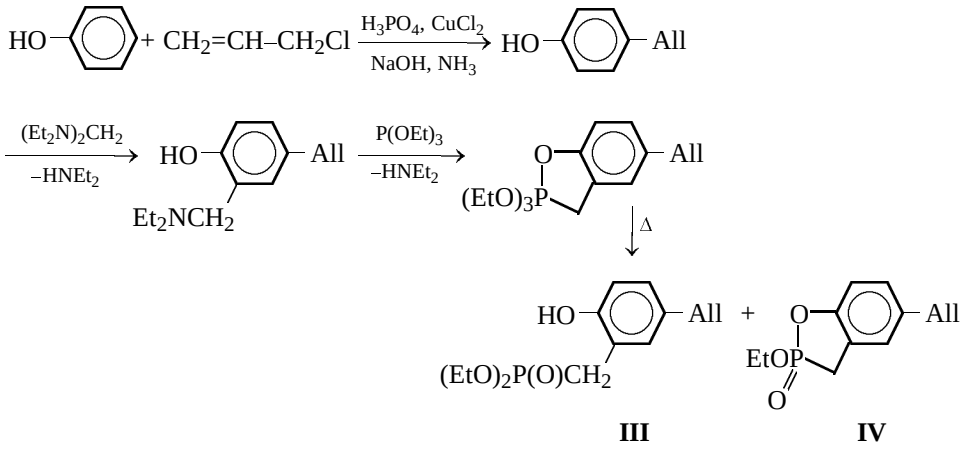


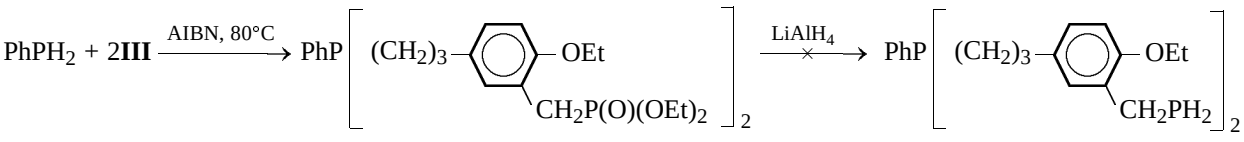
I **B** **II**

2-diethylaminomethyl-4-allylphenol by the Mannich reaction. The latter compound under relatively mild conditions reacts with triethyl phosphite following the Arbuzov reaction pattern to give compound **III**. The by-product of this reaction is 5-allyl-2-ethoxy-2-oxo-1,2λ^5-oxaphosphindane **IV**. The amount of this compound increases at overheating of the reaction mixture. Products **III** and **IV** were separated by vacuum distillation.



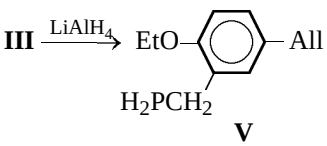
III **IV**

However, an attempt to obtain the branched phosphine from more complex phosphonate **III** failed. Though phenylphosphine readily added to this compound in the presence of azobisisobutyronitrile (the ^{31}P NMR spectra of the reaction mixture contained only the signals of the bridging phosphino group at –26.59 ppm and terminal phosphonate groups at 25.45 ppm), after the reduction of adduct **C** the signal of the bridging tertiary phosphino group disappeared. Several signals in the range from –122 to –124 ppm indicated cleavage of the bridging fragment. Probably, the negative role was played by the tendency of arylalkylphosphonates to the cleavage of the P–C bond under the conditions of reduction.



C

At the same time, reduction of phosphonate **III** gives 5-allyl-2-ethoxybenzylphosphine **V** in satisfactory yield.



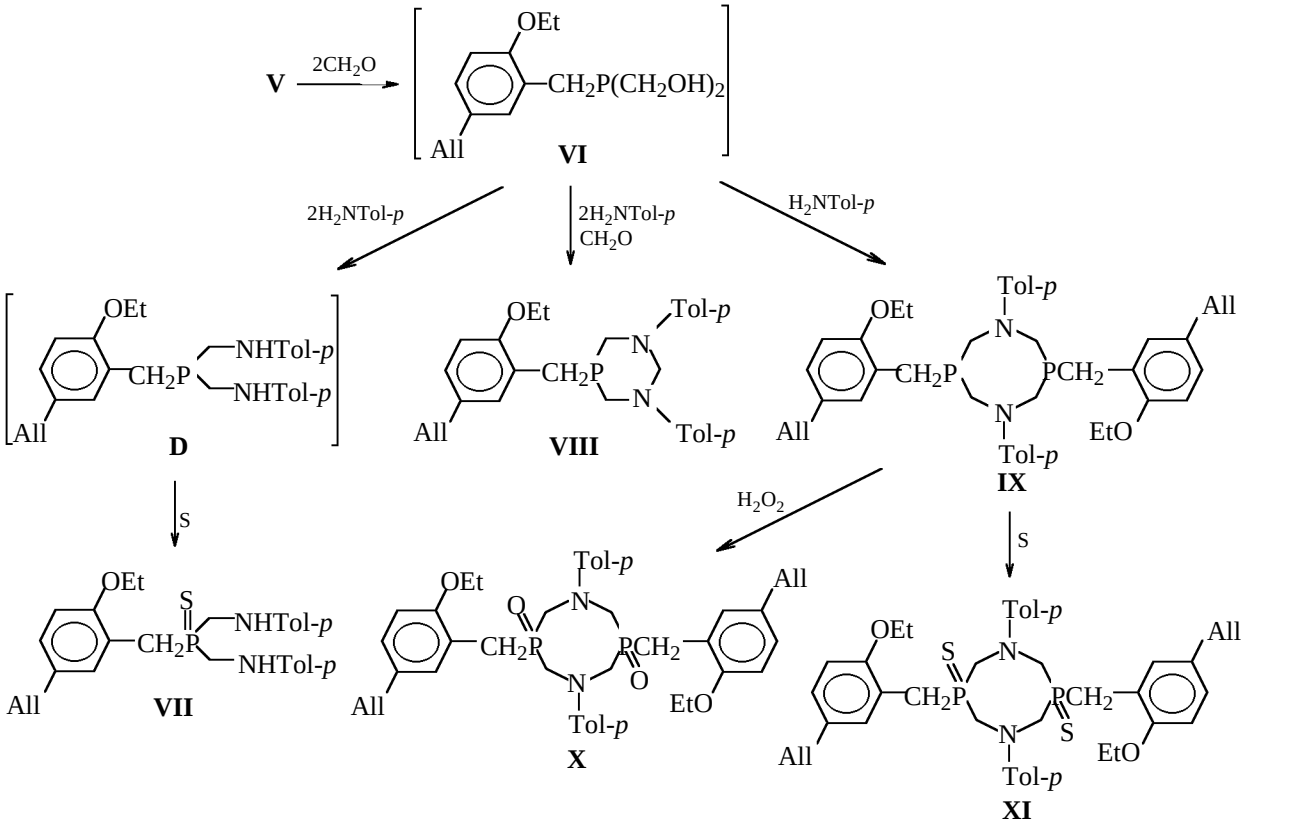
V

Phosphine **V** on careful heating to 100–110°C adds two formaldehyde molecules to give the corresponding bis(hydroxymethyl)(5-allyl-2-ethoxybenzyl)phosphine **VI** which, without further purification, was used for preparing cyclic and acyclic aminomethylphosphines and their derivatives containing one or two allyl groups capable of polymerization. For example, the reaction of **VI** with two equivalents of *p*-toluidine

in benzene yields bis(*p*-toluidinomethyl)(5-allyl-2-ethoxybenzyl)phosphine **D**.

In the ^{31}P NMR spectrum of the reaction mixture, the signal with the chemical shift δ_P –29.44 ppm, belonging to compound **D**, was predominant, but we failed to isolate this product pure. Therefore, we converted crude phosphine **D** to the corresponding phosphine sulfide **VII** by the reaction with elemental sulfur. The IR spectrum of **VII** contains the characteristic bands of stretching vibrations of the N–H bonds at 3324 and 3408 cm^{-1}, double bond of allyl group at 1638 cm^{-1}, and P=S bond at 700 cm^{-1}. The ^{31}P NMR spectrum contains one signal with the chemical shift δ_P 49.55 ppm. The ratio of the integral intensities of the corresponding signals in the ^1H NMR spectrum of **VII** suggests the presence of two *p*-tolyl and one 5-allyl-2-ethoxyphenyl fragments. The signals of the methylene protons of ethoxy group and P–CH_2–N and P–CH_2–Ar fragments overlap to give a complex multiplet in the range 3.30–3.55 ppm. The analytical data for **VII** are consistent with its empirical formula.

Similarly to the case of bis(hydroxymethyl)aryl- and bis(hydroxymethyl)benzylphosphines [2, 4], introduction of an additional mole of formaldehyde into this reaction leads to the closure of the six-membered ring and formation of 1,3-di-*p*-tolyl-5-(5'-allyl-2'-ethoxybenzyl)-1,3,5-diazaphosphorinane **VIII**, which is stable to hydrolysis and oxidation with atmospheric oxygen in the crystalline state and in solutions.



The analytical data for **VIII** are consistent with its empirical formula. No N–H stretching bands are observed in its IR spectrum, which confirms the cyclic structure. In the ^{31}P NMR spectrum, compound **VIII** gives a signal at –39.94 ppm, which disagrees with the values characteristic of the previously known 1,3-diaryl-5-phenyl-1,3,5-diazaphosphorinanes (average –60 ppm [5]). The cause of the unusual chemical shift of phosphorus is, most probably, the substitution of the phenyl group by the functionalized benzyl group. The ^1H NMR spectrum confirms the suggested structure of **VIII**. For example, the ratio of the integral intensities of the signals belonging to *p*-tolyl groups (the singlet of methyl protons and *AB* system of protons of phenylene fragments) and 5-allyl-2-ethoxyphenyl substituent (the triplet of methyl protons of

ethoxy group, the doublet of methylene protons of allyl group, the multiplet of the proton at the double bond, and the doublet of the aromatic proton at C^3) indicates the presence of two tolyl and one allylethoxyphenyl fragments in the molecule. Also, the doublet of doublets of equatorial protons of the P–CH_2–N fragment at 3.39 ppm ($^2J_{HH}$ 15.2 Hz, $^2J_{PH}$ 16.2 Hz) and the doublet of doublets of the N–CH_2–N fragment at 4.17 ppm ($^2J_{HH}$ 13 Hz, $^4J_{PH}$ 2 Hz), characteristic of phosphorinanes, are clearly identified in the spectrum. The signals of axial protons of the P–CH_2–N and N–CH_2–N fragments overlap with the signals of the methylene protons of the ethoxy group and the terminal protons of the double bond, respectively, and form complex multiplets at 3.65–3.76 and 5.85–6.00 ppm. The nonequivalence of the methylene protons of the heteroring shows that it has the *chair* conformation. The signal of one of the P–CH_2–N protons is obscured, which does not allow unambiguous determination of the orientation of the substituent at phosphorus. However, the coupling constant $^2J_{PH_e}$ is close to that observed for 1,3-di-*p*-tolyl-5-phenyl-1,3,5-diazaphosphorinane ($^2J_{PH_e}$ 16 Hz) [6], for which the preferred equatorial orientation of the substituent at phosphorus is known; this fact suggests the similar conformation of diazaphosphorinane **VIII** also.

Reaction of compound **VI** with an equimolar amount of *p*-toluidine in ethanol yielded the expected 1,5-di-*p*-tolyl-3,7-di(5-allyl-2-ethoxybenzyl)-1,5,3,7-diazadiphosphacyclooctane **IX**. The absence of vibration bands of amino and hydroxy groups in the IR spectrum of **IX** also counts in favor of its cyclic structure. Contrary to diazaphosphorinane **VIII**, compound **IX** has the chemical shift of phosphorus characteristic of 1,5,3,7-diazadiphosphacyclooctanes [2–4] (–48.95 ppm). The ^{1}H NMR spectrum of **IX** is typical of diazadiphosphacyclooctanes. It shows that, in solutions, this compound has the *chair-chair* conformation with the equatorial orientation of substituents at phosphorus, characteristic of these heterorings. This follows from the fact that the signal of axial protons of the heteroring is a doublet of doublets at 3.76 ppm with the coupling constant $^2J_{HH}$ 15.25 Hz and small $^2J_{PH}$ (3.75 Hz), which corresponds to the dihedral angle lone electron pair–P–C–H close to 180°. Phosphine **IX** is well soluble only in DMF and DMSO, though its solubility is to some extent higher than that of the previously known diazadiphosphacyclooctanes with phenyl groups at phosphorus. Compound **IX** is stable against hydrolysis and oxidation with atmospheric oxygen, but it is oxidized with hydrogen peroxide and adds sulfur to form the corresponding dioxide **X** and disulfide **XI**. The signals of **X** and **XI** in the ^{31}P NMR spectra (39.73 and 45.71 ppm, respectively) are shifted downfield as compared to the signals of 3,7-diphenyl-3,7-dioxo- (28–30 ppm) and 3,7-diphenyl-3,7-dithioxo-1,5,3λ^5,7λ^5-diazadiphosphacyclooctanes (36–38 ppm) [7]. However, the IR and ^{1}H NMR spectra of these compounds show that the heterocyclic structure is preserved. In the IR spectra of the products **X** and **XI**, the absorption bands of amino and hydroxy groups are absent, and in the ^{1}H NMR spectrum the ring protons give a pattern typical of diazadiphosphacyclooctane derivatives: two doublets at 4.04 and 4.21 ppm ($^2J_{HH}$ 16.1 Hz) for disulfide **XI** and a doublet at 3.78 ppm ($^2J_{HH}$ 15 Hz) and a doublet of doublets at 4.14 ppm ($^2J_{HH}$ 15, $^2J_{PH}$ 5.2 Hz) for dioxide **X**. Small values of $^2J_{PH}$ (0–5.2 Hz) are indicative of the equatorial orientation of the P=X bonds in both heterorings.

Thus, starting from diethyl allylphosphonate, we prepared a new trisphosphine, bis(3-phosphinopropyl)-phenylphosphine, and oligomers containing 1,5,3,7-diazadiphosphacyclooctane fragments linked with phosphine-containing bridges. Starting from diethyl 5-allyl-2-ethoxybenzylphosphonate, we prepared new aminomethylphosphines and their derivatives containing allyl groups. The presence of unsaturated groups and the sufficient stability of these compounds make them promising as comonomers in copolymerization with various organic monomers to give new phosphorus-containing polymer materials.

EXPERIMENTAL

The IR spectra (mulls in mineral oil) were recorded on Specord M-80 and UR-20 spectrometers. The ^{31}P NMR spectra were taken on Bruker WM-250 (101 MHz) and Bruker MSL-400 (161 MHz) spectrometers. The ^{1}H NMR spectra were measured on a Bruker WM-250 spectrometer.

p-Allylphenol was prepared according to [8].

All manipulations with phosphines were carried out in an inert atmosphere.

Bis(3-phosphinopropyl)phenylphosphine I. A mixture of 2.78 g of phenylphosphine, 11.76 g of diethyl allylphosphonate, and 0.15 g of azobis(isobutyronitrile) was heated for 8 h at 80°C in a weak flow of argon. A solution of the resulting bis[3-(diethoxyphosphoryl)propyl]phenylphosphine in 30 ml of absolute diethyl ether was added dropwise to a suspension of 1.58 g (10% excess) of $LiAlH_4$ in 10 ml of ether at a temperature not higher than –25°C. The temperature of the reaction mixture was gradually raised to 0°C, and the mixture was stirred for several hours. Then the reaction mixture was treated with 3 ml of

degassed water at cooling with ice and then with 33 ml of 18% HCl. The organic layer was separated and dried over $MgSO_4$ for a day. The volatiles were removed in a water-jet pump vacuum, and the residue was fractionated in a vacuum. Yield of 0.56 g (7.81%), bp 160°C (0.1 mm). ^{31}P NMR spectrum, δ_P, ppm: –26.5, –137 ($^1J_{PH}$ 145 Hz).

Oligo{3-[3'-(propyleno)phenylphosphino]propyl-1,5-di-*p*-tolyl-1,5,3,7-diazadiphosphacyclooctane} II. Paraform, 0.24 g, was added to 0.56 g of **I**, and the mixture was heated until it became homogeneous. The product was dissolved in 15 ml of absolute ethanol, and 0.43 g of *p*-toluidine was added. The reaction mixture was refluxed for several days until a powder-like precipitate formed. It was filtered off and dried for several hours in a vacuum (0.1 mm). Yield of **II** 0.34 g (31%), mp 76°C. IR spectrum (mineral oil), ν, cm^{-1}: 796 (C–H_{ar}), 984 (P–C_{ar}), 1514 (C=C_{ar}), 1620 (C=C_{ar}), 3025 (C–H_{ar}). ^{31}P NMR spectrum (DMF), δ_P, ppm: –26.88, –48.31. Found, %: C 70.34; H 7.25; N 5.53; P 17.25. $(C_{30}H_{39}N_2P_3)_n$. Calculated, %: C 69.22; H 7.55; N 5.38; P 17.85.

Diethyl 5-allyl-2-ethoxybenzylphosphonate III. *p*-Allylphenol, 53.78 g, was placed in a flask equipped with a reflux condenser, 63.38 g of bis(diethylamino)methane was added, and the mixture was left for 3 days. The released diethylamine (22.1 g) was removed in a water-jet pump vacuum at 60°C. The residue was placed in a three-necked flask equipped with an argon inlet tube, a thermometer, a descending condenser, and a collector and filled with argon. Triethyl phosphite, 73 g (10% excess), was added. The mixture was heated to 160°C (bath temperature 175°C), and 20 g of diethylamine was distilled off. The residue was 2,2,2-triethoxy-5-allyl-1-oxa-2-phosphaindane (δ_P –26 ppm). It was refluxed at 170°C for 12 h. The reaction progress was monitored by the ^{31}P NMR spectra. 5-Allyl-2-ethoxy-2-oxo-1,2λ^5-oxaphosphindane **IV** (δ_P 45 ppm) was formed along with **III**. Compound **III** was isolated by fractional distillation in a vacuum; the fraction with bp 140–170°C (0.2 mm) was collected. Yield 42.08 g (33%). ^{31}P NMR spectrum, δ_P, ppm: 25.

5-Allyl-2-ethoxybenzylphosphine V. A solution of 8.01 g of **I** in 30 ml of absolute diethyl ether was added dropwise to a suspension of 1.07 g (10% excess) of lithium aluminum hydride in 40 ml of ether at –30°C under dry argon. The mixture was stirred for a day at room temperature, and then 2.03 ml of distilled degassed water and 23 ml of 18% HCl were successively added dropwise with stirring and cooling with ice. The organic layer was removed and dried overnight over $MgSO_4$. The residue after removing the ether was fractionated in a vacuum. Yield of **V** 2.46 g (46%), bp 160–187°C (0.1 mm). ^{31}P NMR spectrum (C_6H_6), δ, ppm: –128.48 ($^1J_{PH}$ 194 Hz).

Bis(*p*-tolylaminomethyl)(5-allyl-2-ethoxybenzyl)-phosphine sulfide VII. Paraform, 0.334 g, was added to 1.16 g of **V**, and the mixture was heated on a water bath until it became homogeneous. A solution of 1.195 g of *p*-toluidine in 10 ml of benzene was added to the resulting compound **VI**. The mixture was stirred for a day at room temperature, the volatiles were removed in a vacuum, and the residue was treated with 0.18 g of sulfur in 10 ml of benzene. The mixture was heated until sulfur dissolved. The next day, the solvent was removed in a vacuum, and the residue was crystallized from acetonitrile at 0°C. The crystals were additionally recrystallized from acetonitrile. Yield of **VII** 0.8 g (30%), mp 88°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 700 (P=S), 806 (C–H_{ar}), 1612 (C=C_{ar}), 1638 (C=C), 3324 (N–H), 3408 (N–H). ^1H NMR spectrum (C_6D_6), ppm (*J*, Hz): 1.07 t (3H, OCH_2CH_3, $^3J_{HH}$ 6.7), 2.21 s (6H, $CH_3 \cdot C_6H_4$), 3.25 d (2H, $CH_2CH{=}CH_2$, $^3J_{HH}$ 6.8), 3.30–3.55 m (8H, PCH_2N, PCH_2Ar, OCH_2CH_3), 4.39 br.s (2H, NH), 5.04–5.12 m (2H, $CH_2CH{=}CH_2$), 5.89–6.06 m (1H, $CH_2CH{=}CH_2$), 6.47 d (4H, *o*-C_6H_4, $^3J_{HH}$ 9), 6.52 d (1H, C^3H_{ar}, $^3J_{HH}$ 8.8), 6.96 d (4H, *m*-C_6H_4, $^3J_{HH}$ 8.8), 7.01 d (1H, C^4H_{ar}, $^3J_{HH}$ 8.8). ^{31}P NMR spectrum, δ_P, ppm: 49.54. Found, %: C 70.01; H 7.56; N 5.65; P 6.09; S 6.91. $C_{28}H_{35}N_2OPS$. Calculated, %: C 70.30; H 7.32; N 5.86; P 6.49; S 6.69.

1,3-Di-*p*-tolyl-5-(5'-allyl-2'-ethoxybenzyl)-1,3,5-diazaphosphorinane VIII. Paraform, 0.91 g, was added to 2.11 g of **V**. The mixture was heated on a water bath until it became homogeneous. The resulting solution of formaldehyde in **VI** was treated with a solution of 2.17 g of *p*-toluidine in 15 ml of benzene. The mixture was stirred for a day at room temperature, the solvent was removed in a vacuum, and the residue was crystallized from acetonitrile at 0°C. Yield of **VIII** 1.9 g (40%), mp 106°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 808 (C–H_{ar}), 1424 (C–N), 1512 (C=C_{ar}), 1619 (C=C_{ar}), 1638 (C=C). ^1H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 1.25 t (3H, OCH_2CH_3, $^3J_{HH}$ 6), 2.24 s (6H, $CH_3C_6H_4$), 3.23 d (2H, $CH_2CH{=}CH_2$, $^3J_{HH}$ 6.5), 3.37 s (2H, P–CH_2Ar), 3.39 d.d (2H, PCH_eN, $^2J_{PH}$ 16.2, $^2J_{HH}$ 15.2), 3.65–3.76 m (4H, PCH_aN, OCH_2CH_3), 4.17 d.d (1H, NCH_eN, $^2J_{HH}$ 13, $^4J_{PH}$ 2), 4.95–5.11 m (3H, NCH_aN, $CH_2CH{=}CH_2$), 5.85–6.00 m (1H, $CH_2CH{=}CH_2$), 6.64 d (1H, C^3H_{ar}, $^3J_{HH}$ 7.5), 6.90–7.30 m (C^4H_{ar}, C^6H_{ar}), 6.99 d (*o*-C_6H_4, $^3J_{HH}$ 7), 7.07 d (*m*-C_6H_4, $^3J_{HH}$ 7) (total integral intensity 10H). ^{31}P NMR spectrum, δ, ppm: –39.94. Found, %: C 75.71; H 8.36; N 6.45;

P 6.49. $C_{29}H_{38}N_2OP$. Calculated, %: C 75.00; H 8.24; N 6.00; P 6.72.

1,5-Di-*p*-tolyl-3,7-di(5′-allyl-2′-ethoxybenzyl)-1,5,3,7-diazadiphosphacyclooctane IX. Paraform, 1.23 g, was added to 4.27 g of **V**, and the mixture was heated on a water bath until it became homogeneous. The resulting compound **VI** was dissolved in 25 ml of ethanol, and a solution of 2.23 g of *p*-toluidine in 20 ml of ethanol was added. The mixture was refluxed on a water bath for 3 h. The white precipitate was filtered off, washed with ethanol, and crystallized from acetonitrile. Yield of **IX** 2.6 g (37%), mp 198–200°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 790 (C–H_{ar}), 1614 (C=C_{ar}), 1638 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.36 t (6H, OCH_2CH_3, $^3J_{HH}$ 6.9), 2.06 s (6H, $CH_3C_6H_4$), 2.76 s (4H, PCH_2Ar), 3.31 d (4H, $CH_2CH{=}CH_2$, $^3J_{HH}$ 6.3), 3.76 d.d (4H, PCH_aN, $^2J_{HH}$ 15.25, $^2J_{PH}$ 3.75), 3.93–4.10 m (8H, OCH_2CH_3, PCH_eN), 4.98–5.10 m (4H, CH_2=CH), 5.85–6.00 m (2H, CH_2=CH), 6.04 d (4H, *o*-C_6H_4, $^3J_{HH}$ 8.3), 6.67 d (4H, *m*-C_6H_4, $^3J_{HH}$ 8.3), 6.91–7.19 m (6H, C_6H_3). ^{31}P NMR spectrum (DMF), δ_P, ppm: –48.97. Found, %: C 74.93; H 7.34; N 4.67; P 8.75. $C_{42}H_{52}N_2O_2P_2$. Calculated, %: C 74.34; H 7.67; N 4.12; P 9.14.

1,5-Di-*p*-tolyl-3,7-di(5′-allyl-2′-ethoxybenzyl)-3,7-dioxo-1,5,3λ^5,7λ^5-diazadiphosphacyclooctane X. To a suspension of 0.2 g of **IX** in 3 ml of acetone, we added a solution of 0.1 g of 33% H_2O_2 in 3 ml of acetone. The mixture was stirred at room temperature for 3 days. The precipitate was filtered off, washed with acetone, and crystallized from DMF. Yield of **X** 1.99 g (95%), mp 245–250°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 792 (C–H_{ar}), 1184 (P=O), 1614 (C=C_{ar}), 1638 (C=C), 3072 (C–H_{ar}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.30 t (6H, OCH_2CH_3, $^3J_{HH}$ 7), 2.16 s (6H, $CH_3C_6H_4$), 3.11 d (4H, PCH_2Ar, $^2J_{PH}$ 11.3), 3.78 d (4H, PCH_aN, $^2J_{HH}$ 15), 3.99 q (4H, OCH_2CH_3, $^3J_{HH}$ 7), 4.14 d.d (4H, PCH_eN, $^2J_{HH}$ 15, $^2J_{PH}$ 5.2), 4.98–5.11 m (4H, CH_2=CH), 5.86–6.02 m (2H, CH_2=CH), 6.76–7.12 m (14H, C_6H_4, C_6H_3). ^{31}P NMR spectrum (in pyridine), δ_P, ppm: 39.73. Found, %: C 71.89; H 7.65; N 3.71; P 8.73. $C_{42}H_{52}N_2O_4P_2$. Calculated, %: C 71.05; H 7.32; N 3.94; P 8.72.

1,5-Di-*p*-tolyl-3,7-di(5′-allyl-2′-ethoxybenzyl)-3,7-dithioxo-1,5,3λ^5,7λ^5-diazadiphosphacyclooctane XI. Sulfur, 0.039 g, and 5 ml of benzene were added to 0.41 g of **IX**. The mixture was heated until the reactants dissolved. The precipitate that formed after cooling of the reaction mixture was filtered off, washed with acetonitrile, and dried. Yield 0.2 g (44%), mp 115°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 792 (C–H_{ar}), 1616 (C=C_{ar}), 1640 (C=C), 3080 (C–H_{ar}). ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.99 t (6H, OCH_2CH_3, $^3J_{HH}$ 7), 2.11 s (6H, $CH_3 \cdot C_6H_4$), 3.24 d (4H, $CH_2CH{=}CH_2$, $^3J_{HH}$ 6.5), 3.36 d (4H, PCH_2Ar, $^2J_{PH}$ 11.75), 3.54 q (4H, OCH_2CH_3, $^3J_{HH}$ 7), 4.04 d (4H, PCH_aN, $^2J_{HH}$ 16.1), 4.21 d (4H, PCH_bN, $^2J_{HH}$ 16.1), 5.00–5.10 m (4H, CH_2=CH), 5.86–6.02 m (2H, CH_2=CH), 6.50 d (2H, C^3H_{ar}, $^3J_{HH}$ 8), 6.90–7.05 m (C^4H_{ar}), 6.94 d (*o*-C_6H_4, $^3J_{HH}$ 8.2), 6.67 d (*m*-C_6H_4, $^3J_{HH}$ 8.2) (total integral intensity 10H), 7.40 s (2H, C^6H_{ar}). ^{31}P NMR spectrum (DMF), δ_P, ppm: 45.71. Found, %: C 70.41; H 7.56; N 3.63; P 8.57; S 9.22. $C_{42}H_{52}N_2O_4P_2S$. Calculated, %: C 70.99; H 7.32; N 3.94; P 8.73; S 9.01.

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