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Synthesis and Ionophoric Properties of α,ω-Diphosphorylated Aza Podands: II.[1] Kabachnik–Fields Reaction as a Method for Design of α,ω-Diphosphorylated Aza Podands and Their Use for Determination of Metal Ions

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Abstract—Methods of the design of podands with α-aminomethylphosphine oxide terminal groups with the purpose of investigation of the ionophoric properties of the podands and their use as components of ion-selective electrodes are analyzed. The most convenient procedure is a one-pot synthesis based on the Kabachnik–Fields reaction in a system comprising a dialkyl(aryl)phosphinous acid, formaldehyde, and a diamine. An alternative procedure is two-stage and involves the reaction of a primary amine with a phosphinous acid and formaldehyde to form an α-aminomethyldialkyl(aryl)phosphine oxide in the first stage and cross-linking of two molecules of this compound via reaction with a dihalooligoether of the corresponding length in the second. Advantages and disadvantages of both procedures are considered. Electrode-active properties of the prepared aza podands are studied to show that ion-selective electrodes on their basis can be used for selective determination of low concentrations of alkali and alkaline-earth metal ions.

One of the most promising fields in the chemistry of host–guest complexes is design of polyfunctional host molecules with preset properties, capable of effectively binding inorganic and organic molecules. Various complex-forming agents that can play the role of a host are nowadays used in ion-selective electrodes, membrane transport, and as biologically active compounds, catalysts, etc. Podands with donor terminal groups hold much promise in this respect [2]. Of them the most extensively studied are oligoethers with amino and amido terminal groups [3], that have found wide application as components of ion-selective electrodes for metal cations [4, 5]. Considerable recent attention has been attracted to podands with phosphine oxide and phosphonate terminal groups, as potent complex-forming agents for alkali metal cations and effective neutral carriers and extractants for rare-earth metals [4–9]. The available published data on the complex-forming ability of aminophosphonates and aminophosphine oxides suggest that these compounds, too, may serve as effective reagents for extraction and separation of metal ions [9, 10].

At the same time, the information on the synthesis and properties of podands containing α-aminoalkylphosphoryl terminal groups is scarce. We set ourselves the task to develop procedures for preparing such structure with the aim to study their ionophoric properties and utility as components of ion-selective electrodes. It might be expected that introduction of nitrogen atoms in phosphorylated podands would significantly affect their extractive, transporting, and ionophoric properties and endow the organophosphorus compounds with features inherent in monofunctional aminophosphoryl carriers. These expectations were based on the structural similarity of phosphorylated aza podands having two α-aminomethylphosphine oxide terminal groups to macrocyclic ligands, such as crown ethers or cryptands, on the one side, and four-coordinate phosphorus compounds, aminophosphonates and phosphine oxides on the other; eventually, this would predetermine specific complex-forming properties of such podands.

Analysis of published data on the synthesis of phosphorylated compounds, as well as podands having terminal nitrogen-containing functional groups enabled us to outline a number of possible ways to constructing the target compounds. One of them might include the reduction of the nitro or nitroso incorporates in the structure of podands, like that

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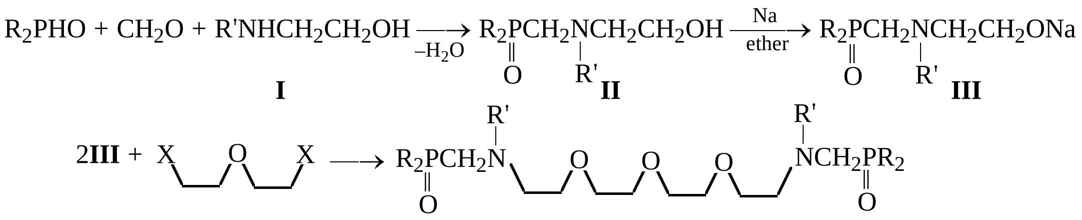
[1] For communication I, see [1].

described in [12]. However, this protocol seemed unlikely to hold promise, because compounds containing phosphoryl, nitro, and nitroso groups in one molecule are usually synthesized by multistage and, therefore, practically unfeasible procedures. Moreover, the reduction of the nitro and nitroso groups, which in the frames of this strategy would lead to amino groups, might touch the phosphoryl centers. For the above reasons, we ruled out this synthetic approach to phosphorylated aza podands.

More attractive seemed the synthetic strategy based on the creation of the α-aminomethylphosphoryl skeleton P(O)C–N by means of the Kabachnik–Fields reaction in a three-component system comprising a hydrophosphoryl and a carbonyl compounds, and an amine. One of the participants of this process might be alkanolamine **I**. This compound could be converted into hydroxyl-substituted aminophosphoryl compound **II** that is easy to covert into alcoholate **III**. Subsequent reaction of the latter with α,ω-dihaloethers or other bifunctional compounds with easily leaving groups, such as tosyl, would provide target aza podand **IV** as the final product [Scheme (1)].

Scheme 1.

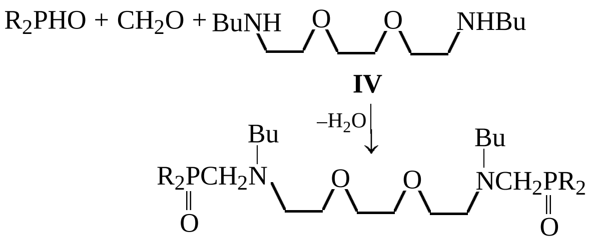


This strategy was subjected to experimental testing. As the phosphorus-containing components we used *N*-(β-hydroxyethyl)-α-aminomethylphosphine oxide derivatives prepared by means of the Kabachnik–Fields reaction from dialkyl- or diarylphosphinous acids, Paraform, and secondary amines with a β-hydroxyethyl substituent **I**. Aminomethylphosphorylated alcohol **II** prepared in this manner was treated with metallic sodium in ether to obtain sodium derivative **III** whose suspension was treated with the corresponding α,ω-dihalooligoether.

However, this method did not lead to the desired result. After removal of sodium chloride, in the ^{31}P NMR spectrum of the reaction mixture we observed several groups of signals presumably belonging to the phosphorus atoms in phosphine oxide and phosphine structures. This result is probably associated with the fact that the described reaction pathway was complicated by the redox processes yielding phosphines and phosphonium salts, that develop on treatment of *N*-alkyl-*N*-(hydroxyethyl)aminomethylphosphine oxides with sodium. Our attempts to carry out the analogous reaction with ditosyl derivatives of oligoethers failed. Hence, this method, too, proved to be unsuitable for our purposes.

The Kabachnik–Fields reaction in a system comprising a hydrophosphoryl compound, formaldehyde, and α,ω-bis(alkylamino)oligoether **IV**, i.e. the “bifunctional version” of a classical Kabachnik–Fields reaction, was found to be a more successful approach [Scheme (2)].

Scheme 2.



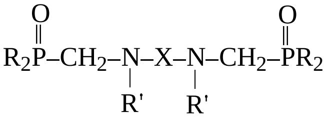
VI–IX

R = pentyl (**V**), *p*-Tol (**VII**), octyl (**VIII**), decyl (**IX**).

This process was carried out with aliphatic (diamyl-, dioctyl-, didecyl-) and an aromatic (di-*p*-tolyl-) phosphinous acids. *N*,*N*'-Dibutyl-1,10 diaza-4,7-dioxadecane **IV** was chosen as the bifunctional amine. The phosphine oxide–Paraform–diamine molar ratio was 2 : 2 : 1. The reaction was carried out in boiling benzene or toluene, using a Dean–Stark trap. The reaction progress was controlled by the amount of water, as well as by means of TLC and ^{31}P NMR spectroscopy.

After the reaction had been complete, the solvent was removed in a vacuum, and the residue was dried

Table 1. Characteristics of phosphorylated aza podands of the general formula



$$R_2\overset{O}{\overset{\|}{P}}-CH_2-\underset{R'}{N}-X-\underset{R'}{N}-CH_2-\overset{O}{\overset{\|}{P}}R_2$$

Comp. no.	R	R'	X	n_D^{20}	R_f	Yield, %	IR spectrum, ν(P=O), cm^{-1}	δ, ppm
VI	Pentyl	Bu	TEG[a]	1.4763	0.407	64	1165	46
VII	*p*-Tol	Bu	TEG	[b]	0.45	68–74	1190	24.7
VIII	Octyl	Bu	TEG	1.4735	0.588	64	1150	44.53
IX	Decyl	Bu	TEG	[b]	0.484	76	1140	43.2
X	Octyl	Bu	$(CH_2)_2$	1.472	0.35	99 (73)	1140	49
XI	Decyl	–	$N(CH_2CH_2)_2N$	[c]	0.297	67	1160	51

Table 1. (Contd.)

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	P		C	H	P
VI	65.1	11.75	9.3	$C_{36}H_{78}N_2O_4P_2$	67.55	12.41	9.1
VII	73.74	9.21	6.66	$C_{44}H_{62}N_2O_4P_2$	73.84	8.76	6.96
VIII	69.23	12.3	7.5	$C_{48}H_{102}N_2O_4P_2$	70.1	11.76	7.4
IX	71.19	12.5	6.57	$C_{56}H_{118}N_2O_4P_2$	70.9	12.54	6.43
X	70.97	12.63	8.33	$C_{44}H_{94}N_2O_2P_2$	71.12	12.52	8.43
XI	71.69	12.47	8.05	$C_{46}H_{96}N_2O_2P_2$	71.83	12.31	7.93

[a] TEG = $CH_2CH_2OCH_2CH_2OCH_2CH_3$ [b] Tar. [c] Solid.

to constant weight and subjected to column chromatography on silica gel. Characteristics of products **VI**–**IX** are listed in Table 1.

Podands **VI**–**IX** are viscous liquids readily soluble in most organic solvents. Their purity was controlled by TLC and elemental analysis, and the structure was assessed by IR and NMR spectroscopy. The IR spectra contain a characteristic sharp peak at 1140–1190 cm^{-1} due to P=O stretching vibrations. Stretching vibrations of C–O bonds appear in the range 1050–1100 cm^{-1}, and symmetric and antisymmetric vibrations of CH_2 and CH_3 groups, as characteristic multiplets at 3050–3100 cm^{-1}. Aromatic aza podands **VII** is additionally identified by the characteristic bands at 750–805 cm^{-1}, belonging to out-of-plane deformation vibrations of the aromatic ring and at 1600 cm^{-1}, belonging to double bonds of the tolyl group.

The ^{31}P NMR spectra of the aliphatic phosphine oxides all contain a singlet signal at 42–51 ppm and those of the aromatic phosphine oxides, a signal at 25 ppm.

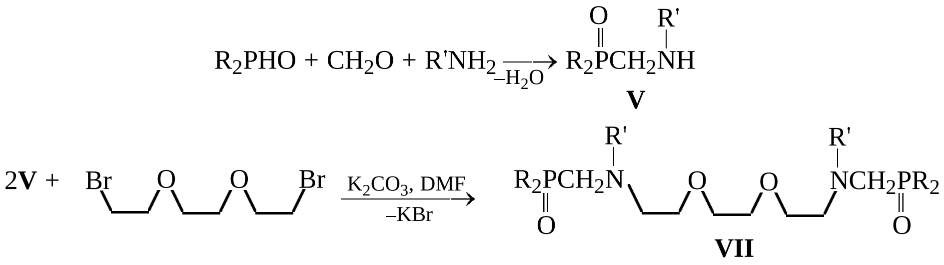
In ^1H NMR spectra of the phosphorylated 2,11-diaza-5,8-dioxadodecanone with tolyl substituents on phosphorus (compound **VII**) there are a doublet of doublets at 7.86 and 7.46 ppm, characteristic of aromatic systems, and a well-defined singlet at 2.6 ppm from the *p*-methyl substituents of the tolyl groups on phosphorus. The oxyethylene chain is identified by a set of signals: The singlet at 3.63 ppm (4H) belongs to protons of the symmetrical $O–CH_2–CH_2–O$ system of the central ethylenedioxy fragment, the α-methylene $P–CH_2–N$ group gives a doublet at 3.61 ppm (4H, $^2J_{PH}$ 15.3 Hz); and the $N–CH_2CH_2–O$ fragment gives two well-defined signals: a triplet of the OCH_2 group at 3.62 ppm (4H, $^3J_{HH}$ 5.9 Hz) and a triplet of the $N–CH_2$ group at 2.96 ppm (4H, $^3J_{HH}$ 5.6 Hz). Protons of the butyl group attached to nitrogen appear as a well-resolved group of signals in the range 1.02–2.84 ppm, characteristic of alkyl protons. Regretfully, the ^1H NMR spectra of aza podands with alkyl substituents on phosphorus proved to be poorly informative.

The latter synthetic approach was applied to success to prepare bis(aminoalkyl)phosphine oxides containing bridging ethylenediamine and piperazine fragments (compounds **X** and **XI**, respectively). Characteristics of these products are listed in Table 1. Compound **X** is liquid, and it was purified by column chromatography. Compound **XI** crystallizes as white needles and was purified by crystallization from hexane.

The developed one-stage synthesis of bis(α-aminomethyl)phosphorylated ligands **VI**–**XI** offers some undoubted advantages. The target compounds are formed in high or nearly quantitative yields. The reaction proceeds under mild conditions and its progress is controlled by simple methods.

Disadvantages of this method should also be mentioned. First of all this is the limited possibility of varying of the bridging polyether fragment in podands (no more than two oxyethylene units can be introduced). Furthermore, we came up against significant difficulties in attempted synthesis of aza podands with more lipophilic substituents on nitrogen, since diaminooligoethers with long hydrocarbon chains were hard to prepare pure. The example of diaminophosphine oxide **VII** was used to show that there is one more successful synthetic approach to phosphorylated aza podands. By means of the Kabachnik–Fields reaction we prepared α-aminophosphine oxide **XII** which was involved in reaction with 1,8-dibromo-4,7-dioxaoctane in the presence of anhydrous potassium carbonate in DMF (Scheme 3).

Scheme 3.



R = *p*-Tol, R' = Bu.

Spectral characteristics (^{31}P NMR and IR) of the samples of phosphorylated aza podand **VII**, obtained by both the above-described methods are completely identical. Our opinion is that the latter method is the most promising. In this case, organic radicals of any desired structure can be easily introduced to the phosphorus and nitrogen atoms of the aminophosphine oxides prepared by the Kabachnik–Fields reaction. This type compounds are easily purified by usual methods. Moreover, the dibromooligoethers used in this procedure are comparatively available and can be purified by vacuum distillation.

Hence, we have developed two relatively facile and convenient procedures for preparing phosphorylated podands, based on the Kabachnik–Fields reaction. The first of them is a one-pot synthesis in a three-component system comprising a hydrophosphoryl and a carbonyl compounds, and a diaminooligoether, which provides the target compounds in extremely high yields. The alternative procedure is a two-stage process involving the synthesis of the α-aminophosphine oxide synthon by reaction of a hydrophosphoryl compound with a carbonyl compound and a primary amine, followed by cross-linking of two molecules of the phosphorylated secondary amine with a dihalooligoether of corresponding length. Though these procedures both are rather facile and practically feasible, each of them has its merits and faults. The choice of a suitable one depends on the desired hydrophobic–hydrophilic balance or lipophilic characteristics of the target podand. Undoubtedly, the desired dimensions of the potential pseudocavity and number of potential coordination centers should be taken into account. Using the devised procedures we carried out the first synthesis of new podands with α-aminophosphoryl terminal groups, which allowed as to explore their use as electrode-active components of ion-selective electrodes for chemical analysis.

In the short preliminary report [1] we mentioned that ion-selective electrodes doped with aza podand **VII** can used for determination of cesium and rubidium ions in the presence of other ions. In the present work we present the results of a more extended and thorough investigation of the feasibility for determination of alkali and alkaline-earth metal ions of ion-selective electrodes containing aza podands with tolyl (**VII**) and octyl (**VIII**) substituents on phosphorus. The choice of these two of all our prepared phosphorylated aza podands (Table 1) was motivated, first, by the fact that their phosphorus-containing functional groups are fairly strongly differ in structure and, consequently, in lipophilicity. Then, as found by special investigations, these aza podands exhibit the highest selectivity, among the synthesized compounds, to heavy alkali and alkaline-earth metal cations in membrane transport (the results of this study will be reported elsewhere).

According to published data, the most sensitive to alkali and alkaline-earth metal cations among neutral carriers used in ion-selective electrodes are oligoethers with the low-polarity amido and amino terminal groups [3, 4], as well as natural antibiotics, such as nigericin, monensin, and valinomicin [13]. One of the most important factors controlling the selectivity of ion-selective electrodes is compliance of the structure of the carrier to coordination demands of the ion. At the same time, an important role belongs to correct selection of the membrane phase, since the electrostatic interaction between the membrane solvent and the complex of the cation with neutral carrier strongly effects the stability of such complexes [4]. In solvents with a high dielectric permeability, the selectivity of complex formation with double-charged cations is higher than with single-charged cations with the same radius. Therefore, nitroaromatic solvents are usually used as membrane solvents in ion-selective electrodes on the basis of neutral carriers sensitive to doble-charged ions [4].

To study the ionophoric properties of the aza podands, we made ion-selective electrodes with liquid membranes. Their construction was analogous to that described in [14]. The body of the electrode is a polyethylene pipette tip packed with a Teflon powder impregnated with a liquid membrane. Phosphorylated 2,11-diaza-5,8-dioxadodecanes with tolyl ((**VII**)) and octyl (**VIII**) substituents on phosphorus were used as active components of the liquid membranes. The membranes were solutions of the podands in nitrobenzene or *o*-nitrophenyl octyl ether containing equimolar (with respect to carrier) amount of sodium nitrophenylborate added to suppress the anionic function of the electrode.

Potentiometric measurements with membrane ion-selective electrodes were carried out in the following galvanic transfer circuit.

$$\mathrm{Ag}\,|\,\mathrm{AgCl,\ KCl}\,\vdots\,\underset{\mathrm{MCl}}{1\times10^{-2}\text{–}1\times10^{-5}\ \mathrm{M}}\,|\,\mathrm{Membrane}\,|\,\underset{\mathrm{MCl}}{1\times10^{-2}\ \mathrm{M}}\,\vdots\,\mathrm{AgCl}\,|\,\mathrm{Ag}.$$

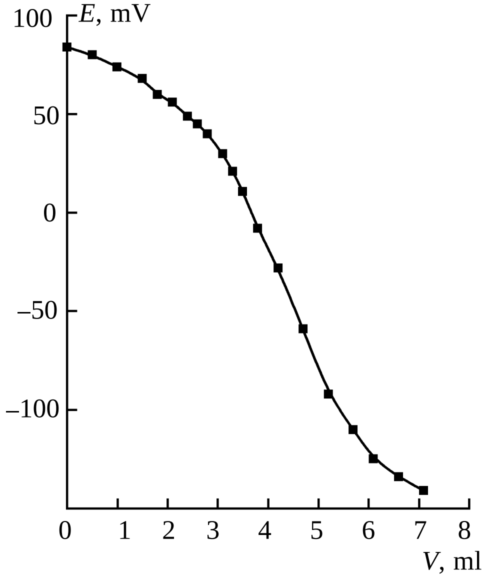
Here M is a metal to be determined. The internal electrode solution is a standard solution of the corresponding salt.

We found that ion-selective electrodes doped with aza podands **VII** and **VIII** give a response on alkali and alkaline-earth metal ions, and the selectivity of the electrodes significantly depends on the structure of the podand. Hence, aza podand **VII** exhibits the highest affinity and selectivity to ions of heavy alkali metals, such as cesium and rubidium.

From Table 2 it follows that the electrode containing this podand is characterized by electrode function slopes of 56.27 ± 1.65 mV for rubidium cation and 62.7 ± 1.77 for cesium cation. These values are close to the theoretical slopes found from the Nernst equation for single-charged cations, which implies reversibility of the processes on the interface. We found that the described electrode is sensitive to cesium and rubidium ions in the concentration range 10^{-2}–10^{-5} M. It should be emphasized that a high selectivity of

Table 2. Characteristics of ion-selective electrodes with liquid membranes on the basis of phosphorylated aza podands **VII** and **VIII**

Cation	Detection limit $C_{\min}$, M	Slope, $E/pC(M)$, mV
	Ionophore **VII**	
Rb^+	1.0×10^{-5}	56.3 ± 1.7
Cs^+	1.0×10^{-5}	62.7 ± 1.8
	Ionophore **VIII**	
Li^+	1.0×10^{-4}	57.9 ± 1.0
Na^+	1.0×10^{-3}	–
K^+	1.0×10^{-3}	–
NH_4^+	1.0×10^{-4}	44.9 ± 0.3
Rb^+	1.0×10^{-4}	–
Mg^{2+}	5.0×10^{-5}	28.7 ± 1.8
Ca^{2+}	1.0×10^{-5}	31.1 ± 1.3
Sr^{2+}	5.0×10^{-5}	29.6 ± 1.5
Ba^{2+}	1.0×10^{-5}	31.7 ± 1.4



Potentiometric titration curve of RbCl with the indicator electrode on the basis of aza podand **VII**.

the simultaneous determination of potassium and rubidium ions is attained. The log rubidium/potassium selectivity coefficient $-\log k_{pot}(Rb^+/K^+)$ 1.2, i.e. the sensitivity to rubidium is more that an order of magnitude higher than to potassium. A still higher selectivity was found for the rubidium/ammonium cation pair, $-\log k_{pot}(Rb^+/NH_4^+)$ 1.38. The lowest are the rubidium/barium (0.72), rubidium/lithium (0.89) and rubidiun/sodium (0.83) selectivities. Aza podand **VII** containing aromatic fragments exhibits the highest affinity to heavy alkaline and alkaline-earth metal cations.

Aliphatic aza podand **VIII** was found to be the most selectivite for barium cation. In this case, $-\log k_{pot}(Ba^{2+}/M)$ decreases in order K^+ (2.24), Na^+ (1.82), NH_4^+ (1.41), Li^+ (1.36), Ca^{2+} (0.75), and Rb^+ (0.51). Hence, here, too, complex formation occurs in preference to the heavy barium ion compared to ammonium and most alkali metal ions, which allows barium to be determined in the presence of the latter ions. Note that the selectivity for the heaviest barium and rubidium is the lowest. This fact may imply similarity in the character of complex formation of these two ions.

Note that the ion-selective electrode containing octyl-substituted aza podand **VIII** is feasible for determination double-charged metal ions (detection limit 10^{-5} M). The detection limit for light metal ions is much lower (10^{-3}–10^{-4}, Table 2).

Comparison of the ionophoric properties of aza podands with tolyl (**VII**) and octyl (**VIII**) substituents shows that the aromatic compound exhibits the highest sensitivity to the single-charged rubidium cation, while its aliphatic analog is the most suitable for determination of the double-charged barium ion. However, in both cases podands **VII** and **VIII** are best complementary to larger radius ions, thus providing one more evidence showing that an ion to be determined should fit the size of the potenial pseudocavity.

The practical feasibility of ion-selective electrodes on the basis of phosphorylated aza podands we tested using the example of electrodes with a podand **VII**–doped liquid membrane. With this electrode we performed potentiometric titration of rubidium chloride with sodium tetraphenylborate. The titration curve is presented in the figure. In the equivalence point we observe a strong potential jump, which suggest the applicability of the indicator electrodes for potentiometric titration of rubidium salts.

Hence, we have developed a new type of ionophores having the structure of α,ω-aminomethylphosphorylated oligoethers, which can be used as components of ion-selective electrodes. We have also established the feasibility of such electrodes for determination of heavy alkali and alkaline-earth metal cations in low concentrations in the presence of sodium, potassium, and ammonium ions.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were recorded on a Varian Unity NMR spectrometer (300 MHz) and on a custom-made spectrometer with a working frequency of 8 MHz, external references TMS and 85% phosphoric acid. The IR spectra were recorded on a Specord M-80 spectrometer.

The electrode characteristics of ion-selective electrodes were measured after preliminary 24-h exposure of the membranes to standard solutions of cations to be determined. The measurements were performed at constant temperature (20 ± 2°C) under continuous stirring in a temperature-controlled cell.

Potentiometric measurements with ion-selective electrodes as indicator electrodes were carried out on an I-130 pH-meter–millivoltmeter. The reference electrode was an EVL-1M3 silver chloride electrode.

The starting dialkylphosphinous acids were obtained according to the procedure in [15] by reactions of diethyl hydrogen phosphite with the corresponding aryl- or alkylmagnesium halides. Intermediate α-aminophosphine oxide **XII** was synthesized by means of the Kabachnik–Fields reaction. α,ω-Dibutylaminoethers were prepared by alkylation of α,ω-dihaloethers. Reaction progress and product purity were controlled by TLC on Silufol plates (eluents 1:1 acetonitrile–chloroform and 1:4 acetone–chloroform) using reference compounds, developer iodine vapor. For better visualization the plates were treated with water.

Purification of the reaction products was carried out on a column (70 × 5 cm) of Silica gel L100/400 (LaChema), eluent 1:9 methanol–chloroform. The sorbent was preliminary exposed to the eluent for 1 day. The samples was diluted with a little chloroform before application to the column. The average time of elution was about 4 h. The solvents were purified by standard procedures [16].

1,10-Dibutyl-1,10-diaza-4,7-dioxadecane (IV). Dibutylamine, 27 g, was heated to boil, and 15 g of 1,8-dibromo-4,7-dioxaoctane was added dropwise. Addition of each drop was accompanied by heat evolution, and the reaction mixture boiled without heating. After the addition was complete, the reaction mixture was refluxed for 5 h, cooled to room temperature, and washed with a solution of 4.34 g of sodium hydroxide in 15 ml of water. The product and the aqueous layer were extracted with ether (3 × 20 ml), and the combined extracts were dried over sodium sulfate for a day. The solvent and excess butylamine were removed in a vacuum. The crude product was distilled in a vacuum to obtain 6.2 g (32%) of compound **IV** as a colorless liquid, bp 122-125°C (38 Pa), n_D^{20} 1.4513. Found, %: C 64.52; H 12.43. $C_{14}H_{32}N_2O_2$. Calculated, %: C 64.62; H 12.30.

(Aminomethyl)butyldi(*p*-tolyl)phosphine oxide (V). To solution of 2.92 g of *n*-butylamine in 20 ml of benzene, 0.13 g of Paraform was added. The resulting mixture was treated with a solution of 2.3 g of di(*p*-tolyl)phosphinous acid in 15 ml of benzene, refluxed with a Dean–Stark trap for 4 h, and then let to stand for 2 h. The residual solvent, butylamine, and water were removed in a vacuum to give 3.03 g of a viscous light yellow oil. According to TLC (Silufol, elution with 4:1 chloroform-acetone), it was an almost pure compound which can be used in further syntheses. Crystallization from hexane–benzene gave a pure low-melting crystalline product **V**, yield after purification 2.8 g (92%), R_f 0.35 (elution with 4:1 chloroform–acetone). ^{31}P NMR spectrum: δ_P 42 ppm (benzene). Found, %: C 72.5; H 8.11; P 9.4. $C_{19}H_{26}NOP$. Calculated, %: C 72.38; H 8.25; P 9.84.

1,12-Bis(diphenylphosphinoyl)-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane (VI). To a solution of 5.8 g of 1,10-dibutyl-1,10-diaza-4,7-dioxadecane (**XII**) in 30 ml of benzene, 1.34 g of Paraform was added. Cooling of the reaction mixture was observed. After that, 5.31 g of diamylphosphinous acid in 20 ml of benzene was added, and the reaction mixture was refluxed with a Dean–Stark trap for 6.5 h. Over this period, 0.7 ml of water (88%) was collected. The solvent was removed in a vacuum until constant weight. The residual light yellow oil, 11.6 g, was purified by column chromatography. Characteristics of compounds **VI**–**XI** are listed in Table 1.

1,12-Bis[di(*p*-tolyl)phosphinoyl]-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane (VII). *a*. A mixture of 2.76 g of di(p-tolyl)phosphinous acid, 0.36 g of Paraform, and 1.56 of compound **XII** was refluxed in benzene with a Dean-Stark trap for 40 min. Over this period, about 95% of water was collected. After that the mixture was refluxed for an additional 40 min and then evaporated to constant weight. The residual viscous liquid was purified by column chromatography to obtain 3.3 g (74%) of a light yellow viscous liquid.

b. To a solution of 3.05 g of compound **V** in 20 ml of DMF, 1.32 g of 1,8-dibromo-4,7-dioxaoctane was added dropwise with stirring at 50°C in the presence of 0.7 g of potassium carbonate. After the addition was complete, the reaction mixture was heated for 5 h at 70°C (bath temperature). After that it was cooled, washed with water, extracted with chloroform, and dried oved sodium sulfate. Then chloroform was removed, and the residue was subjected to a vacuum until constant weight. The crude product was purified by column chromatography as described above to obtain 2.43 g (68%) of product **VII** whose R_f and spectral characteristics were similar to those of the above sample.

1,12-Bis(dioctylphosphinoyl)-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane (VIII). A mixture of 6.53 g of dioctylphosphinous acid, 0.72 g of Paraform, 3.1 g of compound **XII**, and 30 ml of benzene was refluxed for 4 h with the removal of water. After 0.3 ml (75%) of water evolved, 0.2 g of Paraform was added, and the resulting mixture was refluxed for 2 h. The solvent was removed, and the residue was exposed to a vacuum to constant weight to obtain 9.8 g of a crude light yellow product which was purified by column chromatography under the above-described conditions (eluent 1:1 chloroform–acetonitrile) to give 6.5 g (64%) of a yellow resinous product.

1,12-Bis(didecylphosphinoyl)-2,11-dibutyl-2,11-diaza-5,8-dioxadodecane (IX). A mixture of 3.3 g of didecylphosphinous acid, 0.3 g of Paraform, and 1.3 g of compound **XII** was refluxed for 2 h in benzene with removal of water. After that, the solvent was removed in a vacuum, the residue was dissolved in toluene, *p*-toluenesulfonic acid was added, and the mixture was refluxed for an additional 2 h. A total of 0.2 ml of water (100%) was removed. The mixture was cooled, washed with aqueous potassium bicarbonate and two portions of water, and dried over anhydrous magnesium sulfate. The product was purified by column chromatography to give 3.6 g (76%) of a resinous product (elution with 1 : 1 chloroform–acetonitrile).

1,6-Bis(dioctylphosphinoyl)-2,5-dibutyl-2,5-diazahexane (X). A mixture of 8.22 g of dioctylphosphinous acid, 0.9 g of Paraform, and 2.58 g of *N*,*N*'-dibutylethylenediamine was refluxed in toluene with removal of water for 3 h. Over the reaction period, 0.25 ml of water was collected. The toluene was removed in a vacuum, and the residue was heated for 6 h at 145°C to obtain 11 g (99%) of a crude product. Column chromatography gave 8.1 g of a viscous light yellow liquid.

***N*,*N*'-Bis(didecylphosphinoylmethyl)piperazine (XI)**. A mixture of 7.20 g of didecylphosphinous acid, 0.6 g of Paraform, and 0.86 g of piperazine was refluxed in toluene with removal of water. After water no longer separated, the reaction mixture was refluxed for an additional 1.5 h, and the toluene was then removed in a vacuum. The solid residue was twice crystallized from hexane to give 5.6 g (67%) of a pure product, white downy crystals.

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