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Synthesis of New Liophilic Functionalized Aminomethylphosphine Oxides and Their Acid–Base and Membrane-Transport Properties Toward Acidic Substrates

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Abstract—A large number of new lipophilic mono- and bisphosphinylamines including those possessing additional potential centers of coordination was synthesized on the basis of the Kabachnik–Fields reaction, and acid–base and membrane transport properties of the synthesized compounds toward the mono- and polybasic carboxylic acids were studied. By their basicity all the synthesized aminophosphine oxides were shown to be inferior to their aliphatic amine precursors. Introduction of the second phosphinyl group so strongly decreases the basicity that the determination of pK_a by potentiometric method becomes impossible. Interrelation between the structure of aminophosphinyl carrier and substrate and the efficiency of the membrane transport of acidic substrates are discussd.

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A vital problem of contemporary analytical, coordination and environmental chemistry is the creation of new highly effective extractants for the separation and concentration of the mixtures of substrates of different origin, both natural and technogenic. An acknowledged and promising method of solution of this problem is the application of the membrane technology based on the liquid impregnated membranes. In a large series of investigations [1–13] we have established high efficiency and selectivity of the membrane transfer of different substrates of organic and inorganic nature at the application of functionalized phosphoryl compounds, and first of all aminophosphoryl compounds, the analogs of natural amino acids. Thus, the high efficiency was shown of the membrane transport of the ions of alkaline and alkaline earth metals by phosphorylated azapodands [11], and of the transfer through the liquid membranes by mono- and diphosphorylated amines of mono- and polybasic carboxylic acids [12, 13].

Among the many aminophosphoryl compounds we have investigated the most suitable for the transfer of acids we believe to be the aminophosphine oxides with one or two phosphinyl groups located at different distances from the carrier basic center, the nitrogen atom [13]. Due to the absence of labile ester bonds the aminophosphine oxides are stable in acidic and alkaline media and show a high rate of transfer of monobasic (acetic) and dibasic (glutaric) acids that we have explained by the formation in the source aqueous phase of strong "substrate–carrier" N-complexes with the participation of one or two basic centers of the carrier. As to polybasic hydroxy acids, tartaric and citric, a sharp drop in the transfer flow rate for these substrate is connected obviously with the presence in them of highly hydrophilic hydroxy and carboxy groups not connected with the basic centers of the carrier and capable to form strong hydrogen bonds with water molecules to retain the formed complexes in the source aqueous phase.

For further examination of the relationship between structure of aminophosphine oxide carriers and their membrane-transport properties with respect to acid substrates we perfomed the purposeful synthesis of new aminophosphoryl compounds containing one or two aminomethylphosphinyl groups and possessing an increased lipophilicity due to the introduction of long-chain substituents to the nitrogen and phosphorus atoms. Their formulas and characteristics are given in Table 1. In addition, it seems important to trace the effect of the introduction to their molecules of additional functional groups capable of coordination

Table 1. Aminophosphoryl compounds

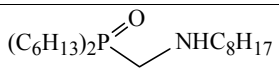
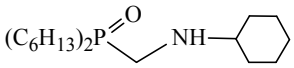
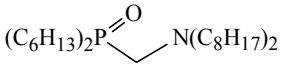
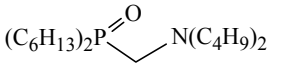
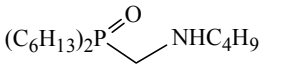
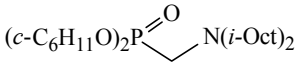
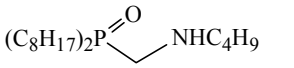
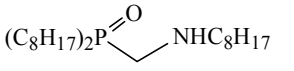
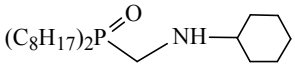
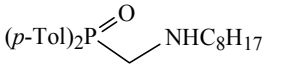
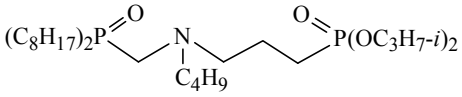
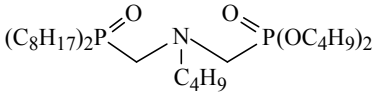
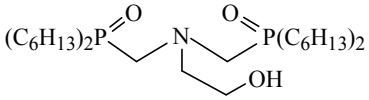
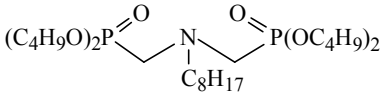
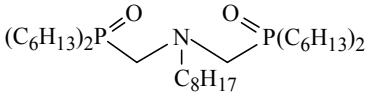
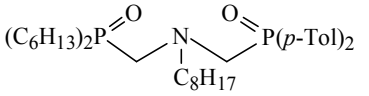
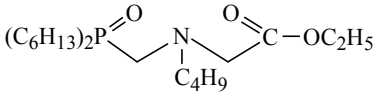
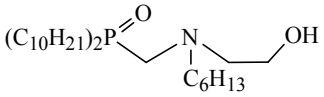
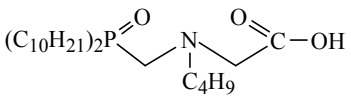
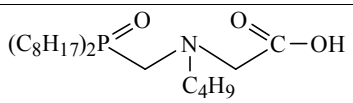
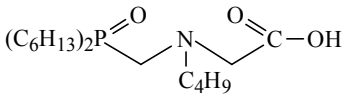
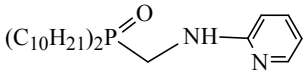
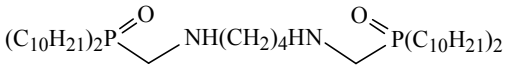
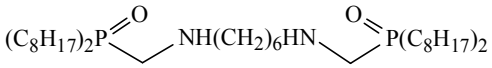
Comp. no.	Formula	mp, °C	n_D^{20} (n_D^f)	δ_P, ppm[a]	R_f[b]
I		28	–	48	0.65
II		[c]	1.4870	45	0.58
III		[c]	1.4652	47	0.66
IV		[c]	1.4648	47	0.53
V		[c]	1.4710	44	0.57
VI		[c]	1.4729	25	0.54
VII		[c]	1.4719	45	0.57
VIII		36	–	48	0.68
IX		[c]	1.4760	43	0.61
X		[c]	1.4749	27	0.4
XI		[c]	1.4650	45, 31	
XII		[c]		43, 26	
XIII		89	–	46	0.15
XIV		[c]	1.4520	25	0.52
XV		[c]	1.4729	44	0.53
XVI		[c]	1.5190	45, 27	0.45
XVII		[c]	1.4652	49	0.46
XVIII		[c]	1.4728	47[d]	0.60
XIX		65	–	53	0.51

Table 1. (Contd.)

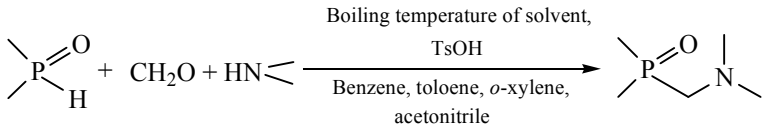
Comp. no.	Formula	mp, °C	n_D^{20} (n_D^t)	δ_P, ppm[a]	R_f[b]
XX		29	–	53	0.46
XXI		[c]		53	0.4
XXII		69		53[e]	
XXIII		80	–	46	0.30
XXIV		82		43	0.15

[a] External reference 85% H_3PO_4, solvent toluene. [b] Most of R_f values of the obtained aminophosphoryl compounds were measured with the eluent chloroform–acetone (3:1), Silufol UV 254. [c] External reference 85% H_3PO_4, solvent acetonitrile. [d] External reference 85% H_3PO_4, solvent chloroform. [e] Undistillable viscous liquid (oil).

with the proton substrates, that, in our opinion, could facilitate or, conversely, hinder the formation of the substrate–carrier complex, which should affect the value of the flow at the transport through the membrane. The revealed regularities could obviously serve as a basis for purposeful introduction into the molecule of the carrier of certain functional groups and thus regulate consciously the efficiency and selectivity of the membrane transport of substrates with a certain structure.

For the synthesis of target substances **I–XXIV** we used the classical one-pot Kabachnik-Fields method emp;oying ternary system of dialkylphosphinous acid–form-aldehyde–amine as well as the multistep methods of synthesis developed by us specifically for this purpose. We carried out a investigation of the reaction conditions (solvent, catalyst, temperature) with respect to the reactivity of reagents and the stability of the target products. Moreover, owing to technological constraints to the use of column chromatography for the highly lipophilic objects we developed an original "oxalate" method for purification of the aminophosphoryl compounds that consists in the treatment of the crude aminophosphine oxide with oxalic acid taken in a small excess, recrystallization of the formed salt, and release of the phosphorylated amine by a weak alkalinization. The purity of the aminophosphoryl compounds thus obtained (control by TLC and NMR ^{31}P) was almost 100%. In addition, we used the method of microwave activation of the Kabachnik–Fields reaction, which reduces the reaction duration from hours to 10–20 minutes.

Synthesis of aminophosphoryl compounds **I, II, V, VII–X** containing a phosphoryl center and aminomethyl group with a secondary nitrogen atom was carried out for 1–4 h using the three-component Kabachnik–Fields reaction with *p*-toluenesulfonic acid as a catalyst, in boiling benzene or toluene as solvents.



The completion of the reaction was monitored by TLC, by the amount of formed water collected in a Dean-Stark trap, and by ^{31}P NMR spectroscopy. The structure of the compounds was proved by NMR (^1H, ^{31}P) and IR spectroscopy, elemental analysis, and mass spectrometry. The IR spectra of aminophosphoryl compounds contain a signal in the region of 1100–1200 cm^{-1} characteristic of P=O group. The completion of the reaction with secondary amines was determined by the disappearance of the NH signal at ~3300 cm^{-1}. In the ^{31}P NMR spectra the completion of the reaction is shown by the appearance of a singlet at

44–49 ppm characteristic of the most aminophosphoryl compounds with phosphine oxide structure [2, 3]. In some cases this signal is accompanied by a signal at ~51 ppm indicating the presence in the reaction mixture of hydroxymethylphosphine oxide, the product of the competitive route along Abramov's reaction. In the spectra of the aminomethylphosphonates and compound **X** with the acceptor *p*-tolyl group at the phosphorus atom the signal of parent product is shifted upfield to 22–30 ppm in agreement with the published data [2].

In the ^{1}H NMR spectra of all obtained aminophosphoryl compounds of this group were observed a typical doublet of the methylene groups P–CH_2 and a triplet of methylene group at the nitrogen atom N–CH_2, or a multiplet of N–CH proton. More detailed identification of signals is not possible because of the presence of multiplets and broad singlets of long-chain hydrocarbon substituents.

The synthesis of aminophosphoryl compounds in the described above conditions in some cases is complicated by the formation of hydroxymethylphosphine oxide. This product of the side reaction is formed in 10–30% yield. The separation of these substances from mixtures by traditional methods of distillation or recrystallization was not always possible, and we used the new method we developed: preparation of the set of aminophosphoryl compound with oxalic acid, recrystallization of the salt, and isolation of the target aminophosphoryl compound by weak alkalinization. This method of purification can be used for oily aminophosphoryl compounds; it replaces effectively the time-consuming method of column chromatography.

The reaction with the participation of secondary amines in nonpolar solvents proceeds less actively than with primary amines since the iminium intermediate formed in the course of the reaction [14] is less stable in the nonpolar solvent than imine, and it is rapidly decomposed into the initial formaldehyde and secondary amine. By the example of dihexyl-*N*,*N*-dibutylaminomethylphosphine oxide **IV** we showed that regardless the duration of stirring the reagents in boiling *o*-xylene the ratio of the side dihexyl-α-hydroxymethylphosphine oxide (δ 51 ppm) and aminophosphine oxide **IV** (δ 47 ppm) reaches, according to the data of ^{31}P NMR spectroscopy, 3:4 and is not changed. However, after removing the solvent in a vacuum and heating the mixture to 210°C the reaction proceeds to the end with formation of amine **IV**, as follows from the data of NMR spectroscopy and elemental analysis. At the same time analogous operation at the synthesis of dihexyl-*N*-octylaminophosphine oxide **I** (heating the reaction mixture without a solvent to 210°C) does not prevent the side reaction giving the hydroxymethylphosphine oxide. Moreover, after prolonged heating the strong tarring of the mixture is observed, and in the NMR spectra appear additional signals indicating formation of oxidation products. The same pattern is observed also in the case of dihexyl-*N*,*N*-dioctylaminomethylphosphine oxide **III**.

We succeeded in preventing the undesirable side reactions of formation and decomposition of hydroxymethylphosphine oxides in the synthesis of aminophosphine oxides with the tertiary nitrogen atom by replacing the nonpolar solvents by the more polar acetonitrile. We suggest that in this case in the reaction with secondary amine the intermediately formed iminium cation is better stabilized. Monitoring the reaction course by tracing isolation of water in the Dean–Stark trap becomes impossible, and the completion of the synthesis was checked by TLC and by NMR spectroscopy. The reaction was carried out at the solvent boiling point in the presence of catalytic amount of *p*-toluenesulfonic acid. In all cases in acetonitrile the reaction proceeded successfully in 2–4 h, the signals of side product hydroxymethylphosphine oxide in the NMR spectra were not registered. For removing the catalyst, into the reaction mixture after the reaction completion was added sodium carbonate at stirring and heating to 50°C. Then the mixture was washed with water, organic fraction was dried over magnesium sulfate, filtered, and then evaporated to dryness. The products were obtained in high yield (85%) in the form of white crystals or light oily substance; in the latter case we used "oxalate" method for the purification of aminophosphoryl compounds.

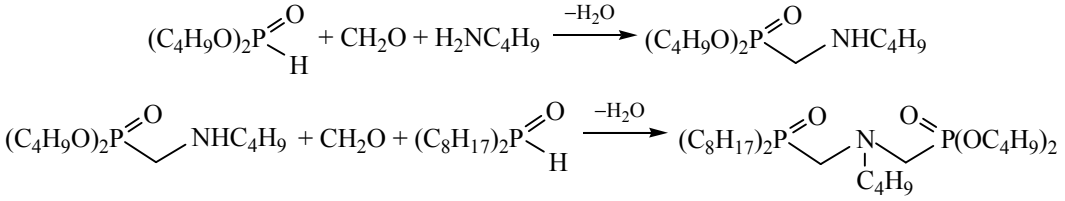
The information that appeared recently in the literature on the microwave activation of the Kabachnik–Fields reaction with the participation of ketones and phosphites [15–17] impelled us to use this method for the preparation of lipophilic aminomethylphosphine oxides by the three-component Kabachnik–Fields reaction with paraform and respective amines using an ordinary cooking microwave furnace at the maximum regime of heating (720 W). In this case we, however, encountered the same complications which were characteristic for the syntheses of aminophosphine oxides in nonpolar solvents described above. Thus, the reaction with the dioctylphosphinous acid, paraform and dibutylamine, according to the data of NMR

spectra, proceeded with the formation of two products: ~20% of hydroxymethylphosphine oxide and ~80% of the desired aminophosphine oxide **IV**. After heating for 30 min the signal of the by-product did not disappear. A similar situation was observed also in the case of didecylphosphinous acid and di-2-ethylhexylamine: the formation of the by-product reached approximately 30%, and the ratio of the target compound and by-product did not change at the prolonged heating (50 min).

These complications do not appear in the reactions of primary amines: the almost quantitative yield of the final aminophosphoryl compounds **II** and **VII** is achieved at heating for ~20 min. Obviously, the Kabachnik–Fields reaction with the participation of secondary amines is controlled by steric factors. While the reaction with dibutylamine in the medium of a nonpolar solvent or without it proceeds readily, in the case of secondary amines with the bulky radicals (octyl, 2-ethylhexyl) the rates of formation of imines and products of their further hydrophosphorylation ("imine" way of Kabachnik–Fields reaction) and of Abramov reaction ("hydroxyphosphine oxide" way) apparently become comparable.

The conditions we found for the three-component Kabachnik–Fields reaction for obtaining monophosphorylated amines we applied to the synthesis of diphosphorylated amines **XII–XVI**. In this case for obtaining symmetrical diphosphinylamines **XIV** and **XV** the appropriate hydrophosphoryl compounds, formaldehyde and primary amine in the ratio 2:2:1 were introduced into the reaction. The most suitable solvents for the synthesis of the phosphonate derivatives **XII** and **XIV** proved to be benzene and toluene; the best results at the synthesis of bis-phosphine oxides **XV** and **XVI** were reached at the use of acetonitrile as the medium.

The synthesis of asymmetrical diphosphinylamines was carried out in two stages. The monoaminophosphoryl compound formed during the first stage was used without purification and isolation in the reaction with paraform and the corresponding hydrophosphoryl compound. This procedure allowed the prevation of the formation of hydroxymethylphosphoryl compound. Thus, by the two-stage version the synthesis was performed of asymmetrical aminophosphoryl compound **XII**: to the preliminarily obtained *N*-[(dibutoxyphosphoryl)methyl]butylamine dissolved in acetonitrile were added phosphinous acid and paraform:

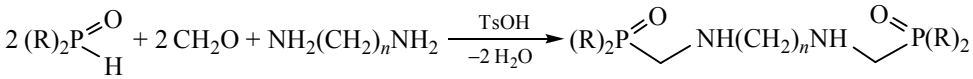


XII

The second stage of reaction, as follows from the data of ^{31}P NMR spectroscopy, proceeds completely. This is confirmed by the presence of two signals: a peak at 48 ppm corresponding to the phosphine oxide phosphorus atom, and a signal at 26 ppm which belongs to phosphorus atom of phosphonate group.

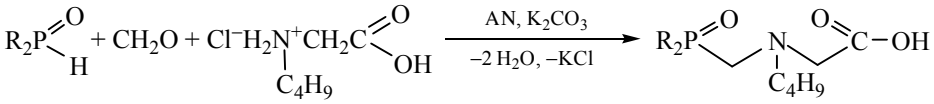
For the synthesis of *N*,*N*'-bisdiaminophosphine oxides **XXIII** and **XXIV** we introduced the respective primary 1,4-and 1,6-diamines into the reaction with phosphinous acids and paraform employing general procedure with toluene as a solvent. According to the data of ^{31}P NMR spectra, the formation of dioctylphosphinyl compound **XXIV** proceeds without any complications: one signal at 47 ppm is observed and the signal of the initial compound is absent.

Compound **XXIII** was analogously prepared when didecylphosphinous acid was used as a hydrophosphoryl component. However, in this case for an increase in the solvent polarity we used 1:2 mixture of DMF with benzene, which allowed not to elevate the reaction temperature and thus to avoid tarring. In the ^{31}P NMR spectrum one signal at 46 ppm was fixed.



R = $C_{10}H_{21}$, n = 4 (**XXIII**); R = C_8H_{17}, n = 6 (**XXIV**).

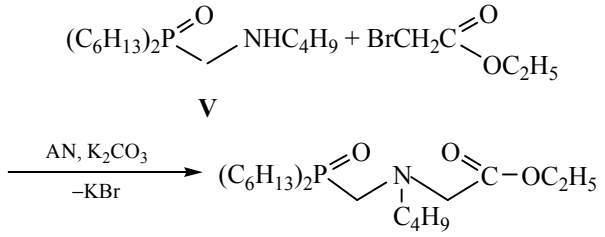
We developed two methods for the synthesis of aminophosphoryl compounds with the aminoacid group. The first was the traditional Kabachnik–Fields reaction: interaction of phosphinous acid with the carbonyl component and the corresponding ammonium chloride derivative of the acid in acetonitrile. Into the reaction mixture 0.45 mol of K_2CO_3 was added for binding the formed hydrochloric acid. The remaining 0.05 mol of hydrochloric acid had to perform the role of a catalyst. The reactions were completed approximately in 2 h. By the data of ^{31}P NMR spectra the yield of the product is close to quantitative, only one peak appeared at –53 ppm of compound **XIX** or **XX**.



XIX, XX

R = $C_{10}H_{21}$ (**XIX**), C_8H_{17} (**XX**).

The second method consists in the "construction" of the aminoacid with the use of aminophosphine oxide as the amino component. This strategy is based on the two-stage process, which makes it possible also to obtain aminophosphine oxides with the ester group.



V

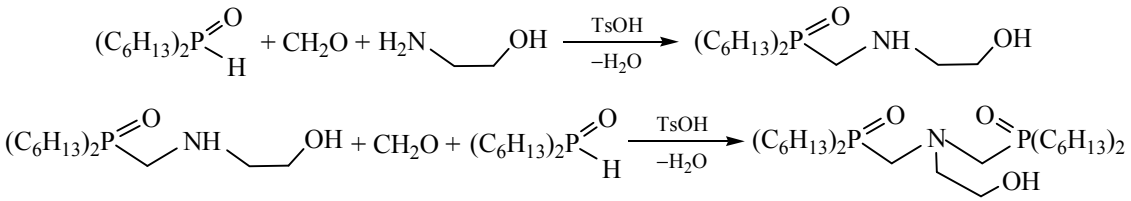
XVII

The aminophosphine oxide **V** obtained by this method undergoes reaction with ethyl bromoacetate in acetonitrile with 1.5 molar excess of K_2CO_3. In the ^{31}P NMR spectrum to the reaction product **XVII**, the phosphorylated ester of aminoacetic acid, corresponds a singlet at 53 ppm, the formation of other phosphorus-containing products was not registered.

The structure of this compound was studied also by GC–MS method. One peak at 2.72 min is present on the chromatogram; splitting of this signal of ion current probably indicates the formation of a sufficiently stable dimer which also is fixed in the mass-spectrum. Furthermore, a peak of the protonated molecule is also seen (474.10), of its dimer (947.19), and of the complex with didecylphosphoryl cation (810).

For the synthesis of promising membrane-transport carriers and extractants containing as the additional potential center of coordination the hydroxy group, we brought aminoalcohols to the Kabachnik–Fields reaction. The reaction with the participation of ethanolamine in the medium of acetonitrile afforded the final product in the form of a viscous liquid, whose salt with oxalic acid was obtained, recrystallized, and transformed into aminophosphoryl compound **XVIII** to which in the ^{31}P NMR spectrum corresponded a singlet at 51 ppm.

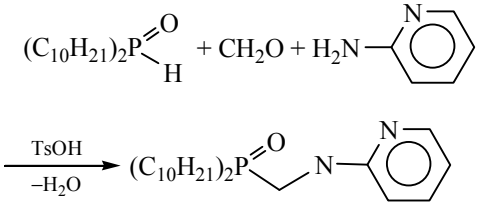
For introduction into this molecule of the second phosphoryl group to obtain diphosphorylated aminoethanol **XIII** we used the two-stage version of the reaction in order to avoid the formation of hydroxymethylphosphine oxide.



XIII

In the first stage for the condensation of dihexylphosphinite with paraform and aminoethanol a 1:2 mixture of DMF with benzene was used as a solvent. Further the solvent was distilled off and the second part of the synthesis, the reaction of dihexyl-*N*-2-hydroxyethylaminomethylphosphine oxide with paraform and dihexylphosphinous acid, was carried out in the medium of acetonitrile. In the ^{31}P NMR spectrum of compound **XIII** recrystallized from hexane a singlet is present at 46 ppm.

We believe that the promising pathway for the creation of the polyfunctional carriers of acids consists in the introduction into the molecule of an aminophosphoryl compound, together with the aminomethyl group, of other organonitrogen basic function, for example, pyridine ring. We undertook an attempt of the synthesis of aminophosphine oxides on the basis of α-aminopyridine in *o*-xylene at heating during five days. However, reaction did not proceed to the end, the formation of by-products was observed, and it was impossible to isolate the final product even by the "oxalate" purification. Under the milder conditions, at the use of acetonitrile and dioxane as solvents, according to the ^{31}P NMR spectra the reaction proceeded completely enough, although not to the end (in the acetonitrile approximately up to 10% of phosphinous acid was present, in dioxane, about 5%); in this case the formation of by-products, first of all, of hydroxyphosphine oxide, was not observed. After removal of the solvent on the rotary evaporator the residue was dissolved in benzene and washed initially with aqueous alkali and then with water. According to the data of TLC and ^{31}P NMR spectroscopy (singlet at 30.8 ppm) the product did not contain foreign matter. The yield of pure didecyl-β-(2-pyridyl)aminophosphine oxide **XXII** was about 70%.



XXII

The method of the synthesis of the first representative of γ-aminophosphoryl compounds, the diphosphorylated amine **XI,** we described earlier [13].

The compounds of phosphine oxide and phosphonate structure (Table 1) we synthesized form a basis for studying their extraction and membrane transport properties toward diverse substrates. We assumed that introduction of additional functional groups capable to form both N-complexes with acidic substrate and complexes with metal ions would give a possibility to reveal the interrelation between their structure and practically useful properties including the studied membrane transport, extraction and, later, ionofor properties, etc. This, in turn, would open a way to the selection of complementary pairs substrate–carrier and thus would allow to optimize the processes of the membrane and liquid extraction of the objects of different nature.

The protolytic equilibria with the participation of aminophosphoryl compound occur in all the processes at their practical appliction (membrane transport, extraction, and complex formation). Therefore we determined the ionization constants (pK_a) of the conjugate acids of the aminophosphine oxides obtained by us.

Earlier [2, 18] we determined the ionization constants of a wide range of α-aminophosphonates in water and in the water–2-propanol media with the water content 50 and 25 vol %, and revealed linear correlations between the values of pK_a determined in the media with different content of water. For the comparability of these results we also have determined the ionization constants of a series of newly synthesized aminophosphoryl compounds in the medium of aqueous 2-propanol containing 50 vol % of water to ensure a sufficiently high solubility of the compounds investigated. The values of pK_a of lipophilic α-aminophosphine oxides and a number of the functionalized derivatives are given in [19].

For the estimation of the effect of introduction of phosphinyl groups to the amine molecule we determined also the ionization constants of aliphatic and aromatic amines of different structure, mainly the amine precursors of the corresponding aminophosphoryl compound. The values of their pK_a differ little from each other and vary in the range of 8–10 units. The analysis of the influence of the aminophosphoryl compound structure on its basicity in the investigated series allows to derive a number of the most general regularities connecting the structure and the basicity of the studied lipophilic aminophosphoryl compounds. First of all, it should be noted that like α-aminophosphonates [2], the α-aminophosphine oxides are considerably inferior by the basicity to their precursors, the non-posphorylated amines: the pK_a values of amines and the corresponding aminophosphine

Table 2. Difference in basicity of aminophopshine oxides and parent amines

Amine	Aminophosphine oxide	ΔpK_a
$C_4H_9NH_2$	**V**	9.74 − 5.70 = 4.04
$C_8H_{17}NH_2$	**I**	9.49 − 5.51 = 3.98
o-$C_6H_{11}NH_2$	**IX**	9.68 − 5.65 = 4.13
$(C_4H_9)_2NH$	**IV**	9.60 − 4.47 = 5.13
$HOCH_2CH_2(C_6H_{13})NH_2$	**XVIII**	8.87 − 3.90 = 4.97

oxides differ approximately by 4 units in the case of primary amines and by 5 units for the secondary amines. This change in the basicity of amines as a result of their phosphorylation is completely undestandable if we consider the significant electron-acceptor effect of the phosphoryl group. For the illustration of the aforesaid in Table 2 are compared the values of pK_a of aminophosphine oxides and the respective amine precursors.

We determined for the first time the ionization constants of *N,N'*-bis-phosphorylated 1,6-diaminohexane **XXIV**. In this case the influence on the basicity of the introduction of phosphinyl groups is clearly seen: the change in pK_a at the both stages of dissociation occurs in the same range as in the case of monobasic amines. Thus, to 1,6-hexamethylenediamine correspond the values of pK_{a1} = 10.06 and pK_{a2} = 9.08; for its 1,6-bis(dioctylaminomethylphosphinyl) derivative are obtained the values of pK_{a1} = 5.90 and pK_{a2} = 5.42, i.e., the difference in the acidity ΔpK_a for two stages is respectively 4.16 and 3.66 pK_a units.

It is noteworthy that we failed to determine the precise values of the pK_a of bis-phosphorylated amines **XIV–XVI**. Under the conditions of titration selected by us the necessary portion of the protonated form of these compounds was not reached. However, this fact is completely understandable: if we proceed from the assumption that the introduction of the second methylenephosphoryl group contributes the same as the mono-phosphorylation, then the pK_a of bis-phosphorylated amines must have values less than 1.7.

The fact of the low basicity of bis-phosphorylated amines is very remarkable. We suggest that lipophilic bisphosphorylated amines are of undoubted interest as new extraction reagents, since a weak affinity to proton must lead to an essential difference in the behavior of these reagents at the extraction of metals from the acidic media as compared to the widely utilized at present aliphatic amines or the neutral organophosphorus reagents. Thus, a new possibility appears of creating on their basis reagents with the specific properties like enhanced selectivity.

Earlier we established that α- and β-aminophosphoryl compounds could be used as selective extractants of the ions of noble metals [3–5] and as ionophores in the ion-selective electrodes [1]. Also, they are of undoubted interest as carriers in the processes of the membrane extraction of organic and inorganic substrates [6, 20]. A study of the influence of structure of the functionalized phosphoryl carriers on the efficiency of the membrane transport of proton-donor substrates [21] and of interphase ion transfer of metals [5, 6] made it possible to establish the influence of "additional" donor functional groups on the ability of phosphoryl extractants to complexation. A similar comparison for mono- and diphosphorylated phosphine oxides and phosphonates as the membrane carriers of proton-donor substrates has not been performed so far.

The aminophosphoryl carriers synthesized by us we investigated in the processes of the membrane extraction of organic acids of the moderate strength differing by the number of functional groups: acetic, glutaric, tartaric and citric. The sequential growth of the number of hydrophilic carboxy and hydroxy groups in them should have strongly affected their ability "to utilize" certain basic centers of carriers, and also to form the H-bond complexes of different strength with the molecules of water in the source phase.

The purposeful selection of the aminophosphoryl carriers by structure we accomplished taking into account that, as had been established earlier [21], among the functionalized phosphoryl compounds which contain hydroxy, alkoxy and amino groups located in different position with respect to phosphorus atom, the most effective membrane transfer of acids was observed just in the case of amino derivatives: the flow value of the transfer by aminophosphonates considerably exceeded that of oxygen analogs. Obviously the hydrogen binding of the transferred substrate acid by nitrogen centers is much stronger than by oxygen centers. Introduction into the molecule of the carrier of the second phosphoryl group to the α-position (compounds **XII–XVI**) or the γ-position (compound **XI**) with respect to nitrogen atom not only

changes (decreases) the electron density on the latter [6], but also creates obvious steric hindrances for the com-plexation, especially for the large molecules of polybasic acids. Thus, we were able to estimate the efficiency and the selectivity of membrane extraction and the concentration of acid substrate taking complementary pairs substrate–aminophosphoryl carrier.

As the membrane solvent we selected low polar phenylcyclohexane, which excludes the possibility of the specific solvation both of carriers and of the complexes formed in the membrane phase.

We repeatedly have indicated [8, 21] that in the processes of the membrane transfer through the liquid impregnated membranes the simple dependences between the structure and the transport properties of carriers usually cannot be found, since the efficiency of the transfer depends both on the carrier binding with the substrate and on the ease of the reextraction into the receiving phase. Furthermore, in the case of polyfunctional complexones of the type of the aminophosphoryl compounds under study, into the binding with the transferred substrate can be involved at once not all centers of coordination, for example, by steric reasons. It is important also that the rate of transfer is connected also with the the characteristics of the medium viscosity of all phases that also cannot be completely estimated.

At the same time, analysis of the results of determining the flow values of transfer of organic acids by different aminophosphoryl compounds through the liquid membranes listed in Table 3 makes it possible to reveal some trends in the interrelation between the structure of the partners interacting at the complex formation and the efficiency of the transfer. This interrelation is manifested distinctly at the analysis of the transfer of monobasic acetic acid. The comparison of flow values for phosphorylamines **I–X** confirms the fact we have noted earlier [21] that the center of the carrier protonation is the nitrogen atom, while the phosphoryl oxygen atom is not involved into the binding the substrate or little affects the transfer efficiency. The phosphoryl carriers not containing nitrogen atoms sharply increase their efficiency at the transfer of monobasic acids upon the replacement of electron-acceptor alkoxy substituents at phosphorus by the donor alkyl groups. In this case the comparison of the flow values of the transfer in the series of phosphine oxides and phosphonate **VI** shows that the replacement of donor alkyl groups in phosphine oxide amines by the acceptor cyclohexyloxy substituents at the phosphoryl center does not decrease, but on the contrary, increases the flow intensity. Undouptedly, together with the basicity of amino center, an important role in the case of phosphonate **VI** belongs to the high lipophilicity of the carrier caused by the presence of two isooctyl groups at the nitrogen atom.

Table 3. Values of flows (P) at the membrane transport of acetic, glutaric, citric and tartaric acids. Concentration of carrier in the membrane phase 0.1 M, concentration of substrate in source phase 0.2 M. Error of measuring P ± 10%

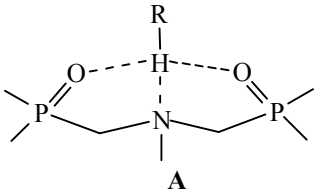
Comp. no.	$P\times10^6$, mol m^{-2} min^{-1}			
	Acetic	Glutaric	Citric	Tartaric
I	170	79	19	0.06
IV	100	2.0	–	–
V	73	3.0	4.0	–
VI	200	0.3	13	0.06
VIII	190	260	95	2.0
IX	170	6.0	–	0.6
X	79	0.3	–	1.0
XI	420	330	23	11
XII	610	250	60	35
XIII	410	100	62	34
XIV	240	15	2.0	1.0
XV	460	240	30	18
XVI	500	280	25	15
XVII	500	140	4.0	3.0
XVIII	710	450	38	11
XIX	150	29	2.0	2.0
XX	78	14	1.0	1.0
XXI	110	10	1.5	–
XXII	270	150	34	12
XXIII	300	6.0	–	–
XXIV	390	100	74	34

The transport properties of two aminophosphine oxides **I** and **VIII**, phosphonate **VI**, diphosphine oxide **XV** and phosphorylated γ-phosphonate **XI** we already described in [13]. For the completeness of consideration we use some data from that publication that which in essence well agree with newly obtained data for aminophosphoryl compounds lacking additional centers of coordination. The majority of monophos-

phorylated aminophosphine oxides **I**, **IV**, **VII**, and **IX** possesses a moderate efficiency of the acetic acid transfer, in the range of 100–200 P, and in these cases, obviously, the solvate mechanism operates which assumes the formation of the aminoacid *N*-complexes. Falling out from this series of phosphine oxides of compound **X** is due undoubtedly to the presence at the phosphorus atom of two acceptor tolyl groups. As to the low transport properties of secondary amine **V**, this fact most likely is connected with the insufficient lipophilicity of the carrier. Previously we showed [1, 5] that the acceptable interphase distribution was achieved at the presence in the molecule of aminophosphoryl compound no less than 20 carbon atoms.

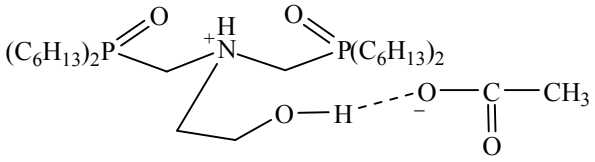
The sharp increase in the flow value of the acetic acid transfer in the case of diphosphorylated amines **XII–XVII** is natural to connect with "involvemnt" into the complex formation with acetic acid also of other centers of basicity: one or two phosphoryl oxygen atoms. We initially expressed it as assumption [13], but now it is confirmed by the experimental data obtained in this study: diphosphine oxides **XV** and **XVI**, phosphonatephosphine oxide **XIV,** and, especially, "mixed" diphosphorylamine **XII** demonstrate high transport efficiency with respect to acetic acid. In this case the high result obtained with the latter compound, as we assume, is caused by the optimum combination of the basic properties of the carrier with its hydrophilic–lipophilic balance.

With respect to α,α-diphosphorylamines **XII, XIV–XVI** it would be possible to use the model of the tricentric hydrogen binding of hydrogen atom with nitrogen and two oxygen atoms of phosphoryl groups (complex **A**). However, this assumption requires serious experimental testing, for example, at the level of X-ray diffraction analysis on the specially synthesized models that we intend to make in future.



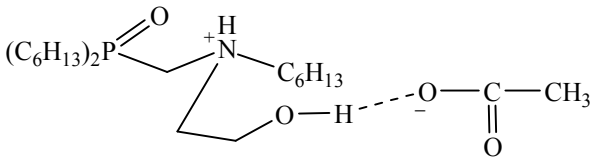
A

Noteworthy is a sufficiently high transport activity of diphosphine oxide **XIII** containing hydroxyethyl group at the nitrogen atom. It is expectable owing to the increased hydrophilic nature of this reagent that leads to its retention in the source phase or, at least, hampers its complexing with the proton-donor substrate. However, this carrier displays high activity not only with respect to acetic acid, but also toward other selected substrates. The possible reason for this phenomenon can be the ability of hydroxyl to bind into complex **B** the acetate anion "liberated" after the protonation of nitrogen.



B

In this connection a special interest presentes an example of the phosphorylated aminoalcohol **XVIII**, which demonstrates exclusively high transport activity. On the basis of the above suggested model of participation of a hydroxy group in "additional" binding of the transferred acid substrate (acetic acid), the structure appearing in this case can be represented in the form H-bound complex **C**.



C

Thus, the presence of "additional" hydrophilic function in the carrier capable of forming with the molecule of substrate one or more additional hydrogen bonds is favorable for the process of the membrane transport of proton-donor substrate.

We attempted to verify this assumption by the example of the phosphorylated amino acids **XIX–XXI**. It turned out that in this case the flow values at the transfer of acetic acid are quite moderate and are comparable with those of α-aminophosphine oxides **I, IV, V,** and **IX**. It seems that the additional proton-donor carboxylic groups do not participate in the process of binding the substrate. This is possible only in two cases. First, the acidic groups are not dissociated under the conditions of the interphase transfer, and the center of binding is the tertiary nitrogen atom, a highly improbable version. Second, phosphine oxides **XIX–XXI** like any amino acids are zwitter-ions due to "internal" protonation of nitrogen by the carboxyl group. In this case the carboxylate anion and/or phosphoryl group should behave as the

center of coordination with the acid substrate. As we have established earlier [21], these functional groups are less effective in the processes of the membrane transport of acids than the amino centers of carriers. It is very significant that the ester **XVII** incapable of various prototropic processes shows high membrane transport activity with respect to acetic acid as compared with the activity of diphosphine oxides **XV** and **XVI**.

Diphosphorylated diamines **XXIII** and **XXIV** exceed in the effeiciency of the transfer of acetic acid their "monoamine" analogs. Possibly in these cases each amino group operates as an independent center of coordination, and the highest activity of 1,6-diaminohexene derivative **XXIV** is connected with the comparatively favorable steric conditions for the formation of N-complexes with all nitrogen atoms, which are sufficiently "distant" from each other.

The interrelation "structure–efficiency of transfer" seems more ambiguous in the case of dicarboxylic glutaric acid. Although in this case the tendency is observed of an increase in the transfer by the diphosphoryl carriers, however it is not so clearly expressed as for the monobasic acid substrate. The high index for phosphine oxide **VIII** can be understood as the participation of both carboxy groups of acid in the protonation of two basic centers of the phosphorylated amine, as the relative steric accessibility of the second atom of nitrogen, and as the suitable hydrophilic–lipophilic balance. Approximately the same factors can determine a comparatively high rate of transfer of this dicarboxylic acid by diphosphorylated amines **XI, XII, XV,** and **XVI**.

A possibility of both basic centers of α-aminophosphonates to bind hydrogen simultaneously was previously shown in the study of the membrane transport of α-hydroxy acids [22–23]. The X-ray structure of the complex reveals the protonation of amino center by the carboxy group while the phosphoryl oxygen atom is connected by a hydrogen bond with the hydroxyl proton of the transferred acid. It is interesting that the hydroxy proton of substrate is connected also with one of the atoms of acylate anion, thus forming a tricentric hydrogen bond; we noted above a possibility of existence of the latter.

In the formation of complexes by diphosphorylated amines with the acid substrate an important role, besides the basicity of the centers of protonation, obviously plays the steric effect. In this sense the essential difference in the efficiency of the transfer is obvious: sterically completely hindered α,α-diphosphinylamines **XV** and **XVI** due obviously to screening of the nitrogen center are less accessible for the bulky glutaric acid than α,γ-analog **XI**. The reason for the low performance at the transfer of glutaric acid by phosphine oxides **II** and **III** and especially by phosphonate **VI** can be the unfavorable hydrophilic–lipophilic balance of the carrier (previously such difference at the change in the length of hydrocarbon groups at the phosphorus atom has been observed at the study of membrane transport with the participation of phosphorylated azapodands [3]). Another possible cause of the observed phenomenon is the presence of the second hydrophilic carboxy group not connected with the carrier, which retains substrate in the source phase because of the strong hydrogen bonds with the medium. However, the absence of transfer via the formation of complex with phosphonate **VI** can be due to the specific properties of the complex, for example, to poor solubility in the membrane organic phase. The anomalously high index of transfer characteristic of phosphorylated ethanolamine **XVIII** appeared also in the case of glutaric acid. The most plausible explanation is the formation of a complex of the same type as that formed by acetic acid, while the "extra" carboxylic group is connected by hydrogen bond with the phosphoryl oxygen. However, this hypothesis needs experimental confirmation.

The relatively low flow values of the transfer of glutaric acid by diaminodiphosphine oxides **XXIII** and **XXIV** can be understood only by eclipsing of nitrogen atoms by the large dialkylphosphinyl groups, which hamper the complexing with the large molecule of dicarboxylic acid. At the same time quite accessible nitrogen atom of pyridine fragment in phosphine oxide **XXII** makes this carrier completely suitable for the transport of dibasic acids.

The effect of "additional" hydrophilic group which we had observed earlier for the transfer of dicarboxylic acids and hydroxy acids by the functionalized phosphoryl carriers [21] was fully found also in this study. The low flow values of transfer of di- and tricarboxylic hydroxy acids, tartaric and citric, obviously is connected just with the high hydrophilic nature of the *N*-complexes of phosphorylated amines with these substrate: the number of basic centers is insufficient for binding all proton-donor functional groups of these substrates. The free extra hydroxy and carboxylic groups enter into the hydrogen bonding with the molecules of water and therefore are retained in the source phase.

Thus, the results of this work show that the performance of the membrane transport of the substrate of different nature is provided only at the complementary cooperation of carrier with the transferred substance. Thus, at the ion transfer of metals by phosphorylated azapodands [11] or at the use of aminophosphoryl compounds in the ion-selective electrodes [9] an important role belongs to the correspondence of the size of ion and potential pseudocavity formed by the podand. In the processes of the membrane transport of acidic substrate the accounting is important for the acid–base interactions of proton donor with the potential electron-donor centers of the complex-forming agent, and for the presence or absence of "additional" hydrophilic groups in the substrate and the carrier. Obviously, the speciic feature of hydrophilic-lipophilic balance both in the carrier and in the complex formed by it should be taken into consideration, although the exact estimation of this factor is difficult. This fully corresponds also to the estimation of the steric factors, essential at the formation of the complexes transferred into the membrane phase. Nevertheless, the laws governing the change in the transport properties of carriers in the dependence on their structure and nature of the transferred substrate that we revealed make it possible to a certain approximation to optimize the processes of membrane transport by the selection of complementary substrate–carrier pairs.

EXPERIMENTAL

The ^{31}P NMR spectra were registered on a Varian Unity instrument with the operating frequency 300 MHz (external reference 85% phosphoric acid) in the solution of deuterochloroform; the ^{1}H NMR spectra were taken on Varian Unity instruments with operating frequencies 300 and 400 MHz (internal reference TMS) from the condensed phase or solution in benzene. The IR spectra were registered on a Specord-M80 spectrometer.

The completion of the reactions was monitored by the volume of isolated water in Dean–Stark trap as compared with the calculated volume of water (in the case of nonpolar solvent) and by the method of thin-layer chromatography with references on silica gel (Silufol). The mobile phase is a mixture of chloroform and acetone (3: 1); development by treatment with iodine vapor and then by distilled water.

For the syntheses were used the solvents of the "analytically pure" and "chemically pure" grade which when necessary were purified additionally employing known procedures. Primary and secondary amines produced by Acros Organics were used. Toluenesulfonic acid is of "chemically pure" grade. Other substances if necessary were synthesized from the commercially accessible reagents employing standard procedures.

At the potentiometric titration of aminophosphoryl compounds were used ES-1060 glass electrode, ESr-1010 silver chloride electrode filled with 3 M solution of KCl, universal ionomer I-160MI, and a thermostat U15 MLW. For the preparation of solutions was used 2-propanol of "chemically pure" grade, potassium chloride of "extra pure" grade, and bidistilled water. Processing of analytical data was accomplished on the computer using original software on the base of VisualBasic compiler.

The research of membrane transport properties of aminophosphoryl compounds was carried out on the installation we described in [24]. As a hydrophobic matrix for the impregnated membranes were used the porous filters "Vladipor" MFFK-4, with the size of pores 0.6 μm that were Teflon matrix on the polyester support. The acid–base titration was performed with the use of a 10 ml burette, a change in pH was fixed by a laboratory ionomer I-30 measuring the potential of glass electrode relative to the silver chloride reference electrode.

General procedure of the synthesis of aminomethylphosphoryl compounds in three-component system of hydrophosphoryl compound, formaldehyde, and amine. In a round-bottom three-neck 100 ml flask equipped with a mechanic stirrer, a Dean–Stark trap, and a reflux condenser were mixed 50 mmol of phosphoryl compound, 52.5 mmol of paraform, 52.5 mmol of amine, 35 ml of anhydrous nonpolar high-boiling solvent (benzene, toluene, o-xylene), and 100 mg of *p*-toluenesulfonic acid. The obtained mixture was refluxed with stirring till complete liberation of water into the trap. The course of reaction was monitored by measuring the volume of water in the Dean–Stark trap, by the method of TLC, and also by ^{31}P NMR spectra of the sampes. At the end of the reaction into the solution ~500 mg of K_2CO_3 was added, and the mixture was refluxed for 10 min for the removal of catalyst. The mixture was then cooled, washed with water (3×5 ml), and dried over anhydrous $MgSO_4$. The filtrate was evaporated in a vacuum on the rotary evaporator. The obtained

substances were oily or crystalline compounds; the yields of aminophosphoryl compounds are 60–95%.

Oily residue was treated with a calculated amount of oxalic acid in diethyl ether. The separated white crystalline precipitate was recrystallized from acetone, treated with aqueous solution of alkali to neutral reaction, and the target aminophosphoryl compound was extracted with toluene, the extract was dried over anhydrous magnesium sulfate, then the solvent was removed in a vacuum. The methods of synthesis and the characteristic of compounds **I, VI, VII, XI** and **XV** were described earlier [13].

Dihexyl-*N*-cyclohexylaminomethylphosphine oxide (II). n_D^{20} = 1.4870, yield 98%, R_f 0.58. Found, %: N 4.73, P 8.59 $C_{19}H_{40}N_2OP$. Calculated, %: N 4.28, P 9.46; ^{31}P NMR spectrum: 45 ppm. ^{1}H NMR spectrum, ppm: 2.84 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.33 br.s (CH), 1.78–0.83 m [$(CH_3)_2$, $(CH_2)_{15}$, NH].

Dihexyl-*N*,*N*-dioctylaminomethylphosphine oxide (III). n_D^{20} = 1.4652, yield 80%, R_f 0.51. IR spectrum, ν, cm^{-1}: 1158 (P=O); ^{31}P NMR spectrum: 47 ppm.

Dihexyl-*N*,*N*-dibutylaminomethylphosphine oxide (IV). n_D^{20} = 1.4648, yield 85%, R_f 0.53 .Found, %: N 4.46. $C_2{}^1H_{46}NOP$. Calculated, %: N 3.90; IR spectrum, ν, cm^{-1} : 1161 (P=O). ^{31}P NMR spectrum: 47 ppm. ^{1}H NMR spectrum, ppm: 2.69 d (CH_2, $^2J_{P–H}$ = 7.2 Hz), 2.49 t [$(CH_2)_2$, $^3J_{C–H}$ = 6.6 Hz], 1.67–0.87 m [$(CH_3)_4$, $(CH_2)_{14}$].

Dihexyl-*N*-butylaminomethylphosphine oxide (V). n_D^{20} = 1.4710, yield 81%, R_f 0.57. Found, %: N 4.62 $C_{17}H_{38}NOP$. Calculated, %: N, 4.62. IR spectrum, ν, cm^{-1}: 1144 (P=O). ^{31}P NMR spectrum: 44 ppm. ^{1}H NMR spectrum ppm: 2.85 d (CH_2, $^2J_{P–H}$ = 8.7 Hz), 2.62 t (CH_2, $^3J_{C–H}$ = 5.7 Hz), 1.67–0.81 m [$(CH_3)_3$, $(CH_2)_{12}$, NH].

Dioctyl-*N*-butylaminomethylphosphine oxide (VII). n_D^{20} = 1.4719, yield 98%, R_f 0.57. Found, %: N 4.40 $C_{21}H_{46}NOP$. Calculated, %: N 3.92; ^{31}P NMR spectrum: 45 ppm; ^{1}H NMR spectrum, ppm: 2.86 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.63 t (CH_2, $^3J_{C–H}$ = 7.5 Hz), 1.7–0.89 m [$(CH_3)_3$, $(CH_2)_{17}$, NH].

Dioctyl-*N*-cyclohexylaminomethylphosphine oxide (IX). n_D^{20} = 1.4760, yield 82%, R_f 0.61. Found, %: N 3.48, P 7.67. $C_{23}H_{48}NOP$. Calculated, %: N 3.63; P, 8.03. IR spectrum, ν, cm^{-1}: 1147 (P=O); ^{31}P NMR spectrum: 43 ppm. ^{1}H NMR spectrum ppm: 2.84 d [(CH_2) $^2J_{P–H}$ = 8.1 Hz], 1.78–0.80 m [$(CH_3)_2$, $(CH_2)_{19}$, NH, CH].

Oxalic derivative of phosphine oxide IX. mp = 145°C, yield 90%. Found, %: C 63.42, N 2.99, H 11.45. $C_{25}H_{50}NO_5P$. Calculated, %: C 63.13, N 2.94, H 10.60.

Di-*p*-tolyl-*N*-octylaminomethylphosphine oxide (X). n_D^{20} = 1.4749, yield 80%, R_f 0.4. Found, %: N 3.72, P 7.94. $C_{23}H_{34}NOP$. Calculated, %: N, 3.77; P, 8.34.; IR spectrum, ν, cm^{-1}: 1121 (P=O); ^{31}P NMR spectrum: 27 ppm. ^{1}H NMR spectrum, ppm: 7.60 m $(CH)_4$, 7.25 m $(CH)_4$, 3.46 d (CH_2, $^2J_{P–H}$ = 7.2 Hz), 3.02 t (CH_2, $^3J_{C–H}$ = 6.9 Hz), 1.46 br.s (CH_3), 1.25 m $(CH_2)_6$, 0.94 m $(CH_3)_2$.

Oxalic derivative of phosphine oxide X. mp = 153°C, yield 86%. Found, %: C 65.04, N 3.11, H 7.82 $C_{25}H_{36}NO_5P$. Calculated, %: C 65.06, N 3.03, H 7.86.

***N*-[(Dibutoxyphosphoryl)methyl]-*N*-[(dioctylphosphinyl)methyl]butylamine (XII).** Yield 60%. ^{31}P NMR spectrum: (C_6H_6, 300 Hz); δ, ppm: 43; 26.

Dihexyl-*N*-2-hydroxyethyl-*N*-(dihexylphosphinylmethyl)phosphine oxide (XIII). mp = 89°C, yield 45%, R_f 0.15. Found, %: N 2.61, H 12.17, C 62.86. $C_{28}H_{61}NO_3P_2{\cdot}H_2O$. Calculated, %: N 2.60, H 11.86, C 62.31. IR spectrum, ν, cm^{-1}: 1145 (P=O), 3240 (OH); ^{31}P NMR spectrum: 46 ppm. ^{1}H NMR spectrum, ppm: 3.09 d [$(CH_2)_2$, $^2J_{P–H}$ = 4.8 Hz], 3.01 t (CH_2, $^3J_{C–H}$ = 4.8 Hz), 3.66 t (CH_2, $^3J_{C–H}$ = 4.8 Hz), 2.67 br.s (OH), 1.8–1.1 m [$(CH_3)_4$, $(CH_2)_{20}$].

Dibutyl *N*-octyl-*N*-(dibutyloxyphosphinylmethyl) phosphonate (XIV). n_D^{20} = 1.4520, yield 90%, R_f 0.52. Found, %: N 2.78. $C_{26}H_{57}NO_6P_2$. Calculated, %: N 2.59. IR spectrum, ν, cm^{-1}: 1027 (P=O); ^{31}P NMR spectrum: (C_6H_6, 300 Hz); 25 ppm.

Dihexyl-*N*-octyl-*N*-(di-*p*-tolylphosphinylmethyl) phosphine oxide (XVI). n_D^{20} = 1.5190, yield 70%, R_f 0.55. Found, %: N 2.91. $C_{36}H_{61}NO_2P_2$. Calculated, %: N 2.33. IR spectrum, ν, cm^{-1}: 1121 (P=O), 1179 (P=O). ^{31}P NMR spectrum: 45, 27 ppm. ^{1}H NMR spectrum, ppm: 7.74 m $(CH)_4$, 7.38 m $(CH)_4$, 3.59 d (CH_2, $^2J_{P–H}$ = 5.4 Hz), 3.05 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.92 t (CH_2, $^3J_{C–H}$ = 4.2 Hz), 2.38–0.93 m [$(CH_3)_5$,$(CH_2)_{16}$].

Dihexyl-*N*-butyl-*N*-ethoxycarbonylaminomethylphosphine oxide (XVII). n_D^{20} = 1.4652, yield 95%, R_f 0.4. Found, %: N 3.71, P 7.27. $C_{21}H_{44}NO_3P$. Calculated, %: N 3.60, P 7.95. IR spectrum, ν, cm^{-1}: 1156 (P=O). ^{31}P NMR spectrum: 49 ppm. ^{1}H NMR spectrum ($CDCl_3$, 300 Hz); ppm: 4.11 q (CH_2 $^3J_{C–H}$ = 6 Hz), 3.39 s (CH_2), 2.99 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.68 t (CH_2, $^3J_{C–H}$ = 6 Hz), 1.69–0.85 m [$(CH_3)_4$, $(CH_2)_{12}$].

Didecyl-*N*-hexyl-*N*-(2-hydroxyethyl)aminomethylphosphine oxide (XVIII). n_D^{20} = 1.4728, yield 77%, R_f 0.66. Found, %: N 3.71, P 7.27 $C_{21}H_{44}NO_3P$. Calculated, %: N 3.60, P 7.95. IR spectrum, ν, cm^{-1}: 1138 (P=O), 3300 (OH). ^{31}P NMR spectrum: (C_6H_6, 300 Hz); 47 ppm. ^1H NMR spectrum ($CDCl_3$, 300 Hz); ppm: 3.61 t (CH_2, $^3J_{C–H}$ = 4.8 Hz), 2.21 d (CH_2, $^2J_{P–H}$ = 4.2 Hz), 2.73 t (CH_2, $^3J_{C–H}$ = 4.8 Hz), 2.58 t (CH_2, $^3J_{C–H}$ = 7.2 Hz), 1.1–0.8 m [$(CH_3)_3$, $(CH_2)_{23}$].

Didecyl-*N*-butyl-*N*-carboxymethylaminomethylphosphine oxide (XIX). mp = 50°C, yield 90%, R_f 0.47. Found, %: %: N 3.79, P 7.73, C 62.44, H 11.80. $C_{19}H_{40}NO_3P$. Calculated, %: N 3.87, P 8.57, C 63.13, H 11.15. ^{31}P NMR spectrum: 53 ppm. ^1H NMR spectrum, ppm: 3.51 s (CH_2), 3.06 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.73 t (CH_2, $^3J_{C–H}$ = 6 Hz), 1.75–0.85 m [$(CH_3)_3$, $(CH_2)_{11}$].

Oxalic derivative of phosphine oxide XIX. mp = 50°C, yield 90%, R_f 0.66. Found, %: C 63.78, N 2.48, H 11.43. $C_3{}^1H_{64}NO_6P$. Calculated, %: C 64.44, N 2.48, H 11.19.

Dioctyl-*N*-butyl-*N*-carboxymethylaminomethylphosphine oxide (XX). mp = 65°C, yield 90%, R_f 0.51. ^{31}P NMR spectrum: (C_6H_6, 300 Hz); 53 ppm. ^1H NMR spectrum, ppm: 3.48 s (CH_2), 3.06 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.73 t (CH_2, $^3J_{C–H}$ = 6 Hz), 1.75–0.85 m [$(CH_3)_3$, $(CH_2)_{11}$].

Dioctyl-*N*-butyl-*N*-carboxymethylaminomethylphosphine oxide (XXI). mp = 84°C, yield 90%, R_f 0.46. Found, %: N 2.94. $C_{23}H_{48}NO_3P$. Calculated, %: N 3.35. IR spectrum, ν, cm^{-1}: 1027 (P=O). ^{31}P NMR spectrum: 53 ppm. ^1H NMR spectrum, ppm: 3.71 s (CH_2), 3.28 d (CH_2, $^2J_{P–H}$ = 6 Hz), 2.90 t (CH_2, $^3J_{C–H}$ = 6 Hz), 1.91–0.97 m [$(CH_3)_3$, $(CH_2)_{17}$] .

Didecyl-β-(2-piridyl)aminophosphine oxide (XXII). Yield 90%. ^{31}P NMR spectrum: (C_6H_6, 300 Hz); 30.7 ppm.

Oxalic derivative of phosphine oxide XXII. Yield 80%. Found, %: C 63.85. $C_{28}H_{51}N_2O_5P$. Calculated, %: C 63.56.

***N*,*N*-Bis(didecylphosphinylmethyl)tetramethylenediamine (XXIII).** mp = 80°C, yield 75%, R_f 0.3. Found, %: C 72.03. $C_{46}H_{98}N_2O_2P_2$. Calculated, %: C 71.45. IR spectrum, ν, cm^{-1}: 1150 (P=O), 3280 (NH). ^{31}P NMR spectrum: 46 ppm. ^1H NMR spectrum, ppm: 2.87 d [$(CH_2)_2$, $^2J_{P–H}$ = 7.8 Hz], 2.66 t [$(CH_2)_2$, $^3J_{C–H}$ = 6 Hz], 1.8–0.8 m [$(CH_3)_4$, $(CH_2)_{32}$, $(NH)_2$].

***N*,*N*-Bis(didecylphosphinylmethyl)hexamethylenediamine (XXIV).** mp = 82°C, yield 85%, R_f 0.15. Found, %: N 4.03, C 69.94, H 13.28. $C_{40}H_{86}N_2O_2P_2$. Calculated, %: N 4.07, C 69.72, H 12.58. IR spectrum, ν, cm^{-1}: 1148 (P=O), 3275 (NH). ^{31}P NMR spectrum: 43 ppm. ^1H NMR spectrum, ppm: 2.88 d [$(CH_2)_2$, $^2J_{P–H}$ = 5.4 Hz], 2.65 t [$(CH_2)_2$, $^3J_{C–H}$ = 6.9 Hz], 1.8–0.8 m [$(CH_3)_4$, $(CH_2)_{32}$, $(NH)_2$].

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