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Effect of the Structure of Functionalized Phosphoryl Carriers on the Membrane Transport of Proton-Donor Substrates

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Abstract — A series of phosphoryl compounds functionalized in the side chain were synthesized, and their membrane-transport properties with respect to proton-donor substrates of various acidity were studied. It was found that the efficiency of phase transport of the strong monobasic perchloric acid correlates with the basicity of the phosphoryl carriers in a series of carriers containing oxygen-containing functional groups. The transport flow sharply increases in going to phosphorylated amines, whereas phosphoramidates in their efficiency are closer to phosphonates than to amines. The efficiency of transport of dibasic acids (oxalic and tartaric) is low, since the hydroxy and carboxy groups not bound to the carrier make ionic associates highly hydrophilic. Fine details of the structure–transport acitivity relationship in the series of phosphorus compounds were discussed. Three-dimensional correlation analysis was used to compare the structure of the carriers with their characteristics: basicity of amine centers, atomic charges of oxygen and nitrogen, and hardness and hydrophobicity parameters.

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Liquid and membrane extraction play an important role in technological processes involving concentration and selective separation of mineral, organic, and biological substrates. The most common extractants and carriers for the latter are neutral organophosphorus compounds, such as tributyl phosphate and trioctylphosphine oxide [1], as well as polyether podands with terminal phosphoryl groups [2]. In a series of previous works we showed that α- and β-aminated phosphoryl compounds exhibit a high efficiency in phase transport. This equally relates to liquid extraction of metal ions [3] and mineral acids [4], as well as to transport of inorganic acids through liquid membranes [5]. Of particular importance is that research into phase transport of acids is quite urgent, since separation of, for example, metal ions by means of liquid and membrane extraction is most frequently performed from aqueous solutions of mineral acids [5, 6].

In the present work we studied substituent effects on transport properties with respect to acidic substrates of compounds of the phosphonate and phosphine oxide structure, containing, along with phosphoryl, other donor oxygen- and nitrogen-containing functional groups that, too, can serve as coordination centers. These substituents differ in electronic nature and, on the one hand, exert different effects on the basic phosphoryl center and thus predetermine its coordination power and efficiency of the carrier as a whole, and on the other hand, can function as competitive and additional coordination centers. We studied the membrane-transport properties of a series of phosphoryl compounds $R_2P(O)R'$ (**I**–**XIII**) functionalized in the side chain, with respect to acids of various nature, viz. the strong monobasic perchloric acid, two medium-strength dibasic organic acids oxalic and tartaric, and a relatively weak proton donor having, in addition, a potentially alternative basic amine center, aminoethanol that can act both as proton donor and proton acceptor. Table 1 lists the formulas of the radicals R and R' and experimental and calculated characteristics of the corresponding carriers.

The organophosphorus carriers studied in the present work were synthesized using traditional methods of organophosphorus chemistry [7]. Trioctylphosphine oxide (**I**) was prepared by the reaction of phosphorus oxychloride with octylmagnesium bromide, and phosphonates **II**–**IV**, by the Michaelis–

Table 1. Transport flows of substrates and calculated characteristic of carriers $R_2P(O)R'$

Comp. no.	R	R'	Substrate transport flow $\prod \times 10^6$, mol m^{-2} min^{-1}				log *P*	Total hardness	Charge on P(O), ē	Charge on N, ē	pK_b
			perchloric acid	oxalic acid	tartaric acid	ethanolamine					
I	Oct	Oct	140	280	114	5.32	9.20	221.26	–0.63		
II	2-Et-HexO	Oct	0.43	49	6.1	1.46	11.92	230.64	–0.69		
III	2-Et-HexO	CH_2OAm	0.89	35	0.50	1.74	9.53	206.93	–0.65		
IV	2-Et-HexO	$CH_2O(CH_2)_2OAm$	1.6	32	0.46	0.45	9.35	230.54	–0.74		
V	Dec	CH_2OH	97	80	0.75	6.2	7.22	206.82	–0.65		
VI	DecO	CH_2OH	0.60	5.0	0.10	12.5	7.51	213.74	–0.69		
VII	Dec	OH	17	2.04	0.02	241	7.51	200.94	–0.66		
VIII	DecO	OH	1.7	1.80	0.10	372	7.79	204.42	–0.73		
IX	2-Et-HexO	NBu_2	0.55	66	0.17	0.37	11.09	220.25	–0.65	–0.61	7.40
X	2-Et-HexO	NEt_2	0.22	63	0.32	0.38	8.98	199.11	–0.69	–0.64	7.25
XI	2-Et-HexO	NHBu	2.5	49	0.11	0.34	10.04	202.54	–0.67	–0.60	7.17
XII	2-Et-HexO	$CH_2NBuOct$	420	105	1.4	–	10.71	250.62	–0.74	–0.03	9.55
XIII	DecO	CH_2NBu_2	407	98	0.03	11.1	10.87	263.52	–0.67	–0.04	9.37
XIV	*i*-PrO	NC(O)Ph					2.91	120.57	–0.64	–0.58	1.91
XV	*i*-PrO	NC(S)Ph					2.99	119.39	–0.65	–0.46	1.35

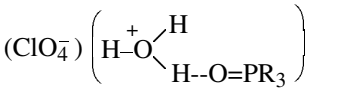
Becker reaction of sodium bis(2-ethylhexyl) hydrogen phosphite with octyl bromide, chloromethyl pentyl ether, and ethylene glycol butyl chloromethyl ether, respectively. Hydroxymethyl derivatives **V** and **VI** were prepared by the Abramov reaction of didecylphosphinic acid and didecyl hydrogen phosphite, respectively, with Paraform. Acids **VII** and **VIII** were prepared by the oxidation of the corresponding hydrophosphoryl compounds with nitrogen dioxide. Aminophosphonates **XII** and **XIII** were synthesized by the Kabachnik–Fields reaction [8] and phosphoramidates **IX**–**XI**, by the Todd–Atherton reaction [9].

We expected that changes in the basicity of the phosphoryl group in polyfunctional organophosphorus reagents, caused by different electronic effects of substituents, as well as the presence in the molecules of "additional" nitrogen- and oxygen-containing groups, would specifically affect the membrane-transport properties of each carrier to the chosen substrates. As reference we took trioctylphosphine oxide (**I**) which has a single potential coordination center, the phosphoryl oxygen atom. Compounds **III**–**VI**, **XII**, and **XIII** contain additional basic coordination centers, oxygen or nitrogen. In should therewith borne in mind that in aminophosphonates **XII** and **XIII** the amino group is more basic than phosphoryl [8]. Furthermore, compounds **V**–**VIII** and **XI** contain proton-donor fragments that can form intramolecular hydrogen bonds with the phosphoryl group [8] or intermolecular hydrogen bonds with substrate molecules.

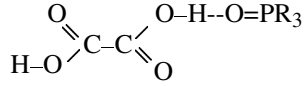
Thus, in our opinion, we could account for a variety of structural factors on such properties of the chosen series of compounds as electronic effects of substituents, their hydrophilicity and lipophilicity, and role of competitive intramolecular hydrogen bonding.

The range of substrates on this stage of research was restricted by hydrophilic compounds capable of forming H complexes with the phosphoryl group. As membrane solvent we chose the nonpolar tridecane, which excludes the possibility of specific solvation of both carriers and complexes that form in the membrane phase.

The results listed in Table 1 show that the transport properties of the four-coordinate phosphorus derivatives studied vary over a wide range. To explain the resulting data, one should primarily account for the nature of substrate–carrier ionic associates formed in the membrane phase. According to [10], there are two mechanisms of extraction with neutral organophosphorus compounds, hydrate–solvate and solvate, depending on the strength of the acid. Perchloric acid, like some other strong inorganic acids, is extracted by the hydrate–solvate mechanism, i.e. a species that passes into the organic phase is ionic associate **XVI** comprising the hydroxonium cation H-bonded with



XVI

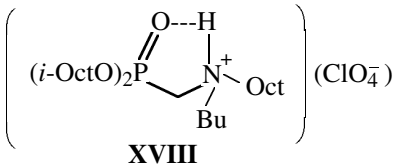


XVII

the extractant phosphoryl group and the perchlorate counter ion.

Weak organic and inorganic acids are extracted by the solvate mechanism which suggests formation of H complexes **XVII**. In the case, the extraction efficiency will be controlled by the hydration energy of the acid molecule and the energy of the H bond formed, i.e. by the strength and hydrophilicity of associate **XVII**. Most likely, such complexes are formed between our studied carries and oxalic and tartaric acids.

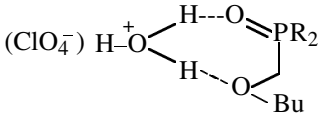
In the membrane extraction of perchloric acid, the transport properties of the carriers should be affected by the basicity of the phosphoryl group and the effect of additional coordination. The highest transport flow is characteristic of the strongest bases, α-aminophosphonates **XII** and **XIII**, and it is 3 times higher than that for phosphine oxide **I**. This is naturally connected with the fact that the tertiary nitrogen atom in α-aminophosphonates is more basic than the oxygen atom in trioctylphosphine oxide. At the same time, it should be emphasized that the transport properties of aminophosphonates and the other carriers are not fully correct to compare, since amino compounds extract acids by a different mechanism: Like in the extraction with higher aliphatic amines, a species that passes into the organic phases is the ionic associate of the corresponding acid anion and protonated aminophosphonate. With perchloric acid, ionic associate **XVIII** may occur.



XVIII

Replacement of donor alkyl groups at the phosphoryl center by acceptor alkoxy groups (compound pairs **I** and **II**, **V** and **VI**, and **VII** and **VIII**) always appreciably decreases the transport efficiency by decreasing the electron density on the phosphoryl oxygen. The presence or absence of proton-donor groups in the side chain of the carrier (cf., for example, compounds **III**, **IV**, on the one hand, and **V**, **VI**, on the other) has no considerable effect of the general regularity: In oxygen-containing compounds, the key role belongs to the electronic effect of the substituent on phosphorus.

The increase of the flow over the series **II**–**IV** is probably explained by additional coordination: Introduction of it is not fully oxygen atoms make possible formation of solvate complex **XIX** whose relatively higher strength is determined by additional H bonding with this oxygen atom.

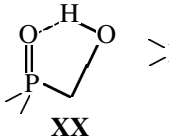


XIX

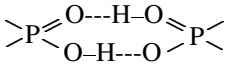
As noted above, the transport of oxalic and tartaric acid occurs by the solvate mechanism. Here, too, the basicity of the phosphoryl group is the key factor. In particular, the transport flow of oxalic acid decreases alone the series **I**–**IV**, in parallel with the decreasing basicity of the phosphoryl oxygen atom.

Therewith, the effect of additional coordination does not obviously reveal itself, since phosphonates **III** and **IV** that contain, along with the phosphoryl oxygen, other potential coordination centers transport oxalic acid slower than unsubstituted phosphonate **II**; the oxygen-containing functional groups function exclusively as electron-acceptor substituents and decrease the electron density on the phosphoryl center.

The transport properties of phosphoryl compounds with respect to oxalic acid are strongly affected by proton-donor substituents that increase the flow more than 3 times for phosphine oxide **V** and almost 2 orders of magnitude for hydroxy derivatives **VI**–**VIII** compared with reference phosphine oxide **I.** The most probable reasons for this effect are competitive H bonding of the phosphoryl oxygen in intramolecular H complexes **XX** of hydroxymethylphosphoryl compounds **V** and **VI** and dimerization of acids **VII** and **VIII** in the membrane phase to form very stable cyclic H complexes **XXI**, which is characteristic of oxygen acids of phosphorus in the highest oxidation state [11].



XX



XXI

Interactions of this type prevent formation of H complexes between protic carriers with the fairly weak oxalic acid, which makes the carriers less efficient. With the strong perchloric acid, the described intra- or intermolecular H bonding exerts no competitive effects.

With tartaric acid, a similar tendency in the effect of the structure of phosphoryl carriers on their transport properties is observed. As would be effected all carriers transport tartaric acid slower than oxalic, since the former substrate is more hydrophilic, having hydroxy groups that form H bonds with carriers. General-

Table 2. Atomic parameters used in calculating pK_b for organophosphorus amines

Atom	χ	R	δ_i^b
H	2.10	0.30	0.76 ± 0.06
C_{sp^3}	2.10	0.77	0.08 ± 0.04
C_{ar}	2.45	0.67	–2.46 ± 0.11
O_{sp^3}	3.05	0.66	–9.54 ± 0.24
O_{sp^2}	4.60	0.62	–9.82 ± 0.71
S_{sp^2}	2.74	0.94	–3.50 [a]
P_{sp^3}	2.26	1.10	–16.8 [a]

[a] Calculated by Eq. (2).

ly, the monobasic perchloric acid is much more efficiently transported by all the organophosphorus bases than dibasic acids. The obvious reson for this phenomenon is the high hydrophilicity of H complexes between phosphoryl carriers and substrates containing "additional" proton-donor groups, hydroxyls and carboxyls, that do not bind with carriers, thus making the H-bonded associates formed by these substrates with carriers highly hydrophilic. Notably, even phosphorylated amines **XII** and **XIII** that are quite effective carriers for perchloric acid radically (4 times) decrease the transport flow of oxalic acid and exhibit almost no transport activity with respect to tartaric acid.

Bis(2-ethylhexyl) phosphoramidates **IX**–**XI** occupy special place in the series of phosphoryl membrane carriers (Table 1). They most effectively transport oxalic acid, while perchloric and tartaric acids have much lower transport flows. It should be emphasized that phosphoramidates rank much below the more basic trioctylphosphine oxide and compare with bis-(2-ethylhexyl) octylphosphonate (**II**) in transport efficiency with respect to perchloric and oxalic acids. Our results are well consistent with the above-described general regularities of the membrane transport of acids with four-coordinate phosphorus derivatives. Obviously, the amide nitrogen atom in phosphorus acid amides scarcely exhibits basic properties and is not protonated with even fairly strong acids. Moreover, it is well known that strong electron-acceptor groups, such as trifluouromethanesulfonyl, tosylcarbamoyl, 2,4-dinitrophenyl, etc., in hydrazines [12] or secondary amines [13] make these compounds strong NH acids comparing in strength with carboxylic acids. The nitrogen atom in phosphoramidates is bound with the fairly strong electron-acceptor phosphoryl group (the σ^* constants of the dialkoxyphosphoryl group vary within the range 1.78–2.21; for comparison, the Taft constant of the 2,4-dinitrophenyl group is 1.9 [14]), which makes it less basic. Note that recently Sokolov et al. [15] reported the high mobility of the NH proton in *N*-(thio)acyl(thio)amidophosphates. Their pK_a values in aqueous ethanol are 7–11. Moreover, among numerous reactions characteristic of these compounds, we found no no reactions where the amide nitrogen atom exhibits its basic or nucleophilic properties. According to [16], diisopropyl phosphoramidate and phosphoramidothioate, too, exhibit pronounced acidic properties (mean pK_a in 50% ethanol 12.4).

The above findings explain the fact that in their transport properties the phosphoramidate carriers compare with phosphonates **II** and **III**, rather than with phosphorylated amines **XII** and **XIII**. The reason for such a high selectivity of oxalic acid transport with phosphoramidates (as well as trioctylphosphine oxide) is not clear. Probably, we deal here with more complex hydrogen associates formed by the dibasic acid and phosphoryl associates, whose structure should be studied in more detail, and we plan this work for future.

We tried to express the dependence of the transport properties of the organophosphorus carriers studied on their structure by means of three-dimensional correlation analysis [17]. The basicities pK_b of phosphoramidates **IX**–**XI** and aminophosphonates **XII** and **XIII** were calculated by Eq. (1) [18].

$$pK_{R_3N} = 9.12 + \sum_{i}^{N-1} \frac{\delta_i^b}{r_{rc-i}^2}. \quad (1)$$

Here N is the number of atoms in a molecule; rc, N_{sp^3} atom considered as the protonation center; r°_{rc-i}, distance between the ith atom and nitrogen; and δ_i^b, parameter reflecting the ability of an atom of a certain type to contribute to pK_b.

Table 2 lists the δ_i^b values for all-type atoms constituting the compounds studied (the atom types are assigned according to [19]). For the P_{sp^3} and S_{sp^2} atoms whose parameters had not been known, we calculated them by Eq. (2) taking account of their electronegativity (χ_i) and covalent radius (R_i).

$$\delta_i^b = -32.14(\chi_i - 2.17)R_i^2. \quad (2)$$

The calculated values are listed in Table 2. The calculated pK_b values of phosphorus amides and phosphonamidates are listed in Table 1. For comparison we also give in Table 1 the calculated pK_b values for two *N*-acylphosphoramidates **XIV** and **XV**. The calculated basicity characteristic of nitrogenous bases are well consistent with available experimental results.

Thus, phosphoramidates **IX**–**XI** proved to be almost neutral nitrogen compounds: Their pK_b span the range 7.2–7.5. These values provide convincing evidence for the "phosphoryl" rather than "amine" nature of the proton-acceptor properties of these carriers. The calculated basicity parameters of α-aminophosphonates **XII** and **XIII**, pK_b 9.55 and 9.37, respectively, with the experimental pK_a values of their conjugate acids (pK_a 4–6) measured in [8]. With *N*-benzoylphosphoramidate **XIV** and its thio analog **XV**, too, the calculated pK_b values correspond to the experimental and above-mentioned acidities in aqueous ethanol (pK_a 9–11). The calculated basicity parameters of the latter two compounds can be considered perceived with caution, since they take no account of the resonance interaction of functional groups, which is probably quite considerable. These results provide evidence for the adequacy of the calculation methods we used to estimate the basicity of the nitrogen centers in the carriers studied.

We found that the oxalic acid transport flows with five phosphorus–nitrogen compounds **IX**–**XIII** fairly correlate with the basicity parameters of the latter [Eq. (3)].

$$\Pi = 19.562\text{p}K_b - 83.191 \quad (R\ 0.9794). \qquad (3)$$

Regretfully, we failed to obtain fair correlations for the other reaction series. This is not surprising, since, as mentioned above, the character of complex formation with different acids should vary from one carrier to another and, strictly speaking, certain assumption should be made in relating the transport flows for each acid with all the carriers studied to a single reaction series.

For the same reasons we could not reveal definite correlations between the transport flows and the charge on nitrogen and phosphoryl oxygen, as well as the octanol–water partition coefficients of the carriers (log *P*), calculated in the present work as a measure of the hydrophobicity of the latter (see Experimental).

At the same time, we found that the total molecular rigidity parameters (η_{MOL}) of the organophosphorus carriers studied (Table 1), calculated by formula (4) we proposed in [20, 21], correlate well with the perchloric acid transport flows [Eq. (5)].

$$\eta_{MOL} = \Sigma \frac{1}{2\sum_{i\neq 1}^{N-1} \frac{R_j^2 + R_i^2}{r_{j-i}^2}}, \qquad (4)$$

$$\Pi = 6.2325\eta_{MOL} - 1283.2 \quad (R\ 0.9794). \qquad (5)$$

Correlation (5) gives us grounds to suggest that the interaction (transport) of perchloric acid with the carriers can obviously be described in terms of the hard and soft acids and bases concept.

Thus, the quantitative correlations between the transport properties of organophosphorus carriers and some of their characteristics obtained both experimentally and theoretically allowed us to reveal a number of above tendencies relating the structure and properties of these compounds. At the same time, it should be borne in mind that the structure–membrane properties for various carriers may not be unambiguous and simple, since the efficiency of membrane transport depends on a great number of factors. In the case of acidic substrates, along with basicity, the efficiency of membrane transport can be affected, according to [22], by the viscosity of membrane phase, surface tension on the interface, and other characteristic that are not always readily accounted for.

To assess the effect of the structure of phosphoryl compounds on their transport properties with respect to proton donors containing their own basic center, amino group, we chose aminoethanol as substrate. The undeniable advantage of this reference compound is its high hydrophobicity. Furthermore, we found in a special experiment, ethanolamine is not transferred through hydrophobic membranes in the absence of carriers.

The results listed in Table 1 suggest that the effect of carrier structure on the flow of this substrate is quite different from what we observed with the other acids, even though the general tendency of the flow rate to increase with increasing basicity of the carrier is preserved. This primarily relates to proton-donor carriers, i.e. hydroxymethyl derivatives **V** and **VI**. With these carriers, the flows are appreciable higher that with other derivatives of close basicity, for example, phosphorylated esters **III** and **IV**, whereas with oxalic acid the opposite tendency took place. However, this effect is especially clearly pronounced with relatively strong acids, viz. didecylphosphinic acid (**VII**) and didecyl hydrogen phosphate (**VIII**). There is no doubt that this fact is explained by the presence in the substrate molecule of a highly basic amino group that forms salts or H complexes with the corresponding protic functional groups of the carriers.

With phosphoryl compounds containing no proton-donor groups, the transport rate decreases with decreasing basicity. No evidence for additional coordination for carriers with oxygen-containing substituents was observed. Thus, the transport of aminoethanol with phosphoryl carriers features the "reverse" acid–base relation: With acids, phosphoryl reagents act as

basic cariers, whereas aminoethanol is more effectively transported by proton-donor (acidic) carriers.

Our present results open up possibilities for purposeful selection of molecular structure in carrier–substrate pairs for optimizing both the rate of membrane transport and the selectivity of phase transport. Naturally, research into complementary carrier–substrate relations cannot confined to compounds of specific classes (in our case, acids and basic phosphoryl compounds) and should be extended to other important objects, such as ion metals, amino acids, and neutral and organoelement molecules. These problems will be the subject of our further studies.

EXPERIMENTAL

The octanol–water partition coefficients log *P* were calculated by the MOE program (Molecular Operational Environment; Version 2003.10, Chemical Computation Group Inc., Montreal, Canada, 2004), and the charges of the nitrogen and phosphoryl oxygen are determined by the PM3 method using the MOE program.

Membrane extraction was studies using a "beaker-in-beaker" temperature-controlled cell whose design is described in [23]. Vladipor MFFK-4 porous filters (Teflon matrix on a polyether support; pore size 0.6 μm) were used as the hydrophobic matrix for impregnated membranes; the source phase contained a 0.2 M substrate solution and the receiving phase contained doubly distilled water. The membrane was impregnated with tridecane solutions of neutral carriers. Substrate solutions were prepared by dissolving accurately weighed samples in doubly distilled water or by diluting more concentrated solutions. When required, the substrate concentration was determined more accurately by titrimetry. All carrier solutions were prepared by dissolving accurately weighed samples in corresponding solvents. Conductivity measurements were performed at 25°C every 5 min using a conductometer.

Calibration dependences were obtained by measuring the electrical conductivities of substrate solutions of varied concentrations in a temperature-controlled cell, after which electrical conductivity–time linear plots were constructed (25°C, *R* 10 kΩ).

Measurement of membrane transport flow *(typical experiment).* The outer beaker of the cell was loaded with a substrate solution and the inner beaker equipped with the conductometer sensor, with 7.5 ml of doubly distilled water; measurements were performed every 5 min. The flows ∏ were calculated using a specially developed Vizual UNMK 2002 software [5] by the equation $\prod = \tan\alpha\, V/S$, where $\tan\alpha$ is the slope of the concentration–time kinetic dependence; *V*, volume of the receiving phase; and *S*, membrane surface area. The resulting flows are listed in Table 1.

Synthesis and characteristics of organophosphorus carriers.

Trioctylphosphine oxide. mp 55°C (published data [1]: 50–55°C), δ ^{31}P 50 ppm.

Bis(2-ethylhexyl) octylphosphonate (II). Bis(2-ethylhexyl) phosphite, 37 ml, was added dropwise over the course of 30 min to a mixture of 40 ml of ether, 60 ml of benzene, and 2.57 g of metallic sodium. After the metal had dissolved completely, 16.38 g of freshly distilled octyl bromide was added. The mixture was refluxed for 1 h and left overnight. Sodium bromide that dropped was separated by centrifugation, and the solution was washed with distilled water (5.50 ml) and dried with sodium sulfate. The solvent was removed in a rotary evaporator, and the residue was distilled in a vacuum. Yield 70%, bp 164°C (0.2 mm Hg), n_D^{20} 1.4475, δ_P 33.2 ppm.

Bis(2-ethylhexyl) (pentyloxymethyl)phosphonate (III) was prepared in a similar way from 35 g of sodium bis(2-ethylhexyl) phosphite and 15.02 g of chloromethyl pentyl ether. Yield 31.26 g (70%), bp 164°C (0.25 mm Hg), n_D^{20} 1.4452, δ_P 22,3 ppm.

Bis(2-ethylhexyl) [(2-butoxyethoxy)methyl]-phosphonate (IV) was prepared in a similar way from 18.36 g of sodium bis(2-ethylhexyl) phosphite and 10 g of ethylene glycol butyl chloromethyl ether. Yield 16.23 g (65%), bp 175°C (0.25 mm Hg), n_D^{20} 1.4462, δ_P 22.3 ppm.

Didecyl (hydromethyl)phosphonate (VI). A mixture of 0.2 g of metallic sodium, 60 ml of absolute benzene, 17.5 g of didecyl hydrogen phosphite was heated until the metal dissolved completely, after which 1.45 g of Paraform was added with stirring. The mixture was stirred for 3 h at 60°C. Excess Paraform was filtered off, and the filtrate was washed with distilled water (6.50 ml) and dried with sodium sulfate. Excess Paraform and solvent were removed on a rotary evaporator, and the residue was heated to 80°C in a water-jet-pump vacuum to obtain an almost pure hydroxyphosphonate **VI** as a colorless liquid. Yield 50%. bp 168°C (0.25 mm Hg), n_D^{20} 1.4523, δ_P 25.6 ppm.

Didecyl(hydromethyl)phosphine oxide (V) was prepared in a similar way from didecylphosphinic acid and Paraform. mp 47°C, δ_P 54.8 ppm.

Didecylphosphinic acid (VII) was prepared by

the procedure described in [24]. mp 84°C, δ_P 59.9 ppm (chloroform). Published data [24]: mp 85–86°C, δ_P 59.4 ppm.

Didecyl hydrogen phosphate (VIII). Nitrogen dioxide obtained by the action of concentrated nitric acid on a saturated solution of sodium nitrite was barboted through a solution of 15 g of didecyl hydrogen phosphite in 20 ml of benzene until an intense yellow color appeared. Benzene was removed on a rotary evaporator, and the solid precipitate was twice recrystallized from hexane to obtain 10 g (60%) of compound *VIII* as colorless crystals. mp 47°C {published data [25]: mp 46–47°C), δ_P 0.9 ppm (chloroform).

Bis(2-ethylhexyl) diethylphosphoramidate (X). Carbon tetrachloride, 7.546 g, was added dropwise to a mixture of 15 g of bis(2-ethylhexyl) hydrogen phosphite and 8.96 g of diethylamine at 0–5°C. The reaction mixture was let to stand for 30 min at this temperature and then for 1 h at room temperature, the amine hydrochloride was filtered off on a glass frit and washed with hexane, the filtrate was washed with 5% HCl and twice with water, and dried with Na_2SO_4. The solvent was removed in a vacuum, and the residue was distilled in a vacuum, bp 132°C (0.15 mm Hg), to obtain 16 g (87%) of amide **X**, n_D^{20} 1.4421, δ_P 11 ppm.

Bis(2-ethylhexyl) dibutylphosphoramidate (IX) was synthesized in a similar way from 25 g of bis(2-ethylhexyl) hydrogen phosphite, 26.34 g of dibutylamine in 10 ml of hexane, and 8 ml of CCl_4 in 20 ml of hexane. Yield 30.5 g (88%), bp 159°C (0.3 mm Hg), n_D^{20} 1.4461, δ_P 10.7 ppm.

Bis(2-ethylhexyl) butylphosphoramidate (XI) was synthesized in a similar way from 25 g of bis(2-ethylhexyl) hydrogen phosphite, 14.9 g of dibutylamine in 10 ml of hexane, and 8 ml of CCl_4 in 20 ml of hexane. Yield 26.5 g (86%), bp 157°C (0.2 mm Hg), n_D^{20} 1.4455, δ_P 11.3 ppm.

Bis(2-ethylhexyl) (*N*-butyl-*N*-octylamino)methylphosphonate (XII) was synthesized as described in [3].

Didecyl (*N,N*-dibutylamino)methylphosphonate (XIII). Paraform, 2.3 g, was gradually added to a mixture of 25 g of didecyl hydrogen phosphite and 8.9 g of dibutylamine, heated on a boiling water bath, the mixture was heated at 80°C until Paraform had dissolved completely and then heated on a boiling water bath for 1 h. After cooling, the reaction mixture was diluted with equal volume of benzene, the resulting solution was passed through a column of Al_2O_3, and the solvent was removed on a rotary evaporator. Yield 26.4 g (76%), n_D^{20} 1.4511, δ_P 25.7 ppm.

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