SYNTHESES OF NEW TRIETHYLENE GLYCOL BIS(ALKYL PHOSPHATE)S AS POTENTIAL COMPLEXING AGENTS

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A series of triethylene glycol bis(alkyl phosphate)s HO(RO)P(O)(OCH$_2$CH$_2$)$_3$OP(O)(OR)OH **4** (R = octyl (**4a**), 1-methylheptyl (**4b**), 2-ethylhexyl (**4c**), nonyl (**4d**), decyl (**4e**), dodecyl (**4f**), hexadecyl (**4g**), octadecyl (**4h**)) has been synthesized with the expectation that these compounds could be effective complexing and/or extraction agents for metal cations. The compounds were characterized by ^{31}P NMR, ^{1}H NMR, ^{13}C NMR and IR spectroscopy, MALDI-TOF mass spectroscopy and elemental analysis.

Keywords: Bis(phosphate); Bis(alkyl phosphate); Oligoethers; Polyethers; Phosphorylation; Phosphates; O-ligands; Extraction; Potentiometry.

Organophosphorus compounds have been commonly used as complexing and extraction agents for metal ions. More effective are those which contain two P=O groups in one molecule, which increases the probability of the formation of stable chelate complexes, *e.g.* diphosphinoylalkanes R$_2$P(O)(CH$_2$)$_n$P(O)R$_2$ (n = 1, 2) form six- and seven-membered chelate rings[1].

The polyethers with the –(CH$_2$CH$_2$O)$_n$– chain rank among to polydentate ligands capable of forming chelate complexes with metal ions. Particularly cyclic polyethers (crowns) are widely used for metal complexation because of their selectivity for certain ions and relatively good solubility of the complexes in nonpolar solvents. The selectivity depends on the size and conformation of the ring, the number of oxygen atoms in the crown molecule, and the charge and coordination number of the ion[2]. Both simple crowns[3] and their derivatives with side-chain substituents or with substituents bonded to the crown ring[4] are used in solvent extractions. The presence of

a certain substituent often leads to the selectivity of the crown for the extraction of a group of metal ions or for single metal ion only[5].

Since linear polyethers have more flexible chains as compared with crowns, they are able to conform better to the size of metal cation, and to form pseudomacrocycle complexes. In some cases the formed complexes are readily extracted into the organic phase but the selectivity for particular metals is lower than in the case of crowns[6]. In some extraction experiments, linear polyethers were used as synergic agents, *e.g.* in extraction of alkaline and alkaline-earth metals with bis(1,2-dicarbollyl)cobaltate[7], and in extraction of rare-earth metals[8].

In the course of our search for new phosphorus extraction agents, we considered as promising to combine complexing properties of polyether chains with phosphate groups. Similar compounds were described in the literature as tensides and emulsifying agents[9] but only few experiments have been reported which examine their complexing and extraction properties[6,10]. The compounds of the type $Ph_2P(O)CH_2–X–CH_2P(O)Ph_2$ (X = polyether chain) are more effective complexing and extraction agents for alkaline and heavy metals than crown ethers. Their extraction capability depends on the arrangement of the donor atoms in the polyether chain and the ability to form stable five- and six-membered chelate rings[11].

This paper reports the syntheses of new triethylene glycol bis(alkyl phosphate)s $HO(RO)P(O)(OCH_2CH_2)_3OP(O)(OR)OH$ **4** (R = octyl (**4a**), 1-methylheptyl (**4b**), 2-ethylhexyl (**4c**), nonyl (**4d**), decyl (**4e**), dodecyl (**4f**), hexadecyl (**4g**), octadecyl (**4h**)) whose good extraction and complexing ability could be expected. Furthermore, if fixed on a solid support, they could be used in column chromatography for separation of metal cations from aqueous solutions. The prepared compounds were characterized by ^{31}P NMR, ^1H NMR, ^{13}C NMR and IR spectroscopy, MALDI-TOF mass spectroscopy and thermal and elemental analyses. It was found that these compounds have good extraction and complexing ability to bivalent and trivalent metal ions, especially to rare-earth metals. The results of the extraction experiments and complex formation will be reported in a separate communication.

RESULTS AND DISCUSSION

Syntheses

In the syntheses of new triethylene glycol bis(alkyl phosphate)s **4a–4h**, approaches A and B were used (Scheme 1) which were based on published pro-

cedures[9a,12]. Transesterification and side reactions leading to mixtures of products[13] can be expected in both cases. The approach A used to obtain products **3a**–**3h** by the reaction of triethylene glycol (TEG) with alkyl dichlorophosphate (Scheme 1) was not successful because it did not yield any compound of the type **3**, which was probably caused by trans-esterification of the expected product and/or various side reactions[14].
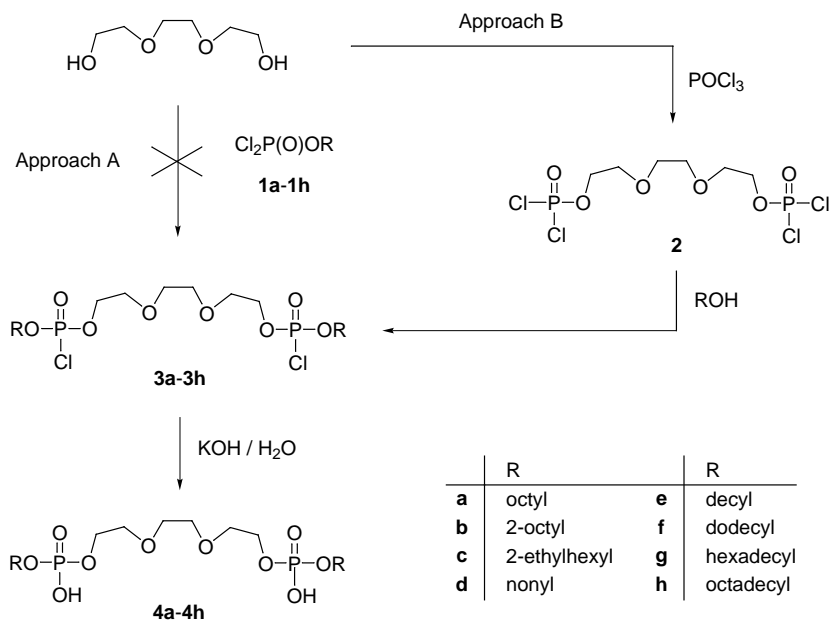
Therefore, the approach B was applied. A similar procedure was published for syntheses of dialkyl bis(phosphate)s $HO(RO)P(O)O(CH_2)_nOP(O)(OR)OH$ ($n = 2, 3, 4$)[9a]. In the first step, $POCl_3$ reacted with TEG in molar ratio 3 : 1 yielding triethylene glycol bis(dichlorophosphate) **2**, which then reacted with the corresponding alcohol in molar ratio 1 : 2 (Scheme 1). The resulting reaction mixture was then hydrolyzed using water or aqueous solution of KOH to yield required compounds **4a**–**4h**. Several purification procedures for the prepared compounds **4a**–**4h** such as separation of synthesized species between two solvents[15], anion-exchange chromatography using basic ion exchangers, liquid–liquid extraction of the Cu salt[16] and recrystallization of solids from non-polar solvents, were tested. The solubility of **4f**, **4g** and **4h** in non-polar solvents increases rapidly with tempera-

ture which enabled us to obtain pure compounds by recrystallization from petroleum ether (yields of **4f**, **4g** and **4h** were 50, 55 and 46%, respectively).

^{31}P NMR chemical shifts of the new compounds **2**, **3a**–**3h**, **4a**–**4h** are in good agreement with chemical shifts of similar phosphoric acid diester derivatives[9,17] (Tables I and II). The other observed but not discussed signals in the spectra of crude products were ascribed to phosphoric acid and its mono- and triesters[14]. ^{1}H and ^{13}C NMR spectra of **4f**–**4h** are in good agreement with the proposed structure of these compounds (Fig. 1) and with the data published for similar compounds[9]. The MALDI-TOF MS observed masses correspond to the expected masses of compounds **4a**–**4h** as shown in Table II. This fact confirms compositions of the prepared compounds. The HR-MS was also used for examination of **4a**–**4h** but only fragments with low masses and no molecular peaks were detected.

TABLE I
^{31}P NMR chemical shifts[a] of triethylene glycol bis(alkyl chlorophosphate)s **3a**–**3h**

Compound	δ, ppm	Multiplet[b], Hz	Integral intensity, %
3a	5.16 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 8.5$	68
3b	4.0; 4.09 m (two isomers)		66
3c	5.89 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.8$	74
3d	5.59 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.8$	67
3e	5.16 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.8$	66
3f	5.22 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 8.5$	66
3g	5.59 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 8.5$	71
3h	5.79 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 8.0$	77

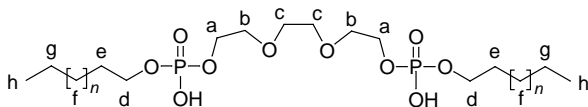[a] In CH_2Cl_2. [b] tt means triplet of triplet; atom denotation in Fig. 1.
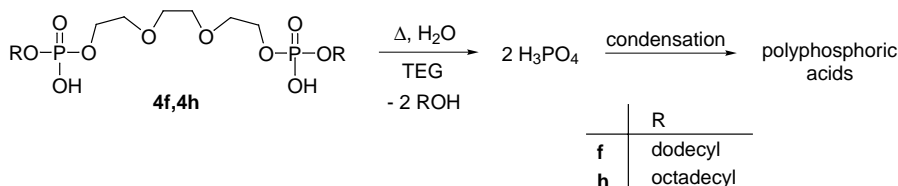

FIG. 1
Carbon atom denotation for **4f**–**4h** (n = 8, 12, 14)

Thermogravimetric Analysis

Thermal stability of **4f**–**4h** was determined using thermogravimetry in air. Since all compounds decompose in a very similar way (Scheme 2), we give here only decomposition of **4f** as an example (Fig. 2).

$$RO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-O\diagdown\diagup O\diagdown\diagup O\diagdown\diagup O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-OR \quad \xrightarrow[\substack{TEG \\ -\,2\,ROH}]{\Delta,\,H_2O} \quad 2\,H_3PO_4 \quad \xrightarrow{\text{condensation}} \quad \text{polyphosphoric acids}$$

4f,4h

	R
f	dodecyl
h	octadecyl

SCHEME 2

The melting point of **4f** is approximately 60 °C and the decomposition begins approximately at 220 °C. After heating to 280 °C, about 71% of the sample mass was lost, which corresponds to removal of the organic part of the molecule (endothermic effect) which burns in the presence of oxygen to CO_2 and H_2O (exothermic effect). Further heating leads to condensation of H_3PO_4 to polyphosphoric acids $(HPO_3)_n$. The mass loss above 280 °C cor-

TABLE II
^{31}P NMR chemical shifts[a] and MALDI-TOF MS molecular masses of triethylene glycol bis(alkyl phosphate)s **4a**–**4h**

Comp.	δ, ppm	Multiplet[b], Hz	Integral intensity %	Molecular mass		
				Formula	Calculated	Found
4a	1.02 m		69	$C_{22}H_{48}O_{10}P_2$	534.56	534.1
4b	1.0 m		67	$C_{22}H_{48}O_{10}P_2$	534.56	533.1
4c	0.13 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 8.5$	74	$C_{22}H_{48}O_{10}P_2$	534.56	533.7
4d	0.27 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.0$	67	$C_{24}H_{52}O_{10}P_2$	562.4	561.9
4e	–0.5 m		66	$C_{26}H_{56}O_{10}P_2$	590.4	590.2
4f	0.11 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.0$	66	$C_{30}H_{64}O_{10}P_2$	646.78	647.1
4g	0.23 tt	$^3J_{PH(a)} = {}^3J_{PH(d)} = 7.0$	71	$C_{38}H_{80}O_{10}P_2$	760.0	761.5
4h	0.71 m		77	$C_{42}H_{88}O_{10}P_2$	815.1	815.4

[a] In CH_2Cl_2. [b] tt means triplet of triplet; atom denotation in Fig. 1.

responds to evaporation of the condensation water, total degradation and evaporation of polyphosphoric acid at the end of heating. Relative thermal stability of the compounds might enable their possible use in extractions at elevated temperatures.

Potentiometry

We obtained the dissociation constant of **4f** $pK_a = 2.1(1)$ in a mixed organic solvent (MeOH–water 90 : 10, v/v) medium using potentiometry. We did not observe any side chemical reaction such as dimerization in the concentration range around 10^{-3} mol dm^{-3} as was proved by potentiometry and/or ^{31}P NMR spectroscopy. Applying the simple Born model[18] $pK_a = f(1/\varepsilon_r)$, we can predict the dissociation constant in a pure solvent (*e.g.* water). Equations based on the Born model can be used only for relative comparison as was pointed out previously[18]. If the difference of pK_a in a mixed solvent medium (water–ethanol 20 : 80, v/v) and in pure water is equal to 1.3 for the general series of dialkyl phosphates[19], then the pK_a estimate for **4f** in pure water is by 1.3 logarithmic unit lower than pK_a in the mixed organic solvent and dissociation constant would be equal to 2.1 – 1.3 = 0.8 at ionic strength 0.1 mol dm^{-3}. We calculated this rough estimate of dissociation constant in pure water for two reasons. First, for comparison with other values published in literature for aqueous solutions obtained mainly by sol-
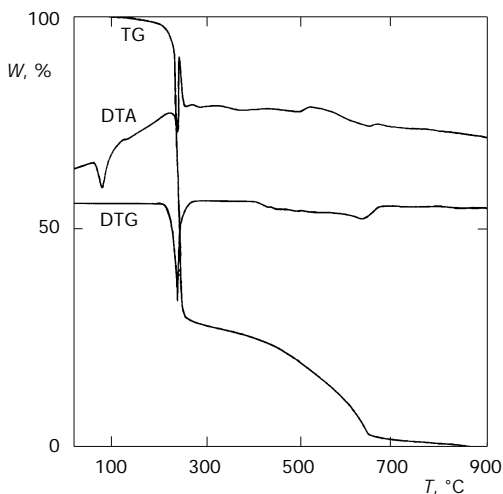

FIG. 2
Thermogravimetric analysis of **4f**

vent extraction. Second, to use potentiometry as experimental method for determination of dissociation constant with sufficient accuracy.

The dissociation constants of similar compounds (dibutyl phosphate[20,21] 1.0 or 0.8, dihexyl phosphate[20] 1.1, dioctyl phosphate[20,22] 1.2 or 1.3) obtained by solvent extraction are in a good agreement with the value obtained for **4f** (0.8). The discrepancies can be ascribed to diferences in temperature and ionic supporting electrolyte.

CONCLUSION

Syntheses of new triethylene glycol bis(alkyl phosphate)s $HO(RO)P(O)(OCH_2CH_2)_3OP(O)(OR)OH$ is possible *via* approach B. Crude products contain limited amounts of byproducts. The purification was possible only with solid compounds by recrystallization from petroleum ether.

EXPERIMENTAL

Chemicals and Methods

All chemicals and solvents were obtained from Fluka and were purified and dried by standard methods. NMR spectra were recorded on a FT NMR spectrometer Avance DRX 500 (Bruker, Karlsruhe, Germany) at working frequencies of 202.460 MHz (^{31}P), 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shift values are given in ppm (δ-scale) relative to 85% H_3PO_4 as an external standard (^{31}P) and TMS as an internal standard (^{1}H, ^{13}C), coupling constants (*J*) are given in Hz. The numbering of atoms follows from Fig. 1. IR spectra (in cm^{-1}) were recorded in Nujol on an Equinox 55/S/NIR FTIR spectrometer (Bruker, Germany). Mass spectrometric analyses were performed on a MALDI-TOF mass spectrometer Kompact Maldi III (Shimadzu Corp., Kyoto, Japan; matrix: dihydroxybenzoic, 2-cyano-3-(4-hydroxyphenyl)propenoic or 5-chlorosalicylic acids). Melting points were measured using a Boëtius melting point apparatus (VEB Wägetechnik Rapido, Dresden, DDR). Thermogravimetric analysis (TG) was performed on air using an Orion Derivatograph OD-102 (Budapest, Hungary), the temperature range 20–1 000 °C, heating rate 10 °C min^{-1}, mass of the analyzed sample about 100 mg.

Potentiometric titrations were carried out on Radiometer titration equipment (Copenhagen, Denmark), which contained a pH-meter PHM 84, automatic burette ABU 80 and digital titrator TTT 81 with a microprocessor unit. The potentiometric cell consisted of a reference electrode Radiometer K 401 and indicator glass electrode Radiometer G202 B. In order to keep constant temperature 25.0 ± 0.1 °C, a double-wall jacket cell was used. The ionic strength 0.1 mol dm^{-3} was maintained by potassium chloride in a mixed organic medium (water–methanol 10 : 90, v/v). During all measurements, gaseous argon was passed through solution. The potentiometric cell was calibrated by titration of 0.004 M hydrochloric acid (25 cm^3) with 0.01 M sodium hydroxide solution at a fixed ionic strength of 0.1 mol dm^{-3}. Knowing [H$^+$] values calculated from titration curve and measured potential values, the parameters of calibration function were determined using of OPIUM program[23]

$$E = E_0 + g\log[\text{H}^+] + j_\text{a}[\text{H}^+] + j_\text{b}\frac{10^{-\text{p}K_\text{w}}}{[\text{H}^+]},$$

where term E_0 includes the standard potential of the electrode, g corresponds to value of the Nernstian slope and last two terms describe the contributions of ions H^+ and OH^- to the liquid-junction potential (in our case, they were neglected because the $-\log[\text{H}^+]$ range of titration curves was 2.2–11.7). The reliability of function of glass electrode in the mixed organic solvent medium was confirmed by the determined parameters mentioned above ($\text{p}K_\text{w}$ = 14.31, E_0 = 358.2 mV and Nernstian slope g = 58.1 mV/$-\log[\text{H}^+]$). The dissociation constant of partly soluble compound **4f** was determined by the same method (0.002 M solution of **4f** titrated at least twice under the same conditions):

$$\log\beta = \log\left(\frac{[\text{H}_2\text{L}]}{[\text{H}^+]^2[\text{L}^{2-}]}\right) = 4.2(2).$$

Because of independence of both acid groups (they are far apart and do not influence each other), we can estimate the protonation constant for the first step as

$$\log\beta_{\text{p,1}} = \log\left(\frac{[\text{HL}]^-}{[\text{H}^+][\text{L}^{2-}]}\right) = 2.1(1).$$

Procedures

Triethylene Glycol Bis(dichlorophosphate) (**2**)

A solution of triethylene glycol (8 cm^3, 0.06 mol) in CH_2Cl_2 (20 cm^3) was added dropwise over 2 h at laboratory temperature to an excess of POCl_3 (16.6 cm^3, 0.18 mol) in CH_2Cl_2 (5 cm^3). Dry nitrogen gas was bubbled through the reaction mixture overnight to remove released HCl and to protect the reaction mixture from air moisture. The reaction vessel was kept in the dark during the reaction. The solvent and excess of POCl_3 were then evaporated in vacuum, and the colourless viscous liquid product was isolated and stored in the dark. The yield was 98% based on triethylene glycol. ^{31}P NMR (CH_2Cl_2): 6.6 t, $^3J_{\text{PH(a)}}$ = 9.8 (denotation of atoms in Fig. 1). ^1H NMR (CDCl_3): 3.55 s, 4 H (CH_2-c); 3.68 m, 4 H (CH_2-b); 4.36 m, 4 H (CH_2-a). ^{13}C NMR (CDCl_3): 70.18 d, 2 C (CH_2-b), $^3J_{\text{C(b)P}}$ = 8.8; 71.84 s, 2 C (CH_2-c); 73.20 d, 2 C (CH_2-a), $^2J_{\text{C(a)P}}$ = 9.7. For $\text{C}_6\text{H}_{12}\text{Cl}_4\text{O}_6\text{P}_2$ (383.9) calculated: 36.94% Cl, 16.14% P; found: 36.66% Cl, 15.83% P.

Triethylene Glycol Bis(alkyl Chlorophosphate) **3a**–**3h**. General Procedure

A solution of an alcohol (46.5 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise over 2.5 h to a solution of **2** (8.91 g, 23.2 mmol) in CH_2Cl_2 (5 cm^3) at laboratory temperature. The reaction was carried out in nitrogen atmosphere. Nitrogen gas was bubbled through the reaction mixture overnight. The solvent was evaporated in vacuum after reaction, a colourless, viscous crude product was isolated and directly used in the hydrolysis step. The ^{31}P NMR characteristic of compounds **3a**–**3h** is given in Table I.

Triethylene Glycol Bis(alkyl Phosphate)s 4a–4e by Hydrolysis of 3a–3e. General Procedure

A mixture of CH_2Cl_2–H_2O 2 : 1, v/v (15 cm^3) was added dropwise to a solution of crude **3a–3e** (10.0 g) in dichloromethane at laboratory temperature. Nitrogen gas was bubbled through the reaction mixture overnight. From white suspensions, water and the solvent were evaporated in vacuum and colourless, viscous crude compounds **4a–4e** were isolated. The ^{31}P NMR data of the products and results of MALDI-TOF MS determinations are given in Table II. All attempts to purify the products by the mentioned methods failed.

Triethylene Glycol Bis(alkyl Phosphate)s 4f–4h by Hydrolysis of 3f–3h. General Procedure

An equimolar amount of a 0.5 M aqueous KOH solution was added dropwise at laboratory temperature to a solution of crude **3f–3h** in dichloromethane. The reaction mixture was purged with nitrogen gas overnight. A thick white suspension was formed. Water and the solvent were evaporated in vacuum and the colourless solid crude products were isolated and purified by recrystallization from petroleum ether. Colourless microcrystalline powders were obtained. The products were characterized by elemental analysis, ^{31}P NMR (Table II), ^1H NMR, ^{13}C NMR (denotation of atoms in Fig. 1) and IR spectroscopy, MALDI-TOF MS (Table II) and thermogravimetric analysis (Fig. 2).

Compound **4f**. ^1H NMR (CDCl$_3$): 0.92 t, 6 H (CH$_3$-h), $^3J_{H(h)H(g)}$ = 7; 1.25–1.45 s + m, 36 H (CH$_2$-f + g); 1.71 tt, 4 H (CH$_2$-e), $^3J_{H(e)H(f)}$ = $^3J_{H(e)H(d)}$ = 7; 3.74 s, 4 H (CH$_2$-c); 3.78 m, 4 H (CH$_2$-b); 4.07 m, 4 H (CH$_2$-d); 4.25 m, 4 H (CH$_2$-a); 10.95 s, 2 H (OH). ^{13}C NMR (CDCl$_3$): 14.05 s (CH$_3$-h); 22.64 s (CH$_2$-g); 25.38, 29.13, 29.30, 29.48, 29.54, 29.59, 29.62 and 31.88 s (CH$_2$-f); 30.15 d, J_{CP} = 7; 66.68 d, J_{CP} = 5.3; 67.82 d, J_{CP} = 7; 69.97 d, J_{CP} = 5.3; 70.61 s (CH$_2$-c). IR: 2 882 (s, CH$_2$ stretching), 2 726 (broad, w, P–OH stretching), 1 219 (s, P=O stretching), 1 061 (s, P–O–C stretching asym.). The yield was 50% based on triethylene glycol bis(dichlorophosphate). M.p. 60–63 °C. For $C_{30}H_{64}O_{10}P_2$ (646.8) calculated: 55.71% C, 9.97% H, 9.58% P; found: 55.9% C, 9.8% H, 9.5% P.

Compound **4g**. ^1H NMR (CDCl$_3$): 0.93 t, 6 H (CH$_3$-h), $^3J_{H(h)H(g)}$ = 7; 1.25–1.45 s + m, 52 H (CH$_2$-f + g); 1.72 tt, 4 H (CH$_2$-e), $^3J_{H(e)H(f)}$ = $^3J_{H(e)H(d)}$ = 7; 3.57 s, 4 H (CH$_2$-c); 3.80 m, 4 H (CH$_2$-b); 4.07 dt, 4 H (CH$_2$-d), $^3J_{H(d)H(e)}$ = $^3J_{H(d)P}$ = 7; 4.25 m, 4 H (CH$_2$-a); 10.38 s, 2 H (OH). ^{13}C NMR (CDCl$_3$): 14.04 s (CH$_3$-h); 22.64 s (CH$_2$-g); 25.40, 29.15, 29.32, 29.50, 29.56, 29.63, 29.66 and 31.88 s (CH$_2$-f); 30.17 d, J_{CP} = 7.1; 66.60 d, J_{CP} = 5.3; 67.78 d, J_{CP} = 6.2; 69.97 d, J_{CP} = 5.3; 70.58 s (CH$_2$-c). IR: 2 880 (s, CH$_2$ stretching), 2 730 (broad, w, P–OH stretching), 1 221 (s, P=O stretching), 1 060 (s, P–O–C stretching asym.). The yield was 55% based on triethylene glycol bis(dichlorophosphate). M.p. 60–66 °C. For $C_{38}H_{80}O_{10}P_2$ (760.0) calculated: 60.13% C, 10.62% H, 8.17% P; found: 60.1% C, 10.5% H, 8.2% P.

Compound **4h**. ^1H NMR (CDCl$_3$): 0.94 t, 6 H (CH$_3$-h), $^3J_{H(h)H(g)}$ = 7; 1.26–1.47 s + m, 60 H (CH$_2$-f + g); 1.73 tt, 4 H (CH$_2$-e), $^3J_{H(e)H(f)}$ = $^3J_{H(e)H(d)}$ = 7; 3.76 s, 4 H (CH$_2$-c); 3.80 m, 4 H (CH$_2$-b); 4.08 m, 4 H (CH$_2$-d); 4.25 m, 4 H (CH$_2$-a); 9.9 broad s, 2 H (OH). ^{13}C NMR (CDCl$_3$): 14.06 s (CH$_3$-h); 22.65 s (CH$_2$-g); 25.42, 29.17, 29.33, 29.52, 29.58, 29.64, 29.68 and 31.9 s (CH$_2$-f); 30.18 d, J_{CP} = 7.1; 66.55 d, J_{CP} = 5.3; 67.76 d, J_{CP} = 5.3; 69.98 d, J_{CP} = 5.3; 70.57 s (CH$_2$-c). IR: 2 878 (s, CH$_2$ stretching), 2 728 (broad, w, P–OH stretching), 1 220 (s, P=O stretching), 1 058 (s, P–O–C stretching asym.). The yield was 46% based on triethylene glycol bis(dichlorophosphate). M.p. 64–69 °C. For $C_{42}H_{88}O_{10}P_2$ (815.1) calculated: 61.89% C, 10.88% H, 7.60% P; found: 61.9% C, 10.8% H, 7.5% P.

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