Synthesis of calix[4]resorcinarenes, containing phosphoryl fragments at the lower rim of the molecule

A. R. Burilov,[a] I. R. Knyazeva,[a] Yu. M. Sadykova,[a] M. A. Pudovik,[a]★ W. D. Habicher,[b] I. Baier,[b] and A. I. Konovalov[a]

[a]A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 275 2253. E-mail: pudovik@iopc.knc.ru
[b]Institute of Organic Chemistry, Dresden University of Technology,
*13 Mommsenstrasse, D-01062 Dresden, Germany.**
Fax: +49 (351) 463 4093

Reaction of resorcinol with phosphorylated acetals or ethoxyvinylphosphonic acid esters in acidic media leads to calix[4]resorcinarenes, containing dialkoxyphosphoryl fragments at the lower rim of the molecule. When the alkyl substituent in alkoxy groups at phosphorus atom is not very long, a partial hydrolysis of the initially formed products takes place to give calixarenes with alkoxyhydroxyphosphoryl fragments.

Key words: acetals, vinylphosphonic acids, resorcinols, calix[4]resorcinarenes, organophosphorus compounds.

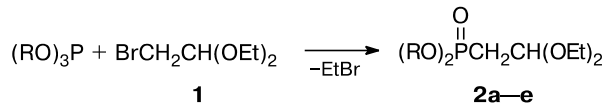
Exploration of chemistry of calix[*n*]arenes, in particular calix[4]resorcinarenes, is one of the most promising and intensively developing trends in organic chemistry.[1—3] The simplicity of their synthesis and the ability to form complexes of the "guest—host" type with various in structure organic compounds and metal ions, as well as the tendency to self-association, leading to supramolecular ensembles, are the conditions of it. All the properties described above make this class of compounds very prospective from the point of view of creation of new types of complex-forming agents and the metal ions extragents, as well as new catalytic systems. The most widely used approach to the formation of calixarene matrix includes the reaction of polyphenols with aldehydes and their derivatives. However, it has certain limitations, since the question about influence of the starting aldehyde and polyphenol structures on the composition of the forming final products is not entirely clear. It is known[4—6] that unsubstituted aliphatic and aromatic aldehydes, as well as aliphatic aldehydes with functional substituents, separated from the reaction center by four—eight carbon atoms, afford calix[4]resorcinarenes by condensation with resorcinol in acidic media. At the same time, such structures are not formed in the reaction of α-halogen-substituted aliphatic aldehydes with resorcinol.[5] Within the framework of approach under discussion, there is no information about a possibility of the synthesis of calixarenes by the reaction of resorcinol with aldehydes, containing functional substituents, separated from the carbonyl group by two—three carbon atoms.

Calix[4]resorcinarenes, bearing phosphoryl-substituted alkyl groups at the lower rim of the molecule, are of particular interest as complex-forming agents and extragents. Methods for the preparation of compounds of this type are not described in the literature, which, apparently, is mainly connected with the difficulties in the synthesis of phosphorylated aliphatic aldehydes. It should be also noted that so far the attempts to obtain calixarenes, bearing phosphorus-containing alkyl fragments at the lower rim of the molecule, by phosphorylation of the already made calixarene matrix failed and it is doubtful whether such an approach will be implemented in the nearest future. We came to a conclusion that the synthesis of calix[4]resorcinarenes, phosphorylated at the lower rim of the molecule, most likely can be fulfilled during formation of calixarene matrix. Since, as it was already mentioned above, phosphorylated aldehydes are not easily available, we tried to perform the "acetal" method, *i.e.*, we decided to involve into condensation with resorcinol phosphorylated acetals. The latter can be easily obtained by the Arbuzov reaction, *viz.*, by interaction of trialkylphosphites with bromoacetaldehyde acetal **1**. Some of the phosphono acetals were described earlier[7] and we extended this series by preparation of compounds **2a—e** (Scheme 1).

* Institut für organische Chemie, Technische Universität Dresden, 13 Mommsenstraβe, D-01062 Dresden, Germany.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1102—1106, June, 2007.

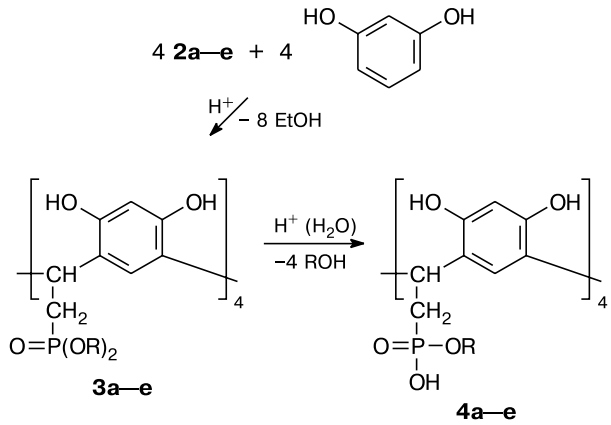
Scheme 1



R = Et (**a**), Pr (**b**), Pr^i (**c**), Bu (**d**), Bu^i (**e**)

Phosphono acetals react with resorcinol under heating in acidic media, giving rise to calix[4]resorcinarenes with phosphorylmethyl groups at the lower rim of the molecule in high yields. The synthetic outcome of the reaction is considerably affected by the experimental conditions. Thus, heating of equimolar amounts of resorcinol and acetals **2a**—**e** for 3 h at 50—60 °C leads to a mixture of full esters of phosphonic acid **3a**—**e** (δ_P 29.90 (**3a**)) as the main products and a small amount of partially hydrolyzed products **4a**—**e** (δ_P 32.21 (**4a**)) (Scheme 2). Eventually, hydrolytically labile calixarenes **3a**—**e** completely turned into compounds **4a**—**e**, which were isolated and characterized.

Scheme 2

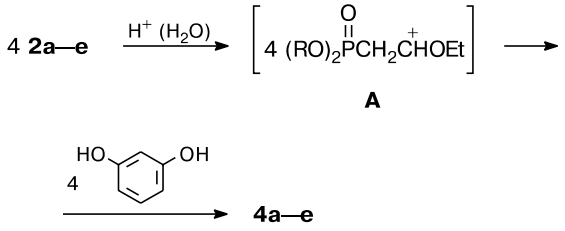


R = Et (**a**), Pr (**b**), Pr^i (**c**), Bu (**d**), Bu^i (**e**)

Calixarenes **4a**—**e** were obtained as powders white in color, soluble in ethanol and DMF, as well as in a mixture of these solvents with water. Their ^{31}P NMR spectra have one signal each in the region δ 30—33. Position of the signal slightly changes depending on the size of the R substituent. In the ^{1}H NMR spectrum, there are signals for the protons of methyl groups (δ 1.10—1.40), methylene groups adjacent to phosphorus atom (δ 1.63—3.20), methylene groups next to oxygen atom (δ 2.70—4.20), and methyne groups (δ 5.07—5.90), as well as of the protons in *ortho*- (δ 6.26—6.77) and *meta*-positions (δ 7.25—7.32) of the aromatic ring. In the IR spectra, the absorption bands of P=O (1170—1220 cm^{-1}) and OH groups (3100—3580 cm^{-1}) are observed.

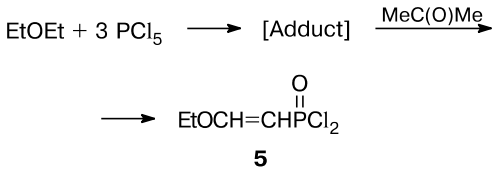
It is safe to suggest that phosphorylated carbocations **A**, resulting from protonation of acetals **2a**—**e**, serve as the intermediates in electrophilic substitution reactions between phosphono acetals and resorcinol in acidic media (Scheme 3).

Scheme 3



As it follows from the stated above, the use of the phosphorylated acetals allowed one to obtain a series of calixarenes, phosphorylated at the lower rim of the molecule. However, the insufficient versatility should be mentioned as a disadvantage of the "acetal" method, since for the synthesis of the key phosphorylated acetals, a set of phosphites of various structure is required. Taking into account the hypothesis of the participation of intermediates **A** in the key step of the formation of calixarene framework, we suggested that carbocations of the similar type can be generated by the use of ethoxyvinylphosphonates in the reaction with calixarenes in acidic media. The common representative of this series, (β-ethoxyvinyl)dichlorophosphonate (**5**), can be easily obtained from available and inexpensive reagents: diethyl ether, phosphorus pentachloride, and acetone[8] (Scheme 4).

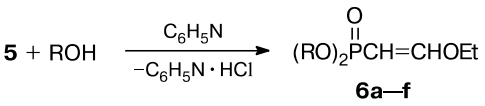
Scheme 4



The challenge for the use of dichlorophosphonate **5** is due to the possibility of easy variations of substituents at phosphorus atom. This can be accomplished by the reaction of dichlorophosphonate **5** with alcohols in the presence of a base (Scheme 5).

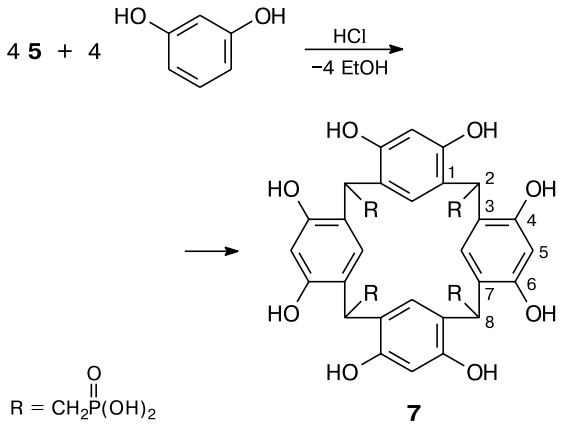
The suggested possibility of the utilization of ethoxyvinylphosphonates in the synthesis of calix[4]resorcinarenes was confirmed by reaction of dichlorophosphonate **5** with resorcinol in acidic media, which led to water-soluble calix[4]resorcinarene **7**, containing four fragments of phosphonic acid at the lower rim of calixarene matrix (Scheme 6).

Scheme 5



R = Et (**a**), Pr (**b**), Pr^i (**c**), Bu (**d**), C_7H_{15} (**e**), $C_{12}H_{25}$ (**f**)

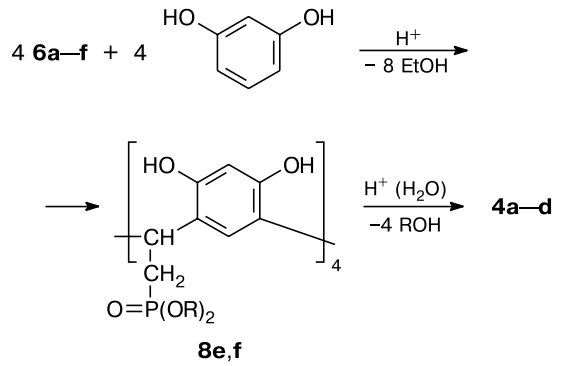
Scheme 6



The stability of compound **7** in acidic media makes it a prospective extragent of the rare earth metals from strong acidic solutions. At the same time we anticipate that the presence of acid functions will make it possible to synthesize new water-soluble salt-like structures, including the tubular ones, by its reaction with organic amines and diamines.

The acid-catalyzed reaction of vinylphosphonates **6a—f** with resorcinol in aqueous alcohols also gave calix[4]resorcinarenes (Scheme 7). It should be also noted that, similarly to the case of phosphorylated acetals, if alkyl substituent is not too long, condensation products **4a—d** with alkoxy and hydroxy groups at phosphorus atom are eventually formed. The longer the alkyl substituent in the starting phosphonate the more stable the obtained compounds are toward hydrolysis, resulting in isolation of calixarenes **8e,f** with dialkoxyphosphoryl fragments at the lower rim of the molecule.

Scheme 7



8: R = C_7H_{15} (**e**), $C_{12}H_{25}$ (**f**)

Experimental

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer (400.13, 100.62, and 166.93 MHz, respectively) in D_2O, CD_3OD, and $CDCl_3$ solutions. The δ values are given relatively to the signals of residual protons of the deuterated solvent (^{1}H, ^{13}C) or to the external standard, 85% aq. H_3PO_4 (^{31}P). IR spectra were recorded on a UR-20 spectrometer in the region 500—3700 cm^{-1} in Nujol mulls. Mass spectra were recorded on a MALDI 2 V5.2.0 instrument (1,8,9-trihydroxyanthracene as the matrix).

Diethyl 2,2-diethoxyethylphosphonate (2a). A mixture of triethylphosphite (16.6 g, 100 mmol) and bromoacetaldehyde diethyl acetal (**1**) (29.55 g, 150 mmol) was heated with stirring (4 h, 170—180 °C), distilling the forming during the reaction ethylbromide and excess of the acetal off. After fractional distillation *in vacuo*, compound **2a** was obtained (18.8 g, 74%), b.p. 92 °C (0.03 Torr), n_D^{20} 1.4280. Found (%): P, 12.14. $C_{10}H_{23}O_5P$. Calculated (%): P, 12.20. ^{1}H NMR ($CDCl_3$), δ: 0.73 (t, 6 H, Me, $^3J_{H,H}$ = 7.05 Hz); 0.86 (t, 6 H, Me, $^3J_{H,H}$ = 7.31 Hz); 1.69 (dd, 2 H, PCH_2, $^3J_{H,H}$ = 5.48 Hz, $^2J_{P,H}$ = 18.69 Hz); 3.08 (m, 2 H, OCH_2, $^3J_{H,H}$ = 7.05 Hz); 3.18 (m, 2 H, OCH_2, $^3J_{H,H}$ = 7.05 Hz); 3.63 (m, 4 H, OCH_2, $^3J_{H,H}$ = 7.31 Hz); 4.41 (dt, 1 H, CH, $^3J_{H,H}$ = 5.48 Hz, $^3J_{P,H}$ = 15.48 Hz). ^{31}P NMR ($CDCl_3$), δ: 22.21.

Dipropyl 2,2-diethoxyethylphosphonate (2b) was obtained similarly from tripropylphosphite (8.32 g, 40 mmol) and bromoacetal **1** (11.82 g, 60 mmol). The yield was 8.8 g (55%), b.p. 102—105 °C (0.03 Torr), n_D^{20} 1.4330. Found (%): P, 10.79. $C_{12}H_{27}O_5P$. Calculated (%): P, 10.99. ^{31}P NMR ($CDCl_3$), δ: 26.93.

Diisopropyl 2,2-diethoxyethylphosphonate (2c) was obtained similarly from triisopropylphosphite (8.32 g, 40 mmol) and bromoacetal **1** (11.82 g, 60 mmol). The yield was 7.36 g (46%), b.p. 70—72 °C (0.03 Torr), n_D^{20} 1.4360. Found (%): P, 10.82. $C_{12}H_{27}O_5P$. Calculated (%): P, 10.99. ^{1}H NMR ($CDCl_3$), δ: 1.03, 1.04 (both t, 3 H each, Me, $^3J_{H,H}$ = 7.05 Hz); 1.15 (d, 12 H, Me, $^3J_{H,H}$ = 6.27 Hz); 1.98 (dd, 2 H, CH_2P, $^3J_{H,H}$ = 5.48 Hz, $^2J_{P,H}$ = 18.65 Hz); 3.38 (q, 2 H, OCH_2, $^3J_{H,H}$ = 7.05 Hz); 3.48 (q, 2 H, OCH_2, $^3J_{H,H}$ = 7.05 Hz); 4.54 (m, 2 H, OCH, $^3J_{H,H}$ = 6.27 Hz, $^3J_{H,H}$ = 12.28 Hz); 4.71 (dt, 1 H, CH, $^3J_{H,H}$ = 5.48 Hz, $^3J_{P,H}$ = 7.12 Hz). ^{31}P NMR ($CDCl_3$), δ: 20.64.

Dibutyl 2,2-diethoxyethylphosphonate (2d) was obtained similarly from tributylphosphite (10.0 g, 40 mmol) and bromoacetal **1** (11.82 g, 60 mmol). The yield was 6.0 g (55%), b.p. 102—105 °C (0.03 Torr), n_D^{20} 1.4330. Found (%): P, 9.82. $C_{14}H_{31}O_5P$. Calculated (%): P, 10.00. ^{31}P NMR ($CDCl_3$), δ: 26.93.

Diisobutyl 2,2-diethoxyethylphosphonate (2e) was obtained similarly from triisobutylphosphite (5.0 g, 20 mmol) and bromoacetal **1** (5.91 g, 30 mmol). The yield was 4.0 g (65%), b.p. 118—120 °C (0.03 Torr), n_D^{20} 1.4340. Found (%): P, 9.79. $C_{14}H_{31}O_5P$. Calculated (%): P, 10.00. ^{1}H NMR ($CDCl_3$), δ: 1.07 (t, 6 H, Me, $^3J_{H,H}$ = 7.10 Hz); 1.14—1.50 (m, 14 H, $(CH_3)_2CH$); 1.93 (dd, 2 H, PCH_2, $^3J_{H,H}$ = 5.43 Hz, $^2J_{P,H}$ = 17.60 Hz); 3.42, 3.54 (both q, 2 H each, OCH_2, $^3J_{H,H}$ = 7.10 Hz);

4.63 (m, 4 H, OCH_2); 4.84 (dt, 1 H, CH, $^3J_{H,H}$ = 5.43 Hz, $^3J_{P,H}$ = 7.15 Hz). ^{31}P NMR ($CDCl_3$), δ: 26.09.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(ethoxyhydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4a).
A. Acetal **2a** (3.69 g, 14.5 mmol) was added dropwise with cooling to a mixture of resorcinol (1.6 g, 14.5 mmol), water (10 mL), ethanol (5 mL), and conc. hydrochloric acid (3.6 mL). The reaction mixture was heated with stirring (1 h, 50—60 °C) and kept for 10 h at 20 °C. The oil layer was decanted, triturated with acetonitrile, and filtered. The solvent was evaporated and the residue was dried *in vacuo* (40 °C, 0.04 Torr) until the weight was constant. Compound **4a** was obtained (2.0 g, 56%), m.p. 193—195 °C. Found (%): C, 48.81; H, 5.72; P, 12.88. $C_{40}H_{52}O_{20}P_4$. Calculated (%): C, 49.18; H, 5.33; P, 12.70. ^{1}H NMR (CD_3OD), δ: 1.40 (t, 12 H, Me, $^3J_{H,H}$ = 7.0 Hz); 1.63 (m, 8 H, CH_2P); 3.95 (m, 8 H, OCH_2); 5.07 (br.m, 4 H, CH); 6.50 (s, 4 H, *o*-H arom.); 7.25 (s, 4 H, *m*-H arom.). ^{13}C NMR ((CD_3)$_2$CO), δ: 17.35 (q, Me, $^1J_{C,H}$ = 124.4 Hz); 63.45 (t, CH_2O, $^1J_{C,H}$ = 142.6 Hz); 79.64 (dd, CH, $^1J_{C,H}$ = 149.0 Hz, $^2J_{C,P}$ = 7.0 Hz); 102.55 (d, *m*-C arom., $^1J_{C,H}$ = 155.9 Hz); 123.4 (s, C arom.—CH); 139.25 (d, *o*-C arom., $^1J_{C,H}$ = 153.55 Hz); 154.37 (s, C arom.—OH). ^{31}P NMR (CD_3OD), δ: 32.21. MS, *m/z*: 976.

B. A mixture of resorcinol (0.61 g, 5.5 mmol), water (3 mL), ethanol (3 mL), conc. hydrochloric acid (0.6 mL), and phosphonate **6a** (1.15 g, 5.5 mmol) was heated with stirring (1 h, 50 °C) and kept 3 days at 20 °C. The solvent was evaporated *in vacuo*, the residue was re-precipitated from ethanol with water, the product was filtered off and kept *in vacuo* (40 °C, 0.04 Torr) until the weight was constant. The yield was 1.2 g (85%), m.p. 192—194 °C. Found (%): C, 49.87; H, 5.47; P, 12.42. $C_{40}H_{52}O_{20}P_4$. Calculated (%): C, 49.18; H, 5.33; P, 12.70. IR, ν/cm^{-1}: 1190 (P=O); 1615 (C=C arom.); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 32.23.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(propoxyhydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4b).
A. Product **4b** (8.1 g, 79%), m.p. 201—203 °C, was obtained similarly to compound **4a** (method ***A***) from resorcinol (4.4 g, 40 mmol), water (50 mL), ethanol (50 mL), conc. hydrochloric acid (7.75 mL), and acetal **2b** (11.28 g, 40 mmol). Found (%): C, 50.45; H, 5.53; P, 12.07. $C_{44}H_{60}O_{20}P_4$. Calculated (%): C, 51.16; H, 5.81; P, 12.02. ^{1}H NMR (CD_3OD), δ: 1.49 (br.m, 20 H, CH_3CH_2); 1.81 (m, 8 H, CH_2P); 4.01 (m, 8 H, OCH_2); 5.10 (br.m, 4 H, CH); 6.23 (s, 4 H, *o*-H arom.); 7.30 (s, 4 H, *m*-H arom.). IR, ν/cm^{-1}: 1160 (P=O); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 33.30.

B. Product **4b** (1.41 g, 89%), m.p. 201—203 °C, was obtained similarly to compound **4a** (method ***B***) from resorcinol (0.68 g, 6.18 mmol), water (8 mL), ethanol (6 mL), conc. hydrochloric acid (1.1 mL), and vinylphosphonate **6b** (1.45 g, 6.18 mmol). Found (%): C, 51.22; H, 5.62; P, 11.79. $C_{44}H_{60}O_{20}P_4$. Calculated (%): C, 51.16; H, 5.81; P, 12.02. IR, ν/cm^{-1}: 1160 (P=O); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 33.15.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(isopropoxyhydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4c).
A. Product **4c** (4.43 g, 86%), m.p. 233—235 °C (decomp.), was obtained similarly from resorcinol (2.2 g, 20 mmol), water (10 mL), ethanol (10 mL), conc. hydrochloric acid (1.0 mL), and acetal **2c** (5.64 g, 20 mmol). Found (%): C, 50.97; H, 5.56; P, 11.57. $C_{44}H_{60}O_{20}P_4$. Calculated (%): C, 51.16; H, 5.81; P, 12.02. ^{1}H NMR (CD_3OD), δ: 1.46 (d, 24 H, Me, $^3J_{H,H}$ = 6.8 Hz); 1.83 (m, 8 H, CH_2P); 3.85 (m, 4 H, OCH); 5.17 (br.m, 4 H, CH); 6.26 (s, 4 H, *o*-H arom.); 7.28 (s, 4 H, *m*-H arom.). IR, ν/cm^{-1}: 1162 (P=O); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 30.82.

B. Product **4c** (0.45 g, 89%), m.p. 233—235 °C (decomp.), was obtained similarly from resorcinol (0.22 g, 2 mmol), water (3 mL), ethanol (2 mL), conc. hydrochloric acid (0.4 mL), and phosphonate **6c** (0.47 g, 2 mmol). Found (%): C, 50.94; H, 5.40; P, 11.54. $C_{44}H_{60}O_{20}P_4$. Calculated (%): C, 51.16; H, 5.81; P, 12.02. IR, ν/cm^{-1}: 1160 (P=O); 1610 (C=C arom.); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 30.90.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(butoxyhydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4d).
A. Product **4d** (4.0 g, 74%), m.p. 166—168 °C, was obtained similarly from resorcinol (2.2 g, 20 mmol), water (8 mL), ethanol (30 mL), conc. hydrochloric acid (2.4 mL), and acetal **2d** (6.2 g, 20 mmol). Found (%): C, 52.55; H, 6.43; P, 11.85. $C_{48}H_{68}O_{20}P_4$. Calculated (%): C, 52.94; H, 6.25; P, 11.40. ^{1}H NMR (CD_3OD), δ: 1.10 (t, 12 H, Me, $^3J_{H,H}$ = 7.0 Hz); 1.55 (br.m, 16 H, CH_2); 1.89 (m, 8 H, CH_2P); 4.20 (m, 8 H, OCH_2); 5.17 (br.m, 4 H, CH); 6.48 (s, 4 H, *o*-H arom.); 7.32 (s, 4 H, *m*-H arom.). ^{13}C NMR (CD_3OD), δ: 13.99 (q, Me, $^1J_{C,H}$ = 124.4 Hz); 19.64 (t, $(CH_2)_2$, $^1J_{C,H}$ = 122.06 Hz); 33.48 (t, CH_2P, $^1J_{C,H}$ = 125.60 Hz); 66.71 (t, CH_2O, $^1J_{C,H}$ = 142.60 Hz); 69.65 (dd, CH, $^1J_{C,H}$ = 150.90 Hz, $^2J_{C,P}$ = 7.04 Hz); 104.05 (d, *m*-C arom., $^1J_{C,H}$ = 155.90 Hz); 122.53 (s, C arom.—CH); 129.96 (d, *o*-C arom., $^1J_{C,H}$ = 154.60 Hz); 154.26 (s, C arom.—OH). ^{31}P NMR (CD_3OD), δ: 31.14. MS, *m/z*: 1088.

B. Product **4d** (4.5 g, 84%), m.p. 166—168 °C, was obtained similarly from resorcinol (2.20 g, 20 mmol), water (10 mL), ethanol (7 mL), conc. hydrochloric acid (2 mL), and vinylphosphonate **6d** (5.28 g, 20 mmol). Found (%): C, 52.48; H, 6.39; P, 11.09. $C_{48}H_{68}O_{20}P_4$. Calculated (%): C, 52.94; H, 6.25; P, 11.40. IR, ν/cm^{-1}: 1190 (P=O); 1615 (C=C arom.); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 31.76.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(isobutoxyhydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (4e) was obtained similarly (method ***A***) from resorcinol (1.1 g, 10 mmol), water (20 mL), ethanol (20 mL), conc. hydrochloric acid (4.75 mL), and phosphono acetal **2e** (3.1 g, 10 mmol). The yield was 6.8 g (67%), m.p. 247—250 °C (decomp.). Found (%): C, 52.60; H, 6.15; P, 11.04. $C_{48}H_{68}O_{20}P_4$. Calculated (%): C, 52.94; H, 6.25; P, 11.40. IR, ν/cm^{-1}: 1165 (P=O); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 32.90.

Diethyl 2-ethoxyvinylphosphonate (6a). A solution of phosphonic dichloroanhydride **5** [8] (6 g, 32 mmol) in benzene (12.0 mL) was added dropwise with stirring and cooling to a mixture of ethanol (2.94 g, 64 mmol) and pyridine (5.2 mL, 64 mmol) in benzene (20 mL). The reaction mixture was stirred for 3 h at 20 °C, the formed precipitate of pyridine hydrochlo-

ride was filtered off, the filtrate was concentrated, and the residue was fractionally distilled. Compound **6a** (4.7 g, 72%) was obtained, b.p. 83 °C (0.04 Torr), n_D^{20} 1.4500. Found (%): P, 14.81. $C_8H_{17}O_4P$. Calculated (%): P, 14.90. ^{1}H NMR ($CDCl_3$), δ: 0.81 (t, 3 H, $C\underline{H}_3CH_2OC$, $^3J_{H,H}$ = 6.86 Hz); 0.84 (t, 6 H, $C\underline{H}_3CH_2OP$, $^3J_{H,H}$ = 7.20 Hz); 3.42 (q, 2 H, $COCH_2$, $^3J_{H,H}$ = 6.86 Hz); 3.54 (dq, 4 H, CH_2OP, $^3J_{H,H}$ = 7.20 Hz, $^3J_{P,H}$ = 7.20 Hz); 4.21 (dd, 1 H, CHP, $^3J_{H,H}$ = 13.28 Hz, $^2J_{P,H}$ = 9.95 Hz); 6.87 (dd, 1 H, OCH, $^3J_{H,H}$ = 13.28 Hz, $^3J_{P,H}$ = 11.66 Hz). IR, ν/cm^{-1}: 950—1050 ($POCH_2$); 1250 (P=O); 1615 (C=C); 3030 (=HC). ^{31}P NMR (CD_3OD), δ: 22.23.

Dipropyl 2-ethoxyvinylphosphonate (6b) was obtained similarly from propanol (3.12 g, 52 mmol), pyridine (4.2 mL, 52 mmol), benzene (25 mL), and compound **5** (4.9 g, 26 mmol). The yield was 4.2 g (69%), b.p. 90—92 °C (0.04 Torr), n_D^{20} 1.4510. Found (%): P, 13.06. $C_{10}H_{21}O_4P$. Calculated (%): P, 13.14. ^{1}H NMR ($CDCl_3$), δ: 0.56 (t, 6 H, Me, $^3J_{H,H}$ = 7.36 Hz); 0.94 (t, 3 H, Me, $^3J_{H,H}$ = 6.99 Hz); 1.29 (m, 4 H, CH_2); 3.53 (m, 6 H, OCH_2P, OCH_2); 4.32 (dd, 1 H, =CHP, $^3J_{H,H}$ = 13.60 Hz, $^2J_{P,H}$ = 9.56 Hz); 6.79 (dd, 1 H, OCH=, $^3J_{H,H}$ = 13.60 Hz, $^3J_{P,H}$ = 11.77 Hz). IR, ν/cm^{-1}: 1240 (P=O); 1620 (C=C); 3040 (=HC). ^{31}P NMR ($CDCl_3$), δ: 21.69.

Diisopropyl 2-ethoxyvinylphosphonate (6c) was obtained similarly from propan-2-ol (3.12 g, 52 mmol), pyridine (4.2 mL, 52 mmol), and compound **5** (4.94 g, 26 mmol). The yield was 3.6 g (59%), b.p. 92—93 °C (0.04 Torr), n_D^{20} 1.4475. Found (%): P, 12.87. $C_{10}H_{21}O_4P$. Calculated (%): P, 13.14. ^{1}H NMR ($CDCl_3$), δ: 0.88 (br.m, 15 H, Me, ($C\underline{H}_3$)CH); 3.46 (q, 2 H, OCH_2,$^3J_{H,H}$ = 6.62 Hz); 4.18 (m, 2 H, CHOP); 4.29 (dd, 1 H, =CHP, $^3J_{H,H}$ = 13.24 Hz, $^2J_{P,H}$ = 10.29 Hz); 6.75 (dd, 1 H, OCH=, $^3J_{H,H}$ = 13.24 Hz, $^3J_{P,H}$ = 12.71 Hz). IR, ν/cm^{-1}: 1260 (P=O); 1635 (C=C); 3030 (=HC). ^{31}P NMR ($CDCl_3$), δ: 19.46.

Dibutyl 2-ethoxyvinylphosphonate (6d) was obtained similarly from *n*-butanol (8.35 g, 44 mmol), pyridine (7.1 mL, 88 mmol), and compound **5** (8.35 g, 44 mmol). The yield was 8.2 g (70%), b.p. 142 °C (0.02 Torr), n_D^{20} 1.4720. Found (%): P, 11.47. $C_{12}H_{25}O_4P$. Calculated (%): P, 11.74. ^{31}P NMR ($CDCl_3$), δ: 21.64.

Diheptyl 2-ethoxyvinylphosphonate (6e) was obtained similarly from heptanol (11.14 g, 96 mmol), pyridine (7.7 mL, 96 mmol), and compound **5** (9.0 g, 48 mmol). The yield was 10.9 g (66%), b.p. 170 °C (0.02 Torr). Found (%): P, 9.33. $C_{16}H_{33}O_4P$. Calculated (%): P, 9.68. IR, ν/cm^{-1}: 1240 (P=O); 1620 (C=C); 3030 (=HC). ^{31}P NMR ($CDCl_3$), δ: 21.62.

Didodecyl 2-ethoxyvinylphosphonate (6f) was obtained similarly from dodecanol (6.51 g, 35 mmol), pyridine (2.8 mL, 35 mmol), and compound **5** (3.30 g, 17.5 mmol). The yield was 7.2 g (84%). Compound **6f** was further used without additional purification. Found (%): P, 5.94. $C_{28}H_{57}O_4P$. Calculated (%): P, 6.35. IR, ν/cm^{-1}: 1250 (P=O); 1620 (C=C); 3030 (=HC). ^{31}P NMR ($CDCl_3$), δ: 21.52.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(dihydroxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (7). A mixture of resorcinol (0.76 g, 6.9 mmol), water (7 mL), ethanol (5 mL), conc. hydrochloric acid (1 mL), and compound **5** (1.30 g, 6.9 mmol) was heated with stirring (0.5 h, 60 °C) and kept for 5 days at 20 °C. The solvent was evaporated, the residue was re-precipitated from ethanol with diethyl ether, the product was dried *in vacuo* (40 °C, 0.04 Torr) until the weight was constant. Product **7** was obtained (1.1 g, 92%), m.p. >350 °C. Found (%): C, 44.35; H, 4.71; P, 13.48. $C_{32}H_{36}O_{20}P_4$. Calculated (%): C, 44.44; H, 4.16; P, 13.05. ^{1}H NMR (D_2O), δ: 1.07 (m, 8 H, PCH_2); 3.79 (m, 4 H, CH); 6.28 (s, 4 H, *o*-H arom.); 7.04 (s, 4 H, *m*-H arom.). IR, ν/cm^{-1}: 995—1024 (P(O)OH); 1195 (P=O); 1620 (C=C arom.); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 28.28.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(diheptyloxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (8e) was obtained similarly to compound **4a** from resorcinol (1.20 g, 11 mmol), water (12 mL), ethanol (8 mL), conc. hydrochloric acid (1.8 mL), and phosphonate **6e** (3.80 g, 11 mmol). The yield was 3.8 g (85%), m.p. 138 °C. Found (%): C, 63.67; H, 9.35; P, 8.02. $C_{88}H_{148}O_{20}P_4$. Calculated (%): C, 64.07; H, 8.98; P, 7.62. IR, ν/cm^{-1}: 1240 (P=O); 1610 (C=C arom.); 3100—3580 (OH). ^{31}P NMR (CD_3OD), δ: 32.77.

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetra[(didodecyloxyphosphoryl)methyl]pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (8f) was obtained similarly from resorcinol (1.51 g, 13.7 mmol), water (15 mL), ethanol (10 mL), conc. hydrochloric acid (2.3 mL), and vinylphosphonate **6f** (6.69 g, 13.7 mmol). The yield was 6.5 g (89%), m.p. 128 °C. Found (%): C, 69.18; H, 10.98; P, 5.36. $C_{128}H_{228}O_{20}P_4$. Calculated (%): C, 69.56; H, 10.32; P, 5.61. IR, ν/cm^{-1}: 1210 (P=O); 1620 (C=C); 3100—3580 (OH). ^{31}P NMR ($CDCl_3$), δ: 33.25.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32136).

References

1. C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, 1989, 132.
2. J. Vicens and V. Böhmer, *Calixarenes*: *a Versatile Class of Macrocyclic Compounds*, Kluwer Acad. Publ., Dordrecht, 1991, 15.
3. Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens, *Calixarenes 2001*, Kluwer Acad. Publ., Dordrecht—Boston—London, 2001.
4. R. J. Egbering, P. L. Cobben, W. Verboom, S. Harkema, and D. N. Reinhoudt, *J. Inclusion Phenom.*, 1992, 151.
5. L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, and D. J. Cram, *J. Org. Chem.*, 1989, 1305.
6. E. U. Thoden van Velzen, J. F. Engbersen, and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1994, 3597.
7. V. V. Kormachev and M. S. Fedoseev, *Preparativnaya khimiya fosfora* [*The Preparative Chemistry of Phosphorus*], UrO RAS Publ., Perm, 1992, 189 (in Russian).
8. A.s. 883047; *Byul. Izobret.*, 1981, No. 43.

Received December 2, 2005;
in revised form February 19, 2006