Russian Journal of General Chemistry, Vol. 73, No. 6, 2003, pp. 909–917. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 6, 2003, pp. 961–969.

Phosphorylation of Dialkylaminomethyl-substituted Calix[4]resorcinolarenes with Hexaalkylphosphorous Triamides and Phosphorus(V) Dichlorides

A. R. Burilov, D. I. Kharitonov, N. I. Bashmakova, T. B. Makeeva, I. L. Nikolaeva, M. A. Pudovik, and A. I. Konovalov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Received June 1, 2001

Abstract — A series of aminophosphino cavitands were synthesized by reactions of dialkylaminomethyl-substituted calix[4]resorcinolarenes with hexaalkylphosphorous triamides, and their properties were studied. New aminoalkylated (thio)phosphato(phosphonato) cavitands were prepared by phosphorylation of dialkylaminomethyl-substituted calix[4]resorcinolarenes with phosphorus(V) dichlorides in the presence of a base. Their reactions with electrophilic alkylating agents (methyl trifluoromethanesulfonate, methyl iodide, and triethyloxonium tetrafluoroborate) were examined.

Up to now, some experimental data have been reported on cyclophosphorylation of calix[4]resorcinolarenes having no other substituents in the aromatic rings [1–4]. We have recently succeeded in synthesizing cyclic chlorophosphates on the basis of calix[4]resorcinolarenes [5]. These products can also be modified. The present state-of-the-art in the calixarene chemistry is characterized by extensive development of methods for their functionalization at the oxygen and carbon atoms, which make it possible to introduce various reactive moieties capable of participating in new reactions. Such reactions could lead to a variety of spatially organized structures, e.g., cavitands, carceplexes, hemicarceplexes, etc. [6].

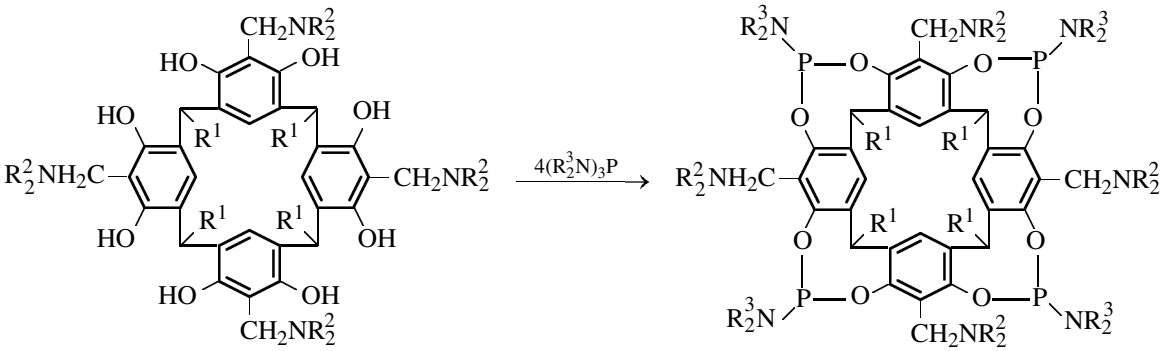
Calix[4]resorcinolarenes having aminomethyl fragments in the *ortho* position with respect to the aromatic hydroxy groups attract a keen interest as initial sterically organized matrix. The first representative of this series has recently been synthesized by the Mannich reaction of calixarene, formaldehyde, and secondary amine [7]. We have developed a convenient procedure for the preparation of short- and long-chain aminoalkylated calix[4]resorcinolarenes by reaction of unsubstituted calixarenes with bis(dimethylamino)-methane [8]. It is important that the presence in calixarene molecules of dialkylaminomethyl groups provides the possibility for their further quaternization with a view to improve their solubility in polar solvents. Phosphorylation of dialkylaminoalkyl-substituted calix[4]resorcinolarenes was not reported previously. In the present work we examined their reactions with hexaalkyl phosphorous triamides and phosphorus(V) acid dichlorides.

In keeping with published data, calix[4]resorcinolarenes react with hexaalkylphosphorous triamides at a molar reactant ratio of 1 : 4 at 20°C, yielding P(III)-containing cavitands [9, 10]. Introduction of dialkylaminomethyl fragments into the *ortho* positions to the hydroxy groups turned out to considerably reduce the reactivity of calix[4]resorcinolarenes toward phosphorous triamides. A probable reason is formation in the initial structures of a different intramolecular hydrogen bond system which involves the nitrogen atoms, which leads to reduced acidity of the phenolic hydroxy groups.

Dialkylaminomethyl-substituted calix[4]resorcinolarenes **Ia**–**Ii** failed to react with hexaalkylphosphorous triamides at room temperature. The reaction occurs only on heating in boiling benzene (8–12 h). Regardless of the initial calixarene–phosphorous triamide ratio (1 : 1 to 1 : 4), the phosphorylated products had a composition of 1 : 4; the reactant ratio affects only the yield of final cavitands **IIa**–**IIk**.

Unlike unsubstituted analogs, macrocyclic P(III)-containing cavitands **IIa**–**IIk** are readily hydrolyzed by the action of atmospheric moisture. Interestingly, cavitand **IIc** having methyl groups on all nitrogen atoms is capable of undergoing an unusual ring–chain transformation with participation of water molecules. Hydrolytic cleavage of the endocyclic P–O bonds in the dioxaphosphocine fragments gives P–H derivative

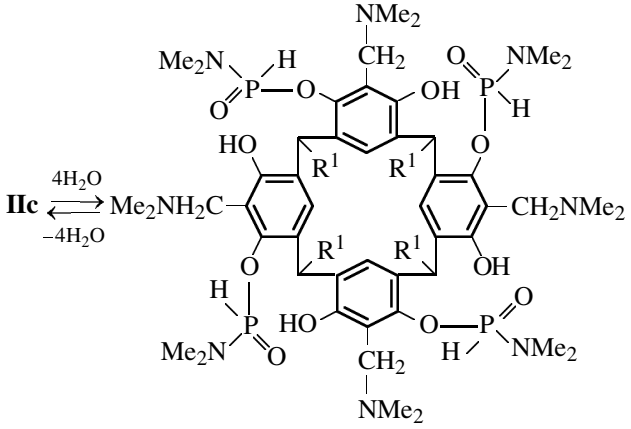
1070-3632/03/7306-0909 $25.00 © 2003 MAIK "Nauka/Interperiodica"



Ia–Ii **IIa–IIk**

I, $R^1 = R^2 =$ Me (**a**); $R^1 =$ Me, $R^2 =$ Et (**b**); $R^1 =$ Et, $R^2 =$ Me (**c**); $R^1 = R^2 =$ Et (**d**); $R^1 =$ Et, $R^2 =$ Pr (**e**); $R^1 =$ Pr, $R^2 =$ Me (**f**); $R^1 = C_6H_{13}$, $R^2 =$ Me (**g**); $R^1 = C_6H_{13}$, $R^2 =$ Et (**h**); $R^1 = C_{11}H_{23}$, $R^2 =$ Me (**i**); **II**, $R^1 = R^2 = R^3 =$ Me (**a**); $R^1 = R^2 =$ Me, $R^3 =$ Et (**b**); $R^1 =$ Et, $R^2 = R^3 =$ Me (**c**); $R^1 = R^3 =$ Me, $R^2 =$ Et (**d**); $R^1 = R^2 =$ Et, $R^3 =$ Me (**e**); $R^1 =$ Et, $R^2 =$ Pr, $R^3 =$ Me (**f**); $R^1 =$ Pr, $R^2 = R^3 =$ Me (**g**); $R^1 = C_6H_{13}$, $R^2 = R^3 =$ Me (**h**); $R^1 = C_6H_{13}$, $R^2 =$ Me, $R^3 =$ Et (**i**); $R^1 = C_{11}H_{23}$, $R^2 = R^3 =$ Me (**j**); $R^1 =$ Me, $R^2 = R^3 =$ Et (**k**).

III. Heating of the latter in benzene with simultaneous removal of water (azeotrope) results in the reverse ring closure to initial cyclic P(III)-cavitand **IIc**. No such transformation occurs with the other alkyl derivatives, so that the reaction is specific for the given system.

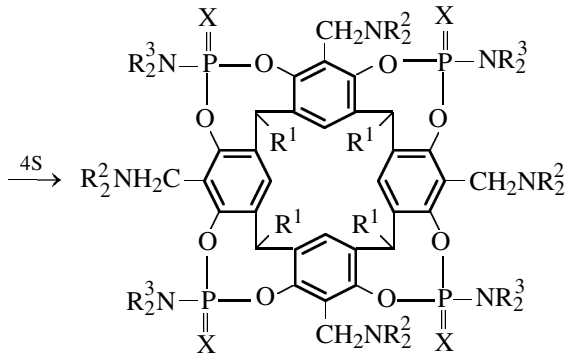


III

Cavitands **IIc**, **IId**, **IIh**, **IIi**, and **IIk** take up elemental sulfur on prolonged heating to afford the corresponding stable phosphoramidothioates **IVa**–**IVe**.

We tried to extend the series of phosphorylating agents suitable for cyclophosphorylation of dialkylaminomethylated calix[4]resorcinolarenes. For this purpose, we examined their reactions with phosphorus (V) acid dichlorides. According to published data [1–4], P(V) dichlorides react with calix[4]resorcinolarenes in the presence of a base (such as triethylamine or pyridine) to afford cyclic phosphorus-containing cavitands. We anticipated that a combination of dialkylaminomethyl and hydroxy groups in a single molecule will make it possible to effect cyclophosphorylation of calix[4]resorcinolarenes with P(V) dichlorides in the absence of an external base, for the substrate molecule contains four basic tertiary amino groups. The final products of such reactions could be novel cavitands having both cyclic phosphorus-containing and ammonium fragments.

IIc, IId, IIh, IIi, IIk

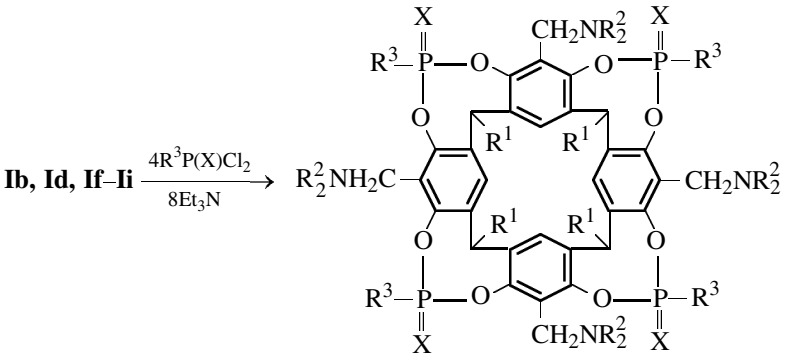


IVa–IVe

IV, $R^1 =$ Et, $R^2 = R^3 =$ Me (**a**); $R^1 = C_6H_{13}$, $R^2 = R^3 =$ Me (**b**); $R^1 = C_6H_{13}$, $R^2 =$ Me, $R^3 =$ Et (**c**); $R^1 = R^3 =$ Me, $R^2 =$ Et (**d**); $R^1 =$ Me, $R^2 = R^3 =$ Et (**e**).

We have found that reactions of dialkylaminomethylcalix[4]resorcinolarenes with dichlorophosphates and dichlorophosphonates give unstable cyclophosphorylation products which can be detected by ^{31}P NMR spectroscopy. These intermediates are then converted into complex mixtures of cyclic and acyclic

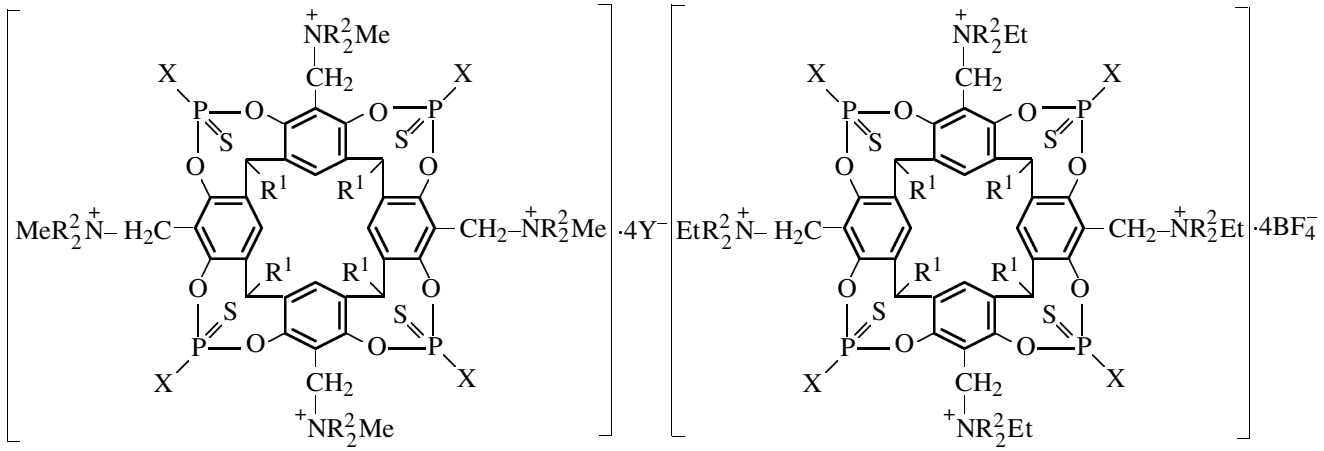
phosphorylation products which are very difficult to separate. Therefore, the experimental conditions were changed, and phosphorylation of calixarenes **Ib**, **Id**, and **If**–**Ii** with ethyl phosphorodichloridate, *S*-ethyl phosphorodichlorothioate, phenyl phosphorodichloridate, *O*-phenyl phosphorodichlorothioate, and phenylphosphonothioic dichloride (ratio 1 : 4) was performed in the presence of 8 equiv of triethylamine. The reactions took 24 h at 20°C and afforded cyclic P(V)-containing cavitands **Va**–**Vm**. Among these, stable were compounds having a thiolic or thionic sulfur atom on the phosphorus. According to the ^{31}P NMR data, the oxygen analogs underwent fast transformations to give inseparable mixtures of products.



Va–**Vm**

V, R^1 = Me, R^2 = Et, R^3 = SEt, X = O (**a**); R^1 = Me, R^2 = Et, R^3 = OPh, X = S (**b**); R^1 = Me, R^2 = Et, R^3 = Ph, X = S (**c**); R^1 = R^2 = Et, R^3 = Ph, X = S (**d**); R^1 = Pr, R^2 = Me, R^3 = OPh, X = S (**e**); R^1 = C_6H_{13}, R^2 = Me, R^3 = SEt, X = O (**f**); R^1 = C_6H_{13}, R^2 = Me, R^3 = OPh, X = S (**g**); R^1 = C_6H_{13}, R^2 = Me, R^3 = Ph, X = S (**h**); R^1 = C_6H_{13}, R^2 = Et, R^3 = SEt, X = O (**i**); R^1 = C_6H_{13}, R^2 = Et, R^3 = OPh, X = S (**j**); R^1 = C_6H_{13}, R^2 = Et, R^3 = Ph, X = S (**k**); R^1 = $C_{11}H_{23}$, R^2 = Me, R^3 = SEt, X = O (**l**); R^1 = $C_{11}H_{23}$, R^2 = Me, R^3 = OPh, X = S (**m**).

The resulting cyclic phosphorus-containing dialkylaminomethylated cavitands were brought into reactions with electrophilic alkylating agents, methyl trifluoromethanesulfonate, triethyloxonium tetrafluoroborate, and methyl iodide. The alkylation with the above reagents involved all four nitrogen atoms of the substrate, regardless of the initial reactant ratio.



VIa–**VIe** **VIIa**–**VIIf**

VI, R^1 = Me, R^2 = Et, X = NEt_2, Y = $CF_3SO_3^-$ (**a**); R^1 = C_6H_{13}, R^2 = Me, X = NEt_2, Y = $CF_3SO_3^-$ (**b**); R^1 = R^2 = Et, X = OPh, Y = $CF_3SO_3^-$ (**c**); R^1 = C_6H_{13}, R^2 = Me, X = NEt_2, Y = I^- (**d**); R^1 = C_6H_{13}, R = Me, X = OPh, Y = I^- (**e**); **VII**, R^1 = Me, R^2 = Et, X = NMe_2 (**a**); R^1 = Me, R^2 = Et, X = NEt_2 (**b**); R^1 = C_6H_{13}, R^2 = Me, X= NMe_2 (**c**); R^1 = C_6H_{13}, R_2 = Me, X = NEt_2 (**d**); R^1 = C_6H_{13}, R^2 = Me, X = Ph (**e**); R^1 = Me, R^2 = Et, X = OPh (**f**).

Table 1. Yields, melting points, and elemental analyses of compounds **IIa**–**IIk**, **III**, **IVa**–**IVe**, and **Va**–**Vn**

Comp. no.	Yield, %	mp, °C	Found, %					Formula	Calculated, %				
			C	H	N	P	S		C	H	N	P	S
IIa	84	240[a]	57.51	7.33		10.92		$C_{52}H_{76}N_8O_8P_4$	58.64	7.14		11.65	
IIb	67	230[a]	62.19	8.58	9.67	9.81		$C_{60}H_{92}N_8O_8P_4$	61.22	7.82	9.52	10.54	
IIc	96	140[a]	59.58	7.32	6.93	10.85		$C_{56}H_{84}N_8O_8P_4$	60.00	7.50	6.89	11.07	
IId	77	230[a]	61.45	8.28	9.17	9.61		$C_{60}H_{92}N_9O_8P_4$	61.22	7.82	9.52	10.54	
IIe	78	160[a]	61.97	7.99	9.13	9.77		$C_{64}H_{100}N_8O_8P_4$	62.33	8.11	9.09	10.06	
IIf	64	160[a]			8.43	8.98		$C_{72}H_{116}N_8O_8P_4$			8.33	9.22	
IIg	70	170[a]	61.47	7.90	9.00	10.50		$C_{60}H_{92}N_8O_8P_4$	61.22	7.82	9.52	10.54	
IIh	77	180[a]	65.02	8.60	8.42	9.29		$C_{72}H_{116}N_8O_8P_4$	64.28	8.63	8.33	9.22	
IIi	60	130[a]	66.32	9.30		8.29		$C_{80}H_{132}N_8O_8P_4$	65.93	9.07		8.52	
IIj	61	200[a]	67.44	9.14	6.62	7.17		$C_{92}H_{156}N_8O_8P_4$	67.98	9.60	6.90	7.63	
IIk	64	240[a]	63.05	7.93	8.17	9.14		$C_{68}H_{108}N_8O_8P_4$	63.35	8.38	8.69	9.62	
III	100	170[a]	56.89	7.45		10.29		$C_{56}H_{92}N_8O_{12}P_4$	56.38	7.72		10.40	
IVa	99	300[a]	54.11	6.42	8.98	9.76	9.67	$C_{56}H_{84}N_8O_8P_4S_4$	53.85	6.73	8.97	9.93	10.25
IVb	87	300[a]	58.25	7.21	7.11	8.04	8.25	$C_{72}H_{116}N_8O_8P_4S_4$	58.69	7.88	7.61	8.42	8.69
IVc	97	300[a]	60.45	8.13	7.14	7.52	8.02	$C_{80}H_{132}N_8O_8P_4S_4$	60.61	8.33	7.07	7.83	8.08
IVd	93	300[a]	55.11	6.79	8.22	8.89	9.54	$C_{60}H_{92}N_8O_8P_4S_4$	55.21	7.05	8.59	9.51	9.81
IVe	93	300[a]	57.11	7.33	7.46	8.20	8.66	$C_{68}H_{108}N_8O_8P_4S_4$	57.62	7.63	7.91	8.76	9.04
Va	87	210	55.33	7.43	4.53		10.85	$C_{60}H_{88}N_4O_{12}P_4S_4$	55.04	6.72	4.28		9.78
Vb	86	203	60.23	6.33	3.74	8.43		$C_{76}H_{88}N_4O_{12}P_4S_4$	60.80	5.86	3.73	8.26	
Vc	77	127	62.96	5.62	2.99	8.48	8.83	$C_{76}H_{88}N_4O_8P_4S_4$	63.51	6.13	3.89	8.63	8.91
Vd	80	191	64.22	6.57	3.49	8.49	8.04	$C_{80}H_{96}N_4O_8P_4S_4$	64.34	6.43	3.75	8.31	8.57
Ve	85	174	61.95	5.99	4.07	8.57	8.86	$C_{76}H_{88}N_4O_{12}P_4S_4$	60.80	5.86	3.73	8.26	8.53
Vf	82	209	59.01	7.33	3.56	7.97	8.33	$C_{72}H_{112}N_4O_{12}P_4S_4$	58.52	7.58	3.79	8.39	8.69
Vg	81	167	62.95	6.99	3.58	8.12	7.32	$C_{88}H_{112}N_4O_{12}P_4S_4$	63.29	6.71	3.35	7.43	7.69
Vh	92	174	64.97	7.03	3.02	7.45	7.38	$C_{88}H_{112}N_4O_8P_4S_4$	65.81	6.98	3.49	7.72	8.00
Vi	85	212	60.11	7.90	3.44	6.72		$C_{80}H_{128}N_4O_{12}P_4S_4$	60.45	8.06	3.53	7.81	
Vj	87	156	64.13	7.40	3.07	7.10		$C_{96}H_{128}N_4O_{12}P_4S_4$	64.71	7.19	3.15	6.96	
Vk	89	176	67.41	6.86	3.08	7.02	6.60	$C_{96}H_{128}N_4O_8P_4S_4$	67.13	7.45	3.26	7.22	7.45
Vl	87	210	63.31	7.97	3.15	6.90	7.58	$C_{92}H_{152}N_4O_{12}P_4S_4$	62.87	8.65	3.19	7.06	7.28
Vm	79	132	65.79	8.38	3.01	6.22	6.35	$C_{108}H_{152}N_4O_{12}P_4S_4$	66.53	7.80	2.87	6.36	6.57
Vn	80	200[a]	66.11	6.57	3.29	8.33		$C_{80}H_{96}N_4O_{12}P_4S_4$	66.85	6.68	3.90	8.63	

[a] Decomposition point.

In keeping with the data of [11], alkylation with alkyl halides of P(III)-containing cavitands derived from calix[4]resorcinolarenes gives two kinds of products, quasiphosphonium salts and phosphoranes. The alkylation of cavitand **IIc** was performed using 4 and 8 equiv of methyl trifluoromethanesulfonate. According to the ^{1}H NMR spectra, the reactions take a few minutes at 20°C and involve initial alkylation of the nitrogen atoms in the dialkylaminomethyl groups (reactant ratio 1 : 4) with formation of the corresponding ammonium fragments. In the presence of excess alkylating agent (reactant ratio 1 : 8), alkylation of the phosphorus atoms also occurs to give quasiphosphonium salts (δ_P 47–58 ppm). However, the products were unstable, and we fialed to isolate them. Within a few hours, a complex mixture of products is formed (^{31}P NMR data). The structure of the isolated products was confirmed by the data of elemental analysis and ^{1}H and ^{31}P NMR and IR spectra (Tables 1–5).

Thus, the chemical behavior of cyclic phosphorylated dialkylaminomethyl-substituted calix[4]resorcinolarenes in reactions with electrophilic alkylating agents is determined by the presence of different basic centers. The reactions involve primarily the most basic and, probably, spatially more accessible nitrogen atoms of the dialkylaminomethyl groups. The products are the corresponding ammonium salts which can be regarded as reperesentatives of a new class of

Table 2. Yields, melting points, and elemental analyses of compounds **VIa**–**VIe** and **VIIa**–**VIIf**

Comp. no.	Yield, %	mp, °C	Found, %						Formula	Calculated, %					
			C	H	B	N	P	S		C	H	B	N	P	S
VIa	93	172	43.50	5.94			6.20	12.33	$C_{76}H_{120}F_{12}N_8O_{20}P_4S_8$	44.01	5.79			5.98	12.35
VIb	88	138	46.82	6.77		4.37	5.54	10.32	$C_{88}H_{144}F_{12}N_8O_{20}P_4S_8$	47.14	6.43		5.00	5.53	11.42
VIc	95	107	47.03	5.01			5.50	12.34	$C_{88}H_{108}F_{12}N_4O_{24}P_4S_8$	47.73	4.88			5.60	11.57
VId	87	132	45.63	6.52		4.72	5.03	5.73	$C_{84}H_{144}I_4N_8O_8P_4S_4$	46.84	6.69		5.20	5.76	5.94
VIe	93	139	50.15	6.15		2.82	5.22	5.74	$C_{92}H_{124}I_4N_4O_{12}P_4S_4$	49.37	5.54		2.50	5.54	5.72
VIIa	94	179	45.58	6.29	2.00	5.64	6.73	6.69	$C_{68}H_{112}B_4F_{16}N_8O_8P_4S_4$	46.15	6.33	2.48	6.33	7.01	7.23
VIIb	90	187	49.24	7.10		5.41	6.98	6.84	$C_{76}H_{128}B_4F_{16}N_8O_8P_4S_4$	48.51	6.81		5.95	6.59	6.81
VIIc	96	127	49.58	7.39	1.27	4.85	6.17	7.68	$C_{88}H_{136}B_4F_{16}N_8O_8P_4S_4$	49.47	7.39	1.10	5.78	6.40	6.61
VIId	93	144	50.90	7.40	1.44	4.95	6.13	6.16	$C_{88}H_{152}B_4F_{16}N_8O_8P_4S_4$	51.56	7.42	2.14	5.46	6.05	6.25
VIIe	92	115	55.62	7.01		2.53	4.92	6.46	$C_{112}H_{172}B_4F_{16}N_4O_{12}P_4S_4$	56.85	7.27		2.36	5.24	5.41
VIIf	97	176	50.94	5.45	1.77	2.80	5.08	6.72	$C_{84}H_{108}B_4F_{16}N_4O_{12}P_4S_4$	51.32	5.49	2.24	2.85	6.31	6.51

phosphorylated cavitands having charged hydrophilic ammonium groups on the upper rim and hydrophobic alkyl groups on the lower rim.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^{1}H and ^{31}P NMR spectra were measured, respectively, on Bruker WM-250 and Bruker MSL-400 instruments operating at 250.13 and 166.93 MHz. Residual proton signals of deuterated solvents (acetone-d_6, acetonitrile-d_3, benzene-d_6, and chloroform-*d*) were used as internal reference for ^{1}H NMR spectra, and 85% H_3PO_4 was used as external reference for ^{31}P. Aminoalkylated calixarenes **Ia**–**Ii** were prepared by the procedures described in [7, 8].

33,34,35,36-Tetrakis(dialkylminomethyl)-3,11,19,27-tetrakis(dialkylamino)-2,4,10,12,18,20,26,28-octaoxa-3,11,19,27-tetraphospha-3,7,38,39,40-tetraalkylnonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.1^{24,30}.1^{16,22}.1^{8,14}]tetracosa-1(32),5,7,9(36)13,15,17(35),21,23,25(34),30,29(33)-dodecaenes (IIa–**IIk)** (*general procedure*). A solution of 0.001 mol of calixarene **Ia**–**Ii** and 0.005 mol of hexaalkylphosphorous triamide in 60 ml of benzene was heated under reflux for 4 h, the solvent was removed under reduced pressure (water-jet pump), and the crystalline residue was washed with diethyl ether and dried under reduced pressure (0.002 mm) for 3 h at 110°C. The IR spectra of compounds **IIa**–**IIk** contained the following characteristic absorption bands, ν, cm^{-1}: 1210 (P–O–C_{arom}), 1610 (C=C_{arom}).

5,11,17,19-Tetrakis(dimethylaminomethyl)-6,12,18,24-tetrakis(dimethylaminophosphinoyl)-2,8,14,20-tetraethyl-4,10,16,22-tetrahydroxypentacyclo[19.3.1.1^{3,7}.1^{15,19}]octacoza-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (III). Compound **IIc**, 1 g, was dissolved in 25 ml of diethyl ether, 0.1 g of water was added, and the mixture was kept for 12 h at 20°C. The solvent was removed, and the crystalline residue was dried under for 2 h at 50°C under reduced pressure (0.02). Yield 1.06 g (quantitative).

Transformation of compound III into cavitand IIc. A solution of 1.1 g of compound **III** in 25 ml of dry benzene was heated for 2 h at 80°C with simultaneous removal of water (as azeotrope). The solvent was removed, and the residue was dried for 3 h at 100°C under reduced pressure (0.02 mm). Yield of **IIc** 1.035 g (quantitative).

37,38,39,40-Tetraalkyl-33,34,35,36-tetrakis(dialkylaminomethyl)-3,11,19,27-tetrakis(dialkylamino)-2,4,10,12,18,20,26,28-octaoxa-3λ^5,11λ^5,19λ^5,27λ^5-tetraphosphanonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.1^{24,30}.1^{16,22}.1^{8,14}]-tetracosa-1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaene 3,11,19,27-tetrasulfides (VIa–**VIe).** A solution of 0.001 mol of cavitand **IIc**, **IId**, **IIh**, **IIi**, or **IIk** and 0.004 mol of sulfur in 50 ml of dry benzene was heated for 8 h at 80°C. The solvent was removed, and the residue was dried for 3 h at 110°C under reduced pressure (0.02 mm). IR spectrum, ν, cm^{-1}: 1610 (C=C_{arom}).

33,34,35,36-Tetrakis(dialkylaminomethyl)-37,38,39,40-tetramethyl-3,11,19,27-tetra-R-2,4,10,12,18,20,26,28-octaoxa-3λ^5,11λ^5,19λ^5,27λ^5-tetraphosphanonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.1^{24,30}.1^{16,22}.1^{8,14}]-tetracosa-1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaene 3,11,19,27-

Table 3. ^{1}H and ^{31}P NMR spectra of compounds **IIa**–**IIk**, **III**, and **IVa**–**IVe** in chloroform-*d*

Comp. no.	X	^{1}H NMR spectrum, δ, ppm (*J*, Hz)						^{31}P NMR spectrum, δ_P, ppm
		R^1	R^2	R^3	CH_2	CH	*m*-H	
IIa		1.71 d (12H, CH_3, 7.0)	2.17 s (24H, CH_3N)	2.85 d (24H, CH_3, 10.5)	3.56 s (8H)	4.75 q (4H, 7.0)	7.36 s (4H)	138.86
IIb		2.2 d (12H, CH_3, 7.0)	1.95 s (24H, CH_3N)	1.01 t (24H, CH_3, 6.9) 2.85 m (16H, CH_2)	3.32 s (8H)	5.26 q (4H, 7.0)	7.2 s (4H)	141.04
IIc		0.88 t (12H, CH_3, 6.9), 1.28 m (8H, CH_2)	2.14 s (24H, CH_3N)	2.78 d (24H, CH_3, 10.3)	3.21 s (8H)	4.61 t (4H, 6.9)	7.17 s (4H)	139.22
IId		–	–	–	–	–	–	139.81
IIe		0.86 t (12H, CH_3, 6.5), 1.24 m (8H, CH_2)	1.15 t (24H, CH_3, 7.0), 2.28 m (16H, CH_2)	2.67 d (24H, CH_3, 10.47)	3.27 s (8H)	4.59 t (4H, 6.9)	7.12 s (4H)	141.16
IIf		0.90 t (12H, CH_3, 7.4), 2.09 m (8H, CH_2)	1.30 t (24H, CH_3, 6.7), 1.84 m (16H, CH_2), 2.37 m (16H, CH_2N)	2.63 d (24H, CH_3, 9)	3.86 m (8H)	4.39 t (4H, 6.7)	7.18 s (4H)	127.86
IIg		0.96 t (12H, CH_3, 7.0), 1.37 m (8H, CH_2), 2.46 m (8H, CH_2CH)	2.29 s (24H, CH_3)	2.67 d (24H, CH_3, 9.6)	3.71 s (8H)	4.30 t (4H, 7.0)	7.21 s (4H)	129.53
IIh		0.98 t (12H, CH_3, 7.0), 1.25 m [32H, $(CH_2)_4$], 2.10 m (8H, CH_2CH)	2.28 s (24H, CH_3)	2.65 d (24H, CH_3, 9.0)	3.87 s (8H)	4.51 t (4H, 7.0)	7.17 s (4H)	140.11
IIi		1.12 m (12H, CH_3), 1.28 m [32H, $(CH_2)_4$]	2.28 s (24H, CH_3)	0.85 t (24H, CH_3, 7.0), 3.36 m (16H, CH_2)	3.85 s (8H)	4.50 t (4H, 7.0)	7.15 s (4H)	140.51
IIj		0.84 t (12H, CH_3, 6.7), 1.23 m [72H, $(CH_2)_9$], 2.14 m (8H, CH_2CH)	–	2.69 d (24H, CH_3, 9.0)	3.88 s (8H)	4.35 t (4H, 7.0)	7.10 s (4H)	127.55
IIk		–	–	–	–	–	–	140.24
III		0.98 t (12H, CH_3, 6.9), 1.32–1.42 m (8H, CH_2)	2.44 s (24H, CH_3)	2.59 d (24H, CH_3, 11)	3.32 s (8H)	4.55 t (4H, 6.9)	7.17 (4H)	17
IVa[a]	S	0.93 t (12H, CH_3, 7.0), 1.28 m (8H, CH_2)	2.20 s (24H, CH_3)	2.66 d (24H, CH_3, 10.28)	3.88 s (8H)	4.24 t (4H, 7.0)	7.16 s (4H)	65.64
IVb	S							65.67
IVc	S	0.83 t (12H, CH_3, 7.0), 1.29 m [32H, $(CH_2)_4$]	2.24s (24H, CH_3)	1.12 t (24H, CH_3, 7.0), 3.05 m (16H, CH_2)	3.53 s (8H)	4.56 t (4H, 7.0)	7.15 s (4H)	65.15
IVd	S							65.15
IVe	S							65.15

[a] In benzene-d_6.

tetraoxides(sulfides) Va–Vn. A solution of 0.004 mol of phosphorus(V) dichloride in 10 ml of benzene was added to a solution of 0.001 mol of calixarene **Ib**, **Id**, or **If**–**Ii** and 0.008 mol of triethylamine in 15 ml of benzene. After 24 h, triethylamine hydrochloride was filtered off, the solvent was removed from the filtrate, and the crystalline residue was washed with diethyl ether and dried for 10 h at 20°C under reduced pressure (0.02 mm). IR spectrum: ν(C=C_{arom}) 1610 cm^{-1}.

37,38,39,40-Tetraalkyl-33,34,35,36-tetrakis-(methyldialkylammoniomethyl)-3,11,19,27-tetra-R-2,4,10,12,18,20,26,28-octaoxa-3λ^5,11λ^5,19λ^5,27λ^5-tetraphosphanonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.-1^{24,30}.1^{16,22}.1^{8,14}]tetracosa-1(32),5,7,9(36),13,15,-17(35),21,23,25(34),30,29(33)-dodecaene 3,11,19,27-

Table 4. ^{1}H and ^{31}P NMR spectra of compounds **Va**–**Vn** in chloroform-*d*

Comp. no.	X	^{1}H NMR spectrum, δ, ppm (*J*, Hz)						^{31}P NMR spectrum, δ_P, ppm
		R^1	R^2	R^3	CH_2	CH	*m*-H	
Va	O	–	1.34 m (24H, CH_3), 3.21 m (16H, CH_2)	1.41 m (24H, CH_3, 3.12 m (8H, CH_2)	1.14 s (8N)	5.01 q (4H, 7.0)	7.42 s (4H)	19.31
Vb	S	1.92 d (12H, CH_3, 7.0)	1.32 t (24H, CH_3N, 7.0), 3.11 m (16H, CH_2)	7.66 s (20N, C_6H_5)	3.74 s (8H)	4.93 q (4H, 7.0)	7.42 s (4H)	48.46
Vc	S							77.35
Vd	S	0.97 m (24H, CH_3, 1.12 m (8H, CH_2)	1.23 t (12H, CH_3, 6.9), 2.34 m (16H,	7.65 s (20H, C_6H_5) 10.47)	3.13 s (8H)	4.65 t (4H, 7.0)	7.42 s (4H)	78.27
Ve	S	0.93 t (12H, CH_3, 7.0), 1.36 m (8H, CH_2), 2.24 m (8H, CH_2C)	2.70 s (24H, CH_3)	7.63 s (20H, C_6H_5)	3.72 s (8H)	4.63 t (4H, 7.0)	7.11 s (4H)	48.25
Vf	O	0.89 m (12H, CH_3, 1.33 m [32H, $(CH_2)_4$], 2.26 m (8H, CH_2C)	2.96 s (24H, CH_3)	1.18 m (12H, CH_3), 3.32 m (8H, CH_2)	3.73 c (8H)	4.45 t (4H, 7.0)	7.13 s (4H)	19.59
Vg	S	0.89 m (12H, CH_3, 1.33 m [32H, $(CH_2)_4$], 2.27 m (8H, CH_2C)	2.96 s (24H, CH_3)	7.63 s (20H, C_6H_5)	3.93 s (8H)	4.65 t (4H, 7.9)	7.13 s (4H)	49.08
Vh	S	0.88 m (12H, CH_3), 1.32 m [32H, $(CH_2)_4$], 2.27 m (8H, CH_2C)	2.93 s (24H, CH_3)	7.66 s (20H, C_6H_5)	4.01 s (8H)	4.67 t (4H, 7.0)	7.12 s (4H)	76.54
Vi	O	0.82 m (12H, CH_3), 1.44 m [32H, $(CH_2)_4$], 2.26 m (8H, CH_2C)	1.12 m (24H, CH_3), 2.83 m (16H, CH_2)	3.44 m (8H, CH_2S)	4.18 m (8H)	4.81 t (4H, 7.0)	7.32 s (4H)	17.93
Vj	S	0.92 t (12H, CH_3, 7.0), 2.22 m (8H, CH_2)	1.1 m (24H, CH_3), 3.05 m (16H, CH_2)	7.47 s (20H, C_6H_5)	3.93 s (8H)	4.93 t (4H, 7.0)	7.42 s (4H)	48.67
Vk	S	0.91 m (12H, CH_3), 1.50 m [32H, $(CH_2)_4$], 2.25 m (8H, CH_2C)	1.10 m (24H, CH_3), 3.02 m (16H, CH_2)	7.62 s (20H, C_6H_5)	4.04 s (8H)	4.75 t (4H, 7.0)	7.42 s (4H)	79.88
Vl	O	0.92 m (12H, CH_3), 1.27 m [72H, $(CH_2)_9$], 2.25 m (8H, CH_2C)	2.63 s (12H, CH_3)	1.08 m (12H, CN_3), 3.03 m (8H, CH_2)	4.18 s (8H)	4.75 t (4H, 7.0)	7.32 s (4H)	18.39
Vm	S	0.92 m (12H, CH_3), 1.15 m [72H, $(CH_2)_9$], 2.23 m (8H, CH_2C)	2.60 m (24H, CH_3)	7.53 s (20H, C_6H_5)	3.83 s (8H)	4.65 t (4H, 7.0)	7.42 s (4H)	49.47
Vn								48.14

tetrasulfide tetrakis(trifluoromethanesulfonates) VIa–VIc. A mixture of 0.0005 mol of cavitand **IVc**, **IVe**, or **Vn** and 0.0025 mol of methyl trifluoromethanesulfonate in 15 ml of benzene was kept for 24 h at 20°C. The precipitate was filtered off, washed with benzene, reprecipitated from acetonitrile with hexane, and dried for 4 h at 40°C under reduced pressure (0.02 mm). IR spectrum: ν, cm^{-1}: 690 (P=S), 1610 (C=C_{arom}).

37,38,39,40-Tetrahexyl-33,34,35,36-tetrakis(trimethylammoniomethyl)-3,11,19,27-tetra-R-2,4,10,12,18,20,26,28-octaoxa-3λ^5,11λ^5,19λ^5,27λ^5-tetraphosphanonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.1^{24,30}.1^{16,22}.1^{8,14}]tetracosa-1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaene 3,11,19,27-tetrasulfide tetraiodides VId and VIe were synthesized following the above procedure from 0.0006 mol of cavitand **IVa** or **Vg**, respectively, and 0.003 mol of methyl iodide. IR spectrum, ν, cm^{-1}: 690 (P=S), 1610 (C=C_{arom}).

37,38,39,40-Tetraalkyl-33,34,35,36-tetrakis(dialkylethylammoniomethyl)-3,11,19,27-R-2,4,10,12,-

Table 5. ^{1}H and ^{31}P NMR spectra of compounds **VIa**–**VIe** and **VIIa**–**VIIf** in acetone-d_6

Comp. no.	Y	^{1}H NMR spectrum, δ, ppm (*J*, Hz)						^{31}P NMR spectrum, δ_P, ppm
		R^1	R^2	R^3	CH_2	CH	*m*-H	
VIa	$CF_3SO_3^-$	1.96 d (12H, CH_3, 7.0)	1.24 t (24H, CH_3, 7.0), 3.14 s (12H, CH_3N), 3.32 m (16H, CH_2)	1.42 t (24H, CH_3, 7.0), 3.77 (16H, CH_2)	4.53 s (8H)	4.97 q (4H, 7.0)	7.21 s (4H)	63.76
VIb	$CF_3SO_3^-$	0.72 t (12H, CH_3, 7.0), 1.22 m [32H, $(CH_2)_4$], 2.47 m (8H, CH_2C)	3.31 s (36H, CH_3N)	1.01 m (24H, CH_3), 3.35 m (8H, CH_2)	3.78m (8H)	4.62 t (4H, 7.0)	7.15 s (4H)	63.11
VIc	$CF_3SO_3^-$	0.95 t (12H, CH_3, 6.9), 2.63 m (8H, CH_2)	1.32 t (24H, CH_3, 7.0), 2.99 s (12H, CH_3N), 3.12 m (16H, CH_2)	7.61 s (20H, C_6H_5)	4.17 s (8H)	4.77 t (4H, 7.0)	7.41 s (4H)	48.94
VId	I^-	0.92 m (12H, CH_3), 1.34 m [32H, $(CH_2)_4$]	2.65 s (36H, CH_3N)	1.01 t (24H, CH_3, 7.0), 3.06 m (16H, CH_2)	3.92 s (8H)	4.47 t (4H, 7.0)	7.14 s (4H)	63.26
VIe[a]	I^-	0.92 m (12H, CH_3), 1.34 m [32H, $(CH_2)_4$], 2.56 m (8H, CH_2C)	2.83 s (12H, CH_3N)	7.52 s (20H, C_6H_5)	3.21 m (8H)	4.64 t (4H, 7.0)	7.12 s (4H)	50.12
VIIa	B^-F_4	1.71 d (12H, CH_3, 7.4)	1.42 t (24H, CH_3, 7.0), 3.14 s (12H, CH_2)	2.54 d (24H, CH_3, 10.5)	4.19 s (8H)	4.67 q (4H, 7.0)	7.15 s (4H)	64.68
VIIb	B^-F_4	1.12 t (12H, CH_3, 7.0)	1.33 m (36H, CH_3), 3,57 m (24H, CH_2)	1.51 m (24H, CH_3), 3.14 m (16H, CH_2)	4.41 s (8H)	4.94 q (4H, 7.0)	7.29 s (4H)	64.78
VIIc	B^-F_4	0.93 t (12H, CH_3, 7.0), 1.32 m [32H, $(CH_2)_4$], 2.57 m (8H, CH_2C)	1.48 s (12H, CH_3), 2.94 s (24H, CH_3N), 3.53 m (8H, CH_2)	3.16 m (12H, CH_3, 10.4)	3.78 s (8H)	4.56 t (4H, 7.0)	7.29 s (4H)	64.89
VIId[a]	B^-F_4	0.95 t (12H, CH_3, 7.0), 1.25 m [32H, $(CH_2)_4$], 2.57 m (8H, CH_2C)	1.37 m (12H, CH_3), 2.88 s (24H, CH_3N), 2.98 m (8H, CH_2)	1.41 m (12H, CH_3), 3.01 m (16H, CH_2)	3.63 s (8H)	4.52 t (4H, 7.0)	7.29 s (4H)	63.42
VIIe[a]	B^-F_4	0.92 m (12H, CH_3), 1.34 m [32H, $(CH_2)_4$], 2.64 m (8H, CH_2C)	1.52 t (12H, CH_3, 7.0), 2.92 m (8H, CH_2), 3.37 s (24H, CH_3N)	7.67 s (20H, C_6H_5)	3.71 s (8H)	4.98 t (4H, 7.0)	7.42 s (4H)	69.42
VIIf	B^-F_4	2.07 d (12H, CH_3, 7.4)	1.24 t (36H, CH_3, 7.0), 3.01 m (24H, CH_2)	7.66 s (20H, C_6H_5)	4.11 s (8H)	4.99 q (4H, 7.0)	7.62 s (4H)	48.57

[a] In acetonitrile-d_3.

18,20,26,28-octaoxa-3λ^5,11λ^5,19λ^5,27λ^5-tetraphosphanonacyclo[29.3.1.1^{21,25}.1^{13,17}.1^{5,9}.1^{6,32}.1^{24,30}.1^{16,22}.1^{8,14}]tetracosa-1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaene 3,11,19,27-tetrasulfide tetrakis(tetrafluoroborates) VIIa–VIIf. Triethyloxonium tetrafluoroborate, 0.0025 mol, was added with stirring to a solution of 0.0005 mol of cavitand **IVb**–**IVe**, **Vb**, or **Vh** in 15 ml of an equimolar benzene–chloroform mixture. After 24 h, the crystalline precipitate was filtered off, washed with benzene, reprecipitated from acetonitrile with hexane, and dried for 4 h at 40°C under reduced pressure (0.02 mm). IR spectrum of **VIIa**–**VIIf**, ν, cm^{-1}: 690 (P=S), 1610 (C=C$_{arom}$).

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project nos. 99-03-32999 and 98-03-04105).

REFERENCES

1. Lippmann, T. and Dalcanale, E., and Mann, G., *Tetrahedron Lett.,* 1994, vol. 35, no. 35, p. 1685.
2. Lippmann, T., Wilde, H., Dalcanale, E., Mavilla, L., Mann, G., Heyer, U., and Spera, S., *J. Org. Chem.,* 1995, vol. 60, no. 1, p. 235.
3. Dalcanale, P. and Dutasta, J.P., *Tetrahedron Lett.,* 1995, vol. 36, no. 36, p. 9325.
4. Kazakova, E.Kh., Davletshina, G.R., and Konovalov, A.I., *Zh. Obshch. Khim.,* 1996, vol. 66, no. 3, p. 407.
5. Nikolaeva, I.L., Burilov, A.R., Kharitonov, D.I., Khabikher, V.D., Pudovik, M.A., and Konovalov, A.I., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 2, p. 333.
6. Vicens, J. and Bohmer, V., *Calixarenes, a Versatile Class of Macrocyclic Compounds,* Dordrecht: Kluwer Academic, 1991, p. 15.
7. Yohichi, M. and Tahanao, M., *Tetrahedron Lett.,* 1993, vol. 34, no. 46, p. 7433.
8. Burilov, A.R., Nikolaeva, I.L., Makeeva, T.B., Pudovik, M.A., Reznik, B.C., and Konovalov, A.I., *Zh. Obshch. Khim.,* 1997, vol. 67, no. 5, p. 870.
9. Nifant'ev, E.E., Maslennikova, V.I., Vasyanina, L.K., and Panina, E.V., *Zh. Obshch. Khim.,* 1994, vol. 64, no. 1, p. 154.
10. Burilov, A.R., Nikolaeva, I.L., Galimov, R.D., Pudovik, M.A., and Reznik, B.C., *Zh. Obshch. Khim.,* 1995, vol. 65, no. 10, p. 1745.
11. Nifant'ev, E.E., Maslennikova, V.I., Sinitsina, E.N., and Vasyanina, L.N., *Zh. Obshch. Khim.,* 1997, vol. 67, no. 11, p. 1925.