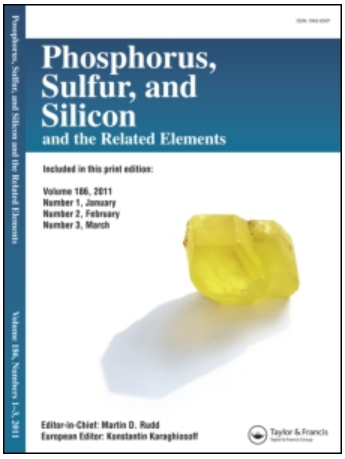

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SYNTHESIS OF NEW PHOSPHORUSCONTAINING THREE-DIMENSIONAL STRUCTURES ON THE BASIS OF CALIX[4] RESORCINARENES

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SYNTHESIS OF NEW PHOSPHORUS-CONTAINING THREE-DIMENSIONAL STRUCTURES ON THE BASIS OF CALIX[4] RESORCINARENES

ALEXANDER I. KONOVALOV, VLADIMIR S. REZNIK, MICHAEL A. PUDOVIK, ELLA KH. KAZAKOVA, ALEXANDER R. BURILOV, IRINA L. NIKOLAEVA, NELLY A. MAKAROVA, GUZEL R. DAVLETSCHINA, LUDMILA V. ERMOLAEVA, RUSTEM D. GALIMOV and ASIJA R. MUSTAFINA

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Phosphorylation of calix[4]resorcinarenes with long chain aliphatic radicals (R=C_6, C_7, C_9) (1a,b,c) with a number of P(III) derivatives i.e. triamido- and diamidophosphites, triphenylphosphite, mono- and polyhalogenides of P(III) is described. A series of phosphoamide cavitands **(2)**,(3) were obtained. A new three-dimensional "container"- like structures, in which tetraresorcinol fragments are connected by means of phosphite bridges **(13,14)** were formed in the reaction of **(Ib)** with (-) bis(N,N-diethylamido)menthylphosphite , phosphorus trichloride and triphenylphosphite. Phosphorylation of calix[4]resorcinarene **(1c)** with chloroanhydrides of chloromethylphosphonic and bis(chloromethyl)phosphinic acids results in completely or partially posphorylated products depending on the reaction conditions. The synthesis of dimeric "head to head" macrocyclic derivative of chlormethylphosphonic acid **(19)** is described. Structures and properties of synthesized compounds were discussed on the basis of physical and quantum chemical methods.

Keywords: Phosphorylation; calix[4]resorcinarenes; carceplex; cavitands.

INTRODUCTION

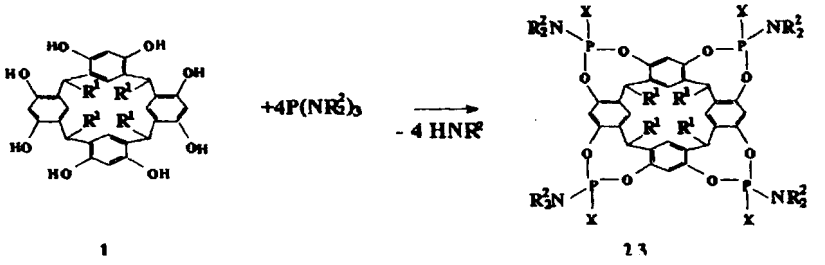
Cyclodextrins, crown ethers and calixarenes are prominent in host-guest chemistry. Cyclodextrins mainly connect organic molecules, while crown ethers mainly form complexes with metal and ammonium ions. Calixarenes and their derivatives can selectively involve both organic and inorganic guests. Long chain

calix[4]resorcinarenes are of great interest because of their accessible synthesis, sufficient solubility and "bowl-like" conformation. The molecular design of new three-dimensional structures with calixaren as a basis can be achieved with the use of a wide range of reagents and methods of organophosphorus chemistry. The purpose of this work is to synthesize new three-dimensional structures with three- and four-coordinated phosphorus atoms on the basis of longchain calix[4]resorcinarenes as key starting materials and to investigate their properties.

RESULTS AND DISCUSSION

Phosphorylalion with phosphorus (III) triamides

Phosphorylation of some calixarenes with phosphorus triamides was described earlier[1,2]. We obtained a series of new phosphorus-containing cavitands by phosphorylation of calixarenes **(1a,b,c)** with phosphorus triamides in the molar ratios of 1:4. Phosphorylation proceeds at room temperature in non-polar media and gives rise to phosphoamide cavitands **(2a,b,c,d,e)** in high yields. According to the nuclear magnetic spectroscopy data they possess a C_4 symmetry and bind two molecules of diethylamine. The removal of diethylamine can be attained by washing it out with water. Unlike acyclic amidophosphites cavitands **(2)** are stable to alcohols and water and add elemental sulfur only in severe conditions with the formation of compounds **(3a,b).**

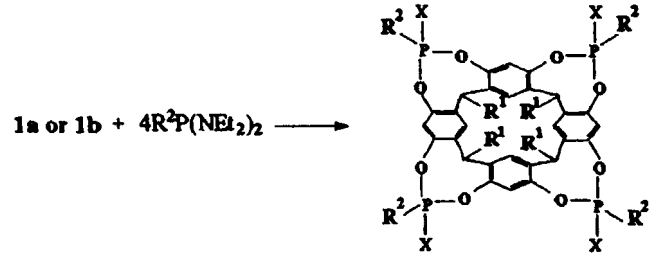


1 2

1. a. $R^1 = {}^1C_6H_{13}$;b.$R^1 = C_7H_{15}$;c. $R^1 = C_9H_{19}$
2. a. $R^1 = C_6H_{13}$, R^2= Me, X= l.e.p.; b.$R^1 = C_6H_{13}$, R^2 = Et, X= l.e.p.; c. $R^1 = C_7H_{15}$, R^2= Me, X=l.e.p.; d. $R^1 = C_7H_{15}$, R^2=Et, X=l.e.p; e. $R^1 = C_9H_{19}$, R^2=Et, X=l.e.p.
3. a. $R^1 = C_6H_{13}$, R^2=Me, X=S; b. $R^1 = C_7H_{15}$, R^2=Et, X=S

Phosphorylation with phenyl- and alkyldiamidophosphites

The interaction of long chain calixresorcinarenes (**1a,b**) with phenyl-, methyl-and ethyldiamidophosphites unexpectedly resulted in the formation of phosphatocavitands (**4,5a,b**). Phosphitocavitands were obtained only when hexyl- and octhyldiamidophosphites were used as phosphorylating agents. Phosphites (**6a,b**) were converted into thiophosphates (**7a,b**) when heated with sulfur.



4-7

4. $R^1=C_7H_{15}$, R^2=OPh, X=O
5. a. $R^1=C_6H_{13}$, R^2=OMe, X=O; b. $R_1=C_6H_{15}$, R^2=OEt, X=O
6. a. $R^1=C_6H_{13}$, $R^2=OC_6H_{13}$, X=l.e.p.; b. $R^1=C_7H_{15}$, $R^2=OC_8H_{17}$, X=l.e.p.
7. a. $R^1=C_6H_{13}$; $R^2=OC_6H_{13}$, X=S; b. $R^1=C_7H_{15}$, $R^2=OC_8H_{17}$, X=S

Phosphorylation with (-) bis(N,N-diethylamido)menthylphosphite (8)

The molecular cavity of calixarenes can be used for the chiral recognition of molecules after asymmetric modification. Asymmetry can be caused by the structure of calixarene or can be induced by the introduction of chiral fragments. We have used an optically active organophosphorus compound-(-)bis(N,N-diethylamido)menthylphosphite (**8**) as the chiral agent[3]. Phosphorylation was conducted in mild conditions with different ratios of initial reagents (1:8, 1:4, 1:2). In all cases the optically active phosphorylated products, containing acyclic amidomenthylphosphite fragments were obtained. A completely phosphorylated product contains six acyclic amidomenthylphosphite fragments with $\delta^{31}P$ 147.6 ppm and one cyclic menthylphosphite fragment with $\delta^{31}P$ 133. 1 ppm (**9**). The latter reacts with elemental sulfur forming an optically active product (**10**), which contains two kinds of non-equivalent four-coordinated phosphorus atoms with $\delta^{31}P$ 67.5 and 55.4 ppm. Since the signal $\delta^{31}P$ 133.1 ppm could be caused by the admixture of initial bis-(N,N-diethylamido)menthylphosphite ($\delta 6^{31}P$ 133.1 ppm), we have added some sulfur and obained bis(N,N-diethylamido) menthylthiophosphate with $\delta^{31}P$ 76.67 ppm. This value differs from that of the product (**10**).

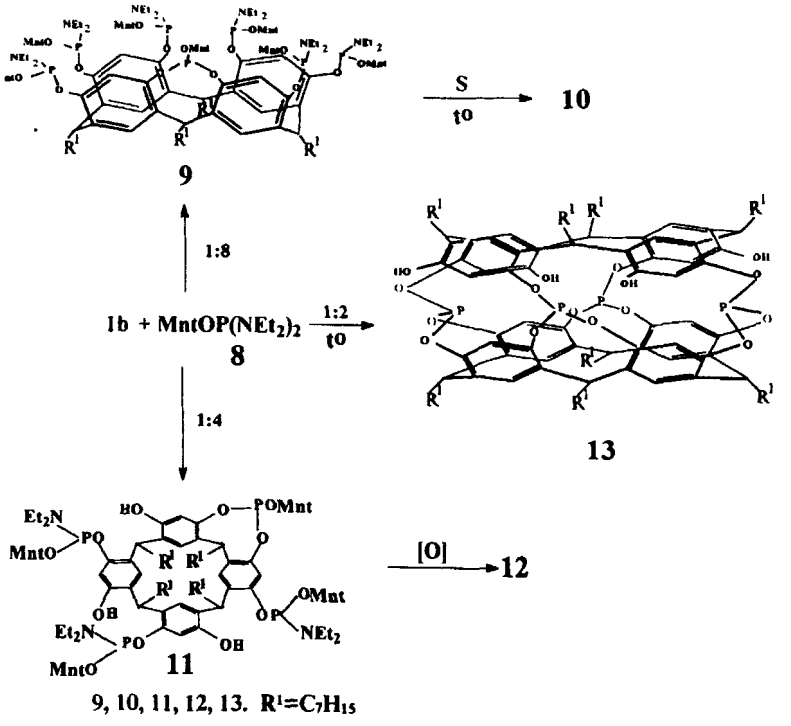
When the ratio 1:4 of the initial reagents was used, the compound with one cyclic menthylphosphite fragment ($\delta^{31}P$ 133. 1 ppm) and three acyclic amido-menthylphosphite groups ($\delta^{31}P$ 147.0 ppm) was obtained (**11**). This optically active compound was transformed into phosphate (**12**) [($\delta^{31}P$ −14.8, 3.68 ppm), m.p. 85–86° C , $[\alpha]^{20}578 = -31$ (benzene)] with oxidation of peracetic acid.

TABLE I NMR data of cavitands 2, 3, 4, 7, 15

N	*R*	*Y*	*X*	$\delta^{31}P$,*pp m*	*NMR*
2a	C_6H_{13}	$N(CH_3)_2$	LP	144.8	(C_6D_6) δ, ppm: 0.73(t, 12H, $\underline{CH_3}$-CH_2, $^3J_{HH}$6.5 Hz), 1.22–1.54(m, 32H, $\underline{CH_3}$-$\underline{CH_2}$-CH_2-CH_2), 2.39, (m, 8H, -$\underline{CH_2}$-CH), 2.53(d, 12H, CH_3N,$^3J_{PH}$ 10.9 H_z), 4,95 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 7.00–7.21 (m, 8H, Harom).
2b	C_6H_{13}	$N(C_2H_5)_2$	LP	144.75	(C_6D_6) δ, ppm: 1.01 (t, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 7.0 Hz), 1.04–1.18 (m, 12H, $\underline{CH_3}$-CH_2), 1.32–1.45 (m, 32H, $(CH_2)_4$, 2.48 (m, 8H, -$\underline{CH_2}$-CH), 3.28 (m, 16H, $\underline{CH_3}$-CH_2-N,), 5.14 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 7.05–7.34 (m, 8H, Harom).
2c	C_7H_{15}	$N(CH_3)_2$	LP	142.60	(C_6D_6) δ, ppm: 1.39–1.49 (m, 12H, $\underline{CH_3}$-CH_2,$^3J_{HH}$6.5 Hz), 1.89 (m, 40H, $(CH_2)_5$), 2.89(mM 8H, -$\underline{CH_2}$-CH), 3.38 (d, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 10.9 Hz), 5.18 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 6.55–7.52 (m, 8H, Harom).
2d	C_7H_{15}	$N(C_2H_5)_2$	LP	143.09	(C_6D_6) δ, ppm: 1.10 (t, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 7.0 Hz), 1.25–1.30 (m, 12H, $\underline{CH_3}$-CH_2), 1.58–1.64 (mM, 40H, $(CH_2)_5$), 2.65 (m, 8H, $\underline{CH_2}$-CH), 3.30 (m, 16H, CH_2-N), 5.10 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 6.82–7.15 (m, 8H, Harom).
2e	C_9H_{19}	$N(C_2H_5)_2$	LP	144.26	(C_6D_6) δ, ppm:1.07 (t, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 7.0 Hz), 1.25–1.30 (m, 12H, $\underline{CH_3}$-CH_2), 1.60–1.68 (m, 56H, $(CH_2)_7$), 2.70 (m, 8H, -$\underline{CH_2}$-CH), 3.42 (m, 16H, CH_2-N), 5.22 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 7.01–7.20 (m, 8H, Harom).
3a	C_6H_{13}	$N(CH_3)_2$	S	70.88	(C_6D_6) δ, ppm: 0.95 (t, 12H, $\underline{CH_3}$-CH_2, $^3J_{HH}$ 7.0 Hz), 1.45–1.55 (m, 32H, $(CH_2)_4$, 2.42 (m, 8H, -$\underline{CH_2}$-CH), 2.72 (d , 24H, J_{PH} 12.4 Hz), 4.75 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 7.00–7.15 (m, 8H, Harom).
3b	C_7H_{15}	$N(C_2H_5)_2$	S	67.93	(C_6D_6) δ, ppm: 0.98 (t, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 7.0 Hz), 1.35–1.42 (m, 12H, $\underline{CH_3}$-CH_2), 1.60–1.68 (m, 40H, $(CH_2)_5$), 2.50 (m, 8H, -$\underline{CH_2}$-CH), 3.39 (m, 16H, CH_2-N), 4.95 (t, 4H, $\underline{C}CH_2$, $^3J_{HH}$ 7,0 Hz), 6.95–7.15 (m, 8H, Harom).
7a	C_6H_{13}	OC_6H_{13}	S	57.5	(C_6D_6) δ, ppm: 0.80–0.93 (m, 24H, $\underline{CH_3}$-CH_2-N, $^3J_{HH}$ 7.0 Hz), 1.29–1.35 (m, 64H ($\underline{CH_2}$4-CH, $(\underline{CH_2})_4O$), 2.68–2.74 (m, 8H, -$\underline{CH_2}$-CH), 4.33 (m, 8H, CH_2O $^3J_{HH}$ 7,0 Hz, $^3J_{PH}$ 13.2 Hz), 4.85 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 6.75–7.20 (m, 8H, Harom).

N	R	Y	X	$\delta^{31}P$,pp m	NMR
7b	C_7H_{15}	OC_8H_{17}	S	59.25	(CD_3CO) δ, ppm: 0.84–0.92 (m, 24H, CH_3), 1.24–1.30 (m, 88H, $(CH_2)_6$; $(CH_2)_5$), 2.74–2.80 (m, 8H, -$\underline{CH_2}$-CH), 4.30 (m, 8H, $\underline{CH_2}O$, $^3J_{HH}$7,05 Hz, $^3J_{PH}$ 13.2 Hz), 4.70 (t, 4H, CH-, $^3J_{HH}$ 7,0 Hz), 6.60 (s, 4Horto), 7.19 (s, 4Hmeta)
4	C_7H_{15}	C_6H_5	O	11.26	(C_6D_6) δ, ppm: 1.14 (t, 12H, $\underline{CH_3}$-CH_2, $^3J_{HH}$ 7,0 Hz), 1.47–1.52 (m, 40H, $(CH_2)_5$), 2.57–2.62 (m, 8H, -$\underline{CH_2}$-CH), 5.02 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 6.95 (s, 4Horto), 7.05–7.44 (m, 4Hmeta, 20H, Harom).
15	C_6H_{13}	$C_6H_4O_2$	LP	132.60	1.05–1.16 (m, 12H, $\underline{CH_3}$-CH_2), 1.25–1.32 (m, 32H, $(CH_2)_4$), 2.01 (m, 8H, -$\underline{CH_2}$-CH), 4.60 (t, 4H, $\underline{CH}$-CH_2, $^3J_{HH}$ 7,0 Hz), 6.50–7.20 (m, 24Harom), 8.44 (s, 4H, $\underline{OH}$)

The reaction with the ratio 1:2 of reagents at room temperature yields a product which contains acyclic and cyclic fragments ($\delta^{31}P$ 146 and 133.1 ppm) with the ratio of the signal intensity 3:1 as in the reaction with the ratio 1:4. We assume that an identical product was obtained in both reactions. When the reaction mixture was heated in dioxane there appeared a signal of the cyclic phosphite fragment ($\delta^{31}P$ 133.9 ppm). The product of the reaction is a powder, which does not have any optical activity and does not contain a menthyl fragment. All these spectral and elemental analysis data and the lack of optical activity make it possible for us to propose a globe-shaped structure **(13)** for it. Molecular modelling supports this conclusion. Examination of the model octol **(1)** and amidophosphitocavitand **(2)** (in which the pendant R^1 groups and substituents R^2 at nitrogen atom are replaced by hydrogen) by MNDO-PM3 quantum chemical calculations shows that carcerand may be formed. According to the calculations both **(1)** and **(2)** have a C_4 symmetry, the latter with two isomers. The *isomer(oooo)* with all the phosphorus lone electron pairs oriented in the opposite direction from the cave is by 9.3 kcal/mol more stable than another one **(iiii)** with the pairs pointing towards the centre. During the shell closure (after one of the P-O bonds has been formed), only the alternating oxygen atom of the nearest ring is complemental to the nearby phosphorus atom. The distance between the adjacent phosphorus atoms is 6.5 A and close to the one between alternating oxygen atoms. The distance between adjacent oxygen atoms is 4.8 A (when they are placed on the same benzene ring), and - 3.2 A. (when they are placed on different benzene rings). Semi-empirical calculations of the model carcerand **(13)** (in which all the substituents R are replaced by H), has shown that the structure **(13)** is placed in minimum on the potential energy surface. The P-O bonds of the phosphacyne cycle are not the same (1.629 and 1.621 A). The third P-O bond is 1.625 A. One octol



hemisphere is turned around one long polar axis with respect to another one by about 16°, therefore carcerand probably exists as two diastereomeric species. The distance between opposite bridge phosphorus atoms is 7.7 A and shorter by 1.7 than in (**2**). It must be noted, that the phosphorus unshared electron pairs face the shell inward, thus the equatorial position is electronegative. The equatorial short axes are 4.1 A. This value limits the molecular shape of the guests to be incorporated.

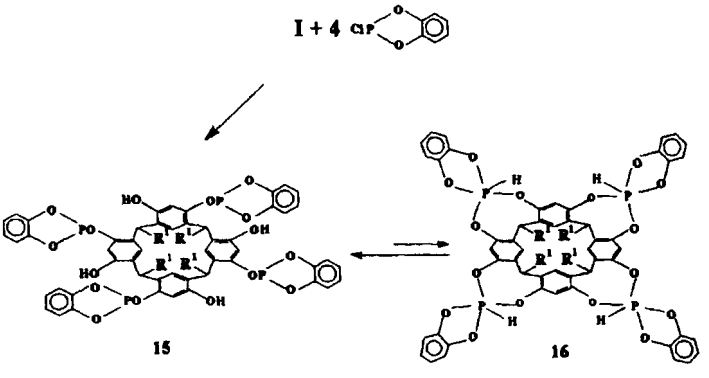
It may be assumed, that when heated the initially formed phosphorylation product (**11**) is converted into dioxaphosphocane cycles. The subsequent intermolecular interaction of the product formed with the calixarene molecules present in reaction mixture followed by shell closures yields the final "container"-like structure with the tetraresorcinol fragments connected with phosphite bridges. It must be pointed out that the elemental data prove that each molecule of the compound (**13**) involves eight molecules of diethylamine. The addition of elemental sulphur to compound (**13**) gives rise to the product with the signals $\delta^{31}P$ 56.2 , 56.4 ppm in ^{31}P NMR spectrum, with the stretching vibration of O-H bond –3400 cm^{-1} in the IR-spectrum and the m.p. 99–100° C.

Phosphorylation with phosphorus *(III)* halides

The phosphorylation of (**1a,b**) with phosphorus trichloride in the absence of a base with the ratio 1:2 of reagents gives rise to high yields of compounds (**14a,b**), with a structure similar to (**13**) according to analytical, ^{31}p NMR (δ^{31}P 129 ppm) and ^{1}H NMR data. Besides an isomeric structure with free HO-groups in both calixaren units may be proposed. This structure can be the result of dimerization of phosphacavitand with two phosphorus atoms. But the geometric considerations mentioned above show that in this case there is no complementarity. The shell-closing reaction was observed as a result of the prolonged boiling of strongly diluted calixarene solutions with thriphenylphosphite with the 1:2 ratio of the reagents. The final products have identical analytical and spectral properties.

$$2(1) + PCl_3 \longrightarrow \textbf{13 or 14} \longleftarrow P(OPh)_3 + 2(1)$$

Phosphorylation of four retained hydroxy-groups of (**14a,b**) with excess of phosphorus trichoride yields a compound, which contains both phosphite (δ^{31}P 129 ppm) and chlorophosphite (δ^{31}P 172 ppm) fragments. This product was also observed in the absence of a base with the ratio 1:4 of the reagents. The phosphorylation of calixarenes (**1a,b**) with alkyldichlorophosphites in the presence of a base results in the formation of cyclic compounds (**5a,b**) with four coordinated (δ^{31}P –10- –11 p.p.m) phosphorus atoms. Meanwhile the interaction of compound (**1a**) with pyrocatechinchlorophosphite in the presence of a base (with ratio of 1:4 or 1: 8) proceeds with the formation of phosphite (**15**). It could be mentioned that an abundance of pyrocatechinechlorophosphite does not lead to the phosphorylation of all hydroxy-groups. On the basis of nuclear magnetic resonance data it was shown that phosphite (**15**) (δ^{31}P 132.60 ppm) is in the equilibrium with its P-H-form (**16**) (δ^{31}P –18.30 ppm, JPH 715 Hz), which is about five per cent.



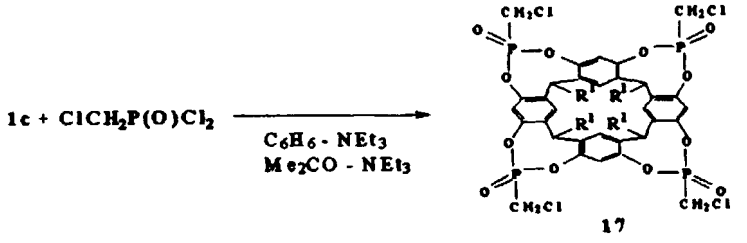
15 16

15, 16. $R^1 = C_6H_{13}$

Phosphorylation with phosphorus (IV) chlorides

Chloromethylphosphonic and chloromethylphosphinic acid chlorides were also used as phosphorylating agents. In this way we wanted to introduce phosphoryl groups connected with chloromethyl groups[4] into the calixaren molecules.

The course of the reaction of (**1c**) with chloromethyldichlorophosphonate depends on the reaction conditions. In the system of C_6H_6 - NEt_3 the reaction results in a crystalline substance with the m. p. 135–137° C, soluble in C_6H_6, Me_2CO, CH_2Cl_2, $CHCl_3$. The latter has been proved (owing to the absence of the stretching O-H bond vibrations in IR-spectra) to be a completely phosphorylated product. The ^{31}P NMR spectra shows a slightly broadened main signal $\delta^{31}P$ 12.37 ppm. The molecular mass obtained by ebulioscopy is 1440, this value being larger than that, calculated for the assumed structure (**17**) - 1370. This difference may be owing to the inclusion of the molecule NEt_3 into the molecular cavity of (**17**). The ^1H NMR spectra of (**17**) shows the signal of methyn protons of an aldehyde bridge to be twice less than the broad signal of methylene protons of the chloromethyl groups. The reaction in the system of acetone-NEt_3 results in a product with similar spectral properties. The ^{31}P NMR spectrum contains a signal $\delta^{31}P$ 12.62 ppm and the elemental analysis data are in accordance with the structure (**17**).



17

$R^1 = C_9H_{19}$

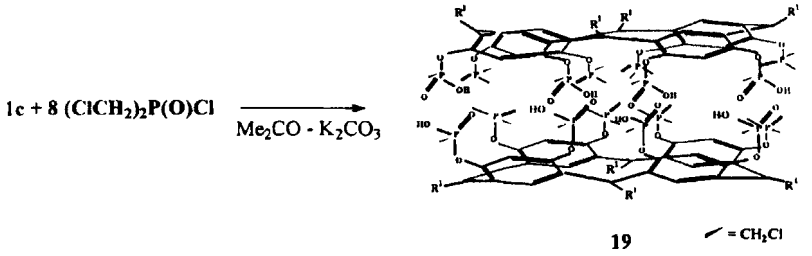
When the system CH_2Cl_2 - K_2CO_3 was used in the same reaction, the product, with a signal $\delta^{31}P$ 10.54 ppm was obtained. In its IR-spectra the stretching of O-H bond vibrations is observed and the ^1H NMR spectra contains two signals of equal intensity assigned to methyn and methylene protons. The spectral and analytical data make it possible for us to assume, that the product obtained contains four hydroxy groups and it may have symmetry either C_{2v} with nearby dibenzophosphocyne cycles, or Cs, when the cycles are opposite each other (**18** $R^1 = C_9H_{19}$).

Phosphorylation of (**1c**) with bis(chloromethyl)chlorophosphinate in the C_6H_6-NEt_3 system gives a complex picture in the ^{31}P NMR spectra. The same reaction in the Me_2CO - K_2CO_3 yields a product with a signal $\delta^{31}P$ 29.04 ppm.

This is a brittle glass-like substance melting at 120° C, well soluble in C_6H_6 and other organic solvents. Its ^{13}C NMR spectra has all the signals typical for (**1c**) and a signal of C-atoms of chloromethyl groups at 35.47 ppm (J_{pc}103.9 Hz). The ^1H NMR spectra of the product obtained in deuteroacetone contains all the signals typical for (**1c**) plus two signals at 3.77 and 3.88 ppm, which belong to the methylene protons of the chloromethyl groups. These signals are four times as intensive as the triplet signal of methyn protons of the aldehyde bridges at 4.42 ppm. The analysis of spectral and analytical data make it possible for us to assume that this is a completely phosphorylated product with eight chloromethyl groups. Some additional information on the structure of the product was obtained by the measurement of its molecular mass (M.m. 4239). It is twice as large as that for one macrocyclic molecule. On addition the pH-metric data show that the product dissociates stepwise (pK_1 3.7; pK_2 3.6; pK_3 5.1), which confirms the acidic character of the product.

We consider that this reaction results in the macrocyclic derivative of chlormethylphosphonic acid (**19**), in which two molecules are connected in a dimeric structure of the type "head to head".

The unusual elimination of chlormethyl fragments, is probably caused by a combination of several factors: by the active nature of the methylene group, by the presence of a base in the solution, by the solvating nature of the solvent (acetone), which can take part in the reaction.



19. $R^1 = C_9H_{19}$

The properties of *calixrecorcin[4]arenes* and their monoamidophosphites

The multipoint hydrodgen bonding plays an important part in the selective binding of some sugars, poliols and dicarboxylic acids with calixresorcinarens (1)[5]. The substitution of protons of the hydroxy-groups by four monoamidophosphite fragments preserves a "container"-like conformation, but leads to the modification of the selectivity of the cavitand (**2**) owing to the appearance of new donor centers on the "rim" of the molecule. The cavitand (**2**) is sufficiently soluble in

non-polar solvents and stable to the hydrolysis of the phosphorus-nitrogen bond in neutral and alkaline media, so it can be used as an extragent of organic compounds from water solutions.

TABLE II NMR ^1H spectroscopy data for free "guests" in $CDCl_3$ and "guests" after their extraction from water solution into $CDCl_3$ solution of cavitand **2** (C= 0.01M)

	"GUEST"	δ ^1H free "guests", ppm	δ ^1H bound "guests", ppm	stoichiometry
1	$(CH_3CH_2)_2NH$ $C_g = 0.1M$	2.62(CH_2) 1.08(CH_3) 0.74(NH)	~2.1-2.4	1:2
2	$(CH_3CH_2)_3N$ $C_g = 1M$	2.42(CH_2) 0.92(CH_3)	2.7; 2.4; 2.0; 1.6	1:8
3	NH_2 CH_2^1 CH_2^2–OH $C_g = 0.1M$	2.62 CH_2(1) 3.42 CH_2(2) 2.70 (NH_2) 7.22 (OH)	~2.1-2.4	1:2
4	$N(CH_3)_2$ CH_2^1 CH_2^2—OH $C_g = 0.1M$	4.5 (OH) 3.2 CH_2(2) 2.0 CH_2(1) 1.8 (CH_3)	3.5 CH_2(2) ~2.5-1.8 CH_2(1), CH_3	1:2
5	$N(CH_3)_2$ CH_2^1 CH_2^2—OH $C_g = 1M$	4.5 (OH) 3.2 CH_2(2) 2.0 CH_2(1) 1.8 (CH_3)	5.4 (OH) 3.6 CH_2(2) 2.5 CH_2(1) 2.2 (CH_3)	1:20
6	COOH CH^1–NH_2 CH_2^2 $(CH_2^4)_2$ CH_2^3–NH_2 $C_g = 0.02M$	3.5 CH(1)* 3.0 CH_2(2)* 2.5 CH_2(3)* 1.5 CH_2(4)* * - in D_2O	2.47 2.28	1:2

From NMR ^1H data it is evident that the cavitand (**2**) is firstly obtained with two molecules of $NHEt_2$ as guests, the latter can be reextracted by water or substituted by other amine molecules. Mixing of the cavitand $CHCl_3$ solution with water leads to reextraction of Et_2NH, which is accompanied by the dissapearance of Et_2NH signals in the NMR ^1H spectra without ane changes in the NMR ^{31}P

spectra. Mixing of the cavitand $CHCl_3$ solution with the water solution of some amine derivatives leads to the dissapearance of Et_2NH signals and the appearance of new guest widened signals, which differ from the absorbance of free guest molecules. It was found that the cavitand forms "host-guest" complexes with Et_2NH, Et_3N, $H_2NCH_2CH_2OH$, $Me_2NCH_2CH_2OH$ and $HOCOCH(NH_2)(CH_2)_4NH_2$ with the stoichiometry 1:2. The complexation induced shifts the guest protons absorbance in NMR 'H spectra are presented in the Table I. It is well known, that in most cases "host-guest" complexation is accompanied by the up-field shift of the guest absorbance in the NMR 'H spectra. From the table it is evident, that the complexation of the cavitand (**2d**) with $HOCOCHOCH(NH_2)(CH_2)_4NH_2$ and $H_2NCH_2CH_2OH$ is accompanied by the up-field shift of the guest protons absorbance in NMR 'H spectra. The lack of up-field shift for the cavitand complexes with NEt_3, Et_2NH and $Me_2NCH_2CH_2OH$ is due to the rapid exchange between free and bound molecules.

The complexation with metal ions is mainly determined in accordance with the "size-match" rule. Due to the "size-match" rule calixresorcinarenes (**1**) bind only bulky cations like tetra-alkylammonium cations in water-organic alkaline media. As was shown by the quantum chemical calculation the diameter of the upper rim of a cavitand (**2**) is large, which makes it possible to coordinate large size guests. According to our data calixresorcinarenes bind cobalt complexes with amines and aminoacids in the weak alkaline water-organic media.[6]

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EXPERIMENTAL

All the syntheses were performed in dry solvents under argon. ^1H NMR and ^{13}C spectra were recorded on a Varian VM–250 (250 MHz) and Varian UNITY–300 (75.43 MHz) spectrometer with TMS as an internal standard. ^{31}P NMR spectra were recorded on a Bruker CXP-l00 spectrometer (36.47 MHz, 85% H_3PO_4 as an external standard) Quantum chemical calculations were performed using the AMPAC program[8] with the full optimization of geometrical parameters.

Amidophosphitocavitands (2a-e).

A solution of the corresponding amide (10.0 mmol) in benzene (30 ml) was slowly added to a suspension of octol (**1**) (2.5 mmol) in benzene (20 ml) under stirring at 80 °C. Cavitands (**2a-e**) were recrystallized from benzene and dried in vacuum.

Amidophosphitocavitand (2a) (stereoisomer).

Yield 75%. M.p. 240–242°C. $C_{60}H_{88}N_4O_8P_4$. 1116. Calc. C 63.94, H 8.27, N 5.36, P 11.79. Found C 64.52, H 7.89, N 5.02, P 11.11.

Amidophosphilocavitand (2b) (stereoisomer).

Yield 90%. M.p.186–187°C. $C_{68}H_{104}N_4O_8P_4$. 1228. Calc. C 66.12, H 8.00, P 10.45. Found C 66.45, H 8.47, P 10.10.

Amidophosphitocavitand (2c) (stereoisomer).

Yield 75%. M.p,198–200°C. $C_{64}H_{96}N_4O_8P_4$. 1172. Calc. C 64.60, H 8.36, N 5.38, P 10.26. Found C 65.08, H 8.14, N 4.75, P 10.51.

Amidophosphitocavitand (2d) (stereoisomer).

Yield 92%. M.p. 208–209°C. $C_{72}H_{112}N_4O_8P_4$. 1284. Calc. C 67.28, H 8.72, N 4.36, P 9.65. Found C 66.89, H 8.12, N 4.06, P 9.20

Amidophosphilocavitand (2e) (stereoisomer).

Yield 89%. M.p,127°C. $C_{80}H_{128}N_4O_8P_4$. 1396. Calc. C 68.77, H 9.16, N 4.01, P 8.88. Found C 69.10, H 8.96, N 3.94, P 8.85.

Thiophosphatocavitands (3a,b, 7a,b).

A solution of the corresponding cavitand **(2)** or **(6)** (1.28 mmol) and sulfur (5.30 mmol) in benzene (40 ml) was stirred for 1 hr at 80 °C.Thiophosphatocavitands (3a,b, 7a,b) were dried in vacuum.

Amidothiophosphatocavitand (3a).

Yield 94%. M.p. 116-l17°C. $C_{60}H_{88}N_4O_8P_4S_4$. 1244. Calc. C 57.88, H 7.07, N 4.50, P 9.97. Found C 57.60, H 6.88, N 4.31, P 9.72.

Amidothiophosphatocavitand (3b).

Yield 87%. M.p.107–108° C. $C_{72}H_{112}N_4O_8P_4S_4$. 1412. Calc. C 61.18, H 7.93, P 8.78, S 9.06. Found C 60.76, H 7.60, P 8.26, S 9.02.

Thiophosphatocavitand (7a).

Yield 79%. $C_{76}H_{116}O_{12}P_4S_4$. 1472. Calc. C 61.95, H 7.88, P 8.42, S 8.69. Found C 61.32, H 7.46, P 8.40, S 8.57.

Thiophosphatocavitand (7b).

Yield 77%. $C_{88}H_{140}O_{12}P_4S_4$. 1640. Calc. C 64.39, H 8.54, P 7.56, S 7.80. Found C 64.25, H 8.40, P 7.54, S 7.60.

Phosphatocavitand (4). Octol (1b)

(0.2 mmol) and tetraethyldiamidophenylphosphite (0.8 mmol) in benzene (60 ml) were heated for 1.5 hr at 80°C. The solvent was removed under reduced pressure. The residue was dried for 1 hr at 90°C(0.002). Yield 85%. M.p. 93–95°C. $C_{80}H_{92}O_{12}P_4$. 1368. Calc. C 70.17, H 6.72, P 9.06. Found C 69.85, H 7.12, P 9.10.

Phosphatocavitands (5a,b).

Dichlorophosphite (12 mmol) was added to the solution of octol **(1a,b)** (3 mmol), Et_3N (24 mmol) in benzene (50 ml) at 10°C and the mixture was stirred for I hr. The precipitate was filtered, the solvent was removed and the product was dried in vacuum.

Phosphatocavitand (5a).

Yield 48%. $C_{56}H_{84}O_{16}P_4$. 1136. Calc. C 59.15, H 7.39, P 10.91. Found C 60.20, H 7.59, P 10.65.

Phosphatocavitand (5b).

Yield 55%. $C_{60}H_{92}O_{16}P_4$. 1180. Calc. C 60.02, H 7.80, P 10.51. Found C 60.85, H 7.55, P 10.30.

(-) Bis (N, N-diethylamido) menthylphosphite (8).

(-)-Menthol (2 mmol) and hexamethyltriamidophosphite (2 mmol) in dry dioxan (15ml) were heated for 10 h. The solvent was removed under reduced pressure, the residue was distilled. Yield 93%, b.p. 113°C(0.09); n^{20}_D=1.4751, ^{31}P n.m.r.: 133.2, $[\alpha]^{22}_{578} = -50.5$ (in benzene). $C_{18}H_{39}N_2OP$. Calc. C 65.45; H 11.81, N 8.48, P 9.14 %. Found C 65.73, H 11.61, N 8.52, P 9.17 %.

Menthylphosphitocavitands (9,11).

(-)Bis (N,N-diethylamido)menthylphosphite **(8)** (0.38 mmol) and octol **(1b)** (0.095 mmol) in benzene (30 ml) were stirred for 0.5 hr. Benzene was removed under reduced pressure, the residue was dried for 20 hr at 25–35°C(0.005).

Menthylphosphitocavitand (9).

M.p. 61–63°; $[\alpha]^{20}578$ =–36 (benzene). $C_{150}H_{265}N_6O_{15}P_7$. 2606. Calc. C 69.00, H 10.17, N 3.22, P 8.32 %. Found C 69.49, H 10.78, N 2.72., P 7.58 %.

Menthylphosphitocavitand (11).

M.p. 63–65°C; $[\alpha]^{20}_{578}$ =–12(benzene). $C_{104}H_{110}N_2O_{12}P_4{}^*$ $2(C_2H_5)_2NH$. 1835. Calc. C 70.44, H 10.06, N 2.93, P 6.49 %. Found C 69.72, H 11.06, N 3.25., P 7.27 %.

Phosphitocarceplex (13).

(-)Bis (N,N-diethylamido)menthylphosphite **(8)** (0.38 mmol) and octol **(1b)** (0.19 mmol) in benzene (30 ml) were stirred for 2 hr at 90–95°C. Benzene was removed and the residue was dried for 8 hr at 90°C (0.002). $C_{112}H_{148}O_{16}P_4{}^*$ 8 $(C_2H_5)_2NH$. 2456. Calc. C 70.36; H 9.61; N 4.56; P 5.05. Found C 70.37; H 10.48; N 5.54.; P 5.77.

Thiophosphatocavitand (10).

A suspension of cavitand (9) (0.1 mmol) and sulfur (0.45 mmol) in xylol (15 ml) was boiled for 8 hr. A surplus of the sulfur was filtered and the solvent removed under reduced pressure. The residue was purified with chromatography on silicagel coloumn, eluent $CHCl_3$-C_6H_6 (1:1), m.p. 71–73°, $[\alpha]^{20}578$ = –+14 benzene). $C_{150}H_{265}N_6O_{15}P_7$. 2830 (calculated). Calc.C 63.60; H 9.36; N 2.96; P 7.66, S 7.91%

Found C 64.07; H 10.43; N 2.34.; P 6.66, S 8.54%. 3000 (measurement).

Phosphitocarceplex (14a).

(Method A). A solution of octol **(1a)** (6 mmol) in benzene (50 ml) was added to a solution of PCl_3 (12 mmol) in benzene (20 ml). The reaction mixture was heated for 0.5 hr at 80°C, the solvent was removed and residue was dried for 1 hr at 70°C(0.002). Yield 70%. M.p 223–227°C. ^{31}P n.m.r. (C_6D_6): 129.0. $C_{104}H_{132}O_{16}P_4$. 1760. Calc. C 70.91, H 7.50, P 7.05. Found C 70.69, H 7.98, P 6.83.

(Method B). A solution of octol **(1a)** (6 mmol) and triphenylphosphite (12 mmol) in benzene (50 ml) was heated for 2 hr at 800°C. The solvent was removed, the residue was dried in vacuume. Yield 60%. M.p. 225–227°C. ^{31}P n.m.r.(C_6D_6): 129.0. ^{1}H n.m.r.(C_6D_6): 0.95 (t, 24H, $\underline{CH_3}$-CH_2, $^{3}J_{HH}$ 7.0 Hz), 1.20–1.23 (m, 64H, $(CH_2)4$), 2.39 (m, 16H, -$\underline{CH_2}$-CH), 4.75 (t, 8H, CH-, $^{3}J_{HH}$ 7,0 Hz), 6.71 (m, 16H, Harom), 10.25 (s, 4H, $\underline{OH}$). $C_{104}H_{132}O_{16}P_4$. 1760. Calc. C 70.91, H 7.50, P 7.05. Found C 70.52, H 7.85, P 6.94.

Phosphitocarceplex (14b).

Yield 65%. M.p. 195–198°C. ^{31}P n.m.r. (C_6D_6) : 130.8. ^{1}H n.m.r (C_6D_6): 0.87 (t, 24H, $\underline{CH_3}$-CH_2, $^{3}J_{HH}$ 7.0 Hz), 1.18–1.23 (m, 80H, $(CH_2)_5$), 2.29 (m, 16H, -$\underline{CH_2}$-CH), 4.59 (t, 8H, $\underline{CH}$-, $3J_{HH}$ 7,0 Hz), 6.59–7.15 (m, 16H, Harom), 10.35 (s, 4H, $\underline{OH}$). $C_{112}H_{148}O_{16}P_4$. 1872. Calc. C 71.79, H 7.90, P 6.62. Found C 71.80, H 8.12, P 6.46

Phosphatocavitand (16).

Pyrocatechinchlorophosphite (12 mmol) was added to the solution of octol **(1a)** (3 mmol), Et_3N (12 mmol) in benzene (50 ml) at 10°C and the mixture was stirred for 10 hr. Et_3NHCl was filtered, the solvent was removed and the product was dried in vacuum. Yield 95%. M.p. 65–67°C. $C_{76}H_{84}O_{16}P_4$. 1376. Calc. C 66.28, H 6.10, P 9.01. Found C 65.71, H 6.41, P 9.28

Compounds (17,18,19).

Chloromethylphosphonic acid chloride (1.6 mmol) [or bis(chloromethyl) phosphinic acid chloride (0.8 mmol)] in dry benzene (or Me_2CO_3, or CH_2CL_2) (60 ml) was added to the solution of octol (1c) (0.2 mmol), triethylamine (or K_2CO_3) (1.6 mmol) in benzene (or Me_2CO_3, or CH_2Cl_2) (100 ml). The mixture was stirred for 24 hr at room temperature centrifuged and decanted. The solvent was removed under reduced pressure and the product was dried for 36 hr in vacuum.

Compound (17)

Yield 75 %. M.p.135–137°C. ^{1}H n.m.r [$(CD_3)CO$]: 1.02 (t,12H, $C\underline{H_3}$- CH_2,$^{3}J_{HH}$ 7.0 Hz), 1.22, 1.35–1.44 (m, 56H, $C\underline{H_2}$), 2.67– 3,1 (m, 16H, $C\underline{H_2}$), 3.6–4.1 (m, 8H, P(O)$C\underline{H_2}$Cl), 4.3–4.5 (m, 4H,$C\underline{H}$), 4.7–4.8 (m, 4H), 6.90–7.3 and 7.9–8.2 (m, 8H, CH arom.) ^{31}P n.m.r.: 12.37. $C_{68}H_{96}C_{14}O_{12}P_4Et_3N$ 1440 (calculated); 1472 (measurement).

Compound (18).

Yield 80 %. M.p. 145–147°C. ^{1}H n.m.r [$(CD_3)CO$],: 1.04 (t,12H, $\underline{CH}_3$-CH_2, $^{3}J_{HH}$ 7.0 Hz), 1.27–1.44 (m, 56H, $C\underline{H}_2$), 2.43, (m, 8H, $C\underline{H}_2$) , 3.66 (s, 4H, P(O)$C\underline{H}_2$Cl), 3.88 (s, 4H, P(O)$C\underline{H}_2$Cl), 4.45 (t, 4H,C$\underline{H}$), 6.52, 6,78 (s, 4H,CH arom) and 7.49, 7.70, 7.86 (4H, C$\underline{H}$ arom.). ^{31}P n.m.r. ($C6D_6$): 10.5. $C_{66}H_{96}Cl_2O_{10}P_2$. Calc. C 67.00, H 8.12, Cl 6.00, P 5.24. Found C 69.05;, H 8.73,Cl 6.89; P 5.24.

Compound (19).

Yield 92 %. M.p. 120° C. ^{1}H n.m.r [$(CD_3)CO$] : 1.04 (t,12H, $C\underline{H}_3$-CH_2, $^{3}J_{HH}$ 7.0 Hz), 1.35–1.44 (m, 56H, $C\underline{H}_2$), 2.29 (m, 8H, $C\underline{H}_2$), 3.77, (s, 8H, P(O)$C\underline{H}_2$Cl), 3.81 (s, 8H, P(O)$C\underline{H}_2$Cl) , 4.3 (t, 4H,CH) , 6.50, (s, 4H, C$\underline{H}$ arom.), 7.59 (s, 4H, C$\underline{H}$ arom.) ^{31}P n.m.r.: 29.04 . ^{13}C n.m.r.: ($CDCl_3$): 14.76 (s, CH_3), 23.39 (s, CH_2), 28.70 (s, CH_2), 30.04 (s, CH_2), 30.43 (s, CH_2), 32.64 (s, CH_2), 34.05 (arom.-C-arom), 35.47 (d, P-CH_2-Cl, J PC 103.9 Hz), 103.41 (s, Carom), 124.72 (s, C-arom), 125.17 (s, Carom), 151.67 (s,Carom). $C_{72}H_{112}C_{18}O_{24}P_8$ * 4 Me_2CO. 2024.6 (monom), 4049 (dimer). Calc. C 47.27;, H 6.75, Cl 13.32; P 11.63. Found C 47.64, H 6.33, Cl 13.65; P 11.96. 4239 (measurement).

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