ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 3, pp. 458–468. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © E.M. Kasymova, A.R.Burilov, N.A. Mukmeneva, S.V. Bukharov, G.N. Nugumanova, M.A. Pudovik, A.V. Chernova, R.R. Shagidullin, A.I. Konovalov, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 3, pp. 494–504.

Synthesis and Some Properties of Tetrakis-3,5-di-*tert*-butyl-4-hydroxybenzylated Calix[4]resorcinols

E. M. Kasymova[a], A. R. Burilov[a], N. A. Mukmeneva[b], S. V. Bukharov[b], G. N. Nugumanova[b], M. A. Pudovik[a], A. V. Chernova[a], R. R. Shagidullin[a], and A. I. Konovalov[a]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Acad. Arbuzova 8, Kazan, Tatarstan, 420088 Russia*
Fax: (843 2) 75 2253
e-mail: pudovik@iopc.knc.ru
[b] *Kazan State Technological University, Kazan, Tatarstan, Russia*

Received November 16, 2006

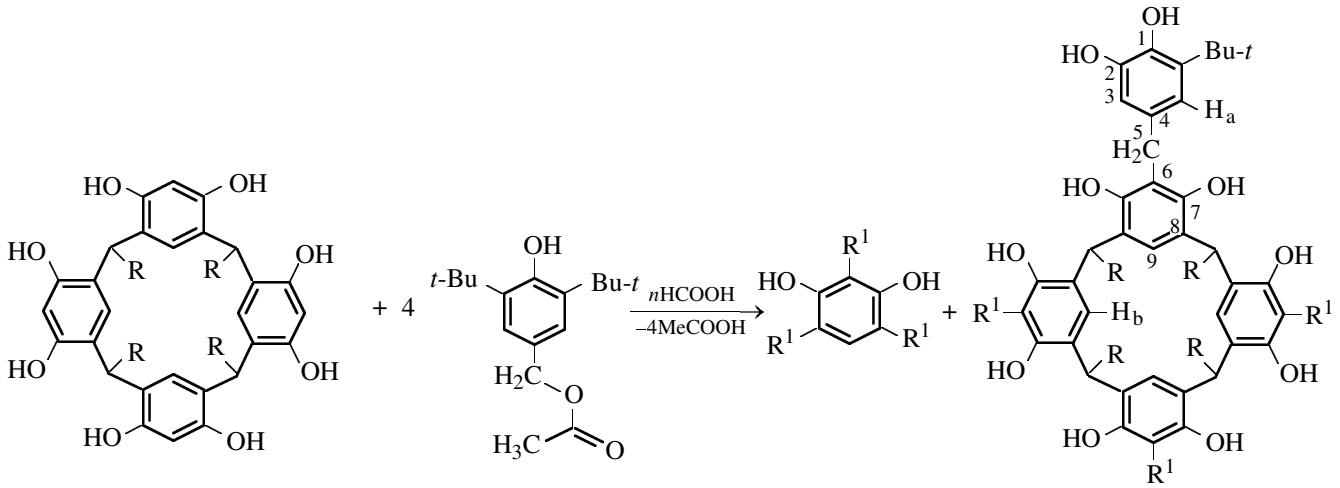
Abstract — A method for the synthesis of new calix[4]resorcinols tetra-3,5-di-*tert*-butyl-4-hydroxybenzyl derivatives is developed. Their interaction with methyldichlorophosphonate, dimethyldichlorosilane in the presence of a base leads to formation of organophosphorus-organosilicon cavitands. Acetylation of hydroxybenzylated calix[4]resorcinols with acetic anhydride leads to products of either incomplete or full acetylation depending on experimental conditions.
DOI: 10.1134/S1070363207030206

One of perspective and intensively developing lines of investigation in organic chemistry comprises research in the field of calix[n]arens and in particular calix [4]resorcinols [1–4]. It is caused by an ease of their synthesis, opportunity of C- and O-functionalisation, ability to form complexes of host–guest type with organic compounds of various structure and metal ions. Combination of properties mentioned above makes use of this class compounds perspective for creation of new type complexing agents, metal ions extractants and new catalytic systems. One of the peculiarities of calix[4]resorcinols is their tendency to selfassociation leading to a formation of supramolecular ensembles. As a consequence, they are low soluble in organic solvents, have diffuse melting points and in some cases reduced reactivity. We have assumed that introduction of bulky groups into calixarene molecules should prevent their aggregation and as a consequence would substantially improve solubility in organic solvents and enhance their reactivity. We choose a bulky 3,5-di-*tert*-butyl-4-hydroxybenzyl fragment as a substituent which is of interest from one more point of view. Investigation of antioxidant properties of tetramethylcalix[4]resorcinol and some of its derivatives has shown an opportunity of creation a new group of highly effective inhibitors of polymers thermal-oxidative degradation on the basis of calixarenes [5, 6]. In that aspect modification of tetraalkylcalix[4]resorcinols by introduction of sterically hindered phenol fragments into their aromatic rings could be a perspective method to increase their antioxidizing activity.

In the present work we investigated an interaction of calix[4]resorcinols **Ia**–**Id** with 3,5-di-*tert*-butyl-4-hydroxybenzylacetate (**II**), which application allows to introduce under mild conditions sterically hindered phenol fragments into the molecules of various compounds [7].

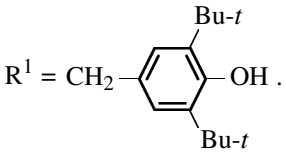
Interaction of compound **Ia** with benzylacetate **II** in acetone solution in the presence of chloric acid leads to formation of two products: 2,4,6-tris(3,5-di-*tert*-buty-4-hydroxybenzyl)resorcinol (**III**) and 4,6,10,12,16,18,22,24-octahydroxy-5,11,17,19-tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (**IVa**) in a ratio of 70 : 30%. The major product, substituted resorcinol **III**, is isolated and characterized by spectral methods and also by comparison of its constants with published data [8].

Change the ratio of reagents **Ia** and **II** to 1 : 12 has led to increase of a product **III** yield up to 95%. Thus, we found a new direction of calixarene reaction with



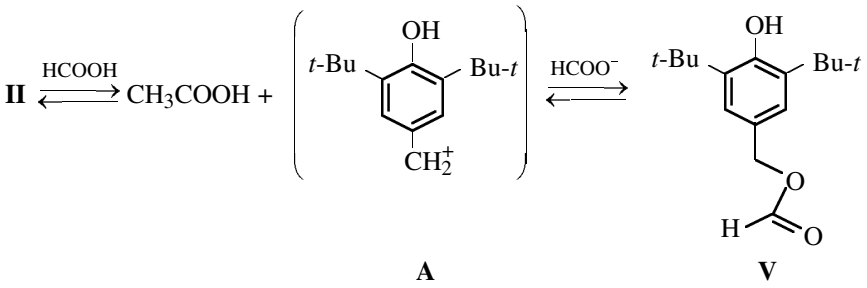
Ia–Id **II** **III** **IVa–IVd**

I, IV, R = Me (**a**), Et (**b**), Pr (**c**), C_5H_{11} (**d**),



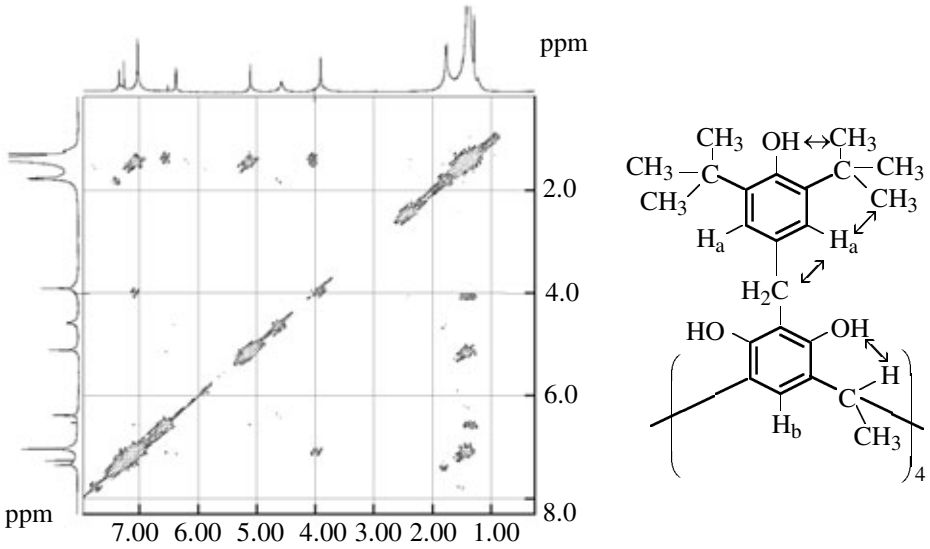
electrophilic reagents, leading to a full destruction of a macro cyclic matrix and formation of tris-benzylated resorcinol.

With the purpose of optimization the method of tetra-benzylated calixarene **IVa** synthesis we used formic acid instead of chloric acid as the acidic catalyst. This replacement influenced essentially the synthetic result of reaction: the calixarene **IVa** yield increased from 30 up to 80%.



A **V**

As we suggest, this influence of formic acid is connected with the course of starting compound **II** transacylation reaction and formation of benzylformate **V** [9]. As formate group seems to be better leaving group than the acetate one, benzylformate **V** is the best benzylating agent in comparison with benzylacetate. Analysis of homonuclear correlation ^{1}H NMR spectra showed that C-benzylated calix[4]-resorcinol **IVa** has a "cone" conformation (see figure). This conclusion follows from the fact that compound **IVa** methine proton quartet is located in the field of 4.5 ppm, same as calixarene **Ia** methine proton quartet, having according to X-ray structural analysis a "cone" conformation [10]. According to published data, a change of a "cone" conformation by "1,3-alternant" in phenol calixarenes leads to displacement of methine protons signal by ~1 ppm [11]. In the 2D ROESY spectrum of compound **IVa** in chloroform (see figure) only trivial cross-peaks $H_a \leftrightarrow$ *t*-Bu, OH$\leftrightarrow$*t*-Bu are present, that confirm realization of a "cone" conformation.



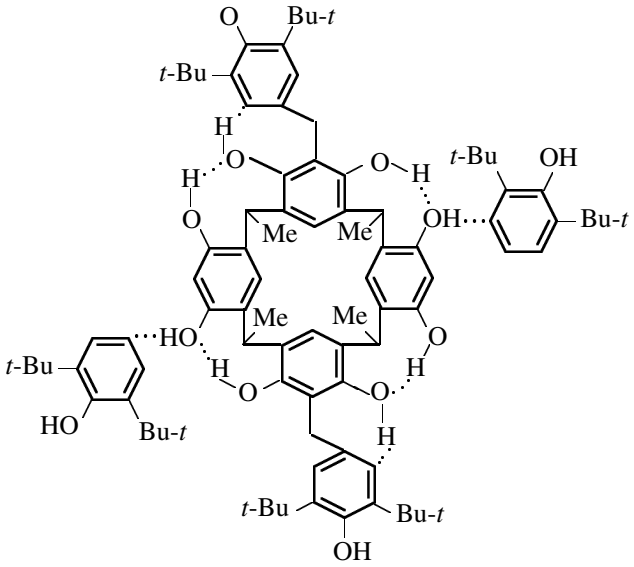
2D ROESY spectrum of compound **IVa**.

Analysis of hydroxyl groups stretching vibrations region in calixresorcinol **IVa** IR spectra allows to make certain conclusions concerning character of hydrogen bonds with participation of OH groups and hence on the supramolecular structure of this compound. In the spectrum of compound **IVa** crystal sample the hydroxyl groups stretching vibrations are displayed in the form of two major absorption bands, narrow with a maximum at 3642 cm^{-1}, having a shoulder at 3615 cm^{-1}, and wide asymmetrical at 3435 cm^{-1} with a number of shoulders. In the spectra of calixarene **IVa** solutions in CCl_4 position of main ν_{OH}. bands maxima practically does not change. At the same time, passing on from the crystal sample spectrum to the spectra of solutions (© 10^{-4}) an obvious change of the peak intensity ratio of the bands at 3640 and 3430 cm^{-1} is observed in favor of a high-frequency component. The peak intensity ratio D_{3640}/D_{3430} increases from 0.7 for crystals up to 1.02 for solutions. Simultaneously the contours of both bands become a little simpler: the high-frequency band shoulder at 3615 cm^{-1} disappears and a weak maximum at 3597 cm^{-1} appears, and the absorption of the lowfrequency band shoulder at 3495 cm^{-1} decreases. Further dilution of the solution down to the concentration of 3×10^{-5} M leaves unchanged the spectral pattern in the region of ν_{OH}. Mentioned above allows to assign the band at 3640 cm^{-1} to vibrations of 2,6-di-*tert*- butylphenol fragment free hydroxyl group as it is observed in the region typical of the sterically hindered phenols [12]. Absorption at 3430 cm^{-1} should be attributed to calix[4]resorcinol backbone resorcinol hydroxyls connected by intramolecular hydrogen bonds OH···OH [13]. The weak peak at 3595 cm^{-1} in the solution spectrum corresponds to absorption of hydroxyl groups of this fragment connected from behind by OH···O–H (so-called pseudo-free hydroxyls [14]) which can form with involvement of their protons the additional intramolecular hydrogen bonds with π-electrons located near benzyl rings [14]. Growth of free ν_{OH} bonds intensity, as well as noted above change in the band contours observed in the spectra of compound **IVa** under crystal-solution transition, confirm the fact that a part of di-*tert*-butylphenol hydroxyls in a solid phase participates in intermolecular hydrogen bonds breaking off under the substance dilution.

For specification of possible number and position of bands components at 3640 and 3430 cm^{-1} a decomposition of these bands contours in a version of "Local Least Squares" algorithm and Lorentz–Gauss bands configuration is carried out. In the spectrum of the solid sample the results of decomposition are the following: in the free ν_{OH} region there is a second component at 3619 cm^{-1} alongside with major peak at 3641 cm^{-1}. Band ν_{OH} bound 3435 cm^{-1} is resolved into five components with approximate maxima at 3546, 3494, *3438*, 3330, and 3145 cm^{-1}. After decomposition of a solution spectrum alongside with singlet at 3644 cm^{-1} (ν_{OH} free) there are 8 components at 3597, 3551, 3524, 3492, 3461, *3429*, *3386*, and *3280* cm^{-1} in the field of ν_{OH} (bound).

In the spectra of compounds **IVa** diluted solutions in CCl_4 (down to 3×10^{-5} M) the absence of resorcinol backbone free OH groups bands, which by analogy to resorcinol and data [15] for calixarenes are expected

to be located in the region of 3616–3620 cm^{-1}, indicates the retaining in molecules **IVa**, both in a crystal and solutions, of the above-described intramolecular hydrogen bonds on the upper rim of calix[4]resorcinol rings, i.e. a primary "cone" conformation. It is obvious that in case of "alternant" forms along with the bound OH groups the above-mentioned free hydroxyls bands should be observed. Retaining the complex structured character of the band at 3430 cm^{-1} also in solutions confirms the "cone" asymmetry and heterogeneity that can be a consequence of the presence of bulky *tert*-butyl substituents in the molecule.

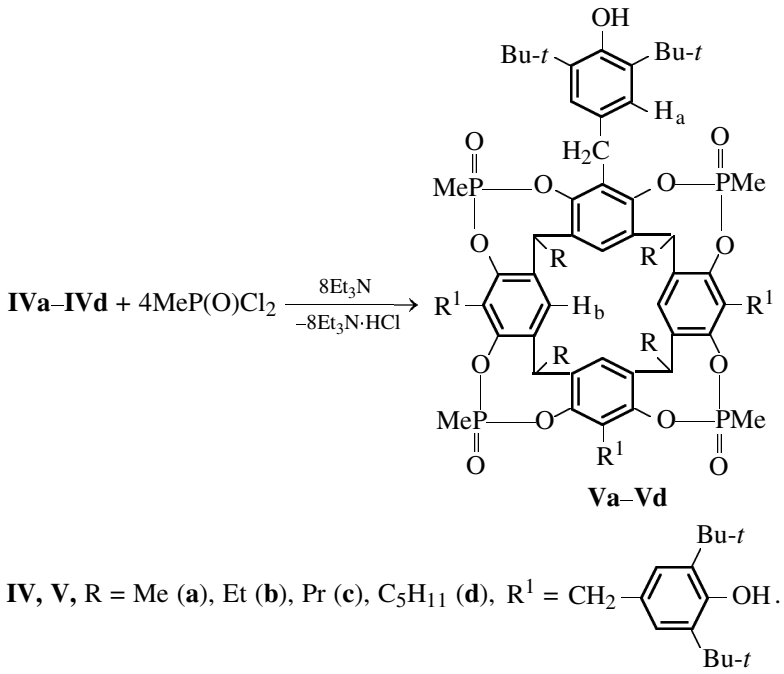


As it was already mentioned above, the formation of benzylated resorcinol **III** appeared to be unexpected for us as there were no publications on the opportunity of calixarene ring cleavage under the action of electrophilic reagents. By special experiments it has been found out that in double system: calixarene **I**–chloric or formic acid the splitting of macrocycle does not occur. It could be assumed, that formation of compound **III** is a result of calixarenes **I** and/or **IV** complete benzylation by benzyl carbocation (**A**), generated in the reaction conditions. Actually, when acetone solution of compounds **IVa** and **II** in the ratio of 1 : 8 was standing during 24 hours in the presence of chloric or formic acid in ^1H NMR spectrum of the reaction mixture the signals of calixarene **IVa** 1.74 d (12H, Me, $^3J_{HH}$ 7.0 Hz), 4.60 q (4H, CH, $^3J_{HH}$ 7.0 Hz), 6.34 s (8H, OH) practically disappeared, and the signals of nonequivalent methylene and hydroxyl (in the benzyl fragment) groups of compound **III**: 3.80 s (4H, CH_2), 3.92 s (2H, CH_2), 4.85 s (2H, OH), 5.09 s (1H, OH) were observed. Thus, it is possible to conclude, that formation of the product **III** in reaction of calixarene **I** with benzylacetate **II** probably occurs as a result of compound **IVa** calixarene ring splitting under the action of benzyl carbocation (**A**) and the acid catalyst.

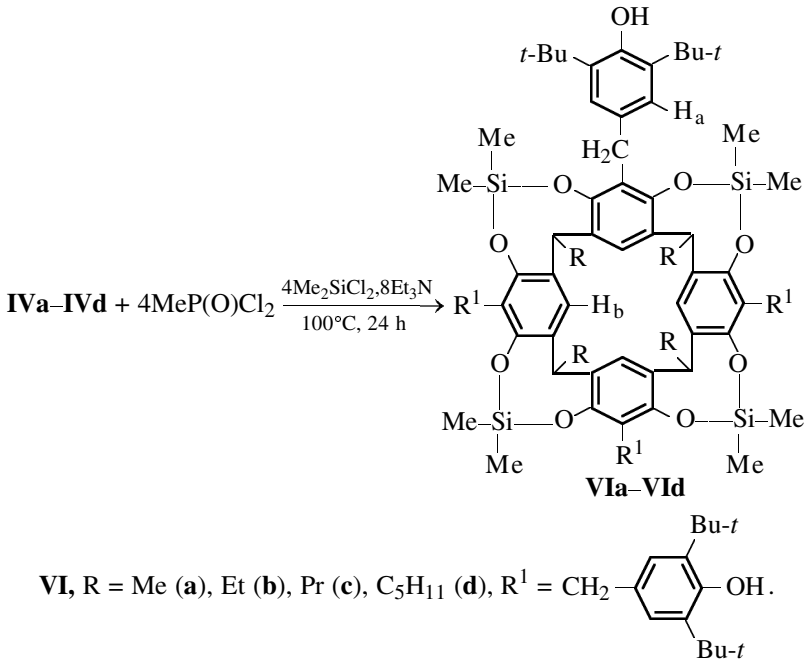
Developed on an example of tetramethyl derivative **Ia** the method of calixarene matrix benzylation have been extended also to other calixarenes. Interaction of tetraethyl(propyl-, pentyl-) calix[4]resorcinols **Ib**–**Id** with benzylacetate **II** in the presence of formic acid leads to formation of tetrabenzylated calix[4]resorcinols **IVb**–**IVd** with high yields and to small amounts of tris-benzylated resorcinol **III**. As expected, compounds **IVa**–**IVd** are well soluble in nonpolar organic solvents and have narrow melting points, that indirectly confirm the breaking of their aggregation.

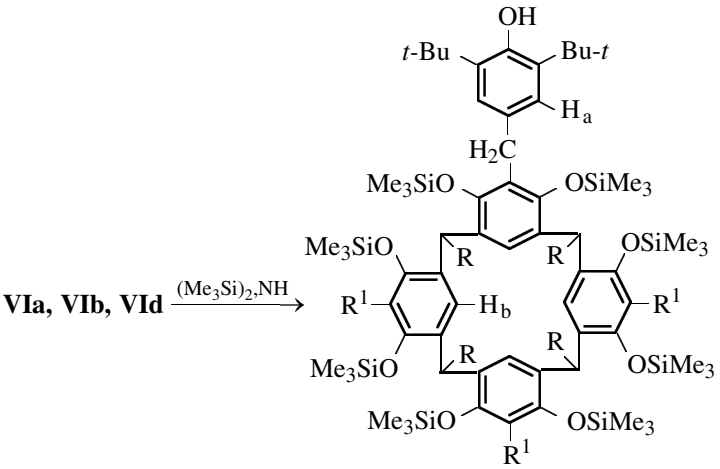
The prepared tetrabenzylated calix[4]resorcinols **IVa**–**IVd** are studied in phosphorilation, silylation and acetylation reactions. Recently the researchers have paid a great attention to calixarenes phosphorilated derivatives, which are of interest as complexing agents, extractants of metal ions, basic compounds for synthesis of new types of spatially organized structures: carceplex, tubes, etc. [16]. With the purpose of preparation of phosphorous containing cavitands we studied phosphorylation of calixarenes **IVa**–**IVd** by methyldichlorophosphonate in the presence of a base. As a result the compounds **Va**–**Vd** were obtained and their structure were confirmed by

the data of IR, ^1H, ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis. It should be noted that obtained spectral and analytical data indicate the presence of hydrochloride triethylamine admixture in the synthesized compounds, probably as a part of molecular complex which is not possible to avoid.

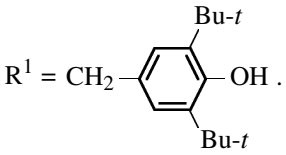


According to published data, phenols silylation can be carried out with use of some halogen- or nitrogen containing organosilicon compounds [17]. It was found, that at interaction of calixarenes **IVa**–**IVd** with dimethylchlorosilane in toluene in the presence of triethylamine (24 h, 100°C) organosilicon cavitands **VIa**–**VId** were formed, which structure was proven by IR the ^1H, ^{13}C NMR spectroscopy and mass spectrometry data.



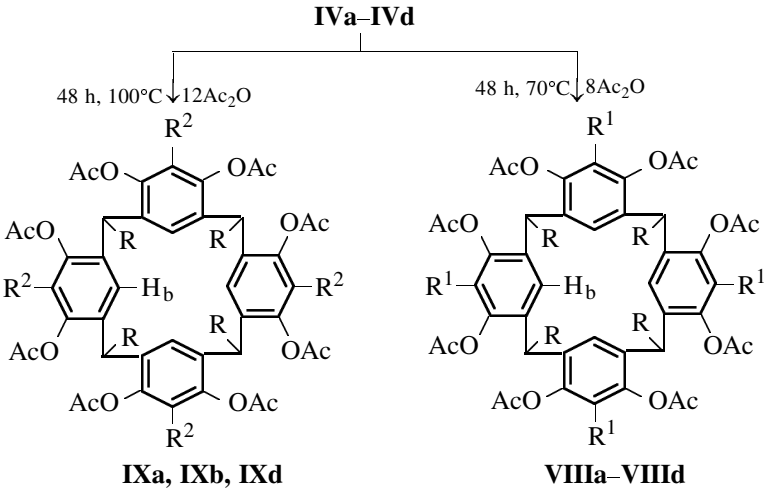


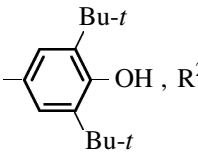
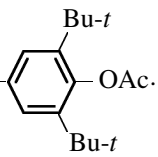
VII, R = Me (**a**), Et (**b**), Pr (**c**), C_5H_{11} (**d**),



As a result of resorcinols **IVa**, **IVb**, and **IVd** silylation by hexamethyldisilazane the octasilylderivatives **VIIa**, **VIIb**, and **VIId** were prepared.

Interaction of calix[4]resorcinols **IVa**–**IVd** with acetic anhydride in the presence of pyridine catalytic quantity was carried out at double excess of the acylating agent at long heating (24 h, 70°C). Under these conditions, acylation of calixarene matrix hydroxyl groups occurs with the formation of compounds **VIIIa**–**VIIId**. In their IR spectra there is an absorption band in the region of 3640 cm^{-1} characteristic of the benzyl fragment hydroxyl group in the molecules of compounds **IVa**–**IVd**, and also a band of stretching vibrations at 1780 cm^{-1}, characteristic of carbonyl group.



VIIIa–**VIIId**, **IXa**–**IXd**, R + Me (**a**), Et (**b**), Pr (**c**), C_5H_{11} (**d**), $R^1 = CH_2$  , $R^2 = CH_2$  .

It was possible to carry out complete acylation of calixarenes **IVa**, **IVb**, and **IVd** in acetic anhydride as a solvent at long heating of the reaction mixture (48 h, 100°C). In the ^{1}H NMR spectrum of compound **IXa** a singlet peak is observed in the field of 2.15 ppm corresponding to acyl groups methyl protons whereas singlet signals of OH groups protons (at 5.07 and 6.84 ppm) are absent. In the IR a spectrum of compound **IXa** there are no bands of stretching vibrations, characteristic of hydroxyl groups. It should be noted that in the ivestigated reactions tetrabenzylated calixarenes **IVa**–**IVd** displayed rather low reactivity in comparison with starting calixarenes **Ia**–**Id**, that can be caused by the presence of bulky 3,5-di*tert*-butyl-4-hydrobenzyl groups in ortho-positions of calixarene backbone.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker MSL-400 spectrometer at 400.13, 100.62, and 166.93 MHz, respectively, relative to residual protons of deuterated solvent (*D*-acetone, $CDCl_3$) and external reference 85% H_3PO_4. The mass spectra were obtained on MALDI-2 V-5.2.0 spectrometer (1,8,9-trihydroxyanthracene matrix).

2,4,6-Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-resorcinol (III). 0.08 ml of 72% chloric acid was added to a solution of 1.0g of calixarene **Ia** and 4.1 g of benzylacetate **II** in 20 ml of acetone. The reaction mixture was kept for 24 hours at 20 °C and then poured into water. The precipitate formed was filtered off, washed with water to pH 7 and dried for 48 h at 20°C. According to ^{1}H NMR spectroscopy data the reaction product obtained (3.4 g) was a mixture of compounds **III** and **IV** in a ratio of 70 : 30%. After recristallisation from hexane 1.2 g (35%) of compound **III** was obtained, mp 153–154°C (151–154°C [8]). Found, %: C 79.85; H 9.70. $C_{51}H_{72}O_5$ Calculated, %: C 80.10; H 9.42.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.13,7.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (IVa). A mixture 3.0 g calixarene **Ia**, 6.9 g benzylacetate **II**, 55 ml acetone and 65 ml of formic acid was kept for 24 h at 20°C, poured into 100 ml of water, and a solution of sodium bicarbonate was added to povide pH 5–6. The precipitate formed was filtered off, washed with water and dried in air. We obtained 7.75 g of powder, which according to ^{1}H NMR spectroscopy data was a mixture of compounds **III** and **IVa**. The main reaction product **IVa** was isolated by column chromatography on silica gel (pentane–acetone, 7 : 3). Yield 2.6 g (33%) of compound **IVa**, mp 230°C (decomp.). IR spectrum (¤Br), ν, cm^{-1}: 3440, 3640 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 1.39 s (72H, CMe_3), 1.77 d (12H, Me, $^3J_{HH}$ 7.0), 3.89 s (8H, CH_2), 4.60 q (4H, CH, $^3J_{HH}$ 7.0), 5.08 s (4H, OH), 6.34 s (8H, OH), 7.0 s (8H, H_a), 7.33 s (4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 20.5 q (C^{11}, $^1J_{CH}$ 125.0), 28.3 d (C^{10}, $^1J_{CH}$ 130.0), 29.4 t (C^5, $^1J_{CH}$ 90.0), 30.2 q (CMe_3, $^1J_{CH}$ 120.0), 34.3 s (CMe_3), 114.0 s (C^8), 121.6 d (C^9, $^1J_{CH}$ 150.0), 125.0 d (C^3, $^1J_{CH}$ 150.0), 125.5 s (C^6), 128.9 s (C^4), 136.5 s (C^2), 149.0 s (C^7), 152.6 s (C^1). Found, %: C 77.69; H 8.65. $C_{92}H_{120}O_{12}$. Calculated, %: C 77.97; H 8.47.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetraethylpentacyclo[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-dodecaen (IVb) was prepared similarly to the previous one from 2.0 g of calixarene **Ib**, 4.2 g of benzylacetate **II**, 45 ml of acetone, 55 ml of formic acid. Yield of **IVb** 1.5 g (31%), mp 200°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.93 d (12H, Me, $^3J_{HH}$ 6.97), 1.38 s (72H, CMe_3), 2.18 m (8H, CH_2), 3.93 s (8H, CH_2), 4.23 t (4H, CH, $^3J_{HH}$ 7.0), 5.09 s (4H, OH), 6.53 s (8H, OH), 6.99 s (8H, H_a), 7.34 s (4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 12.07 q (C^{12}, $^1J_{CH}$ 125.0), 27.19 t (C^{11}, $^1J_{CH}$ 125.0), 28.4 d (C^{10}, $^1J_{CH}$ 130.0), 29.65 t (C^5, $^1J_{CH}$ 90.0), 33.07 q (CMe_3, $^1J_{CH}$ 120.0), 30.9 s (CMe_3), 113.66 s (C^8), 121.4 d (C^9, $^1J_{CH}$ 150.0), 124.14 d (C^3, $^1J_{CH}$ 150.0), 124.26 s (C^6), 128.46 s (C^4), 136.23 s (C^2), 149.22 s (C^7), 152.2 s (C^1). Found, %: C 78.59; H 8.50. $C_{96}H_{128}O_{12}$. Calculated, %: C 78.26; H 8.70.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetrapropylpentacyclo[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-dodecaen (IVc) was prepared similarly to the previous one from 2.0 of calixarene **Ic**, 3.81 g of benzylacetate **II**. Yield 1.3 g (31%), mp 205°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.90 t (12H, Me, $^3J_{HH}$ 6.97), 1.39 s (72H, CMe_3), 1.68 m (8H, CH_2), 2.18 m (8H, CH_2), 3.95 s (8H, CH_2), 4.33 t (4H, CH, $^3J_{HH}$ 7.0), 5.09 s (4H, OH), 6.53 s (8H, OH), 6.99 s (8H, H_a), 7.34 s (4H, H_b). Found, %: C 78.72; H 8.70. $C_{100}H_{136}O_{12}$. Calculated, %: C 78.95; H 8.95.

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetrapenthylpentacyclo[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-dodecaen (IVd) was prepared similarly to the previous one from 2.0 of calixarene **Id** and 3.25 g of benzylacetate **II**. Yield 1.28 g (30%), mp 190°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 0.89 t (12H, Me, $^3J_{HH}$ 6.97), 1.37 s (72H, CMe_3), 1.57 m (24H, CH_2), 2.20 m (8H, CH_2CH), 3.91 s (8H, CH_2), 4.51 t (4H, CH, ^3J 7.0), 5.09 s (4H, OH), 6.28 s (8H, OH), 6.97 s (8H, H_a), 7.25 s (4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 13.09 q (C^{15}, $^1J_{CH}$ 150.0), 21.73 t (C^{12-14}, $^1J_{CH}$ 125.0), 25.49 q (C^{11}, $^1J_{CH}$ 125.0), 27.47 d (C^{10}, $^1J_{CH}$ 130.0), 29.7 t (C^5, $^1J_{CH}$ 90.0), 31.83 q (CMe_3), $^1J_{CH}$ 120.0), 33.39 s (CMe_3), 111.65 s (C^8), 119.52 d (C^9, $^1J_{CH}$ 150.0), 122.36 d (C^3, $^1J_{CH}$ 150.0), 126.5 s (C^6), 128.9 s (C^4), 134.22 s (C^2), 147.15 s (C^7), 150.29 s (C^1). Found, %: C 79.32; H 9.50. $C_{108}H_{152}O_{12}$. Calculated, %: C 79.02; H 9.27.

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-tetramethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetraphospha-37,38,39,40-tetramethylnonacyclo[29,3,1,1^{21,25},1^{13,17},1^{5,9}]-tetracosa[16,32,124,30,116,22,18,14]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (Va). 0.06 g of methyldichlorophpsphonate was added to a mixture of 0.2 g of calixarene **IVa**, 10 ml of anhydrous acetonitrile, 0.1 g triethylamine. The reaction mixture was kept for 32 h at 80°C, triethylamine hydrochloride was separated, the solvent was removed and the residue was reprecipitated to hexane from chloroform and dried in vacuum (5 h, 20°C, 04 mm Hg). Yield 0.1 g (43%), mp 145–147°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm, (*J*, Hz): 0.88 br.m. (12H, Me), 1.38 s (72H, CMe_3), 1.80 m (12H, MeP), 3.93 s (8H, CH_2Ph), 4.55 q (4H, CH, $^3J_{HH}$ 6.9), 6.45 s (4H, OH), 6.98–7.21 m (8H, H_a, 4H, H_b). ^{31}P NMR spectrum, δ_P, ppm: 22.63, 18.48. Found, %: C 70.03; H 8.11; P 7.19. $C_{96}H_{124}O_{16}P_4$. Calculated, %:, C 69.55; H 7.54; P 7.47. *m/z* 1679 (*M* + Na), 1793 (*M* + $Et_3N\cdot HCl$).

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-tetramethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetraphospha-37,38,39,40-tetraethylnonacyclo[29,3,1,1^{21,25},1^{13,17},1^{5,9}]-tetracosa-[1^{6,32},1^{24,30},1^{16,22},1^{8,14}]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (Vb) was prepared similarly to the previous one from 1.0 of calixarene **IVb**, 0.5 g of triethylamine and 0.4 g of methyldichlorophpsphonate. Yield 0.6 g (52%), mp 143°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 0.89 m (12H, Me), 1.38 m (72H, CMe_3), 1.83 m (12H, MeP), 2.17 m (8H, CH_2), 3.85 s (8H, CH_2Ph), 4.56 t (4H, CH, ^3J 6.9), 6.50 s (4H, OH), 7.08 m (8H, H_a, 4H, H_b). ^{31}P NMR spectrum, δ_P, ppm: 22.62, 18.40. Found, %: C 70.56; H 7.99; P 6.94. $C_{100}H_{132}\cdot O_{16}P_4$. Calculated, %: C 70.07; H 7.76; P 7.23.

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-tetramethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetraphospha-37,38,39,40-tetrapropylnonacyclo[29,3,1,1^{21,25},1^{13,17},1^{5,9}]-tetracosa-[1^{6,32},1^{24,30},1^{16,22},1^{8,14}]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (Vc) was prepared similarly to the previous one from 1.0 g of calixarene **IVc**, 0.5 g of triethylamine and 0.4 g of methyldichlorophpsphonate. Yield 0.5 g (58%), mp 150°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm. (*J*, Hz): 0.88 t (12H, Me, ^3J 6.9), 1.34 m (72H, CMe_3), 1.60 m (8H, CH_2), 1.80 m (12H, MeP), 2.20 m (8H, CH_2), 3.82 s (8H, CH_2Ph), 4.42 t (4H, CH, ^3J 6.9), 5.92 s (4H, OH), 6.08 m (8H, H_a, 4H, H_b). ^{31}P NMR spectrum, δ_P, ppm: 22.64, 18.43. Found, %: C 70.34; H 8.10; P 6.81. $C_{104}H_{140}O_{12}P_4$. Calculated, %: C 70.57; H 7.97; P 7.00.

33,34,35,36- Tetrakis(3,5- di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-tetramethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetraphospha-37,38,39,40-tetrapenthylnonacyclo[29,3,1,1^{21,25},1^{13,17},1^{5,9}]-tetracosa[1^{6,32},1^{24,30},1^{16,22},1^{8,14}]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (Vd) was prepared similarly to the previous one from 1.0 of calixarene **IVd**, 0.5 g of triethylamine, 0.5 g of methyldichlorophpsphonate. Yield 0.57 ' (52%), mp 147–150°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 m (12H, Me), 1.36 m (72H, CMe_3), 1.63 m (24H, CH_2), 1.81 m (12H, MeP), 2.21 m (8H, CH_2), 3.93 s (8H, CH_2Ph), 4.52 t (4H, CH, ^3J 6.9), 5.95 s (4H, OH), 6.08 m (8H, H_a, 4H, H_b). ^{31}P NMR spectrum, δ_P, ppm: 23.30, 18.90. Found, %: C 72.04; H 9.09; P 6.25. $C_{112}H_{156}O_{16}P_4$. Calculated, %: C 71.46; H 8.35; P 6.58. *m/z* 1903 (*M* + Na), 1919 (*M* + K), 2017 (*M* + $Et_3N\cdot HCl$).

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-octamethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetrasila-37,38,39,40-tetramethylnonacyclo[29,3,1,1^{21,25},1^{13,17},1^{5,9}]tetracosa[1^{6,32},1^{24,30},1^{16,22},1^{8,14}]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (VIa). 0.16 g of triethylamine were added dropwise to 0.2 g of calixarene **Ia** in 10 ml toluene at a constant stirring under argon. 0.14 g of dimethylchlorosylane were added to a reaction mixture, then it was kept for 24 h at 100°C, triethylamine hydrochloride precipitate was filtered off. The solvent was removed and reaction product was recrystallized with hexane from chloroform and dried in vacuum of oil pump (2 h, 60°C, 0.01 mm Hg.). Yield 0.10 g (48%), mp 159°C. ^{1}H NMR spectrum

($CDCl_3$), δ, ppm (*J*, Hz): 0.08 m (24H, $SiMe_2$), 0.87 m (12H, Me), 1.41 m (72H, CMe_3), 3.59 s (8H, CH_2Ph), 4.50 q (4H, CH, $^3J_{HH}$ 6.9), 5.01 s (4H, OH), 7.17 m (8H, H_a, 4H, H_b). Found, %: C 73.84; H 9.01; Si 6.44. $C_{100}H_{136}O_{12}Si_4$. Calculated, %: C 73.13; H 8.35; Si 6.84. *m/z* 1663 (*M* + Na).

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-octamethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetrasila-37,38,39,40-tetraethylnonacyclo[29,3,1,$1^{21,25}$,$1^{13,17}$,$1^{5,9}$]tetracosa[$1^{6,32}$,$1^{24,30}$,$1^{16,22}$,$1^{8,14}$]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (VIb) was prepared similarly to the previous one from 0.5 of calixarene **IVb**, 0.27 g of triethylamine and 0.18 g of dimethylchlorosilane. Yield 0.32 g (53%), mp 157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm. (*J*, Hz): 0.08 s (24H, $SiMe_2$), 0.85 m (12H, Me), 1.38 m (72H, CMe_3), 2.17 m (8H, CH_2CH) 3.59 s (8H, CH_2Ph), 4.47 t (4H, CH, $^3J_{HH}$ 6.9), 5.01 s (4H, OH), 7.14 m (8H, H_a, 4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 q ($SiMe_2$, $^1J_{CH}$ 120.0), 12.52 q (C^{12}, $^1J_{CH}$ 125.0), 25.65 t (C^{11}, $^1J_{CH}$ 125.0), 29.38 d (C^{10}, $^1J_{CH}$ 130.0), 30.34 t (C^5, $^1J_{CH}$ 90.0), 35.57 q (CMe_3, $^1J_{CH}$ 120.0), 34.28 s (CMe_3), 125.47 s (C^8), 130.14 d (C^9, $^1J_{CH}$ 150.0), 131.26 d (C^3, $^1J_{CH}$ 150.0), 131.8 s (C^6), 135.35 s (C^4), 148.21 s (C^2), 151.82 s (C^7), 157.93 s (C^1). Found, %: C 73.98; H 8.88; Si 6.14. $C_{104}H_{144}O_{12}Si_4$. Calculated, %:, C 73.54; H 8.54; Si 6.61. *m/z* 1695.5.

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-octamethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetrasila-37,38,39,40-tetrapropylnonacyclo[29,3,1,$1^{21,25}$,$1^{13,17}$,$1^{5,9}$]tetracosa-[$1^{6,32}$,$1^{24,30}$,$1^{16,22}$,$1^{8,14}$]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (VIc) was prepared similarly to the previous one from 0.2 of calixarene **IVc**, 0.27 g of triethylamine and 0.2 g of dimethylchlorosilane. Yield 0.09 g (46%), mp 161°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.08 s (24H, $SiMe_2$), 0.84 m. (12H, Me), 1.41 s (72H, CMe_3), 1.69 m (8H, CH_2Me), 2.19 m (8H, CH_2CH) 3.59 s (8H, CH_2Ph), 4.50 t (4H, CH, $^3J_{HH}$ 6.9), 5.01 s (4H, OH), 7.19 m (8H, H_a, 4H, H_b). Found, %: C 73.20; H 11.03; Si 6.82. $C_{108}H_{152}O_{12}Si_4$. Calculated, %:, C 73.92; H 10.94; Si 6.40.

33,34,35,36-Tetrakis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3,11,19,27-octamethyl-2,4,10,12,18,20,26,28-octaoxy-3,11,19,27-tetrasila-3,7,38,39,40-tetrapentylnonacyclo[29,3,1,$1^{21,25}$,$1^{13,17}$,$1^{5,9}$]tetracosa-[$1^{6,32}$,$1^{24,30}$,$1^{16,22}$,$1^{8,14}$]1(32),5,7,9(36),13,15,17(35),21,23,25(34),30,29(33)-dodecaen (VId) was prepared similarly to the previous one from 0.2 of calixarene **IVd**, 0.1 g of triethylamine and 0.08 g of dimethylchlorosilane. Yield 0.13 g (52%), mp 170 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 0.08 s (24H, $SiMe_2$), 0.85 t (12H, Me, $^3J_{HH}$ 6.90), 1.42 m (72H, CMe_3), 1.70 m (24H, $(CH_2)_3$), 2.18 m (8H, CH_2CH), 3.57 s (8H, CH_2Ph), 4.52 t (4H, CH, $^3J_{HH}$ 6.9), 5.01 s (4H, OH), 7.15–7.23 m (8H, H_a, 4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.75 q ($SiMe_2$, $^1J_{CH}$ 125.0), 11.56 q (C^{15}, $^1J_{CH}$ 140.0), 21.73 t (C^{12-14}, $^1J_{CH}$ 125.0), 25.49 q (C^{11}, $^1J_{CH}$ 125.0), 27.47 d (C^{10}, $^1J_{CH}$ 130.0), 30.7 t (C^5, $^1J_{CH}$ 90.0), 33.97 q (CMe_3, $^1J_{CH}$ 120.0), 35.4 s (CMe_3), 115.65 s (C^8), 125.52 d (C^9, $^1J_{CH}$ 150.0), 128.36 d (C^3, $^1J_{CH}$ 150.0), 130.5 s (C^6), 135.9 s (C^4), 144.22 s (C^2), 150.15 s (C^7), 155.29 s (C^1). Found, %: C 75.18; H 9.58; Si 5.74. $C_{116}H_{168}O_{12}Si_4$. Calculated, %: C 74.63; H 9.07; Si 6.02. *m/z* 1887 (*M* + Na).

4,6,10,12,16,18,22,24-Octatrimethysiloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIa). A mixture of 0.2 g of compound **IVa**, 5 ml of anhydrous toluene and 0.7 g of hexamethyldisilazane was heated for 36 h at 90°C, solvent was removed, the residue was recrystallized with hexane from chloroform, solvent was removed, the residue was dried in vacuum of oil pump (4 h, 40°C, 0.4 mm Hg). Yield 0.15 g (53%), mp 143°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.06 s (72H, $SiMe_3$), 1.36 m (72H, CMe_3), 1.76 m (12H, Me,), 3.94 s (8H, CH_2Ph), 4.41 m (4H, CH), 6.2 s (4H, OH), 7.21 m (8H, H_a), 7.51 s (4H, H_b). Found, %: C 70.36; H 9.58; Si 10.74. $C_{116}H_{184}O_{12}Si_8$. Calculated, %: C 69.82; H 9.29; Si 11.26.

4,6,10,12,16,18,22,24-Octatrimethysiloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetraethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIb) was prepared similarly to the previous one from 1.0 g of calixarene **IVb** and 7 ml of hexamethyldisilazane. Yield 0.16 g (59%), mp 157°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm, (*J*, Hz): 0.07 s (72H, $SiMe_3$), 0.91 m (12H, Me), 1.41 m (72H, CMe_3), 2.32 m (8H, CH_2CH) 3.93 s (8H, CH_2Ph), 4.30 t (4H, CH, $^3J_{HH}$ 7.00), 6.45 s (4H, OH), 7.13 m (8H, H_a, 4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm, (*J*, Hz): 0.75 q ($SiMe_3$, $^1J_{CH}$ 125.0), 11.52 q (C^{12}, $^1J_{CH}$ 125.0) 25.65 t (C^{11}, $^1J_{CH}$ 140.0), 29.38 d (C^{10}, $^1J_{CH}$ 130.0), 30.34 t (C^5, $^1J_{CH}$ 90.0), 34.57 q (CMe_3, $^1J_{CH}$ 120.0), 33.78 s (CMe_3), 125.47 s (C^8), 130.14 d (C^9, $^1J_{CH}$ 150.0), 131.26 d (C^3, $^1J_{CH}$ 150.0), 131.8 s (C^6), 135.35 s (C^4), 148.21 s (C^2), 151.82 s (C^7), 157.93 s (C^1). Found, %: C 70.61; H 9.81; Si

10.26. $C_{120}H_{192}O_{12}Si_8$. Calculated, %:, C 70.26; H 9.43; Si 10.95.

4,6,10,12,16,18,22,24-Octatrimethysiloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetrapentylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIId) was prepared similarly to the previous one from 1.0 of calixarene **IVd** and 6 ml of hexamethyldisilazane. Yield 0.21 g (61%), mp 146°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 0.08 s (72H, $SiMe_3$), 0.85 m (12H, Me), 1.41 m (72H, CMe_3), 1.96 m [24H, $(CH_2)_3$], 2.30 m (8H, CH_2CH), 3.59 s (8H, CH_2Ph), 4.50 t (4H, CH, $^3J_{HH}$ 6.9), 6.11 s (4H, OH), 7.14 s (8H, H_a), 7.23 s (4H, H_b). Found, %: C 70.81; H 9.78; Si 10.26. $C_{120}H_{192}O_{12}Si_8$. Calculated, %: C 70.26; H 9.43; Si 10.95.

4,6,10,12,16,18,22,24-Octaacetyloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIIa). A mixture of 0.5 of calixarene **IVa**, 6.57 ml of acetic anhydride and 0.66 ml of pyridine was heated for 24 h at 70°C. Acetic anhydride was removed in vacuum of water-jet pump (1 h, 40°C, 0.01 mm Hg), the residue was dissolved in chloroform, the organic phase was separated water-jet air pump, dried over $MgSO_4$ and poured into 150 ml of pentane. Precipitated product was dried in vacuum (3 h, 50°C, 0.04 mm Hg). Yield 0.21 g (34%) of compound **VIIIa**, mp 155°C. 1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 t (12H, Me, $^3J_{HH}$ 6.97), 1.35 s (72H, CMe_3), 1.75 s [24H, OC(O)Me], 3.58 m (8H, CH_2), 4.35 m (4H, CH), 5.0 s (4H, OH), 6.85 s (8H, H_a), 7.33 s (4H, H_b). Found, %: C 73.98; H 8.11. $C_{108}H_{136}$·O20. Calculated, %:, C 74.32; H 8.02. *m/z* 1775 (*M* + Na)

4,6,10,12,16,18,22,24-Octaacetyloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetraethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIIb) was prepared similarly to the previous one from 1 g of calixarene **IVb**, 6 ml of acetic anhydride and 0.6 ml of pyridine. Yield 0.23 g (38%), mp 148°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 t (12H, Me, $^3J_{HH}$ 6.97), 1.35 s (72H, CMe_3), 1.77 s [24H, OC(O)Me], 2.21 m (8H, CH_2), 3.62 m (8H, CH_2), 4.40 m (4H, CH), 5.0 s (4H, OH), 6.85 s (8H, H_a), 7.33 s (4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 13.02 q (C^{12}, $^1J_{CH}$ 125.0), 20.89 q (CH3C(O), $^1J_{CH}$ 130.0), 28.32 t (C^{11}, $^1J_{CH}$ 140.0), 29.84 t (C^5, $^1J_{CH}$ 90.0), 30.67 d (C^{10}, $^1J_{CH}$ 130.0), 32.82 s (*C*Me_3), 34.68 q (C*Me*$_3$, $^1J_{CH}$ 120.0), 125.55 s (C^8), 126.24 d (C^9, $^1J_{CH}$ 150.0), 127.2 d (C^3, $^1J_{CH}$ 150.0), 130.03 s (C^6), 135.97 s (C^4), 149.21 s (C^2), 151.82 s (C^7), 152.37 s (C^1), 168.71 s [C(O)]. Found, %: C 73.44; H 8.20. $C_{112}H_{144}O_{20}$. Calculated, %:, C 73.94; H 7.81.

4,6,10,12,16,18,22,24-Octaacetyloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetrapropylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIIc) was prepared similarly to the previous one from 1.0 of calixarene **IVc**, 6 ml of acetic anhydride and 0.6 ml of pyridine. Yield 0.20 g (33%), mp 150°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 t (12H, Me, ^3J 6.97), 1.36 s (72H, CMe_3), 1.50 m (8H, CH_2), 1.71 s [24H, OC(O)Me], 2.19 m (8H, CH_2), 3.58 m (8H, CH_2), 4.32 m (4H, CH), 5.0 s (4H, OH), 6.85 s (8H, H_a), 7.33 s (4H, H_b). Found, %: C 74.13; H 8.82. $C_{116}H_{152}O_{20}$. Calculated, %: C 74.65; H 8.21.

4,6,10,12,16,18,22,24-Octaacetyloxy-5,11,17,23-tetra(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetrapentylpentacycl[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (VIIId) was prepared similarly to the previous one from 1 g of calixarene **IVd**, 6 ml of acetic anhydride and 0.6 ml of pyridine. Yield 0.21 g (35%), mp 153°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 m (12H, Me), 1.27 s (72H, CMe_3), 1.50 m [24H, $(CH_2)_3$], 1.71 s [24H, OC(O)Me], 2.17 m (8H, CH_2), 3.83 m (8H, CH_2), 4.23 m (4H, CH), 5.0 s (4H, OH), 6.95 s (8H, H_a), 7.33 s (4H, H_b). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 11.54 q (C^{15}, $^1J_{CH}$ 150.0), 20.89 q [(CH_3C(O), $^1J_{CH}$ 130.0], 21.73 t (C$^{12–14}$, $^1J_{CH}$ 125.0), 25.49 q (C^{11}, $^1J_{CH}$ 125.0), 29.84 t (C^5, $^1J_{CH}$ 90.0), 30.67 d (C^{10}, $^1J_{CH}$ 130.0), 32.82 s (CMe_3), 34.68 q (CMe_3, $^1J_{CH}$ 120.0), 125.55 s (C^8), 126.24 d (C^9, $^1J_{CH}$ 150.0), 127.2 d (C^3, $^1J_{CH}$ 150.0), 130.03 s (C^6), 134.6 s (C^4), 137.26 s (C^2), 148.82 s (C^7), 152.37 s (C^1), 168.71 s [C(O)]. Found, %: C 73.12; H 9.04. $C_{124}H_{168}O_{20}$. Calculated, %: C 73.27; H 8.56. *m/z* 2016 (*M* + K).

4,6,10,12,16,18,22,24-Octaacyl-5,11,17,23-tetra-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (IXa). A mixture of 0.3 g of calixarene **IVa** and 7 ml of acetic anhydride was heated for 48 h at 100°C. When acetic anhydride was removed the residue was dissolved in 10 ml methylene chloride and this solution was poured into100 ml of hexane. Precipitated product was dried in vacuum water-jet air pump (2 h, 100°C, 0.4 mm Hg). Yield 0.15 g (60%) of compound

IXa, mp 151°C. ^{1}H NMR spectrum (CD_3OD), δ, ppm, (*J*, Hz): 0.89s (12H, Me), 1.33 s (72H, CMe_3), 1.76 s [24H, OC(O)Me], 2.10 m [12H, OC(O)Me], 3.62 s (8H, CH_2), 4.11 q (4H, CH, $^3J_{HH}$ 6.9), 6.9 m (8H, H_a), 7.17 s (4H, H_b). Found, %: C 72.92; H 8.12. $C_{116}H_{144}O_{24}$. Calculated, %: C 72.48; H 7.55.

4,6,10,12,16,18,22,24-Octaacyl-5,11,17,23-tetra-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetra-ethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (IXb) was prepared similarly to the previous one from 1.0 of calixarene **IVb** and 10 ml of acetic anhydride. Yield 0.16 g (64%), mp 200°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 t (12H, Me, $^3J_{HH}$ 7.02), 1.34 m (72H, CMe_3), 1.79 m [24H, OC(O)Me], 2.15 m [12H, OC(O)Me], 2.35 m (8H, CH_2CH), 3.84 s (8H, CH_2), 4.22 t (4H, CH, $^3J_{HH}$ 7.0), 6.9 s (8H, H_a), 7.19 s (4H, H_b). Found, %: C 73.20; H 7.80. $C_{120}H_{152}O_{24}$. Calculated, %: C 72.85; H 7.74. *m/z* 1999 (*M* + Na).

4,6,10,12,16,18,22,24-Octaacyl-5,11,17,23-tetra-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,8,14,20-tetra-pentylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen (IXd) was prepared similarly to the previous one from 1.0 g of calixarene **IVd** and 10 ml of acetic anhydride. Yield 0.10 g (51%), bp 167 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.85 t (12H, Me, $^3J_{HH}$ 6.97), 1.34 m (72H, CMe_3), 1.62 m [24H, OC(O)Me], 2.03 s [12H, OC(O)Me], 2.17 m [24H, $(CH_2)_3$], 2.38 m (24H, CH_2CH), 3.84 s (8H, CH_2), 4.22 t (4H, CH, $^3J_{HH}$ 7.0), 6.9 s (8H, H_a), 7.19 s (4H, H_b). Found, %: C 74.27; H 8.81. $C_{132}H_{176}O_{24}$. Calculated, %: C 73.85; H 8.26.

ACKNOWLEDGMENTS

This research was financially supported by the Russian Foundation for Basic Research (project no. 05-03-32136).

REFERENCES

1. Asfari, Z., Bohmer, V., Harrowfield, J., and Vicens, J., *Calixarenes,* Dordrecht: Kluwer Academic Publ., 2001, p. 43.
2. Izatt, R.M. and Christensen, J.J., *Synthesis of Macrocycles: Design of Selective Complexing Agents,* New York: Wiley, 1987, p. 95.
3. Gutsche, C.D., *Calyxarenes.* Cambridge: Royal Society of Chemistry, 1989, p. 132.
4. Vicens, J. and Bohmer, V., *Calyxarenes, a Versatile Class of Macrocyclic Compounds,* Dodrecht: Kluwer Acad. Publ., 1991, p. 15.
5. Ehrhardt, D., *Gummi, Fasern Kunststoffe,* 1992, vol. 45, no. 5, p. 231.
6. Ehrhardt, D., *Gummi, Fasern Kunststoffe,* 1992, vol. 45, no. 7, p. 358.
7. Bukharov, S.V., Nugumanova, G.N., and Mukmeneva, N.A., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 12, p. 1977.
8. Bukharov, S.V., Litvinov, I.A., Gubaydullin, A.T., Nugumanova, G.N., and Mukmeneva, N.A., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 2, p. 290.
9. Brunetti, H. and Schmidt, A., USA Patent 3 821 334, *C. A.,* 1973, vol. 78. 15 828k.
10. Hogberg, A.G., *J. Org. Chem.,* 1980, vol. 45, no. 22, p. 4498.
11. Tunstad, L.M., Tucker, J.A., Dalcanale, E., Weiser, J., Bruant, J.A., Sherman, J.C., Helgeson, R.C., Knobler, C.B., and Cram, D.J., *J. Org. Chem.,* 1989, vol. 54, no. 6, p. 1305.
12. Belamy, L., *Novie dannie po IK spektram slozhnih molekul* (New Data on IK spectra of Complex Molecules), Moscow: Mir, 1971, p. 112.
13. Kovalenko, V.I., Chernova, A.V., Shagidullin, R.R., Doroshkina, G.M., Borisoglebskaya, E.A., and Nikitin, V.G., Abstaract of Papers, *V Vserossiyskaya konferentsiya "Structura i dinamika molekulyarnyh system"* (Russian Conf. "Structure and dynamics of Molecular Systems"), Kazan–Moscow, 1998, part 1, p. 126.
14. Lutz, B.T, Astarboa, G., Van der Maas, J.H, Janssen, R.G., Verboom, W., Reinhoudt, D.N., *Vibrational* Spectroscopy, 1995, vol. 10, p. 29.
15. Groenen, L.C., Steinuender, E., Lutz, B.T.G., Van der Maas, J.H., Reinhoudt, D.N., *J. Chem. Soc. Perkin Trans 2,* 1992, p. 1893.
16. Antipin, I.S., Kazakova, E.H., Habiher, V.D., and Konovalov, A.I., *Usp. Khim.,* 1998, vol. 67, no. 4, p. 995.
17. Neda, I., Siedentop, T., Vollbrecht, A., Thoennesse, H., Jones, P.G., and Schmutzler, R., *Chem. Sci.,* 1998, vol. 53, p. 841.