Russian Journal of General Chemistry, Vol. 71, No. 11, 2001, pp. 1786–1792. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 11, 2001, pp. 1887–1894.
Original Russian Text Copyright © 2001 by Alekseeva, Mazepa, Gren'.

Synthesis and Conformational Characteristics of Benzyl-Substituted *p-tert*-Butylcalixarenes

E. A. Alekseeva, A. V. Mazepa, and A. I. Gren'

Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine, Odessa, Ukraine

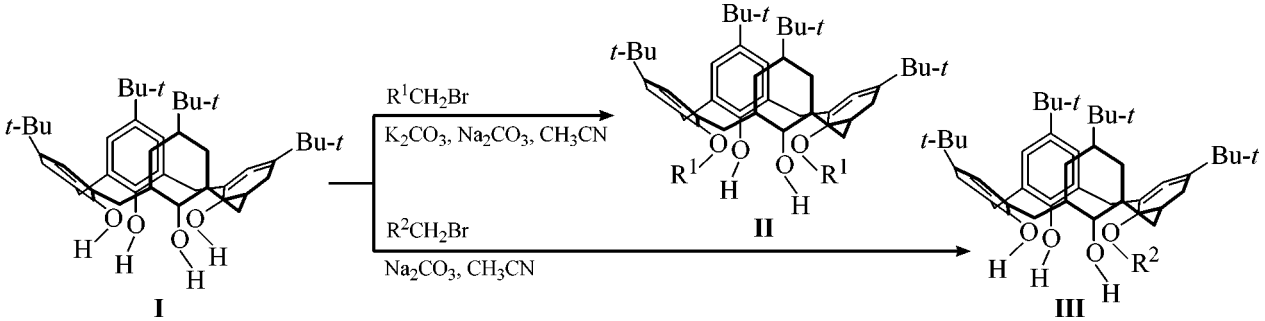
Received April 10, 2000

Abstract—(*m*-Methylbenzyloxy)-, bis(*p*-methylbenzyloxy)-, and bis(*m*-methylbenzyloxy)-*p-tert*-butylcalix[4]-arenes were prepared by reactions of *p-tert*-butylcalix[4]arene with *p*- and *m*-methylbenzyl bromides in the presence of alkali metal carbonates. Silylation of these derivatives gave (*m*-methylbenzyloxy)bis(trimethylsilyloxy)-, bis(*m*-methylbenzyloxy)bis(trimethylsilyloxy)-, and bis(*p*-methylbenzyloxy)bis(trimethylsilyloxy)-*p-tert*-butylcalix[4]arenes. With phase-transfer catalysis, bis(*p*-methylbenzyloxy)bis(2-propenyloxy)- and bis(*m*-methylbenzyloxy)bis(2-propenyloxy)-*p-tert*-butylcalix[4]arenes were obtained. Alkylation of the monosubstituted calixarene yields the corresponding trisubstituted derivative.

Interest in the calixarene chemistry is due to the possibility of preparing from these compounds synthetic receptors selectively binding metal ions and neutral molecules [1–3]. Numerous studies of the complexing power of calixarenes and their derivatives and of the complexation selectivity show that the selectivity depends on many factors, including the conformational state of calixarene molecules. The most stable conformational isomers of *p-tert*-butylcalix[4]arene (**I**) molecules are *cone*, *partial-cone*, 1,2-*alternate*, and 1,3-*alternate* (see table) [1–7]. It is also known that introduction into the *p-tert*-butylcalix[4]arene lower rim of such bulky substituents as benzyl groups fixes the *cone* and *partial-cone* conformations [8]. Arylation of calixarene **I** was studied only in a few papers. For example, Gutsche and Reddy [8] studied the reaction of **I** and its di- and triethers in the *cone* and *partial-cone* conformations with *p*-substituted benzyl bromides in the presence of various bases (NaH, $KOSiMe_3$, K_2CO_3) in acetone and in DMF–THF. The reaction yields a mixture of the tetrasubstituted derivative (in the *cone* and *partial-cone* conformations) with a minor amount of the trisubstituted derivative. It was shown that reaction of **I** with *p*-substituted benzyl bromides in the presence of excess NaH yields tetrasubstituted calixarene derivatives in the *cone* conformation, whereas with K_2CO_3 diethers in the *cone* and *partial-cone* conformations are formed. Although the yield of target products in arylation of calixarenes was studied in relation to many factors (electronic effect of the *p*-substituent, temperature, natures of the solvent and base), the influence of the steric structure of the substituent on formation of particular reaction products practically was not examined.

In this work we studied how the structure of the arylating agent affects the composition, prevailing conformations, and yields of products in the reaction of calixarene **I** with *p*- and *m*-methylbenzyl bromides in the presence of sodium and potassium carbonates, using the procedure described in [9], and also performed further functional substitution of the products.

Compound **I** reacts with *p*-methylbenzyl bromide in the presence of Na_2CO_3 or K_2CO_3 (molar ratio 3 : 7 : 3.25) to form 1,3-bis(*p*-methylbenzyloxy)-*p-tert*-



II, R^1 = *p*-MeC_6H_4; **III**, R^2 = *m*-MeC_6H_4.

1070-3632/01/7111-1786 $25.00 © 2001 MAIK "Nauka/Interperiodica"

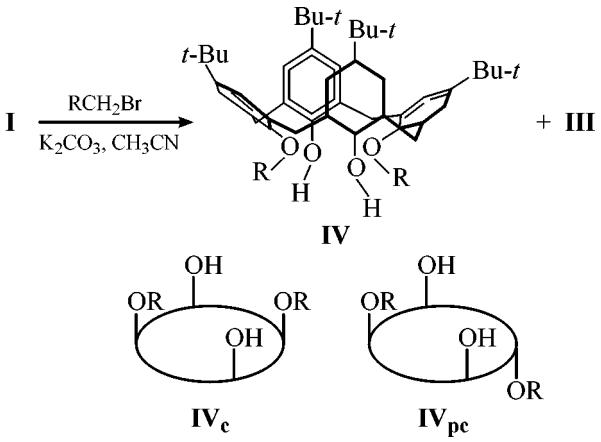
^{1}H NMR signals of the main molecular fragments of *p-tert*-butylcalix[4]arene **I** and its derivatives

Comp. no.	Conformation	Multiplicity and intensity of signals		
		t-Bu	CH_2	ArH
I	*Cone*	s (36H)	2 d (4H)	s (8H)
	Partial-cone	3 s (1 : 2 : 1)	d.d.d (2H) or d.d (2H) and s (4H)	2 s (2H) and d.d (2H) or 4 s (1 : 1 : 1 : 1)
	1,2-*Alternate*	1 s (36H)	1 s and 2 d (1 : 1)	2 s (1 : 1)
	1,3-*Alternate*	1 s (36H)	1 s (8H)	1 s (8H)
II	*Cone*	2 s (1 : 1)	2 d (4H, *J* 13.6 Hz)	2 s (4H)
III	"	2 s (1 : 3)	2 d (2H, *J* 13.2 Hz) and d (4H)	2 d (2H, *J* 2.8 Hz) and 2 s (2H)
$\mathbf{IV_c}$	"	2 s (1 : 1)	2 d (4H, *J* 12.4 Hz)	2 s (4H)
$\mathbf{IV_{pc}}$	*Partial-cone*	3 s (1 : 1 : 2)	2 d (2H, *J* 13.4 Hz) and d (4H, *J* 14.4 Hz)	2 d (2H, *J* 3.2 Hz) and 2 s (2H)
V	*Cone*	3 s (1 : 2 : 1)	d.d.d (2H, *J* 12.8 Hz)	2 s (2H) and 2 d (2H, *J* 3.1 Hz)
VI	"	2 s (1 : 1)	d.d.d (2H, *J* 12.8 Hz)	2 s (4H)
$\mathbf{VII_c}$	*Distorted cone*	4 s (1 : 1 : 1 : 1)	t.d.d (1H, *J* 12.6 Hz) and d (2H, *J* 12.6 Hz)	t.d.d (1H) and d (2H, *J* 2.7 Hz)
$\mathbf{VII_{pc}}$	*Partial-cone*	3 s (2 : 1 : 1)	d.d.d (2H, *J* 13.0 Hz)	2 s (2H) and 2 d (2H, *J* 3.0 Hz)
VIII	*Cone*	3 c (1 : 2 : 1)	d.d.d (2H, *J* 12.8 Hz)	3 s (1 : 2 : 1)
IX	*Distorted cone*	4 s (1 : 1 : 1 : 1)	2 d (2H, *J* 13.0 Hz) and 2 m (2H)	2 s (2H) and 2 d (2H, *J* 2.7 Hz)
X	*Cone*	4 s (1 : 1 : 1 : 1)	4 d (1H, *J* 12.7 Hz) and 2 m (2H)	2 d (2H) and m (4H)

butylcalix[4]arene **II** in a high yield. The ^{1}H NMR spectrum of this compound suggests its *cone* conformation [8] (see table). Contrastingly, with *m*-methylbenzyl bromide in the presence of Na_2CO_3 under similar conditions only the monosubstituted product **III** is formed even after refluxing for 23 h. According to the spectrum, the molecules of **III** exist in the *cone* conformation [10].

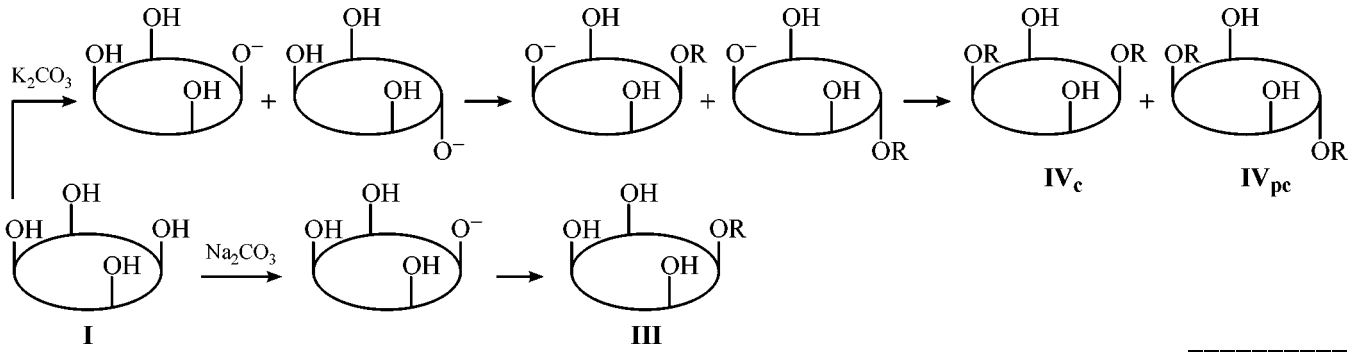
The ^{1}H NMR spectrum of **III** contains two doublets and two singlets (2H each) from the aromatic protons of the macroring. The *tert*-butyl protons give rise to two singlets with the ratio of integral intensities of 1 : 3, and the protons of the methylene bridges give a doublet at δ 3.42 ppm (4H) and doublets of doublets at 4.22 and 4.34 ppm (2H each). This pattern is apparently due to the effect of the aromatic substituent.

With Na_2CO_3 replaced by K_2CO_3, other conditions being the same, a mixture of **III** with the disubstituted product, 1,3-bis(*m*-methylbenzyloxy)-*p*-*tert*-butylcalix[4]arene (**IV**), is formed, with the monosubstituted derivative prevailing. Their ratio after TLC separation (Al_2O_3, hexane–chloroform, 3 : 1) is 7 : 3. The molecules **III**, as follows from the ^{1}H NMR spectrum of the isolated compound, exist in the *cone* conformation. The ^{1}H NMR spectrum of the second component (**IV**) suggests the presence of two conformers. These conformers were separated by preparative TLC on Al_2O_3 in the system hexane–chloroform, 4 : 1. The fact that the ^{1}H NMR spectrum of one of the conformers of **IV** contains two singlets from *tert*-butyl protons (18H each), two signals from aromatic protons of the macrocyclic system (4H each), and a doublet of doublets from the methylene bridge protons (*J* 12.4 Hz) suggests that a part of the molecules of **IV** exist in the *cone* conformation ($\mathbf{IV_c}$). The ^{1}H NMR spectrum of the other conformer contains three singlets from the *tert*-butyl protons with the ratio of the integral intensities of 1 : 1 : 2, a doublet of doublets (2H each, *J* 13.4 Hz, Δδ 1.05 ppm) and a singlet (4H) from the methylene bridge protons, and two singlets and a doublet of doublets (*J* 3.2 Hz) from the aromatic protons. The presence of two sets of proton signals from the OCH_2 and CH_3 groups of the methylbenzyl substituent suggests that in this compound the substituents are located on different sides of the ring plane. Such a pattern indicates that these molecules exist in the *partial-cone* conformation ($\mathbf{IV_{pc}}$). The ratio of the conformers $\mathbf{IV_c}$ and $\mathbf{IV_{pc}}$ is 3 : 2.



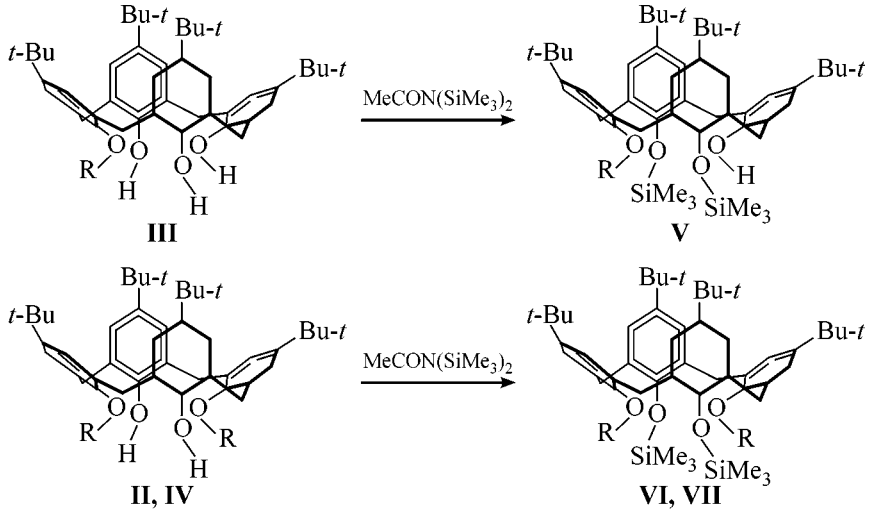
R = *m*-MeC_6H_4.

In accordance with the published data [8–12] that alkylation reactions in the presence of weak bases are stepwise and that the distribution of the conformers in the final product is influenced by the template factor, we suggested that the reaction with *m*-methylbenzyl bromide in the presence of sodium carbonate occurs via formation of the conical conformer in the first stage. The incorporated substituent sterically hinders the approach of the second molecule of the arylating agent to the monophenoxide anion formed from the monoether. The lack of the template effect and the size of the potassium cation allow the calixarene molecules to take in the course of the reaction the conformations of *partial-cone* and so-called *flattened cone*; in the process, the distance between the phenolic OH groups increases, and the approach of the second molecule of the arylating agent and base becomes easier.



In order to examine how the steric structure of the substituent affects further functional substitution of calixarene benzyl derivatives, we performed a number of transformations of **II**–**IV**.

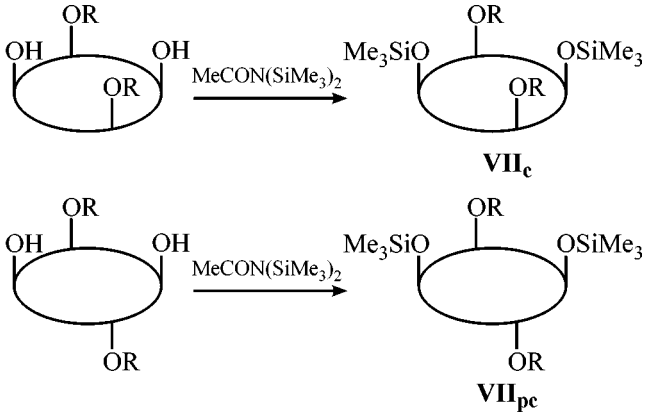
To confirm the structure and composition of **II**–**IV**, we silylated these compounds under conditions that usually ensure complete substitution of phenolic protons. We found that in the monosubstituted benzyl derivative **III** the silylation occurred only at the two hydroxy groups adjacent to the benzyl substituents, yielding (*m*-methylbenzyloxy)bis(trimethylsilyloxy)-*p*-*tert*-butylcalix[4]arene (**V**), whereas silylation of **II**, $\mathbf{IV_c}$, and $\mathbf{IV_{pc}}$ yielded the corresponding bis(*p*-methylbenzyloxy)bis(trimethylsilyloxy)- (**VI**) and bis(*m*-methylbenzyloxy)bis(trimethylsilyloxy)-*p*-*tert*-butylcalix[4]arenes ($\mathbf{VII_c}$, $\mathbf{VII_{pc}}$).



R = *m*-$MeC_6H_4CH_2$ (**III**–**V, VII**), *p*-$MeC_6H_4CH_2$ (**II, VI**).

The ^{1}H NMR spectrum of the silylated conical isomer $\mathbf{VII_c}$ contains two signals of equal intensity from the trimethylsilyl protons and four singlets from *tert*-butyl protons, which is apparently due to certain dis-

tortion of the *cone* shape, resulting in increased distance between the substituents in the calixarene molecule (see table):



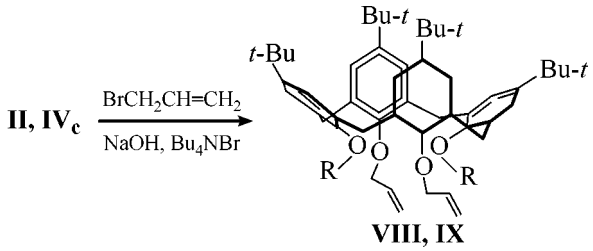
R = *m*-$MeC_6H_4CH_2$.

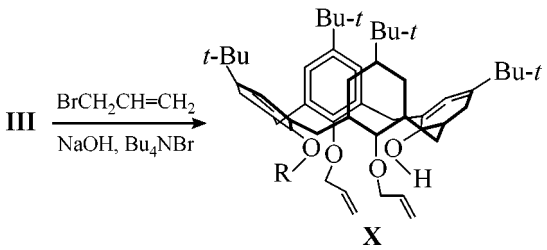
The ^{1}H NMR spectrum of **VII$_{pc}$** (*partial-cone* conformation) contains three singlets from the *tert*-butyl protons (ratio of integral intensities 2 : 1 : 1), two doublets and two singlets from aromatic protons, and two pairs of doublets (*J* 12 Hz, Δδ 2.04 ppm) from the methylene protons of calixarene. The presence in the ^{1}H NMR spectrum of **VII$_{pc}$** of two resonance signals from trimethylsilyl protons and two signals from the CH_3 protons of the methylbenzyl moiety indicates that silylation of the initial calixarene **IV$_{pc}$** does not involve the ring inversion, and the benzyl substituents are located on different sides of the macroring plane.

Alkylation of **II** and **IV**c with allyl bromide under conditions of phase-transfer catalysis [13] in the presence of Bu_4NBr and NaOH yields bis(*p*-methylbenzyloxy)bis(2-propenyloxy)- (**VIII**) and bis(*m*-methylbenzyloxy)bis(2-propenyloxy)-*p*-*tert*-butylcalix[4]arenes (**IX**). However, when compound **III** was alkylated under conditions suggesting hydrogen substitution in all the three OH groups of the calixarene, the only reaction product was (*m*-methylbenzyloxy)bis(2-propenyloxy)-*p*-*tert*-butylcalix[4]arene (**X**). Its ^{1}H NMR spectrum contains four singlets from the *tert*-butyl protons with δ 0.85, 0.87, 1.34, and 1.5 ppm (9H each). The arene protons of the macroring give rise to a doublet of doublets with δ 7.09 and 7.1 ppm (2H each) and a multiplet at 7.15–7.2 ppm (4H) originating from superposition of doublets. The methylene protons of the calixarene ring of **X** give four doublets with δ 3.095, 4.7, 4.74, and 4.80 ppm (1H each, *J* 12.7 Hz) and two multiplets with δ 4.35–4.39 and 4.42–4.49 ppm (2H each), which are due to superposition of doublets with a small Δδ. Observation of four signals from the *tert*-butyl protons of the calixarene and of doublets from each methylene bridge proton (Δδ < 0.6) suggests distortion of the *cone* conformation of these molecules.

In the spectrum of calixarene **VIII**, the *tert*-butyl protons give three singlets with δ 0.84, 0.867, and 1.338 ppm (intensity ratio 1 : 2 : 1); the arene protons of the calixarene core also give three singlets with δ 7.079, 7.097, and 7.153 ppm. The methylene protons give two pairs of doublets with δ 3.023, 3.084 and 4.37, 4.72 ppm (*J* 12.8 Hz). Such a pattern of the arene and methylene proton signals indicates that molecules of **VIII** occur in the *cone* conformation, and the magnetic nonequivalence of the protons of the opposite phenolic fragments bearing benzyl substituents suggests certain distortion of this conformation.

A different pattern is observed in the ^{1}H NMR spectrum of calixarene **IX**. The *tert*-butyl protons in this case give four signals of equal intensity with δ 0.8, 0.85, 1.31, and 1.33 ppm. The methylene protons of this compound give rise to two doublets with δ 3.07 and 4.7 ppm (1H each, *J* 13 Hz) and two multiplets in the ranges 4.32–4.39 and 4.4–4.5 ppm (2H each), probably originating from overlapping doublets with Δδ < 0.2–0.3 ppm. The aromatic protons of the calixarene give a doublet of doublets with δ 7.08 and 7.1 ppm and a pair of singlets with δ 7.15 and 7.18 ppm. The presence of two resonance signals from the methyl and methylene components of the substituent and fragments of the aryl residue indicates that the molecules of this compound occur in the *distorted cone* conformation in which each *tert*-butylphenol ring is a unique fragment nonequivalent to the other fragments.

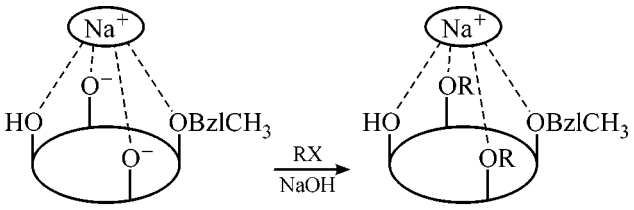




R = *p*-$MeC_6H_4CH_2$ (**II, IX**), *m*-$MeC_6H_4CH_2$ (**VIII, X**).

The results of phase-transfer alkylation, along with those of silylation of **II**, are due to the template effect

of the sodium ion, fixing the calixarene molecule in the *cone* conformation, and also to the steric effect of the methyl group in the *m*-position of the benzyl substituent, shielding the oxygen atom of the phenoxide anion from the molecule of the alkylating agent as shown in the scheme. Therefore, inversion of the phenol rings is hindered, and further reaction becomes impossible. At the same time, the *p*-methylbenzyl substituent does not hinder sterically the alkylation, and the products of total substitution are formed:



diphenoxide anion formed from **II** — alkylation product

Thus, introduction of such bulky substituents as *m*-methylbenzyl groups with further modification of the resulting derivatives is an example of synthesis of unsymmetrical calixarenes; it can be used for introducing and removing protective groups in synthesis of calixarenes of the required structure with three different substituents in the molecule.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer (300 MHz, ~10% solutions in CCl_4, internal reference TMS). As eluents for column chromatography we used 3 : 1 and 4 : 1 hexane–chloroform mixtures. All solvents were preliminarily purified by distillation and dried over 3 Å or 4 Å molecular sieves.

5,11,17,23-Tetra-*tert*-butyl-25-[(*m*-methylbenzyl)-oxy]-26,27,28-trihydroxycalix[4]arene III. A mixture of 6 mmol of **I**, 14 mmol of *m*-methylbenzyl bromide, and 7.5 mmol of Na_2CO_3 in 100 ml of acetonitrile was refluxed with stirring for 23 h, after which the solvent was distilled off, the residue was washed with 50 ml of 5% HCl, the products was extracted with chloroform, the organic layer was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was recrystallized from 1-butanol. Yield 85%; mp 218°C, R_f 0.75 (Al_2O_3, eluent hexane–chloroform, 3 : 1). ^{1}H NMR spectrum, δ, ppm: 1.20 s (9H, *t*-Bu), 1.21 s (27H, *t*-Bu), 2.45 s (3H, Me), 3.42 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.2 Hz), 4.22 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.2 Hz), 4.34 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.2 Hz), 5.132 s (2H, CH_2O), 6.95 d (2H, Ar–H, $^4J_{HH}$ 2.8 Hz), 7.05 d (2H, Ar–H, $^4J_{HH}$ 2.8 Hz), 7.12 s (2H, Ar–H), 7.13 s (2H, Ar–H), 7.27–7.52 m (4H, Bzl), 9.39 s (2H, OH), 9.99 s (1H, OH). Found, %: C 83.14; H 8.59. $C_{52}H_{64}O_4$. Calculated, %: C 82.94; H 8.57.

Di(methylbenzyl) derivatives of calixarene II and IV. A mixture of 6 mmol of **I**, 14 mmol of *m*- or *p*-methylbenzyl bromide, and 7.5 mmol of Na_2CO_3 or K_2CO_3 in 100 ml of acetonitrile was refluxed with stirring for 23 h, after which the solvent was distilled off, the residue was washed with 50 ml of 5% HCl, the reaction product was extracted with chloroform, the organic layer was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was recrystallized from chloroform–1-butanol, 1 : 3.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*p*-methylbenzyl)oxy]calix[4]arene II. Yield 86%, mp 256°C, R_f 0.78 (Al_2O_3, eluent hexane–chloroform, 3 : 1). ^{1}H NMR spectrum, δ, ppm: 0.934 s (18H, *t*-Bu), 1.281 s (18H, *t*-Bu), 2.438 s (6H, Me), 3.26 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.6 Hz), 4.221 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.6 Hz), 5.028 s (4H, CH_2O), 6.776 s (4H, Ar–H), 7.032 s (4H, Ar–H), 7.23–7.38 m (8H, Bzl), 7.27 s (2H, OH), Found, %: C 84.17; H 8.49. $C_{60}H_{88}O_4$. Calculated, %: C 84.07; H 8.47.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*m*-methylbenzyl)oxy]calix[4]arene [*cone* (IV_c)]. mp 240°C, R_f 0.75 (Al_2O_3, eluent hexane–chloroform, 4 : 1). ^{1}H NMR spectrum, δ, ppm: 0.951 s (18H, *t*-Bu), 1.238 s (18H, *t*-Bu), 2.284 s (3H, Me), 3.273 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.4 Hz), 4.279 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.4 Hz), 5.01 s (4H, CH_2O), 6.706 s (4H, Ar–H), 7.038 s (4H, Ar–H), 7.34 s (2H, OH), 7.16–7.57 m (8H, Bzl). Found, %: C 84.17; H 8.49. $C_{60}H_{88}O_4$. Calculated, %: C 84.07; H 8.47.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(*m*-methylbenzyl)oxy]calix[4]arene [*partial-cone* (IV_{pc})]. mp 258°C, R_f 0.35 (Al_2O_3, eluent hexane–chloroform, 4 : 1). ^{1}H NMR spectrum, δ, ppm: 0.94 s (9H, *t*-Bu), 0.99 s (9H, *t*-Bu), 1.27 s (18H, *t*-Bu), 2.33 s (3H, Me), 2.36 s (3H, Me), 3.21 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.4 Hz), 4.14 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.4 Hz), 4.26 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.4 Hz), 4.94 s (2H, CH_2O), 4.96 s (2H, CH_2O), 7.05 d (2H, Ar–H, $^4J_{HH}$ 3.2 Hz), 7.12 d (2H, Ar–H, $^4J_{HH}$ 3.2 Hz), 7.16 s (2H, Ar–H), 7.18 s (2H, Ar–H), 7.21 s (2H, OH), 7.25–7.5 m (8H, Bzl). Found, %: C 84.17; H 8.49. $C_{60}H_{88}O_4$. Calculated, %: C 84.07; H 8.47.

5,11,17,23-Tetra-*tert*-butyl-25-[(*m*-methylbenzyloxy]-26,28-bis(trimethylsilyloxy)-27-hydroxycalix[4]arene (V). A solution of 10 mmol of *N*,*N*-bis(trimethylsilyl)acetamide in 10 ml of CH_3CN was added dropwise under nitrogen to a solution of 1 mmol of **III** in 25 ml of CH_3CN. The mixture was refluxed with stirring for 6 h. Then the solvent was distilled off, and the crude product was recrystallized from toluene–MeCN, 1 : 2. Yield 80%, mp 244–246°C. ^{1}H NMR spectrum, δ, ppm: 0.047 s (18H, Me_3Si), 0.84 s (9H, *t*-Bu), 1.29 s (18H, *t*-Bu), 1.31 s (9H, *t*-Bu), 1.94 s (3H, Me), 2.865 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 2.93 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.20 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.25 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 5.21 s (2H, CH_2O), 6.37 s (2H, Ar–H), 6.43 d (2H, Ar–H, $^4J_{HH}$ 3.1 Hz), 6.98 d (2H, Ar–H, $^4J_{HH}$ 3.1 Hz), 7.03 s (2H, Ar–H), 7.12–7.38 m (2H, 3H, Bzl). Found, %: C 77.72; H 9.01. $C_{58}H_{80}O_4Si_2$. Calculated, %: C 77.62; H 8.99.

Silylated di(methylbenzyl)-substituted calixarenes VI and VII_c. A solution of 6.66 mmol of *N*,*N*-bis(trimethylsilyl)acetamide in 5 ml of MeCN was added dropwise under nitrogen to a solution of 1 mmol of **II** or **IV** in 25 ml of MeCN. The mixture was refluxed with stirring for 6 h. Then the solvent was distilled off, and the crude product was recrystallized from toluene–MeCN, 1 : 2.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*p*-methylbenzyl)oxy]-26,28-bis(trimethylsilyloxy)calix[4]arene VI. Yield 78%, mp 276–278°C. ^{1}H NMR spectrum, δ, ppm: 0.087 s (18H, Me_3Si), 0.919 s (18H, *t*-Bu), 1.362 s (18H, *t*-Bu), 2.331 s (6H, Me), 2.98 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 3.22 d (4H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.27 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.417 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 6.37 s (2H, CH_2O), 6.44 s (4H, Ar–H), 7.10 s (2H, Ar–H), 7.18–7.42 m (8H, Bzl). Found, %: C 79.25; H 8.88. $C_{66}H_{88}O_4Si_2$. Calculated, %: C 79.15; H 8.86.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*m*-methylbenzyl)oxy]-26,28-bis(trimethylsilyloxy)calix[4]arene VII_c. Yield 80%, mp 280–281°C. ^{1}H NMR spectrum, δ, ppm: 0.07 s (9H, Me_3Si), 0.084 s (9H, Me_3Si), 0.874 s (9H, *t*-Bu), 0.897 s (9H, *t*-Bu), 1.27 s (9H, *t*-Bu), 1.353 s (9H, *t*-Bu), 2.26 s (3H, Me), 2.3 s (3H, Me), 2.865 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 2.93 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 4.20 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 4.25 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 5.10 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 5.21 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 5.25 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.6 Hz), 6.37 br.s (4H, CH_2O), 6.4 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 6.44 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 6.98 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.03 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.1 d (2H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.12 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.22 d (1H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.15–7.38 m (8H, Bzl). Found, %: C 79.25; H 8.88. $C_{66}H_{88}O_4Si_2$. Calculated, %: C 79.15; H 8.86.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*m*-methylbenzyl)oxy]-26,28-bis(trimethylsilyloxy)calix[4]arene VII_{pc}. Yield 76%, mp 295–297°C. ^{1}H NMR spectrum, δ, ppm: 0.04 s (9H, Me_3Si), 0.082 s (9H, Me_3Si), 0.9 s (18H, *t*-Bu), 1.29 s (9H, *t*-Bu), 1.31 s (9H, *t*-Bu), 1.94 s (3H, Me), 2.1 s (3H, Me), 2.28 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 2.87 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 4.32 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 4.41 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 6.4 s (2H, CH_2O), 6.438 s (2H, CH_2O), 6.5 d (1H, Ar–H, $^4J_{HH}$ 3.0 Hz), 6.56 d (2H, Ar–H, $^4J_{HH}$ 3.0 Hz), 7.12 s (2H, Ar–H), 7.15 s (2H, Ar–H), 7.2–7.42 m (8H, Bzl). Found, %: C 79.25; H 8.88. $C_{66}H_{88}O_4Si_2$. Calculated, %: C 79.15; H 8.86.

Alkylated di(methylbenzyl)-substituted calixarenes VIII and IX. A mixture of 2 mmol of **III** or $\mathbf{IV_c}$ and 10 mmol of allyl bromide in 50 ml of toluene, 2 ml of 50% aqueous NaOH, and 0.2 mmol of Bu_4NBr was stirred at 90–100°C for 6 h. After cooling, 20 ml of water was added, and the organic phase was separated and washed successively with 40 ml of 5% HCl and 40 ml of water. The solution was dried over Na_2SO_4, the solvent was removed at reduced pressure, and the crude product was recrystallized from methanol–$CHCl_3$, 3 : 1.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*p*-methylbenzyl)oxy]-26,28-bis(2-propenyloxy)calix[4]arene VIII. Yield 90%, mp 193–195°C. ^{1}H NMR spectrum, δ, ppm: 0.84 s (9H, *t*-Bu), 0.867 s (18H, *t*-Bu), 1.338 s (9H, *t*-Bu), 2.33 s (3H, Me), 2.38 s (3H, Me), 3.023 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 3.084 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.37 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.5 d (1H, CH_2=, *J* 8.54 Hz), 4.6 d (1H, CH_2=, *J* 8.54 Hz), 4.67 m (2H, CH_2O), 4.73 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.8 Hz), 4.8–4.96 m (2H, CH_2=), 5.3 m (2H, CH_2O), 6.37 m (2H, CH=), 6.434 s (2H, CH_2O), 6.466 s (2H, CH_2O), 7.079 s (2H, Ar–H), 7.097 s (4H, Ar–H), 7.153 s (2H, Ar–H), 7.195–7.35 m (8H, Bzl). Found, %: C 84.67; H 8.62. $C_{66}H_{80}O_4$. Calculated, %: C 84.57; H 8.60.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*m*-methylbenzyl)oxy]-26,28-bis(2-propenyloxy)calix[4]arene IX. Yield 92%, mp 215°C. ^{1}H NMR spectrum, δ, ppm: 0.8 s (9H, *t*-Bu), 0.85 s (9H, *t*-Bu), 1.31 s (9H, *t*-Bu), 1.33 s (9H, *t*-Bu), 2.31 s (3H, Me), 2.34 s (3H, Me), 3.07 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 4.32–4.39 m (2H, $ArCH_2Ar$), 4.4–4.5 m (2H, $ArCH_2Ar$), 4.52–4.61 m (2H, CH_2=), 4.65 m (2H, CH_2O), 4.7 d (2H, $ArCH_2Ar$, $J_{H_AH_B}$ 13.0 Hz), 4.73–4.9 m (2H, CH_2=), 5.1–5.2 m (2H, CH_2O), 6.37 m (2H, CH=), 6.44 s (2H, CH_2O), 6.5 s (2H, CH_2O), 7.08 d (2H, Ar–H, $^4J_{HH}$ 2.8 Hz), 7.1 d (2H, Ar–H, $^4J_{HH}$ 2.8 Hz), 7.15 s (2H, Ar–H), 7.18 s (2H, Ar–H), 7.2–7.45 m (8H, Bzl). Found, %: C 84.67; H 8.62. $C_{66}H_{80}O_4$. Calculated, %: C 84.57; H 8.60.

5,11,17,23-Tetra-*tert*-butyl-25-[(*m*-methylbenzyl)-oxy]-26,28-bis(2-propenyloxy)-27-hydroxycalix[4]-arene X. A mixture of 2 mmol of **III** and 15 mmol of allyl bromide in 75 ml of toluene, 3 ml of 50% aqueous NaOH, and 0.3 mmol of Bu_4NBr was stirred at 90–100°C for 8 h. After cooling, 30 ml of water was added, and the organic phase was separated and washed successively with 60 ml of 5% HCl and 60 ml of water. The solution was dried over Na_2SO_4, the solvent was removed at reduced pressure, and the residue was recrystallized from methanol–$CHCl_3$, 3 : 1. Yield 94%, mp 200–201°C. ^{1}H NMR spectrum, δ, ppm: 0.85 s (9H, *t*-Bu), 0.87 s (9H, *t*-Bu), 1.34 s (9H, *t*-Bu), 1.5 s (9H, *t*-Bu), 2.35 s (3H, Me), 3.095 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.7 Hz), 4.35–4.39 m (2H, $ArCH_2Ar$), 4.42–4.49 m (2H, $ArCH_2Ar$), 4.5–4.55 m (2H, CH_2=), 4.65 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.7 Hz), 4.74 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.7 Hz), 4.80 d (1H, $ArCH_2Ar$, $J_{H_AH_B}$ 12.7 Hz), 4.83–4.91 m (2H, CH_2=), 5.18 m (4H, CH_2O), 6.3–6.4 m (2H, CH=), 6.46 s (2H, CH_2O), 7.08 d (2H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.1 d (2H, Ar–H, $^4J_{HH}$ 2.7 Hz), 7.15–7.2 m (4H, Ar–H), 7.21–7.3 m (4H, Bzl). Found, %: C 83.71; H 8.74. $C_{58}H_{72}O_4$. Calculated, %: C 83.61; H 8.71.

REFERENCES

1. Vicens, J. and Bohmer, V., *Calixarenes*, Dordrecht: Kluwer Academic, 1991.
2. Ikeda, A. and Shinkai, S., *Chem. Rev.*, 1997, vol. 97, no. 5, pp. 1713–1734.
3. Arduini, A., McGregor, W.M., Paganuzzi, D., Pochini, A., Secchi, A., Ugozzoli, F., and Ungaro, R., *J. Chem. Soc., Perkin Trans. 2*, 1996, no. 1, pp. 839–846.
4. Casnati, A., *Gazz. Chim. Ital.*, 1997, vol. 127, no. 11, pp. 637–649.
5. Gutsche, C.D., Dhawan, B., No, K.H., and Muthukrishnan, R., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 16, pp. 3782–3881.
6. Araki, K., Iwamoto, K., Shinkai, S., and Matsudo, T., *Chem. Lett.*, 1989, no. 4, pp. 1747–1749.
7. Gutsche, C.D. and Pagoria, P.F., *J. Org. Chem.*, 1985, vol. 50, no. 26, pp. 5795–5802.
8. Gutsche, C.D. and Reddy, P.A., *J. Org. Chem.*, 1991, vol. 56, no. 15, pp. 4783–4791.
9. Iwamoto, K., Araki, K., and Shinkai, S., *Tetrahedron*, 1991, vol. 47, no. 25, pp. 4325–4342.
10. Alekseeva, E.A., Bacherikov, V.A., and Gren', A.I., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 5, pp. 866–867.
11. Iwamoto, K., Araki, K., and Shinkai, S., *J. Org. Chem.*, 1991, vol. 56, no. 16, pp. 4955–4962.
12. Iwamoto, K., Fujimoto, K., Matsuda, T., and Shinkai, S., *Tetrahedron Lett.*, 1990, vol. 31, no. 49, pp. 7169–7172.
13. Bitter, I., Grun, A., Agai, B., and Toke, L., *Tetrahedron*, 1995, vol. 51, no. 28, pp. 7835–7840.