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Selective Upper-Rim Adamantylation of Calix[4]arenes*

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Abstract—Lower-rim mono- and diacylated calix[4]arenes [acyl = C_6H_5CO, 3,5-$(NO_2)_2C_6H_3CO$] undergo selective adamantylation with 3-Y-1-adamantanols (Y = H, *i*-Pr, 4-MeC_6H_4) in trifluoroacetic acid at the free phenolic fragments of the macroring. The reaction provides a convenient preparative route to di-, tri-, and tetraadamantylated calix[4]arenes.

Design of new molecular receptors is one of the most important problems of organic chemistry. From this viewpoint, very promising compounds are calix[*n*]arenes (*n* usually equals 4, 6, or 8) which have been extensively studied in the last two decades. Valuable properties of calixarenes originate from the presence of a hydrophobic aromatic cavity and the possibility for both upper- and lower-rim modification by appropriate functional groups. As a result, these compounds can be widely used as models for simulation of biochemical processes, molecular recognition, membrane transfer, and enzymatic catalysis. In this connection, important problems are both synthesis of new types of calixarenes and development of procedures for their selective functionalization.

Prior to our studies, adamantylcalix[*n*]arenes were not reported. The first representatives were obtained in 1993 [4]. In 1994 we developed a new procedure for modification of calix[4]arene via reaction with 1-hydroxyadamantane and 3-alkyl-1-hydroxyadamantanes in trifluoroacetic acid (TFA). This reaction gives exhaustively adamantylated derivatives [5]. Later on, the procedure was applied to calix[6]arene [6]. In 1996–97 we showed that 3-substituted 1-hydroxyadamantanes as adamantylating agents provide the possibility for upper-rim functionalization of calix[4 or 6]arenes by adamantyl fragments containing various groups [6, 7]. Finally, with the use of 1-hydroxyadamantanes having electron-acceptor substituents in position *3* we succeeded in finding conditions for selective adamantylation of calix[4]arene. The latter reacted with 3-(4-methylsulfonylphenyl)-1-hydroxyadamantane in trifluoroacetic acid/xylene to give 70% of the corresponding triadamantyl derivative [7, 8]. Diadamantyl derivatives were isolated only as mixtures of 1,2- and 1,3-isomers. On the other hand, such derivatives with functional groups in the adamantane fragments, especially those with distal arrangement of the adamantyl substituents, attract attention as “building blocks” in supramolecular synthesis, specifically for creation of selective receptors for metal cations and organic molecules.

In all the above cases [5–8], the adamantylation was performed with calixarenes having free hydroxy groups. We now propose a general procedure for selective adamantylation of calix[4]arenes, which is based on the difference in the reactivity of alkylated (or acylated) and free phenolic fragments in calix[4]arenes with respect to carbocationic adamantyl intermediates in trifluoroacetic acid.

The reactions were carried out in excess TFA using chloroform as co-solvent. As starting compounds we used calix[4]arenes selectively alkylated or acylated at the lower rim: 25,27-dipropoxy, 25,27-bis(benzyloxy), 25,27-bis(benzoyloxy), 25,26,27-tris(benzoyloxy), 25-(3,5-dinitrobenzoyloxy), and 25,27-bis(3,5-dinitrobenzoyloxy) derivatives **I**–**VI** with unsubstituted *para*-positions and 5,17-di-*tert*-butyl-26,28-bis(3,5-dinitrobenzoyloxy)calix[4]arene (**VII**) (Scheme 1).

1,3-Dipropyl ether **I** turned out to be resistant to TFA, but its reaction with 1-adamantanol was not selective: it resulted in exhaustive adamantylation at the *para*-positions of both phenolic and ether fragments with formation of tetraadamantyl derivative **VIII** (Scheme 2). We did not succeed in selectively obtaining the desired 5,17-bis(1-adamantyl) derivative by varying the reaction conditions such as TFA amount and temperature; in all cases intractable mixtures of partially and exhaustively admantylated

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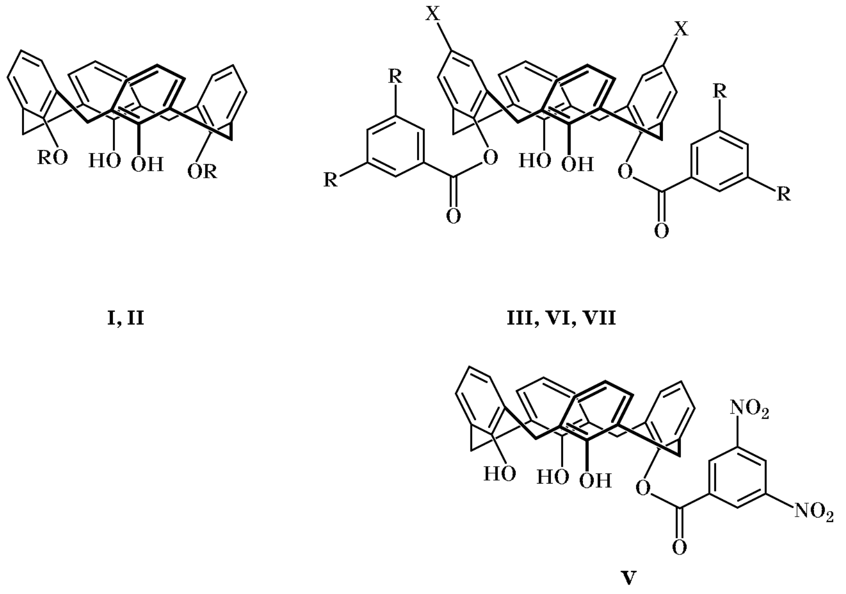
Scheme 1.



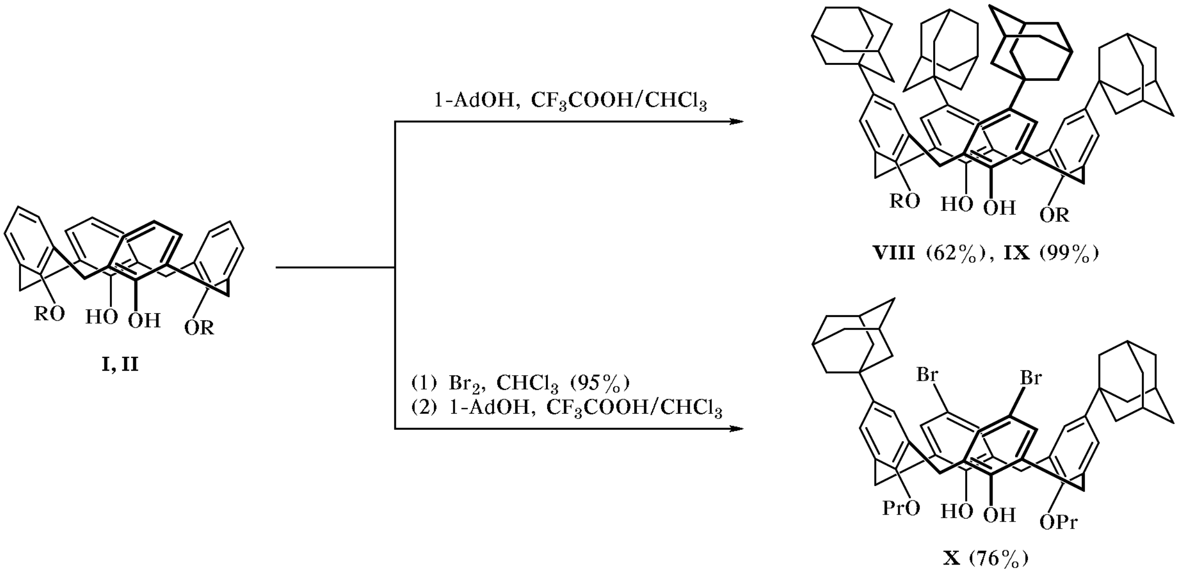
I, R = Pr; **II**, R = CH_2Ph; **III**, R = X = H; **VI**, R = NO_2, X = H; **VII**, R = NO_2, X = *t*-Bu.

products were formed. 1,3-Dibenzyl ether **II** undergoes dealkylation in TFA even at room temperature. Its reaction with 1-adamantanol yields *p*-tetrakis-(1-adamantyl)calix[4]arene (**IX**) (Scheme 2).

Thus, lower-rim alkylation does not allow us to effect selective upper-rim adamantylation of calixarenes. By selective bromination of **I** at the *para*-positions of phenolic rings we obtained the corresponding dibromide whose adamantylation gave 11,23-diadamantyl derivative (**X**).

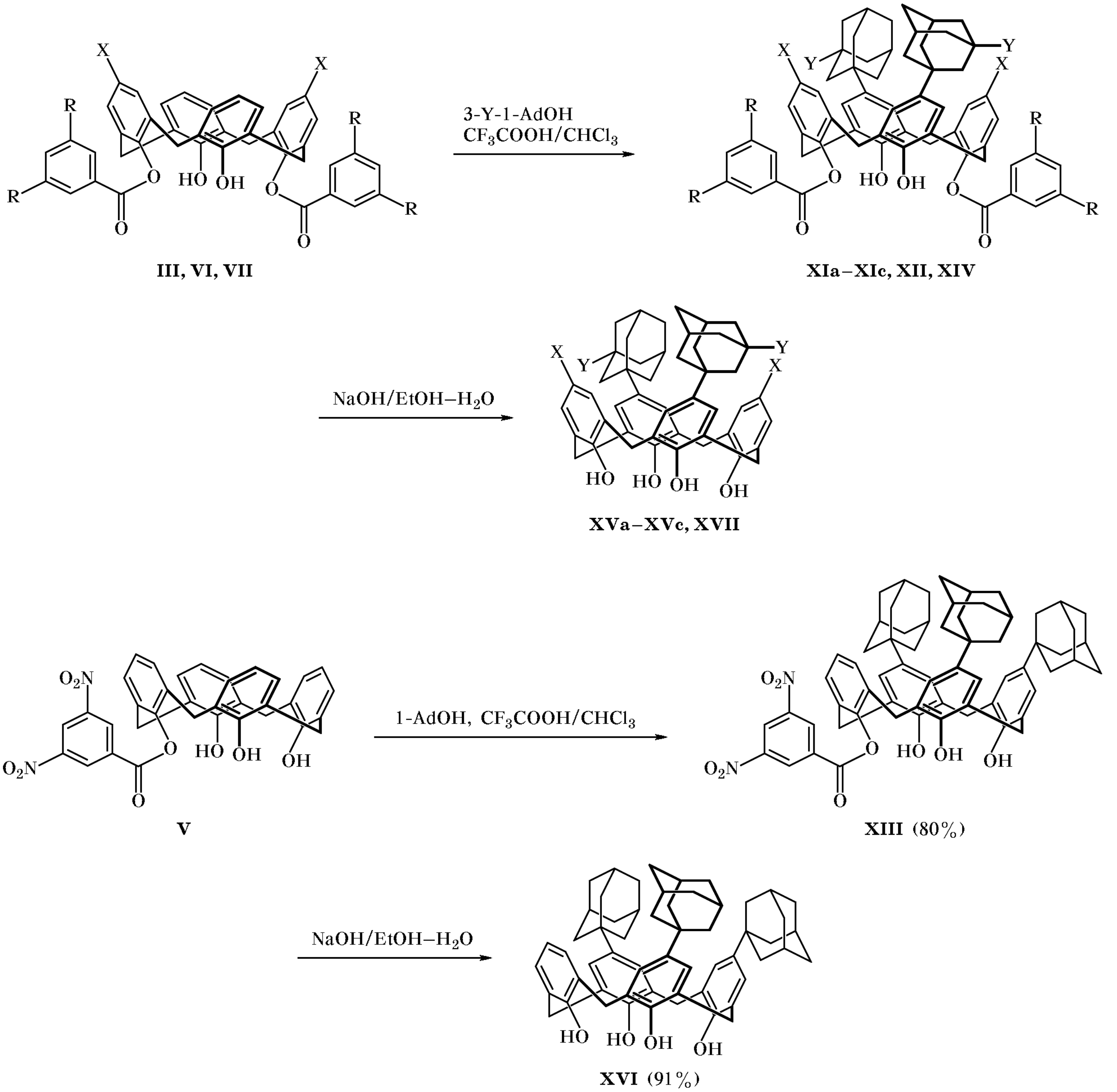
The reaction of partially acylated 1,3-bis(benzoyloxy)calix[4]arene (**III**) with 3-Y-substituted 1-hydroxyadamantanes (Y = H, *iso*-C_3H_7, 4-$CH_3C_6H_4$) in TFA gave calixarenes **XIa**–**XIc** having two adamantyl

Scheme 2.



I, R = Pr; **II**, R = CH_2Ph; **VIII**, R = Pr; **IX**, R = H.

Scheme 3.

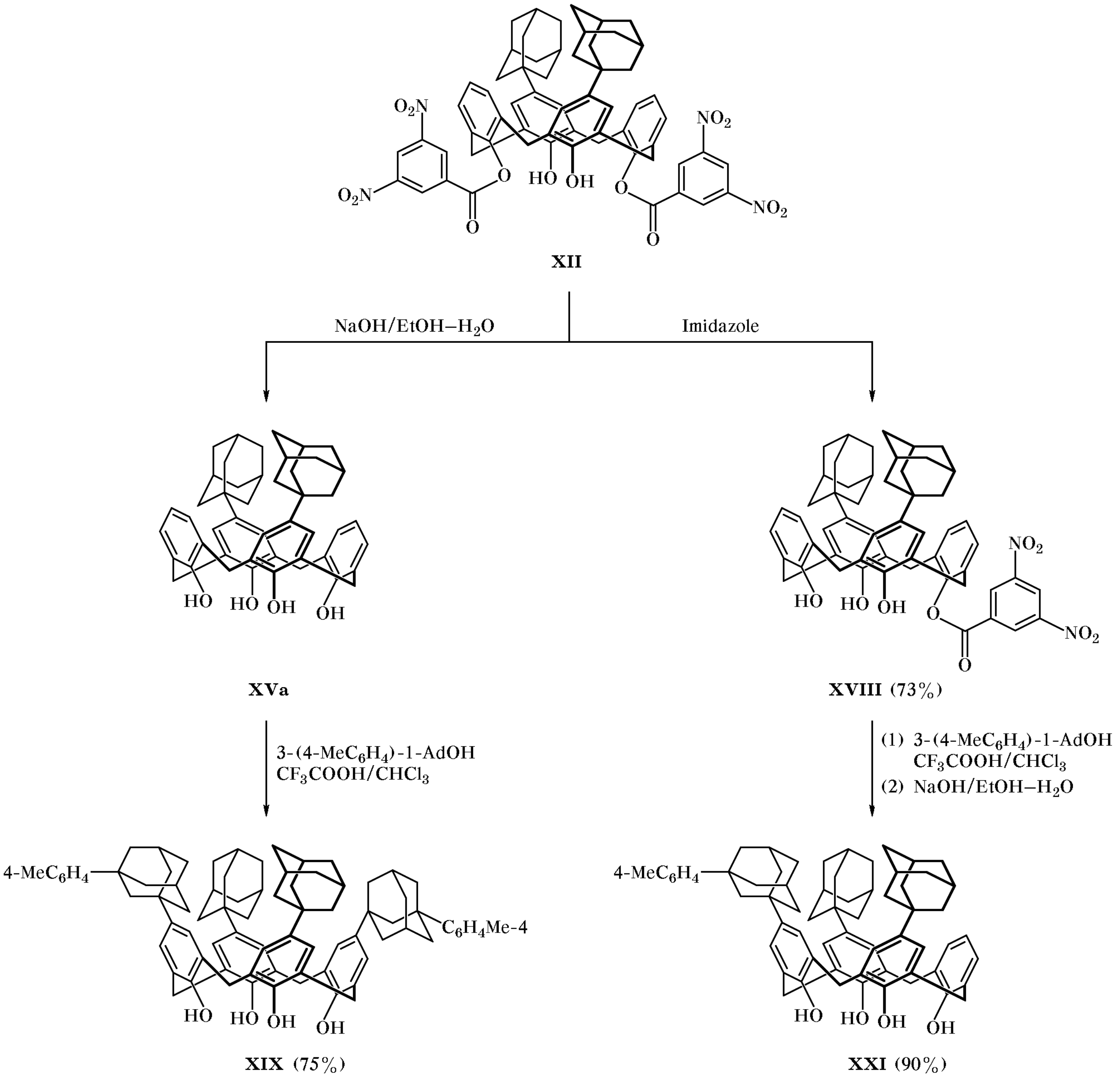


III, R = X = H; **VI**, R = NO_2, X = H; **VII**, R = NO_2, X = *t*-Bu; **XIa**, R = X = Y = H (90%); **XIb**, R = X = H, Y = *i*-Pr (89%); **XIc**, R = X = H, Y = 4-MeC_6H_4 (63%); **XII**, R = NO_2, X = Y = H (76%); **XIV**, R = NO_2, X = *t*-Bu, Y = H (86%); **XVa**, X = Y = H (92%); **XVb**, X = H, Y = *i*-Pr (77%); **XVc**, X = H, Y = 4-MeC_6H_4 (81%); **XVII**, X = *t*-Bu, Y = H (89%).

groups in the *para*-positions of the phenol rings. It should be emphasized that the adamantylation was selective in a narrow temperature range, from 45 to 55°C. At higher temperature the reaction was accompanied by partial debenzoylation of the initial ester to produce complex reaction mixtures. At lower temperature the reaction was very slow. Less active tris(benzoyloxy)calix[4]arene **IV** almost did not react with adamantanols below 75°C, while above that temperature debenzoylation occurred.

3,5-Dinitrobenzoyloxy derivatives **V**–**VII** are more resistant to hydrolysis in acid medium. No deacylation occurred in TFA even under reflux. The reaction of 25,27-bis(3,5-dinitrobenzoyloxy)calix[4]arene (**VI**) with 1-adamantanol gave 76% of upper-rim diadamantylated calixarene **XII** (Scheme 3). Under similar

Scheme 4.



conditions, from monoacyl derivative **V** we obtained 80% of product **XIII** having three adamantyl groups at the upper rim. 5,17-Di-*tert*-butyl-26,28-bis(3,5-dinitrobenzoyloxy)calix[4]arene (**VII**) obtained by selective dealkylation of the corresponding tetra-*tert*-butyl derivative reacted with 1-adamantanol to afford calix[4]arene **XIV** with distal *tert*-butyl and adamantyl groups.

The acyl protection can readily be removed from the synthesized adamantylcalix[4]arenes by alkaline hydrolysis. As a result, compounds **XV**–**XVII** were obtained (Scheme 3).

The product of selective upper-rim 1,3-diadamantylation, calix[4]arene **XII**, was used as starting compound for synthesis of calix[4]arenes **XIX**–**XXI** with four or three differently substituted adamantyl fragments on the upper rim. In the first case, further adamantylation of calix[4]arene **XII** was performed after hydrolysis. In the second case, we used a procedure utilizing imidazole [9] to remove one of the two acyl groups in **XII**, and the resulting monoacyl derivative **XVIII** was subjected to further adamantylation.

Our results show that the reaction in trifluoroacetic acid of 3-substituted 1-hydroxyadamantanes with calix[4]arenes selectively acylated at the lower rim provides a selective synthetic route to upper-rim adamantylated derivatives.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VRX-300 spectrometer in $CDCl_3$ (75.4 MHz for ^{13}C) using tetramethylsilane as internal reference. Preparative column chromatography was performed on Silicagel 40/60 μm. Silufol-254 and DC Alufolien Kieselgel 60 F_{256} plates (Merck) were used for thin-layer chromatography; spots were visualized by UV irradiation. Initial calixarenes and adamantylating agents were synthesized by known methods: calix[4]-arene [10, 11], 25,27-dipropoxycalix[4]arene (**I**) [12], 5,17-dibromo-25,27-dipropoxycalix[4]arene [13], 25,27-bis(benzyloxy)calix[4]arene (**II**) [14], 25,27-bis-(benzoyloxy)calix[4]arene (**III**) [15], 25,26,27-tris-(benzoyloxy)calix[4]arene (**IV**) [11], 25,27-bis(3,5-dinitrobenzoyloxy)calix[4]arene (**VI**) [9], 5,7-di-*tert*-butyl-26,28-bis(3,5-dinitrobenzoyloxy)calix[4]arene (**VII**) [9, 16], 1-adamantanol [17, 18], 3-isopropyl-1-adamantanol [19]; 3-(4-methylphenyl)-1-adamantanol [20]. 25-(3,4-Dinitrobenzoyloxy)calix[4]arene (**V**) was synthesized from calix[4]arene and 3,5-dinitrobenzoyl chloride in acetonitrile in the presence of 1-methyl-imidazole by analogy with the synthesis of *p-tert*-butyl derivative reported in [9]. The yield of **V** was 75%. The solvents used in this work were purified and dehydrated by standard procedures.

Typical procedure for adamantylation of calix-arenes. A flask was charged with required amounts of calixarene, adamantylating agent, and chloroform. The flask was filled with argon, and trifluoroacetic acid and lithium perchlorate as catalyst were added. The reactant ratio calixarene–adamantylating agent–TFA was as a rule 1 : 3–4 : 40–60. The amount of chloroform (by volume) was the same as the amount of TFA. Lithium perchlorate was taken in an amount of 6×10^{-2} mol per mole of calixarene. The reaction mixture was heated (oil bath) to a required temperature in a stream of argon. The progress of the reaction was monitored by TLC, following the disappearance of the initial calixarene. When the reaction was complete, the mixture was evaporated to dryness.

Typical procedure for removal of acyl protection from adamantylated calixarenes XI–XIV and XX. A mixture of acylated calixarene (0.15 mmol), sodium hydroxide (1 g), THF (30 ml), ethanol (10 ml), and water (4 ml) was refluxed for 18–20 h and evaporated. Dilute hydrochloric acid, 15 ml, was added to the solid residue, and the products were extracted into chloroform or methylene chloride. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography using 1 : 1 hexane–chloroform as eluent.

5,11,17,23-Tetrakis(1-adamantyl)-25,27-dipropoxycalix[4]arene (VIII) was synthesized from 100 mg (0.2 mmol) of calixarene **I**, 120 mg (0.8 mmol) of 1-adamantanol, and 0.6 ml (8 mmol) of trifluoroacetic acid; reaction temperature 60–65°C, reaction time 8 h. The reaction mixture was evaporated, 5–10 ml of water was added to the residue, and the mixture was left overnight. The precipitate was filtered off and washed with water and methanol. Yield of **VIII** 130 mg (62%), mp 210–212°C, R_f 0.59 (chloroform–hexane, 1 : 2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: C_{Ad}: 35.40, 35.26 (C^1), 43.66, 43.21 (C^2), 29.10, 28.89 (C^3), 36.92, 36.79 (C^4); C_{cavity}: 150.69, 149.64, 146.65, 141.47, 132.68, 127.83 (C_{arom}), 124.88, 124.38 (CH_{arom}); 31.50 ($Ar\mathbf{C}H_2Ar$); C_R: 78.08 ($O\mathbf{C}H_2CH_2CH_3$), 23.36 ($OCH_2\mathbf{C}H_2CH_3$), 10.72 ($OCH_2CH_2\mathbf{C}H_3$). Found, %: C 85.31; H 8.57. $C_{74}H_{92}O_4$. Calculated, %: C 85.01; H 8.87.

5,11,17,23-Tetrakis(1-adamantyl)calix[4]arene (IX) was synthesized from 100 mg (0.17 mmol) of calixarene **II**, 104 mg (0.68 mmol) of 1-adamantanol, and 0.5 ml (6.62 mmol) of trifluoroacetic acid; reaction temperature 60–65°C, reaction time 9 h. The mixture was treated as described above for compound **VIII**. Yield of **IX** 158 mg (99%). The constants and ^{1}H and ^{13}C NMR spectral parameters of the product were identical to those given in [5].

5,17-Dibromo-11,23-bis(1-adamantyl)-26,28-dipropoxycalix[4]arene (X) was synthesized from 100 mg (0.15 mmol) of 5,17-dibromo-26,28-dipropoxycalix[4]arene, 91 mg (0.6 mmol) of 1-adamantanol, and 0.48 ml (6.4 mmol) of trifluoroacetic acid; reaction temperature 70–75°C, reaction time 12 h. After removal of the solvent, the solid residue was washed with boiling methanol and was subjected to column chromatography using 1 : 9 carbon tetrachloride–hexane as eluent. Yield of **X** 106 mg (76%), mp 365–367°C, R_f 0.54 (chloroform–hexane, 1 : 2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.26 s (2H, OH), 7.13 s (4H, H_{arom}), 6.86 s (4H, H_{arom}), 4.24 d.d (4H, $ArC\mathbf{H}_2Ar$), 3.91 t (4H, $OC\mathbf{H}_2CH_2CH_3$), 3.28 d.d (4H, $ArC\mathbf{H}_2Ar$), 2.05–1.95 m (7H, $OCH_2C\mathbf{H}_2CH_3$, CH, adamantane), 1.60–1.75 m (24H, CH_2, adamantane), 1.21 t (6H, $OCH_2CH_2C\mathbf{H}_3$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.61 (C^1), 42.81 (C^2), 28.74 (C^3), 36.55 (C^4); C_{cavity}: 152.26, 149.94, 147.87, 132.02, 130.51 (CH_{arom}), 130.33 (C_{arom}), 125.33 (CH_{arom}), 110.41 (C_{arom}), 31.50 ($Ar\mathbf{C}H_2Ar$);

C_R: 78.16 ($O\mathbf{C}H_2CH_2CH_3$), 23.29 ($OCH_2\mathbf{C}H_2CH_3$), 10.72 ($OCH_2CH_2\mathbf{C}H_3$). Found, %: C 69.19; H 6.84; Br 16.91. $C_{54}H_{62}Br_2O_4$. Calculated, %: C 69.38; H 6.68; Br 17.09.

5,17-Bis(1-adamantyl)-25,27-bis(benzoyloxy)calix[4]arene (XIa) was synthesized from 1 g (1.6 mmol) of calixarene **III**, 0.98 g (6.4 mmol) of 1-adamantanol, and 5 ml (66 mmol) of trifluoroacetic acid. Reaction temperature 55°C, reaction time 10 h. After removal of the solvent, the solid residue was refluxed with methanol, and the precipitate was filtered off and dried. Yield of **XIa** 1.3 g (90%), mp 318–320°C, R_f 0.61 (chloroform–hexane, 2 : 1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.22 (C^1), 43.13 (C^2), 28.86 (C^3), 36.63 (C^4); C_{cavity} + C_R: 164.66 (OCOPh), 150.39, 145.46, 142.93 (C_{arom}), 133.56 (CH_{arom}), 132.54 (C_{arom}), 130.33 (CH_{arom}), 129.10 (C_{arom}), 129.04, 128.84 (CH_{arom}), 127.17 (C_{arom}), 126.57, 125.35 (CH_{arom}), 33.27 ($Ar\mathbf{C}H_2Ar$). Found, %: C 82.91; H 6.99. $C_{62}H_{60}O_6$. Calculated, %: C 82.64; H 6.71.

25,27-Bis(benzoyloxy)-5,17-bis(3-isopropyl-1-adamantyl)calix[4]arene (XIb) was synthesized as described above for compound **XIa** from 0.1 g (0.16 mmol) of calixarene **III**, 0.12 g (0.62 mmol) of 3-isopropyl-1-adamantanol, and 1 ml (13 mmol) of trifluoroacetic acid. Yield of **XIb** 140 mg (89%), mp 323–325°C, R_f 0.70 (chloroform–hexane, 2 : 1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 37.55 [$(CH_3)_2\mathbf{C}H$], 16.40 [$(\mathbf{C}H_3)_2CH$], 35.01 (C^1), 45.43 (C^2), 36.37 (C^3), 42.81 (C^4, C^{10}), 29.25 (C^5, C^7), 35.39 (C^6), 38.21 (C^8, C^9); C_{cavity} + C_R: 164.71 (OCOPh), 150.47, 145.49, 142.92, 133.61 (C_{arom}), 132.54 (CH_{arom}), 130.35 (CH_{arom}), 129.13 (C_{arom}), 129.04, 128.89 (CH_{arom}), 127.24 (C_{arom}), 126.63, 125.42 (CH_{arom}), 33.24 ($Ar\mathbf{C}H_2Ar$). Found, %: C 82.61; H 7.58. $C_{68}H_{72}O_6$. Calculated, %: C 82.89; H 7.37.

25,27-Bis(benzoyloxy)-5,17-bis[3-(4-methylphenyl)-1-adamantyl]calix[4]arene (XIc) was synthesized as described above for compound **XIa** from 0.25 g (0.4 mmol) of calixarene **III**, 0.39 g (1.6 mmol) of 3-(4-methylphenyl)-1-adamantanol, and 2 ml (26 mmol) of trifluoroacetic acid. After evaporation of the reaction mixture, the residue was washed with boiling methanol and was subjected to column chromatography using hexane–chloroform as eluent. Yield of **XIc** 270 mg (63%) (500 mg before chromatographic treatment), mp 208–210°C, R_f 0.65 (chloroform–hexane, 2 : 1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 20.79 ($Ph\mathbf{C}H_3$), 147.62, 134.99, 128.73, 124.68 ($CH_3\mathbf{C}_6H_5$); 36.37 (C^1), 49.08 (C^2), 36.80 (C^3), 42.39 (C^4, C^{10}), 29.47 (C^5, C^7), 35.71 (C^6), 42.04 (C^8, C^9); C_{cavity} + C_R: 164.51 (OCOPh), 150.54, 145.40, 142.24, 133.60 (C_{arom}), 132.43, 130.30 (CH_{arom}), 129.09 (C_{arom}), 129.01, 128.85 (CH_{arom}), 127.30 (C_{arom}), 126.57, 125.37 (CH_{arom}), 33.14 ($Ar\mathbf{C}H_2Ar$). Found, %: C 84.78; H 7.01. $C_{76}H_{72}O_6$. Calculated, %: C 84.41; H 6.71.

5,17-Bis(1-adamantyl)-25,27-bis(3,5-dinitrobenzoyloxy)calix[4]arene (XII) was synthesized from 0.81 g (1 mmol) of calixarene **VI**, 0.45 g (3 mmol) of 1-adamantanol, and 3.9 ml (50 mmol) of trifluoroacetic acid; reaction temperature 65°C, reaction time 30 h. After evaporation of the reaction mixture, the residue was washed with boiling methanol and was subjected to column chromatography using hexane–chloroform as eluent. Yield of **XII** 1.45 g (76%), mp 243–245°C, R_f 0.62 (chloroform–hexane, 2 : 1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.61 (C^1), 43.51 (C^2), 29.01 (C^3), 36.78 (C^4); C_{cavity} + C_R: 163.55 (OCOAr), 149.96, 148.75, 144.52, 144.21 (C_{arom}), 132.75 (CH_{arom}), 131.81 (CH_{arom}), 129.35 (C_{arom}), 127.67, 127.53 (CH_{arom}), 125.70 (C_{arom}), 123.08 (CH_{arom}), 32.01 ($Ar\mathbf{C}H_2Ar$). Found, %: C 68.71; H 5.50; N 5.01. $C_{62}H_{56}N_4O_{14}$. Calculated, %: C 68.88; H 5.22; N 5.18.

5,11,17-Tris(1-adamantyl)-25-(3,5-dinitrobenzoyloxy)calix[4]arene (XIII) was synthesized from 0.15 g (0.2 mmol) of calixarene **V**, 0.21 g (1.5 mmol) of 1-adamantanol, and 0.3 ml (3.8 mmol) of trifluoroacetic acid; reaction temperature 60°C, reaction time 12 h. After evaporation of the reaction mixture, the residue was washed with boiling methanol. Yield of **XIII** 0.20 g (80%), mp 260–262°C, R_f 0.38 (chloroform–hexane, 2 : 1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.52, 34.92 (C^1), 43.04, 42.80 (C^2), 29.01, 28.54 (C^3), 36.80, 36.41 (C^4); C_{cavity} + C_R: 159.82 (OCOPh), 149.11, 148.53, 148.42, 143.83, 132.65, 132.16 (C_{arom}), 130.34, 129.50, 128.91 (CH_{arom}), 127.57, 127.41 (C_{arom}), 125.61 (CH_{arom}), 125.46 (C_{arom}), 124.38, 122.30, 122.02 (CH_{arom}), 35.40, 31.72 (1 : 1, $Ar\mathbf{C}H_2Ar$). Found, %: C 76.71; H 6.51; N 2.91. $C_{65}H_{68}N_2O_9$. Calculated, %: C 76.45; H 6.71; N 2.74.

11,23-Bis(1-adamantyl)-5,17-di-*tert*-butyl-26,28-bis(3,5-dinitrobenzoyloxy)calix[4]arene (XIV) was synthesized from 0.92 g (1 mmol) of calixarene **VII**, 0.45 g (3 mmol) of 1-adamantanol, and 3.9 ml (50 mmol) of trifluoroacetic acid, following the procedure described above for compound **XII**. Yield of **XIV** 1.03 g (80%), mp 216–218°C. Found, %: C 70.70; H 5.85; N 4.98. $C_{70}H_{72}N_4O_{14}$. Calculated, %: C 70.45; H 6.08; N 4.70.

5,17-Bis(1-adamantyl)calix[4]arene (XVa) was obtained by alkaline hydrolysis of compound **XIa**. Yield of **XVa** 92%, mp 241–243°C, R_f 0.51 (chloroform–hexane, 1:2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.46 (C^1), 43.15 (C^2), 28.87 (C^3), 36.65 (C^4); C_{cavity}: 148.51, 146.63, 144.84 (C_{arom}), 128.86 (CH_{arom}), 128.37, 127.37 (C_{arom}), 125.28, 122.16 (CH_{arom}), 32.12 ($Ar\mathbf{C}H_2Ar$). Found, %: C 83.55; H 7.90. $C_{48}H_{52}O_4$. Calculated, %: C 83.20; H 7.56.

5,17-Bis(3-isopropyl-1-adamantyl)calix[4]arene (XVb) was obtained by alkaline hydrolysis of compound **XIb**. Yield of **XVb** 77%, mp 237–239°C. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: C_{Ad}: 37.55 $[(CH_3)_2\mathbf{C}H]$, 16.40 $[(\mathbf{C}H_3)_2CH]$, 35.01 (C^1), 45.43 (C^2), 36.37 (C^3), 42.81 (C^4, C^{10}), 29.25 (C^5, C^7), 35.39 (C^6), 38.21 (C^8, C^9); C_{cavity}: 148.55, 146.33, 144.55 (C_{arom}), 128.26 (CH_{arom}), 128.38, 127.23 (C_{arom}), 125.20, 122.00 (CH_{arom}), 32.32 ($Ar\mathbf{C}H_2Ar$). Found, %: C 83.21; H 8.51. $C_{54}H_{64}O_4$. Calculated, %: C 83.46; H 8.30.

5,17-Bis[3-(4-methylphenyl)-1-adamantyl]calix[4]arene (XVc) was obtained by alkaline hydrolysis of compound **XIc**. Yield of **XVc** 81%, mp 243–245°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 20.78 ($\mathbf{C}H_3Ph$), 147.60, 134.99, 128.74, 124.70 ($CH_3\mathbf{C}_6H_5$), 36.55 (C^1), 48.85 (C^2), 36.80 (C^3), 42.27 (C^4, C^{10}), 29.46 (C^5, C^7), 35.73 (C^6), 42.27 (C^8, C^9); C_{cavity}: 148.45, 146.77, 144.17 (C_{arom}), 128.88 (CH_{arom}), 128.24, 127.49 (C_{arom}), 125.32, 122.20 (CH_{arom}), 32.12 ($Ar\mathbf{C}H_2Ar$). Found, %: C 85.54; H 7.18. $C_{62}H_{64}O_4$. Calculated, %: C 85.28; H 7.39.

5,11,17-Tris(1-adamantyl)calix[4]arene (XVI) was obtained by alkaline hydrolysis of compound **XIII**. Yield of **XVI** 91%, mp 259–261°C, R_f 0.80 (chloroform–hexane, 1:2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.45 (C^1), 43.12, 43.06 (2:1, C^2), 28.87 (C^3), 36.68 (C^4); C_{cavity}: 148.73, 146.58, 146.24, 144.71, 144.65 (C_{arom}), 128.79 (CH_{arom}), 128.45, 127.67, 127.65, 127.28 (C_{arom}), 125.45, 125.17, 122.04 (CH_{arom}), 32.53, 32.17 (1:1, $Ar\mathbf{C}H_2Ar$). Found, %: C 84.55; H 7.98. $C_{58}H_{66}O_4$. Calculated, %: C 84.22; H 8.04.

11,23-Bis(1-adamantyl)-5,17-di-*tert*-butylcalix[4]arene (XVII) was obtained by alkaline hydrolysis of compound **XIV**. Yield of **XVII** 89%, mp 186–188°C, R_f 0.59 (chloroform–hexane, 1:2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.45 (C^1), 43.10 (C^2), 28.88 (C^3), 36.70 (C^4); $C_{t\text{-}Bu}$: 33.94, 31.38; C_{cavity}: 146.61, 146.52, 144.25, 144.18, 127.64, 127.53 (C_{arom}), 125.85, 125.36 (CH_{arom}), 32.59 ($Ar\mathbf{C}H_2Ar$). Found, %: C 83.71; H 8.75. $C_{56}H_{68}O_4$. Calculated, %: C 83.54; H 8.51.

5,17-Bis(1-adamantyl)-25-(3,5-dinitrobenzoyloxy)calix[4]arene (XVIII). A solution of 0.3 g (4.4 mmol) of imidazole in 8 ml of acetonitrile was added to a solution of 0.4 g (0.37 mmol) of calixarene **XII** in 8 ml of chloroform. The mixture was stirred for 30 min at room temperature, 3 ml of 1 N hydrochloric acid was added, and the mixture was stirred for an additional 20 min. The product was extracted into chloroform, and the extracts were washed with water until neutral reaction, dried over $MgSO_4$, and evaporated. The residue was washed with boiling methanol. Yield of **XVIII** 240 mg (73%), mp 265–267°C, R_f 0.29 (chloroform–hexane, 2:1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.01 (C^1), 42.91 (C^2), 28.58 (C^3), 36.42 (C^4); C_{cavity} + C_R: 159.90 (OCOPh), 149.11, 148.53, 148.42, 143.83, 132.65, 132.16 (C_{arom}), 130.34, 129.50, 128.91, 128.19 (CH_{arom}), 127.57, 127.41 (C_{arom}), 125.61 (CH_{arom}), 125.46 (C_{arom}), 124.38, 122.30, 122.02 (CH_{arom}), 35.40, 31.72 (1:1, $Ar\mathbf{C}H_2Ar$). Found, %: C 74.28; H 6.31; N 3.40. $C_{55}H_{54}N_2O_9$. Calculated, %: C 74.47; H 6.14; N 3.16.

5,17-Bis(1-adamantyl)-11,23-bis[3-(4-methylphenyl)-1-adamantyl]calix[4]arene (XIX) was synthesized from 0.28 g (0.4 mmol) of calixarene **XVa**, 0.39 g (1.6 mmol) of 3-(4-methylphenyl)-1-adamantanol, and 2 ml (26 mmol) of trifluoroacetic acid, following the procedure described below for compound **XXI**. Yield of **XIX** 0.33 g (75%), mp 223–225°C, R_f 0.72 (chloroform–hexane, 1:2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.47 (C^1), 43.11 (C^2), 28.83 (C^3), 36.79 (C^4); $C_{3\text{-}Tol\text{-}1\text{-}Ad}$: 20.75 ($\mathbf{C}H_3C_6H_4$), 147.66, 134.90, 128.68, 124.58 ($CH_3\mathbf{C}_6H_4$); 36.70 (C^1), 48.90 (C^2), 36.56 (C^3), 42.28 (C^4, C^{10}), 29.55 (C^5, C^7), 35.84 (C^6), 42.28 (C^8, C^9); C_{cavity}: 146.71, 146.22, 144.66, 144.18, 127.82, 127.55 (C_{arom}), 125.43 (CH_{arom}), 32.59 ($Ar\mathbf{C}H_2Ar$). Found, %: C 86.51; H 7.98. $C_{82}H_{92}O_4$. Calculated, %: C 86.27; H 8.12.

5,17-Bis(1-adamantyl)-11-[3-(4-methylphenyl)-1-adamantyl)]-25-(3,5-dinitrobenzoyloxy)calix[4]arene (XX) was synthesized from 89 mg (0.1 mmol) of compound **XVIII**, 100 mg (0.4 mmol) of 3-(4-methylphenyl)-1-adamantanol, and 1 ml (13 mmol) of trifluoroacetic acid; reaction temperature 60°C, reaction time 12 h. The mixture was then treated as described above for compound **XIII**. Yield of **XX** 81 mg (73%). The product was immediately brought into alkaline hydrolysis.

5,17-Bis(1-adamantyl)-11-[3-(4-methylphenyl)-1-adamantyl]calix[4]arene (XXI) was obtained by alkaline hydrolysis of compound **XX**. Yield of **XXI** 60 mg (90%), mp 263–265°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: C_{Ad}: 35.44 (C^1), 43.11 (C^2), 28.84 (C^3), 36.66 (C^4); $C_{3\text{-Tol-1-Ad}}$: 20.77 ($\mathbf{C}H_3C_6H_4$), 147.67, 134.88, 128.64, 124.55 ($CH_3\mathbf{C}_6H_4$); 36.50 (C^1), 48.72 (C^2), 36.75 (C^3), 42.31 (C^4, C^{10}), 29.52 (C^5, C^7), 35.84 (C^6), 42.24 (C^8, ^{9}); C_{cavity}: 148.78, 146.57, 146.31, 144.75, 144.06 (C_{arom}), 128.80 (CH_{arom}), 128.48, 127.73, 127.19 (C_{arom}), 125.42, 125.14, 121.98 (CH_{arom}), 32.44, 32.18 (1:1, $Ar\mathbf{C}H_2Ar$). Found, %: C 85.39; H 8.15. $C_{65}H_{72}O_4$. Calculated, %: C 85.11; H 7.91.

REFERENCES

1. Gutsche, C.D., *Host Guest Complex Chemistry: Macrocycles: Synthesis, Structures, Applications,* Vögtle, F. and Weber, E., Eds., Berlin: Springer, 1985. Translated under the title *Khimiya kompleksov "gost'–khozyain." Sintez, struktury i primenenie,* Moscow: Mir, 1988, pp. 445–495.
2. Gutsche, C.D., *Calixarenes: Monographs in Supramolecular Chemistry,* Stoddart, J.F., Ed., Cambridge: The Royal Society of Chemistry, 1989, vol. 1, p. 1.
3. Bohmer, V., *Angew. Chem.*, 1995, vol. 107, no. 4, pp. 785–818.
4. Lubitov, I., Shokova, E., and Kovalev, V., *Synlett.*, 1993, no. 9, pp. 647–649.
5. Khomich, A.N., Shokova, E.A., and Kovalev, V.V., *Synlett.*, 1994, no. 12, pp. 1027–1028.
6. Kovalev, V., Shokova, E., and Khomich, E., Abstracts of Papers, *4th Int. Conf. on Calixarenes,* Parma, Italy, August 31–September 4, 1997, p. 140.
7. Kovalev, V., Shokova, E., Khomich, A., and Luzikov, Yu., *New J. Chem.*, 1996, vol. 20, no. 4, pp. 483–492.
8. Shokova, E., Khomich, A., and Kovalev, V., *Tetrahedron Lett.*, 1996, vol. 37, no. 4, pp. 543–546.
9. See, K.A., Fronczek, F.R., Watson, W.H., Kashyap, R.P., and Gutsche, C.D., *J. Org. Chem.*, 1991, vol. 56, no. 26, pp. 7256–7268.
10. Gutsche, C., Iqbal, M., and Stewart, D., *J. Org. Chem.*, 1986, vol. 51, no. 5, pp. 742–745.
11. Gutsche, C. and Lin, L., *Tetrahedron,* 1986, vol. 42, no. 6, pp. 1633–1640.
12. Arduini, A., Fabbi, M., Mantovani, M., Mirone, L., Pochini, A., Secchi, A., and Ungaro, R., *J. Org. Chem.*, 1995, vol. 60, no. 5, pp. 1454–1457.
13. Linnane, P., James, T.D., and Shinkai, S., *J. Chem. Soc., Chem. Commun.*, 1995, no. 19, pp. 1997–1998.
14. Van Loon, J.-D., Arduini, A., Verboom, W., Ungaro, R., van Hummel, G., Harkema, S., and Reinhoudt, D., *Tetrahedron Lett.*, 1989, vol. 30, no. 20, pp. 2681–2684.
15. Chun-mei Shu, Wen-chin Liu, Ming-chung Ku, Fa-shin Tang, Mei-ling Yeh, and Lee-gin Lin, *J. Org. Chem.*, 1994, vol. 59, no. 13, pp. 3730–3733.
16. Kanamathareddy, S. and Gutsche, C., *J. Org. Chem.*, 1995, vol. 60, no. 19, pp. 6070–6075.
17. Stetter, H., Schwarz, M., and Hirschhorn, A., *Chem. Ber.*, 1959, vol. 92, no. 7, pp. 1629–1635.
18. Shokova, E.A., Knopova, S.I., Nguen Dang K'en, and Kazanskii, B.A., *Neftekhimiya,* 1973, vol. 13, no. 4, pp. 585–591.
19. Kovalev, V., Rozov, A., and Shokova, E., *Tetrahedron,* 1996, vol. 52, no. 11, pp. 3983–3990.
20. Kovalev, V.V., Knyazeva, I.V., and Shokova, E.A., *Zh. Org. Khim.*, 1986, vol. 22, no. 4, pp. 776–780.