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LETTERS TO THE EDITOR

Unusual Reaction of Tetramethylcalix[4]resorcinolarene with 3,5-Di-*tert*-butyl-4-hydroxybenzyl Acetate

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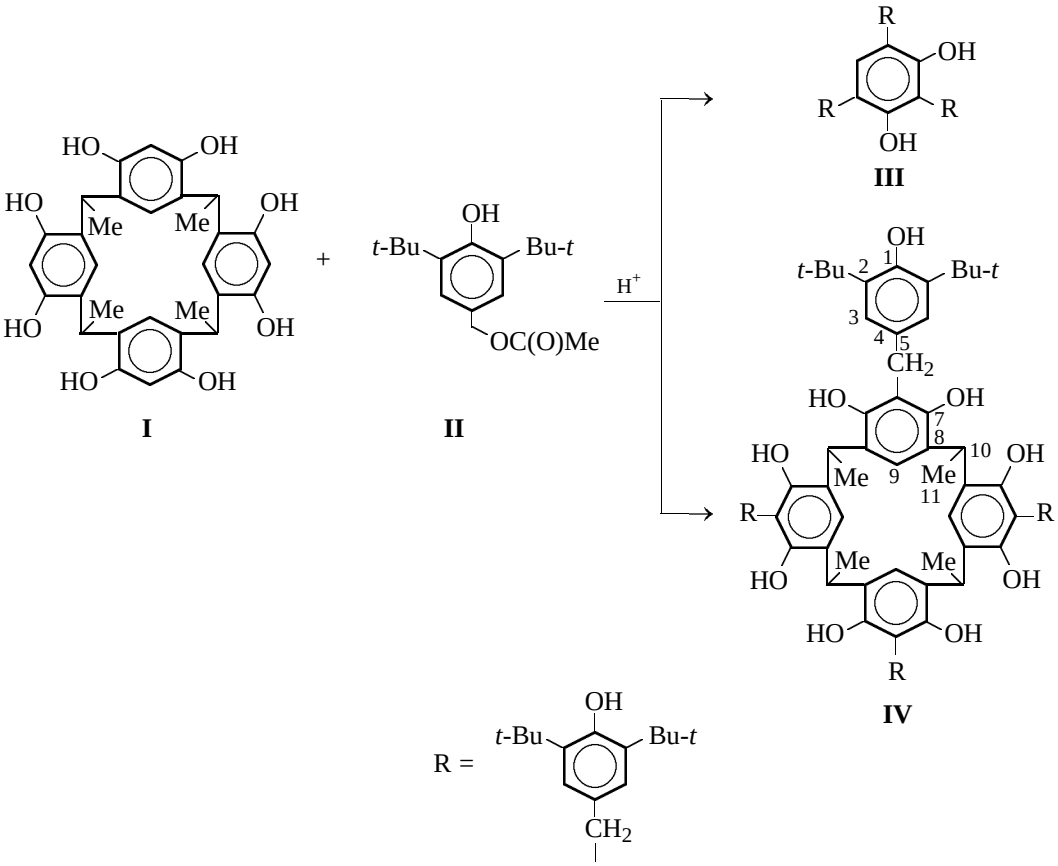
In the recent time, calix[4]resorcinolarenes and their derivatives which have a cup-like structure and are capable of binding both organic molecules and ions attract increased interest [1–4]. The stability of calixarene macrocycles and the possibility of modifying them by organic and organometallic reagents makes the chemistry of these compounds quite a promising field of studies.

We were the first to reveal that calix[4]resorcinolarene (**I**) reacts with 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate (**II**) in the presence of perchloric acid to give 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol (**III**). A small amount of compound **IV** was also isolated.



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It should be noted that no macrocycle opening occurs in the binary system calixarene–perchloric acid. Therefore, the formation of compound **III** is the result of transalkylation of calixarene **I** with the 3,5-di-*tert*-butyl-4-hydroxybenzyl cation generated during the process.

Reaction of tetramethylcalix[4]resorcinolarene with 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate. To a solution of 1 g of calixarene **I** and 4.1 g of ester **II** in 20 ml of acetone we added 0.08 ml of 72% perchloric acid. The mixture was kept for 24 h at 20°C and poured into water, and the precipitate was washed with water to neutral reaction and dried for 2 days at 20°C. We thus obtained 3.4 g of a product which, according to the ^{1}H NMR data, was a mixture of 2,4,6-tris(3,5-di-*tert*-butyl-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[19.3.1.1^{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-dodecaene (**IV**) at a ratio of 70 : 30. Recrystallization of the crude product from hexane gave 1.2 g (35%) of compound **III** with mp 153–154°C [5]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 s (54H, CMe_3), 3.92 s (6H, CH_2), 4.87 s (2H, OH), 5.09 s (1H, OH), 5.16 s (2H, OH), 6.93 s (1H, H_{arom}), 7.12 s (6H, H_{arom}). Found, %: C 79.85; H 9.70. $C_{51}H_{72}O_5$. Calculated, %: C 80.10; H 9.42. The mother liquor obtained after separation of compound **III** was evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ether (8 : 2 to 1 : 1) as eluent. We thus isolated 0.5 g (15%) of compound **IV** with mp 230°C (decomp.). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.37 s (72H, CMe_3), 1.73 d (12H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.89 s (8H, CH_2), 4.60 q (4H, CH, $^3J_{HH}$ 7.0 Hz), 5.72 s (4H, OH), 7.18 s (8H, H_{arom}), 7.52 s (4H, N_{arom}), 7.88 s (8H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, 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 77.65; H 8.65. $C_{92}H_{120}O_{12}$. Calculated, %: C 77.97; H 8.47.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 and 50 MHz, respectively, using the solvent (chloroform-*d* and acetone-d_6) signals as reference.

ACKNOWLEDGMENTS

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