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SHORT COMMUNICATIONS

Synthesis of 3,5-Di-*tert*-butyl-4-hydroxyphenylsulfanylmethyl-Substituted Tetramethylcalix[4]resorcinarenes

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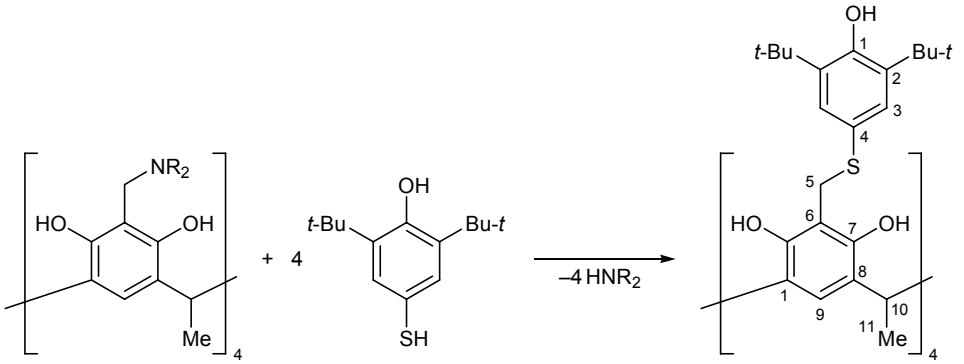
Dialkylaminomethyl-substituted calix[4]resorcinarenes have been reported long ago [1], but further transformations of these compounds were reported in a few publications [2–4], and the described transformations did not involve the dialkylaminomethyl group therein. An exception was the formation of the corresponding ammonium salts [5, 6] and thioamides [7]. Products of nucleophilic replacement of dialkylamino group in the above calix[4]resorcinarenes were not reported. On the other hand, deamination of phenolic Mannich bases is their typical reaction [8].

Deamination of freshly prepared dialkylaminomethyl-substituted calix[4]resorcinarenes **Ia** and **Ib** by the action of 2,6-di-*tert*-butyl-4-sulfanylphenol (**II**) resulted in the formation of previously unknown calixarene **III** containing sterically hindered phenylsulfanyl fragments (yield 68–72%). We also found that the duration of storage of initial compound **Ib** does not affect the yield of **III**. By contrast, the reaction of benzenethiol **II** with calixarene **Ia** preliminarily stored for 3 months gave a mixture of products of partial replacement of the dimethylamino groups (according to the ^{1}H NMR data) even after heating for 66 h. The reactivity of calix[4]resorcinarene **Ia** can be restored after prolonged storage by washing with dimethyl sulfoxide and then with water, followed by drying in air. Presumably, the reactivity of aminomethyl calixarene derivatives **Ia** and **Ib** depends on their supramolecular organization.

According to [9], molecules of calix[4]resorcinarene **Ia** in crystal are linked to dimers where dimethylaminomethyl groups of neighboring molecules enter the macroring cavity in each other; therefore, these groups become spatially inaccessible for nucleophilic attack. Such associates are likely to dissociate by the action of solvent, whereas prolonged drying favors the



Ia, **Ib** **II** **III**

R = Me (**a**), Et (**b**).

formation of the dimers. Compound **Ib** in crystal does not give rise to analogous dimers.

5,11,17,19-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenylsulfanylmethyl)-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-4,6,10,12,-16,18,22,24-octaol (III). A mixture of 0.6 g of calixarene **Ia**, 0.8 g of thiol **II**, and 20 ml of *o*-xylene was stirred for 14 h at 125°C in a stream of argon. The solvent was removed under reduced pressure, and the residue was washed with hexane. Yield 0.82 g (68%), off-white powder, mp >168°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 s (72H, CMe_3), 1.68 d (12H, Me, ^3J = 7.29 Hz), 4.07 s (8H, CH_2S), 4.50 q (4H, CH, ^3J = 7.29 Hz), 5.17 s (4H, OH), 7.06 s (8H, 3-H), 7.26 s (4H, 9-H), 7.60 s (8H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.18 q (C^{11}, J_{CH} = 127.15 Hz), 28.18 d (C^{10}, J_{CH} = 126.79 Hz), 30.15 q (C**Me**$_3$, J = 126.07 Hz), 31.21 t (C^5, J_{CH} = 143.33 Hz), 34.40 s (**C**Me$_3$), 111.04 s (C^8), 122.55 s (C^6), 126.10 s (C^4), 127.90 (C^9, J_{CH} = 160 Hz), 129.86 d (C^3, J = 160 Hz), 136.89 s (C^2), 149.74 s (C^7), 154.21 s (C^1). Found, %: C 72.84; H 9.12; O 10.01; S 8.03. $C_{92}H_{120}O_{12}S_4$. Calculated, %: C 71.50; H 7.77; O 12.44; S 8.29.

Calixarene **III** was also synthesized in a similar way from 0.6 g of compound **Ib** and 0.74 g of thiol **II** in 20 ml of *o*-xylene. Yield 0.80 g (72%).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-600 spectrometer operating at 600 and 150 MHz, respectively.

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