Letters to the Editor

Unusual reaction of resorcinol or methylresorcinol with 2-dimethylamino-1,1-dimethylpropanal

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Calix[4]resorcinarenes are mainly synthesized by condensation of resorcinol and its derivatives with aliphatic and aromatic aldehydes.[1—3] Recently,[4] the synthetic potentialities of this method were extended by using phosphorylated acetals in the reaction with resorcinol to give calix[4]resorcinarenes with phosphinoylalkyl substituents on the lower rim of the molecule. Their aminoalkyl analogs are of particular interest since they can be used as starting reagents (through involvement of the amino group) for the synthesis of novel cavitands, container-type calixarenes, and nanosized tubes. We believed that such calixarenes might be obtained by reactions of resorcinol with amino aldehydes. However, the condensation of resorcinol or 2-methylresorcinol with β-amino aldehyde **1** did not give the expected calixarene **2**. Instead, compounds **3a,b** were formed from three resorcinol molecules and two molecules of the amino aldehyde. It should be noted that the reaction outcome is insensitive to the ratio between the reagents, the reaction time, and the temperature.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument (400.13 MHz) in $(CD_3)_2O$. The δ values are referenced to signals for the residual protons of the deuterated solvent. Mass spectra were recorded on a MALDI 2 V5.2.0 instrument using a 1,8,9-trihydroxyanthracene matrix. Amino aldehyde **1** was prepared according to a known procedure.[5]

4,6-Bis[1-(2,4-dihydroxyphenyl)-3-dimethylamino-2,2-dimethylpropyl]resorcinol (3a). Amino aldehyde **1** (3.48 g, 26.9 mmol) was added to a stirred mixture of resorcinol (4.45 g, 40.2 mmol), water (43.4 mL), EtOH (43.4 mL), and conc. HCl (6.7 mL). The reaction mixture was left at 20 °C for seven days and neutralized with an alkali solution. The high-melting powdery product thus formed was filtered off, washed with water, and dried *in vacuo* (80 °C, 0.4 Torr) to a constant weight to give compound **3a** (5.32 g, 72%), m.p. > 300 °C. Found (%): C, 69.96; H, 7.73; N 4.71. $C_{32}H_{44}N_2O_6$. Calculated (%): C, 69.54; H, 8.02; N, 5.07. ^{1}H NMR ($(CD_3)_2O$), δ: 1.12 (s, 6 H, C$\underline{H_3}$); 1.20 (s,

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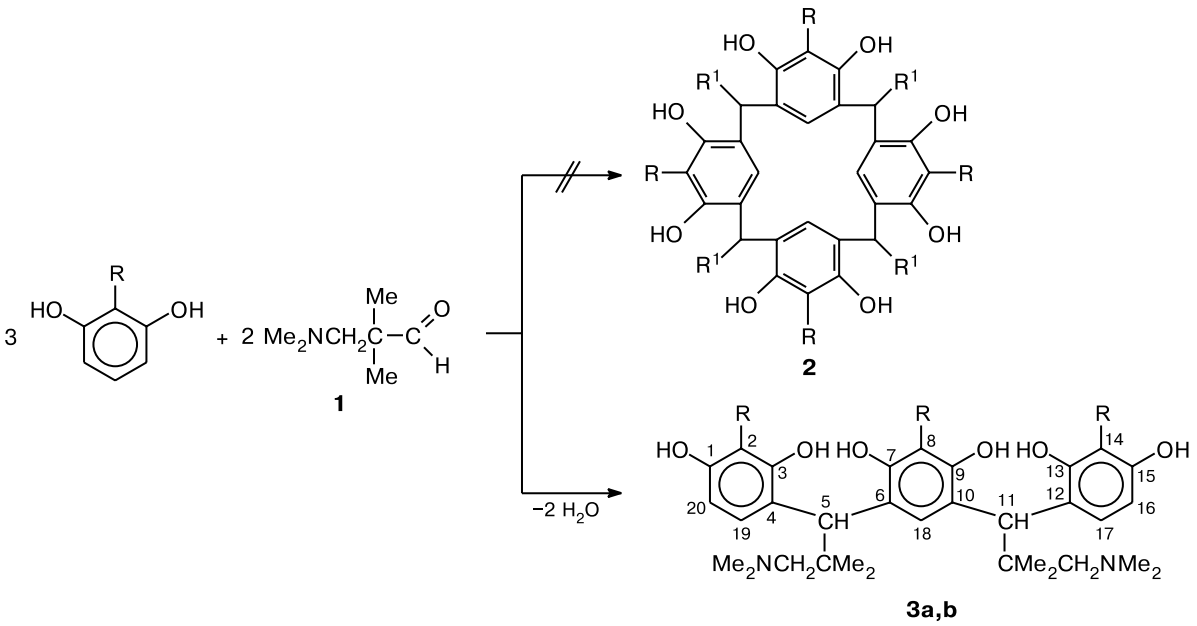

2: R′ = $CMe_2CH_2NMe_2$
3: R = H (**a**), Me (**b**)

6 H, C<u>H</u>$_3$); 2.39 (s, 12 H, NC<u>H</u>$_3$); 5.17 (s, 1 H, C<u>H</u>); 5.19 (s, 1 H, C<u>H</u>); 6.31 (s, 3 H, C(2)H, C(8)H, C(14)H); 6.80—7.30 (m, 5 H, C(16)H, C(17)H, C(18)H, C(19)H, C(20)H). MS, *m/z*: 553. IR, ν/cm^{-1}: 1600 (arom.), 3100—3500 (OH).

4,6-Bis[1-(2,4-dihydroxy-3-methylphenyl)-3-dimethylamino-2,2-dimethylpropyl]-2-methylresorcinol (3b) was obtained analogously from 2-methylresorcinol (2.46 g, 19.8 mmol), EtOH (8 mL), water (15 mL), conc. HCl (4 mL), and amino aldehyde **1** (2.58 g, 20 mmol). The yield of compound **3b** was 1.09 g (34%), m.p. > 300 °C. Found (%): C, 69.14; H, 8.13; N, 3.25. $C_{35}H_{50}N_2O_6$. Calculated (%): C, 70.68; H, 8.47; N, 4.71. IR, ν/cm^{-1}: 1600 (CH arom.), 3100—3500 (OH). ^{1}H NMR ($(CD_3)_2O$), δ: 1.05 (s, 12 H, C<u>H</u>$_3$); 1.95 (s, 9 H, C<u>H</u>$_3$C$_{arom}$); 2.30 (s, 12 H, NC<u>H</u>$_3$); 5.11 (s, 2 H, C<u>H</u>); 6.31 (m, 2 H, C(16)H, C(20)H); 7.45 (m, 2 H, C(17)H, C(18)H, C(19)H). ^{13}C NMR ($(CD_3)_2O$), δ: 9.34 (<u>C</u>H$_3$Ar); 21.52 (CH_3C); 26.74 (CH); 36.84 (C); 46.05 (<u>C</u>H$_3$N); 70.13 (<u>C</u>H$_2$N); 105.81, 106.02 (C(17), C(18), C(19)); 110.67 (C(16), C(20)); 121.26, 121.50 (C(4), C(6), C(10), C(12)); 127.02 (C(2), C(8), C(14)); 154.30, 156.10 (C(1), C(3), C(7), C(9), C(13), C(15)). MS, *m/z*: 595.

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References

1. C. D. Gutsche, *Calixarenes,* The Royal Society of Chemistry, Cambridge, 1989, 132.
2. J. Vicens and V. Böhmer, *Calixarenes, a Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, 1991, 15.
3. Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens, *Calixarenes-2001*, Kluwer Academic Publishers, Dordrecht—Boston—London, 2001, 57.
4. E. V. Popova, Yu. M. Volodina, A. R. Burilov, M. A. Pudovik, W. D. Habicher, and A. I. Konovalov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1815 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1968].
5. C. Mannich, B. Lesser, and F. Silten, *Ber.*, 1932, **65**, 378.

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