ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 3, pp. 548–549. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.I. Maslennikova, A.V. Burikhina, L.K. Vasyanina, E.E. Nifant'ev, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 3, pp. 519–520.

LETTERS TO THE EDITOR

Amination of Calix[4]resorcinarenes. First Synthesis of Calix[4]phenylenediamines

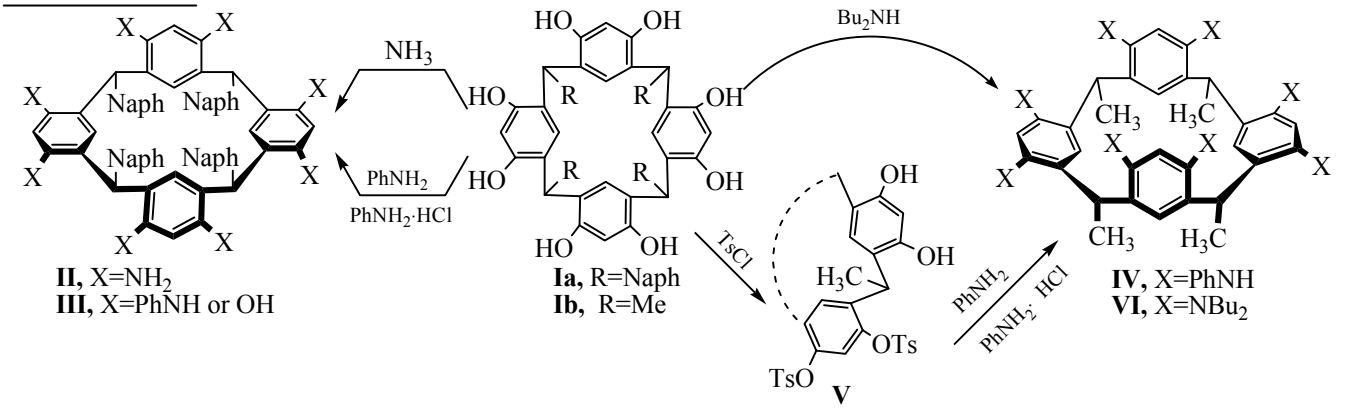
V. I. Maslennikova, A. V. Burikhina, L. K. Vasyanina, and E. E. Nifant'ev

Moscow State Pedagogical University, Nesvizhskii per. 3, Moscow, 119021 Russia
email: him-vim@mail.ru

Received October 29, 2009

DOI: 10.1134/S1070363210030333

Calix[4]resorcinarenes form a convenient platform for the construction on their basis of complex macroheterocyclic and supramolecular systems of different architecture, which is associated with the conformational lability and high reactivity of these compounds [1–3]. The replacement of the hydroxy groups by other functions will change the properties of the calixarene system and expand the range of basic macrocycles. Here we report the first data on the substitution of hydroxy groups in the molecules of calix[4]resorcinarenes by amino groups. As substrates for the amination tetranaphthylresorcynarene (**Ia**), which has a *chair* conformation with *rttt* configuration of aryl groups, and tetramethylresorcynarene (**Ib**) in the *crown* conformation with *rccc* configuration of alkyl groups were used. Reactions of resorcinarenes **I** with ammonia, aniline, and dibutylamine were performed in a CEM "Discover" microwave reactor.



The reaction of calix[4]resorcinarene **Ia** with ammonia mainly led to the substitution of hydroxy groups in the molecule and to the formation of calix[4]-phenylenediamine (**II**). In the reaction with aniline occurred partial modification of **Ia**, and as a result a mixture of compounds **III** was obtained differing by the ratio of functional groups. We failed to obtain a peraminated compound in this case.

In the reaction of calix[4]resorcinarene **Ib** with ammonia dominated the process of oligocondensation. The reaction of **Ib** with aniline proceeded with the formation of partially aminated dimeric compounds. Molecules of these compounds contain the calixarene calyxes connected through two or three nitrogen-containing spacers. The product of peramination **IV** was obtained by using tetratosylated resorcinarene **V** as an intermediate. We succeeded to implement the direct amination leading to the formation of octaamino derivative **VI** only by the reaction of resorcinarene **Ib** with dibutylamine.

4,6,10,12,16,18,22,24-Octaamino-2,8,14,20-tetranaphthylpentacyclo[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-dodecane (II). A suspension of 0.1 g of resorcinarene **Ia**

in 0.34 ml of 40% aqueous ammonia was heated for 30 min at 160°C under microwave irradiation (50–150 W, 2455 MHz). The precipitate formed was filtered, washed with water, and dried at 50°C (1 mm Hg). Yield of compound **II** 0.045 g (45.7%), mp. 310°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 3.75 s (16H, NH_2), 5.66 s (2H, H^{3h}), 6.30 s (2H, H^{3v}), 6.34 s (2H, H^5), 6.36 s (4H, H^1), 6.76 s (2H, H^5), 6.77 d.d (4H, H_{Naph}), 6.79 d (4H, H_{Naph}), 7.00 d.d (4H, H_{Naph}), 7.11 d.d (4H, H_{Naph}), 7.37 d (4H, H_{Naph}), 7.43 d (4H, H_{Naph}), 7.53 d (4H, H_{Naph}). Found,%: C 82.32, H 5.29; N 11.14. $C_{68}H_{56}N_8$. Calculated,%: C 82.90; H 5.73; N 11.38.

4,6,10,12,16,18,22,24-octakis(phenylamino)-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-dodecane (IV). Resorcinarene **Ib** was tosylated using the procedure [4]. Compound **IV** was synthesized by analogy with product **II** by the interaction of 0.4 g of the tetratosylated resorcinarene **V**, 1.27 ml of aniline, and 0.4 g of aniline hydrochloride within 40 min at 150°C. Excess aniline was distilled off with water vapor. The products obtained were separated using column chromatography (SiO_2 100–250 μm, benzene–dioxane 1:1). Yield of compound **IV** 0.0172 g (4%), R_f 0.83 (benzene–dioxane 1:1). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.52 d (6H, CH_3), 1.56 d (6H, CH_3), 3.56 q (2H, CH), 4.02 m (2H, CH), 6.63–7.26 m (48H, $H_{arom.}$). Found, %: C 83.32; H 7.79; N 8.64. $C_{88}H_{96}N_8$. Calculated, %: C 83.50; H 7.64; N 8.85.

4,6,10,12,16,18,22,24-Octakis(dibutilamino)-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-dodecane (VI) is synthesized by analogously with compound **II** by the reaction of 0.1 g of resorcinarene **Ib** and 0.25 ml of 40% aqueous solution of dibutylamine over 20 min at 150°C. Yield of compound **VI** 0.123 g (46.7%), mp 272°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (24H, $(CH_2)_3CH_3$), 1.78 d (12H, $CHCH_3$), 1.83–1.85 m (32H, $NCH_2(CH_2)_2$·CH_3), 3.72–3.74 m (16H, NCH_2), 4.55 q (4H, $CHCH_3$), 6.11 s (4H, H^3), 7.23 s (4H, H^5). Found, %: C 80.32; H 11.79; N 7.64. $C_{96}H_{168}N_8$. Calculated, %: C 80.38; H 11.81; N 7.81. Mass-spectrum, *m/z:* 1440 $[M]^+$.

The ^{1}H NMR spectra were obtained on a JEOL spectrometer with operating frequency 400 MHz, internal reference TMS. The mass spectra were recorded on a KRATOS COMPACT (MALDI TOF – MS) device.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 09-03-00201).

REFERENCES

1. Cram, D.J., *Angew. Chem., Int. Ed. Engl*., 1988, no. 27, p. 1009.
2. Timmerman, P., Verboom, W., and Reinhoudt, D.N., *Tetrahedron*, 1996, vol. 52, no. 8, p. 2663.
3. Nifantiev, E.E., Maslennikova, V.I., and Merkulov, R.V., *Acc. Chem. Res.,* 2005, vol. 38, no. 2, p. 108.
4. Lukin, O.V., Pirozenko, V.V., and Shivanyuk, A.N., *Tetrahedron Lett*., 1995, vol. 36, no. 42, p. 7725.