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DIMROTH REARRANGEMENT IN SYNTHESIS OF A HETERODITOPIC RECEPTOR

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We showed earlier [1] that calix[4]arenes containing a sulfamide moiety with NH protons on the "upper rim" and four ethoxycarbonyl groups on the "lower rim" can exhibit the properties of a heteroditopic receptor, i.e., they can simultaneously chelate cations and anions. In this paper, by reacting tetrakis(azidosulfonyl)calixarene **1** with N-cyclohexylcyanoacetamide in the presence of a catalytic amount of sodium ethoxide, we obtained tetrakis(5-amino-1,2,3-triazol-1-ylsulfonyl)calixarene **2**, which when boiled with excess triethylamine undergoes a Dimroth rearrangement to form tetrakis[(1H-1,2,3-triazol-5-yl)-aminosulfonyl]calixarenes **3** (Scheme 1).

We used the membrane transport method to study the chelating properties of the synthesized compounds [1]. In a study of transport through a liquid impregnated membrane, we showed that the initial sodium sulfate flux for compound **2** was $1.37 \cdot 10^{-6}$; for **3**, $6.95 \cdot 10^{-5}$; for 5-tosylamino-1,2,3-triazole-4-(N-cyclohexyl)-carboxamide, $7.50 \cdot 10^{-10}$ mol·sec^{-1}·m^{-2}. The cooperative heteroditopic effect compared with compound **1**, which can chelate only cations, was 1.9 and 95 respectively for compounds **2** and **3**.

Thus we have shown that calixarene **2** (containing a triazole ring with an unsubstituted amino group at the 5 position of the heterocycle) weakly chelates anions while calixarene **3** (containing an isomeric triazole ring with a sulfamoyl group) exhibits the properties of a ditopic receptor.

The ^{1}H NMR spectra were taken on a Bruker DRX-400 (400 MHz) in $CDCl_3$, internal standard TMS.

25,26,27,28-Tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis(1-(5-amino-4-N-cyclohexyl-carbamoyl-1,2,3-triazol-1-yl)sulfonyl)calix[4]arene (2). A suspension of calix[4]arene **1** (119 mg, 0.1 mmol) and cyclohexyl cyanoacetamide (66 mg, 0.4 mmol) in alcohol (7 ml) was stirred for 15 h at 40°C; the precipitate was filtered out and crystallized from alcohol. Yield 0.1 g (60%); mp 249°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.58 (8H, s, ArH); 6.55 (8H, br. s, NH_2); 5.19 (4H, d, *J* = 13.7, CHAr); 4.88 (8H, s, OCH_2); 3.80 (8H, t, *J* = 4.1, OCH_2); 3.50 (4H, d, *J* = 13.7, CHAr); 3.34-3.38 (4H, m, CH); 1.2-2.2 (40H, m, C_6H_{10}); 1.13 (12H, t, *J* = 4.1, CH_3). Found, %: N 15.29. $C_{80}H_{100}N_{20}O_{24}S_4$. Calculated, %: N 15.11.

25,26,27,28-Tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis-(N-(4-N-cyclohexylcarbamoyl-1H-1,2,3-triazol-4-yl)sulfamoyl)calix[4]arene (3). A solution of calix[4]arene **2** (93 mg, 0.05 mmol) in ethanol (30 ml) and triethylamine (5 ml) was boiled for 3 h, the solvent was evaporated, and the residue was crystallized from ethanol. Yield 88%; mp 217°C (decomposes). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.00 (1H, br. s, NH); 7.50 (8H, s, ArH); 6.86 (4H, s, NH); 5.13 (4H, d, *J* = 13.7, CHAr); 4.88 (8H, s, OCH_2); 3.80 (8H, t, *J* = 4.1, OCH_2); 3.56 (4H, d, *J* = 13.7, CHAr); 3.34-3.38 (4H, m, CH); 1.2-2.2 (40H, m, CH); 1.12 (12H, t, *J* = 4.1, CH_3). Found, %: N 14.99. $C_{80}H_{100}N_{20}O_{24}S_4$. Calculated, %: N 15.11.

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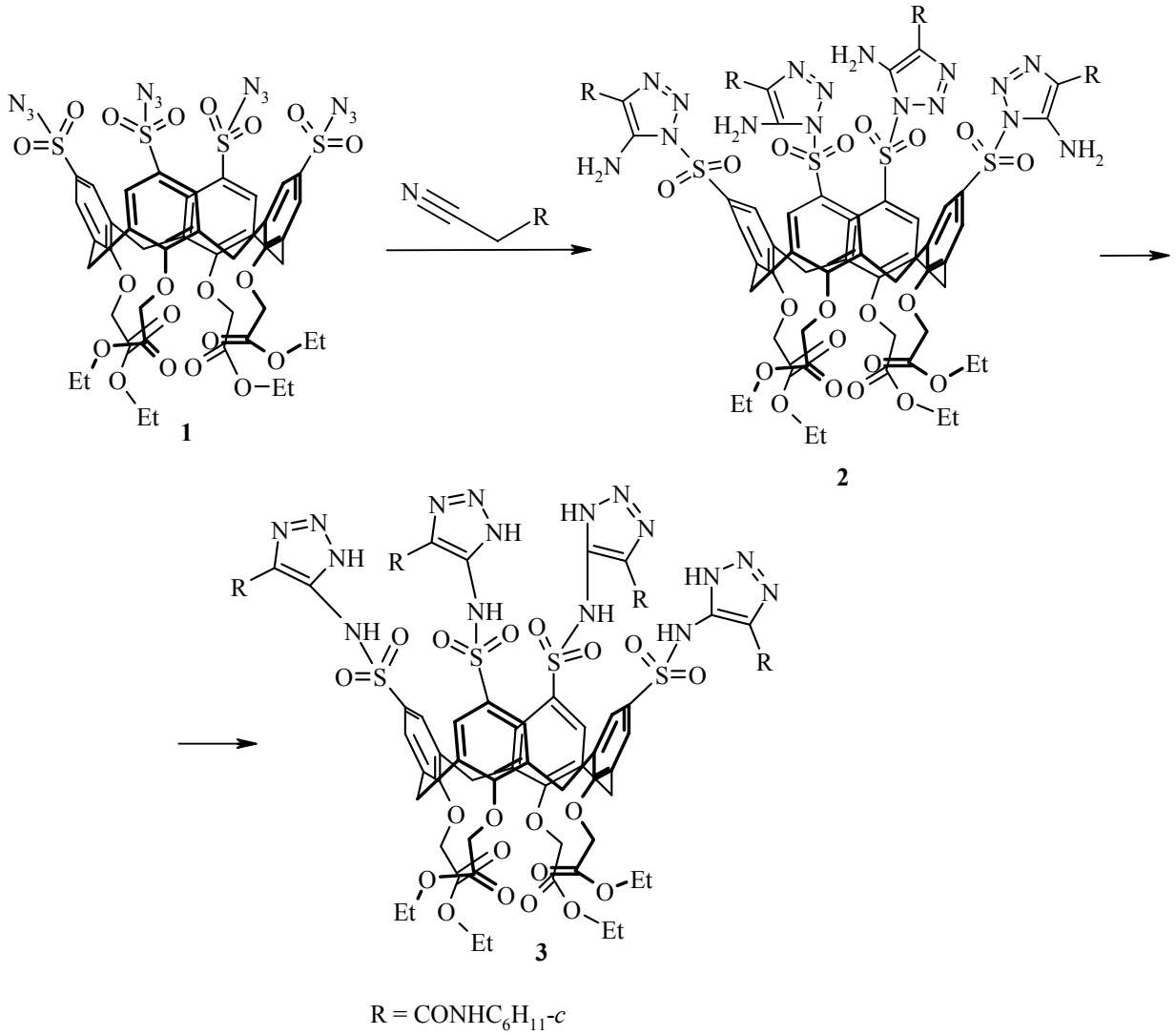
Scheme 1



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