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SHORT COMMUNICATIONS

Reaction of 4-Chloro-*N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]-benzenesulfonamide with Diaza-18-crown-6

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We recently showed that *N*-(2,2,2-trichloro-1-arylethyl)arenesulfonamides **I** react with secondary amines [1–3] through dichloroaziridine and imidoyl chloride intermediates (**A** and **B**) to give *N*′-arylsulfonyl-(amino)arylacetimidamide derivatives **II** (Scheme 1).

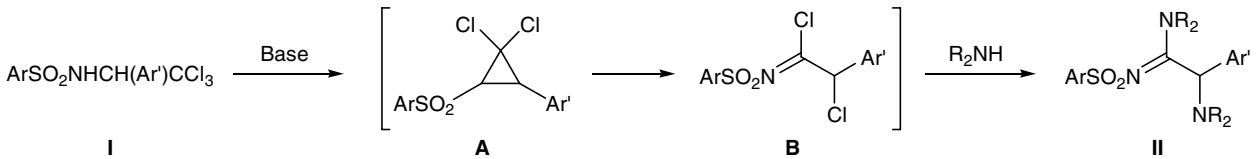
In continuation of our studies on reactions of sulfonamides **I** with secondary amines, we examined the reaction of 4-chloro-*N*-[2,2,2-trichloro-1-(*p*-tolyl)-ethyl]benzenesulfonamide (**Ia**) with diaza-18-crown-6. It is well known that crown-like compounds and their functional derivatives are used as selective extractants for metal ions, reagents for separation of enantiomers, materials for ion-selective membranes, and biologically active compounds. The present study was aimed at determining main pathways of reactions of sulfonamides like **I** with diamines, taking into account that the presence of two secondary amino groups in the reagent could give rise to not only amidine derivatives like **II** but also intramolecular heterocyclization products due to participation of both NH groups of the diaza crown ether and two C–Cl bonds in intermediate **B**. Also, the possibility for formation of oligomeric structures in which the SO_2N=C fragments are linked by diaza crown ether moieties cannot be ruled out.

We have found that the reaction of amide **Ia** with diaza-18-crown-6 gives a mixture of compounds **III** and **IV** at a ratio of 9:1 (Scheme 2). In the ^{1}H and ^{13}C NMR spectra of the major product (compound **III**) we observed signals from the chlorobenzene and toluene fragments, C=N group, and CH–N moiety. The IR spectrum of this product showed the presence in its molecule of a sulfonyl group and a double C=N bond. These data together with the relative intensities of signals from aromatic protons, CH=N, and methylene protons in the macroring, as well as the absence of NH signal in the ^{1}H NMR spectrum and of NH absorption in the IR spectrum, correspond to structure **III**. The ^{1}H and ^{13}C NMR spectral patterns of minor product **IV** were consistent with those typical of previously reported amidine derivatives **II** [1–3]. No oligomeric amidine ensembles were detected.

Studies on reactions of *N*-polychloroethyl amides with difunctional nitrogen-centered nucleophiles are now in progress with a view to develop a chemoselective procedure for the synthesis of bicyclic diaza compounds.

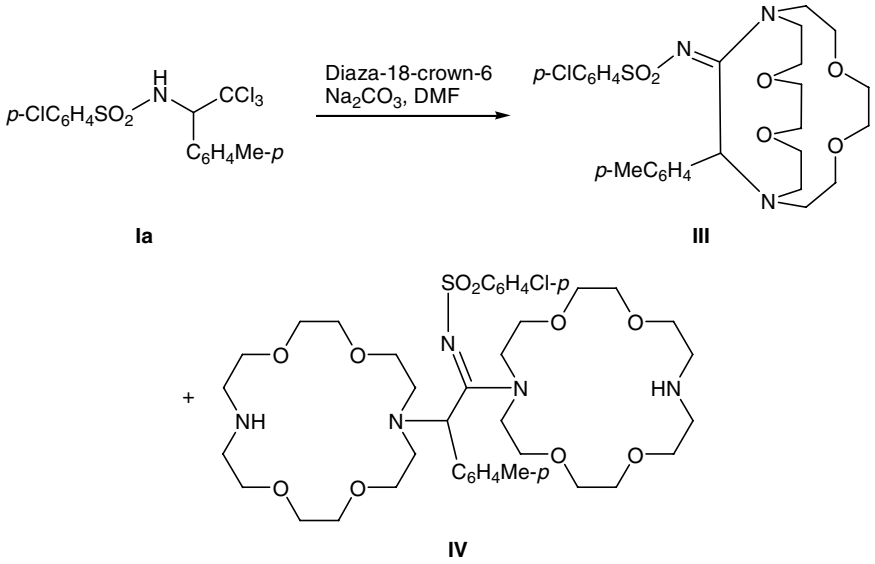
Reaction of 4-chloro-*N*-[2,2,2-trichloro-1-(*p*-tolyl)ethyl]benzenesulfonamide (Ia) with diaza-18-crown-6. A mixture of 2.1 g (0.005 mol) of amide **Ia**, 4.0–6.5 g (0.015–0.025 mol) of diaza-18-crown-6, 2.1 g (0.02 mol) of sodium carbonate, and 30 ml of dimethylformamide was stirred for 1 h at 90–100°C.

Scheme 1.



I A B II

Scheme 2.



The mixture was cooled, diluted with 50 ml of water, shaken, kept for 2 h at 0°C, and filtered, the filtrate was kept for 2 days, and the precipitate was filtered off, dried, and recrystallized from diethyl ether or hexane. We thus isolated 2.3 g of a mixture of compounds **III** and **IV** at a ratio of 9:1.

4-Chloro-*N*-[20-(4-tolyl)-4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]icosan-19-ylidene]benzenesulfonamide (III). IR spectrum, ν, cm^{-1}: 1110, 1270 (SO_2); 1600 (C=N); 2850–2940 (C–H_{aliph}); 3060 (C–H_{arom}). ^1H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3); 2.40, 2.84, 2.88, 3.11, 3.29, 3.43–3.63, 4.07, 4.21, 4.62, 5.43 m (24H, CH_2); 5.45 s (1H, CHN); 6.87 s (4H, C_6H_4); 7.08, 7.18 (4H, C_6H_4, *AA′BB′*). ^{13}C NMR spectrum, δ_C, ppm: 21.11 (CH_3); 52.23, 53.12, 53.33, 53.70, 68.91, 69.32, 69.85, 70.76, 71.00, 72.85, 73.44, 75.46 (CH_2); 69.63 (CHN); 127.12, 127.90, 128.53, 129.37, 134.86, 136.22, 136.68, 143.81 (C_{arom}); 162.14 (N=C).

***N*-[1,2-Bis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)-2-(4-tolyl)ethylidene]-4-chlorobenzenesulfonamide (IV).** ^1H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3); 2.39, 2.49, 2.63, 3.01, 3.05, 3.43–3.63, 4.04, 4.16, 4.58, 4.60 m (48H, CH_2); 6.18 s (1H, CHN); 6.90, 7.03 (4H, C_6H_4, *AA′BB′*); 7.11, 7.19 (4H, C_6H_4, *AA′BB′*). ^{13}C NMR spectrum, δ_C, ppm: 21.11 (CH_3); 52.86, 52.91, 53.65, 53.84, 58.34, 62.88, 65.97, 67.23, 67.86, 68.38, 68.82, 69.45, 71.36, 75.46 (CH_2); 70.28 (CHN); 127.37, 128.22, 129.37, 130.19, 130.95, 136.98, 138.26, 142.41 (C_{arom}); 168.88 (N=C).

The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 and 101.61 MHz, respectively, using $CDCl_3$ as solvent and hexamethyldisiloxane as internal reference.

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