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SHORT COMMUNICATIONS

Unusual Transformations of *N*-[2,2,2-Trichloro-1-(4-methylphenyl)ethyl]-4-chlorobenzenesulfonamide by the Action of Dipropylamine

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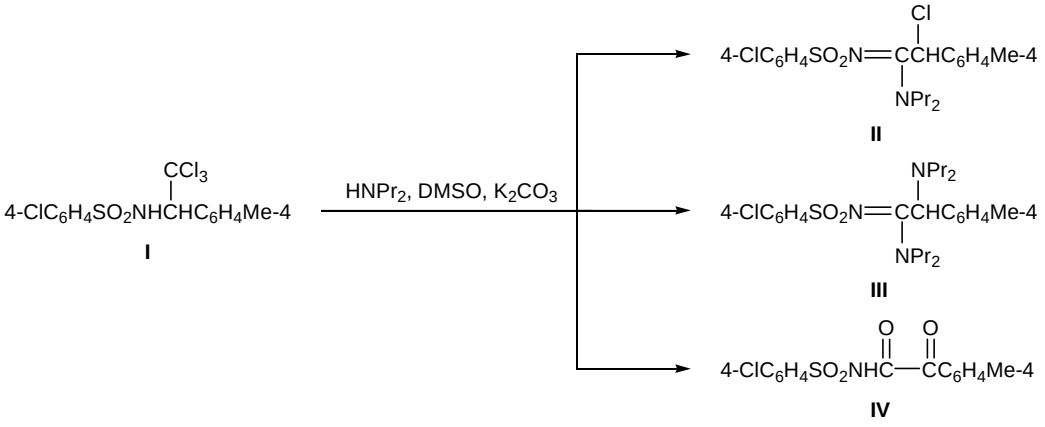
We have revealed unusual transformations in the series of accessible *N*-(1-aryl-2,2,2-trichloroethyl)-arenesulfonamides [1, 2] by the action of secondary amines in dimethylformamide or dimethyl sulfoxide. These transformations are accompanied by rearrangement, and they result in formation of a mixture of products. The reaction of *N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]-4-chlorobenzenesulfonamide (**I**) with an equivalent amount of dipropylamine in the presence of excess sodium or potassium carbonate gave a mixture of compounds from which we isolated *N*-[2-chloro-1-dipropylamino-2-(4-methylphenyl)-ethylidene]-4-chlorobenzenesulfonamide (**II**) and *N*-[1,2-bis(dipropylamino)-2-(4-methylphenyl)-ethylidene]-4-chlorobenzenesulfonamide (**III**). When the reaction was performed in the presence of excess amine, no compound **II** was isolated. The reaction in DMSO, apart from compounds **II** and **III**, afforded *N*-[1,2-dioxo-2-(4-methylphenyl)ethyl]-4-chlorobenzenesulfonamide (**IV**). The yield of the latter decreases as the amount of dipropylamine increases.

The structure of products **II**–**IV** was confirmed by the data of elemental analysis and NMR spectroscopy (^{1}H, ^{13}C, ^{13}C JMOD, ^{13}C RGGD, two-dimensional techniques). A probable reaction mechanism leading to amidines **II** and **III** includes intermediate formation of 2,2-dichloro-1-(4-chlorophenylsulfonyl)-3-(4-methylphenyl)aziridine and its subsequent transformations by the action of secondary amine. Compound **IV** could be formed via hydrolysis of the aziridine intermediate, followed by oxidation of the hydrolysis product with DMSO.

Study of the discovered transformations is now in progress with a view to elucidate their mechanism and develop effective methods for the preparation of new polyfunctional sulfonamide derivatives.

Reaction of *N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]-4-chlorobenzenesulfonamide (I) with dipropylamine. A mixture of 4.13 g (0.01 mol) of amide **I**, 2.12 g (0.02 mol) of sodium carbonate, 1.37 ml (0.01 mol) of dipropylamine, and 25 ml of DMSO was stirred for 1.5 h at 90°C. The mixture was



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cooled to room temperature, diluted with 25 ml of water, and filtered. The filtrate was acidified, and the precipitate of oxo amide **IV** was filtered off, dried, and purified by recrystallization from carbon tetrachloride. The material insoluble in water was dried over P_2O_5 under reduced pressure and quickly washed with diethyl ether. From the undissolved material, we isolated first compound **III** by treatment with hot hexane and then compound **II** by treatment with carbon tetrachloride.

***N*-[2-Chloro-1-dipropylamino-2-(4-methylphenyl)ethylidene]-4-chlorobenzenesulfonamide (II).** Yield 0.8 g (18%), mp 140–141°C. IR spectrum, ν, cm^{-1}: 1120, 1260 (SO_2); 1520–1590 br (N=C, C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.52 t, 0.80 t, 1.25–1.60 m, and 2.98–3.33 m [14H, N(C_3H_7)$_2$]; 2.34 s (3H, 4-C**H**$_3C_6H_4$); 7.29 s (1H, CHCl); 7.17 and 7.31 (4H, *AA'BB'* system, 4-MeC_6**H**$_4$); 7.43 and 7.89 (4H, *AA'BB'* system, 4-ClC_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 10.83, 11.38, 19.58, 20.63, 50.89, 51.32 (C_3H_7); 21.12 (4-**C**H$_3C_6H_4$); 55.00 (CHCl); 125.60, 129.50, 131.40, 137.88 (Me**C**$_6H_4$); 127.74, 129.50, 138.23, 142.20 (ClC_6H_4); 162.34 (N=C). Found, %: C 57.34; Cl 16.30; N 6.83; S 7.32. $C_{21}H_{26}Cl_2N_2O_2S$. Calculated, %: C 57.14; Cl 16.06; N 6.35; S 7.26.

***N*-[1,2-Bis(dipropylamino)-2-(4-methylphenyl)-ethylidene]-4-chlorobenzenesulfonamide (III).** Yield 1.26 g (25%), mp 143–146°C. IR spectrum, ν, cm^{-1}: 1130, 1300 (SO_2); 1520–1590 br (N=C, C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.57, 0.65, 0.79, 1.57, 2.48, 2.71, 3.26, and 4.22 m (28H, C_3H_7); 2.29 s (3H, 4-C**H**$_3C_6H_4$); 5.97 s (1H, C**H**NPr_2); 7.10 and 7.45 (4H, *AA'BB'* system, 4-MeC_6**H**$_4$); 7.37 and 7.89 (4H, *AA'BB'* system, 4-ClC_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 10.77, 11.49, 11.94, 19.16, 20.07, 50.62, 51.36, 52.67 (C_3H_7); 21.15 (4-**C**H$_3C_6H_4$); 68.36 (**C**HNR_2); 127.61, 128.63, 137.05, 142.81 (Me**C**$_6H_4$); 128.01, 129.08, 134.39, 136.99 (ClC_6H_4); 164.93 (N=C). Found, %: C 64.01; Cl 7.82; N 8.59; S 7.03. $C_{27}H_{40}ClN_3O_2S$. Calculated, %: C 64.07; Cl 7.92; N 8.31; S 6.33.

***N*-[2-Oxo-2-(4-methylphenyl)acetyl]-4-chlorobenzenesulfonamide (IV).** Yield 0.5 g (15%), mp 147–150°C. IR spectrum, ν, cm^{-1}: 1160, 1350 (SO_2); 1660 (4-MeC_6H_4C=O); 1720 (NC=O); 3230 (NH). ^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, C**H**$_3C_6H_4$); 7.25 and 7.53 (4H, *AA'BB'* system, 4-MeC_6**H**$_4$); 8.07 and 8.16 (4H, *AA'BB'*, 4-ClC_6H_4), 9.73 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 21.97 (4-**C**H$_3C_6H_4$); 129.50, 129.71, 130.08, 131.60, 134.55, 136.29, 141.25, 147.16 (4-ClC_6H_4, MeC_6H_4); 158.25 (NC=O); 183.06 (4-MeC_6H_4**C**=O). Found, %: C 55.95; Cl 11.55; N 4.97; S 9.85. $C_{15}H_{12}ClNO_4S$. Calculated, %: C 55.99; Cl 11.02; N 4.35; S 9.96.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.6 MHz for ^{1}H and 100.61 MHz for ^{13}C using $CDCl_3$ as solvent (*c* = 5–10%) and HMDS as internal reference. The IR spectra were measured in KBr on a Specord IR-75 instrument.

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