

SHORT
COMMUNICATIONS

Unexpected Transformations of Arenesulfonic Acids *N*-(1-Aryl-2,2,2-trichloroethyl)amides in the Presence of Alkylthiols

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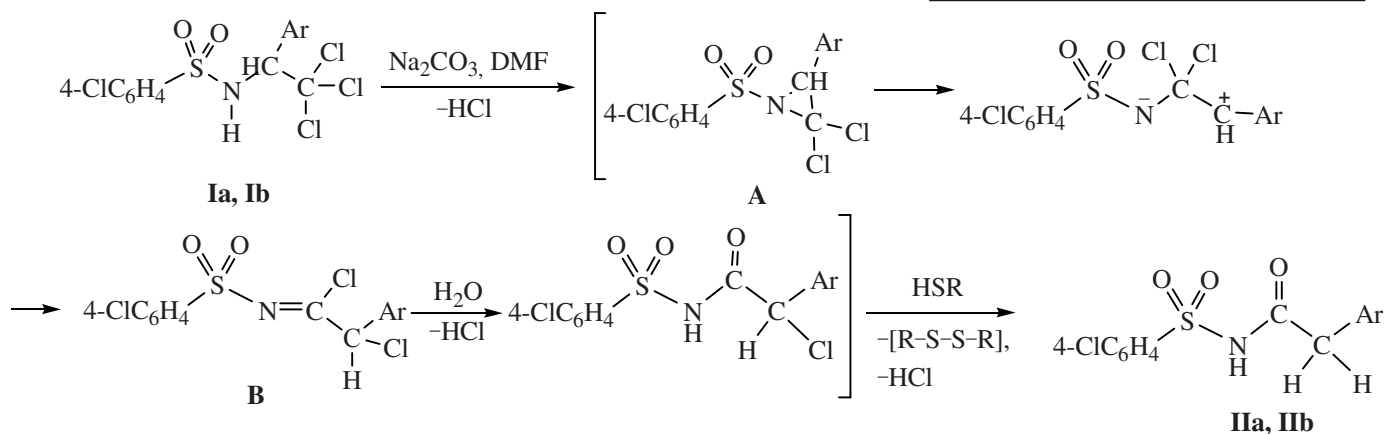
We formerly demonstrated [1] that accessible arenesulfonic acids *N*-(1-aryl-2-polychloroethyl)amides [2, 3] in aprotic highly polar media in the presence of inorganic bases suffered cyclization into chlorine-containing *N*-sulfonylaziridines whose further transformations essentially depended on the reagents character and conditions.

We discovered uncommon transformations occurring in DMF in the presence of sodium carbonate and propanethiol or mercaptoethanol. It was shown by an example of compounds **Ia** and **Ib** with the above thiols that the process proceeded with the formation of arylacetic acids *N*-arenesulfonamides **IIa** and **IIb** whose structure was unambiguously proved by spectral methods and confirmed by elemental analysis.

Apparently dichloroaziridine intermediates **A** undergo recyclization into imidoylchloride intermediates **B** [1] that under the reaction conditions are hydrolyzed at the imidoylchloride moiety and are reduced involving the chloromethyl group.

In this process evidently mercaptan is a reducer that is oxidized into the corresponding disulfide.

4-Chloro-*N*-[2-(4-chlorophenyl)acetyl]benzenesulfonamide (IIa). For 1 h a mixture was stirred at 100°C of 2.17 g (5 mmol) of 4-chlorobenzenesulfonic acid *N*-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]amide (**Ia**), 2.12 g (20 mmol) of Na₂CO₃, 1.56 g (20 mmol) of mercaptoethanol or 1.52 g (20 mmol) of propanethiol in 15 ml of DMF. The reaction mixture was cooled, diluted with 50 ml of water, filtered, the filtrate was acidified with 10% hydrochloric acid till neutral, the reaction mixture was left standing for 24 h, the formed precipitate of compound **IIa** was separated, dried, washed with cold ether till colorless washings, and recrystallized from hexane. Yield 0.88 g (51%), mp 206–208°C. IR spectrum, ν, cm⁻¹: 1170, 1360 (SO₂), 1690 (C=O), 3100 (NH). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 3.58 s (2H, CH₂), 7.17, 7.33 AA'BB' (4H, C₆H₄), 7.68, 7.89 AA'BB' (4H, C₆H₄), 12.45 br.s (1H, NH). ¹³C NMR spectrum (DMSO-*d*₆), δ, ppm: 41.38 (CH₂), 128.51, 129.57, 129.78, 131.51,



Ar = 4-ClC₆H₄ (**a**), 4-MeOC₆H₄ (**b**); R = Pr, CH₂CH₂OH

131.95, 132.96, 138.14, 138.97 ($2C_6H_4$), 169.56 (C=O). Found, %: C 48.57; Cl 20.78 N 4.35; S 9.01. $C_{14}H_{11}Cl_2NO_3S$. Calculated, %: C 48.85; Cl 20.60; N 4.07; S 9.31.

4-Chloro-N-[2-(4-methoxyphenyl)acetyl]benzenesulfonamide (IIb) was similarly obtained from 2.15 g (5 mmol) of amide **Ib**. Yield 0.73 g (43%), mp 137–140°C. IR spectrum, ν , cm^{-1} : 1170, 1365 (SO_2), 1680 (C=O), 3150 (NH). 1H NMR spectrum ($CDCl_3$), δ , ppm: 3.53 s (2H, CH_2), 3.80 s (3H, OCH_3), 6.85, 7.06 *AA'BB'* and 7.49, 7.94 *AA'BB'* (8H, $2C_6H_4$), 8.55 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ , ppm: 42.33 (CH_2), 54.93 (CH_3), 114.32, 123.59, 128.91, 129.54, 130.11, 136.30, 140.40, 158.99 ($2C_6H_4$), 168.74 (C=O). Found, %: C 53.37; Cl 10.12; N 4.29; S 9.28. $C_{15}H_{14}ClNO_4S$. Calculated, %: C 53.02; Cl 10.43; N 4.12; S 9.44.

1H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 (400.6, 100.61 MHz respectively), internal reference HMDS. IR spectra were recorded on a spectrophotometer Bruker IFS-25 from samples pelletized with KBr.

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