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SHORT COMMUNICATIONS

Spirocyclization in a Three-Component Reaction of Trifluoromethanesulfonamide with Paraformaldehyde and Malonamide

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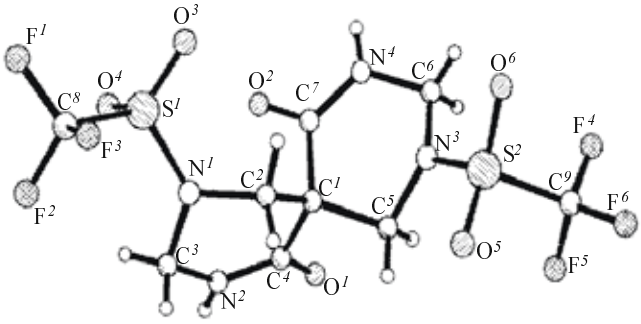
We formerly demonstrated that the reaction of the trifluoromethanesulfonamide $CF_3SO_2NH_2$ with the paraformaldehyde depending on the reaction conditions led to the formation of various linear and cyclic condensation products [1]. A three-component reaction between trifluoromethanesulfonamide, acetamide, and paraformaldehyde gave rise to *N*-[(trifluoromethanesulfonyl)aminomethyl]acetamide $CF_3SO_2NHCH_2NHCOCH_3$ [1]. In extension of this research we investigated a three-component condensation involving trifluoromethanesulfonamide, malonamide, and paraformaldehyde. Similarly to the previous findings [1] it was presumable to obtain linear and/or cyclic products of paraformaldehyde and trifluoromethanesulfonamide condensation at one or both amide groups of the malonamide. It turned out unexpectedly that alongside the formerly prepared bis(trifluoromethanesulfonylamino)methane (**I**) the reaction gave also 4,10-bis(trifluoromethanesulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**II**).

The ^{1}H NMR spectrum of compound **II** contains a singlet from the NH proton at 8.8 ppm and two *AB*-quartets from uncoupled CH_2 groups at 4.0 and 4.8 ppm; in the ^{13}C NMR spectrum appears a signal at 25.5 ppm, two CH_2 resonances in the region 50–56 ppm, a quartet of the CF_3 group, and a peak of the amide group at 165 ppm. The absorption band of C=O in the IR spectrum is observed at 1680–1690 cm^{-1}, at higher frequency than in the spectra of linear amides. The structure of compound **II** unambiguously determined by the X-ray diffraction analysis is given below.

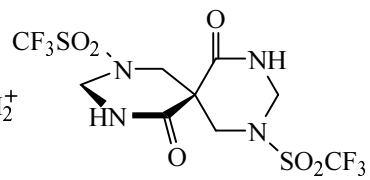


The formation of the spirocyclic compound **II** indicated that the heteocyclization occurred not only at both amide groups of the malonamide, but that its active methylene group was also involved in the process along the scheme.

$$CF_3SO_2NH_2 + CH_2O + CH_2(CONH_2)_2$$

$$\xrightarrow{[H^+]} (CF_3SO_2NH)_2CH_2^+$$

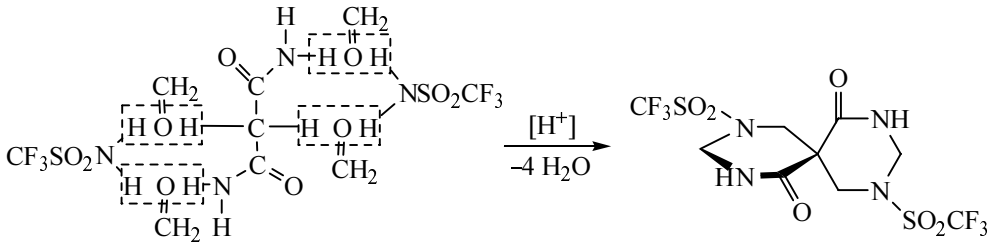
I



II

Reaction between trifluoromethanesulfonamide, paraformaldehyde, and malonamide. To a solution of 2 g of malonamide in 50 ml of concn. H_2SO_4 was added 8.76 g of trifluoromethanesulfonamide, and the reaction mixture was heated till the latter dissolved completely (~60°C). On cooling the solution to 45°C was added by

Scheme.



small portions while vigorously stirring 2.36 g of paraformaldehyde. On completion of the addition the mixture was heated to 80–90°C and stirred for 5 h, then it was poured into the ice water, the separated precipitate (4.8 g) was filtered off, dried in air, and treated with a mixture ether–hexane, 1:2. We obtained 2.52 g of **bis(trifluoromethanesulfonylamino)methane (I)** identical to an authentic sample [1]. The insoluble residue was **4,10-bis(trifluoromethanesulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (II)**. Yield 2.27 g, mp 240–242°C. IR spectrum, ν, cm^{-1}: 3180, 3040, 2906, 1692, 1680, 1395, 1380, 1210, 1170, 1100, 970, 585. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.95 d (1H, H^A in NCH_2N), 4.14 d (1H, H^B in NCH_2N, J_{AB} 13.3 Hz), 4.76 d (1H, $H^{A'}$ in NCH_2C), 4.85 d (1H, $H^{B'}$ in NCH_2C, $J_{A'B'}$ 11.0 Hz). Proton signal of $H^{A'}$ is slightly split (J 1.0 Hz) due to the coupling with the NH proton. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.46 (C<u>C</u>C), 49.35 br (C<u>C</u>N), 56.11 (NCN), 119.28 q (CF_3, J_{CF} 322.3 Hz), 165.58 (CO). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –76.41. Found, %: C 24.00; H 2.28; F 25.02; N 12.22; S 14.94. $C_9H_{10}F_6N_4O_6S_2$. Calculated, %: C 24.11; H 2.25; F 25.43; N 12.50; S 14.30.

The reaction progress was monitored by TLC on Silufol UV-254 plates, eluent hexane–ether–acetone, 1:2:1. IR spectra were recorded on a spectrophotometer Specord 75IR from smples pelletized with KBr. NMR spectra were registered on a spectrometer Bruker DPX-400 at operating frequencies 400 (^1H), 100 (^{13}C), and 376 MHz (^{19}F), the chemical shifts of ^1H and ^{13}C were measured from the signal of the solvent and were reported relative to TMS. The ^{19}F chemical shift is reported relative to CCl_3F. The crystals for the X-ray diffraction analysis were grown from methanol solution, crystal size 0.24 × 0.14×0.10 mm, colorless, monoclinic, space group $P2_1/c$, a 12.743(3), b 11.572(2), c 11.626(2) Å, β 103.12(3)°, V 1669.6(6) $Å^3$, Z 4, C 1.784 g/cm^3. The X-ray diffraction study was performed on a diffractometer Enraf Nonius CAD4, MoK_α radiation, without correction for radiation absorption in the sample, the structure solved based on 3271 reflections with $I > 2\sigma(I)$.

REFERENCES

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