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SHORT COMMUNICATIONS

Unusual Reaction of *N*-(2,2,2-Trichloroethylidene)trifluoromethanesulfonamide with Pyrrole

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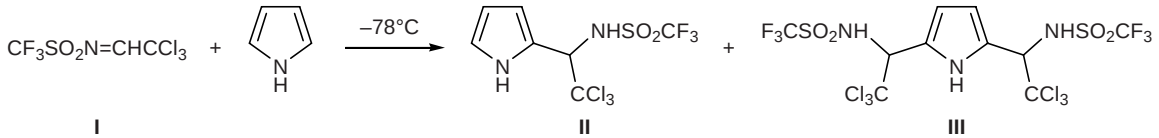
As we showed previously, 4-chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide reacts with pyrrole to give 4-chloro-*N*-[2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethyl]benzenesulfonamide in 37% yield [1]. Unexpectedly, by reaction of pyrrole with an equimolar amount of strongly electrophilic *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide on cooling [2] we obtained a mixture of *N*-[2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethyl]trifluoromethanesulfonamide (**II**) and *N*,*N*′-[1*H*-pyrrole-2,5-diylbis(2,2,2-trichloroethane-1,1-diyl)]bis(trifluoromethanesulfonamide) (**III**) at a ratio of ~2:1.

Initial imine **I** was synthesized by reaction of *N*,*N*-dichlorotrifluoromethanesulfonamide with trichloroethylene and was used without isolation from the reaction mixture [2]. We also found conditions ensuring formation of compounds **II** and **III** as the only products. By adding imine **I** to 4 equiv of pyrrole in a chlorinated hydrocarbon we obtained compound **II**. In the reaction of 2 equiv of imine **I** with pyrrole (the latter was added to the former), the major product was bis-amide **III**. Unusual formation of disubstituted pyrrole **III** may be rationalized in terms of higher electrophilicity of the CH=N group in **I**, as compared to analogous N-substituted arenesulfonamides, which favors repeated amidoalkylation of compound **II** to give product **III**. It should be noted that there have been no published data on the formation of 2,5-disubstituted derivatives like **III** in C-amidoalkylation of pyrrole.

***N*-[2,2,2-Trichloro-1-(1*H*-pyrrol-2-yl)ethyl]trifluoromethanesulfonamide (II).** A solution of 2.68 g (0.04 mol) of pyrrole in 12 ml of methylene chloride was cooled to –78°C, and cold reaction mixture obtained as described in [2] (it contained 0.01 mol of imine **I**) was added dropwise under stirring. The mixture was then allowed to warm up to room temperature, and the precipitate was filtered off, washed with hexane and water, and dried under reduced pressure. Yield 2.94 g (85%), mp 147°C. ^{1}H NMR spectrum, δ, ppm: 5.39 s (1H, CHN), 6.04 m (1H, 4-H), 6.45 m (1H, 3-H), 6.79 m (1H, 5-H), 10.94 br.s (1H, NH), 11.08 s (1H, 1-H). ^{13}C NMR spectrum, δ_C, ppm: 66.59 (**C**HCCl$_3$), 101.23 (CCl$_3$), 107.98 (C^4), 108.75 (C^3), 118.45 (C^5), 123.43 (C^2), 119.09 q (CF$_3$, $^1J_{CF}$ = 322.5 Hz). Found, %: C 24.12; H 1.72; Cl 31.15; N 7.95; S 9.57. $C_7H_6Cl_3F_3N_2O_2S$. Calculated, %: C 24.33; H 1.75; Cl 30.78; N 8.11; S 9.28.

***N*,*N*′-[1*H*-Pyrrole-2,5-diylbis(2,2,2-trichloroethane-1,1-diyl)]bis(trifluoromethanesulfonamide) (III).** A solution of 0.67 g (0.01 mol) of pyrrole in 6 ml of methylene chloride was cooled to –50°C and added dropwise under stirring to a mixture containing 0.02 mol of imine **I** (prepared as described in [2] and diluted with 5 ml of methylene chloride), cooled to –50°C. The mixture was allowed to warm up to room temperature and kept for 1 h, and the precipitate was filtered off, washed on a filter with hexane and a small amount of water, and dried under reduced pressure.



I **II** **III**

Yield 4.61 g (74%), mp 190°C. ^{1}H NMR spectrum, δ, ppm: 5.29 s (2H, CH), 6.51 d (2H, 3-H, 4-H, $^3J_{HH}$ = 2.3 Hz), 11.11 br.s (2H, NH), 11.66 s (1H, 1-H). ^{13}C NMR spectrum, δ_C, ppm: 66.98 (**C**HCCl$_3$), 101.07 (CCl$_3$), 109.72 (C^3, C^4), 119.41 q (CF$_3$, $^1J_{CF}$ = 322.5 Hz), 124.39 (C^2, C^5). Found, %: C 19.47; H 0.99; Cl 34.55; N 6.70; S 10.05. $C_{10}H_6Cl_6F_6N_3O_4S_2$. Calculated, %: C 19.28; H 0.97; Cl 34.14; N 6.74; S 10.29.

The structure of the products was proved by the ^{1}H and ^{13}C NMR spectra using HMBC-^{13}C and HSQC-^{13}C techniques. The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.6 MHz for ^{1}H and 100.61 MHz for ^{13}C from 10% solutions in DMSO-d_6; the chemical shifts were measured relative to hexamethyldisiloxane as internal reference.

REFERENCES

1. Mirskova, A.N., Drozdova, T.I., Levkovskaya, G.G., Kukharev, B.F., Kalikhman, I.D., and Voronkov, M.G., *Zh. Org. Khim.*, 1989, vol. 25, p. 1312.
2. Rozentsveig, I.B., Levkovskaya, G.G., Kondrashov, E.V., Evstaf'eva, I.T., and Mirskova, A.N., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1559.