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SHORT COMMUNICATIONS

2,5-Diphenyl-1,4-(trifluoromethylsulfonyl)piperazine from *N*-(2-bromo-2-phenylethyl)trifluoromethanesulfonamide

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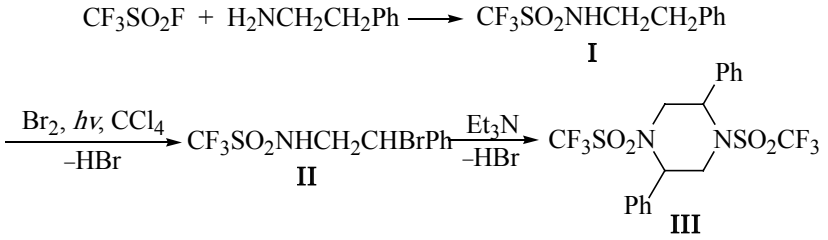
Aiming at preparation of unsaturated derivatives of trifluoromethanesulfonamide containing a fragment $CF_3SO_2NHCH{=}CH–$ we synthesized by the bromination of *N*-(2-phenylethyl)trifluoromethanesulfonamide (**I**) N-(2-bromo-2-phenylethyl)trifluoromethanesulfonamide (**II**) and carried out the dehydrobromination of compound **II** with triethylamine. It turned out unexpectedly that the reaction product was 2,5-diphenyl-1,4-(trifluoromethylsulfonyl)piperazine (**III**). By the ^1H and ^{13}C NMR data and the melting point compound **III** was identical to the substance that we had obtained by the styrene reaction with trifluoromethylsulfonylnitrene and whose structure we had established with the use of XRD analysis [1] (Scheme 1).

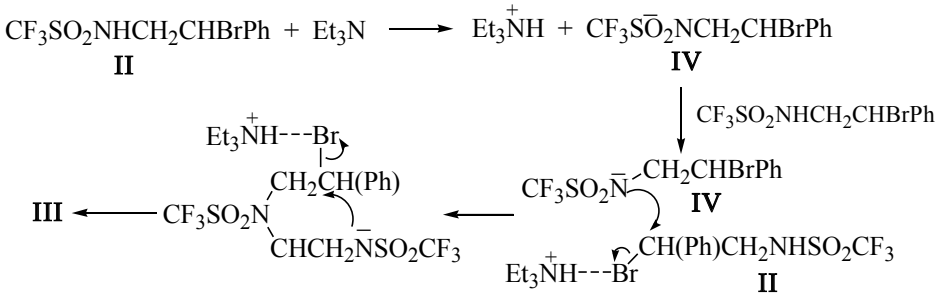
As showed the ^1H and ^{13}C NMR data the expected *N*-(2-phenylethenyl)trifluoromethanesulfonamide $CF_3SO_2NHCH{=}CHPh$ or its tautomer *N*-(2-phenylethylidene)trifluoromethanesulfonamideC $F_3SO_2N{=}$ $=CHCH_2Ph$ were lacking in the reaction mixture.

Evidently due to the high NH-acidity of compound **II** first the treatment with the triethylamine generated the amide anion **IV**, then the substitution occurs of bromide

Scheme 1.



Scheme 2.



in the second molecule **II** with electrophilic assistance of the triethylammonium cation.

***N*-(2-Phenylethyl)trifluoromethanesulfonamide (I)**. A mixture of 1.0 ml (0.12 mol) trifluoromethanesulfonyl fluoride CF_3SO_2F frozen with liquid nitrogen and 50 ml (0.47 mol) of 2-phenylethylamine was placed into a pressure reactor and heated for 12 h at 70–80°C, then cooled with liquid nitrogen, the reactor was opened, the formed thick syrupy mass was diluted with water, acidified with HCl (overall volume 400 ml), strirred for 2 h, and extracted with ethyl ether. The extract was dried with $MgSO_4$, the solvent was distilled off, the residue was distilled in a vacuum. Yield 16.5 g (53%), bp 106°C (2 mm Hg). IR spectrum, ν, cm^{-1}: 3320 (NH), 1604, 1455, 1373, 1232, 1198, 1147, 1071, 701, 610. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.83 m (2H, CH_2Ph), 3.38 m (2H, CH_2N), 7.25 m (5H, Ph), 9.44 m (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.95 (CPh), 44.83 (NC), 119.85 q (CF_3, J_{CF} 322.4 Hz), 126.50 (C^p), 128.42 (C^m), 128.83 (C^o), 137.91 (C^I). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –77.76. Found, %: C 42.19; H 3.98; F 23.33; N 6.62; S 12.78. $C_9H_{10}F_3NO_2S$. Calculated, %: C 42.69; H 3.98; F 22.51; N 5.53; S 12.66.

***N*-(2-Bromo-2-phenylethyl)trifluoromethanesulfonamide (II)**. To a solution of 3.8 g (15 mmol) of compound **I** in 25 ml of CCl_4 was added dropwise 1 ml (3.1 g, 19 mmol) of Br_2 over 3 h while stirring and irradiation with an UV lamp. The residue after evaporation of the solvent was dried in a deep vacuum. Yield 5 g (98%). IR spectrum, ν, cm^{-1}: 3313 (NH), 1601, 1429, 1377, 1234, 1199, 1145, 1073, 699, 610. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 m (2H, CH_2N), 5.04 d.d (1H, CHBr, *J* 8.1, 6.6 Hz), 5.39 уш.t (1H, NH, *J* 6.0 Hz), 7.41 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 50.98 (CHBr), 52.38 (CH_2), 119.57 q (CF_3, J_{CF} 32.8 Hz), 127.69 (C^m), 129.34 (C^o), 129.66 (C^p), 140.52 (C^I). Found, %: C 31.98; H 2.72; Br 24.61; F 17.21; N 4.23; S 9.23. $C_9H_9BrF_3NO_2S$. Calculated, %: C 32.55; H 2.73; Br 24.06; F 17.16; N 4.22; S 9.65.

2,5-Diphenyl-1,4-(trifluoromethylsulfonyl)piperazine (III). A solution of 5 g (15 mmol) of compound **II** and 15 ml (0.1 mol) of triethylamine in 50 ml of CCl_4 was heated under reflux for 2 h, the solvent and excess triethylamine was distilled off, the residue was dried and subjected to column chromatography on silica gel, eluents hexane, hexane–ethyl ether, 1 : 2, ethyl ether, methanol. Yield 0.65 g (9%). Colorless crystals, mp 128°C. IR spectrum, ν, cm^{-1}: 1403, 1229, 1202, 1122, 1028, 956, 876, 759, 742, 699, 611, 498. ^1H NMR spectrum (CD_3CN), δ, ppm: 4.01 d.d [1H, 3(6)-H_{trans}, *J* 15.2, 11.4 Hz], 4.40 d.d [1H, 3(6)-H_{cis}, *J* 15.6, 6.7 Hz], 5.32 d.d [1H, 2(5)-H, *J* 10.8, 6.8 Hz], 7.46 m (5H, Ph). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 48.63 (CH_2), 61.66 (CH), 120.47 q (CF_3, J_{CF} 321.0 Hz), 127.50 (C^o), 129.99 (C^m), 130.17 (C^p), 137.74 (C^I). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –77.34.

IR spectra were recorded on a spectrophotometer Bruker Vertex 70 from thin film or pellets with KBr. NMR spectra were registered on a spectrometer Bruker DPX 400 at operating frequencies 400 (^1H), 100 (^{13}C), 386 MHz (^{19}F), chemical shifts are reported with respect to TMS (^1H, ^{13}C) and CCl_3F (^{19}F).

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