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SHORT COMMUNICATIONS

N-Methyl-*N*-(2-phenylethenyl)trifluoromethanesulfonamide

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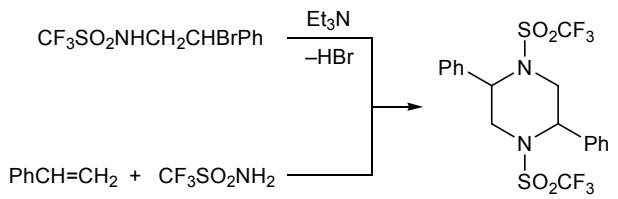
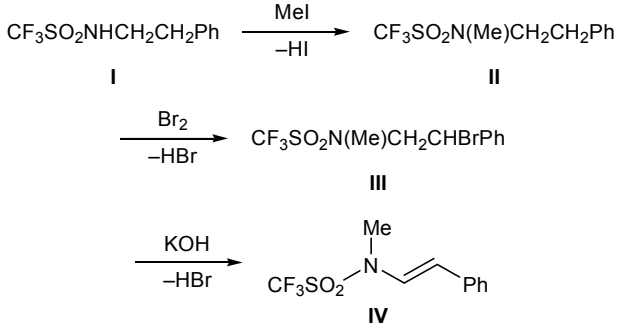
There are only a few published data on *N*-alkenyl-substituted sulfonamides of the general formula $R^1SO_2N(R^2)–C(R^3)=CR^4R^5$. Hydrostannylation of *N*-tosyl-substituted ynamines $TsN(Bzl)C{\equiv}CSiMe_3$ [1] and TsN(Bzl)C≡CH [2] led to the corresponding *N*-tosyl enamines $TsN(Bzl)C(SnBu_3)=CHSiMe_3$ [1] and $TsN(Bzl)C(SnBu_3)=CH_2$, and coupling of the latter with various organic halogen compounds RX afforded *N*-benzyl-*N*-(1-R-vinyl)-*p*-toluenesulfonamides $TsN(Bzl)C(R)=CH_2$; *N*-alkenylsultams were synthesized from *N*-alkynyl precursors [3]. Unsaturated derivatives of trifluoromethanesulfonamide containing a $CF_3SO_2N(R)CH=CHR'$ fragment were not reported so far. With a view to obtain *N*-(2-phenylethenyl)-trifluoromethanesulfonamide $CF_3SO_2NHCH=CHPh$ we previously synthesized *N*-(2-phenylethyl)trifluoromethanesulfonamide whose bromination gave *N*-(2-bromo-2-phenylethyl)trifluoromethanesulfonamide, and the latter was subjected to dehydrobromination by the action of triethylamine [4]. Unexpectedly, the product of this reaction was 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine (Scheme 1); its ^1H and ^{13}C NMR spectra and melting point were identical to those of a sample synthesized by us previously from styrene and trifluoromethanesulfonamide (its structure was proved by X-ray analysis [5]).

Scheme 1.



Obviously, dehydrohalogenation may be accompanied by heterocyclization process only when the initial trifluoromethanesulfonamide contains an NH proton. To rule out this possibility *N*-(2-phenylethyl)-trifluoromethanesulfonamide (**I**) was preliminarily subjected to methylation with methyl iodide. *N*-Methyl-*N*-(2-phenylethyl)trifluoromethanesulfonamide (**II**) thus formed was brominated to *N*-(2-bromo-2-phenylethyl)-*N*-methyltrifluoromethanesulfonamide (**III**), and dehydrobromination of the latter with alcoholic alkali afforded *N*-methyl-*N*-[(*E*)-2-phenylethenyl]trifluoromethanesulfonamide (**IV**) (Scheme 2) as the first representative of *N*-alkenyl-substituted trifluoromethanesulfonamide derivatives.

Scheme 2.



According to the NMR data, the reaction was not accompanied by side processes. The purity of intermediate products **II** and **III** was checked by ^1H NMR spectroscopy, and the structure of compound **IV** was confirmed by its ^1H, ^{13}C, and ^{19}F NMR spectra and elemental analysis. *trans* Configuration of the double bond in molecule **IV** followed from the coupling constant $^3J_{HH}$ = 14.4 Hz. By comparing the ^1H and ^{13}C NMR spectra of compound **IV** and styrene the following substituent shielding constants of the *N*-methyltrifluoromethanesulfonamide moiety $CF_3SO_2N(Me)$ for olefinic protons and carbons were determined:

^{1}H NMR: σ_{gem} = 1.35, σ_{cis} = –0.3 ppm; ^{13}C NMR: σ_α = 10.7, σ_β = –20.8 ppm; signals were assigned using the ^{1}H–^{13}C HSQC and HMBC techniques.

***N*-Methyl-*N*-(2-phenylethyl)trifluoromethanesulfonamide (II).** Methyl iodide, 1.86 ml (0.03 mol), was added dropwise to a mixture of 2.53 g (0.01 mol) of *N*-(2-phenylethyl)trifluoromethanesulfonamide (**I**) (prepared according to [4]), 10 ml of *N*,*N*-dimethylformamide, and 5.5 g (0.04 mol) of potassium carbonate, the mixture was stirred for 2 h at 25°C, the precipitate was filtered off and washed with a small amount of DMF, the filtrate was evaporated, and the residue was distilled under reduced pressure. Yield 75%, bp 102°C (0.5 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.98 t (2H, PhC**H**$_2$, J = 7.6 Hz), 3.03 s (3H, NCH_3), 3.60 br.s (2H, NCH_2), 7.25 m (2H, *m*-H), 7.30 m (1H, *p*-H), 7.36 m (2H, *o*-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.87 (Ph**C**H$_2$), 35.58 (NCH_3), 52.40 (NCH_2), 120.16 q (CF_3, J_{CF} = 323.8 Hz), 126.90 (C^p), 128.70 (C^m), 128.72 (C^o), 137.02 (C^i). ^{19}F NMR spectrum ($CDCl_3$): δ_F –75.29 ppm.

***N*-(2-Bromo-2-phenylethyl)-*N*-(methyl)trifluoromethanesulfonamide (III).** Compound **II**, 1.6 g (6 mmol), was dissolved in 10 ml of carbon tetrachloride, and 0.5 ml (0.01 mol) of bromine was added dropwise over a period of 3 h under stirring and UV irradiation. The product was isolated by vacuum distillation. Yield 59%, bp 92°C (0.5 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.01 s (3H, NCH_3), 3.99 br.s (1H, NCH_2), 4.10 d.d (1H, NCH_2, J = 14.0, 8.0 Hz), 5.53 t (1H, CHBr, J = 7.6 Hz), 7.39 m (3H, *m*-H, *p*-H), 7.55 d (2H, *o*-H, J = 7.1 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 35.54 (NCH_3), 50.26 (NCH_2), 56.01 (CHBr), 119.73 q (CF_3, J_{CF} = 324.7 Hz), 128.09 (C^o), 128.76 (C^m), 129.08 (C^p), 138.05 (C^i). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.03 ppm.

***N*-Methyl-*N*-[(*E*)-2-phenylethenyl]trifluoromethanesulfonamide (IV).** Compound **III**, 0.83 g (2.4 mmol), was added dropwise over a period of 1 h under stirring to a solution of 0.39 g (7 mmol) of potassium hydroxide in 10 ml of anhydrous methanol. The product was isolated by vacuum distillation. Yield 49%, bp 80–82°C (0.5 mm). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.34 s (3H, NCH_3), 6.43 d (1H, PhC**H**=, J = 14.4 Hz), 7.17 d (1H, NCH=, J = 14.4 Hz), 7.22 t (1H, *p*-H, J = 7.3 Hz), 7.31 t (2H, *m*-H, J = 7.5 Hz), 7.41 d (2H, *o*-H, J = 7.5 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 34.21 (NCH_3), 115.87 (Ph**C**H=), 119.48 q (CF_3, J_{CF} = 325.5 Hz), 124.82 (NCH=), 125.90 (C^m), 127.33 (C^p), 128.72 (C^o), 134.66 (C^i). ^{19}F NMR spectrum ($CDCl_3$): δ_F –74.43 ppm. Found, %: C 44.98; H 3.06; N 5.13; S 11.50. $C_{10}H_{10}F_3NO_2S$. Calculated, %: C 45.28; H 3.80; N 5.28; S 12.09.

The NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 (^{1}H), 100 (^{13}C), or 386 MHz (^{19}F); the chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or CCl_3F (^{19}F).

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