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SHORT COMMUNICATIONS

N-Propargyltrifluoromethanesulfonamide

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N-Propargylsulfonamides are synthesized by reactions of propargylamines with sulfonyl chlorides [1] or of tosylamides with propargyl carbonate [2] (along with isomeric *N*-allenylsulfonamides), and also by the $InCl_3$-catalyzed substitution of the acetate group of propargyl acetate by the tosylamide residue [3]. The synthesis of fluorine-containing *N*-propargylsulfonamides was not described up till now.

We have recently synthesized first *N*-allyltriflamide derivatives $CF_3SO_2NHCH_2CH{=}CH_2$ and $CF_3SO_2{\cdot}\ NHCH_2CBr{=}CH_2$, but the attempt to perform the dehydrobromination of the latter in order to obtain *N*-propargyltriflamide or its isomer *N*-allenyltriflamide was unsuccessful [4], apparently due to the high acidity of the substrate. The preliminary protection of the nitrogen atom made it possible to carry successfully the dehydrobromination of the N-protected substrate $CF_3SO_2N(CH_2Ph)CH_2CBr{=}CH_2$ and to obtain *N*-allenyl-*N*-benzyltriflamide $CF_3SO_2N{\cdot}(CH_2Ph)CH{=}C{=}CH_2$ [4]. The careful analysis of the IR and NMR spectra revealed the presence in the reaction product of a small (~3%) admixture of the isomeric *N*-benzyl-*N*-propargyltriflamide $CF_3SO_2N(CH_2Ph){\cdot}CH_2C{\equiv}CH$ [4], as seen from the appearance of the absorption band ν(≡C–H) 3299 cm^{-1} in the IR spectrum and of the minor signals in the NMR spectra: a triplet at 2.4 ppm, $^4J_{HH}$ 2.4 Hz (≡CH) in the ^1H NMR spectrum and signals at 74.6 (≡CH) and 35.9 ppm ($\underline{C}H_2C{\equiv}CH$) in the ^{13}C NMR spectrum.

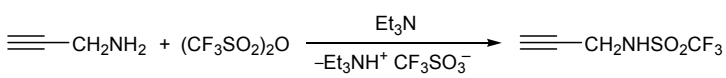
In this work we synthesized for the first time NH-unsubstituted propargyltriflamide (**I**) by the reaction of propargylamine with trifluoromethanesulfonic acid anhydride (Scheme 1).

To avoid the subsequent reaction of amide **I** with the trifluoromethanesulfonic acid anhydride the latter was taken in a deficit with respect to propargylamine. The structure and the composition of compound **I** were unambiguously proved by IR and ^1H, ^{13}C, ^{19}F spectra and by elemental analysis. The signals of the isomeric *N*-allenyltriflamide were absent from the NMR spectra. In the IR spectrum recorded from thin film the vibration bands ν(≡C–H) and ν(NH) are overlapped and form a single band at 3307 cm^{-1}; in CCl_4 solution the bands are separated and individual bands are observed: ν(≡C–H) at 3395 and ν(NH) at 3311 cm^{-1}.

N-Propargyltriflamide (**I**) does not suffer rearrangement into *N*-allenyltriflamide $CF_3SONH{\cdot}CH{=}C{=}CH_2$ or *N*-(prop-1-ynyl)triflamide $CF_3SO_2NH{\cdot}C{\equiv}CCH_3$ under the treatment with potassium butoxide in DMSO-d_6, as shows the lack in the ^1H NMR spectrum of signals in the region 1.5–2.0 ($C{\equiv}CCH_3$) and 4.5–6.5 ppm ($HC{=}C{=}CH_2$).

***N*-Propargyltrifluoromethanesulfonamide (I)**. To a mixture of 6.0 g (7.5 mL, 0.11 mol) of propargylamine, prepared by the Gabriel method from propargyl bromide and phthalimide [5] with subsequent heating with ethanolamine, and 16.6 g (23 mL, 0.16 mol) of triethylamine was added dropwise 23.3 g (14 mL, 0.083 mol) of trifluoromethanesulfonic acid anhydride, the reaction mixture was stirred for 2 h at 50°C, excess Et_3N was evaporated on a rotary evaporator, the residue was acidified with 10–15% HCl till pH 5,

Scheme 1.



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treated with ether (6 × 20 mL), the extract was dried with $MgSO_4$, ether was evaporated, the residue was distilled. Yield 6 g (40%), bp 50°C (10 mmHg). Pure for analysis substance was obtained by column chromatography on silica gel 0.125–0.200 mm. IR spectrum (film), ν, cm^{-1}: 3307, 2985, 2946, 2883, 2135, 1436, 1375, 1233, 1145, 1070, 996, 938, 853. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 t (1H, ≡CH, ^4J 2.5 Hz), 4.08 d.d (2H, CH_2, ^3J 5.5, ^4J 2.3 Hz), 5.58 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 33.74 (NCH_2), 73.86 (≡CH), 76.99 (–C≡), 119.53 q (CF_3, J_{CF} 320.7 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –76.69. Found, %: C 25.21; H 2.57; F 30.37; N 7.15; S 16.79. $C_4H_4F_3NO_2S$. Calculated, %: C 25.67; H 2.15; F 30.46; N 7.48; S 17.13.

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

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