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SHORT COMMUNICATIONS

Dedicated to Academician M.G.Voronkov on occasion of his 80th birthday

Trifluoromethanesulfonyl Azide as a Convenient Reagent for Synthesis of Triazoles

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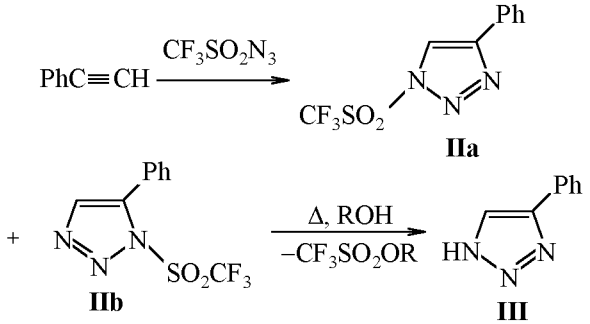
Trifluoromethanesulfonyl azide $CF_3SO_2N_3$ (**I**) is known to react with various substrates either with liberation of nitrogen or as a source of nitrene [1–3]; it usually acts as amidating agent or, more rarely, as diazotizing agent with respect to amino group [4, 5] or azidating agent [6]. There are no published data on reactions of azide **I** with alkynes. We were the first to examine the reaction of trifluoromethanesulfonyl azide (**I**) with phenylacetylene, which resulted in formation 1,2,3-triazole derivatives. Unlike *p*-toluenesulfonyl azide which reacts with phenylacetylene to give the corresponding triazole in 49% yield under reflux for 6 days [7], azide **I** gives rise to 1,3-cycloaddition products in a similar yield but under milder conditions and at a much higher rate (by an order of magnitude). By heating azide **I** with phenylacetylene in ethanol we obtained 4-phenyl-1*H*-1,2,3-triazole (**III**) as the major product; it was formed as a result of solvolysis of intermediate 4- and 5-phenyl-1-trifluoromethylsulfonyl-1*H*-1,2,3-triazoles **IIa** and **IIb**.



We succeeded in isolating *N*-substituted triazole **II** by carrying out the reaction under mild conditions which exclude solvolysis (CH_2Cl_2, 30–40°C). Heating of pure triazole **II** in ethanol also resulted in its transformation into 4-phenyl-1*H*-1,2,3-triazole (**III**) due to high nucleofugicity of the CF_3SO_2 group. The hydrolysis of structurally related triazole derived from *p*-toluenesulfonyl azide occurs only in 90% sulfuric acid [7]. Thus the examined reaction provides a convenient method for preparation of difficultly accessible substituted 1*H*-1,2,3-triazoles.

In the ^{1}H NMR spectrum of triazole **II**, apart from signals belonging to the major product **IIa**, we observed signals at δ 7.58 (m, *p*-H, *m*-H), 8.00 (m, *o*-H), and 9.16 ppm (s, =CH) at a ratio of 3 : 2 : 1. Presumably, these signals belong to the minor isomer, 5-phenyl-1-trifluoromethylsulfonyl-1*H*-1,2,3-triazole (**IIb**). The isomer ratio **IIa** : **IIb** is 4 : 1.

Trifluoromethanesulfonyl azide $CF_3SO_2N_3$ (I). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 119.26 q ($^1J_{C,F}$ = 322.5 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.28 ppm; isotope shift $\delta(^{12}C) - \delta(^{13}C)$ = 0.13 ppm. ^{15}N NMR spectrum ($CDCl_3$), δ_N, ppm: –136.21 (=N=), –150.96 (=N–), –250.31 (S–N=).

4-Phenyl-1-trifluoromethylsulfonyl-1*H*-1,2,3-triazole (II). To a solution of 2 g (0.02 mol) of phenylacetylene in 20 ml of CH_2Cl_2 we added a solution of 3.5 g (0.02 mol) of azide **I** in 10 ml of CH_2Cl_2, and the mixture was stirred for 10–15 h at 40°C until the initial azide disappeared (according to TLC). The solvent was distilled off, and the liquid residue was subjected to column chromatography on silica gel using ether–hexane (2 : 1) as eluent. Yield 2.7 g (48%), mp 150–155°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.62 m (3H, *p*-H, *m*-H), 8.04 m (2H, *o*-H), 9.20 s (1H, =CH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 120.77 q (CF_3, $^1J_{C,F}$ = 322.5 Hz), 125.66

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(C^o), 127.14 (C^5), 128.25 (C^p), 129.01 (C^m), 130.18 (C^i), 145.12 (C^4). ^{19}F NMR spectrum ($CDCl_3$): δ_F −74.79 ppm. Found, %: C 39.16; H 2.52; F 19.84; N 14.85; S 11.44. $C_9H_6F_3N_3O_2S$. Calculated, %: C 38.99; H 2.18; F 20.56; N 15.16; S 11.56.

4-Phenyl-1*H*-1,2,3-triazole (III). To a solution of 3.26 g (0.032 mol) of phenylacetylene in 50 ml of ethanol we added 5.6 g (0.032 mol) of azide **I**, and the mixture was heated for 10 h at 70°C under stirring. It was then cooled and poored into ice water, and the precipitate was filtered off and recrystallized from ethanol. Yield 2.3 g (50%), mp 143–145°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.33 t (1H, *p*-H, J = 7.4 Hz), 7.43 t (2H, *m*-H, J = 7.6 Hz), 7.33 d (2H, *o*-H, J = 7.5 Hz), 8.33 s (1H, 5-H), 11.5 v.br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 125.62 (C^o), 127.28 (C^5), 128.12 (C^p), 128.93 (C^m), 130.34 C^i), 145.24 (C^4).

The NMR spectra were obtained on a Bruker DPX-400 instrument at 400 MHz for ^1H, 100 MHz for ^{13}C, 46 MHz for ^{15}N, and 376 MHz for ^{19}F. Solutions in $CDCl_3$ or neat substance (^{15}N) were examined. Hexamethyldisiloxane was used as internal reference for ^1H and ^{13}C. The chemical shifts are given relative to TMS (^1H, ^{13}C), CCl_3F (^{19}F), and CH_3NO_2 (^{15}N).

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