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SHORT COMMUNICATIONS

N,*N*-Diformyltrifluoromethanesulfonamide

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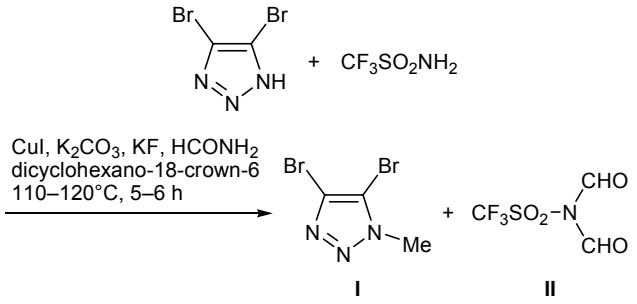
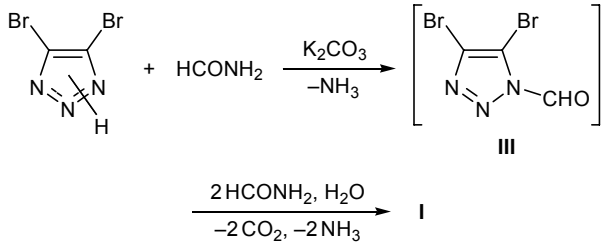
In continuation of our studies on trifluoromethylsulfonyl derivatives of azoles [1–3] we made an attempt to perform cross coupling of trifluoromethanesulfonamide with 4,5-dibromo-1,2,3-triazole by analogy with copper(I) iodide-catalyzed amidation of aryl bromides with 2,2,2-trifluoroacetamide [4]. However, targeted *N*,*N*′-bis(trifluoromethylsulfonyl)-2*H*-1,2,3-triazole-4,5-diamine was not formed, but the reaction in formamide unexpectedly produced 4,5-dibromo-1-methyl-1*H*-1,2,3-triazole (**I**) and *N*,*N*-diformyltrifluoromethanesulfonamide (**II**) (Scheme 1).

Scheme 1.



Compound **I** displayed in the ^{1}H NMR spectrum only one singlet at δ 4.06 ppm, whereas its ^{13}C NMR spectrum contained signals assignable to methyl (δ_C 37 ppm) and two nonequivalent olefinic carbon atoms (C^4, δ_C 122 ppm, and C^5, δ_C 114 ppm); these findings indicated that the methyl group in molecule **I** is linked to the N^1 atom. The IR and UV spectra of **I** coincided with those reported in [5] where methylation of 4,5-dibromo-1,2,3-triazole with dimethyl sulfate was shown to give a 1:1 mixture of compound **I** and isomeric 4,5-dibromo-2-methyl-2*H*-1,2,3-triazole, which differed by spectral parameters. Obviously, the only source of methyl group in **I** may be formamide molecule, and the process is likely to involve reduction of the aldehyde group in intermediate **III** with formamide on heating (Scheme 2), by analogy with the reduction with formamide of a nitro group [6].

Scheme 2.



The formation of 1-methyl rather than 2-methyl isomer may be rationalized in terms of charge-controlled reaction of 4,5-dibromo-1,2,3-triazolate anion with formamide. This follows from the fact that the negative charge in 4,5-dibromo-1,2,3-triazolate anion is localized mainly on the N^1 and N^3 atoms (–0.88 *e*; cf. –0.19 *e* on N^2), whereas the contribution of N^2 to the highest occupied molecular orbital of the anion exceeds by an order of magnitude the overall contribution of the N^1 and N^3 atoms.

The ^{1}H NMR spectrum of *N*,*N*-diformyltrifluoromethanesulfonamide (**II**) contained a singlet at δ 8.7 ppm as the only signal, and the CF_3 and C=O carbon nuclei resonated in the ^{13}C NMR spectrum at δ_C 120 and 170 ppm, respectively. Due to the presence of two carbonyl groups, absorptions bands due to their symmetric and antisymmetric stretching vibrations were observed in the IR spectrum of **II** in the region 1610–1640 cm^{-1}.

N,*N*-Diformyltrifluoromethanesulfonamide (**II**) is the first representative of *N*-formyl-substituted trifluoromethanesulfonamide and is one of a few representatives of *N*-formyl amides. We have found only

one early publication on the synthesis of *N*-formylarenesulfonamides $ArSO_2NHCHO$ by reaction of arenesulfonamide sodium salts $ArSO_2NHNa$ with formic acid esters HCOOR [7]. Diformyl derivatives of sulfonamides were not reported previously. As concerns *N*-formyl-substituted carboxylic acid amides, only *N*,*N*-diformylformamide $HCON(CHO)_2$ (triformamide) and *N*,*N*-diformylacetamide $HCON(CHO)_2$ were reported [8]. Taking the above stated into account, we tried to synthesize compound **II** as target product under various conditions. Compound **II** can be separated from excess formamide only by column chromatography. The best result was obtained by reacting trifluoromethanesulfonamide sodium salt CF_3SO_2NHNa with formamide in the presence of a catalytic amount of CuI. An attempt to effect formylation of trifluoromethanesulfonamide by heating with formic acid in boiling toluene with simultaneous removal of water (as in the formylation of amines) [9] was unsuccessful due to extremely low basicity of trifluoromethanesulfonamide which was recovered from the reaction mixture.

Reaction of 4,5-dibromo-1*H*-1,2,3-triazole with trifluoromethanesulfonamide in the presence of copper(I) iodide in formamide. Trifluoromethanesulfonamide, 1.7 g (11 mmol), and 4,5-dibromo-1,2,3-triazole, 1.13 g (5 mmol), were dissolved in 20 ml of formamide, 0.2 g (0.55 mmol) of dicyclohexano-18-crown-6, 0.5 g (0.55 mmol) of potassium fluoride, and 5 mol % of copper(I) iodide were added, and 0.83 g (5.5 mmol) of potassium carbonate was then added in small portions (strong foaming was observed). The mixture was heated to 110–120°C over a period of 5–6 h (vigorous evolution of ammonia was observed), cooled, poured into a saturated aqueous solution of sodium chloride, and extracted with two portions of ethyl acetate. The combined extracts were dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue, ~1.7 g of a yellow–green glassy material, was subjected to column chromatography on silica gel to isolate 0.16 g (13%) of compound **I** as colorless crystals with mp 117°C (published data [5]: mp 116.5–117.5°C) and ~0.3 g (13%) of compound **II** as white finely crystalline powder with mp ~280°C (sublimes).

1-Methyl-4,5-dibromo-1*H*-1,2,3-triazole (I). ^{1}H NMR spectrum: δ 4.06 ppm, s (CH_3). ^{13}C NMR spectrum, δ_C, ppm: 37.01 (CH_3), 114.08 (C^5), 122.00 (C^4).

***N*,*N*-Diformyltrifluoromethanesulfonamide (II).** IR spectrum (KBr), ν, cm^{-1}: 2916, 2902, 1650, 1612, 1328, 1317, 1215, 1132, 962, 770, 649, 601. ^{1}H NMR spectrum: δ 8.73 ppm, s (CHO). ^{13}C NMR spectrum, δ_C, ppm: 120.37 q (CF_3, J_{CF} = 323.5 Hz), 170.55 (CHO). ^{19}F NMR spectrum: δ_F –79.39 ppm. Found: *m*/*z* 204.9656 $[M]^+$. $C_3H_2F_3NO_4S$. Calculated: *M* 204.9657.

Reaction of trifluoromethanesulfonamide sodium salt with formamide. A mixture of 5 g (0.029 mol) of trifluoromethanesulfonamide sodium salt and 0.28 g (1.5 mmol) of copper(I) iodide in 50 ml of formamide was heated under stirring for 6–8 h at 140–150°C. The mixture gradually turned blue due to liberation of ammonia and formation of copper–ammonia complex. The progress of the reaction was monitored by TLC, following disappearance of initial trifluoromethanesulfonamide. The mixture was cooled, poured into a saturated aqueous solution of sodium chloride, and extracted with two portions of ethyl acetate. The extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure. According to the ^{1}H NMR data, the residue, 4.87 g, contained ~50% of target compound **II** together with formamide and water. Compound **II** was separated from formamide by column chromatography on silica gel using hexane–diethyl ether (3:1 to 1:3) and hexane–diethyl ether–propan-2-ol (2:3:1) as eluents.

The IR spectrum was recorded on a Bruker Vertex 70 spectrometer. The NMR spectra were measured on a Bruker DPX 400 instrument at 400 (^{1}H), 100 (^{13}C), and 376 MHz (^{19}F) from solutions in DMSO-d_6; the chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or trichlorofluoromethane (^{19}F). The progress of reactions was monitored by TLC on Silicagel 60 UV-254 plates using hexane–diethyl ether–propan-2-ol (2:3:1) as eluent.

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