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SHORT COMMUNICATIONS

Reaction of Trifluoro-*N*-(oxo-λ^4-sulfanylidene)methanesulfonamide with Pyrazolidin-3-ones

B. A. Shainyan* and L. L.Tolstikova

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
**e-mail: bagrat@irioch.irk.ru*

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Abstract—Trifluoro-*N*-(oxo-λ^4-sulfanylidene)methanesulfonamide reacted with 1-phenylpyrazolidin-3-one and 4-methyl-1-phenylpyrazolidin-3-one to give 1-phenyl-1,2-dihydro-3*H*-pyrazol-3-ones. A probable oxidation mechanism was proposed.

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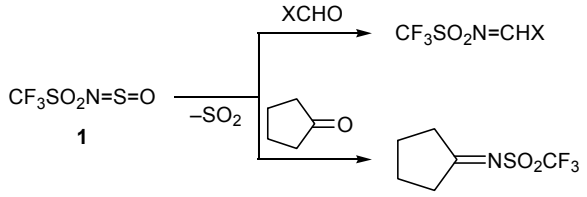
Trifluoro-*N*-(oxo-λ^4-sulfanylidene)methanesulfonamide $CF_3SO_2N{=}S{=}O$ (**1**), as well as its perfluoroalkyl analogs, is known to react with aromatic and heterocyclic aldehydes and cyclopentanone to give the corresponding *N*-ylidene derivatives [1, 2] (Scheme 1).

Scheme 1.

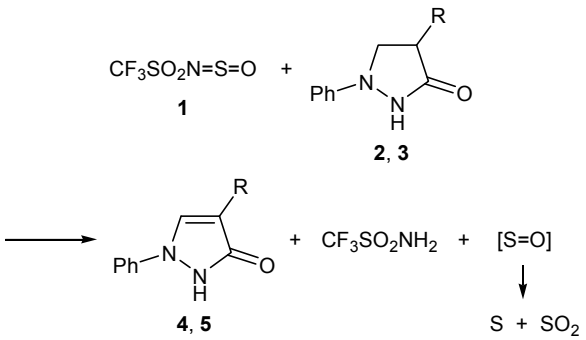


X = Ar, Ht.

With the goal of extending the series of ylidene derivatives of trifluoromethanesulfonamide and elucidating general character of the above condensation, compound **1** was brought into reaction with 1-phenylpyrazolidin-3-ones **2** and **3** possessing a pharmacophoric pyrazolone fragment. The reactions were carried out at room temperature or on cooling (–30 to –20°C) in methylene chloride, chloroform, or benzene in the absence of a catalyst. However, instead of expected *N*-(pyrazolidin-3-ylidene) derivatives, we isolated oxidation products, 1-phenyl-1,2-dihydro-3*H*-pyrazol-3-ones **4** and **5** in high yields (>80%; Scheme 2).

Upon addition of sulfonamide **1** to a solution of **2** or **3**, the mixture instantaneously turned violet, but it became colorless after stirring for 5 h. Oxidation products **4** and **5** are poorly soluble in the solvents used, so that they precipitated as the reaction progressed; the products can also be precipitated with acetonitrile and separated from trifluoromethanesulfonamide by washing with water. The formation of $CF_3SO_2NH_2$ was confirmed by the ^{19}F NMR spectra which contained a signal at δ_F –79 ppm (cf. δ_F –78 to –77 ppm for $Ht{=}NSO_2CF_3$). The melting points and ^1H and ^{13}C NMR spectra of **4** and **5** coincided with those reported in [3–6]. The IR spectra of **4** and **5** displayed strong absorption bands at 1600 and 1550 cm^{-1} typical of stretching vibrations of C=C bond and bending vibrations of NH group, respectively.

Scheme 2.



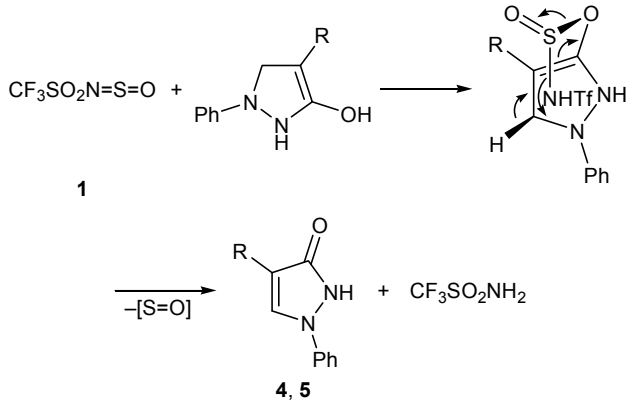
2, **4**, R = H; **3**, **5**, R = Me.

Unlike pyrazolidinones **2** and **3**, compound **1** failed to react with 1-methylpyrrolidin-2-one, pyrrolidine-2,5-dione, 2,4-dihydro-3*H*-1,2,4-triazol-3-one, and 5,5-diethylhexahydropyrimidine-2,4,6-trione, regardless of the solvent nature (CH_2Cl_2, benzene, or no

solvent), catalyst [$SOCl_2$, $Y(OTf)_3$, $AlCl_3$], and temperature (from –30°C to the boiling point).

Compounds **4** and **5** and their enol tautomers were obtained previously by oxidation of pyrazolidinones with Fe(III), MnO_2, sulfur, or benzoquinone [7–9]. We have found no examples of using *N*-(oxo-λ⁴-sulfanylidene)sulfonamides as oxidants in any reactions. Presumably, the oxidation mechanism involves addition of the enol tautomer of **2** or **3** to the N=S bond of **1**, followed by rearrangement with elimination of trifluoromethanesulfonamide molecule and sulfur(II) oxide which undergoes disproportionation to sulfur(IV) oxide and elemental sulfur [10] (Scheme 3).

Scheme 3.



1-Phenyl-1,2-dihydro-3*H*-pyrazol-3-one (4). A solution of 0.32 g (2 mmol) of 1-phenylpyrazolidin-3-one (**2**) in 3 mL of methylene chloride was cooled to –30°C, and a solution of 0.40 g (2.05 mmol) of compound **1** in 1 mL of methylene chloride was added under argon. The mixture instantaneously turned dark violet and was stirred for 3 h at room temperature and evaporated under reduced pressure (water-jet pump). The oily residue, 0.32 g, was treated with acetonitrile and dried under reduced pressure. Yield 0.25 g (80%), yellow crystals, mp 158°C [3, 4]. ^{1}H NMR spectrum, δ, ppm: 5.80 d (1H, CH, ^3J = 2.4 Hz), 7.17 t (1H, H_{arom}, J = 7.3 Hz), 7.41 t (2H, H_{arom}, J = 7.9 Hz), 7.67 d (2H, H_{arom}, J = 7.8 Hz), 8.20 d (1H, CH, ^3J = 2.4 Hz), 10.20 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 94.5, 116.9, 124.8, 128.6, 129.5, 140.0, 162.8. The spectral parameters of **4** were consistent with those given in [3, 4].

4-Methyl-1-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (5) was synthesized in a similar way from 0.17 g (1 mmol) of 4-methyl-1-phenylpyrazolidin-3-one (**3**) in 1 mL of methylene chloride and 0.19 g (1.01 mmol) of **1** in 1 mL of methylene chloride at room temperature. Yield 0.15 g (88%), yellow powder, mp 209°C [5, 6]. ^{1}H NMR spectrum, δ, ppm: 1.90 s (3H, CH_3), 7.12 t (1H, *p*-H, J = 7.3 Hz), 7.38 t (2H, *m*-H, J = 8.1 Hz), 7.60 d (2H, *o*-H, J = 7.8 Hz), 8.01 s (1H, =CH), 10.14 (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 7.0, 103.3, 116.2, 123.9, 126.5, 129.3, 139.9, 161.4. The spectral parameters of **5** coincided with those given in [5, 6].

The IR spectra (400–4000 cm^{-1}) were recorded in KBr on a Varian 3100 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.62 MHz, respectively, using DMSO-d_6 as solvent and reference.

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