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Reaction of *N*-Sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ with Carbonyl Compounds

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Abstract—*N*-Sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ reacts with salicylaldehyde, 2-furaldehyde, 2-thiophenecarbaldehyde, 3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde, and 2-phenyl-2*H*-1,2,3-triazole-4-carbaldehyde to afford the corresponding *N*-aryl(hetaryl)methylidenetrifluoromethanesulfonamides in high yields. Reactions of the latter with aniline give no adducts at the C=N bond but transamination products. The reaction of trifluoromethanesulfonamide with phenyl isocyanate led to formation of *N*,*N'*-diphenylurea instead of expected *N*-phenyl-*N'*-(trifluoromethylsulfonyl)urea.

N-Sulfinyl amides derived from carboxylic and sulfonic acids are highly reactive compounds which are widely used in the synthesis of heterocycles. Reactions of *N*-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ with aldehydes lead to formation of the corresponding imines having a trifluoromethylsulfonyl group on the nitrogen atom. As early as 1986, Yagupol'skii and co-workers proposed a new principle for design of superstrong electron-acceptor substituents and noted that an aldehyde group is the simplest moiety where the effect of replacement of the oxygen atom by the $=NSO_2CF_3$ group may be observed [1]. Heating of substituted benzaldehydes with *N*-trifluoromethanesulfonyl isocyanate $CF_3SO_2N{=}C{=}O$ [2] or more accessible *N*-sulfinyltrifluoromethanesulfonamide [1] gives rise to the corresponding *N*-benzylidenetrifluoromethanesulfonamides (Scheme 1).

Scheme 1.

$$YC_6H_4CHO + CF_3SO_2N{=}X{=}O \xrightarrow[-XO_2]{} YC_6H_4CH{=}NSO_2CF_3$$

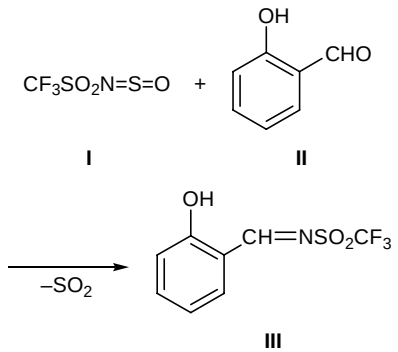
X = C, S; Y = H, *m*-F, *p*-F.

Substituted *N*-benzylideneperfluoroalkanesulfonamides $R_FSO_2N{=}CHAr$ were synthesized in up to 84% yield by reactions of *N*-sulfinylperfluoroalkanesulfonamides R_FSO_2NSO with aromatic aldehydes [3, 4].

With a view to extend the series of nucleophiles and elucidate general character of this reaction, in the present work we examined reactions of *N*-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ (**I**) with a number of heterocyclic aldehydes, salicylaldehyde, and dimethylformamide. We also explored an alternative synthetic route to heterocumulenes of the trifluoromethanesulfonyl series on the basis of addition of trifluorosulfonamide to isocyanates.

It is known [5] that $RSO_2N{=}S{=}O$ heterocumulenes are very readily converted into the corresponding sulfonamides in the presence of proton donors such as water, alcohols, and amines. Therefore, it was reasonable to examine the behavior of *N*-sulfinyltrifluoromethanesulfonamide (**I**) in reaction with salicylaldehyde (**II**) which possesses both carbonyl and hydroxy group. Aldehyde **II** turned out to react in a way similar to other aromatic aldehydes [3], and heating of the reaction mixture in boiling benzene for 8 h resulted in formation of *N*-(2-hydroxybenzylidene)trifluoromethanesulfonamide (**III**) in 88% yield (Scheme 2).

Scheme 2.



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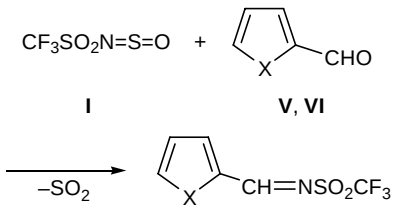
The reaction successfully occurred at room temperature in the presence of a catalytic amount of $AlCl_3$.

The formation of imine **III** could also be expected in the reaction of salicylaldehyde with trifluoromethanesulfonamide ($CF_3SO_2NH_2$, **IV**). However, compound **II** failed to react with sulfonamide **IV** even on prolonged heating (30 h) in boiling benzene. The reason is the low nucleophilicity of amide **IV**. Addition of thionyl chloride to the mixture favors formation of the desired imine **III**; according to the ^{19}F NMR data, the conversion was 26% after heating for 11 h in boiling benzene.

Reactions of *N*-sulfinylperfluoroalkanesulfonamides R_FSO_2NSO [3, 4] or *N*-sulfinylarenesulfonamides $ArSO_2NSO$ [5–7] with aldehydes require elevated temperature and in some cases addition of Lewis acids as catalysts (see above). We found that compound **I** reacts with 2-furaldehyde (**V**) and 2-thiophenecarbaldehyde (**VI**) to give compounds **VII** and **VIII** in more than 80% yield even at room temperature in the absence of a catalyst (Scheme 3).

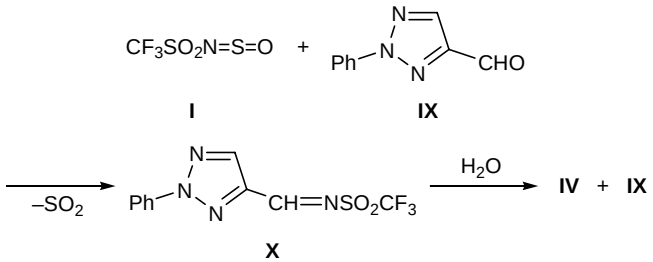
Scheme 3.



V, **VII**, X = O; **VI**, **VIII**, X = S.

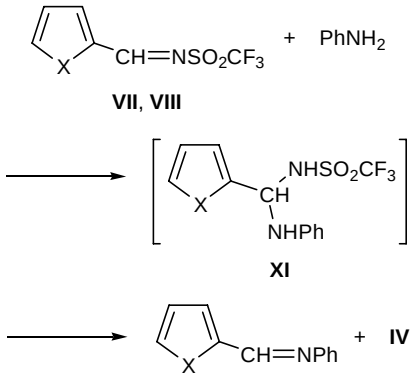
The reaction of **I** with 2-phenyl-2*H*-1,2,3-triazol-4-carbaldehyde (**IX**) occurs less readily, and the complete conversion of **IX** is reached only on prolonged heating (for more than 30 h) in carbon tetrachloride. The product, 2-phenyl-4-trifluoromethylsulfonyliminomethyl-2*H*-1,2,3-triazole (**X**) readily undergoes hydrolysis on treatment with water or on exposure to atmospheric moisture. As a result, trifluoromethanesulfonamide (**IV**) and initial aldehyde **IX** are obtained (Scheme 4).

Scheme 4.



N-Sulfonyl derivatives of trichloroacetaldehyde imine are known to readily take up various OH, NH, and CH acids [8]. Taking these data into account, we tried to obtain adducts **XI** by reaction of imines **VII** and **VIII** with aniline. However, the reactions resulted in formation of only transamination products **XII** and **XIII** which were likely to be formed according to Scheme 5. The ^1H NMR spectrum of the product obtained from compound **VII** and aniline coincided with the spectrum of an authentic sample of *N*-(2-furylmethylidene)aniline (**XII**) prepared by reaction of furaldehyde with aniline. Also, the ^1H NMR spectra of **XII** and **XIII** coincided with those reported in [9, 10]; in addition, the spectra of the reaction mixtures contained a signal at δ 5.5 ppm due to protons of the NH_2 group in amide **IV**. In the ^{19}F NMR spectrum we observed a single signal at about δ_F –78 ppm, which also belongs to amide **IV**. Presumably, intermediate adducts are unstable owing to high nucleofugality of the trifluoromethanesulfonamide residue and weaker electron-acceptor power of the furyl or thienyl group as compared to CCl_3 group.

Scheme 5.

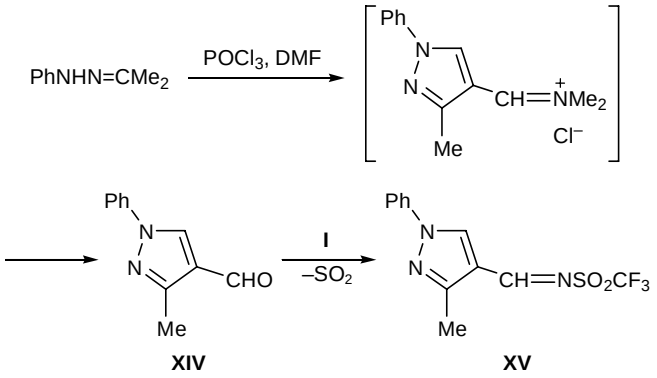


VII, **XII**, X = O; **VIII**, **XIII**, X = S.

3-Methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**XIV**) smoothly reacted with compound **I** to give more than 90% of the corresponding sulfonyliminomethyl derivative **XV**. Compound **XIV** was synthesized by the Vilsmeier reaction of acetone phenylhydrazone [11, 12] (Scheme 6).

Taking into account that N,N-disubstituted formamides react with *N*-sulfinylarenesulfonamides in a way similar to aromatic aldehydes, i.e., with elimina-

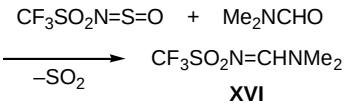
Scheme 6.



XIV **XV**

tion of SO_2 [5], we performed reaction of *N*,*N*-dimethylformamide with *N*-sulfinyltrifluoromethanesulfonamide (**I**) and obtained *N*-(dimethylaminomethylidene)trifluoromethanesulfonamide (**XVI**) (Scheme 7). We previously synthesized compound **XVI** by reaction of trifluoromethanesulfonamide (**IV**) sodium salt with 2-phenyl-2*H*-1,2,3-triazole-4-carbonyl chloride in dimethylformamide [13].

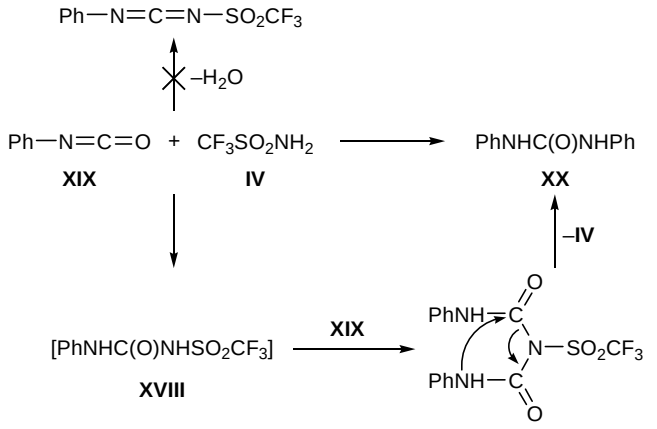
Scheme 7.



XVI

In the presence of proton donors, heterocumulene **I** is very readily converted into trifluoromethanesulfonamide (**IV**). Unlike **IV**, structurally related trifluoromethanesulfonyl isocyanate ($CF_3SO_2N=C=O$, **XVII**) smoothly takes up, e.g., aniline, to afford substituted urea $CF_3SO_2NHC(O)NHPh$ (**XVIII**) which is a strong NH acid [2]. An alternative route to new NH acids of the trifluoromethanesulfonamide series may be addition of **IV** to isocyanates. However, the reaction of amide **IV** with phenyl isocyanate (**XIX**) led to formation of *N*,*N*′-diphenylurea (**XX**) rather than compound **XVIII**. The reaction is likely to follow a mechanism shown in Scheme 8.

Scheme 8.



XVIII

It should be noted that analogous reaction of amide **IV** with chlorosulfonyl isocyanate $ClSO_2N=C=O$ also gives *N*,*N*′-disubstituted urea $(ClSO_2NH)_2CO$ [2].

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer from samples prepared as KBr pellets. The NMR spectra were obtained on a Bruker DPX-400 spectrometer at 400 (^1H), 100 (^{13}C), or 376 MHz (^{19}F) using HMDS as internal reference; the chemical shifts are given relative to TMS (^1H, ^{13}C) and CCl_3F (^{19}F). The progress of reactions was monitored by TLC using Silufol UV-254 plates.

***N*-(2-Hydroxybenzylidene)trifluoromethanesulfonamide (III).** Salicylaldehyde, 0.24 g (2 mmol), was added under vigorous stirring to a solution of 0.39 g (2 mmol) of *N*-sulfinyltrifluoromethanesulfonamide in 3 ml of benzene. The mixture was heated for 8 h at 75°C, cooled, and evaporated under reduced pressure (water-jet pump) to obtain 0.44 g (88%) of crude product **III** with mp 40–42°C. The product was purified by vacuum sublimation at a residual pressure of 1 mm. Yellow crystals, mp 54–56°C. IR spectrum, ν, cm^{-1}: 1620, 1580, 1550, 1450, 1380, 1360, 1290, 1220, 1180, 1140, 1110, 900, 830, 600. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.12–7.67 m (4H, H_{arom}), 9.14 s (1H, OH), 10.49 s (1H, CH=N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 118.79 (C^3), 119.35 (CF_3, J = 318.8 Hz), 120.71 (C^1), 121.15 (C^5), 136.84 (C^4), 140.57 (C^6), 163.86 (C^2), 180.05 (C=NSO_2). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.85 ppm. Found, %: C 38.12; H 2.56; F 22.22; N 5.60; S 12.95. $C_8H_6F_3NO_3S$. Calculated, %: C 37.95; H 2.39; F 22.51; N 5.53; S 12.66.

***N*-(2-Furylmethylidene)trifluoromethanesulfonamide (VII).** Freshly distilled 2-furaldehyde, 0.192 g (2 mmol), was added under stirring to 0.39 g (2 mmol) of *N*-sulfinyltrifluoromethanesulfonamide (**I**). After stirring for 15 min at room temperature, the mixture solidified to give grayish crystals with mp 129–130°C, yield 0.37 g (82%). IR spectrum, ν, cm^{-1}: 3160, 3140, 1590, 1510, 1450, 1390, 1340, 1310, 1290, 1190, 1170, 1110, 1020, 920, 820, 780, 600. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.81 d.d (1H, 4-H, J = 3.6, 1.6 Hz), 7.67 d (1H, 3-H, J = 3.6 Hz), 7.96 d (1H, 5-H, J = 1.6 Hz), 8.85 s (1H, N=CH). ^{13}C NMR spectrum

($CDCl_3$), δ_C, ppm: 115.14 (C^4), 119.15 (CF_3, J_{CF} = 321.7 Hz), 130.92 (C^3), 149.00 (C^2), 152.94 (C^5), 163.16 (CH=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.88 ppm. Found, %: C 32.02; H 1.76; F 24.99; N 6.53; S 13.89. $C_6H_4F_3NO_3S$. Calculated, %: C 31.72; H 1.77; F 25.09; N 6.17; S 14.12.

***N*-(2-Furylmethylidene)aniline (XII).** Freshly distilled aniline, 0.08 g (0.88 mmol), was added under stirring to a solution of 0.20 g (0.88 mmol) of *N*-(2-furylmethylidene)trifluoromethanesulfonamide (**VII**) in 1 ml of $CDCl_3$. After 15 min, the mixture turned dark red. Signals in the ^1H NMR spectrum of the mixture coincided with those of an authentic sample of *N*-(2-furylmethylidene)aniline prepared by reaction of 2-furaldehyde (**V**) with aniline ($CDCl_3$), δ, ppm: 6.56 d.d (1H, 4-H, *J* = 3.4, 1.7 Hz), 6.97 d (1H, 3-H, *J* = 3.4 Hz) 7.27 m (3H, *o*-H, *p*-H), 7.40 t (2H, *m*-H, *J* = 7.7 Hz), 7.62 br.s (1H, 5-H), 8.29 s (1H, N=CH); published data [9], δ, ppm: 6.42, 6.83, 7.17, 7.27, 7.49, 8.17.

***N*-(2-Thienylmethylidene)trifluoromethanesulfonamide (VIII).** A solution of 0.22 g (2 mmol) of 2-thiophenecarbaldehyde in 1 ml of benzene was added under stirring at 7 to 10°C to a solution of 0.39 g (2 mmol) of *N*-sulfinyltrifluoromethanesulfonamide (**I**) in 2 ml of benzene. The mixture was stirred for 10 h at room temperature and evaporated under reduced pressure to obtain brownish crystals with mp 92°C. Yield 0.36 g (75%). IR spectrum, ν, cm^{-1}: 1560, 1540, 1340, 1290, 1200, 1180, 1105, 860, 810, 640, 590. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.35 d.d (1H, 4-H, *J* = 3.9, 4.9 Hz), 8.01 s (1H, 3-H, *J* = 3.9 Hz), 8.07 s (1H, 5-H, *J* = 4.9 Hz), 9.18 s (1H, N=CH); a weak coupling between the 3-H and CHN protons was observed: the 3-H signal at δ 8.01 ppm was additionally split with a constant of ~1 Hz, and the CHN signal at δ 9.18 ppm was broadened. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 119.15 (CF_3, J_{CF} = 320.0 Hz), 130.00 (C^4), 137.50 (C^3), 141.47 (C^5), 142.90 (C^2), 170.71 (CH=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.84 ppm. Found, %: C 29.69; H 1.62; F 23.42; N 6.02. $C_6H_4F_3NO_2S_2$. Calculated, %: C 29.63; H 1.66; F 23.43; N 5.76.

***N*-(2-Thienylmethylidene)aniline (XIII).** Freshly distilled aniline, 0.065 g (0.69 mmol), was added under stirring to a solution of 0.17 g (0.69 mmol) of *N*-(2-thienylmethylidene)trifluoromethanesulfonamide (**VIII**) in 1 ml of $CDCl_3$. After 15 min, the mixture turned dark. Its ^1H NMR spectrum contained the following signals, δ, ppm: 7.12 d.d (1H, 4-H, *J* = 5.0, 3.7 Hz), 7.48 d (1H, 3-H, *J* = 3.7 Hz) 7.23 m (3H, *o*-H, *p*-H), 7.39 t (2H, *m*-H, *J* = 7.7 Hz), 7.50 d (1H, 5-H, *J* = 5.0 Hz), 8.55 s (1H, N=CH); cf. 7.02, 7.36, 7.13, 7.29, 7.38, 8.35 [9]; 7.0–7.5 m (8H), 8.51 s (1H, N=CH) [10].

2-Phenyl-4-trifluoromethylsulfonyliminomethyl-2*H*-1,2,3-triazole (X). 2-Phenyl-2*H*-1,2,3-triazole-4-carbaldehyde (**IX**), 0.36 g (2.1 mmol), was added in portions under vigorous stirring to a solution of 0.51 g (2.6 mmol) of *N*-sulfinyltrifluoromethanesulfonamide (**I**) in 8 ml of carbon tetrachloride. The mixture was heated for 32 h at 75°C, cooled, and evaporated under reduced pressure (water-jet pump) to obtain 0.55 g (87%) of compound **X** as yellowish crystals with mp 115°C. IR spectrum, ν, cm^{-1}: 1590, 1480, 1350, 1210, 1200, 1180, 1105, 830, 790, 740, 600. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.53 m (3H, *p*-H, *m*-H), 8.15 d (2H, *o*-H), 8.52 s (1H, 5-H), 9.41 s (1H, CH=N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 119.02 (CF_3, *J* = 321.6 Hz), 119.67 (C^o), 129.72 (C^m), 129.77 (C^p), 135.47 (C^4), 138.37 (C^1), 143.42 (C^5), 170.20 ($C=NSO_2$). ^{19}F NMR spectrum ($CDCl_3$): δ_F –77.60 ppm. Found, %: C 39.33; H 2.39; F 18.65; N 18.28; S 10.75. $C_{10}H_7F_3N_4O_2S$. Calculated, %: C 39.48; H 2.32; F 18.73; N 18.41; S 10.54.

***N*-(3-Methyl-1-phenyl-1*H*-pyrazol-4-ylmethylidene)trifluoromethanesulfonamide (XV).** 3-Methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**XIV**) [11, 12], 0.37 g (0.002 mol), was added under stirring to a solution of 0.39 g (2 mmol) of *N*-sulfinyltrifluoromethanesulfonamide (**I**) in 3 ml of benzene. The mixture was kept for two days at room temperature and evaporated to obtain grayish crystals with mp 80–82°C. Yield 0.62 g (94%). IR spectrum, ν, cm^{-1}: 1560, 1490, 1350, 1200, 1180, 1160, 1100, 840, 750, 700, 600. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.53 m (3H, *p*-H, *m*-H), 8.15 d (2H, *o*-H), 8.52 s (1H, 5-H), 9.41 s (1H, CH=N). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 119.02 (CF_3, *J* = 321.6 Hz), 119.67 (C^o), 129.72 (C^m), 129.77 (C^p), 135.47 (C^4), 138.37 (C^1), 143.42 (C^5), 170.20 ($C=NSO_2$). ^{19}F NMR spectrum ($CDCl_3$): δ_F –77.04 ppm. Found, %: F 17.49; S 9.93. $C_{12}H_{10}F_3N_3O_2S$. Calculated, %: F 17.96; S 10.11.

***N*-(Dimethylaminomethylidene)trifluoromethanesulfonamide (XVI).** A solution of 0.15 g (2 mmol) of anhydrous dimethylformamide in 1 ml of chloroform was added dropwise under stirring to 0.3 g (2 mmol) of *N*-sulfinyltrifluoromethanesulfonamide (**I**). The mixture was stirred for 30 min at room temperature and evaporated to obtain 0.21 g (50%) of sulfonamide **XVI** as a crystalline substance with mp 90–

92°C [13]. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of the product coincided with those reported in [13].

Reaction of trifluoromethanesulfonamide with phenyl isocyanate. Phenyl isocyanate (**XIX**), 2.6 ml (0.024 mol), was added to a solution of 2.98 g (0.02 mol) of trifluoromethanesulfonamide (**IV**) in 10 ml of anhydrous THF, and the mixture was heated for 3 h under reflux. After 1 h, colorless needle-shaped crystals began to separate from the solution. The mixture was cooled, and the precipitate was filtered off, washed with cold anhydrous THF, and dried under reduced pressure. Yield of *N*,*N'*-diphenylurea (**XX**) 0.68 g, mp 235–236°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.93 t (1H, *p*-H), 7.26 t (2H, *m*-H), 7.45 d (2H, *o*-H), 8.63 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 118.75 (C^o), 122.39 (C^p), 129.35 (C^m), 153.10 (C=O).

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