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Reactions of *N*-Sulfinyltrifluoromethanesulfonamide with Carboxylic Acids

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Abstract—Phenylacetic, diphenylacetic, salicylic, and cinnamic acids reacted with *N*-sulfinyltrifluoromethanesulfonamide (CF_3SO_2NSO) to give the corresponding *N*-acyltrifluoromethanesulfonamides CF_3SO_2NHCOR (R = $PhCH_2$, Ph_2CH, *o*-HOC_6H_4, PhCH=CH). The reaction of *N*-sulfinyl-trifluoromethanesulfonamide with 3-hydrazinobenzoic acid occurred at the hydrazino group of the latter with conservation of the carboxy group and without elimination of SO_2, and the product was 3-(2-sulfinylhydrazino)benzoic acid $OSNNHC_6H_4CO_2H$.

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Reactions of *N*-sulfinylamines RN=S=O and fluorine-containing heterocumulenes, such as $R_FSO_2N=S=O$, $C_6F_5N=S=O$, and $R_FSO_2N=C=O$, with aromatic aldehydes [1, 2], dimethylformamide [2], and carboxylic acids [3] have been extensively studied, and they are widely used in organic synthesis [1–8]. These reactions are accompanied by elimination of SO_2 or CO_2, and the products have the general formula RN=Y where Y = CHAr, $CHNMe_2$, or C(OH)R′, respectively. Reactions of *N*-sulfinylperfluoroalkanesulfonamides with carboxylic acids, followed by prototropic tautomerization, yield mixed carboxylic sulfonic acid imides $R_FSO_2NHC(O)R'$. *N*-Sulfinylamines and *N*-sulfinylperfluoroalkanesulfonamides react with carboxylic acids in the presence of HCl or $SOCl_2$ [3–5] as catalyst on prolonged heating at 150–160°C [3].

The conditions of the reactions of heterocumulenes with carboxylic acids strongly depend on the acidity of the latter. For example, fluorosulfonyl isocyanate FSO_2NCO reacts with acetic and chloroacetic acids with heat evolution, and the yield reaches 94%, whereas the reactions with stronger di- and trichloroacetic acids require prolonged heating, and the yield decreases to 50 and 21%, respectively [6]. *N*-Sulfinylperfluoroalkanesulfonamides also react with acetic acid under milder conditions (60°C) than with stronger benzoic acids (150–160°C) [3]. Reactions of only acetic, benzoic, and *p*-iodobenzoic acids with *N*-sulfinylperfluoroalkanesulfonamides have been reported [3]. In the present work we examined the behavior of *N*-sulfinyltrifluoromethanesulfonamide (CF_3SO_2NSO, **I**) with other functionally substituted, as well as with strong polyhalogenated, carboxylic acids, namely phenylacetic (**II**), diphenylacetic (**III**), salicylic (**IV**), cinnamic (**V**), 3-hydrazinobenzoic (**VI**), trichloroacetic, pentafluoropropionic, and perfluorononanoic (perfluoropelargonic) acids.

Acids **II** and **III** smoothly reacted with compound **I** at room temperature with formation of the corresponding *N*-acyltrifluoromethanesulfonamides **VII** and **VIII** in nearly quantitative yield (Scheme 1).

Scheme 1.

$CF_3SO_2N=S=O$ (**I**) + PhCHXCOOH (**II**, **III**) → ($-SO_2$) $CF_3SO_2NHC(O)CHXPh$ (**VII**, **VIII**)

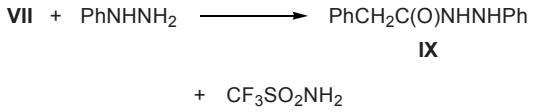
II, **VII**, X = H; **III**, **VIII**, X = Ph.

The product structure was proved by elemental analysis, IR spectroscopy (NHCO stretching vibration band at 1720 cm^{-1}), and ^1H (δ_{NH} 8.2–8.3 ppm) and ^{13}C NMR ($\delta_{C=O}$ 170 ppm). Addition of a catalytic amount of thionyl chloride strongly accelerates the process: for example, the reaction time for phenylacetic acid (**II**) shortens from 6 h to 10 min.

The reaction of compound **VII** with phenylhydrazine involved cleavage of the N–C bond and replace-

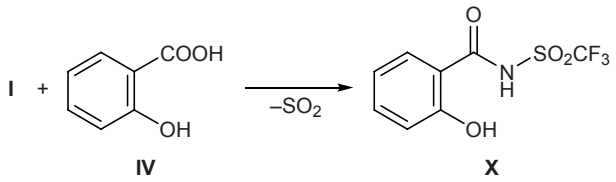
ment of the trifluoromethanesulfonamide group by the phenylhydrazine residue (Scheme 2). The reaction was carried out in methylene chloride at –40°C, and the yields of trifluoromethanesulfonamide and *N*′-phenyl-(phenyl)acetohydrazide (**IX**) were quantitative; compound **IX** thus obtained was identical to a sample described in [9].

Scheme 2.



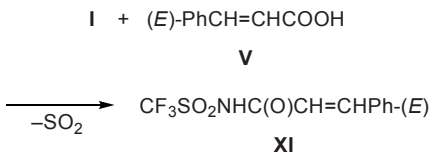
We previously showed that, despite easy addition of proton donors to heterocumulenes, the hydroxy group in salicylaldehyde does not disappear in the reaction with compound **I**, which occurs only at the aldehyde group [2]. Likewise, i.e., with conservation of the hydroxy group, salicylic acid (**IV**) reacted with compound **I** (Scheme 3). The ^{1}H NMR spectrum of product **X** contained two broadened downfield singlets with equal intensities, which were assigned to the OH and NH protons.

Scheme 3.



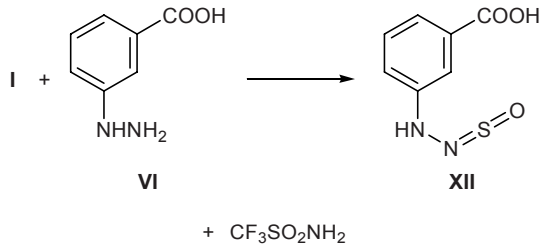
Cinnamic acid (**V**) reacted with *N*-sulfinyltrifluoromethanesulfonamide (**I**) to afford trifluoro-*N*-[(2*E*)-3-phenylprop-2-enoyl]methanesulfonamide (**XI**) (Scheme 4). Here, the double bond remained intact: in the ^{1}H NMR spectrum of the product we observed two doublets from vinylic protons at δ 6.45 and 7.27 ppm (J = 15.6 Hz).

Scheme 4.



Unexpected results were obtained in the reaction of compound **I** with 3-hydrazinobenzoic acid (**VI**). Unlike published data [3] and the above described reactions (Schemes 1, 3, and 4) where mixed trifluoromethanesulfonic and carboxylic acid imides $CF_3SO_2NHC(O)R'$ were formed, the reaction of **I** with hydrazino acid **VI** did not involve the carboxy group (according to the ^{1}H and ^{13}C NMR and mass spectra). The elemental analysis of the product showed the absence of fluorine, and it was assigned the structure of 3-(2-sulfinylhydrazino)benzoic acid (**XII**) (Scheme 5).

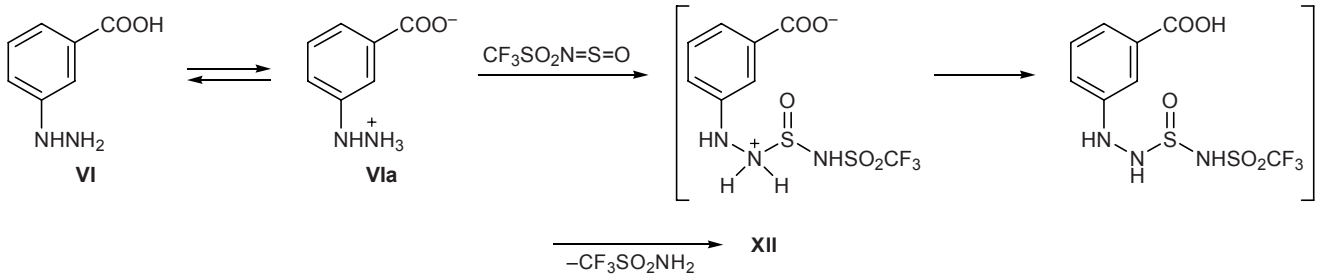
Scheme 5.



The second product formed in this reaction was trifluoromethanesulfonamide, which was separated from compound **XII** by recrystallization from ethanol. The mass spectrum of **XII** contained the molecular ion peak with m/z 198, and its fragmentation pattern was consistent with the assumed structure. Compound **XII** displayed in the ^{1}H NMR spectrum signals from four aromatic protons and downfield signals from protons of the COOH and NH groups at δ 13.0 and 12.8 ppm, respectively. In the ^{13}C NMR spectrum of **XII** we observed signals from aromatic carbon atoms and carboxy group, while no CF_3 signal was present. The ^{1}H signal at δ 13 ppm disappeared upon addition of D_2O (simultaneously, a signal from water appeared at about δ 4.8 ppm). In going from acid **VI** to compound **XII**, the signal from the carboxy carbon atom almost did not change its position, whereas the C^3 signal displaced upfield by 10.5 ppm, indicating that the reaction involved the hydrazine fragment rather than the carboxy group.

Unusual behavior of 3-hydrazinobenzoic acid (**VI**) toward *N*-sulfinyltrifluoromethanesulfonamide is likely related to specificity of its structure. The IR spectrum of a crystalline sample of **VI** contains absorption bands at 2000–3000 cm^{-1} due to stretching vibrations of the NH_3^+ group and at 1360 cm^{-1} due to stretching vibrations of the carboxylate group. The ^{1}H NMR spectrum of acid **VI** in DMSO-d_6 lacks signal assignable to COOH group, but broadened signals from NH (δ 6.9 ppm, 1H) and NH_3^+ groups (δ 3.5 ppm, 3H) were present. These data suggest that 3-hydrazinobenzoic acid in crystal and in solution exists as zwitterion **VIa**. Presumably, the reaction occurs as addition of the hydrazinium fragment in the zwitterionic form of acid **VIa** at the N=S bond of heterocumulene **I**,

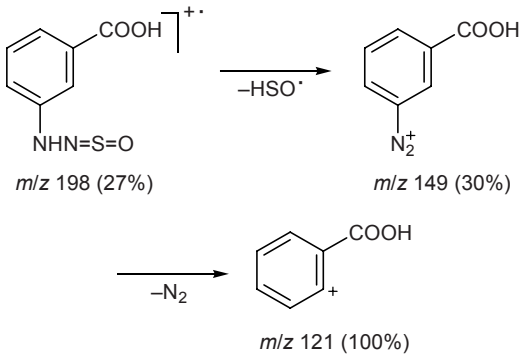
Scheme 6.



followed by elimination of trifluoromethanesulfonamide molecule from the adduct (Scheme 6).

Decomposition of the molecular ion of **XII** under electron impact involves elimination of HSO$^{\cdot}$ radical and subsequent elimination of nitrogen molecule from the diazonium ion thus formed (Scheme 7).

Scheme 7.



Compound **XII** is fairly stable, and it does not undergo hydrolysis to initial acid **VI** even on recrystallization from aqueous ethanol. *N*-Sulfinyl derivatives **XII** and **I** show different reactivities toward nucleophiles since the N=S=O heterocumulene fragment in the latter is linked to one of the strongest electron-withdrawing groups, CF_3SO_2, which sharply facilitates hydrolysis of compound **I**. By contrast, the N=S=O fragment in **XII** is contiguous to the NH group, and conjugation with unshared electron pair on the NH nitrogen atom hampers nucleophilic attack on the N=S=O group.

We have found no published data on *N*-sulfinyl-substituted hydrazines or their analogs having an N–N=X=Y moiety. Therefore, the reaction of 3-hydrazinobenzoic acid (**VI**) with compound **I** may be regarded as the first example of reactions of *N*-sulfinylsulfonamides with hydrazines, and compound **XII**, as the first representative of hydrazine heterocumulenes.

We failed to obtain products of reactions of *N*-sulfinyltrifluoromethanesulfonamide (**I**) with polyhalogenated carboxylic acids. Obviously, the reason is reduction of the reactivity of acids with rise in their acidity. No reaction occurred between compound **I** and trichloroacetic acid at room temperature even in the presence of thionyl chloride, whereas prolonged heating of the reaction mixture resulted in strong tarring. The only fact indicating formation of expected *N*-(2,2,2-trichloroacetyl)trifluoromethanesulfonamide $CF_3SO_2NHCOCCl_3$ was the presence in the ^{19}F NMR spectrum of the reaction mixture of a signal at δ_F –76 ppm, i.e., in the region typical of analogous compounds **VII**, **VIII**, **X**, and **XI**. According to the NMR data, no mixed trifluoromethanesulfonic and carboxylic acid imides were formed when compound **I** was heated with pentafluoropropionic or perfluorononanoic acid with *N*-sulfinyl amide **I** at the boiling point over a period of 1 h in the presence of thionyl chloride.

EXPERIMENTAL

The IR spectra were recorded in mineral oil or KBr on an IKS-29 spectrometer. The mass spectra (electron impact, 70 eV) were obtained on a TRACE DSQ II GC–MS system (Thermo); samples were injected as dispersions in DMSO. The NMR spectra were measured on a Bruker DPX-400 instrument at 400 (^1H), 100 (^{13}C), and 376 MHz (^{19}F); the chemical shifts were determined relative to tetramethylsilane (^1H, ^{13}C) and trichlorofluoromethane (^{19}F).

Trifluoro-*N*-(phenylacetyl)methanesulfonamide (VII). *a*. Phenylacetic acid (**II**), 0.27 g (2 mmol), was added to 0.78 g (4 mmol) of compound **I**, the mixture was stirred for 6 h at room temperature until it crystallized completely, kept for 16 h more, and evaporated to dryness. Yield 0.50 g (94%), mp 129°C. IR spectrum, ν, cm^{-1}: 3200, 1720, 1440, 1400, 1390, 1240, 1200, 1180, 1140, 880, 700, 600, 490. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.77 s (2H, CH_2), 7.36–7.23 m (5H, H_{arom}), 8.21 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$),

δ_C, ppm: 43.56 (CH_2), 120.68 q (CF_3, $^1J_{CF}$ = 318.0 Hz), 128.50 (C^m), 129.35 (C^p), 129.49 (C^o), 131.09 (C^1), 168.07 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.31 ppm. Found, %: C 39.96; H 3.25; F 21.90; N 5.37; S 12.39. $C_9H_8F_3NO_3S$. Calculated, %: C 40.45; H 3.02; F 21.33; N 5.24; S 12.00.

b. The reaction was carried out as described above but with addition of 0.1 ml of thionyl chloride. The mixture was stirred for 10 min at room temperature. Yield 0.50 g (94%).

***N*-(2,2-Diphenylacetyl)trifluoromethanesulfonamide (VIII)** was obtained from 0.39 g (2 mmol) of compound **I** and 0.21 g (1 mmol) of diphenylacetic acid (**III**) according to method *b*. Yield 0.31 g (91%), mp 120°C. IR spectrum, ν, cm^{-1}: 3150, 1720, 1460, 1390, 1240, 1200, 1140, 1090, 890, 690, 590. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.01 s (1H, CH), 7.19–7.32 m (10H, H_{arom}), 8.32 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 59.01 (CH), 119.04 q (CF_3, $^1J_{CF}$ = 322.4 Hz), 128.31 (C^m), 128.68 (C^p), 129.19 (C^o), 135.89 (C^1), 169.28 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F –75.38 ppm. Found, %: C 52.38; H 3.51; N 4.28; S 10.02. $C_{15}H_{12}F_3NO_3S$. Calculated, %: C 52.48; H 3.52; N 4.08; S 9.34.

***N*′-Phenyl(phenyl)acetohydrazide (IX).** A solution of 0.24 g (0.89 mmol) of compound **VII** in 2 ml of methylene chloride was cooled to –40°C, a solution of 0.096 g (0.89 mmol) of phenylhydrazine in 2 ml of methylene chloride was added dropwise under stirring, and the mixture was stirred for 15 min at that temperature and was left overnight at –12°C. The white precipitate was filtered off and dried. Yield 0.07 g (35%), mp 175–176°C; published data [9]: mp 175°C. The filtrate was treated with cold methylene chloride, and the precipitate of *N*-trifluoromethanesulfonamide, 0.13 g (100%), was filtered off. Evaporation of the filtrate gave an additional 0.13 g (65%) of compound **IX**. Overall yield 0.20 g (100%). IR spectrum, ν, cm^{-1}: 3280, 3200, 3030, 1660–1640, 1600, 1490, 960, 740, 680. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.49 s (2H, CH_2), 6.66 m, (3H, *o*-H and *p*-H in PhNH), 7.09 t, (2H, *m*-H in PhNH, *J* = 7.8 Hz), 7.32 m (4H, *o*-H and *m*-H in PhC), 7.24 m (1H, *p*-H in PhC), 7.73 s (1H, N**H**Ph), 9.86 s (1H, NHCO). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 40.46 (CH_2), 112.03 (C^o in NPh), 118.43 (C^p in NPh), 126.48 (C^p in PhC), 128.24 (C^m in NPh), 128.62 (C^o in PhC), 128.98 (C^m in PhC), 135.90 (C^1 in PhC), 149.27 (C^1 in NPh), 169.92 (C=O).

Trifluoro-*N*-(2-hydroxybenzoyl)methanesulfonamide (X). A mixture of 0.49 g (2.5 mmol) of compound **I**, 0.28 g (2 mmol) of salicylic acid (**IV**), and 0.05 ml of thionyl chloride was stirred for 1 h at 60–80°C and left overnight. It was then evaporated to dryness, and trifluoromethanesulfonamide was removed by sublimation. Yield of **X** 0.44 g (75%), mp 132°C. IR spectrum, ν, cm^{-1}: 3400, 3200, 1680, 1605, 1470–1440, 1380, 1240, 1210, 1190, 1130, 880, 740, 600, 490. ^1H NMR spectrum ($CDCl_3$–CD_3CN), δ, ppm: 6.96 m (2H, 3-H, 5-H), 7.47 t (1H, 4-H, *J* = 7.7 Hz), 7.80 d (1H, 6-H, *J* = 7.7 Hz), 9.85 br.s (1H, NH), 10.55 br.s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$–CD_3CN), δ_C, ppm: 113.97 (C^1), 117.82 (C^3), 119.20 q (CF_3, *J* = 322.1 Hz), 120.51 (C^5), 130.11 (C^6), 136.65 (C^4), 159.07 (C^2), 165.11 (C=O). ^{19}F NMR spectrum ($CDCl_3$–CD_3CN): δ_F –75.41 ppm. Found, %: C 36.39; H 2.39; N 5.05; S 11.63. $C_8H_6F_3NO_4S$. Calculated, %: C 35.69; H 2.25; N 5.20; S 11.91.

Trifluoro-*N*-[(2*E*)-3-phenylprop-2-enoyl]-methanesulfonamide (XI). A mixture of 0.39 g (2 mmol) of compound **I** and 0.15 g (1 mmol) of cinnamic acid (**V**) was stirred for 1 h at room temperature and left overnight. The mixture was treated with anhydrous diethyl ether, the precipitate of trifluoromethanesulfonamide was separated, and the filtrate was evaporated to dryness. Yield 0.24 g (86%), mp 165°C. IR spectrum, ν, cm^{-1}: 3190, 1700, 1620, 1440, 1380, 1240, 1200, 1140, 1095, 870, 760, 600. ^1H NMR spectrum ($CDCl_3$–CD_3CN), δ, ppm: 6.45 d (1H, =CHCO, *J* = 15.6 Hz), 7.34 m (3H, *m*-H, *p*-H), 7.47 m (2H, *o*-H), 7.72 d (1H, PhC**H**=, *J* = 15.6 Hz), 9.77 s (1H, SO_2NH). ^{13}C NMR spectrum ($CDCl_3$–CD_3CN), δ_C, ppm: 116.19 (=C**H**CO), 118.75 q (CF_3, $^1J_{CF}$ = 321.6 Hz), 128.09 (C^o), 128.58 (C^m), 130.90 (C^p), 132.94 (C^1), 147.05 (Ph**C**H=), 161.99 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.52 ppm. Found, %: C 43.05; H 2.87; N 5.22; S 10.94. $C_{10}H_8F_3NO_3S$. Calculated, %: C 43.01; H 2.89; N 5.02; S 11.48.

3-Hydrazinobenzoic acid (VI). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.51 br.s (3H, NH_3^+), 6.92 br.s (1H, NH), 6.97 d (1H, 4-H, *J* = 7.4 Hz), 7.16 m (2H, 5-H, 6-H), 7.38 s (1H, 2-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 112.23 (C^4), 115.76 (C^2), 117.73 (C^6), 128.64 (C^5), 131.27 (C^1), 152.54 (C^3), 168.05 (C=O).

3-(2-Sulfinylhydrazino)benzoic acid (XII). A solution of 0.30 g (2 mmol) of 3-hydrazinobenzoic acid (**VI**) in 2 ml of methylene chloride was cooled to

–78°C, a solution of 0.49 g (2.5 mmol) of compound **I** in 2 ml of methylene chloride was added dropwise under stirring, the mixture was stirred for 15 min at –40°C, left overnight at –12°C, and evaporated to dryness, and the residue was recrystallized from ethanol. Yield 0.25 g (62%), sublimes at 230°C. IR spectrum, ν, cm^{-1}: 3420 (OH), 3194 (NH), 1684 (C=O), 1592, 1524, 1273, 1200, 1082. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.48 t (1H, 5-H, J = 7.8 Hz), 7.61 m (2H, 4-H, 6-H), 7.94 s (1H, 2-H), 12.81 s (1H, NH), 13.03 br.s (1H, COOH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 115.24 (C^4), 118.76 (C^2), 124.15 (C^6), 129.72 (C^5), 132.06 (C^1), 142.00 (C^3), 166.83 (COOH). Mass spectrum, m/z (I_{rel}, %): 198 (27) $[M]^+$, 149 (30) [M – HSO], 121 (100) [149 – N_2]. Found, %: C 42.04; H 2.85; N 13.87; S 16.01. $C_7H_6N_2O_3S$. Calculated, %: C 42.42; H 3.05; N 14.13; S 16.18.

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