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2-Benzothiazolyl-*N*-(arenesulfonyl)-sulfinimidoyl Fluorides

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ABSTRACT: *2-Benzothiazolyl-N-(arenesulfonyl)-sulfinimidoyl fluorides were synthesized by the treatment of benzothiazolyl-2-sulfur trifluoride with sulfonamides. The reaction of 2-benzothiazolyl-N-(p-toluenesulfonyl)-sulfinimidoyl fluoride with tert-butylamine and morpholine gave 2-benzothiazolyl-N-(arenesulfonyl)-sulfinimidoyl amides. The reaction of 2-benzothiazolyl-N-(p-toluenesulfonyl)-sulfinimidoyl fluoride or 2-benzothiazolyl-^{15}N-(p-tosyl)sulfinimidoyl fluoride with S-trimethylsilylbenzenethiol gave di(benzothiazolyl-2) disulfide, fluorotrimethylsilane and N,N′-bis(p-toluenesulfonyl)-N,N′-bis(phenylthio)-hydrazine or ^{15}N,^{15}N′-bis(p-toluenesulfonyl)-^{15}N,^{15}N′-bis(phenylthio)-hydrazine, respectively.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:352–356, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20102

INTRODUCTION

A characteristic feature of present synthetic organic sulfur chemistry is the development of iminoanalogs of oxysulfur compounds in various valency, containing S=N multiple bond. The replacement of an oxygen atom in the group S=O for NR results in a wide change of structural and chemical properties depending of the radical R [1–7].

The derivatives of sulfinimidoyl acids R—S(X)=NR (X = Hlg, OR, NR_2) are a most investigated class of sulfur iminoderivatives. First of all, these are sulfinimidoyl chlorides, which are prepared by the reaction of divalent sulfur compounds with *N*-chlorocompounds or chlorine [5]. Sulfinimidoyl fluorides are practically unexplored compounds that, apparently, are connected with the absence of convenient methods of their preparation. The known syntheses of sulfinimidoyl fluorides are based on the use of remote and toxic reagents: perfluoroalkens [8], thiazyl fluoride [9], fluorine [10–12], trifluoromethylsulfur trifluoride [12–14] and these methods result only in perfluorosulfinimidoyl fluorides.

In this work we report about the synthesis and some chemical properties of the first representatives of heterocyclic sulfinimidoyl fluorides, namely 2-benzothiazolyl-*N*-(arenesulfonyl)-sulfinimidoyl fluorides.

RESULTS AND DISCUSSION

Earlier, a convenient preparation of the benzothiazolyl-2-sulfur trifluoride **1** was developed. This method consists in the reaction of di(benzothiazolyl-2) disulfide **2** with chlorine in the presence of excess potassium fluoride [15]. It allowed to avoid the use of fluorine or silver difluoride, which were usually used for aryl- and perfluoroalkylsulfur trifluoride synthesis [16–18].

Dedicated to Professor Alfred Schmidpeter on the occasion of his 75th birthday.

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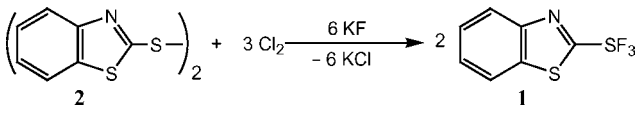
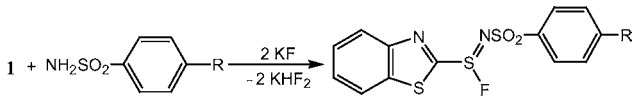


2 **1**

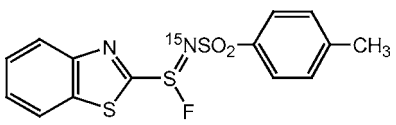
We have found that **1** reacts with benzenesulfonamides in the presence of potassium fluoride as an acceptor of hydrogen fluoride. As a result 2-benzothiazolyl-*N*-(arenesulfonyl)-sulfinimidoyl fluorides **3a–c** were obtained.



3, R = H (**a**), Me (**b**), Cl (**c**)

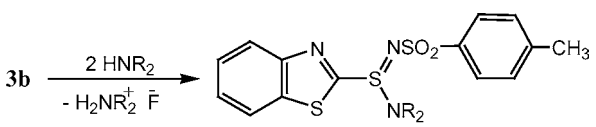
The reaction proceeds at mixing of the reagents in acetonitrile at 20°C. The yields of **3a–c** are 60–65%. Compounds **3a–c** are crystal substances which are easily hydrolyzed. They are stable at room temperature and decompose at melting point. They are soluble in chloroform, acetonitrile, benzene, toluene, and practically insoluble in ether, petroleum ether, and hexane. The structure of **3a–c** was established by their ^{1}H,^{19}F NMR, IR, and mass-spectral data. The signals of **3a–c** are observed in the ^{19}F NMR spectra at δ = 2–5 ppm (relative to CCl_3F). An intense absorption is observed at 1070 cm^{-1} in the IR spectra.

The use of *p*-toluenesulfonamide with the isotope ^{15}N in this reaction has allowed to prepare **3b***. The comparison of the IR-spectra of the compounds **3b** and **3b*** unambiguously allowed to assign the absorption at 1070 cm^{-1} to the N=S group (see the Experimental section).



3b*

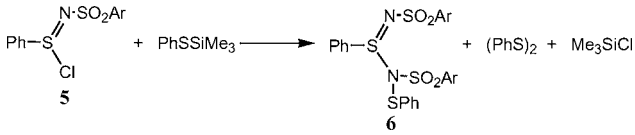
As a rule, the known sulfinimidoyl chlorides easily react with amines with the formation of sulfinimidoyl amides [19]. Similarly **3b** form **4a,b** by the reactions with tert-butylamine and morpholine. The excess of amine was used as the acceptor of hydrogen fluoride.



4a NR_2 = $NHCMe_3$

4b NR_2 = $N(C_2H_4)_2O$

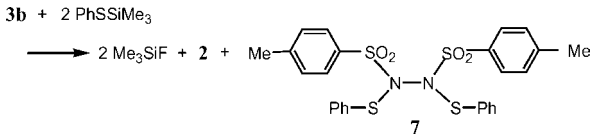
The reaction of **3** with *S*-trimethylsilylbenzenethiol was of great interest for us. It is known [20–22] that the reactions of sulfinimidoyl chlorides with benzenethiol or *S*-trimethylsilylbenzenethiol do not result in thioethers as the products of the chlorine replacement products for arylthio-group. For example, the mixture of sulfinimidoyl amide **6** and disulfide was formed in the reaction of chloride **5** with *S*-trimethylsilylbenzenethiol [21,22].



5 **6**

The formation of **6** allows to assume the course of the reaction on halogenophilic mechanism. The positive character of chlorine in the molecules of sulfinimidoyl chlorides was discussed [23]. The use of sulfinimidoyl fluorides in the reaction with *S*-trimethylsilylbenzenethiol allowed to exclude the course of the reaction on halogenophilic mechanism.

It appeared that the reaction of **3b** with *S*-trimethylsilylbenzenethiol proceeds at room temperature with separation of fluorotrimethylsilane and formation of **2** and *N*,*N*′-bis(*p*-toluenesulfonyl)-*N*,*N*′-bis(phenylthio)-hydrazine **7**.

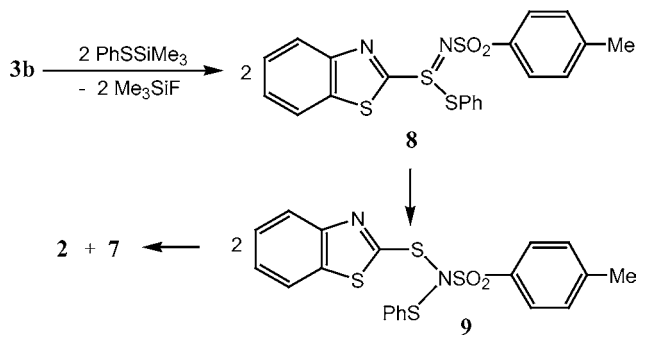


7

The structure of the **7** was established on the basis of the ^{1}H, ^{13}C NMR spectra and also the comparison of its IR spectrum with that of the ^{15}N derivative **7***, prepared from fluoride **3b***.

The absorption of 1070 cm^{-1} characteristic for S=N group is absent in the IR spectrum of the **7**. ^{1}H, ^{13}C NMR spectra of **7** and ^{15}N NMR of **7*** confirm the symmetric structure. The fact that *m/e* peak, which corresponds to the half of the molecular weight, is observed in the mass-spectrum of **7** also confirm the symmetrical structure. The spectral pictures would be more complex if **7** had a structure similar to **6**.

We can propose the following scheme of the reaction based on the structure of the obtained products. Sulfinimidoyl thiophenyl **8** which is formed on the first stage of the reaction transforms to sulfonamide **9**. It is known that the compounds with the similar structure are unstable and easily undergo the homolytic break on N–S bond with subsequent symmetrization of radicals [24,25].



EXPERIMENTAL

The reactions of the substances sensitive to oxygen and air moisture were conducted in the atmosphere of dry argon. The solvents were dried by distillation with P_4O_{10}. ^1H, ^{19}F, ^{15}N, ^{13}C NMR spectra were recorded on a Varian VRX-300 spectrometer at 299.9, 282.2, 20.266, 75.429 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to TMS ($\delta_H = 0.00$) as the internal standard for hydrogen nuclei, $(CD_3)_2SO$ ($\delta_C = 39.52$) as the standard for carbon nuclei, C_6F_6 ($\delta_F = -162.9$) as the internal standard for fluorine nuclei, and $H_2NC(O)H$ ($\delta_N = 264.00$) as the standard for nitrogen nuclei. The mass spectra were obtained on a MX-1321 mass spectrometer. The spray-dried potassium fluoride was used. Evaporation of solutions and drying of compounds were conducted in 0.12 mmHg vacuum.

Starting Materials

Benzothiazolyl-2-sulfur trifluoride (**1**) was synthesized from **2** with chlorine in acetonitrile at the presence of excess potassium fluoride according to [15].

General Procedure for the Synthesis of **3a–c**

The solution of sulfonamide (13.43 mmol) in 15 mL of acetonitrile was added during 1 h to the mixture of **1** (3.00 g, 13.44 mmol) and KF (1.70 g, 29.30 mmol) in 25 mL of acetonitrile. The reaction mixture was stirred at room temperature. The precipitate was filtered, washed with 15 mL of acetonitrile, dried in vacuum and extracted with 30 mL of dry chloroform. The solvent was evaporated in vacuum. The residue is **3a–c**.

*2-Benzothiazolyl-N-(phenylsulfonyl)-sulfinimidoyl Fluoride (***3a***).* The solution of benzenesulfonamide (2.11 g) was added to the mixture of **1** and KF in acetonitrile. The reaction mixture was stirred during 12 h. Yield, 2.92 g (64%); mp 108–109°C (decomp.); ^{19}F NMR ($CDCl_3$): $\delta = 3.89$ (s, 1F); ^1H NMR ($CDCl_3$): $\delta = 7.52–7.67$ (m, 6H, Ar—H), 7.98–8.03 (m, 3H, Ar—H), 8.19–8.22 (m, 1H, Ar—H); IR (KBr): $\nu = 1075$ (S=N); MS: *m/z* (%) = 321 [(M^+—F), 5], 141 ($C_6H_5SO_2^+$, 43), 77 ($C_6H_5^+$, 100). Anal. Calcd for $C_{13}H_9FN_2O_2S_3$ (340.4): C, 45.87; H, 2.66; F, 5.58; N, 8.23; S, 28.26%. Found: C, 46.19; H, 2.73; F, 5.66; N, 8.30; S, 27.90%.

*2-Benzothiazolyl-N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (***3b***).* The solution of *p*-toluenesulfonamide (2.30 g) was added to the mixture of **1** and KF in acetonitrile. The reaction mixture was stirred during 48 h. Yield, 2.86 g (60%); mp 97–99°C (decomp.); ^{19}F NMR ($CDCl_3$): $\delta = 4.56$ (s, 1F); ^1H NMR ($CDCl_3$): $\delta = 2.49$ (s, 3H, CH_3), 7.34 (d, 2H, J(H.H) = 8.10 Hz, Ar—H), 7.59–7.68 (m, 2H, Ar—H), 7.89 (d, 2H, J(HH) = 8.70 Hz, Ar—H), 7.99–8.02 (m, 1H, Ar—H), 8.20–8.23 (m, 1H, Ar—H); IR (KBr): $\nu = 1070$ (S=N); MS: *m/z* (%) = 336 (M^+—F, 6), 155 [(4-$CH_3C_6H_4SO_2)^+$, 46], 91 [(4-$CH_3C_6H_4^+$), 100]. Anal. Calcd for $C_{14}H_{11}FN_2O_2S_3$ (354.4): C, 47.44; H, 3.13; F, 5.36; N, 7.90; S, 27.14%. Found: C, 47.34; H, 3.20; F, 5.23; N, 7.56; S, 27.20%.

*2-Benzothiazolyl-N-(p-chlorobenzenesulfonyl)-sulfinimidoyl Fluoride (***3c***).* The solution of *p*-chlorobenzenesulfonamide (1.80 g) was added to the mixture of **1** and KF in acetonitrile. The reaction mixture was stirred during 72 h. Yield, 1.87 g (53%); mp 115–117°C (decomp.). ^{19}F NMR ($CDCl_3$): $\delta = 2.79$ (s, 1F); ^1H NMR ($CDCl_3$): $\delta = 7.51–7.55$ (m, 2H, Ar—H), 7.61–7.70 (m, 2H, Ar—H), 7.93–7.98 (m, 2H, Ar—H), 8.01–8.04 (m, 1H, Ar—H), 8.22–8.25 (m, 1H, Ar—H); IR (KBr): $\nu = 1070$ (S=N); MS: (*m/z*, %) = 174 (4-$ClC_6H_4SO_2^+$, 23), 135 ($C_7H_3NS^+$, 100). Anal. Calcd for $C_{13}H_8ClFN_2O_2S_3$ (374.8): C, 41.65; H, 2.15; F, 5.07; N, 7.47; S, 25.66%. Found: C, 41.87; H, 1.83; F, 5.23; N, 7.55; S, 25.97%.

*2-Benzothiazolyl-^{15}N-(p-toluenesulfonyl)-sulfinimidoyl Fluoride (***3b****).* The solution of ^{15}N-*p*-toluenesulfonamide (2.31 g) was added to the mixture of **1** and KF in acetonitrile. The reaction mixture was stirred during 48 h. Yield, 1.62 g (34%); mp 97–98°C (decomp.). ^{19}F NMR ($CDCl_3$): $\delta = 4.51$ [d, $J(^{15}NF) = 41.39$ Гц]. ^1H NMR ($CDCl_3$): $\delta = 2.44$ (s, 3H, CH_3), 7.35 (d, 2H, J(HH) = 8.10 Hz, Ar—H), 7.60–7.69 (m, 2H, Ar—H), 7.90 (d, 2H, J(HH) = 8.40 Hz, Ar—H), 8.00–8.03 (m, 1H, Ar—H), 8.20–8.23 (m, 1H, Ar—H); IR (KBr): $\nu = 1045$ (S=N^{15}); MS: (*m/z*, %) = 337 (M^+—F, 1), 155 [(4-$CH_3C_6H_4SO_2)^+$, 36], 91 [(4-$CH_3C_6H_4^+$), 100]. Anal. Calcd for $C_{14}H_{11}FN^{15}NO_2S_3$ (355.4): C, 47.31; H, 3.12; F, 5.34; N, 8.16; S, 27.07%. Found: C, 47.34; H, 3.20; F, 5.23; N, 7.86; S, 27.20%.

General Procedure for the Synthesis of **4a,b**

The solution of amine in 10 mL of benzene was added during 0.5 h to the solution of **3b** (0.50 g, 1.41 mmol) in 25 mL of benzene. The reaction mixture was stirred at room temperature during 12 h. The precipitate was filtered, washed with 10 mL of benzene, dried in vacuum, washed with 50 mL of water and dried in vacuum. The residue is **4a,b**.

*2-Benzothiazolyl-N-(p-toluenesulfonyl)-sulfinimidoyl tert-Butylamide (***4a***).* The solution of tert-butylamine (0.20 g, 2.73 mmol) was added to the solution of **3b**. Yield, 0.45 g (80%); mp 181–183°C (decomp.). ^{1}H NMR ($CDCl_3$): $\delta = 1.49$ (s, 9H, CH_3), 2.30 (s, 3H, CH_3), 5.56 (s, 1H, NH), 7.07 (d, 2H, J(HH) = 8.10 Hz, Ar—H), 7.46–7.56 (m, 2H, Ar—H), 7.63 (d, 2H, J(HH) = 8.10 Hz, Ar—H), 7.91 (d, 2H, J(HH) = 7.81 Hz, Ar—H); MS: (*m/z*, %) = 321 [M^+—C_4H_9N—CH_3, 5], 166 [$(C_7H_4NS_2)^+$, 6], 155 [$(4\text{-}CH_3C_6H_4SO_2)^+$, 39], 135 [$(C_7H_4NS)^+$, 24], 91 [$(4\text{-}CH_3C_6H_4)^+$, 100]. Anal. Calcd for $C_{18}H_{21}N_3O_2S_3$. (407.6): C, 53.04; H, 5.19; N, 10.31; S, 23.60%. Found: C, 52.86; H, 5.25; N, 10.14; S, 23.45%.

*2-Benzothiazolyl-N-(p-toluenesulfonyl)-sulfinimidoyl Morpholide (***4b***).* The solution of morpholine (0.25 g, 2.87 mmol) was added to the solution of **3b**. Yield, 0.53 g (90%); *mp* 154–155°C (from methanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H, CH_3), 3.06 (dt, 2H, $J(HH)' = 12.00$ Hz, $J(HH)'' = 4.50$ Hz, CH_2), 3.39 (dt, 2H, $J(HH)' = 12.00$ Hz, $J(HH)'' = 4.50$ Hz, CH_2), 3.71 (t, 4H, $J(HH)'' = 4.50$ Hz, CH_2), 7.27 (d, 2H, J(HH) = 6.90 Hz, Ar—H), 7.50–7.61 (m, 2H, Ar—H), 7.87 (d, 2H, J(HH) = 8, 40 Hz, Ar—H), 7.96 (d, 1H, J(HH) = 7.20 Hz, Ar—H), 8.12 (d, 1H, J(HH) = 8.40 Hz, Ar—H); MS: (*m/z*, %) = 336 [M^+—C_4H_8NO, 8], 155 [$(4\text{-}CH_3C_6H_4SO_2)^+$, 20], 91 [$(4\text{-}CH_3C_6H_4)^+$, 65], 86 [$(C_4H_8NO)^+$, 100]. Anal. Calcd for $C_{18}H_{19}N_3O_3S_3$. (421.6): C, 51.28; H, 4.54; N, 9.97; S, 22.82%. Found: C, 51.30; H, 4.55; N, 10.14; S, 22.83%.

The Reaction of **3b** *with S-Trimethylsilylbenzenethiol*

The solution of *S*-trimethylsilylbenzenethiol (0.52 g, 2.86 mmol) in 5 mL acetonitrile was added dropwise with stirring to the solution of **3b** (1.00 g, 2.83 mmol) in 15 mL acetonitrile at room temperature. The reaction mixture was stirred at room temperature during 12 h. The precipitate of **2** was filtered, washed with 15 mL of acetonitrile, and dried in vacuum. Yield, 0.39 g (83%); mp 177–178°C [Lit. [26], 178–180°C]. The filtrate was evaporated in vacuum. 0.95 g of oily residue was treated with 10 mL ether; the formed crystals of **7** were filtered and dried in vacuum. Yield, 0.30 g (38%); mp 125–126°C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (s, 6H, CH_3), 7.14–7.23 (m, 10H, Ar—H), 7.47 (d, 4H, J(HH) = 7.50 Hz, Ar—H), 7.79 (d, 4H, J(HH) = 8, 10 Hz, Ar—H); ^{13}C NMR ($CDCl_3$): $\delta = 21.61$ (CH_3), 127.65 (Ar—C), 128.93 (Ar—C), 129.54 (Ar—C), 131.00 (Ar—C), 134.50 (Ar—C), 137.27 (Ar—C), 144.04 (Ar—C); MS: (*m/z*, %) = 279 (M^+/2, 23), 124 [$C_6H_5SN^+$, 100]. Anal. Calcd for $C_{26}H_{24}N_2O_4S_4$ (556.7): C, 56.09, H, 4.34; N, 5.03; S, 23.03%. Found: C, 56.28; H, 4.29; N, 5.09; S, 23.00%.

The Reaction of **3b*** *with S-Trimethylsilylbenzenethiol*

S-Trimethylsilylbenzenethiol (0.35 g, 19.19 mmol) was added dropwise with stirring to the solution of **3b*** (0.70 g, 1.97 mmol) in 15 mL of benzene at room temperature. The reaction mixture was stirred at room temperature during 12 h. The precipitate of **2** was filtered, washed with 5 mL of benzene, and dried in vacuum. Yield, 0.25 g (78%); mp 177–178°C (Lit. [26], 178–180°C). The filtrate was evaporated in vacuum. 0.58 g of oily residue was treated with 5 mL of ether; the formed crystals of **7*** were filtered and dried in vacuum. Yield, 0.13 g (24%); mp 125–127°C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (s, 6H, CH_3), 7.14–7.23 (m, 10H, Ar—H), 7.47 (d, 4H, J(HH) = 7.50 Hz, Ar—H), 7.79 (d, 4H, J(HH) = 8, 10 Hz, Ar—H); ^{15}N NMR (DMSO): $\delta = 330.00$; MS: (*m/z*, %) = 280 (M^+/2, 17), 124 [$C_6H_5SN^+$, 100]. Anal. Calcd for $C_{26}H_{24}{}^{15}N_2O_4S_4$ (558.7): C, 55.89; H, 4.33; N, 5.37; S, 22.95%. Found: C, 55.65; H, 4.02; N, 5.56; S, 23.01%.

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