Efficient synthesis of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl fluoride – the key agent in the preparation of compounds with superstrong electron-withdrawing groups and strong acidic properties

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N-(Trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl fluoride **4** was prepared by the oxidative fluorination of *N*-(trifluoromethylsulfinyl)trifluoromethanesulfonamides **3a**,**b** which are formed by the reaction of trifluoromethyltrimethylsilane with *N*-(sulfinyl)trifluoromethanesulfonamide in the presence of fluoride ions. Addition of MF to *N*-(sulfinyl)trifluoromethanesulfonamides affords the stable *N*-(fluorosulfinyl)trifluoromethanesulfonamides **2a**,**b**. Reaction of **4** with *N*-nucleophiles readily forms the corresponding amides **6**–**8**.

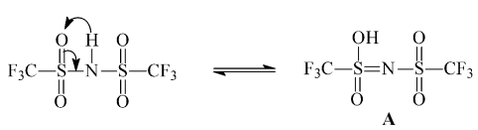
Introduction

The attractive physical and chemical properties of trifluoromethanesulfonic acid (Tf-OH) and its derivatives have led to a wealth of new compounds and applications in many fields of chemistry.[1] Recently, there has been a sustained interest in bis(perfluoroalkylsulfonyl)imides derivatives as Lewis acid catalysts, fluorination reagents of aromatic compounds, electrolytes for lithium batteries and fuel cells, and even as bioactive molecules.[2]

We have demonstrated with mono- and bis-*N*-(trifluoromethylsulfonylimino)-substituted aza analogs of arenesulfonyl halides that the replacement of the oxygen atom of sulfonyl halides by the $=NSO_2CF_3$ group leads to an impressive rise of the electron-withdrawing strength of these groups[3] and to uncommon reactivity of such halides.[4]

Bis(perfluoroalkylsulfonyl)imides are the strongest acids known to date. Gas phase acidity measurements have shown that the acidity of $(CF_3SO_2)_2NH$ is in excess of TfOH by 8 kcal mol^{-1} (~6 pK_a units).[3b] An explanation for the increased acidity of the NH-acid compared with the OH-acid is the possible existence of the tautomeric forms of $(CF_3SO_2)_2NH$ in which the proton is bonded to the oxygen atom (see structure **A**).

Examples of this type of tautomer have been observered with aryl- and trialkylsilyl ethers, prepared by direct arylation of the anion $^-N(SO_2CF_3)_2$ during pyrolysis of arenediazonium bis(trifluoromethylsulfonyl)amide[5] and *via* silylation of the NH-acid by silanes containing bulky groups.[6] However these compounds cannot be used as starting materials to obtain a variety of acid **A** derivatives. Therefore the obtention of *N*-(trifluoromethylsulfonylimino)trifluoromethanesulfonyl halides and amides, as precursors to the $CF_3S(O)=NSO_2CF_3$ (Tf-aza-triflyl group) appeared highly desirable.



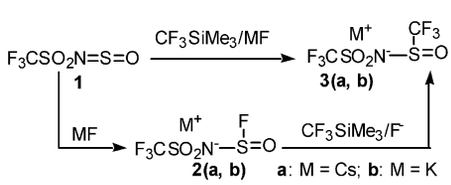
A

Results and discussion

For the synthesis of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl halides we initially tried the preparation of the corresponding *N*-(trifluoromethylsulfinyl)trifluoromethanesulfonamides derivatives and subsequent oxidation to the S(VI)-derivatives.

By addition of CsF, or KF, to the *N*-(sulfinyl)trifluoromethanesulfonamide **1**[7] the salts **2a**–**b** were prepared in quantitative yields. The salts **2a**–**b** are colourless crystals which are stable in an Ar-atmosphere at room temperature for a long time in contrast with $(R_F)N=S(O)F^-$ and $(SF_5)N=S(O)F^-$ anions,[8] probably due to the presence of stronger π-electron-withdrawing substituents on the nitrogen atom and the absence of the protogenic solvents in this reaction.

The salts **3a** and **3b** can be prepared by transformation of the S-bonded fluorine atom of salts **2a** and **2b** into CF_3 group *via* Ruppert's reagent or by direct addition of CF_3SiMe_3 to sulfonamide **1** in the presence of excess MF in THF at room temperature (Scheme 1).



Scheme 1 Preparation of salts **2a**–**b** and **3a**–**b**.

The best results were obtained with the following reagent ratio: **1**–MF–CF_3SiMe_3 = 1 : 2 : 1. Excess MF is needed to maintain the basic medium and to avoid the formation of side-products. The salts **3a** and **3b** were obtained in quantitative yield as colourless crystals. We have previously described an alternative method for preparation of the salt **3b**.[9]

Oxidative fluorination of sulfonamides, iminofluorosulfinates and sulfur difluoroimides with fluorine, xenon difluoride to the corresponding sulfur(VI) fluorides has been described

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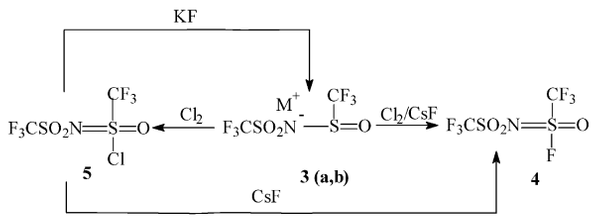
previously.[10] In this study, however, we have developed a novel method of oxidative fluorination of the *N*-(trifluoromethylsulfinyl)trifluoromethanesulfonamides **3a** and **3b** with chlorine in the presence of caesium fluorides in 70–75% yield (Scheme 2).



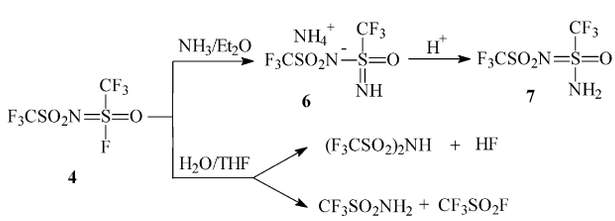
Scheme 2 Preparation of the fluoride **4** and chloride **5**.

The reaction path for this method is not simply an oxidation by chlorine, followed by chlorine ⟶ fluorine (Halex) substitution. The monitoring by ^{19}F NMR of the oxidative fluorination reaction also showed the absence of chloride **5** in the reaction mixture. Evidently, the reaction of the oxidative fluorination occurs *via* addition of two chlorine atoms, fast substitution of one chlorine atom for fluorine and then elimination of CsCl.

Chloride **5** has been obtained by the reaction of chlorine on salts **3a** and **3b**. The reactions of chloride **5** with such nucleophiles as ammonia, pyridine or KF led to its complete reduction, due to the positive nature of chlorine atom, forming salts similar to salts **3a** and **3b**. However, the reaction of chloride **5** with CsF without solvent at room temperature for 7 days led to the formation of fluoride **4** with 80% yield. This reaction can be explained in two ways: a) as slow formation of ClF at first followed by fast reaction with formed salt **3a**, starting chloride **5** or fluoride **4** and with partial decomposition; b) addition of CsF to the S=N double bond of chloride **5** with formation of an adduct that converts into fluoride **4** and CsCl.

N-(Trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl fluoride **4** is a colourless liquid which may be distilled at atmospheric pressure (bp 100 °C). It slowly undergoes hydrolysis (by action of water in THF solution at room temperature for a week) involving two reaction centres of the molecule at equal rates: through the S=N bond with the formation of trifluoromethanesulfonamide and trifluoromethanesulfonyl fluoride or through the S–F bond with formation of $(CF_3SO_2)_2NH$ and HF.

Fluoride **4** reacts with gaseous ammonia in Et_2O at −20 °C to form the ammonium salt of *N*-(trifluoromethylsulfonimidoyl)trifluoromethanesulfonamide **6** in quantitative yield (Scheme 3). Salt **6** is a hygroscopic colourless solid, soluble in Et_2O, THF, melting without decomposition (mp 116 °C).

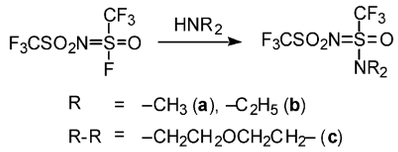


Scheme 3 Properties of fluoride **4**.

The aqueous solution of the salt **6**, when passed through an ion-exchange resin (Dowex 50 WX8–200) gives free *N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidamide **7** in 70% yield. This compound appears as colourless crystals that may be distilled *in vacuo* (bp 70 °C/0.4 mmHg).

The acidity of amide **7** has been calculated.[11] These calculations show that the deprotonation enthalpy (DPE) has a value of 293.5 kcal mol^{-1}, which is in excess of $TfNH_2$ by 23.5 kcal mol^{-1} (~16pK_a units). The physical and chemical properties of amide **7** are under investigation.

N-(Trifluoromethylsulfonyl)-*N*′,*N*′-(dialkyl)trifluoromethanesulfonimidamides **8a**–**c** were obtained by reaction of the fluoride with secondary amines in Et_2O at room temperature (Scheme 4).



Scheme 4 Preparation of amides **8(a–c)**.

Conclusion

In conclusion, to the best of our knowledge, this is the first report of the addition of CF_3SiMe_3 to a S=N bond of *N*-(sulfinyl)sulfonamide. We have developed an interestingly simple yet efficient method for the synthesis of the sulfonimidoyl fluorides $CF_3SO_2N{=}SO(CF_3)F$. This compound and the chlorine analogue are novel reagents, as exemplified by the formation of the amide derivative. We expect these compounds to serve as synthons for the introduction of the super attracting groups according to Yagupolskii's proposition.[3,4]

Experimental

General

All compounds were handled under a dry Ar atmosphere. THF was distilled from sodium benzophenone ketyl; Et_2O was distilled from $LiAlH_4$. CsF and KF were dried at 180 °C for 18 h. Chlorine was dried over P_2O_5.

^{1}H and ^{19}F spectra were recorded with a Varian VX-300 spectrometer at 299.8 and 282.2 MHz respectively with hexamethyldisiloxane (HMDS) and CCl_3F as standards. *N*-(Sulfinyl)trifluoromethanesulfonamide **1** was prepared as reported elsewhere.[7] Trifluoromethyltrimethylsilane was purchased from ABCR, Karlsruhe.

N-(Fluorosulfinyl)trifluoromethanesulfonamides of Cs (2a) and K (2b)

To a stirred suspension of 15 mmol MF in dry THF (10 ml), a solution of *N*-(sulfinyl)trifluoromethanesulfonamide **1** (3 g, 15 mmol) in THF (10 ml) was added slowly at 20 °C and stirred for 30 min at room temperature. THF was removed *in vacuo*. **2a**: ^{19}F NMR (THF): δ_F 67.4 (1F, s, SF), −79.78 (3F, s, CF_3); analytical data: $CsCF_4NO_3S_2$, calc.: C 3.47, N 4.03; found: C 3.09, N 3.77%; **2b**: ^{19}F NMR (THF): δ_F 67.0 (1F, s, SF), −79.62 (3F, s, CF_3); analytical data: $KCF_4NO_3S_2$ calc.: C 4.74, N 5.53; found: C 4.50, N 5.31%.

N-(Trifluoromethylsulfinyl)trifluoromethanesulfonamides of Cs (3a) and K (3b)

To a stirred suspension of 30 mmol MF in dry THF (10 ml), a solution of *N*-(sulfinyl)trifluoromethanesulfonamide **1** (3 g, 15 mmol) in THF (10 ml) was added slowly at 20 °C and stirred for 30 min at room temperature. THF then trifluoromethyltrimethylsilane (2.5 g, 17 mmol) were added dropwise at 20 °C. The mixture was stirred for 2 h, and the excess of MF was filtered off . The solvent was removed *in vacuo*. The salts can be recrystallised from THF, CH_3OH or H_2O. **3a**: ^{19}F NMR (THF): δ −79.50 (3F, s, CF_3), −82.19 (3F, s, CF_3); analytical data: $CsC_2F_6NO_3S_2$ calc.: C 6.04, N 3.53; found: C 5.74, N 3.38%; **3b**: ^{19}F NMR (THF): δ −79.20 (3F, s, CF_3), −81.0 (3F, s, CF_3).

N-(Trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl fluoride 4

N-(Sulfinyl)trifluoromethanesulfonamide **1** (1 equiv.) was slowly added dropwise to a suspension of CsF (2 equiv.) in

THF at 20 °C. The reaction mixture was stirred at room temperature for 0.5 h then CF_3SiMe_3 (1 equiv.) was slowly introduced. The reaction mixture was stirred at room temperature for 2 h. The reaction vessel was then connected to a vacuum line, THF was removed at room temperature and Cl_2 (1 equiv.) was condensed at −40 °C. The reaction mixture was allowed to warm to +20 °C over a period of 1 h and kept at this temperature during 1 h. The fluoride **4** was collected at −50 °C. Purification was accomplished by distillation at atmospheric pressure. Bp 110–111 °C **4**: ^{19}F NMR (THF): δ +46 (q, 1F, S–F, J = 17 Hz), −72.4 (d, 3F, CF_3, J = 17 Hz), −78.6 (s, 3F, CF_3); analytical data: $C_2F_7NO_3S_2$ calc.: C 8.48, N 4.95; found: C 8.83, N 5.02%.

N-(Trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl chloride 5

Cl_2 (20 mmol) was condensed onto dry salt **3a** and **3b** (10 mmol) in a Pyrex glass vessel equipped with a Kontes® PTFE stopcock at −50 °C. The reaction mixture was allowed to warm to +20 °C over a 2 h period and was kept at room temperature during 2 h. The reaction vessel was connected to a vacuum line, the volatile products were collected at −40 °C; bp 42–43 °C/12 mmHg. Yield: 65%. ^{19}F NMR (CH_2Cl_2): δ −73.20 (3F, s, CF_3), −78.40 (3F, s, CF_3); analytical data: $C_2ClF_6NO_3S_2$ calc.: C 8.01, N 4.67, Cl 11.85; found: C 7.90, N 4.55, Cl 11.7%.

Ammonium salt of the *N*-(trifluoromethylsulfonimidoyl)trifluoromethanesulfonamide 6

Fluoride **4** (3 g, 10.6 mmol) was dissolved in 30 ml of Et_2O and ammonia was bubbled through this solution at −20 °C for 30 min (until NH_4F-production had ceased). Compound **6** was removed by filtration, the solvent was distilled off *in vacuo*. **6**: ^{19}F NMR (D_2O): δ −80.0 (s, 3F, CF_3), −82.1 (s, 3F, CF_3); ^{1}H NMR ($(CD_3)_2SO$): δ 7.1 (s, 4H, NH_4^+), 4.6 (s, 1H, NH) analytical data: $C_2H_5F_6N_3O_3S_2$ calc.: C 8.08, N 14.14, H 1.68; found: C 8.40, N 14.01, H 2.04%.

N-(Trifluoromethylsulfonyl)trifluoromethanesulfonimidamide 7

The salt **6** was dissolved in minimum quantity of water and was passed through an ion-exchange resin (Dowex 50 WX8–200). Water was extracted with Et_2O, and the mixture was dried and concentrated. The product was distilled under high vacuum. **7**: mp 50 °C; Yield 60%; ^{19}F NMR (THF): δ −78.2 (s, 3F, CF_3), −79.2 (s, 3F, CF_3); ^{1}H NMR (CD_3CN): δ 7.88 (s, 2H, NH_2) analytical data: $C_2H_2F_6N_2O_3S_2$ calc.: C 8.57, N 10.0, H 0.71; found: C 8.53, N 9.97, H 0.70%.

N-(Trifluoromethylsulfonyl)-*N′*,*N′*-(dialkyl)trifluoromethanesulfonimidamide 8a–c

Fluoride **4** (3 g, 10.6 mmol) was dissolved in 30 ml of Et_2O and secondary amide (21.2 mmol) was added at room temperature under stirring. In 1 h the precipitate was removed, filtrate was distilled off, the residue was distilled for **8a**,**b** or recrystallised for **8c** from hexane. **8a**: Yield 78%; bp 150–151 °C; ^{19}F NMR (CH_2Cl_2): δ 75.2 (s, 3F, CF_3), −79.2 (s, 3F, CF_3); ^{1}H NMR ($CDCl_3$): δ 3.21 (s, 6H, CH_3); analytical data: $C_4H_6F_6N_2O_3S_2$ calc.: C 15.6, N 9.09, H 1.95; found: C 15.21, N 9.17, H 2.06%. **8b**: Yield 89%; bp 173–175 °C; ^{19}F NMR (CH_2Cl_2): δ 75.8 (s, 3F, CF_3), −79.1 (s, 3F, CF_3); ^{1}H NMR ($CDCl_3$): δ 1.39 (t, 6H, CH_3, J = 7 Hz), 3.8 (q, 4H, CH_2, J = 7 Hz); analytical data: $C_6H_{10}F_6N_2O_3S_2$ calc.: C 21.4, N 8.3, H 2.98; found: C 21.26, N 8.47, H 3.17%. **8c**: Yield 91%; mp 60–62 °C; ^{19}F NMR (CH_2Cl_2): δ −75.7 (s, 3F, CF_3), −79.4 (s, 3F, CF_3); ^{1}H NMR ($CDCl_3$): δ 3.5–3.7 (m, 4H, CH_2), 3.8–3.9 (m, 4H, CH_2); analytical data: $C_6H_8F_6N_2O_4S_2$ calc.: C 20.57, N 8.0, H 2.29; found: C 20.50, N 8.04, H 2.20%.

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