ELSEVIER

Journal of Fluorine Chemistry 115 (2002) 129–132

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

N-(Trifluoromethylsulfonyl)trifluoromethanesulfinimidic acid and its salts

Yurij L. Yagupolskii*, Andrej V. Bezdudnyi, Lev M. Yagupolskii

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 Murmanskaya Street, Kiev 02094, Ukraine

Received 23 November 2001; received in revised form 26 January 2002; accepted 26 January 2002

Abstract

Lithium, sodium and potassium *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidates were obtained by the reaction of the corresponding sulfinimidoyl chloride with alkali metal trimethylsilanolates. The potassium and sodium salts were converted to the free acid, having predominantly the amidic tautomeric structure, $CF_3S(O)NHSO_2CF_3$, by treatment with concentrated H_2SO_4 or with H^+-cationite.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidic acid; Alkali metal trimethylsilanolates; Tautomerism

1. Introduction

The replacement of an sp^2 oxygen atom (=O) by the group $=NSO_2CF_3$ in various substituents significantly raises the value of their σ constants which amount thereafter up to 1.4–1.75 [1,2]. Such substituents strongly affect the reactivity of compounds [3] and, in particular, their acidity [4,5]. For example, the acidity of *p*-toluenesulfonamide, after substitution of $=NSO_2CF_3$ groups for both oxygen atoms, grows by 25 pK_a units in the vapor phase and by 13 pK_a units in dimethyl sulfoxide [5]. In searching for novel superstrong acids, it is worthwhile to prepare and investigate more closely the analogs of very strong, by themselves, trifluoromethanesulfinic ($pK_a = 0.6$ [6]) and trifluoromethanesulfonic acids with oxygen atoms replaced by imino groups $=NSO_2CF_3$.

Only imidoyl chloride was reported out of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidic acid derivatives [7]. In the present work, we describe the synthesis of the indicated acid, its salts and some transformations of the compounds.

2. Results and discussion

Hydrolysis of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidoyl chloride (**1**), prepared by oxidative imination of bis(trifluoromethyl) disulfide with *N*,*N*-dichlorotrifluoromethanesulfonamide [7], gave a difficult-to-separate mixture of products from which we failed to isolate the corresponding free acid. For this reason, we prepared at first its alkali metal salts by reacting sulfinimidoyl chloride **1** with two equivalents of lithium, sodium or potassium trimethylsilanolate in dimethoxyethane (DME) (Scheme 1).

Salts **2a–c** are crystalline substances, resistant to atmospheric oxygen and moisture, soluble in polar solvents.

The sodium (**2b**) and potassium (**2c**) salts do not react with alkyl halides CH_3I or $C_6H_5CH_2Br$. The potassium salt was transformed into silver salt **2d** by treatment with $AgBF_4$ in methanol (Scheme 2).

The silver salt is methylated smoothly with methyl iodide at the nitrogen rather than at the oxygen atom (Scheme 3). In ^1H NMR spectrum, the product **3** displays a single signal at 2.17 ppm which corresponds to the $N–CH_3$ group. The structure of **3** was confirmed by the independent synthesis from trifluoromethanesulfinyl chloride and the *N*-sodium salt of *N*-methyltrifluoromethanesulfonamide (Scheme 3).

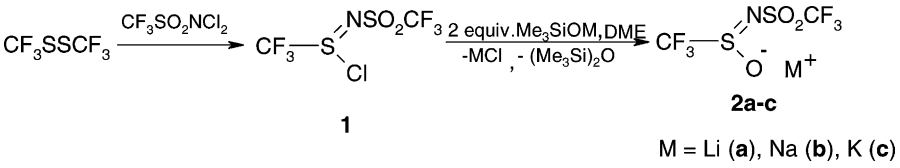
By reacting with tributyltin chloride in benzene, silver salt **2d** was converted into compound **4** (Scheme 4) whose ^{19}F NMR spectrum is very similar to those of salts **2a–c**. This finding confirms the salt structure of **4**.

Sodium salt **2b** was prepared also by another synthetic route, from trifluoromethanesulfinyl chloride and the *N*-sodium salt of *N*-(trimethylsilyl)trifluoromethanesulfonamide (Scheme 5). The samples of the sodium salt obtained by the two different methods are identical in properties.

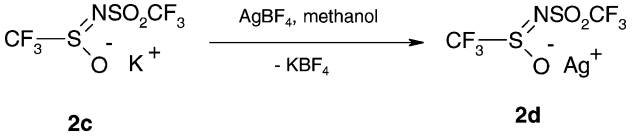
Free *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidic acid (**5**) was prepared by two methods—by passing aqueous solutions of its potassium or sodium salt through H^+-cationite DOWEX 50WX8-200 and by treatment of the potassium salt with concentrated sulfuric acid and

* Corresponding author. Tel.: +38-44-5510652; fax: +38-44-5436843.
E-mail address: yurii@fluor-ukr.kiew.ua (Y.L. Yagupolskii).

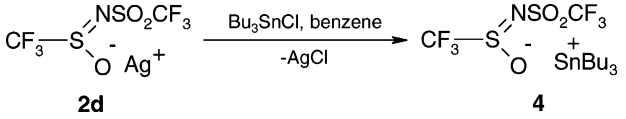
0022-1139/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-1139(02)00036-2



Scheme 1.



Scheme 2.



Scheme 4.

subsequent extraction of the acid with dichloromethane (Scheme 6).

In ^{1}H NMR spectra taken in $CDCl_3$ or $(CD_3)_2SO$ compound **5** shows a broadened singlet at 8.7 or 10.9 ppm which evidently belongs to a N–H proton because a H–O proton is expected to resonate in much lower field. In the IR spectrum of neat **5** there is observed an intense absorption band at 3380 cm^{-1} (ν_{NH}), but in CCl_4 solution a new band appears at 3080 cm^{-1} (ν_{OH}). Therefore, in accordance with the rules of tautomerism, acid **5** exists predominantly in the amidic form, that is, the proton is located at the less electronegative site, namely at the nitrogen rather than at the oxygen atom. However, for the anion of the acid, particularly in its salts, the contribution of the resonance structure with the negative charge localized on the oxygen far exceeds that of the nitrogen-centered anion.

3. Experimental

3.1. General

^{1}H and ^{19}F NMR spectra were recorded on a Varian XR-300 spectrometer (299.95 and 282.2 MHz) using TMS and CCl_3F as internal standards. All the reactions were carried out under anhydrous conditions with exclusion of atmospheric moisture.

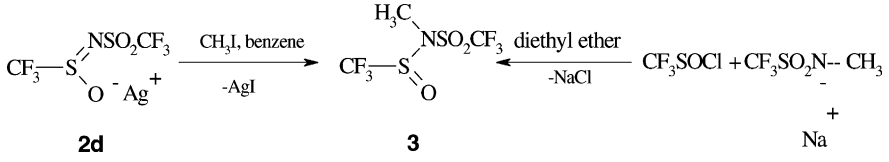
Alkali metal trimethylsilanolates were Aldrich products and were used as received. *N*-Sodium salts of *N*-methyltrifluoromethanesulfonamide [8,9] and *N*-(trimethylsilyl)-trifluoromethanesulfonamide [10] and trifluoromethanesulfinyl chloride [11] were prepared by the published methods.

3.2. Lithium N-(trifluoromethylsulfonyl)trifluoromethanesulfinimidate (*2a*)

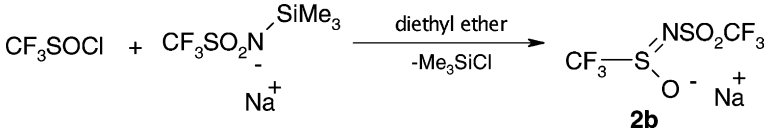
To a stirred solution of lithium trimethylsilanolate (0.19 g, 2 mmol) in 2 ml of DME was added dropwise, over 20 min, sulfinimidoyl chloride **1** [7] (0.28 g, 1 mmol) dissolved in 3 ml of DME. When the addition was complete, the mixture was stirred for a further 2 h and volatiles were removed in vacuum. The residue was extracted with diethyl ether (2× 10 ml). The extract was separated and concentrated. The solid product was washed with benzene (3 ml) and dried. Yield 0.22 g (81%).^{19}F NMR (DME) δ_F: −79.4 (s, CF_3), −80.4 (s, CF_3). Anal. calcd. for $C_2F_6LiNO_3S_2$: C, 8.86; N, 5.17. Found: C, 8.51; N, 5.02%.

3.3. Sodium N-(trifluoromethylsulfonyl)trifluoromethanesulfinimidate (*2b*)

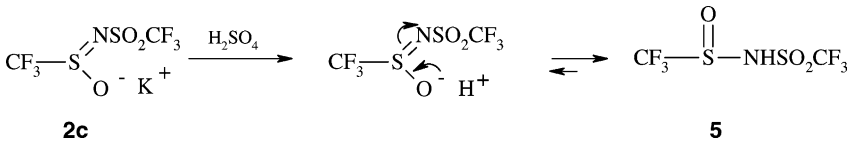
(A) In a three-necked flask fitted with a thermometer, dropping funnel, and a drying tube, a solution of sulfinimidoyl chloride **1** (14.2 g, 50 mmol) in 50 ml of DME was added, over 2 h, to a stirred and cooled to 0−5 °C solution of sodium trimethylsilanolate (11.2 g, 100 mmol) in 50 ml of DME at such a rate that the temperature of the reaction mixture was maintained at 20 °C. Stirring was continued for a further 2 h and the sodium chloride precipitated was filtered off. The solvent was evaporated under water-jet pump vacuum and the residue was stirred with benzene (60−80 ml) until crystals appeared. They were separated by filtration and dried in vacuum. Yield 12.48 g (87%), dec. 208−209 °C. ^{19}F NMR (DME) δ_F: −78.5 (s, CF_3),



Scheme 3.



Scheme 5.



Scheme 6.

−80.1 (s, CF_3). Anal. calcd. for $\tilde{N}_2F_6NNaO_3S_2$: C, 8.36; N, 4.88. Found: C, 8.41; N, 5.03%.

(B) To a stirred solution of the *N*-sodium salt of the *N*-(trimethylsilyl)trifluoromethanesulfonamide (0.5 g, 2 mmol) in 10 ml of diethyl ether was added dropwise a solution of trifluoromethanesulfinyl chloride (0.32 g, 2 mmol) in 5 ml of diethyl ether. The mixture was stirred for 1 h. After evaporation of the solvent, the residue was treated with benzene as above. Yield 0.38 g (65%).

*3.4. Potassium N-(trifluoromethylsulfonyl)trifluoromethanesulfinimidate (**2c**)*

Salt **2c** was prepared from potassium trimethylsilanolate (12.8 g, 100 mmol) and sulfinimidoyl chloride **1** (14.2 g, 50 mmol) by a procedure similar to that described for **2b** (Method A). Yield 11.5 g (76%), dec. 181−182 °C. ^{19}F NMR (DME) δ_F: −79.5 (s, CF_3), −80.9 (s, CF_3). Anal. calcd. for $C_2F_6KNO_3S_2$: C, 7.92; N, 4.62. Found: C, 8.07; N, 4.90%.

*3.5. Silver N-(trifluoromethylsulfonyl)trifluoromethanesulfinimidate (**2d**)*

To a solution of silver tetrafluoroborate (1.95 g, 11 mmol) in 20 ml of anhydrous methanol was added a solution of the potassium salt **2c** (3.2 g, 11 mmol) in 10 ml of the same solvent. The mixture was stirred for 1.5 h, then solids were removed by filtration, the filtrate was concentrated in vacuum and the product was extracted from the residue with diethyl ether. Yield 3.67 g (93%), dec. 162−164 °C. ^{19}F NMR (diethyl ether) δ_F: −78.8 (s, CF_3), −79.7 (s, CF_3). Anal. calcd. for $C_2AgF_6NO_3S_2$: C, 6.17; N, 3.50. Found: C, 6.45; N, 3.76%.

*3.6. N-Methyl-N-(trifluoromethylsulfinyl)trifluoromethanesulfonamide (**3**)*

(A) To a solution of silver salt **2d** (0.3 g, 0.8 mmol) in 5 ml of benzene was added methyl iodide (1.0 g, 7 mmol) and the mixture was stirred for 1 h. The solvent was evaporated in vacuum and the residue was crystallized from a 3:1 mixture of hexane and benzene. Yield 0.16 g (71%).

(B) To a suspension of the *N*-sodium salt of *N*-methyltrifluoromethanesulfonamide (0.61 g, 3.7 mmol) in 15 ml diethyl ether was added a solution of trifluoromethanesulfinyl chloride (0.58 g, 3.7 mmol) in 3 ml of diethyl ether. The mixture was stirred for 8 h, filtered and the filtrate was concentrated. The product was purified as above. Yield 0.63 g (60.5%), mp 83−84 °C. ^{1}H NMR ($CDCl_3$) δ: 2.17 (s, CH_3). ^{19}F NMR ($CDCl_3$) δ_F: −74.2 (s, CF_3), −76.0 (s, CF_3). Anal. calcd. for $C_3H_3F_6NO_3S_2$: C, 12.90; H, 1.07; N, 5.34. Found: C, 12.74; H, 0.96; N, 5.02%.

*3.7. Tributyltin N-(trifluoromethylsulfonyl)trifluoromethanesulfinimidate (**4**)*

To a solution of silver salt **2d** (0.4 g, 1.1 mmol) in 5 ml of benzene was added tributyltin chloride (0.35 g, 1.1 mmol) dissolved in 2 ml of benzene. The mixture was stirred for 1 h and filtered. The filtrate was evaporated in vacuum and the residue was washed with hexane and dried to give a viscous, undistillable in vacuum substance. Yield 0.54 g (90.4%). ^{1}H NMR ($CDCl_3$) δ: 0.83−0.90 (9H, m), 1.23−1.6 (18H, m). ^{19}F NMR ($CDCl_3$) δ_F: −78.9 (s, CF_3), −79.6 (s, CF_3). Anal. calcd. for $C_{14}H_{27}F_6NO_3S_2Sn$: C, 30.34; H, 4.88; N, 2.53. Found: C, 30.80; H, 5.03; N, 2.79%.

*3.8. N-(Trifluoromethylsulfonyl)trifluoromethanesulfinimidic acid (**5**)*

(A) To potassium salt **2c** (0.48 g, 1.6 mmol) was added 5 ml of concentrated sulfuric acid. The mixture was stirred for 2 h and extracted with dichloromethane (10 ml). The upper layer was separated and concentrated in vacuum to leave an oily substance. Yield 0.26 g (62%).

(B) A solution of **2b** (0.8 g) in 5 ml of water was passed through cationite DOWEX 50WX8−200 (20 g). The aqueous effluent was evaporated in vacuum. The product was extracted from the residue with diethyl

ether and dried under a high vacuum. Yield 0.41 g (55.6%). ^{1}H NMR δ: 8.7 (br.s, NH; in $CDCl_3$) or 10.9 (br.s, NH; in $(CD_3)_2SO$). ^{19}F NMR ($CDCl_3$) δ_F: −74.2 (s, CF_3), −75.8 (s, CF_3). IR (neat): ν 3380, 3290 (N–H) cm^{-1}. IR (CCl_4): ν 3380 (N–H), 3080 (HO) cm^{-1}.

Anal. calcd. for $C_2HF_6NO_3S_2$: C, 9.06; H, 0.38; N, 5.28. Found: C, 8.76; H, 0.60; N, 5.35%.

References

[1] L.M. Yagupolskii, Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents (in Russian), Naukova Dumka, Kiev, 1988.
[2] L.M. Yagupolskii, V.I. Popov, N.V. Pavlenko, I.I. Maletina, A.A. Mironova, R.Yu. Gavrilova, V.V. Orda, Zh. Org. Khim. 22 (1986) 2169–2173.
[3] L.M. Yagupolskii, S.V. Shelyazhenko, I.I. Maletina, V.N. Petrik, E.B. Rusanov, A.N. Chernega, Eur. J. Org. Chem. (2001) 1225–1233.
[4] I.A. Koppel, R.W. Taft, F. Anvia, S. Zhu, L. Hu, K. Sung, D.D. DesMarteau, L.M. Yagupolskii, Yu.L. Yagupolskii, N.V. Ignat'ev, N.V. Kondratenko, A.Y. Volkonskii, V.M. Vlasov, R. Notario, P. Maria, J. Am. Chem. Soc. 116 (1994) 3047–3057.
[5] I.A. Koppel, J. Koppel, I. Leito, I. Koppel, M. Mishima, L.M. Yagupolskii, J. Chem. Soc., Perkin Trans. 2 (2001) 229–232.
[6] S. Braverman, T. Pechenick, Y. Zafrani, Tetrahedron Lett. 42 (2001) 1391–1393.
[7] Yu.L. Yagupolskii, A. Haas, T.I. Savina, A.V. Bezdudnyi, L.M. Yagupolskii, Zh. Org. Khim. 35 (1999) 1802–1805.
[8] R.D. Trepka, J.K. Harrington, J.W. Belisle, J. Org. Chem. 39 (1974) 1094–1098.
[9] C. Guo, R.L. Kirchmeier, J.M. Shreeve, J. Fluorine Chem. 52 (1991) 29–36.
[10] D.D. Desmarteau, M. Wits, J. Fluorine Chem. 52 (1991) 7–12.
[11] H.W. Roesky, S. Tutkunkarder, Chem. Ber. 107 (1974) 508–517.