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Trifluoromethanesulfonylimides of arenehydroxamic acids and their aza Lossen rearrangement

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Dedicated to Professor Dr. Alois Haas on his 75th birthday.

Abstract

Trifluoromethanesulfonylimides of arenehydroxamic acids ArC(=NSO_2CF_3)NHOH (**1**), analogues of arenehydroxamic acids, in which sp^2 hybridized oxygen atom is replaced by the much stronger electron-withdrawing group =NSO_2CF_3, have been synthesized, and the abilities of these compounds to undergo transformations similar to the Lossen rearrangement have been studied.

At heating *O*-trimethylsilyl or *O*-tosyl derivatives of acids **1** rearrange to carbodiimides ArN=C=NSO_2CF_3 or products of their hydration, the corresponding carbamides. Interaction of acids **1** with sulfinyl chloride or phosphorus pentachloride results in formation of *N*-trifluoromethylsulfonyl-*N*′-arenechloroformamidines, ArNHC(Cl)=NSO_2CF_3, which were transformed into their morpholine derivatives and thus characterized.

Keywords: Hydroxamic acids; Rearrangements; X-ray structure; Formamidines

1. Introduction

Rearrangements of organic compounds via migration of a substituent with its electron pair from carbon atom to nitrogen atom are widely used in synthetic organic chemistry for preparation of isocyanates and amines from amides of carboxylic acids (Hofmann rearrangement), azides (Curtius), hydroxamic acids or their derivatives (Lossen), amides from oximes (Beckmann) [1].

We have found earlier that replacement of an sp^2-hybridized oxygen atom by the =NSO_2CF_3 group in various substituents enhances their electron-withdrawing power, resulting in a dramatic change in the properties of corresponding organic compounds, e.g., their acidity increases significantly [2,3], halogen atoms in the corresponding aromatic compounds become more active in reactions of nucleophilic substitution [4], and dyestuffs are coloured more intensively [5].

We have also established that the replacement of oxygen in the chloranhydride of a carboxylic acid by the =NSO_2CF_3 group enabled an aza-Curtius rearrangement to be carried out, and, in addition, to perform the reaction in more mild conditions. This rearrangement resulted in the formation of the carbodiimide RN=C=NSO_2CF_3 [6].

Taking into account these observations, it would be of interest to study the effect of replacement of carbonyl oxygen in hydroxamic acids by =NSO_2CF_3 group on the course of a Lossen-type rearrangement.

2. Results and discussion

Trifluoromethanesulfonylimides of arenehydroxamic acids have not been described in the literature. We tried to prepare these compounds by reaction of hydroxylamine hydrochloride with *N*-trifluormethylsulfonylarencarboximidoyl chlorides at the presence of triethylamine or sodium hydride (similarly to corresponding azides [6]), but a mixture of products was formed. Positive results were finally achieved by reaction of chloranhydrides of arenehydroxamic acids with the monosodium salt of trifluormethanesulfonamide in dimethylformamide

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[1] Crystal structure analysis.
[2] IR-spectra.

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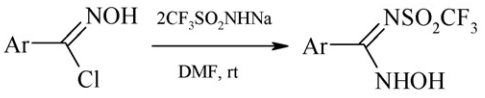
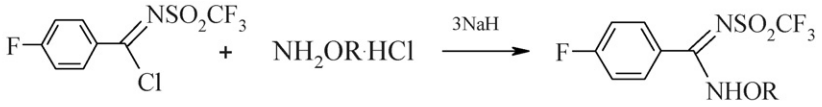


1a-f

Ar = 4-XC_6H_4-

Comp.	1a	1b	1c	1d	1e	1f
X	H	OCH_3	$OCHF_2$	F	Cl	NO_2
Yield [%]	70	65	71	69	74	90

Scheme 1.



2a-c

Comp.	2a	2b	2c
R	Me	Et	Allyl
Yield [%]	75	66	64

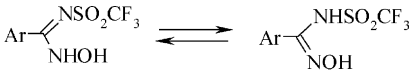
Scheme 2.

(DMF) solution (similarly to arenesulfonamide monosodium salts [7]). Trifluoromethanesulfonylimides of arenehydroxamic acids **1a–f** were isolated with good yields (Scheme 1).

Starting from *O*-alkylated hydroxylamines we have prepared *O*-alkylated trifluoromethanesulfonylimides of arenehydroxamic acids **2a–c** in high yield by reaction with *N*-trifluoromethylsulfonylarenecarboximidoyl chlorides [6] in the presence of sodium hydride (Scheme 2).

Trifluoromethanesulfonylimides of arenehydroxamic acids **1a–f** and *O*-alkylated trifluoromethanesulfonylimides of arenehydroxamic acids **2a–c** are colorless (except yellow nitrocompound **1f**) crystalline materials.

Trifluoromethanesulfonylimides of arenehydroxamic acids may exist in two tautomeric forms (**A** and **B**).



A **B**

On the basis of ^1H and ^{19}F NMR spectra, IR spectra and X-ray analysis of the compounds **1**, we have established that they have the structure of hydroxamic acid **A** in both solution and in solid.

The analysis of ^{19}F NMR spectra of the compounds with fixed C=NSO_2CF_3 and C–$NHSO_2CF_3$ groups has confirmed that a signal of the =NSO_2CF_3 group is in the range −78 to −80 ppm, and that of $NHSO_2CF_3$ group—at −75 to −77 ppm [6]. In ^{19}F NMR spectra of the compounds **1a–f** signals at −79 to −80 ppm are observed, which correspond to the structure **A**. In their IR-spectra (both in KBr tablets and in chloroform or methylene chloride solutions) of the compounds in which tautomerism is impossible a band at 1565–1590 cm^{-1} is typical for vibrations of the fragment C=N in the C=NSO_2CF_3 group. In the IR-spectra of **1a–f** compounds (in $CHCl_3$) absorption bands at 1590–1595 cm^{-1} are observed, which correspond to tautomeric form **A** and agree with the ^{19}F NMR data of these compounds. The results of X-ray analysis for **1a** confirm the existence of the **1a–f** compounds in the form **A** (Fig. 1).

The perspective view of the molecule **1a** and selected geometrical parameters are given in Fig. 1 from a single crystal

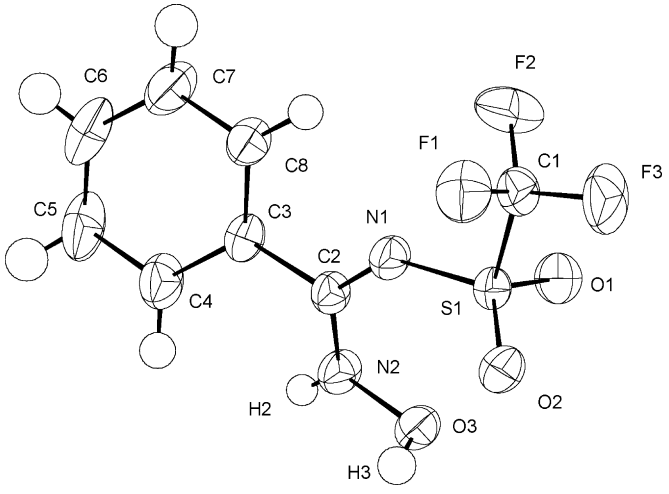


Fig. 1. Perspective view and labelling scheme for the molecule **1a**. Selected bond lengths (Å) and angles (°): S(1)–O(1) 1.426(2), S(1)–O(2) 1.432(1), S(1)–N(1) 1.562(2), S(1)–C(1) 1.825(2), O(3)–N(2) 1.381(2), N(1)–C(2) 1.315(2), N(2)–C(2) 1.307(2), C(2)–C(3) 1.482(2); S(1)N(1)C(2) 129.5(1), O(3)N(2)C(2) 120.8(2), N(2)O(3)H(3) 100(2).

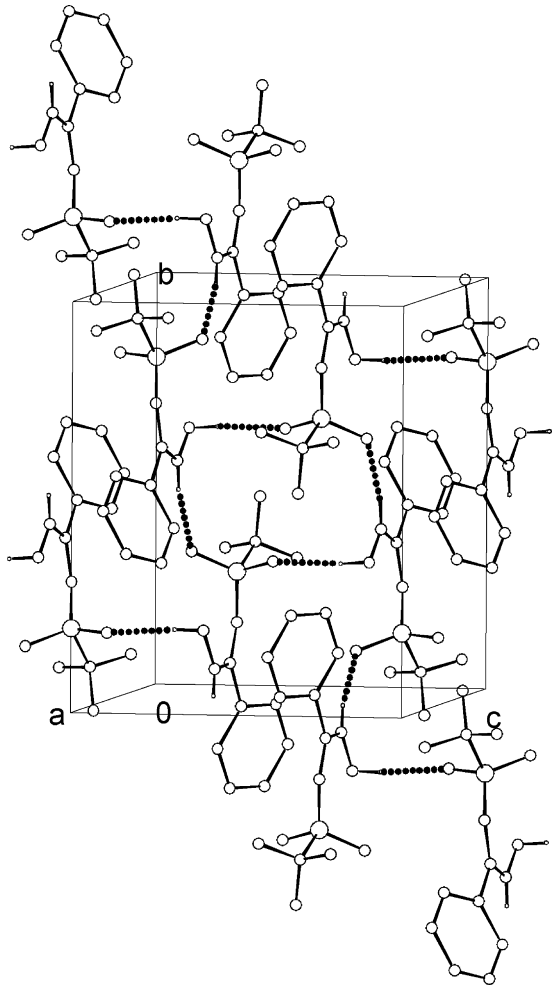
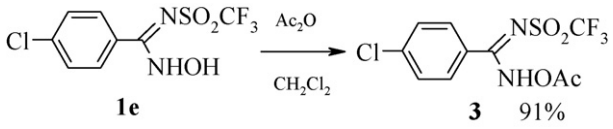


Fig. 2. Crystal packing of the compound **1a**.



1e **3** 91%

Scheme 3.

X-ray study. The central O(3)N(1)N(2)C(2)C(3) bond system is planar (deviations from the least-square plane do not exceed 0.004 Å). The S(1) atom is 0.237 Å above this plane. The benzene ring C(3–8) is twisted out of this plane by 29.5°. The N(2) atom has a trigonal–planar bond configuration (sum of the bond angles 359.6°). Due to the $n_{N(2)}$–$\pi_{C(2)=N(1)}$ conjugation the N(2)–C(2) bond of 1.307(2) Å is significantly shortened in comparison with the standard value for the N(sp^2)–C(sp^2) single bonds of 1.43–1.45 Å [8,9]. In the solid state the molecules of **1** are joined in nets by the N(2)–H···O(2) (N···O 2.878(2), O···H 2.04(3) Å, NHO 165(2)°) and O(3)-H···O(1) (O···O 2.759(2) Å, O···H 1.94(2) Å, OHO 175(2)°) hydrogen bonds (Fig. 2).

Our attempts to carry out rearrangement of compounds **1** under the conditions of the classic Lossen rearrangement, thermolysis of the sodium salt of the *O*-acyl derivative, were unsuccessful. Trifluoromethanesulfonylimide of 4-chlorophenylhydroxamic acid **1e**, acylated by acetic anhydride in dichloromethane, to form acetyl derivative **3**, was chosen as a model compound (Scheme 3).

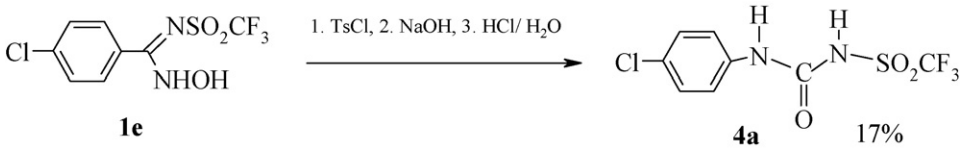
However, on further heating, the sodium salt of **3**, obtained in situ by its reaction with sodium hydride in anhydrous DMF, was probably transformed into a rearrangement product, namely, a carbodiimide which decomposed at high temperature. As a result, trifluoromethanesulfonamide and tarry products only were obtained from reaction mixture.

An attempt to use an ester of a stronger acid, namely trifluoroacetic, for this reaction was also unsuccessful. A positive result was achieved after tosyl chloride was chosen as an esterification agent (similarly to [10]). The tosyl residue is a good leaving group, so rearrangement with formation of carbamide **4a** occurs under the action of aqueous alkali (Scheme 4).

It was found earlier that trimethylsilyl esters of arenehydroxamic acids underwent the Lossen rearrangement [11]. We have obtained trimethylsilyl esters of trifluoromethanesulfonylimides of 4-fluoro- and 4-chlorophenylhydroxamic acids (**5a**, **b**) by reaction of compounds **1d**, **e** with hexamethyldisilazane (HMDS) in acetonitrile solution. In this case, in contrast to silylation of usual hydroxamic acids, resulting in *O*,*O*′-bis-trimethylsilyl derivatives [11], only monosilylation occurs, which was confirmed by ^{1}H and ^{19}F NMR spectra. Compounds **5** underwent thermal decomposition in boiling toluene. Morpholine was then added to the reaction mixture in order to obtain stable derivatives. As a result, mixture of carbamide **4** and trifluoromethylsulfonylamidinomorpholine **6** is formed, obviously due to competitive bonding of not only morpholine, but also water to the resulting carbodiimide (Scheme 5).

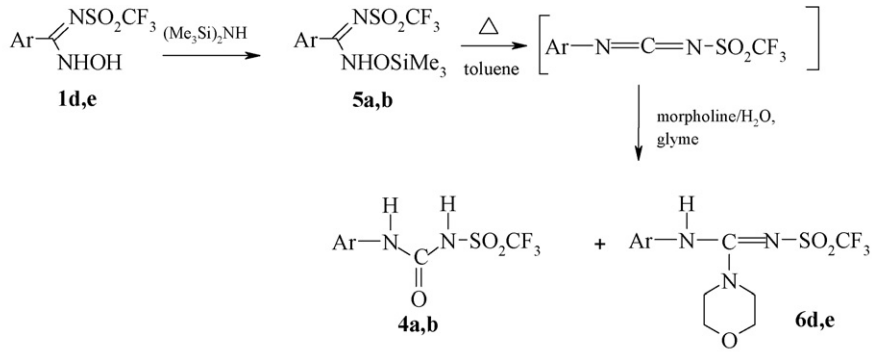
The low yields of key products obtained within Schemes 4 and 5 may be rationalized by the fact that transient formed carbodiimides ArN=C=NSO_2CF_3 were unstable at the temperature necessary for the rearrangement realization.

It is known that hydroxamic acids and their derivatives undergo a Lossen rearrangement by the action of acid dehydration agents, e.g. sulfinyl chloride. When heating the



1e **4a** 17%

Scheme 4.



1d,e — 5a,b — 4a,b — 6d,e

Ar = 4-FC_6H_4 (**1d**, **4b**, **5b**, **6d**), 4-ClC_6H_4 (**1e**, **4a**, **5a**, **6e**)

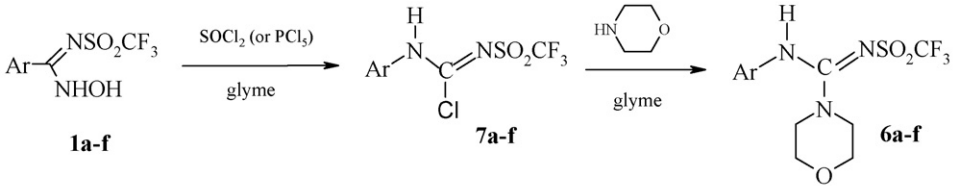
Ar	4-ClC_6H_4			4-FC_6H_4		
Comp.	**4a**	**5a**	**6e**	**4b**	**5b**	**6d**
Yield [%]	5	97	7	5	91	6

Scheme 5.

solutions of compounds **1** in glyme with sulfinyl chloride or phosphorus pentachloride the rearrangement occurs to form *N*-trifluoromethylsulfonyl-*N*′-arenechloroformamidines **7**. Chloroformamidines **7** are found to be compounds unstable at storage or to hydrolysis, therefore, only three of them, namely, **7a**, **7d**, and **7f** were isolated and characterized by NMR-spectra and elemental analysis. All **7a–f** were characterized in the form of their morpholine derivatives **6** (Scheme 6).

We first assumed, that this transformation proceeded by the classical mechanism of triplet rearrangements [1] with formation of a carbodiimide, as shown in Scheme 5, with further addition of HCl. In order to check this assumption we obtained carbodiimide **8** from *N*-trifluoromethylsulfonyl-(4-fluorophenyl)carboximidoyl chloride, with the use of aza Curtius reaction [6], and passed the dry HCl flow through its boiling solution in glyme. It was found, however, that under these conditions hydrogen chloride did not add to carbodiimide **8** with formation of *N*-trifluormethylsulfonyl-*N*′-(4-fluorophenyl) chloroformamidine **7d** (Scheme 7).

This result suggests that under the action of sulfinyl chloride or phosphorus pentachloride the trifluoromethanesulfonylimides of arenehydroxamic acids **1a–f** undergo a Lossen-type rearrangement which includes a five-membered cyclic transition complex (Scheme 8).



1a-f — **7a-f** — **6a-f**

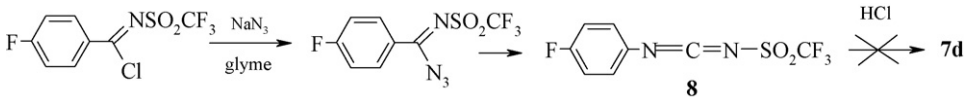
Ar = 4-XC_6H_4-

Comp.	**6a**	**6b**	**6c**	**6d**	**6e**	**6f**
X	H	OCH_3	$OCHF_2$	F	Cl	NO_2
Yield [%]	88	66	65	65	67*	65

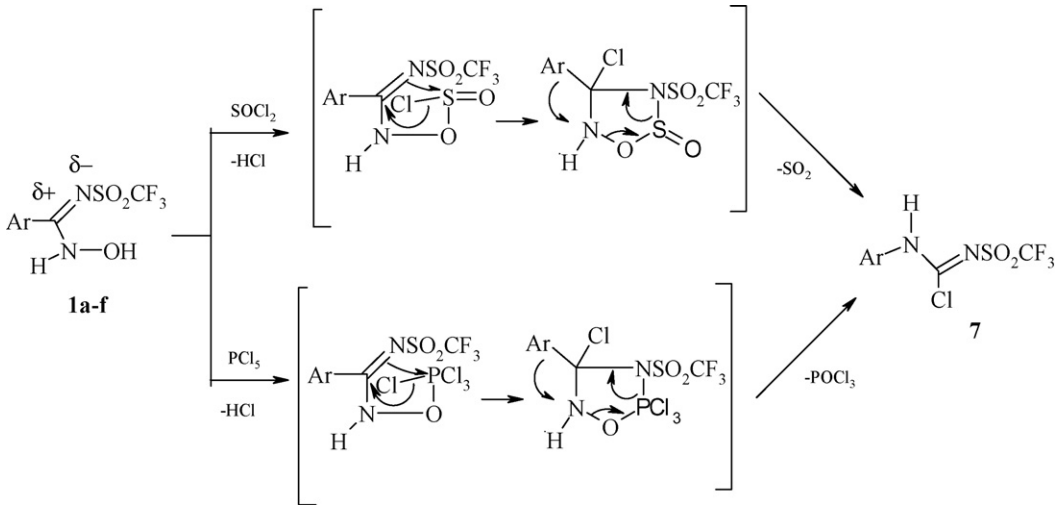
With PCl_5 yield 65%

Comp.	**7a**	**7d**	**7f**
X	H	F	NO_2
Yield [%]	88	85	90

Scheme 6.



Scheme 7.



Scheme 8.

Chloroformamidines **7**, formed in the course of this reactions were found to be thermally much more stable then corresponding carbodiimides, that enabled to obtain products up to Scheme 6 with good yields.

O-Alkylated trifluoromethanesulfonylimides of arenehydroxamic acids **2** do not enter into rearrangements under the action of sulfinyl chloride and phosphorous pentachloride.

We have earlier established [6], that Curtius reaction for the compounds, in which sp^2 oxygen atom is replaced by the group $=NSO_2CF_3$, proceeds under more mild conditions (−5 to 0 °C) than for azides of carboxylic acids. It can be accounted for by the weakening of the N–N bond in azides due to the strong electron-withdrawing affect of the $=NSO_2CF_3$ group. In the case of trifluoromethanesulfonylimides of arenehydroxamic acids **1** Lossen rearrangement proceeds under more severe conditions. This can be explained by the strengthening of the N–O bond in hydroxyaminogroup. As a result of coupling with the $=NSO_2CF_3$ group an electron pair of nitrogen atom N(2) shifts to form a partial double bonding. It is confirmed by X-ray analysis, namely, length of N(2)–C(2) bond is 1.307 Å instead of 1.43–1.45 Å in the compounds with the typical N(sp^2)–C(sp^2) bond. Emergence of a partial positive charge on N(2) atom strengthens N(2)–O(3) bond because of withdrawing the electron density from O(3) atom.

3. Experimental

3.1. General

Moisture-sensitive reactions were carried out under dry argon using flame-dried glassware. All chemicals were of reagent grade or were purified by standard methods before use. Solvents were distilled from the appropriate drying agents immediately prior to use. Some reactions were monitored by thin-layer chromatography (TLC) on precoated silica gel Kieselgel 60 F/UV_{254} plates (Merck); spots were visualized with UV light. Purification of most products was performed by column chromatography (CC) on silica gel, 70–230 mesh 60A (Aldrich). ^1H and ^{19}F NMR spectra were recorded at 299.5 MHz and 282.2 MHz, respectively, with a Varian VXR-300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si and CCl_3F, respectively, as internal standards. Coupling constants are given in Hz. IR spectra were recorded with a Spekord M 40 instrument (KBr tablet or solution in $CHCl_3$). Melting points were determined in open capillaries and are uncorrected. Elemental analysis was performed in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kiev.

3.2. General procedure for the synthesis of trifluoromethanesulfonylimides of arenehydroxamic acids (*1a–f*)

A solution of arenehydroxamic acid chloranhydride (0.003 mol) in anhydrous DMF (10 mL) was added dropwise to a stirred mixture of monosodium salt of trifluoromethanesulfonamide (0.006 mol) in anhydrous DMF (10 mL) at 0 °C in 20 min. After stirring for 24 h at room temperature, the reaction mixture was poured into ice. The product was extracted with diethyl ether (3 × 15 mL), ether layer was washed with water (2 × 15 mL), and dried with Na_2SO_4. Distillation of ether, and recrystallization (from

chloroform/hexane) of resultant precipitate gave analytically pure **1**.

*3.2.1. Phenylhydroxamic acid trifluoromethanesulfonylimide (**1a**)*

mp 126–128 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ 7.51–7.78 (5H, m, ArH), 10.00–10.60 (1H, w s, NH), 11.00–12.00 (1H, w s, OH); ^{19}F NMR ([D$_6$]acetone): δ–79.4 (s, 3F, SO_2CF_3); IR (KBr): ν 3400, 3285, 3240 (O–H), 1608 (C=N), 943 cm^{-1} (N–O). Anal. calcd for $C_8H_7F_3N_2O_3S$: C 35.82, H 2.63, N 10.44. Found: C 35.90, H 2.54, N 10.48.

*3.2.2. 4-Methoxyphenylhydroxamic acid trifluoromethanesulfonylimide (**1b**)*

mp 138–140 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ 3.65 (3H, s, OCH_3), 6.76–7.30 (4H, dd, ArH), 7.94–8.06 (1H, w s, NH), 8.45 (1H, s, OH); ^{19}F NMR ([D$_6$]acetone): δ −79.6 (s, 3F, SO_2CF_3); IR (KBr): ν 3310 (O–H), 1606 (C=N), 943 cm^{-1} (N–O). Anal. calcd for $C_9H_9F_3N_2O_4S$: C 36.24, H 3.04, N 9.39. Found C 35.92, H 2.87, N 9.07.

*3.2.3. 4-Difluoromethoxyphenylhydroxamic acid trifluoromethanesulfonylimide (**1c**)*

mp 134–135 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ 7.19 (1H, t, $J_{H,F}$ = 73 Hz, $OCHF_2$), 7.28–7.83 (4H, dd, ArH), 10.20–10.60 (1H, w s, NH), 11.00–11.80 (1H, w s, OH); ^{19}F NMR ([D$_6$]acetone): δ −79.2 (s, 3F, SO_2CF_3), −82.9 (d, $J_{H,F}$ = 73 Hz, 2F, $OCHF_2$); IR (KBr): ν 3325 (O–H), 1606 (C=N), 943 cm^{-1} (N–O). Anal. calcd for $C_9H_7F_5N_2O_4S$: C 32.34, H 2.11, N 8.38. Found C 32.51, H 1.98, N 8.46.

*3.2.4. 4-Fluorophenylhydroxamic acid trifluoromethanesulfonylimide (**1d**)*

mp 139–141 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ 7.29–7.37 (2H, m, ArH), 7.82–7.87 (2H, m, ArH), 9.84–10.32 (1H, w s, NH), 11.48–11.93 (1H, w s, OH); ^{19}F NMR ([D$_6$]acetone): δ −76.8 (s, 3F, SO_2CF_3), −108.8 (s, 1F, ArF); IR (KBr): ν 3220 (O–H), 1600 cm^{-1} (C=N). Anal. calcd for $C_8H_6F_4N_2O_3S$: C 33.57, H 2.11, N 9.79. Found C 33.70, H 2.05, N 9.68.

*3.2.5. 4-Chlorophenylhydroxamic acid trifluoromethanesulfonylimide (**1e**)*

mp 157 °C (dec). ^{1}H NMR ([D$_6$]acetone): δ 7.58–7.79 (4H, dd, ArH), 10.50–11.50 (2H, w s, NH + OH); ^{19}F NMR ([D$_6$]acetone): δ −79.7 (s, 3F, SO_2CF_3); IR (KBr): ν 3315 (O–H), 1616 (C=N), 943 cm^{-1} (N–O). Anal. calcd for $C_8H_6ClF_3N_2O_3S$: C 31.75, H 2.00, N 9.25. Found C 31.85, H 2.05, N 9.30.

*3.2.6. 4-Nitrophenylhydroxamic acid trifluoromethanesulfonylimide (**1f**)*

mp 152–154 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ 8.03–8.36 (4H, dd, ArH), 10.60–11.80 (2H, w s, NH + OH); ^{19}F NMR ([D$_6$]acetone): δ −75.4 to −79.7 (w s, 3F, SO_2CF_3); IR (KBr): ν 3285 (O–H), 1626 (C=N), 943 cm^{-1} (N–O). Anal. calcd for $C_8H_6F_3N_3O_5S$: C 30.68, H 1.93, N 13.42. Found C 30.79, H 1.81, N 13.30.

*3.3. General procedure for the synthesis of O-substituted trifluoromethanesulfonylimides of arenehydroxamic acids (**2a–c**)*

A solution of 4-fluoro-*N*-(trifluoromethylsulfonyl)benzimidoyl chloride [6] (0.57 g, 0.002 mol) in anhydrous THF (10 mL) was added dropwise to a stirred mixture of *O*-alkylhydroxylamine hydrochloride (0.002 mol) and sodium hydride (0.15 g, 0.006 mol) in anhydrous THF (25 mL) at 0 °C in 20 min. After stirring for 72 h at room temperature and refluxing for 30 min, the solvent was evaporated in vacuo. The residue was dissolved in water and filtered, filtrate was acidified with conc. HCl at 0 °C. The precipitate formed was filtered off, washed with water and dried. Recrystallization (from benzene/hexane) gave analytically pure **2**.

*3.3.1. 4-Fluorophenyl-O-methylhydroxamic acid trifluoromethanesulfonylimide (**2a**)*

mp 105–107 °C. ^{1}H NMR ($CDCl_3$): δ 4.03 (3H, s, OCH_3), 7.07–7.13 (2H, m, ArH), 7.58–7.62 (2H, m, ArH), 7.85 (1H, s, NH); ^{19}F NMR ($CDCl_3$): δ −76.8 (s, 3F, SO_2CF_3), −108.7 (s, 1F, ArF); IR (KBr): ν 3225 (N–H), 1610 cm^{-1} (C=N). Anal. calcd for $C_9H_8F_4N_2O_3S$: C 36.01, H 2.69, N 9.33. Found C 36.23, H 2.83, N 9.57.

*3.3.2. 4-Fluorophenyl-O-ethylhydroxamic acid trifluoromethanesulfonylimide (**2b**)*

mp 92–93 °C. ^{1}H NMR ($CDCl_3$): δ 1.34 (3H, t, OCH_2CH_3), 4.28 (2H, quart, OCH_2CH_3), 7.06–7.12 (2H, m, ArH), 7.58–7.63 (2H, m, ArH), 7.80 (1H, s, NH); ^{19}F NMR ($CDCl_3$): δ −77.0 (s, 3F, SO_2CF_3), −111.6 (s, 1F, ArF). Anal. calcd for $C_{10}H_{10}F_4N_2O_3S$: C 38.22, H 3.21, N 8.91. Found C 38.09, H 2.77, N 9.16.

*3.3.3. 4-Fluorophenyl-O-allylhydroxamic acid trifluoromethanesulfonylimide (**2c**)*

mp 82–83 °C. ^{1}H NMR ([D$_6$]acetone): δ 4.71 (2H, d, OCH_2–$CH=CH_2$), 5.32–5.50 (2H, m, OCH_2–$CH=CH_2$), 6.03–6.16 (1H, m, OCH_2–$CH=CH_2$), 7.27–7.33 (2H, m, ArH), 7.81–7.86 (2H, m, ArH), 10.00–12.00 (1H, w s, NH); ^{19}F NMR ([D$_6$]acetone): δ −78.5 (s, 3F, SO_2CF_3), −108.2 (s, 1F, ArF). Anal. calcd for $C_{11}H_{10}F_4N_2O_3S$: C 40.49, H 3.09, N 8.58. Found C 40.70, H 2.89, N 8.56.

*3.4. 4-Chlorophenyl-O-acetylhydroxamic acid trifluoromethanesulfonylimide (**3**)*

A solution of acetic anhydride (1 mL) in anhydrous methylene chloride (10 mL) was added dropwise to a stirred suspension of **1e** (0.3 g, 0.001 mol) in anhydrous methylene chloride (10 mL) at 5 °C in 20 min. After stirring for 2 h at room temperature (the completion of reaction was controlled with $FeCl_3$ probe) the solvent was evaporated in vacuo (0.05 Torr). The residue afforded spectral pure **3** (0.31 g). mp 120–121 °C. ^{1}H NMR ([D$_6$]acetone): δ 2.25 (3H, s, $OCOCH_3$), 7.55–7.65 (4H, dd, ArH), 10.00–12.00

(1H, w s, NH); ^{19}F NMR ([D$_6$]acetone): δ −78.9 (s, 3F, SO_2CF_3).

3.5. Aza Lossen rearrangement with tosyl chloride

3.5.1. N-(4-Chlorophenyl)-N′-trifluoromethylsulfonylurea (4a)

Tosyl chloride (0.19 g, 0.001 mol) was added in portions to a stirred solution of **1e** (0.3 g, 0.001 mol) in 2N aqueous sodium hydroxide (2 mL) at 0 °C in 20 min. After stirring for 4 h at room temperature, the reaction mixture was neutrolized with conc. HCl at 0 °C. The product was extracted with diethyl ether (3 × 15 mL), ether layer was washed with water (2 × 15 mL), and dried with Na_2SO_4. Distillation of ether, and recrystallization (from chloroform) of resultant precipitate gave 0.05 g of **4a** (from **5a**, 0.03 g). mp 220 °C. ^{1}H NMR ([D$_6$]DMSO): δ 7.19–7.53 (4H, dd, ArH), 9.00 (1H, s, NH); ^{19}F NMR ([D$_6$]DMSO): δ −75.8 (s, 3F, SO_2CF_3). Anal. calcd for $C_8H_6ClF_3N_2O_3S$: C 31.75, H 2.00, N 9.25. Found C 31.83, H 1.96, N 9.31.

3.5.2. N-(4-Fluorophenyl)-N′-trifluoromethylsulfonylurea (4b)

Yield 0.03 g, mp 136–140 °C. ^{1}H NMR ([D$_6$]acetone): δ 7.10–7.60 (4H, m, ArH), 9.10 (1H, s, NH); ^{19}F NMR ([D$_6$]acetone): δ −79.3 (s, 3F, SO_2CF_3), −116.1 (s, 1F, ArF). Anal. calcd for $C_8H_6F_4N_2O_3S$: C 33.57, H 2.11, N 9.78. Found C 33.61, H 2.08, N 9.83.

3.6. General procedure for the synthesis of O-silylated trifluoromethanesulfonylimides of arenehydroxamic acids (5a, b)

The mixture of **1** (0.002 mol), HMDS (0.97 g, 0.006 mol), and acetonitrile (10 mL) was stirred for 72 h at room temperature. After evaporation of solvent in vacuo the residue was pure enough for further reactions.

3.6.1. 4-Chlorophenyl-O-trimethylsilylhydroxamic acid trifluoromethanesulfonylimide (5a)

Yield 0.73 g, ^{1}H NMR ([D$_6$]DMSO): δ 0.02 (9H, s, $Si(CH_3)_3$), 5.27 (1H, s, NH), 7.34–7.67 (4H, dd, ArH); ^{19}F NMR ([D$_6$]DMSO): δ −77.8 (s, 3F, SO_2CF_3).

3.6.2. 4-Fluorophenyl-O-trimethylsilylhydroxamic acid trifluoromethanesulfonylimide (5b)

Yield 0.65 g, ^{1}H NMR ([D$_6$]DMSO): δ 0.02 (9H, s, $Si(CH_3)_3$), 7.23–7.29 (2H, m, ArH), 7.91–7.96 (2H, m, ArH); ^{19}F NMR ([D$_6$]DMSO): δ −77.1 (s, 3F, SO_2CF_3), −110.2 (s,1F, ArF).

3.7. Aza Lossen rearrangement with O-silylated trifluoromethanesulfonylimides of arenehydroxamic acids (5a, b). N-Arene-N′-trifluoromethylsulfonylureas (4a, b) and 4-(N-arene-N′-trifluoromethylsulfonylamidino)morpholines (6d, e)

Substance **5** (0.002 mol) was refluxed in toluene (15 mL) solution for 30 min. Reaction mixture was evaporated to dryness, residue was dissolved in anhydrous glyme (15 mL) and treated with solution of morpholine (0.002 mol) in glyme (5 mL) at 0 °C. After stirring for 24 h at room temperature the solvent was distilled off. Column chromatography (eluent hexane/ethylacetate 2:1) afforded compounds **4** and **6**.

3.8. Aza Lossen rearrangement with sulfinyl chloride (method A). 4-[N-Arene-N′-trifluoromethylsulfonylamidino]morpholines (6a–f) and N-trifluoromethylsulfonyl-N′-arenechloroformamidines (7a, d, f)

A solution of $SOCl_2$ (0.4 g, 0.0033 mol) in anhydrous glyme (5 mL) was added dropwise to a stirred solution of **1** (0.003 mol) in anhydrous glyme (10 mL) at 5 °C in 20 min. After refluxing for 1 h, the solvent was evaporated in vacuo (0.05 Torr). Products **7a**, **7d**, and **7f** were recrystallized from anhydrous ether/hexane. Others **7** were used without isolation. Compound **7** was dissolved again in glyme and treated with morpholine (0.3 g, 0.0033 mol). After stirring for 24 h at room temperature, precipitated morpholine hydrochloride was filtered off, the filtrate was concentrated to dryness, and the residue was purified by column chromatography (eluent benzene/ethylacetate 20:1) and following crystallization (from benzene/hexane).

3.8.1. 4-[N-Phenyl-N′-trifluoromethylsulfonylamidino]morpholine (6a)

mp 115–116 °C; Ref. [6] 112–114 °C. ^{1}H NMR (CD_3CN): δ 3.51 (4H, m, $2CH_2$), 3.67 (4H, m, $2CH_2$), 7.15–7.26 (3H, m, ArH), 7.38–7.44 (2H, m, ArH), 8.15–8.32 (1H, w s, NH); ^{19}F NMR (CD_3CN): δ −79.1 (s, 3F, SO_2CF_3); IR (KBr): ν 3405 (N–H), 1611 (C=N), 1575 cm^{-1} (amide II).

3.8.2. 4-[N-(4-Methoxyphenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6b)

mp 142–144 °C. ^{1}H NMR (CD_3CN): δ 3.50 (4H, m, $2CH_2$), 3.80 (4H, m, $2CH_2$), 3.88 (3H, s, OCH_3), 6.72–7.68 (4H, dd, ArH), 8.21–8.35 (1H, w s, NH); ^{19}F NMR (CD_3CN): δ −79.5 (s, 3F, SO_2CF_3); IR (KBr): ν 3400 (N–H), 1610 (C=N), 1580 cm^{-1} (amide II). Anal. calcd for $C_{13}H_{16}F_3N_3O_4S$: C 42.50, H 4.39, N 11.44. Found C 42.64, H 4.21, N 11.48.

3.8.3. 4-[N-(4-Difluoromethoxyphenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6c)

mp 132–134 °C. ^{1}H NMR (CD_3CN): δ 3.52 (4H, m, $2CH_2$), 3.67 (4H, m, $2CH_2$), 6.76 (1H, t, $J_{H,F}$ = 73 Hz, $OCHF_2$), 7.10–7.30 (4H, m, ArH), 8.17 (1H, s, NH); ^{19}F NMR (CD_3CN): δ −79.1 (s, 3F, SO_2CF_3), −81.8 (d, $J_{H,F}$ = 73 Hz, 2F, $OCHF_2$); IR (KBr): ν 3290 (N–H), 1615 (C=N), 1583 cm^{-1} (amide II). Anal. calcd for $C_{13}H_{14}F_5N_3O_4S$: C 38.71, H 3.50, N 10.42. Found C 38.82, H 3.33, N 10.49.

3.8.4. 4-[N-(4-Fluorophenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6d)

From **5b** yield 0.04 g, mp 144–146 °C; Ref. [6] 142–144 °C. ^{1}H NMR ([D$_6$]acetone): δ 3.62 (4H, m, $2CH_2$), 3.78 (4H, m,

$2CH_2$), 7.22–7.32 (4H, m, ArH), 8.15–8.30 (1H, w s, NH); ^{19}F NMR ([D_6]acetone): δ −78.8 (s, 3F, SO_2CF_3), −116.6 (s, 1F, ArF); IR (KBr): ν 3330 (N–H), 1575 (C=N), 1537 cm^{-1} (amide II).

3.8.5. 4-[N-(4-chlorophenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6e)

From **5a** yield 0.05 g, mp 150–152 °C; Ref. [6] 148–150 °C. ^{1}H NMR (CD_3CN): δ 3.53 (4H, m, $2CH_2$), 3.68 (4H, m, $2CH_2$), 7.15–7.40 (4H, dd, ArH), 8.09–8.22 (1H, w s, NH); ^{19}F NMR (CD_3CN): δ −79.1 (s, 3F, SO_2CF_3).

3.8.6. 4-[N-(4-Nitrophenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6f)

mp 218–220 °C; Ref. [6] 217–219 °C. ^{1}H NMR (CD_3CN): δ 3.63 (4H, m, $2CH_2$), 3.73 (4H, m, $2CH_2$), 7.33–8.22 (4H, dd, ArHH), 8.40–8.60 (1H, w s, NH); ^{19}F NMR (CD_3CN): δ −79.1 (s, 3F, SO_2CF_3).

3.8.7. N-Trifluoromethylsulfonyl-N′-phenylchloroformamidine (7a)

mp 104–106 °C. ^{1}H NMR ($CDCl_3$): δ 7.25–7.49 (5H, m, ArH), 8.06 (1H, w s, NH); ^{19}F NMR ($CDCl_3$): δ −79.5 (s, 3F, SO_2CF_3). Anal. calcd for $C_8H_6ClF_3N_2O_2S$: C 33.52, H 2.11, Cl 12.37. Found C 33.39, H 2.00, Cl 11.98.

3.8.8. N-Trifluoromethylsulfonyl-N′-4-fluorophenylchloroformamidine (7d)

mp 112–114 °C. ^{1}H NMR ($CDCl_3$): δ 7.14 (2H, m, ArH), 7.56 (2H, m, ArH), 7.96 (1H, w s, NH); ^{19}F NMR ($CDCl_3$): δ −79.0 (s, 3F, SO_2CF_3), −116.0 (s, 1F, ArF). Anal. calcd for $C_8H_5ClF_4N_2O_2S$: C 31.54, H 1.65, Cl 11.63. Found C 31.38, H 2.03, Cl 11.32.

3.8.9. N-Trifluoromethylsulfonyl-N′-4-nitrophenylchloroformamidine (7f)

mp 147–149 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 7.40–8.21 (4H, dd, ArH), 8.40 (1H, w s, NH); ^{19}F NMR ($CDCl_3$): δ −77.8 (s, 3F, SO_2CF_3). Anal. calcd for $C_8H_5ClF_3N_3O_4S$: C 28.97, H 1.52, Cl 10.68. Found C 28.68, H 1.74, Cl 10.44.

3.9. Aza Lossen rearrangement with phosphorus pentachloride (method B). 4-[N-(4-Chlorophenyl)-N′-trifluoromethylsulfonylamidino]morpholine (6e)

PCl_5 (0.63 g, 0.003 mol) was added in portions to a stirred solution of **1e** (0.91 g, 0.003 mol) in anhydrous glyme (15 mL) at 5 °C. After refluxing for 1 h, the solvent was evaporated in vacuo (0.05 Torr). The residue afforded spectral pure **7e**. It was dissolved again in glyme and treated with morpholine (0.3 g, 0.0033 mol). After stirring for 24 h at room temperature, precipitated morpholine hydrochloride was filtered off, the filtrate was concentrated to dryness, and the residue was purified by column chromatography (eluent benzene/ethylacetate 20:1) and following crystallization (from benzene/hexane) to give 0.72 g **6e**.

3.10. X-ray crystallography

All crystallographic measurements were performed at 293 K on a Bruker SMART 6K CCD diffractometer. The intensity data were collected within the range $2.7 < \theta < 29.3^\circ$ ($-12 < h < 13$, $-15 < k < 14$, $-12 < l < 12$) using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities of 9418 reflections (28718 unique, $R_{int} = 0.014$) were measured. Data were corrected for Lorentz and polarisation effects and an absorption correction using the Sadabs procedure [12] was applied.

3.10.1. Structure solution and refinement

The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation using the CRYSTALS program package [13]. In the refinement 1710 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in the different Fourier maps and refined isotropically. Convergence was obtained at $R = 0.031$ and $R_w = 0.034$, GOF = 1.116 (182 refined parameters; obs./variabl. 9.4). Chebushev weighting scheme [14] with parameters 0.74, 0.88, 0.63, 0.24, and 0.10 was used. Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this materials should quote the full literature citation and reference number CCDC 613386.

3.10.2. Crystal data for 1a

$C_8H_7F_3N_2O_3S$, $M = 268.2$, monoclinic, $a = 9.8787(4)$, $b = 11.6982(4)$, $c = 9.4291(3)$ Å, $\beta = 97.966(3)^\circ$, $V = 1079.14(7)$ Å^3, $Z = 4$, $d = 1.65$ g cm^{-1}, space group $P2_1/c$ (N 14), $\mu = 0.34$ cm^{-1}, F(0 0 0) = 544, crystal size ca. 0.14 mm × 0.22 mm × 0.49 mm.

References

[1] M.B. Smith, J. March, March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 5th ed., Wiley–Interscience Publishers, 2001, pp. 1410–1417.
[2] I. Leito, I. Kaljurand, I.A. Koppel, L.M. Yagupolskii, V.M. Vlasov, J. Org. Chem. 63 (1998) 7868–7874.
[3] P. Burk, I.A. Koppel, I. Koppel, L.M. Yagupolskii, R.W. Taft, J. Comput. Chem. 17 (1996) 30–41.
[4] V.N. Boiko, N.V. Kirii, L.M. Yagupolskii, J. Fluor. Chem. 67 (1994) 119–123.
[5] L.M. Yagupolskii, V.N. Petrik, Y.L. Slominskii, Tetrahedron Lett. 43 (2002) 3957–3959.
[6] 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.
[7] E.A. Abrazhanova, L.F. Pronskii, Vop. Khim. Khim. Tekhnol., Respub. Mezhvedom. Temat. Nauch. -Tekh. Sb. (1972) 36–39;
E.A. Abrazhanova, L.F. Pronskii, Chem. Abstr. 78 (1973) 110806k.
[8] M. Burke-Laing, M. Laing, Acta Crystallogr. Sect. B 32 (1976) 3216–3224.
[9] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin II (Suppl.) (1987) 1–19.

[10] E.A. Abrazhanova, L.F. Pronskii, Zh. Org. Khim. 9 (4) (1973) 780–783; E.A. Abrazhanova, L.F. Pronskii, Chem. Abstr. 79 (1973) 42110x.
[11] J. Rigaudy, E. Litwyn, P. Wallach, N.K. Cuong, Tetrahedron Lett. 21 (1980) 3367–3370.
[12] G.M. Sheldrick, SADABS: Program for Scaling and Correction of Area Detector Data, University of Gottingen, Germany, 1996.
[13] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, CRYSTALS Issue 10, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996.
[14] J.R. Carruthers, D.J. Watkin, Acta Crystallogr. Sect. A 35 (1979) 698–699.