N-(Trifluoromethylsulfonyl)arenesulfonimidoyl and *N,N'*-Bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl Chlorides

L. M. Yagupolskii, R. Yu. Garlyauskajte, N. V. Kondratenko
Institute of Organic Chemistry of the Ukrainian Academy of Sciences, 252094, Kiev, Ukraine

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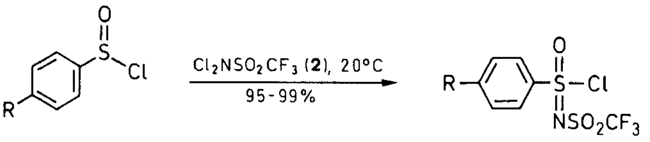
Dedicated to Professor Alois Haas on the occasion of his 60th birthday

N-(Trifluoromethylsulfonyl)arenesulfonimidoyl chlorides **3a–e** and *N,N'*-bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl chlorides **6a–e** are obtained by *N,N*-dichlorotrifluoromethanesulfonamide oxidative imination of arene sulfonyl chlorides **1a–e** and diaryl disulfides **4a–e**, respectively. The electron nature of the new substituents possessing high electron-accepting ability is also determined.

Recently[1,2] we have suggested a method for constructing superstrong electron-acceptor substituents in which the values of σ_p-constants exceed the magnitude of 1.1. It consists in the substitution of an oxygen atom in different groups by the trifluoromethylsulfonylimino group. When substituting the oxygen atom in the trifluoromethylsulfonyl group with the trifluoromethylsulfonylimino group the σ_p-constant of the new substituent, a *N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl group, reached the order of magnitude 1.40. To substitute the second oxygen atom by a trifluoromethylsulfonylimino group it was necessary to develop new synthetic methods. It was possible to realize this through the example of diphenyl sulfone with the use of the strong iminizing agent *N,N*-dichlorotrifluoromethanesulfonamide. We have shown that diphenyl sulfoxide and *S,S*-diphenylsulfilimine are iminated by this reagent.[3]

The paper presented is aimed to synthesize arenesulfonyl chloride derivatives in which one or both oxygen atoms are substituted by the trifluoromethylsulfonylimino group. Arenesulfinyl chlorides in contrast to phenyl trifluoromethyl sulfoxide react with *N,N*-dichlorotrifluoromethanesulfonamide **2** at 20 °C to afford *N*-(trifluoromethylsulfonyl)arenesulfonimidoyl chlorides **3** almost in quantitative yield:



1a-e **3a-e**

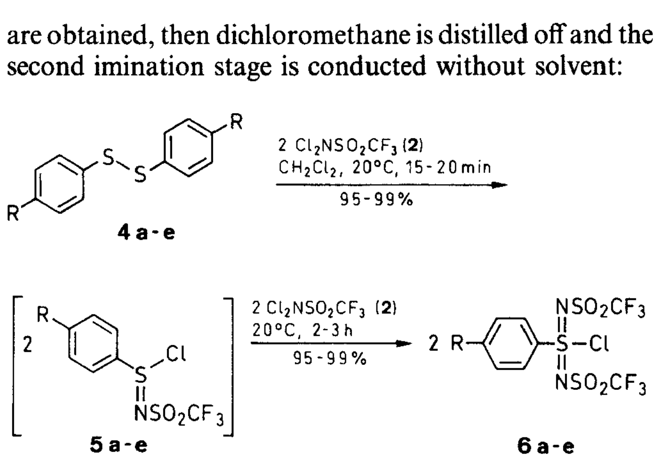
1,3	R	1,3	R
a	H	**d**	Me
b	Cl	**e**	NO2
c	F		

Table 1. *N*-(Trifluoromethylsulfonyl)arenesulfonimidoyl Chlorides **3a–e** and *N,N*-Bis(trifluoromethylsulfonylarenesulfonodiimidoyl Chlorides **6a–e**

Product	Yield (%)	Molecular Formula[a]	mp (°C)
3a	91	$C_7H_5ClF_3NO_3S_2$ (307.5)	oil
3b	90	$C_7H_5Cl_2F_3NO_3S_2$ (342)	oil
3c	91	$C_7H_4ClF_4NO_3S_2$ (325.5)	oil
3d	92	$C_8H_7ClF_3NO_3S_2$ (321.5)	oil
3e	88	$C_7H_4ClF_3N_2O_5S_2$ (352.5)	55–56
6a	98	$C_8H_5ClF_6N_2O_4S_3$ (438.5)	oil
6b	100	$C_8H_4Cl_2F_6N_2O_4S_3$ (473)	oil
6c	95	$C_8H_4ClF_7N_2O_4S_3$ (456.5)	oil
6d	96	$C_9H_7ClF_6N_2O_4S_3$ (452.5)	oil
6e	98	$C_8H_4ClF_6N_3O_6S_3$ (483.5)	70–71

[a] Satisfactory microanalyses obtained: C ±0.28, H ±0.06, N ±0.13, Cl ±46, except for **3c**: N +0.56.

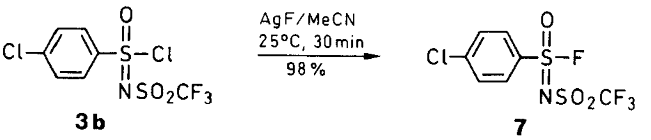
Other arene sulfonic acid *N,N*-dichloro- and *N*-sodium-*N*-chloroamides participate in this reaction.[4] Using the powerful iminizing reagent **2** we have successfully produced a new type of compound from diarene disulfides – analogs of arenesulfonyl chlorides in which both oxygen atoms are substituted by the trifluoromethylsulfonylimino group. The reaction is successively carried out, first in dichloromethane solution at 20–25 °C the *N*-(trifluoromethylsulfonylarenesulfinimidoyl chlorides are obtained, then dichloromethane is distilled off and the second imination stage is conducted without solvent:



4a-e **5a-e** **6a-e**

4-6	R	4-6	R
a	H	**d**	Me
b	Cl	**e**	NO2
c	F		

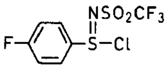
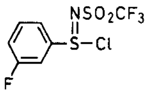
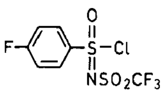
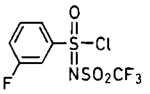
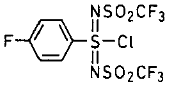
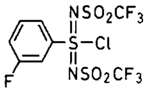
The chlorine atoms in the chlorides may be substituted for fluorine by treatment with silver fluoride in acetonitrile or on heating with antimony(III) fluoride without solvent.



3b **7**

The σ-constants of analogs of the SOCl and SO_2Cl groups in which oxygen atoms are substituted for one or two trifluoromethylsulfonylimino groups are determined (calculated by equations given in the publication[5]) using the ^{19}F NMR method. In the case when both oxygen

Table 2. Chemical Shifts in the ^{19}F NMR Spectra and σ-Constants of Substituents $S(Cl){=}NSO_2CF_3$, $S(Cl)(O){=}NSO_2CF_3$, $S(Cl)({=}NSO_2CF_3)_2$

Compound	^{19}F NMR (CD_2Cl_2/CCl_3F)	σ_I	σ_R	σ_P
	99.44 (F), 77.46 (CF_3)	1.11	0.24	1.35
	106.46 (F), 77.48 (CF_3)			
	96.9 (F), 78.1 (CF_3)	1.12	0.32	1.49
	106.4 (F), 78.0 (CF_3)			
	94.7 (F), 77.2 (CF_3)	1.36	0.34	1.70
	104.7 (F), 77.15 (CF_3)			

atoms are substituted by trifluoromethylsulfonylimino groups the σ_p-constant is the highest (except for $\overset{+}{N}{\equiv}N\ BF_4^-$),[6] it equals 1.70.

The ^{19}F NMR spectra were obtained on a Bruker WP-200 instrument in CD_2Cl_2 relative to CCl_3F. CH_2Cl_2 was distilled twice from CaH_2. Et_2O was distilled from $LiAlH_4$. MeCN was at first distilled from P_2O_5, then from CaH_2.

N-(Trifluoromethylsulfonyl)arenesulfonimidoyl Chlorides 3a–e; General Procedure:

In an Ar-flushed flask with a bubble counter and a P_2O_5 tube **1a–e** (1 mmol) was inserted and **2** (1.1 mmol) was added. The reaction occurred at 20 °C up to the cessation of Cl_2 elimination. Little excess of **2** and traces of Cl_2 were removed in vacuo without heating (water-jet pump).

N,*N*′-Bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl Chlorides 6a–e; General Procedure:

$CF_3SO_2NCl_2$ (2 mmol) in CH_2Cl_2 (2 mL) were dropped into a solution of diarene disulfide **4a–e** (1 mmol) in CH_2Cl_2 (2 mL). When Cl_2 elimination was over (15–20 min) the solvent was distilled off in vacuo at 25 °C. Then additional $CF_3SO_2NCl_2$ (2.2 mmol) was added to **5a–e**. The excess of **2** was removed 2–3 h later in vacuo.

4-Chloro-*N*-(trifluoromethylsulfonyl)benzenesulfonimidoyl Fluoride (7):

Sulfonimidoyl chloride **3b** (1.7 g, 5 mmol) was stirred at 25 °C in anhydr. MeCN (2.5 mL) with AgF (0.8 g, 6 mmol) for 30 min. The precipitated AgCl was filtered off, MeCN was evaporated in vacuo and the product distilled off; yield: 1.6 g (98 %); bp 100–110 °C/0.04 mm.

		C	H	F
$C_7H_4ClF_4NO_3S_2$	calc.	25.81	1.23	23.35
(325.5)	found	25.88	1.31	23.10

^{19}F NMR (CD_2Cl_2/CCl_3F): δ = 78.39 (CF_3), −72.81 (F-S).

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