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The Unusual Reactivity of the Mono- and Bis- N-(Trifluoromethylsulfonyl)-substituted Azaanalogs of Arenesulfonochlorides

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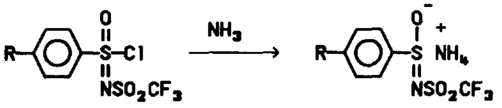
Abstract: *The reactions of N-(trifluoromethylsulfonyl)arenesulfonimidoyl- and N,N'-bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl chlorides of general formulas* $Ar-S(O)(=NSO_2CF_3)Cl$ *(1) and* $Ar-S(=NSO_2CF_3)_2Cl$ *(2) with ammonia have been investigated and found to yield the ammonium salts of [N-(trifluoromethylsulfonyl)arenesulfinylimino]-N'-(trifluoromethylsulfonyl)amides. The high oxidative ability of the chlorides (1,2) have been shown. Thus, chlorides (2) react with benzene or trifluoromethylbenzene, to form the chlorobenzene or 3-chloro-trifluoromethylbenzene. The fluorides of the general formulas* $Ar-S(O)(=NSO_2CF_3)F$ *and* $Ar-S(=NSO_2CF_3)_2F$ *have been prepared. Their interaction with ammonia leads to the usual formation of corresponding amides. The electron nature of new electron withdrawing substituents have been investigated.*

INTRODUCTION

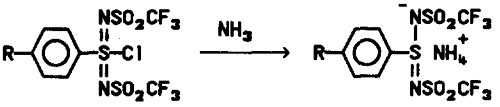
Recently, we have developed the facile synthesis of N-(trifluoromethylsulfonyl)arenesulfonimidoyl- and N,N'-bis(trifluoromethylsulfonyl) arenesulfonodiimidoyl chlorides [1]. The σ-constants of $-SOCl$ and $-SO_2Cl$ group analogs in which oxygen atoms are replaced for one or two trifluoromethylsulfonylimino groups are determined using the ^{19}F NMR method. In the case of $-S(=NSO_2CF_3)_2Cl$ group the σ_p-constant is equal to 1.70. The present study is due to the reactivity of the above mentioned chlorides.

RESULTS AND DISCUSSION

Reactivity of the mono- and bis-N-(trifluoromethylsulfonyl)-substituted azaanalogs arensulfonochlorides. We have investigated the reactions of chlorides (1,2) with ammonia. In contrast to the usual results of the common reactions of sulfonochlorides with ammonia it was shown that the chlorides (1,2) are reduced with ammonia and ammonium salts (3) and (4), respectively, are formed. It can be suggested, that the initial step of this reaction is the oxidative chlorination of ammonia by chlorides (1) and (2) leading to the formation of NH_2Cl, N_2H_4 and thus to NH=NH. The latter can be considered as a source of hydrogen atoms to form compound (3) and (4).



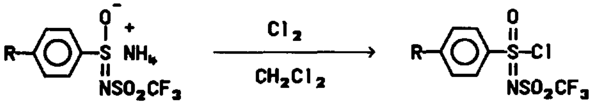
1(a-e) 3(a-e)



2(a-e) 4(a-e)

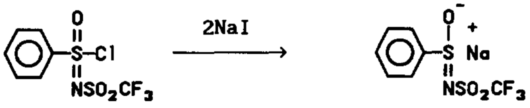
R = H(a),Cl(b),F(c),CH_3(d),NO_2(e)

Compounds (3) and (4) are white solids, insoluble in benzene, but in CH_2Cl_2 and Et_2O they are partially soluble. The salts (3,4) melt with decomposition. Ammonium salts (3) react with chlorine in CH_2Cl_2 to form the starting sulfonimidoyl chlorides (1).

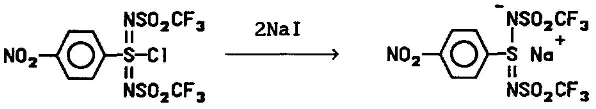


3(a-e) 1(a-e)

All attempts to oxidize the salts (4) into the chlorides (2) by either chlorine, or SO_2Cl_2, or t-BuOCl failed. The salts (3) and (4) do not react with HCl in ether solution, and in aqueous solution the hydrolysis takes place to form trifluorometanesulfonamide. Sodium salts (5) and (6) can be obtained by reduction of chlorides (1) and (2) by NaI respectively.



1a 5



2e 6

The exotermic reaction takes place by addition of dry benzene to arenesulfonodiimidoyl chlorides (2). At first starting chloride (2) dissolves in benzene and then the white solid of compound (7) precipitates. The ^{19}F NMR spectra of this substance contains one signal of CF_3-groups (δ=-77.48 ppm for (7c)). The reaction mixture was analysed using the GC method and the chlorobenzene was detected.

For the determination of the structure of compound (7) an X-ray structural study has been performed. The general view of molecule (7e) with atom numbering and principal bond lengths is shown in Figure 1. The central atom of sulfur S1, has a noticeable distorted pyramidal bond configuration with scattering of bond angles from 98.7(1) through to 107.2(1)$^{\circ}$. The double bond S1=N1 lies practically in the plane of the benzene ring, the torsion angle C2-C1-S1-N1 is 1.5(2)$^{\circ}$. The bond lengths with participation of sulfur and nitrogen atoms are as expected.

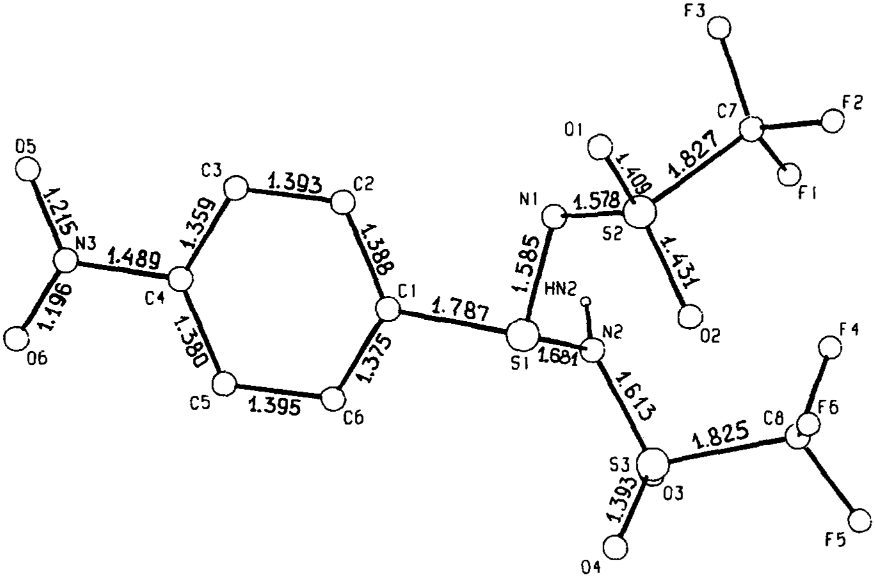
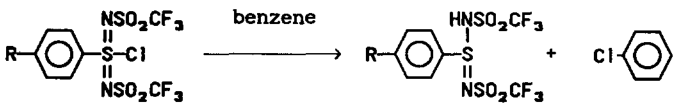


Fig.1

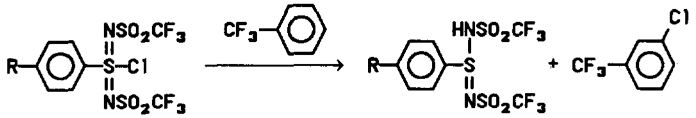
Thus, the arenesulfonylimidoyl chlorides (2) when reacting with as weak a C-nucleophilic agent as benzene are reduced smoothly to [N-(trifluoromethylsulfonyl)arenesulfinylimino]-N'-(trifluoromethylsulfonyl) amides (7).



2(a,c,e) 7(a,c,e)

R = H (a), F (c), NO_2 (e)

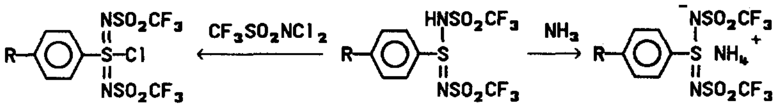
Chlorides (2) proved to be powerful chlorinating agents that react even with trifluoromethylbenzene, at ambient temperature, in spite of the fact that the CF_3-group inhibits activity of the benzene ring. In this case the time of reaction increases markedly.



2(a,e) 7(a,e)

R = H (a), NO_2 (e)

Compounds (7) do not react with chlorine even when heated at 100°C under pressure. The oxidative chlorination of compounds (7) was carried out by reaction with the N,N-dichlorotrifluoromethanesulfonylamide without solvent at ambient temperature. In this case $CF_3SO_2NCl_2$ shows a powerful ability to chlorinate and can be used to form chlorides (2). Ammonium salts (4) are formed by the reaction of compounds (7) with ammonia in ether solution at ambient temperature. The structure of salt (4) has been proved by this reaction.

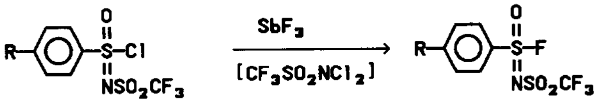


2(a,c,e) 7(a,c,e) 4(a,c,e)

R = H (a), F (c), NO_2 (e)

The chlorides (1) and (2) are extremely sensitive to moisture, though under dry Ar they are stable over a period of more than two months.

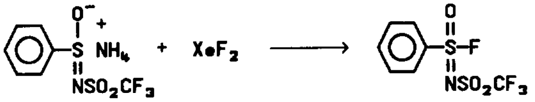
Synthesis and reactivity of the mono- and bis-N-(trifluoromethylsulfonyl)-substituted azaanalogs of arenesulfonofluorides. The chlorine atoms in the chlorides (1) can be substituted by fluorines by treatment with silver fluoride in CH_3CN solution [1]. The utilization of CsF has no advantages and arenesulfonimidoyl fluorides (8) were obtained with a yield of 20% only. The Swarts's reaction with SbF_3 in the presence of $CF_3SO_2NCl_2$ is the most convenient route to fluorides (8).



1(a-e) 8(a-e)

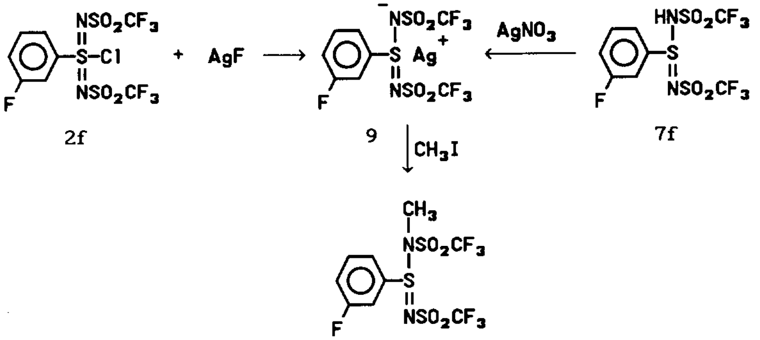
R = H(a), Cl(b), F(c), CH$_3$(d), NO$_2$(e)

The compound (8a) has been obtained also in quantitative yield by heating of ammonium salt (3a) with xenon difluoride.



3a 8a

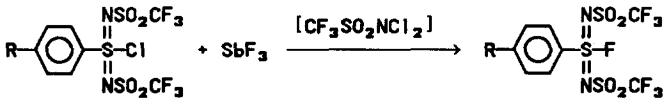
In contrast to chlorides (1) in which one oxygen atom of $-SO_2Cl$ group is replaced by a $=NSO_2CF_3$ fragment, bis(substituted) azaanalogs - chlorides (2) possess a more positive chlorine atom which is diffucult to substitute by fluorine atom by usual methods. Thus, for example the treatment of chlorides (2) with alkali-metal fluorides, ZnF_2 was unsuccessful. The action of silver fluoride results in reduction of chlorides (2) and the silver salt (9) is formed. Compound (9) was also obtained by an alternative route from compound (7). The methylation of salt (9) by excess of CH_3I occurs at the nitrogen atom and leads to compound (10).



2f 9 7f

10

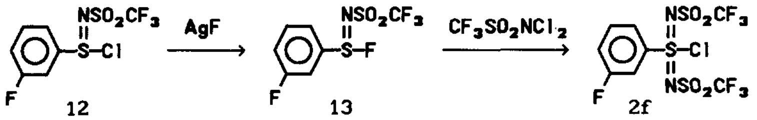
It was found that N,N'-bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl fluorides (11) can be obtained only by heating chlorides (2) with antimony (III) fluoride without solvent and in the presence of $CF_3SO_2NCl_2$, the last one presumably to generate SbF_3Cl_2 *in situ* which promotes the reaction under mild conditions. It is of interest, that neither antimony (V) chloride, nor chlorine promotes this reaction. Fluorides (8) and (11) are stable to air moisture and may be distilled under high *vacuo*.



2(a,c,d,f) 11(a,c,d,f)

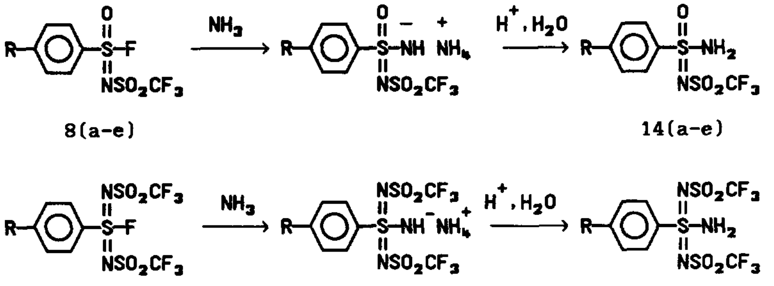
R = H(a),4-F(c),CH_3(d), 3-F(f)

The chlorine atom in the N-(trifluoromethylsulfonyl)arenesulfynimidoyl chloride (12) may be substituted by a fluorine atom by treatment of silver fluoride in acetonitrile. However, our attempts to synthesize fluorides (11) starting from compound (13) using $CF_3SO_2NCl_2$ as oxidative imination agent failed. The reaction is accompainied by substitution of a fluorine atom by a chlorine one and chloride (2f) is formed.



12 13 2f

Fluorides (8) and (11) react with ammonia (liquid or gaseous) to form ammonium salts of compounds (14) and (15) respectively, which give the corresponding amides by treatment with H_2SO_4.



8(a-e) 14(a-e)

11(a,c,d,f) 15(a,c,d,f)

R = H(a),Cl(b),4-F(c),CH_3(d),NO_2(e),3-F(f)

Thus, it was shown that the arenesulfonimidoyl- and arenesulfonodiimidoyl halogens possess a different reactivity towards nucleophilic agents. For confirmation of the structure of compounds (14) X-ray structural study was performed. The general view of the molecule (14b) with atom numbering and principal bond lengths is shown in Figure 2. A sulfur atoms have pyramidal bond configuration with the scattering of the bond angles from $100.19(8)^{\circ}$ to $120.55(8)^{\circ}$. The bond S1-N1 lies in the plane of the benzene ring and the fragment C1-S1-N1-S2 is transoic. The presence of an electron donating NH_2-group bonded to sulfur atom S1 leads to over distribution of bond lengths in the central fragment. The bond S=N is lengthened and S-N bond shortened to 1.559 and 1.576 Å respectively in comparison with ordinary values (1.51 and 1.61 Å respectively) [2].

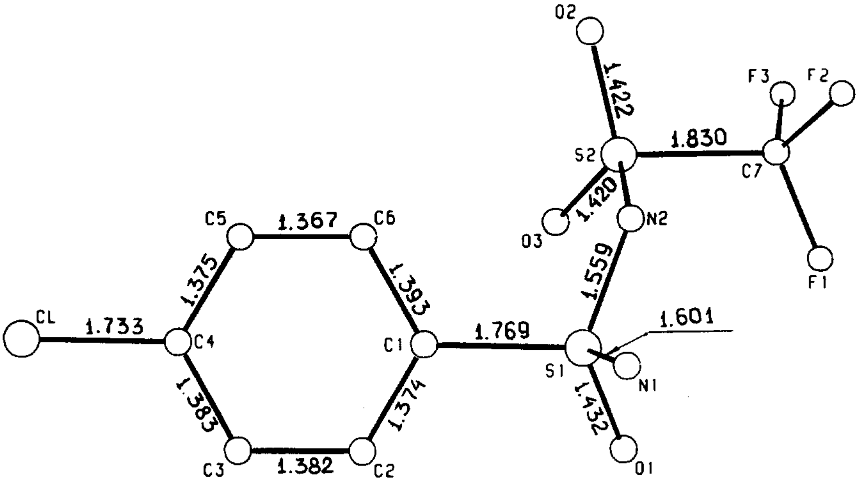
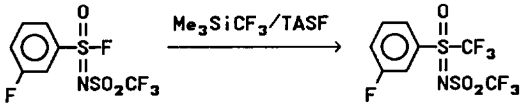


Fig.2

Arenesulfonimidoyl- (14) and arenesulfonodiimidoyl- (15) amides are white solids, soluble in organic solvents and stable to hydrolysis. The amide (14b) does not give a depression of melting point at mixing test with the product obtained by independent way [3].

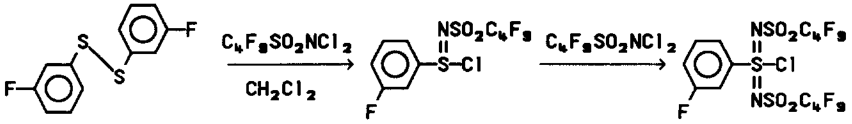
The reaction of arenesulfonimidoyl fluorides (8f) with (trifluoromethyl)trimethyl silane in the presence of catalytic amounts of tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF) [4] leads to the N-(trifluoromethylsulfonyl)arenetrifluoromethyl sulfoximine (16) in 70% yield.



8f 16

Electron nature of the new super strong electronwithdrawing substituents. The σ-constants of analogs of SO_2F-groups in which oxygen atoms are substituted by one or two CF_3SO_2N= groups were determined (calculated by the equations given in the publication [5]) using the ^{19}F NMR method. For the group $-S(=NSO_2CF_3)_2F$ the σ_p-constant is the highest, it is equal to 1.76 (see Table I).

The substitution of CF_3-groups by more electronegative n-C_4F_9-groups at the R_fSO_2N= fragment seems to lead to the further increase of electron-accepting character of the sulfur containing substituents. Therefore we have synthesized N-(perfluorobutylsulfonyl)-arenesulfynimidoyl (17) and N,N'-bis(perfluorobutylsulfonyl)arenesulfonodiimidoyl (18) chlorides.



17 18

Table I Hammett-Taft's σ-Constants of Substituents

Substituent	σ_I	σ_R	σ_P
$-S(=NSO_2CF_3)Cl$	1.10	0.24	1.34
$-S(=NSO_2C_4F_9)Cl$	1.12	0.24	1.36
$-S(O)(=NSO_2CF_3)Cl$	1.14	0.32	1.46
$-S(O)(=NSO_2CF_3)F$	1.11	0.37	1.48
$-S(=NSO_2CF_3)_2Cl$	1.36	0.34	1.70
$-S(=NSO_2C_4F_9)_2Cl$	1.37	0.32	1.69
$-S(=NSO_2CF_3)_2F$	1.37	0.41	1.78

The σ-constants of substituents $-S(=NSO_2C_4F_9)Cl$ and $-S(=NSO_2C_4F_9)_2Cl$ are given in Table I. It was found that values of σ-constants for both types of substituents with the central sulfur atom in (+4) and (+6) valence stages $-S(=NSO_2R_f)Cl$ and $-S(=NSO_2R_f)_2Cl$ do not depend on the length of perfluoroalkyl chain of R_f (R_f = CF_3, C_4F_9) and field effects are negligible in this case.

CONCLUSIONS

It was shown, that compounds (1) and (2) are reduced under the action of C-, N-nucleophiles. N-(Trifluoromethylsulfonyl)arenesulfonimidoyl- and N,N'-bis(trifluoromethylsulfonyl)arenesulfonodiimidoyl fluorides (8) and (11) were obtained by Swarts's reaction from the corresponding chlorides.There properties were compared with the reactivity of starting chlorides (1,2). The amides (14,15) have been synthesized by reaction of fluorides (8), (11) with ammonia.

EXPERIMENTAL

General remarks

CH_2Cl_2 was distilled twice over CaH_2. Et_2O and THF were distilled over $LiAlH_4$. MeCN was at first distilled from P_2O_5, then from CaH_2. Benzene was distilled twice from Na. SbF_3 was dried *in vacuo* (water-jet pump) at 160°C during 12 h. All compounds were handled in dry Ar atmosphere.

The ^{19}F NMR spectra were recorded on a Bruker WP-200 (200MHz) spectrometer with CCl_3F as the internal standard. Infrared spectra were recorded either neat or as double mulls (Nujol), as $CDCl_3$, CCl_4, CH_2Cl_2 solutions, as KBr disks on a UR-20 spectrometer. ^1H NMR spectra were recorded on a Gemini (200MHz) against internal HMDS. All new compounds were analyzed (for C,H,N,F). GC analyses were performed on a Chrom-5 instrument fitted with a flame-ionization detector on a PEGA (polyethyleneglycol 20M) column.

An X-ray structural study of the compounds (7e) and (14b) was performed with a CAD-4-ENRAF-NONIUS diffractometer using graphite monochromated Mo-K_α(7e) and Cu-K_α(14b) radiation (the ratio of the scanning rates $\omega/s = 1.2$). Both structures were solved by direct methods and refined by full-matrix least squares techniques in the anisotropic approximation. All hydrogens were located in the difference Fourier maps and were included in the final refinement with the fixed position and thermal (B_{iso}=5A^o) parameters. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS programmer package [6].

Starting materials

N-(Trifluoromethylsulfonyl)arenesulfonimidoyl (1a-e) and N,N'-bis-(trifluoromethylsulfonyl)arenesulfonodiimidoyl (2a-e) chlorides were obtained by N,N-dichlorotrifluoromethanesulfonamide [7] oxidative imination of arenesulfonyl chlorides and diaryldisulfides, respectively [1].

AgF was obtained by reaction of the sulfur tetrafluoride with silver trifluoroacetate.

$$CF_3COOAg + SF_4 \longrightarrow CF_3COF + AgF + SOF_2$$

Silver trifluoroacetate (10g, 45mmol) was transfered to an evacuated 50ml stainless steel autoclave with platinum bushing. SF_4 (7g, 65mmol) was added by transfer under pressure. The mixture was heated at 100°C over a time period of about 10h, cooled and the volatile products were removed *in vacuo*. The remaining solid AgF was washed out with Et_2O (3×100) from tracks of CF_3COOAg. Yield 5.5g (92%) AgF.

Me_3SiCF_3 was obtained according to Marchenko-Ruppert method [8]. TASF was purchased from Fluka AG.

I. *Reactions of chlorides (1) and (2)*

a) with ammonia

Ammonia was bubbled at 0-5°C through a solution (1mmol) of chlorides (1) or (2) in 10 *ml* Et_2O. *After the* NH_4Cl-*production had stopped, it was removed by filtration, the solvent* was distilled off *in vacuo*. The remaining residue was washed with CH_2Cl_2. The analytical data, melting points and ^{19}F NMR data are given in Table II. The ammonia salts (3) and (4) were obtained in 95-97% yields.

IR (KBr): 950-1050 (O-S-N, N-S-N); 1350-1500,2800-3400 (NH_4^+)

for (3a): $\nu_{as}(SO_2)$=1295 $\nu_s(SO_2)$=1140 $\nu(CF_3)$=1180 (max)
for (3b): $\nu_{as}(SO_2)$=1330 $\nu_s(SO_2)$=1150 $\nu(CF_3)$=1190 (max)
for (4b): $\nu_{as}(SO_2)$=1290 $\nu_s(SO_2)$=1135 $\nu(CF_3)$=1165(max)

^1H NMR for (3b): δ=6.07(br.S.,4H), δ=7.438-7.587(M.,4H) (MeCN/HMDS)

b) with NaI

The solution of NaI (2 mmol) in MeCN was added to a concentrated solution of (1a) or (2e) (1mmol) in CH_3CN. The reaction mixture was stirred for 15 min at ambient temperature. The NaCl was removed by filtration, MeCN was evaporated. The remaining residue was washed out with CH_2Cl_2.

Compound (5a) was obtained in 98% yield as a white powder, m.p. (decomp.) 185-187°C.
Compound (6c): 90% yield, m.p. (decomp.) 235-237°C

c) with AgF

The solid AgF was added to solution of (2f) (1mmol) in 10 ml CH_3CN under stirring at 22°C. AgCl was filtered off and the solvent was removed *in vacuo*. The solid white precipitate (9) was washed with CH_2Cl_2.

M.p. (decomp.) 190-220°C. NMR ^{19}F (CH_3CN): δ_1=-78.2ppm(CF_3), δ_2=-110.2(F_{ar}).

$C_8H_4N_2O_4S_3F_7Ag$ (529): calc.: C 18.11; H 0.94; N 5.28; F 25.1.
Found: C 18.14; H 0.84; N 4.86; F 26.0.

Table II Ammonium salts of [N-(Trifluoromethylsulfonyl)arene- sulfinylimino]-N'-(trifluoromethylsulfonyl)amides (3a-e) and 4(a-e)

Pro-duct	Molecular Formula	M.p. (°C)	^{19}F NMR (CH_3CN/CCl_3F)	Analtical data				
					C	H	N	F
2a	$C_7H_9F_3N_2O_3S_2$ (290)	135–137	-78.13(CF_3)	calc.	28.97	3.10	9.66	19.66
				found	28.92	3.07	9.63	19.96
2b	$C_7H_8ClF_3N_2O_3S_2$ (324.5)	180–181	-78.26(CF_3)	calc.	25.89	2.47	8.63	17.57
				found	25.64	2.32	8.56	17.82
2c	$C_7H_8F_4N_2O_3S_2$ (308)	176–177	-78.26(CF_3) -111.64(F_{ar})	calc.	27.27	2.60	9.09	24.68
				found	27.06	2.78	8.98	24.84
2d	$C_8H_{11}F_3N_2O_3S_2$ (304)	108–109	-78.19(CF_3)	calc.	31.58	3.62	9.21	18.75
				found	31.81	3.37	9.25	19.02
2e	$C_7H_8F_3N_3O_5S_2$ (335)	164–165	-78.26(CF_3)	calc.	25.07	2.39	12.54	17.01
				found	25.32	2.49	12.30	17.13
4a	$C_8H_9F_6N_3O_4S_3$ (421)	124-126	-78.13(CF_3)	calc.	22.80	2.14	9.98	27.08
				found	23.13	1.95	9.87	27.48
4b	$C_8H_8ClF_6N_3O_4S_3$ (455.5)	163-165	-78.13(CF_3)	calc.	21.08	1.76	9.22	25.03
				found	20.98	1.74	8.86	25.02
4c	$C_8H_8F_7N_3O_4S_3$ (439)	168-170	-78.13(CF_3) -108.34(F_{ar})	calc.	21.87	1.82	9.57	30.30
				found	21.52	1.52	9.23	30.46
4d	$C_9H_{11}F_6N_3O_4S_3$ (435)	145-147	-78.13(CF_3)	calc.	24.83	2.53	9.66	26.20
				found	24.92	2.43	9.33	26.30
4e	$C_8H_8F_6N_4O_6S_3$ (466)	180-183	-78.13(CF_3)	calc.	20.60	1.72	12.02	24.46
				found	20.92	1.78	11.80	24.62

d) with benzene

[N-(trifluoromethylsulfonyl)arenesulfinyl]-N'-(trifluoromethylsulfonyl)amides

The benzene (or trifluoromethylbenzene) (1ml) was added to chlorides (2a,c,e) (0.2mmol) under stirring at 22°C. Sometime the after chloride (2) dissolved (1-3min), the white solid precipitate of compounds (7) precipitated. In the case of the reaction with benzene the process is exothermically low. The precipitate was filtrated. The compounds (7) were obtained in quantitative yields. The melting points, reaction conditions, analytical data and ^{19}F NMR data are given in Table III.

IR: (CH_2Cl_2): 840(N-S-N), 1350(as, SO_2), 1130 (s,SO_2), 1200-1240 (CF_3).

Table III [N-(Trifluoromethylsulfonyl)arenesulfinylimino]-N'-(trifluoromethylsulfonyl) Amides 7(a,c,e)

Product	Molecular Formula	M.p. (°C)	$^{\tau}$reac (min) with PhH	$^{\tau}$reac. (h) with CF_3–Ar	^{19}F NMR (CH_2Cl_2/CCl_3F)	Analytical data			
							C	N	F
7a	$C_8H_6F_6N_2O_4S_3$ (404)	95	90	960	-77.7 (CF_3)	calc.	23.76	6.83	28.20
						found	23.63	6.96	28.03
7c	$C_8H_5F_7N_2O_4S_3$ (422)	118	80	840	-77.48 (CF_3) -100.75 (F_{ar})	calc.	22.75	6.64	31.51
						found	22.37	6.60	31.30
7e	$C_8H_5F_6N_3O_6S_3$ (449)	139	10	96	-77.93 (CF_3)	calc.	21.38	9.35	25.39
						found	21.26	9.37	25.21

II. *Reactions of ammonia salts (3)*

a) with Cl_2

The solution of Cl_2 (3mmol) in CH_2Cl_2 was added dropwise to suspension (3) (1mmol) in CH_2Cl_2 under stirring. The pricipitate of NH_4Cl was filtered off and CH_2Cl_2 was removed *in vacuo*. The chlorides (1) were obtained in 100% yields as yellow oils. ^{19}F NMR spectrum corresponds to the literature data [1].

b) with XeF_2

The salts (3) (1mmol) in CH_3CN with XeF_2 (1.1mmol) were heated in a quartz round-bottomed flask, which was dried under Ar atmosphere at 40-50°C. The time of the reaction was 3-5h. The solution was evaporated, the remaining residue was dissolved in CH_2Cl_2 and the NH_4F was removed off by filtration. CH_2Cl_2 was distilled off *in vacuo* and the remaining oil was dried under high *vacuo* at 22°C over time of about 30 min (from volatile by-products).

III *Reactions of amides (7)*

a) with $CF_3SO_2NCl_2$

Amide (7) (1mmol) was transferred to a flask which was dried under Ar atmosphere with extraneous moisture protection (tube with P_2O_5). At ambient temperature the N,N-dichlorinetrifluoromethanesulfonamide (2mmol) was added. Mixture was stirred for 5-6 h at ambient temperature. Then the excess of $CF_3SO_2NCl_2$ and CF_3SO_2NHCl was distilled off under high *vacuo*. The yield of (2) was quantitative. ^{19}F NMR spectrum corresponds to the literature data [1].

b) with ammonia

Compound (7) (1mmol) was dissolved in Et_2O (10ml) and an excess of ammonia was bubbled through for 20 min at ambient temperature. Et_2O was evaporated *in vacuo*. The remaining residue was washed with CH_2Cl_2 and dried *in vacuo* at 22°C. The resulting salt at the mixing test to not give the depression of melting point with the respective salt was obtained independent procedure (by reaction of chlorides (2) with ammonia; see Table II)

c) with $AgNO_3$

To solution of compound (7) (1mmol) in NH_4OH (1 ml) the solution of $AgNO_3$ (1mmol) in water was added. The precipitate (9) was filtrated and dried under high *vacuo* at 30°C.

IV *Fluorides (8) and (11)*

Chloride (1) or (2) (8mmol), SbF_3 (10mmol) and a few drops (0.1mmol) of $CF_3SO_2NCl_2$ were placed in a two-neck flask dried under Ar atmosphere with extraneous moisture protection. The mixture was stirred and heated over a Bunsen flame (the temperature inside the flask never exceeded 70°C) over time of about 2-3 min. At the end of the process Et_2O (20 ml) was added at 22°C. The ether solution was washed with cold aqueous solution of HCl (at ratio 1:1) and distilled water, then dried ($MgSO_4$) and concentrated. The product (8) or (11) were distilled under high *vacuo*. Yields 60-80% were obtained. Physical data are given in Tables IV, V.

V *Reaction of silver salt (9) with* CH_3I

To salt (9) (0.53g., 1mmol) freshly-distilled CH_3I (2ml) was added. The mixture was stirred for 0.5h at 30°C. The excess of CH_3I was removed. The remainder was dissolved in CH_2Cl_2, filtered under Ar atmosphere and concentrated *in vacuo*. Yield of (10) 56%.

^{19}F NMR (CH_2Cl_2): δ_1=-106.5(F_{arom}); δ_2=-74.6(s.3F); δ_3=-78.4(s.3F)

^1H NMR (benzene): δ_1=3.63 (s.3H); δ_2=6,3(m. 4H)

VI *Reactions of fluorides (8), (11)*

a) with ammonia

Method A

Fluoride (8) or (11) (1mmol) was dissolved in Et_2O (10ml). To the solution ammonia was bubled for 30 min at ambient temperature. Et_2O was distilled off *in vacuo*. The concentrated solution of the remainder in water was acidificated by H_2SO_4(conc.) at 0-5°C (pH=1) and extracted with Et_2O, dried ($MgSO_4$) and concentrated. The products (14) and (15) were recrystallized from benzene.

Table IV **N-(Trifluoromethylsulfonyl)arenesulfonimidoyl Fluorides (8(a-f)**

Product	Molecular Formula	^{19}F NMR (CH_2Cl_2/ CCl_3F)	B.p.(°C)/ P(mmHg)	Analytical data			
					C	H	F
8a	$C_7H_5F_4NO_3S_2$ (291)	-78.329(CF_3) +73.0(S-F)	85-95/ 0.04	calc. found	28.87 28.73	1.72 1.79	26.12 26.30
8b	$C_7H_4ClF_4NO_3S_2$ (325.5)	-78.32(CF_3) +73.85(S-F)	100-110/ 0.04	calc. found	25.81 25.88	1.23 1.31	23.34 23.10
8c	$C_7H_7F_5NO_3S_2$ (309)	-95.45($F_{ar.}$) -78.38(CF_3) +74.30(S-F)	95-100/ 0.04	calc. found	27.18 27.22	1.29 1.33	30.74 30.52
8d	$C_8H_7F_4NO_3S_2$ (305)	-78.13(CF_3) +73.13(S-F)	85-100/ 0.04	calc. found	31.48 31.62	2.30 2.32	24.92 24.65
8e	$C_7H_4F_4N_2O_5S_2$ (336)	-78.19(CF_3) +73.48(S-F)	70-90/ 0.01	calc. found	25.00 25.17	1.19 1.10	22.62 22.38
8f	$C_7H_4F_5NO_3S_2$ (309)	-106.72($F_{ar.}$) -78.38(CF_3) +73.0(S-F)	85-95/ 0.04	calc. found	27.18 27.28	1.29 1.32	30.74 30.78

Table V **N,N'-Bis(Trifluoromethylsulfonyl)arenesulfonodiimidoyl Fluorides 11(a,c,d,f)**

Product	Molecular Formula	^{19}F NMR (CH_2Cl_2/CCl_3F)	Analytical data				
				C	H	N	F
11a	$C_8H_5F_7N_2O_4S_3$ (422)	-77.48(CF_3) +67.56(S-F)	calc. found	22.75 22.67	1.18 1.19	6.64 6.65	31.52 30.96
11c	$C_8H_4F_8N_2O_4S_3$ (440)	-92.45($F_{ar.}$) -77.41(CF_3) +69.70(S-F)	calc. found	21.82 21.73	0.91 1.11	6.36 6.28	34.55 33.98
11d	$C_9H_7F_7N_2O_4S_3$ (436)	-77.50(CF_3) +68.60(S-F)	calc. found	24.77 24.65	1.60 1.72	6.42 6.45	30.50 30.02
11f	$C_8H_4F_8N_2O_4S_3$ (440)	-104.7($F_{ar.}$) -77.30(CF_3) +68.30(S-F)	calc. found	21.82 21.76	0.91 1.02	6.36 6.38	34.55 34.14

Method B

Fluoride (8) or (11) (1mmol) was situated in a two-necked flask with ammonia (2-3ml) was condensed. The mixture was stirred at ambient temperature. The excess of NH_3 was removed. Further work-up is performed according to method A . The melting points, analytical data and ^{19}F NMR data are given in Table VI.

IR (KBr):for (14a) ν_{as}(O-S-N)=1288;ν_s(O-S-N)=1070;$\nu_{as}(SO_2)$=1340; $\nu_s(SO_2)$=1140; $\nu(CF_3)$=1210; $\nu_{as}(NH_2)$=3372; $\nu_s(NH_2)$=3260.

Table VI **N-(Trifluoromethylsulfonyl)arenesulfonimidoyl (14 a-f) and N,N'-Bis-(trifluoromethylsulfonyl)arenesulfonodiimidoyl (15 a,d) Amides**

Product	Molecular Formula	M.p. (°C)	^{19}F NMR (CH_3CN/CCl_3F)	Analytical data	C	H	N	F
14a	$C_7H_7F_3N_2O_3S_2$ (288)	105	-78.8(CF_3)	calc. found	29.17 29.34	2.43 2.42	9.72 9.59	19.79 19.61
14b	$C_7H_6ClF_3N_2O_3S_2$ (322,5)	132	-78,77(CF_3)	calc. found	26.05 25.89	1.86 1.72	8.68 8.49	17.67 17.54
14c	$C_7H_6F_4N_2O_3S_2$ (306)	106	-102.63($F_{ar.}$) -78.64(CF_3)	calc. found	27.45 27.21	1.96 1.82	9.15 9.14	24.84 24.85
14d	$C_8H_9F_3N_2O_3S_2$ (302)	115	-78.77(CF_3)	calc. found	31.79 31.63	2.98 2.91	9.27 9.16	18.87 18.84
14e	$C_7H_6F_3N_3O_5S_2$ (333)	137	-78.7(CF_3)	calc. found	25.23 24.71	1.80 1.63	12.61 13.03	17.12 16.71
14f	$C_7H_6F_4N_2O_3S_2$ (306)	108	-109.57($F_{ar.}$) -78.8(CF_3)	calc. found	27.45 27.24	1.96 1.65	9.15 9.34	24.84 24.71
15a	$C_8H_7F_6N_3O_4S_3$ (419)	107	-78.5(CF_3)	calc. found	22.91 22.67	1.67 1.70	10.02 9.90	27.21 27.15
15d	$C_9H_9F_6N_3O_4S_3$ (433)	132	-78.60(CF_3)	calc. found	24.94 24.76	2.08 2.17	9.70 9.52	26.33 26.13

b) with Me_3SiCF_3

A solution of Me_3SiCF_3 (0.9g.,6.4mmol) in THF (2ml) was added dropwise to a stirred suspension of fluoride (8a) (1g.,3.2mmol) and TASF (0.09g.,0.32mmol) in THF (15ml) at -20°C. Then the temperature was increased to 22°C. The mixture was stirred for 1h,then treated with water (20ml). The organic phase was washed with water, dried ($MgSO_4$) and concentrated. The product (16) was purified by column chromatography on SiO_2 with benzene/-petroleum ether (in ratio 1:4) as the mobile phase. A 70% yield (0.8g.,2.2mmol) was obtained.

B.p.136-137°C/0.7mmHg; ^{19}F NMR(CH_2Cl_2):δ_1=-106.44(F_{ar}); δ_2=-75.47(s.3F); δ_3=-78.26 (s.3F)
IR (CH_2Cl_2):ν_{as}(O-S-N)=1306; ν_s(O-S-N)=1056; ν_{as}(SO_2)=1382; ν_s(SO_2)=1130; ν(CF_3)=1221.

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