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Electrochemical fluorination of *N,N,N',N'*-tetramethylsulfondiamides [1]

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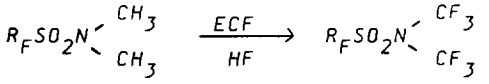
Abstract

The electrochemical fluorination of *N,N,N',N'*-tetramethylsulfondiamides gives the corresponding perfluorinated *N,N,N',N'*-tetrakis(trifluoromethyl)sulfondiamides. The nature of the partially fluorinated by-products is determined by specific adsorption of starting compounds on the surface of the Ni anode.

Keywords: Electrochemical fluorination; Simons process; Perfluoroalkyldisulfondiamides

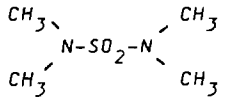
1. Introduction

In the previous report [1] we have described the electrochemical synthesis of new *N,N*-bis(trifluoromethyl)perfluoroalkanesulfonamides based on electrochemical fluorination of *N,N*-dimethylperfluoroalkanesulfonamides in liquid $(HF)_x$ (Simons process, ECF).

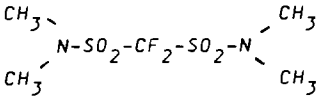


$R_F = CF_3;\ C_4F_9$

The influence of the nature of starting compound and the temperature of the cell on the yield of perfluoro- and partially-fluorinated compounds was demonstrated. To clarify the mechanism of the ECF process we investigated the electrochemical fluorination of *N,N,N',N'*-tetramethylsulfondiamides (compounds 1 and 2) in liquid $(HF)_x$.



(1)



(2)

[1] Dedicated to Prof. Dr. mult. A. Haas, Bochum, on the occasion of his 65th birthday.

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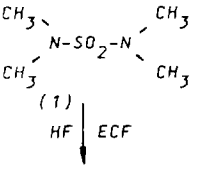
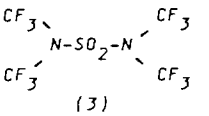
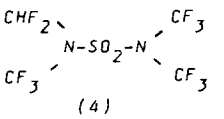
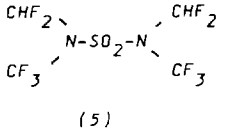
2. Results and discussion

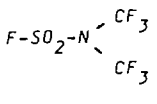
ECF of *N,N,N',N'*-tetramethylsulfondiamide (1) in anhydrous hydrogen fluoride solution leads to the formation of a mixture of perfluoro and partially fluorinated compounds (3–7) in a total yield up to 30%.



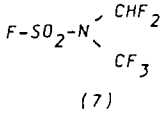
(1)

HF | ECF

	Yield[a], %	Contents in the reaction mixture[a], %
 (3)	11	43
 (4)	4	15
 (5)	3	11



(6) 8 18



(7) 2 5

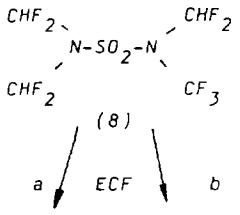
others 8

[a] Estimated by GC.

Gaseous products gave IR-spectra identical to those of the gaseous phase from ECF of $CF_3SO_2N(CH_3)_2$ [1] and they reflect the presence of products of fragmentation of starting material, such as:

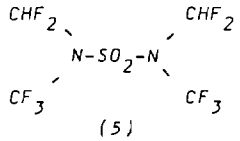
$FSO_2N(CF_3)_2$, $FN(CF_3)_2$ and SO_2F_2

Relatively high contents of the compounds (6,7) in the reaction mixture indicate that cleavage of the S–N bond is a parallel process which takes place at the first stages of the ECF of compound (1). Replacement of hydrogen atoms in the starting compound (1) by fluorine proceeds step by step and partially-fluorinated compounds (4) and (5) are precursors for the formation of perfluorinated compound (3). On the other side, compound (5) is formed by fluorination of precursor (8). Compound (8) was found among other products in the reaction mixture. (See Table 1.)

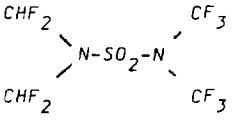


(8)

a ECF b

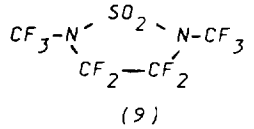


(5)



has not been found in the reaction mixture

Compound (8) can be fluorinated in two possible ways: (a) and (b), but only the product (5) was detected in the reaction mixture by NMR ^{19}F spectroscopy (see Table 1). It indicates that fluorination takes place preferably on the mostly hydrogenated side of the starting molecule (8). In the NMR ^{19}F spectra of the reaction mixture small signals: −56.5 m and −92.7 m; $J_{F,F}=7$ Hz with integral intensity 3:2 are present. These signals can be related to compound (9).

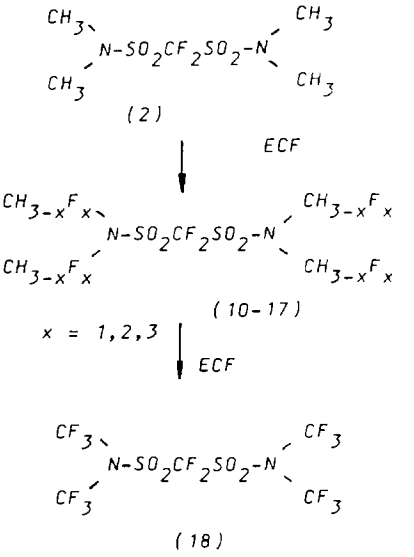


(9)

The formation of cyclic compounds via electrochemical fluorination of organic molecules is possible [2] owing to the radical mechanism of this process.

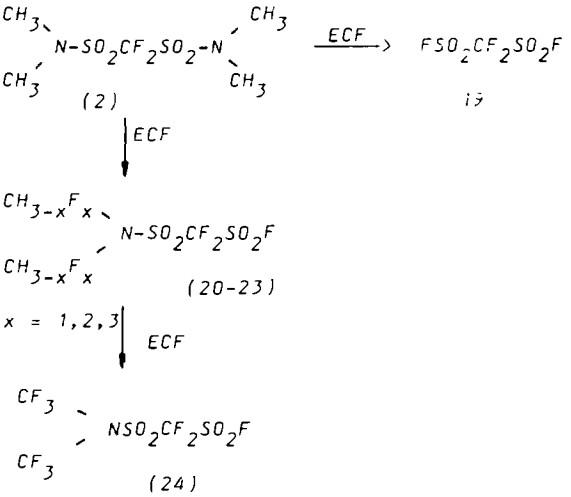
Electrochemical fluorination of compound (2) leads to the formation of a much more complicated mixture of perfluoro- and partially-fluorinated products than compound (1). According to GC-analysis the liquid phase, collected from the cell, contains more than 20 compounds. The resulting mixture after electrochemical fluorination was separated by distillation into several narrow fractions, each containing 2–3 compounds, which were further characterized by ^{19}F- and ^{1}H-NMR spectra. The results show that electrochemical fluorination of compound (2) proceeds in several parallel ways, such as:

(a) replacement of hydrogen atoms in starting compound (2) by fluorine, that leads to the formation of partially-fluorinated compounds (10–17) and finally of perfluorinated compound (18) (see Table 1).



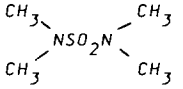
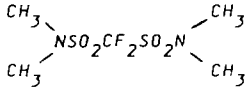
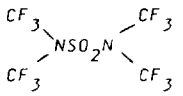
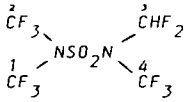
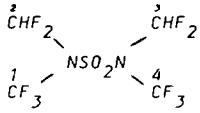
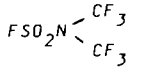
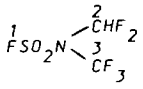
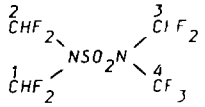
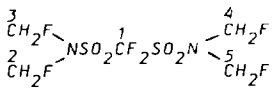
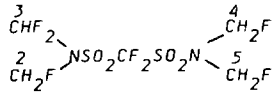
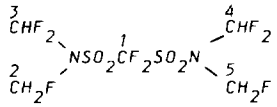
(2) ECF (10-17) x = 1,2,3 ECF (18)

(b) cleavage of the S–N bond, followed by fluorination of the resulting fragments



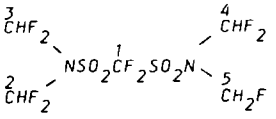
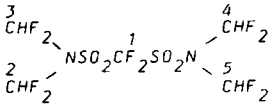
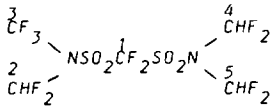
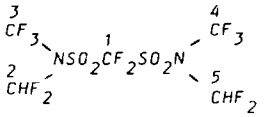
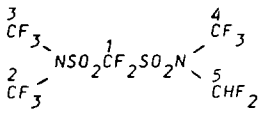
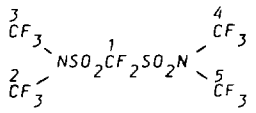
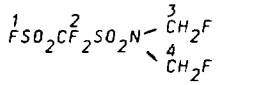
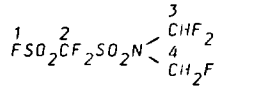
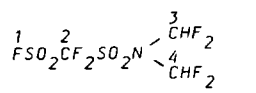
(2) ECF (20-23) x = 1,2,3 ECF (24)

Table 1
NMR data

Compound	^{19}F, δ(ppm)	^{1}H, δ(ppm)
 (1)		2.82 (s)
 (2)	−100.4 (m)	3.06 (t) $^{5}J_{H,F}$ = 1.0 Hz
 (3)	−53.4 (s)	
 (4)	−53.6 (m, 6F^{1,2}) −54.0 (m, 3F^{4}) −97.2 (dqm, 2F^{3}) $^{4}J_{F^3,F^4}$ = 10.3 Hz $^{6}J_{F^3,F^2}$ = 1.7 Hz	6.95 (tq) $^{2}J_{H,F^3}$ = 56.0 Hz $^{4}J_{H,F^4}$ = 1.8 Hz
 (5)	−54.1 (tm, 6F^{1,4}) −97.0 (dqm, 4F^{2,3}) $^{4}J_{F^1,F^2}$ = 10.6 Hz	6.94 (tq) $^{2}J_{H,F^2}$ = 56.3 Hz $^{4}J_{H,F^1}$ = 1.7 Hz
 (6) [3]	61.2 (sep, 1F) −54.0 (d, 6F) $J_{F,F}$ = 6.1 Hz	
 (7) [3]	60.1 (tq, 1F^{1}) −54.1 (tdd, 3F^{3}) −96.9 (dqd, 2F^{2}) $^{4}J_{F^1,F^2}$ = 6.1 Hz $^{4}J_{F^2,F^3}$ = 9.9 Hz $^{4}J_{F^1,F^3}$ = 6.1 Hz	6.92 (tq) $^{2}J_{H,F}$ = 56.4 Hz $^{4}J_{H,F}$ = 1.7 Hz
 (8)	−53.9 (tm, 3F^{4}) −97.0 (dm, 4F^{1,2}) −91.1 (dm, 2F^{3}) $^{4}J_{F^3,F^4}$ = 10.3 Hz	6.79 (tt, 2H^{1,2}) 6.95 (tq, 1H^{3}) $^{2}J_{H,F^1}$ = 58.1 Hz $^{2}J_{H,F^3}$ = 56.9 Hz
 (10)	−102.6 (p, 2F^{1}) −170.0 (tm, 4F) $^{5}J_{F^1,F^2}$ = 5.9 Hz	5.57 (d) $^{2}J_{H,F}$ = 53.0 Hz
 (11)	−101.8 (tdt, 2F^{1}) −95.0 (dm, 2F^{3}) −168.8 (ttt, 1F^{2}) −170.0 (tm, 2F^{4,5}) $^{5}J_{F^1,F^2}$ = 8.3 Hz $^{5}J_{F^1,F^4}$ = 6.0 Hz $^{5}J_{F^1,F^3}$ = 2.3 Hz $^{4}J_{F^2,F^3}$ = 8.9 Hz	5.57 (d, 4H^{4,5}) 5.64 (d, 2H^{2}) 6.87 (t, 1H^{3}) $^{2}J_{H,F^2}$ = 51.5 Hz $^{2}J_{H,F^3}$ = 58.0 Hz $^{2}J_{H,F^4}$ = 53.0 Hz
 (12)	−101.2 (tp, 2F^{1}) −95.0 (dm, 4F^{3,4}) −168.8 (ttt, 2F^{2,5}) $^{4}J_{F^2,F^3}$ = 8.9 Hz $^{5}J_{F^1,F^2}$ = 8.7 Hz $^{5}J_{F^1,F^3}$ = 2.3 Hz	5.64 (d, 4H^{2,5}) 6.87 (t, 2H^{3,4}) $^{2}J_{H,F^2}$ = 51.5 Hz $^{2}J_{H,F^3}$ = 58.0 Hz

(continued)

Table 1 (continued)

Compound		^{19}F, δ(ppm)	^{1}H, δ(ppm)
	(13)	−100.2 (m, 2F^{1}) −95.0 (dm, 6F^{2,3,4}) −168.9 (ttt, 1F^{5}) $^{4}J_{F^4,F^5}$ = 8.9 Hz $^{5}J_{F^1,F^5}$ = 8.6 Hz	5.64 (d, 2H^{5}) 6.82 (tt, 2H^{2,3}) 6.86 (t, 1H^{4}) $^{2}J_{H,F^2}$ = 57.2 Hz $^{2}J_{H,F^4}$ = 57.5 Hz $^{2}J_{H,F^5}$ = 51.5 Hz $^{2}J_{H^2,F^3}$ = 6.4 Hz
	(14)	−99.4 (m, 2F^{1}) −94.9 (dm, 8F) $^{5}J_{F^1,F^2}$ = 4.7 Hz	6.82 (tt) $^{2}J_{H,F}$ = 57.2 Hz $^{4}J_{H^2,F^3}$ = 6.2 Hz
	(15)	−50.9 (ttd, 3F^{3}) −98.0 (m, 2F^{1}) 95.0 (dm, 6F^{2,4,5}) $^{4}J_{F^2,F^3}$ = 10.4 Hz $^{5}J_{F^1,F^3}$ = 6.9 Hz	6.82 (tt, 2H^{4,5}) 6.89 (tq, 1H^{2}) $^{2}J_{H,F^2}$ = 56.0 Hz $^{2}J_{H,F^4}$ = 56.9 Hz $^{4}J_{H^2,F^3}$ = 1.9 Hz $^{4}J_{H^4,F^5}$ = 6.3 Hz
	(16)	−50.9 (ttd, 6F^{3,4}) −96.7 (m, 2F^{1}) −95.0 (dm, 4F^{2,5}) $^{4}J_{F^2,F^3}$ = 10.4 Hz $^{5}J_{F^1,F^3}$ = 7.0 Hz	6.89 (tq) $^{2}J_{H,F^2}$ = 56.0 Hz $^{4}J_{H^2,F^3}$ = 1.9 Hz
	(17)	−51.0 (m, 3F^{4}) −51.2 (t, 6F^{2,3}) −95.3 (m, 2F^{1}) −94.8 (dm, 2F^{5}) $^{4}J_{F^4,F^5}$ = 10.4 Hz $^{5}J_{F^1,F^2}$ = 5.6 Hz	6.90 (tq) $^{2}J_{H,F}$ = 56.0 Hz $^{4}J_{H^5,F^4}$ = 1.9 Hz
	(18)	−51.2 (t, 12F) −94.0 (m, 2F^{1}) $^{5}J_{F^1,F^2}$ = 5.6 Hz	
$FSO_2CF_2SO_2F$ [a]	(19) [4]	47.6 (t, 2F) −96.9 (t, 2F) $^{3}J_{F,F}$ = 6.8 Hz	
	(20)	47.6 (t, 1F^{1}) −99.5 (dt, 2F^{2}) −170.4 (tm, 2F^{3,4}) $^{3}J_{F^1,F^2}$ = 5.9 Hz $^{4}J_{F^2,F^3}$ = 6.2 Hz	5.59 (d) $^{2}J_{H,F}$ = 52.6 Hz
	(21)	48.2 (t, 1F^{1}) −99.0 (m, 2F^{2}) −94.8 (dm, 2F^{3}) −169.1 (ttt, 1F^{4}) $^{3}J_{F^1,F^2}$ = 5.9 Hz $^{4}J_{F^3,F^4}$ = 8.9 Hz $^{5}J_{F^2,F^4}$ = 8.8 Hz	5.67 (d, 2H^{4}) 6.96 (t, 1H^{3}) $^{2}J_{H,F^4}$ = 51.2 Hz $^{2}J_{H,F^3}$ = 55.8 Hz
	(22)	48.5 (t, 1F^{1}) −98.1 (dp, 2F^{2}) −94.9 (dm, 4F^{3,4}) $^{3}J_{F^1,F^2}$ = 5.9 Hz $^{5}J_{F^2,F^3}$ = 5.0 Hz	6.83 (tt) $^{2}J_{H,F}$ = 57.1 Hz $^{4}J_{H^5,F^4}$ = 6.3 Hz

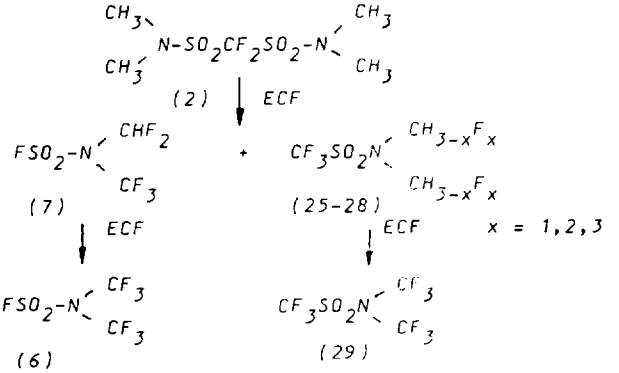
(*continued*)

Table 1 (continued)

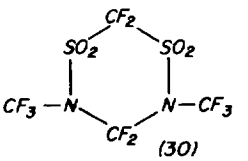
Compound			^{19}F, δ(ppm)	^{1}H, δ(ppm)
$FSO_2\overset{2}{C}F_2SO_2N\begin{matrix}\diagup\overset{3}{C}F_3\\ \diagdown\overset{4}{C}HF_2\end{matrix}$	(23)		48.8 (t, 1F^1) −50.9 (m, 3F^3) −96.9 (m, 2F^2) −94.8 (dm, 2F^4) $^3J_{F^1,F^2}$ = 5.9 Hz	6.90 (tq) $^2J_{H,F}$ = 56.0 Hz $^4J_{H^4,F^3}$ = 1.9 Hz
$FSO_2\overset{2}{C}F_2SO_2N\begin{matrix}\diagup\overset{3}{C}F_3\\ \diagdown\overset{4}{C}F_3\end{matrix}$	(24)		49.3 (t, 1F^1) −51.2 (t, 6F^{3,4}) −95.2 (dsep, 2F^2) $^3J_{F^1,F^2}$ = 5.7 Hz $^5J_{F^2,F^3}$ = 5.3 Hz	
$\underline{\overset{1}{C}F_3}SO_2N\begin{matrix}\diagup\overset{2}{C}H_2F\\ \diagdown\overset{3}{C}H_2F\end{matrix}$	(25)	[1]	−77.7 (t, CF_3) $^5J_{F,F}$ = 5.8 Hz	
$\underline{\overset{1}{C}F_3}SO_2N\begin{matrix}\diagup\overset{2}{C}HF_2\\ \diagdown\overset{3}{C}H_2F\end{matrix}$	(26)	[1]	−77.2 (dt, CF_3) $^5J_{F^1,F^3}$ = 7.6 Hz $^5J_{F^1,F^2}$ = 2.0 Hz	
$\underline{\overset{1}{C}F_3}SO_2N\begin{matrix}\diagup\overset{2}{C}HF_2\\ \diagdown\overset{3}{C}HF_2\end{matrix}$	(27)	[1]	−76.7 (p, CF_3) $^5J_{F^1,F^2}$ = 4.0 Hz	
$\underline{\overset{1}{C}F_3}SO_2N\begin{matrix}\diagup\overset{2}{C}F_3\\ \diagdown\overset{3}{C}HF_2\end{matrix}$	(28)	[1]	−75.6 (m, CF_3^1)	
$\underline{\overset{1}{C}F_3}SO_2N\begin{matrix}\diagup\overset{2}{C}F_3\\ \diagdown\overset{3}{C}F_3\end{matrix}$	(29)	[1]	−74.2 (sep, CF_3^1) $^5J_{F^1,F^2}$ = 4.0 Hz	

[a] NMR ^{19}F spectra were recorded without solvent, using CD_3CN-film.

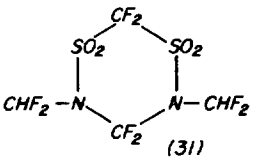
(c) cleavage of C–S bond and formation of partially and perfluorinated bis(polyfluoroalkyl)amidosulfofluorides (6,7) and *N,N-bis*(polyfluoroalkyl)trifluoromethanesulfonamides (25–29).



(d) formation of cyclic products is not a main process, but nevertheless small signals in the NMR ^{19}F-spectra of some fractions can be related to the structures (30) and (31).



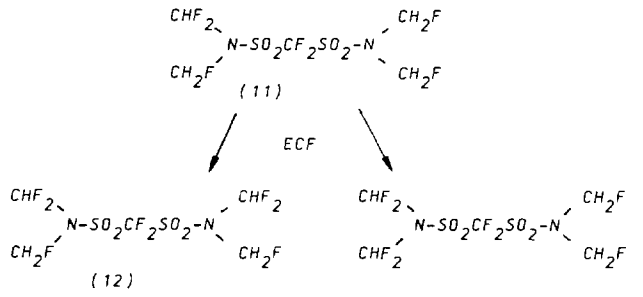
NMR ^{19}F (δ, ppm):
−48.9 t (6 F)
−57.0 sep. (2 F)
−97.4 m (2 F)
$J^4_{F,F}$ = 17.1 Hz
$J^5_{F,F}$ = 0.9 Hz



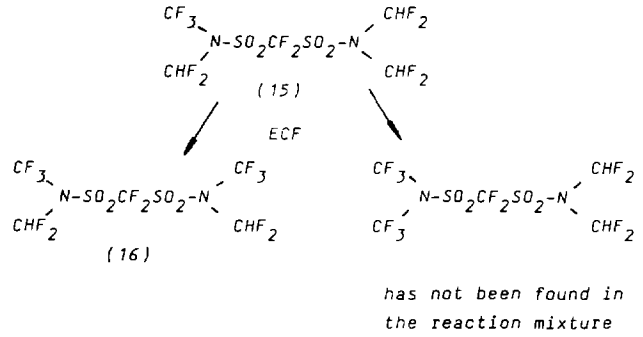
NMR ^{19}F (δ, ppm):
−60.2 p (2 F)
−94– −96 m (CHF_2)
−98.7 p (2 F)
$J^4_{F,F}$ = 13.0 Hz
$J^5_{F,F}$ 1.6 Hz
$J_{H,F}$ = 56 Hz
NMR ^{1}H (δ, ppm): 6,96 t

Obviously, the reaction mixture mostly contains perfluorinated compounds (18), (19), (24), (29) (all together ~45% of the mixture) and partially-fluorinated compounds with one and two hydrogen atoms (~40%).

The results, obtained by electrochemical fluorination of compound (2), clearly indicate that the ECF process leads not only to the replacement of hydrogen atoms by fluorine but also causes cleavage of C–S and S–N bonds, that reduce the yield of perfluorinated product (18). The presence of partially-fluorinated compounds (10–17) in the reaction mixture testifies that ECF is a consecutive step by step process and again fluorine atoms are introduced into the molecule preferably at the mostly hydrogenated position, for example:



and



Such a selectivity of the process of the electrochemical fluorination of *N,N*-dimethylsulfonamides must be related to the specific adsorption of these molecules on the surface of the Ni anode.

3. Experimental details

3.1. Apparatus

A Simons type cell described elsewhere [5] was used with nickel electrodes and an effective anodic area of 375 cm^2. The total volume of the electrolytic bath was 280 ml.

3.2. Analytical procedures

Gas chromatography was undertaken with a Perkin-Elmer Gas chromatograph on packed column (4% OV 101 on Chromosorb G AW DMCS) of length 1.5 m and 2 mm i.d. at 40 °C and 50 °C. Temperature of the injector was 140 °C and an FID detector was used at a temperature of 200 °C. The carrier gas was He. IR spectra were recorded on a NICOLET 20 DXB instrument in the gas phase.

MS spectra were taken at 17 eV by EI-method on an AMD 604 instrument. ^{19}F- and ^{1}H-NMR spectra were taken in $CDCl_3$ solution with a Bruker WP 80 SY instrument, using CCl_3F and $Si(CH_3)_4$ respectively, as internal references.

3.3. Chemicals

$(CH_3)_2NSO_2N(CH_3)_2$ (1) was prepared as published [6]. $(CH_3)_2NSO_2CF_2SO_2N(CH_3)_2$ (2) (m.p. 71–72 °C) was synthesized in 74% yield by the interaction of $FSO_2CF_2SO_2F$ [4] with dimethylamine. Details will be given in a separate publication.

3.4. Electrochemical fluorination of *N,N,N',N'*-tetramethylsulfondiamide (1)

$(CH_3)_2NSO_2N(CH_3)_2$ (84.5 g, 0.556 mol) was added in four portions (20.0 g at the start; 22.8 g after 95.8 Ah; 21.7 g after 180.4 Ah; 20.0 g after 275.3 Ah) to 245 g liquid HF, previously electrolyzed in the ECF cell over 48 h. The temperature of the cell was maintained at 2 °C and the temperature of the condenser was −30 °C. The gaseous products from the cell passed through two PTFE traps cooled to −78 °C. The electrolysis (Voltage: 4.2–4.9 V; current density: 0.53 Adm^{-2}) was finished after 409.2 Ah of electricity (114.4% of theory) had been consumed and 200 g of liquid products were removed from the cell. After cooling to −20 °C, separating the organic layer from the HF phase, washing it with water and 1% $NaHCO_3$ solution, and drying with Na_2SO_4, 21.3 g (mixture I) of crude product was obtained. According to GC analysis this mixture contained 45% of (3), 22% of (4), 16% of (5), 7% of (6) + (7) and 10% of other compounds.

Diluting the HF phase from the cell with ice-water additionally gave 13.5 g (mixture II) of fluorinated products with consisted of 30% of (3), 24% of (4), 17% of (5), 14% of (6) + (7) and 15% of other compounds.

137 g of liquid products together with HF were obtained from the traps. After separating the organic layer from the HF phase, washing it with ice-water and 1% $NaHCO_3$ solution, and drying with Na_2SO_4, 19 g (mixture III) of crude product was obtained. According to GC analysis and NMR spectra this mixture contains 50% of (3), 47% of (6) and 3% of other products. Fractionated distillation of mixtures (I), (II) and (III) gave perfluorinated compounds (3) and (6) as pure substances which were characterised by ^{19}F- and ^{1}H-NMR spectroscopy (Table 1). A fraction boiling at 102–105 °C contains mainly compounds (4) and (5) with one and two hydrogen atoms. The residue after fractional distillation was examinated by ^{19}F- and ^{1}H-NMR spectroscopy. Compound (8) with three hydrogen atoms was found as a main product in this mixture. *N,N,N',N'*-Tetrakis(trifluoromethyl)sulfondiamide (3): b.p. 85–86 °C. MS (*m/z*): 368 (M^+). IR, (cm^{-1}): 664,4, 721.6, 990.3, 1158.4, 1194.7,

1260.1, 1268.3, 1327.6, 1483.1. *N,N-bis*(trifluoromethyl)-amidosulfonylfluoride (6): b.p. 30–31 °C [3].

3.5. Electrochemical fluorination of difluoromethane-N,N,N',N'-tetramethyldisulfondiamide (2)

$(CH_3)_2NSO_2CF_2SO_2N(CH_3)_2$ (93.8 g, 0.35 mol) was added in six portions (20.0 g at the start, 20.0 g after 50.2 Ah, 16.2 g after 91.9 Ah, 18.6 g after 136.1 Ah, 10.0 g after 180.1 Ah, 9.0 g after 215,4 Ah) to 232 g of liquid HF previously electrolyzed in the ECF cell over 48 h. The temperature of the cell was maintained at 0 °C and the temperature of the condenser was −30 °C. The gaseous products from the cell passed through two PTFE traps cooled to −78 °C. The electrolysis (voltage: 4.5–5.0 V; current density: 0.51 A dm^{-2}) was finished after 258.3 Ah of electricity (114% of theory) has been consumed and 205 g of liquid products were removed from the cell.

After cooling to −78 °C solid product was separated from the HF phase and washed with water and 1% $NaHCO_3$ solution. After drying by Na_2SO_4 43 g of crude product was obtained. Diluting the HF phase from the cell and from the traps with ice-water additionally gave 9 g and 1.2 g fluorinated substances respectively.

By fractionated distillation the reaction mixture was separated into several narrow fractions, which were investigated by GC and ^{19}F- and ^{1}H-NMR spectroscopy (Table 1).

Difluoromethane-*N,N,N',N'*-tetrakis(difluoromethyl)disulfondiamide (14) was isolated from the mixture by crystallisation and purified by recrystallisation from pentane, m.p. 51–52 °C. Analysis: Found: C, 15.22; S, 15.83%. Calc. for $C_5H_4F_{10}N_2O_4S_2$: C, 14.64; S, 15.63%. MS, EI (70 eV) *m/z* (% rel. int.): 51 (100, CHF_2), 60 (10.1), 69 (42.2), 78 (54.1, SO_2N), 79 (18.9), 92 (12.0), 94 (68.4, CHFNSO), 96 (88.8), 97 (29.4), 98 (11.7), 110 (85.5, $CHFNSO_2$), 116 (15.0), 162 (20.5), 164 [36.0, $(CHF_2)_2NSO$], 180 [64.6, $(CHF_2)_2NSO_2$], 211 (11.8).

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