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Electrochemical fluorination of *N,N,N′,N′*-tetramethylethylenediamine

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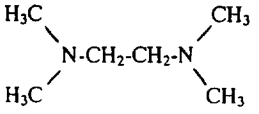
Abstract

The electrochemical fluorination of *N,N,N′,N′*-tetramethylethylenediamine was carried out in a modified Simons type cell using anhydrous hydrogen fluoride as a solvent. Effects of various experimental parameters like concentration of amine, temperature, and current density etc. were investigated. In addition to perfluoro-*N,N,N′,N′*-tetramethylethylenediamine, cyclic, cleavage, and partially fluorinated products were obtained and characterized by gas chromatography, IR spectroscopy, nuclear magnetic resonance and mass spectra. A plausible reaction pathway for the electrochemical fluorination of *N,N,N′,N′*-tetramethylethylenediamine has been proposed based on the products obtained. © Elsevier Science S.A.

Keywords: Electrochemical fluorination; *N,N,N′,N′*-tetramethylethylenediamine; Perfluoro-*N,N,N′,N′*-tetramethylethylenediamine

1. Introduction

Many investigations have been made on the electrochemical fluorination (ECF) of amines and their derivatives as possible candidates for medicinal and other industrial applications of the corresponding perfluoro compounds [1–4]. However, only few reports have been found in the literature about the chemical [5] and electrochemical [1,4] fluorination of alkyl substituted diamines. Though perfluorotetraalkyldiamines are prospective inert liquids for electronic industry [1] and also used as insecticide activator [4], no details about the preparation and physical properties have been reported. Rendell et al. [5] have investigated the fluorination of *N,N,N′,N′*-tetramethylethylenediamine (1) using cobalt trifluoride. However, partially fluorinated tetramethylethylenediamines along with cleavage and cyclization products were obtained in this case. In general, ECF leads to substitution of hydrogen atoms by fluorine atoms, carbon–carbon and carbon–heteroatom bond formation [6], as well as carbon–carbon and carbon–heteroatom bond cleavage [7,8]. The reports cited in the literature about the ECF of substituted diamines are mainly concerned with the corresponding perfluoro compounds. No details have been published about the mechanism and by products formed during the electrochemical fluorination of substituted diamines. Hence it was decided to investigate the ECF of *N,N,N′,N′*-tetramethylethylenediamine (1) in detail.



(1)

2. Experimental details

2.1. Electrochemical cell

The electrolytic cell used in this study is a stainless steel cylindrical cell having a capacity of 280 ml, containing a pack of alternate anodes and cathodes (effective anode area = 3.8 dm^2). Teflon spacers were used to keep the electrodes apart at a distance of about 4 mm. The electrolyte could be drained through a ball valve in the cell bottom. The cell was provided with a liquid level indicator made of a Teflon tube. Gaseous products were collected in PTFE FEP traps kept at −78 °C after passing through a condenser kept at −30 °C.

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Table 1
Effect of experimental parameters

Experiment	Current (A dm^{-2})	Cell voltage (V)	Concentration of amine (%)	TMEDA added (g)	Cell temperature (°C)	Electricity passed (%)	Products obtained (g)
1	0.53	4.9–5.1	10	105	−10	101	73
2	0.53	4.8–5.0	10	100	−5	102	84
3	0.53	4.6–4.7	10	100	+10	104	55
4[a]	0.53	4.9–5.0	10	105	0	115	105
5	0.39	4.5–4.7	10	101	0	104	87
6	0.53	4.7–4.8	5	102	0	103	106

[a] During electrolysis the electrolyte becomes brown. Completion of electrolysis was indicated by the colour change (brown to colourless), and sudden increase of cell voltage and decrease of current. In this experiment electrolyte was light yellow,the current and voltage were steady. Hence the electrolysis was continued further and finally explosions occured in the contents of the traps.

2.2. Analytical procedures

Gas chromatograms were recorded on a Perkin-Elmer gas chromatograph on a packed column (4% OV 101 on chromosorb G-AW DMCS, 80/100 mesh) of length 2.5 m and 2 mm i.d at 40 °C. Temperatures of the injector and detector (TCD) were 120 °C and 250 °C respectively. Helium was used as carrier gas.

Gas chromatography (GC)–mass spectra were measured using a Varian MAT-311 A at 70 eV by the EI method.

^{19}F and ^{1}H nuclear magnetic resonance (NMR) spectra were measured for neat liquids without solvent using a special technique (CD_3CN film) on a Brucker WP 80 SY spectrometer (80.1 MHz for ^{1}H and 75.4 MHz for ^{19}F). CCl_3F and TMS were used as internal references. The resonance at high field of the reference was designated as negative.

IR spectra were recorded on a Nicolet 20 DXB instrument. Volatile samples were measured in a 10 cm gas cell using KBr windows. Other samples were recorded as neat liquids.

2.3. Electrochemical fluorination of N,N,N′,N′-tetramethylethylenediamine

About 200 g HF were fed into the electrochemical cell and dried by pre-electrolysis for about 30–40 h to remove moisture and to activate the electrodes. The mixture of tetramethylethylenediamine (Aldrich, 99.0%) and HF was prepared separately.[3] Calculated quantities of this mixture were added into the cell at intervals of 24 h to maintain steady concentration of amine. Electrolysis was carried out under galvanostatic conditions. The cell voltage was maintained between 4.5 and 5.0 V. In every experiment, about 100–105 g of tetramethylethylenediamine were added. The electrolysis was stopped after passing 104% of the theoretical quantity of electricity. Experimental details are recorded in Table 1.

At the end of the electrolysis, nonvolatile products together with HF were drained from the cell. Organic layers obtained from both the cell and cooling traps were separated from the HF phase. Volatile products were passed through traps containing 5% aqueous NaOH, finally collected in a trap kept at −78 °C, and dried. Nonvolatile products were washed free from HF with water and dried. Additionally, the HF phase obtained from the cell and traps was diluted with ice–water to separate partially fluorinated compounds. In this study about 90% of the products obtained condensed in the traps. Only small amounts of partially fluorinated compounds were isolated separately from the HF phase. The mixture of products obtained from the cell and traps was separated by distillation into various fractions. According to the NMR ^{19}F and ^{1}H spectra (Table 3):

Fraction (I) (b.p. < 19 °C) contained mostly:
perfluorotrimethylamine (9),
perfluorodimethylethylamine (13),
octaflurotrimethylamine (8),
heptafluorotrimethylamine (7);

Fraction (II) (b.p. 19–40 °C):
perfluorodimethylethylamine (13),
difluoromethylperfluoromethylethylamine (12);

Fraction (III) (b.p. 50–60 °C):
perfluoro-*N,N*-dimethylimidazolidine (22);

Fraction (IV) (b.p. 60–100 °C):
perfluoro-*N,N*-dimethylpiperazine (24) and
perfluoro-*N,N,N′,N′*-tetramethylethylenediamine (4)

Residue, b.p. > 100 °C.

The total amounts of compounds (7), (8), (9), (12), (13), (22), (4) and (24) were estimated in all fractions by ^{19}F NMR spectroscopy and results are given in Table 2.

Partially fluorinated amines (7) and (8) can be separated from perfluorotrimethylamine (9) and perfluorodimethylethylamine (13) by ethanol extraction as follows:

The mixture (fraction I) is stirred in a distillation flask with ethanol (1:1 v/v) and perfluorotrimethylamine (9) is slowly distilled off. During the distillation temperature of the column and the condenser is kept at −10 °C. After the separation of perfluorotrimethylamine (9) the residue in the

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[3] **CAUTION**: The reaction between tetramethylethylenediamine (1) and HF is highly exothermic. The amine–HF mixture should be prepared in an efficient hood by dropwise addition of diamine to precooled HF.

Table 2
Effect of experimental parameters on product distribution

Experiment	Distribution of products (g) / (%w/w) [a]							
	(4) + (24)	(22)	(13)	(9)	(8)	(7)	(12)	(m)
1	7.3	12.2	12.9	21.7	5.4	2.0	1.2	10.3
	(10.0)	(16.7)	(17.7)	(29.7)	(7.4)	(2.7)	(1.6)	(14.0)
2	10.0	10.5	16.9	22.1	11.3	1.8	2.6	8.8
	(11.9)	(12.5)	(20.0)	(26.3)	(13.5)	(2.1)	(3.1)	(10.5)
3	6.7	12.8	8.5	10.1	4.5	1.6	0.6	10.2
	(12.2)	(23.3)	(15.1)	(18.4)	(9.2)	(2.9)	(1.1)	(18.5)
4	19.9	20.3	15.0	28.0	9.0	2.2	0.6	10.0
	(18.9)	(19.3)	(14.3)	(26.7)	(8.6)	(2.1)	(0.6)	(9.5)
5	7.5	14.4	15.4	27.0	9.0	2.9	1.3	9.5
	(8.6)	(16.6)	(17.7)	(31.0)	(10.3)	(3.3)	(1.5)	(10.9)
6	6.3	12.7	22.9	33.3	10.2	2.4	2.5	15.7
	(5.9)	(12.0)	(21.6)	(31.4)	(9.6)	(2.3)	(2.4)	(14.8)

(4)—Perfluorotetramethylethylenediamine, (24)—Perfluorodimethylpiperazine, (22)—Perfluorodimethylimidazolidine, (13)—Perfluorodimethylethylamine, (9)—Perfluorotrimethylamine, (8)—Octafluorotrimethylamine, (7)—Heptafluorotrimethylamine, (12)—Difluoromethylperfluoromethylethylamine (m)—Minor products and loss of products during purification.

[a] Estimated by NMR ^{19}F spectroscopy.

Notes: (a) Cell drainings contain mainly compounds (4), (24) + (22). (b) Amounts of compounds (4) and (24) were 55% and 45% respectively.

distillation flask can be divided into two parts: ethanol layer and high boiling fluoroamines, mainly (13), at the bottom. Further distillation of the ethanol layer gives mostly partially fluorinated amines (7,8), which were characterised by NMR spectra (see Table 3). The products of the reaction between perfluoro-*N*-fluoroamines (10) and (14) with ethanol can be isolated by the distillation of the bottom layer as a high boiling fraction in the range 90–100 °C.

$$R^1R^2N{-}F + C_2H_5OH \rightarrow \underset{(26,\ 27)}{R^1R^1R^2N{-}OC_2H_5}$$

where $R^1 = CF_3$, $R^2 = CF_3$ or C_2F_5.

Formation of *N*-ethoxyperfluorodialkylamines (26,27) was confirmed by ^{19}F and ^1H NMR spectroscopy and GC–MS data (Table 4).

The additional distillation of the high boiling fraction (IV) at 87 °C gave a mixture of perfluoro tetramethylethylenediamine (4) and perfluorodimethylpiperazine (24). The reported boiling point of perfluorodimethylpiperazine is 84 °C [15]. Even after repeated distillation a mixture of perfluorotetramethylenediamine (4) (80%) and perfluorodimethylpiperazine (24) (20%) was obtained. GC–MS data for this mixture are as follows.

GC–MS,EI (70 eV), *m/e* (% rel.int):

m/e 366 (0.9, $C_6F_{14}N_2$), 347 (51, $C_6F_{13}N_2$), 297 (43.3, $C_5F_{11}N_2$), 259 (30.9, $C_5F_9N_2$), 209 (26.9, $C_4F_7N_2$), 171 (7.2, C_2F_7N), 164 (97.1, C_3F_6N), 119 (92.1, C_2F_5), 114 (99.3, C_2F_4N), 100 (93.5, C_2F_4), 69 (base peak, CF_3). These observed mass spectral data are similar to that reported for perfluoro-1,4-dimethylpiperazine (24) [15].

m/e 252 (13.1, $C_4F_{10}N$), 202 (67.4, C_3F_8N), 152 (1.4, C_2F_6N), 133 (2.7, C_2F_5N), 69 (base peak, CF_3), 50 (33.2, CF_2). These observed *m/e* values are related to perfluoro-*N,N,N′,N′*-tetramethylethylenediamine (4). To the knowledge of the authors the spectral data for the compound (4) are reported for the first time.

2.4. *Separation of perfluorotrimethylamine (9) from perfluorodimethylethylamine (13)*

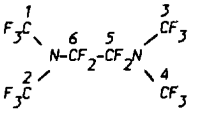
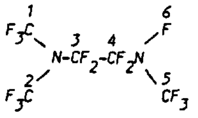
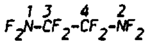
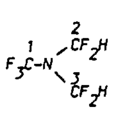
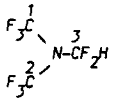
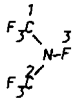
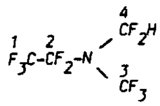
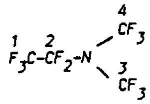
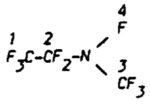
Bürger et al. [6] have reported that perfluorotrimethylamine (20%) and perfluoro dimethylethylamine (80%) formed an azeotropic mixture boiling at 21 °C which could not be separated by repeated distillation. We adopted a different procedure for the separation of perfluorotrimethylamine (9) from perfluorodimethylethylamine (13). Separation of perfluoro trimethylamine was carried out at low temperature by keeping the temperature of the column well below the boiling point of perfluorodimethylethylamine. In this way we obtained 99% pure perfluorotrimethylamine (9) (b.p. = − 10 °C). The purity of this compound was checked by NMR spectra.

3. Results and discussion

3.1. *Effect of variables and product distribution*

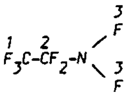
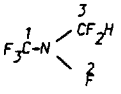
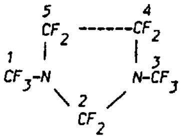
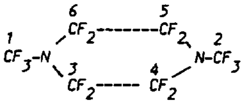
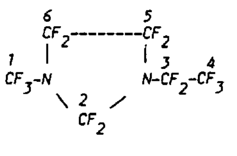
Details of experimental variables studied and the product distribution pattern are given in Tables 1 and 2 respectively. Examination of the product distribution pattern clearly indicates that electrochemical fluorination of tetramethylethylenediamine (1) gave about 90% of the cleavage and cyclization products in all the experiments irrespective of the variables. However, the best yield of perfluorotetramethylethylenediamine (4) was obtained at 0 °C in 10% amine concentration and at 0.53 A dm^{-2} (Expt. 4, Table 2).

Table 3
NMR data and boiling point of the products

Products	^{19}F δ (ppm)	^{1}H δ (ppm)	bp (°C)
 (4)	−53.0 (m, 12F^{1-4}) −93.1 (m, 4$F^{5,6}$) $^{4}J_{F-F}$ = 7.4 Hz		87
 (5)	−55.4 (m, 6F1,2) −76.3 (m, 3F^{5}) −90.9 (br, 2F^{3}) −92.5 (m, 2F^{4}) −95.9 (br, 1F^{6})		70–75
 $F_2N-CF_2-CF_2-NF_2$ (6) [a]	+16.4 (br, 4$F^{1,2}$) −115.7 (t, 4$F^{3,4}$) $^{3}J_{F-F}$ = 8.7 Hz		−1.6 [9]
 (7) [a] [10]	−56.5 (qi, 3F^{1}) −97.4 (dq, 4$F^{2,3}$) $^{2}J_{F-H}$ = 57.5 Hz $^{4}J_{F1}$ = 6.9 Hz	6.55 (t, 2H) $^{2}J_{H-F}$ = 56.7 Hz	26–30
 (8) [a] [10]	−56.1 (t, 6$F^{1,2}$) −98.4 (dsept, 2F^{3}) $^{2}J_{F-H}$ = 56.1 Hz $^{4}J_{F1-F3}$ = 7.8 Hz	6.56 (t, 1H^{3}) $^{2}J_{H-F}$ = 56.0 Hz	8
$(CF_3)_3-N$ (9) [10]	−55.7 (s, 9F)		−10
 (10) [a]	−70.8 (d, 6$F^{1,2}$) −87.8 (br, 1F^{3}) $^{3}J_{F-F}$ = 19.6 Hz		−37 [9]
 (12) [a] [6]	−52.6 (m, 3F^{3}) −86.5 (br, 3F^{1}) −96.1 (dm, 2F^{4}) −99.4 (m, 2F^{2})	6.5 (t, 1H^{4}) $^{2}J_{H-F}$ = 55.5 Hz	35
 (13) [a] [6]	−53.3 (tq, 6$F^{3,4}$) −85.1 (Sept, 3F^{1}) −96.6 (Sept, 2F^{2}) $^{4}J_{F2-F3}$ = 15.3 Hz $^{5}J_{F1-F3}$ = 5.6 Hz		20
 (14) [a]	−68.2 (dt, 3F^{3}) −83.2 (d, 3F^{1}) −89.5 (br, 1F^{4}) −112.2 (dq, 2F^{2}) $^{3}J_{F4-F3}$ = 13.1 Hz $^{3}J_{F4-F2}$ = 12.6 Hz $^{4}J_{F4-F1}$ = 15.0 Hz		−3.8 [11]

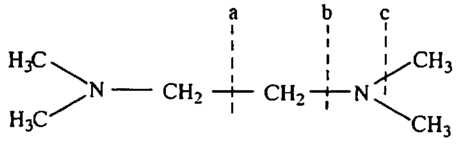
(*continued*)

Table 3 (*continued*)

Products	^{19}F δ (ppm)	^{1}H δ (ppm)	bp (°C)
 (15) [a]	+15.9 (br, $2F^3$) −81.3 (t, $3F^1$) −119.7 (s, $2F^2$) $^4J_{F^1-F^3}=8.6$ Hz		−34 [12]
 (17)	−71.8 (dt, $3F^1$) −105.8 (br, $1F^2$) −113.0 (dq, 2F3) $^2J_{F-H}=56.4$ Hz $^3J_{F^1-F^2}=16.4$ Hz $^4J_{F^1-F^3}=6.4$ Hz	6.21 (t, 1H) $^2J_{H-F}=56.0$ Hz	−7.5 [13]
 (22) [14]	−56.5 (tt, $6F^{1,3}$) −63.4 (m, $2F^2$) −92.8 (qt, $4F^{4,5}$) $^4JF^1–F^2=^4JF^1–F^5=7.3$ Hz		57
 (24) [15]	−53.3 (m, $6F^{1,2}$) −92.5 (q, $8F^{3-6}$) $^4J_{F-F}=13.2$ Hz		87
 (25)	−56.4 (tt, 3F1) −61.1 (m, $2F^2$) −84.4 (tt, $3F^4$) −92.1 (m, $2F^5$) −92.4 (m, $2F^6$) −98.3 (tt, $2F^3$) $^4J_{F^1-F^2}=^4J_{F^1-F^6}=7.4$ Hz $^4J_{F^3-F^5}=^4J_{F^3-F_2}=10.5$ Hz $^5J_{F^4-F_5}=^4J_{F^4-F^2}=7.2$ Hz		70–75

[a] NMR was recorded at −20 °C; br = broad, d = doublet, m = multiplet, q = quartet, qi = quintet, s = singlet, sept = septet, t = triplet.

During the ECF of tetramethylethylenediamine (1) cleavage of the molecule is possible in three different ways as shown below.

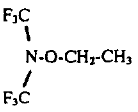
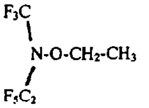


(a) carbon–carbon bond cleavage between two methylene groups, (b) carbon–nitrogen bond cleavage between methylene carbon and nitrogen, and (c) carbon–nitrogen bond cleavage between methyl carbon and nitrogen. The products related to all these three types of cleavage were obtained. However, the yield of products from the third type of cleavage is very low.

Quantitative analysis of the products reveals the following conclusions. At low concentration of amine (compare Expts. 4 and 6, Table 2), the amount of cleavage products is significantly higher than the amount of cyclic products and perfluorotetramethylethylene diamine (4). At high concentrations of amine, the yield of perfluorotetramethylethylene diamine (4) is higher. By raising the temperature of the cell from −10 °C to 0 °C, the overall yield of fluorinated products increases from 20% to 29% (compare Expts. 1,2,4, Table 1). Further increase in the temperature of the cell to +10 °C leads to degradation of the starting material and the formation of volatile products (Expt. 3, Tables 1 and 2). Overall yield is high at higher current density (compare Expts. 4 and 5, Table 1). In general carbon–carbon bond cleavage occurs more extensively, when compared to carbon–nitrogen bond cleavage, under all the conditions used.

Two types of cyclic products were obtained from ECF of tetramethylethylenediamine (1) (Table 3). A six-membered cyclic product, perfluoro-1,4-dimethylpiperazine (24) was formed by cyclization between methyl carbons (carbon–carbon cyclization), and cyclization between methyl carbon and nitrogen (carbon–nitrogen cyclization) leads to the formation of perfluoro-1,3-dimethylimidazolidine (22), a five

Table 4
Spectral data of *N*-ethoxydiperfluoroalkylamines (26) and (27)

Products	NMR data (ppm) [a]	GC–MS, *m/z* (%rel.int)
 $(F_3C)_2N\text{-}O\text{-}CH_2\text{-}CH_3$ (26) [16]	^{19}F -55.4 (s, 6F) ^{1}H 1.34 (t, 3H) 4.36 (q, 2H) $J_{H\text{-}H} = 7.2$ Hz	198 (7.4, M + 1), 181 (7.4, $C_3F_6HNO^+$), 180 (98.1, $C_3F_6NO^+$), 112 (11, $C_2F_3HNO^+$), 99 (1.8, CF_3NO^+), 92 (97.8, $C_2F_2NO^+$), 73 (9.2, C_2FNO^+), 69 (100, CF_3^+), 58 (2.2, $C_2H_4NO^+$) 50 (5.2, CF_2^+), 45 (90.4, $C_2H_5O^+$), 44 (8.7, $C_2H_4O^+$), 43 (18.8, $C_2H_3O^+$), 42 (2.7, $C_2H_2O^+$).
 $(F_3C)(F_5C_2)N\text{-}O\text{-}CH_2\text{-}CH_3$ (27)	^{19}F -53.9 (m, 3F) -83.5 (q, 3F) -95.2 (q, 2F) $^{4}J_{F\text{-}F} = 16.2$ Hz $^{5}J_{F\text{-}F} = 5.4$ Hz ^{1}H 1.27 (t, 3H) 4.22 (q, 2H) $J_{H\text{-}H} = 7.1$ Hz	231 (2, $C_4F_8HNO^+$), 230 (38.7, $C_4F_8NO^+$), 228 (4.9 $M-F^+$), 202 (1, $C_3F_8N^+$), 164 (10.5, $C_3F_6N^+$), 142 (38.5, $C_3F_4NO^+$), 119 (34.5, $C_2F_5^+$), 114 (12.6, $C_2F_4N^+$), 100 (4.1, $C_2F_4^+$), 69 (100, CF_3^+), 50 (8.1, CF_2^+), 45 (85.5, $C_2H_5O^+$), 44 (4.3, $C_2H_4O^+$) 43 (15.1, $C_2H_3O^+$), 42 (2.6, $C_2H_2O^+$).

[a] Solvent: $CDCl_3$.

membered cyclic product. Distribution of these products clearly indicates that carbon–nitrogen cyclization is favoured over carbon–carbon cyclization (compare the yields of the products (22) and (24), Table 2).

Extensive degradation of tetramethyethylenediamine (1) during electrochemical fluorination yielding highly volatile products like perfluorodimethylamine (10), b.p. = −34 °C [9] or perfluoroethylamine (15), b.p. = −37 °C [12] causes

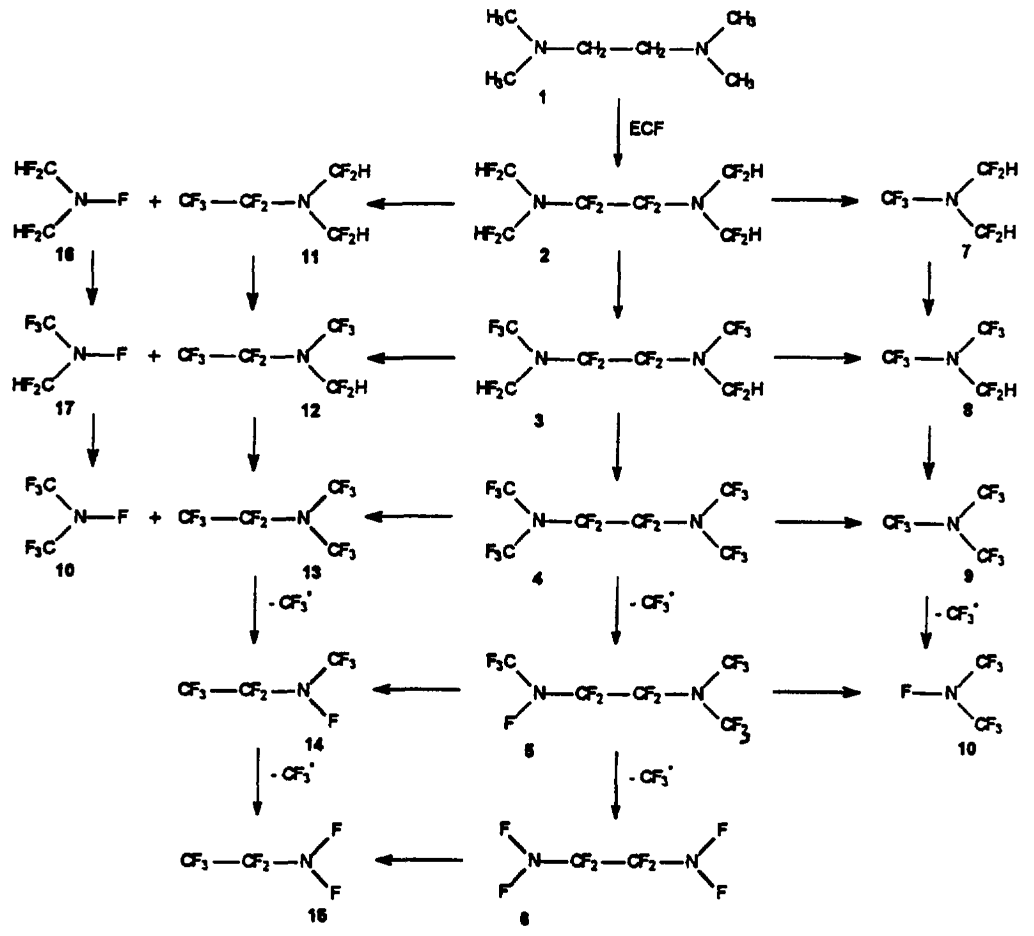


Fig. 1. Schematic representation of formation of perfluoro and partially fluorinated compounds by the ECF of *N,N,N′,N′*-tetramethylethylenediamine.

a low yield of perfluorotetramethyl-ethylenediamine (4). NMR data for the products obtained are given in Table 3.

3.2. *Reaction pathways for electrochemical fluorination of N,N,N′,N′-tetramethylethylenediamine (1)*

Various perfluoro and partially fluorinated compounds (Table 3) were found in the reaction mixture after ECF of tetramethylethylenediamine. The results clearly indicate that the ECF of tetramethylethylenediamine proceeds in three parallel ways, (a): substitution of hydrogen atoms by fluorine atoms, (b): degradation of tetramethylethylenediamine and intermediates, and (c): formation of cyclic products.

Partially fluorinated products (7, 8) obtained from the ECF of diamine (1) and products (2, 3, 19) which can be revealed by NMR in the residue of high boiling products clearly indicate the stepwise fluorination of tetramethylethylenediamine as suggested by Sartori et al. [3]. According to the proposed mechanism [3,7], the high valence nickel fluorides (NiF_3, NiF_4 etc.) formed on the electrode surface during electrolysis cause oxidative fluorination of the organic compounds. The fluorination always starts at the carbon having higher electron density in a symmetrical way by stepwise substitution of hydrogen. A schematic representation of the reaction sequence of the electrochemical fluorination of tetramethylethylenediamine is depicted in Fig. 1. The presence of cleav-

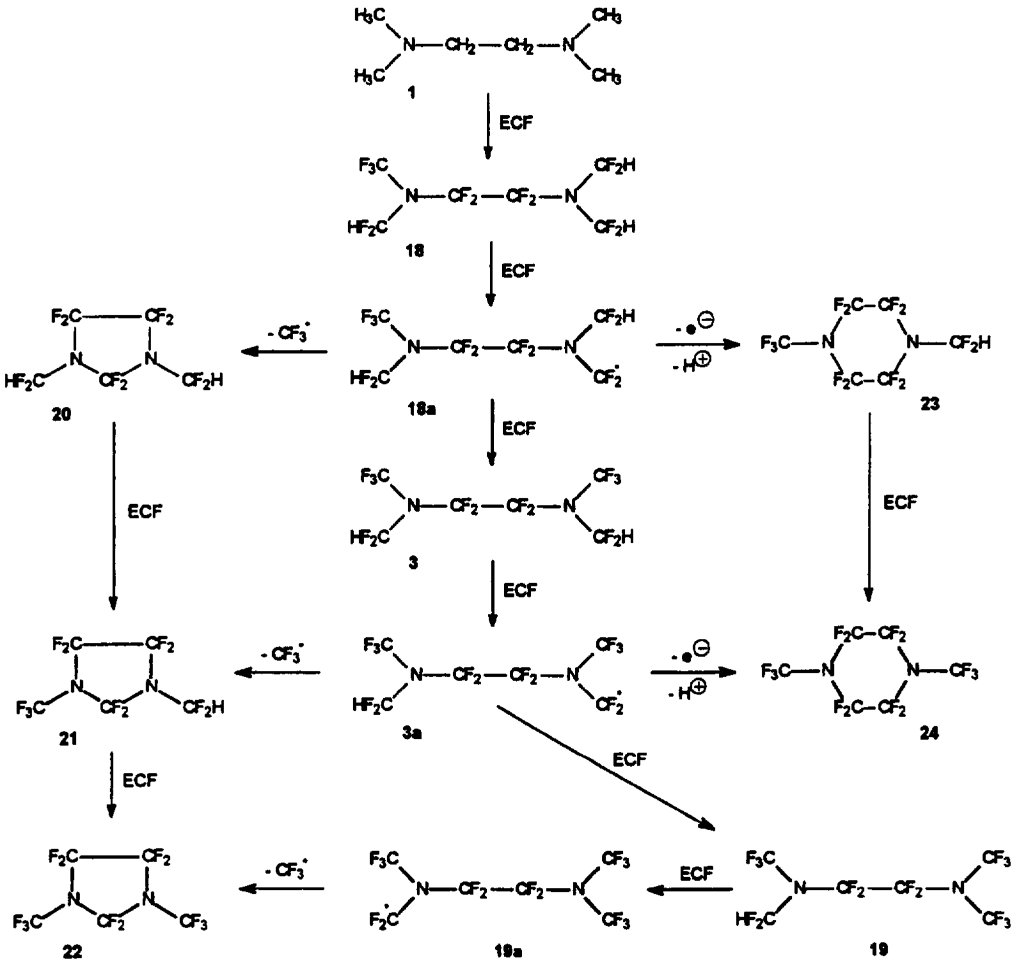


Fig. 2. Schematic representation of formation of cyclic products by ECF of *N,N,N′,N′*-tetramethylethylenediamine.

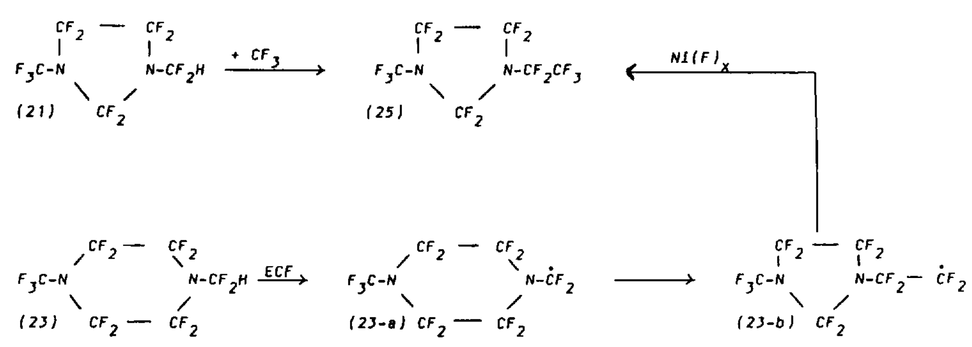


Fig. 3. Schematic representation of formation perfluoro-1-methyl-3-ethyl imidazolidine by ECF of *N,N,N′,N′*-tetramethylethylenediamine.

age products in the reaction mixture reflects the side cleavage process which takes place in parallel with the substitution of hydrogen by fluorine on the way from compound (1) to compound (4). Perfluorotetramethylethylenediamine (4) itself may undergo degradation by splitting off trifluoromethyl radicals forming compounds of the types (5,6), which were identified among the products.

Fig. 2 shows the formation of cyclic products. According to the results obtained, compounds (3, 18, 19) seem to be intermediates for the formation of cyclic products. The key step in this process is the formation of stable electrophilic radicals by the oxidation of intermediates (3, 18, 19) by nickel fluorides at $-CHF_2$ position as shown in Fig. 2.

The intermediate radical (3-a) has two possibilities for cyclization. Intramolecular radical attack may take place either at the partially fluorinated carbon or at the nitrogen to form six or five-membered cyclic products respectively. Indeed both products were obtained. The five membered cyclic product (22) was obtained in nearly twice the amount of the six membered cyclic product (24), (Table 2). This clearly indicates that carbon–nitrogen cyclization is more predominant than carbon–carbon cyclization due to the favourable attack by the electrophilic radical (3-a) [17] on the nitrogen bearing a lone pair of electrons.

Perfluoro-1-methyl-3-ethylimidazolidine (25) which was found in the reaction mixture is not formed directly from tetramethylethylenediamine or intermediates with linear structure. It may be formed either by the replacement of hydrogen at $-CHF_2$ position of the partially fluorinated compound (21) by the addition of trifluoromethyl radical [6], or by the rearrangement of the intermediate radical (23-a) as shown in Fig. 3. The later way seems to be preferable because it resembles the general mechanism proposed for the formation of cyclic compounds.

4. Conclusion

Electrochemical fluorination of tetramethylethylenediamine results in the formation of fluorinated products in an overall yield up to 30%. The products obtained clearly indicate that the ECF of tetramethylethylenediamine proceeds via indirect oxidative fluorination by the high valence nickel fluoride films formed on the electrode surfaces as proposed by Sartori et al. [3,7]. Cleavage, cyclization, and the formation of volatile products are the main reasons for low yield of perfluorotetramethylethylenediamine.

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