Syntheses and properties of compounds containing the bis(trifluoromethyl)amido group

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Zusammenfassung

Das Ziel dieser Arbeit war die Entwicklung von (i) Synthesewegen zu Salzen mit dem $[N(CF_3)_2]^-$-Anion und (ii) Methoden zur Einführung der Bis(trifluoromethyl)-aminogruppe in organische Substanzen unter Verwendung dieser Salze.

Die als Ausgangsverbindungen verwendeten N,N-Bis(trifluoromethyl)perfluor-alkylsulfonamide und N,N-Bis(trifluoromethyl)perfluorakylacylamide wurden durch elektrochemische Fluorierung hergestellt. Es konnte gezeigt werden, dass diese Substanzen ideale Ausgangstoffe für die Herstellung von Salzen mit dem $[N(CF_3)_2]^-$-Anion sind.

Die neuen stabilen $[N(CF_3)_2]^-$-Salze mit Tetraalkylammonium- oder Phosphonium-Kationen konnten in organischen Reaktionen verwendet werden und eine Reihe neuer Verbindungen mit der Bis(trifluoromethyl)aminogruppe wurde auf diese Weise erhalten.

Da das $[N(CF_3)_2]^-$-Anion ein schwaches Nukleophil ist und leicht ein Fluorid-Anion abspaltet, kam es zu Konkurrenzreaktionen zwischen dem $[N(CF_3)_2]^-$- und dem Fluorid-Anion in organischen Synthesen.

Die elektrochemischen Eigenschaften von N,N-Bis(trifluoromethyl)perfluoralkyl-sulfonamiden, N,N-Bis(trifluoromethyl)perfluoralkylacylamiden und dem $[N(CF_3)_2]^-$-Anion wurden untersucht. Die Eignung des $[N(CF_3)_2]^-$-Anions für elektrochemische Synthesen ließ sich nachweisen.

Summary

The aim of this thesis was to develop (i) a convenient route to materials containing the $[N(CF_3)_2]^-$-anion and (ii) methods for the introduction of the bis(trifluoromethyl)amino-group into organic substances by using these materials.

Electrochemical fluorination was used for the syntheses of the starting compounds N,N-bis(trifluoromethyl)perfluoroalkylsulfonamides and N,N-bis(trifluoromethyl)-perfluoroalkylacylamides. It was shown that these compounds can be used for the convenient generation of the $[N(CF_3)_2]^-$-anion and different salts were prepared, and their properties and reactivity investigated.

The new stable $[N(CF_3)_2]^-$-salts with tetraalkylammonium and phosphonium cations can be used in common organic syntheses. In this manner new organic compounds bearing the bis(trifluoromethyl)amino group were synthesized.

It was shown that the $[N(CF_3)_2]^-$-anion is a weak nucleophile which can easily split off a fluorine-anion which leads to competitive reactions between the $[N(CF_3)_2]^-$- and fluoride anion with organic compounds.

The electrochemical properties of N,N-bis(trifluoromethyl)perfluoroalkyl-sulfonamides, N,N-bis(trifluoromethyl)perfluoroalkylacylamides and the $[N(CF_3)_2]^-$-anion were investigated. It was shown that the $[N(CF_3)_2]^-$ anion can be used in electrochemical syntheses.

CONTENTS

1 Introduction and aim of this work

Though the minerals containing fluorine are quite widespread in the Earth's crust, naturally occurring organo-fluorine compounds are very rare. Systematic knowledge of organic fluorine chemistry and its practical utilization tends to grow slowly, compared to the advances in other fields of organic chemistry. Until 1899 the bibliography to Moissan's monograph[1] collected all work and aspects of fluorine chemistry in ca. 840 articles. With the inorganic chemistry's progress in development of new fluorinating agents, evolution of organo-fluorine chemistry is supported. The first fluorinating agents such as alkali metal fluorides are known since 1820, pure anhydrous hydrogen fluoride since 1856, and fluorine itself since 1886. The chemistry of organo-fluorine compounds started to grow rapidly during the Second World War, when it became driven much more by the advances in technology rather than by pure academic curiosity. Organo-fluorine compounds found their application in industrial processes ranging from the processing of nuclear fuel and microchip fabrication to the fire–fighting foams and inhalation anesthetics. However, their preparation is not straightforward because ordinary synthetic methods are not always applicable to the preparation of fluorinated organic compounds. Fluorination of an organic compound strongly affects its physical properties and chemical reactivity. The unique characteristics of the C-F bond are the result of the high ionization potential of fluorine as well as the element's low polarizability. The properties of the C-F bond are manifested in very weak intermolecular forces and low surface energy. In addition, the extreme

Pauling electronegativity of fluorine polarizes the C-F bond by electron withdrawal and makes this bond partially ionic. The “fluorine influence” in organic chemistry stems from a combination of properties associated with the fluorine atom: its high electronegativity and relatively small size, its tightly bound lone-pair electrons and the excellent match between the bonding orbitals of fluorine and carbon.

The dimethylamino group is an important building block in organic chemistry. It is a part of many biological active compounds and dyes. Therefore, the syntheses of compounds containing the fluorinated dimethylamino group are of interest for the subsequent studies of their properties. For example, the changes in properties may include changes in color and stability of the dyes. Research in new compounds containing the bis(trifluoromethyl)amino group is strongly dependent on (i) its convenient synthesis and (ii) methods for introduction of this moiety into organic compounds.

At the start of my research work in the area of fluorine chemistry and electrochemical fluorination, I was involved in the synthesis of new compounds - perfluorinated amides of sulphonic acids. This lead finally to the development of new methods of synthesis and applications of the $[N(CF_3)_2]^-$-anion.

2 Review of the literature

2.1 Sources for the bis(trifluoromethyl)imido anion

Salts of weak acids such as HNR_2, HPR_2 and $HAsR_2$ (R = alkyl or aryl substituent) have been known for a long time, and are of widespread importance in inorganic and organic synthesis[2]. Despite their importance, and irregardless of the growing interest in the fluorine-containing compounds in the last decades, only very few salt-like bis(perfluoroorgano)element compounds $M[N(R_F)_2]$, $M[P(R_F)_2]$ (M = electropositive metal; $R_F = CF_3$, C_6F_5, etc.) have been reported[3-5]. These types of compounds are considered to be very unstable, because the formation of MF is energetically favored, especially in the case of small cations[6].

The synthesis of the bis(trifluoromethyl)imido-anion is generally based on the fluoride ion addition an perfluoro-2-azapropene, $CF_3N=CF_2$[7-9]. $CF_3N=CF_2$ can be prepared in 78 % yield by fluorination of $CCl_3N=CCl_2$ with excess of NaF in sulfolane at 150 °C[10] or by photolysis of $CF_3N(CF_2CFCl_2)Cl$ (Yield: 65-70 %)[11]. Perfluoro-2-azapropene is a gas at room temperature (B.p. −33 °C[9]) and to make use of this compound special equipment is required.

The very reactive, covalently bound mercury (II) bis(trifluoromethyl)imid, was synthesized at first by Young and co-workers[12] according to equation (1).

$$2\,CF_3N=CF_2 \;+\; HgF_2 \longrightarrow (CF_3)N-Hg-N(CF_3)_2 \qquad (1)$$

This liquid, volatile compound is a good reagent for the introduction of $N(CF_3)_2$ - groups into organic molecules[7, 13], but it is extremely moisture-sensitive and very reactive. The synthesis of $Hg(N(CF_3)_2)_2$ is a difficult, time-consuming task that requires special equipment and expensive starting materials.

Caesium bis(trifluoromethyl)imid, $Cs[N(CF_3)_2]$, is another possible reagent for the synthesis of bis(trifluoromethyl)amino compounds. This salt can be prepared simply by introducing perfluoro-2-azapropene into a suspension of caesium fluoride in dry acetonitrile[14] equation (2):

$$CF_3N{=}CF_2 \quad + \quad CsF \quad \longrightarrow \quad Cs[N(CF_3)_2] \qquad (2)$$

It was isolated as a solid material that decomposes at temperatures above 90 °C[15] but all attempts to reproduce this experiment in gram scale were unsuccessful.

A disadvantage of this method is the formation of a dimeric by-product (3):

$$CF_3N{=}CF_2 \quad + \quad Cs[N(CF_3)_2] \quad \longrightarrow \quad CF_3{-}N{=}CF{-}N(CF_3)_2 \quad + \quad CsF \qquad (3)$$

This process seems to be nearly unavoidable and leads to the formation of a product mixture.

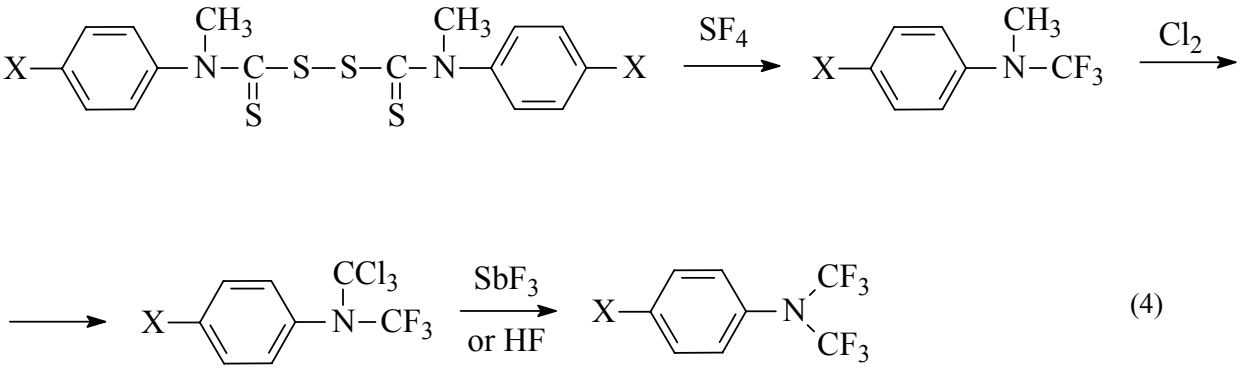
2.2 Methods of introduction of the $N(CF_3)_2$ group into organic compounds

There are two methods for introducing of the $N(CF_3)_2$ groups into organic compounds:

(i) conversion of suitable organic substituents into $N(CF_3)_2$,

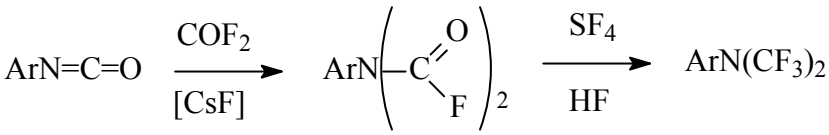
(ii) direct introduction of the $N(CF_3)_2$ group.

The synthesis of N,N'-bis(trifluoromethyl)aniline, according to (4), belongs to the first type (i) [16]:



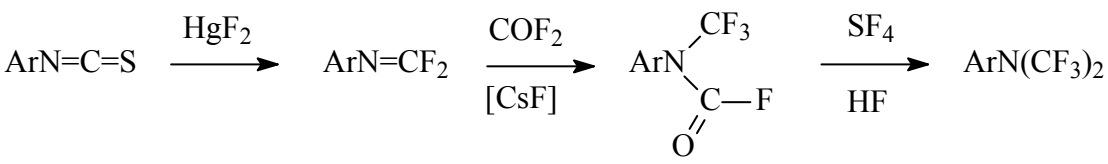
(4)

In another route arylisocyanates (5) [17]:



(5)

or aryl isothiocyanates (6) were used as starting compounds:



(6)

For the second type of reactions (ii) starting reagents, that already contain the $N(CF_3)_2$-group, are required.

N-halogenoamines are suitable for such kind of reactions. N-chloro, N-bromo and N-iodobis(trifluoromethyl)amines can be obtained from mercury(II) bis(trifluoromethyl)imide (7) [18]:

$$(CF_3)_2N-Hg-N(CF_3)_2 + 2\,X_2 \longrightarrow 2\;X-N(CF_3)_2 + HgX_2 \qquad (7)$$

X= Cl, Br, I

or from bis(trifluoromethyl)hydroxylamine (8) [19]:

$$HO-N(CF_3)_2 + PCl_5 \longrightarrow Cl-N(CF_3)_2 + POCl_3 + HCl \qquad (8)$$

These compounds are convenient reagents for the introduction the $N(CF_3)_2$-group by addition to unsaturated moieties (9)[20-23]:

$$X-N(CF_3)_2 + RCH{=}CH_2 \longrightarrow X-CHR-CH_2-N(CF_3)_2 + X-CH_2-CHR-N(CF_3)_2 \qquad (9)$$

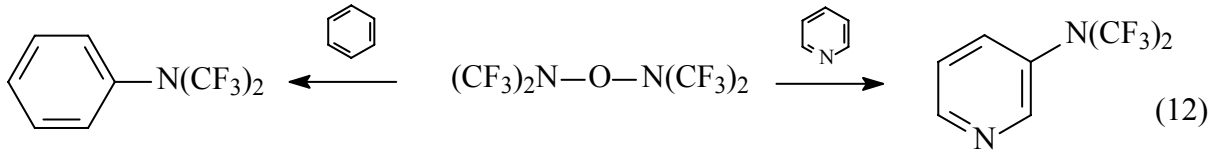
X= Cl, Br, I; R= Alk

There are only a few examples of the direct introduction of $N(CF_3)_2$-group into aromates. Because N-halogenobis(trifluoromethyl)amines are weak nucleophiles, it is impossible to use them for Friedel-Crafts reactions.

A method for introduction of the $N(CF_3)_2$-groups into aromatic systems via $[N(CF_3)_2]^{\cdot}$-radicals, generated from perfluoro-2,4-dimethyl-3-oxa-2,4-diazapentane (10-12), has been developed[24]:

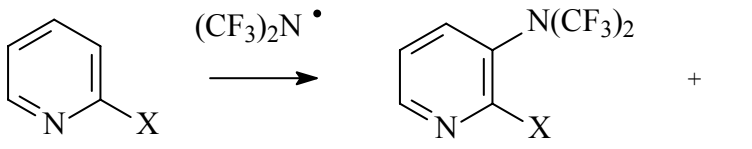
$$(CF_3)_2N-O-N(CF_3)_2 \xrightarrow{\Delta} (CF_3)_2N^{\bullet} + (CF_3)_2N-O^{\bullet} \qquad (10)$$

$$(CF_3)_2N^{\bullet} + ArH \longrightarrow (CF_3)_2NArH^{\bullet} \longrightarrow \longrightarrow ArN(CF_3)_2 \qquad (11)$$



(12)

The disadvantages of this method are the formation of a mixture of isomeric products, which are difficult to separate, and loss of half of the $N(CF_3)_2$-groups as by-products[25].



(13)

X	%	%
Cl	28.5	27
F	32.5	41.5

The methods of introduction of the bis(trifluoromethyl)amino group into organic compounds described above are not very practical. They are very cumbersome from both point of views (i) technical, due to the need for special equipment, and difficulties in the syntheses of starting materials and (ii) difficulties in scaling up. Therefore, development of a new, simple and practical method for introduction of the bis(trifluoromethyl)amino group into organic compounds is an essential and promising challenge.

3 Results and discussion

3.1 Syntheses of perfluoroorganic compounds by electrochemical fluorination

Electrochemical fluorination (ECF) was used to synthesize the starting materials, *i.e.* ($C_2F_5SO_2F$, $C_2F_5C(O)F$), which were converted into dialkyl-sulfonamides or -acylamides. The amides again were treated by ECF to obtain perfluoro dialkylamides. The results of the ECF process are strongly dependent on the choice of the starting material, and the influence of its structure on the yield of fluorinated products was studied. For example, the electrochemical fluorination of ethanesulphonyl-chloride and -fluoride clearly demonstrate the influence of the nature of the starting material on the result of the ECF-process.

3.1.1 Principles of the electrochemical fluorination

Electrochemical synthesis of fluoroorganic compounds is an important industrial method. Since its development by Simons at the beginning of the 40-th and first publication in 1949[26], ECF has been used to synthesize many fluoro-containing substances (primarily, perfluorinated organic compounds). This process is named "Simons process".

In the ECF anhydrous hydrogen fluoride (aHF) as solvent and nickel electrodes are used. The choice of nickel as electrode material is crucial, because the fluorination

is not conducted by fluorine itself, but rather by the nickel fluorides (III) or (IV) that are formed on the surface of the electrodes[27].

To evaluate the mechanism of the electrochemical fluorination several studies were performed. At first, Simons suggested a two steps mechanism – (i) oxidation of the fluoride anion to atomic fluorine, and then (ii) replacement of hydrogen atoms in the organic molecule by fluorine (i.e., radical fluorination) [28]. However, this mechanism did noto explain the failure of fluorinated products when platinum electrodes were used. Later a four steps mechanism of ECF has been suggested[29] according to (14):

$$
\begin{aligned}
&\mathrm{R\text{-}H} \xrightarrow[\mathrm{HF}]{-\,e} [\,\mathrm{R\text{-}H}\,]^{+\bullet} \\
&[\,\mathrm{R\text{-}H}\,]^{+\bullet} \xrightarrow{-\,H^{+}} [\,\mathrm{R}\,]^{\bullet} \\
&[\,\mathrm{R}\,]^{\bullet} \xrightarrow{-\,e} [\,\mathrm{R}\,]^{+} \\
&[\,\mathrm{R}\,]^{+} \xrightarrow{F^{-}} \mathrm{R\text{-}F}
\end{aligned}
\qquad (14)
$$

Finally Sartori et al.[27] included nickel fluorides as intermediates in the mechanism. This assumption also explained the important role of adsorption of the starting molecules on the surface of the nickel electrodes during the process of electrochemical fluorination.

Therefore, the mechanism of ECF consists of two distinct and independent stages:

(i) Formation of fluorinating agents – nickel fluorides – on the surface of the electrodes (electrochemical process);

$$3\,HF + Ni^0 - 3e \longrightarrow NiF_3 + 3H^+ \quad (15)$$

(ii) Interaction of the nickel fluorides with the organic substrate dissolved in aHF that results in a replacement of hydrogen atoms by fluorine (chemical process).

Anode:

$$R{-}H + NiF_3 \longrightarrow R^{\cdot} + NiF_2 + HF \quad (16)$$

$$R^{\cdot} + NiF_3 \longrightarrow R^+ + NiF_2 + F^- \quad (16a)$$

$$R^+ + F^- \longrightarrow R{-}F \quad (16b)$$

$$2\,NiF_2 + 2\,HF - 2e \longrightarrow 2\,NiF_3 + 2\,H^+ \quad (16c)$$

Cathode:

$$2\,H^+ + 2e \longrightarrow H_2 \quad (16d)$$

The starting material is oriented, absorbed at the surface of the nickel anode, fluorinated and desorbed. This radical stepwise fluorination mechanism was confirmed recently by ECF of some model compounds[30]. Formation of isomers were rationalized by cyclization and ring opening processes.

Based on this knowledge about the mechanism of ECF it is possible to explain the product distribution pattern and partially predict results of the ECF. For first insights in the electrochemical properties of a starting substance analytical electrochemical method such as voltammetry can be used.

3.1.2 Cyclic voltammetry

Early contributions to cyclic voltammetry or voltamperometry (CVA) were made by investigators including Randles[31], Nicholson and Shain[32, 33], Kalthoff and Tomsicek[34]. Over the past couple of decades potential sweep techniques, such as CVA, have been applied to an ever increasing range of systems, preliminary mechanistic investigations[35].

This technique has grown in popularity so much, that obtaining a cyclic voltamperogramm of a new electrochemical system (or substance) is often the first experiment performed by the electrochemist, giving valuable information as to the presence of electroactive species in solution or at the electrode surface.

A three-electrode system is typically used in voltammetry of organic compounds in non-aqueous solutions[36] (Fig. 1).

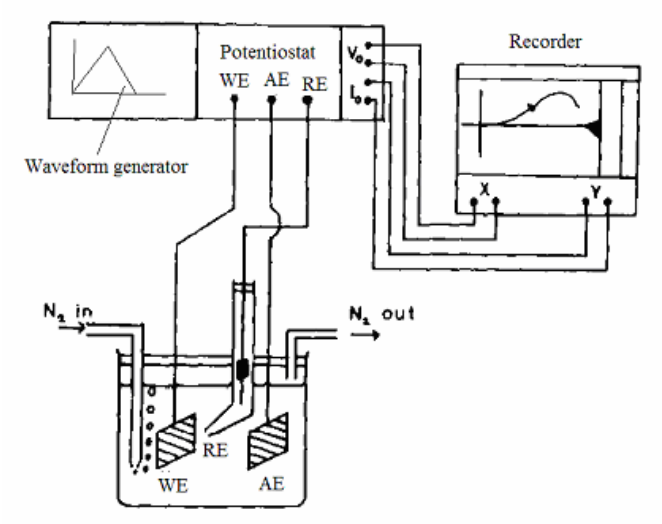


Fig. 1 A schema of the cell used for CVA

One electrode is a working electrode WE (typically glassy carbon or platinum). Another one is counter or auxiliary electrode AE (platinum wire or plate). These

two electrodes placed into solution form an electrical chain. The third electrode is the reference electrode (RE). The potential at the WE is monitored and controlled very precisely with respect to the RE via a potentiostat. Using the RE into the system gives the possibility to regulate the potential of the working electrode by the potentiostat independently from the voltage applied to working and auxiliary electrodes. The desired voltage as function of time is imposed on the WE by waveform generator.

The current flowing between the WE and AE is usually measured as the potential drop V across a resistor connected in series with the WE and AE. The current does not flow through the reference electrode because of the very high input impedance between RE and WE. When the potential of the working electrode is more positive than that of a redox couple present in the solution, the corresponding species may be oxidized (*i.e*. electrons going from the solution to the electrode) and produce an *anodic* current. Similarly, on the return scan, as the working electrode potential becomes more negative than the reduction potential of a redox couple, reduction (*i.e.* electrons flowing away from the electrode) may occur to cause a *cathodic* current.

The potential of the working electrode is changed linearly with time (Fig. 2). The scan rate (v) and the polarity of the working electrode can be varied by the potentiostat. The measured dependence of the current between working and auxiliary electrodes (I) from the potential (E) of working electrode result in the

cyclovoltamperogram and then plotted out directly via an XY chart recorder. The scan rate of the potential is usually in the range from 0.020 $V \cdot s^{-1}$ to 100 $V \cdot s^{-1}$ [37]

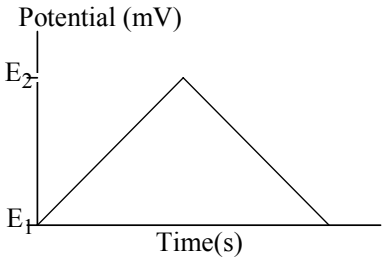
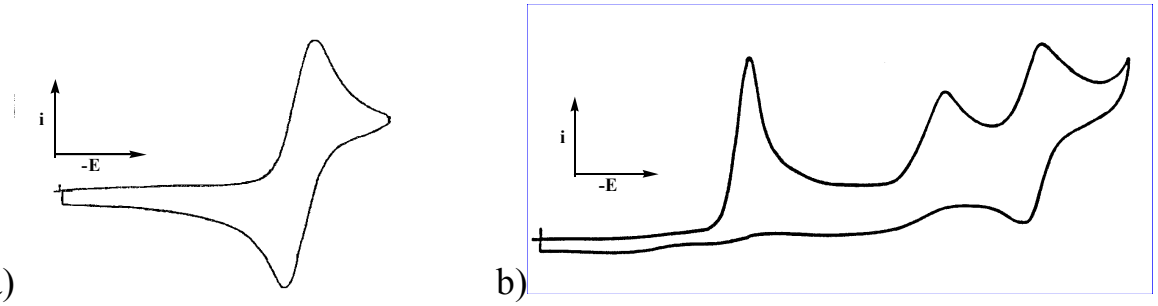


Fig. 2 Development the potential with time in CVA

By the CVA measurement the product which is formed on the electrode surface via electrochemical reaction (17) can be detected in the reverse scan.

$$Ox + ne \rightleftharpoons Red \qquad (17)$$

The dependence of the current on potential in CVA exhibits a peak. In the case of reversible process the species which is formed via an electrochemical reaction are stable enough to be detected on the reverse scan (Fig 3a). If the electrochemically generated species undergo rapid chemical reaction, they can not be detected during the reverse scan (absence of the reverse peak on the CVA, Fig 3b)



a) b)

Fig. 3 Reversible (a) and irreversible (b) systems

The basic parameters for a cyclic voltammograms and their signs are shown on Fig. 4

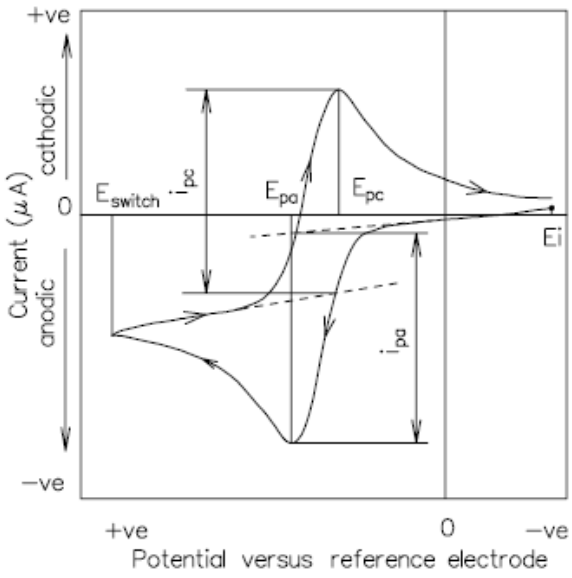


Fig. 4 Basic parameters for the cyclic voltammetry:

ip_A : Anodic peak current (oxidation)

Ep_A : Potential of anodic process

ip_C : Cathodic peak current (reduction)

Ep_C : Potential of cathodic process

E_{switch}: Point of reverse switching of the potential sweep

E_i : Starting point

The current response **Ip** for a reversible system is described by Randles-Sevcik equation[38] (18).

$$\mathbf{Ip = 0.4463\ n\ F\ A\ C\ (n\ F\ \nu\ D\ /\ R\ T)^{1/2}} \qquad (18)$$

Ip : Forward peak current (A)

n : number of electrons,

F : Faraday's constant (96485 C / mol),

A : electrode area (m^2),

C : concentration (mol/l)

R is the universal gas constant (8.314 J / mol·K),

T is the absolute temperature (K), and

D is the analytic's diffusion coefficient (m^2/sec).

ν is the potential scan rate ($V \cdot s^{-1}$)

A test of the reversibility of the system (Fig. 5) is (i) to check whether a plot of I_p as a function of $\nu^{1/2}$ is linear and passes through origin, (ii) the current ratio between reverse and forward peaks is constant and equal to 1.0, (iii) E_p is independent of ν, (iv) the separation between the potentials of the forward and reverse peaks ΔE_P at 25 °C is equal to 59/n mV (n being the number of electron exchanged per molecule of O_x) and such value maintains constant with scan rate. The experimental measurements of the peak current I_p allows to calculate one of parameters appearing in the equation.

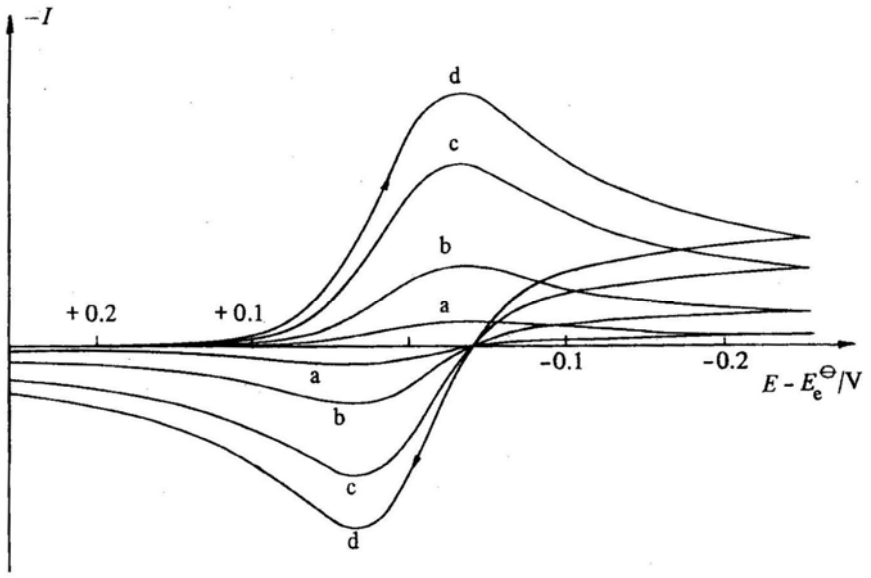


Fig. 5 Reversible system and its dependence from the scan rate.
(a, b, c, d : Voltamperograms with different scan rate (ν). $\nu_a < \nu_b < \nu_c < \nu_d$)

In case of irreversible system (i) E_p depends from scan rate, (ii) no current ratio exist (Fig. 6)

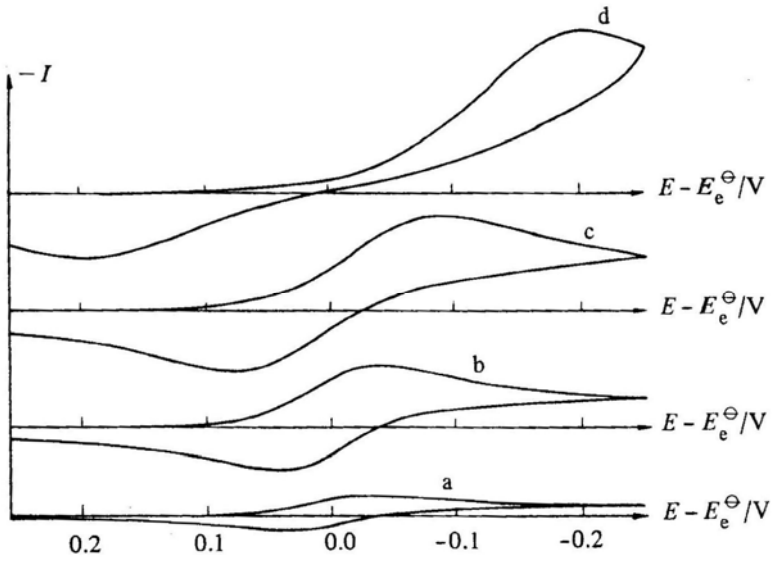


Fig. 6 Irreversible system and its dependence from the scan rate.
(a, b, c, d : Voltamperograms with different scan rate (ν). $\nu_a < \nu_b < \nu_c < \nu_d$)

The materials normally used as working electrodes are: platinum, gold, mercury, and carbon. The glassy carbon electrode (a patented material) is particularly suitable for non-aqueous solvents. It is isotropic, impermeable to gases, resistant to chemical attack and has a high conductivity.

A working electrode should have a rather small surface (10^{-2} and 10^{-1} cm^2) to ensure low currents in the circuit. The working electrode may be a rod with insulated edges and a mantle, which eliminates peripheral contributions in such a way that diffusion to the electrode is perpendicular to the plane surface (Fig. 7).

No strict limitations are imposed on selecting a reference electrode. However, the ions of the reference electrode should not interact with species of the studied solution. Usually electrodes such as saturated calomel (SCE) or silver-silver

chloride are equipped with an appropriate noninterfering salt bridge to prevent direct contact of aqueous electrolyte with the non-aqueous solution in the cell.

The reference electrode must be placed as close as possible to the surface of the working electrodes seen in Figure 7.

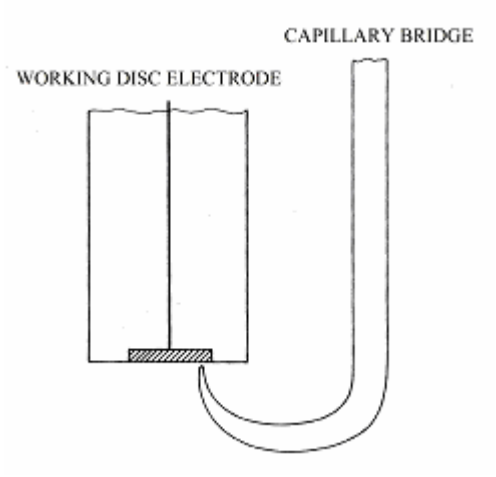


Fig. 7 Disc electrode with capillary bridge.

The auxiliary electrode, which placed directly in the solution under study, is usually made of platinum wire that is coiled around the working electrode (Fig. 8).

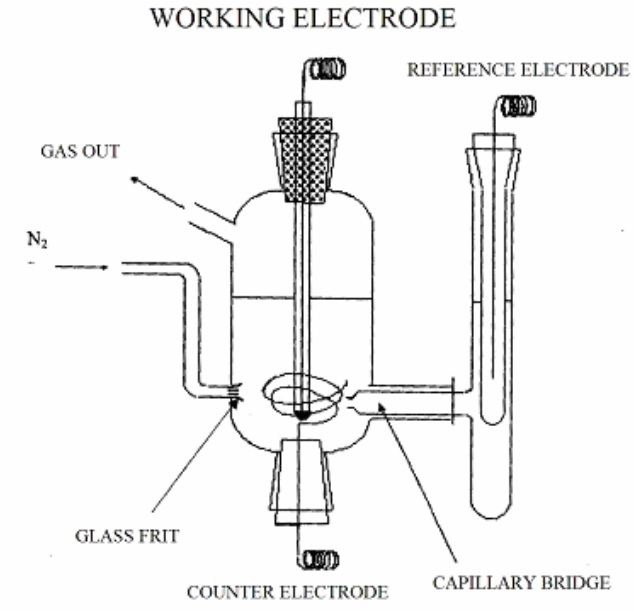


Fig. 8 Typical electrochemical cell

Because oxygen is electrochemically active it must be removed from the measuring sample via saturation of the solution with argon or nitrogen.

The rotating ring-disk electrode (RRDE, Fig. 9) is a two working electrodes system, consisting of a disk electrode, which is concentrically surrounded with a ring electrode separated by an insulator. The gap between both electrodes is small. From mechanical point of view both electrodes are **one** system which rotates about a same axis. However, electrically both electrodes are **independent** and can be used for two independent measurements in the same time.

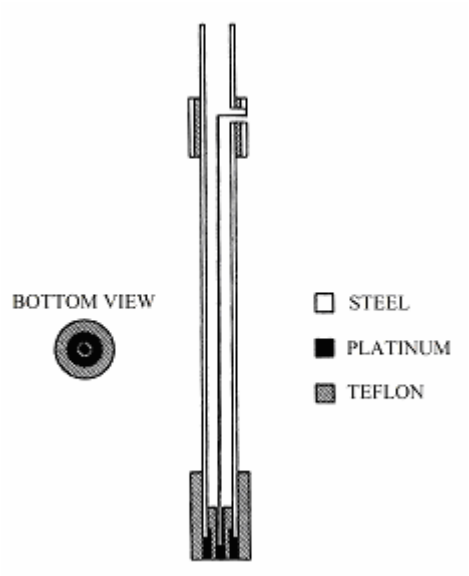


Fig. 8 Rotating ring-disc electrode.

The advantage of this form of electrodes is that products produced by the disc electrode may be monitored at the ring electrode. Thus the potential of the ring can be kept at a level which is different from the potential of the disc electrode to give the possibility register a specific response (oxidation or reduction) for a transient or

unstable product. The ratio between disk current and ring current depends on quantity of product which can reach to the ring from the disk.

The RRDE found extensive application for the study of the kinetics and mechanisms of chemical reactions and short-lived intermediates in electrochemical processes.

All methods described above were used to rationalize the results of the electrochemical fluorinations performed in this work.

The data collected by electrochemical measurements of different ethylsulfonylhalides play a key role to understand the product pattern and yields of the ECF. In detail it will be described in the next chapter.

3.1.3 Synthesis of $C_2F_5SO_2F$

The aim of this work was to found the best source for the $[N(CF_3)_2]^-$-anion. It was supposed that perfluorodimethylsulfonamides can be used for this purpose. The ECF of N,N-dimethyl-trifluoromethylsulfonylamide was reported[39] but the yield of the perfluorinated product was low. It was known[39, 40] that increasing of the length of alkyl group can decrease the solubility of the perfluorinated product and increase its yield. For this reason it was decided to synthesize perfluoroethylsulfonylamide.

But perfluoroethylsulfonyl fluoride is not commercially available. The electrochemical fluorination of ethylsulfonylchloride could be the simplest way to synthesize this compound. The reasons for the choice were two-fold (i) this substance is commercially available and (ii) the synthesis of perfluoroethylsulfonylfluoride from ethylsulfonylchloride was already reported[41] to yield 79% by ECF. However, all attempts to reproduce this result were unsuccessful. A complex mixture of perfluorinated, partially-fluorinated and chloride-fluoride-ethylsulfonyl-fluorides was formed and the yield of the desired product was very low (16%). Thus, it was necessary to find an alternative way to produce pentafluoroethylsulfonylfluoride.

To improve the yield of perfluoroethylsulfonylfluoride the parent compound $C_2H_5SO_2F$ was considered as starting material because (i) it does not contain chlorine, and therefore formation of chlorinated products is not possible; and (ii) it

already contains fluorine which enhances its stability[27]. It was found, that the presence of fluorine in the starting material is of crucial importance to improve the yield of the perfluorinated product.

While the Simons process with ethylsulfonylfluoride results in the formation of pentafluoroethylsulfonylfluoride in 82% yield, the ECF of ethylsulfonylchloride gives a complex mixture of perfluorinated and partially fluorinated compounds together with large amounts of chloro-fluoro-ethanes and chloro-fluoro-ethylsulfonyl fluorides (Tables 2-8). This result indicate that (i) during the ECF of ethylsulfonylchloride, a significant decomposition of the starting material takes place (only 35 g of fluorinated products from 136.4 g of starting material were obtained) and (ii) the chlorination of the starting material and intermediates proceeds in parallel with the Simons process.

What is the reason for such drastic difference in the fluorination of two similar compounds? For an answer let us review the processes that occur during the electrochemical fluorination of alkylsulfonyl chlorides and -fluorides.

If methyl- and butylsulfonylchlorides are used as starting materials for the synthesis of perfluoromethyl and buthylsulfonylfluorides via the Simons process, it can be assumed that, chlorine is replaced by fluorine by action of aHF as it takes place in the case of acyl chlorides[42]. However, it was found that chlorine in alkanesulfonyl chlorides cannot be exchanged by fluorine simply by dissolving it in anhydrous hydrogen fluoride. Rather, it is very rapidly replaced by fluorine in the presence of SbF_5[43]. During ECF in anhydrous hydrogen fluoride, the

replacement of chlorine in sulfonyl chlorides proceeds via oxidation instead of a nucleophilic substitution. As a result, an S–F bond is formed and chlorine atoms leave presumably via the formation of mixed nickel chloro-fluoride intermediates.

The Simons cell is not equipped with a diaphragma. The main cathodic process is the electrochemical reduction of protons with the formation of hydrogen, eqn (19).

$$H^+ + e \longrightarrow H^\bullet \quad (19)$$

In the case of the electrochemical fluorination of alkylsulfonylchlorides, the reduction by cathodically formed hydrogen or the direct electrochemical reduction of the starting material is also possible to some extent, eqn. (20) and (21).

$$RSO_2Cl + 2\,H^\bullet \longrightarrow RSO_2H + HCl \quad (20)$$

$$RSO_2Cl + 2\,e \longrightarrow RSO_2^- + Cl^- \quad (21)$$

Chloride anions resulting from this process are anodically oxidized to Cl_2. As a result, the volatile products trapped at –78 °C[44, 45 1995] sometimes are yellow-green due to the presence of dissolved chlorine.

Alkylsulfonylfluorides are reduced at much more negative cathodic potentials than alkylsulfonylchlorides (See Table 1).

Table 1 Reduction potentials of alkylsulfonylhalides

Compound	$E_p^{red.}$, V (vs.SCE)	I_p , μA
CH_3SO_2F	**>2.3**	
CH_3SO_2Cl	–1.30	105
$ClCH_2SO_2Cl$	–0.90	190
$CH_3CH_2SO_2F$	**>2.3**	

Compound	$E_p^{red.}$, V (vs.SCE)	I_p , μA
$CH_3CH_2SO_2Cl$	−1.34	184
$ClCH_2CH_2SO_2Cl$	−0.99	332

Concentration of substrate: 2×10^{-3} M. Electrode: glassy carbon. Supporting electrolyte: 0,1 M Tetrabutylammonium tetrafluoroborate in CH_3CN. Reference electrode: SCE (E_p^{ox} ferrocene = 0.425 V). Scan rate: 0.2 $V\cdot s^{-1}$.

This is probably the reason for the higher yield of perfluoroalkylsulfonylfluorides obtained by ECF of alkylsulfonylfluorides as starting materials.

Chlorine that formed during the electrochemical fluorination of alkylsulfonylchlorides can chlorinate the starting material and intermediates.

All these reasons may be responsible for the drastic differences between the results of the ECF of ethylsulfonylchloride and ethylsulfonylfluoride.

In the ^{19}F NMR spectra of the mixture collected in the trap at −78 °C after the ECF of ethylsulfonylchloride about 40 different compounds were observed. These compounds can be divided into three groups: fluorinated alkylsulfonylfluorides and chlorides (Table 2)

Table 2 Compounds containing SO_2F and SO_2Cl groups

	Compound	Contents in the mixture, mol %	^{19}F NMR
1.	$CF_3CF_2SO_2F$	38.1	-113.1 d (2F,CF_2) -80.3 d (3F,CF_3) 44.9 qt (1F,SO_2F) $J^4_{F,F}$ = 6.8 Hz $J^3_{F,F}$ = 6.3 Hz

	Compound	Contents in the mixture, mol %	^{19}F NMR
2.	$ClCF_2CF_2SO_2F$	3.8	-107.6 dt (2F,CF_2) -67.7 dt (2F,$CClF_2$) 46.6 tt (1F, SO_2F) $J^4_{F,F}$ = 8.0 Hz $J^3_{F,F}$ = 5.5 Hz $J^3_{F,F}$ = 2.6 Hz
3.	$CF_3CFClSO_2F$	1.3	-122.3 q (1F,CClF) -77.3 dd (3F,CF_3) 42.0 q (1F, SO_2F) $J^4_{F,F}$ = 9.4 Hz $J^3_{F,F}$ = 6.8 Hz
4.	$CF_3CF_2SO_2Cl$	0.5	-109.7 s (2F,CF_2) -78.0 s (3F,CF_3)
5.	CF_3CHFSO_2F	<0.1	-191.2 dqd (1F,CHF) -74.3 ddd (3F,CF_3) 52.2 qdd (1F, SO_2F) $J^4_{F,F}$ = 9.5 Hz $J^3_{F,F}$ = 7.0 Hz $J^3_{F,F}$ = 11.4 Hz $J^2_{H,F}$ = 44.5 Hz $J^3_{H,F}$ = 5.1 Hz $J^3_{H,F}$ = 2.3 Hz
6.	CF_3SO_2F	<0.1	-73.0 d (3F,CF_3) 37.6 q (1F,SO_2F) $J^3_{F,F}$ = 18.0 Hz
7.	CF_2ClSO_2F	<0.1	-59.4 d (2F,CF_2Cl) 31.1t (1F, SO_2F) $J^3_{F,F}$ = 8.0 Hz

Table 3 Compounds containing the CF_3 group

	Formula	Contents in the mixture, mol %	^{19}F NMR
1.	CF_3CF_3	0.5	-87.0 s (3F,CF_3)
2.	CF_3CHF_2	1.1	-137.0 d (2F,CHF_2) -86.5 s (3F,CF_3) $J^2_{H,F}$ = 56.0 Hz
3.	CF_3CH_2F	1.9	-241.0 tq (1F,CH_2F) -78.3 dt (3F,CF_3) $J^3_{F,F}$ = 16.0 Hz $J^3_{H,F}$ = 8.0 Hz
4.	CF_3CH_3	1.5	-61.5 q (3F,CF_3) $J^3_{H,F}$ = 13.0 Hz

	Formula	Contents in the mixture, mol %	^{19}F NMR
5.	CF_3CF_2Cl	5.8	-86.0 s (3F,CF_3) -74.5 s (2F,CF_2Cl)
6.	CF_3CCl_2F	1.1	-84.1 d (3F,CF_3) -77.0 q (1F,CCl_2F) $J^3_{F,F}$ = 5.5 Hz
7.	CF_3CHClF	3.4	-156.8 dq (1F,CHClF) -82.5 dd (3F,CF_3) $J^3_{F,F}$ = 10.3 Hz $J^2_{H,F}$ = 47.0 Hz $J^3_{H,F}$ = 4.0 Hz
8.	CF_3CH_2Cl	3.3	-72.4 t (3F,CF_3) $J^3_{H,F}$ = 8.0 Hz

Table 4 Compounds containing the CHF_2 group

	Formula	Contents in the mixture, mol %	^{19}F NMR
1.	CHF_2CF_3	1.1	(see Table 3)
2.	CHF_2CHF_2	<0.5	-138.7 d (CHF_2) $J^2_{H,F}$ = 52.0 Hz
3.	CHF_2CH_2F	<0.5	-130.1 ddt (CHF_2) $J^3_{F,F}$ = 16.0 Hz $J^2_{H,F}$ = 55.0 Hz $J^3_{H,F}$ = 13.0 Hz
4.	CHF_2CH_3	1.1	-109.9 dq (CHF_2) $J^2_{H,F}$ = 58.0 Hz $J^3_{H,F}$ = 21.0 Hz
5.	CHF_2CF_2Cl	3.4	-133.2 dt (2F,CHF_2) -73.7td (2F,CF_2Cl) $J^3_{F,F}$ = 7.0 Hz $J^2_{H,F}$ = 54.0 Hz $J^3_{H,F}$ = 2.3 Hz
6.	CHF_2CCl_2F	<0.5	-127.5 dd (2F,CHF_2) -67.3 dt (1F,CCl_2F) $J^3_{F,F}$ = 14.0 Hz $J^2_{H,F}$ = 54.6 Hz $J^3_{H,F}$ = 3.5 Hz

	Formula	Contents in the mixture, mol %	^{19}F NMR
7.	CHF_2CHClF	3.4	-156.3 dddd (1F,CHClF) -131.6 dddd ($1F^b$,CHF_2) -129.3 dddd ($1F^a$,CHF_2) $J^2_{F}a_{,F}b$ = 298 Hz $J^2_{H,F}a$ = 55.2 Hz $J^2_{H,F}b$ = 54.1 Hz $J^3_{F}a_{,F}$ = 12.5 Hz $J^3_{H,F}a$ = 6.3 Hz $J^3_{F}b_{,F}$ = 16.0 Hz $J^3_{H,F}b$ = 5.1 Hz $J^2_{H,F}$ = 50.0 Hz
8.	CHF_2CH_2Cl	0.8	-120.3 dt (CHF_2) $J^2_{H,F}$ = 55.0 Hz $J^3_{H,F}$ = 13.0 Hz
9.	CHF_2CHCl_2	< 0.1	-123.8 dd (CHF_2) $J^2_{H,F}$ = 56.0 Hz $J^3_{H,F}$ = 7.0 Hz

Table 5 Compounds containing the CF_2Cl group

	Formula	Contents in the mixture, mol %	^{19}F NMR
1.	CF_2ClCF_3	5.8	(see Table 3)
2.	CF_2ClCHF_2	3.4	(see Table 4)
3.	CF_2ClCH_2F	1.5	-226.1 tt (1F,CH_2F) -66.9 dt (2F,CF_2Cl) $J^3_{F,F}$ = 20.6 Hz $J^2_{H,F}$ = 46.5 Hz $J^3_{H,F}$ = 10.0 Hz
4.	CF_2ClCH_3	< 0.1	-47.6 q (CF_2Cl) $J^3_{H,F}$ = 8.0 Hz
5.	CF_2ClCF_2Cl	1.7	-70.9 s (CF_2Cl)
6.	$CF_2ClCHFCl$	1.1	-148.7 dt (1F,CHFCl) -70.1 ddd ($1F^a$,CF_2Cl) -67.5 ddd ($1F^b$,CF_2Cl) $J^2_{F}a_{,F}b$ = 174 Hz $J^3_{F}a_{,F}$ = 15.4 Hz $J^3_{F}b_{,F}$ = 15.2 Hz $J^2_{H,F}$ = 48.2 Hz $J^3_{H,F}a$ = 5.1 Hz $J^3_{H,F}b$ = 3.5 Hz $J^3_{H,F}$ = 13.0 Hz
7.	CF_2ClCH_2Cl	1.0	-59.6t (CF_2Cl) $J^3_{H,F}$ = 11.0 Hz

Table 6 Compounds containing the CCl_2F group.

	Formula	Contents in the mixture, mol %	^{19}F NMR
1.	CCl_2FCF_3	1.1	(see Table 3.)
2.	CCl_2FCHF_2	0.5	(see Table 4.)
3.	CCl_2FCH_2F	< 0.1	-210.8 td (1F,CH_2F) -73.0 d (1F,CCl_2F) $J^3_{F,F}$ = 21.5 Hz $J^2_{H,F}$ = 47.3 Hz
4.	CCl_2FCH_3	1.4	-46.1 q (CCl_2F) $J^3_{F,F}$ = 20,6 Hz
5.	$CCl_2FCHFCl$	< 0.1	-139.9 dd (1F,CHFCl) -69.4 d (1F,CCl_2F) $J^3_{F,F}$ = 22.0 Hz $J^2_{H,F}$ = 48.4 Hz

Table 7 Compounds containing the CHFCl group.

	Formula	Contents in the mixture, mol %	^{19}F NMR
1.	$CHFClCF_3$	3.4	(see Table 3.)
2.	$CHFClCHF_2$	2.3	(see Table 4.)
3.	$CHFClCH_2F$	< 0.1	-220.3 tdd (1F, CH_2F) -146.6 dm (1F, CHFCl) $J^2_{H,F}$ = 47.3 Hz $J^2_{H,F}$ = 40.5 Hz $J^3_{H,F}$ = 8.6 Hz $J^3_{F,F}$ = 19.3 Hz
4.	$CHFClCH_3$	< 0.1	-135.4 dq (CHFCl) $J^2_{H,F}$ = 52.0 Hz $J^3_{H,F}$ = 8.0 Hz
5.	$CHFClCF_2Cl$	1.1	(see Table 5.)
6.	$CHFClCFCl_2$	< 0.1	(see Table 6.)
7.	$CHFClCHCl_2$	< 0.1	-137.3 dd (CHFCl) $J^2_{H,F}$ = 55.0 Hz $J^3_{H,F}$ = 7.0 Hz

8.	$CHFClCH_2Cl$	< 0,1	-137.9 ddd (CHFCl) $J^2_{H,F}$ = 5.0 Hz $J^3_{H,F}a$ = 12.5 Hz $J^3_{H,F}b$ = 22.8 Hz

Table 8 Sulfur containing side products.

	Formula	**Contents in the mixture, mol %**	^{19}F NMR
1.	SO_2F_2	10.5	33.3 s
2.	SOF_2	3.8	74.5 s
3.	SSF_2	5.0	79.7 s
4.	SF_6	< 0.1	59.6 s
5.	SOF_4	< 0.1	100.0 s

chloro-fluoro ethanes (Table 3-7) and sulfur-containing side products (Table 8). The main product in this mixture is pentafluoroethylsulfonylfluoride in proportion of 38 mol. % (see Table 2). α- and β-chlorotetrafluoroethylsulfonylfluorides were also found in significant quantity, but the starting molecule does not contain a chlorine atom at α- and β- position.

Furthermore the electrochemical behavior of ethylsulfonylchloride was studied by means of cyclic voltammetry (see Fig. 9), and it was found that this compound is reduced irreversibly on the glassy carbon electrode at a potential of -1.34 V (vs. SCE, E_p^{ox} ferrocene = 0.425 V), (21). After cathodic scan, an irreversible wave appeared in the anodic area at the potential of 1.15 V. The anodic wave reflects the electrochemical oxidation of chloride ions generated in the cathodic process.

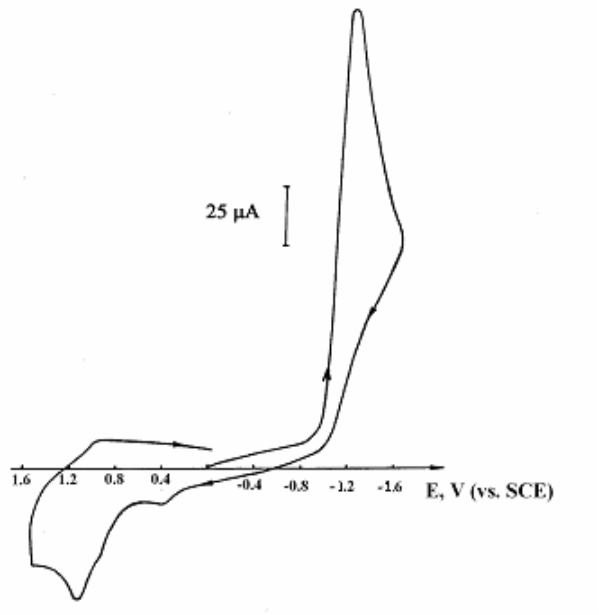


Fig.9

Cyclic voltammogram of ethylsulfonylchloride.

Concentration: $2x10^{-3}$ M. Electrode: glassy carbon. Supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. Scan rate: 0.2 $V \cdot s^{-1}$

The chlorine atoms generated in this way play a key role in the formation of chlorinated products and the decomposition of the starting material, because chloroethylsulfonylchlorides are reduced even more easily. For example, 2-chloroethylsulfonyl chloride shows the reduction peak in the cyclic voltammogram at -0.99 V (vs. SCE, E_p^{ox} ferrocene = 0.425 V) (see Fig.10), which is 0.35 V more positive than the reduction potential of $C_2H_5SO_2Cl$.

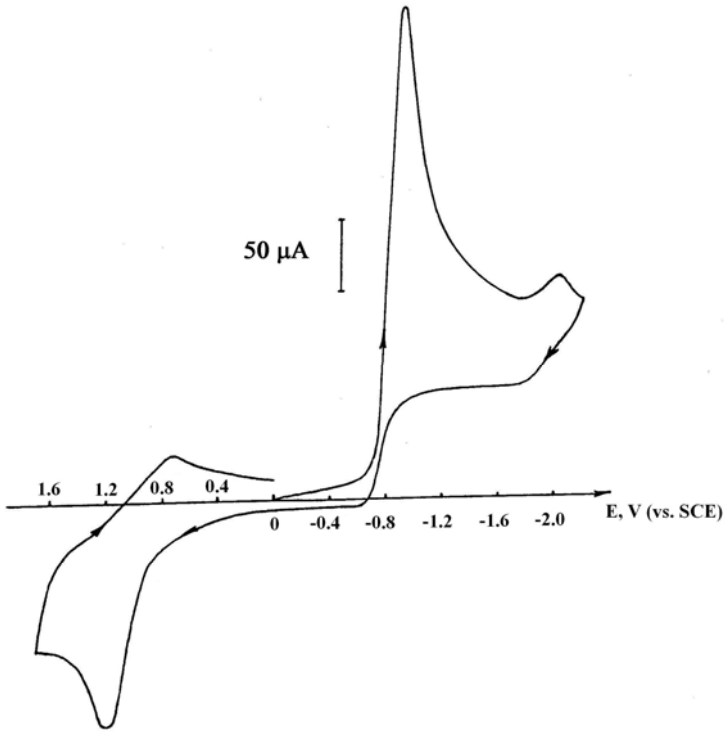


Fig. 10

Cyclic voltammogram of 2-chloroethylsulfonylchloride.

Concentration: $2x10^{-3}$ M. Electrode: glassy carbon. Supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. Scan rate: 0.2 $V \cdot s^{-1}$

Nearly the same difference is found in the reduction potentials of methylsulfonyl chloride and chlorometylsulfonylchloride (Table 1). Hence, the introduction of a chlorine atom into the aliphatic chain of alkylsulfonylchlorides shifts the reduction potentials to less negative values. If chloride anions are formed in the Simons process (first by the reduction of $C_2H_5SO_2Cl$) a cyclic process is triggered: chlorination - reduction - chlorination which causes a severe decomposition of ethylsulfonylchloride during the ECF. The sulfinic acids, which are formed by the cathodic reduction of chloroethylsulfonylchlorides, are not stable during the

Simons process. This strongly reduces the yield of the desired perfluoroethylsulfonylfluoride. The instability of chloroethylsulfinic acids, which decompose by elimination of SO_2 and other electrochemically-active species, is probably the reason why the reduction current of 2-chloroethylsulfonyl chloride is nearly twice to that of $C_2H_5SO_2Cl$ (see Table 1).

α- and β-chlorotetrafluoroethylsulfonylfluorides are formed in parallel with pentafluoroethylsulfonylfluoride. It is remarkable that the yield of β-chlorotetrafluoroethylsulfonylfluoride is more than twice as high as that of α-chlorotetrafluoroethylsulfonylfluoride. This means that the chlorination process preferably takes place at the β-position of ethylsulfonyl chloride. In any case, the total yields of these two chlorinated sulfonylfluorides are much less than that of $C_2F_5SO_2F$ (see Table 2). The direct or indirect cathodic reduction of chloroethylsulfonylchlorides strongly decreases the probability of these molecules to survive the Simons process.

The formation of $C_2F_5SO_2Cl$ (Table 2) indicates that the S–Cl bond can remain untouched.

Decomposition of chloroethylsulfonylchlorides during the ECF process leads to the formation of a large amount of chlorinated fluoroethanes. The total amount of these substances in the mixture trapped at -78 °C is 29 mol %, consisting mostly of

mono-chlorinated compounds (22 mol %). The amount of fluorinated dichloro-ethanes is 7 mol %, and that of trichloro-ethanes is less than 0.2 mol %. These data clearly indicate that the introduction of even one chlorine atom into the aliphatic chain is sufficient to cause severe decomposition of the starting material during the ECF process.

The formation of large amounts of sulfur-containing side products (see Table 8) indicates that the C–S bond is also weak. The cleavage of this bond is probably accelerated by the introduction of a chlorine atom into α-position of the starting molecule.

The cleavage of the C–C bond during the ECF of $C_2H_5SO_2Cl$ is not a process of significant importance, as the yields of CF_3SO_2F and $ClCF_2SO_2F$ are very low (see Table 2). The influence of this process on the yield of $C_2F_5SO_2F$ is even less in the case of the ECF of ethylsulfonylfluoride.

The result indicate that the large differences in the yield of $C_2F_5SO_2F$ produced by ECF of $C_2H_5SO_2Cl$ or $C_2H_5SO_2F$ are determined by the chlorination process that takes place during the ECF of ethylsulfonylchloride.

The differences in yields of CF_3SO_2F obtained by ECF of CH_3SO_2Cl or CH_3SO_2F (only 10 - 20 %) are much smaller, because the alkyl group is shorter and the probability of chlorination during the ECF is much lower.

3.1.4 Electrochemical fluorination of N,N-dialkyl(perfluoroalkyl)sulfamides

In the previous chapter the important role of starting material for the ECF was shown. Because N,N-dimethylpentafluoroethylsulfonylamide is not easy to obtain, different methyl-, ethyl trifluoromethylsulfonamides were used as model compounds for ECF because they are commercially available (CF_3SO_2F, CH_3SO_2Cl, $C_2F_5SO_2Cl$).

To find the best starting material for the preparation of perfluoro-N,N-dimethylalkylsulfonamides via ECF some experiments have been carried out and the results are collected in Table 9. The electrochemical fluorination of N,N-dimethylmethylsulfonamide gives a very low yield of $CF_3SO_2N(CF_3)_2$. But replacement of the CH_3-group bounded to sulphur by the CF_3-group improved the result. $CF_3SO_2N(CF_3)_2$ can be obtained in 24 % yield by ECF of $CF_3SO_2N(CH_3)_2$ (see Table 9). The reported[39] yield of $CF_3SO_2N(CF_3)_2$ is 35 % but it is probably depended on the cell. By using a bigger cell a yield of 47 % was obtained. All ECF experiments reported here were done in the same cell to give comparable results. Surprisingly, the ECF of $CF_3SO_2NH(CH_3)$, results mostly in decomposition products, most likely, due to insufficient protection of the S-N bond. Increasing in the length of the alkyl group e.g. in the $CF_3SO_2N(C_2H_5)_2$ or $C_2H_5SO_2N(CH_3)_2$ leads to complete decomposition of the starting material.

Table 9 Results of the ECF of different dialkylsulfonamides.

Sulfamide	Yield of perfluorinated product after ECF, %
$CH_3SO_2N(CH_3)_2$	< 5
$CF_3SO_2N(CH_3)_2$	24
$CF_3SO_2NH(CH_3)_2$	-
$CF_3SO_2N(C_2H_5)_2$	-
$C_2H_5SO_2N(CH_3)_2$	-
$C_2F_5SO_2N(CH_3)_2$	30

Taking into account these results, $CF_3SO_2N(CH_3)_2$ and $C_2F_5SO_2N(CH_3)_2$ are the only possible candidats for the ECF for the preparation of the compounds containing the desired $N(CF_3)_2$ group. The detailed synthesis of $C_2F_5SO_2N(CF_3)_2$ will be described later.

4 New sources of the bis(trifluoromethyl)imido group.

4.1 Sulfamides

4.1.1 Synthesis of sulfamides

Perfluorinated sulfonamides were prepared by electrochemical fluorination of the corresponding partially fluorinated sulfonamides[39, 46]:

$$FSO_2N(CH_3)_2 \longrightarrow FSO_2N(CF_3)_2 \quad (22)$$

Yield 31%

$$CF_3SO_2N(CH_3)_2 \longrightarrow CF_3SO_2N(CF_3)_2 \quad (23)$$

Yield 35 %

$$(CH_3)_2NSO_2N(CH_3)_2 \longrightarrow (CF_3)_2NSO_2N(CF_3)_2 \quad (24)$$

Yield: 11%

The starting materials are easily prepared from commercially available sulfonyl fluorides and dimethylamine (25-26).

$$SO_2F_2 + 2\,HN(CH_3)_2 \longrightarrow FSO_2N(CH_3)_2 + [(CH_3)_2NH_2]F \quad (25)$$

$$CF_3SO_2F + 2\,HN(CH_3)_2 \longrightarrow CF_3SO_2N(CH_3)_2 + [(CH_3)_2NH_2^+][F^-] \quad (26)$$

Perfluorinated sulfonamides are stable colorless liquids, which can be stored for a long time at room temperature ($FSO_2N(CF_3)_2$ b.p. 30-31 ^oC[47]; $CF_3SO_2N(CF_3)_2$ b.p. 56-57 ^oC[39] and $(CF_3)_2NSO_2N(CF_3)_2$ b.p. 85-86 ^oC[46] respectively). To work with these compounds, no special precautions or equipment are required. They are water stable (even not mixable with water), and fairly good soluble in organic

solvents (acetonitrile, ethylenglycoldimethylether, DMF and others). These characteristics make them very suitable for organic syntheses.

Synthesis of N,N-bis(trifluoromethyl)-pentafluoroethylsulfamide $C_2F_5SO_2N(CF_3)_2$

The starting material N,N-dimethylpentafluoroethylsulfamide was prepared in three steps. It was found, that the reaction of ethylsulfonylchloride with KHF_2 in water results in a high yield (90 %) ethylsulfonylfluoride (27),

$$C_2H_5SO_2Cl + KHF_2 \longrightarrow C_2H_5SO_2F + KF + HCl \qquad (27)$$

which was converted into pentafluoroethylsulfonylfluoride (28) by ECF

$$C_2H_5SO_2F \xrightarrow[Ni]{e,\ HF} C_2F_5SO_2F \qquad (28)$$

Yield: 82%

and the reaction of $C_2F_5SO_2F$ with dimethylamine leads to the formation of $C_2F_5SO_2N(CH_3)_2$ (29).

$$C_2F_5SO_2F + 2\ HN(CH_3)_2 \longrightarrow C_2F_5SO_2N(CH_3)_2 + [(CH_3)_2NH_2]F \qquad (29)$$

Finally the electrochemical fluorination of $C_2F_5SO_2N(CH_3)_2$ leads to the desired product (30)

$$C_2F_5SO_2N(CH_3)_2 \xrightarrow[Ni]{e,\ HF} C_2F_5SO_2N(CF_3)_2 \qquad (30)$$

In comparison to $CF_3SO_2N(CF_3)_2$, N,N-bis(trifluoromethyl)pentafluoro-ethylsulfonylamide is obtained in higer yield; however, the improvement is not very significant. It seems, that the pentafluoroethyl group is still not long enough

to make the perfluorinated product insoluble in aHF. Again, increase of the length of the perfluoroalkyl chain bonded to the sulphur increase the probability of S-N bond cleavage and precipitation of not completely fluorinated products from aHF (the content of polyfluorinated products is significant).

Results of fluorination are collected in the Table 10.

Table 10 Composition of the product obtained by electrochemical fluorination of $C_2F_5SO_2N(CH_3)_2$

No.	Compound	Content in the mixture, %	Yield, %
1.	$CF_3CF_2SO_2(CF_3)_2$	44	38
2.	$CF_3CF_2SO_2(CF_3)CF_2H$	27	25
3.	$CF_3CF_2SO_2(CF_2H)_2$	16	15
4.	$CF_3CF_2SO_2(CF_2H)CFH_2$	4	4
5.	$CF_3CF_2SO_2(CFH_2)_2$	1	1
6.	$CF_3CF_2SO_2F$	8	17

Synthesis of N,N,N´,N´-tetrakis(trifluoromethyl)sulfondiamide $(CF_3)_2NSO_2N(CF_3)_2$

It was interesting to synthesize a compound bearing two $N(CF_3)_2$-groups in the molecule. Tetramethylsulfonyldiamide was considered to be a possible starting material for its preparation.

Tetramethylsulfonyldiamide was prepared from cheap and commercially available thionylchloride by the reaction with dimethylamine (31).

$$SO_2Cl_2 + 4\,HN(CH_3)_2 \longrightarrow (CH_3)_2NSO_2N(CH_3)_2 + 2\,[H_2N(CH_3)_2]\,Cl \qquad (31)$$

Following ECF results in a mixture of per- and polyfluorinated products (32).

$$(CH_3)_2NSO_2N(CH_3)_2 \xrightarrow[HF]{e,\ Ni} (CF_3)_2NSO_2N(CF_3)_2 + (CF_3)_2NSO_2N(CF_3)CHF_2 + CHF_2(CF_3)NSO_2N(CF_3)CHF_2 \quad (32)$$

After several fractional distillations pure $(CF_3)_2NSO_2N(CF_3)_2$ was obtained in 1 % yield.

From Table 9 we can see that only $CF_3SO_2N(CH_3)_2$ and $C_2F_5SO_2N(CH_3)_2$ can be considered as convenient starting materials for the ECF. However, pentafluoroethylsulfonylfluoride is commercial not available.

Polyfluorinated products formed during the ECF can be used a repeated fluorination. It was found that additional ECF of the polyfluorinated product mixture resulted in a nearly pure perfluorinated product. For example in an additional ECF of the mixture: $CF_3SO_2N(CF_3)_2CF_2H$, $CF_3SO_2N(CF_2H)_2$, and $CF_3SO_2N(CF_2H)_2CFH_2$ the desired $CF_3SO_2N(CF_3)_2$ was obtained in 99 % purity and 64 % yield. It made the process of the ECF of $CF_3SO_2N(CH_3)_2$ and $C_2F_5SO_2N(CH_3)_2$ as source for the $[N(CF_3)_2]^-$ anion even more attractive.

At present $CF_3SO_2N(CH_3)_2$ remains the most suitable starting material for big scale ECF.

4.2 Chemical properties of fluorinated sulfamides.

Reactions with fluorides.

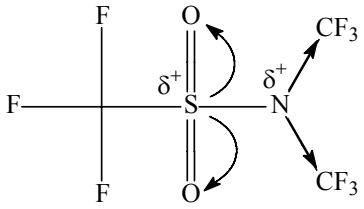
The bis(trifluoromethyl)aminogroup is an electron-withdrawing group with the Hammett sigma constant close to the trifluoromethyl group (Table 11).

Table 11 Hammett Sigma Constants[48, 49]

Group	σ_{meta}	σ_{para}	σ_I
CF_3	0.43	0.54	0.42
$N(CH_3)_2$	-0.15	-0.83	0.06
$N(CF_3)_2$	0.49	0.50	0.49

The strong electron-withdrawing CF_3 groups bonded to nitrogen effectively shift the electron density from nitrogen atom to the CF_3 groups. That makes the bis(trifluoromethyl)amino group non-basic, for example bis(trifluoromethyl)-anilines do not show basic properties and do not form salts with strong acids[17]. Bis(trifluoromethyl)amine can not be protonated even with HCl and did not give a solid Lewis acid/base addition product with boron trifluoride[12].

According to the electronic structure of N,N-bis(trifluoromethyl)-trifluoromethylsulfonamide the $N(CF_3)_2$ -anion can be obtained via nucleophilic attack on the S-N bond, for example by the fluoride-anion.



Indeed, it was found that perfluorinated sulfonamides readily react with metal fluorides to form the corresponding sulfonylfluorides and bis(trifluoromethyl)imido-salts (33).

$$x\ R_FSO_2N(CF_3)_2 + MF_x \longrightarrow x\ R_FSO_2F + M[N(CF_3)_2]_x \qquad (33)$$

R_F = F or C_nF_{2n+1} ; n = 1 - 4

M = Na, K, Rb, Cs, Ag, Cu, Hg ; x = 1 , 2

To increase the efficiency of this method, sulfamides with two bis(trifluoromethyl)amido-groups were considered, because they produce two moles of the $[N(CF_3)_2]^-$ anion (46).

$$(CF_3)_2N(SO_2CF_2)_mSO_2N(CF_3)_2 + (3\text{-}x)\ MF_x \longrightarrow F(SO_2CF_2)_mSO_2F + (3\text{-}x)\ M^+\ [^-N(CF_3)_2]_x \qquad (33a)$$

m = 0 ; 1

However, the synthesis of perfluorinated-diamides via ECF yielded a mixture of per- and polyfluorinated products and its isolation is very difficult. Therefore they can not be recommended for the large scale synthesis of the $[N(CF_3)_2]^-$ anion.

Perfluorinated sulfonylfluorides, which are formed as by-products (33) are either a gas at room temperature or very volatile liquids. The presence of these compounds

in the acetonitrile solution after reaction with metal fluorides does not cause any problems for the application of imido-salts as reagents for the introduction of $N(CF_3)$-groups into organic or inorganic molecules.

The sulfonylfluorides can be collected and used again for the synthesis of the starting material for the ECF, equation (26).

The method described above gives the possibility to transform $N(CH_3)_2$-groups into $N(CF_3)$-groups and using the cheap and commercially available dimethylamine.

Reaction with NaF

When using sodium fluoride, the reaction proceeds very slowly, due to the low solubility of NaF in organic solvents. Due to the low stability of salts with small cations, the decomposition of sodium bis(trifluoromethyl)imide at room temperature proceeds faster than its formation equation (34).

$$2\ CF_3SO_2N(CF_3)_2 \xrightarrow{NaF} 2\ CF_3SO_2F + CF_3{-}N{=}CF{-}N(CF_3)_2 \qquad (34)$$

Nevertheless the intermediate formation of sodium bis(trifluoromethyl)imide can be confirmed by trapping it with bromaceticethyl ester (35).

$$CF_3SO_2N(CF_3)_2 + NaF + BrCH_2C(O)OEt \longrightarrow (CF_3)_2NCH_2C(O)OEt + CF_3SO_2F + NaBr \qquad (35)$$

Reaction with KF

The reaction with potassium fluoride is faster and a solution of potassium bis(trifluoromethyl)imide (for example, in acetonitrile) (36), was obtained, which

$$CF_3SO_2N(CF_3)_2 \xrightarrow{KF} CF_3SO_2F + K[N(CF_3)_2] \quad (36)$$

slowly decomposes (37-38) at room temperature.

$$K[N(CF_3)_2] \rightleftharpoons CF_3-N=CF_2 + KF \quad (37)$$

$$CF_3-N=CF_2 + K[N(CF_3)_2] \longrightarrow CF_3-N=CF-N(CF_3)_2 + KF \quad (38)$$

Reaction with RbF

The best results were obtained by using rubidium fluoride. It has a relatively good solubility in organic polar solvents, and the size of the rubidium cation matches perfectly to stabilize the bis(trifluoromethyl)imide anion. The reaction with RbF in acetonitrile (39) occurs within a few minutes, and the resulting solution contains only rubidium bis(trifluoromethyl)imide and trifluoromethylsulfonylfluoride.

$$CF_3SO_2N(CF_3)_2 + RbF \longrightarrow CF_3SO_2F + Rb[N(CF_3)_2] \quad (39)$$

Reaction with CsF

Caesium fluoride is better soluble in organic polar solvents then the other alkali metal fluorides. From this point of view the caesium salt should be more stable and it was described as such an material[15]. However, a side reaction was observed (41), which was probably due to the high activity of caesium bis(trifluoromethyl)imide:

$$CF_3SO_2N(CF_3)_2 \xrightarrow{CsF} CF_3SO_2F + Cs[N(CF_3)_2] \quad (40)$$

$$CF_3SO_2N(CF_3)_2 + Cs[N(CF_3)_2] \longrightarrow CF_3-N=CF-N(CF_3)_2 + CsF + CF_3SO_2F \quad (41)$$

Therefore, it was not possible to prepare a pure solution of caesium bis(trifluoromethyl)imide.

Reaction with AgF

AgF is soluble in most organic polar solvents, and the silver cation is fairly large to stabilize the bis(trifluoromethyl)imide anion. The reaction takes place under mild conditions and in a short time (41). The drawbacks of this reagent are its high cost and sensitivity to light.

$$CF_3SO_2N(CF_3)_2 \xrightarrow{AgF} CF_3SO_2F + Ag[N(CF_3)_2] \quad (46)$$

Reaction with CuF_2

$$CF_3SO_2N(CF_3)_2 \xrightarrow{CuF_2} CF_3SO_2F + Cu[(N(CF_3)_2]_2 \quad (43)$$

Copper salts are widely used in organic syntheses[50]. By this reason, some experiments to prepare copper salt with the bis(trifluoromethyl)imide anion were carried out. The reaction with copper fluoride takes place at 80 °C in a closed vessel (due to the volatility of N,N-bis(trifluoromethyl)sulfonylamide). But, at this temperature, many side processes take place. The yield and purity of copper (II) bis(trifluoromethyl)imide obtained in this reaction were not satisfactory.

Reaction with HgF_2

$$2\ CF_3SO_2N(CF_3)_2 + HgF_2 \longrightarrow 2\ CF_3SO_2F + (CF_3)_2N-Hg-N(CF_3)_2 \qquad (44)$$

The reaction takes place at 85 °C and results in moderate yields of mercury (II) bis(trifluoromethyl)imide (44).

The syntheses of Cd, Zn, Cu, Ag salts by using $Rb[N(CF_3)_2]$

The reaction of N,N-bis(trifluoromethyl)-trifluoromethylsulfonylamide or -acylamides with ZnF_2 and CdF_2 at room temperature proceeds very slowly, due to their low solubility in organic solvents. At elevated temperature only decomposition products were observed.

However, such salts can be prepared by treatment of $Rb[N(CF_3)_2]$ with metal triflates, $M[OSO_2CF_3]_x$, which have a good solubility in different organic solvents. The reaction between $Rb[N(CF_3)_2]$ and metal triflates (45), in organic solvent proceeds very fast.

$$x\ Rb[N(CF_3)_2] + M[OSO_2CF_3]_x \longrightarrow M[N(CF_3)_2]_x + x\ Rb[OSO_2CF_3] \qquad (45)$$

M= Ag, Zn, Cd; x = 1,2

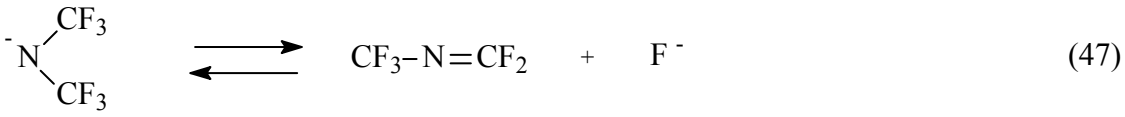
Rubidium triflate has a low solubility in organic solvents and can be separated by decantation at low temperature. The purification of the salts can be carried out through extraction with dichloromethane.

Reaction with $[NR_4]F$

Tetraalkylammonium fluorides also react with N,N-bis(trifluoromethyl)trifluoromethylsulfonylamide. This reaction leads to the corresponding tetraalkylammonium-bis(trifluoromethyl)imides which can be isolated as stable solid materials (46).

$$CF_3SO_2N(CF_3)_2 + [(CH_3)_4N]F \longrightarrow CF_3SO_2F + [(CH_3)_4N][N(CF_3)_2] \quad (46)$$

In solution, the $[N(CF_3)_2]^-$ anion is in equilibrium with perfluoroazapropene (47):

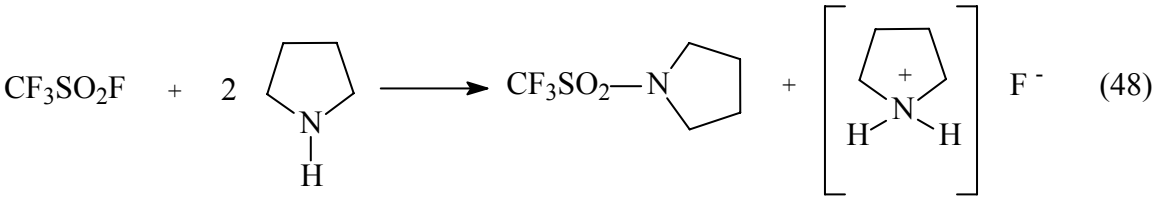


$$CF_3{-}N{=}CF_2 + F^- \quad (47)$$

That explains the low stability of the $[N(CF_3)_2]^-$ anion in the presence of metal cations. There are two possible ways to increase the stability of such imido salts (i) change cation (as it was shown above with tetramethylammonium cation) and (ii) change of the anion structure.

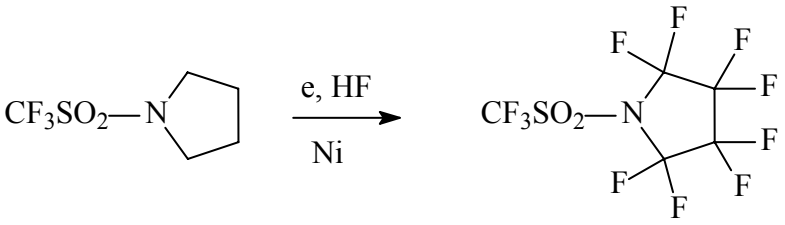
In attempt to prevent equilibrium (47) octafluoro-1-trifluoromethanesulfonyl-pyrrolidine was synthesized.

By the reaction of trifluoromethylsulfonylfluoride with pyrrolidine the corresponding sulfamide was prepared (48)



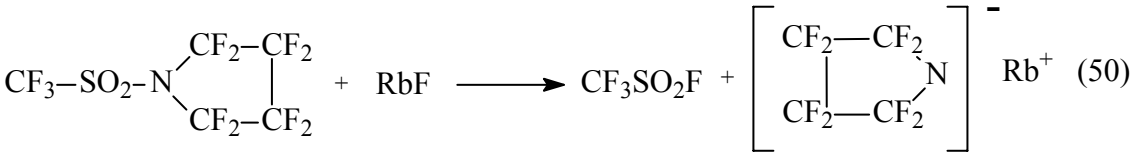
$$CF_3SO_2F + 2 \longrightarrow CF_3SO_2{-}N + F^- \quad (48)$$

After ECF the desired $CF_3SO_2N[-C_4F_8-]$ was obtained in 5 % yield (49).



(49)

It was expected, that the reaction with the fluoride anion (50) will yield an imido salt probably more stable then the bis(trifluoromethyl)imido salt.

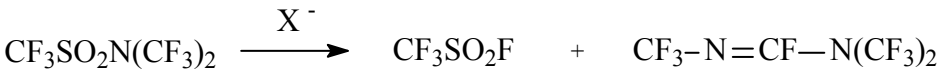


(50)

However, only a mixture of products was obtained.

Reactions with other nucleophiles

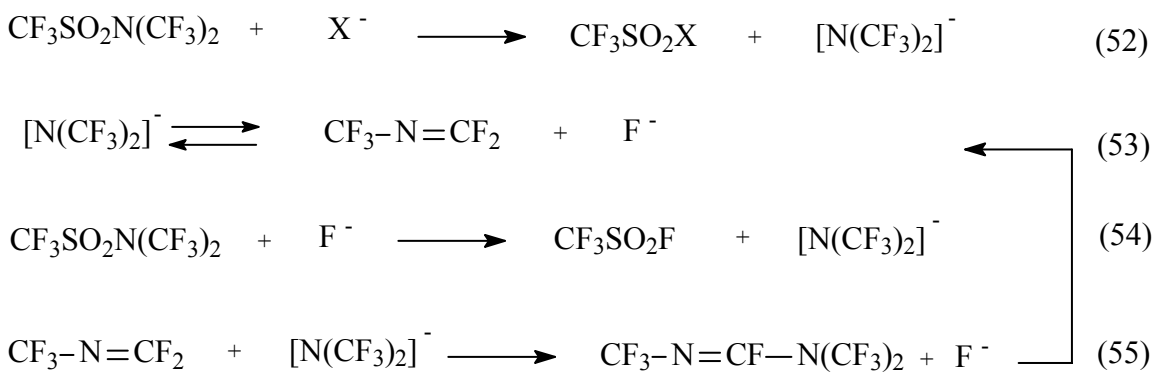
The behavior of sulfamides towards others nucleophiles, such as chlorides, bromides, iodides and others, was also investigated and a mixture of CF_3SO_2F and CF_3-N=CF-N$(CF_3)_2$ was observed (51).



(51)

X = Cl, Br, I

Most likely, the interaction of sulfamides with these nucleophiles proceeds in accordance with the following scheme:

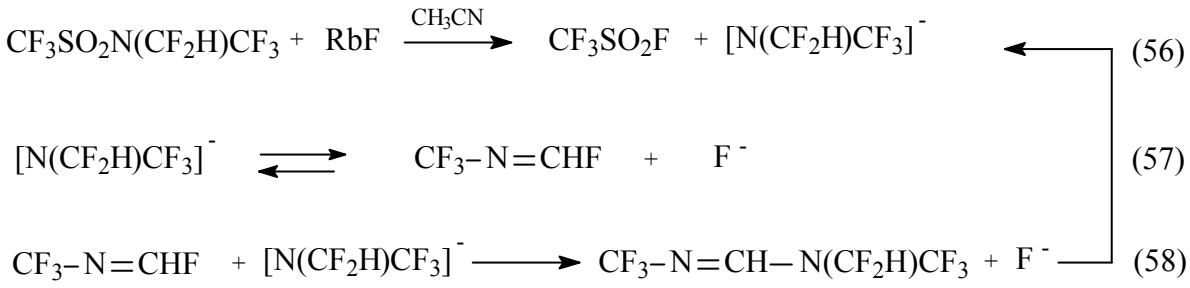


The fluoride anion generated in reaction (53) has a higher nucleophilicity than other nucleophiles, and therefore the reaction with fluoride proceeds faster.

During the electrochemical fluorination of sulfonamides, a considerable amount of polyfluorinated products were formed and its utilization was important task. It was interesting to study their chemical behavior in comparison to the perfluorinated products.

Salts containing the (difluoromethyl)amino group are unknown. And therefore the synthesis of N-trifluoromethyl-N'-difluoromethylimido-anion using $CF_3SO_2N(CF_2H)CF_3$ was attempted. The latter compound was formed in sufficient quantity by ECF of $CF_3SO_2N(CH_3)_2$.

However, due to instability of N-trifluoromethyl-N'-difluoromethylimide salts at room temperature, the reaction proceeds as follows:



Even a catalytic amount of fluoride anion converts completely the compound $CF_3SO_2N(CF_2H)CF_3$ into CF_3-N=CH-N(CF_2H)CF_3.

For the complete investigation of all possible sources of the $[N(CF_3)_2]^-$ anion another class of compounds – acylamides were studied and the results described in the next chapter.

4.2 Acylamides

4.2.1 Synthesis of acylamides

Synthesis of trifluoroacylbis(trifluoromethyl)amide, $CF_3C(O)N(CF_3)_2$

Another potential source of the $[N(CF_3)_2]^-$ anion is trifluoroacyl-bis(trifluoromethyl)amide. This compound can be obtained by ECF of N,N-dimethyltrifluoroacylamide in 5% yield[51].

$$CF_3C(O)N(CH_3)_2 \xrightarrow[HF]{e\ ,\ Ni} CF_3C(O)N(CF_3)_2 + FC(O)N(CF_3)_2 + CF_3C(O)F \quad (59)$$

Primarily decomposition products, including bis(trifluoromethyl)carbamyl fluoride, $(CF_3)_2NC(O)F$ were formed.

This experiment was repeated and the results confirmed. The low yield of trifluoroacyl-bis(trifluoromethyl)-amide is probably due to its high solubility in aHF that allows further fluorination and decomposition during the electrolysis. To verify this assumption, it was decided to investigate the ECF of the homologues N,N-dimethylperfluoropropioneamide with the longer perfluorinated chain to decrease the solubility in aHF.

Synthesis of pentafluoropropionebis(trifluoromethyl)amide $C_2F_5C(O)N(CF_3)_2$

Electrochemical fluorination of $C_2F_5C(O)N(CH_3)_2$.

The starting material $C_2F_5C(O)N(CH_3)_2$ was synthesized via $C_2H_5C(O)Cl$, by electrochemical fluorination.

$$C_2H_5C(O)Cl + aHF \longrightarrow C_2H_5C(O)F + HCl \quad (60)$$

Since chlorine in propionylchloride was replaced by fluorine during dissolving in anhydrous hydrogen fluoride (60), and the hydrogen chloride was allowed to evaporate, chlorination of the alkyl group was not observed (61).

$$C_2H_5C(O)F \xrightarrow[Ni]{e,\ aHF} C_2F_5C(O)F \quad (61)$$

Yield: 27 %

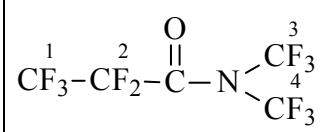
Pentafluoropropionylfluoride readily react with dimethylamine in ether to form pentafluoropropiondimethylamide (62).

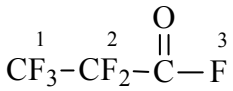
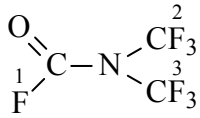
$$C_2F_5C(O)F + 2\ HN(CH_3)_2 \longrightarrow C_2F_5C(O)N(CH_3)_2 + [H_2N(CH_3)_2]F \quad (62)$$

$C_2F_5C(O)N(CH_3)_2$ was fluorinated by the means of ECF in anhydrous hydrogen fluoride (63) and the resulting products are listed in Table 12. The yield of perfluoro-N,N-dimethylpropionamide, $C_2F_5C(O)N(CF_3)_2$ was still very low (5 % estimated by NMR).

$$C_2F_5C(O)N(CH_3)_2 \xrightarrow[Ni]{e,\ aHF} \underset{5\ \%}{C_2F_5C(O)N(CF_3)_2} + \underset{22\ \%}{C_2F_5C(O)F} + \underset{0.6\ \%}{F(O)CN(CF_3)_2} \quad (63)$$

Table 12 Composition of the product obtained by electrochemical fluorination of $C_2F_5C(O)N(CH_3)_2$

Compound	B.p., °C	^{19}F, δ (ppm)**	Yield, %
	49-50	-55.06 t ($6F^{3,4}$) -81.76 m ($3F^{1}$) -118.75 m ($2F^{2}$) $^{5}J_{F3,F2}$ = 8.0 Hz	5

Compound	B.p., °C	^{19}F, δ (ppm)**	Yield, %
	-26.5[52]	+23.73 tq (1F^{3}) -83.39 d (3F1) -121.90 d (2F^{2}) $^{4}J_{F3,F1}$ = 4.5 Hz $^{3}J_{F2,F3}$ = 7.7 Hz	22
	13-15 [51, 53]	+5.38 sp (1F^{1}) -56.47 d (6F^{2,3}) $^{4}J_{F1,F3}$ = 17.0 Hz	0.6

*trapped at –78 ^{0}C
** spectra were measured at – 40 °C.

Synthesis of N,N-bis(trifluoromethyl)perfluorobutyramide $C_3F_7C(O)N(CF_3)_2$

Perfluorobutyrchloride can be prepared from the commercially available heptafluorobutanoic acid and phosphorous pentachloride (64).

$$C_3F_7C(O)OH + PCl_5 \longrightarrow C_3F_7C(O)Cl + POCl_3 + HCl \qquad (64)$$

Reaction with dimethylamine in ether results in the dimethylamide (65).

$$C_3F_7C(O)Cl + 2\ HN(CH_3)_2 \longrightarrow C_3F_7C(O)N(CH_3)_2 + [H_2N(CH_3)_2]Cl \qquad (65)$$

This compound was fluorinated by means of ECF under two different conditions. The main difference between these two experiments was in (i) the temperature and (ii) the time between the fillings of the cell with the starting material. In experiment (II), the cell was re-filled with N,N-dimethylheptafluorobutyramide every two hours to keep the Ni-electrodes active with the fluorination of the starting material but not with fluorination of the desired product. This procedure increased the contents of $C_3F_7C(O)N(CF_3)_2$ in the resulting product from 10% in

experiment (I) to 16% in experiment (II) (see Table 13), that corresponds to a yield of 8% (estimated by NMR). Pure perfluoro-N,N-dimethylbutyramide was isolated by fractional distillation.

$$C_3F_7C(O)N(CH_3)_2 \xrightarrow[Ni]{e,\ aHF} C_3F_7C(O)N(CF_3)_2 + C_3F_7C(O)N(CF_2H)CF_3 + C_3F_7C(O)(CF_2H)_2 + \\ + F(O)CN(CF_3)_2 + C_3F_7C(O)F \quad (66)$$

Table 13 Composition of the product obtained by electrochemical fluorination of $C_3F_7C(O)N(CH_3)_2$

Compound	B.p., °C	^{19}F *, δ (ppm)	^{1}H, δ (ppm)	Contents in the mixture, %, wt.	
				Experiment	
				I	II
$CF_3^1-CF_2^2-CF_2^3-C(=O)-N(CF_3^4)(CF_3^5)$	72-73	-54.90 t ($6F^{4,5}$) -80.18 t ($3F^1$) -115.75 m ($2F^3$) -124.57 m ($2F^2$) $^4J_{F1,F3}$ = 9.5 Hz $^5J_{F5,F3}$ = 7.8 Hz		10.2	15.7
$CF_3^1-CF_2^2-CF_2^3-C(=O)-N(CHF_2^4)(CF_3^5)$	90-91	-54.82 m ($3F^5$) -80.12 t ($3F^1$) -99.56 dqt ($2F^4$) -114.30 m ($2F^3$) -124.79 m ($2F^2$) $^4J_{F1,F3}$ = 9.5 Hz $^4J_{F4,F5}$ = 10.9 Hz $^5J_{F4,F3}$ = 4.0 Hz	7.57 t (1H) $J_{H,F}$ = 55.3 Hz	6.1	4.4
$CF_3^1-CF_2^2-CF_2^3-C(=O)-N(CHF_2^4)(CHF_2^5)$	-	-80.07 t ($3F^1$) -99.78 dt ($4F^{4,5}$) -113.99 m ($2F^3$) -125.07 m ($2F^2$) $^4J_{F1,F3}$ = 9.5 Hz $^5J_{F4,F3}$ = 5.0 Hz	7.47 t (2H) $J_{H,F}$ = 57.02 Hz	7.2	2.7
$F^1-C(=O)-N(CF_3^2)(CF_3^3)$	13-15	(See Table 1)		0.7	5.3
$CF_3^1-CF_2^2-CF_2^3-C(=O)-F^4$ *	7-9 [54]	+24.70 t ($1F^4$) -80.90 t ($3F^1$) -119.20 m ($2F^3$) -127.00 m ($2F^2$) $^4J_{F1,F3}$ = 8.0 Hz		62.8	48.1

Compound	B.p., °C	^{19}F *, δ (ppm)	^{1}H, δ (ppm)	Contents in the mixture, %, wt.	
				Experiment	
				I	II
$CF_3-CF_2-CF_2-C(=O)-N(CH_3)_2$ (starting material)		(See Experimental Part)		-	13.2
$CF_3CF_2CF_3$ *	-38 [55]	-82.30 s (6F) -131.00 s (2F)		1.3	4.0
others				11.7	6.6

* ^{19}F NMR spectra were recorded at –40 °C.

However, the main compound in the product mixture was still perfluorobutyryl fluoride.

These results can be reasonably explained by the still high solubility of $C_3F_7C(O)N(CF_3)_2$ in aHF, which is further fluorinated even in the presence of the starting material $C_3F_7C(O)N(CH_3)_2$. Therefore after every re-filling of the cell with starting material, the cell voltage decreases sharply at the beginning of the experiment and remains practically unchanged at the end of the experiment (see Fig. 11).

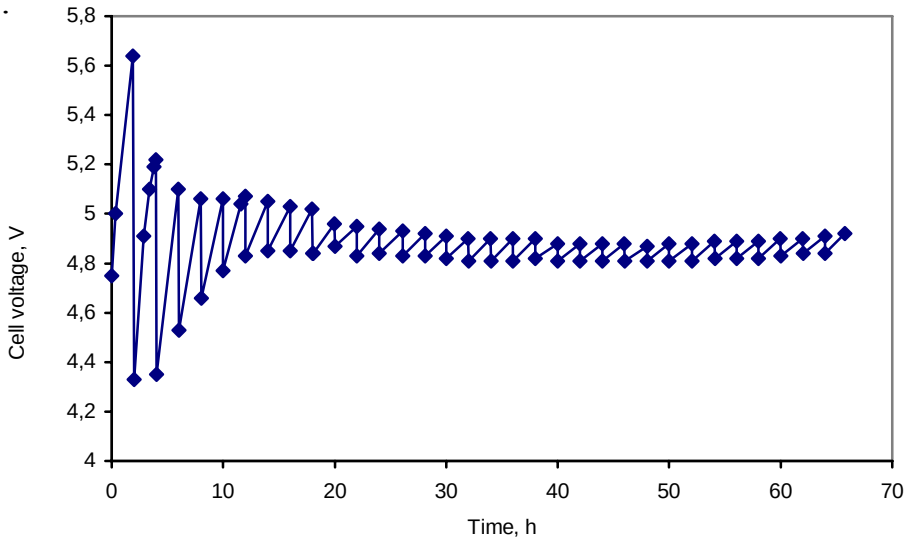


Fig. 11

Development of the cell voltage with time.

It can be concluded the aHF in the cell is saturated with soluble materials that keep the conductivity of the solution constant irrespective of addition of starting material.

The presence of partially fluorinated compounds, such as: $C_3F_7C(O)N(CF_3)(CHF_2)$ and $C_3F_7C(O)N(CHF_2)(CHF_2)$ in the reaction mixture, confirms again that the ECF is a step-wise process[43] .

The obtained N,N-bis(trifluoromethyl)perfluoroacylamides were used further as starting materials for the preparation of $[N(CF_3)_2]^-$ salts.

4.2.2 Chemical properties of fluorinated acylamides

Reaction of N,N-bis(trifluoromethyl)perfluoroacylamides with fluorides.

N,N-bis(trifluoromethyl)perfluoroacylamides readily react with metal fluorides (67) similar to the perfluoroalkylsulfamides, and can be used as sources for the preparation of bis(trifluoromethyl)imido-salts:

$$R_FC(O)N(CF_3)_2 + 2MF \longrightarrow [R_FCF_2O]\,M + M\,[N(CF_3)_2] \quad (67)$$

R_F = F or C_nF_{2n+1} ; n = 2,3

M = Rb, Cs

A mixture of N,N-bis(trifluoromethyl)imide and perfluoroalkoxy salts are formed in this reaction. Therefore, two moles of metal fluorides were needed for this reaction. Perfluoroalkoxydes exist in equilibrium with perfluoroacylfluorides according to equation (68) but it is not possible to obtain pure N,N-bis(trifluoromethyl)imido-salts by pumping off the acylfluoride.

$$CF_3{-}CF_2{-}CF_2{-}O^- \rightleftharpoons CF_3{-}CF_2{-}C(=O)F + F^- \quad (68)$$

The low yield of perfluorinated compounds and impossibility to prepare pure $[N(CF_3)_2]^-$ salts in the case of N,N'-bis(trifluoromethyl)perfluoroalkylacylamides make them not a source for large scale syntheses of compounds containing the $N(CF_3)_2$-group.

5 **Salts containing the bis(trifluoromethyl)imido anion.**

5.1 Syntheses of bis(trifluoromethyl)imido salts with organic cations

Inorganic salts with the $[(CF_3)_2N]^-$-anion can be prepared only in solution and are thermally unstable. In contrast the stable solid salt $[N(CH_3)_4][N(CF_3)_2]$ can be obtained from the corresponding fluoride as described above. Analogous syntheses of other quaternary ammonium or phosphonium salts are not straight forward, because the anhydrous fluorides are difficulty to obtain.

Previous attempts to prepare $[(C_6H_5)_4As][(CF_3)_2N]$ and $[(C_2H_5)_4N][(CF_3)_2N]$ failed [15].

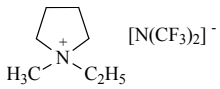
However, such salts can be easily synthesized via exchange reactions between $Rb[N(CF_3)_2]$ and ammonium or phosphonium salts, e.g., tetrabutylammonium tetrafluoroborate (69).

$$Rb[N(CF_3)_2] + [(C_4H_9)_4N]BF_4 \xrightarrow{CH_3CN} [(C_4H_9)_4N][N(CF_3)_2] + Rb[BF_4]\downarrow \qquad (69)$$

Other ammonium or phosphonium salts with different anions, for example Cl^-, Br^- can be used for this reaction in the same manner. The low solubility of rubidium halogenides in acetonitrile allows the simple separation. The $[N(CF_3)_2]^-$ salts with organic cations can be easily isolated from the solution by evaporation of the solvent, and used as a convenient reagents for the introduction of $(CF_3)_2N$ -group into organic molecules.

Quaternary ammonium- and phosphonium- salts with the $[N(CF_3)_2]^-$-anion are much more stable than alkali metal salts. They melt without decomposition (Table 14).

Table 14 Melting points of some $[N(CF_3)_2]^-$ salts with organic cation

Salt	Melting point, °C
$[(CH_3)_4N]^+[N(CF_3)_2]^-$	120-125
$[(C_2H_5)_4N]^+[N(CF_3)_2]^-$	88-90
$[(n\text{-}C_4H_9)_4N]^+ [N(CF_3)_2]^-$	123-125
	85
$[(C_2H_5)_4P]^+[N(CF_3)_2]^-$	85-86
$[Ph_3(PhCH_2)P]^+[N(CF_3)_2]^-$	114-115

Some bis(trifluoromethyl)imides, for example with: 1-butyl-3-methyl-imidazolium, 1,1-butyl-methylpyrrolidinium cations are liquid at room temperature (co-called ionic liquids) and can be used in reactions without solvent[56].

5.2 Preparation of diazonium salts containing the bis(trifluoromethyl)imdo anion

Aryldiazonium bis(trifluoromethyl)imides were prepared from the corresponding tertafluoroborates by an exchange reaction with rubidium bis(trifluoromethyl)-imide in acetonitrile at –35°C (70).

$$[ArN_2]^+[BF_4\}^- + Rb[N(CF_3)_2] \xrightarrow[CH_3CN]{-35\,^\circ C} [ArN_2][N(CF_3)_2] + Rb[BF_4]\downarrow \quad (70)$$

These salts are stable below –35°C and start to decompose above this temperature to yield $HN(CF_3)_2$ as the main product.

5.3 Chemical properties of salts with the bis(trifluoromethyl)imido anion

Replacement of active halogen

The $[N(CF_3)_2]^-$-anion is a nucleophile, which can be used in S_N2 (or S_N1) types reactions. $Rb[N(CF_3)_2]$ readily reacts with methyliodide in acetonitrile yielding bis(trifluoromethyl)methylamine (72):

$$CH_3I + Rb[N(CF_3)_2] \xrightarrow{CH_3CN} CH_3N(CF_3)_2 + RbI \qquad (72)$$

This route to bis(trifluoromethyl)methyl amine is more simple then the one described in the literature (73) [57]

$$CH_3F + CF_3{-}N{=}CF_2 \xrightarrow[-40°C\text{ to RT}]{SbF_5} CH_3{-}N(CF_3)_2 \qquad (73)$$

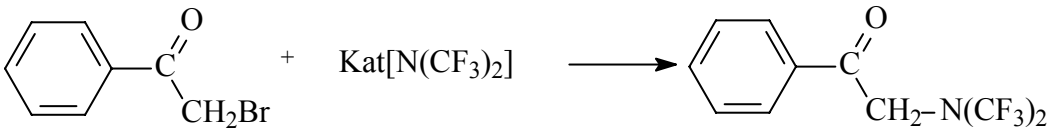
The reactions of $Cs[N(CF_3)_2]$ with halogenacetic ester (74) is described in the literature[4] .

$$Br{-}CH_2{-}C(=O)OEt + Cs[N(CF_3)_2] \longrightarrow (CF_3)_2N{-}CH_2{-}C(=O)OEt + CsBr \qquad (74)$$

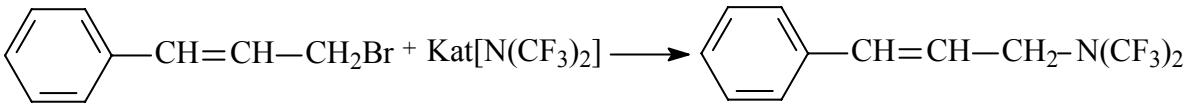
The reported yield of 45 % was increased to 90% by use of $Rb[N(CF_3)_2]$ in the course of this work.

Obtained esters bearing the $[N(CF_3)_2]$-group can be used for common organic reactions, for example preparation of hydrazides.

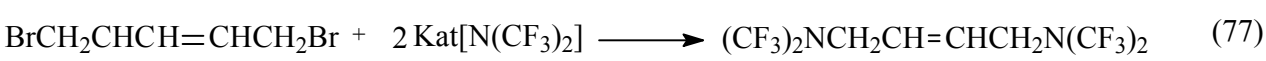
The tetraalkylammonium salts formed the substituted product in quantitative yield (75).



(75)



(76)



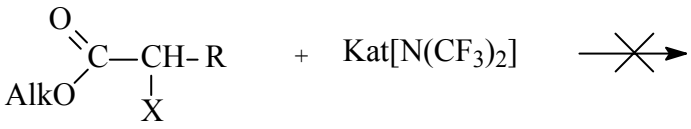
(77)

$$Kat = Rb^{+} ; [(Alk)_4N]^{+} ; [(Alk)_4P]^{+}$$

The tetraalkylammonium salts are highly soluble in dichloromethane. Therefore the reaction can be carried out at low temperature. That is important for the syntheses of reactive compounds, for example bearing a double bond (76-77).

Reaction with esters of α-halogencarbonic acids

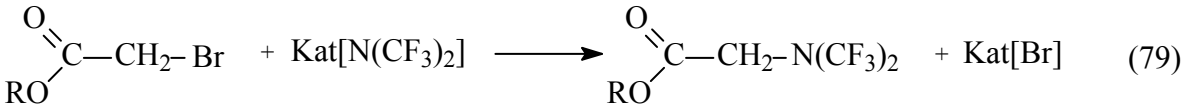
Surprisingly, no reaction was observed between α-halogenocarbonic esters with long alkyl chains and bis(trifluoromethyl)imido salts (78).



(78)

R= Me, Ph; Kat= $[Bu_4N]^{+}$

Whereas halogenoacetic esters readily react with bis(trifluoromethyl)imido salts in nearly quantitative yield (79).

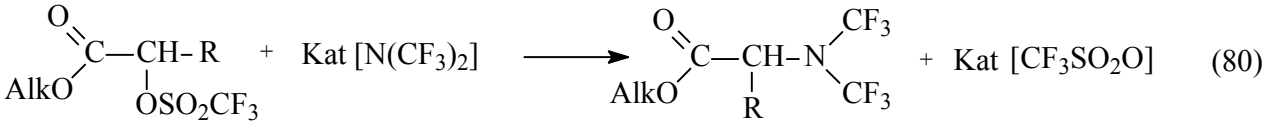


(79)

Kat= $[Et_4N]^+$, $[Bu_4N]^+$; R= Et, $PhCH_2$

This behavior may be due to the low nucleophilicity of the $[N(CF_3)_2]^-$-anion and the steric hindrances at the reaction center in the case of an S_N2 mechanism.

The replacement of the halogen by a better leaving group (for example, trifluoromethylsulfonyl), results in a change of the reaction mechanism, which becomes probably S_N1. The reaction between triflates esters and $[N(CF_3)_2]^-$ -salts proceeds within several minutes exothermally (80).

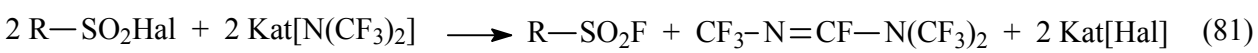


(80)

Kat= $[Et_4N]^+$, $[Bu_4N]^+$; Alk=Me, Et

Substitution of halogen in acyl- and sulfonyl-halides.

All attempts to exchange the halogen atom in -SO_2Hal, -C(O)Hal by the $[N(CF_3)_2]^-$-anion failed. Fluoride, which is generated from bis(trifluoromethyl)amide-anion according to equilibrium (47) react much faster, then the bis(trifluoromethyl)amide-anion resulting in the corresponding fluorides (81):



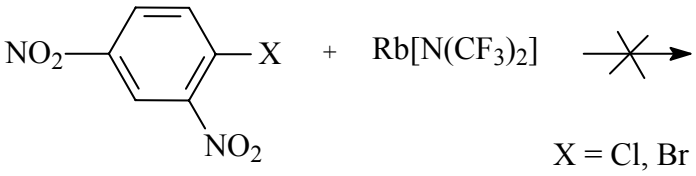
(81)

Kat= Rb, $[Et_4N]^+$, $[Bu_4N]^+$; X=Cl, Br R= Alkyl, aryl

The reactions take place at room temperature within some minutes and bis(trifluoromethyl)amide-salts act as soft fluorinating reagents.

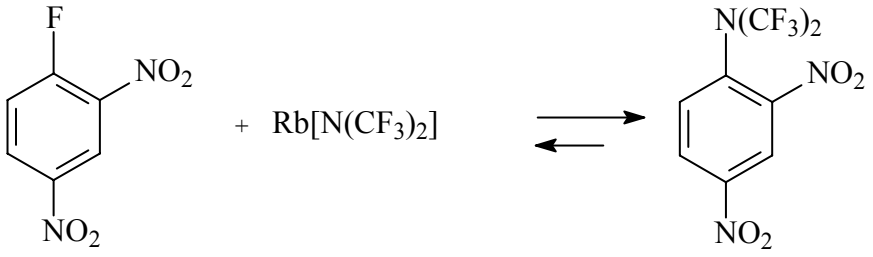
Substitution of halogen in activated aromatic systems

Replacement of halogen in aromatic systems by the bis(trifluoromethyl)amino-group failed (82).



(82)

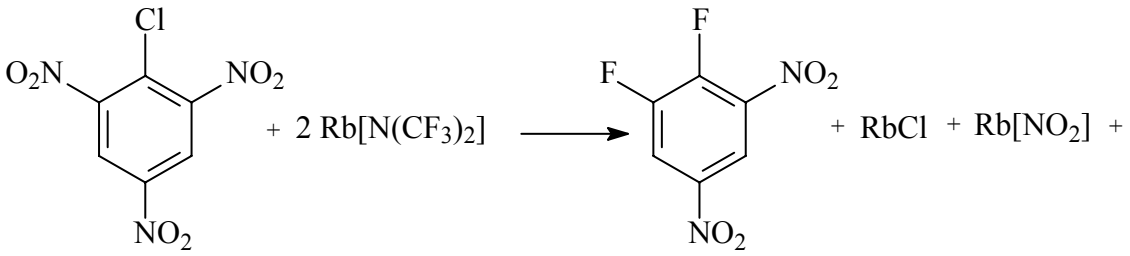
Only in the case of strong activated systems (2,4-dinitrofluorobenzene), nucleophilic substitution with a yield of 30 % was observed (83).



(83)

The low yield may be due to an equilibrium reaction.

Reaction of 2,4,6-trinitrochlorobenzene with $Rb[N(CF_3)_2]$ proceeds more easy and leads to the replacement of one chloro and nitro group (84).

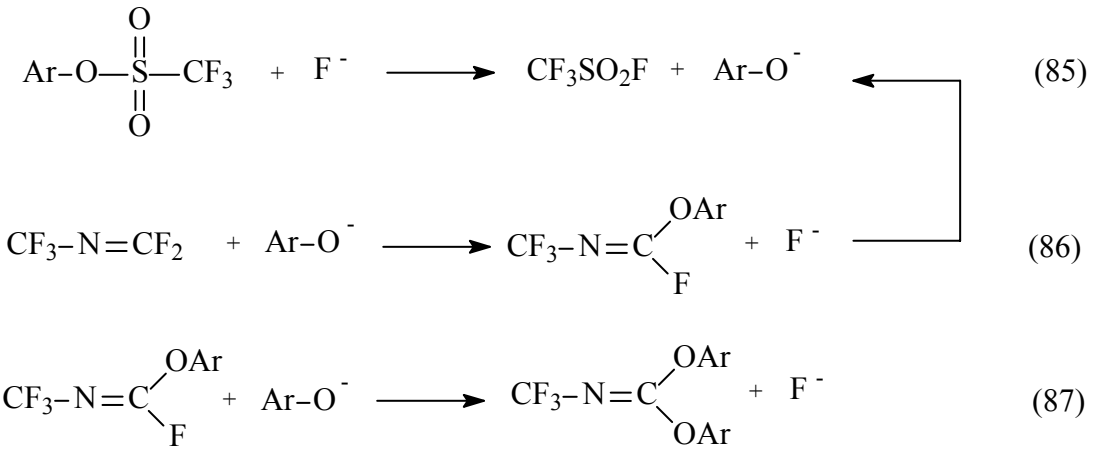


(84)

The nucleophilic substitution of the nitro-group by fluoride is known[58] e.g. fluorodenitration of 2-nitrobenzonitrile with tetramethylammonium fluoride. In our case due to equilibrium (47) the free fluoride anion was formed.

Reaction with trifluoromethylsulfone aryl esters

To increase the reactivity of aromatic systems for the reaction with the $[N(CF_3)_2]^-$-anion the trifluoromethylsulfonyl group as leaving group was used. However substituting products were not found. Again, the fluoride anion formed in equilibrium (47) is much more active than the $[N(CF_3)_2]^-$-anion for the nucleophilic substitution (85-87).



(85)

(86)

(87)

The structure of the resulting product in reaction (87) was confirmed by X-ray crystallography (Fig 12).

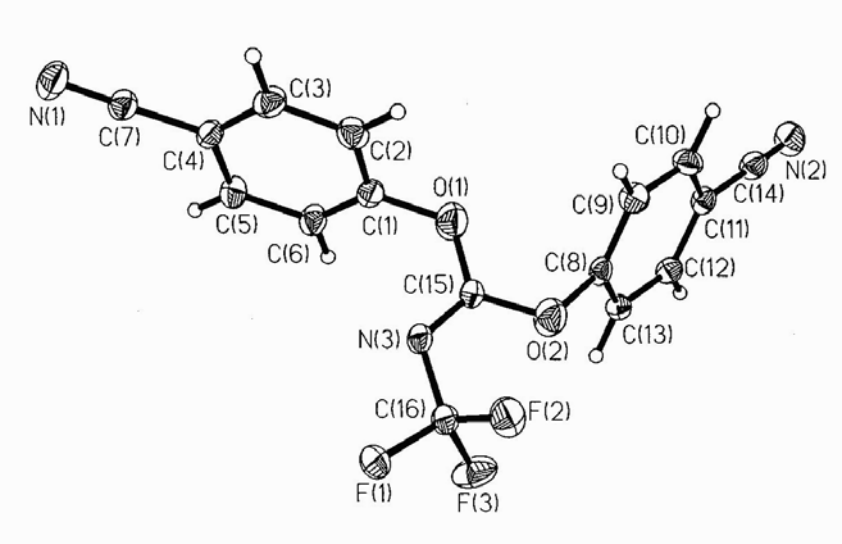


Fig. 12

Structure of CF_3-N=C(O-C_6H_4-CN)$_2$

The compound crystallised from acetonitrile to give colourless prisms. The orthorhombic space group Aba2 contains 8 molecules in the unit cell. The bonds and angles are all as expected (Table 15b).

Table 15. Crystal data and structure refinement

Chemical formula	$C_{16}H_8F_3N_3O_2$
Formula weight	331.25
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Aba2
Unit cell dimensions	a = 15.034(8) Å b = 21.269(9) Å c = 9.313(5) Å
Volume	2978 $Å^3$

Z, calculated density	8, 1.478 Mg/m^3
Absorption coefficient	0.126 mm^{-1}
F(000)	1344
Crystal size	0.45 x 0.26 x 0.21 mm
Theta range	2.35 to 27.03 ^{o}
Limiting indices	0<h>19, -27<k>0, -11<l>
Reflections collected / unique	1740 / 1740 [R(int) = 0.0000]
Completeness to H = 27.03	99.9 %
Absorption correction	psi-scan
Max. and min. transmission	0.760 and 0.677
Refinement method	full-matrix least-squares (F^2)
Data / restraints / parameters	1740 / 1 / 219
Doodness-of-fit on F^2	1.064
Final R indices [I>2r(I)]	R1 = 0.0254, wR2 = 0.0641
R indices (all data)	R1 = 0.0281, wR2 = 0.0657
Absolute structure parameter	-0.1(7)
Extinction coefficient	0.0023(4)
Largest diff. peak and hole	0.162 und -0.165 eA^{-3}

Table 15a. Coordinates and coefficients of the equivalent isotropic temperature factors [$Å^2$] without H atoms) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
C(1)	0.76652(11)	0.6851(1)	0.6845(2)	0.024(1)
C(2)	0.68388(13)	0.6794(1)	0.7470(2)	0.029(1)
C(3)	0.61612(12)	0.7185(1)	0.6992(2)	0.029(1)
C (4)	0.63244(11)	0.7611(1)	0.5897(2)	0.023(1)
C(5)	0.71721(12)	0.7670(1)	0.5296(2)	0.027(1)
C(6)	0.78515(12)	0.7286(1)	0.5796(2)	0.027(1)
C(7)	0.55963(12)	0.7989(1)	0.5351(2)	0.027(1)
C(8)	0.96653(11)	0.5760(1)	0.8346(2)	0.022(1)
C(9)	0.93178(12)	0.5753(1)	0.9710(2)	0.027(1)
C(10)	0.98791(12)	0.5868(1)	1.0859(2)	0.027(1)

C(11)	1.07817(11)	0.5991(1)	1.0604(2)	0.023(1)
C(12)	1.11163(11)	0.5991(1)	0.9213(2)	0.024(1)
C(13)	1.05574(12)	0.5872(1)	0.8068(2)	0.023(1)
C(14)	1.13682(13)	0.6125(1)	1.1795(2)	0.028(1)
C(15)	0.84977(11)	0.5932(1)	0.6621(2)	0.021(1)
C(16)	0.82369(11)	0.5231(1)	0.4792(2)	0.024(1)
F(1)	0.77260(8)	0.5196(1)	0.3612(1)	0.036(1)
F(2)	0.80602(8)	0.4711(1)	0.5552(2)	0.037(1)
F(3)	0.90779(8)	0.5176(1)	0.4329(2)	0.042(1)
N(1)	0.50025(11)	0.8272(1)	0.4939(2)	0.038(1)
N(2)	1.18391(12)	0.6245(1)	1.2718(2)	0.037(1)
N(3)	0.80507(9)	0.5786(1)	0.5513(2)	0.022(1)
O(1)	0.83596(8)	0.6460(1)	0.7360(2)	0.026(1)
O(2)	0.91459(8)	0.5575(1)	0.7158(2)	0.027(1)

Table 15b Bond lengths [Å]

C(1)-C(6)	1.374(3)
C(1)-C(2)	1.377(3)
C(1)-O(1)	1.418(2)
C(2)-C(3)	1.387(3)
C(3)-C(4)	1.387(3)
C(4)-C(5)	1.397(3)
C(4)-C(7)	1.450(2)
C(5)-C(6)	1.389(3)
C(7)-N(1)	1.144(2)
C(8)-C(9)	1.373(3)
C(8)-C(13)	1.387(3)
C(8)-O(2)	1.410(2)
C(9)-C(10)	1.385(3)
C(10)-C(11)	1.402(3)
C(11)-C(12)	1.390(3)
C(11)-C(14)	1.445(3)
C(12)-C(13)	1.381(3)

C(14)-N(2)	1.143(3)
C(15)-N(3)	1.269(2)
C(15)-O(2)	1.332(2)
C(15)-O(1)	1.334(2)
C(16)-F(2)	1.339(2)
C(16)-F(3)	1.341(2)
C(16)-F(1)	1.343(2)
C(16)-N(3)	1.388(2)

Table 15c. Bond angles [°]

C(6)-C(1)-C(2)	122.90(17)
C(6)-C(1)-O(1)	119.00(16)
C(2)-C(1)-O(1)	118.05(17)
C(1)-C(2)-C(3)	118.36(19)
C(2)-C(3)-C(4)	119.80(18)
C(3)-C(4)-C(5)	120.98(17)
C(3)-C(4)-C(7)	119.11(16)
C(5)-C(4)-C(7)	119.89(17)
C(6)-C(5)-C(4)	118.91(18)
C(1)-C(6)-C(5)	118.99(17)
N(1)-C(7)-C(4)	177.7(2)
C(9)-C(8)-C(13)	122.88(17)
C(9)-C(8)-O(2)	120.80(16)
C(13)-C(8)-O(2)	115.88(17)
C(8)-C(9)-C(10)	118.76(17)
C(9)-C(10)-C(11)	119.43(19)
C(12)-C(11)-C(10)	120.56(17)
C(12)-C(11)-C(14)	119.64(16)
C(10)-C(11)-C(14)	119.79(19)
C(13)-C(12)-C(11)	119.98(16)
C(12)-C(13)-C(8)	118.38(18)
N(2)-C(14)-C(11)	178.2(2)
N(3)-C(15)-O(2)	123.62(17)
N(3)-C(15)-O(1)	122.83(15)

O(2)-C(15)-O(1)	113.56(15)
F(2)-C(16)-F(3)	106.59(15)
F(2)-C(16)-F(1)	105.93(14)
F(3)-C(16)-F(1)	105.77(16)
F(2)-C(16)-N(3)	113.96(16)
F(3)-C(16)-N(3)	114.81(15)
F(1)-C(16)-N(3)	109.12(14)
C(15)-N(3)-C(16)	119.61(15)
C(15)-O(1)-C(1)	115.75(14)
C(15)-O(2)-C(8)	122.74(14)

Table 15d. Coefficients of the anisotropic temperature factors [$Å^2$]
The anisotropic temperature factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11}+...+2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.025(1)	0.021(1)	0.025(1)	-0.005(1)	-0.007(1)	0.004(1)
C(2)	0.032(1)	0.027(1)	0.027(1)	0.001(1)	0.002(1)	0.001(1)
C(3)	0.023(1)	0.032(1)	0.033(1)	-0.001(1)	0.003(1)	0.002(1)
C(4)	0.022(1)	0.023(1)	0.026(1)	-0.005(1)	-0.004(1)	0.004(1)
C(5)	0.026(1)	0.027(1)	0.029(1)	0.005(1)	-0.001(1)	0.001(1)
C(6)	0.020(1)	0.030(1)	0.030(1)	0.002(1)	0.000(1)	0.003(1)
C(7)	0.023(1)	0.029(1)	0.030(1)	-0.004(1)	-0.003(1)	0.002(1)
C(8)	0.021(1)	0.021(1)	0.024(1)	-0.002(1)	-0.008(1)	0.003(1)
C(9)	0.016(1)	0.035(1)	0.030(1)	-0.001(1)	-0.001(1)	0.000(1)
C(10)	0.024(1)	0.034(1)	0.022(1)	-0.001(1)	0.002(1)	0.002(1)
C(11)	0.020(1)	0.025(1)	0.025(1)	-0.001(1)	-0.006(1)	0.002(1)
C(12)	0.017(1)	0.026(1)	0.030(1)	-0.001(1)	0.000(1)	0.000(1)
C(13)	0.023(1)	0.024(1)	0.022(1)	0.000(1)	0.001(1)	0.002(1)
C(14)	0.026(1)	0.027(1)	0.030(1)	-0.002(1)	-0.003(1)	0.002(1)
C(15)	0.019(1)	0.022(1)	0.023(1)	0.002(1)	-0.002(1)	0.002(1)
C(16)	0.020(1)	0.027(1)	0.025(1)	-0.002(1)	-0.004(1)	0.002(1)
F(1)	0.040(1)	0.038(1)	0.029(1)	-0.010(1)	-0.015(1)	0.009(1)

F(2)	0.053(1)	0.023(1)	0.036(1)	0.001(1)	-0.009(1)	-0.003(1)
F(3)	0.022(1)	0.052(1)	0.051(1)	-0.019(1)	0.005(1)	0.006(1)
N(1)	0.026(1)	0.039(1)	0.047(1)	-0.003(1)	-0.007(1)	0.009(1)
N(2)	0.037(1)	0.040(1)	0.034(1)	-0.005(1)	-0.013(1)	0.000(1)
N(3)	0.019(1)	0.024(1)	0.023(1)	0.000(1)	-0.004(1)	0.002(1)
O(1)	0.028(1)	0.023(1)	0.026(1)	-0.002(1)	-0.009(1)	0.006(1)
O(2)	0.026(1)	0.025(1)	0.029(1)	-0.005(1)	-0.012(1)	0.006(1)

Table 15e. Hydrogen coordinates and coefficients of the isotropic temperature factors [$Å^2$]

Atom	x	y	z	U
H(2A)	0.6733	0.6494	0.8220	0.035(2)
H(3A)	0.5580	0.7160	0.7415	0.035(2)
H(5A)	0.7282	0.7976	0.4559	0.035(2)
H(6A)	0.8441	0.7319	0.5407	0.035(2)
H(9A)	0.8697	0.5669	0.9862	0.035(2)
H(10A)	0.9649	0.5868	1.1821	0.035(2)
H(12A)	1.1735	0.6078	0.9048	0.035(2)
H(13A)	1.0783	0.5865	0.7103	0.035(2)

As it was shown above, salts with the $[N(CF_3)_2]^-$-anion can be used in common organic syntheses. But difficulties in introduction of the $[N(CF_3)_2]$-group into aromatic systems forced us to attempt a electrochemical synthesis.

5.4 Electrochemical properties

N,N-bis(trifluoromethyl) poly- and per- fluoroalkylsulfamides

The $[N(CF_3)_2]^-$-anion can be generated from N,N-bis(trifluoromethyl)-perfluoroalkylsulfamides not only via chemical interaction with fluoride, but also in an electrochemical way. N,N-bis(trifluoromethyl)perfluoroalkylsulfamides are electrochemically active compounds. Their potentials of electrochemical oxidation and reduction were measured by cyclic voltamperometry (CVA) (Table 16).

As expected the more fluorine atoms in the alkyl group bonded to nitrogen are present, the more easily the compound can be reduced and the more difficulty can be oxidized.

Table 16 Potentials of electrochemical reduction and oxidation of fluorinated sulfonamides.

$R^1SO_2N(R^2)R^3$

R^1	R^2	R^3	E_p^{red}, V	E_p^{ox}, V
CH_3	CH_3	CH_3	no reduction	+ 2.58
CF_3	CH_3	CH_3	no reduction	no oxidation
CF_3	CF_2H	CF_2H	-2.58	no oxidation
F	CF_3	CF_3	-2.50	no oxidation
CF_3	CF_3	CF_2H	-2.40	no oxidation
CF_3	CF_3	CF_3	-2.12	no oxidation
$N(CF_3)_2$	CF_3	CF_3	-2.10	no oxidation

Contrary to the electrochemical behavior of N,N-dimethylmethansulfonamide which shows only an oxidation peak, the N,N-bis(trifluoromethyl)-trifluoromethylsulfonamide shows an irreversible reduction peak at high cathodic potentials (Fig. 13).

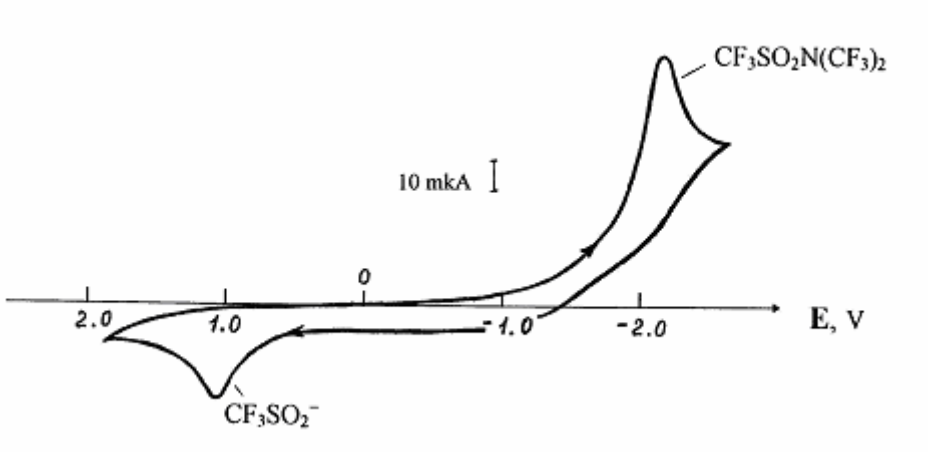
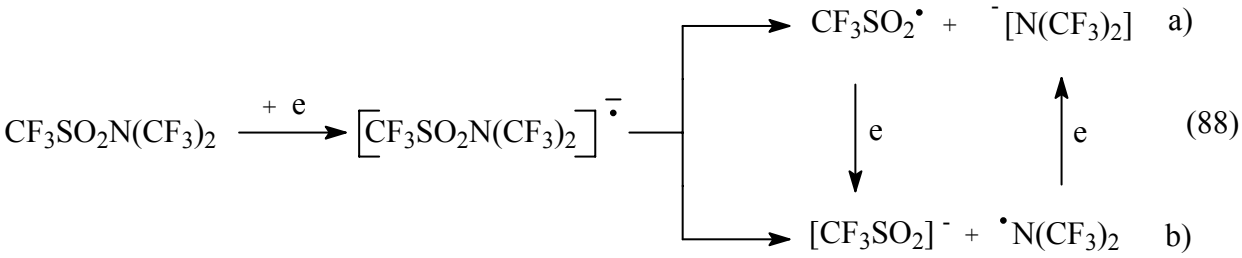


Fig. 13

Cyclic voltammogram of $CF_3SO_2N(CF_3)_2$.

The mechanism of the electrochemical reduction of $CF_3SO_2N(CF_3)_2$ can be formulated in the following way (88):



Formation of the $[CF_3SO_2]^-$-anion during the electrochemical reduction of $CF_3SO_2N(CF_3)_2$ was confirmed by the registration of its oxidation peak on the

CVA (Fig. 13). After several scans a second peak at -2.20 V appears on the CVA (Fig. 14).

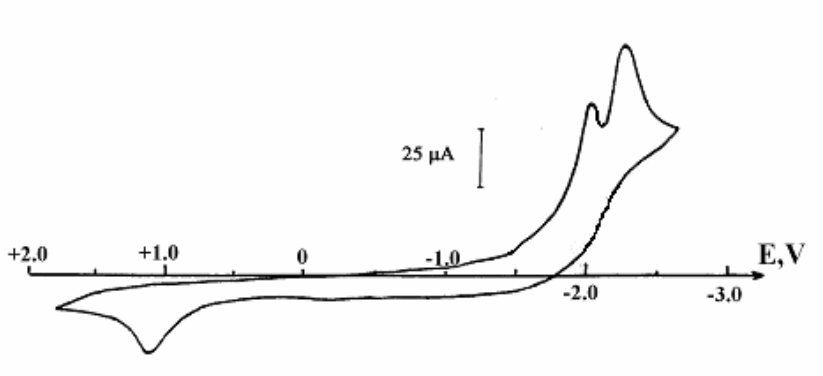


Fig. 14

Cyclic voltammogram of $CF_3SO_2N(CF_3)_2$ after several scans.

This peak belongs to CF_3SO_2F, which was confirmed in a separate experiment (Fig. 15). Electrochemical reduction of CF_3SO_2F shows the same position of the reduction peak and the same oxidation peak which belongs to trifluoromethylsulfinate anion (approved by addition of sodium salt of trifluoromethylsulfinic acid with following increasing of the oxidation peak)

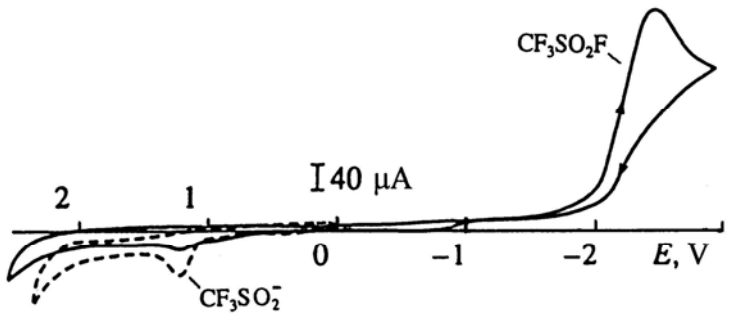
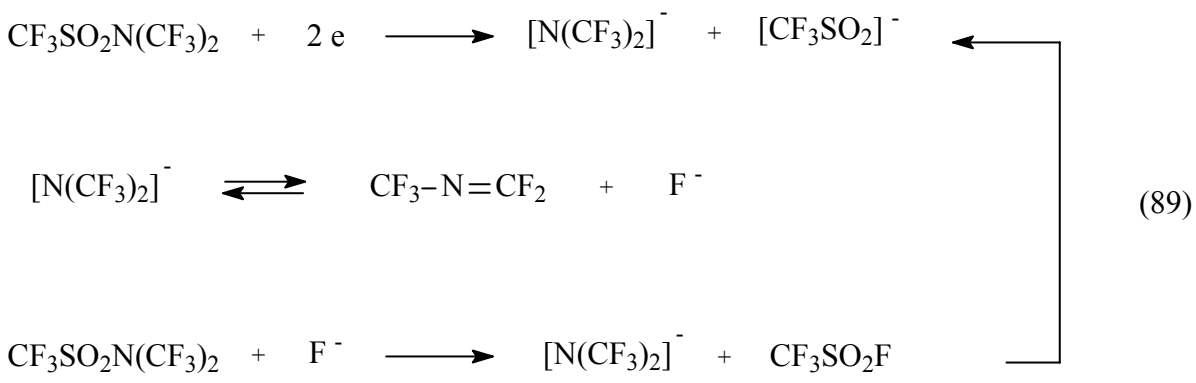


Fig. 15

Cyclic voltammogram of CF_3SO_2F.

Coulometric measurements of the electrochemical reduction of $CF_3SO_2N(CF_3)_2$ show a consumption of electricity of less than 0.3 F/mol. It means that for the conversion of the starting compounds we need only 1/3 of the necessary electrons. This is only possible in chain reactions and rationalized in the following scheme (89):



(89)

Perfluoro- and N,N-dimethylperfluoroalkylacylamides

A similar electrochemical behavior was observed on N,N-dimethylacylamides. The more fluorine atoms in the molecule are present, the easier it can be reduced. The difference in the electrochemical potentials between N,N-dimethyl-heptafluorobutyrylamide and it perfluorinated analogue is 1.5 volts (Table 17).

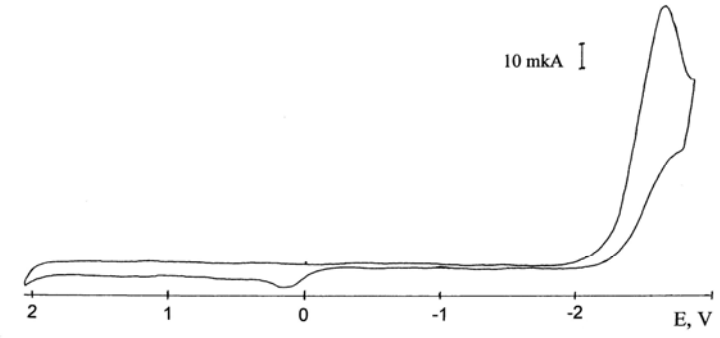


Fig. 16

Cyclic voltammogram of N,N-dimethylheptafluorobutyrylamide.

Concentration: $5x10^{-3}$ M. Electrode: glassy carbon. Supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. Scan rate: 0.2 $V \cdot s^{-1}$

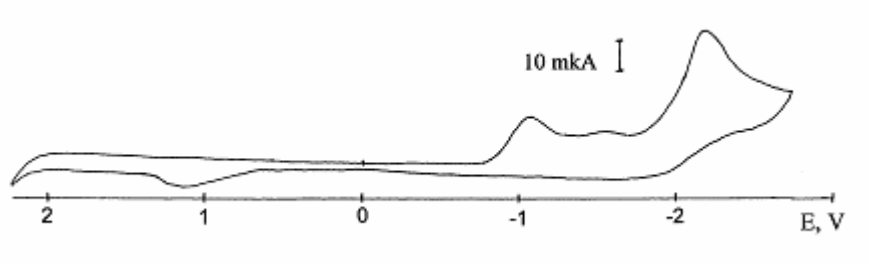


Fig. 17

Cyclic voltammogram of N,N-bis(trifluoromethyl)heptafluorobutyrylamide.

Concentration: $5x10^{-3}$ M. Electrode: glassy carbon. Supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. Scan rate: 0.2 $V \cdot s^{-1}$

Table 17 Potentials of electrochemical reduction and oxidation of fluorinated acylamides

$R^1C(O)N(R^2)_2$

N^o	R^1	R^2	$E_p^{red\,1}$, V	$E_p^{red\,2}$, V	E_p^{ox}, V
1.	C_2F_5	CH_3	no reduction	-	
2.	C_3F_7	CH_3	-2.68	-	
3.	C_2F_5	CF_3	-1.18	-2.20	
4.	C_3F_7	CF_3	-1.08	-2.16	

Electrochemistry of the bis(trifluoromethyl)imino anion

Anodic substitution reactions are well known for different kind of nucleophiles. The overall reaction may be represented as in Eq. 90

$$R\text{-}E + Nu^- \longrightarrow R\text{-}Nu + E^+ + 2e \qquad (90)$$

The nucleophile Nu^- (or NuH) may be RO^-, $RCOO^-$, NO_2^-, SCN^-, N_3^-, CN^-, and some another anions; the electrophile (E^+) is most commonly H^+, but could be a carbocation or an alkoxonium ion. Anodic substitution reactions therefore allow for a net substitution by a nucleophile, a reaction not easily achieved by ordinary chemical means. Specifically, this makes possible the direct formation of a C-O or C-N bond by substitution of a C-H bond[59].

However, aliphatic amines and their derivatives are not suitable for anodic substitution reactions, because they are easily oxidizable[59]. The $[N(CF_3)_2]^-$-anion

seems to be an exception from this rule, due to the high oxidation potential (1.74V, Fig. 18). The one-step electrochemical introduction of the $N(CF_3)_2$-group into organic molecules is of great interest.

Tetrabutylammonium bis(trifluoromethyl)imide is a very convenient source for the $[N(CF_3)_2]^-$-anion in electrochemistry. The acetonitrile solution of this salt shows (Fig. 18a) an irreversible peak in the cyclic voltammogram at 1.74 V (vs. SCE, E_p^{ox} ferrocene = 0.425 V), which corresponds to the anodic oxidation of the $[N(CF_3)_2]^-$-anion.

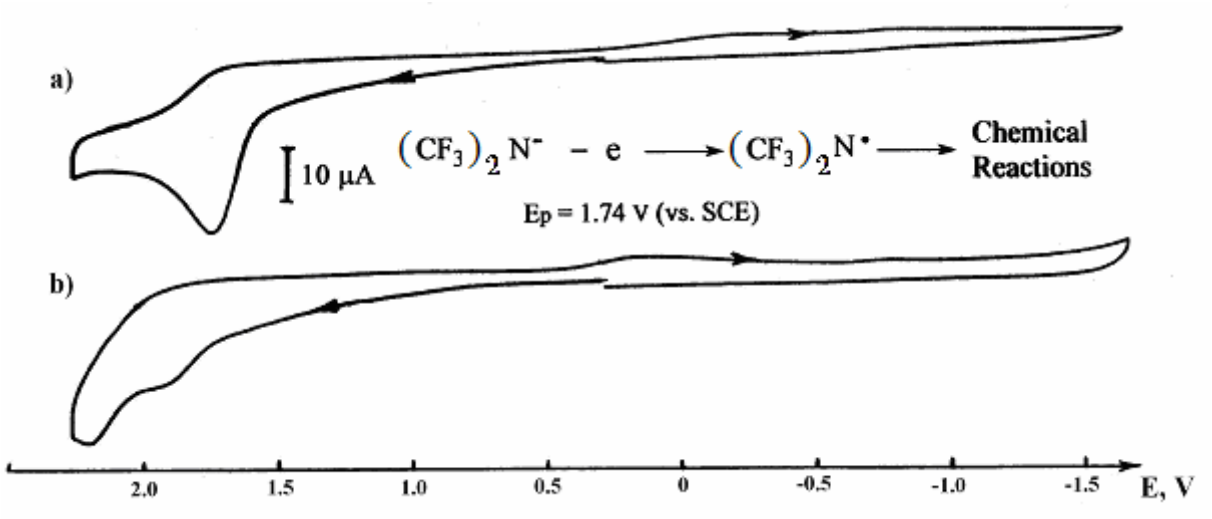


Fig. 18

Cyclic voltammogram of $[(C_4H_9)_4N][N(CF_3)_2]$.

Concentration: 1.6×10^{-3} M. Electrode: glassy carbon. Supporting electrolyte: 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN. Scan rate: 0.2 $V \cdot s^{-1}$

This one electron process yield the amino radical $[N(CF_3)_2]^{\cdot}$ which can undergo the following chemical reactions (Fig. 18b).

$$^{-}N(CF_3)_2 - e \longrightarrow {}^{\bullet}N(CF_3)_2 \quad (91)$$

$$2\,{}^{\bullet}N(CF_3)_2 \longrightarrow (CF_3)_2N-N(CF_3)_2 \quad (92)$$

$${}^{\bullet}N(CF_3)_2 + Sol-H \longrightarrow (CF_3)_2NH + Sol^{\bullet} \quad (93)$$

$$(CF_3)_2NH \rightleftharpoons CF_3-N=CF_2 + HF \quad (94)$$

$$CF_3-N=CF_2 + {}^{-}N(CF_3)_2 \longrightarrow CF_3-N=CF-N(CF_3)_2 + F^{-} \quad (95)$$

$$^{-}N(CF_3)_2 + HF \longrightarrow (CF_3)_2NH + F^{-} \quad (96)$$

This cascade of reactions (91-96) leads to the decomposition of the $[N(CF_3)_2]^-$-anion in a chemical way, with the formation of bis(trifluoromethyl)amine and F^- as the main products.

To determine the nature of intermediate species the method of a rotating ring-disk electrode (RRDE) was used.

By the electrochemical oxidation of the $[N(CF_3)_2]^-$-anion on the disk electrode the corresponding current response was registered on the ring electrode (Fig. 19). It means that some species formed during the oxidation on the disc electrode can reach the ring and participate in the electrochemical process on the ring electrode. The current intensity on the ring electrode is very low. It means that the life-time of $N(CF_3)_2$-radicals at these conditions is very short.

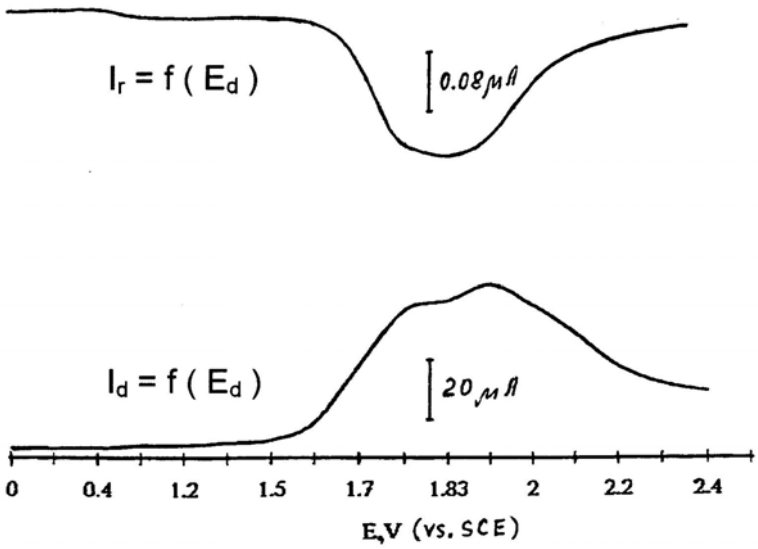


Fig. 19

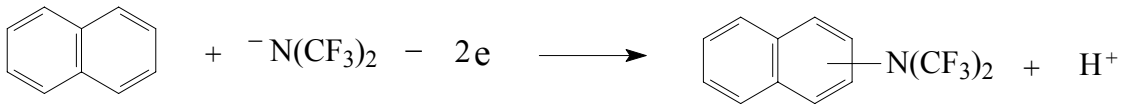
Voltammogram of $[N(CF_3)_2]^-$-anione on rotating disk-ring electrode.
Disk electrode: glassy carbon; Ring electrode: Pt; $\omega = 50\ s^{-1}$
Electrolyte: 0.1 M $Bu_4N[BF_4]$ in CH_3CN

Taking into account the high potential of oxidation of the $[N(CF_3)_2]^-$-anion, the direct anodic substitution with this anion's is possible (97), if the substrate is oxidized at less positive potentials.

$$Ar{-}H + {}^{-}N(CF_3)_2 - 2e \longrightarrow Ar{-}N(CF_3)_2 + H^+ \qquad (97)$$

In the case of aromates: benzene (E_{ox}= +2.62 V), toluene (E_{ox}= +1.98 V), with the oxidation potential higher than the oxidation potential of the $[N(CF_3)_2]^-$-anion, only bis(trifluoromethyl)amine and the fluoride anion were observed in the reaction mixture by ^{19}F NMR spectroscopy. The aromatics remained practically unreacted.

The electrochemical oxidation of naphthalene (E_{ox}= +1.34 V) in the presence of $[N(CF_3)_2]^-$-anion (98) leads to the formation of the substituted product (mixture of isomers) in low yield.



(98)

The low yield of the substituted product can be explained by the parallel generation of proton, which occurs during this process and causes the decomposition of $[N(CF_3)_2]^-$-anion according to the equations (91-96).

6 Experimental part

Electrochemical measurements and synthesis.

Voltammetric measurements were carried out with the RDE-3 potentiostat from "Pine Instrument Company" (USA). Cyclic voltammograms were obtained with a three-electrode system using a glassy carbon disk (∅ 2.29 mm) as the working electrode and a platinum wire as the counter electrode. All measurements were carried out with a saturated calomel electrode (SCE) as the reference with capillary bridge (E_p^{ox} ferrocene = 0.425 V) to prevent the diffusion of water into the measured solution.

For the preparative scale electrolysis the cell made from glassy carbon (cell body) was used (anode). Platinum wire was applied for the cathode.

Analytical procedures

^{19}F and ^{1}H NMR spectra were measured of neat liquids on the Bruker Avance: DRX500, DRX-300, Avance-250, WP 80 SY (Bruker) spectrometers.

^{1}H-NMR-Spectra:

Bruker Avance DRX500	(500. 13MHz)
Bruker DRX-300	(300.13 MHz)
Avance-250	(250.13 MHz)
WP 80 SY (Bruker)	(80.13 MHz)

^{19}F-NMR-Spectra:

Bruker Avance DRX500	(470.59 MHz)
Bruker DRX-300	(282.41 MHz)
Avance-250	(235.36 MHz)
WP 80 SY (Bruker)	(75.39 MHz)

^{31}P-NMR-Spectra:

Bruker Avance DRX500	(202.46 MHz)
Bruker DRX-300	(121.49 MHz)
Avance-250	(101.25 MHz)

For perfluorinated compounds and solutions in aHF spectra were recorded using FEP sample tube inside a 5 mm thin walled NMR tube (Wilmad, Type 537PPT) with an acetone-D_6 and acetonitrile-D_3 film as an external lock and CCl_3F as internal or TMS as external references.

For other compounds spectra were recorded in glass NMR-tubes (Wilmad, Type 507PP) in deuterated solvents from Deutero GmbH and Merck KGaA.

Gas-chromatographic analyses were undertaken with a Perkin-Elmer gas-chromatograph using a column (4% OV 101 on Chromosorb GAW DMCS) of length 2.5 m and 2 mm i.d. at 40 °C. The temperature of the injector was 100 °C and the temperature of the FID detector was maintained at 250 °C. The carrier gas was He.

The elementalanalysator “Carlo Erba” Model 1106 was used for elemental

analyses. The accuracy is:

Carbon ±0.3%
Sulphur ±0.3%
Hydrogen ±0.3%
Nitrogen ±0.2%

Mass spectra were measured with Varian MAT 311A spectrometer (EI-ion source 70 eV).

The B 510 K "Fa. Büchi Laboratoriumstechnik AG" was used for the melting point determinations.

Equipment

For all synthesis the common glass equipment (if no special comments) was used. The argon (4.8) and nitrogen (5.0) were used for the protection of moisture sensitive reactions and compounds.

The special equipment made from FEP (tetrafluoroethylen-hexafluoroplopylen-blockpolymer, m.p. ca. 270 °C, working temperature ca. 205 °C), PFA (Bohlender GmbH, MN, USA) and Teflon® was used for work with aHF. The FEP capillaries ($Ø_e$= 1.5, $Ø_i$= 0.7; $Ø_e$= 3.0; $Ø_i$= 2.0 mm) was used for transferring of aHF and moisture sensitive solutions in argon or nitrogen atmosphere. The Teflon® stopper with two opening was used for the outcoming vessels. In one opening the capillary

was placed. Second opening was used for increasing the pressure of argon or nitrogen in the vessel (< 500 hPa). In the incoming vessel the second opening was used for the protective atmosphere operated by an open T-joint and a flow of inert gas.

For handling and storing moisture sensitive compounds a Glovebox (M. Braun, MB-100G) with a residual water content of < 1 ppm was used.

Two ECF cell mainly used in this work (Fig. 20) [41, 60] were made of stainless steel, and had a cooling sleeve for maintaining a constant temperature of the cell body at approximately 0 °C (the boiling point of HF is 19.5 °C) and a reflux condenser held at -20 to -30 °C to condense the HF vapour. To trap the volatile products, which easily leave the aHF solution with the flow of the hydrogen formed during ECF and HF PFA traps are used. Traps are cooled to -78 °C with the mixture of dry ice and ethanol. To remove the HF from the gaseous products, the electrolyses gas can be passed through a bed of NaF and scrubbed with aqueous KI or Na_2SO_3 to remove OF_2. Pre-electrolysis of a HF is used to remove traces of water. The aHF solution of the starting material is added to the cell in intervals, to maintain its concentration at a level of ca. 5%. Typical parameters of an electrochemical fluorination are: voltage 4-6 V and current density 0.5 to 2.0 A/dm^2. The Ni-electrodes form a stack of alternating anodes and cathodes. There is no diaphragma between the anodes and cathodes. Fluorinated products are

generally not soluble in the electrolyte and are collect at the bottom of the cell due their high densities. Two different types of cells were used for the ECF:

Cell No.	Total volume, cm^3	Effective anodic area, dm^2
1.	360	4.58
2.	1500	15.6

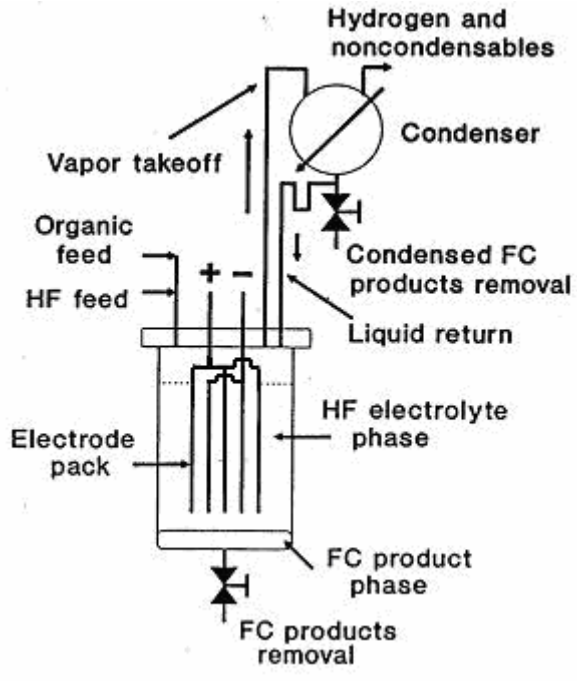


Fig. 20

Typical cell for the electrochemical fluorination

The special protective equipment was used during work with aHF:

Eyes: appropriate protective eyeglasses or chemical safety goggles.

Face: protection helmet with mask European Standard EN166.

Skin: appropriate protective gloves to prevent skin exposure.

Clothing: appropriate protective clothing to prevent skin exposure and chemical apron.

Chemicals

Ethanesulfonylchloride	≥ 98 %, (Fluka)
Hydrogen fluoride	≥ 99 %, (Bayer AG)
Acetonitrile anhydrous	Selectipur (Merck KGaA)
KHF_2	99 % (Aldrich)
Diethylether	Selectipur (Merck KGaA)
CF_3SO_2F	98 %, AEP (Angarsk, Russia)
Dimethylamine	99+%, (Aldrich)
SO_2Cl_2	97 %, (Aldrich)
Pyrrolidine	99 %, spray dried (Aldrich)
KF	99 %, (Aldrich)
RbF	99 %, (Aldrich)
$C_4F_9SO_2N(CF_3)_2$	Dr. N. Ignatiev
$C_2H_5C(O)Cl$	≥ 98 %, (Fluka)
$C_3F_7C(O)OH$	99 %, (Aldrich)
AgF	99 %, (Aldrich)
$Ag[OSO_2CF_3]$	≥ 98 %, (Aldrich)
HgF_2	99+%, (Aldrich)
CuF_2	≥ 98 %, (Fluka)
$Cu[OSO_2CF_3]\cdot CH_3CN$	L. Zinovyeva
$Zn[OSO_2CF_3]_2\cdot CH_3CN$	L. Zinovyeva
$Cd[OSO_2CF_3]_2\cdot 2CH_3CN$	L. Zinovyeva
$[(CH_3)_4N]F$	97 %, (Aldrich)
$[(C_4H_9)_4N]Cl$	≥ 98 %, (Merck KGaA)
$[(C_4H_9)_4P][BF_4]$	synthesized and purified as described.[61]
$[(C_4H_9)_4P]Br$	≥ 98 %, (Fluka)
$[Ph_3(PhCH_2)P]Cl$	99 %, (Acros)

$BrCH_2COOC_2H_5$	≥ 98 %, (Fluka)
Hydrazine hydrate	98 %, (Aldrich)
p-Nitrobenzaldehyde	98 %, (Aldrich)
$C_6H_5CH_2Br$	99 %, (Aldrich)
CH_3I	99 %, (Aldrich)
2,4-Dinitrofluorobenzene	98 %, (Aldrich)
2-Bromacetophenone	98 %, (Aldrich)
Ph-CH=CH-CH_2Br	97 %, (Aldrich)
Br-CH_2-CH=CH-CH_2Br	99 %, (Aldrich)
Naphthalene	≥ 99 %, (Aldrich)

Experiments

Electrochemical fluorination of ethanesulfonylchloride.

(i) The cylindrical cell No.1 was used, temperature of the cell body was maintained at -1 °C and the temperature of the condenser was kept at -30 °C. Ethanesulfonyl chloride (136.4 g ;1.06 mol) was added in twelve portions (11.5 g at the beginning ; 10.2 g after 28.6 A·h ; 10.8 g after 55.9 A·h ; 15.0 g after 81.9 A·h ; 9.6 g after 123.4 A·h ; 15.9 g after 144.0 A·h ; 9.0 g after 184.1 A·h ; 13.2 g after 205.7 A·h ; 10.4 g after 239.9 A·h ; 13.7 g after 266.3 A·h ; 12.1 g after 301.4 A·h ; 5.0 g after 327.7 A·h) to 306 g of liquid hydrogen fluoride previously electrolysed in the cell during 48 h at a cell voltage of 4.9 - 5.2 V. The gaseous products from the cell were passed through the condenser and two PTFE traps held at -78 °C. The electrolysis, which proceeded at a cell voltage of 4.9 - 5.3 V and a current density of 0.47 - 0.55 A/dm^2, was finished after the consumption of 378 A·h (110.9 % of the theoretical amount of electricity). During the electrolysis, the amount of the liquid in the cell was kept constant by occasional addition of hydrogen fluoride. The liquid products collected in both cold traps were separated from the HF-layer unified and studied by ^{19}F NMR spectroscopy at -40 °C. The acetone-d_6 and CCl_3F were used as lock and standard for NMR measurements. Altogether 35 g of fluorinated material was obtained.

(ii) This experiment was carried out as experiment (i), but the temperature of the cell body was maintained to 5 °C and the temperature of the condenser was kept at -15 °C. Ethanesulfonyl chloride (107.3 g; 0.83 mol) was added in twelve equal portions every 24 A·h to 305 g of liquid hydrogen fluoride previously electrolysed in the cell during 48 h at a cell voltage of 5.0 - 5.2 V. The electrolysis proceeded at a cell voltage of 4.4 - 5.3 V with a current density of 0.44 A/dm^2 and was finished after 356.7 A·h of electricity were consumed (132.8 % of the theoretical amount of electricity). The liquid products (39 g) were collected in the traps in the same way as in the previous experiment. After low temperature distillation of this material and washing in the vapour phase at room temperature with water (for removing traces of HF) and concentrated sulfuric acid (for drying), 32 g of a liquid containing 85 % of $C_2F_5SO_2F$ (yield : 16 %) was isolated. After reaction of this material with $Ba(OH)_2 \cdot 8H_2O$, followed by treatment of the Ba-salts with 100 % sulfuric acid, a mixture of $C_2F_5SO_2OH$ (96 mol %) and $ClCF_2CF_2SO_2OH$ (4 mol %) was obtained.

^{19}F NMR , ppm: -79.7 s (3F), -115.9 s (2F) ($C_2F_5SO_2OH$) ; -66.8 s (2F), -110.1 s (2F) ($ClCF_2CF_2SO_2OH$).

MS for $C_2F_5SO_2OH$: m/s 50 (CF_2), 64 (SO_2), 65 (SO_2H), 69 (CF_3), 81 (SO_3H), 100 (C_2F_4), 119 (C_2F_5), 183 ($C_2F_5SO_2$).

MS for $ClCF_2CF_2SO_2OH$: m/s 36 (Cl), 85 ($ClCF_2$), 135 (C_2F_4Cl), 215 (M^+-H^+).

Synthesis of $C_2H_5SO_2F$

342 g (2.66 mol) of $C_2H_5SO_2Cl$ was placed in PE bottle (total volume 1000 cm^3) and cooled down in an ice bath to 0 °C. The solution of 228.2 g (2.93 mol) of KHF_2 in 540 cm^3 water was slowly added to the cold $C_2H_5SO_2Cl$. The reaction mixture was stirred at 0 °C for 1 h and additionally at room temperature for 24 hs. The layer at the bottom was separated and dried over $MgSO_4$. After distillation 255g of pure $C_2H_5SO_2F$ (b.p. 76-78 °C) was obtained. Yield: 86 %.

Electrochemical fluorination of ethanesulfonylfluoride.

The cell No.2 was used for this experiment, temperature of the cell body was maintained at 0 °C and the temperature of the condenser was kept at -25 °C. Ethanesulfonyl fluoride (1115.6 g; 9.96 mol) was added in twenty-seven portions to 1140 g of liquid hydrogen fluoride previously electrolyzed in the cell during 111 h at the cell voltage 4.5 - 5.2 V. The electrolysis proceeded at a cell of voltage of 4.8 - 5.2 V and a current density of 0.20 -0.32 A/dm^2 and was finished after 3492.2 A·h of electricity were consumed (130.9 % of the theoretical amount of electricity). The liquid products collected in the traps held at -78 °C were periodically separated from HF which was reused in the cell. Altogether 1651 g of pure $C_2F_5SO_2F$ (95%) was obtained. Yield: 82.1 %.

Synthesis of $C_2F_5SO_2N(CH_3)_2$

N,N'dimethylpentafluoroethylsulfonylamide was synthesized by reacting of pentafluoroethylsulfonylfluoride with dimethylamine. 81.0 g (0.40 mol) of pentafluoroethylsulfonylfluoride were condensed to the stirred solution of 46.0 g (1.02 mol) of diethylamine in 250 cm^3 of dry ether cooled in ice-water. The reaction mixture was stirred 12 h at room temperature. ca. 250 cm^3 water was added, stirred and reaction mixture was extracted with diethyl ether (3x100 cm^3). The ether solution was washed with diluted HCl (to pH=6) and ether was distilled off. The residue was redistilled. 77.8 g of N,N'-dimethyl-pentafluoroethylsulfonylamide (B.p. 160-165 °C) was obtained. Yield: 85 %.

^{19}F NMR spectrum (Lock: CD_3CN; Standard: internal CCl_3F), δ, ppm: -79.8 s (CF_3); -115.6 s (CF_2). ^1H NMR spectrum (Lock: CD_3CN; Standard: internal TMS), δ, ppm: 3.06 s ($2CH_3$).

Electrochemical fluorination of $C_2F_5SO_2N(CH_3)_2$.

The temperature of the cell body (No.1) in this experiment was maintained at 0 °C and the temperature of the condenser was kept at –30 °C.

75 g (0.33 mol) of $C_2F_5SO_2N(CH_3)_2$ was added portionwise (25g at the start; 25 g after 35.1 A·h; 25 g after 69.5 A·h) to 324 g of liquid hydrogen fluoride previously electrolysed in the cell for 24 h. The gaseous products from the cell were passed through a condenser and two FEP traps held at –78 ^{o} C. The electrolysis, which

proceeded at a cell voltage of 4.8 – 5.2 V and a current density of 0.66 A/dm^2, was completed after consumption of 130.72 A·h (123 % of the theoretical amount calculated on a 12 electron process). 3.73 g of a transparent liquid (basically $C_2F_5SO_2F$) was obtained from the trap after separation from the HF layer. Diluting the HF from the cell with ice-water gave additionally 95 g of the fluorinated product mixture.

After several fractional distillations $C_2F_5SO_2N(CH_3)_2$ was isolated (33.6 g) as a pure compound; B.p. 78 °C. Yield: 30 % (isolated), 38 % (by NMR).

^{19}F NMR-spectra (lock: CD_3CN, standart: CCl_3F) δ, ppm: -79.8 s (3F, CF_3); -112.0 s (2F, CF_2); -52.1 s (6F, $2CF_3$).

Synthesis of $CF_3SO_2N(CH_3)_2$

N,N'-dimethyl-trifluoromethylsulfonylamide was synthesized by reacting of trifluoromethylsulfonylfluoride with dimethylamine. 308.6 g (2.03 mol) of trifluoromethylsulfonylfluoride were condensed (in ca. 20 g portions) to the stirred solution of 186 g (4.13 mol) of dimethylamine in 350 cm^3 of dry ether cooled in ice-water. The reaction mixture was stirred 12 h at room temperature. ca. 500 cm^3 water was added, stirred and reaction mixture was extracted with diethyl ether (5x100 cm^3). The ether solution was washed with diluted HCl (to pH=6) and ether was distilled off. The residue was redistilled. 332.6 g of N,N'dimethyl-trifluoromethylsulfonylamide (B.p. 150-151 °C) was obtained. Yield: 93 %.

^{19}F NMR spectrum (Lock: $CDCl_3$; Standard: internal CCl_3F), δ, ppm: -75.1 h (CF_3;

$^{5}J_{H,F}$=1.2 Hz) ^{1}H NMR spectrum (Lock: $CDCl_3$; Standard: internal TMS), δ, ppm: 3.05 q ($2CH_3$) [39].

Electrochemical fluorination of $CF_3SO_2N(CH_3)_2$.

(i) The cell No.1 was used for this experiment, temperature of the cell body was maintained at 0 °C and the temperature of the condenser was kept at -30 °C. 165 g (0.93 mol) $CF_3SO_2N(CH_3)_2$ was added in eleven portions (20 g at the start; 11.3 g after 39.3 A·h; 18.8 g after 62.6 A·h; 10.0 g after 101.7 A·h; 17.5 g after 121.3 A·h; 12.5 g after 156.7 A·h; 18.1 g after 180.9 A·h; 12.5 g after 217.6 A·h; 18.1 g after 243.1 A·h; 12.5 g after 279.3 A·h; 13.7 g after 302.9 A·h) to 317 g of liquid hydrogen fluoride previously electrolyzed in the cell during 48 h at the cell voltage 5.0 - 5.2 V. The electrolysis proceeded at a cell voltage of 4.5 - 5.1 V and a current density of 0.55 A/dm^2 and was finished after 374.8 A·h of electricity were consumed (125 % of the theoretical amount of electricity). The 27.4 g of liquid products was collected in the traps held at -78 °C. It was obtained 99.8 g of products from the cell and dilution of the HF-solution from the cell with ice-water gave as additionally 29.9 g of mixture of products. After unification and washing with cold water mixture of the products was dried over magnesium sulphate. Following fractional distillation gave 63.3 g pure $CF_3SO_2N(CF_3)_2$. Yield: 24 %.

^{19}F NMR spectrum (Lock: $CDCl_3$; Standard: internal CCl_3F), δ, ppm: -51.6 q (6F; $^{5}J_{F,F}$=4 Hz), -74.6 h (3F) [39].

(ii) The cell No.2 was used for this experiment, temperature of the cell body was maintained at 0 °C and the temperature of the condenser was kept at -25 °C. 746.14 g (4.22 mol) $CF_3SO_2N(CH_3)_2$was added in nine portions (66 g at the start; 68.42 g after 122.08 A·h; 69 g after 245.6 A·h; 62 g after 482.4 A·h; 93.32 g after 651.9 A·h; 105.9 g after 844.4 A·h; 105.6 g after 1036.3 A·h; 94.9 g after 1207.0 A·h; 81.0 g after 1356.0 A·h) to 1260 g of liquid hydrogen fluoride previously electrolyzed in the cell during 48 h at the cell voltage 4.5 - 5.2 V. The electrolysis proceeded at a cell voltage of 4.9 - 5.1 V and a current density of 0.51 A/dm^2 and was finished after 1692 A·h of electricity were consumed (124.7 % of the theoretical amount of electricity). The liquid products collected in the traps held at -78 °C was periodically separated from HF which was reused in the cell. It was obtained 85 g mixture of products from the traps, 319 g from the cell and dilution of the HF-solution from the cell with ice-water gave as additionally 299 g of mixture of products. After unification and washing with cold water mixture of the products was dried over magnesium sulphate. Following fractional distillation gave 560 g pure $CF_3SO_2N(CF_3)_2$. Yield: 47 %.

Electrochemical fluorination of a mixture containing $CF_3SO_2N(CH_3)CF_2H$, $CF_3SO_2N(CF_2H)_2$ and $CF_3SO_2N(CFH_2)CF_2H$

The cell No.1 was used for this experiment, temperature of the cell body was maintained at 5 °C and the temperature of the condenser was kept at -20 °C. 210.6 g of the mixture consisted of: 56.3 % $CF_3SO_2N(CH_3)CF_2H$; 35.8 % $CF_3SO_2N(CF_2H)_2$ and 7.9 % $CF_3SO_2N(CFH_2)CF_2H$ was added in four portions (74.5 g at the start; 29.8 g after 18.9 A·h; 63.3 g after 33.45 A·h; 43 g after 55.5 A·h) to 330 g of liquid hydrogen fluoride previously electrolyzed in the cell during 24 h at the cell voltage 5.2 V. The electrolysis proceeded at a cell voltage of 5.10-5.15 V and a current density of 0.17 A/dm^2 and was finished after 100.8 A·h of electricity were consumed (149 % of the theoretical amount of electricity). The liquid products collected in the traps held at -78 °C. It was obtained 19 g mixture of products from the traps ($CF_3SO_2N(CF_3)_2$, CF_3SO_2F, $FN(CF_3)_2$), 70 g $CF_3SO_2N(CF_3)_2$ (98% purity) from the cell and dilution of the HF-solution from the cell with ice-water gave as additionally 70 g $CF_3SO_2N(CF_3)_2$ (98% purity). After unification and washing with cold water mixture of the products was dried over magnesium sulphate. Following fractional distillation gave 150 g pure $CF_3SO_2N(CF_3)_2$. Yield: 64 %.

Synthesis of $(CH_3)_2NSO_2N(CH_3)_2$

N,N,N',N'-Tetramethylsulfonyldiamide was prepared from SO_2Cl_2 by the reaction with dimethylamine. 250.0 g (1.85 mol) in 100 cm^3 $CHCl_3$ of thionyl

chloride were dropwise added to the stirred solution of 391.0 g (8.69 mol) of dimethylamine in 250 cm^3 of dry chloroform cooled in ethanol bath to -20 °C. The temperature of the condenser was -78 °C. After addition, the reaction mixture was left overnight at room temperature. The white deposit was dissolved in ca. 500 cm^3 and reaction mixture was extracted with five portions (100 cm^3) of ether. After removing the ether, the residue was recrystallized from chloroform to give 222.3 g of N,N,N',N'-Tetramethylsulfonyldiamide (m.p. 74 °C). Yield: 79 %.

^{1}H NMR spectrum (Lock: $CDCl_3$; Standard: internal TMS), δ, ppm: 2.82 s (CH_3) [46].

Electrochemical fluorination of $(CH_3)_2NSO_2N(CH_3)_2$

The cell No.1 was used for this experiment, temperature of the cell body was maintained at 0 °C and the temperature of the condenser was kept at -30 °C.

139.5 g (0.92 mol) of N,N,N',N'-Tetramethylsulfonyldiamide was added in eighteen portions (8.4 g at the start and nine times every 24 h; 7.1 g after 35.6 A·h and nine times every 24 h) to 325 g of liquid hydrogen fluoride previously electrolyzed in the cell during 44 h at the cell voltage 5.00 V. The electrolysis proceeded at a cell voltage of 4.80-5.20 V and a current density of 0.66 A/dm^2 and was finished after 645.9 A·h of electricity were consumed (109.4 % of the theoretical amount of electricity). The liquid products were collected in the traps held at -78 °C. It was obtained 14.9 g mixture of products from the traps, 44.0 g from the cell and dilution of the HF-solution from the cell with ice-water gave

additionally 23.4 g. After unification and washing with cold water the products mixture was dried over magnesium sulphate. Following fractional distillation resulted in 3.6 g pure $(CF_3)_2SO_2N(CF_3)_2$. Yield: 1 %.

Synthesis of $CF_3SO_2N[-CH_2-]_4$

N-(trifluoromethylsulfonyl)-pyrrolidine was synthesized by treatment of trifluoromethylsulfonylfluoride with pyrrolidine in presence of triethylamine. 74.9 g (0.493 mol) of trifluoromethylsulfonylfluoride were condensed to the stirred solution of 34.97 g (0.492 mol) of pyrrolidine, 50 g (0.495 mol) triethylamine in 250 cm^3 of dry ether cooled in ice-water. The reaction mixture was stirred 8 h at room temperature. The white deposit was filtered off and washed with three portions (50 cm^3) of ether. The ether solution was washed with diluted HCl (to pH=6) and distilled off. The residue was distilled. 93.72 g of N-(trifluoromethylsulfonyl)-pyrrolidine (B.p. 88 °C) was obtained. Yield: 94 %.

^{19}F NMR spectrum (Lock: $CDCl_3$; Standard: internal CCl_3F), δ, ppm: -75.5 s (CF_3)

^1H NMR spectrum (Lock: $CDCl_3$; Standard: internal TMS), δ, ppm: 2.02 m ($2CH_2$) 3.54 m ($2CH_2'$).

Electrochemical fluorination of $CF_3SO_2N[-CH_2-]_4$.

The temperature of the cell body (No.1) in this experiment was maintained at 0 °C and the temperature of the condenser was kept at −30 °C.

88.7 g of $CF_3SO_2N[-CH2-]_4$ was added portionwise (22g at the start; 22.3 g after 45.3 A·h; 21.9 g after 88.81 A·h; 22.5 g after 141.1 A·h) to 322 g of liquid hydrogen fluoride previously electrolyzed in the cell for 24 h. The gaseous products from the cell were passed through a condenser and two FEP traps at –78 °C. The electrolysis, which proceeded at a cell voltage of 4.83 – 5.12 V and a current density of A/dm^2, was completed after consumption of 225.1 A·h (120.3 % of the theoretical amount calculated on a 16 electron process). 55.0 g of a transparent liquid was obtained from the trap after separation from the HF layer. It consists of: 44 % CF_3SO_2F, 39 % C_4F_{10} and 17 % of N-fluoro-octafluoropyrrolidine.

Diluting the HF from the cell with ice-water additionally gave 13 g of nearly pure $CF_3SO_2N[-CF2-]_4$.

By the fractional distillation $CF_3SO_2N[-CF2-]_4$ was isolated (6.08 g) as a pure compound; B.p. 97 °C. Yield: 5 %

^{19}F NMR-spectra (lock: CD_3CN, standart: CCl_3F) δ, ppm: -75.6 m (3F, CF_3); -90.7 m (4F, 2 N-CF_2); -133.1 s (4F, 2CF_2).

Electrochemical fluorination of $C_2H_5C(O)Cl$

The cell No.2 was used for this experiment, temperature of the cell body was maintained at -1 °C and the temperature of the condenser was kept at -30 °C. Propanoylchloride (240 g; 2.59 mol) was added in eight portions (30 g at the start;

30 g after 173.9 A·h; 30 g after 260.8 A·h; 30 g after 347.7 A·h; 30 g after 434.7 A·h; 30 g after 521.6 A·h; 30 g after 608.5 A·h; 30 g after 695.5 A·h) to 330 g of liquid hydrogen fluoride previously electrolyzed in the cell during 48 h at the cell voltage 4.90 V. The electrolysis proceeded at a cell of voltage of 4.8 - 5.2 V and a current density of 0.66 A/dm^2 and was finished after 882.55 A·h of electricity were consumed (127 % of the theoretical amount of electricity). At the end of the ECF the temperature of the cell body was increased to 18 °C and the temperature of the condenser up to -25 °C for 2 h. The liquid products collected in the traps held at -78 °C was separated from HF. Altogether 110.3 g of pure $C_2F_5C(O)F$ (95%) was obtained. Yield: 26 %.

Synthesis of $C_2F_5C(O)N(CH_3)_2$

N,N-Dimethylpentafluoropropionamide, $C_2F_5CON(CH_3)_2$, was synthesized by reacting of pentafluoropropanoyl fluoride with dimethylamine. 102.0 g (0.614 mol) of pentafluoropropanoyl fluoride were bubbled through the stirred solution of 75.0 g (1.66 mol) of dimethylamine ("Aldrich", 99+%) in 500 cm^3 of dry ether cooled in ice-water. The reaction mixture was kept overnight at room temperature, the white deposit was filtered off and washed with three portions (50 cm^3) of ether. The ether was distilled off and the residue was distilled at reduced pressure. 85.0 g of N,N-Dimethylpentafluoropropionamide (B.p. 98-100 °C at 18.4 kPa) [62] was obtained. Yield: 72 %. ^{19}F NMR spectrum (Lock: acetone-D_6 ; Standard: internal CCl_3F), δ, ppm: -82.0 s (CF_3), -115.0 m (CF_2). ^{1}H NMR spectrum (Lock: acetone-

D_6 ; Standard: internal TMS), δ, ppm: 3.04 t (CH_3 $^5J_{H,F}$ = 1.0 Hz), 3.23 t (CH'_3 $^5J_{H',F}$ = 2.4 Hz).

Electrochemical fluorination of $C_2F_5C(O)N(CH_3)_2$

The temperature of the cell body (No.1) in this experiment was maintained at 0 °C and the temperature of the condenser was kept at –30 °C.

90.0 g of N,N-dimethylpentafluoropropionamide was added in four portions (25 g at the start; 25 g after 54.0 A·h; 20 g after 86.8 A·h; 20 g after 128.4 A·h) to 337 g of liquid hydrogen fluoride previously electrolysed in the cell for 25 h. The gaseous products from the cell were passed through the condenser and two FEP traps held at –78 ^{o} C. The electrolysis, which proceeded at a cell voltage of 4.3 – 5.1 V and a current density of 0.66 A/dm^2, was completed after consumption of 183.7 A·h (121 % of the theoretical amount calculated on a 12 electron process). 23.0 g of a transparent liquid was obtained from the trap after separation from the HF layer.

According to ^{19}F NMR spectra this mixture contains three main substances (see Table 12). By the fractional distillation pure perfluoro-N,N-dimethyl-propioamide was isolated (3.6 g, 5 % yield); B.p. 49-50 °C.

Synthesis of $C_3F_7C(O)N(CH_3)_2$

N,N-Dimethylheptafluorobutyramide was prepared from heptafluorobutyryl chloride by the reaction with dimethylamine. 132.5 g (0.57 mol) of heptafluorobutyryl chloride were slowly (≈ 1.5 g per min) added to the stirred solution of 71.0 g (1.58 mol) of dimethylamine in 500 cm^3 of dry ether cooled in ice-water. After addition, the reaction mixture was refluxed for one hour and left overnight at room temperature. The white deposit was filtered off and washed with three portions (50 cm^3) of ether. After removing the ether, the residue was distilled at reduced pressure to give 121.7 g of N,N-dimethylheptafluorobutyramide (B.p. 107 °C at 14.7 kPa)[63] (Yield: 89 %). ^{19}F NMR spectrum (Lock: acetone-D_6 ; Standard: internal CCl_3F), δ, ppm: -79.5 t (CF_3 $^4J_{F,F}$ = 9.5 Hz), -111.6 m (CF_2), -125.0 s (CF_2),. ^1H NMR spectrum (Lock: acetone-D_6 ; Standard: internal TMS), δ, ppm: 3.1 t (CH_3, $^5J_{H,F}$ = 0.8 Hz), 3.23 t (CH_3, $^5J_{H,F}$ = 2.4 Hz).

Electrochemical fluorination of N,N-dimethylheptafluorobutyramide

Experiment (I).

The temperature of the cell body (No.1) in this experiment was maintained at -15 °C and the temperature of the condenser was kept at –30 °C.

140.4 g of N,N-dimethylheptafluorobutyramide was added in six portions (22.4 g at the start; 27 g after 30.2 A·h; 22 g after 73.6 A·h; 27 g after 102.0 A·h; 22 g after 141.6 A·h; 20 g after 175.6 A·h) to 338 g of liquid HF previously electrolysed in the cell for 17 h. The gaseous products from the cell were passed

through the condenser and two FEP traps held at −78 ^{o} C. The electrolysis, which proceeded at a cell voltage of 4.6 – 5.5 V and a current density of 0.66 A/dm^2, was completed after consumption of 226.5 A·h (121 % of the theoretical amount calculated on a 12 electron process). 70.5 g of a transparent liquid was obtained from the trap after separation from the HF layer. This mixture was analysed by ^{19}F NMR spectroscopy.

Dilution of the HF-solution from the cell with ice-water gave in addition 32.2 g of a transparent liquid, which was dried over magnesium sulphate and analysed by means of gas-chromatography and ^{19}F NMR spectroscopy.

Table 13 shows the total contents of fluorinated compounds in the mixture, isolated after ECF of N,N-dimethylheptafluorobutyramide.

By fractional distillation of the material from the trap (after warming up to the room temperature 4.9 g remained) together with the product obtained from the HF from the cell (32.2g), the following compounds were isolated as pure substances (for NMR data see Table 13):

a) Perfluoro-N,N-dimethylbutyramide, $C_3F_7CON(CF_3)_2$ (4.8 g; b.p. 72-73 °C) (isolated yield: 3.0 %).

b) N-(trifluoromethyl)-N-(difluoromethyl)heptafluorobutyramide, $C_3F_7CON(CF_3)(CHF_2)$; (4.6 g; b.p. 90-91 °C)

The ^{19}F NMR spectrum of the last fraction (5.76 g; b.p. 108 - 115 °C) shows the presence of N,N-bis(difluoromethyl)heptafluorobutyramide, $C_3F_7CON(CHF_2)_2$, as the main component.

Experiment (II).

The temperature of the cell body in this experiment was maintained at 0 °C and the temperature of the condenser was kept at –30 °C.

132.0 g of N,N-dimethylheptafluorobutyramide was added in 33 equal portions (4 g each) every 2 hours to 333 g of liquid HF previously electrolysed in the cell over 45 h. The gaseous products from the cell were passed through the condenser and two FEP traps held at –78 ^{o} C. The electrolysis, which proceeded at a cell voltage of 4.3 – 5.6 V and a current density of 0.66 A/dm^2, was completed after consumption of 199.7 A·h (113 % of the theoretical amount calculated on a 12 electron process). 57.1 g of a transparent liquid was obtained from the trap after separation from the HF layer. Dilution of the HF-solution from the cell with ice-water gave in addition 35.4 g of a transparent liquid, which was dried over magnesium sulphate.

Analyses of both samples and isolation of the pure compounds were carried out as described in Experiment (I). Data are given in the Table 13.

Potassium bis(trifluoromethyl)imid

2.85 g (10 mmol) of $CF_3SO_2N(CF_3)_2$ was added to 0.58 g of KF suspended in 5 cm^3 of dry acetonitrile and the reaction mixture was stirred at room temperature for 1 hour. The ^{19}F NMR signal at – 39.7 ppm (s) belongs to the $K[N(CF_3)_2]$ salt.

The published value for $Cs[N(CF_3)_2]$ and $K[N(CF_3)_2]$ supposedly in CH_3CN is – 34.2 ppm (broad singlet) relatively to CF_3COOH (external standard)[4].

Rubidium bis(trifluoromethyl)imid from $CF_3SO_2N(CF_3)_2$.

To 2.185 g (21 mmol) of RbF in 10 cm^3 of dry CH_3CN which are placed in a glass flask equipped with a condenser dropwise 6.13 g (21 mmol) of $CF_3SO_2N(CF_3)_2$ was added. The reaction mixture was stirred at room temperature till all RbF was dissolved (some minutes). The resulting mixture was examined by ^{19}F NMR spectroscopy. The signal at – 37.5 ppm (s) belongs to the $Rb[N(CF_3)_2]$. This was confirmed by addition to the reaction mixture of an identical sample of $Rb[N(CF_3)_2]$ which was prepared by the known procedure[14] from RbF and perfluoro(2-azapropene) in the acetonitrile solution.

The same procedure was used for the preparation of $Rb[N(CF_3)_2]$ salt from with RbF and $FSO_2N(CF_3)_2$.

The acetonitrile solution of $Rb[N(CF_3)_2]$ is stable at room temperature in closed container for a long time and can be used for the chemical reactions without additional purification.

Preparation of rubidium bis(trifluoromethyl)imid from $C_4F_9SO_2N(CF_3)_2$.

To 0.041 g (0.39 mmol) of RbF in 1 cm^3 of dry CH_3CN which are placed in a glass flask 0.170 g (0.39 mmol) of $C_4F_9SO_2N(CF_3)_2$ was added. The reaction

mixture was stirred at room temperature until all RbF was dissolved (some minutes). The ^{19}F NMR signal at – 37.8 ppm (s) belongs to $Rb[N(CF_3)_2]$ salt.

Preparation of rubidium bis(trifluoromethyl)imid from $(CF_3)_2NSO_2N(CF_3)_2$.

To 0.064 g (0.61 mmol) of RbF in 1.5 cm^3 of dry CH_3CN which are placed in a glass flask 0.120 g (0.32 mmol) of $(CF_3)_2NSO_2N(CF_3)_2$ was added. The reaction mixture was stirred at room temperature till all RbF was dissolved. The ^{19}F NMR signal at – 37.2 ppm (s) belongs to the $Rb[N(CF_3)_2]$ salt.

Preparation of rubidium bis(trifluoromethyl)imid from $C_3F_7CON(CF_3)_2$.

To 0.092 g (0.88 mmol) of RbF suspended in 1.5 cm^3 of dry CH_3CN in a glass flask 0.160 g (0.45 mmol) of $C_3F_7CON(CF_3)_2$ was added. The reaction mixture was stirred at room temperature until all RbF was dissolved (approximately 10 min.). The ^{19}F NMR signal at –37.2 ppm (s) belongs to the $Rb[N(CF_3)_2]$ and the signals at –29.0 ppm, –80.8 ppm, –122.3 ppm and –125.9 ppm reflect the presence of $[CF_3CF_2CF_2CF_2O]^-$-anion in the reaction mixture.

After addition of $BrCH_2COOC_2H_5$ to the reaction mixture and heating at 80^o C during one hour the formation of substituted product $(CF_3)_2NCH_2COOC_2H_5$, was fixed by ^{19}F NMR spectroscopy and GC analyses.

Preparation of silver bis(trifluoromethyl)imid from $CF_3SO_2N(CF_3)_2$.

To 0.080 g (0.63 mmol) of AgF in 1 cm^3 of dry CH_3CN which were placed in a glass flask equipped with a condenser 0.180 g (0.63 mmol) of $CF_3SO_2N(CF_3)_2$ was added. The reaction mixture was stirred at room temperature for two hours. The ^{19}F NMR signal at – 47.0 ppm (s) belongs to the $Ag[N(CF_3)_2]$. After addition of $C_6H_5CH_2Br$ to the reaction mixture and heating at 80° C during 10 minutes the formation of $C_6H_5CH_2N(CF_3)$, was observed by ^{19}F NMR spectroscopy and GC analyses.

Preparation of silver bis(trifluoromethyl)imid from $Ag[OSO_2CF_3]$

The cold (-20°C) solution of $Rb[N(CF_3)_2]$, which was obtained from 0.083 g (0.79 mmol) of RbF and 0.227 g (0.79 mmol) of $CF_3SO_2N(CF_3)_2$ in 3.2 cm^3 of dry acetonitrile, was added at -20°C to the stirred solution of 0.205 g (0.79 mol) of $Ag[OSO_2CF_3]$ in 1.8 cm^3 of dry acetonitrile. The mixture was stirred one hour more at -20 °C. During that time a white deposit was formed. The solvent, acetonitrile was pumped off at -20 °C and to the residue 4 cm^3 of dry dichloromethane was added. After 10 min of stirring at -20 °C the solution was separated from the deposit and the solvent was pumped off at -20 °C. 0.149 g of white crystalline $Ag[N(CF_3)_2]\cdot CH_3CN$ was obtained. Yield 62.3 %.

Analysis (amperometric titration): Found, %: Ag^+ 35.76; calculated for the $Ag[N(CF_3)_2]\cdot CH_3CN$, %: Ag^+ 35.85.

^{19}F NMR spectra (lock CD_2Cl_2, standard CCl_3F), ppm: -44.6 s, (CF_3).

^{1}H NMR spectra (lock CD_2Cl_2 , standard TMS), ppm: 2.08 s, CH_3CN.

^{109}Ag NMR spectra (lock CD_2Cl_2 , standard: chemical shift of 1 M $AgNO_3$ in D_2O assigned to 0), ppm: 316.2 s, Ag.

Preparation of mercury (II) bis(trifluoromethyl)imid from $CF_3SO_2N(CF_3)_2$.

The mixture of 0.17 g (0.54 mmol) of HgF_2 , 0.32 g (1.1 mmol) of $CF_3SO_2N(CF_3)_2$ and 2 cm^3 of dry CH_3CN was heated for 10 hours at 85 ^oC in a PTFE FEP cylinder which was placed inside a stainless-steel autoclave. After cooling, the clear liquid was separated from the deposit. The ^{19}F NMR signal at –46.3 ppm (s) belongs to $Hg(N(CF_3)_2)_2$ in accordance with published value of – 48.7 ppm (broad singlet)[18].

Preparation of copper (II) bis(trifluoromethyl)imid from $CF_3SO_2N(CF_3)_2$.

The mixture of 0.11 g (1.1 mmol) of CuF_2 , 0.98 g (3.4 mmol) of $CF_3SO_2N(CF_3)_2$ and 1.5 cm^3 of dry CH_3CN was heated for 10 hours at 80 ^oC in a FEP cylinder which was placed inside a stainless-steel autoclave. After cooling, the clear liquid was separated from the deposit and heated up to 80 ^oC in an argon stream to remove all volatile products. The ^{19}F NMR signal at –55.8 ppm (broad singlet) (Lock: CD3CN film) belongs to the $Cu[N(CF_3)_2]_2$. After addition of

$Rb[N(CF_3)_2]$ to this solution only one average signal at −38.0 ppm (broad singlet) was observed in the ^{19}F NMR spectra.

Preparation of copper(I) bis(trifluoromethyl)imid from $Cu[OSO_2CF_3]\cdot CH_3CN$.

The solution of $Rb[N(CF_3)_2]$, which was obtained from 0.080 g (0.766 mmol) of RbF and 0.218 g (0.766 mmol) of $CF_3SO_2N(CF_3)_2$ in 3.2 cm^3 of dry acetonitrile, was added at room temperature to the stirred solution of 0.194 g (0.766 mol) of $Cu[OSO_2CF_3]\cdot CH_3CN$ in 1.8cm^3 of dry acetonitrile. The mixture was stirred for one hour and the solvent was pumped off at room temperature. To the white residue 4 cm^3 of dry dichloromethane were added. After 10 min of stirring at room temperature the solution was separated from the deposit and the solvent was pumped off room temperature. 0,150 g of white crystalline $Cu[N(CF_3)_2]\cdot CH_3CN$ were obtained. Yield 76.5 %.

^{19}F NMR spectra (lock CD_2Cl_2, standard CCl_3F), ppm: -44.8 s, (CF_3).

^1H NMR spectra (lock CD_2Cl_2 , standard TMS), ppm: 2.03 s, CH_3CN.

Preparation of zinc bis(trifluoromethyl)imid from $Zn[OSO_2CF_3]_2\cdot CH_3CN$.

The cold (-45°C) solution of $Rb[N(CF_3)_2]$, which was obtained from 0.080 g (0.766 mmol) of RbF and 0.218 g (0.766 mmol) of $CF_3SO_2N(CF_3)_2$ in 3.2 cm^3 of dry propionitrile, was added at -45°C to the stirred solution of 0.155 g (0.383 mol)

of $Zn[OSO_2CF_3]_2 \cdot CH_3CN$ in 1.8 cm^3 of dry propionitrile. During the mixing of the reagents a white deposit was formed. The mixture was stirred for one hour at -45 °C , cooled down to -78 °C and was kept two hours at this temperature without stirring. To the solution, which was separated from the deposit, a small quantity (≈ 30%) of CD_3CN was added and the mixture was investigated by ^{19}F NMR spectroscopy at -40 °C. The signal at -44.83 ppm belongs to the salt $Zn[N(CF_3)_2]_2$, co-ordinated with the solvent.

The solvent was pumped off at -30 °C and the white solid residue shows in CD_2Cl_2 solution by NMR spectroscopy the presence of propionitrile in the salt $Zn[N(CF_3)_2]_2 \cdot C_2H_5CN$. The salt has a low stability at room temperature.

^{19}F NMR spectra at -40°C (lock: CD_2Cl_2, standard: CCl_3F), ppm: -46.0 s, (CF_3). Position of the signal depends on the concentration.

^1H NMR Spectra at -40°C (lock: CD_2Cl_2 , standard: TMS), ppm: 1.08 t (CH_3); 2.25 q (CH_2), C_2H_5CN.

Preparation of cadmium bis(trifluoromethyl)imid from Cd$[OSO_2CF_3]_2 \cdot 2CH_3CN$.

The cold (-45°C) solution of $Rb[N(CF_3)_2]$ salt, which was obtained from 0.080 g (0.766 mmol) of RbF and 0.218 g (0.766 mmol) of $CF_3SO_2N(CF_3)_2$ in 3.2 cm^3 of dry propionitrile, was added at -45°C to the stirred solution of 0.188 g (0.383 mol) of $Cd[OSO_2CF_3]_2 \cdot 2CH_3CN$ in 1.8 cm^3 of dry propionitrile. During the

mixing of the reagents a white deposit was formed. The mixture was stirred for one hour at -45 °C , cooled to -78 °C and kept for two hours at this temperature without stirring. To the solution, which was separated from the deposit, a small quantity (≈ 30% by volume) of CD_3CN was added and the mixture was investigated by ^{19}F NMR spectroscopy at -40 °C. The signal at -42.5 ppm belongs to the salt $Cd[N(CF_3)_2]_2$, co-ordinated with the solvent. At room temperature the signal of $N(CF_3)_2$ group in the ^{19}F NMR spectra is shifted to -45.4 ppm. The salt $Cd[N(CF_3)_2]_2 \cdot nC_2H_5CN$ has a low stability in the solid state at room temperature.

Tetramethylammonium bis(trifluoromethyl)imide

To the solution of 0.017 g (0.18 mmol) of $[(CH_3)_4N]F$ in 0.5 cm^3 of dry dichloromethane 0.052 g (0.18 mmol) of $CF_3SO_2N(CF_3)_2$ was added at - 40 °C. The reaction mixture was warmed up to room temperature, diluted with the same volume of dry acetonitrile and investigated by ^{19}F NMR spectroscopy. The signal at -40.8 s (lock CD_3CN, reference substance: CCl_3F) belongs to the salt $[(CH_3)_4N][N(CF_3)_2]$. After evaporation of the solvent 0.037 g of white, very hygroscopic, material was obtained. Yield: 90 %.

Tetrabutylammonium bis(trifluoromethyl)imide

(i) The solution of 4.63 g (19.5 mmol) of $Rb[N(CF_3)_2]$, which was prepared from 2.04 g (19.5 mmol) of RbF and 5.56 g (19.5 mmol) of $CF_3SO_2N(CF_3)_2$ in 20 cm^3 of

dry acetonitrile, was added to the stirred solution of 6.40 g (19.4 mmol) of $[(C_4H_9)_4N][BF_4]$ in 5 cm^3 of dry acetonitrile. The deposit of $Rb[BF_4]$ was filtered off and washed with dry acetonitrile. After removing the solvent in vacuum, 7.5 g of white solid $[(C_4H_9)_4N][N(CF_3)_2]$ was obtained. Yield: 98%, m.p.: 123 – 125 °C. Elemental analysis ,%: C 54.67 , H 9.56 , F 28.70 , N 7.15 ; calculated ,%: C 54.80 , H 9.20 , F 28.90 , N 7.10. ^{19}F NMR spectrum (reference substance: CCl_3F) : -38.3 s (Lock: CD_3CN) ; -37.7 s (Lock: CD_2Cl_2).

(ii) The solution of 0.568 g (2.39 mmol) of $Rb[N(CF_3)_2]$, which was prepared from 0.25 g (2.39 mmol) of RbF and 0.69 g (2.39 mmol) of $CF_3SO_2N(CF_3)_2$ in 2 cm^3 of dry acetonitrile, was added to the solution of 0.66 g (2.37 mmol) of $[(C_4H_9)_4N]Cl$ in 1 cm^3 of dry acetonitrile. The deposit of RbCl was filtered off and washed with dry acetonitrile. After removing of the solvent in vacuum, 0.77 g of a white solid $[(C_4H_9)_4N][N(CF_3)_2]$ was obtained. Yield: 82 %. ^{19}F NMR spectrum of this material coincides with the spectrum of the salt obtained in the previous experiment.

Tetrabutylphosphonium bis(trifluoromethyl)imide

The solution of 0.62 g (2.61 mmol) of $Rb[N(CF_3)_2]$, which was prepared from 0.273 g (2.61 mmol) of RbF and 0.75 g (2.63 mmol) of $CF_3SO_2N(CF_3)_2$ in 2 cm^3 of dry acetonitrile, was added to the solution of 0.883 g (2.60 mmol) of $[(C_4H_9)_4P]Br$ in 1 cm^3 of dry acetonitrile. The deposit of RbBr was filtered off and washed with

dry acetonitrile. After removing the solvent in vacuum, 0.97 g of a white solid $[(C_4H_9)_4P][N(CF_3)_2]$ was obtained. Yield: 91 %, m.p.: 85-86 °C. ^{19}F NMR spectrum (lock: CD_3CN, reference substance: CCl_3F), ppm: -36.5 s.

Triphenyl-benzyl-phosphonium bis(trifluoromethyl)imide

The solution of 0.522 g (2.20 mmol) of $Rb[N(CF_3)_2]$, which was prepared from 0.23 g (2.20 mmol) of RbF and 0.63 g (2.21 mmol) of $CF_3SO_2N(CF_3)_2$ in 3 cm^3 of dry acetonitrile, was added to the suspension of 0.84 g (2.16 mmol) of $[Ph_3(PhCH_2)P]Cl$ in 1 cm^3 of dry acetonitrile and the mixture was stirred during 10 min at room temperature. The deposit of RbCl was filtered off and washed with dry acetonitrile. After removing the solvent in vacuum, 0.96 g of a white solid $[Ph_3(PhCH_2)P][N(CF_3)_2]$ was obtained. Yield: 88 %, m.p.: 114-115 °C. ^{19}F NMR spectrum (lock: CD_3CN, reference substance: CCl_3F), ppm : -36.66 s.

All another $[N(CF_3)_2]$-salts with different organic cations can be obtained in the similar way.

Reaction of $CF_3SO_2N(CF_3)CF_2H$ with RbF

To the solution of 0.114 g (0.426 mmol) of $CF_3SO_2N(CF_3)CF_2H$ in 0.5 cm^3 of dry acetonitrile-d_6 0.010 g (0.010 mmol) of RbF was added at room temperature. The reaction mixture was investigated by NMR spectroscopy.

The main product is CF_3-N=CH-$N(CF_3)CF_2H$.

^{19}F NMR spectra (lock acetone-d_6, standard CCl_3F), δ, ppm: −57.9 s (CF_3); −60.9 s (CF_3); −57.9 s (CF_3). : −104.6 bs (CF_2H)

^{1}H NMR spectra (lock acetone-d_6, standard TMS), δ, ppm: 7.3 tq (CF_2H, $^{2}J_{H,F}$ =57 Hz, $^{4}J_{H,F}$ =1 Hz); 8.4 s (CH).

Reaction of tetramethylammonium bis(trifluoromethyl)imid with ethylsulfonylchloride.

To the solution of 10.08 g (44.64 mmol) $[Me_4N][N(CF_3)_2]$ in 10 cm^3 of dry CH_2Cl_2 5.73 g (44.64 mmol) of ethylsulfonylchloride was added. The reaction proceeds within few minutes. The mixture was kept stirred for 15 min. After, all volatile products was distilled off in vacuum (0.1 mm Hg) at 130 °C and collected in trap cooled with liquid nitrogen. Trap was warmed up to the room temperature, dichloromethane was distilled off and ethylsulfonylfluoride was redistilled. 4.65 g of pure ethylsulfonylfluoride was obtained. B.p. 76-78 °C. Yield 93 %.

Application of bis(trifluoromethyl)imides for introduction of the $N(CF_3)_2$ - group into organic compounds:

Reaction of rubidium bis(trifluoromethyl)imid with ethyl bromoacetate.

To the solution of $Rb[N(CF_3)_2]$ which was obtained from 2.185 g (20.9 mmol) of RbF and 6.127 g (21.5 mmol) of $CF_3SO_2N(CF_3)_2$ in dry acetonitrile 3.13 g (18.7 mmol) of $BrCH_2COOC_2H_5$ was added. The mixture was kept boiling for one hour

and subsequently treated with water. The water insoluble liquid material was collected, washed with water and dried with $MgSO_4$. After distillation 2.73 g of pure $(CF_3)_2NCH_2COOC_2H_5$ was obtained. Yield 61%, b. p. 127-128 ^oC[4].

^{19}F NMR spectra (lock acetone-d_6, standard CCl_3F), δ, ppm: −57.0 s ($2CF_3$).

^1H NMR spectra (lock acetone-d_6, standard TMS), δ, ppm: 4.3 s (CH_2).

Reaction of tetrabutylammonium bis(trifluoromethyl)imid with ethyl bromoacetate.

To the solution of 0.837 g (2.12 mmol) of $[(C_4H_9)_4N][N(CF_3)_2]$ in 2 cm^3 of dry dichloromethane 0.271 g (1.62 mmol) of the ethyl bromoacetate, $BrCH_2COOC_2H_5$, was added and the reaction mixture refluxed for 2 h. After addition of water the organic layer was extracted with three portions (10 cm^3) of dichloromethane. The extract was dried with $MgSO_4$ and solvent was distilled off. The remaining product, $(CF_3)_2NCH_2COOC_2H_5$, was identified by GC. Yield: 93%.

Reaction of ethyl bis(trifluoromethyl)aminoacetate with hydrazine hydrate.

To the solution of 0.715 g (2.99 mmol) of $(CF_3)_2NCH_2C(O)OC_2H_5$ in isopropanol 0.5 g hydrazine hydrate (9.98 mmol) was added. The mixture was kept boiling during three hours. Isopropanol was distilled off in vacuum (0.1 mm Hg) and the residue was recrystallized from benzene. 0.600 g of $(CF_3)_2NCH_2C(O)NN\text{-}NH_2$ was obtained. Yield: 89 %. M.p.=113-114 °C

^{19}F NMR spectra (lock $CDCl_3$, standard CCl_3F), ppm: -59.7 s, (CF_3).

^{1}H NMR spectra (lock $CDCl_3$, standard TMS), δ, ppm: 3.69 bs (NH); 3.93 s (CH_2); 7.76 bs (NH_2)

Reaction of $(CF_3)_2NCH_2C(O)NH\text{-}NH_2$ with p-nitrobenzaldehyde.

To the solution of 0.220 g (0.98 mmol) of $(CF_3)_2NCH_2C(O)NH\text{-}NH_2$ in 2 cm^3 of hot benzene 0.150 g (0.99 mmol) of p-nitrobenzaldehyde was added. The mixture was kept boiling during one hour. The yellow crystals were precipitated after cooling down the reaction mixture to the room temperature. 0.350 g of $(CF_3)_2NCH_2C(O)NH\text{-}N{=}CH\text{-}C_6H_4\text{-}NO_2$ was obtained. Yield 100% M.p. 195 °C

^{19}F NMR spectra (lock acetone-d_6, standard CCl_3F), δ, ppm: −56.8 s (CF_3).

^{1}H NMR spectra (lock acetone-d_6, standard TMS), δ, ppm: 4.756 s (CH_2); 7.96 d (2H); 8.17 s (CH); 8.22 d (2H); 10.86 bs (NH).

Reaction of rubidium bis(trifluoromethyl)imid with benzyl bromide.

To the solution of $Rb[N(CF_3)_2]$ which was obtained from 0.882 g (8.44 mmol) of RbF and 2.5 g (8.77 mmol) of $CF_3SO_2N(CF_3)_2$ in 7 cm^3 of dry acetonitrile 1.27 g (7.4 mmol) of $C_6H_5CH_2Br$ was added. The mixture was kept boiling for one hour and subsequently treated with water. The water insoluble liquid material was extracted with diethylether (3×25 cm^3), washed with water and dried with $MgSO_4$. After distillation 1.35 g of pure $C_6H_5CH_2N(CF_3)_2$ was obtained. Yield 75%, b.p. 151-152 ^oC.

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), δ, ppm: −56.8 t (CF_3, $^4J_{H,F}$ =1.5 Hz).

^1H NMR spectra (lock CD_3CN, standard TMS), δ, ppm: 4.5 q (CH_2)

The reaction of $Rb[N(CF_3)_2]$ with benzyl chloride was done in the same way as described above, except that the reaction mixture was kept boiling for 10 hours.

Reaction of rubidium bis(trifluoromethyl)imid with methyliodide.

To the solution of $Rb[N(CF_3)_2]$, which was obtained from 0.189 g (1.81 mmol) of RbF and 0.530 g (1.86 mmol) of $CF_3SO_2N(CF_3)_2$ in 3 cm^3 of dry acetonitrile 0.250 g (1.76 mmol) of CH_3I was added. The mixture was stirred at room temperature for 30 min. The yellow precipitate was filtered off and solution was examined by NMR spectroscopy. Yield of $(CF_3)_2NCH_3$ was 90 % (NMR data). Solution was diluted with water and extracted with CD_2Cl_2 (0.5 cm^3).

^{19}F NMR spectra (lock CD_2Cl_2, standard CCl_3F), ppm: -61.25 s, ($2CF_3$).

^1H NMR spectra (lock CD_2Cl_2, standard TMS), ppm: 2.90 hep ($2CH_3$, $^4J_{H,F}$ = 1.3 Hz).

Reaction of rubidium bis(trifluoromethyl)imid with 2,4-dinitrofluorobenzene.

To the solution of $Rb[N(CF_3)_2]$ which was obtained from 0.304 g (2.91 mmol) of RbF and 0.850 g (2.98 mmol) of $CF_3SO_2N(CF_3)_2$ in 2 cm^3 of dry acetonitrile 0.258 g (1.39 mmol) of 2,4-dinitrofluorobenzene was added. The mixture was kept under reflux for 6 hours and was examined by ^{19}F NMR spectroscopy. It was the mixture

of 2,4-dinitrofluorobenzene and 2,4-dinitro-N,N-bistrifluoromethylaniline (ratio 1:2).

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -55.16 s, ($2CF_3$).

Reaction of rubidium bis(trifluoromethyl)imid with 4-cyanophenyltriflate.

To the solution of $Rb[N(CF_3)_2]$ which was obtained from 0.112g (1.07 mmol) of RbF and 0.320 g (1.12 mmol) of $CF_3SO_2N(CF_3)_2$ in 2 cm^3 of dry acetonitrile 0.270 g (1.08 mmol) of 4-cyanophenyltriflate was added. The mixture was kept stirred during 1 hour and acetonitrile was distilled off in vacuum (0.1 mm Hg). The rest, white solid material, after dissolving in dry CH_2Cl_2 was filtered and after evaporation of the dichloromethane 0.191 g of white solid material left. It was examined by ^{19}F NMR spectroscopy:

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -54.0 s, (CF_3).

^{1}H NMR spectra (lock CD_3CN, standard TMS), ppm: 8.13 d (2CH, $^{3}J_{H,H}$ = 9.3 Hz); 8.24 d (2CH, $^{3}J_{H,H}$ = 9.3 Hz).

It was found (after determination of the crystal structure) that this material corresponds to the following formula: CF_3-N=C(-O-C_6H_4-CN)$_2$. Yield: 54 %.

Reaction of tetrabutylammonium bis(trifluoromethyl)imid with ethyl 2-(trifluoromethyl-sulfonyloxy)propionate.

To the solution of 3.2 g (11.35 mmol) $[Et_4N][N(CF_3)_2]$ in 15 cm^3 of dry CH_2Cl_2 2.18 g (8.72 mmol) of ethyl 2-(trifluoromethyl-sulfonyloxy)propionate was added.

The reaction proceeds within few minutes exothermically. The mixture was kept stirred for 15 min. After, all volatile products was distilled off in vacuum (0.1 mm Hg) at 130 °C and collected in trap cooled with liquid nitrogen. Trap was warmed up to the room temperature, dichloromethane was distilled off and 2.05 g of pure ethyl 2-(bis(trifluoromethyl)amino)propionate left. Yield 93 %.

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -54.2 s, (CF_3).

^{1}H NMR spectra (lock CD_3CN, standard TMS), ppm: 1.26 t (CH_3, $^{3}J_{H,H}$ = 7 Hz); 1.56 d (CH_3, $^{3}J_{H,H}$ = 7 Hz); 4.21 m (CH); 4.49 q (CH_2, $^{3}J_{H,H}$ = 7 Hz).

Reaction of tetrabutylammonium bis(trifluoromethyl)imid with 2-bromacetophenone.

To the solution of 4.48 g (11.37 mmol) $[Bu_4N][N(CF_3)_2]$ in 50 cm^3 of dry CH_2Cl_2 2.18 g (10.95 mmol) of 2-bromacetophenone was added. The mixture was kept stirred for 3 hours. After, all volatile products was distilled off in vacuum (0.1 mm Hg) at 130 °C and collected in trap cooled with liquid nitrogen. Trap was warmed up to the room temperature, dichloromethane was distilled off and 2.67 g of pure bis(trifluoromethyl)aminoacetophenone left. Yield 90 %.

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -55.9 s, (CF_3).

^{1}H NMR spectra (lock CD_3CN, standard TMS), ppm: 4.92 s (CH_2); 7.54-7.67-7.97 m (6H, Ph)

Reaction of tetrabutylammonium bis(trifluoromethyl)imid with Ph-CH=CH-CH_2Br.

To the solution of 3.27 g (8.29 mmol) $[Bu_4N][N(CF_3)_2]$ in 5 cm^3 of dry CH_2Cl_2 1.47 g (8.03 mmol) of Ph-CH=CH-CH_2Br was added. The mixture was kept stirred for 4 hours. After, all volatile products was distilled off in vacuum (0.1 mm Hg) at 110 °C and collected in trap cooled with liquid nitrogen. Trap was warmed up to the room temperature, dichloromethane was distilled off and 1.98 g of pure 1-Phenyl-3-bis(trifluoromethyl)amino-prop-1-en left. Yield 97% .

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -56.3 s, (CF_3).

^{1}H NMR spectra (lock CD_3CN, standard TMS), ppm: 4.09 s (CH_2); 6.66 d (CH, $^3J_{H,H}$=16 Hz); 6.26 dt (CH, $^3J_{H,H}$=16 Hz; $^3J_{H,H}$=6 Hz); 7.26-7.43 m (6H, Ph)

Reaction of tetrabutylammonium bis(trifluoromethyl)imid salt with Br-CH_2-CH=CH-CH_2-Br

To the solution of 4.86 g (12.33 mmol) $[Bu_4N][N(CF_3)_2]$ in 25 cm^3 of dry CH_2Cl_2 1.19 g (5.56 mmol) of BrCH_2-CH=CH-CH_2Br (predominantly *trans*-form) was added. The mixture was kept stirred for 7 hours. After, all volatile products was distilled off in vacuum (0.1 mm Hg) at 100 °C and collected in trap cooled with liquid nitrogen. Trap was warmed up to the room temperature, dichloromethane was distilled off and 1.81 g of pure 1,4-di[bis(trifluoromethyl)amino]but-2-en left. Yield 91 % .

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -56.2 s, (CF_3).

^{1}H NMR spectra (lock CD_3CN, standard TMS), ppm: 4.09 m (CH_2); 5.85 m (CH).

Electrochemical synthesis with $[Bu_4N][N(CF_3)_2]$

Electrochemical oxidation of $[Bu_4N][N(CF_3)_2]$ in presence of naphthalene was carried out in an divided cell equipped with a platinum cathode and glassy carbon anode. The cell was charged with 30 cm^3 of acetonitrile solution containing 1.3 g tetrabutylammonium tetrafluoroborate, 1.58 g (4.0 mmol) of $[Bu_4N][N(CF_3)_2]$ and 0.171 g (1.3 mmol) naphthalene was added to the cell. Before electrolysis, the oxygen in the system was removed by passing argon through the solution. After that, the stirred mixture was electrolyzed by supplying regulated DC power at 10 mA/cm^2 until 2 F/mole has been passed through the cell. Acetonitrile was distilled off, and dry rest was sublimed in vacuum (0.1 mm Hg) and collected in trap cooled with liquid nitrogen. Collected white crystals 0.07 g (yield 18 %) was examined by ^{19}F NMR spectroscopy.

^{19}F NMR spectra (lock CD_3CN, standard CCl_3F), ppm: -55.7 s, ($2CF_3$).

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