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Comparative fluorination of *N,N*-dialkylamidosulfonyl halides

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Abstract

N,N-Bis(trifluoromethyl)amidosulfonyl fluoride and lower fluorinated analogues can be obtained by electrochemical fluorination as well as by CoF_3-fluorination of *N,N*-dimethylamidosulfonyl fluoride or chloride. The CoF_3 process is especially useful for the synthesis of lower fluorinated compounds. The new compounds are potential insecticides.

Keywords: Fluorination; *N,N*-Dialkylamidosulfonyl halides; NMR spectroscopy; Electrochemical fluorination; Cobalt trifluoride

1. Introduction

The electrochemical fluorination in anhydrous HF (ECF, Simons' process) has proved to be a one-step synthesis of perfluorinated, functionalized organic compounds, used in large-scale industrial production [1]. A variety of organic compounds with different heteroatoms have been successfully fluorinated by ECF, e.g. compounds with C–O, C–S, C–N, C–P, C–As and C–Sb bonds [2]. However, *N,N*-disubstituted amidosulfonyl halides, i.e. compounds with an S–N bond, have not been subject to ECF.

Fluorination by means of CoF_3, another well-established perfluorination method, is nearly exclusively used for the fluorination of hydrocarbons, i.e. for compounds having neither functional groups nor heteroatoms [3]. Only a few papers or patents deal with the CoF_3-fluorination of compounds of the latter type, e.g. of amines [4] or fluorinated amines [5], but *N,N*-disubstituted amidosulfonyl halides have not been subject to CoF_3-fluorination.

Thus it was an interesting task to use comparatively ECF as well as CoF_3 for the fluorination of *N,N*-dimethylamidosulfonyl fluoride and *N,N*-dimethylamidosulfonyl chloride, respectively. The results of these investigations are reported here.

2. Results and discussion

The results of ECF as well as CoF_3 fluorination are shown in Table 1. The ECF of *N,N*-dimethylamidosulfonyl fluoride (**1**) resulted with moderate yield of a crude product consisting mainly of *N,N*-bis(trifluoromethyl)amidosulfonyl fluoride (**2**) (total yield varying from 20% to 30%), a highly volatile substance, b.p. 32–33 °C, besides some *N*-trifluoromethyl-*N*-difluoromethylamidosulfonyl fluoride (**3**), b.p. 52–53 °C and *N,N*-bis(difluoromethyl)amidosulfonyl fluoride (**4**), b.p. 86–88 °C. In addition, gaseous decomposition products were formed, such as SO_2F_2, NF_3, CF_4 and $(CH_xF_{3-x})(CH_yF_{3-y})NF$, as expected. Compounds **2–4** could be separated by distillation and characterized individually by ^{19}F NMR (**2**, **3**, **4**) and ^1H NMR (**3**, **4**) spectroscopy and by elemental analysis. Tentative electrofluorination of *N,N*-dimethylamidosulfonyl chloride (**6**) yielded principally the same spectrum of products; hence the ECF was not studied in detail.

Fluorination of **1** over CoF_3 at 300–350 °C yielded a crude product whose composition was very similar to that obtained by ECF. However, at lower fluorination temperature, i.e. at 200–250 °C, compounds fluorinated to a lower extent became dominant, with compound **4** now being the main product and with substantial formation of *N*-difluoromethyl-*N*-fluoromethylamidosulfonyl fluoride (**5**). With compound **6** as substrate, fluorination over CoF_3 gave results which were nearly identical to those of compound **1** at the same respective tem-

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Table 1
Products from ECF and CoF_3 fluorination of *N,N*-dialkylamidosulfonyl halides

Educt	Products	Yield (%)		
		By ECF	By CoF_3 at 200–250 °C	By CoF_3 at 300–350 °C
$(CH_3)_2NSO_2F$ (**1**)	$(CF_3)_2NSO_2F$ (**2**)	31	5.9	44
	$CF_3(CHF_2)NSO_2F$ (**3**)	8	6.6	12
	$(CHF_2)_2NSO_2F$ (**4**)	4	38.5	4
	$CHF_2(CH_2F)NSO_2F$ (**5**)	–	11.9	–
$(C_2H_5)_2NSO_2F$ (**7**)	$(C_2F_5)_2NSO_2F$ (**8**)	10	–	

Table 2
Biological activity of polyfluoro-*N,N*-dimethylfluorosulfonamides

Compound	LC_{50} (g l^{-1})				LD_{50} (mg kg^{-1})
	Grain louse	House fly	Rice beetle	Spider mite	Mouse
$(CF_3)_2NSO_2F$	0.0453	0.0077	0.1130	0.1700	500
CF_3, CHF_2 > N–SO_2F	0.0910	0.0500	–	0.1100	800
$(CHF_2)_2NSO_2F$	0.0340	0.0065	0.0442	0.0310	1000
$C_2H_4Cl_2$	0.0430	0.0160	0.0470	0.0650	–
CH_3SO_2F	0.0001	0.00072	0.01	0.0038	3.5

peratures, both in terms of the product spectra and the overall yields.

Fluorination of *N,N*-diethylamidosulfonyl fluoride (**7**) corresponds to that of the dimethyl compound **1**. Whereas ECF gave predominantly the perfluoro product *N,N*-bis(pentafluoroethyl)amidosulfonyl fluoride (**8**) in about 10% yield, fluorination over CoF_3 at moderate temperature (200–250 °C) gave, however, a complex mixture of fluorinated amidosulfonyl fluorides not containing the perfluoro compound **8**.

The new class of compounds was evaluated concerning its biological activity against insects. Compounds **2**, **3** and **4** were tested in comparison with 1,2-dichloroethane and methylsulfonyl fluoride, against grain louse, house fly, rice beetle and spider mite; in addition, their toxicity against mice was determined. The results given in Table 2 show that of the three amidosulfonyl fluorides tested, compound **4**, i.e. the one with the lowest degree of fluorination, exhibits the highest activity against insects, but only about one-tenth that of methylsulfonyl fluoride. However, its toxicity against warm-blooded animals is the lowest, about 0.3% of that of methylsulfonyl fluoride. Thus, as for possible biological application, the partially fluorinated dimethylamidosulfonyl fluoride is superior to the fully fluorinated one.

The successful perfluorination of different *N,N*-dialkylamidosulfonyl fluorides as well as chlorides by both ECF and CoF_3 indicates an unexpected stability of the S–N bond under these oxidative fluorinative conditions. Likewise, the results demonstrate the broad applicability of both methods for the perfluorination even of compounds bearing such functional groups.

On the other hand, the differences in the results obtained with CoF_3 at higher or lower temperature, respectively, show that this method is more flexible compared to ECF in terms of the predominant synthesis of partially fluorinated compounds. This means that, in principle, the CoF_3 process offers the possibility of adjusting the extent of fluorination within certain limits simply by varying the reaction temperature. Thus, CoF_3 fluorination at moderate temperature opens a new access to partially fluorinated compounds, whose properties can sometimes be even more valuable than those of the respective perfluorinated ones.

3. Experimental details

The ECF cell used has already been described [6]. ECF was carried out at about 10 °C, the reflux condenser being maintained at −20 °C and followed by three traps maintained at −20 °C, −50 °C and −78 °C, respectively. When the ECF process had finished, the traps were warmed to 0 °C, their contents combined together with any product drained from the cell and freed from HF by separation of the organic layer followed by its repeated distillation over NaF pellets. The product mixtures obtained were fractionally distilled and the components individually analyzed or the mixtures characterized by GC and NMR methods.

Fluorinations by CoF_3 were done in a conventional [3] horizontal nickel tube-type reactor of 1 m length, filled with 3 kg CoF_3 to about one-half of its volume, and fitted with a central horizontal paddle shaft to stir the CoF_3 gently. The substrate was introduced as a vapour by means of an additional stream of nitrogen (20 l h^{-1}). The CoF_3 reactor was heated in a manner designed to maintain a temperature gradient along the tube with the lower temperature at the inlet side. The gas stream from the reactor (N_2, vapour of products and possibly unreacted substrate) was passed through three traps, kept at 50 °C, −20 °C and −78 °C, respectively. After the fluorination reaction, the condensates from the traps were freed from HF and fractionally distilled. The products obtained were characterized by ^{19}F and ^{1}H NMR spectroscopy.

^{19}F and ^{1}H NMR spectra were measured with a Bruker WP 200 instrument, using F-11 and TMS, respectively, as external references, ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 75.4 MHz, with HMDS as internal reference. Gas chromatography was done with a Varian 3700 GC instrument using packed columns (10% FS 16 on N-AW-DMCS, 3.7 mm) or on a Varian 3400 capillary GC (60 m capillary coated with DB 5 silicon phase).

3.1. ECF of compound 1

N,N-Dimethylamidosulfonyl fluoride (104 g) was added in four portions (39.2 g at the beginning, 20.4 g after 107.5 A h, 27.6 g after 157 A h, 16.8 g after 218.4 A h) to 500 ml of anhydrous HF in the ECF cell. Electrolysis was complete after passage of 250 A h through the cell. From the cooling traps 85 g of crude product were obtained, which were distilled to give five fractions: (i) (70%) b.p. 29–35 °C; (ii) (5%) b.p. 35–45 °C; (iii) (15%) b.p. 45–50 °C; (iv) (4%) b.p. 50–75 °C; and (v) (5%) b.p. 75–100 °C. According to GC, fraction (i) consisted mainly (85%–90%) of compound **2**, fraction (ii) of **2** (32%) and **3** (53%), fraction (iii) of **3** (85%) and **4** (10%), fraction (iv) of **3** (40%) and **4** (50%), and fraction (v) of **4** (75%). Compounds **2–4** were separated in more than 95% concentration by further distillation. Besides these compounds, gaseous fluorinated cleavage products such as NF_3, CF_4, SO_2F_2 were found in the H_2 stream leaving the cell, but these amounts were not determined.

Compound **2**: b.p. 32–33 °C. Analysis for $C_2F_7NSO_2$: Calc.: F, 56.57; N, 5.96%. Found: F, 56.45; N, 5.48%. ^{19}F NMR δ: −53.23 (d, $J_{F,F}$ = 5.9 Hz, 6F, CF_3); 62.05 (m, $J_{F,F}$ = 5.9 Hz, 1F, SO_2F) ppm.

Compound **3**: b.p. 52–53 °C. ^{19}F NMR δ: 61.12 (m, J = 6 Hz, 1F, SO_2F); −53.5 (m, 3F, CF_3); −97.1 (dm, $J_{F,F}$ = 6 Hz, $J_{H,F}$ = 54.5 Hz, 2F, CHF_2) ppm. ^{1}H NMR δ: 7.68 (tm, $J_{H,F}$ = 54.6 Hz, 1H, CHF_2) ppm. ^{13}C NMR δ: 117.8 (q, $J_{C,F}$ = 271 Hz, CF_3); 110.5 (t, $J_{C,F}$ = 262 Hz, CHF_2) ppm.

Compound **4**: b.p. 86–88 °C. Analysis for $C_2H_2F_4NSO_2F$: Calc.: C, 12.07; H, 1.00; F, 42.71%. Found: C, 12.61; H, 1.03; F, 41.27%. ^{19}F NMR δ: 61.05 (t, $J_{H,F}$ = 6.6 Hz, 1F, SO_2F); −97.04 (dh, $J_{H,F}$ = 56.7 Hz, $J_{H,F}$ = 6.6 Hz, 4F, CHF_2) ppm. ^{1}H NMR δ: 7.5 (tt, $J_{H,F}$ = 56.7 Hz, $J_{H,F}$ = 6.6 Hz, 2H, CHF_2) ppm. ^{13}C δ: 109.53, 109.51 (diastereotopic groups of triplets, both $J_{C,F}$ = 259 Hz, CHF_2) ppm.

N,N-Dimethylamidosulfonyl chloride (**6**) yielded under similar conditions a crude product with a GC composition nearly identical to those derived from the ECF of **1**.

Likewise, *N,N*-diethylamidosulfonyl fluoride (**7**) was electrofluorinated (starting with an 8% w/v solution, no further educt added) yielding a mixture of perfluorinated compounds, about 50% of them being *N,N*-bis(pentafluoroethyl)amidosulfonyl fluoride (**8**) (total yield about 10%).

Compound **8** (from the product mixture): ^{19}F NMR δ: 67.3 (ph, $^{4}J_{F,F}$ = 10 Hz, $^{5}J_{F,F}$ = 2.5 Hz, 1F, SO_2F); −81.7 (pd, $^{3}J_{F,F}$ = 5 Hz, $^{5}J_{F,F}$ = 2.5 Hz, 6F, CF_3); −89.6 (dh, $^{4}J_{F,F}$ = 10 Hz, $^{3}J_{F,F}$ = 5 Hz, 4F, CF_2) ppm.

3.2. CoF_3 fluorination of compound 1

At moderate temperature

N,N-Dimethylamidosulfonyl fluoride (90 g) was evaporated over a period of 3 h at 200 °C and the vapour passed through the reactor held at 200 °C (inlet) to 250 °C (outlet). The reactor was purged with N_2 for an additional 30 min. The resulting products (102 g) were condensed, freed from HF by treatment with NaF and fractionally distilled, yielding 5.9% of **2**, 6.6% of **3**, 38.5% of **4** and 11.9% of *N*-(difluoromethyl)-*N*-(fluoromethyl)amidosulfonyl fluoride (**5**).

Compound **5**: b.p. 95–105 °C. ^{19}F NMR δ: 58.7 (m, 1F, SO_2F); −96.5 (dt, $J_{H,F}$ = 56.4 Hz, $J_{F,F}$ = 6.6 Hz, 2F, CHF_2); −172.3 (tq, 1F, CH_2F) ppm. ^{1}H NMR δ: 7.5 (td, $J_{H,F}$ = 56.4 Hz, 1H, CHF_2); 5.9 (dq, $J_{H,F}$ = 56.5 Hz, 2H, CH_2F) ppm. ^{13}C NMR δ: 110.14 (t, $J_{C,F}$ = 256 Hz, CHF_2); 81.59 (d, $J_{C,F}$ = 211 Hz, CH_2F) ppm.

Under similar conditions, 53 g of compound **6** were fluorinated yielding 65 g of crude product, consisting of **2** (13.5%), **4** (47.6%) and **5** (33%).

At higher temperature

Compound **1** (60 g) was fluorinated at 300–350 °C over 2 h, resulting in 75 g of crude product composed mainly of **2** (total yield, 44%), **3** (12%) and **4** (4%).

Fluorination of **6** under like conditions gave similar results while CoF_3 fluorination of **7** at 200–250 °C resulted in a complex mixture of fluorinated compounds, which according to GC and ^{19}F NMR contained no **8** (no further identification of individual compounds was attempted).

3.3. Biological activity testing

The insecticidal activity was measured in serial tests, applying 5, 25, 40, 60, 80, 100 or 150 μl, respectively, of the substance to be tested on a paper strip, which was brought immediately into a hermetically closed glass box containing several petri dishes with about 20–30 test insects in each. After 3 h at 22 °C, the numbers of living and dead insects were counted and compared with those of a control experiment. The toxicity against warm-blooded animals was determined with mice as test animals by intramuscular injections

of increasing amounts of the substances to be tested into groups of mice each. The concentration at which 50% of the mice were killed is the LD_{50} value.

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