Organic compounds bearing a difluoroaminooxy group

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A preparative method for the synthesis of *C*- and *N*-difluoroaminooxy compounds was elaborated. The method involves the reaction of *N,N*-difluoro-*O*-fluorosulfonyl hydroxylamine with the corresponding alkoxides and *N*-oximide salts. It was shown that *N*-difluoroaminooxy compounds can add to olefins at the double bond.

Key words: difluoroamino group, fluorination, difluoroaminooxy compounds, synthesis.

At present, only a few organic compounds containing a difluoroaminooxy group (F_2NO—) are known.[1–4] The main methods of their synthesis are reactions of tetrafluorohydrazine (N_2F_4) or difluoroamine (HNF_2) with fluorooxyperfluoroalkanes,[1,2] perfluorinated hypochlorites and peroxides,[1] as well as reactions of fluorinated olefins with nitrogen trifluoride oxide or its complexes with arsenic, antimony, or boron fluorides.[1,3,4]

Our first attempts to synthesize difluoroaminooxy compounds revealed that the above substances are rather difficult to prepare. Thus, sufficiently pure perfluoro-*tert*-butyl peroxide (**1**) used as the initial reagent was obtained only by the oxidation of perfluoro-*tert*-butyl alcohol with chlorine trifluoride according to the modified procedure.[5]

$$(CF_3)_3COH + ClF_3 \longrightarrow \underset{\mathbf{1}}{[(CF_3)_3CO]_2}$$

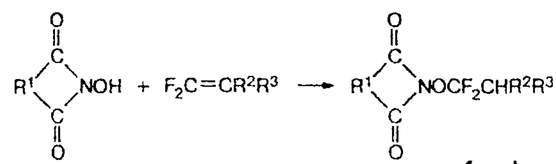
The reaction of peroxide **1** with 50—60% N_2F_4 occurred only under rather drastic conditions (90 °C, pressure ~2 atm, reaction time from 20 to 40 h) to give 2-(difluoroaminooxy)perfluoro-2-methylpropane (**2a**) in 38% yield.

$$\underset{\mathbf{1}}{[(CF_3)_3CO]_2} + N_2F_4 \longrightarrow \underset{\mathbf{2a}}{(CF_3)_3CONF_2}$$

Another possible route to such compounds involves direct fluorination of organic hydroxylamine derivatives with cleavage of the C—N bonds by analogy with the fluorination of Schiff's bases[6] and isocyanates.[7] *O*-Polyfluoroalkyl-substituted oximes **3** and *N*-polyfluoroalkoxy-substituted dicarboximides **4**, whose representatives have been synthesized earlier by addition of fluoroolefins to ketoximes,[8–12] were chosen as the starting compounds. Substituted oximes **3** and oximides **4** were obtained by the reaction of perfluorinated ethylene, propene, isobutene, and oct-1-ene with acetoxime, ethyl α-hydroximinoethyl ether, ethyl cyanohydroximinoacetate, and *N*-hydroxysuccin- and -phthalimides.

$$R^1R^2C{=}NOH + F_2C{=}CFR^3 \longrightarrow \underset{\mathbf{3a-e}}{R^1R^2C{=}NOCF_2CHFR^3}$$

	a	b	c	d	e
R^1	Me	Me	Me	COOEt	Me
R^2	Me	Me	Me	CN	OEt
R^3	F	CF_3	C_6F_{13}	CF_3	C_6F_{13}



4a—d

	a	b	c	d
R^1	CH_2CH_2	CH_2CH_2	CH_2CH_2	*o*-phenylene
R^2	F	CF_3	F	F
R^3	CF_3	CF_3	C_6F_{13}	CF_3

The addition occurred smoothly in DMF at room temperature in the presence of catalytic amounts of NaOH. In the general case, the adduct yield increases in passing from perfluoroethylene to perfluoropropene and perfluoroisobutene in accordance with the activity of the perfluoroolefins in nucleophilic reactions.

Fluorination of compounds **3a—e** and **4a—d** was studied both under heterogeneous conditions (on solid carriers such as NaF or KF) and in organic solvents. These are destructive processes of decomposition of the initial compounds that are predominant under rather drastic conditions of heterogeneous fluorination or when the reaction is carried out in solvents at increased temperatures, the processes being accompanied by cleavage of not only the C—N bonds but possibly also the O—C bonds. This is indirectly evidenced by the large

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number of highly volatile reaction products (GLC) and by their green to blue color characteristic of nitroso compounds. Somewhat less ambiguous results were obtained upon fluorination under milder conditions (−30 to −15 °C, a solution of Freon-113 or a mixture of Freon-113 with acetonitrile in the presence of NaF). However, in this case, the main reaction pathway is also fluorination of the hydrocarbon fragment of the initial molecule rather than the C—N bond (^{19}F NMR). It was shown with acetone *O*-(2-hydroperfluoropropyl)oxime (**3b**) as an example that the reaction under these conditions yields a mixture containing three main products with boiling points close to one another. Two of them were isolated by preparative GLC and identified as 1-fluoro- (**5**) and 1,1-difluoropropanal *O*-(2-hydrohexafluoropropyl)oximes (**6**).

$$Me_2C{=}NOCF_2CHFCF_3 \xrightarrow{F_2} \rightarrow FCH_2C(Me){=}NOCF_2CHFCF_3 + F_2CHC(Me){=}NOCF_2CHFCF_3$$
5 **6**

This rather mild substitution of fluorine atoms for the hydrogen atoms of the methyl group may be explained by the imine-enamine tautomerism known for similar compounds:

$$H_3\overset{Me}{\overset{|}{C}}{=}NOCF_2CHFR_F \rightleftharpoons H_2C{=}\overset{Me}{\overset{|}{C}}NHOCF_2CHFR_F$$

R_F = F, CF_3, C_6F_{13}

In particular, this is evidenced by a low-intensity signal at δ 7.5—7.7 in the ^{1}H NMR spectra of compounds **3a—c** and **4a—d**.

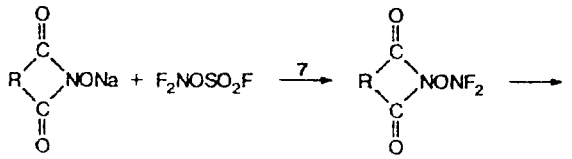
It is known[13] that addition of fluorine at the C=C double bond occurs quite vigorously even under the mildest conditions, and subsequent elimination of HF may result in the observed compounds **5** and **6**.

In connection with this, we further studied *N*,*N*-difluoro-*O*-(fluorosulfonyl)hydroxylamine (F_2NOSO_2F) as a possible reagent for oxydifluoroamination of organic compounds. Earlier, this hydroxylamine had been successfully used in electrophilic *C*-[14,15] and *N*-difluoroamination.[16,17] It was established that treatment of sodium and lithium 1,1,3-trihydroperfluoroalkoxides (C_3—C_5) and perfluoro-*tert*-butoxide in a mixture of solvents (CH_2Cl_2—MeCN, 1 : 1 and 1 : 2, by volume), which allows one to difluoroaminate salts of nitro compounds,[16] results only in disproportionation of F_2NOSO_2F into FNO and SO_2F_2 even at $T < 0$ °C. The spectra of reaction products showed only fluorosulfates of the corresponding alcohols. Attempts to change the direction of process by replacing alkoxides by a mixture of fluorinated alcohol with pyridine, Et_3N, pyridine *N*-oxide, and $Et_3N{\rightarrow}O$ resulted, in the case of pyridine and Et_3N, in a similar decomposition. In the presence of *N*-oxides, the reaction did not occur, the reagents being recovered virtually unconsumed. Attention was attracted to the high stability and the good solvent action of fluorine-containing alcohols with respect to F_2NOSO_2F. That is why, in accordance with an earlier assumption that F_2NOSO_2F may be a much more promising synthetic agent in slightly polar solvents,[16] we tested fluorine-containing ethers, in particular, methyl 2,2,3,3-tetrafluoropropyl ether $MeOCH_2CF_2CHF_2$ (**7**), for difluoroamination of alkoxides. Using ether **7**, we obtained difluoroaminooxy compounds **2a,b** from lithium and sodium perfluoro-*tert*-butoxides in good yields and from lithium *tert*-butoxide in satisfactory yield.

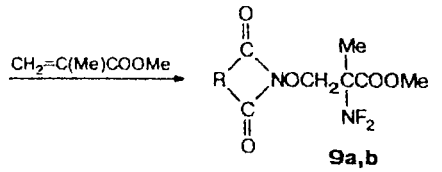
$$(CF_3)_3COLi + F_2NOSO_2F \xrightarrow{7} (CF_3)_3CONF_2$$
2a

$$Bu^tOLi + F_2NOSO_2F \xrightarrow{7} Bu^tONF_2$$
2b

Further, we succeeded in difluoroaminating sodium *N*-hydroxysuccin- and -phthalimide. However, because reaction products **8a,b** containing the $>NONF_2$ group are most likely to be unstable,* they were immediately treated with methyl methacrylate to give addition products **9a,b**, which were finally isolated and identified.



8a,b



9a,b

R = CH_2CH_2 (**a**), *o*-phenylene (**b**)

In conclusion, it should be noted that pure F_2NOSO_2F, unlike tetrafluorohydrazine (N_2F_4) and difluoroamine (HNF_2), is much less sensitive to external factors and thus more preferred.

F_2NOSO_2F can be stored at room temperature in nickel or stainless steel test tubes passivated with F_2 as long as one year and longer. But even when it began to decompose spontaneously into FNO and SO_2F_2,** no dangerous consequences were observed. Usually, its de-

* Earlier,[18] one representative of these compounds, $(CF_3)_2NONF_2$, was described. It remained stable at no higher than −30 °C and decomposed on heating.

** Decomposition indications such as increasing pressure in the test tube and appearance of light blue color upon condensation (−70 °C) in a glass trap seem to be a result of the reaction of FNO with the glass and the formation of nitrogen oxides.

Table 1. The main physicochemical characteristics of the compounds synthesized

Compound	Yield (%)	B.p./°C (*p*/Torr) [M.p./°C]	n_D^{20}	Found / Calculated (%) C	H	F	N	Molecular formula
2a	38.2 (*A*) 70 (*B*)	36—37	1.27	16.51 16.72	—	72.23 72.82	5.07 4.88	$C_4F_{11}NO$
2b	23.6	69—71	—	38.27 38.40	7.38 7.20	29.94 30.40	11.43 11.20	$C_4H_9F_2NO$
3a	12.5	27 (12)	1.3507	34.81 34.69	3.95 4.07	43.23 43.90	8.30 8.09	$C_5H_7F_4NO$
3b	32	51 (30)	1.3460	—	—	—	—	$C_6H_7F_6NO$
3c	22	42—45 (1.5)	1.3305	28.86 27.98	1.58 1.48	63.02 64.21	3.33 2.86	$C_{11}H_7F_{16}NO$
3d	39.5	96—104 (8)	1.3781	31.51 32.85	2.61 2.03	38.41 39.04	8.43 9.58	$C_8H_6F_6N_2O_3$
3e	10	63—70 (4)	1.3375	28.10 28.63	1.62 1.79	58.67 60.44	3.39 2.78	$C_{12}H_9F_{16}NO_2$
4a	80	[57—58]	—	32.51 31.70	2.07 1.89	42.34 43.02	4.89 5.28	$C_7H_5F_6NO_3$
4b	73	[114]	—	31.52 30.48	2.01 1.59	47.60 48.25	4.03 4.44	$C_8H_5F_8NO_3$
4c	20	[76.5]	—	28.46 27.96	0.93 0.97	59.11 59.03	2.74 2.72	$C_{12}H_5F_{16}NO_3$
4d	86	[110]	—	41.93 42.17	1.61 1.60	35.19 36.42	4.36 4.47	$C_{11}H_5F_6NO_3$
5	—	—	1.3482	29.12 29.81	2.91 2.49	—	4.83 5.82	$C_6H_6F_7NO$
6	—	—	1.3351	26.33 27.81	2.08 1.93	—	5.03 5.42	$C_6H_5F_8NO$
9a	26.3	—	—	39.80 40.60	4.20 4.51	14.00 14.29	10.20 10.53	$C_9H_{12}F_2N_2O_5$
9b	72	—	—	50.10 49.68	4.00 3.82	11.90 12.10	8.80 8.92	$C_{13}H_{12}F_2N_2O_5$

composition was completed at room temperature over 2—3 days so that F_2NOSO_2F was not detected by chromatography. Keeping the test tube cooled with solid CO_2 substantially inhibits the process and allows one to use F_2NOSO_2F for synthetic purposes.

However, when mixed with organic compounds, F_2NOSO_2F can easily decompose explosively, as in the case of N_2F_4. Thus, our attempt to add F_2NOSO_2F (like $ClOSO_2F$)[19] to tetrafluoroethylene in the gaseous phase in a glass reactor (earlier,[20] this reaction had been carried out in an autoclave at 98—106 °C) showed that the pressure remains high for 4 days. In the end, when the glass valve connecting the manometer with the reactor containing equimolar amounts of the reagents at nearly atmospheric pressure was turned for the next time, the experiment was over with a blast that destroyed the reactor completely.

The physicochemical and spectral characteristics of the compounds obtained are summarized in Tables 1 and 2, respectively.

Experimental

Caution! Even though compounds ***2a*** *and* ***2b*** *are less sensitive to external factors than similar compounds containing the —$NONF_2$ group, all manipulations involving them and, especially, crude reaction mixtures require corresponding protective measures.*

^{19}F NMR (56.45 MHz, CF_3COOH as the external standard) and ^1H NMR (60 MHz, with respect to Me_4Si) spectra were recorded on a Perkin—Elmer R-20 instrument. The purity of the compounds was checked by GLC on an LKhM-8MD instrument (3000 × 4 mm column, 20% FST-5 on Chromosorb P (80—100 mesh), helium as the carrier gas).

Perfluoro-*tert*-butyl peroxide (1). Perfluoro-*tert*-butyl alcohol (23 g) and chlorine trifluoride (8 g) were placed at −78 °C in a stainless steel autoclave 0.3 L volume evacuated to 1 Torr. The autoclave was gradually heated to 20 °C. Gage pressure was slowly reduced to 1 atm, and then the autoclave was evacuated at 1 Torr with collecting volatile products with b.p. −78 °C in a quartz trap containing calcined KF (10 g). Fractionation gave a colorless liquid (**1**) (12 g, 53%), b.p. 53—54 °C (150 Torr), n_D^{20} 1.28 (*cf.* Ref. 5).

2-(Difluoroaminooxy)perfluoro-2-methylpropane (2a). *A.* Perfluoro-*tert*-butyl peroxide (**1**) (6 g) was placed in a Pyrex reactor 1 L volume evacuated to 1 Torr. Then, a gaseous mixture of N_2F_4 with CO_2 (1 : 1, by volume) was supplied to a pressure of 0.5 atm. The reaction mixture was kept at 20 °C for 170 h, 60 °C for 6 h, 70 °C for 1 h, 80 °C for 2 h, and 90 °C for 34 h. After cooling, the reactor was evacuated at 1 Torr, and the products collected in a trap cooled to −100 °C. Fractionation gave a colorless liquid (**2a**) (1.95 g, 38.2%), b.p. 36—37 °C, compound **1** (1.75 g) being recovered.

Table 2. The ^{19}F and ^{1}H NMR spectral parameters of the compounds synthesized

Compound	^{19}F NMR [a]	^{1}H NMR [b]
	δ (*J*/Hz)	
2a	−3.7 (s, CF_3); −210.9 (br.s, ONF_2)	—
2b	−140 (br.s, ONF_2)	—
3a	15.7 (m, CF_2); 60.9 (dt, CF_2H, $^2J_{H-F}$ = 54, $^3J_{F-F}$ = 6)	1.55 (m, CH_3); 5.6 (t, CHF_2, J_{H-F} = 54)
3c	−2.84 (dm, OCF_2, $^3J_{H-F}$ = 21); 3.85 (t, CF_3, $^3J_{F-F}$ = 6); 40.75, 41.50, 43.02, 45.35 (CF_2); 94.62 (dm, CFH, $^2J_{H-F}$ = 52)	—
3d	−2.21 (m, CF_2); 7.17 (m, OCF_2); 135.60 (dm, CFH, $^2J_{H-F}$ = 45)	2.92 (t, CH_3); 5.20 (q, CH_2); 5.85 (dm, CHF, $^2J_{H-F}$ = 45)
3e	1.12 (dd, OCF_2, $^3J_{H-F}$ = 15, $^3J_{F-F}$ = 6); 4.26 (t, CF_3, $^3J_{F-F}$ = 6); 41.40, 45.82, 46.90, 49.25 (CF_2)	—
4a	−3.99 (m, CF_3); 5.24 (m, OCF_2); 133.36 (dq, CFH, $^2J_{H-F}$ = 41.4, $^3J_{F-F}$ = 10.8)	2.86 (s, CH_2); 5.81 (dq, CHF, $^2J_{H-F}$ = 41.5, $^3J_{H-F}$ = 6)
4b	−14.8 (dt, CF_3, $^3J_{F-F}$ = 10.8, $^3J_{H-F}$ = 7.8); −10.2 (m, OCF_2)	2.86 (s, CH_2); 5.11 (q, CHF, $^3J_{H-F}$ = 7.8)
4c	0.69 (dm, OCF_2, $^3J_{H-F}$ = 10); 3.84 (t, CF_3, $^3J_{F-F}$ = 6); 40.90, 45.35, 46.10, 48.75, (CF_2); 77.41 (m, CFH)	2.86 (s, CH_2); 5.20 (m, CHF)
4d	−5.83 (m, CF_3); −3.98 (m, OCF_2); 96.45 (m, CFH)	—
5	−1.25 (m, CF_3); 7.1 (m, OCF_2); 136.7 (dq, CFH, $^2J_{H-F}$ = 32); 140.7 (t, CFH_2, $^2J_{H-F}$ = 35.3)	1.55, 1.72 (both m, CH_3);[c] 4.30, 4.14 (both dm, CH_2F, $^2J_{H-F}$ = 35.3);[c] 4.60 (dq, CHF, $^2J_{H-F}$ = 32, $^3J_{H-F}$ = 6)
6	−1.22 (m, CF_3); 7.84 (m, OCF_2); 44.64 (d, CHF_2, $^2J_{H-F}$ = 52.6); 137.2 (m, CHF)	1.78 (s, CH_3); 4.56 (dm, CHF, $^2J_{H-F}$ = 32, $^3J_{H-F}$ = 6); 5.47 (t, CHF_2, $^2J_{H-F}$ = 52.6)
9a	−122 (s, NF_2)	—
9b	−120.7 (s, NF_2)	—

[a] CF_3COOH as the external standard.

[b] With respect to Me_4Si.

[c] The double set of signals for the CH_3 and CHF groups in the ^1H NMR spectrum apparently corresponds to *syn*- and *anti*-isomers **5**.

B. F_2NOSO_2F (6.3 g, 0.042 mol) was condensed in a suspension of sodium perfluoro-*tert*-butoxide (10.3 g, 0.04 mol) in 20 mL of methyl 2,2,3,3-tetrafluoropropyl ether (**7**) in an atmosphere of N_2 at −30 °C. The reaction mixture was heated to 22 °C over 1 h, stirred at 22—25 °C for 4 h, and purged with N_2. The organic layer was separated and fractionated to give a colorless liquid (**2a**) (8 g, 70%), b.p. 36—37 °C, n_D^{20} 1.27, d_4^{20} 1.750, the content of the main component >95% (GLC and ^{19}F NMR).

Under similar conditions, 2-(difluoroaminooxy)-2-methylpropane (**2b**) was obtained from sodium *tert*-butoxide in 23.6% yield.

Acetone *O*-(2-hydrohexafluoropropyl)oxime (3b). Hexafluoropropene (0.1 mol) was passed with stirring at ~20 °C through a solution of acetoxime (7.3 g, 0.1 mol) in 60 mL of DMF in the presence of NaOH (2 g). The reaction mixture was kept for 2 h, treated with water, and the products were extracted with ether (2×50 mL). The combined extracts were washed with water (3×50 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Rectification gave compound **3b** (7.1 g) as a colorless liquid (*cf.* Ref. 11).

Compounds **3a**, **3c—e**, and **4a—d** were obtained under similar conditions.

Fluorination of acetone *O*-(2-hydrohexafluoropropyl)oxime (3b). A mixture of F_2+He (30 vol. % F_2) was passed with stirring at −20 to −15 °C through a solution of compound **3b** (16 g, 0.07 mol) in 100 mL of Freon-113 in the presence of NaF (60 g) at a rate of 3.5 L h^{-1} for 5 h. Then, the reaction mixture was purged with N_2 and heated to room temperature. The precipitate was filtered off, and the filtrate was concentrated *in vacuo* to give a light blue liquid (9.9 g) containing seven components (GLC). Two main compounds, 1-fluoropropanal *O*-(2-hydrohexafluoropropyl)oxime (**5**) and 1,1-difluoropropanal *O*-(2-hydrohexafluoropropyl)oxime (**6**), were isolated by preparative chromatography on a PAKhV-03 chromatograph (column 1500 × 8 mm, 20% FST-5 on Chromosorb P (80—100 mesh), helium as a carrier gas).

Methyl 2-difluoroamino-2-methyl-3-(succinimidooxy)-propionate (9a). F_2NOSO_2F (4.5 g, 0.03 mol) was added to sodium *N*-hydroxysuccinimide (4.1 g, 0.03 mol) in 40 mL of methyl 2,2,3,3-tetrafluoropropyl ether (**7**) in an atmosphere of He at 0—5 °C over 1 h. The reaction mixture was kept at 20 °C for 6 h and purged with He. The precipitate was filtered off, and a solution of a freshly prepared methyl methacrylate (3 g, 0.03 mol) in 6 mL of ether **7** was added to the filtrate. The resulting solution was kept at 20 °C for 12 h, and the precipitate was filtered off. The filtrate was concentrated to give a highly viscous oil (**9a**) (2.1 g, 26.3%).

Methyl 2-difluoroamino-2-methyl-3-(phthalimidooxy)-propionate (**9b**) was obtained under similar conditions.

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