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THE ADDITION OF NITROSYL FLUORIDE TO FLUORO-OLEFINES

THE REACTION MECHANISM

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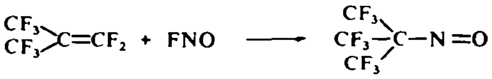
Abstract—The addition of nitrosyl fluoride to fluoro-olefines in tetramethylenesulphone has been investigated. In the fluoro-olefines series the reaction mechanism reverses: the addition of nitrosyl fluoride to fluoro derivatives of ethylene proceeds by an electrophilic mechanism while the addition to higher fluoro-olefines is a nucleophilic reaction.

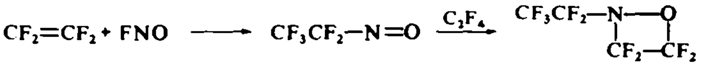
The reaction of nitrosyl fluoride with perfluoropropylene occurs only at 140–150° vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, hexafluoropropylene and perfluoroisobutylene. In these reactions only perfluoroisobutylene proved capable of smooth addition of nitrosyl fluoride giving tertiary nitrosoperfluoroisobutane:



$$(CF_3)_2C{=}CF_2 + FNO \longrightarrow (CF_3)_3C{-}N{=}O$$

The reaction of nitrosyl fluoride with perfluoropropylene occurrs only at 140–150° in presence of activated carbon impregnated by calcium sulfate. The yield of 2-nitrosoperfluoropropane $(CF_3)_2CFN{=}O$, was small since under these conditions homolytic nitration of perfluoropropylene by nitrogen oxides takes place.

Tetrafluoroethylene in the presence of $CaSO_4/C$ reacts with FNO at 70–80 giving perfluoro-N-ethyloxazetidine:



The hydrogen-containing fluoro-olefines $CF_2{=}CHF$ and $CF_2{=}CH_2$ react with nitrosyl fluoride at room temperature in inert solvents yielding in the first case trifluoroacetaldehyde, trifluoroacetic acid and perfluoronitrosoethane and in the second case— a substance, whose structure was assigned as $CF_3CH_2\overline{N{-}O{-}N(OH){-}C}HCF_3$. All these reactions were performed in an autoclave. Barr and Haszeldine[2] found that the reaction of FNO an $CF_2{=}CF_2$ in a sealed glass tube at room temperature gave, together with oxazetidine, the products of homolytic nitration by nitrogen oxides, i.e. 1,2-dinitrotetrafluoroethane and difluoronitro acetyl fluoride. Later the reaction

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[1] I. L. Knunyants, E. G. Bychovskaya, V. N. Frosin and Ya. M. Kisel, *Dokl. Akad. Nauk SSSR* **132**, 123 (1960).

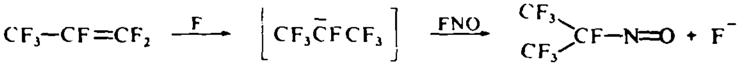
[2] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.* 1151 (1960).

of nitrosyl fluoride with tetrafluoroethylene, hexafluoropropylene and perfluoroisobutylene was investigated by Andreades[3] whose results in principle confirm the data obtained previously [1,2]

Since perfluoroisobutylene readily undergoes nucleophilic addition reactions, it was assumed that FNO is added to fluoro-olefines by a nucleophilic mechanism. The addition of potassium fluoride to the reaction mixture described by Knunyants *et al.*[1] corresponds to such a concept though in this work interpretation of the reaction mechanism is not given and the role of KF remains uncertain.

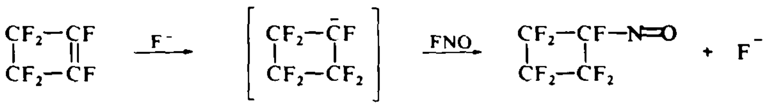
According to Andreades[3] the addition of nitrosyl fluoride to perfluoroisobutylene proceeds without a catalyst. On the basis that fluoro-olefines tend to react with nucleophilic reagents, Andreades suggested that FNO addition proceeds by a nucleophilic mechanism. This was not proved experimentally nor were any conclusions drawn from the assumption.

The nucleophilic character of nitrosyl fluoride addition has been fully confirmed in this work for the higher perfluoro-olefines. Hexafluoropropylene in the presence of potassium fluoride in tetramethylenesulphone smoothly adds nitrosyl fluoride at temperatures as low as 30–35° giving 2-nitrosoperfluoropropane in about 90% yield:



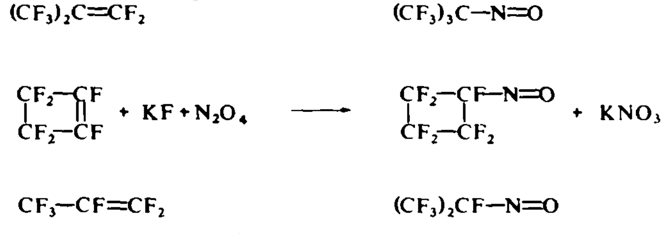
$$CF_3{-}CF{=}CF_2 \xrightarrow{F^-} \left[CF_3\bar{C}FCF_3\right] \xrightarrow{FNO} (CF_3)_2CF{-}N{=}O + F^-$$

Similarly perfluorocyclobutene gives the formerly inaccessible nitrosoperfluorocyclobutane in above 70% yield.



But perfluorocyclobutene without a catalyst and solvent does not react with nitrosyl fluoride even at 120°.

It has been found that fluoronitrosation of fluoro-olefines takes place by the action of potassium fluoride and dinitrogen tetroxide in tetramethylenesulphone. Perfluoroisobutylene under these conditions in an autoclave at room temperature yields tertiary nitrosoperfluoroisobutane in approximately 60% yield; simultaneously further oxidation of nitrosocompound proceeds giving perfluoro-t-butylnitrite the hydrolysis of which leads to perfluoro-t-butyl alcohol[4] (in about 10% yield). The same reaction at 100° gives perfluoro-t-butyl alcohol in about 80% yield. Interaction of perfluorocyclobutene with N_2O_4 and KF in tetramethylenesulphone at 40° gives nitrosoperfluorocyclobutane (51%) with 40% conversion of perfluorocyclobutene. Perfluoropropylene under similar conditions undergoes 53% conversion and yields 21·5% of nitrosocompound.



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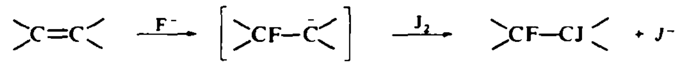
[3] S. Andreades, *J. Org. Chem.* 27, 4163 (1962).

[4] I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Chem. Ser.* 923 (1964).

This reaction resembles that found by Krespan[5] for obtaining perfluoroiodoalkanes from fluoro-olefines, potassium fluoride and iodine:



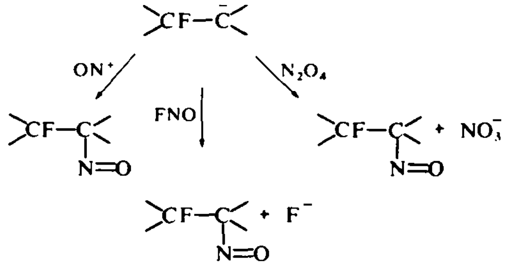
In the system KF-N_2O_4-fluoro-olefine the following equilibria are possible:

$$KF \rightleftharpoons K^+ + F^-$$

$$N_2O_4 \rightleftharpoons ON^+ + NO_3^-$$

$$ON^+ + F^- \rightleftharpoons FNO$$

Nitrosoalkane may be generated as follows:



The reaction of N_2O_4 with fluoro-olefines in the absence of potassium fluoride proceeds by a radical mechanism and yields fluorine-containing 1,2-dinitrocompounds, nitronitrites and dinitrites, depending on the structure of the fluoro-olefine. For example, perfluoropropylene at room temperature adds N_2O_4 giving $CF_3CF(NO_2)CF_2NO_2$ and $CF_3CF(ONO)CF_2NO_2$, hydrolysis of which yields nitroperfluoroacetone.[7] But in the presence of potassium fluoride nucleophilic fluoronitrisation of perfluoropropylene occurs giving 2-nitrosoperfluoropropane.

It has, therefore, been established that the addition of nitrosyl fluoride to higher perfluoro-olefines proceeds by a nucleophilic mechanism and a method for the synthesis of formerly inaccessible perfluoronitrosoalkanes from fluoro-olefines has been developed.

The addition of nitrosyl fluoride to fluorine derivatives of ethylene—trifluorochloroethylene $CF_2{=}CFCl$ (the reaction of which with FNO has not been studied) and tetrafluoroethylene $CF_2{=}CF_2$—in tetramethylenesulphone in the presence of potassium fluoride failed, indicating that the mechanism of FNO addition to fluoroethylenes is different. In the case of trifluorochloroethylene and tetrafluoroethylene, the nitrosyl fluoride may act as an electrophilic reagent in accordance with examples of nitrosation of tetraflouroethylene by an electrophilic mechanism.[8,9] As boron

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[*] Recently the possibility of NOF synthesis from KF and N_2O_4 was demonstrated.[6]

[5] C. G. Krespan, *J. Org. Chem.* 27, 1813 (1962).

[6] Ch. T. Ratcliffe and J. M. Shreeve, *Chem. Commun.* No. 19, 674 (1966).

[7] I. L. Knunyants, A. V. Fokin and V. A. Komarov, *ZhVKhO imeni Mendeleyeva* 7, 709 (1962); *Izv. Akad. Nauk SSSR, Chem. Ser.* 466 (1966).

[8] A. I. Titov, *Dokl. Akad. Nauk SSSR* **149**, 619 (1963).

[9] J. D. Park, A. P. Stephani and J. Lacher, *J. Org. Chem.* **26**, 3319, 4017 (1961).

trifluoride could be an appropriate catalyst, the interaction of FNO with $CF_2{=}CFCl$ and $CF_2{=}CF_2$ in the presence of BF_3 in tetramethylenesulphone was investigated and found to proceed at 30–35° and giving a 30% yield of monochloroperfluoronitrosoethane. The product was investigated by F^{19} NMR and proved to be identical with α-chloroperfluoro nitrosoethane $CF_3CFCl{-}N{=}O$ obtained earlier by another method.[10] This was confirmed by a comparison with the F^{19} NMR spectrum of β-chloroperfluoronitrosoethane $CF_2ClCF_2{-}N{=}O$ obtained by ClNO addition to tetrafluoroethylene in the presence of $AlCl_3$.[8]

Compound	Chemical shift (ppm) relative to $C_6H_5CF_3$ (internal standard)		Relative intensity
	δ_1	δ_2	
$CF_3CFClNO$	6·6	61·8	3:1
CF_2ClCF_2NO	15·6	55·0	1:1

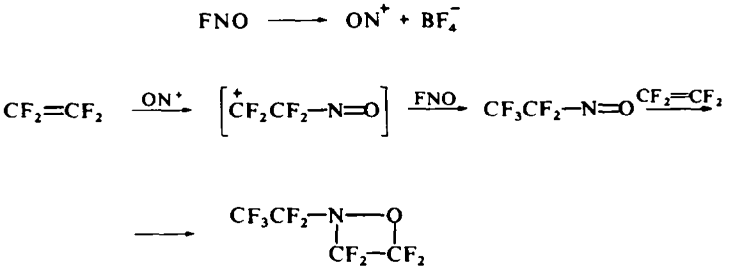
The formation of α-chloroperfluoronitrosoethane corresponds to the polarization of the starting reagents:

$$FNO + BF_3 \longrightarrow ON^+ + BF_4^-$$

$$\overset{\delta+}{C}F_2{=}\overset{\delta-}{C}FCl \xrightarrow{ON^+} \left[\overset{+}{C}F_2CFCl{-}N{=}O\right] \xrightarrow{FNO} CF_3CFCl{-}N{=}O$$

Together with nitroso compound considerable amounts of liquids which could not be distilled were obtained.

Reaction of nitrosyl fluoride with tetrafluoroethylene in the presence of boron trifluoride in tetramethylenesulphone was performed at 30–50°. Together with indistillable nitrogen and fluorine containing polymers, liquids boiling up to 50° were obtained. These products were a mixture of perfluoro-N-ethyl-oxazetidine whose formation in the reaction of tetrafluoroethylene with nitrosyl fluoride was stated earlier,[1–3] and a substance with b.p. of 34–35° proved to be perfluoro-(2-oxazetidinyl) acetyl fluoride. The formation of perfluoro-N-ethyloxazetidine can be representated as follows:



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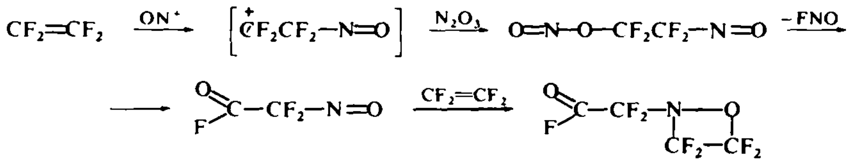
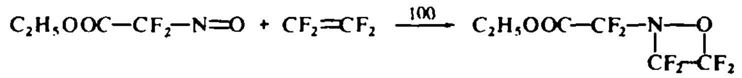
[10] I. L. Knunyants, L. S. German, I. N. Rozhkov and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Chem. Ser.* 250 (1966).

The formation of perfluoro-(2-oxazetidinyl) acetyl fluoride may result from the partial hydrolysis of nitrosyl fluoride:

$$2\,FNO \xrightarrow{H_2O} N_2O_3 + 2HF$$

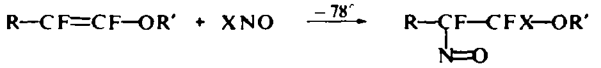


The structure of this compound was confirmed by conversion to the methyl and ethyl esters of perfluoro-(2-oxazetidinyl)-acetic acid and by an alternative synthesis of the ethyl ester:



The formation of perfluoro-(2-oxazetidinyl) acetyl fluoride, during conjugate addition, starting with an attack on the double bound by the $O{=}N^+$ cation confirms that the reaction of nitrosyl fluoride with tetrafluoroethylene proceeds by an electrophilic mechanism.

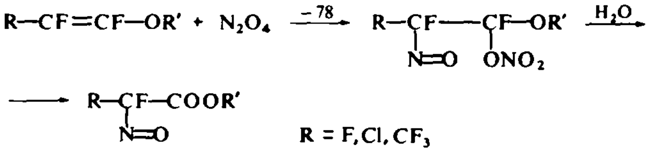
The ability of fluoro-ethylenes to be nitrosated by an electrophilic mechanism indicates that the double bond in these compounds has not fully lost its electron-donating properties characteristic for the carbon–carbon double bond. These properties are even more apparent in a special class of fluoro-olefines—the alkylperfluorovinyl ethers, in which there is conjugation of the double bond with an unshared electron pair of the oxygen atom, e.g. $CF_3CF{=}CF{-}\ddot{O}{-}R$. As was shown recently.[11] alkylperfluorovinyl ethers readily add FNO and ClNO giving fluorine-containing nitrosoethers:



$$R{-}CF{=}CF{-}OR' + XNO \xrightarrow{-78^\circ} R{-}\underset{\substack{|\\ N{=}O}}{C}F{-}CFX{-}OR'$$

$X = F, Cl$
$R = F, Cl, CF_3$
$R' = CH_3, C_2H_5$

It was also found[12] in relation to alkylperfluorovinyl ethers that dinitrogen tetroxide is a nitrosating agent. In nitrosyl-nitrate form it yields after hydrolysis of the adducts the esters of α-nitrosoperfluorocarboxylic acids:



$$R{-}CF{=}CF{-}OR' + N_2O_4 \xrightarrow{-78} R{-}\underset{\substack{|\\ N{=}O}}{C}F{-}\underset{\substack{|\\ ONO_2}}{C}F{-}OR' \xrightarrow{H_2O} R{-}\underset{\substack{|\\ N{=}O}}{C}F{-}COOR'$$

$R = F, Cl, CF_3$
$R' = C_2H_5$

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[11] B. L. Dyatkin, R. A. Bekker, Yu. S. Konstantinov and I. L. Knunyants, *Dokl. Akad. Nauk SSSR* **165**, 1305 (1965).

[12] B. L. Dyatkin, R. A. Bekker and I. L. Knunyants, *Dokl. Akad. Nauk SSSR* **166**, 106 (1966).

There is no doubt that nitrosation of alkylperfluorovinyl ethers proceeds by an electrophilic mechanism. It is precisely for this reason that perfluoroisobutenyl ethers $(CF_3)_2C{=}CFOR$ are less active in these reactions. They do not add dinitrogen tetroxide and nitrosyl chloride and addition of nytrosyl fluoride proceeds only in an autoclave at room temperature.

Relative to alkylperfluorovinyl ethers and fluoro ethylenes in which the electron density of the double bond is high enough, it has therefore been proved that nitrosyl fluoride acts as an electrophilic reagent and its reactions with these fluoro-olefines start with an attack on the double bond by the $O{=}N^+$ cation. In passing to higher perfluoro-olefines where the electron-accepting properties of double bound prevail, nitrosyl fluoride acts as a nucleophilic reagent and the initial stage of the reaction consists in an attack on the double bond by the F^- anion. The mechanism of nitrosyl fluoride addition to perfluoromethacrylyl fluoride $CF_2{=}C(CF_3)COF$[13] and bis-trifluoromethylketene $(CF_3)_2C{=}C{=}O$[14] is undoubtedly the same.

This reversion of the addition mechanism in fluoro-olefines series occurs also for halogenation, hydrohalogenation and some other reactions and it is therefore quite a general phenomenon.[15]

EXPERIMENTAL

Addition of nitrosyl fluoride to perfluoropropylene

2-*Nitrosoperfluoropropane*. Perfluoropropylene (32·0 g, 0·214 mole), FNO (13·5 g, 0·28 mole), powdered dry KF (7 g) and tetramethylenesulphone (25 ml) were shaken in a 100 ml stainless steel autoclave at 30–35° for 9 hr. Volatile reaction products were distilled through a wash bottle with conc H_2SO_4 into a trap cooled to −78° and distilled. 2-Nitrosoperfluoropropane (37·5 g, 88%) was obtained as a deep-blue liquid, b.p. −11–−9°. According to GLC the substance was identical with 2-nitrosoperfluoropropane, obtained earlier.[1,16] Reported: b.p. −13°[1]; −11–−9°.[16]

Reaction of perfluoropropylene with potassium fluoride and dinitrogen tetroxide

A mixture of perfluoropropylene (8 g, 0·053 mole), N_2O_4 (7·5 g, 0·082 mole), KF (15 g, 0·26 mole) and tetramethylenesulphone (30 ml) was shaken in a 50 ml autoclave for 9 hr at 40°. Volatile reaction products were isolated as above and 5 g of mixture was obtained containing, according to GLC, 2-nitrosoperfluoropropane (24%) and starting perfluoropropylene (76%). Conversion—53%, yield—10·6% on the charged and 21·5% on the reacted perfluoropropylene.

Addition of nitrosyl fluoride to perfluorocyclobutene

Nitrosoperfluorocyclobutane. Perfluorocyclobutene (8 g, 0·05 mole), FNO (3·9 g, 0·08 mole), KF (5 g) and tetramethylenesulphone (20 ml) were shaken for 6 hr at 35° and treated as before to give nitrosoperfluorocyclobutane (7·7 g, 73·5%), b.p. 22·5–23·5°, in the form of a deep-blue liquid giving a blue crystalline mass at −78°. (Mol. wt., Found: 211·6, calc. 211·1.) IR spectrum ν_{max} 1593 (strong) cm^{-1}. (Found: C, 22·77; F, 62·91. C_4F_7NO requires: C, 22·76; F, 63·02%.)

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[13] Yu. A. Cheburkov, N. Mukhamadaliev and I. L. Knunyants, *Dokl. Akad. Nauk SSSR* **165**, 127 (1965).

[14] N. Mukhamadaliev, Yu. A. Cheburkov and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Chem. Ser.* 1982 (1965).

[15] B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, *Uspekhi Chimii* 35, 979 (1966).

[16] B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Chem. Ser.* 1715 (1965).

Reaction of perfluorocyclobutene with potassium fluoride and dinitrogen tetroxide

By a similar method perfluorocyclobutene (9·8 g, 0·06 mole), N_2O_4 (5·5 g, 0·06 mole) and KF (15 g, 0·26 mole) in tetramethylenesulphone (15 ml) at 40° for 9 hr gave a mixture (8·4 g) containing (according GLC) nitrosoperfluorocyclobutane (30%) and starting perfluorocyclobutene (70%). The mixture was easily separated by distillation. Conversion was 40%, nitrosocompound yield 20% on the charged and and 51% on the reacted perfluorocyclobutene.

Reaction of perfluoroisobutylene with potassium fluoride and dinitrogen tetroxide

A. Perfluoroisobutylene (10 g, 0·05 mole), N_2O_4 (12 g, 0·13 mole), KF (15 g, 0·26 mole) and tetramethylenesulphone (15 ml) were shaken in a 50 ml stainless steel autoclave for 20 hr at 100°. Volatile reaction products were distilled under low vacuum (up to 150 mm Hg) through a wash bottle with conc H_2SO_4 into a trap, cooled to -78°, and redistilled with H_2SO_4. The reaction gave perfluoro-t-butyl alcohol (9·4 g, 79·4%) b.p. 45–47° indentified by GLC with an authentic sample.[4] reported: b.p. 45°.[4]

B. Perfluoroisobutylene (10 g, 0·05 mole), N_2O_4 (4·6 g, 0·05 mole), KF (15 g, 0·26 mole) and tetramethylenesulphone (15 ml) were shaken in a 50 ml autoclave for 24 hr at room temp. Reaction products were distilled under low vacuum through H_2SO_4 into a trap cooled to -78° and redistilled. The reaction gave t-nitrosoperfluoroisobutane, b.p. 24°, indentified by GLC with the substance, obtained earlier.[1] reported: b.p. 24°.[1] The distillation of a high-boiling residue from H_2SO_4 gave perfluoro-t-butyl alcohol, b.p. 44–47°.

Addition of nitrosyl fluoride to trifluorochloroethylene

Trifluorochloroethylene (10·2 g, 0·08 mole), FNO (7·8 g, 0·16 mole) and 1 g of BF_3 in 10 ml of tetramethylenesulphone were shaken in a 50 ml autoclave for 4 hr at 25–35° to give a blue gas distillation of which gave α-chloroperfluoronitrosoethane with b.p. -5 – -3°, reported: b.p. $-4·5$ 3°.[10] The liquid part of the reaction mixture when poured into water gave an oil (8 g) representating a polymer which could not be distilled.

Reaction of nitrosyl fluoride with tetrafluoroethylene

Tetrafluoroethylene (7·5 l.) was condensed into a 50 ml stainless steel autoclave containing a soln of BF_3 (6 g) in tetramethylenesulphone (10 ml) and FNO (6·7 g) and the mixture was shaken for 8 hr at 40–50°. The autoclave was cooled to room temp and excess fluoro-olefine (about 5·5 l.) was fed into a gasometer. Volatile reaction products were distilled from the autoclave under low vacuum into a trap, cooled to -78°. The condensate was distilled and the fraction with b.p. of up to 50° was treated after cooling by EtOH. The substance which did not react with alcohol was collected in a trap at -78°. The reaction mixture was washed with water, the organic layer was separated, dried with $CaCl_2$ and distilled to give ethyl perfluoro-(2-oxazetidinyl) acetate (2 g), b.p. 48·5–49·5°/46 mm, n_D^{20} 1·3335, d_4^{20} 1·4421. (Found: C, 28·60; H, 2·02; F, 44·20; N, 5·69. $C_6H_5F_6NO_3$ requires: C, 28·51; H, 1·99; F, 45·04; N, 5·53%.)

The substance was obtained by an alternative synthesis from ethyl nitrosodifluoroacetate[12] and tetrafluoroethylene (heating in autoclave at 100° for 5 hr in difluorodichloromethane soln), the yield was equal to 10% (in the main polymer is formed), b.p. 49°/50 mm. The samples were identified by GLC method.

The trap content (1 g) was perfluoro-N-ethyloxazetidine, b.p. 23–24°. The substance was identical with an authentic sample by GLC, reported: b.p. 24°.[1]

By thorough distillation of the fraction with b.p. of up to 50° perfluoro-(2-oxazetidinyl) acetyl fluoride, b.p. 34–35° could be isolated. (Found: N, 6·16. $C_7F_6NO_2$ requires: N, 5·78%.)

IR spectrum of the substance shows an intensive absorption band at 1890 cm^{-1}. Mass spectrum: 180 (M − COF), 13; 130 (C_2F_4NO; M-COF-CF_2), 11; 119 (C_2F_5), 7; 114 (C_2F_4N), 39; 100 (C_2F_4), 14; 95 (C_2F_3N), 13; 69 (CF_3), 100; 50 (CF_2), 14; 47 (COF), 30; 44 (CO_2), 19.

Methyl perfluoro-(2-oxazetidinyl) acetate was obtained from acid fluoride and MeOH, b.p. 44°/48 mm, n_D^{20} 1·3257, d_4^{20} 1·5411. (Found: C, 24·87; H, 1·06; F, 46·98; N, 5·83. $C_5H_3F_6NO_2$ requires: C, 25·16; H, 1·26; F, 47·68; N, 5·86%.)

Mass spectrum: 239 (M), 0·8; 180 (M-$COOCH_3$), 19; 130 (C_2F_4NO; M-$COOCH_3$ − CF_2), 14; 114 (C_2F_4N), 12·5; 109 (CF_2COOCH_3), 10; 81 (C_2F_3), 7; 69 (CF_3), 20; 59 ($COOCH_3$), 100; 44 (CO_2), 25.

Gas–liquid chromatography. Analysis and identifications were carried out using a thermal conductivity detector. Helium was used as a carrier gas. Chromatography conditions are given below.

Packing	t°	Analyzed objects
20% $H(CF_2CF_2)_nCH_2OH$, b.p. 125–160°/1 mm, on Al_2O_3	room	R_fNO
30% 1,4-Butanediol di-n-butirate on INZ-600	room	R_fNO, oxazetidines
20% Reoplex-400 on Chromosorb-W	100	$(CF_3)_3COH$
20% Tiocol on Chromosorb-W	100	$(CF_3)_3COH$
20% liquid poly-trifluoro-chloroethylene on solid	100	oxazetidines