R-PCPU with R = H, m-Cl, and m-$CH_3$ were obtained by the reaction of anthranilonitrile with the corresponding substituted phenyl isocyanate according to Breukink and Verkade [7] and recrystallized from 3:1 benzene—ethanol.

The structures of the compounds synthesized and their purity were monitored by elemental analysis and IR spectroscopy. The IR spectra of the PCPU solutions during the cyclization were taken on a UR-10 spectrometer.

## CONCLUSIONS

The isomerizational cyclization of N-phenyl-N'-(o-cyanophenyl)urea in solution in the presence of bases is a one-step reaction with an equilibrium step involving proton abstraction as the rate-limiting step.

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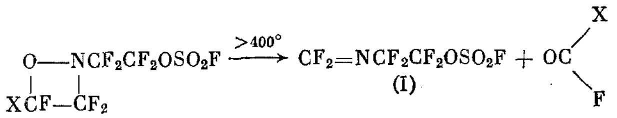
# PERFLUOROAZOMETHINES WITH FLUOROSULFATE GROUPS

A. V. Fokin, Yu. N. Studnev,
A. I. Rapkin, V. G. Chilikin,
and O. V. Verenikin

UDC 541.11:542.92:547.414.7'226

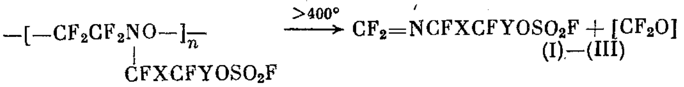
The pyrolysis of the adducts of fluoroolefins and nitrosofluoroalkanes is commonly used for the preparation of perfluoroazomethines [1]. An example of the pyrolysis of a copolymer of trifluoronitrosomethane with trifluoroacrylyl fluoride has also been reported [2].

In the present work, we studied the pyrolysis of adducts of 2-nitrosoperfluoroalkyl fluorosulfates with fluoroolefins containing fluorosulfate groups in the side chain. The pyrolysis of 1,2-oxazetidines with a fluorosulfonyloxytetrafluoroethyl group at N-2 proceeds with retention of the fluorosulfate group.



X = Cl, $CF_3O$.

Perfluoroazomethines with fluorosulfate groups were also obtained in the pyrolysis of the corresponding nitrosofluoro polymers.



$$-[-CF_2CF_2\underset{\substack{|\\ CFXCFYOSO_2F}}{N}O-]_{n}- \xrightarrow{>400^\circ} CF_2=NCFXCFYOSO_2F + [CF_2O] \quad (I)-(III)$$

X = Y = F (I); X = Cl, Y = F (II); X = F, Y = $CF_3O$ (III).

Analogous results were obtained from the pyrolysis of "mixed" nitrosofluoro polymers.

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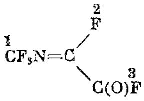
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1443-1446, June, 1985. Original article submitted November 2, 1984.

0568-5230/85/3406-1322 $09.50

TABLE 1. $^{19}F$ NMR Spectral Parameters of Products Obtained

| Compound | δ, ppm | J, Hz |
|---|---|---|
| $\overset{1,2}{F_2}C{=}NC\overset{3}{F_2}C\overset{4}{F_2}OSO_2\overset{5}{F}$ (I)* | $\delta_1\ -51{,}64$ d, $\delta_2\ -35{,}14$ d, $\delta_3\ 18{,}86$ t, $\delta_4\ 11{,}28$ d, $\delta_5\ -126{,}98$ t | $J_{12}=93$, $J_{3N}=10{,}2$, $J_{45}=9{,}6$ |
| $\overset{1,2}{F_2}C{=}NC\overset{3}{F}ClC\overset{4}{F_2}OSO_2\overset{5}{F}$ (II) | $\delta_1\ -52{,}06$ d, $\delta_2\ -34{,}95$ d, $\delta_3\ 18{,}05$ m, $\delta_4\ 8{,}56$ m, $\delta_5\ -127{,}3$ t | $J_{12}=90$, $J_{45}=8{,}5$ |
| $\overset{1,2}{F_2}C{=}NC\overset{3}{F_2}C\overset{4}{F}(OC\overset{5}{F_3})OSO_2\overset{6}{F}$ (III) | $\delta_1\ -49{,}63$ d, $\delta_2\ -32{,}23$ d, $\delta_3\ 20{,}73$ m, $\delta_4\ 17{,}43$ m, $\delta_5\ -21{,}13$ d. d. t, $\delta_6\ -126{,}94$ m | $J_{12}=92$, $J_{45}=12{,}4$, $J_{35}=J_{46}=2{,}8$ |
| $C\overset{1}{F_3}OC\overset{2}{F}{=}NC\overset{3}{F_2}C\overset{4}{F_2}OSO_2\overset{5}{F}$ (IV) | $\delta_1\ -17{,}72$ d, $\delta_2\ -47{,}95$ m, $\delta_3\ 17{,}54$ d. t, $\delta_4\ 11{,}05$ d. d. t, $\delta_5\ -127{,}07$ t | $J_{12}=8{,}5$, $J_{23}=18{,}1$, $J_{24}=4{,}5$, $J_{34}=1{,}6$, $J_{45}=8{,}5$ |
| $C\overset{1}{F}Cl{=}NC\overset{2}{F}ClC\overset{3}{F_2}OSO_2\overset{4}{F}$ (V) | $\delta_1\ -86{,}47$ m, $\delta_2\ 25{,}34$ m, $\delta_3\ 8{,}68$ m, $\delta_4\ -127{,}3$ t | $J_{34}=8{,}5$ |
|  (VI) | $\delta_1\ -20{,}41$ d, $\delta_2\ -55{,}28$ d q., $\delta_3\ -98{,}96$ d | $J_{12}=14{,}1$, $J_{23}=20{,}9$ |
| $\overset{1}{F}SO_2OC\overset{2}{F_2}N(OSO_2\overset{3}{F})C\overset{4}{F_2}C\overset{5}{F_2}OSO_2\overset{6}{F}$ (VII) | $\delta_{1,6}\ -129{,}27$ t and $-127{,}78$ t, $\delta_2\ -13{,}92$ m, $\delta_3\ -121{,}08$ m, $\delta_4\ 24{,}71$ m, $\delta_5\ 6{,}25$ m | $J_{12}=J_{56}=8{,}5$ |
| $\overset{1}{F}SO_2OC\overset{2}{F_2}N(Cl)C\overset{3}{F_2}C\overset{4}{F_2}OSO_2\overset{5}{F}$ (VIII) | $\delta_{1,5}\ -127{,}87$ t and $-127{,}72$ t, $\delta_2\ 20{,}14$ d t, $\delta_3\ -17{,}54$ t t, $\delta_4\ 5{,}95$ d t | $J_{12}=J_{45}=8{,}5$, $J_{23}=13{,}0$, $J_{34}=3{,}4$ |
| COFCl | $-61{,}81$ s | |
| $C\overset{1}{F_3}OC(O)\overset{2}{F}$ | $\delta_1\ -16{,}63$ d, $\delta_2\ -62{,}75$ q | $J_{12}=10{,}7$ |

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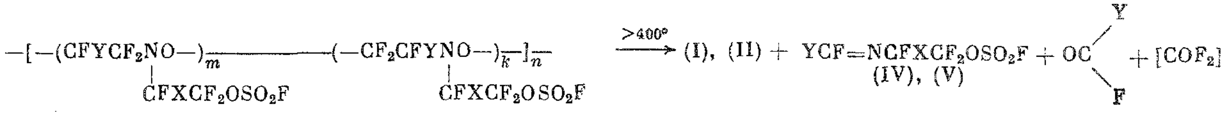
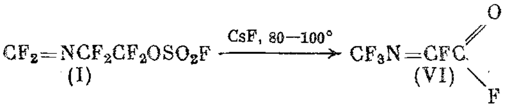
* Here and subsequently, the $^{19}F$ NMR signals for fluorine atoms close to nitrogen are broadened.



$$-[-(\underset{CFXCF_2OSO_2F}{CFYCF_2NO}-)_m-(-\underset{CFXCF_2OSO_2F}{CF_2CFYNO}-)_k-]_n \xrightarrow{>400^\circ} \text{(I), (II)} + \underset{\text{(IV), (V)}}{YCF{=}NCFXCF_2OSO_2F} + OC(Y)F + [COF_2]$$

X = F, Y = $CF_3O$ (IV); X = Y = Cl (V).

Thus, the pyrolysis of the products of the reaction of 2-nitrosopolyfluoroalkyl fluorosulfates with fluoroolefins gave previously unreported perfluoroazomethines with fluorosulfate groups which hold interest for the synthesis of fluoronitrogen compounds [1]. These pyrolytic reactions characteristically yield fluoroazomethines with a terminal double bond. This feature may be related to the low tendency of these compounds to isomerize. Thus, fluoroazomethine (I) does not isomerize by the action of CsF at 40-50°C but undergoes cleavage and double bond migration at 80-100°C.



$$\underset{\text{(I)}}{CF_2{=}NCF_2CF_2OSO_2F} \xrightarrow{\text{CsF, 80—100}^\circ} \underset{\text{(VI)}}{CF_3N{=}CFC(O)F}$$

Fluoroazomethine (I) under mild conditions adds at the double bond of peroxydisulfuryl difluoride and chlorine fluorosulfate

$$CF_2{=}NCF_2CF_2OSO_2F + XOSO_2F \rightarrow \underset{\text{(VII), (VIII)}}{FSO_2OCF_2N(X)CF_2CF_2OSO_2F}$$

X = $OSO_2F$ (VII); Cl (VIII).

## EXPERIMENTAL

The $^1H$ and $^{19}F$ NMR spectra were taken on a Hitachi R-20 spectrometer at 60 and 56.45 MHz relative to HMDS and $CF_3CO_2H$ (external standard) (Table 1). The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph on a 3 m × 3 mm column packed

TABLE 2. Characteristics of Products Synthesized

| Compound | bp, °C (p, mm Hg) | $d_4^{20}$ | $n_D^{20}$ | Chemical formula | Found/Calculated, % | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | Cl | F | N | S |
| (I) | 77–78 | 1,738 | 1,3061 | $C_3F_7NO_3S$ | 13,78/13,69 | – | 50,73/50,57 | 5,48/5,32 | 12,36/12,17 |
| (II) | 65–69 (180) | 1,768 | 1,3364 | $C_3ClF_6NO_3S$ | 12,48/12,88 | 12,51/12,70 | 40,56/40,79 | 5,21/5,01 | 11,40/11,45 |
| (III) | 78–80 | 1,704 | 1,3059 | $C_4F_9NO_4S$ | 14,39/14,59 | – | 51,67/51,98 | 4,15/4,26 | 9,51/9,73 |
| (IV) | 80–84 | 1,725 | 1,3020 | $C_4F_9NO_4S$ | 14,41/14,59 | – | 51,72/52,98 | 4,16/4,26 | 9,52/9,73 |
| (V) | 25–28 (3) | 1,789 | 1,3670 | $C_3Cl_2F_5NO_3S$ | 12,33/12,16 | 23,89/23,65 | 32,40/32,10 | 4,51/4,73 | 10,68/10,81 |
| (VI) | 26–27 * | 1,589 | <1,3 | $C_3F_5NO$ | 22,39/22,36 | – | 60,21/59,01 | 8,79/8,70 | – |
| (VII) | 90–92 (60) | 1,953 | 1,3422 | $C_3F_9NO_9S_3$ | 7,49/7,81 | – | 36,85/37,10 | 3,51/3,04 | 20,80/20,82 |
| (VIII) | 42–45 (80) | 1,859 | 1,3358 | $C_3ClF_8NO_6S_2$ | 9,26/9,06 | 8,99/8,93 | 38,21/38,24 | 3,92/3,52 | 8,08/8,05 |

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* See the work of Banks et al. [2].

with 5% SE-30 on Chromaton N-AW-DMCS, 3 m × 3 mm column packed with QF-1 on TND-TSM, and a 2 m × 3 mm column packed with 5% XE-60 on Chezasorb AW-HMDS with helium as the carrier gas. The physical constants for the products are given in Table 2.

Perfluoro-3-azabuten-3-yl Fluorosulfate (I). a) A 4.5-g sample of 2-(2-fluorosulfonyloxytetrafluoroethyl)-4-chlorotrifluoro-1,2-oxazetidine was added dropwise to a flask heated over 400°C. The pyrolysis products were collected in a trap at −100°C. Fractionation gave 3 g (88%) (I) and 1 g COFCl, bp −60°C.

b) Under the conditions of the above experiment, 10 g 2-(2-fluorosulfonyloxytetrafluoroethyl)-4-trifluoromethoxytrifluoro-1,2-oxazetidine gave 5.6 g (84.1%) (I) and about 2 g $CF_3OC(O)F$ with bp from −53 to −56°C.

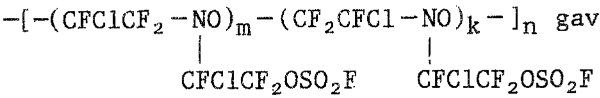
c) A sample of 17 g nitrosofluoro polymer $-[-CF_2CF_2\underset{\substack{|\\ CF_2CF_2OSO_2F}}{N}-O-]_n$ was subjected to pyrolysis in a flask heated over 400°C with collection of the products in a trap at −78°C. Fractionation yielded 11.9 g (87.5%) (I).

2-Chloroperfluoro-3-azabuten-3-yl Fluorosulfate (II). Under the conditions of experiment c, 22 g nitrosofluoro polymer $-[-CF_2-CF_2-\underset{\substack{|\\ CFClCF_2OSO_2F}}{N}-O-]_n$ gave 16 g (83.4%) (II).

1-Trifluoromethoxyperfluoro-3-azabuten-3-yl Fluorosulfate (III). Under the conditions of experiment c, 6.5 g nitrosofluoro polymer $-[-CF_2CF_2-\underset{\substack{|\\ CF_2CF(OCF_3)OSO_2F}}{N}-O-]_n$ gave 4 g (74.1%) (III).

Perfluoro-3-azabuten-3-yl Fluorosulfate (I) and 4-Trifluoromethoxyperfluoro-3-azabuten-3-yl Fluorosulfate (IV). Under the conditions of experiment c, 8 g nitrosofluoro polymer $-[-(CF(CF_3O)CF_2-\underset{\substack{|\\ CF_2CF_2OSO_2F}}{N}O)_m-(CF_2CF(CF_3O)-\underset{\substack{|\\ CF_2CF_2OSO_2F}}{N}-O)_k-]_n$ gave 6.5 g of a 1:3 mixture of (I) and (IV) as indicated by gas−liquid chromatography and $^{19}F$ NMR spectroscopy. Fractionation gave the individual compounds in addition to about 1 g $CF_3OC(O)F$, bp from −53 to −56°C.

2-Chloroperfluoro-3-azabuten-3-yl Fluorosulfate (II) and 2,4-Dichloroperfluoro-3-azabuten-3-yl Fluorosulfate (V). Under conditions of experiment c, 16 g nitrosofluoro polymer



$-[-(CFClCF_2-\underset{\substack{|\\ CFClCF_2OSO_2F}}{N}O)_m-(CF_2CFCl-\underset{\substack{|\\ CFClCF_2OSO_2F}}{N}O)_k-]_n$ gave 11 g of a 1:2 mixture of (II) and (V) as indicated by gas–liquid chromatography and $^{19}F$ NMR spectroscopy. Fractionation gave the individual products as well as 1.5 g COFCl, bp −60°C.

Acid Fluoride of Perfluoro-3-aza-2-butenoic Acid (VI). A mixture of 11.3 g (I) and 2 g CsF was heated with a reflux condenser for 0.5 h at 80-100°C. The products formed were collected in a trap at −78°C. Fractionation gave 4.5 g (65.2%) (VI).

1,2,4-Tris(fluorosulfonyloxy)perfluoro-2-azabutane (VII). A mixture of 3.5 g (13.3 mmoles) (I) and 3 g (15 mmoles) $S_2O_6F_2$ was maintained for 5 days in a sealed vessel at 20°C and then fractionated to yield 3.9 g (64%) (VII).

1,4-Bis(fluorosulfonyloxy)-2-chloroperfluoro-2-azabutane (VIII). A sample of 1.8 g (13.3 mmoles) chlorine fluorosulfate was added dropwise with stirring to 3.5 g (13.3 mmoles) (I) at 20°C, maintained for 5 h, and fractionated to yield 4.2 g (79%) (VIII).

## CONCLUSIONS

The pyrolysis of adducts of 2-nitrosopolyfluoroalkyl fluorosulfates with fluoroolefins gives previously unreported fluorosulfonyloxyfluoroazomethines.

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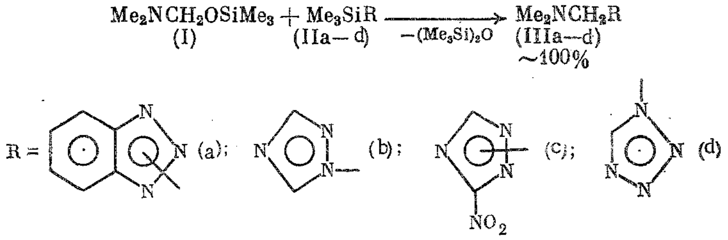
# NONAQUEOUS AMINOMETHYLATION OF SILYLATED POLYNITROGEN HETEROCYCLES

A. V. Kalinin, É. T. Apasov,
S. L. Ioffe, V. P. Kozyukov,
and Vik. P. Kozyukov

UDC 542.91:547.1'128

1-Trimethylsilyl-3,5-dimethylpyrazole reacts with trimethylsiloxymethyldiethylamine at 130-160°C to give the condensation product in 70% yield [1].

In a study of the condensation of trimethylsiloxymethyldimethylamine (I) [2] with trimethylsilyl derivatives of triazole and tetrazole (IIa-d), we showed that this reaction is an effective, general, and rather mild method for the nonaqueous aminomethylation of polynitrogen aromatic heterocycles.



$$\underset{(I)}{Me_2NCH_2OSiMe_3} + \underset{(IIa-d)}{Me_3SiR} \xrightarrow[-(Me_3Si)_2O]{} \underset{\substack{(IIIa-d)\\ \sim 100\%}}{Me_2NCH_2R}$$

We should stress that, in contrast to the condensation described in our previous work [1], the condensation of (I) proceeds in an inert solvent at 20°C. The acceleration of the

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Institute for the Chemistry and Technology of Heteroorganic Compounds, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1447-1449, June, 1985. Original article submitted November 21, 1984.

0568-5230/85/3406-1325 $09.50