Reaction of hexafluoropropylene and its oligomers with acetone oxime

V. F. Snegirev, M. Yu. Antipin, and Yu. T. Struchkov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Reactions of perfluoropropylene and its oligomers with acetone oxime in the presence of a base afford perfluoroalkyl and/or perfluoroalkenyl ethers of acetone oxime. When heated to 100 °C, the 3-perfluoro-2-methyl-2-pentenyl ether of acetone oxime (**3**) is quantitatively converted to 4-hydroxy-3-methyl-5,5-bistrifluoromethyl-4-pentafluoroethyl-1-pyrroline (**4**), the structure of which was established by X-ray diffraction analysis. A convenient one-stage synthesis of perfluoro-3-isopropyl-4-methyl-3-penten-2-one (**7**) was proposed.

Key words: hexafluoropropylene; perfluoro-2-methyl-2-pentene; perfluoro-3-isopropyl-4-methyl-2-pentene; *O*-perfluoroalkyl- and *O*-perfluoroalkenyl acetone oximes, synthesis; 4-hydroxy-2-methyl-5,5-bistrifluoromethyl-4-pentafluoroethyl-1-pyrroline, X-ray structural analysis; perfluoro-3-isopropyl-4-methyl-3-penten-2-one.

It is known[1–3] that the reactions of ketoximes with the simplest fluoro-containing olefins afford only the addition products, namely *O*-fluoroalkylketoximes.

In this work, we demonstrated that perfluoropropylene reacts with acetone oxime in the presence of a base to give the adduct (**1**):

$$CF_3CF{=}CF_2 + HON{=}C(CH_3)_2 \xrightarrow[\text{diglyme, 0 °C}]{\text{KOH}} CF_3CHF{-}CF_2{-}O{-}N{=}C(CH_3)_2$$

1

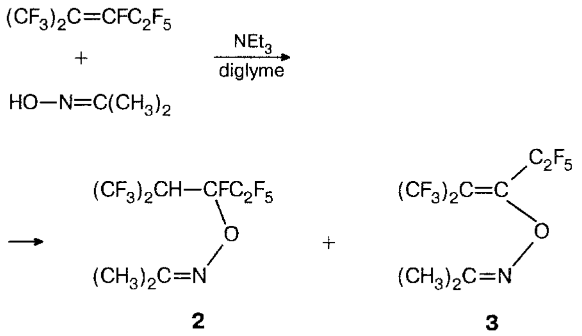
Attempts to dehydrofluorinate this product with a powdered alkali with the aim of preparing the perfluoropropenyl ether of acetone oxime failed, whereas treatment with a 50 % alkaline aqueous solution results in the complete mineralization of the initial compound.

Unlike simple olefins, perfluoro-2-methyl-2-pentene (a dimer of hexafluoropropylene) reacts with acetone oxime to yield both the adduct (**2**) and the product of the replacement of the vinyl fluorine atom (**3**); the yield of the latter increases with an increase in the amount of the base (Scheme 1).

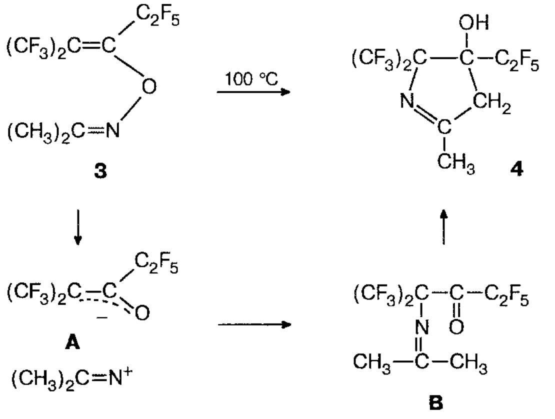
Adduct **2** is readily dehydrofluorinated with powdered KOH in ether and is converted to vinyl ether **3**.

The prepared compounds are markedly different in their thermal stability. Adduct **2** is a stable compound which undergoes no change when allowed to stand at 150 °C for a day, whereas compound **3** is stable only when it is stored at temperatures below 30 °C. When heated to 100 °C for 1 h, ether **3** is quantitatively converted to pyrroline (**4**).

Scheme 1



Scheme 2



Apparently, the heterolytic cleavage of the O—N bond occurs first. Evidently, this bond breaks easily owing to the strong electron-acceptor effect of the

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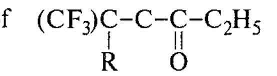
perfluoroalkyl groups, because the mesomeric anion (**A**), as is known,[4] is a readily leaving group (Scheme 2).

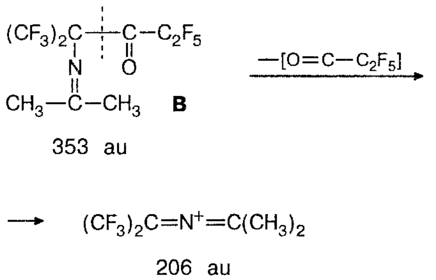
The nascent ionic pair is stabilized through the transfer of a cationoid particle from the oxygen atom to the carbon atom of the mesomeric anion **A**. Therefore, the migration of the methyl group in the cationoid fragment from the carbon atom to the nitrogen atom, which is typical of the Beckmann rearrangement, does not occur in this case.

Monitoring the process of the isomerization of **3** to **4** by ^{19}F NMR spectroscopy shows that initially the intermediate **B** is actually formed. In the ^{19}F NMR spectrum signals typical of  $(CF_3)\underset{R}{\underset{|}{C}}-C-\underset{O}{\underset{\|}{C}}-C_2H_5$ compounds, namely, those at δ −10.1 (t, $(CF_3)_2$), 4.5 (s (CF_3)), and 39.6 (heptete (CF_2)); $J_{(CF_3)_2-CF_2} = 7.6$ Hz, appear.

All attempts to isolate the unstable ketone **B** proved unsuccessful because it is completely converted to the cyclic product **4**.

The isomerization **3** → **B** occurs during the chromatographic analysis of a virtually pure sample (^{19}F NMR) of compound **3**. When the temperature of the vaporizing chamber was gradually changed, two peaks with different R_f could be observed on the chromatograms; the relative area of the second peak increases from 0 % (100 °C) to 100 % (200 °C). The peak corresponding to the cyclic compound **4** does not appear.

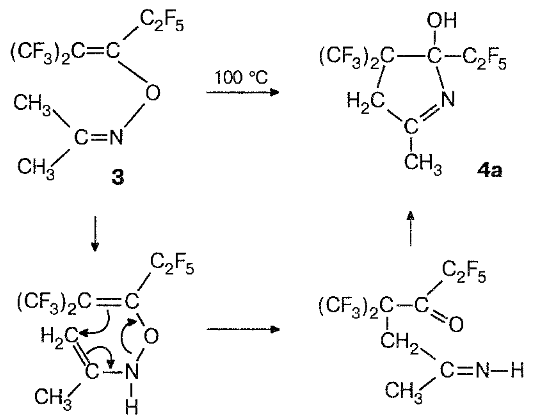
This must be taken into account when samples of compound **3** are studied by mass spectrometry and, especially, by gas chromatography/mass spectrometry techniques (GC-MS). As the temperature of the inlet chamber increases, the character of the mass spectrum is substantially changed. Thus, the peak of the molecular ion (353 au) is retained, but a new peak with a mass of 206 and intensity of 100 % appears.



The structure of compound **4**, which is the product of the thermolysis of the fluoroalkenyl ether of acetone oxime **3**, was established by X-ray structural analysis (*cf.* Refs. 3, 5). First, we suggested that when heated, ether **3** undergoes the Claisen rearrangement with subsequent intramolecular cyclization (Scheme 3).

On the basis of the ^{19}F and ^{1}H NMR, IR, and mass spectroscopy data, we were unable to determine which of the isomeric structures, **4** or **4a**, is correct for the obtained crystalline compound. By means of X-ray structural analysis we unambiguously determined that this compound has the structure of **4** rather than **4a**. Hence, ether **3** does not undergo the Claisen rearrangement, and the driving force for its conversion is the lability of the N—O bond and its susceptibility to heterolytic cleavage.

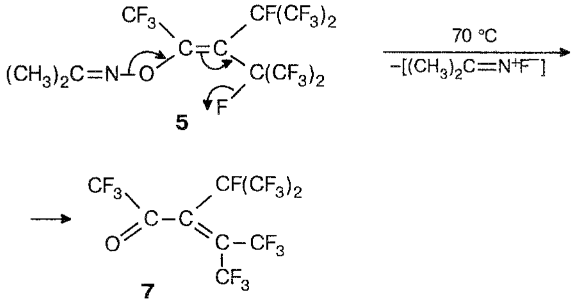
Scheme 3



Perfluoro-2-methyl-3-isopropyl-2-pentene (**C**) and perfluoro-3-isopropyl-4-methyl-2-pentene (**D**) (trimers of hexafluoropropylene) in an aprotic polar solvent in the presence of fluoride ions are in a state of reversible mutual isomerization. The ratio of the isomers in the equilibrium mixture is 2 : 1.

The reaction of trimers of hexafluoropropylene with acetone oxime evidently proceeds by the mechanism typical of the reaction of these olefins with *O*-nucleophiles[6] to yield two isomeric ethers (**5** and **6**) — the products of vinyl and allyl substitution in molecules of olefins **D** and C, respectively (Scheme 4) (the ratio of isomers was determined by ^{19}F NMR spectroscopy).

Two compounds were separated by the distillation of the mixture at 40 °C (after treatment with water and drying): allyl ether **6** and vinyl ketone **7**, which we have obtained previously.[7]



Even when the products of the reaction are heated to only 70 °C, their decomposition becomes observable. Apparently, vinyl ether **5** is less thermically stable than the allyl ether **6**. On heating, it is completely converted to ketone **7**. Evidently, after heterolytic cleavage of the N—O bond, the mesomeric anion formed is unstable and is stabilized through the elimination of the fluoride ion.

Scheme 4

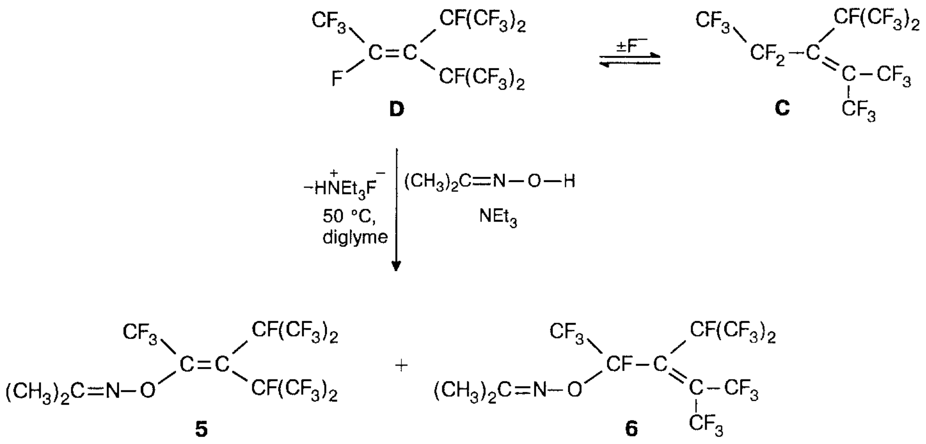


Table 1. Bond lengths (*d*) in compound **4**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
F(1)—C(9)	1.333(4)	F(9)—C(6)	1.326(4)	C(1)—C(7)	1.498(5)
F(2)—C(9)	1.337(5)	F(10—C(6)	1.347(4)	C(2)—C(4)	1.545(5)
F(3)—C(9)	1.346(5)	F(11)—C(6)	1.316(5)	C(3)—C(4)	1.595(5)
F(4)—C(8)	1.334(5)	O—C(4)	1.393(4)	C(3)—C(8)	1.549(5)
F(5)—C(8)	1.331(4)	O—H(O)	0.83(6)	C(3)—C(9)	1.546(5)
F(6)—C(8)	1.335(4)	N—C(1)	1.272(4)	C(4)—C(5)	1.554(5)
F(7)—C(5)	1.344(4)	N—C(3)	1.477(4)	C(5)—C(6)	1.546(5)
F(8)—C(5)	1.363(4)	C(1)—C(2)	1.506(5)		

If the reaction mixture obtained after the reaction of olefins with oxime (complete homogenization) has been completed, is allowed to stand for 2 h at 70 °C, the only product is vinyl ketone **7**. Evidently, under the reaction conditions (the presence of the fluoride ion in an aprotic polar solvent), the isomeric ethers **5** and **6** formed are in a state of a dynamic equilibrium. Apparently, owing to the thermal lability of ether **5**, the increase in temperature (40 → 80 °C) causes the shift of the equilibrium of the system to the right $\mathbf{6} \xrightleftharpoons{\pm F^-} \mathbf{5} \longrightarrow \mathbf{7}$.

It should be mentioned in conclusion, that among the prepared ethers **1**, **2**, **3**, **5**, and **6**, only ethers **3** and **5** are thermally unstable. Hence, it is the presence of the C=C multiple bond, directly attached to the oxygen atom, that substantially reduces the stability of the N—O bond in *O*-fluoroalkenyl ketoximes.

Experimental

The ^{19}F and ^{1}H NMR spectra (δ) were obtained on a Bruker WP-200 spectrometer (188.4 and 200 MHz), with CF_3COOH and TMS as external standards; mass spectra were recorded on a VGMS 70-70e chromatographic mass spectrometer, the energy of ionizing electrons was 70 eV (*m/z*, assumed assignments, intensities, %, are given).

X-ray diffraction analysis of a single crystal of compound **4** was performed on a Siemens P3/PC automated four-circle diffractometer at −124 °C (Mo-*K*α radiation, graphite monochromator, θ/2θ-scan technique, $2\theta \le 46°$). Crystals of **4** are orthorhombic, at −124 °C: $a = 8.330(2)$, $b = 10.884(3)$, $c = 13.286(3)$ Å, $V = 1204.6(9)$ Å^3, $d_{\text{calc}} = 1.947$ g cm^{-3}, $Z = 4$, the space group is $P2_12_12_1$. Of the total 1418 independent reflections, 1245 observed reflections with $|F| \ge 4\sigma(F)$ were used in subsequent calculations and refinement. The structure was solved by the direct method and refined anisotropically (isotropically for H) by the full-matrix least-squares procedure to $R = R_w = 0.033$. All calculations were performed on an IBM PC/AT personal computer using the SHELXTL PLUS program package.

The bond lengths and bond angles for compound **4** are given in Tables 1 and 2, respectively; atomic coordinates and temperature factors are listed in Table 3. The overall view of the molecule and the atomic numbering scheme is given in Fig. 1. Geometric parameters for crystalline molecule **4** are close to the expected values. The heterocycle adopts an envelope conformation: the C(3), N, C(1), and C(2) atoms are coplanar within 0.019 Å, and the deviation of the C(4) atom from the mean plane through the remaining four atoms of the cycle is 0.420 Å (toward the oxygroup). The C(3)—N—C(1)—C(2) torsion angle around the N=C(1) double bond is −4.9°, and the N=C(1) bond length (1.272(4) Å) is about normal for bonds of this type (the typical value is 1.279 Å, see Ref. 8). The presence of the bulky electron-accepting CF_3 and C_2F_5 groups at the C atoms of the heterocycle causes slight elongation of the N—C(3) (to 1.477(4) Å) and C(3)—C(4) (to 1.595 Å) bonds compared to their usual values. In molecule **4**,

Table 2. Bond angles (ω) in compound **4**

Angle	ω/deg	Angle	ω/deg
C(4)—O—H(O)	116(4)	F(7)—C(5)—C(6)	106.9(3)
C(1)—N—C(3)	109.6(3)	F(8)—C(5)—C(6)	105.4(3)
N—C(1)—C(2)	115.6(3)	C(4)—C(5)—C(6)	114.5(3)
N—C(1)—C(7)	122.4(3)	F(9)—C(6)—F(10)	107.3(3)
C(2)—C(1)—C(7)	122.1(3)	F(9)—C(6)—F(11)	109.2(3)
C(1)—C(2)—C(4)	102.6(3)	F(10)—C(6)—C(11)	106.8(3)
N—C(3)—C(4)	104.9(3)	F(9)—C(6)—C(5)	111.0(3)
N—C(3)—C(8)	107.5(3)	F(10)—C(6)—C(5)	108.4(3)
C(4)—C(3)—C(8)	112.9(3)	F(11)—C(6)—C(5)	113.7(3)
N—C(3)—C(9)	104.0(3)	F(4)—C(8)—F(5)	107.2(3)
C(4)—C(3)—C(9)	116.6(3)	F(4)—C(8)—F(6)	106.0(3)
C(8)—C(3)—C(9)	110.1(3)	F(5)—C(8)—F(6)	108.4(3)
O—C(4)—C(2)	113.)(3)	F(4)—C(8)—C(3)	111.7(3)
O—C(4)—C(3)	111.1(3)	F(5)—C(8)—C(3)	112.4(3)
C(2)—C(4)—C(3)	100.8(3)	F(6)—C(8)—C(3)	110.9(3)
O—C(4)—C(5)	101.7(3)	F(1)—C(9)—F(2)	106.4(3)
C(2)—C(4)—C(5)	112.5(3)	F(1)—C(9)—F(3)	107.1(3)
C(3)—C(4)—C(5)	118.3(3)	F(2)—C(9)—F(3)	107.8(3)
F(7)—C(6)—F(8)	107.2(3)	F(1)—C(9)—C(3)	112.7(3)
F(7)—C(5)—C(4)	111.9(3)	F(2)—C(9)—C(3)	110.5(3)
F(8)—C(5)—C(4)	110.5(3)	F(3)—C(9)—C(3)	112.0(3)

Table 3. Fractional atomic coordinates (×10^4,×10^3 for H atoms) and their equivalent isotropic (×10^3) and isotropic for H atoms (×10^2) temperature factors

Atom	*x*	*y*	*z*	U/Å^2
F(1)	1563(3)	8333(2)	3665(2)	38(1)
F(2)	430(3)	7138(2)	2603(2)	35(1)
F(3)	175(3)	9112(2)	2455(2)	38(1)
F(4)	−151(3)	9751(2)	4734(2)	38(1)
F(5)	−2127(3)	10223(2)	3774(2)	36(1)
F(6)	−2513(3)	9183(2)	5139(2)	34(1)
F(7)	−2069(3)	7441(2)	1506(2)	35(1)
F(8)	−2978(3)	9232(2)	1968(2)	34(1)
F(9)	−5254(3)	6547(2)	1941(2)	41(1)
F(10)	−4765(3)	7721(2)	674(2)	43(1)
F(11)	−5958(3)	8451(2)	1968(2)	39(1)
O	−4253(3)	8171(2)	3675(2)	23(1)
N	−930(4)	7153(3)	4524(2)	21(1)
C(1)	−1655(4)	6166(3)	4288(2)	21(1)
C(2)	−2768(5)	6256(3)	3397(3)	22(1)
C(3)	−1297(4)	8116(3)	3775(3)	20(1)
C(4)	−2895(4)	7657(3)	3230(2)	19(1)
C(5)	−3147(4)	7997(3)	2105(3)	23(1)
C(6)	−4828(5)	7678(3)	1687(3)	28(1)
C(7)	−1394(5)	4984(3)	4841(3)	25(1)
C(8)	−1531(5)	9337(3)	4355(3)	27(1)
C(9)	234(4)	8182(4)	3121(3)	29(1)
H(O)	−444(7)	796(5)	426(4)	7(2)
H(21)	−388(4)	593(3)	356(2)	1(1)
H(22)	−236(6)	584(5)	280(4)	5(1)
H(71)	−63(7)	510(5)	547(5)	8(2)
H(72)	−256(7)	455(5)	503(4)	7(2)
H(73)	−64(7)	448(6)	445(4)	8(2)

there are a number of shortened intramolecular contacts between the fluorine atoms of the CF_3 and C_2F_5 groups. In particular, the nonbonded distances F(1)···F(4), F(2)···F(7), F(7)···F(10), and F(8)···F(11) are shortened to 2.537(6), 2.562(6), 2.521(6), and 2.623(6) Å (the sum of the van der Waals radii of fluorine is 2.80 Å; see Ref. 9). In the crystal, molecules are linked in infinite chains through intermolecular hydrogen bonds of the O—H···N′ type (the N' atom is related to the basis N atom by the $-0.5+x$, $1.5-y$, $1-z$ operation). The parameters for this H-bond that can be referred to the bond of medium strength are as follows: O···N′ 2.793(4) Å, O—H(O) 0.83(6) Å, H(O)···N′ 2.04(6) Å, the angle at the H(O) atom is 151(5)°. There are no shortened intermolecular contacts other than the above-mentioned H-bond.

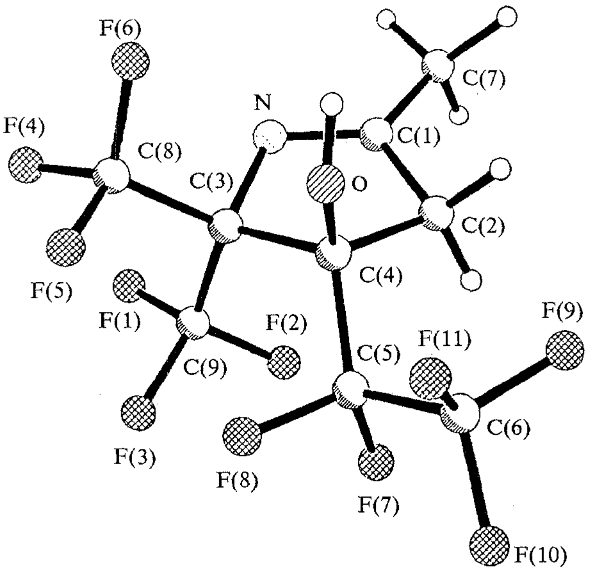


Fig. 1. The overall view of the pyrroline molecule **4**.

1,1,2,3,3,3-Hexafluoropropyl ether of acetone oxime (1). Hexafluoropropylene was passed through a mixture of acetone oxime (7.3 g, 0.1 mol), triethylamine (10 mL), diglyme (100 mL), and 25 g of a 50 % KOH aqueous solution with intense stirring, until the uptake of hexafluoropropylene was completed. Then the mixture was successively treated with a 5 % HCl solution and water. The organic phase was dried with $MgSO_4$ and 18.9 g (85 %) of ether **1**, b.p. 135 °C or 80 °C (100 Torr), was obtained by distillation. ^{1}H NMR ($CDCl_3$), δ: 2.4 (br s, 6 H, 2 CH_3); 5.6 (dtq, 1 H, CH, J_{H-F} = 43 Hz, J_{H-CF_3} = J_{H-CF_2} = 6 Hz). ^{19}F NMR, δ: −1.3 (ddt, 3 F, CF_3, J_{CF-CF} = 11 Hz, $J_{CF_3-CF_2}$ = 8 Hz, J_{CF_3-H} = 6 Hz); 6.6 (the center of the AB system, 2 F, CF_2, J_{A-B} = 156 Hz); 120.2 (dtq, 1 F, CF, J_{F-H} = 43 Hz, J_{F-CF_3} = J_{F-CF_2} = 11 Hz). Mass spectrum, *m/z* (I_{rel} (%)): 223 $[M]^+$(39), 208 $[M-CH_3]^+$(5), 204 $[M-F]^+$(1), 151 $[CF_3CHFCF_2]^+$(8), 101 $[CF_3CHF]^+$(5), 72 $[(CH_3)C{=}^+N{=}O]$ (56), 69 $[CF_3]^+$(28), 56 $[(CH_3)C{=}^+N]$ (100). Found (%): C, 32.33; H, 3.07; F, 51.61; $C_6H_7F_6ON$. Calculated (%): C, 32.29; H, 3.14; F, 51.12.

3-(2-Trifluoromethyl-1,1,1,3,4,,5,5,5-nonafluoro)pentyl ether of acetone oxime (2). Absolute triethylamine (1.0 g, 0.01 mol) was added dropwise with stirring and cooling to 0 °C to a mixture of perfluoro-2-methyl-2-pentene (15 g, 0.05 mol), acetone oxime (3.7 g, 0.05 mol), and absolute diglyme (20 mL). After 1 h, the mixture was treated with a 5 % HCl solution and water. The mixture was dried with Mg_2SO_4. 11.9 g (64 %) of compound **2**, b.p. 40—42 °C (10 Torr), was obtained by distillation. Mass spectrum, *m/z* (I_{rel} (%)): 373 $[M]^+$(5), 354 $[M-F]^+$(2), 119 $[C_2F_5]^+$(3), 72 $[(CH_3)_2C{=}^+N{=}O]$ (17), 69 $[CF_3]^+$(16), 56 $[(CH_3)_2C{=}^+N]$ (100). ^1H NMR ($CDCl_3$), δ: 1.95 and 1.97 (m, 6 H, 2 CH_3); 4.65 (m, 1 H, CH). ^{19}F NMR ($CDCl_3$), δ: −16.6 (m, 3 F, CF_3); −16.0 (m, 3 F, CF_3); 3.2 (d, 3 F, CF_3, J = 11 Hz); 33.2 (m, 1 F, CF); 44.4 (the AB system, 2 F, CF_2, J_{A-B} = 290 Hz). Found (%): C, 29.03; H, 1.77; F, 61.52. $C_9H_7F_{12}ON$. Calculated (%): C, 28.95, H, 1.88, F, 61.13.

3-Perfluoro-2-methyl-2-pentenyl ether of acetone oxime (3). Powdered KOH (2.0 g, 0.035 mol) was slowly added with stirring to a mixture of the 3-(2-trifluoromethyl-1,1,1,3,4,5,5,5-nonafluoro)pentyl ether of acetone oxime (**2**) (11.2 g, 0.03 mol) and absolute ether (20 mL). Then the reaction mixture was boiled for 10 min, cooled, and treated with a 5 % HCl solution and water. Then the mixture was dried with $MgSO_4$. 7.6 g (72 %) of compound **3**, b.p. 38—40 °C (12 Torr), was obtained by distillation. ^1H NMR ($CDCl_3$), δ: 1.95 and 1.98 (s, 6 H, 2 CH_3). ^{19}F NMR ($CDCl_3$), δ: −20.8 (tqq, 3 F, $CF_3{}^a$); −17.9 (q, 3 F, $CF_3{}^b$, $J_{CF_{3a}-CF_{3b}}$ = 10 Hz); 3.8 (q, 3 F, $CF_3{}^c$, $J_{CF_{3a}-CF_{3c}}$ = 3 Hz); 37.5 (q, 2 F, CF_2, $J_{CF_2-CF_{3a}}$ = 19 Hz). IR ($CDCl_3$), ν/см$^{-1}$: 1646 (C=C). Found (%): C, 31.08; H, 1.75; F, 59.47. $C_9H_6F_{11}ON$. Calculated (%): C, 30.59; H, 1.70; F, 59.21.

4-Hydroxy-3-methyl-5,5-bistrifluoromethyl-2-pentafluoroethyl-1-pyrroline (4). Compound **3** in a sealed ampule was placed in a thermostat (100 °C). The NMR spectra were recorded every 30 min. 7.1 g (0.02 mol) of the 3-perfluoro-2-methyl-2-pentenyl ether of acetone oxime (**3**) was kept in a sealed ampule for 3 h at 100 °C. 5.9 g (83 %) of compound **4**, m.p. 134 °C, was obtained by recrystallization from chloroform. IR ($CDCl_3$), ν/см$^{-1}$: 1657 (C=N). Mass spectrum, *m/z* (I_{rel} (%)): 353 $[M]^+$(4), 334 $[M-F]^+$(4), 234 $[M-C_2F_5]^+$(19), 191 $[(CF_3)_2C{=}N{-}CH{=}CH_2]^+$(100), 172 $[CF_2{=}C(CF_3){-}{}^+N{-}CH{=}CH_2]$ (22), 150 $[CF_3{-}CF{=}CF_2]^+$(12), 122 $[CF_3{-}C{\equiv}{}^+N{-}CH{=}CH_2]$ (5), 119 $[C_2F_5]^+$(3), 69 $[CF_3]^+$(9), 41 $[CH_3{-}C{\equiv}N]^+$(13). ^1H NMR, δ in $(CD_3)_2C{=}O$: 2.28 (s, 3 H, CH_3); 3.14, 3.23, 3.52 and 3.61 (s, AB system, CH_2, J_{A-B} = 18 Hz); 6.72 (s, 1 H, OH); in $CDCl_3$: 2.20 (s, 1 H, OH); 2.32 (s, 3 H, CH_3); 2.91, 3.00, 3.31 and 3.40 (s, AB system, CH_2, J_{A-B} = 18 Hz); in C_6F_6: 2.35 (s, 3 H, CH_3); 2.74 (s, 1 H, OH); 2.88, 2.97, 3.30 and 3.39 (s, CH_2, AB system, J_{A-B} = 18 Hz). ^{19}F NMR ($(CD_3)_2C{=}O$), δ: −11.8 (dq, 3 F, $CF_3{}^a$, $J_{CF_{3a}-CF_{3b}}$ = 12 Hz, $J_{CF_{3a}-F_B}$ = 23 Hz), −10.1 (ddq, 3 F, $CF_3{}^b$, $J_{CF_{3a}-CF_{3b}}$ = 12 Hz, $J_{CF_{3b}-F_A}$ = 30 Hz, $J_{CF_{3b}-FB}$ = 12 Hz); 1.4 (s, 3 F, $CF_3{}^c$); 37.7 and 39.1 (q, 1 F, F_A); 44.1 and 45.5 (qq, 1 F, F_B) (AB system, CF_2, J_{A-B} = 274 Hz). Found (%): C, 30.94: H, 1.89; F, 59.17; $C_9H_6F_{11}ON$. Calculated (%): C, 30.59; H, 1.70; F, 59.21.

The reaction of trimers of hexafluoropropylene with acetone oxime. 10 g (0.1 mol) of absolute triethylamine was added dropwise with stirring and cooling (0 °C) to a mixture of perfluoro-2,4-dimethyl-3-ethyl-2-pentene and perfluoro-4-methyl-3-isopropyl-2-pentene (45 g, 0.1 mol; trimers of hexafluoropropylene in a ratio of 2 : 1). Then the mixture was stirred for 15 h at room temperature, treated with a 5 % HCl solution and water, and dried with $MgSO_4$. According to ^{19}F NMR data, the obtained product is a mixture of two isomers (a 1 : 1 ratio): the 2-perfluoro-4-methyl-3-isopropyl-2-pentenyl (**5**) and 4-perfluoro-2-methyl-3-isopropyl-2-pentenyl (**6**) ethers of acetone oxime. The product was placed into a sealed ampule and allowed to stand for 3 h at 100 °C. The lower transparent pale-yellow bulky layer was distilled. 12.7 g (29.7 %) of perfluoro-3-isopropyl-4-methyl-3-penten-2-one (**7**), b.p. 108—100 °C, was obtained. Mass-spectrum, *m/z* (I_{rel} (%)): 409 $[M-F]^+$(5), 359 $[M-CF_3]^+$(54), 293 $[(CF_3)_2C{=}C{=}C(CF_3){-}{}^+CF_2]$ (6), 243 $[(CF_3)_2C{=}C{=}CF{-}{}^+CF_2]$ (11), 181 $[CF_2{=}C(CF_3){-}{}^+CF_2]$ (8), 97 $[CF_3{-}C{\equiv}{}^+O]$ (12), 69 $[CF_3]^+$(100); the ^{19}F NMR and IR spectra are in complete agreement with those reported previously;[7] 18.6 g (37 %) of compound **6**, b.p. 97—100 °C (28 Torr). Mass spectrum, *m/z* (I_{rel} (%)): 503 $[M]^+$(1), 484 $[M-F]^+$(5), 434 $[M-CF_3]^+$(89), 119 $[C_2F_5]^+$(2), 72 $[(CH_3)_2C{=}^+N{=}O]$ (48), 69 $[CF_3]^+$(64), 56 $[(CH_3)_2C{=}^+N]$ (100). ^1H NMR ($CDCl_3$), δ: 1.51 and 1.57 (m, 6 H, 2 CH_3). ^{19}F NMR ($CDCl_3$), δ: −19.8 (dm, 3 F, $CF_3{}^a$); −17.5 (dqq, 3 F, $CF_3{}^b$); −9.2 (dm, 3 F, $CF_3{}^c$); −7.8 (qq, 3 F, $CF_3{}^d$); −3.5 (m, 3 F, $CF_3{}^e$); 19.1 (qqm, 1 F, CF^f); 82.0 (qm, 1 F, CF^g); J_{a-g} = 53 Hz, J_{b-f} = 28 Hz, J_{a-b} = J_{b-d} = J_{d-e} = 14 Hz. Found (%): C, 28.81; H, 1.31; F, 63.88. $C_{12}H_6F_{17}ON$. Calculated (%): C, 28.63; H, 1.19; F, 64.21. ^{19}F NMR for ether **5** ($CDCl_3$), δ: −16.7 (d, 3 F, $CF_3{}^a$, J_{a-d} = 57 Hz); −4.4 (s, 6 F, $(CF_3{}^b)_2$, −3.8 (d, 6 F, $(CF_3{}^c)_2$, J_{c-e} = 34 Hz); 89.6 (qd, 1 F, CF^d, J_{d-e} = 8 Hz); 92.3 (heptet d, 1 F, CF^e).

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