Reaction of perfluoro-2-methyl-2-pentene with cycloalkanone oximes: new examples of the Beckmann—Chapman rearrangement

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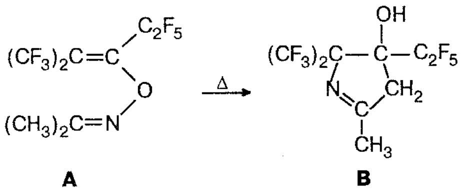
The base-catalyzed reaction of cycloalkanone oximes (**1a,b**) with perfluoro-2-methyl-2-pentene (PFMP) initially affords the addition products, *i.e.*, fluoroalkyl ethers (**2a,b**). In the presence of KOH, the latter undergoes dehydrofluorination to give perfluoroalkenyl ethers (**3a,b**). Thermolysis of ethers **3a,b** results in compounds of two types — pyrrolines (**4a,b**) and *N*-perfluoroalkenyl lactams (**5a,b**). The latter are also prepared from PFMP and the corresponding lactams. The structure of *N*-[perfluoro-(2-methyl-2-penten-3-yl)]-2-pyrrolidone (**5c**) was established by X-ray diffraction study.

Key words: perfluoro-2-methyl-2-pentene; fluoroalkyl ethers of cycloalkanone oximes; fluoroalkenyl ethers of cycloalkanone oximes; thermal rearrangement; fluoroalkylpyrrolines; *N*-fluoroalkenyl lactams, X-ray analysis.

Previously we demonstrated[1] that the thermolysis of the *O*-substituted oxime (**A**) prepared from perfluoro-2-methyl-2-pentene (PFMP) and acetone oxime results in quantitative isomerization to give the corresponding pyrroline (**B**).

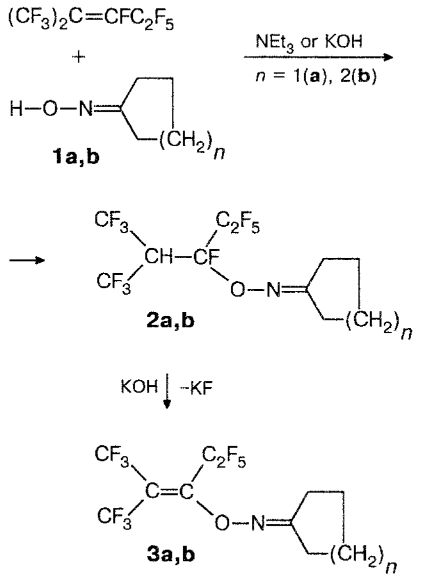


A **B**

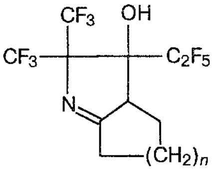
The aim of this work is to synthesize analogous derivatives of cyclic ketones and to study their properties.

Cyclopentanone oxime (**1a**) and cyclohexanone oxime (**1b**) react with PFMP only in the presence of catalytic amounts of bases to give adducts **2a, b** and the products of their dehydrofluorination **3a,b** (no more than 10%). When the saturated ethers **2a,b** and powdered KOH are heated in Et_2O, compounds **3a,b** are also obtained in preparative yields (~70 %) (Scheme 1).

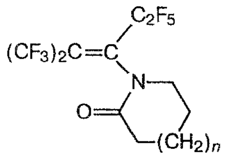
Scheme 1



As may be expected, the thermal stability of vinyl ethers **3a,b** is rather limited. They can be distilled without decomposition under a vacuum only at temperatures not exceeding 70 °C. When heated to 100 °C, these compounds are completely converted. However, in contrast to the thermolysis of ether **A**, which is isomerized only to pyrroline **B** under the same conditions, in the case under consideration, two types of products, **4** and **5**, are formed. In the case of cyclopentanone derivative, **3a**, the major product is **4a**, whereas in the case of cyclohexanone derivative **3b**, the major product is of the second type (**5b**):



4a,b



5a,b

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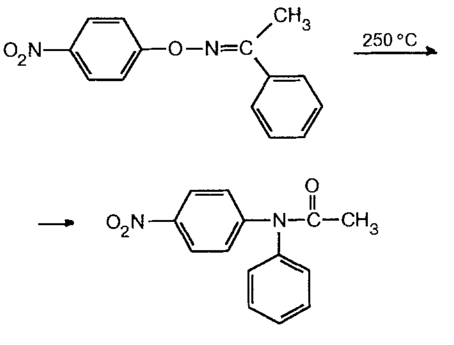
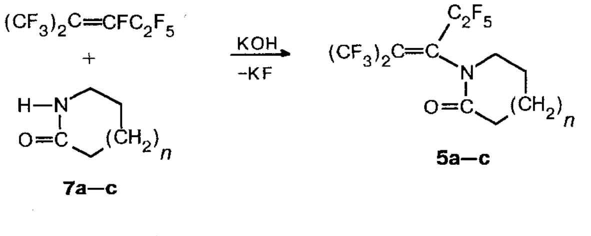
Apparently, the formation of products of the first type — pyrrolines **4a,b** — is analogous to the isomerization **A** → **B** (*cf.* Ref. 1).

In these two cases, the formation of the products of the second type — lactams **5a,b** — according to Scheme 2 is of most interest.*

Evidently, the lability of the O—N bond and its susceptibility to heterolytic cleavage are the driving forces for the thermolysis. However, in the first case (route *A*), the transient cationoid species migrates from the O atom to the C atom of the mesomeric anion in the unchanged form, and the ions are stabilized through the formation of the C—N bond, whereas in the second case (route *B*), the cationoid species undergoes a change, that is, the cycle expands and the positive charge moves from the N atom to the C atom (*i. e.*, processes typical of the Beckmann rearrangement take place). In the latter case, the charged particles are stabilized owing to the formation of the C—O bond, after which the fluoroalkenyl group migrates from the O atom to the N atom in the intermediate imido ethers **6a,b**. This migration was previously observed[2] for *O*-aryl oximes containing electron-withdrawing substituents in the aromatic ring (the Beckmann—Chapman rearrangement), for example:



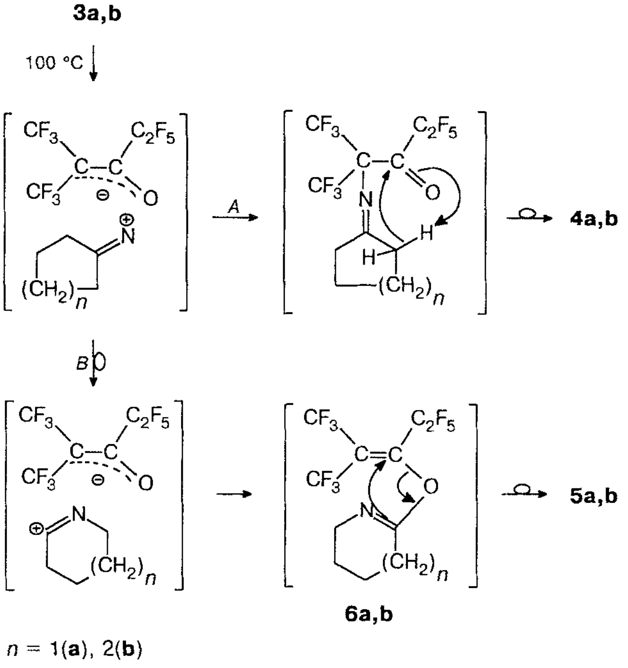
In our case, hitherto unprecedented, the role of the electron-withdrawing substituent in this rearrangement is played by the perfluoroalkenyl group. It should to be mentioned that *N*-(perfluoroalkenyl)lactams of the type **5** may be readily obtained by back synthesis from the corresponding lactams (**7a—c**) and PFMP in the presence of a base.



7a—c **5a—c**

n = 1(**a**), 2(**b**), 0(**c**)

Scheme 2



Lactams **5a—c** are unstable in acidic media; when their ethereal solutions are boiled with a 5 % HCl solution, they are readily hydrolyzed to give the corresponding ketones, $(CF_3)_2CH—C(O)—C_2F_5$.

It is known,[3] that the Beckmann rearrangement proceeds much more readily for the oximes of cyclic ketones than for those of acyclic ketones. Evidently, this fact accounts for the absence of *N*-fluoroalkenylacetamide, when ether **A** is subjected to thermolysis.

The structures of bicyclic compounds **4a,b** are based unambiguously on a spectroscopic evidence. Thus, their ^{19}F NMR spectra are virtually no different from the spectrum of pyrroline **B** (Table 1), the structure of which has been established previously by X-ray structural analysis. In their mass spectra, ions of high intensity have been observed, which apparently correspond to the elimination of the C_2F_5 and $C_2F_5—C{=}O$ groups from the molecular ion.

The fragment ions $[M—CF_3]^+$ are dominant in the mass spectra of lactams **5a—c**. In order to establish unambiguously the structure of *N*-fluoroalkenyl lactams **5a—c**, we used X-ray diffraction method, because the possibility of the formation of isomeric compounds **6** (the intermediates of the Beckmann—Chapman rearrangement) as a result of attack by the *O*-rather than by the *N*-nucleophilic center of the initial lactams **7a—c** at the multiple bond of perfluoro-2-methyl-2-pentene could not be otherwise excluded.

The geometric parameters for molecule **5c** have the normal values, which are similar to those found previously[4] in the 3-(4-methylphenoxy)perfluoro-2-methyl-2-pentene molecule. Among the characteristic features

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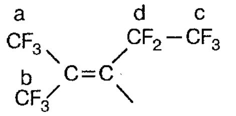
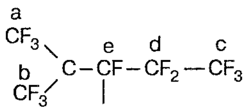
* Under conditions, in which pyrrolines **3a** and **3b** are eliminated, hydrolysis of lactams **4a,b** occurs.

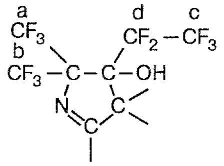
Table 1. ^{19}F NMR spectra (CDCl$_3$) for compounds of the three structural types studied



3a,b, 5a—c



2a,b



B, 4a,b

Compound	δ					Spin-spin interaction constant, *J*/Hz
	a	b	c	d*	e	
2a	−16.5	−16.0	3.2	43.8(A) 44.5(B)	32.5	10.9(c—e), 295(A—B)
2b	−16.6	−16.1	3.4	44.1(A) 44.9(B)	33.7	10.8(c—e), 297(A—B)
3a	−20.8	−17.9	3.8	37.5	–	10(a—b), 19.8(a—d), 3.4(a—c)
3b	−21.0	−18.2	3.6	37.4	–	9.2(a—b), 18.3(a—b), 4.1(a—c)
5a	−19.9	−15.9	3.9	32.1	–	9.3(a—b), 18.4(a—d), 6.7(a—c)
5b	−20.0	−15.0	3.6	32.7	–	9.5(a—b), 8.6(a—c), 19.9(a—d)
5c	−21.4	−14.1	4.1	29.4(A) 35.1(B)	–	9.2(a—b), 7.6(a—c), 36.6(a—B), 298(A—B)
4a	−11.5	−10.3	1.9	40.7(A) 44.5(B)	–	32(b—A), 25.5(a—B), 11.5(a—c), 11.5(b—B), 280(A—B)
4b	−11.3	−10.6	2.0	38.0(A) 40.4(B)	–	31.8(b—A), 24.7(a—B), 11.5(a—c), 12.0(b—B), 282(A—B)
B	−11.8	−10.1	1.4	38.5(A) 44.7(B)	–	30.7(b—A), 23.1(a—B), 12.0(b—B), 11.5(a—c), 275(A—B)

* Signal CF$_2$(d) — the **AB** system.

of the molecular geometry a slight twisting about the C(6)=C(7) double bond should to be mentioned: the C(10)—C(6)—C(7)—C(9), C(10)—C(6)—C(7)—C(8), N(1)—C(6)—C(7)—C(8), and N(1)—C(6)—C(7)—C(9) torsion angles are −11.5, 162.7, −20.2, and 165.7°, respectively; the double bond is planar within 0.120 Å. The five-membered cycle adopts an envelope conformation with the 0.49 Å deviation of the C(3) atom from the plane accommodating the remaining four atoms (which are coplanar within 0.01 Å). The dihedral angle between the mean planes through the ring and the double bond is 69.8°.

Experimental

The ^{19}F and ^{1}H NMR spectra were obtained on a Bruker WP-200 spectrometer (188.4 and 200 MHz) using CF$_3$COOH and TMS, respectively, as external standards. Mass spectra (electron impact) were obtained on a VGMS 70-70e gas chromatography—mass spectrometry instrument; the energy of the ionizing electrons was 70 eV (*m/z*, assumed assignments, intensities, %, are given).

X-ray diffraction analysis of compound **5** was performed on a Siemens P3/PC automated four-circle diffractometer (λMo-*K*α radiation, graphite monochromator, $\theta/2\theta$-scan technique, $2\theta \le 54°$) at −100 °C. Crystals of **6c** are monoclinic; at −100 °C: $a = 8.326(2)$, $b = 10.155(3)$, $c = 15.250(3)$ Å, $\beta = 100.19(3)°$, $V = 1269(2)$ Å^3, $d_{\text{calc}} = 1.911$ g cm^{-3}, $Z = 4$, the space group $P2_1/n$. Of the 2565 measured reflections, a total of 1755 independent observed reflections with $I \ge 3.5\sigma(I)$ were used in subsequent calculations and refinement of the structure. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method. The positions of the hydrogen atoms were determined geometrically and were used in calculations with fixed positional and isotropic thermal parameters (0.05 Å^2). The final refinement converged to $R = R_w = 0.028$, GOF = 1.26. The overall view of molecule **5c** in the crystal and the atomic numbering scheme are shown in Fig. 1. Coordinates and thermal parameters for non-hydrogen atoms in structure **5c** are given in Table 2; the bond lengths and bond angles are listed in Tables 3 and 4. All calculations were performed on an IBM PC/AT personal computer using the SHELXTL PLUS program package.

3-(2-Trifluoromethyl-1,1,1,3,4,4,5,5,5-nonafluoro)pentyl ethers of cycloalkanone oximes (2a,b). 1.0 g (0.01 mol) of absolute NEt$_3$ was added dropwise with stirring and cooling (0 °C) to a mixture of perfluoro-2-methyl-2-pentene (15 g, 0.05 mol) with 0.05 mol of cyclopentanone or cyclohexanone oximes (**1a,b**) in absolute diglyme (20 mL). After 1 h, the reaction mixture was treated with a 5 % HCl solution, then with water, and dried with MgSO$_4$. From PFMP and **1a** there was obtained 12.6 g (63 %) of the 3-(2-trifluoromethyl-1,1,1,3,4,4,5,5,5-nonafluoro)pentyl ether of cyclopentanone oxime **2a**, b. p. 71—73 °C (10 Torr). Mass spectrum, *m/z* (I_{rel}

Table 2. Fractional atomic coordinates for nonhydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors ($\times 10^3$) in structure **5c**

Atom	*x*	*y*	*z*	*U*/Å
F(1)	387(1)	7246(1)	7121(1)	33(1)
F(2)	36(1)	8887(1)	6228(1)	38(1)
F(3)	481(2)	6952(1)	5744(1)	37(1)
F(4)	4590(1)	9070(1)	5780(1)	35(1)
F(5)	3719(2)	7160(1)	5305(1)	44(1)
F(6)	2135(2)	8846(1)	5108(1)	43(1)
F(7)	6105(1)	7332(1)	6776(1)	35(1)
F(8)	5979(1)	6734(1)	8122(1)	38(1)
F(9)	6206(2)	9947(1)	7352(1)	50(1)
F(10)	6175(2)	9259(2)	8678(1)	51(1)
F(11)	8119(2)	8686(2)	8004(1)	63(1)
O(1)	1986(2)	10008(1)	7916(1)	33(1)
N(1)	3073(2)	7929(2)	8157(1)	20(1)
C(2)	3180(3)	6883(2)	8840(1)	28(1)
C(3)	1864(3)	7296(2)	9362(1)	29(1)
C(4)	1815(3)	8784(2)	9279(1)	27(1)
C(5)	2255(2)	9035(2)	8375(1)	23(1)
C(6)	3705(2)	7869(2)	7364(1)	21(1)
C(7)	2734(2)	8005(2)	6566(1)	22(1)
C(8)	903(2)	7790(2)	6434(1)	27(1)
C(9)	3317(3)	8259(2)	5692(1)	30(1)
C(10)	5559(2)	7703(2)	7518(1)	27(1)
C(11)	6533(2)	8925(3)	7893(2)	37(1)

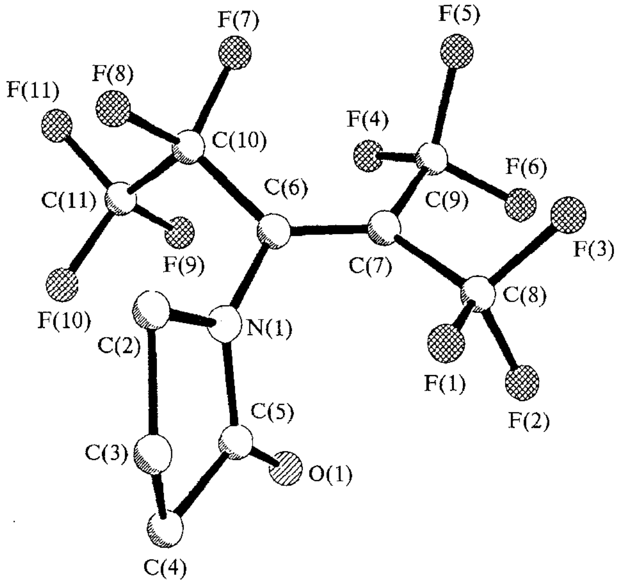


Fig. 1. The overall view of *N*-perfluoroalkenyl-α-pyrrolidone **5c**.

Table 3. Bond lengths (*d*) in structure **5c**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
F(1)—C(8)	1.322(2)	F(9)—C(11)	1.324(3)	C(3)—C(4)	1.516(3)
F(2)—C(8)	1.335(2)	F(10)—C(11)	1.328(3)	C(4)—C(5)	1.510(3)
F(3)—C(8)	1.350(2)	F(11)—C(11)	1.324(2)	C(6)—C(7)	1.344(2)
F(4)—C(9)	1.330(2)	O(1)—C(5)	1.210(2)	C(6)—C(10)	1.529(3)
F(5)—C(9)	1.333(3)	N(1)—C(2)	1.480(3)	C(7)—C(8)	1.518(3)
F(6)—C(9)	1.345(2)	N(1)—C(5)	1.384(2)	C(7)—C(9)	1.519(3)
F(7)—C(10)	1.346(2)	N(1)—C(6)	1.403(3)	C(10)—C(11)	1.536(3)
F(8)—C(10)	1.351(2)	C(2)—C(3)	1.523(3)		

Table 4. Bond angles (ω) in structure **5c**

Angle	ω/deg	Angle	ω/deg
C(2)—N(1)—C(5)	112.6(2)	F(3)—C(8)—C(7)	108.1(2)
C(2)—N(1)—C(6)	126.2(2)	F(4)—C(9)—F(5)	107.8(2)
C(5)—N(1)—C(6)	121.2(2)	F(4)—C(9)—F(6)	105.6(2)
N(1)—C(2)—C(3)	102.2(2)	F(5)—C(9)—F(6)	106.8(2)
C(2)—C(3)—C(4)	104.0(2)	F(4)—C(9)—C(7)	112.9(2)
C(3)—C(4)—C(5)	103.7(2)	F(5)—C(9)—C(7)	113.0(2)
O(1)—C(5)—N(1)	124.9(2)	F(6)—C(9)—C(7)	110.3(2)
O(1)—C(5)—C(4)	128.1(2)	F(7)—C(10)—F(8)	106.5(2)
N(1)—C(5)—C(4)	107.0(2)	F(7)—C(10)—C(6)	112.5(1)
N(1)—C(6)—C(7)	121.3(2)	F(8)—C(10)—C(6)	108.5(2)
N(1)—C(6)—C(10)	113.2(1)	F(7)—C(10)—C(11)	107.7(2)
C(7)—C(6)—C(10)	125.4(2)	F(8)—C(10)—C(11)	106.2(1)
C(6)—C(7)—C(8)	122.3(2)	C(6)—C(10)—C(11)	114.9(2)
C(6)—C(7)—C(9)	125.3(2)	F(9)—C(11)—F(10)	107.9(2)
C(8)—C(7)—C(9)	112.2(1)	F(9)—C(11)—F(11)	108.3(2)
F(1)—C(8)—F(2)	107.3(2)	F(10)—C(11)—F(11)	108.0(2)
F(1)—C(8)—F(3)	106.1(2)	F(9)—C(11)—C(10)	111.4(2)
F(2)—C(8)—F(3)	106.7(1)	F(10)—C(11)—C(10)	110.7(2)
F(1)—C(8)—C(7)	114.5(1)	F(11)—C(11)—C(10)	110.4(2)
F(2)—C(8)—C(7)	113.6(2)		

(%)): 399 $[M]^+$(9), 380 $[M-F]^+$(3), 360 $[M-HF_2]^+$(1), 179 $[(CF_3)_2CH-C\equiv O^+]$(1), 119$[C_2F_5]^+$(3), 113 $[CF_2=CH-{}^+CF_2]$(2), 99 $[(\overline{CH_2)_4C}=N-OH]^+$(6), 98 $[(\overline{CH_2)_4C}={}^+N=O]$(10), 82 $[(\overline{CH_2)_4C}={}^+N]$(100), 69 $[CF_3]^+$(17), 68 $[C_5H_8]^+$(17), 67 $[C_5H_7]^+$(15), 55 $[C_4H_7]^+$(74), 54 $[C_4H_6]^+$(19), 53 $[C_4H_5]^+$(6), 41 $[C_3H_5]^+$(18). Found (%): C, 33.18; H, 2.29; F, 57.43. $C_{11}H_9F_{12}ON$. Calculated (%): C, 33.08; H, 2.26; F, 57.14. Using the same procedure, from oxime **1b** and PFMP there was prepared 13.8 g (67%) of the 3-(2-trifluoromethyl-1,1,1,3,4,4,5,5,5-nonafluoro)pentyl ether of cyclohexanone oxime **2b**, b.p. 80—82 °C (10 Torr). Mass spectrum, *m/z* (I_{rel}(%)): 413 $[M]^+$(20), 394 $[M-F]^+$(4), 374 $[M-HF_2]^+$(1), 359 $[M-2HF-CH_2]^+$(8), 179 $[(CF_3)_2CH-C\equiv{}^+O]$(3), 119 $[C_2F_5]^+$(5), 113 $[(\overline{CH_2)_5C}=N-OH]^+$ and [CF2=CH—+CF2](14), 112 $[(\overline{CH_2)_5C}={}^+N=O]$(19) , 96 $[(\overline{CH_2)_5C}={}^+N]$(100) , 82 $[C_6H_{10}]^+$(19), 81 $[C_6H_9]^+$(17), 79 $[C_6H_7]^+$(6), 69 $[CF_3]^+$(3), 68 $[C_5H_8]^+$(15), 67 $[C_5H_7]^+$(20), 58 $[C_4H_{10}]^+$(15), 55 $[C_4H_7]^+$(67), 54 $[C_4H_6]^+$(17), 53 $[C_4H_5]^+$(8), 42 $[C_3H_6]^+$(34), 41 $[C_3H_5]^+$(44). Found (%): C, 35.07; H, 2.73; F, 55.02. $C_{12}H_{11}F_{12}ON$. Calculated (%): C, 34.87; H, 2.66; F, 55.21.

***O*-(3-(2-Trifluoromethyl)perfluoro-2-pentenyl)cycloalkanone oximes (3a,b).** Powdered KOH (2.0 g, 0.035 mol) was slowly added with stirring to a solution of 0.03 mol of a polyfluoroalkyl ether (**2a** or **2b**) in absolute ether (20 mL). The reaction mixture was heated to boiling and left to boil 10 min. The mixture was cooled, treated successively with a 5 % HCl solution and water, and the organic layer was dried with $MgSO_4$. The extract was evaporated, and the residue was distilled under a vacuum. The yield of the 3-perfluoro-2-methyl-2-pentenyl ether of cyclopentanone oxime **3a** was 7.9 g (70 %), b.p. 74—76 °C (10 Torr). IR ($CDCl_3$), ν/cm^{-1}: 1647 (C=C). Found (%): C, 35.07; H, 2.19; F, 56.02. $C_{11}H_8F_{11}ON$. Calculated (%): C, 34.83; H, 2.11; F, 55.15. Similarly, from **2b** (00.3 mol) there was obtained 8.1 g (68 %) of the 3-perfluoro-2-methyl-2-pentenyl ether of cyclohexanone oxime **4b**, b.p. 81—83 °C (10 Torr). IR ($CDCl_3$), ν/cm^{-1}: 1646 (C=C). Found (%): C, 36.88; H, 2.73; F, 53.02. $C_{12}H_{10}F_{11}ON$. Calculated (%): C, 36.64; H,2.54; F, 53.18.

4-Hydroxy-5,5-bistrifluoromethyl-4-pentafluoroethyl-2,3-trimethylene-1-pyrroline (4a). A solution of the polyfluoroalkyl ether of cyclopentanone oxime (**3a**) (7.6 g, 0.01 mol) in absolute Et_2O (15 mL) was allowed to stand for 1 h at 100 °C in a sealed ampule. Based on ^{19}F NMR data, the reaction mixture consisted of **4a** and lactam **5a** in the ratio of 3:1. Then 5 mL of a 3 % HCl solution was added, the mixture was stirred for 1 h at 35 °C, then the organic layer was dried with $MgSO_4$, and the ether was removed under a vacuum. 3.6 g (47 %) of pyrroline **4a**, m.p. 87 °C, was obtained by recrystallization from chloroform. IR (KBr), ν/cm^{-1}: 1687 (C=N), 3360 (OH). ^1H NMR ($CDCl_3$), δ: 2.0 (m, 2 H, CH_2); 2.3 (m, 2 H, CH_2); 2.6 (m, 2 H, CH_2); 3.3 (br s, 1 H, OH); 3.7 (t, 1 H, CH, J = 9.8 Hz). Mass spectrum, *m/z* (I_{rel} (%)): 379 $[M]^+$(8.4), 378 $[M-H]^+$(1.3), 360 $[M-F]^+$(22.9), 351 $[M-C_2H_4]^+$(22.2), 310 $[M-CF_3]^+$(1.6), 282 $[M-CF_3-C_2H_4]^+$(7.5), 260 $[M-C_2F_5]^+$(34.1), 232 $[M-C_2F_5-CO]^+$(110), 231 (2.6), 230 (3.1), 214 (6.5), 204 $[M-C_2F_5-C_3H_4O]^+$(6.6), 190 $[M-C_3F_5-C_4H_6O]^+$(2.3), 184 $[M-C_2F_6-C_3H_3O]^+$(5.7), 119 $[C_2F_5]^+$(7.5), 95 $[CF_3-C\equiv N]^+$(21.8), 69 $[CF_3]^+$(23.6), 67 $[C_2F_7]^+$(32.0), 55 $[C_4H_7]^+$(14.0), 51 $[CHF_2]^+$(3.8), 41 $[C_3H_5]^+$(20.8), 39 $[C_3H_3]^+$(15.3). Found (%): C, 34.17; H, 2.02; F, 55.63. $C_{11}H_8F_{11}ON$. Calculated (%): C, 34.83; H, 2.11; F, 55.15.

4-Hydroxy-5,5-bistrifluoromethyl-4-pentafluoroethyl-2,3-tetramethylene-1-pyrroline (4b). A solution of the 3-perfluoro-2-methyl-2-pentenyl ether of cyclohexanone oxime **3b** (7.9 g, 0.02 mol) in absolute Et_2O (15 mL) was allowed to stand for 1 h in a sealed ampule at 100 °C. Based on ^{19}F NMR data, the reaction mixture consisted of pyrroline **4b** and lactam **5b** in a ratio of 1:1. 3% aqueous HCl (5 mL) was added to the reaction mixture, and the mixture was stirred for 1 h at 35 °C. Then the mixture was washed with water, dried with $MgSO_4$, the ether was removed under a vacuum, and **4b** (m. p. 65 °C) was obtained by recrystallization from chloroform in a yield of 3.3 g (41%). IR (KBr), ν/cm^{-1}: 1685 (C=N), 3340 (OH). ^1H NMR ($CDCl_3$), δ: 1.9 (m, 4 H, 2×CH_2); 2.2 (m, 2 H, CH_2); 2.6 (m, 2 H, CH_2); 3.2 (br s, 1 H, OH); 3.6 (t, 1 H, CH, J = 9.7 Hz). Mass spectrum, *m/z* (I_{rel} (%)): 393 $[M]^+$(55.0), 393 $[M-H]^+$(3.2), 375 $[M-H_2O]^+$(5.8), 374 $[M-F]^+$(35.2), 373 $[M-HF]^+$(3.0), 365 $[M-C_2H_4]^+$(7.9), 364 $[M-C_2H_5]^+$(17.1), 354 $[M-HF_2]^+$(3.0), 324 $[M-CF_3]^+$(3.7), 306 $[M-CF_3-H_2O]^+$(2.3), 274 $[M-C_2F_5]^+$(74.7), 246 $[M-C_2F_5-CO]^+$(100.0), 245 (14.2), 244 (72.6), 243 (7.0), 242 (64.5), 204 (10.0), 201 (18.1), 193 (47.6), 153 (11.8), 122 (12.3), 119 $[C_2F_5]^+$(11.6), 109 (15.5), 81 $[C_6H_{10}]^+$(56.4), 79 (27.9), 77 (13.4), 69 $[CF_3]^+$(28.7), 67 $[C_5H_8]^+$(12.7), 55 (34.3), 53 (24.6), 41 (54.3), 39 (26.9). Found (%): C, 37.13; H, 2.41; F, 53.37. $C_{12}H_{10}F_{11}ON$. Calculated (%): C, 36.64; H, 2.54; F, 53.18.

***N*-[3-(2-Trifluoromethyl)perfluoro-2-pentenyl]lactams (5a—c).** 2.8 g (0.05 mol) of powdered KOH was slowly added with stirring to a mixture of 15 g (0.05 mol) of PFMP and 0.05 mol of the initial lactam (**7a—c**) in 20 mL of absolute diglyme. After 1 h, 50 mL of Et_2O was added to the reaction mixture, and the mixture was dried with $MgSO_4$. The ether was removed under a vacuum. Recrystallization from alcohol afforded:

from α-piperidone **7a** (4.9 g) — 9.2 g (49 %) of **5a**, m. p. 63 °C. IR (KBr), ν/cm^{-1}: 1647 (C=C), 1710 (C=O). Mass spectrum, *m/z* (I_{rel} (%)): 379 $[M]^+$(1), 360 $[M-F]^+$(5), 332 $[M-F-CO\ \text{or}\ -C_2H_4]^+$(6), 310 $[M-CF_3]^+$(100), 254 $[M-CF_3-C_3H_4O]^+$(10), 290 $[M-F-C_4H_6O]^+$(3), 282 $[M-CF_3-CO\ \text{or}\ -C_2H_4]^+$(3), 204 $[M-C_2F_5-C_3H_4O]^+$(4), 190 $[M-C_2F_5-C_4H_6O]^+$(7), 83 $[C_5H_7O]^+$(4), 82 $[C_5H_6O]^+$(7), 69 $[CF_3]^+$(10), 56 $[C_3H_4O]^+$(2), 55 $[C_3H_3O]^+$(31), 54 $[C_3H_2O]^+$(6), 53 $[C_3HO]^+$(3), 51 $[CHF_2]^+$(2), 42 $[C_3H_6\ \text{or}\ C_2H_2O]^+$(7), 41 $[C_3H_5\ \text{or}\ C_2HO]^+$(15). Found (%): C, 35.01; H, 2.19; F, 55.27. $C_{11}H_8F_{11}ON$. Calculated (%): C, 34.83; H, 2.11; F,55.15.

from caprolactam **7b** (5.6 g) — 10.0 g (51 %) of **5b**, m. p. 49 °C. IR (KBr), ν/cm^{-1}: 1648 (C=C), 1690 (C=O). Mass spectrum, *m/z* (I_{rel} (%)): 393 $[M]^+$(2), 374 $[M-F]^+$(2), 346 $[M-F-CO\ \text{or}\ -C_2H_4]^+$(2), 336 $[M-3F]^+$(4), 324 $[M-CF_3]^+$(100), 310 $[M-CF_3-CH_2]^+$(3), 296 $[M-CF_3-C_2H_4\ \text{or}\ -CO]^+$(5), 290 $[M-F-C_5H_8O]^+$(6), 282 $[M-CF_3-C_2H_2O]^+$(2), 254 $[M-CF_3-C_4H_6O]^+$(2), 190 $[M-C_2F_5-C_5H_{10}O]^+$(7), 204 $[M-C_2F_5-C_4H_6O]^+$(3), 145 $[C_2F_5C=]$(2), 97 $[CF_3-C\equiv O]^+$(9), 69 $[CF_3]^+$(69), 68 $[C_5H_8\ \text{or}\ C_4H_4O]^+$(55), 67 $[C_5H_7]^+$(13), 56 $[C_4H_8\ \text{or}\ C_3H_4O]^+$(4), 55 $[C_4H_7\ \text{or}\ C_3H_3O]^+$(38), 54 $[C_4H_6\ \text{or}\ C_3H_2O]^+$(2), 53 $[C_4H_5\ \text{or}\ C_3HO]^+$(4), 51 $[CHF_2]^+$(3), 43 $[C_3H_7]^+$(5), 42 $[C_3H_6\ \text{or}\ C_2H_2O]^+$(11), 41 $[C_3H_5\ \text{or}\ C_2HO]^+$(67). Found (%): C, 36.31; H, 2.41; F, 53.41. $C_{12}H_{10}F_{11}ON$. Calculated (%): C, 36.64; H, 2.54; F, 53.18.

from α-pyrrolidone **7c** (4.3 g) - 9.8 g (54 %) of **5c**, m. p. 56 °C. IR (KBr), ν/cm^{-1}: 1646 (C=C), 1755 (C=O). Mass spectrum, *m/z* (I_{rel} (%)): 365 $[M]^+$(5), 346 $[M{-}F]^+$(11), 326 $[M{-}HF_2]^+$(2), 318 $[M{-}F{-}CO$ or $-C_2H_4]^+$(2), 310 $[M{-}C_3H_3O]^+$(10), 308 $[M{-}3F]^+$(1), 296 $[M{-}CF_3]^+$(100), 290 $[M{-}F{-}C_3H_4O]^+$(13), 276 $[M{-}F{-}C_4H_6O]^+$(2), 268 $[M{-}CF_3{-}CO$ or $-C_2H_4]^+$(4), 240 $[M{-}CF_3C_3H_4O]^+$(1), 204 $[M{-}C_2F_5{-}3CH_2$ or $-C_2H_2O]^+$(1), 190 $[M{-}C_2F_5{-}C_3H_4O]^+$(6), 145 $[C_2F_5{-}C{\equiv}N]^+$(4), 119 $[C_2F_5]^+$(1), 69 $[CF_3]^+$(24), 68 $[C_4H_4O]^+$(7), 56 $[C_3H_4O]^+$(5), 55 $[C_3H_3O]^+$(39), 51 $[CHF_2]^+$(3), 42 $[C_3H_6$ or $C_2H_2O]^+$(11), 41 $[C_3H_5$ or $C_2HO]^+$(43). Found (%): C, 33.01; H, 1.74; F, 57.19. $C_{10}H_6F_{11}ON$. Calculated (%): C, 32.70; H, 1.63; F, 56.95.

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