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# Reactions of Polyfluoroalkanethioamides with Tris(diethylamino)phosphine

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**Abstract**—Structure of reaction products obtained from tris(diethylamino)phosphine with *N,N*-dialkylpolyfluoroalkanethioamides depends on the length of the polyfluoroalkyl substituent in the latter. In the case of morpholides of perfluorothiopropionic and perfluorothiobutyric acids the main reaction products are fluoro-containing aminoacetylenes: 4-(perfluoroalkan-1-yn-1-yl)morpholines, and also tris(diethylamino)phosphine sulfide and tris(diethylamino)difluorophosphorane. From morpholides or piperidides of ω-*H*-perfluorothiovaleric acid with a longer perfluoroalkyl substituents amides of *cis*- and *trans*-perfluoropent-2-enethiocarboxylic acids were obtained.

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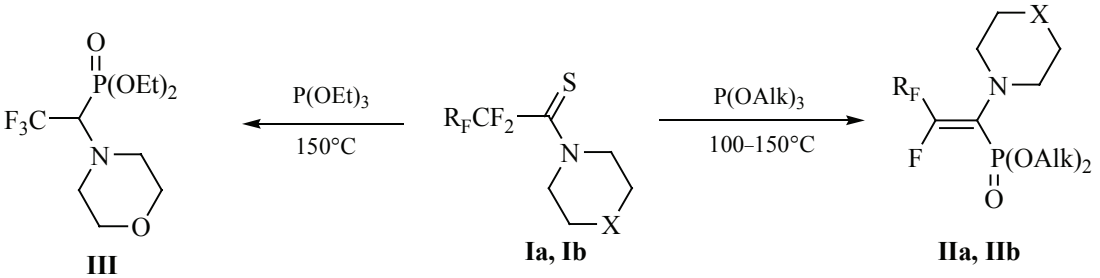
One of the widespread modern approaches to the synthesis of organofluorine compounds consists in the utilization of simple reactive fluorine-containing molecules (building-blocks) for the preparation of more complex substances. Compounds of diverse classes are used as these building-blocks [1]. In particular, the research in our laboratory on the synthetic opportunities provided by chlorides, esters, and thioesters of perfluoroalkanethiocarboxylic acids made it possible to develop procedures for the preparation of fluorinated heterocyclic compounds of diverse classes [2]. Among the other derivatives of the perfluoroalkanethiocarboxylic acids possessing promising opportunities for the application in organic synthesis amides of these acids stand out against the acyl halides and the esters due first of all to their higher availability [3, 4].

We showed formerly that reactions of perfluoroalkanethioamides with organometallic compounds (*C*-nucleophiles) could be used for the preparation of fluorine-containing keten-*N,S*-acetals [5] and heterocyclic substances [6], and the reaction of polyfluoroalkanethiocarboxylic acids *N,N*-dialkylamides **I** with trialkyl phosphites led to the formation of fluorine-containing derivatives of $\alpha$-aminophosphonates of saturated and un-

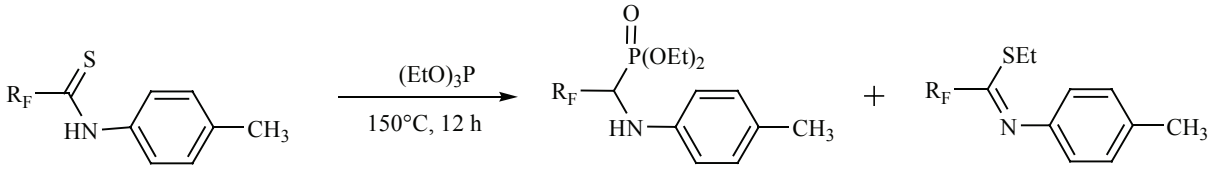
**Scheme 1.**




**III** **Ia, Ib** **IIa, IIb**

$R_F = CF_3$, X = O (**a**); $R_F = C_2F_5$, X = $CH_2$ (**b**).

**Scheme 2.**




**IVa, IVb** **Va, Vb** **VIa, VIb**

$R_F = CF_3$ (**a**), $H(CF_2)_4$ (**b**).

saturated structure [7] (Scheme 1).

The reaction of *N*-*p*-tolyl thioamides **IVa, IVb** with triethyl phosphite under similar conditions provided the derivatives of *α*-aminophosphonates **Va, Vb** and of *S*-ethylthioimidates **VIa, VIb** (Scheme 2). Yet the polyfluoroalkanethiocarboxylic acids *N*-alkylamides did not react with triethyl phosphite at a prolonged heating at 150°C.

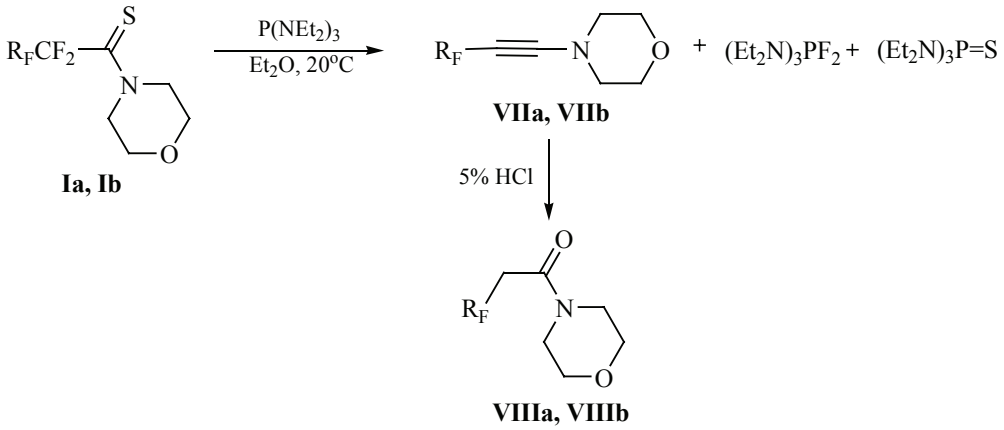
The disadvantage of these reactions consists in the necessity of prolonged heating at relatively high temperature. Therefore the attempts to study in these reactions the behavior of more nucleophilic derivatives of the three-valent phosphorus appeared promising.

The goal of this study was the investigation of reactions between *N,N*-dialkylperfluoroalkanethioamides **Ia–Id** with such phosphorus-containing nucleophile as tris(diethylamino)phosphine.

We found that in contrast to trialkyl phosphites the tris(diethylamino)phosphine reacted with thioamides **I** already at room temperature. In the event of thioamides **Ia, Ib** the main reaction products were 4-(perfluoroalkan-1-yn-1-yl)morpholines **VIIa, VIIb** formed in the yields no less than 90% (according to $^{19}F$ NMR spectra of the reaction mixture), and also tris(diethylamino)phosphine sulfide and tris(diethylamino)difluorophosphorane (Scheme 3). Ynamines **VIIa, VIIb** were isolated from the reaction mixtures as solutions in diethyl ether by distillation in a vacuum into a trap cooled by liquid nitrogen. Like the known compounds of this type with trifluoromethyl substituent [8, 9] these compounds are thermally unstable and slowly decompose at the attempt to isolate them in the individual state by evaporation of diethyl ether at the atmospheric pressure. The formation of ynamines **VII** was proved by the hydrolysis of their ether solutions to amides **VIIIa, VIIIb** (Scheme 3).

On the contrary, the main products of the reaction of *ω*-*H*-perfluorothiovaleric acid amides **Ic, Id** with tris(diethylamino)phosphine were morpholide **Xa** and

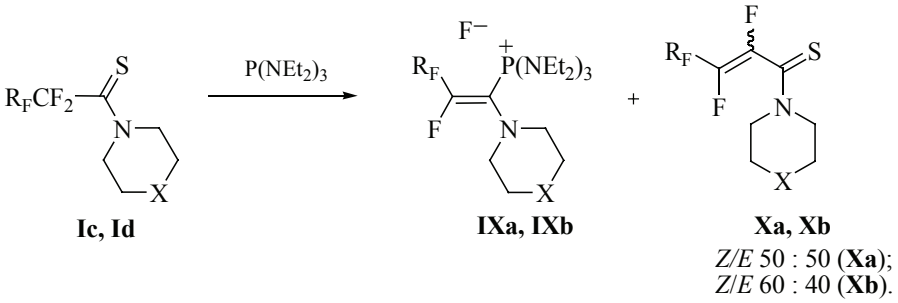
**Scheme 3.**




**Ia, Ib** **VIIa, VIIb** **VIIIa, VIIIb**

$R_F = CF_3$ (**a**), $CF_3CF_2$ (**b**).

**Scheme 4.**



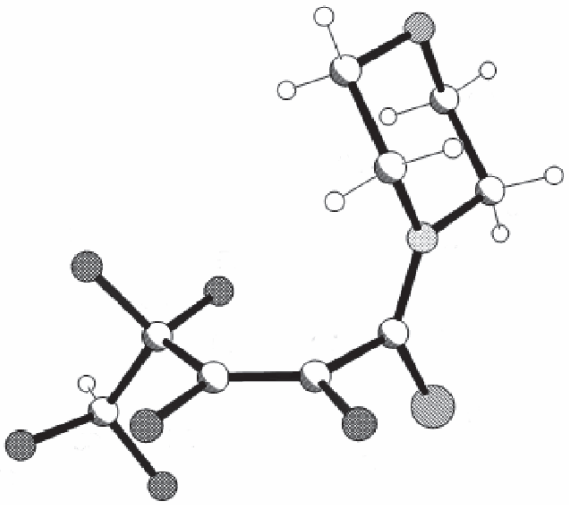

**Ic, Id** **IXa, IXb** **Xa, Xb**

*Z*/*E* 50 : 50 (**Xa**);
*Z*/*E* 60 : 40 (**Xb**).

**I**, $R_F = H(CF_2)_3$, X = O (**c**); $R_F = H(CF_2)_3$, X = $CH_2$ (**d**); **IX**, $R_F = H(CF_2)_3$, X = O (**a**); $R_F = H(CF_2)_3$, X = $CH_2$ (**b**); **X**, $R_F = H(CF_2)_2$, X = O (**a**); $R_F = H(CF_2)_2$, X = $CH_2$ (**b**).

piperidide **Xb** of perfluoro-2-pentenethiocarboxylic acid existing as mixtures of *cis*- and *trans*-isomers. Besides tris(diethylamino)phosphonium fluorides **IXa, IXb** were isolated from the reaction mixture in 13−15% yield (Scheme 4).

It should be noted that compounds **X** are the specimens of previously virtually unknown type of derivatives of α,β-unsaturated thiocarboxylic acids containing fluorine atoms at the C=C bond. The first representative of this type thioamide was described in [4].



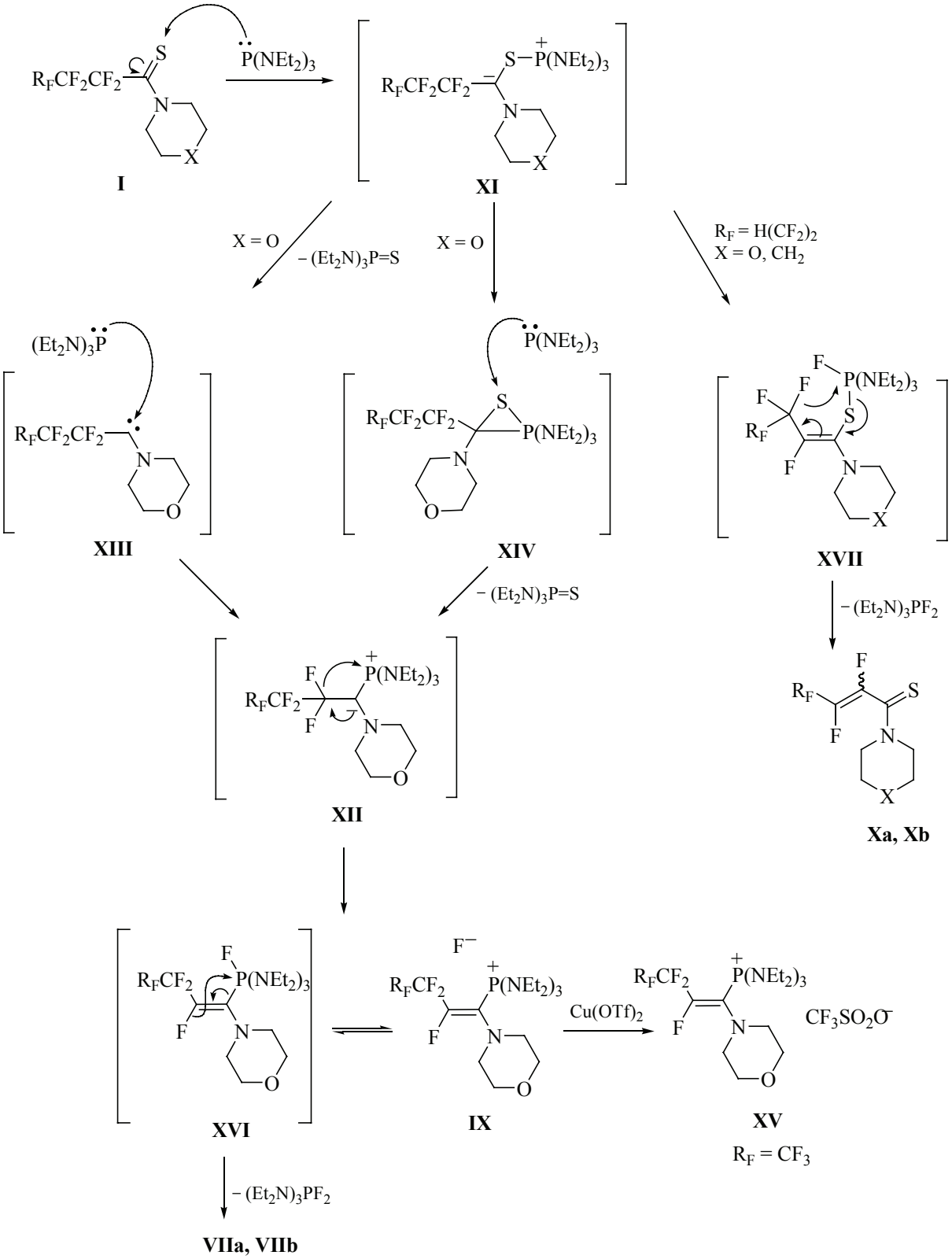
General view of the molecule of (*2Z*)-2,3,4,4,5,5-hexafluoropent-2-enethiocarboxylic acid morpholide (**Xa**). Main geometric parameters are as follows: $C^5$–$C^6$ 1.4934(18), $C^5$–$S^1$ 1.6626(13), $C^6$–$C^7$ 1.3214(19), $C^7$–$C^8$ 1.4936(19), $C^8$–$C^9$ 1.534(2) Å; $N^1C^5C^6$ 115.49(11), $C^7C^6C^5$ 128.97(12), $C^6C^7C^8$ 128.28(12), $C^7C^6F^1$ 117.69(12), $F^1C^6C^5$ 113.34(11), $C^6C^7F^2$ 120.16(12), $F^2C^7C^8$ 111.54(11)°.

The structure of *cis*-isomer **Xa** was proved by XRD analysis (see the figure).

Molecule of compound **Xa** has the *cis*-orientation of the fluorine atoms with respect to the double bond $C^6$=$C^7$, torsion angle $F^1C^6C^7F^2$ is –1.02(18)°. The C–F bond lengths are in a fairly narrow range, 1.343(2)–1.3652(16) Å. The morpholine ring has a common structure. The sum of the bond angles at the atom $N^1$ is 359.99(11)°, and the bond $C^5$–$N^1$ is shortened to 1.3307(16) Å, which is considerably less than the standard value of the ordinary C–N bond (1.45 Å) because of the efficient conjugation of the unshared electron pairs of the nitrogen atom with the π-system of the C=S bond.

The obtained experimental findings show that the outcome of the reaction between polyfluoro-alkanethioamides and tris(diethylamino)phosphine is governed by the length of the polyfluoroalkyl substituent. We suggest a scheme of the reaction course including a series of successive transformations: thiophilic attack of the tris(diethylamino)phosphine on the thioamide molecule giving a zwitter-ion **XI** that transforms into ylide **XII** through a stage of formation of carbene **XIII** or three-membered phosphorane **XIV**. The decomposition of ylide **XII** occurs through the stage of formation of fluorophosphoranes **XVI** and phosphonium fluorides **IX** which convert into ynamines **VIIa, VIIb**. The intermediate formation of compound **IX** was confirmed in the case of thioamide **Ib** by the formation of phosphonium salt **XV** at the addition to the reaction mixture of copper(II) triflate. Phosphonium fluorides **IXa, IXb** were isolated in small yields directly from the reaction mixtures in reactions of thioamides **Ic, Id** but here the predominant direction of zwitter-ion **XI** transformation was not the formation of

**Scheme 5.**


I
XI
X = O
– (Et2N)3P=S
X = O
RF = H(CF2)2
X = O, CH2
XIII
XIV
XVII
– (Et2N)3P=S
– (Et2N)3PF2
XII
Xa, Xb
XVI
IX
XV
RF = CF3
Cu(OTf)2
CF3SO2O–
– (Et2N)3PF2
VIIa, VIIb

acetylenes, but of vinylthiophosphorane **XVII** whose decomposition afforded unsaturated thioamides **Xa, Xb** (Scheme 5).

## EXPERIMENTAL

$^1$H and $^{13}$C NMR spectra were registered on a spectrometer Bruker Avance 400 [operating frequencies 400.13 ($^1$H) and 100.62 MHz ($^{13}$C)] in $CDCl_3$, internal reference TMS, $^{19}$F and $^{31}$P NMR spectra were taken on a spectrometer Varian Gemini-200 [operating frequencies 188.14 ($^{19}$F) and 80.95 MHz ($^{31}$P)] in $CDCl_3$, internal reference $C_6F_6$. IR spectra were recorded on an instrument UR-20 from pellets with KBr. Mass spectra were obtained on a GC/MS instrument Hewlett Packard 5890/5972 in the EI mode at 70 eV, mass spectra LC/MS were measured on a spectrometer Agilent 1100 equipped with a mass-selective detector Agilent LC/MSD SL; ionization method ES-API. The elemental analyses were carried out in the analytical laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Melting points were measured on a Boëtius heating block. To column chromatography silica gel Merck 60 (70–230 μm) was applied. TLC was performed on plates Macherey–Nagel; Polygram® Sil G/UV254, development in iodine vapor. The reaction progress was monitored by $^{19}$F and $^{31}$P NMR spectroscopy. All solvents before use were dried and distilled by standard procedures.

Crystals of compound **Xa** monoclinic. $C_9H_9F_6NOS$, $M$ 293.23. Space group $P2_1/c$; $a$ 6.7128(2), $b$ 8.6074(2), $c$ 10.6208(3) Å; α 69.709(1), β 76.664(1), γ 84.120(2)°, $V$ 559.89(3) Å$^3$, $Z$ 2, $d_{calc}$ 1.739 g/cm$^3$, μ 0.358 mm$^{-1}$, $F$(000) 296. XRD analysis of a single crystal of the size 0.44 × 0.25 × 0.12 mm was carried out at –100°C on a diffractometer Bruker Smart Apex II (λMo$K_\alpha$-radiation, graphite monochromator, $\theta_{max}$ 30.49°, spheric segment $-7 \le h \le 9$, $-12 \le k \le 12$, $-15 \le l \le 14$). Overall 10178 reflections were collected, among them 3284 were independent (R-factor of averaging 0.0322). The correction for extinction was introduced by multiscanning procedure using SADABS program ($T_{min}/T_{max}$ = 0.8300/0.9583). The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation using Bruker SHELXTL software [10]. All hydrogen atoms were placed geometrically and refined in the rider model. The refinement was performed using 3284 independent reflections, among them 2629 reflections with $I > 2\sigma(I)$ (163 refined parameters, 16.1 reflection per parameter. A weight scheme was used: $\omega = 1/[\sigma^2(Fo^2) + (0.0337P)^2 + 0.161P]$, where $P = (Fo^2 + 2Fc^2)/3$, the ratio of the maximum (average) shift to the error in the last cycle 0.001 (0.000). The final values of the divergence $R_1(F)$ 0.0351, $wR_2(F^2)$ 0.0808 with respect to reflections with $I > 2\sigma(I)$; $R_1(F)$ 0.0467, $wR_2(F^2)$ 0.0871, $GOF$ 1.063 for all independent reflections. The residual electron density from the difference Fourier series after the last refinement cycle was 0.37 and –0.27 e/Å$^3$. The structural data are deposited in the Cambridge Crystallographic Data Center, CCDC 931671.

**Reaction of *N*-*p*-tolyl polyfluoroalkanethioamides IVa, IVb with triethyl phosphite**. A mixture of 15.0 mmol of thioamide **IVa, IVb** and 7.47 g (45.0 mmol) of triethyl phosphite was heated in an argon atmosphere for 9 h at 150°C. The reaction mixture was distilled in a vacuum (0.08 mm Hg) at 100–130°C with subsequent purification by column chromatography on silica gel (eluent hexane–ethyl acetate, 70 : 30). The corresponding phosphonates **Va, Vb** and *S*-ethylthioimidates **VIa, VIb** were isolated.

**Diethyl 1-[(4-methylphenyl)amino](2,2,2-trifluoroethyl) phosphonate (Va)**. Yield 0.20 g (40%), yellow crystals, mp 70–72°C (from hexane). $^1$H NMR spectrum, δ, ppm: 1.129 m (6H, $POCH_2C\underline{H}_3$), 2.25 s (3H, $CH_3$), 4.18 m (5H, CH + $POC\underline{H}_2CH_3$), 6.63 d (2H$_{Ar}$, $^3J_{H,H}$ 8.4 Hz), 7.02 d (2H$_{Ar}$, $^3J_{H,H}$ 8.4 Hz). $^{13}$C NMR spectrum, δ, ppm: 16.4 m ($POCH_2\underline{C}H_3$), 20.5 s ($CH_3$), 54.7 d.q (CH, $^1J_{C,P}$ 153.3, $^2J_{C,F}$ 31.5 Hz), 63.8 d ($PO\underline{C}H_2CH_3$, $^2J_{C,P}$ 7.7 Hz), 64.2 d ($PO\underline{C}H_2CH_3$, $^2J_{C,P}$ 6.3 Hz), 113.9 s (CH, Ar), 124.1 q.d ($CF_3$, $^1J_{C,F}$ 283.4, $^2J_{C,P}$ 10.9 Hz), 129.1 s (C$_{tert}$, Ar), 130.0 s (CH, Ar), 143.2 d (C$_{tert}$, Ar, $^3J_{C,P}$ 6.6 Hz). $^{19}$F NMR spectrum, δ, ppm: – 69.8 m (3F, $CF_3$). $^{31}$P{$^1$H} NMR spectrum, δ, ppm: 15.8 q ($^3J_{P,F}$ 8.2 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 326 $[M+1]^+$. Found, %: C 47.89; H 5.87; N 4.47; P 9.48. $C_{13}H_{19}F_3NO_3P$. Calculated, %: C 48.00; H 5.89; N 4.31; P 9.52. $M$ 325.26.

**Diethyl 1-[(4-methylphenyl)amino]-(2,2,3,3,4,4,5,5-octafluoropentyl)phosphonate (Vb)**. Yield 0.14 g (20%), yellow liqid. $^1$H NMR spectrum, δ, ppm: 1.27 m (6H, $POCH_2C\underline{H_3}$), 2.24 s (3H, $CH_3$), 4.05–4.20 m (5H, CH + $POC\underline{H}_2CH_3$), 6.01 t.t (1H, $HCF_2$, $^2J_{H,F}$ 52.0, $^3J_{H,F}$ 5.5 Hz), 6.60 d (2H$_{Ar}$, $^3J_{H,H}$ 8.4 Hz), 7.02 d (2H, Ph, $^3J_{H,H}$ 8.4 Hz). $^{19}$F NMR spectrum, δ, ppm: –112.8 d.m (1F, $CF_AF_B$, $^2J_{F,F}$ 282.9 Hz), –118.1 d.m (1F, $CF_AF_B$, $^2J_{F,F}$ 282.9 Hz), –124.2 m (2F, $CF_2$), –131.5 m (2F, $CF_2$), –138.7 m (2F, $HCF_2$). $^{31}$P NMR spectrum, δ, ppm: 14.8 m.

Mass spectrum, *m/z* ($I_{rel}$, %): 457 (10.1) $[M]^+$, 320 (100), 169 (15.7), 118 (13.0), 91 (11.3). Found, %: C 42.10; H 4.47; N 3.04; P 6.74. $C_{16}H_{20}F_8NO_3P$. Calculated, %: C 42.02; H 4.41; N 3.06; P 6.77. *M* 457.30.

**Ethyl-*N*-(4-methylphenyl)-2,2,2-trifluoroethaneimidothionate (VIa)**. Yield 0.07 g (20%), yellow liquid. $^1$H NMR spectrum, δ, ppm: 1.20 m (3H, $SCH_2C\underline{H_3}$), 2.35 s (3H, $CH_3$), 2.95 m (2H, $SC\underline{H_2}CH_3$), 6.85 m (2H, Ar), 7.18 m (2H, Ar). $^{19}$F NMR spectrum, δ, ppm: –68.9 s ($CF_3$). Mass spectrum, *m/z* ($I_{rel}$, %): 247 $[M]^+$, 186 (88.62), 150 (63.9), 91 (100), 65 (34.9). Found, %: C 53.39; H 4.81; N 5.69; S 12.93. $C_{11}H_{12}F_3NS$. Calculated, %: C 53.43; H 4.89; N 5.66; S 12.97. *M* 247.28.

**Ethyl-*N*-(4-methylphenyl)-2,2,3,3,4,4,5,5-octafluoropentanimidothionate (VIb)**. Yield 0.34 g (60%), yellow liquid. $^1$H NMR spectrum, δ, ppm: 1.10 t (3H, $SCH_2C\underline{H_3}$, $^3J_{H,H}$ 7.5 Hz), 2.36 s (3H, $CH_3$), 2.67 q (2H, $SC\underline{H_2}CH_3$, $^3J_{H,H}$ 7.5 Hz), 6.21 t.t (1H, $HCF_2$, $^2J_{H,F}$ 52.2, $^3J_{H,F}$ 5.6 Hz), 6.88 d ($2H_{Ar}$, $^3J_{H,H}$ 7.8 Hz), 7.18 d ($2H_{Ar}$, $^3J_{H,H}$ 7.8 Hz). $^{13}$C NMR spectrum, δ, ppm: 14.7 s ($SCH_2\underline{C}H_3$), 21.1 s ($CH_3$), 26.6 s ($S\underline{C}H_2CH_3$), 105.2–110.8 m [$4CF_2$, $H(CF_2)_4$], 119.0 s (CH, Ar), 129.8 s (CH, Ar), 135.7 s ($C_{tert}$, Ar), 144.2 s ($C_{tert}$, Ar), 152.8 t (C=N, $^2J_{C,F}$ 27.5 Hz). $^{19}$F NMR spectrum, δ, ppm: –109.9 m (2F, $CF_2$), –123.1 m (2F, $CF_2$), –129.3 m (2F, $CF_2$), –138.1 d.m (2F, $HCF_2$, $^2J_{F,H}$ 52.2 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 379 (36.1) $[M]^+$, 318 (75.6), 178 (61.2), 150 (79.1), 91 (100). Found, %: C 44.25; H 3.53; N 3.48; S 8.53. $C_{14}H_{13}F_8NS$. Calculated, %: C 44.33; H 3.45; N 3.69; S 8.45. *M* 379.31.

**Fluorine-containing aminoacetylenes VIIa, VIIb and polyfluoroalkanecarboxylic acids morpholides VIIIa, VIIIb**. To a solution of 18.0 mmol of thioamide **Ia** in 20 ml of diethyl ether was added under argon 0.82 g (33.0 mmol) of tris(diethylamino)phosphine, and the mixture was stirred for 6 days at room temperature. The solvent and the obtained ynamines **VIIa, VIIb** were distilled off in a vacuum (0.08 mm Hg) into a trap cooled with liquid nitrogen. The signals of the $CF_3CF_2$ group in the $^{19}$F NMR spectrum of ynamine **VIIa** are observed at –87.0 ($CF_3$), –97.0 ppm (2F, $CF_2$), in the spectrum of ynamine **VIIb** this signal of the $CF_3$ group appears at –47.0 ppm in agreement with the described spectra of *N,N*-dibutyl(3,3,3-trifluoro-1-propynyl)amine [8]. The solution of ynamine **VIIa, VIIb** in diethyl ether was stirred for 1h with 15 mL of 5% HCl at room temperature. The organic phase was separated and washed with water. The water phase was extracted with diethyl ether (2 × 15 mL). The combined organic solutions were dried with $Na_2SO_4$, filtered, and evaporated. Amides **VIIIa, VIIIb** were subjected to column chromatography on silica gel, eluent hexane–ethyl acetate, 90 : 10.

**3,3,3-Trifluoropropanoic acid morpholide (VIIIa)** [11]**.** Yield 0.07 g (20%), colorless oily substance. $^1$H NMR spectrum, δ, ppm: 3.18 q (2H, $CH_2$, $^3J_{H,F}$ 10.1 Hz), 3.42 m (2H, morph.), 3.62 m (6H, morph.). $^{19}$F, δ, ppm: –63.7 t (3F, $CF_3$, $^3J_{F,H}$ 10.1 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 198 (100) $[M + 1]^+$. Found, %: C 42.53; H 5.13; N 7.15. $C_7H_{10}F_3NO_2$. Calculated, %: C 42.64; H 5.11; N 7.10. *M* 197.16.

**3,3,3,4,4-Pentafluorobutanoic acid morpholide (VIIIb)**. Yield 0.22 g (50%), colorless crystals, mp 55–58°C. $^1$H NMR spectrum, δ, ppm: 3.22 t (2H, $CH_2$, $^3J_{H,F}$ 17.4 Hz), 3.52 m (2H, morph.), 3.72 m (6H, morph.). $^{13}$C NMR spectrum, δ, ppm: 34.6 t ($CH_2$, $^2J_{C,F}$ 21.7 Hz), 42.5 s ($NCH_2$), 47.1 s ($NCH_2$), 66.5 s ($OCH_2$), 66.7 s ($OCH_2$), 115.0 t.q ($CF_2$, $^1J_{C,F}$ 256.7, $^2J_{C,F}$ 38.3 Hz), 118.6 q.t ($CF_3$, $^1J_{C,F}$ 286.3, $^2J_{C,F}$ 35.8 Hz), 161.3 s (C=O). $^{19}$F NMR spectrum, δ, ppm: –86.4 m (3F, $CF_3$), –116.0 t (2F, $CF_2$, $^3J_{F,H}$ 17.4 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 247 (32.86) $[M]^+$, 232 (23.8), 161 (100), 86 (20.7), 56 (23.3). Found, %: C 38.87; H 4.10; N 5.68. $C_8H_{10}F_6NO_2$. Calculated, %: C 38.88; H 4.08; N 5.67. *M* 247.16.

**Perfluoropent-2-enethiocarboxylic acid amides Xa, Xb and tris(diethylamino)phosphonium fluorides IXa, IXb**. To a solution of 0.5 g (15.0 mmol) of thioamide **Ic, Id** in 20 ml of diethyl ether was added under argon 0.75 g (30.0 mmol) of tris(diethylamino)phosphine, the reaction mixture was stirred for 24 h at room temperature. The formed precipitate of fluoride **IXa** was filtered off, washed with diethyl ether (2 × 15 mL), dried in a vacuum (0.08 mm Hg). At obtaining fluoride **IXb** it separated as an oily fluid insoluble in ether; the solvent was decanted, the residue was washed with diethyl ether (2 × 15 mL), and dried in a vacuum (0.08 mm Hg). At stirring the reaction mixture for 4 days at room temperature the initially formed phosphonium fluorides **IXa, IXb** disappeared. Thus obtained reaction mixture was stirred for 1 h with 15 mL of 5% hydrochloric acid at room temperature. The organic phase was separated and washed with water. The water phase was extracted with diethyl ether (2 × 15 ml). The combined organic solutions were dried with $Na_2SO_4$, filtered, and evaporated. The compounds **Xa, Xb** obtained as a mixture of *cis*- and *trans*-isomers were subjected to column chromatography on silica gel, eluent hexane–ethyl acetate, 90 : 10.

**Tris(diethylamino)(1-morpholino-2,3,3,4,4,5,5-heptafluoropent-1-en-1-yl)phosphonium fluoride (IXa)**. Yield 0.12 g (15%), brown powder, mp 88–92°C. $^1$H NMR spectrum, δ, ppm: 1.29 t (18H, 6CH$_2$C$\underline{H}_3$, $^3J_{H,H}$ 6.8 Hz), 3.05 m [4H, N(CH$_2$)$_2$], 3.28 m (12H, 6C$\underline{H}_2$CH$_3$), 3.76 m [4H, O(CH$_2$)$_2$], 6.26 t.t (HCF$_2$, $^2J_{H,F}$ 51.9, $^3J_{H,F}$ 4.5 Hz). $^{13}$C NMR spectrum, δ, ppm: 12.9 d [PN(CH$_2\underline{C}$H$_3$)$_2$, $^3J_{C,P}$ 2.4 Hz], 40.8 d [PN($\underline{C}$H$_2$CH$_3$)$_2$, $^2J_{C,P}$ 4.2 Hz], 50.6 s (NCH$_2$), 66.2 s (OCH$_2$), 107.3–113.1 m (2$\underline{C}$F$_2$), 107.6 t.t (HCF$_2$, $^1J_{C,F}$ 255.9, $^2J_{C,F}$ 37.8 Hz), 131.7 d.d (CF=*C*, $^1J_{C,P}$ 165.1, $^2J_{C,F}$ 22.8 Hz), 158.7 d.d.t ($\underline{C}$F=C, $^1J_{C,F}$ 278.2, $^2J_{C,F}$ 32.0, $^2J_{C,P}$ 23.3 Hz). $^{19}$F NMR spectrum, δ, ppm: –102.8 m (1F, CF), –114.8 m (2F, CF$_2$), –127.8 m (2F, CF$_2$), –137.6 d.m (2F, HCF$_2$, $^2J_{F,H}$ 51.9 Hz). $^{31}$P{$^1$H} NMR spectrum, δ, ppm: 44.0 d ($^3J_{P,F}$ 6.8 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 527 (100) [*M* + 1]$^+$. Found, %: C 46.24; H 7.20; N 10.23; P 5.73. $C_{21}H_{39}F_8N_4OP$. Calculated, %: C 46.15; H 7.19; N 10.25; P 5.67. *M* 546.52.

**Tris(diethylamino)(1-piperidino-2,3,3,4,4,5,5-heptafluorohex-1-en-1-yl)phosphonium fluoride (IXb)**. Yield 0.11 g (13%), brown oily substance. $^1$H NMR spectrum, δ, ppm: 1.24 m (18H, CH$_2$C$\underline{H}_3$), 1.66 m (6H, CH$_2$), 2.92 m [4H, N(CH$_2$)$_2$], 3.21 (12H, C$\underline{H}_2$CH$_3$), 6.23 t (1H, HCF$_2$, $^2J_{H,F}$ 51.9 Hz). $^{19}$F NMR spectrum, δ, ppm: –105.2 m (1F, CF), –115.1 m (2F, CF$_2$), –127.7 m (2F, CF$_2$), –137.5 d.m (2F, HCF$_2$, $^2J_{F,H}$ 51.9 Hz). $^{31}$P NMR spectrum, δ, ppm: 44.3 m. Mass spectrum, *m/z* ($I_{rel}$, %): 527 (100) [*M* + 1]$^+$. Found, %: C 50.35; H 7.94; N 10.73; P 5.90. $C_{22}H_{41}F_8N_4P$. Calculated, %: C 50.28; H 7.86; N 10.66; P 5.89. *M* 544.55.

**(*2Z*)-2,3,4,4,5,5-Hexafluoropent-2-enethiocarboxylic acid morpholide (Xa)**. Yield 0.15 g (34%), yellow crystals, mp 60–62°C [40°C (0.08 mm Hg) sublimated]. $^1$H NMR spectrum, δ, ppm: 3.69 m (4H, 2CH$_2$), 3.82 t (2H, OCH$_2$, $^3J_{H,F}$ 4.8 Hz), 4.22 t (2H, OCH$_2$, $^3J_{H,H}$ 4.8 Hz), 6.16 t.t (1H, HCF$_2$, $^2J_{H,F}$ 52.7, $^3J_{H,F}$ 4.8 Hz). $^{13}$C NMR spectrum, δ, ppm: 48.4 s (NCH$_2$), 52.7 s (NCH$_2$), 66.1 s (OCH$_2$), 66.3 s (OCH$_2$), 108.6 t.t.d (HCF$_2$, $^1J_{C,F}$ 253.7, $^2J_{C,F}$ 35.1, $^3J_{C,F}$ 2.9 Hz), 110.8 t.m (CF$_2$, $^1J_{C,F}$ 254.3 Hz), 135.7 d.d.t (CF$_2\underline{C}$F, $^1J_{C,F}$ 261.4, $^2J_{C,F}$ 30.7, $^2J_{C,F}$ 21.3 Hz), 145.9 d.d.t (*C*F–CS, $^1J_{C,F}$ 270.1, $^2J_{C,F}$ 15.3, $^3J_{C,F}$ 3.8 Hz), 180.0 d (C=S, $^2J_{C,F}$ 20.6 Hz). $^{19}$F NMR spectrum, δ, ppm: –111.0ч–133.6 br.m (2F, CF$_2$), –117.0 d (2F, CF, $^3J_{H,F}$ 9.2 Hz), –139.0 m (2F, HCF$_2$), –157.2 m (1F, CF). Mass spectrum, *m/z* ($I_{rel}$, %): 293 (100) [*M*]$^+$, 207 (58.8), 192 (88.5), 156 (16.2), 51 (17.0). Found, %: C 36.91; H 3.12; N 4.80; S 10.79. $C_{10}H_{11}F_6NS$. Calculated, %: C 36.86; H 3.09; N 4.78; S 10.94. *M* 293.23.

**(*2E*)-2,3,4,4,5,5-Hexafluoropent-2-enethiocarboxylic acid piperidide (Xb)**. Yield 0.08 g (20%), yellow oily substance. IR spectrum, ν, cm$^{-1}$: 2947 [N(CH$_2$)$_2$], 1493 (C=S). $^1$H NMR spectrum, δ, ppm: 1.76 m (6H, CH$_2$), 3.69 m (2H, NCH$_2$), 4.17 m (2H, NCH$_2$), 6.00 t.m (1H, HCF$_2$, $^2J_{H,F}$ 53.4 Hz). $^{13}$C NMR spectrum, δ, ppm: 24.0 s (CH$_2$), 25.3 s (CH$_2$), 26.9 s (CH$_2$), 49.4 s (NCH$_2$), 53.7 s (NCH$_2$), 109.0 t.t.d (HCF$_2$, $^1J_{C,F}$ 252.6, $^2J_{C,F}$ 37.8, $^3J_{C,F}$ 3.0 Hz), 111.1 t.m (CF$_2$, $^1J_{C,F}$ 253.3 Hz), 135.9 d.d.t (CF$_2\underline{C}$F, $^1J_{C,F}$ 248.4, $^2J_{C,F}$ 44.9, $^2J_{C,F}$ 30.8 Hz), 148.4 d.d.t ($\underline{C}$F–CS, $^1J_{C,F}$ 262.6, $^2J_{C,F}$ 47.9, $^3J_{C,F}$ 3.2 Hz), 180.0 d.d (C=S, $^2J_{C,F}$ 23.6, $^3J_{C,F}$ 2.9 Hz). $^{19}$F NMR spectrum, δ, ppm: –122.3 m (2F, CF$_2$), –134.1 d.t (1F, CF, $^3J_{F,F}$ 141.6, $^3J_{F,F}$ 23.6 Hz), –138.3 d.m (2F, HCF$_2$, $^2J_{F,H}$ 53.4 Hz), –166.6 d.m (1F, CF, $^3J_{F,F}$ 141.6 Hz). Mass spectrum, *m/z* ($I_{rel}$, %): 291 (61.8) [*M*]$^+$, 190 (100), 157 (28.48), 55 (20.0), 41 (20.7). Found, %: C 41.26; H 3.80; N 4.82; S 11.04. $C_{10}H_{11}F_6NS$. Calculated, %: C 41.24; H 3.81; N 4.81; S 11.01. *M* 279.18.

**Tris(diethylamino)(1-morpholino-2,3,3,4,4,4-hexafluorobut-1-en-1-yl)phosphonium trifluoromethylsulfonate (XV)**. To a solution of 0.5 g (15.0 mmol) of thioamide **Ib** in 20 ml of diethyl ether was added under argon 0.8 g (30.0 mmol) of tris(diethylamino)phosphine, and the mixture was stirred for 24 h at room temperature. To the reaction mixture 0.1 g (3 mmol) of copper(II) triflate was added. A brown oily substance separated, immiscible with ether. The solvent was decanted, the residue was washed with water (3 × 15 mL) and dried in a vacuum (0.08 mm Hg). Yield 0.44 g (45%). $^1$H NMR spectrum, δ, ppm: 1.23 m (18H, 6CH$_3$), 3.02 m [4H, N(CH$_2$)$_2$], 3.20 m (12H, 6CH$_2$), 3.72 m [4H, O(CH$_2$)$_2$]. $^{13}$C NMR spectrum, δ, ppm: 13.1 d [PN(CH$_2\underline{C}$H$_3$)$_2$, $^3J_{C,P}$ 3.1 Hz], 40.8 d [PN($\underline{C}$H$_2$CH$_3$)$_2$, $^2J_{C,P}$ 4.0 Hz], 50.9 s (NCH$_2$), 66.5 s (OCH$_2$), 108.0 t.m (CF$_2$, $^1J_{C,F}$ 264.4 Hz), 117.7 q.t (CF$_3$, $^1J_{C,F}$ 289.8, $^2J_{C,F}$ 35.2 Hz), 120.9 q (CF$_3$SO$_2$O, $^1J_{C,F}$ 321.5 Hz), 132.6 d.d (CF=$\underline{C}$, $^1J_{C,P}$ 165.5, $^2J_{C,F}$ 25.1 Hz), 157.8 d.m ($\underline{C}$F=C, $^1J_{C,F}$ 275.4 Hz). $^{19}$F NMR spectrum, δ, ppm: –79.2 s (3F, CF$_3$SO$_2$O), –82.5 m (3F, CF$_3$), –101.7 m (1F, CF), –116.7 m (2F, CF$_2$). $^{31}$P NMR spectrum, δ, ppm: 43.3 m. Mass spectrum, *m/z* ($I_{rel}$, %): 496 [*M* + 1]$^+$, 148 [*M* – 1]$^-$. Found, %: C 39.02; H 6.15; N 8.55; P 4.62; S 5.07. $C_{21}H_{38}F_9N_4O_4PS$. Calculated, %: C 39.13; H 5.94; N 8.69; P 4.81; S 4.97. *M* 644.58.

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