Russian Journal of Organic Chemistry, Vol. 41, No. 3, 2005, pp. 434–439. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 3, 2005, pp. 441–446.

Synthesis of Heterocyclic Compounds Containing Perfluoroalkyl Groups. Reactions of Perfluoro(2-methyl-2-pentene) and Perfluoro(5-aza-4-nonene) with N,S-Dinucleophiles

G. G. Furin[1] and E. L. Zhuzhgov[2]

[1] *Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia*

[2] *Novosibirsk State University, ul. Pirogova 2, 630090, Novosibirsk, Russia*

Received June 30, 2003

Abstract—Perfluoro(2-methyl-2-pentene) and perfluoro(5-aza-4-nonene) react with 1,4,5,6-tetrahydropyrimidine-2-thiol, pyridine-2-thiol, and 1,2,4-triazole-3-thiol to afford fused heterocyclic systems, while their reactions with tetrahydrothiazole-2-thione and pyrimidine-2-thiol result in replacement of the fluorine atom at the double bond. Treatment of 3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-pentenyl isothiocyanate with ammonia gives *N*-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl)thiourea which undergoes ring closure to 4-tetrafluoroethylidene-5,5-bis(trifluoromethyl)-4,5-dihydrothiazol-2-amine. Possible cyclization paths and the effect of the 1,3(N,S)-dinucleophile nature on the direction of nucleophilic addition at the double bond are discussed.

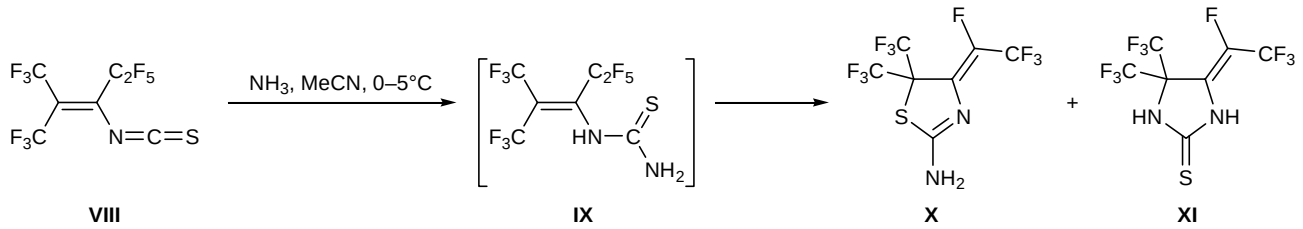
Fluorine-containing heterocycles are important from the viewpoint of design of new medicines and pesticides [1]. The main procedures for their synthesis are based on condensation and intramolecular cyclization processes involving aromatic fluorine atoms and fluorine atoms at the double bond in perfluoroolefins, which are replaced by the action of heteroelement-centered nucleophiles. Taking into account enhanced biological activity of heterocyclic compounds having perfluoroalkyl groups, the above reactions were extensively studied [2–4]. Reactions of perfluoroolefins with difunctional nucleophiles were shown to be effective in the synthesis of heterocyclic systems. These processes include initial addition of a nucleophile at a double bond rather than nucleophilic replacement of a vinyl fluorine atom. The subsequent stabilization of intermediate carbanion gives rise to a new double bond. In reactions with difunctional nucleophiles, attack by the second nucleophilic center on that double bond leads to formation of a heterocyclic system. Possible isomerization via migration of internal double bond to the terminal position by the action of heteroatom in the nucleophilic moiety could produce heterocycles with different structures and sizes. Therefore, it is important to understand the role of fluorine atoms at the double bond and their influence on the reactivity.

We previously studied reactions of internal perfluoroolefins with difunctional nucleophiles [1,3(N,S)-dinucleophiles], which afforded five-membered heterocycles. In the reactions of perfluoro(2-methyl-2-pentene) with thiourea [5] and dihydrobenzimidazole-2-thione [6, 7], 5-tetrafluoroethylidene-4,4-bis(trifluoromethyl)-4,5-dihydrothiazol-2-amine and (2*E*)-2-tetrafluoroethylidene-3,3-bis(trifluoromethyl)-2,3-dihydro[1,3]thiazolo[3,2-*a*]benzimidazole were obtained, respectively. In these cases, initial attack by the sulfur atom in the nucleophile was directed at the carbon atom at the internal double bond of perfluoro(2-methyl-2-pentene). The subsequent cyclization via attack by the second nucleophilic center (nitrogen atom) on the double bond gave rise to heterocyclic system. The presence of a base favors the process. Insofar as difunctional nucleophiles in solution exist in two forms, the most important is to determine nucleophilic center responsible for primary attack on the double-bonded carbon atom. However, it should be kept in mind that the primary reaction center in a difunctional nucleophile cannot be identified on the basis of the final product structure if a substrate contains similar substituents.

The present study was aimed at elucidating how the nature of heterocyclic 1,3(N,S)-dinucleophile affects

1070-4280/05/4103-0434

Scheme 1.



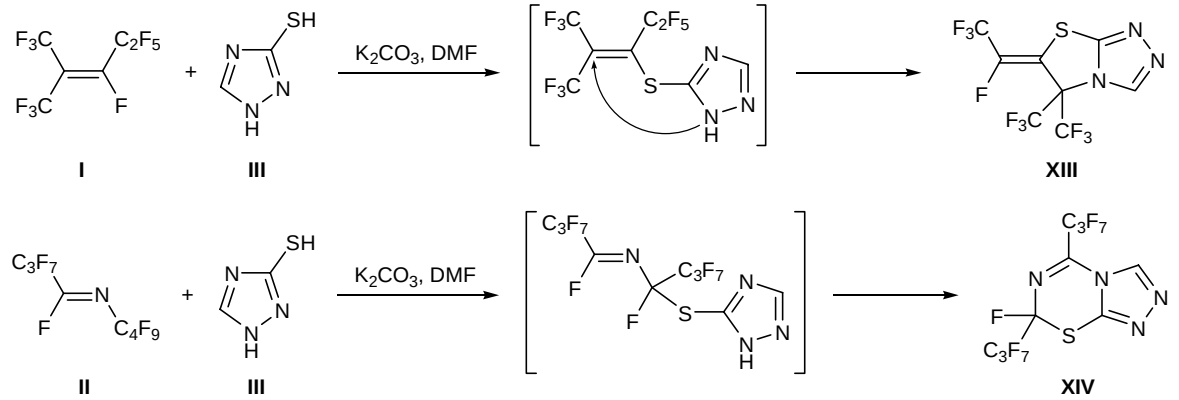
VIII **IX** **X** **XI**

the direction of its primary attack on the double bond in internal perfluoroolefins and synthesizing polycyclic heterocyclic compounds with perfluoroalkyl substituents. As substrates we used perfluoro(2-methyl-2-pentene) (**I**) and perfluoro(5-aza-4-nonene) (**II**), and 1,3(N,S)-dinucleophiles were 1*H*-1,2,4-triazole-3-thiol (**III**), tetrahydrothiazole-2-tione (**IV**), 1,4,5,6-tetrahydropyrimidine-2-thiol (**V**), pyrimidine-2-thiol (**VI**), and pyridine-2-thiol (**VII**); the reactions were carried out in the presence of triethylamine or potassium carbonate as a base.

It might be expected that N-substituted thioureas will also react with perfluoroolefins at the S-nucleophilic center. This assumption was verified by reacting 3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl isothiocyanate (**VIII**) with ammonia. In fact, the initial attack by ammonia at the carbon atom of the N=C=S group is likely to give thiourea derivative **IX** (Scheme 1). The subsequent intramolecular cyclization of **IX** may occur via attack by the S-nucleophilic center at the double bond to afford 4-tetrafluoroethylidene-5,5-bis(trifluoromethyl)-4,5-dihydrothiazol-2-amine (**X**). A heterocycle isomeric to **X** was synthesized previously by reaction of thiourea with internal perfluoroolefin **I**, and its structure was proved by the X-ray diffraction data [5]. As a minor product, we isolated 5-tetrafluoroethylidene-4,4-bis(trifluoromethyl)tetrahydroimidazole-2-thione (**XI**) which was formed via intramolecular attack by the terminal amino group in intermediate **IX**. It should be noted that some cyclic 1,3(N,S)-dinucleophiles, e.g., 2,3-dihydro-1*H*-benzimidazole-2-thione (**XII**) [6, 7] and 5-nitro-2,3-dihydro-1*H*-benzimidazole-2-thione [7], were reported to react with compound **I**, yielding 2,3-dihydro[1,3]-thiazolo[3,2-*a*]benzimidazole derivatives.

The above example demonstrates an important role of structural factors and 1,3(N,S)-dinucleophile nature in reactions of the latter with perfluoroolefins. If primary attack of a 1,3-dinucleophile gives rise to generation of the second active nucleophilic center, the process should be accompanied by formation of a new heterocycle; otherwise, the product formally resulting from replacement of fluorine atom at the double bond is obtained. This conclusion was justified by the reactions of perfluoro(2-methyl-2-pentene) (**I**) and perfluoro(5-aza-4-nonene) (**II**) with 1,2,4-triazole-3-thiol (**III**). The arrangement of the heteroatom triad in the five-membered ring of molecule **III** resembles that in **XII**, and the primary nucleophilic center is the sulfur atom. Initially, product of fluorine replacement at the double bond is formed. Next follows base-catalyzed intramolecular ring closure to give fused heterocyclic systems, 6-tetrafluoroethylidene-5,5-bis(trifluoromethyl)-5,6-dihydrothiazolo[2,3-*c*][1,2,4]triazole (**XIII**) and 7-fluoro-5,7-bis(heptafluoropropyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,5]thiadiazine (**XIV**) (Scheme 2).

Scheme 2.

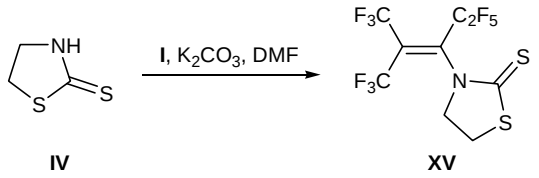


I **III** **XIII**

II **III** **XIV**

The reaction of perfluoroolefin **I** with tetrahydrothiazole-2-thione (**IV**) in dimethylformamide in the presence of K_2CO_3 resulted only in fluorine replacement at the double bond with formation of 3-(3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl)tetrahydrothiazole-2-thione (**XV**) (Scheme 3). It should be noted that thione **IV** reacted under analogous conditions with compound **VIII** via attack by the N-nucleophilic center on the carbon atom of the isothiocyanato group to afford 3-substituted tetrahydrothiazole-2-thione [8]. The subsequent cyclization involving the side-chain double bond and the S-nucleophilic center is possible only via attack by a nucleophile present in the reaction medium (e.g., by fluoride ion) at the carbon atom of the C=S group; this process requires a high concentration of fluoride ions.

Scheme 3.

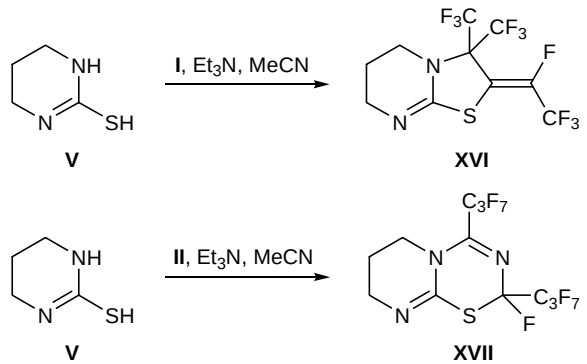


IV **XV**

We previously [9, 10] studied reactions of isothiocyanate **VIII** with azoles, which afforded 1,3-thiazole derivatives, and found a relation between the chemical shift of 6-fluorine atom (at the double bond) and the nature of substituent in position *2* of the thiazole ring ($\delta_{6\text{-}F}$ 20–30 ppm). The product obtained by the reaction of **III** with **I** (Scheme 1) showed in the ^{19}F NMR spectrum a signal at δ_F 54.5 ppm from the fluorine atom at the double bond. This finding indicates formation of structure **XIII** which corresponds to initial attack by the S-nucleophilic center in **III**, as in analogous reaction with thiourea.

Compounds **I** and **II** reacted with 1,4,5,6-tetrahydropyrimidine-2-thiol (**V**) in acetonitrile in the presence of triethylamine to give 2-tetrafluoroethylidene-3,3-bis(trifluoromethyl)-2,3,6,7-tetrahydro-5*H*-thiazolo[3,2-*a*]pyrimidine (**XVI**) and 2-fluoro-2,4-bis(heptafluoropropyl)-2,6,7,8-tetrahydropyrimido[2,1-*b*][1,3,5]thiadiazine (**XVII**), respectively (Scheme 4). In these reactions, compound **V** initially attacks by the thiol group the double C=C and C=N bonds, like in reactions of thiourea with internal perfluoroolefins. Obviously, the thiol tautomer of **V** is more reactive than the thione form. Its attack on the carbon atom at the double bond gives intermediate carbanion which is stabilized via elimination of fluoride ion and regeneration of the double bond; the subsequent intramolecular ring closure with participation of the double bond and endocyclic nitrogen atom leads to final product **XVI** (Scheme 5). Alternative attack on the double bond in **I** by the N-nucleophilic center in **V** would result in formation of isomeric product **XVIII**.

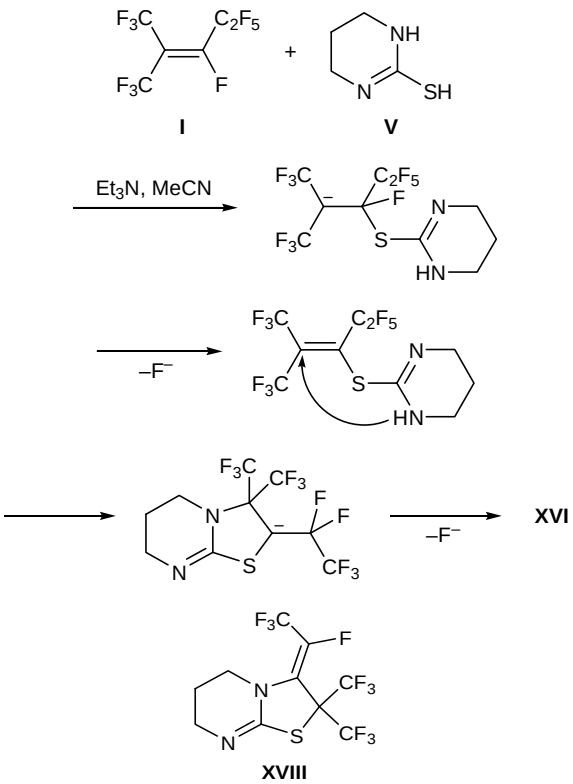
Scheme 4.



V **XVI**

V **XVII**

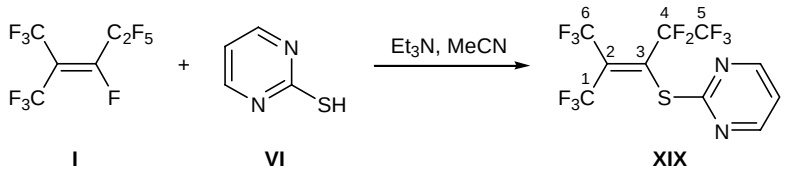
Scheme 5.



XVIII

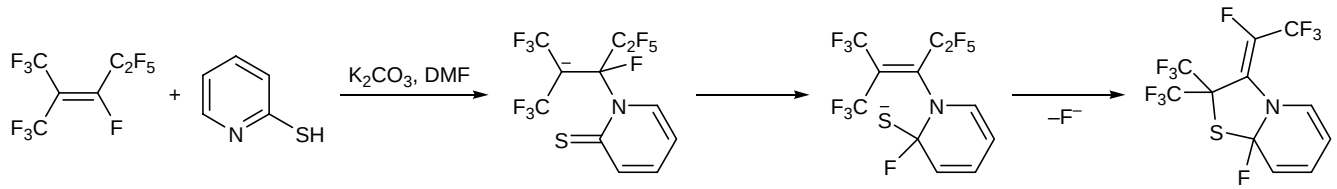
On the other hand, the reaction of **I** with pyrimidine-2-thiol (**VI**) in the presence of triethylamine afforded only compound **XIX** as a result of fluorine replacement at the double bond (Scheme 6, cf. [7]). By contrast, perfluoro(2-methyl-2-pentene) (**I**) reacted with pyridine-2-thiol (**VII**) to give 2-tetrafluoroethylidene-3,3-bis(trifluoromethyl)-2,3-dihydro-8a*H*-

Scheme 6.



I VI XIX

Scheme 7.



I VII A XXI XX

thiazolo[3,2-*a*]pyridine (**XX**) (Scheme 7). In this case, the intramolecular ring closure is governed by the mode of stabilization of intermediate carbanion **A**: migration of fluoride ion from the CF fragment to the C=S carbon atom gives rise to thiolate ion **XXI** which undergoes cyclization to thiazolopyridine **XX**.

It should be noted that the initial reagent may not possess a 1,3-dinucleophile fragment; it is more important that both nucleophilic centers be formed during the reaction with perfluoroolefin. Thus the product structure in reactions of perfluoroolefins with 1,3(N,S)-dinucleophiles is determined by the possibility for generation of a second nucleophilic center after initial nucleophilic attack on the double bond.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP 400SY spectrometer at 400, 100, and 188 MHz, respectively; the chemical shifts were measured relative to TMS (^{1}H, ^{13}C) and C_6F_6 (^{19}F) as internal references; ^{13}C–^{1}H coupling constants were not measured. The IR spectra were recorded on a Specord M-80 spectrometer from solutions in carbon tetrachloride. The electron absorption spectra were measured on a Specord UV-Vis spectrophotometer from solutions in ethanol. The mass spectra (electron impact, 70 eV) were run using a VG 707 OE GC–MS system. The products were isolated by column chromatography on silica gel using CH_2Cl_2–acetone (10:1) as eluent.

Reaction of 3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl isothiocyanate (VIII) with ammonia. A solution of ammonia in acetonitrile was added over a period of 5 min under stirring and cooling with ice water to a solution of 5 g of compound **VIII** in 30 ml of acetonitrile. The mixture was stirred for 0.5 h on cooling and for 1.5 h at room temperature, poured into water, and extracted with methylene chloride. The extract was dried over $CaCl_2$ and evaporated, and the residue was subjected to column chromatography on silica gel using methylene chloride as eluent to isolate 3.4 g of compound **X** and 1.8 g of **XI**.

4-Tetrafluoroethylidene-5,5-bis(trifluoromethyl)-4,5-dihydrothiazol-2-amine (X). mp 112–113°C. IR spectrum (CCl_4, 5%), ν, cm^{-1}: 1200–1300 (C–F); 1360 (C–N); 1590 (C=N); 1630 (δNH); 1670 (C=C); 3320, 3410 (NH_2). UV spectrum, λ_{max}, nm (ε): 210 (8400), 263 (17600). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 97.5 t (3F, 7-F, J = 7 Hz), 96.7 (6F, 8-F, 9-F, J = 22 Hz), 10.7 (1F, 6-F, J = 7, 22 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 161.2 (C^2), 138.2 (C^6, $^1J_{CF}$ = 254.8, $^2J_{CF}$ = 39.7 Hz), 133.8 (C^4, $^2J_{CF}$ = 29.0 Hz), 120.7 (C^8, C^9, $^1J_{CF}$ = 284.9 Hz), 117.9 (C^7, $^1J_{CF}$ = 272.4, $^2J_{CF}$ = 37.2 Hz), 75.2 (C^5, $^1J_{CF}$ = 31.9 Hz). Mass spectrum, m/z (I_{rel}, %): 336 $[M]^+$ (100), 319 $[M - F]^+$ (33.06), 267 $[M - CF_3]^+$ (74.56), 217 $[M - C_2F_5]^+$ (37.68), 190 (3.78), 175 (14.76), 127 (5.73), 100 $[CF_2{=}CF_2]^+$ (3.92), 69 $[CF_3]^+$ (24.63), 60 $[S{=}CNH_2]^+$ (35.71), 42 $[N{=}CNH_2]^+$ (5.01). Found: M^+ 335.9783. $C_7H_2F_{10}N_2S$. Calculated: M 335.9779.

5-Tetrafluoroethylidene-4,4-bis(trifluoromethyl)-2,3-dihydro-1*H*-imidazole-2-thione (XI). mp 134–135°C. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 97.2 (3F, 8-F), 96.4 (3F, 9-F), 98.0 (3F, 7-F), 36.9 (1F, 6-F). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 188.4 (C^2), 135.7 (C^5, $^2J_{CF}$ = 17.0 Hz), 139.2 (C^6, $^1J_{CF}$ = 274, $^2J_{CF}$ = 39 Hz), 120.4 (C^8, C^9, $^1J_{CF}$ = 283.2 Hz), 118.4 (C^7, $^1J_{CF}$ = 280.2, $^2J_{CF}$ = 36.2 Hz), 74.2 (C^4, $^2J_{CF}$ = 32.1 Hz).

Reactions of perfluoro(2-methyl-2-pentene) (I) and perfluoro(5-aza-4-nonene) (II) with N,S-dinucleophiles. Compound **I** or **II**, 5.6 g (0.013 mol), was added over a period of 0.5 h under stirring and cooling with ice water to a solution of 1.5 g (0.013 mol) of N,S-dinucleophile **III–VII** and 5.3 g of K_2CO_3 in 30 ml of dimethylformamide. The mixture was stirred for 1 h at room temperature, heated for 1 h at 70°C, poured into water, and extracted with methylene chloride. The extract was dried over $CaCl_2$ and evaporated, and the residue was either distilled under reduced pressure or subjected to column chromatography on silica gel using methylene chloride–acetone (5:1) as eluent.

6-Tetrafluoroethylidene-5,5-bis(trifluoromethyl)-5,6-dihydrothiazolo[2,3-*c*][1,2,4]triazole (XIII). ^{1}H NMR spectrum, δ, ppm: 5.59 (3-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 95.1 (3F, 12-F), 89.5 (6F, 9-F, 10-F), 51.8 (1F, 11-F). Found, %: C 26.41, 26.64; H 0.30, 0.35; F 52.31, 52.60. M^+ 361. $C_8HF_{10}N_3S$. Calculated, %: C 26.59; H 0.28; F 52.62. *M* 361.

7-Fluoro-5,7-bis(heptafluoropropyl)-7*H*-[1,2,4]-triazolo[3,4-*b*][1,3,5]thiadiazine (XIV). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 83.6 (3F, 15-F), 82.5 (3F, 12-F), 51.5 (1F, 2-F), 44.8 (2F, 13-F), 43.4 (2F, 10-F), 37.0 (2F, 14-F), 36.3 (2F, 11-F). Found, %: C 24.68, 24.87; H 0.18, 0.23; F 57.34, 57.45. M^+ 494. $C_{10}HF_{15}N_4S$. Calculated, %: C 24.29; H 0.20; F 57.69. *M* 494.

3-(3,3,3-Trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenyl)tetrahydrothiazole-2-thione (XV). Yield 5 g (37.6%), bp 82–83°C (0.3 mm). ^{1}H NMR spectrum, δ, ppm: 4.31 t (1H, 9-H, J = 9.3 Hz), 3.53 (1H, 8-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 106.2 t (3F, 1-F, J = 10 Hz), 101.4 s (3F, 6-F), 83.3 s (3F, 5-F), 57.4 and 53.5 (2F, 4-F, *AB* system, J_{FF} = 285.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 202.3 (C^7), 140.3 (C^3, $^2J_{CF}$ = 29.3 Hz), 132.9 (C^2, $^2J_{CF}$ = 31.8 Hz), 118.8 (C^1, $^1J_{CF}$ = 277.4 Hz), 117.6 (C^5, $^1J_{CF}$ = 288.2, $^2J_{CF}$ = 35.7 Hz), 119.4 (C^6, $^1J_{CF}$ = 278.5 Hz), 110.1 (C^4, $^1J_{CF}$ = 262.5, $^2J_{CF}$ = 40.2 Hz), 58.2 (C^9), 30.6 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 399 $[M]^+$ (8.84), 380 $[M - F]^+$ (3.79), 339 $[M - CH_2CH_2S]^+$ (0.96), 330 $[M - CF_3]^+$ (100), 304 $[M - CF_3CH{=}CH]^+$ (19.30), 262 $[M - FCH_2CH_2NS_2]^+$ (0.80), 230 $[M - CF_3CF{=}CF_2]^+$ (11.17), 119 $[C_2F_5]^+$ (1.29), 69 $[CF_3]^+$ (9.72). Found: M^+ 398.9611. $C_9H_4F_{11}NS_2$. Calculated: *M* 398.9609.

2-Tetrafluoroethylidene-3,3-bis(trifluoromethyl)-2,3,6,7-tetrahydro-5*H*-thiazolo[3,2-*a*]pyrimidine (XVI). Yield 3.5 g (57%), mp 173–174°C. IR spectrum, ν, cm^{-1}: 2652, 2755 (C–H); 1675 (C=C_{as}); 1653 (C=C_s); 1528 (C=N); 1350–1335 (C–N); 1269, 1238, 1164 (C–F). UV spectrum, λ_{max}, nm (ε): 249 (13760), 329 (300). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 95.8 (6F, 12-F, 13-F, J_{FF} = 32.0 Hz), 95.5 (3F, 11-F, J_{FF} = 8 Hz), 54.5 sept.q (1F, 9-F, J_{FF} = 32, 8 Hz). ^{1}H NMR spectrum, δ, ppm: 3.85 (7-H), 3.56 (9-H), 2.45 (8-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 158.9 (C^2), 120.2 (C^{12}, C^{13}, $^1J_{CF}$ = 292.1 Hz), 139.8 (C^{10}, $^1J_{CF}$ = 277.7, $^2J_{CF}$ = 41.9 Hz), 117.1 (C^{11}, $^1J_{CF}$ = 274.6, $^2J_{CF}$ = 40.3 Hz), 111.2 (C^5, $^2J_{CF}$ = 16.3 Hz), 76.6 (C^4, $^2J_{CF}$ = 32.5 Hz), 45.3 (C^7), 40.5 (C^9), 18.4 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 376 $[M]^+$ (96.17), 357 $[M - F]^+$ (7.99), 336 $[M - CHCH{=}N]^+$ (29.21), 307 $[M - CH_2CH_2CH_2N{=}CH]^+$ (44.49), 279 (100), 119 $[C_2F_5]^+$ (13.61), 69 $[CF_3]^+$ (87.15), 42 $[CH_2CH_2{=}N]^+$ (65.94), 28 $[CH_2{=}N]^+$ (49.21). Found: M^+ 376.0097. $C_{10}H_6F_{10}N_2S$. Calculated: *M* 376.0092.

2-Fluoro-2,4-bis(heptafluoropropyl)-2,6,7,8-tetrahydropyrimido[2,1-*b*][1,3,5]thiadiazine (XVII). ^{1}H NMR spectrum, δ, ppm: 5.59 (6-H, 8-H), 3.60 (7-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.3 (6F, 13-F, 16-F), 45.6 (1F, 2-F), 45.0 (2F, 11-F), 43.0 (2F, 14-F), 39.8 (2F, 12-F), 36.3 (2F, 15-F). Found, %: C 28.58, 28.67; H 1.24, 1.28; F 55.78, 55.95; N 8.14. M^+ 509. $C_{12}H_6F_{15}N_3S$. Calculated, %: C 28.29; H 1.18; F 55.99; N 8.25. *M* 509.

2-(3,3,3-Trifluoro-1-pentafluoroethyl-2-trifluoromethyl-1-propenylsulfanyl)pyrimidine (XIX). Pyrimidine-2-thiol, 5.6 g (0.05 mol), was added in portions under stirring and cooling with ice water to a mixture of 15 g (0.05 mol) of compound **I** and 5.05 g (0.05 mol) of triethylamine in 50 ml of acetonitrile. The mixture was stirred for 1 h on cooling, for 1 h at 20°C, and for 2 h at 45°C, poured into water, acidified with 5% hydrochloric acid, and extracted with methylene chloride. The extract was dried over $CaCl_2$ and evaporated, and the residue was distilled under reduced pressure. Yield 14.1 g (72%), bp 67–68°C (15 mm). IR spectrum, ν, cm^{-1}: 2895, 2839 (C–H); 1627, 1479 (C=C); 1123, 1031 (C–F); 786 (C–S). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 t (1H, J = 4.9 Hz), 8.57 d (2H, J = 4.9 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 104.2 m (3F, 1-F), 102.3 q (3F, 6-F, J_{FF} = 11.4 Hz), 84.1 q (3F, 5-F, J = 10.3 Hz), 58.3 q (2F, 4-F, J_{FF} = 20.7 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 392 $[M]^+$ (7), 373 $[M - F]^+$ (62), 323 $[M - CF_3]^+$ (85). Found, %: C 30.23, 30.46; H 0.89, 1.21; F 53.67,

53.87. $C_{10}H_3F_{11}N_2S$. Calculated, %: C 30.61; H 0.77; F 53.32.

Reaction of perfluoro(2-methyl-2-pentene) with pyridine-2-thiol. A mixture of 1.4 g of compound **VII** and 3.8 g of triethylamine was added over a period of 10 min under cooling with ice water to a solution of 3.8 g of compound **I** in 30 ml of acetonitrile. The mixture was stirred for 0.5 h on cooling, for 1 h at room temperature, and for 2 h at 45°C, poured into water, acidified with 5% hydrochloric acid, and extracted with methylene chloride. The extract was dried over $CaCl_2$ and evaporated, and the residue was subjected to column chromatography using methylene chloride as eluent to isolate 2.4 g of 8a-fluoro-3-tetrafluoroethylidene-2,2-bis(trifluoromethyl)-2,3-dihydro-8a*H*-thiazolo[3,2-*a*]pyridine (**XX**), bp 86–87°C (0.3 mm). ^{1}H NMR spectrum, δ, ppm: 8.39 (9-H), 7.58 (6-H, 8-H), 7.11 (7-H), 5.80 (5-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 86.7 (6F, 12-F, 13-F), 86.7 (3F, 11-F), 60.7 (1F, 10-F). Found, %: C 35.38; H 1.12; F 51.12; N 3.65. $C_{11}H_4F_{10}NS$. Calculated, %: C 35.48; H 1.07; F 51.07; N 3.76.

This study was performed under financial support by the Ministry of Education of the Russian Federation, "Universities of Russia" program (project no. UR.05.01.014).

REFERENCES

1. Furin, G.G., *Ftorsoderzhashchie geterotsiklicheskie soedineniya* (Fluorine-Containing Heterocyclic Compounds), Novosibirsk: Nauka, 2001, p. 304.
2. *Lekarstvennye sredstva* (Medicines), Mashkovskii, M.D., Ed., Khar'kov: Torsing, 1998, vol. 1, p. 59; vol. 2, p. 592.
3. Filler, R. and Kobayashi, Y., *Biomedical Aspects of Fluorine Chemistry*, Tokyo: Kodansha Elsevier Biomed., 1982, p. 237.
4. Burger, K., Wucherpfenning, U., and Bunner, E., *Adv. Heterocycl. Chem*., 1994, vol. 60, p. 1.
5. Furin, G.G. and Gatilov, Yu.V., *Khim. Geterotsikl. Soedin*., 1993, p. 253.
6. Furin, G.G., Pressman, L.S., Rogoza, A.V., and Salmanov, I.A., *Russ. J. Org. Chem*., 1997, vol. 33, p. 720.
7. Chi, K.-W., Kim, H.-A., Lee, W., Park, T.-H., Lee, U., and Furin, G.G., *Bull. Korean Chem. Soc*., 2002, vol. 23, p. 1017.
8. Rogoza, A.V., Furin, G.G., Gatilov, Yu.V., and Bagryanskaya, I.Yu., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, p. 1027.
9. Furin, G.G., Bagryanskaya, I.Yu., and Gatilov, Yu.V., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1997, p. 1300.
10. Rogoza, A.V. and Furin, G.G., *Russ. J. Gen. Chem*., 1999, vol. 69, p. 1433.