Russian Journal of Organic Chemistry, Vol. 37, No. 11, 2001, pp. 1621–1628. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 11, 2001, pp. 1693–1699.

Reactions of Perfluoro(5-aza-4-nonene) with Hydrazine and Some Its Derivatives

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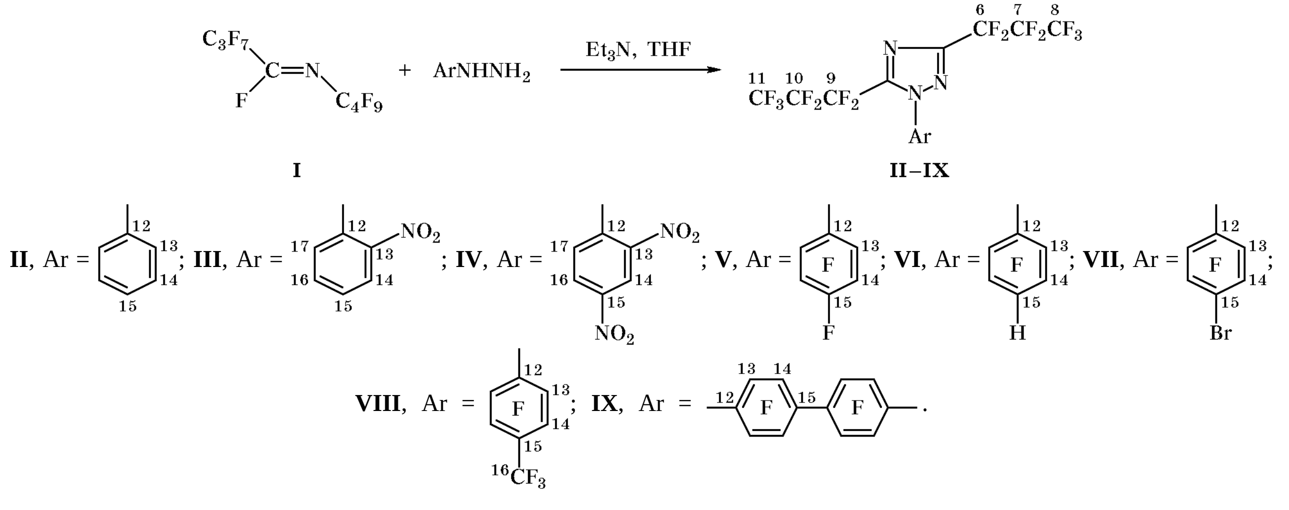
Received October 6, 2000

Abstract—The reaction of perfluoro(5-aza-4-nonene) with hydrazine hydrate in tetrahydrofuran at 0–20°C in the presence of triethylamine yields 2,5-bis(heptafluoropropyl)-1*H*-1,2,4-triazole; under similar conditions perfluoro(5-aza-4-nonene) reacts with arylhydrazines to form 1-aryl-3,5-bis(heptafluoropropyl)-1,2,4-triazoles.

1-Aryl-substituted azoles having perfluoroalkyl groups attract interest as intermediate products in the synthesis of potential biologically active compounds which can be used in medicine and agriculture [1, 2]. As a rule, such products are obtained via introduction of perfluoroalkyl groups into heteroring by various methods [3, 4]. In the recent years, a new approach was developed on the basis of reactions of commercially available perfluoroolefins with difunctional nucleophilic reagents [5–12]. We previously showed [13] that perfluoro(2-methyl-2-pentene) reacts with arylhydrazines in the presence of triethylamine to afford 1-aryl-substituted pyrazole derivatives. The key point of the process is formation of intermediates containing a C=C–C=N–N conjugated bond sequence. Intramolecular cyclization of such intermediates leads to formation of five-membered heterorings. While further developing the above approach, the present work was aimed at finding an initial fluorinated olefin whose reaction with arylhydrazines would give an intermediate having a C=N–N=N–N conjugated bond system. Our previous studies [14] revealed that perfluoro(5-aza-4-nonene) (**I**) reacts with aliphatic and aromatic amidines to form *sym*-triazine

Scheme 1.



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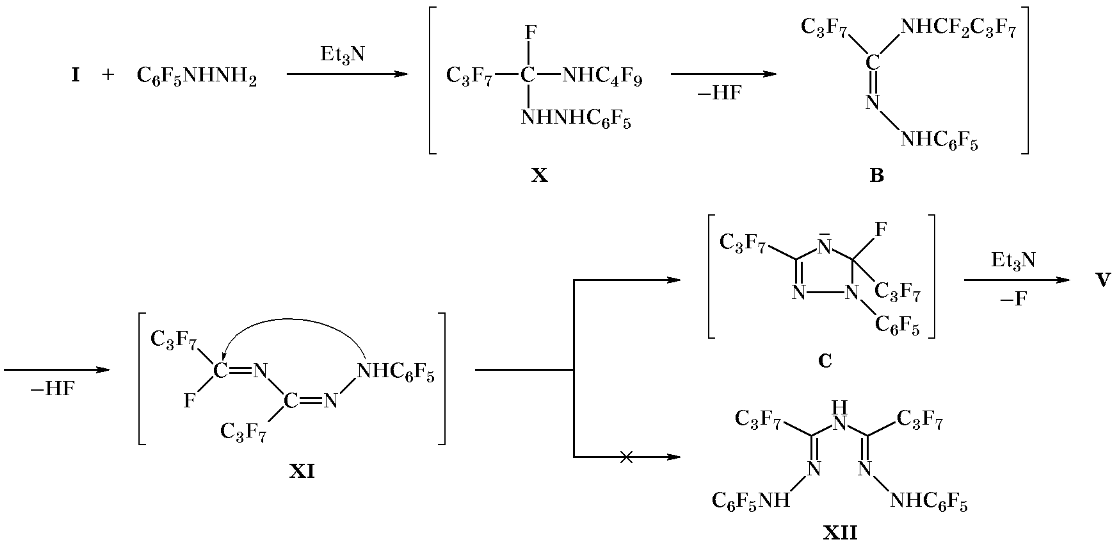
Scheme 2.



derivatives. We now focused on the reactions of **I** with hydrazine hydrate and some its derivatives.

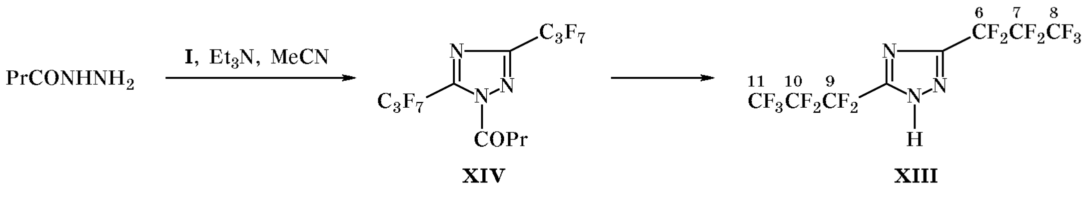
Perfluoro(5-aza-4-nonene) (**I**) reacted with arylhydrazines in tetrahydrofuran in the presence of triethylamine under very mild conditions, yielding 1-aryl-3,5-bis(heptafluoropropyl)-1,2,4-triazoles **II**–**IX** (Scheme 1). Presumably, the final products are formed as follows. Nucleophilic attack on compound **I** by the NH_2 group of pentafluorophenylhydrazine gives intermediate **X** which is capable of losing hydrogen fluoride by the action of triethylamine. Compound **XI** could give rise to two processes. The first of these includes replacement of fluorine at the C=N bond by hydrazino group and subsequent formation of bishydrazone **XII**. The second pathway is intramolecular nucleophilic cyclization with formation of 1,2,4-triazole derivative **V** (Scheme 2). The nature of the aryl group weakly affects the process. In the reaction with 4,4′-dihydrazinooctafluorobiphenyl two triazole rings were formed from the two hydrazine moieties (compound **IX**).

Propionyl hydrazine reacted with flouoroolefin **I** in the presence of triethylamine in acetonitrile to give bis(heptafluoropropyl)-1*H*-1,2,4-triazole (**XIII**) (Scheme 3), presumably as a result of elimination of the *N*-propionyl group from intermediate **XIV**. No dihydrazide formation was observed.

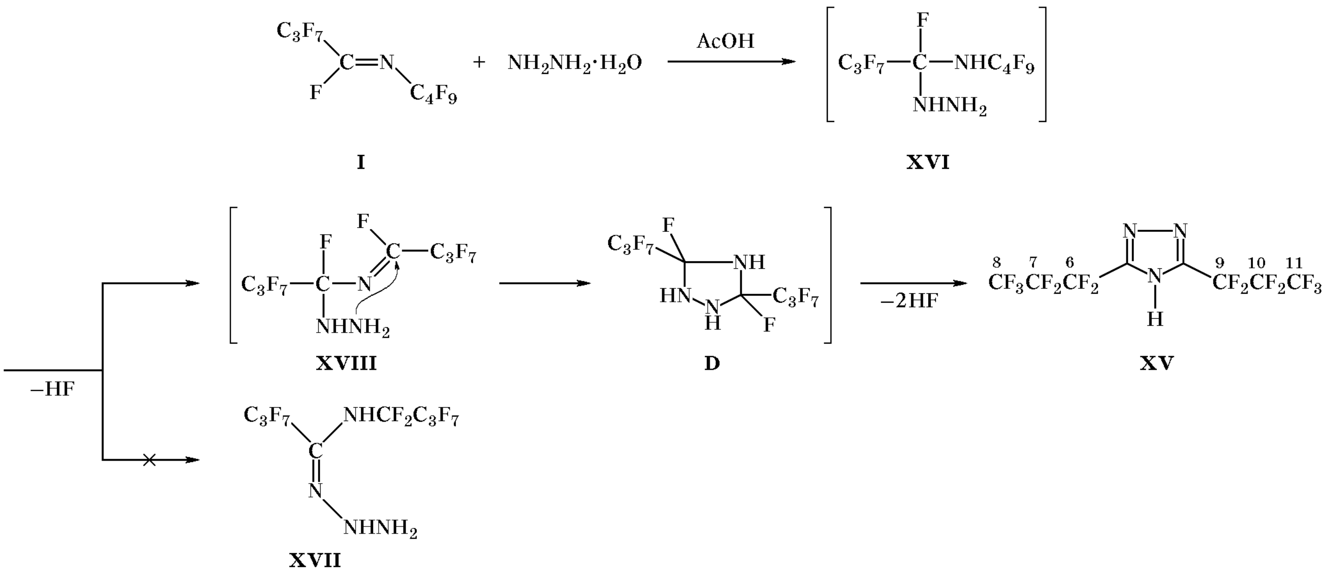
By reaction of compound **I** with hydrazine hydrate in acetic acid we obtained cyclization product **XV** in 42% yield. A possible mechanism of this reaction is shown in Scheme 4. Elimination of hydrogen fluoride from the hydrazino group of primary adduct **XVI** does not occur due to its high basicity, and compound **XVII** is not formed. Instead, HF molecule is released from the $-NH-CF_2C_3F_7$ moiety to give intermediate **XVIII**. Intramolecular cyclization of the latter, followed by loss of two hydrogen fluoride molecules (from intermediate **D**), leads to formation of final product **XV**.

Perfluoro(2-methyl-2-pentene) (**XIX**) behaves like compound **I** in reactions with 2,3,5,6-tetrafluorophenylhydrazine, 4-bromo-2,3,5,6-tetrafluorophenylhydrazine, and propionylhydrazine. The corresponding pyrazole derivatives **XX**–**XXII** were thus obtained (Scheme 5). On the other hand, the reaction of **XIX** with hydrazine hydrate under the same conditions gave isomeric hydrazones **XXIIIa** and **XXIIIb**. Our attempts to effect cyclization of compounds **XXIIIa** and **XXIIIb** by the action of triethylamine in acetonitrile resulted in formation of isomeric perfluoro-

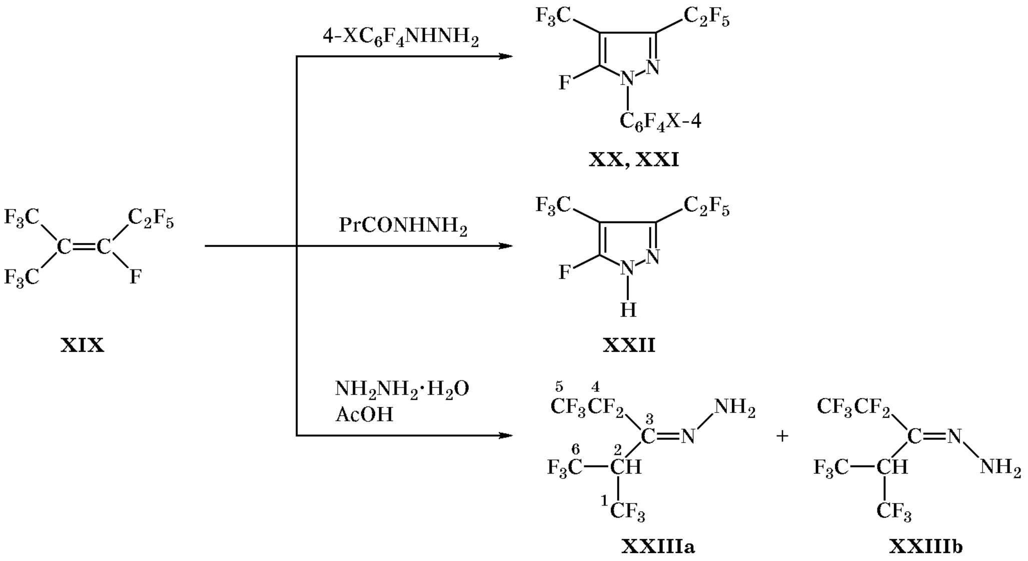
Scheme 3.



Scheme 4.



Scheme 5.



XX, X = H; **XXI**, X = Br.

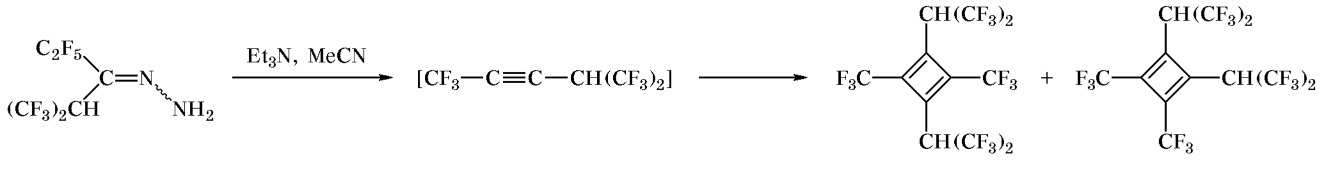
alkylcyclobutadienes **XXIVa** and **XXIVb** at a ratio of 2.3 : 1 (yield 63%) instead of the expected pyrazole derivatives (Scheme 6). Products **XXIVa** and **XXIVb** are likely to be formed via dimerization of intermediate alkyne **XXV**.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP-400SY spectrometer at 400, 100, and 188 MHz, respectively; hexamethyldisiloxane and hexafluorobenzene were used as internal references (^{13}C–^1H coupling constants were not measured). The IR spectra were obtained on a Specord M-80 instrument in CCl_4. The mass spectra (70 eV) were run on a VG 707 OE GC–MS system. Perfluoro(5-aza-4-nonene) (**I**) was synthesized by the procedure described in [15].

Typical procedure for synthesis of fluorinated *N*-aryl-1,2,4-triazoles. A solution of 1 equiv of compound **I** in 10 ml of THF was added over a period of 15 min to a solution of 1 equiv of arylhydrazine and

Scheme 6.



XXIIIa, XXIIIb **XXV** **XXIVa** **XXIVb**

3 equiv of triethylamine in 40 ml of THF on stirring at 0°C. The mixture was stirred for 1 h at 0°C, for 2 h at room temperature, and for 2 h at 50°C. It was then poured into 100 ml of water and extracted with methylene chloride (3 × 70 ml). The extract was dried over Na_2SO_4 and evaporated, and the residue was distilled under reduced pressure or was subjected to column chromatography using hexane–methylene chloride as eluent.

3,5-Bis(heptafluoropropyl)-1-phenyl-1,2,4-triazole (II) was synthesized from 2.48 g (23 mmol) of phenylhydrazine and 9.96 g (23 mmol) of perfluoroolefin **I**. Yield 9.2 g (83%); yellow liquid, bp 81–82°C (0.3 mm). IR spectrum, ν, cm^{-1}: 1658, 1520 (C=N–C=C), 1338 (C–N), 1236–1126 (C–F). ^1H NMR spectrum, δ, ppm: 7.26 (13-H), 7.36 (14-H), 7.31 (15-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 153.0 (C^3, $^2J_{C,F}$ = 29.5 Hz), 144.6 (C^5, $^2J_{C,F}$ = 30.1 Hz), 135.5 (C^{12}), 130.1 (C^{15}), 128.8 (C^{14}), 125.0 (C^{13}), 117.0 (C^8, $^1J_{C,F}$ = 276.8, $^2J_{C,F}$ = 34.4 Hz), 116.8 (C^{11}, $^1J_{C,F}$ = 276.2, $^2J_{C,F}$ = 34.5 Hz), 106.7 (C^7, $^1J_{C,F}$ = 267.5, $^2J_{C,F}$ = 34.4 Hz), 106.3 (C^{10}, $^1J_{C,F}$ = 267.7, $^2J_{C,F}$ = 34.2 Hz), 108.9 (C^6, $^1J_{C,F}$ = 258.8, $^2J_{C,F}$ = 31.6 Hz), 108.5 (C^9, $^1J_{C,F}$ = 258.5, $^2J_{C,F}$ = 31.7 Hz). ^{19}F NMR spectrum, δ_F, ppm: 82.5 t (3F, 11-F, *J* = 9 Hz), 83.8 t (3F, 8-F, *J* = 9 Hz), 53.0 q (2F, 7-F, *J* = 9 Hz), 50.0 q (2F, 10-F, *J* = 9 Hz), 38.2 s (2F, 6-F), 36.4 s (2F, 9-F). Mass spectrum, *m/z* (I_{rel}, %): 481 (73) M^+, 462 (20) $[M-F]^+$, 362 (51) $[M-C_2F_5]^+$, 262 (2) $[M-2C_2F_5]^+$, 169 (2) $[C_3F_7]^+$, 119 (5) $[C_2F_5]^+$, 91 (100) $[C_6H_5N]^+$, 77 (18) $[C_6H_5]^+$, 69 (6) $[CF_3]^+$. Found: *M* 481.0245. $C_{14}H_5F_{14}N_3$. Calculated: *M* 481.0259.

3,5-Bis(heptafluoropropyl)-1-(2-nitrophenyl)-1,2,4-triazole (III) was synthesized from 5.2 g (34 mmol) of 2-nitrophenylhydrazine and 14.7 g (34 mmol) of compound **I**. Yield 14.8 g (83%); yellow liquid, bp 150–151°C (0.5 mm). IR spectrum, ν, cm^{-1}: 1610, 1590, 1545 ($C=C_{arom}$); 1520 (C=C–C=N); 1540 (NO_2, asym.); 1350 (NO_2, sym.); 1320 (C–N); 1220–1150 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.31 (17-H), 7.88 (15-H, 16-H), 7.71 (14-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 154.5 (C^3, $^2J_{C,F}$ = 29.6 Hz), 146.6 (C^5, $^2J_{C,F}$ = 30.5 Hz), 159.9 (C^{12}), 144.2 (C^{13}), 134.7 (C^{14}), 133.1 (C^{15}), 129.6 (C^{16}), 126.1 (C^{17}), 117.8 (C^8, $^1J_{C,F}$ = 286.9, $^2J_{C,F}$ = 30 Hz), 117.5 (C^{11}, $^1J_{C,F}$ = 287.2, $^2J_{C,F}$ = 29.6 Hz), 110.5 (C^6, $^1J_{C,F}$ = 256.8, $^2J_{C,F}$ = 28.7 Hz), 110.4 (C^9, $^1J_{C,F}$ = 259.0, $^2J_{C,F}$ = 31 Hz), 108.6 (C^7, $^1J_{C,F}$ = 266.9, $^2J_{C,F}$ = 27.8 Hz), 108.4 (C^{10}, $^1J_{C,F}$ = 268.7, $^2J_{C,F}$ = 38.4 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.9 t (3F, 8-F, *J* = 9 Hz), 82.5 t (3F, 11-F, *J* = 9 Hz), 53.8 q (2F, 7-F, *J* = 9 Hz), 49.5 q (2F, 10-F, *J* 9 Hz), 37.6 s (2F, 6-F), 36.1 s (2F, 9-F). Mass spectrum, *m/z* (I_{rel}, %): 526 (6) M^+, 507 (49) $[M-F]^+$, 480 (2) $[M-NO_2]^+$, 457 (1) $[M-CF_3]^+$, 407 (27) $[M-C_2F_5]^+$, 195 (1) $[C_3F_7CN]^+$, 169 (54) $[C_3F_7]^+$, 150 (4) $[C_6H_4NO_2N_2]^+$, 119 (9) $[C_2F_5]^+$, 118 (1) $[C_6H_4NO_2]^+$, 106 (87) $[C_6H_4NO]^+$, 100 (5) $[CF_2=CF_2]^+$, 90 (32) $[C_6H_4N]^+$, 78 (100) $[C_6H_6]^+$, 76 (17) $[C_6H_4]^+$, 69 (50) $[CF_3]^+$, 46 (1) $[NO_2]^+$. Found: *M* 526.0124. $C_{14}H_4F_{14}N_4O_2$. Calculated: *M* 526.0110.

1-(2,4-Dinitrophenyl)-3,5-bis(heptafluoropropyl)-1,2,4-triazole (IV) was synthesized from 5.03 g (25 mmol) of 2,4-dinitrophenylhydrazine and 10.8 g (25 mmol) of compound **I**. Yield 7.5 g (53%); brown liquid, bp 104–106°C (0.3 mm). UV spectrum (C_2H_5OH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 228 (11 800), 334 (850). IR spectrum, ν, cm^{-1}: 1590, 1545 ($C=C_{arom}$); 1610, 1520 (C=C–C=N); 1540 (NO_2, asym.); 1350 (NO_2, sym.); 1320 (C–N); 1220–1150 (C–F). ^1H NMR spectrum, δ, ppm: 9.15 d (14-H, *J* = 2.5 Hz), 8.78 d.d (17-H, *J* = 8, 2.5 Hz), 8.02 d (16-H, *J* = 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 155.1 (C^3, $^2J_{C,F}$ = 31 Hz), 146.7 (C^5, $^2J_{C,F}$ = 30 Hz), 145.0 (C^{12}), 134 (C^{13}, C^{15}), 129.1 (C^{16}), 129.0 (C^{14}), 122 (C^{17}), 117.3 (C^8, $^1J_{C,F}$ = 288.1, $^2J_{C,F}$ = 32.8 Hz), 117.6 (C^{11}, $^1J_{C,F}$ = 287.3, $^2J_{C,F}$ = 33.1 Hz), 108.2 (C^7, $^1J_{C,F}$ = 263.4, $^2J_{C,F}$ = 39.5 Hz), 108.3 (C^{10}, $^1J_{C,F}$ = 264.3, $^2J_{C,F}$ = 34.6 Hz), 110.1 (C^6, $^1J_{C,F}$ = 262.4, $^2J_{C,F}$ = 31.2 Hz), 110.2 (C^7, $^1J_{C,F}$ = 257.4, $^2J_{C,F}$ = 31.2 Hz). ^{19}F NMR spectrum

(CDCl$_3$), δ_F, ppm: 82.9 t (3F, 8-F, J = 9 Hz), 82.5 t (3F, 11-F, J = 9 Hz), 54.0 q (2F, 7-F, J = 9 Hz), 49.2 q (2F, 10-F, J = 9 Hz), 37.7 s (2F, 6-F), 36.0 s (2F, 9-F). Mass spectrum, m/z (I_{rel}, %): 571 (3) M^+, 552 (42) $[M-F]^+$, 452 (37) $[M-C_2F_5]^+$, 404 (2) $[M-C_6H_3(NO_2)_2]^+$, 376 (36) $[M-C_3F_7CN]^+$, 348 (17) $[C_3F_7CN, N_2]^+$, 195 (1) $[C_3F_7CN]^+$, 181 (4) $[C_6H_3(NO_2)_2N]^+$, 169 (100) $[C_3F_7]^+$, 145 (2) $[C_2F_5CN]^+$, 119 (11) $[C_2F_5]^+$, 100 (9) $[CF_2=CF_2]^+$, 69 (49) $[CF_3]^+$. Found, %: C 29.42; H 0.53; F 46.58; N 12.26. M 570.9953. $C_{14}H_3F_{14}N_5O_4$. Calculated, %: C 29.34; H 0.45; F 46.68; N 12.47. M 570.9961.

Perfluoro(3,5-dipropyl-1-phenyl-1,2,4-triazole) (V) was synthesized from 4.95 g (25 mmol) of pentafluorophenylhydrazine and 10.8 g (25 mmol) of compound **I**. Yield 12.8 g (90%); yellow liquid, bp 71–72°C (3 mm). UV spectrum (C_2H_5OH), λ_{max}, nm (ε, l mol^{-1} cm): 265 (900). IR spectrum, ν, cm^{-1}: 1527 (C=C), 1520 (C=N), 1338 (C–N), 1236–1126 (C–F). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: 155.9 (C^3, $^2J_{C,F}$ = 30.0 Hz), 147.9 (C^5, $^2J_{C,F}$ = 30.9 Hz), 144.4 (C^{15}, $^1J_{C,F}$ = 253.9 Hz), 144 (C^{13}, $^1J_{C,F}$ = 258.7 Hz), 138.3 (C^{14}, $^1J_{C,F}$ = 258.2 Hz), 117.9 (C^{11}, $^1J_{C,F}$ = 261.7, $^2J_{C,F}$ = 33.2 Hz), 117.4 (C^8, $^1J_{C,F}$ = 253.5, $^2J_{C,F}$ = 33.5 Hz), 111.5 (C^{12}, $^2J_{C,F}$ = 35.8 Hz), 110.2 (C^9, $^1J_{C,F}$ = 258.5, $^2J_{C,F}$ = 32.1 Hz), 109.5 (C^6, $^1J_{C,F}$ = 257.9, $^2J_{C,F}$ = 34.1 Hz), 108.9 (C^{10}, $^1J_{C,F}$ = 267.4, $^2J_{C,F}$ = 34.1 Hz), 108.3 (C^7, $^1J_{C,F}$ = 268, $^2J_{C,F}$ = 33.9 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_F, ppm: 83.5 s (3F, 11-F), 83.1 s (3F, 8-F), 52.6 m (2F, 10-F), 49.7 m (2F, 7-F), 38 m (2F, 9-F), 36.8 m (2F, 6-F), 19.3 m (2F, 13-F), 16.6 m (1F, 15-F), 3.4 m (2F, 14-F). Mass spectrum, m/z (I_{rel}, %): 571 M^+, 552 $[M-F]^+$, 452 $[M-C_2F_5]^+$, 376 $[M-C_3F_7CN]^+$, 357 $[M-C_2F_5CF=C=N]^+$, 257, 224, 169 $[C_3F_7]^+$, 167 $[C_6F_5]^+$, 119 $[C_2F_5]^+$, 69 $[CF_3]^+$. Found: M 570.97830. $C_{14}F_{19}N_3$. Calculated: M 570.97886.

3,5-Bis(heptafluoropropyl)-1-(2,3,5,6-tetrafluorophenyl)-1,2,4-triazole (VI) was synthesized from 1.8 g (10 mmol) of 2,3,5,6-tetrafluorophenylhydrazine, 4.33 g (10 mmol) of compound **I**, and 2.02 g (20 mmol) of triethylamine. Yield 4 g (72%); yellow liquid, bp 134–135°C (3 mm). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 271 (2700). IR spectrum, ν, cm^{-1}: 3086 (C–N), 1650 (C=C), 1631 (C=N), 1531 and 1508 (C=C$_{arom}$), 1345 (C–N), 1236–1187 (C–F). ^{1}H NMR spectrum, δ, ppm: 7.47 (H$_{arom}$). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: 156.1 (C^3, $^2J_{C,F}$ = 30.1 Hz), 148.1 (C^{15}, $^2J_{C,F}$ = 26.4 Hz), 146.3 (C^{13}, $^1J_{C,F}$ = 252.7, $^2J_{C,F}$ = 15.7 Hz), 143.5 (C^{14}, $^1J_{C,F}$ = 259.2, $^2J_{C,F}$ = 15.9 Hz), 118.3 (C^{11}, $^1J_{C,F}$ = 285.7, $^2J_{C,F}$ = 33.2 Hz), 117.9 (C^8, $^1J_{C,F}$ = 283.5, $^2J_{C,F}$ = 33.5 Hz), 110.3 (C^{12}, $^2J_{C,F}$ = 14.2 Hz), 110.2 (C^9, $^1J_{C,F}$ = 258.5, $^2J_{C,F}$ = 32.1 Hz), 109.5 (C^6, $^1J_{C,F}$ = 257.9, $^2J_{C,F}$ = 34.1 Hz), 108.9 (C^{10}, $^1J_{C,F}$ = 267.4, $^2J_{C,F}$ = 34.1 Hz), 108.3 (C^7, $^1J_{C,F}$ = 268, $^2J_{C,F}$ = 33.9 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_F, ppm: 83.4 s (3F, 11-F), 83.0 s (3F, 8-F), 52.3 m (2F, 10-F), 49.8 m (2F, 7-F), 37.8 m (2F, 9-F), 36.7 m (2F, 6-F), 27.1 m (2F, 13-F), 18.3 m (1F, 15-F). Mass spectrum, m/z (I_{rel}, %): 553 (50) M^+, 534 (32) $[M-F]^+$, 434 (78) $[M-C_2F_5]^+$, 239 (0.9) $[M-C_3F_7CN-C_2F_5]^+$, 215 (0.7) $[HC_6F_4N_3C_2]^+$, 177 (2) $[HC_6F_4N_2]^+$, 163 (100) $[HC_6F_4N]^+$, 149 (12) $[HC_6F_4]^+$, 119 (4) $[C_2F_5]^+$, 100 (3) $[CF_2=CF_2]^+$, 69 (22) $[CF_3]^+$. Found: M 552.9873. $C_{14}HF_{18}N_3$. Calculated: M 552.9883.

1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-3,5-bis-(heptafluoropropyl)-1,2,4-triazole (VII) was synthesized from 2.59 g (10 mmol) of 4-bromo-2,3,5,6-tetrafluorophenylhydrazine, 4.33 g (10 mmol) of compound **I**, and 2.02 g (20 mmol) of triethylamine. Yield 3.6 g (57%); yellow liquid, bp 90–91°C (2 mm). UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 250 (3500). IR spectrum, ν, cm^{-1}: 1711 (C=C), 1673 (C=N), 1527 and 1508 (C=C$_{arom}$), 1404 and 1338 (C–N), 1229–1158 (C–F). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: 161.4 (C^3, $^2J_{C,F}$ = 24.6 Hz), 159.1 (C^5, $^2J_{C,F}$ = 26.0 Hz), 155.1 (C^{15}, $^2J_{C,F}$ = 25.3 Hz), 144.8 (C^{13}, $^1J_{C,F}$ = 246.7, $^2J_{C,F}$ = 15.7 Hz), 142.8 (C^{14}, $^1J_{C,F}$ = 257.2, $^2J_{C,F}$ = 15.9 Hz), 118.4 (C^{11}, $^1J_{C,F}$ = 285.1, $^2J_{C,F}$ = 33.8 Hz), 117.9 (C^8, $^1J_{C,F}$ = 283.5, $^2J_{C,F}$ = 33.5 Hz), 110.3 (C^{12}, $^2J_{C,F}$ = 13.8 Hz), 110.2 (C^9, $^1J_{C,F}$ = 258.5, $^2J_{C,F}$ = 32.1 Hz), 109.5 (C^6, $^1J_{C,F}$ 257.5, $^2J_{C,F}$ 34.0 Hz), 108.9 (C^{10}, $^1J_{C,F}$ = 267.4, $^2J_{C,F}$ = 34.1 Hz), 108.3 (C^7, $^1J_{C,F}$ = 268, $^2J_{C,F}$ = 33.9 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_F, ppm: 82.8 s (3F, 11-F), 82.8 s (3F, 8-F), 52.2 m (2F, 10-F), 46.8 m (2F, 7-F), 37.8 m (2F, 9-F), 37.7 m (2F, 6-F), 18.8 m (2F, 13-F), 33.3 m (1F, 15-F). Mass spectrum, m/z (I_{rel}, %): 631 (53) M^+, 612 (20) $[M-F]^+$, 512 (40) $[M-C_2F_5]^+$, 256 (4) $[BrC_6F_4N_3]^+$, 241 (44) $[BrC_6F_4NH]^+$, 229 (4) $[BrC_6F_4]^+$, 169 (12) $[C_3F_7]^+$, 148 (9) $[C_6F_4]^+$, 119 (10) $[C_2F_5]^+$, 100 (5) $[CF_2=CF_2]^+$, 69 (50) $[CF_3]^+$. Found: M 630.9396. $C_{14}BrF_{18}N_3$. Calculated: M 630.8988.

3,5-Bis(heptafluoropropyl)-1-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,2,4-triazole (VIII) was synthesized from 6.2 g (25 mmol) of 2,3,5,6-tetrafluoro-4-trifluoromethylphenylhydrazine and 10.8 g (25 mmol) of compound **I**. Yield 13 g (84%); yellow liquid, bp 80–81°C (3 mm). UV spectrum (EtOH), $\lambda_{\max}$, nm (ε, l mol^{-1} cm^{-1}): 282 (2300). IR spectrum, ν, cm^{-1}: 1658 (C=C), 1514 (C=N), 1510 (C=C$_{\mathrm{arom}}$), 1340 (C−N), 1220–1124 (C−F). ^{13}C NMR spectrum (CDCl$_3$), δ_{C}, ppm: 156.9 (C^3, $^2J_{\mathrm{C,F}}$ = 30.3 Hz), 148.3 (C^5, $^2J_{\mathrm{C,F}}$ = 31.2 Hz), 145 (C^{14}, $^1J_{\mathrm{C,F}}$ = 269.4 Hz), 144.1 (C^{13}, $^1J_{\mathrm{C,F}}$ = 261.9 Hz), 136.2 (C^{15}, $^2J_{\mathrm{C,F}}$ = 32 Hz), 120.7 (C^{16}, $^1J_{\mathrm{C,F}}$ = 275.5 Hz), 118.2 (C^{11}, $^1J_{\mathrm{C,F}}$ = 286.8, $^2J_{\mathrm{C,F}}$ = 33.4 Hz), 117.8 (C^8, $^1J_{\mathrm{C,F}}$ = 286.2, $^2J_{\mathrm{C,F}}$ = 33.5 Hz), 110.7 (C^9, $^1J_{\mathrm{C,F}}$ = 259.5, $^2J_{\mathrm{C,F}}$ = 40.2 Hz), 110.6 (C^6, $^1J_{\mathrm{C,F}}$ = 257.7, $^2J_{\mathrm{C,F}}$ = 39.2 Hz), 108.9 (C^{10}, $^1J_{\mathrm{C,F}}$ = 267.0, $^2J_{\mathrm{C,F}}$ = 38.6 Hz), 108.8 (C^7, $^1J_{\mathrm{C,F}}$ = 268.5, $^2J_{\mathrm{C,F}}$ = 39.7 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_{F}, ppm: 106.8 s (3F, 16-F), 83.5 s (3F, 11-F), 83.1 s (3F, 8-F), 52.5 m (2F, 10-F), 49.7 m (2F, 7-F), 38 m (2F, 9-F), 36.8 m (2F, 6-F), 26.2 m (2F, 13-F), 21.3 m (2F, 14-F). Mass spectrum, *m*/*z* (I_{rel}, %): 621 M^+, 602 $[M-\mathrm{F}]^+$, 502 $[M-\mathrm{C_2F_5}]^+$, 426 $[M-\mathrm{C_3F_7CN}]^+$, 407 $[M-\mathrm{C_2F_5CF{=}C{=}N}]^+$, 306, 231, 216, 169 $[\mathrm{C_3F_7}]^+$, 69 $[\mathrm{CF_3}]^+$. Found: *M* 620.97550. $\mathrm{C_{15}F_{21}N_3}$. Calculated: *M* 620.97567.

4,4′-Bis[3,5-bis(heptafluoropropyl)-1,2,4-triazol-1-yl]octafluorobiphenyl (IX) was synthesized from 4.1 g (11.5 mmol) of 4,4′-dihydrazinooctafluorobiphenyl and 10 g (23 mmol) of compound **I**. Yield 5.4 g (42%); yellow liquid, bp 163–164°C (0.2 mm). UV spectrum (EtOH), $\lambda_{\max}$, nm (ε, l mol^{-1} cm^{-1}): 240 (8200), 280 (1750). ^{13}C NMR spectrum (CDCl$_3$), δ_{C}, ppm: 156.9 (C^3, $^2J_{\mathrm{C,F}}$ = 30.2 Hz), 148.5 (C^5, $^2J_{\mathrm{C,F}}$ = 30.9 Hz), 144.9 (C^{13}, $^1J_{\mathrm{C,F}}$ = 251.9, $^2J_{\mathrm{C,F}}$ = 12.5 Hz), 144.1 (C^{14}, $^1J_{\mathrm{C,F}}$ = 261.7, $^2J_{\mathrm{C,F}}$ = 12.5 Hz), 118.8 (C^{12}, $^2J_{\mathrm{C,F}}$ = 24.4 Hz), 118.5 (C^8, $^1J_{\mathrm{C,F}}$ = 286.8, $^2J_{\mathrm{C,F}}$ = 33.2 Hz), 118.1 (C^{11}, $^1J_{\mathrm{C,F}}$ = 287.1, $^2J_{\mathrm{C,F}}$ = 33.1 Hz), 110.7 (C^{15}, $^2J_{\mathrm{C,F}}$ = 24.6 Hz), 110.5 (C^6, $^1J_{\mathrm{C,F}}$ = 256.8, $^2J_{\mathrm{C,F}}$ = 31.3 Hz), 110.4 (C^9, $^1J_{\mathrm{C,F}}$ = 259.0, $^2J_{\mathrm{C,F}}$ = 31 Hz), 108.9 (C^7, $^1J_{\mathrm{C,F}}$ = 268.9, $^2J_{\mathrm{C,F}}$ = 32.9 Hz), 108.4 (C^{10}, $^1J_{\mathrm{C,F}}$ = 268.7, $^2J_{\mathrm{C,F}}$ = 30.4 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_{F}, ppm: 83.5 t (8-F, *J* = 9 Hz), 83.1 t (11-F, *J* = 9 Hz), 52.5 q (7-F, *J* = 9 Hz), 49.7 q (10-F, *J* = 9 Hz), 37.9 s (6-F), 36.6 s (9-F), 29.1 m (14-F), 19.9 m (13-F). Found, %: C 30.65; F 61.85; N 7.30. $\mathrm{C_{28}F_{36}N_6}$. Calculated, %: C 30.43; F 61.96; N 7.61.

5-Fluoro-3-(pentafluoroethyl)-1-(2,3,5,6-tetrafluorophenyl)-4-trifluoromethyl-1*H*-pyrazole (XX) was synthesized from 3 g (10 mmol) of compound **XIX**, 1.8 g (10 mmol) of 2,3,5,6-tetrafluorophenylhydrazine, and 3.03 g (30 mmol) of triethylamine. Yield 3.5 g (83%); slightly yellowish liquid, bp 69–70°C. IR spectrum, ν, cm^{-1}: 3084 (C−N), 1620 (C=C), 1527 (C=C$_{\mathrm{arom}}$), 1471 and 1887 (C−N), 1225–1160 (C−F). ^{1}H NMR spectrum, δ, ppm: 7.44. ^{13}C NMR spectrum (CDCl$_3$), δ_{C}, ppm: 141.0 (C^3, $^2J_{\mathrm{C,F}}$ = 31.5 Hz), 146.7 (C^{11}, $^1J_{\mathrm{C,F}}$ = 257.3, $^2J_{\mathrm{C,F}}$ = 13.5 Hz), 143.4 (C^{10}, $^1J_{\mathrm{C,F}}$ = 258.8, $^2J_{\mathrm{C,F}}$ = 15.5 Hz), 120 (C^6, $^1J_{\mathrm{C,F}}$ = 267.8 Hz), 118.7 (C^8, $^1J_{\mathrm{C,F}}$ = 286.3, $^2J_{\mathrm{C,F}}$ = 41.4 Hz), 110.3 (C^9, $^2J_{\mathrm{C,F}}$ = 13.4 Hz), 109.4 (C^7, $^1J_{\mathrm{C,F}}$ = 253.8, $^2J_{\mathrm{C,F}}$ = 40.3 Hz), 109.4 (C^{12}, $^2J_{\mathrm{C,F}}$ = 15.5 Hz), 96.0 (C^4, $^2J_{\mathrm{C,F}}$ = 34.3, $^2J_{\mathrm{C,F}}$ = 8.5 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_{F}, ppm: 107.1 d.t (6-F, *J* = 22, 7 Hz), 80.2 s (8-F), 51.8 q (7-F, *J* = 7 Hz), 43.4 q (5-F, *J* = 22 Hz), 27.1 m (11-F), 17.4 m (10-F). Mass spectrum, *m*/*z* (I_{rel}, %): 420 (59) M^+, 401 (29) $[M-\mathrm{F}]^+$, 351 (100) $[M-\mathrm{CF_3}]^+$, 301 (8) $[M-\mathrm{C_2F_5}]^+$, 282 (10) $[M-\mathrm{F}-\mathrm{C_2F_5}]^+$, 263 (5) $[M-2\mathrm{F}-\mathrm{C_2F_5}]^+$, 256 (8) $[M-\mathrm{HC_6F_4N}]^+$, 232 (0.7) $[M-\mathrm{CF_3}-\mathrm{C_2F_5}]^+$, 207 (0.4) $[M-\mathrm{HC_6F_4NCF_2}]^+$, 176 (7) $[\mathrm{C_6F_4N_2}]^+$, 149 (12) $[\mathrm{HC_6F_4}]^+$, 119 (3) $[\mathrm{C_2F_5}]^+$, 100 (2) $[\mathrm{CF_2{=}CF_2}]^+$, 69 (28) $[\mathrm{CF_3}]^+$. Found: *M* 419.9967. $\mathrm{C_{12}HF_{13}N_2}$. Calculated: *M* 419.9932.

1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-5-fluoro-3-pentafluoroethyl-4-trifluoromethyl-1*H*-pyrazole (XXI) was synthesized from 3 g (10 mmol) of compound **XIX**, 2.59 g (10 mmol) of 4-bromo-2,3,5,6-tetrafluorophenylhydrazine, and 3.03 g (30 mmol) of triethylamine. Liquid substance, bp 84–85°C (2 mm). IR spectrum, ν, cm^{-1}: 1623 (C=C), 1539 (C=N), 1503 (C=C$_{\mathrm{arom}}$), 1357 and 1328 (C−N), 1225–1162 (C−F). ^{13}C NMR spectrum (CDCl$_3$), δ_{C}, ppm: 152.3 (C^5, $^1J_{\mathrm{C,F}}$ = 298.8 Hz), 141.3 (C^3, $^2J_{\mathrm{C,F}}$ = 39.6 Hz), 145.7 (C^{11}, $^1J_{\mathrm{C,F}}$ = 255.3, $^2J_{\mathrm{C,F}}$ = 13.5 Hz), 144.4 (C^{10}, $^1J_{\mathrm{C,F}}$ = 263.3, $^2J_{\mathrm{C,F}}$ = 15.5 Hz), 119.6 (C^6, $^1J_{\mathrm{C,F}}$ = 272.8 Hz), 118.2 (C^8, $^1J_{\mathrm{C,F}}$ = 286.1, $^2J_{\mathrm{C,F}}$ = 36.4 Hz), 115.8 (C^{12}, $^2J_{\mathrm{C,F}}$ = 15.5 Hz), 109.7 (C^7, $^1J_{\mathrm{C,F}}$ = 267.9, $^2J_{\mathrm{C,F}}$ = 40.3 Hz), 104.5 (C^9, $^2J_{\mathrm{C,F}}$ = 22.5 Hz), 95.4 (C^4, $^2J_{\mathrm{C,F}}$ = 34.3, $^2J_{\mathrm{C,F}}$ = 8.5 Hz). ^{19}F NMR spectrum (CDCl$_3$), δ_{F}, ppm: 106.7 d.t (6-F, *J* = 22, 7 Hz), 80.4 s (8-F), 51.4 q (7-F, *J* = 7 Hz), 44.1 q (5-F, *J* = 22 Hz), 32.9 m (11-F), 18.7 m (10-F). Mass spectrum, *m*/*z* (I_{rel}, %): 498 (100) M^+, 479 (32) $[M-\mathrm{F}]^+$, 429 (93) $[M-\mathrm{CF_3}]^+$, 256 (2) $[\mathrm{BrC_6F_4N_2}]^+$, 228 (1) $[\mathrm{BrC_6F_4}]^+$, 119 (14) $[\mathrm{C_2F_5}]^+$, 100 (3) $[\mathrm{CF_2{=}CF_2}]^+$, 69 (66) $[\mathrm{CF_3}]^+$. Found: *M* 497.9028. $\mathrm{C_{12}BrF_{13}N_2}$. Calculated: *M* 497.9038.

Reactions of compounds I and XIX with hydrazine hydrate (*general procedure*). Hydrazine hydrate, 2 equiv, was added at 0°C to a solution of compound **I** or **XIX** in 35 ml of acetic acid. The mixture was stirred for 1 h at that temperature, heated for 2 h at 45°C, cooled, poured into 100 ml of water, and treated with methylene chloride (3×70 ml). The extract was washed with water (2×50 ml), dried over $MgSO_4$, and evaporated, and the residue was distilled or subjected to column chromatography on silica gel using hexane–methylene chloride as eluent.

3,5-Bis(heptafluoropropyl)-4*H*-1,2,4-triazole (XV) was synthesized from 17 g (39 mmol) of perfluoro(5-aza-4-nonene) (**I**) and 3.9 g (78 mmol). of hydrazine hydrate. Yield 6.7 g (42%), mp 96–98°C. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 334 (4200). IR spectrum, ν, cm^{-1}: 1620 (C=N), 1450 (C=N), 1350 (C–N), 1120–1220 (C–F). ^{1}H NMR spectrum, δ, ppm: 8.17 (NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 158.7 (C^3, C^5, $^{2}J_{C,F}$ = 25.7 Hz), 117.3 (C^8, C^{11}, $^{1}J_{C,F}$ = 287.3, $^{2}J_{C,F}$ = 33.5 Hz), 110.2 (C^6, C^9, $^{1}J_{C,F}$ = 264.4, $^{2}J_{C,F}$ = 31.4 Hz), 108.0 (C^7, C^{10}, $^{1}J_{C,F}$ = 255.5, $^{2}J_{C,F}$ = 31.8 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 82.97 (6F, 8-F, 11-F), 50.69 (4F, 7-F, 10-F), 36.8 (4F, 6-F, 9-F). Mass spectrum, *m*/*z* (I_{rel}, %): 405 (1) M^+, 386 (26) $[M-F]^+$, 336 (1) $[M-CF_3]^+$, 286 (100) $[M-C_2F_5]^+$, 236 (1) $[M-C_3F_7]^+$, 196 (1) $[C_3F_7C{=}NH]^+$, 169 (5) $[C_3F_7]^+$, 119 (5) $[C_2F_5]^+$, 76 (1) $[CF_2{=}C{=}N]^+$, 69 (33) $[CF_3]^+$. Found: *M* 404.9859. $C_8HF_{14}N_3$. Calculated: *M* 404.9834.

3,3,3-Trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylidenehydrazine XXIIIa/XXIIIb. By the above procedure, from 9 g (30 mmol) of compound **XIX** and 3 g (60 mmol) of hydrazine hydrate we obtained a mixture of isomeric hydrazones **XXIIIa** and **XXIIIb** at a ratio of 2.1 : 1 (GLC) as a yellow liquid, bp 128–129°C. Yield 5 g (53%). IR spectrum, ν, cm^{-1}: 3400, 3500 (NH_2); 2990 (C–H); 1710 (C=N); 1600 (C=N); 1380, 1350 (C–N); 1280–1150 (C–F). Mass spectrum, *m*/*z* (I_{rel}, %): 312 (68) M^+, 293 (17) $[M-F]^+$, 273 (6) $[M-F-HF]^+$, 243 (5) $[M-CF_3]^+$, 193 (100) $[M-C_2F_5]^+$, 161 (23) $[C_2F_5C{=}NNH_2]^+$, 119 (11) $[C_2F_5]^+$, 100 (1) $[CF_2{=}CF_2]^+$, 69 (28) $[CF_3]^+$, 42 (1) $[H_2NN{=}C]^+$. Found, %: C 24.77; H 1.04; F 67.18; N 8.50. *M* 312.0127. $C_6H_3F_{11}N_2$. Calculated, %: C 23.08; H 0.96; F 66.99; N 8.97. *M* 312.0121.

Isomer **XXIIIa**. ^{1}H NMR spectrum, δ, ppm: 3.67 (CH), 6.30 (NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 165.8 (C^3, $^{2}J_{C,F}$ = 27.0 Hz), 113.7 (C^1, C^6, $^{1}J_{C,F}$ = 282.1 Hz), 110.4 (C^5, $^{1}J_{C,F}$ = 288.1, $^{2}J_{C,F}$ = 36.4 Hz), 101.8 (C^4, $^{1}J_{C,F}$ = 260.8, $^{2}J_{C,F}$ = 41.8 Hz), 38.0 (C^2, $^{2}J_{C,F}$ = 32.5 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 102.2 (6F, 1-F, 6-F), 82.0 (3F, 5-F), 52.3 (2F, 4-F).

Isomer **XXIIIb**. ^{1}H NMR spectrum, δ, ppm: 3.67 (CH), 6.10 (NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 165.4 (C^3, $^{2}J_{C,F}$ = 26.8 Hz), 113.6 (C^1, C^6, $^{1}J_{C,F}$ = 282.1 Hz), 110.1 (C^5, $^{1}J_{C,F}$ = 282.9, $^{2}J_{C,F}$ = 36.6 Hz), 103.6 (C^4, $^{1}J_{C,F}$ = 260.5, $^{2}J_{C,F}$ = 34.7 Hz), 35.6 (C^2, $^{2}J_{C,F}$ = 31.2 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 98.3 (6F, 1-F), 79.8 (3F, 5-F), 46.7 (2F, 4-F).

Bis(trifluoromethyl)bis[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclobutadienes XXIVa and XXIVb. A mixture of 6.5 g (21 mmol) of compounds **XXIIIa/XXIIIb** and 4.2 g (42 mmol) of triethylamine in 30 ml of acetonitrile was stirred for 3 h at 80°C. It was then poured into 100 ml of water and treated with methylene chloride (3×70 ml). The extract was washed with water (2×50 ml) and dried over Na_2SO_4. Removal of the solvent, followed by distillation, gave 3.2 g (63%) of a mixture of compounds **XXIVa** and **XXIVb** (ratio 2.3 : 1, according to the GLC data) as a volatile mobile liquid, bp 80–82°C. Mass spectrum, *m*/*z* (I_{rel}, %): 488 (17) M^+, 469 (28) $[M-F]^+$, 419 (8) $[M-CF_3]^+$, 400 (10) $[M-CF_3-F]^+$, 337 (2) $[M-CH(CF_3)_2]^+$, 268 (1) $[M-CF_3-CH(CF_3)_2]^+$, 244 (1) $[(CF_3)_2CHCCCF_3]^+$, 151 (1) $[(CF_3)_2CH]^+$, 119 (7) $[C_2F_5]^+$, 100 (1) $[CF_2{=}CF_2]^+$, 82 (1) $[CF_3CH]^+$, 69 (83) $[CF_3]^+$, 41 (100), 40 (49), 39 (16). Found: *M* 487.9846. $C_{12}H_2F_{18}$. Calculated: *M* 487.9869.

Isomer **XXIVa**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 129.5 (C^2, C^4), 120.3 (C^7, C^8, C^{11}, C^{12}, $^{1}J_{C,F}$ = 282.6 Hz), 119.8 (C^5, C^9, $^{1}J_{C,F}$ = 269.8 Hz), 113.2 (C^1, C^3, $^{2}J_{C,F}$ = 37.8 Hz), 46.6 (C^6, C^{10}, $^{2}J_{C,F}$ = 22.5 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 102.9 (6F, 5-F, 9-F), 96.8 (12F, 7-F, 8-F, 11-F, 12-F).

Isomer **XXIVb**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 120.4 (C^8, C^9, C^{11}, C^{12}, $^{1}J_{C,F}$ = 283.2 Hz), 119.9 (C^5, C^6, $^{1}J_{C,F}$ = 270.3 Hz), 129.6 (C^3, C^4), 114.2 (C^1, C^2, $^{2}J_{C,F}$ = 38.0 Hz), 46.9 (C^7, C^{10}, $^{2}J_{C,F}$ = 22.5 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 100.5 (12F, 8-F, 9-F, 11-F, 12-F), 103.5 (6F, 5-F, 6-F).

5-Fluoro-3-pentafluoroethyl-4-trifluoromethyl-1*H*-pyrazole (XXII). A solution of 15 g (50 mmol) of compound **XIX** and 10.1 g (100 mmol) of triethylamine in 40 ml of acetonitrile was stirred for 2 h at 40°C. It was then cooled to 0°C, and 5.1 g (50 mmol) of propionylhydrazine was added over a period of 15 min, maintaining the temperature at 0°C. The mixture was stirred for 1 h at 0°C and for 3 h at 40°C, 20 ml of DMF was added, and the mixture was heated for 1 h at 40°C, cooled, poured into 100 ml of water, and extracted with methylene chloride (3 × 70 ml). The extract was washed with water (2 × 50 ml), dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. Yield 9.1 g (67%); yellow liquid, bp 60–61°C (0.6 mm). IR spectrum, ν, cm^{-1}: 3400 (NH); 1670 (C=N); 1500 (C=N); 1330, 1380 (C−N); 1140–1220 (C−F). ^1H NMR spectrum, δ, ppm: 8.24 (NH). ^{13}C NMR spectrum (CD_2Cl_2), δ_C, ppm: 150.3 (C^5, $^1J_{C,F}$ = 259.0 Hz), 122.6 (C^3, $^2J_{C,F}$ = 31.9 Hz), 112.1 (C^6, $^1J_{C,F}$ = 266.6, $^2J_{C,F}$ = 5 Hz), 109.6 (C^8, $^1J_{C,F}$ = 285.9, $^2J_{C,F}$ = 37.5 Hz), 100.8 (C^7, $^1J_{C,F}$ = 254.9, $^2J_{C,F}$ = 40.7 Hz), 86.9 (C^4, $^2J_{C,F}$ = 41.6, $^2J_{C,F}$ = 17.1 Hz). ^{19}F NMR spectrum (CD_2Cl_2), δ_F, ppm: 108.1 d.t (3F, 6-F, *J* = 20, 10 Hz), 79.2 s (3F, 8-F), 51.10 q (2F, 7-F, *J* = 10 Hz), 36.1 q (1F, 5-F, *J* = 20 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 272 (47) M^+, 253 (44) $[M-F]^+$, 243 (1) $[M-N_2-H]^+$, 203 (100) $[M-CF_3]^+$, 183 (42) $[M-CF_3-HF]^+$, 155 (12) $[M-CF_3-HF-N_2]^+$, 119 (12) $[C_2F_5]^+$, 69 (58) $[CF_3]^+$. Found, %: C 26.40; H 0.29; F 69.15; N 10.15. $C_6HF_9N_2$. Calculated, %: C 26.47; H 0.37; F 68.87; N 10.29.

3,5-Bis(heptafluoropropyl)-4*H*-1,2,4-triazole (XV). Propionylhydrazide, 3.06 g (30 mmol), was added with stirring at 0°C to a solution of 13 g (30 mmol) of compound **I** and 6.06 g (60 mmol) of triethylamine in 40 ml of acetonitrile. The mixture was stirred for 1 h at 0°C and for 3 h at 50°C, cooled, poured into 100 ml of water, and treated with CH_2Cl_2 (3 × 70 ml). The extract was washed with water (2 × 50 ml) and dried over $MgSO_4$. Distillation followed by column chromatography on silica gel (eluent CH_2Cl_2) gave 7.9 g (65%) of compound **XV**.

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