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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 70th Anniversary

Reactions of Polyfluorinated 2-Arylhydrazono-3-oxocarboxylic Acid Esters with *o*-Phenylenediamine

O. G. Khudina, E. V. Shchegol'kov, Ya. V. Burgart, and V. I. Saloutin

Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi/Akademicheskaya 22/20, Yekaterinburg, 620219 Russia fax: (343)3745954; e-mail: saloutin@ios.uran.ru

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Abstract—Polyfluorinated 2-arylhydrazono-3-oxocarboxylic acid esters react with *o*-phenylenediamine in neutral medium to give mainly the corresponding *o*-aminoanilides which can be converted into 1,5-benzodiazepin-2-ones. In the reactions with ethyl 2-arylhydrazono-3-oxobutanoate and its 4,4-di- and 4,4,4-trifluoro derivatives, ethyl 2-(2-benzimidazolyl)-2-[(4-methylphenyl)hydrazono]ethanoate is also formed.

Depending on the conditions, fluorinated 3-oxocarboxylic acid esters, as well as their fluorine-free analogs, are capable of reacting with *o*-phenylenediamine at the keto group to give 3-arylaminocrotonates and/or 2-methylbenzimidazole [1, 2], at the ester group with formation of *N*-(2-aminophenyl)-3-oxocarboxylic acid amides [1] and/or 3-(2-benzimidazolyl)-1,1,1-trifluoroacetone [3], or at both these to afford 1,5-benzodiazepin-2-ones [1, 4]. 3-Oxocarboxylic acid esters having an alkyl [5], acetyl, or ethoxycarbonyl group [6, 7] or chlorine atom [8] in position *2* react with aromatic *o*-diamines according to the "acid" decomposition pattern which leads to formation of 2-(polyfluoroalkyl)benzimidazoles. Reactions of fluorine-free 2-arylhydrazono-3-oxobutanoates with 3-methylbenzene-1,2-diamine in *o*-xylene on heating give rise to substituted 1,5-benzodiazepin-2-ones which suppress the activity of the central nervous system [9].

The goal of the present work was to examine the reaction of fluorinated 2-arylhydrazono-3-oxocarboxylic acid esters **I** with *o*-phenylenediamine. We have found that esters **Ia**–**Ie** do not react with *o*-phenylenediamine under mild conditions and that the reaction in boiling *o*-xylene or toluene involves the ester fragment to give the corresponding *o*-aminoanilides **IIa**–**IIe** as the major products (Scheme 1, path *1*). The *o*-aminoanilide rather than cyclic 1,2,4,5-tetrahydro-1,5-benzodiazepine structure of compounds **IIa**–**IIe** follows from the presence in their ^{1}H NMR spectra of signals from protons of a primary amino group (δ 3.85–5.35 ppm); in the IR spectra we observed absorption bands due to symmetric and antisymmetric stretching vibrations of that group at 3340–3420 cm^{-1} (see Experimental).

Amides **II** can be converted into 1,5-benzodiazepin-2-ones **III** by heating in boiling *o*-xylene for a long time. In such a way, from *o*-aminoanilides **IIb** and **IId** we obtained 4-fluoroalkyl-1*H*-1,5-benzodiazepine-2,3-dione 3-arylhydrazones **IIIa** and **IIIb** (Scheme 1). It should be noted that small amounts of compounds **IIIa** and **IIIb** are formed directly in the reactions of esters **Ib** and **Id** with *o*-phenylenediamine (according to the TLC data).

The NMR and IR spectral data of compounds **IIIa** and **IIIb** indicate that they exist in solution and in crystal as a single tautomer, namely hydrazone–amide. The formation of intramolecular hydrogen bond in **IIIa** and **IIIb** is confirmed by the reduced frequency of the amide carbonyl absorption (1630–1640 cm^{-1}) in the IR spectrum and by the presence of a downfield broadened singlet from the hydrazone proton (δ 12.48–14.24 ppm) in the ^{1}H NMR spectrum (see Experimental).

Apart from amide **IIc**, the reaction of ester **Ic** with o-phenylenediamine gave *N*,*N*′-phenylenediamide **IV** as a result of subsequent condensation of product **IIc** at the ester group of the second molecule of ester **Ic**.

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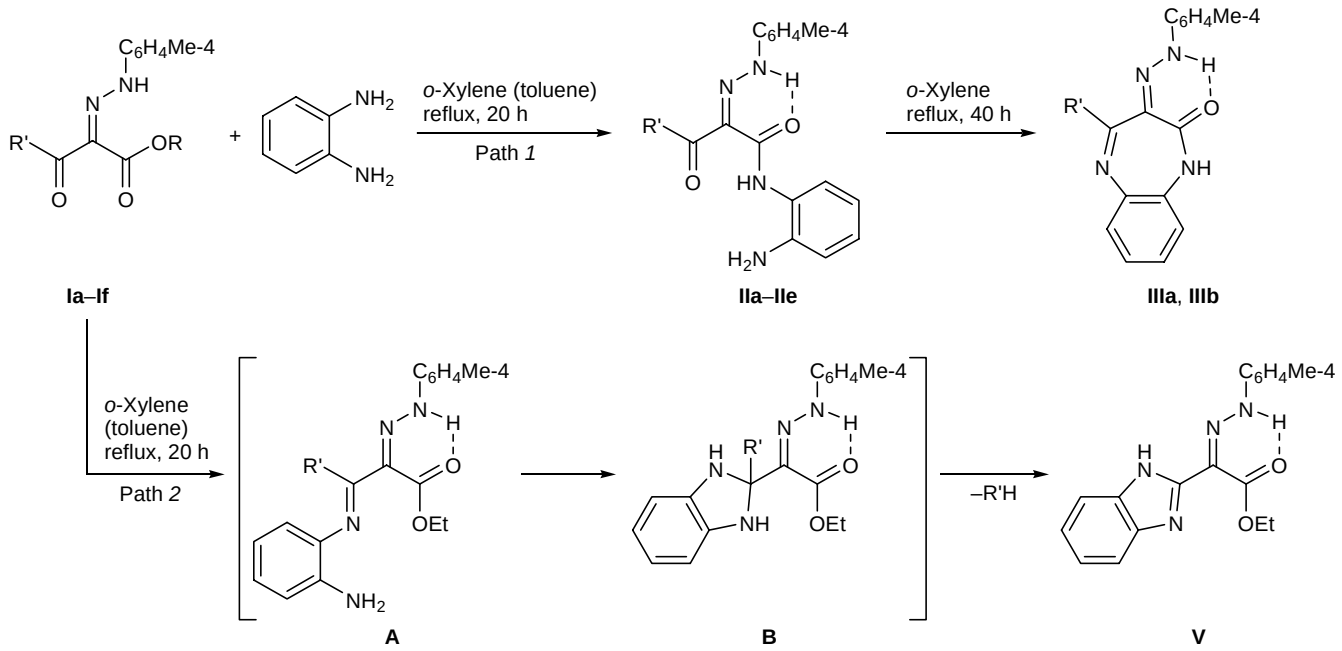
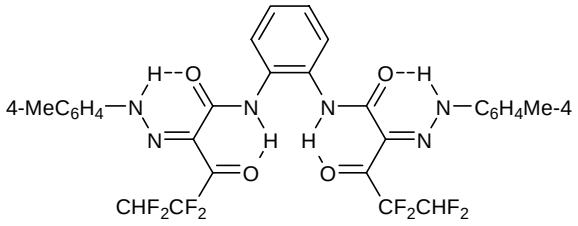
Scheme 1.



Ia, **IIa**, R = Et, R' = C_6F_{13}; **Id**, **IId**, **IIIb**, R = Et, R' = HCF_2; **Ie**, **IIe**, R = Et, R' = Me; **If**, R = Et, R' = CF_3; **Ib**, **IIb**, **IIIa**, R = Me, R' = C_4H_9; **Ic**, **IIc**, R = Me, R' = $H(CF_2)_2$.



IV

Unlike esters **Ia**–**Ic** which contain a "long" polyfluorinated alkyl group (tridecafluorohexyl, nonafluorobutyl, or tetrafluoroethyl), esters **Id** and **Ie** having a "short" difluoromethyl moiety react with *o*-phenylenediamine in boiling *o*-xylene according to both path *1* (to give *o*-aminoanilides **IId** and **IIe**) and path *2*, i.e., at the difluoroacetyl group. In these reactions, we also isolated ethyl 2-(2-benzimidazolyl)-2-(arylhydrazono)acetate (**V**) (Scheme 1). Compound **V** is likely to be formed by cyclization of intermediate 3-(arylimino)butanoate **A** at the C=N bond adjacent to the difluoromethyl group. The resulting 2,2-disubstituted dihydrobenzimidazole **B** readily undergoes aromatization via elimination of difluoromethane molecule to afford ethyl 2-(2-benzimidazolyl)-2-(arylhydrazono)ethanoate (**V**).

It should be noted that the reaction of trifluoromethyl-substituted ester **If** with *o*-phenylenediamine gave a mixture of products, from which we succeeded in isolating only a small amount of ester **V**. This fact can be regarded as an indirect evidence for reduced selectivity of reactions with esters having a short-chain fluoroalkyl group.

Theoretically, 1,5-benzodiazepin-2-ones **III** could be formed by cyclization of not only *o*-aminoanilides **II** but also 3-(arylimino)butanoates **A**. However, we failed to detect the latter by TLC. The chromatograms contained spots belonging to initial esters **I**, *o*-aminoanilides **II,** and benzimidazole **V**. Probably, the transformation of intermediates like **A** into benzimidazole **V** is very fast. On the other hand, we have shown that benzodiazepines **III** can be obtained from *o*-aminoanilides **II**.

Thus the presence of a bulky polyfluoroalkyl group in esters **Ia**–**Ic** favors their selective reaction with *o*-phenylenediamine at the ester group, whereas esters

Id–**If** having di- and trifluoroacetyl moieties react both at the ester and at the fluoroacetyl group.

We also made an attempt to effect reaction of ester **Ib** with *o*-phenylenediamine in acid medium. No reaction occurred in methanol containing a catalytic amount of acetic acid. When methanol was replaced by 1-butanol, a mixture of products was obtained, which we failed to separate. Likewise, the use of a template procedure was unsuccessful. Ester **Ic** did not react with *o*-phenylenediamine on heating in boiling ethanol in the presence of nickel acetate.

We can conclude that esters **I** react with *o*-phenylenediamine in neutral medium (boiling toluene or *o*-xylene) predominantly at the ester group, yielding the corresponding *o*-aminoanilides. However, this reaction pathway is not the only possible in the case of ethyl 2-(arylhydrazono)acetoacetate and its di- and trifluoro analogs. These compounds also give rise to ethyl 2-(2-benzimidazolyl)-2-(arylhydrazono)acetate as a result of concurrent addition of *o*-phenylenediamine at the (fluoro)acetyl group and partial decomposition. The latter process was unexpected; according to published data [2, 5–8], reactions of 3-oxo esters and their 2-alkyl, acetyl, ethoxycarbonyl, and chloro derivatives with *o*-phenylenediamine were accompanied only by "acid" cleavage with formation of 2-(fluoroalkyl)benzimidazoles.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum One Fourier spectrometer in the range from 400 to 4000 cm^{-1}; samples were prepared as mulls in mineral oil. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 spectrometer at 400 and 100.6 MHz, respectively; the chemical shifts were measured relative to tetramethylsilane. The ^{19}F NMR spectra were measured on a Tesla BS-587A instrument (75 MHz) relative to C_6F_6. The elemental analyses were obtained on a Carlo Erba CHNS-O EA 1108 analyzer. The mass spectra were run on a Varian MAT-311A mass spectrometer.

Esters **I** were synthesized by the procedure described in [10]; newly synthesized compounds **Ia**–**Id** and **If** were characterized by spectral data.

Ethyl 2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate (Ia). Yield 53%, yellow powder, mp 50–52°C (from ethanol). IR spectrum, ν, cm^{-1}: 3100, 1590 (NH); 1705, 1660 (C=O); 1530 (C=N, C=C); 1120–1240 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 2.37 s (3H, Me), 4.40 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.0 Hz), 7.22–7.31 m (4H, C_6H_4), 13.55 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 35.73 m (2F, CF_2), 39.12 m (2F, CF_2), 40.57 m (2F, CF_2), 41.89 m (2F, CF_2), 50.34 m (2F, CF_2), 81.01 m (3F, CF_3). Found, %: C 39.40; H 2.31; F 44.70; N 5.12. $C_{18}H_{13}F_{13}N_2O_3$. Calculated, %: C 39.15; H 2.37; F 44.72; N 5.07.

Methyl 2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5,6,6,7,7,7-nonafluoroheptanoate (Ib). Yield 72%, yellow powder, mp 94–96°C (from ethanol). IR spectrum, ν, cm^{-1}: 3070, 1585 (NH); 1680, 1660 (C=O); 1640, 1520, 1500 (C=N, C=C); 1115–1225 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, Me), 3.94 s (3H, OMe), 7.23–7.32 m (4H, C_6H_4), 13.55 br.s (1H, NH). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 38.92 m (2F, CF_2), 43.39 m (2F, CF_2), 52.77 m (2F, CF_2), 82.80 m (3F, CF_3). Found, %: C 41.20; H 2.53; F 38.83; N 6.35. $C_{15}H_{11}F_9N_2O_3$. Calculated, %: C 41.11; H 2.53; F 39.02; N 6.39.

Methyl 2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5-tetrafluoropentanoate (Ic). Yield 66%, yellow powder, mp 79–80°C (from ethanol). IR spectrum, ν, cm^{-1}: 3130, 1580 (NH); 1680, 1660 (C=O); 1640, 1520, 1500 (C=N, C=C); 1070–1230 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, Me), 3.93 s (3H, OMe), 6.34 t.t [1H, $H(CF_2)_2$, $^2J_{HF}$ = 53.2, $^3J_{HF}$ = 5.6 Hz], 7.24–7.30 m (4H, C_6H_4), 13.48 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 24.59 d.t (2F, HCF_2, $^2J_{FH}$ = 53.2, $^3J_{FF}$ = 7.9 Hz), 42.20 m (2F, CF_2). Found, %: C 48.82; H 3.78; F 23.58; N 8.71. $C_{13}N_{12}F_4N_2O_3$. Calculated, %: C 48.76; H 3.78; F 23.73; N 8.75.

Ethyl 2-[(4-methylphenyl)hydrazono]-3-oxo-4,4-difluorobutanoate (Id). Yield 54%, yellow powder, mp 96–98°C (from ethanol). IR spectrum, ν, cm^{-1}: 3180, 1580 (NH); 1690 (C=O); 1640, 1520, 1500 (C=N, C=C); 1110–1220 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.38 s (3H, Me), 4.41 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.1 Hz), 6.70 t (1H, CHF_2, $^2J_{HF}$ = 54.3 Hz), 7.22–7.28 m (4H, C_6H_4), 13.45 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 34.44 d (2F, CHF_2, $^2J_{FH}$ = 54.3 Hz). Found, %: C 54.89; H 4.99; F 13.38; N 9.80. $C_{13}H_{14}F_2N_2O_3$. Calculated, %: C 54.93; H 4.96; F 13.37; N 9.85.

Ethyl 2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,4-trifluorobutanoate (If). Yield 41%, yellow powder, mp 75–76°C (from ethanol). IR spectrum, ν,

cm^{-1}: 3100, 1590 (NH); 1690 (C=O); 1630, 1520, 1500 (C=N, C=C); 1080–1200 (C–F). ^1H NMR spectrum (DMSO-d_6) (mixture of isomers **Ia** and **Ia'**, ~10:3], δ, ppm: **Ia**: 1.28 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.28 s (3H, Me), 4.30 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.1 Hz), 7.18–7.36 m (4H, C_6H_4), 11.65 br.s (1H, NH); **Ia'**: 1.30 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.30 s (3H, Me), 4.25 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.1 Hz), 7.22–7.43 m (4H, C_6H_4), 14.36 br.s (1H, NH). Found, %: C 51.89; H 4.59; F 18.58; N 9.15. $C_{13}H_{13}F_3N_2O_3$. Calculated, %: C 51.66; H 4.34; F 18.86; N 9.27.

Reaction of esters Ia–If with *o*-phenylenediamine (*general procedure*). *o*-Phenylenediamine, 108 mg (1 mmol), was added to a solution of 1 mmol of ester **Ia**–**If** in 10 ml of *o*-xylene (compounds **Ia**–**Id**) or toluene (**Ie**, **If**), and the mixture was heated for 20 h under reflux and evaporated to dryness.

***N*-(2-Aminophenyl)-2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanamide (IIa).** The product was isolated by column chromatography on silica gel (40–100 μm) using chloroform as eluent. Yield 418 mg (68%), yellow powder, mp 132–133°C. IR spectrum, ν, cm^{-1}: 3420, 3340, 3250, 1600 (NH); 1670 (C=O); 1630, 1550, 1520 (C=N, C=C); 1150–1240 (C–F). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.32 s (3H, Me), 5.35 br.s (2H, NH_2), 6.59–7.47 m (8H, $2C_6H_4$), 9.82 br.s and 13.00 br.s (2H, 2NH). Found, %: C 43.18; H 2.27; F 40.08; N 9.03. $C_{22}H_{15}F_{13}N_4O_2$. Calculated, %: C 43.01; H 2.46; F 40.20; N 9.12.

***N*-(2-Aminophenyl)-2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5,6,6,7,7,7-nonafluoroheptanamide (IIb).** Yield 329 mg (64%), yellow powder, mp 146–148°C (from benzene). IR spectrum, ν, cm^{-1}: 3410, 3340, 3250, 1580 (NH); 1650 (C=O); 1535, 1500 (C=N, C=C); 1115–1215 (C–F). ^1H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 2.37 s (3H, Me), 4.83 br.s (2H, NH_2), 6.58–7.44 m (8H, $2C_6H_4$), 9.88 br.s and 14.95 br.s (2H, 2NH). ^{19}F NMR spectrum (DMSO-d_6–CCl_4), δ_F, ppm: 37.46 m (2F, CF_2), 42.18 m (2F, CF_2), 52.34 m (2F, CF_2), 81.80 m (3F, CF_3). Found, %: C 46.39; H 2.94; F 33.64; N 10.86. $C_{20}H_{15}F_9N_4O_2$. Calculated, %: C 46.70; H 2.94; F 33.24; N 10.89.

***N*-(2-Aminophenyl)-2-[(4-methylphenyl)hydrazono]-3-oxo-4,4,5,5-tetrafluoropentanamide (IIc).** The product was isolated by column chromatography on silica gel (100–250 μm) using chloroform as eluent. Yield 150 mg (38%), yellow powder, mp 146–148°C. IR spectrum, ν, cm^{-1}: 3410, 3350, 3240, 3200, 1600 (NH); 1660 (C=O); 1640 sh, 1580, 1550, 1500 (C=N, C=C); 1070–1230 (C–F). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, Me), 5.16 br.s (2H, NH_2), 6.61–7.47 m (8H, $2C_6H_4$), 6.91 t.t [1H, $H(CF_2)_2$, $^2J_{HF}$ = 52.0, $^3J_{HF}$ 5.5 = Hz], 9.91 br.s and 14.50 br.s (2H, 2NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 24.09 d.t (2F, CHF_2, $^2J_{FH}$ = 52.0, $^3J_{FF}$ = 9.7 Hz), 46.75 m (2F, CF_2). Found, %: C 54.48; H 4.07; F 19.08; N 14.03. $C_{18}H_{16}F_4N_4O_2$. Calculated, %: C 54.55; H 4.07; F 19.17; N 14.14.

***N*-(2-Aminophenyl)-2-[(4-methylphenyl)hydrazono]-3-oxo-4,4-difluorobutanamide (IId).** The product was isolated by column chromatography on silica gel (40–100 μm) using chloroform as eluent. Yield 177 mg (51%), yellow powder, mp 140–142°C. IR spectrum, ν, cm^{-1}: 3410, 3340, 3250, 1590 (NH); 1650 (C=O); 1620, 1580, 1500 (C=N, C=C); 1120–1230 (C–F). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, Me), 4.90 br.s (2H, NH_2), 6.57–7.47 m (8H, $2C_6H_4$), 6.81 t (1H, CHF_2, $^2J_{HF}$ = 51.6 Hz), 9.85 br.s and 14.20 br.s (2H, 2NH). Found, %: C 58.68; H 4.47; F 11.08; N 9.03. $C_{17}H_{16}F_2N_4O_2$. Calculated, %: C 58.96; H 4.66; F 10.97; N 9.24.

***N*-(2-Aminophenyl)-2-[(4-methylphenyl)hydrazono]-3-oxobutanamide (IIe).** Yield 186 mg (60%), yellow crystals, mp 161–162°C (from benzene). IR spectrum, ν, cm^{-1}: 3420, 3360, 3240, 3160, 1600 (NH); 1650 (C=O); 1550, 1520 (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s and 2.59 s (6H, 2Me), 3.85 br.s (2H, NH_2), 6.81–7.43 m (8H, $2C_6H_4$), 11.11 br.s and 14.72 br.s (2H, 2NH). Found, %: C 65.76; H 5.71; N 18.12. $C_{17}H_{18}N_4O_2$. Calculated, %: C 65.79; H 5.85; N 18.05.

***N*,*N'*-(1,2-Phenylene)-bis[2-(4-methylphenyl)-hydrazono-3-oxo-4,4,5,5-tetrafluoropentanamide] (IV)** was isolated by column chromatography on silica gel (100–250 μm) using chloroform as eluent. Yield 171 mg (25%), yellow powder, mp 144–146°C. IR spectrum, ν, cm^{-1}: 3350, 3265, 1560 (NH); 1680 sh, 1660 (C=O); 1595, 1555, 1500 (C=N, C=C); 1090–1235 (C–F). ^1H NMR spectrum (DMSO-d_6) (mixture of tautomers **IV** and **IV'**, ~17:3), δ, ppm: **IV**: 2.33 s (6H, 2Me), 6.77 t.t (2H, $2CHF_2$, $^2J_{HF}$ = 52.2, $^3J_{HF}$ = 5.5 Hz), 7.29–7.81 m (12H, $3C_6H_4$), 10.48 s and 14.48 s (4H, 4NH); **IV'**: 2.36 s (6H, 2Me), 7.01 t.t (2H, $2CHF_2$, $^2J_{HF}$ = 52.6, $^3J_{HF}$ = 5.5 Hz), 7.33–7.83 m (12H, $3C_6H_4$), 10.48 s and 14.15 s (4H, 4NH). Mass spectrum, m/z (I_{rel}, %): 685 (24.1) $[M + 1]^+$, 684 (70) $[M]^{+\cdot}$, 396 (25.4), 289 (22.1) $[H(CF_2)_2CO(C{=}NNHC_6H_4Me)CO]^+$, 277 (11.6), 276 (82.9), 135

(14.2), 134 (33.5), 121 (19.5), 119 (19.5) [N=NC$_6$H$_4$-Me]$^+$, 108 (66.1), 107 (100), 106 (78.3) [NHC$_6$H$_4$Me]$^+$, 105 (22.1), 91 (66.1) [C$_6$H$_4$Me]$^+$, 79 (18.4), 77 (11) [C$_6$H$_5$]$^+$. Found, %: C 52.92; H 3.58; F 21.98; N 12.41. $C_{30}H_{24}F_8N_6O_4$. Calculated, %: C 52.64; H 3.53; F 22.20; N 12.28.

Ethyl 2-(2-benzimidazolyl)-2-[(4-methylphenyl)-hydrazono]ethanoate (V). Yield 64 mg (20%; from **Id**), 74 mg (23%; from **Ie**), 81 mg (25%; from **If**); yellow powder, mp 218–220°C. The product was purified by column chromatography using chloroform as eluent and washed with ethanol. IR spectrum, ν, cm^{-1}: 3380, 1575 (NH); 1650 (CO_2Et); 1605, 1535, 1500 (C=N, C=C). ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 1.44 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.35 s (3H, Me), 4.41 q (2H, $OC\mathbf{H}_2CH_3$, J = 7.1 Hz), 7.19–7.72 m (8H, 2C$_6$H$_4$), 12.32 br.s and 15.09 br.s (2H, 2NH). ^{13}C NMR spectrum (DMSO-d_6–CCl_4), δ_C, ppm: 14.26, 20.49, 60.51, 112.77, 114.95, 116.56, 118.24, 122.14, 123.59, 129.82, 132.00, 132.66, 140.20, 140.63, 145.85, 164.49. Mass spectrum, *m*/*z* (I_{rel}, %): 324 (21.7) [M + 1]$^+$, 323 (100) [M]$^{+\cdot}$, 250 (17.2) [M – CO_2Et]$^+$, 249 (19.9), 159 (10.1), 147 (19.1), 144 (55.6), 119 (9.4) [N=NC$_6$H$_4$Me]$^+$, 118 (9.8) [M – EtO$_2$CC=NNHC$_6$H$_4$Me]$^+$, 106 (10.6) [NH-C$_6$H$_4$Me]$^+$, 105 (43.4), 91 (28.1) [C$_6$H$_4$Me]$^+$, 77 (10) [C$_6$H$_5$]$^+$. Found, %: C 66.63; H 5.51; N 17.23. $C_{18}H_{18}N_4O_2$. Calculated, %: C 67.06; H 5.63; N 17.38.

4-Substituted 3-(4-methylphenyl)hydrazono-2,3-dihydro-1*H*-1,5-benzodiazepin-2-ones IIIa and IIIb (*general procedure*). A solution of 1 mmol of *o*-aminoanilide **IIb** or **IId** in 10 ml of *o*-xylene was heated for 40 h under reflux and was then evaporated to dryness.

3-(4-Methylphenyl)hydrazono-4-nonafluorobutyl-2,3-dihydro-1*H*-1,5-benzodiazepin-2-one (IIIa). Yield 279 mg (85%), yellow crystals, mp 203–205°C (from chloroform). IR spectrum, ν, cm^{-1}: 3375, 1580 (NH); 1640 (C=O); 1605, 1535, 1500 (C=N, C=C); 1115–1220 (C–F). ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 2.38 s (3H, Me), 7.27–7.33 m and 7.53–7.79 m (8H, 2C$_6$H$_4$), 14.24 br.s (2H, 2NH). ^{19}F NMR spectrum (DMSO-d_6–CCl_4), δ_F, ppm: 37.35 m (2F, CF_2), 41.75 m (2F, CF_2), 52.13 m (2F, CF_2), 81.76 m (3F, CF_3). Found, %: C 48.46; H 2.43; F 34.64; N 11.25. $C_{20}H_{13}F_9N_4O$. Calculated, %: C 48.40; H 2.64; F 34.45; N 11.29.

4-Difluoromethyl-3-(4-methylphenyl)hydrazono-2,3-dihydro-1*H*-1,5-benzodiazepin-2-one (IIIb). Yield 273 mg (83%), yellow crystals, mp 216-217°C (from chloroform). IR spectrum, ν, cm^{-1}: 3290, 3180, 1575 (NH); 1630 (C=O); 1555, 1500, 1490 (C=N, C=C); 1125–1260 (C–F). ^{1}H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 2.30 s (3H, Me), 6.71 t (1H, CHF_2, $^2J_{HF}$ = 54.9 Hz), 7.09–7.32 m (8H, 2C$_6$H$_4$), 10.41 br.s and 12.48 br.s (2H, 2NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 42.66 d (2F, CHF_2, $^2J_{FH}$ = 54.9 Hz). Found, %: C 61.88; H 4.23; F 11.43; N 17.07. $C_{17}H_{14}F_2N_4O$. Calculated, %: C 62.19; H 4.30; F 11.57; N 17.07.

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