ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 6, pp. 887–896. © Pleiades Publishing, Inc., 2006.
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Fluorine-Containing 3-Arylhydrazono-2,4-dioxobutanoates in Reactions with Difunctional Nucleophiles

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Received April 12, 2005

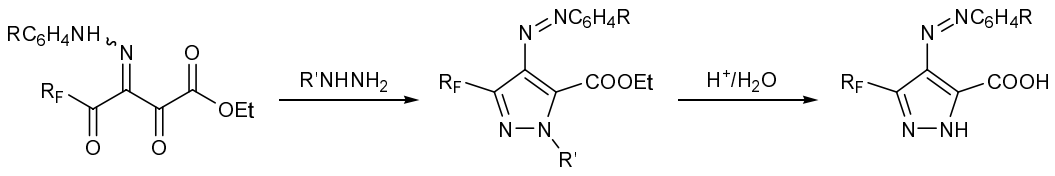
Abstract—3-Arylhydrazono-4-polyfluoroalkyl-2,4-dioxobutanoates reacted with hydrazines to give ethyl 4-aryldiazeno-3-polyfluoroalkyl-1*H*-pyrazole-5-carboxylates, while analogous reactions of ethyl 3-arylhydrazono-4-pentafluorophenyl-2,4-dioxobutanoates resulted in the formation of 4-aryldiazeno-3-pentafluorophenyl-1,2-dihydropyridazine-5,6-diones or 6-aryl-7,8,9,10-tetrafluoro-2-phenyl-2,4a,6,10b-tetradropyridazo[4,3-*c*]cinnoline-3,4-diones, depending on the conditions. Cyclocondensation of ethyl 3-arylhydrazono-4-polyfluoroalkyl(or pentafluorophenyl)-2,4-dioxobutanoates with ethylenediamine led to 3-[1-arylhydrazono-2-oxo-2-polyfluoroalkyl(or pentafluorophenyl)ethyl]-5,6-dihydropyrazin-2(1*H*)-ones, and 3-[1-arylhydrazono-2-oxo-2-polyfluoroalkyl(pentafluorophenyl)ethyl]benzoxazin-2-ones were formed in the condensation with *o*-aminophenol. Pentafluorophenyl-substituted heterocycles were found to undergo intramolecular ring closure to give 3-hetaryl-substituted 1-aryl-5,6,7,8-tetrafluoro-1,4-dihydrocinnolin-4-ones. The reactions of ethyl 3-arylhydrazono-4-pentafluorophenyl-2,4-dioxobutanoates with *o*-aminobenzenethiol gave 3-[7-(2-aminophenylsulfanyl)-1-aryl-5,6,8-trifluoro-4-oxo-1,4-dihydrocinnolin-3-yl]benzothiazin-2-ones; 8a-hydroxy-11,12,13,14-tetrafluoro-10-(4-methoxyphenyl)-2,3,4,5,6,7,8a,10-octahydropyrazino[1',2':4,5][1,4]diazepino[6,7-*c*]cinnolin-8-one was isolated in the condensation of ethyl 3-(4-methoxyphenylhydrazono)-4-pentafluorophenyl-2,4-dioxobutanoate with *N*-(2-aminoethyl)ethane-1,2-diamine.

DOI: 10.1134/S1070428006060133

We previously synthesized polyfluoroalkyl- and pentafluorophenyl-containing 3-arylhydrazono-2,4-dioxobutanoic acid esters and studied some their reactions, in particular with *o*-phenylenediamine [1, 2]. We found that 3-arylhydrazono-4-pentafluorophenyl-2,4-dioxobutanoates are capable of undergoing intramolecular ring closure to give 1-aryl-4-oxo-5,6,7,8-tetrafluoro-3-ethoxalyl-1,4-dihydrocinnolines [1, 2].

In the present work we examined the reactivity of ethyl 3-arylhydrazono-4-polyfluoroalkyl(pentafluorophenyl)-2,4-dioxobutanoates **I** and **II** with respect to various difunctional nucleophiles: hydrazine hydrate, phenylhydrazine, *o*-aminophenol, *o*-aminobenzenethiol, ethane-1,2-diamine, and *N*-(2-aminoethyl)-ethane-1,2-diamine. As we showed previously, 3-arylhydrazono-4-trifluoromethyl-2,4-dioxobutanoates **Ia** and **Ib** react with hydrazine hydrate and phenylhydrazine at the β-dicarbonyl fragment to give pyrazoles **IIIa** and **IIIb**, respectively [1, 2]. In fact, ester **Ic** containing a tetrafluoroethyl group reacted with hydrazine hydrate in a similar way with formation of pyrazole **IIIc** (Scheme 1).

Scheme 1.



Ia–**Ic** **IIIa**–**IIId** **IVa**, **IVb** (93–99%)

Ia, **IIIa**, **IIId**, **IVa**, $R_F = CF_3$, R = H; **Ib**, **IIIb**, $R_F = CF_3$, R = 4-MeO; **IIIa**, **IIIc**, R' = H; **IIIb**, R' = Ph, **IIId**, R' = Me; **Ic**, **IIIc**, **IVb**, $R_F = HCF_2CF_2$, R = 2-Me.

The position of the *N*-phenyl group in pyrazole **IIIb** was not determined [1], though substituted hydrazines could react with 3-aryl-hydrazono-2,4-dioxobutanoates to form regioisomeric 3- and 5-fluoroalkyl-substituted pyrazoles. We performed a model reaction between ethyl 5,5,5-trifluoro-3-phenylhydrazono-2,4-dioxopentanoate (**Ia**) and methylhydrazine and isolated *N*-methylpyrazole **IIId** (Scheme 1). It is known that mutual arrangement of the trifluoromethyl and methyl groups in the pyrazole ring essentially affects the appearance of the NCH_3 proton signal in the ^1H NMR spectrum. In the spectra of 1-methyl-5-trifluoromethylpyrazoles, the NCH_3 group gives a quartet with a coupling constant of 1.2 Hz due to interaction with the trifluoromethyl group on C^5 [3]. The corresponding coupling constant in the spectra of 1-methyl-3-trifluoromethylpyrazoles is smaller than 0.6 Hz or is absent at all [3, 4]. The NCH_3 signal in the ^1H NMR spectrum of pyrazole **IIId**, recorded at a resolution of 0.01 Hz per point, was a singlet; therefore, the trifluoromethyl group in its molecule is attached to the C^3 atom rather than to C^5.

Moreover, the position of the signal from the trifluoromethyl group in the ^{19}F NMR spectrum is also indicative of regioisomeric structure of pyrazoles: Its signal is located at δ_F 99–102 ppm (relative to C_6F_6) in the spectra of 3-trifluoromethyl-substituted isomers and at δ_F ~105 ppm for 5-substituted [4–6]. Trifluoromethyl-substituted pyrazoles **IIIa**, **IIIb**, and **IIId** showed in the ^{19}F NMR spectra a signal at δ_F 99.77–102.63 ppm, i.e., these compounds have the 1-methyl-3-trifluoromethylpyrazole structure. Presumably, fluoroalkyl-containing 3-arylhydrazono-2,4-dioxobutanoates **I** react, at least with substituted hydrazines, initially at the γ-carbonyl group with subsequent ring closure at the α-carbonyl group, thus forming 3-fluoroalkylpyrazoles. By acid hydrolysis of pyrazoles **IIIa** and **IIIc** we obtained the corresponding 4-arylazo-3(5)-fluoroalkylpyrazole-5(3)-carboxylic acids **IVa** and **IVb** (Scheme 1).

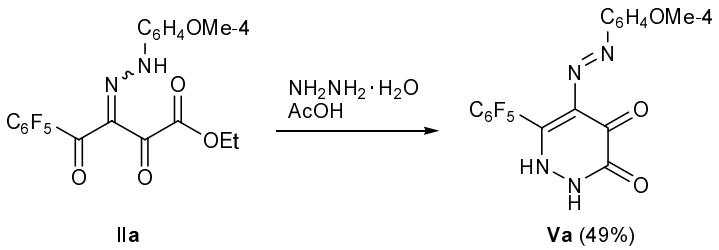
Unlike N-substituted pyrazoles **IIIb** and **IIId** which exist solely in the azo form, compounds **IIIa**, **IIIc**, **IVa**, and **IVb** having no substituent on the nitrogen atom could give rise to azo–hydrazone tautomerism. However, both IR and NMR spectra of these compounds contained only one set of signals corresponding to a single tautomer. Their structure as azo tautomers was determined by electronic absorption spectroscopy: the UV spectra of both N-substituted and unsubstituted pyrazoles **IIIa**, **IIId**, **IVa**, and **IVb** displayed similar absorption patterns (see Experimental).

Replacement of the fluoroalkyl substituent in 3-arylhydrazono-2,4-dioxobutanoates **I** by pentafluorophenyl group (compounds **II**) changed the character of transformations in reactions with hydrazines. The reaction of ethyl 3-(4-methoxyphenylhydrazono)-4-pentafluorophenyl-2,4-dioxobutanoate (**IIa**) with hydrazine hydrate in acetic acid gave pyridazinedione **Va** (Scheme 2) as a result of addition of the difunctional nucleophile at the γ-dicarbonyl fragment. When the reaction was carried out in ethanol or diethyl ether, a mixture of products which were difficult to identify was obtained in all cases (even at room temperature).

The mass spectrum of compound **Va** contained the molecular ion peak with an *m*/*z* value of 412 which is consistent with the assumed structure. In addition, a strong peak from the $[M - 20]^+$ ion (I_{rel} 70.32) was present. This ion has the structure of tetrahydropyridazo[4,3-*c*]cinnoline **A**; it is formed via nucleophilic aromatic substitution of the *ortho*-fluorine atom in the pentafluorophenyl group by the amino group of the arylhydrazone fragment with elimination of hydrogen fluoride molecule. This process (see below) is quite characteristic of the examined compounds containing arylhydrazono and pentafluorophenyl substituents. The other most significant fragment ions originate from stepwise decomposition of the tricyclic pyridazocinnoline system (Scheme 3) [7]. The mass spectrum of **Va** also contained strong peaks corresponding to 4-methoxyphenyldiazonium ion and products of its decomposition [7].

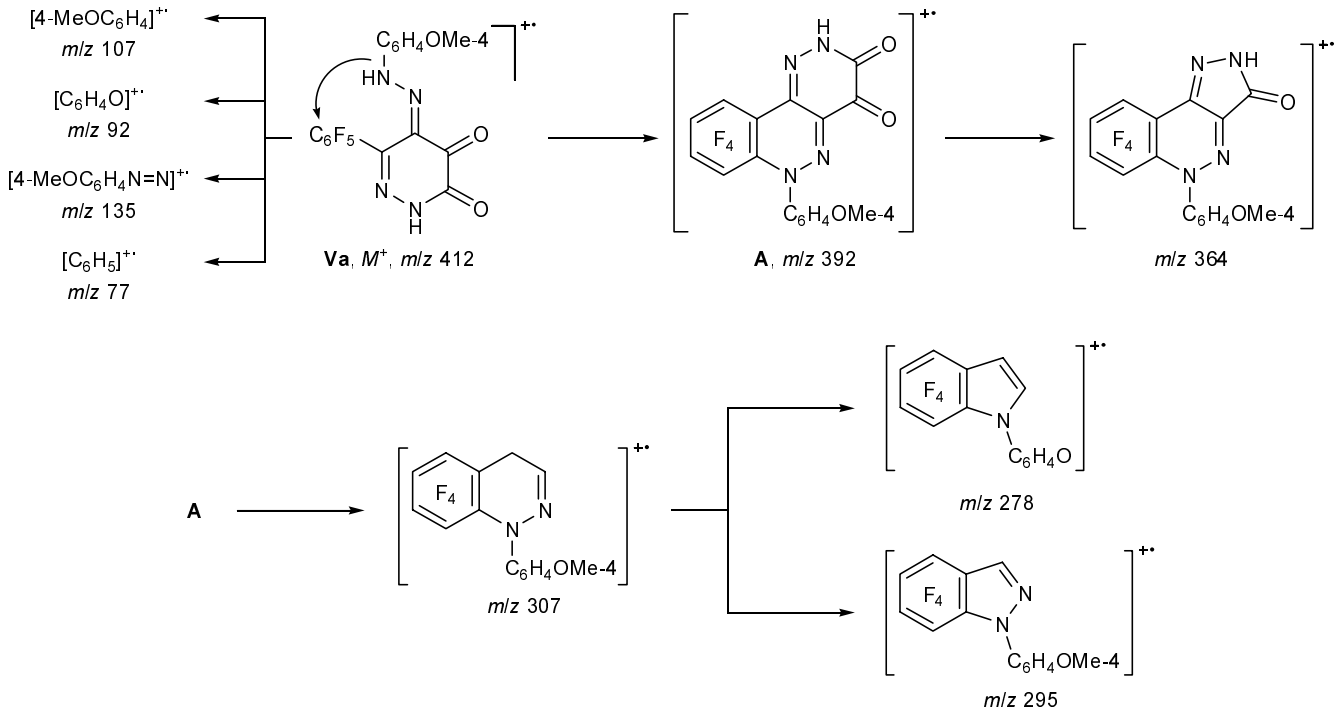
It should be noted that our attempts to effect cyclization of pyridazinedione **Va** to isolate tetrahydro-

Scheme 2.



IIa **Va** (49%)

Scheme 3.



pyridazo[4,3-*c*]cinnoline **A** were unsuccessful; presumably, the reason is instability of the initial compound.

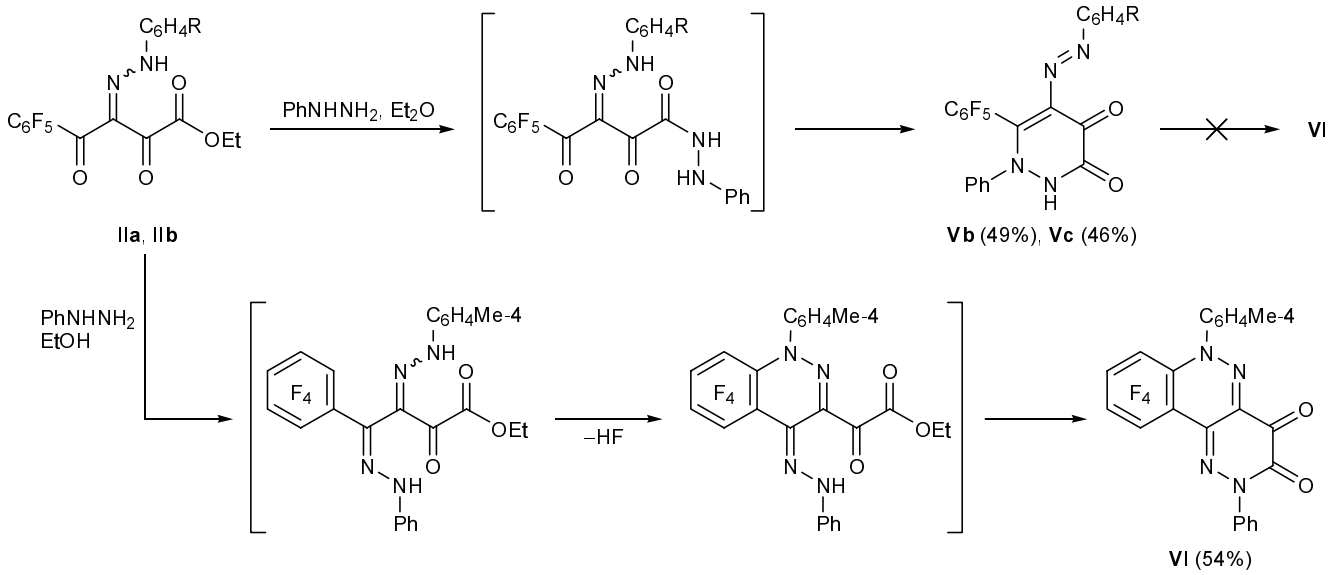
Esters **IIa** and **IIb** reacted with phenylhydrazine in boiling diethyl ether in a similar way: the products were the corresponding pyridazine-5,6-diones **Vb** and **Vc** (Scheme 4). The reactions were regioselective; they involved initial addition of the difunctional nucleophile at the ester group of **IIa** and **IIb**. The structure of pyridazinediones **Vb** and **Vc** was proved by the fact that they cannot undergo intramolecular ring closure to pyridazocinnolines like **VI**, in contrast to alternative products, pyridazine-3,4-diones. No cyclization occurred on treatment of compounds **Vb** and **Vc** with triethylamine in chloroform or with boiling pyridine. An additional support to the assumed structure of compounds **Vb** and **Vc** is the absence of $[M - HF]^+$ ion peak in the mass spectrum of **Vb** (in contrast to **Va**; see Experimental).

Tetrahydropyridazo[4,3-*c*]cinnoline **VI** was obtained when the reaction of ester **IIb** with phenylhydrazine was carried out in boiling ethanol (Scheme 4). Presumably, in this case the addition of the difunctional nucleophile occurred initially at the γ-carbonyl group (as in the reactions with fluoroalkyl-containing analogs); however, the subsequent cyclization gives cinnoline rather than pyrazole structure, and in the final stage thermodynamically more stable (in the given case) pyridazine system is formed.

According to our previous data [8], nonfluorinated acyl(aroyl)pyruvates and their derivatives, including 3-arylhydrazones, generally react with hydrazines to give substituted pyrazoles via initial nucleophilic addition at the α-carbonyl group [8]. The formation of pyridazines in reactions of acyl(aroyl)pyruvate derivatives with hydrazines was observed by us for the first time. The formation of ethyl 3-fluoroalkylpyrazole-5-carboxylates from 3-arylhydrazono-4-polyfluoroalkyl-2,4-dioxobutanoates **I** and substituted hydrazines was also unusual, for both nonfluorinated analogs and unsubstituted polyfluoroacylpyruvates typically give rise to 5-(fluoro)alkylpyrazole-3-carboxylates [8, 9]. A factor responsible for the unusual behavior of esters **I** and **II** in reactions with hydrazines may be considerable electron density redistribution induced by the polyfluoroalkyl (pentafluorophenyl) and arylhydrazone substituents, which reduces the probability for nucleophilic attack by the amino group of hydrazine to occur at the α-carbonyl group of the ester.

Pyridazines **Va**–**Vc** could give rise to amide–imide tautomerism, and compound **Va** having no substituent on the nitrogen atom could be involved additionally in azo–hydrazone and keto–enol equilibria (Scheme 5). However, the IR and ^1H and ^{19}F NMR spectra of com-

Scheme 4.



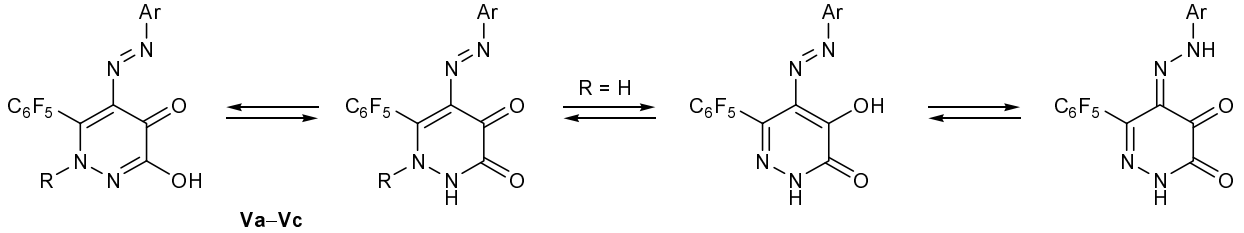
IIa, **Vc**, R = 4-MeO; **IIb**, **Vb**, R = 4-Me.

pounds **Va**–**Vc** indicated that they exist as a single tautomer. The IR spectra of all these compounds, recorded from both crystalline samples (in mineral oil) or solutions in chloroform, contained absorption bands typical of an amide functionality (see Experimental); therefore, they exist in the amide form. Further analysis of the IR spectra of compounds **Va**–**Vc** showed that N-phenyl-substituted pyridazines **Vb** and **Vc** are characterized by strong high-frequency absorption bands due to vibrations of the second carbonyl group. No such band was present in the spectrum of N-unsubstituted pyridazine **Va**. Presumably it exists as the azo–enol–amide tautomer (Scheme 5).

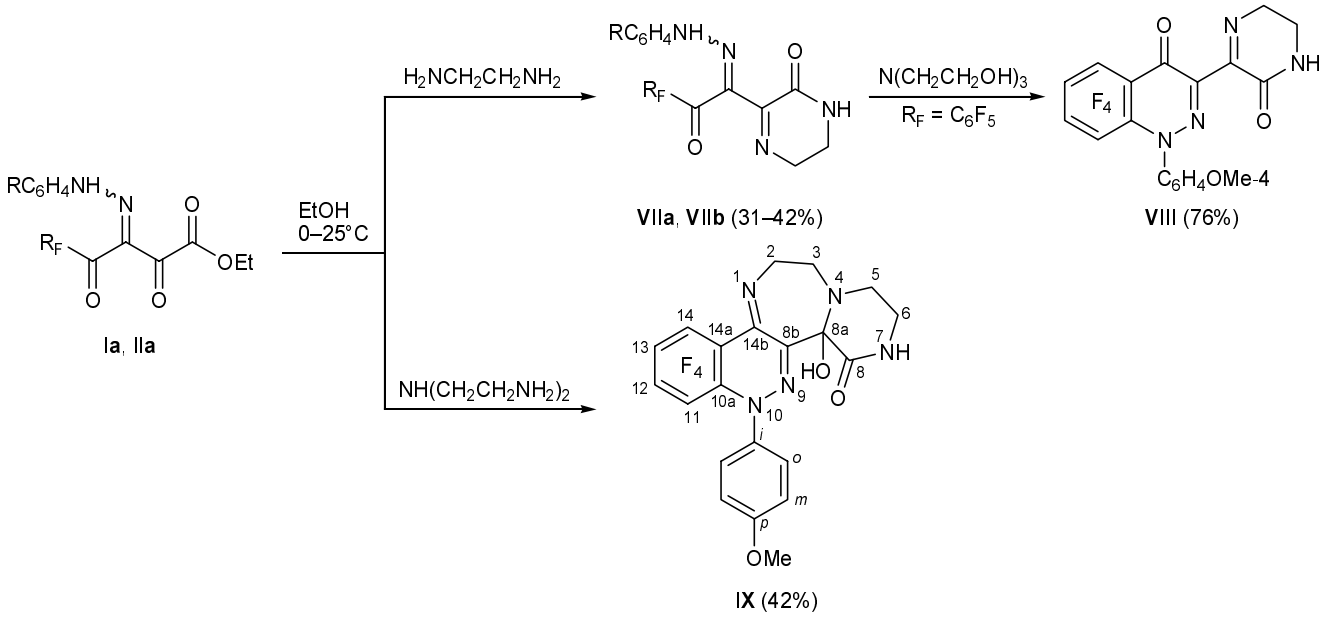
Both trifluoromethyl- and pentafluorophenyl-substituted 3-arylhydrazono-2,4-dioxobutanoates **Ia** and **IIa** underwent cyclocondensation with ethylenediamine at the α-oxo ester fragment in a way similar to unsubstituted fluoroacyl(aroyl)pyruvates [8, 9]. As a result, the corresponding pyrazin-2-one derivatives **VIIa** and **VIIb** were obtained (Scheme 6). Pentafluorophenyl-substituted pyrazin-2-one **VIIb** was subjected to intramolecular cyclization to 5,6,7,8-tetrafluoro-1-(4-methoxyphenyl)-3-(2-oxotetrahydropyrazin-3-yl)cinnolin-4(1*H*)-one (**VIII**) by the action of tris(2-hydroxyethyl)amine (Scheme 6).

Our attempts to perform reactions of 3-arylhydrazono-2,4-dioxobutanoates **I** and **II** with *N*-(2-aminoethyl)ethane-1,2-diamine always resulted in formation of a complex mixture of products which were difficult to separate. The only isolated product was tetracyclic pyrazino[4',3':4,5][1,4]diazepino[6,7-*c*]cinnoline **IX** (Scheme 6). Compound **IX** can be formed via exhaustive interaction between equimolar amounts of *N*-(2-aminoethyl)ethane-1,2-diamine and ester **IIa**, which is accompanied by intramolecular replacement of the *ortho*-fluorine atom in the pentafluorophenyl fragment by the amino group of the arylhydrazone fragment. The formation of heterocyclic system like **IX** and the failure to obtain isolable products in all other cases may be rationalized in terms of, on the one hand, high reactivity of *N*-(2-aminoethyl)ethane-1,2-diamine as polyfunctional nucleophile toward poly-

Scheme 5.



Scheme 6.



Ia, **VIIa**, $R_F = CF_3$, R = H; **IIa**, **VIIb**, $R_F = C_6F_5$, R = 4-MeO.

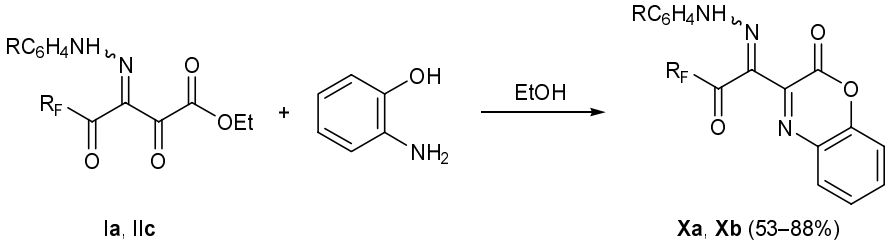
functional electrophilic reagents and, on the other, high stability and low solubility of compound **IX** in the reaction medium. The structure of **IX** was confirmed by the ^1H, ^{13}C, and ^{19}F NMR, IR, and mass spectra and elemental analysis (see Experimental).

Heterocyclization of 3-arylhydrazono-2,4-dioxobutanoates **Ia** and **IIc** with *o*-aminophenol also involved the α-dicarbonyl moiety, regardless of the polyfluorinated substituent in the substrate. The products were substituted benzoxazin-2-ones **Xa** and **Xb** (Scheme 7). The reaction was regioselective since no alternative products were formed. The structure of **Xa** and **Xb** follows from their IR spectra which contain high-frequency carbonyl absorption bands at about ~1750 cm^{-1}, which are typical of lactone group (see Experimental). Insofar as the amino group in *o*-aminophenol is a stronger nucleophile than the hydroxy group, the initial stage in the formation of heterocycles **Xa** and **Xb** is likely to be condensation of the α-carbonyl group in esters **Ia** and **IIa** with the amino group of *o*-aminophenol. It should be noted that nonfluorinated analogs and polyfluoroalkyl(aryl)-containing 3-unsubstituted 2,4-dioxobutanoates react with *o*-aminophenol in a similar way [8, 9].

On the other hand, pentafluorophenyl-substituted 3-arylhydrazono-2,4-dioxobutanoates **IIa** and **IId** reacted with *o*-aminophenol in boiling methanol to give cinnolinylbenzoxazinones **XIa** and **XIb** as a result of subsequent intramolecular ring closure involving the fluorinated benzene ring (Scheme 8).

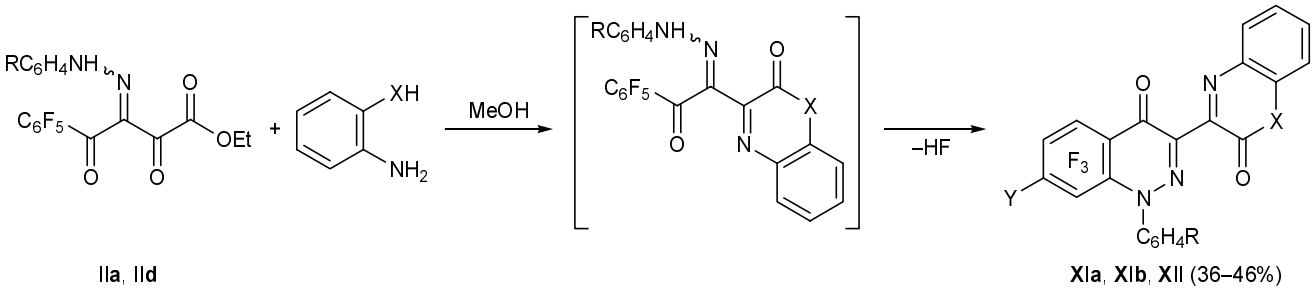
Pyrazin-2-ones **VIIa** and **VIIb** and benzoxazin-2-ones **Xa** and **Xb** can exist each as three tautomers due to keto–enol and azo-hydrazone equilibria. Their spectral data indicate the presence of only one tautomer in each case. The IR spectra of these compounds contained a strong absorption band belonging to a ketone

Scheme 7.



Ia, **Xa**, $R_F = CF_3$, R = H; **IIc**, **Xb**, $R_F = C_6F_5$, R = 4-O_2N.

Scheme 8.



IIa, **IId** **XIa**, **XIb**, **XII** (36–46%)

II, R = 4-MeO (**a**), 4-Br (**d**); **XI**, X = O, Y = F, R = 4-MeO (**a**), 4-Br (**d**); **XII**, R = Br, X = S, Y = 2-$NH_2C_6H_4S$.

carbonyl group (see Experimental); therefore, they were assigned the keto–hydrazone tautomer structure.

We also examined reactions of 3-arylhydrazono-2,4-dioxobutanoates **I** and **II** with *o*-aminobenzenethiol. However, we succeeded in isolating identifiable products only from esters **II**. For example, the reaction of ester **IId** with *o*-aminobenzenethiol in boiling methanol gave cinnolinylbenzothiazinone **XII** (Scheme 8). Here, the heterocyclization process was accompanied by replacement of fluorine atom in the 7-position by the second *o*-aminobenzenethiol molecule. Nucleophilic substitution in the fluorinated aromatic ring becomes possible due to high nucleophilicity of the sulfur atom. Heteroring assemblies analogous to **XI** and **XII** were synthesized by us previously from 1-aryl-3-ethoxalyl-5,6,7,8-tetrafluorocinnolinones [10], but the procedure described in the present work is more advantageous, for it does not include the stage of synthesis of 3-ethoxalylcinnolinones.

We can conclude that 3-arylhydrazono-4-polyfluoroalkyl(pentafluorophenyl)-2,4-dioxobutanoates **I** and **II** are polyfunctional compounds capable of undergoing cyclocondensations with difunctional nucleophilic reagents at the α-, β-, or γ-dicarbonyl fragment, depending on the fluorinated substituent, nucleophile nature, and reaction conditions. Pentafluorophenyl-substituted esters could give rise to subsequent ring closure via intramolecular nucleophilic replacement of the *ortho*-fluorine atom.

EXPERIMENTAL

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} on a Perkin–Elmer Spectrum One Fourier spectrometer from samples dispersed in mineral oil. The UV spectra were measured on a Shimadzu UV-2401 PC spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 instrument (400 and 100 MHz, respectively) using tetramethylsilane as reference. The ^{19}F NMR spectra were run on Tesla BS-587A (75.3 MHz) and Bruker DRX-400 (376 MHz) spectrometers using hexafluorobenzene as reference. The elemental compositions were determined on a Carlo Erba CHNS-O EA 1108 analyzer. The mass spectra (electron impact, 70 eV) were recorded on a Varian MAT-311A instrument with direct sample admission into the ion source.

2-Arylhydrazono-2,4-dioxobutanoates **I** and **II** were synthesized by the procedure described in [1]. Esters **Ic** and **IIb**–**IId** were previously unknown; their yields, melting points and spectral and analytical data are given below.

Ethyl 5,5,6,6-tetrafluoro-3-(2-methylphenylhydrazono)-2,4-dioxohexanoate (Ic). Yield 69%, yellow powder, mp 82–83°C (from isopropyl alcohol). IR spectrum, ν, cm^{-1}: 3070, 1510 (NH); 1730 (CO_2Me); 1660 (COC_2F_4H); 1640 (C=O); 1625 (C=N); 1500 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 t (3H, $CH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.47 s (3H, CH_3), 4.44 q (2H, $C\mathbf{H}_2CH_3$, J = 7.1 Hz), 6.30 t.t (1H, CHF_2, $^2J_{HF}$ = 53.0, $^3J_{HF}$ = 5.4 Hz), 7.26–7.75 m (4H, C_6H_4), 14.89 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 24.78 d.t (2F, $HC\mathbf{F}_2CF_2$, $^2J_{FH}$ = 53.0, $^3J_{FF}$ = 7.2 Hz), 41.47 m (2F, $HCF_2C\mathbf{F}_2$). Found, %: C 50.06; H 3.98; F 20.93; N 7.76. $C_{15}H_{14}F_4N_2O_4$. Calculated, %: C 49.73; H 3.90; F 20.98; N 7.73.

Ethyl 3-(4-methylphenylhydrazono)-4-pentafluorophenyl-2,4-dioxobutanoate (IIb) (a mixture of *Z* and *E* isomers at a ratio of 22 : 78**).** Yield 79%, yellow powder, mp 148–149°C (from isopropyl alcohol). IR spectrum, ν, cm^{-1}: 3060, 1525 (NH); 1735 (CO_2Et); 1660 (COC_6F_5); 1645 (C=O); 1620 (C=N); 1510, 1500 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *Z*/*E*: 1.41 t (3H, $CH_2C\mathbf{H}_3$, J = 7.1 Hz), 2.36 s (3H, CH_3), 4.45 q (2H, $C\mathbf{H}_2CH_3$, J = 7.1 Hz), 7.15 m (4H, C_6H_4); *Z* isomer: 14.94 br.s (1H, NH); *E* isomer:

14.56 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *Z*/*E*: 0.77 m (2F), 11.01 m (1F); *Z*: 20.00 m (2F); *E*: 22.72 m (2F). Found, %: C 53.08; H 2.97; F 22.17; N 6.27. $C_{19}H_{13}F_5N_2O_4$. Calculated, %: C 53.28; H 3.06; F 22.18; N 6.54.

Ethyl 3-(4-nitrophenylhydrazono)-4-pentafluorophenyl-2,4-dioxobutanoate (IIc) (a mixture of *Z* and *E* isomers at a ratio of 24:76**).** Yield 78%, yellow powder, mp 168–169°C (from isopropyl alcohol). IR spectrum, ν, cm^{-1}: 3110, 1605 (NH); 1730 (CO_2Et); 1670 (COC_6F_5); 1645 (C=O); 1625 (C=N); 1530, 1500 (C=C). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: *Z*/*E*: 14.10 br.s (1H, NH); *Z*: 1.26 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1 Hz), 4.21 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.1 Hz), 8.19 m (4H, C_6H_4); *E*: 1.39 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1 Hz), 4.44 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.1 Hz), 8.02 m (4H, C_6H_4). ^{19}F NMR spectrum [$(CD_3)_2CO$], δ_F, ppm: *Z*/*E*: 1.36–2.11 m (2F); *Z*: 12.58 m (1F), 21.04 m (2F); *E*: 12.17 m (1F), 22.73 m (2F). Found, %: C 47.33; H 2.13; F 20.66; N 9.26. $C_{18}H_{10}F_5N_3O_6$. Calculated, %: C 47.07; H 2.20; F 20.68; N 9.15.

Ethyl 3-(4-bromophenylhydrazono)-4-pentafluorophenyl-2,4-dioxobutanoate (IId) (a mixture of *Z* and *E* isomers at a ratio of 31:69**).** Yield 75%, yellow powder, mp 155–156°C (from isopropyl alcohol). IR spectrum, ν, cm^{-1}: 3080, 1520 (NH); 1725 (CO_2Et); 1665 (COC_6F_5); 1640 (C=O); 1615 (C=N); 1495 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *Z*/*E*: 7.00–7.67 m (4H, C_6H_4); *Z*: 1.40 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1 Hz), 4.42 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.1 Hz), 14.79 br.s (1H, NH); *E*: 1.43 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.1 Hz), 4.47 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.1 Hz), 14.42 br.s (NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: *Z*/*E*: –1.21 m (2F); *Z*: 8.94 m (1F), 20.18 m (2F); *E*: 11.83 m (1F), 22.85 m (2F). Found, %: C 43.90; H 2.01; F 19.11; N 5.70. $C_{18}H_{10}BrF_5N_2O_4$. Calculated, %: C 43.84; H 2.04; F 19.26; N 5.68.

Ethyl 4-phenyldiazenyl-3-trifluoromethyl-1*H*-pyrazole-5-carboxylate (IIIa) was described previously [1]. UV spectrum (EtOH), λ_{max}, nm (ε): 216 (6520), 238 (7930), 318 (14680), 429 (830).

Ethyl 4-(2-methylphenyldiazenyl)-3-(1,1,2,2-tetrafluoroethyl)-1*H*-pyrazole-5-carboxylate (IIIc). Ester **Ic**, 465 mg (1.3 mmol), was dissolved in 20 ml of glacial acetic acid, 0.3 ml of 40% hydrazine hydrate was added, and the mixture was stirred for 20 min at room temperature and diluted with 20 ml of distilled water. The precipitate was filtered off and washed with distilled water. Yield 421 mg (90%), orange powder, mp 138–139°C. IR spectrum, ν, cm^{-1}: 3085, 1580 (NH); 1685 (C=O); 1510 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.2 Hz), 2.69 s (3H, CH_3), 4.86 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.2 Hz), 6.43 t.t (1H, CHF_2, $^2J_{HF}$ = 52.5, $^3J_{HF}$ = 5.5 Hz), 7.25–7.67 m (4H, C_6H_4), 11.50 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 25.71 d.t (2F, $HC\mathbf{F}_2CF_2$, $^2J_{HF}$ = 52.5, J_{FF} = 9.2 Hz), 49.36 m (2F, $CHF_2C\mathbf{F}_2$). Found, %: C 50.13; H 3.93; F 21.31; N 15.69. $C_{15}H_{14}F_4N_4O_2$. Calculated, %: C 50.28; H 3.94; F 21.21; N 15.64.

Ethyl 1-methyl-4-phenyldiazenyl-3-trifluoromethyl-1*H*-pyrazole-5-carboxylate (IIId). A solution of 48 mg (1.05 mmol) of methylhydrazine in 2 ml of methanol was added under stirring to a solution of 302 mg (1.00 mmol) of ester **Ia** in 15 ml of methanol. The mixture was stirred for 1 h at 5°C and diluted with 10 ml of distilled water, and the precipitate was filtered off and was purified by column chromatography on silica gel using chloroform as eluent. Yield 140 mg (48%), orange powder, mp 107–108°C. IR spectrum, ν, cm^{-1}: 1715 (C=O), 1500 (C=C). UV spectrum (EtOH), λ_{max}, nm (ε): 208 (10470), 256 (11070), 315 (12390), 438 (750). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, $CH_2C\mathbf{H}_3$, *J* = 7.2 Hz), 4.42 s (3H, NCH_3), 4.43 q (2H, $C\mathbf{H}_2CH_3$, *J* = 7.2 Hz), 7.51–7.89 m (5H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ_F 99.63 ppm, s (CF_3). Found, %: C 51.71; H 3.86; F 17.69; N 16.98. $C_{14}H_{13}F_3N_4O_2$. Calculated, %: C 51.54; H 4.02; F 17.47; N 17.17.

4-Phenyldiazenyl-3(5)-trifluoromethyl-1*H*-pyrazole-5(3)-carboxylic acid (IVa). A mixture of 3.8 ml of distilled water, 4.4 ml of glacial acetic acid, and 0.6 ml of concentrated sulfuric acid was added to 446 mg (1.4 mmol) of pyrazole **IIIa**. The resulting mixture was heated for 50 min at the boiling point and cooled to 0°C, and the precipitate was filtered off and washed with cold water (0–5°C). Yield 396 mg (99%), orange powder, mp 220–221°C (sublimes). IR spectrum, ν, cm^{-1}: 3187, 3060 (NH, OH); 1710 (C=O); 1520 (C=C). UV spectrum (EtOH), λ_{max}, nm (ε): 217 (6040), 237 (7180), 321 (11460), 423 sh (850). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 7.68–7.99 m (5H, C_6H_5), 14.23 br.s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2CO$)]: δ_F 103.28 ppm, s (CF_3). Found, %: C 46.39; H 2.44; F 19.96; N 19.66. $C_{11}H_7F_3N_4O_2$. Calculated, %: C 46.49; H 2.48; F 20.05; N 19.72.

4-(2-Methylphenyldiazenyl)-3(5)-(1,1,2,2-tetrafluoroethyl)-1*H*-pyrazole-5(3)-carboxylic acid (IVb) was synthesized in a similar way from 202 mg (0.6 mmol) of pyrazole **IIIc**. Yield 172 mg (93%),

orange powder, mp 181–183°C. IR spectrum, ν, cm^{-1}: 3185, 3060 (NH, OH); 1700 (C=O); 1510 (C=C). UV spectrum (EtOH), λ_{max}, nm (ε): 216 (7080), 239.5 (9330), 333 (12840), 440 sh (850). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (3H, CH_3), 6.37 t.t (1H, CHF_2, $^2J_{HF}$ = 53.2, $^3J_{HF}$ = 4.3 Hz), 7.36–7.82 m (4H, C_6H_4), 11.50 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 28.85 d.t (2F, HC**F**$_2$CF$_2$, $^2J_{HF}$ = 53.1, $^2J_{FF}$ = 7.2 Hz), 49.28 m (2F, HCF$_2$C**F**$_2$). Found, %: C 47.35; H 2.98; F 22.95; N 17.20. $C_{13}H_{10}F_4N_4O_2$. Calculated, %: C 47.28; H 3.05; F 23.01; N 16.97.

5-Hydroxy-4-(4-methoxyphenyldiazenyl)-3-pentafluorophenylpyridazin-6(1*H*)-one (Va). Ester **IIa**, 444 mg (1 mmol), was dissolved in 10 ml of glacial acetic acid, 0.25 ml of 40% hydrazine hydrate was added, and the mixture was stirred for 1 h at room temperature and diluted with 20 ml of distilled water. The precipitate was filtered off and purified by column chromatography using chloroform–methanol (10:1) as eluent. Yield 189 mg (49%), red powder, mp 230°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3527, 3167, 1579 (NH, OH); 1673 (C=O); 1597 (C=C); 1526, 1499 (C=N, N=N); in $CHCl_3$ (*c* = 0.01 M): 3684, 3621, 3389, 1578 (NH, OH); 1684 (C=O); 1600, 1524, 1502 (C=N, N=N). ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.83 s (3H, OCH_3), 7.35 m (4H, C_6H_4), 8.17 (1H, NH), 14.47 (1H, OH). ^{19}F NMR spectrum [$(CD_3)_2CO$], δ_F, ppm: 0.24 m (2F), 9.47 m (1F), 22.93 m (2F). Mass spectrum, *m*/*z* (I_{rel}, %): 412 (24) $[M]^+$, 392 (70), 364 (6), 307 (8), 295 (22), 278 (11), 264 (10), 135 (39), 107 (100), 92 (26), 77 (36), 64 (14). Found, %: C 49.29; H 2.16; F 22.67; N 13.35. $C_{17}H_9F_5N_4O_3$. Calculated, %: C 49.53; H 2.20; F 23.04; N 13.59.

5-(4-Methylphenyldiazenyl)-6-pentafluorophenyl-1-phenyl-1,2-dihydropyridazine-3,4-dione (Vb). Phenylhydrazine, 108 mg (1 mmol), was added to a solution of 428 mg (1 mmol) of ester **IIb** in 10 ml of diethyl ether, the mixture was heated for 3 h under reflux, and the solvent was evaporated. The residue was purified by column chromatography using chloroform as eluent. Yield 225 mg (46%), dark red powder, mp 161–162°C. IR spectrum, ν, cm^{-1}: in mineral oil: 3264, 1595 (NH); 1688, 1650 (C=O); 1614, 1550, 1523 (C=C, C=N, N=N); in $CHCl_3$ (*c* = 0.01 M): 3684, 3621, 1597 (NH); 1683, 1662 (C=O); 1613, 1530 (C=N, N=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, CH_3), 6.96–7.73 m (9H, C_6H_4, C_6H_5), 14.15 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 1.21 m (2F), 11.64 m (1F), 22.09 m (2F). Found, %: C 58.32; H 2.83; F 20.55; N 11.62. $C_{23}H_{13}F_5N_4O_2$. Calculated, %: C 58.48; H 2.77; F 20.11; N 11.86.

5-(4-Methoxyphenyldiazenyl)-6-pentafluorophenyl-1-phenyl-1,2-dihydropyridazine-3,4-dione (Vc) was synthesized in a similar way from 444 mg (1 mmol) of ester **IIa** and 108 mg (1 mmol) of phenylhydrazine. Yield 225 mg (42%), dark red powder, mp 177–178°C. IR spectrum, ν, cm^{-1}: 3257, 1590 (NH); 1682, 1650 (C=O); 1611, 1560, 1515 (C=C, C=N, N=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (3H, CH_3), 6.91–7.75 m (9H, C_6H_4, C_6H_5), 14.17 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 1.20 m (2F), 11.61 m (1F), 22.15 m (2F). Mass spectrum, *m*/*z* (I_{rel}, %): 488 (100) $[M]^+$, 411 (9), 195 (48), 167 (7), 121 (21), 107 (24), 105 (13), 92 (19), 91 (15), 78 (8), 77 (65), 65 (14). Found, %: C 56.50; H 2.49; F 19.58; N 11.29. $C_{23}H_{13}F_5N_4O_3$. Calculated, %: C 56.57; H 2.68; F 19.45; N 11.47.

7,8,9,10-Tetrafluoro-6-(4-methylphenyl)-2-phenyl-2,6-dihydropyridazino[4,3-*c*]cinnoline-3,4-dione (VI). Phenylhydrazine, 1.43 ml (2.9 mmol), was added to a solution of 1.247 g (2.9 mmol) of ester **IIb** in 25 ml of ethanol. The mixture was heated for 1 min under reflux and cooled to 20°C, and the precipitate was filtered off and washed with chloroform. Yield 189 mg (54%), red powder, mp 244–245°C. IR spectrum, ν, cm^{-1}: 1683, 1665, 1650 (C=O, C=N). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 2.34 s (3H, CH_3), 7.31–7.73 m (9H, C_6H_4, C_6H_5). ^{19}F NMR spectrum [$(CD_3)_2SO$], δ_F, ppm: 2.68 m (1F), 14.97 m (1F), 20.28 m (1F), 30.75 m (1F). Found, %: C 58.74; H 2.63; F 16.01; N 12.16. $C_{23}H_{12}F_4N_4O_2$. Calculated, %: C 58.98; H 2.58; F 16.23; N 11.96.

3-(3,3,3-Trifluoro-2-oxo-1-phenylhydrazonopropyl)-5,6-dihydropyrazin-2(1*H*)-one (VIIa). A solution of 0.1 ml of ethane-1,2-diamine in 5 ml of ethanol was added dropwise on cooling to a solution 302 mg (0.96 mmol) of ester **Ia**. The mixture was stirred for 15 min at 0°C and for 1 h at 30°C and cooled to 0°C, and the precipitate was filtered off and washed with ethanol. Recrystallization from ethanol gave 243 mg (31%) of compound **VIIa** as orange powder with mp 197–198°C. IR spectrum, ν, cm^{-1}: 3380, 3313, 1598 (NH); 1717 ($COCF_3$); 1673 (CONH); 1568, 1540 (C=N, C=C). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 3.32–4.05 m (4H, C_2H_4), 7.19–7.60 m (6H, C_6H_5), 13.08 br.s (2H, NH). ^{19}F NMR spectrum [$(CD_3)_2SO$]: δ_F 85.27 ppm, s (CF_3). Found, %: C 49.88; H 3.40; F 18.53; N 17.72. $C_{13}H_{11}F_3N_4O_2$. Calculated, %: C 50.01; H 3.55; F 18.25; N 17.94.

3-[1-(4-Methoxyphenylhydrazono)-2-oxo-2-pentafluorophenylethyl]-5,6-dihydropyrazin-2(1*H*)-

one (VIIb). Ethane-1,2-diamine, 0.30 ml (6 mmol), was added to a solution of 888 mg (2 mmol) of ester **IIa** in 20 ml of ethanol. The mixture was stirred for 30 min at 15°C, and the precipitate was filtered off and washed with ethanol. Yield 372 mg (42%), orange powder, mp 180–181°C. IR spectrum, ν, cm^{-1}: 3170, 3075, 1598 (NH); 1690 (CONH); 1645 (COC_6F_5); 1540 (C=N, C=C). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 3.74 s (3H, OCH_3), 3.41–3.96 m (4H, C_2H_4), 6.82–7.06 m (4H, C_6H_4), 8.47 br.s (1H, NH), 12.10 br.s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2SO$], δ_F, ppm: 0.88 m (2F), 10.45 m (1F), 21.62 m (2F). Found, %: C 51.94; H 2.93; F 21.62; N 12.73. $C_{19}H_{13}F_5N_4O_3$. Calculated, %: C 51.83; H 2.98; F 21.57; N 12.72.

5,6,7,8-Tetrafluoro-1-(4-methoxyphenyl)-3-(2-oxo-1,2,5,6-tetrahydropyrazin-3-yl)cinnolin-4(1*H*)-one (VIII). Tris(2-hydroxyethyl)amine, 0.4 ml (2.3 mmol), was added to a solution of 285 mg (0.6 mmol) of compound **VIIb** in 100 ml of toluene. The mixture was heated for 2 h under reflux and evaporated, and the residue was washed with a 2:1 ethanol–water mixture. Yield 185 mg (76%), yellow powder, mp 263–264°C. IR spectrum, ν, cm^{-1}: 3353, 1590 (NH); 1695 (CONH); 1640 (C=O); 1584 (C=N). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 1.57 m and 4.47 m (4H, C_2H_4), 3.87 s (3H, OCH_3), 7.43 m (4H, C_6H_4), 8.95 br.s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2SO$], δ_F, ppm: –0.67 m (1F), 12.16 m (1F), 17.47–17.99 m (2F). Found, %: C 54.06; H 3.04; F 17.89; N 13.01. $C_{19}H_{12}F_4N_4O_3$. Calculated, %: C 54.29; H 2.88; F 18.08; N 13.33.

11,12,13,14-Tetrafluoro-8a-hydroxy-10-(4-methoxyphenyl)-2,3,4,5,6,7,8a,10-octahydropyrazino-[1',2':4,5][1,4]diazepino[6,7-*c*]cinnolin-8-one (IX). *N*-(2-Aminoethyl)ethane-1,2-diamine, 0.65 ml (6.0 mmol), was added to a solution of 888 mg (2.0 mmol) of ester **IIa** in 20 ml of ethanol. The mixture was stirred for 1 h at 10°C, and the precipitate was filtered off and washed with cold ethanol. Yield 195 mg (42%), orange powder, mp 260°C (decomp.). IR spectrum, ν, cm^{-1}: 3280, 1590 (NH); 1670 (CONH); 1605, 1575 (C=N, C=C). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 3.76 s (3H, OCH_3), 3.07–3.93 m (8H, C_2H_4), 6.89–7.39 m (4H, C_6H_4), 8.05 br.s (1H, NH), 14.17 br.s (1H, OH). ^{19}F NMR spectrum [$(CD_3)_2SO$], δ_F, ppm: –7.13 m (1F), 10.18 m (1F), 12.30 m (1F), 18.32 m (1F). ^{13}C NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 55.93 (OCH_3); 135.98 (C^p); 114.56–116.45 (C^o, C^m); 129.61 (C^i); 156.23, 168.45 (C^{8b}, C^{14b}); 81.53 (C^{8a}); 175.65 (C^8); 38.11, 49.52, 45.83, 50.28 (C^2, C^3, C^5, C^6); 135.15–147.74 m (C^{11}–C^{14}); 132.72 m, 135.29 m (C^{10a}, C^{14a}). Mass spectrum, *m/z* (I_{rel}, %): 463 (11.08) $[M]^+$, 341 (38), 300 (14), 299 (14), 298 (38), 284 (16), 136 (14), 135 (100), 123 (44), 122 (14), 120 (19), 107 (13). Found, %: C 54.08; H 3.68; F 16.50; N 15.00. $S_{21}H_{17}F_4N_5O_3$. Calculated, %: C 54.43; H 3.70; F 16.40; N 15.11.

3-(3,3,3-Trifluoro-2-oxo-1-phenylhydrazonopropyl)-1,4-benzoxazin-2-one (Xa). A solution of 164 mg (1.5 mmol) of *o*-aminophenol in 10 ml of ethanol was added to a solution of 302 mg (1.0 mmol) of ester **Ia** in 10 ml of ethanol. The mixture was heated for 10 h under reflux and diluted with 50 ml of distilled water, and the precipitate was filtered off and purified by column chromatography on silica gel using chloroform–methanol (10:1) as eluent. Yield 191 mg (53%), yellow powder, mp 176–177°C. IR spectrum, ν, cm^{-1}: 3070, 1560 (NH); 1755 (C=O); 1720 ($COCF_3$); 1530, 1510 (C=C, N=N). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 7.23–8.81 m (9H, C_6H_4, C_6H_5), 13.16 br.s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2SO$]: δ_F 90.75 ppm, s (CF_3). Found, %: C 56.31; H 2.90; F 15.55; N 11.56. $C_{17}H_{10}F_3N_3O_3$. Calculated, %: C 56.52; H 2.79; F 15.78; N 11.63.

3-[1-(4-Nitrophenylhydrazono)-2-oxo-2-pentafluorophenylethyl]-1,4-benzoxazin-2-one (Xb). A solution of 437 mg (4 mmol) of *o*-aminophenol in 5 ml of ethanol was added to a solution of 459 mg (1 mmol) of ester **IIc** in 5 ml of anhydrous ethanol. The mixture was heated for 2 h under reflux, and the precipitate was filtered off and recrystallized from ethanol. Yield 378 mg (75%), yellow powder, mp 197–198°C. IR spectrum, ν, cm^{-1}: 3295, 1610 (NH); 1750 (C=O); 1675 (COC_6F_5); 1645, 1600, 1590 (C=N, C=C). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 6.27–8.28 m (8H, C_6H_4), 8.87 br.s (1H, NH). ^{19}F NMR spectrum [$(CD_3)_2SO$], δ_F, ppm: 6.59 m (2F), 12.08 m (1F), 21.51 m (2F). Found, %: C 52.65; H 2.08; F 18.63; N 11.32. $C_{22}H_9F_5N_4O_5$. Calculated, %: C 52.40; H 1.80; F 18.84; N 11.11.

3-[5,6,7,8-Tetrafluoro-1-(4-methoxyphenyl)-4-oxo-1,4-dihydrocinnolin-3-yl]-1,4-benzoxazin-2-one (XIa). *o*-Aminophenol, 240 mg (2.2 mmol), was added to a solution of 444 mg (1.0 mmol) of ester **IIa** in 10 ml of ethanol. The mixture was heated for 2 h under reflux and cooled to 20°C, and the precipitate was filtered off, washed with diethyl ether, and recrystallized from ethanol. Yield 238 g (51%), yellow powder, mp 209–210°C. IR spectrum, ν, cm^{-1}: 1740 (C=O, lactone); 1635 (C=O); 1595, 1550, 1500 (C=N, C=C). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 3.84 s (3H, OCH_3), 7.05–7.82 m (8H, C_6H_4). ^{19}F NMR spectrum

$[(CD_3)_2SO]$, δ_F, ppm: 19.33 m (2F), 16.05 m (1F), 2.55 m (1F). Found, %: C 58.83; H 2.44; F 16.14; N 8.86. $C_{23}H_{11}F_4N_3O_4$. Calculated, %: C 58.87; H 2.36; F 16.19; N 8.95.

3-[1-(4-Bromophenyl)-5,6,7,8-tetrafluoro-4-oxo-1,4-dihydrocinnolin-3-yl]-1.4-benzoxazin-2-one (XIb) was synthesized in a similar way from 493 mg (1.0 mmol) of ester **IId** and 240 mg (2.2 mmol) of *o*-aminophenol. Yield 243 mg (46%), yellow powder, mp 235–236°C (from ethanol). IR spectrum, ν, cm^{-1}: 1750 (C=O, lactone); 1645 (C=O); 1590, 1560, 1510 (C=N, C=C). ^1H NMR spectrum $[(CD_3)_2SO]$, δ, ppm: 7.37–7.94 m (8H, C_6H_4). ^{19}F NMR spectrum $[(CD_3)_2SO]$, δ_F, ppm: 2.86 m (1F), 16.38 m (1F), 19.26 m (1F), 20.14 m (1F). Found, %: C 51.29; H 1.51; F 14.94; N 8.11. $C_{22}H_8BrF_4N_3O_3$. Calculated, %: C 50.99; H 1.56; F 14.66; N 8.11.

3-[7-(2-Aminophenylsulfanyl)-1-(4-bromophenyl)-5,6,8-trifluoro-4-oxo-1,4-dihydrocinnolin-3-yl]-1,4-benzothiazin-2-one (XII) was synthesized in a similar way from 986 mg (2.0 mmol) of ester **IId** and 75 mg (6 mmol) of *o*-aminobenzenethiol. Yield 455 mg (36%), yellow powder, mp 296°C (decomp.). IR spectrum, ν, cm^{-1}: 3460, 3350, 1620 (NH_2); 1675 (C=O). ^1H NMR spectrum $[(CD_3)_2SO]$, δ, ppm: 5.27 br.s (2H, NH_2), 6.46–9.92 m (12H, C_6H_4). ^{19}F NMR spectrum $[(CD_3)_2SO]$, δ_F, ppm: 17.19 d.d (1F, 5-F, $J_{5,6}$ = 22.0, $J_{5,8}$ = 15.6 Hz), 22.55 d (1F, 6-F, $J_{6,5}$ = 22.0 Hz), 31.64 d (1F, 8-F, $J_{8,5}$ = 15.6 Hz). Found, %: C 52.29; H 1.99; F 8.94; N 8.51. $C_{28}H_{14}BrF_3N_4O_2S_2$. Calculated, %: C 52.59; H 2.21; F 8.91; N 8.76.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 03-03-33118) and by the Russian Foundation for Support of the Russian Science.

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