ISSN 1070-3632, Russian Journal of General Chemistry, 2019, Vol. 89, No. 3, pp. 416–423. © Pleiades Publishing, Ltd., 2019.
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Reactions of 3-(Polyfluoroalkyl)propane-1,2,3-trione-2-oximes with Diaminoarenes

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Received September 27, 2018; revised September 27, 2018; accepted October 4, 2018

Abstract—Novel quinoxaline derivatives have been synthesized via the reaction of 3-trifluoromethyl-1,2,3-propanetrione-2-oximes with 1,2-diaminobenzene or 2,3-diaminonaphthalene: 2-trifluoromethyl-3-aroylquinoxaline and 2-trifluoromethyl-3-aroylbenzo[*g*]quinoxaline. Under similar conditions, 3-R^F-1,2,3-propanetrione-2-oximes [R^F = C_3F_7, $H(CF_2)_4$, C_4F_9, and C_6F_{13}] with the same diaminoarenes have given a mixture of the condensation and fragmentation products in different ratios. The structure of (4-methylphenyl)[3-(trifluoromethyl)benzo[*g*]quinoxalin-2-yl]methanone has been elucidated by means of X-ray diffraction analysis.

Keywords: fluorine-containing lithium 1,3-diketonates, 1,2,3-alkanetrione-2-oximes, 2-R^F-3-benzoylquinoxalines, 2-R^F-3-aroylbenzo[*g*]quinoxalines, (4-methylphenyl)[3-(trifluoromethyl)benzo[*g*]-quinoxalin-2-yl]methanones

DOI: 10.1134/S1070363219030083

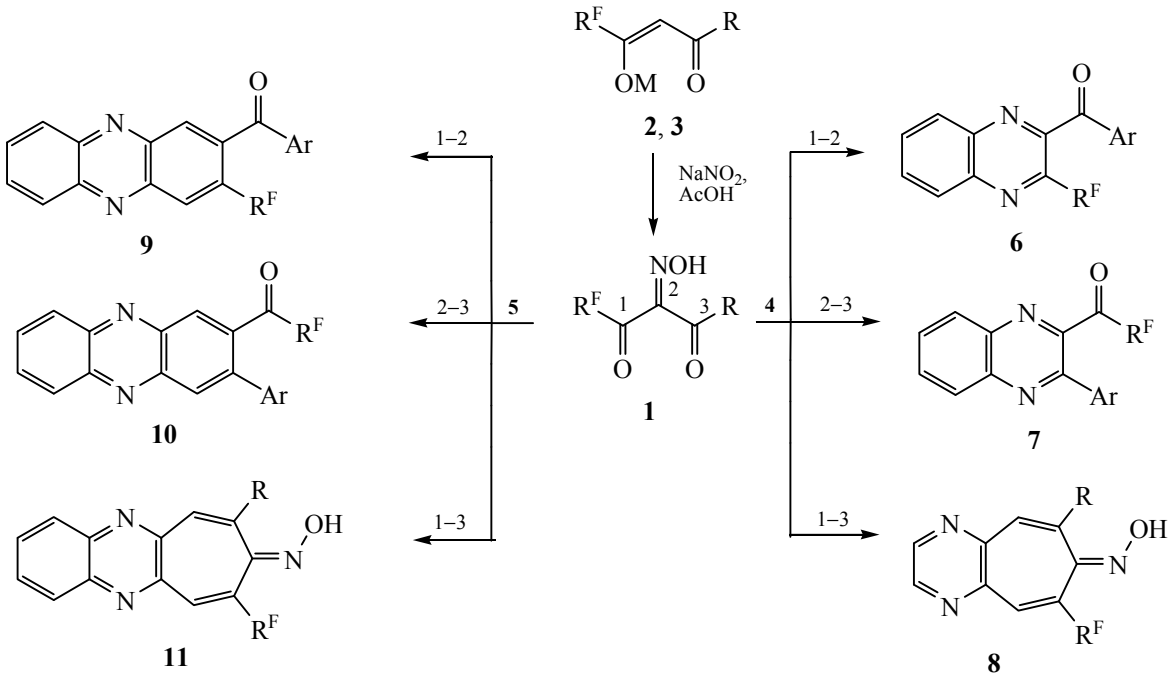
1,2,3-Alkanetrione 2-oximes (2-hydroxyimino-1,3-diketones) are valuable polyfunctional building blocks for targeted synthesis of many acyclic and heterocyclic compounds [1]. However, the properties of 3-polyfluoroalkyl-1,2,3-alkanetrione-2-oximes **1** are almost not investigated as the efficient methods for their synthesis consisting in nitrosation of lithium 3-(polyfluoroalkyl)-1,3-diketonates **3** with sodium nitrite in acetic acid was only recently developed [2][1]. At the same time, the reactivity of compounds bearing fluorinated substituents is substantially different from this of their nonfluorinated analogs, because of strong electron-withdrawing effect of the fluorine atom [6, 7]. Our literature analysis has revealed that the known examples of oximes **1** heterocyclization have been limited to the reactions of **1a** with hydrazine, leading to the formation of 4-hydroxyimino-5-phenyl-3-trifluoromethylpyrazole [8] or 5-phenyl-3-(trifluoromethyl)-1*H*-pyrazole-4-amine [9] and with 1,2-diaminobenzene to give 3-trifluoromethylquinoxaline-2-one or 2-hydroxy-3-hydroxyimino-4-phenyl-2-trifluoromethyl-1*H*-1,5-benzodiazepine [10]. We have earlier shown that the reactions of oximation involving oximes **1** afford 5-hydroxy-5-(polyfluoroalkyl)isoxazol-4(5*H*)-one oximes in high yield [11]. Herein we investigated the reactions of oximes **1a**–**1f** with 1,2-diaminobenzene **4** and 2,3-diaminonaphtha-lene **5**.

Oxime **1** can form several products of condensation with diaminoarenes **4**, **5**, due to the possibility of reaction at the electrophilic centers 1–2, 2–3, 1–3 with the formation of compounds **6**–**11** (Scheme 1).

Moreover, various fragmentations can occur in the course of the reactions, involving the starting oxime **1** and the products of its condensation with 1,2-diaminoarene. It is known that refluxing of oxime **1a** with 1,2-diaminobenzene **4** in methanol affords exclusively to 3-trifluoromethylquinoxaline-2-one **12a**, which is indicative of condensation of diaminoarene **4** with the product of fragmentation of oxime **1a**. Carrying out the reaction in boiling diethyl ether has led to the formation of 2-hydroxy-3-hydroxyimino-4-phenyl-2-trifluoromethyl-1*H*-1,5-benzodiazepine **13a** [10] (Scheme 2). There is no other information about interaction of oximes with diaminoarenes in the literature.

[1] Nitrosation of polyfluoroalkyl-1,3-diketones **2** under similar conditions results in the formation of hydrates of oximes **1** [3] or is accompanied by decomposition of the molecule. The only stable representative of oximes **1**, 3-hydroxyimino-4-phenyl-1,1,1-trifluoromethyl-2,4-butanedione **1a**, has been prepared via this method [4, 5].

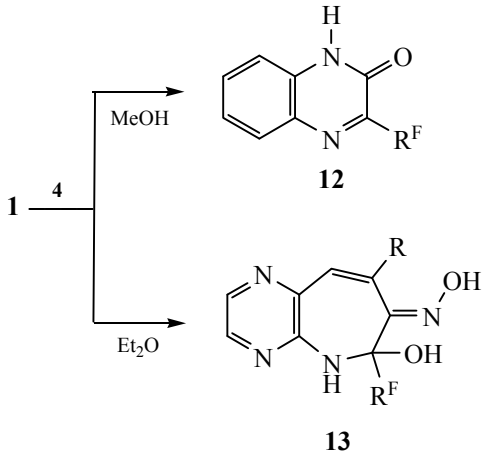
Scheme 1.



M=H (**2**), Li (**3**); R^F = CF_3 (**a**, **b**), C_3F_7 (**c**), C_4F_9 (**d**), $H(CF_2)_4$ (**e**), C_6F_{13} (**f**); R = Ph (**a**, **c**–**f**), 4-$CH_3C_6H_4$ (**b**).

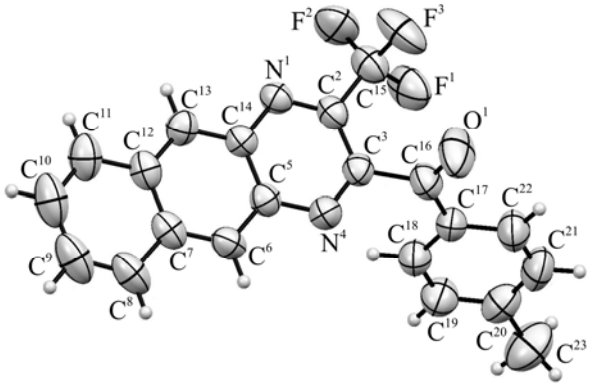
We found that refluxing of oximes **1** with equimolar amounts of diaminoarenes **4** or **5** in methanol or ethanol gave complex mixtures of products, in which compounds **6**–**8** and **9**–**11**, respectively, were detected by the GC–MS method. However, the reaction of oximes **1a** and **1b** with diaminoarenes **4** or **5** in glacial acetic acid at room temperature resulted in predominant formation of the products of condensation at electrophilic centers 1-2: 2-R^F-3-benzoylquinoxalines **6a,b** and 2-R^F-3-aroylbenzo[*g*]quinoxalines **9a, 9b**, respectively. Small amounts of compounds **7, 8, 12** (or **10**, **11, 18**) were also detected in the reaction mixtures by the GC–MS method. Compounds **6a, 6b** and **9a, 9b** were white or light-yellow powders soluble in diethyl ether, methylene chloride, chloroform, and ethanol. The choice between the isomeric structures **6** and **7** (or **9** and **10**) was made basing on the analysis of the data of IR and NMR spectroscopy as well as mass spectrometry. The IR spectra of compounds **6a, 6b** and **9a, 9b** contain narrow strong bands in the range of 1670–1680 cm^{-1}, characteristic of stretching of C=O groups adjacent to aryl substituents (a strong absorption band at 1720–1780 cm^{-1} is characteristic of the trifluoroacetyl carbonyl group).

Scheme 2.



The mass spectra of compounds **6a, 6b** and **9b** contain the peaks of molecular ions M^+ with relative intensity of 6–7%, along with the fragment peaks $[M - ArCO]^+$, $[M - CF_3]^+$, and $[M - CF_3 - ArCO]^+$ with intensity up to 1%. The base peak was that of $[ArCO]^+$ ion. Therefore, fragmentation of molecular ions M^+ of the investigated compounds correspond to the structures of 2-R^F-3-benzoylquinoxalines **6a, 6b** and 2-R^F-3-aroylbenzo[g]quinoxalines **9b**.

^{13}C NMR spectra of compounds **6a, 6b** and **9a** contain a singlet of the carbonyl carbon atom at ~191 ppm. For isomers **7a, 7b** and **10a**, the signal of the



General view of the molecule of compound **9b** according X-ray diffraction analysis (50% thermal ellipsoids are shown).

carbonyl carbon would be a quartet. ^{19}F NMR spectra of compounds **6a, 6b** and **9a** showed the CF_3 signal at δ –65 ppm, whereas the $CF_3C(O)$ group would give a signal at δ ~ –73 ppm [2, 3].

The structure of (4-methylphenyl-[3-(trifluoromethyl)benzo[quinoxalin-2-yl]methanone **9b** was unequivocally elucidated by X-ray diffraction analysis (see figure). The unit cell contained two crystallographically independent molecules exhibiting similar geometry. The selected bond lengths and bond angles are summarized in Tables 1 and 2. The numbers of the corresponding atoms of the second molecule are denoted with index "A." The bond lengths and bond angles of the two molecules coincided with the expected values and were pairwise close. The aroyl fragment in both molecules was practically planar and turned by 69.6° with respect to the heterocycle plane. Significantly shortened intermolecular contacts were not observed in the crystal.

Let us note that the SciFinder and Reaxys databases did not contain any information about quinoxalines of the type **6** and **7** containing simultaneously fluoroalkyl and aroyl substituents. At the same time, quinoxaline and its derivatives are of great importance. The quinoxaline ring is present in numerous antibacterial, antiviral [12], and antituberculosis drugs [13], complex-forming agents, luminophores [14], dyes, organic semiconductors [15], and other practically useful compounds.

Elongation of the fluoroalkyl chain in oximes **1** [R^F = C_3F_7, $H(CF_2)_4$, C_4F_9, or C_6F_{13}] drastically decreased the selectivity of their reaction with diaminoarenes **4** or **5**, leading to the formation of the products of condensation and fragmentation in different ratios (Tables 3 and 4). The amount of the products of fragmentation was increased when carrying out the reactions in AcOH at reflux. The GC–

Table 1. Selected bond lengths in molecule **9b**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
F^1–C^{15}	1.329(3)	N^4–C^5	1.380(3)	F^{1A}–C^{15A}	1.324(3)	N^{4A}–C^{5A}	1.376(3)
F^2–C^{15}	1.338(3)	O^1–C^{16}	1.213(3)	F^{2A}–C^{15A}	1.337(3)	O^{1A}–C^{16A}	1.212(3)
F^3–C^{15}	1.316(3)	C^2–C^{15}	1.497(4)	F^{3A}–C^{15A}	1.329(3)	C^{2A}–C^{15A}	1.511(4)
N^1–C^2	1.301(3)	C^3–C^2	1.439(4)	N^{1A}–C^{2A}	1.296(3)	C^{2A}–C^{3A}	1.437(3)
N^1–C^{14}	1.375(3)	C^{14}–C^5	1.427(3)	N^{1A}–C^{14A}	1.378(3)	C^{14A}–C^{5A}	1.427(3)
N^4–C^3	1.307(3)	C^3–C^{16}	1.522(3)	N^{4A}–C^{3A}	1.306(3)	C^{3A}–C^{16A}	1.516(3)

Table 2. Selected bond angles in molecule **9b**

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
C^2 N^1 C^{14}	116.3(2)	$N^1C^{14}C^{13}$	119.7(2)	$C^{2A}N^{1A}C^{14A}$	116.7(2)	$N^{1A}C^{14A}C^{13A}$	119.6(2)
$C^3N^4C^5$	117.0(2)	$F^1C^{15}F^2$	105.1(2)	$C^{3A}N^{4A}C^{5A}$	117.2(2)	$F^{1A}C^{15A}F^{2A}$	106.3(3)
$O^1C^{16}C^3$	115.8(3)	$F^3C^{15}F^2$	106.6(3)	$O^{1A}C^{16A}C^{3A}$	117.0(3)	$F^{3A}C^{15A}F^{2A}$	106.7(2)
$O^1C^{16}C^{17}$	123.5(3)	$F^3C^{15}F^1$	106.8(2)	$O^{1A}C^{16A}C^{17A}$	123.7(2)	$F^{1A}C^{15A}F^{3A}$	107.0(2)
$N^1C^{14}C^5$	120.9(2)	$C^{17}C^{16}C^3$	120.8(2)	$N^{1A}C^{14A}C^{5A}$	120.4(2)	$C^{17A}C^{16A}C^{3A}$	119.3(2)

Table 3. GC–MS analysis data for the products of the reaction of oxime **1d** with 2,3-diaminobenzene **4**

Comp. no.	Content in the mixture, %[a]	Retention time, min	$[M]^+$, *m/z* (I_{rel}, %)	Characteristic ions, *m/z* (I_{rel}, %)
16d	7.3	11.07	131 (63)	105 (100) $[C_6H_5CO]^+$, 77 (62) $[C_6H_5]^+$, 51 (41) $[C_4H_3]^+$, 38 (5) $[C_3H_2]^+$, 27 (3) $[HCN]^+$
14d	11.9	15.03	336 (26)	317 (8) $[M - F]^+$, 297 (0.5) $[M - HF_2]^+$, 198(6) $[M - F - C_2F_5]^+$, 167 (100) $[M - C_3F_7]^+$, 147 (21) $[M - C_3F_7 - HF]^+$, 140 (14) $[M - C_3F_7 - HCN]^+$, 131 (1) $[C_3F_5]^+$, 116 (6) $[M - C_3F_7 - HCF_2]^+$, 90 (13) $[C_6H_4N]^+$, 69 (11) $[CF_3]^+$, 51 (3) $[C_4H_3]^+$
1d	16.1	19.29	395 (4)	219 (0.7) $[C_4F_9]^+$, 169 (0.3) $[C_3F_7]^+$, 131 (5) $[C_3F_5]^+$, 119 (2) $[C_2F_5]^+$, 105 (100) $[C_6H_5CO]^+$, 77 (48) $[C_6H_5]^+$, 69 (11) $[CF_3]^+$, 51 (16) $[C_4H_3]^+$
6d	13.9	22.75	452 (9)	433 (3) $[M - F]^+$, 424 (2) $[M - CO]^+$, 347 (0.4) $[M - C_6H_5CO]^+$, 283 (0.1) $[M - C_3F_7]^+$, 233 (1) $[M - C_4F_9]^+$, 205 (0.7) $[M - C_4F_9 - CO]^+$, 178 (0.6) $[M - C_6H_5CO - C_3F_7]^+$, 147 (2) $[M - C_6H_5CO - C_4F_8]^+$, 128 (3) $[M - C_6H_5CO - C_4F_9]^+$, 105 (100) $[C_6H_5CO]^+$, 77 (39) $[C_6H_5]^+$, 69 (4) $[CF_3]^+$, 51 (8) $[C_4H_3]^+$
15d	4.7	24.31	194 (100)	167 (5) $[M - HCN]^+$, 140 (2), $[M - 2HCN]^+$, 104 (5) $[C_8H_8]^+$, 90 (8) $[C_7H_6]^+$, 77 (9) $[C_6H_5]^+$, 63 (11) $[C_5H_3]^+$, 51 (6) $[C_4H_3]$
8d	46.0	25.07	467 (39)	450 (100) $[M - OH]^+$, 431 (5) $[M - OH - F]^+$, 262 (20), 231 (36) $[M - C_4F_9 - OH]^+$, 205 (15) $[M - C_4F_9 - CNOH]^+$, 77 (25) $[C_6H_5]^+$, 69 (30) $[CF_3]^+$

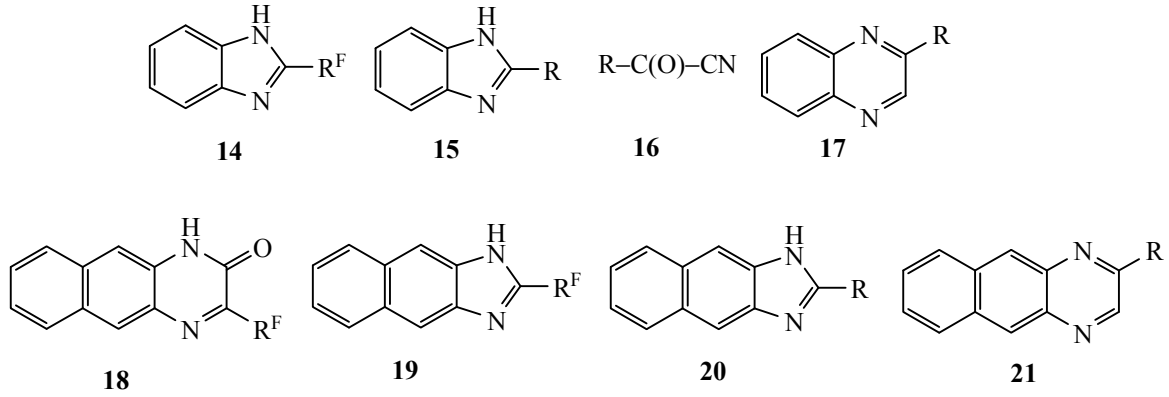
[a] Calculated from the peak areas in the chromatograms using the method of internal normalization.

Table 4. GC–MS analysis data for the products of the reaction of oxime **1c** with 2,3-diaminonaphthalene **5**

Comp. no.	Content in the mixture, %[a]	Retention time, min	$[M]^+$, *m/z* (I_{rel}, %)	Characteristic ions, *m/z* (I_{rel}, %)
16c	9.5	11.07	131 (63)	105 (100) $[C_6H_5CO]^+$, 77 (62) $[C_6H_5]^+$, 51 (41) $[C_4H_3]^+$, 38 (5) $[C_3H_2]^+$, 27 (3) $[HCN]^+$
19c	35.8	20.80	336 (100)	317 (9) $[M - F]^+$, 297 (0.2) $[M - HF_2]^+$, 248 (4) $[M - F - CF_3]^+$, 217 (60) $[M - C_2F_5]^+$, 197 (15) $[M - C_2F_5 - HF]^+$, 190 (11) $[M - C_2F_5 - HCN]^+$, 152 (26) $[C_{11}H_6N]^+$, 145 (37) $[C_{10}H_6F]^+$, 140 (33) $[C_{10}H_6N]^+$, 125 (6) $[C_{10}H_5]^+$, 69 (11) $[CF_3]^+$, 51 (3) $[C_4H_3]$
11c	4.3	27.25	467 (51)	448 (0.5) $[M - F]^+$, 421 (2) $[M - F - HCN]$, 298 (71) $[M - C_3F_7]^+$, 271 (84) $[M - C_3F_7 - HCN]^+$, 140 (100) $[C_{10}H_6N]^+$, 77 (23) $[C_6H_5]^+$, 69 (22) $[CF_3]^+$, 51 (7) $[C_4H_3]^+$
9c	16.3	28.01	452 (7)	433 (0.8) $[M - F]^+$, 424 (3) $[M - CO]^+$, 347 (0.5) $[M - C_6H_5CO]^+$, 283 (2) $[M - C_3F_7]^+$, 207 (1) $[M - C_3F_7 - C_6H_4]^+$, 178 (3) $[M - C_3F_7 - COC_6H_5]^+$, 152 (8) $[M - C_3F_7 - C_6H_5CO - HCN]^+$, 125 (3) $[C_{10}H_5]^+$, 105 (100) $[C_6H_5CO]^+$, 77 (39) $[C_6H_5]^+$, 51 (5) $[C_4H_3]^+$
20c	34.1	31.56	244 (100)	217 (3) $[M - HCN]^+$, 190 (1), $[M - 2HCN]^+$, 140 (28) $[C_{10}H_6N]^+$, 122 (23) $[C_{10}H_2]^+$, 114 (25) $[C_9H_6]^+$, 77 (7) $[C_6H_5]^+$, 63 (5) $[C_5H_3]^+$, 51 (4) $[C_4H_3]^+$

[a] Calculated from the peak areas in the chromatograms using the method of internal normalization.

Scheme 3.



14 **15** **16** **17**

18 **19** **20** **21**

MS analysis showed the presence of condensation products **6–8** in the products of the reaction of oximes **1c**–**1f** with 1,2-diaminobenzene **4** (Scheme 1), along with quinoxalones **12** (Scheme 2), benzimidazoles **14** and **15,** ketonitriles RC(O)CN **16**, and quinoxalines **17**[2] (Scheme 3). Similar products composition was found for the reactions of oximes **1c**–**1f** with 2,3-diamino-naphthalene **5**: 2-R^F-3-aroylbenzo[*g*]quinoxalines **9**, naphthodiazepines **11** (Scheme 1), benzo[*g*]quinoxalones **18**, naphthoimidazoles **19**, **20**, ketonitriles RC(O)CN **16**, and benzo[*g*]quinoxalines **21**[3] were identified (Scheme 3).

The major products were isolated from some of the mixtures obtained upon the reaction of oximes **1c**–**f** with diaminoarenes **4** and **5**. For example, refluxing of oxime **1e** with 1,2-diaminobenzene **4** in the 1 : 1 mixture of Et_2O and EtOH gave 3-R^F-quinoxaline-2-one **12e** as the major product, in line with the data from Ref. [4]. Diazepine **8d** and benzimidazole **14d** were isolated from the products of the reaction of oxime **1d** with 1,2-diaminobenzene **4** (Table 3). The formation of hydrates of benzo- and naphthodiazepines **9** and **11** was not observed in the considered reactions.

In summary, the reactions of 3-polyfluoroalkyl-1,2,3-alkanetrione 2-oximes with 1,2-diamino-benzene and 2,3-diaminonaphthalene were investigated, and new quinoxaline derivatives were obtained.

[2] Apparently, imidazoles **14** and **15** were the products of transformation of 1,5-diazepines **8** in acidic medium [16, 17]. Quinoxalines **17** were the products of the reaction of ketonitriles **16** with 1,2-diaminobenzene.

[3] Probably, naphthoimidazoles **19** and **20** are the products of transformation of naphthodiazepines **11** in acidic medium [16, 17]. Benzo[*g*]quinoxalines **21** are the products of the reaction of ketonitriles **16** with 2,3-diaminonaphthalene.

EXPERIMENTAL

Melting points were determined using Boetius and Stuart SMP3 instruments. IR spectra were recorded for solid samples using a Perkin-Elmer Spectrum One FT-IR spectrometer using a diffuse reflectance unit (DRA) over the 400–4000 cm^{-1} range. ^1H, ^{13}C, and ^{19}F NMR spectra were registered using a Bruker AVANCE-500 spectrometer, TMS and C_6F_6 were used as internal references. Elemental analysis was performed using a Perkin Elmer PE 2400 elemental analyzer.

The reaction products were identified by means of Trace GC Ultra DSQ II gas chromatography–mass spectrometer equipped with a Thermo TR-5ms capillary column (30 m×0.25 mm×0.25 μm, polymethylsiloxane, 5% of phenyl groups) and quadruple mass detector. Scanning of the total ionic current over the 20–1000 Da mass range in electronic ionization mode (70 eV) was performed. Other conditions were as follows: starting temperature of the column 40°C, exposure for 3 min, heating at 10°C/min to 280°C; temperature of injector 250°C, temperature of detector 200°C, temperature of transition chamber 200°C; carrier gas: helium, flow splitting 1 : 50, flow rate 1.0 mL/min.

X-Ray diffraction analysis was performed using an Xcalibur 3 automated single-crystal X-ray diffractometer [MoK_α-radiation, graphite monochromator, ω-scanning with step of 1° at T = 295(2) K]. the empirical absorption correction was applied. The structure was solved and refined using Olex2 software package [18]: the structure was solved using Superflip program [19] and refined by full-matrix least square method over F^2 using ShelXL program [20]. The refinement was performed under anisotropic approxi-

mation for nonhydrogen atoms. Hydrogen atoms were placed in the calculated positions and refined using the *rider* model. Monocrystals of compound **9b** were obtained by crystallization from $CHCl_3$. $C_{21}H_{13}F_3N_2O$, M = 366.33, monoclinic, a = 7.9988(7) Å, b = 36.992(2) Å, c = 11.8595(7) Å, β = 91.304(6)°, V = 3508.2(4) Å^3, space group $P2_1/n$, Z = 8, μ(MoK_α) = 0.109 mm^{-1}, scattering angle 4.76° < 2θ < 52.74°, 12867 total reflections including 6847 independent reflections (R_{int} = 0.0353), 3567 of them with $I > 2\sigma(I)$. Refinement parameters: R_1 = 0.1218, wR_2 = 0.1391 (all data), R_1 = 0.0545, wR_2 = 0.1075 [$I > 2\sigma(I)$], goodness-of-fit factor GooF = 1.010. $\Delta\rho_{\bar{e}}$ = 0.13/–0.17 $\bar{e}$ Å^{-3}. The crystallographic data were deposited at the Cambridge Crystallographic Data Center CCDC 1882664 and are freely available via www.ccdc.cam.ac.uk/data_request/cif.

Oximes **1a**–**1f** were obtained via nitrosation of the corresponding lithium 3-(polyfluoroalkyl)-1,3-diketonates with sodium nitrite in acetic acid [2]. The purity of the products was monitored by TLC on Sorbfil plates (UV-254, eluent $CHCl_3$). The plates were visualized using UV light and an aqueous solution of $Cu(OAc)_2$.

4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1,2,3-hexatrione-2-oxime 1c was obtained as described elsewhere [2] from 2.0 g (6.0 mmol) of lithium diketonate **3c,** 9 mL of acetic acid, and 0.48 g (6.9 mmol) of sodium nitrite, with 1.85 g (89.4%) yield. mp 126–127°C. IR spectrum, ν, cm^{-1}: 1129 s (CF), 1193 s (CF), 1232 m (CF), 1652 s (C=O), 1713 s (C=O), 3271 br (NOH). ^{1}H NMR spectrum, DMSO-d_6, δ, ppm: 7.60–7.66 m (2H, H^m); 7.76–7.80 m (1H, H^p), 7.82–7.86 m (2H, H^o), 14.52 s (1H, OH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –125.03 to –124.99 m (2F, CF_2), –114.93 to –114.82 m (2F, CF_2), –80.29 t (3F, CF_3, $^3J_{FF}$ = 8.96, $^4J_{FF}$ = 2.20 Hz). Found, %: C 42.08; H 1.91; N 4.02; F 38.34. $C_{12}H_6F_7NO_3$. Calculated, %: C 41.76; H 1.75; N 4.06; F 38.53.

3-(1,1,2,2,3,3,4,4-Octafluorobutyl)quinoxalin-2-one (12e). A solution of 0.4 g (1.1 mmol) oxime **1e** and 0.12 g (1.1 mmol) of 1,2-diaminobenzene **4** in 10 mL of the Et_2O : EtOH mixture (1 : 1) was refluxed for 2 h and cooled to room temperature, hexane was added, the formed precipitate was filtered and crystallized from methylene chloride. Yield 0.32 g (84.2%), mp 111°C, t_r 21.98 min. IR spectrum, ν, cm^{-1}: 1128 s (CF), 1168 s (CF), 1278 m (CF), 1674 v. s (C=O), 1612 s (C=N), 2896 w (NH). ^{1}H NMR spectrum, $CDCl_3$, δ, ppm: 6.30 t. t [1H, H$(CF_2)_4$, $^2J_{HF}$ = 51.9, $^3J_{HF}$ = 4.4 Hz, 7.44 d. d (1H, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 0.7 Hz), 7.48 d. d. d (1H, $^3J_{HH}$ = 8.2, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 0.9 Hz), 7.73 d. d. d (1H, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 0.7 Hz), 8.01 d. d (1H, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 0.9 Hz) Ph], 12.69 s (1H, NH). GC–MS (EI, C_2H_5OH, TIC): *m/z* (I_{rel}, %): 346 $[M]^+$ (37), 327 $[M - F]^+$ (7), 195 $[M - HC_3F_6]^+$ (100), 167 $[M - HC_3F_6 - CO]^+$ (68), 147 $[M - HC_3F_6 - CO - HF]^+$ (34), 140 $[M - HC_3F_6 - CO - HCN]^+$ (18), 102 $[C_7H_4N]^+$ (19), 90 $[C_6H_4N]^+$ (34), 69 $[CF_3]^+$ (6), 63 $[C_5H_3]^+$ (13), 51 $[HCF_2]^+$ (13), 39 $[HF_2]^+$ (4). Found, %: C 41.58; H 1.45; N 7.97; F 43.62. $C_{12}H_6F_8N_2O$. Calculated, %: C 41.64; H 1.75; N 8.09; F 43.90.

General procedure of the reaction of oximes 1a–1f with 1,2-diaminobenzene 4 and 2,3-diaminonaphthalene 5. Equimolar amounts of oxime **1** and 1,2-diaminobenzene **4** or 2,3-diaminonaphthalene **5** were dissolved in glacial acetic acid and kept at room temperature until the starting compounds disappeared (TLC monitoring). The reaction mass was poured into the water, extracted with methylene chloride, and filtered through the layer of silica. The solvent was evaporated, the residue was crystallized from the mixture of methylene chloride and hexane (1 : 3). In some cases, the product was additionally purified by column chromatography (eluent: methylene chloride).

Phenyl-[3-(trifluoromethyl)-2-quinoxalinyl]methanone (6a) was obtained from 0.33 g (1.3 mmol) of oxime **1a** and 0.15 g (1.3 mmol) of 1,2-diaminobenzene **4**. Yield 0.19 g (48.7%), mp 78–79°C, t_r 23.02 min. IR spectrum, ν, cm^{-1}: 1169 s (CF), 1186 s (CF), 1235 m (CF), 1596 s (C=N), 1676 vs (C=O). ^{1}H NMR spectrum, $CDCl_3$, δ, ppm: 7.48–7.54 m (2H), 7.64–7.69 m (1H), 7.90–8.01 m (4H), 8.18–8.23 m (1H), 8.28–8.33 m (1H). ^{13}C NMR spectrum, $CDCl_3$, δ, ppm: 120.73 q (CF_3, $^1J_{CF}$ = 276.0 Hz), 128.74, 129.52, 129.93, 130.56, 132.46, 133.20, 134.47, 134.71, 140.40, 141.03 q ($\underline{C}CF_3$, $^2J_{CF}$ = 36.4 Hz), 141.35, 149.13, 191.18 ($\underline{C}$=O). ^{19}F NMR spectrum, $CDCl_3$: δ_F –64.59 ppm. GC-MS (EI, in C_2H_5OH, TIC): *m/z* (I_{rel}, %): 302 $[M]^+$ (7), 283 [*M* – F] (<1), 274 $[M - CO]^+$ (4), 233 $[M - CF_3]^+$ (4), 197 $[M - C_6H_5CO]^+$ (<1), 128 $[M - CF_3 - C_6H_5CO]^+$ (1), 105 $[C_6H_5CO]^+$ (100), 77 $[C_6H_5]^+$ (56), 69 $[CF_3]^+$ (4), 51 $[C_4H_3]^+$ (14). Found, %: C 63.57; H 3.07; N 9.47; F 18.39. $C_{16}H_9F_3N_2O$. Calculated, %: C 63.58; H 3.00; N 9.27; F 18.86.

(4-Methylphenyl)-{3-(trifluoromethyl)-2-quinoxalinyl}methanone (6b) was obtained from 0.2 g (0.8 mmol) of oxime **1b** and 0.083 g (0.8 mmol) of 1,2-

diaminobenzene **4**. Yield 0.16 g (64%), mp 108–109°C, t_r 24.22 min. IR spectrum, ν, cm^{-1}: 1182 s (CF), 1239 s (CF), 1282 m (CF), 1604 m (C=N), 1678 s (C=O). ^1H NMR spectrum, $CDCl_3$, δ, ppm: 2.45 s (3H, CH_3), [7.30 d (2H, $^3J_{HH}$ = 8.1 Hz), 7.81 d (2H, $^3J_{HH}$ = 8.1 Hz) Ar], [(7.95–8.01 m (2H), 8.17–8.23 m (1H), 8.28–8.33 m (1H), quinoxaline ring]. ^{13}C NMR spectrum, $CDCl_3$, δ_C, ppm: 21.86; 95.74; 120.75 q (CF_3, $^1J_{CF}$ = 276.1 Hz), 129.50, 129.53, 129.93, 130.70, 133.34, 133.13, 140.38, 141.04 q ($\underline{C}CF_3$, $^2J_{CF}$ = 36.3 Hz), 141.41, 145.75, 149.40, 190.85 ($\underline{C}$=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F –64.63 ppm. GC-MS (EI, in C_2H_5OH, TIC): *m/z* (I_{rel}, %): 316 $[M]^+$ (6), 301 $[M - CH_3]^+$ (2), 288 $[M - CO]^+$ (1), 247 $[M - CF_3]^+$ (1), 197 $[M - CH_3C_6H_4CO]^+$ (1), 128 $[M - CF_3 - CH_3C_6H_4CO]^+$ (1), 119 $[CH_3C_6H_4CO]^+$ (100), 91 $[CH_3C_6H_4]^+$ (33), 69 $[CF_3]^+$ (3), 65 $[C_5H_5]^+$ (12), 51 $[HCF_2]^+$ (3). Found, %: C 64.54; H 3.51; N 8.78; F 17.69. $C_{17}H_{11}F_3N_2O$. Calculated, %: C 64.56; H 3.51; N 8.86; F 18.02.

(4-Phenyl)-{3-(trifluoromethyl)benzo[*g*]quinoxalin-2-yl}methanone (9a) was obtained from 0.25 g (1.0 mmol) of oxime **1a** and 0.16 g (1.0 mmol) of 2,3-diaminonaphthalene **5**. Yield 0.2 g (57%), mp 158–159°C. IR spectrum, ν, cm^{-1}: 1126 s (CF), 1190 s (CF), 1202 m (CF), 1596 m (C=N), 1673 s (C=O). ^1H NMR spectrum, $CDCl_3$, δ, ppm: 7.49–7.57 m (2H), 7.64–7.72 m (3H), 8.00 d (2H, $^3J_{HH}$ 7.6 Hz), 8.11–8.21 m (2H), 8.77 s (1H), 8.9 s (1H). ^{13}C NMR spectrum, $CDCl_3$, δ_c, ppm: 98.1, 120.67 q (CF_3, $^1J_{CF}$ = 276.2 Hz), 128.25, 128.50, 128.76, 128.84, 129.19, 130.67, 134.47, 134.73, 135.08, 135.59, 136.03, 136.72, 141.51 q ($\underline{C}CF_3$, $^2J_{CF}$ = 36.4 Hz), 148.82, 191.20 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F –64.83 ppm. Found, %: C 67.99; H 3.24; N 7.89; F 15.89. $C_{20}H_{11}F_3N_2O$. Calculated, %: C 68.18; H 3.15; N 7.95; F 16.18.

(4-Methylphenyl)-{3-(trifluoromethyl)benzo[*g*]-quinoxalin-2-yl}methanone (9b) was obtained from 0.2 g (0.77 mmol) of oxime **1b** and 0.12 g (0.77 mmol) of 2,3-diaminonaphthalene **5**. Yield 0.16 g (57%), mp 157.5–158.5°C, t_r 31.23 min. IR spectrum, ν, cm^{-1}: 1138 s (CF), 1185 s (CF), 1204 m (CF), 1604 m (C=N), 1672 s (C=O). ^1H NMR spectrum, $CDCl_3$, δ, ppm: 2.47 s (3H, CH_3), [7.33 d (2H, $^3J_{HH}$ = 8.1 Hz), 7.89 d (2H, $^3J_{HH}$ = 8.1 Hz), C_6H_4], [7.70 m (2H), 8.14 m (2H), 8.24 m (2H)], 8.79 s (1H)], 8.91 s (1H) quinoxaline]. ^{19}F NMR spectrum ($CDCl_3$), δ_F –64.93 ppm. GC-MS (EI, in C_2H_5OH, TIC): *m/z* (I_{rel}, %): 366 $[M]^+$ (7), 351 $[M - CH_3]^+$ (1), 338 $[M - CO]^+$ (2), 297 $[M - CF_3]^+$ (1), 247 $[M - CH_3C_6H_4CO]^+$ (1), 178 $[M - CH_3C_6H_4CO - CF_3]^+$ (2), 152 $[M - CH_3C_6H_4CO - CF_3 - CN]^+$ (7), 119 $[CH_3C_6H_4CO]^+$ (100), 91 $[CH_3C_6H_4]^+$, 65 $[C_5H_5]^+$ (11), 51 $[HCF_2]^+$ (1). Found, %: C 68.82; H 3.35; N 7.71; F 15.07. $C_{21}H_{13}F_3N_2O$. Calculated, %: C 68.85; H 3.57; N 7.65; F 15.56.

The reaction of oxime **1c** with 2,3-diaminonaphthalene **5** gave a mixture of products **16**, **19c**, **11c, 9c, 20c** (GC–MS data) (Table 4).

3-Hydroximino-2-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-4-phenyl-3*H*-1,5-benzodiazepin-3-one (8d) was obtained from 0.3 g (0.76 mmol) of oxime **1d** and 0.082 g (0.76 mmol) of 1,2-diaminobenzene **4**. Column chromatography gave 0.1 g (28%) of compound **8d** and 0.06 g (23%) of benzimidazole **14d**. mp 142–147°C. IR spectrum, ν, cm^{-1}: 1129 s (CF), 1193 s (CF), 1232 m (CF), 1450 m (C=N), 1572 s (C=N), 3134 br (OH). ^1H NMR spectrum, $CDCl_3$, δ, ppm: [7.39–7.46 m (2H), 7.48–7.57 m (3H)] Ph, 7.60–7.77 m (2H), 7.89 s (1H, OH), 8.06 d (2H, $^3J_{HH}$ = 7.3 Hz). Found, %: C 48.67; H 2.15; N 9.01; F 36.25. $C_{19}H_{10}F_9N_3O$. Calculated, %: C 48.84; H 2.16; N 8.99; F 36.59.

The reaction of oxime **1e** with 2,3-diaminonaphthalene **5**, according to GC–MS data, gave a complex mixture, the major components being 2-(1,1,2,2,3,3,4,4-octafluorobutyl)naphthoimidazole **19e** and (4-phenyl)[3-(1,1,2,2,3,3,4,4-octafluorobutyl)benzo-[*g*]quinoxalin-2-yl]methanone **9e. 2-(1,1,2,2,3,3,4,4-Octafluorobutyl)naphthoimidazole (19e)** was isolated by preparative column chromatography, mp 215–217°C, t_r 23.31 min. IR spectrum, ν, cm^{-1}: 1143 s (CF), 1170 s (CF), 1274 m (CF), 1476 m (C=N), 3040–2865 br (NH). GC-MS (EI, in $CHCl_3$, TIC): *m/z* (I_{rel}, %): 368 $[M]^+$ (8), 349 $[M - F]^+$ (1), 317 $[M - HCF_2]^+$ (<1), 297 $[M - HCF_2 - HF]^+$ (<1), 268 $[M - 2CF_2]^+$ (2), 248 $[M - 2CF_2 - HF]^+$ (4), 217 $[M - HC_3F_6]^+$ (30), 197 $[M - HC_3F_6 - HF]^+$ (9), 190 $[M - HC_3F_6 - HCN]^+$ (6), 152 $[C_{11}H_6N]^+$ (19), 145 $[C_{10}H_6F]^+$ (27), 140 $[C_{10}H_6N]^+$ (41), 125 $[C_{10}H_5]^+$ (7), 113 $[C_9H_5]^+$ (26), 69 $[CF_3]^+$ (36), 51 $[HCF_2]^+$ (100), 39 $[HF_2]^+$ (5).

The reaction of oxime **1f** with 2,3-diaminonaphthalene **5**, according to GC–MS data, gave a mixture of products **9f**, **11f**, **19f**, **20f**, **21f**, from which 0.31 g (66%) of **2-(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)naphthoimidazole (19f)** was isolated, mp 148–149°C, t_r 22.32 min. IR spectrum, ν, cm^{-1}: 1144 s (CF), 1202 s (CF), 1238 m (CF), 1479 m (NH), 1588 w (C=N), 3040–2615 br (NH). GC–MS (EI, in C_2H_5OH, TIC): *m/z* (I_{rel}, %): 486 $[M]^+$ (4), 467 $[M - F]^+$ (<1), 367 $[M - C_2F_5]^+$ (<1), 347 $[M - C_2F_5 - HF]^+$ (<1), 317 $[M - C_3F_7]^+$ (2), 298 $[M - C_3F_7 - F]^+$ (4), 278 [*M* –

$C_3F_7 - HF_2]^+$ (1), 248 $[M - C_4F_9 - F]^+$ (5), 217 $[M - C_5F_{11}]^+$ (41), 197 $[M - C_5F_{11} - HF]^+$ (11), 190 $[M - C_5F_{11} - HCN]^+$ (6), 152 $[C_{11}H_6N]^+$ (21), 145 $[C_{10}H_6F]^+$ (34), 140 $[C_{10}H_6N]^+$ (39), 125 $[C_{10}H_5]^+$ (6), 119 $[C_2F_5]^+$ (31), 113 $[C_9H_5]^+$ (18), 69 $[CF_3]^+$ (100), 50 $[CF_2]^+$ (7), 39 $[HF_2]^+$ (5).

FUNDING

This study was performed with financial support from the Russian Foundation for Basic Research (project 18-03-00112 A) in the scope of the State Task no. 0398-2018-0054, using the equipment of the Center for Collective Usage "Spectroscopy and analysis of organic compounds."

CONFLICT OF INTEREST

No conflict of interest was declared by authors.

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