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The transformations of fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds with methylamine

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Abstract

Fluoroalkylated 1,2,3-triketone 2-arylhydrazones and 2-arylhydrazono-3-oxo esters react variously with methylamine depending on the structure of the fluorinated substituent. 2-Arylhydrazono-1,3-dicarbonyl compounds having ''short'' fluoroalkyl substituents condense with methylamine at the carbonyl group attached to the non-fluorinated substituent whereas ones containing a lengthy polyfluoroalkyl substituent undergo haloformic cleavage as a result of the amine addition at the carbonyl group bearing such a substituent. The resulting 2-arylazo-3-(*N*-methyl)amino-1-polyfluoroket-2-en-1-ones and 1-(*N*-methyl)amino-2-arylhydrazono-3-fluoroalkyl-3-oxopropanamides have complexing properties, and they can bind to nickel(II) and copper(II) ions. Nickel chelates can be obtained by a three-component condensation of 2-arylhydrazono-1,3-dicarbonyl compounds and methylamine in the presence of nickel(II) cations.

Keywords: Fluoroalkylated 1,2,3-triketone 2-arylhydrazones; 2-Arylhydrazono-3-oxo esters; Methylamine; Condensation; Haloformic cleavage; Complexation; Metalchelate

1. Introduction

Fluorinated 1,3-dicarbonyl compounds are well-known complex-forming ligands. In addition, they can be used to generate new ligands such as the aminoderivatives, for example. Fluoroalkylated 1,3-diketones react with monoamines to give the regio-isomeric *N*-substituted 1,3-enaminoketones that can be applied as extractive reagents for gas chromatographic determination of transition metals, and their metal complexes are used for various processes as catalysts [1,2]. The substituents in the starting fluoroalkylated 1,3-diketones have a determining impact on the resulting 1,3-enaminoketone structures [3,4]. Fluoroalkyl-containing 3-oxo esters react with monoamines mainly at the polyfluoroacyl carbonyl to provide 3-aminocrotonic ester derivatives [5]. Under high pressure conditions, 3-fluoroalkyl-3-oxo esters and monoamines form amides as a result of condensation at the ester moiety [6]. A side reaction in the reactions of fluoroalkylated 1,3-dicarbonyl compounds with amines is acid cleavage, which produces fluorocarbonic acid amides [3,5].

Herein we report the transformation of fluoroalkylated 1,3-dicarbonyl compounds derivatives, *viz* polyfluroakylated 1,2,3-triketones 2-arylhydrazones **1** and 2-arylhydazono-3-oxo esters **2**, with methylamine with the purpose of getting new promising complexing ligands.

2. Results and discussion

2.1. Reactions of monofluoroalkyl-containing 1,2,3-triketone 2-arylhydrazones with methylamine

Monofluoroalkyl-containing 1,2,3-triketone 2-arylhydrazones **1** have two nonequivalent electrophilic centers (the carbonyl at the fluoroalkyl substituent and the carbonyl at the non-fluorinated substituent). Therefore, they are likely to form two regioisomeric products as a result of the amine condensation at either of the carbonyl groups, as well as the product of dicondensation at both carbonyl groups.

It was found that 1,2,3-triketone 2-arylhydrazones **1a–e** having a ''short'' fluoroalkyl substituent ($C \leq 2$) underwent

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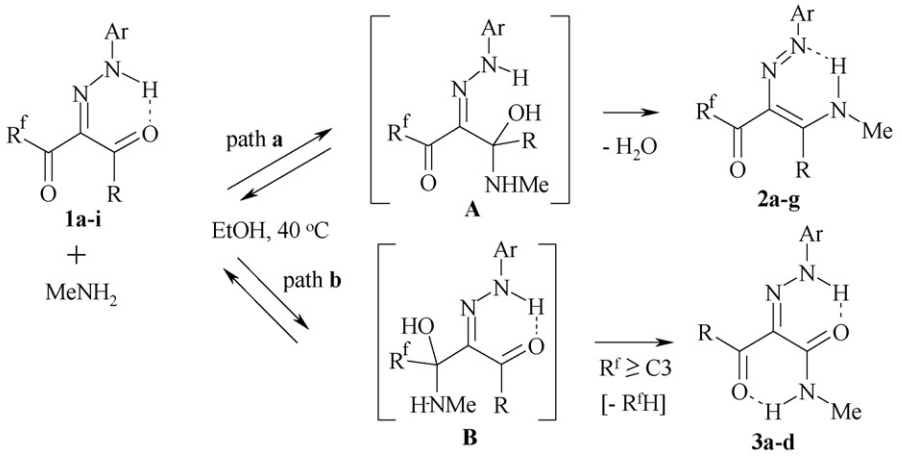


$R^f = CF_3$, R = Me, Ar = Ph (**1a, 2a**), R = Ph, Ar = C_6H_4-Me-4 (**1b, 2b**);
$R^f = H(CF_2)_2$, Ar = C_6H_4-OMe-4, R = Me (**1c, 2c**); R = Ph (**1d, 2d**), R = Bu, Ar = C_6H_4-Me-4 (**1e, 2e**);
$R^f = C_3F_7$, R = Me, Ar = C_6H_4OMe-4 (**1f, 2f, 3a**);
$R^f = C_4F_9$, R = Me, Ar = C_6H_4Me-4 (**1g, 2g, 3b**);
$R^f = H(CF_2)_4$, R = Bu^t, Ar = C_6H_4OMe-4 (**1h, 3c**);
$R^f = C_3F_7$, R = Ph, Ar = C_6H_4Me-4 (**1i, 3d**).

Scheme 1.

monocondensation with methylamine to afford 2-arylazo-1,3-enaminoketones **2a–e** (Scheme 1). The non-fluorinated fragment did not affect the reaction result in contrast to an analogous transformation of 2-nonsubstituted fluorinated 1,3-diketones [4].

The synthesis was carried out using an excess of methylamine and heating in ethanol for 20 min. The reaction was observed by thin-layer chromatography until the starting arylhydrazone **1** was completely converted. However, when chloroform was used as the solvent, no products were observed to be formed.

The regioisomeric structure of compound **2** was determined by NMR spectroscopy. Thus, the multiplet signal was observed in the ^{13}C NMR spectra of compounds **2a**,**b**,**e** at 176–180 ppm (see Section 4), which is typical for the carbon nucleus of a free polyfluoroalkyl moiety. Thus, the amine is shown to have condensed at the carbonyl group bearing the non-fluorinated substituent. The similar structures of products **2c**,**d** were established by comparing their ^1H and ^{19}F NMR data with spectral characteristics of compounds **2a**,**b**,**e**.

It was found that 1,2,3-triketone 2-arylhydrazones **1f–i** containing "long" fluorinated substituents ($C \geq 3$) interacted with methylamine in a manner that depended upon the structure of the non-fluorinated substituent. So, together with the expected 2-arylazo-1,3-enaminoketones **2f**,**g** resulting *via* path ***a*** (Scheme 1), 1-(*N*-methyl)amino-2-arylhydrazono-3-oxobutanamides **3a**,**b** were also obtained in the reactions of *methyl*-substituted arylhydrazones **1f**,**g** with methylamine. Amides **3a**,**b** were likely to have formed as a result of addition of the amine to the carbonyl group bearing the fluoroalkyl substituent followed by a haloformic cleavage of intermediate **B** by the elimination of fluoroalkane (path ***b***) (Scheme 1).

Amides **3c**,**d** were only isolated from the analogous reactions of arylhydrazones **1h**,**i** having fluoroarkyl ($C \geq 3$) and bulky *tert*-butyl or phenyl substituents (Scheme 1).

It is significant that the reactions of arylhydrazones **1** with methylamine were carried out under similar conditions, but more time was required for the full conversion of compounds **1f–i** (approx. 1 h) as compared with arylhydrazones **1a–e**.

Arylhydrazones **1** having the two nonequivalent electrophilic centers are most likely to add methylamine at one of carbonyl atoms forming hemiaminals **A** or **B** as intermediates (Scheme 1). It is obvious that stabilization of the intermediate **A** occurs rapidly due to the elimination of a water molecule to give amine **2** (path ***a***). In comparison with intermediate **A**, hemiaminal **B** should have a greater stability owing to the nearby electron-withdrawing polyfluoroalkyl group effect. The intermediate **B** that has "long" polyfluoroalkyl substituents can be stabilized *via* the elimination of fluoroalkane to give amides **3** (path ***b***). Haloformic cleavage is known to be typical for compounds containing "long" polyfluoroalkyl substituents due to formation of more stable carbanions [7]. The presence of the bulky phenyl or *tert*-butyl substituents in arylhydrazones **1h**,**i** creates difficulties for nucleophilic attack at a nearby carbonyl carbon. Thus one can understand the preferable formation of amides **3c**,**d** in these reactions. In contrast to 2-arylhydrazones **1f–i** with "long" fluorinated substituents, arylhydrazones **1a–e** having "short" fluoroalkyl substituents can form only amines **2** *via* path ***a***.

The compounds **2a–g** potentially exist as complicated tautomeric systems, since azo-hydrazono, keto-enol or imino-enamine tautomerism may be typical for them. Spectral examination (^1H and ^{19}F NMR) of products **2a–g**, however, indicates the presence of only a single tautomer in all cases. In addition, the ^{13}C NMR spectra of compounds **2a**,**b**,**e** exhibit a low-field multiplet signal for the carbonyl carbon atom of polyfluoroacyl moiety. In the ^1H NMR spectra of compounds **2a–g**, the most characteristic signal is a low-field singlet ($\delta \sim 14.67$–14.49 ppm) corresponding to the NH proton of the

arylhydrazone fragment, which takes part in the formation of an intramolecular hydrogen bond. In view of these data, it is supposed that compounds **2** exist in the solution of $CDCl_3$ as a hydrazonoiminoketone (HIK) tautomer.

The HIK tautomer can exist as a *Z*- or *E*-isomer or a mixture of both isomers in which *Z*- and *E*-isomers are stabilized *via* an intramolecular hydrogen bond. The spatial structure of compounds **2** was determined by comparing their NMR characteristics with those of the starting arylhydrazones **1**. Based on NMR spectral data it had been established earlier [8] that the starting arylhydrazones **1** exist in a hydrazonodiketone form where an intramolecular hydrogen bond was realized at the carbonyl group attached to the non-fluorinated substituent whereas the polyfluoroacyl group was unbound. The singlet signals of the CF_3 group of trifluoromethyl-containing substances **1a**,**b** and **2a**,**b** turned out to be observed in the same range ($\delta \sim -70$ ppm) in the ^{19}F NMR spectra in $CDCl_3$. The ^{13}C NMR spectra of compounds **2a**,**b** had quartet signals at $\delta \sim 176$–177 ppm with a spin–spin coupling constant of 30–31 Hz that is typical for a free trifluoroacetyl group. The matching NMR spectral characteristics of substances **2c**–**g** and the starting arylhydrazones **1c**–**g** containing the other polyfluoroalkyl substituents did not show significant differences in their values. Hence, the compounds **2a**–**g** appear to exist in chloroform solution as the *Z*-isomers of HIK tautomeric forms in which intramolecular hydrogen bonds are realized between the arylhydrazone and methylimine fragments, and the polyfluoroacyl groups are free.

The crystal structure of substances **2** was investigated by X-ray diffraction. It was found that in the crystals products **2a**,**b** were *Z*-isomers of the azaenaminoketone (AAK) tautomer in which an intramolecular hydrogen bond was present between $N^3...H^1$ atoms. Thus, the intramolecular distance $N^3...H^1 = 1.89(3)$ Å, angles $N^1–H^1...N^3 = 137.9$, $N^2–N^3...H^1 = 101.8^\circ$ in compound **2a** (Fig. 1) and one $N^3...H^1 = 1.85(6)$ Å, angles $N^1–H^1...N^3 = 134.7$, $N^2–N^3...H^1 = 103.0^\circ$ in substance **2b** (Fig. 2).

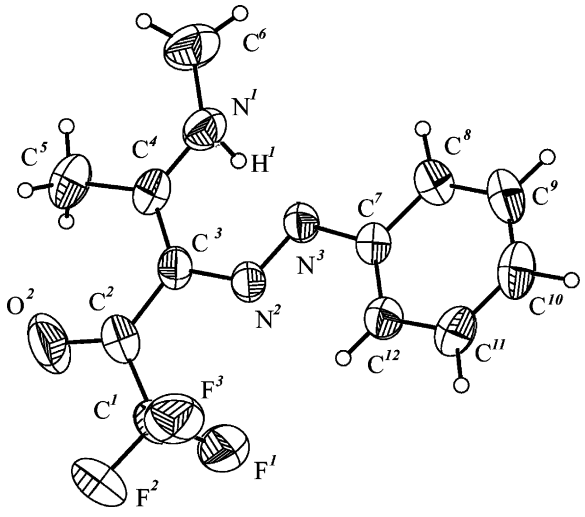


Fig. 1. X-ray structure of 4-(*N*-methyl)amino-1,1,1-trifluoro-3-phenylazopent-3-en-2-one (**2a**).

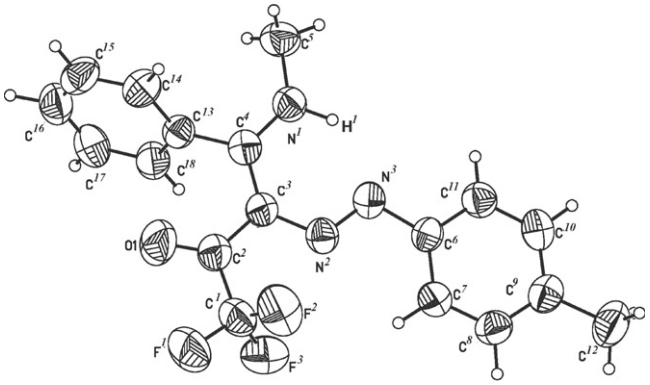
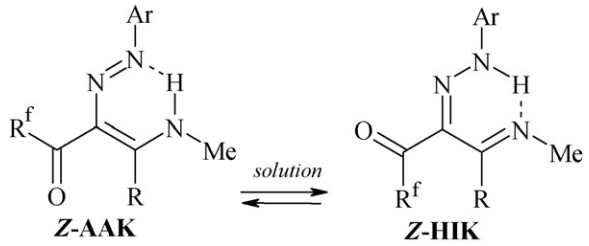


Fig. 2. X-ray structure of 4-(*N*-methyl)amino-3-(4-methylphenyl)azo-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**2b**).



Scheme 2.

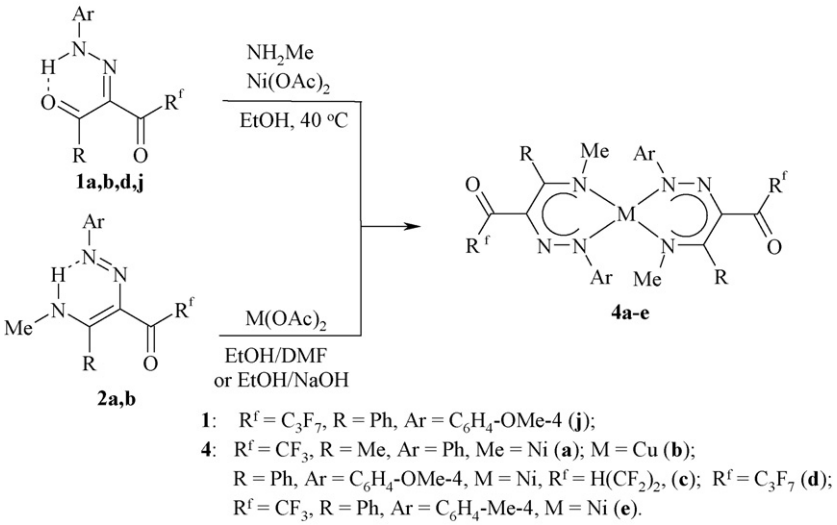
The IR spectra of substances **2a**–**g** in the solid state are very similar. Therefore, we can suppose that products **2c**–**g** exist also as the *Z*-isomer of AAK tautomer.

Obviously, when compounds **2a**–**g** are dissolved, they are subjected to enamino-imine and azo-hydrazone tautomeric transition. So, the AAK tautomers are transforming into HIK tautomers (Scheme 2) since they are the derivatives of the vinylogs of acid amides (''push-pull olefins''), and the formal double bonds in these compounds possess some single bond character [9].

Further, it was found that template condensation of fluoroalkyl-containing 1,2,3-triketone 2-arylhydrazones **1a**,**b**,**d**,**j** with methylamine in the presence of nickel(II) ions leads to the formation of metalchelates **4a**,**c**,**d** (Scheme 3). An alternative method for obtaining of chelates **4** is the treatment of 2-arylazo-3-methylimino-1-polyfluoroalkylket-2-en-1-one **2a**,**b** with metal salts (Scheme 3). The complexes obtained by the latter method can include other metals, e.g. copper(II). An advantage of the template condensation method is the possibility of obtaining metalchelates from ligands having ''long'' fluoroalkyl ($C \geq 3$) and bulky substituents.

The coordinating center with metal ion in the complexes **4** can be formed in different ways (arylhydrazone and methylimine fragments or arylhydrazone and polyfluoroacyl groups or polyfluoroacyl and methylimine moieties).

IR spectra indicated that the absorption bands of the polyfluoroacyl group are similar in chelates **4a**–**e** and the initial imines **2a**,**b** (1675–1665 cm^{-1}). When the ^1H NMR spectra of ligand **2a** and chelate **4a** were compared, it was found that the signals of the *N*-methyl and phenyl group protons had a



1: $R^f = C_3F_7$, R = Ph, Ar = C_6H_4-OMe-4 (**j**);
4: $R^f = CF_3$, R = Me, Ar = Ph, Me = Ni (**a**); M = Cu (**b**);
R = Ph, Ar = C_6H_4-OMe-4, M = Ni, $R^f = H(CF_2)_2$, (**c**); $R^f = C_3F_7$ (**d**);
$R^f = CF_3$, R = Ph, Ar = C_6H_4-Me-4, M = Ni (**e**).

Scheme 3.

diamagnetic shift in the case of complex **4a**. It results from the nickel ion effect on nearby protons. At the same time, the signals of CF_3 group fluorine nuclei were similar to those in the ^{19}F NMR spectra of substances **2a** and **4a** (see Section 4). The ^1H and ^{19}F NMR spectra of compounds **2a** and **4a** were recorded in DMF-d_7.

In accordance with IR and NMR data, it was supposed that the coordination with metal ion in metalchelates **4a–e** was realized *via* the participation of four donor nitrogen atoms of arylhydrazone and methylimine fragments, while polyfluoroacyl group did not participate in the formation of coordinating center. This was supported by X-ray analysis of metalchelate **4a** (Fig. 3).

The nickel atom in complex **4a** (Fig. 3) has plane-squared coordination, and the stepped distortion of molecule is realized in compounds **4a**. Dihedral angle between planes $NiN^{1'}N^{2'}$/$N^1C^{14}C^{12}N^3N^2$ comes to 41.9° and the distance from nickel atom to plane $N^1C^{14}C^{12}N^3N^2$ are equal 0.93(3) Å. Dihedral angels $N^1C^{14}C^{12}N^3N^2$/$C^9C^{28}C^{23}C^{32}C^{20}C^{15}$ and NiN^1N^2/$C^{21}C^{37}O^1C^{36}$ are 23.4° and 44.5°, respectively.

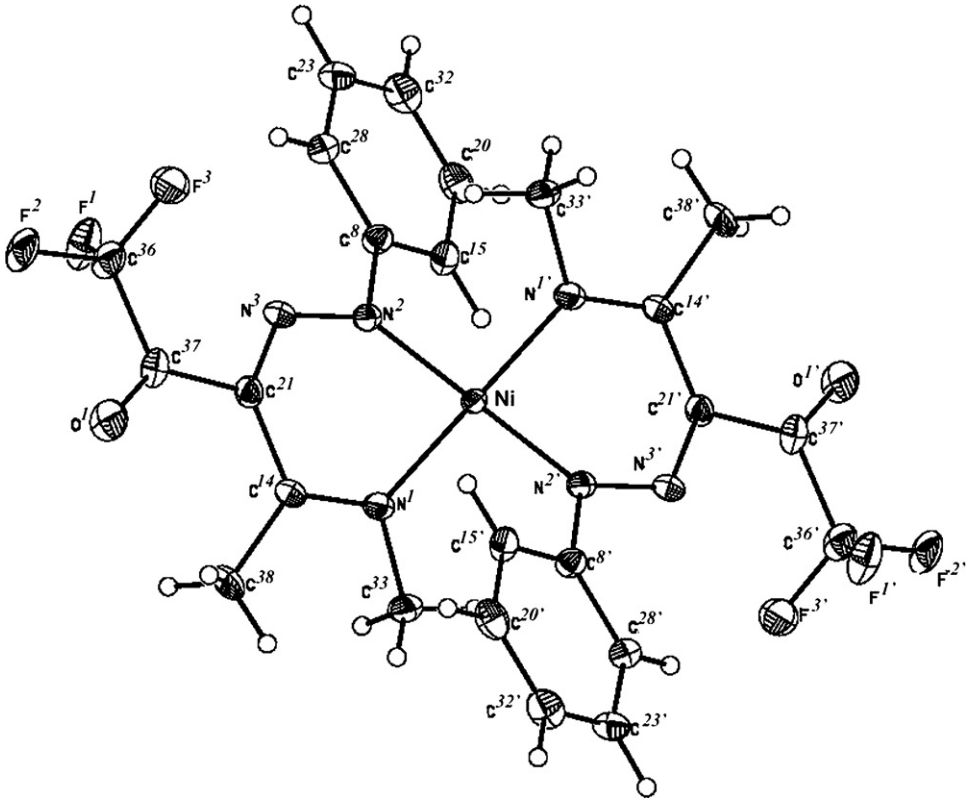
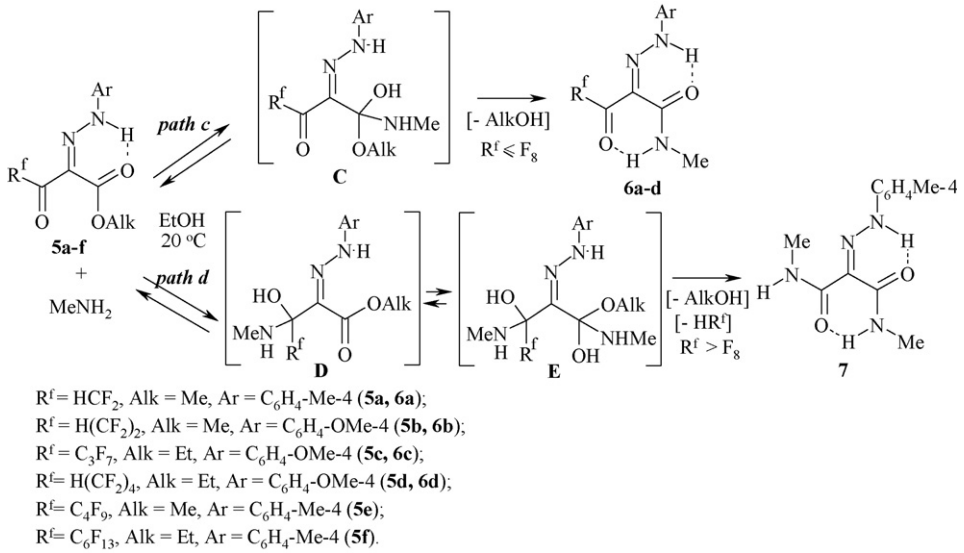


Fig. 3. X-ray structure of molecule bis-{1,1,1-trifluoro-4-[(*N*-methyl)aminato-κ^2N]-3-(phenyldiazenyl-κ^2*N*)pent-3-en-2-one}nickel(II) (**4a**).



R^f = HCF_2, Alk = Me, Ar = C_6H_4-Me-4 (**5a, 6a**);
R^f = $H(CF_2)_2$, Alk = Me, Ar = C_6H_4-OMe-4 (**5b, 6b**);
R^f = C_3F_7, Alk = Et, Ar = C_6H_4-OMe-4 (**5c, 6c**);
R^f = $H(CF_2)_4$, Alk = Et, Ar = C_6H_4-OMe-4 (**5d, 6d**);
R^f = C_4F_9, Alk = Me, Ar = C_6H_4-Me-4 (**5e**);
R^f = C_6F_{13}, Alk = Et, Ar = C_6H_4-Me-4 (**5f**).

Scheme 4.

2.2. Reactions of fluoroalkyl-containing 2-arylhydrazono-3-oxo esters with methylamine

We have studied the interaction of polyfluoroalkyl-containing 2-arylhydrazono-3-oxo esters **5a–f** with methylamine. The 2-arylhydrazono-3-oxo esters **5** have two nonequivalent electrophilic centers (the polyfluoroacyl carbonyl and the ester carbonyl). Thus there is the possibility of formation of various products as a result of the amine condensation at the different reaction centers.

It was found that the basic process in the reactions of compounds **5a–d** with methylamine was the condensation of the amine at the ester moiety to give amides **6a–d** (Scheme 4). However, in the case of esters **6e**,**f** having nonafluorobutyl and tridecafluorohexyl substituents, this reaction direction was accompanied by amine addition at the carbonyl of polyfluoroacyl group followed by formation of diamide **7** as result of haloformic cleavage.

In contrast to the above analogous conversion of arylhydrazones **1**, the reactions of esters **5** with methylamine led to product formation already at 20 °C.

Obviously, esters **5** can add methylamine at both carbonyl groups to form intermediates **C**, **D** (Scheme 4) likely 1,2,3-triketones 2-arylhydrazones **1** (Scheme 1). The stabilization of the intermediates **C** proceeds quickly as a result of elimination of an alcohol molecule to produce the amides **6a–d** (path ***c***). It occurs in the cases of esters **5a–d** having substituents with relatively small content of fluorine atoms ($F \leq 8$). Hemiaminal **D** having greater stability due to the nearby electron-withdrawing polyfluoroalkyl group can add the second amine molecule to give intermediate **E**. The latter can be stabilized *via* the elimination of an alcohol and fluoroalkane molecules to give diamide **7** (path ***d***). This pathway is realized in the cases of esters **5e**,**f** having the high content of fluorine atoms ($F > 8$) in their substituents.

It is noted that ethyl 2-(4-methoxyphenyl)hydrazono-3-oxo-3,3,3-trifluorobutanoate **5g** in its reaction with methylamine forms a mixture of products that is difficult to separate.

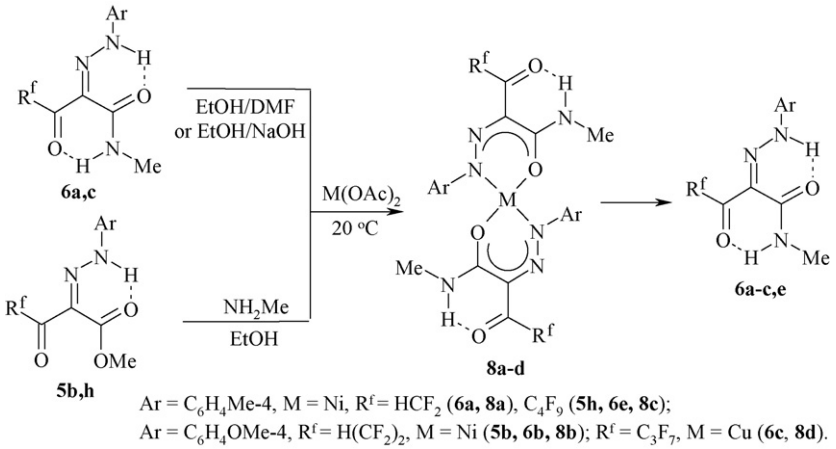
The amides **6a–d** can undergo amide-imide, azo-hydrazono and keto-enol tautomerism. However, spectral examination (^{1}H and ^{19}F NMR) of products **6a–d** indicates the presence of single tautomer in all cases. In the ^{1}H NMR spectra of compounds **6a–d**, the most characteristic signals are doublet ($\delta \sim 2.93$–2.94 ppm, J 5.0 Hz) and broad singlet signals ($\delta \sim 8.75$–8.85 ppm) of the Me–NH groups protons and low-field singlet signal ($\delta \sim 15.23$–15.65 ppm) of arylhydrazone proton. The low-field shift of NH protons testifies to their participation in intramolecular hydrogen bond formation with carbonyl groups of the amide and polyfluoroacyl fragments. The ^{13}C NMR spectrum of amide **6d** has two low-field signals at $\delta \sim 165$ and 179 ppm corresponding to the carbonyl carbon nuclei of amide and the fluoroacetyl groups. These data allows a preference for the hydrazono-ketoamide tautomeric form for amides **6a–d**.

According to ^{1}H, ^{13}C NMR and IR spectral data, the non-fluorinated amides **3a–d** exist in hydrazono-ketoamide tautomeric form similar to the fluoroalkylated ones **6a–d**.

It was found that the amides **6** possess complex-forming properties regarding transition metal ions. So when amides **6a**,**c** were treated with metal acetates, complexes **8a**,**d** were obtained. The analogous metal chelate **8b** was obtained by template condensation of ester **5b** with methylamine in the presence of nickel(II) ions (Scheme 5). Template condensation was used also to obtain of chelate **8c** from ester **5h** bearing the nonafluorobutyl substituent.

In contrast to chelates **4a–e**, complexes **8a–d** were found to be unstable when they were dissolved in solvent (DMF, $CHCl_3$), reverting to the amides **6a–c**,**e** again. The template method may be applied to the synthesis of amides having "long" polyfluorinated substituents, since amide **6e** can be obtained only in this way.

The instability of chelates **8a–d** creates difficulties for studying their structure. According to elemental analysis these complexes have composition of NiL_2, where L is mono-deprotonated ligand. Mass-spectroscopic investigation of chelate **8d** reveals the molecular ion peak corresponding to



Ar = C_6H_4Me-4, M = Ni, R^f = HCF_2 (**6a, 8a**), C_4F_9 (**5h, 6e, 8c**);
Ar = C_6H_4OMe-4, R^f = $H(CF_2)_2$, M = Ni (**5b, 6b, 8b**); R^f = C_3F_7, M = Cu (**6c, 8d**).

Scheme 5.

NiL_2. The IR spectra of products **8a–d** are characterized by a shift of absorption bands corresponding to the carbonyl group vibration at low-frequency compared with the IR spectra of amides **6a–c**,**e**. Besides, the absorption band in compounds **6a–c**,**e** in the range 3300–3290 cm^{-1} is more characteristic for Me–NH group of keto-amide form than for the OH group of a keto-enol form. These data allow us to conjecture that chelates **8a–d** have the structure shown in Scheme 5.

3. Conclusion

In the present work, we have shown that the introduction of the bulky electron-donating arylhydrazone group at the position 2 of fluoroalkylated 1,3-dicarbonyl compounds changes the reaction route with primary amines. In contrast to non-substituted fluoroalkylated 1,3-diketones and 3-oxo esters, the fluoroalkyl substituent size has a decisive impact on the resulting products: 2-arylhydrazono-1,3-dicarbonyl compounds having ''short'' fluoroalkyl substituent condense with methylamine at the carbonyl group attached to non-fluorinated substituent whereas ones containing the lengthy polyfluoroalkyl substituent undergo haloformic cleavage as a result of the amine addition at carbonyl group connected with this substituent. It occurs due to formation of the more stable carbanion in the last case. It was noted that the length of the polyfluoroalkyl substituent has different effect on reactivity of 1,2,3-triketones 2-arylhydrazones and 2-arylhydrazono-3-oxo esters. The resulting 2-arylazo-3-(*N*-methyl)amino-1-polyfluoroket-2-en-1-ones and 1-(*N*-methyl)-2-arylhydrazono-3-fluoroalkyl-3-oxopropanamides have complexing properties and can connect transition metal ions.

4. Experimental

Melting points were measured in open capillaries and are uncorrected. The infrared spectra were recorded on Perkin Elmer Spectrum One FT-IR and Thermo Nicolet 6700 FT-IR spectrometers at 4000–400 cm^{-1} in Nujol mulls. The ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer (^1H, 400 MHz; ^{13}C, 100.6 MHz) relative to $SiMe_4$. The ^{19}F NMR spectra were obtained on a Bruker DRX-400 spectrometer (^{19}F, 376 MHz) using C_6F_6 as an internal standard. The chemical shifts were converted from C_6F_6 to CCl_3F. The microanalyses were carried out on a Perkin Elmer PE 2400 series II elemental analyzer. Mass spectra were recorded on Varian MAT-311A spectrometer. The column chromatography was performed on Merck silica gel 60 (0.063–0.200 mm).

The single crystals of amine **2a**,**b** and **4a** were obtained by crystallization from the mixture CH_2Cl_2:hexane—(4:1). The X-ray studies were performed on 'Xcalibur 3 CCD' diffractometer with ω scanning (φ/ω scanning for **2b**) and graphite monochromatic Mo Kα (Cu Kα for **2a**) radiation. The registration of absorption was carried out analytically by the model of multi-facet crystal using a program ''CrysAlis RED 1.171.28c4'' (''CrysAlis RED 1.171.29'' for **2b**). The crystal structures were solved by direct methods followed by Fourier synthesis with SHELXS-97 and refined with full-matrix least-squares methods for all non-hydrogen atoms with SHELXL-97 software packages [10].

Main crystallographic data for **2a**: $C_{12}H_{12}F_3N_3O$, M = 271.25, space group $P2_1/c$, monoclinic, a = 7.425(4) Å, b = 19.656(4) Å, c = 9.062(2) Å, $\alpha = 90^\circ$, $\beta = 107.01(2)^\circ$, $\gamma = 90^\circ$, V = 1264.7(5) $Å^3$, T = 295(2) K, Z = 4, D_{calc} = 1.425 g/cm^3, μ(Cu Kα) = 0.107 mm^{-1}, 2377 reflections measured, 1881 unique reflections which were used in all calculations. The final R is 0.058. CCDC 612411 contains the supplementary crystallographic data for this compound.[1]

Main crystallographic data for **2b**: $C_{18}H_{16}F_3N_3O$, M = 347.34, space group Pb_c/a, orthorhombic, a = 17.288(8) Å, b = 7.967(2) Å, c = 24.492(3) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, V = 3373.7(4) $Å^3$, T = 295(2) K, Z = 8, D_{calc} = 1.368 g/cm^3, μ(Mo Kα) = 0.110 mm^{-1}, 3407 reflections measured, 1626 unique reflections which were used in all calculations. The final

[1] These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

R is 0.036. CCDC 634088 contains the supplementary crystallographic data for this compound (see the Footnote 1).

Main crystallographic data for **4a**: $C_{25}H_{24}Cl_2F_6N_6NiO_2$, $M = 684.11$, space group $P2_1/n$, monoclinic, $a = 11.055(2)$ Å, $b = 17.381(3)$ Å, $c = 14.455(0)$ Å, $\alpha = 90°$, $\beta = 90.18(4)°$, $\gamma = 90°$, $V = 2777.6(5)$ Å^3, $T = 100(2)$ K, $Z = 4$, $D_{calc} = 1.636$ g/cm^3, μ(Mo Kα) = 0.968 mm^{-1}, 8747 reflections measured, 7157 unique reflections which were used in all calculations. The final *R* is 0.052. CCDC 633787 contains the supplementary crystallographic data for this compound (see the Footnote 1).

The initial fluoroalkyl-containing 1,2,3-triketone of 2-arylhydrazones **1** and 2-arylhydrazono-3-oxo esters **5** were obtained by the known technique [11].

4.1. The interaction of 2-arylhydrazono-1,3-dicarbonyl compounds with methylamine

Method A. A solution of arylhydrazone **1a–i** or **5a–f** (3 mmol) in 30 mL ethanol was bubbled with an excess of methylamine (gas) upon heating (at 20 °C for compounds **5**). The control of the starting reagents conversion was performed by thin-layer chromatography. The resulting residue was filtered off, recrystallized from ethanol. In the case of substances **1f**,**g**, the resulting products were isolated by column chromatography (chloroform as an eluent).

Method B. The compound **8a–d** (1 mmol) was dissolved in chloroform (15 mL) at 20 °C. The resulting solid was filtered off. Then the solvent was evaporated and residue recrystallized from ethanol to give product **6a–c**,**e**.

4.1.1. The interaction of 1,2,3-triketone 2-arylhydrazones with methylamine

*4.1.1.1. (Z)-4-(N-Methyl)amino-1,1,1-trifluoro-3-phenylazo-pent-3-en-2-one (**2a**).* Yield, 74% (method A); mp, 150–152 °C. ^{1}H NMR ($CDCl_3$) δ: 2.62 (s, 3H, Me); 3.19 (s, 3H, NMe); 7.27–7.65 (m, 5H, Ph); 14.67 (br.s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 16.2 (C^{NMe}); 30.2 (C^5); 118.6 (q, C^1, $^1J_{C–F} = 292$ Hz); 121.0 (C^8, C^{12}); 123.8 (C^{10}); 125.2 (C^9, C^{11}); 128.1 (C^7); 151.4 (C^3); 165.7 (C^4); 177.7 (q, C^2, $^2J_{C–F} = 30$ Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −70.2 (s, 3F, CF_3) ppm. ^{1}H NMR (DMF-d_7) δ: 2.69 (s, 3H, Me); 3.37 (s, 3H, NMe); 7.32–7.77 (m, 5H, Ph); 14.15 (br.s, 1H, NH) ppm. ^{19}F NMR (DMF-d_7) δ: −67.2 (s, 3F, CF_3) ppm. IR: 3420, 1610 (NH); 1665 (C=O); 1590, 1570, 1495 (N=N, C=C); 1190–1150 (C–F) cm^{-1}. Analysis: calc. for $C_{12}H_{12}F_3N_3O$: C, 53.1; H, 4.5; F, 21.0; N, 15.5%. Found: C, 53.1; H, 4.6; F, 20.8; N, 15.8%.

*4.1.1.2. (Z)-4-(N-Methyl)amino-3-(4-methylphenyl)azo-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**2b**).* Yield, 71% (method A); mp, 123–125 °C. ^{1}H NMR ($CDCl_3$) δ: 2.40 (s, 3H, Me); 2.92 (s, 3H, NMe); 7.27–7.59 (m, 9H, Ph and C_6H_4); 14.60 (br.s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 21.2 (C^6); 31.7 ($C^{Ph–Me}$); 118.3 (q, C^1, $^1J_{C–F} = 292$ Hz); 120.8 (C^8, C^{12}); 123.1 (C^{10}); 129.0 (C^9, C^{11}); 129.5 (C^7); 126.4 (C^o); 129.8 (C^p); 131.7 (C^m); 138.4 (C^i); 149.0 (C^3); 163.8 (C^4); 176.6 (q, C^2, $^2J_{C–F} = 31$ Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −70.2 (s, 3F, CF_3) ppm. IR: 3350, 1595 (NH); 1680 (C=O); 1590, 1575, 1500 (N=N, C=C); 1185–1130 (C–F) cm^{-1}. Analysis: calc. for $C_{18}H_{16}F_3N_3O$: C, 62.2; H, 4.6; F, 16.4; N, 12.1%. Found: C 62.1; H 4.7; F 16.5; N 12.1%.

*4.1.1.3. (Z)-5-(N-Methyl)amino-4-(4-methoxyphenyl)azo-1,1,2,2-tetrafluorohex-4-en-3-one (**2c**).* Yield, 67% (method A); mp, 145–147 °C. ^{1}H NMR ($CDCl_3$) δ: 2.62 (s, 3H, Me); 3.18 (s, 3H, NMe); 3.86 c (s, 3H, OMe); 6.45 (tt, 1H, $H(CF_2)_2$, $^2J_{H–F} = 54.2$, $^3J_{H–F} = 5.7$ Hz); 7.23–7.42 (m, 4H, C_6H_4); 14.49 (br.s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −137.3 (dt, 2F, HCF_2, $^2J_{F–H} = 54.2$, $^3J_{F–F} = 8.5$ Hz); −121.1 (m, 2F, CF_2) ppm. IR: 3450, 1610 (NH); 1655 (C=O); 1605, 1585, 1500 (N=N, C=C); 1200–1100 (C–F) cm^{-1}. Analysis: calc. for $C_{14}H_{15}F_4N_3O_2$: C, 50.5; H, 4.5; F, 22.8; N, 12.6%. Found: C, 50.2; H, 4.6; F, 22.7; N, 12.8%.

*4.1.1.4. (Z)-5-(N-Methyl)amino-4-(4-methoxyphenyl)azo-1,1,2,2-tetrafluoro-5-phenylpent-4-en-3-one (**2d**).* Yield, 69% (method A); mp, 108–110 °C. ^{1}H NMR ($CDCl_3$) δ: 2.91 (s, 3H, NMe); 3.87 (s, 3H, OMe); 6.42 (tt, 1H, $H(CF_2)_2$, $^2J_{H–F} = 54.0$; $^3J_{H–F} = 5.9$ Hz); 6.98–7.57 (m, 9H, Ph and C_6H_4); 14.29 (s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −137.8 (dt, 2F, HCF_2, $^2J_{F–H} = 54.0$, $^3J_{F–F} = 8.3$ Hz); −121.5 (m, 2F, CF_2) ppm. IR: 3400, 1610 (NH); 1665 (C=O); 1590, 1575, 1495 (N=N, C=C); 1190–1150 (C–F) cm^{-1}. Analysis: calc. for $C_{19}H_{17}F_4N_3O_2$: C, 57.7; H, 4.3; F, 19.2; N, 10.6%. Found: C, 57.6; H, 4.4; F, 19.0; N, 10.7%.

*4.1.1.5. (Z)-5-(N-Methyl)amino-4-(4-methylphenyl)azo-1,1,2,2-tetrafluoronon-4-en-3-one (**2e**).* Yield, 78% (method A); mp, 90–92 °C. ^{1}H NMR ($CDCl_3$) δ: 1.00 (t, 3H, $(CH_2)_3Me$, $^3J_{H–H} = 7.3$ Hz); 1.55, 1.60 (2 m, 4H, $2CH_2$, $^3J_{H–H} = 7.3$ Hz); 2.39 (s, 3H, Me); 3.00 (m, 2H, CH_2, $^3J_{H–H} = 7.3$ Hz); 3.21 (s, 3H, NMe); 6.45 (tt, 1H, $H(CF_2)_2$, $^2J_{H–F} = 54.2$, $^3J_{H–F} = 5.7$ Hz); 7.23–7.42 (m, 4H, C_6H_4); 14.49 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 13.7 (C^{NMe}); 21.2 (C^{Me}); 23.1 (C^9); 28.5, 29.0, 29.4 ($C^{6–8}$); 110.9 (tt, C^1, $^1J_{C–F} = 255$, $^2J_{C–F} = 28$ Hz); 112.3 (tt, C^2, $^1J_{C–F} = 255$, $^2J_{C–F} = 28$ Hz); 120.7 (C^o); 124.3 (C^p); 130.0 (C^m); 138.3 (C^i); 149.7 (C^4); 169.0 (C^5); 180.3 (t, C^3, $^2J_{C–F} = 22$ Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −135.1 (dt, 2F, HCF_2, $^2J_{F–H} = 54.2$, $^3J_{F–F} = 8.2$ Hz); −120.9 (m, 2F, CF_2) ppm. IR: 3400, 1610 (NH); 1670 (C=O); 1605, 1580, 1490 (N=N, C=C); 1200–1100 (C–F) cm^{-1}. Analysis: calc. for $C_{17}H_{21}F_4N_3O$: C, 56.8; H, 5.9; F, 21.2; N, 11.7%. Found: C, 56.7; H, 5.9; F, 21.2; N, 11.9%.

*4.1.1.6. (Z)-2-(N-Methyl)amino-3-(4-methoxyphenyl)azo-5,5,6,6,7,7,7-heptafluorohept-3-en-4-one (**2f**).* Yield, 40% (method A); mp, 112–114 °C. ^{1}H NMR ($CDCl_3$) δ: 2.61 (s, 3H, Me), 3.19 (s, 3H, NMe), 3.85 (s, 3H, OMe), 6.94–7.60 (m, 4H, C_6H_4), 14.56 (br.s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −124.8 (m, 2F, CF_2), −111.5 (m, 2F, CF_2), −81.4 (m, 3F, CF_3) ppm. IR: 3450, 1605 (NH); 1655 (C=O); 1590, 1505, 1495 (N=N, C=C); 1250–1190 (C–F) cm^{-1}. Analysis: calc. for $C_{15}H_{14}F_7N_3O_2$: C, 44.9; H, 3.5; F, 33.1; N, 10.4%. Found: C, 44.9; H, 3.2; F, 32.9; N, 10.6%.

*4.1.1.7. (Z)-2-(N-Methyl)amino-3-(4-methylphenyl)azo-5,5,6,6,7,7,8,8-nonafluorookt-3-en-4-one (**2g**).* Yield, 38% (method A); mp, 100–102 °C. ^{1}H NMR ($CDCl_3$) δ: 2.38 (s, 3H, Me), 2.60 (s, 3H, Me), 3.21 (s, 3H, NMe), 7.21–7.53 (m, 4H, C_6H_4), 14.52 (s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −126.3 (m, 2F, CF_2), −121.4 (m, 2F, CF_2), −111.0 (m, 2F, CF_2), −82.1 (m, 3F, CF_3) ppm. IR: 3470, 1610 (NH); 1660 (C=O); 1600, 1500, 1490 (N=N, C=C); 1245–1130 (C–F) cm^{-1}. Analysis: calc. for $C_{16}H_{14}F_9N_3O$: C, 44.2; H, 3.2; F, 39.3; N, 9.7%. Found: C, 44.2; H, 3.2; F, 39.4; N, 9.6%.

*4.1.1.8. (Z)-1-(N-Methyl)-2-[(4-methoxyphenyl)hydrazono]-3-oxobutanamide (**3a**).* Yield, 35% (method A); mp, 116–118 °C. ^{1}H NMR ($CDCl_3$) δ: 2.50 (s, 3H, Me); 2.90 (d, 3H, NMe, $^3J_{H–H}$ = 5.0 Hz); 3.83 (s, 3H, OMe); 6.92–7.33 (m, 4H, C_6H_4); 9.35 (br.s, 1H, NH–Me); 14.87 (s, 1H, N–NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 25.0, 25.9 (C^{NMe}, C^{OMe}); 55.6 (C^4); 114.8 (C^o); 116.9 (C^m); 125.6 (C^p); 135.6 (C^i); 157.3 (C^2); 166.1 (C^1); 198.8 (C^3) ppm. IR: 3295, 1625 (NH); 1660 (C=O); 1620, 1590, 1540 (C=C, C=N) cm^{-1}. Analysis: calc. for $C_{12}H_{15}N_3O_3$: C, 57.8; H, 6.1; N, 16.9%. Found: C, 57.7; H, 6.2; N, 16.8%.

*4.1.1.9. (Z)-1-(N-Methyl)-2-[(4-methylphenyl)hydrazono]-3-oxobutanamide (**3b**).* Yield, 37% (method A); mp, 123–125 °C. ^{1}H NMR ($CDCl_3$) δ: 2.35 (s, 3H, C_6H_4–Me); 2.51 (s, 3H, Me); 2.90 (d, 3H, NMe, $^3J_{H–H}$ = 5.0 Hz); 7.17–7.27 (m, 4H, C_6H_4); 9.32 (br.s, 1H, NH–Me); 14.78 (s, 1H, N–NH) ppm. IR: 3300, 1620 (NH); 1655 (C=O); 1615, 1590, 1520 (C=C, C=N) cm^{-1}. Analysis: calc. for $C_{12}H_{15}N_3O_2$: C, 61.8; H, 6.5; N, 18.0%. Found: C, 61.8; H, 6.5; N, 18.1%.

*4.1.1.10. (Z)-1-(N-Methyl)-4,4-dimethyl-2-[(4-methoxyphenyl)hydrazono]-3-oxopentanamide (**3c**).* Yield, 55% (method A); mp, 144–146 °C. ^{1}H NMR ($CDCl_3$) δ: 1.41 (s, 9H, $C(Me)_3$), 2.88 (d, 3H, NMe, $^3J_{H–H}$ = 4.9 Hz), 3.82 (s, 3H, OMe), 6.92–7.31 (m, 4H, C_6H_4), 9.49 (br.s, 1H, NH–Me), 15.00 (s, 1H, N–NH) ppm. IR: 3280, 1615 (NH); 1645 (C=O); 1590, 1545, 1510 (C=C, C=N) cm^{-1}. Analysis: calc. for $C_{15}H_{21}N_3O_3$: C, 61.8; H, 7.3; N, 14.4%. Found: C, 62.0; H, 7.5; N, 14.6%.

*4.1.1.11. (Z)-1-(N-Methyl)-3-phenyl-2-[(4-methylphenyl)hydrazono]-3-oxopropanamide (**3d**).* Yield, 62% (method A); mp, 124–126 °C. ^{1}H NMR ($CDCl_3$) δ: 2.31 (s, 3H, Me), 2.97 (d, 3H, NMe, $^3J_{H–H}$ = 5.0 Hz); 7.04–7.12 (m, 4H, C_6H_4), 7.26–7.75 (m, 5H, Ph), 9.45 (br.s, 1H, NH–Me), 14.88 (s, 1H, N–NH) ppm. IR: 3325, 1610 (NH); 1640 (C=O); 1585, 1535, 1510 (C=C, C=N) cm^{-1}. Analysis: calc. for $C_{17}H_{18}N_3O_2$: C, 56.9; H, 4.8; N, 11.7%. Found: C, 57.0; H, 5.0; N, 11.5%.

4.1.2. The interaction of 2-arylhydrazono-3-oxo esters with methylamine

*4.1.2.1. 1-(N-Methyl)-4,4-difluoro-2-[(4-methyphenyl)hydrazono]-3-oxobutanamide (**6a**).* Yields, 72% (method A), 86% (method B); mp, 182–184 °C. ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 3H, Me); 2.94 (d, 3H, NMe, $^3J_{H–H}$ = 5.0 Hz); 6.83 (t, 1H, HCF_2, $^2J_{H–F}$ = 54.5 Hz); 7.21–7.33 (m, 4H, C_6H_4); 8.85 (br.s, 1H, NH–Me); 15.23 (s, 1H, N–NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −128.4 (d, 2F, HCF_2, $^2J_{F–H}$ = 54.5 Hz) ppm. IR: 3340, 1610 (NH); 1665 (C=O); 1590, 1545, 1515 (C=N, C=C); 1140–1050 (C–F) cm^{-1}. Analysis: calc. for $C_{12}H_{13}F_2N_3O_2$: C, 53.5; H, 4.9; F, 14.1; N, 15.6%. Found: C, 53.7; H, 4.8; F, 14.0; N, 15.5%.

*4.1.2.2. 1-(N-Methyl)-4,4,5,5-tetrafluoro-2-[(4-methoxyphenyl)hydrazono]-3-oxopentanamide (**6b**).* Yields, 69% (method A), 84% (method B); mp, 158–160 °C. ^{1}H NMR ($CDCl_3$) δ: 2.93 (d, 3H, NMe, $^3J_{H–H}$ = 5.0 Hz); 3.85 (s, 3H, OMe); 6.37 (tt, 1H, $H(CF_2)_2$, $^2J_{H–F}$ = 53.5, $^3J_{H–F}$ = 5.6 Hz); 6.97–7.52 (m, 4H, C_6H_4); 8.77 (br.s, 1H, NH–Me); 15.51 (s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −140.4 (dt, 2F, HCF_2, $^2J_{F–H}$ = 53.5, $^3J_{F–F}$ = 8.0 Hz); −120.2 (m, 2F, CF_2) ppm. IR: 3345, 1605 (NH); 1655 (C=O); 1590, 1555, 1510 (C=N, C=C); 1250–1155 (C–F) cm^{-1}. Analysis: calc. for $C_{13}H_{13}F_4N_3O_3$: C, 46.6 H, 3.9; F, 22.7; N, 12.5%. Found: C, 46.7; H, 3.6; F, 22.5; N, 12.6%.

*4.1.2.3. 1-(N-Methyl)-4,4,5,5,6,6,6-heptafluoro-2-[(4-methoxyphenyl)hydrazono]-3-oxohexanamide (**6c**).* Yield, 63% (method A), 85% (method B); mp, 117–119 °C. ^{1}H NMR ($CDCl_3$) δ: 2.93 (d, 3H, NMe, $^3J_{H–H}$ = 4.9 Hz); 3.84 (s, 3H, OMe); 6.95–7.52 (m, 4H, C_6H_4); 8.77 (br.s, 1H, NH–Me); 15.64 (s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −125.3 (m, 2F, CF_2), −112.3 (m, 2F, CF_2), −81.5 (m, 3F, CF_3) ppm. IR: 3350, 1605 (NH); 1655 (C=O); 1590, 1545, 1505 (C=N, C=C); 1200–1110 (C–F) cm^{-1}. Analysis: calc. for $C_{14}H_{12}F_7N_3O_3$: C, 41.7; H, 3.0; F, 33.0; N, 10.4%. Found: 41.5; H, 3.1; F, 33.3; N, 10.2%.

*4.1.2.4. 1-(N-Methyl)-4,4,5,5,6,6,7,7-octafluoro-2-[(4-methoxyphenyl)hydrazono]-3-oxoheptanamide (**6d**).* Yield, 68%; mp, 85–87 °C. ^{1}H NMR ($CDCl_3$) δ: 2.93 (d, 3H, NMe, $^3J_{H–H}$ = 4.9 Hz); 3.84 (s, 3H, OMe); 6.15 (tt, 1H, HCF_2, $^2J_{H–F}$ = 52.1, $^3J_{H–F}$ = 5.5 Hz); 6.95–7.40 (m, 4H, C_6H_4); 8.75 (br.s, 1H, NH–Me); 15.65 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 25.3 (C^{NMe}); 55.6 (C^{OMe}); 107.8 (tt, C^4, $^1J_{C–F}$ = 254.6, $^2J_{C–F}$ = 30.5 Hz); 110.3 (tt, C^5, $^1J_{C–F}$ = 255, $^2J_{C–F}$ = 31 Hz); 112.2 (tt, C^6, $^1J_{C–F}$ = 254.6, $^2J_{C–F}$ = 31 Hz); 114.9 (tt, C^6, $^1J_{C–F}$ = 254.6, $^2J_{C–F}$ = 31 Hz); 115.1 (C^o); 118.5 (C^p); 122.7 (C^m); 134.6 (C^i); 158.9 (C^2); 165.8 (C^1); 179.4 (t, C^3, $^2J_{C–F}$ = 22 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −138.2 (dm, 2F, HCF_2, $^2J_{F–H}$ = 52.1 Hz); −129.0 (m, 2F, CF_2); −122.0 (m, 2F, CF_2); −110.8 (m, 2F, CF_2) ppm. IR: 3360, 1610 (NH); 1665 (C=O); 1590, 1540, 1515 (C=N, C=C); 1255–1185 (C–F) cm^{-1}. Analysis: calc. for $C_{15}H_{13}F_8N_3O_3$: C, 41.4; H, 3.0; F, 34.9; N, 9.7%. Found: C, 41.5; H, 3.2; F, 34.7; N, 9.7%.

*4.1.2.5. 1-(N-Methyl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-[(4-methylphenyl)hydrazono]-3-oxoheptanamide (**6e**).* Yield, 87% (method B); mp, 117–119 °C. ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 3H, Me); 2.94 (d, 3H, NMe, $^3J_{H–H}$ = 4.9 Hz); 7.22–7.34 (m, 4H, C_6H_4); 8.73 (br.s, 1H, NH–Me); 15.52 (s, 1H, NH) ppm. ^{19}F NMR ($CDCl_3$) δ: −126.5 (m, 2F, CF_2), −121.9 (m, 2F, CF_2), −111.8 (m, 2F, CF_2), −82.0 (m, 3F, CF_3) ppm. IR: 3345, 1605 (NH); 1660 (C=O); 1595, 1550, 1505 (C=N,

C=C); 1200–1110 (C–F) cm^{-1}. Analysis: calc. for $C_{15}H_{12}F_9N_3O_2$: C, 41.2; H, 2.8; F, 39.1; N, 9.6%. Found: 41.3; H, 2.7.1; F, 39.3; N, 9.5%.

4.1.2.6. 1,1′-(N,N′-Dimethyl)-2-[(4-methylphenyl)hydrazono]-malondiamide (7). Yields, 56% [from ester **5e**] and 51% [from ester **5f**] (method A); mp, 84–86 °C. ^{1}H NMR ($CDCl_3$) δ: 2.33 (s, 3H, Me); 2.90 (d, 3H, NMe, $^3J_{H-H}$ = 5.0 Hz); 2.93 (d, 3H, NMe, $^3J_{H-H}$ = 5.0 Hz); 7.03 (br.s, 1H, NH–Me); 7.11–7.16 (m, 4H, C_6H_4); 9.78 (br.s, 1H, NH–Me); 14.25 (s, 1H, NH) ppm. IR: 3540, 3440, 1610 (NH); 1650 (C=O); 1590, 1540, 1510 (C=N, C=C) cm^{-1}. Analysis: calc. for $C_{12}H_{16}N_4O_2$: C, 58.1; H, 6.5; N, 22.6%. Found: C, 58.0; H, 6.5; N, 22.3%.

4.2. The synthesis of chelates

Method A. A solution of arylhydrazones **1a**,**b**,**d**,**j** or **5b**,**h** (3 mmol) and nickel(II) acetate (0.34 g, 1.5 mmol) in 40 mL ethanol was bubbled methylamine (gas) upon 40 °C (20 °C for esters **5b**,**h**). The resulting precipitate was filtered off. The compounds **4a**,**c**–**e** was isolated by column chromatography (chloroform as an eluent).

Method B. Nickel(II) acetate (1.35 g, 6 mmol) was added to the compound **2a** or **6a** (3 mmol) in DMF (1 mL) and ethanol (6 mL). The mixture was stirring for 1 h at 20 °C. The resulting residue was filtered off; aqueous ethanol (1:1) was used for washing of substance **4a**.

Method C. The 1% NaOH was added to the solution of the compound **2a** or **6c** (3 mmol) in ethanol (30 mL) to pH 9 of reaction mixture. Then copper(II) acetate (0.22 g, 1.5 mmol) in water (10 mL) was dropped to the mixture. It was stirring for 30 min at 20 °C. The resulting precipitate was filtered off; recrystallized from ethanol for compound **4b**.

*4.2.1. Bis-{1,1,1-trifluoro-4-[(N-methyl)aminato-κ^2N]-3-(phenyldiazenyl-κ^2N)pent-3-en-2-one}nickel(II) (**4a**)*

Yields, 82% (method A) and 73% (method B); mp, over 250 °C. ^{1}H NMR (DMF-d_7) δ: 2.58 (s, 3H, Me); 3.09 (s, 3H, NMe); 7.03–7.52 (m, 5H, Ph) ppm. ^{19}F NMR (DMF-d_7) δ: −67.5 (s, 3F, CF_3) ppm. IR: 1670 (C=O); 1595, 1560, 1500 (C=C, C=N); 1170–1150 (C–F) cm^{-1}. Analysis: calc. for $C_{24}H_{22}F_6N_6NiO_2$: C, 48.1; H, 3.7; F, 19.0; N, 14.0%. Found: C, 48.1; H, 3.5; F, 18.8; N, 14.0%.

*4.2.2. Bis-{1,1,1-trifluoro-4-[(N-methyl)aminato-κ^2N]-3-(phenyldiazenyl-κ^2N)pent-3-en-2-one}copper(II) (**4b**)*

Yield, 71% (method C); mp, 227–229 °C. IR: 1675 (C=O); 1600, 1580, 1550 (C=C, C=N); 1200–1100 (C–F) cm^{-1}. MS *m/z* (I_{rel}): 603 (4.46%) $[M]^+$. Analysis: calc. for $C_{24}H_{22}CuF_6N_6O_2$: C, 47.4; H, 3.7; F, 18.9; N, 13.9%. Found: C, 47.2; H, 3.6; F, 19.0; N, 14.1%.

*4.2.3. Bis-{1,1,2,2-tetrafluoro-5-[(N-methyl)aminato-κ^2N]-5-phenyl-4-[(4-methoxyphenyl)diazenyl-κ^2N]pent-4-en-3-one}nickel(II) (**4c**)*

Yield, 78% (method A); mp, over 250 °C. IR: 1665 (C=O); 1560, 1540, 1500 (C=C, C=N); 1175–1140 (C–F) cm^{-1}. Analysis: calc. for $C_{38}H_{32}F_8N_6NiO_4$: C, 53.9; H, 3.8; F, 17.9; N, 9.9%. Found: C, 53.8; H, 3.6; F, 17.8; N, 9.8%.

*4.2.4. Bis-{1,1,2,2,3,3,3-heptafluoro-6-[(N-methyl)aminato-κ^2N]-6-phenyl-5-[(4-methoxyphenyl)diazenyl-κ^2N]pent-5-en-4-one}nickel(II) (**4d**)*

Yield, 68% (method A); mp, over 250 °C. IR: 1660 (C=O); 1605, 1590, 1505 (C=C, C=N); 1250–1160 (C–F) cm^{-1}. Analysis: calc. for $C_{40}H_{30}F_{14}N_6NiO_4$: C, 48.9; H, 3.1; F, 27.1; N, 8.6%. Found: C, 48.8; H, 3.3; F, 27.2; N, 8.4%.

*4.2.5. Bis-{1,1,1-trifluoro-4-[(N-methyl)aminato-κ^2N]-4-phenyl-3-[(4-methylphenyl)diazenyl-κ^2N]but-3-en-2-one}nickel(II) (**4e**)*

Yield, 75% (method A); mp, over 250 °C. ^{1}H NMR ($CDCl_3$) δ: 2.30 (s, 3H, Me), 2.50 (s, 3H, NMe), 7.34–8.06 (m, 4H, C_6H_4) ppm. IR: 1665 (C=O); 1560, 1540, 1500 (C=C, C=N); 1175–1140 (C–F) cm^{-1}. Analysis: calc. for $C_{36}H_{30}F_6N_6NiO_2$: C, 57.6; H, 4.0; F, 15.2; N, 11.2%. Found: C, 57.2; H, 4.0; F, 15.0; N, 11.3%.

*4.2.6. Bis-{4,4-difluoro-N-methyl-3-oxo-2-[2-(4-methylphenyl)hydrazonato-κN]butanamide-κO}nickel(II) (**8a**)*

Yield, 68% (method B); mp, over 250 °C. IR: 3290, 1610 (NH); 1650 (C=O); 1590, 1550, 1505 (C=N, C=C); 1195–1130 (C–F) cm^{-1}. Analysis: calc. for $C_{24}H_{24}F_4N_6NiO_4$: C, 48.4; H, 4.1; F, 12.8; N, 14.1%. Found: C, 48.4; H, 4.0; F, 12.9; N, 14.2%.

*4.2.7. Bis-{4,4,5,5-tetrafluoro-N-methyl-3-oxo-2-[2-(4-methoxyphenyl)hydrazonato-κN]pentanamide-κO}nickel(II) (**8b**)*

Yield, 76% (method A); mp, over 250 °C. IR: 3290, 1605 (NH); 1625 (C=O); 1585, 1550, 1500 (C=N, C=C); 1250–1195 (C–F) cm^{-1}. Analysis: calc. for $C_{26}H_{24}F_8N_6NiO_6$: C, 42.9; H, 3.3; F, 20.9; N, 11.6%. Found: C, 43.0; H, 3.4; F, 20.8; N, 11.5%.

*4.2.8. Bis-{4,4,5,5,6,6,7,7,7-nonafluoro-N-methyl-3-oxo-2-[2-(4-methylphenyl)hydrazonato-κN]heptanamide-κO}nickel(II) (**8c**)*

Yield, 78% (method A); mp, over 250 °C. IR: 3295, 1595 (NH); 1630 (C=O); 1570, 1540, 1505 (C=N, C=C); 1200–1130 (C–F) cm^{-1}. Analysis: calc. for $C_{30}H_{22}F_{18}N_6NiO_4$: C, 38.7; H, 2.4; F, 36.7; N, 9.0%. Found: C, 38.6; H, 2.4; F, 36.56; N, 9.0%.

*4.2.9. Bis-{4,4,5,5,6,6,6-heptafluoro-N-methyl-3-oxo-2-[2-(4-methylphenyl)hydrazonato-κN]hexanamide-κO}copper(II) (**8d**)*

Yield, 80% (method C); mp, 213–215 °C. IR: 3300, 1610 (NH); 1635 (C=O); 1585, 1540, 1505 (C=N, C=C); 1235–1145 (C–F) cm^{-1}. MS *m/z* (I_{rel}): 867 (5.47%) $[M]^+$. Analysis: calc. for $C_{28}H_{22}CuF_{14}N_6O_6$: C, 38.8; H, 2.6; F, 30.6; N, 9.7%. Found: C, 38.9; H, 2.7; F, 30.4; N, 9.5%.

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