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Reactions of 2-Arylhydrazono-1,3-dicarbonyl Compounds with Ethylenediamine

O. G. Khudina, Ya. V. Burgart, N. V. Murashova, and V. I. Saloutin

Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia
e-mail: saloutin@ios.uran.ru

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Abstract—2-Arylhydrazono-1,3-diketones react with ethylenediamine to give, depending on the substituents, dihydro-1,4-diazepine derivative or *N*,*N*′-ethylenebis(1,3-aminovinyl ketones). Treatment of the latter with nickel(II) or copper(II) acetate results in formation of the corresponding metal chelates. Nickel complexes of *N*,*N*′-ethylenebis(1,3-aminovinyl ketones) can also be synthesized from 2-arylhydrazono-1,3-diketones and ethylenediamine on a metal template. Reactions of 2-arylhydrazono-3-oxo esters with ethylenediamine yield *N*,*N*′-ethylenebis(3-alkyl-2-arylhydrazono-3-oxopropionamides). Ethyl 2-arylhydrazonoacetoacetate reacts with ethylenediamine under mild conditions, affording ethyl 2-*p*-tolylazo-3-[2-(2-*p*-tolylhydrazono-1,3-dioxobutylamino)ethylamino]-2-butenoate.

Reactions of 1,3-dicarbonyl compounds with ethylenediamine could give rise to a variety of products. For example, 1,3-diketones, including those containing fluoroalkyl groups, react with ethylenediamine to afford either 1,4-diazepine derivatives [1, 2] or *N*,*N*′-ethylenebis(1,3-aminovinyl ketones) [3], depending on the reaction conditions. Costes *et al.* [4] reported on the formation of a monocondensation product, 1-amino-4-methyl-3-aza-4-hepten-6-one, from acetylacetone. 3-Oxo esters react with ethylenediamine to give heterocyclic compounds of the 1,4-diazepin-5-one [2, 5, 6] and imidazolidine series [6] or open-chain *N*-aminoethyl-3-oxo-3-polyfluoroalkylpropionamides [7] and dialkyl *N*,*N*′-ethylenebis(3-amino-2-butenoates) [5, 7], depending on the substituent nature and reaction conditions.

We previously synthesized fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds and found that their reactions with hydrazine hydrate, phenylhydrazine, thiosemicarbazide, and hydroxylamine lead to formation of such heterocyclic compounds as pyrazoles and isoxazoles [8]. We have found no published data on reactions of 2-arylhydrazono-1,3-diketones and -3-oxo esters with ethylenediamine.

The goal of the present work was to examine the reaction of fluorinated 2-arylhydrazono-1,3-diketones **I** and 2-arylhydrazono-3-oxo esters **II** with ethylenediamine and compare the behavior of these substrates with the behavior of nonfluorinated analogs. We have found that the reactions of fluorine-containing 2-arylhydrazono-1,3-diketones **Ia**–**Ic** with ethylenediamine take different pathways, depending on the structure of the fluorinated group. For example, 1,1-difluoro-3-*p*-tolylhydrazono-2,4-pentanedione (**Ia**) reacts with ethylenediamine in methanol at room temperature to give cyclization product, dihydro-1,4-diazepine **III**, while compounds **Ib** and **Ic** containing longer polyfluoroalkyl groups give rise to open-chain *N*,*N*′-ethylenebis(1,3-aminovinyl ketones) **IVb** and **IVc**, respectively (Scheme 1). The 1,4-diazepine structure of product **III** (rather than tetraazacyclotetradecatetraene structure which could be formed via 2 + 2-condensation) was confirmed by the mass spectra (see Experimental).

Unlike fluorinated compounds **Ib** and **Ic**, the reaction of 3-*p*-methoxyphenylhydrazono-2,4-pentanedione (**Id**) under analogous conditions resulted in formation of an intractable mixture of products. When the same reaction was carried out in diethyl ether, we succeeded in isolating *N*,*N*′-ethylenebis(4-amino-3-*p*-methoxyphenylhydrazono-3-penten-2-one) (**IVd**).

Compounds **IV** are products of condensation of two molecules of 2-arylhydrazono-1,3-diketone **I** at one carbonyl group with one molecule of ethylenediamine in which both amino groups are involved. The reactions with unsymmetrical fluoroalkyl-containing

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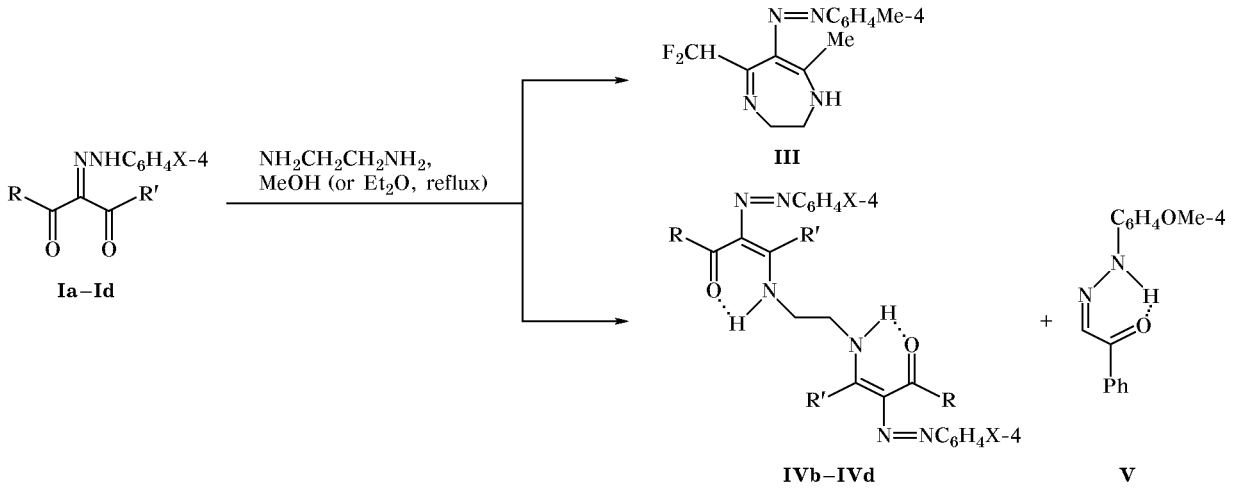
Scheme 1.

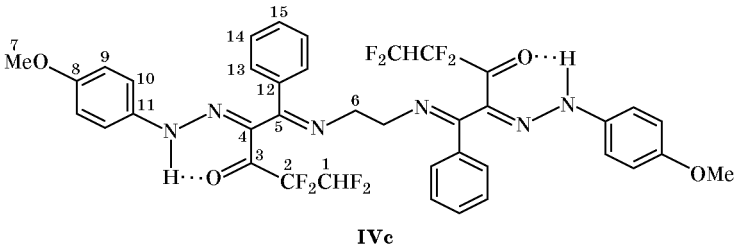


Ia, R = CHF_2, R′ = X = Me; **Ib**, **IVb**, R = $CHF_2(CF_2)_3$, R′ = X = Me; **Ic**, **IVc**, R = CHF_2CF_2, R′ = Ph, X = OMe; **Id**, **IVd**, R = R′ = Me, X = OMe.

2-arylhydrazono-1,3-diketones **I** can occur either at the carbonyl group attached to fluorinated substituent or at the carbonyl group linked to nonfluorinated moiety. The position of the ethylenediamine fragment in compounds **IVb** and **IVc** was determined by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of **IVc** (see below), the triplet signal ($^2J_{CF}$ = 23.3 Hz) from carbon atom at the tetrafluoroethyl group is located in the region typical of a carbonyl carbon atom rather than of a carbon atom at C=C bond [9]. This means that the diamine regioselectively attacks the carbonyl group neighboring to the nonfluorinated substituent. A similar pattern was observed in the reaction of ethylenediamine with fluorinated 1,3-diketones having no substituent in the 2-position [3]. According to the results of quantum-chemical calculations, electron-acceptor fluoroalkyl group induces a greater positive charge on the carbonyl carbon atom attached to nonfluorinated radical [10].

Compounds **IV** could give rise to keto–enol, azo–hydrazone, and amino–imino tautomerism; so that they can exist as four tautomers: keto–azo–amino (KAA), enol–azo–imino (EAI), keto–azo–imino (KAI), and keto–hydrazono–imino (KHI) (Scheme 2). In addition, the two 1,3-ketoamino fragments in molecules **IV** could occur in different tautomeric forms. However, as follows from the NMR data, molecules **IV** are symmetrical: we observed only one set of signals from both fluorinated (^{19}F) and hydrogen-containing (^1H) moieties. These data also indicate that in each case we have only one tautomeric form. The absence of a CH signal in the ^1H NMR spectrum rules out tautomer KAI. The ^{13}C NMR spectrum of **IVc** contains a downfield signal typical of a carbonyl carbon atom; therefore, this compound has structure KAA or KHI. It was impossible to distinguish between tautomers KAA and KHI on the basis of the available spectral data.

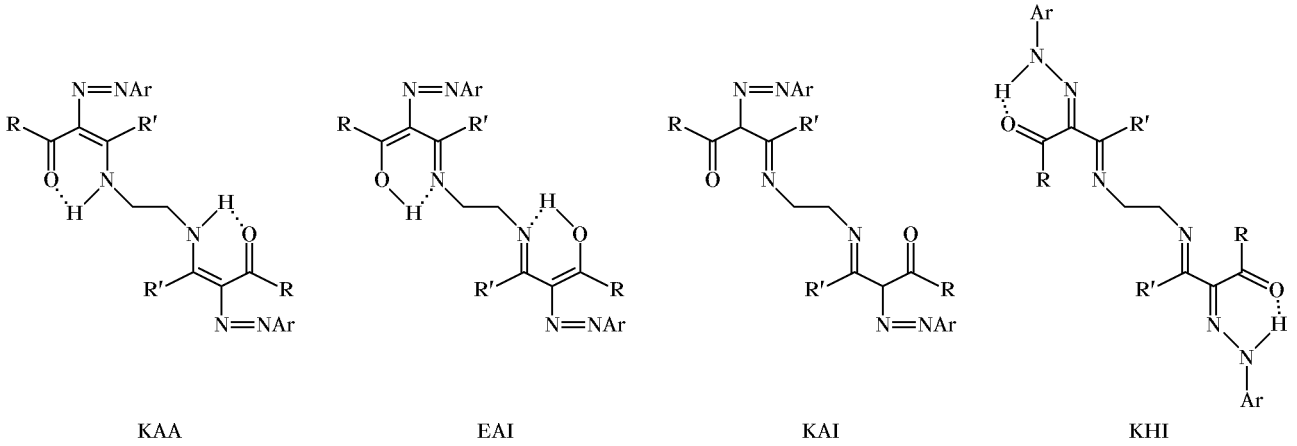
We obtained heterocyclization product, 1,4-diazepine **III**, only in the reaction of 1,1-difluoro-3-*p*-tolylhydrazono-2,4-pentanedione (**Ia**) with ethylenediamine. On the other hand, fusion of 1,3-diketones



IVc

^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 107.76–115.03 (C^1, C^2), 180.36 t (C^3, $^2J_{CF}$ = 23.3 Hz), 160.00 (C^4), 163.85 (C^5), 46.29 (C^6), 55.58 (C^7), 114.74–142.62 (C^8–C^{15}).

Scheme 2.



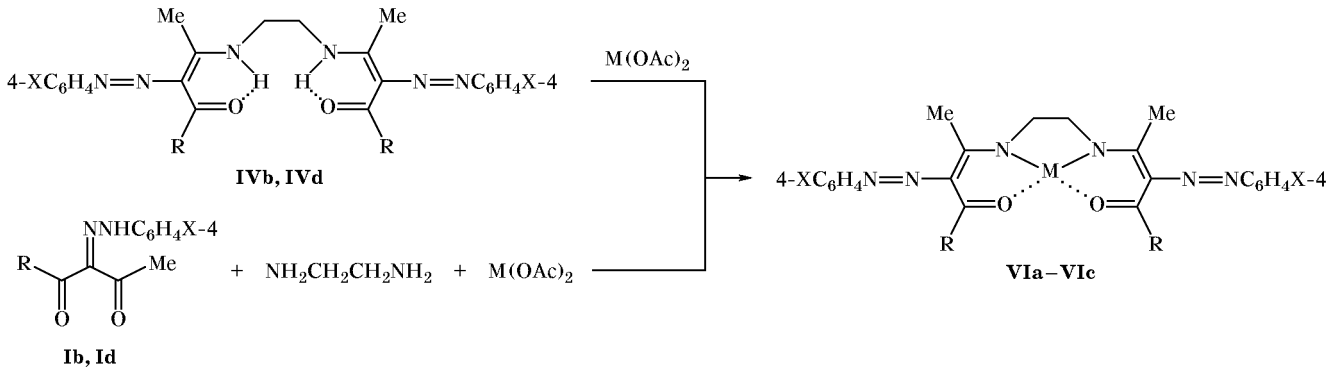
KAA EAI KAI KHI

having no substituent in the 2-position with ethylenediammmonium diperchlorate is known [2] to afford 1,4-diazepine derivatives [2]. 2-Arylhydrazono-1,3-diketones **I** were found to undergo tarring under these conditions. Our attempt to obtain diazepine derivative from 3-*p*-methoxyphenylhydrazono-2,4-pentanedione (**Id**) under the conditions ensuring cyclization of acetylacetone with ethylenediamine (heating in acid medium [1]) resulted in formation of open-chain 2:1 condensation product **IVd**.

Our experimental data inticate that 2-arylhydrazono-1,3-diketones **I** are less reactive toward ethylenediamine than their unsubstituted analogs. Reactions leading to formation of *N*,*N*′-ethylenebis(aminovinyl ketones) from 1,3-diketones are accompanied by heat evolution and are therefore carried out at reduced temperature [3]. 2-Arylhydrazono-1,3-diketones react with ethylenediamine at room temperature, and the conversion of the initial 1,3-diketone is often incomplete. Nevertheless, by-products are formed even under these conditions (TLC). One of the side processes is "acid" cleavage of the molecule of **I**. For instance, we isolated 2-*p*-methoxyphenylhydrazono-1-phenylethanone (**V**) from the product mixture obtained in the reaction of 2-arylhydrazono-1,3-diketone **Ic** with ethylenediamine.

Like unsubstituted analogs [3], *N*,*N*′-ethylenebis-(aminovinyl ketones) **IV** are capable of forming coordination compounds with transition metals. Treatment of compounds **IVb** and **IVd** with nickel or copper acetate gives the corresponding chelates **VIa**–**VIc** (Scheme 3). Related nickel complexes are often synthesized by the template method [11–13]. However, Martin and Olzewski [12] noted that tri- and hexafluoroacetylacetones react with ethylenediamine over a Ni(II) template to afford bis(1,3-diketonato)nickel complexes. According to the data of the same authors [12], no complex formation occurs with 2-phenyl(or methyl)-substituted 1,3-diketones for steric reasons. We have found that nickel complexes **VIb** and **VIc** can be prepared by a one-step template procedure from ethylenediamine and 2-arylhydrazono-1,3-di-

Scheme 3.



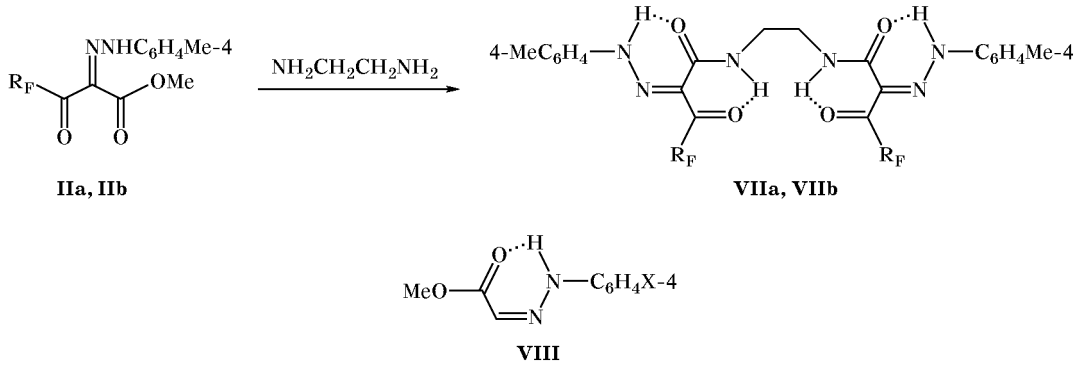
IVb, IVd

Ib, Id

VIa–VIc

Ib, **IVb**, **VIb**, R = $CHF_2(CF_2)_3$, X = Me; **VIa**, M = Cu; **VIb**, M = Ni; **Id**, **IVd**, **VIc**, R = Me, X = OMe; **VIc**, M = Ni.

Scheme 4.



IIa, IIb **VIIa, VIIb** **VIII**

IIa, **VIIa**, R_F = CHF_2CF_2; **IIb**, **VIIb**, R_F = C_4F_9.

ketones **Ib** and **Id** in the presence of nickel(II) acetate. Our attempts to synthesize *N*,*N*′-ethylenebis(aminovinyl ketone) **IVa** having a difluoromethyl group by template method were unsuccessful; instead, a large number of by-products were formed.

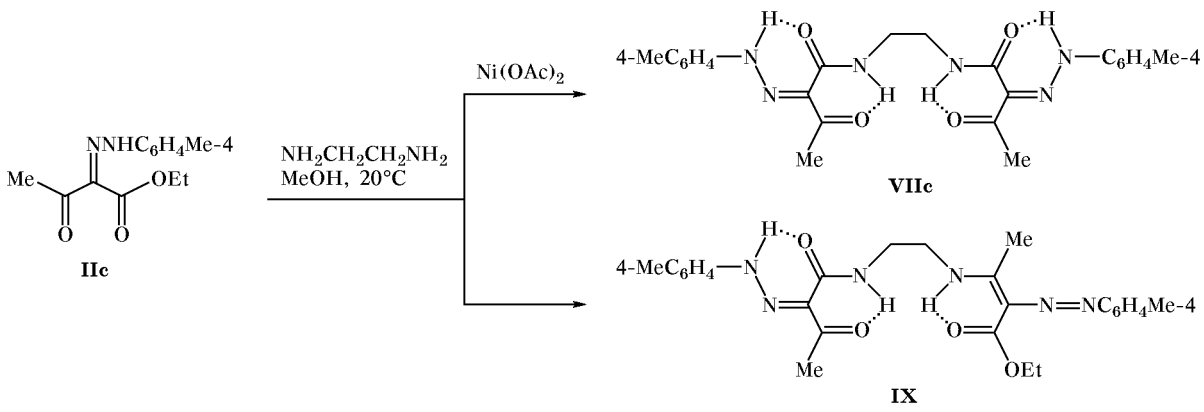
3-Oxo esters are capable of reacting with ethylenediamine at the ketone group [5, 7], ester fragment [7], or both these simultaneously [2, 5, 6]. We examined reactions of 2-arylhydrazono-3-oxo esters **IIa** and **IIb** with ethylenediamine and found that the products are bisamides **VIIa** and **VIIb** (Scheme 4). They are formed by condensation of one ethylenediamine molecule with two molecules of 3-oxo ester **II** at the ester group.

Unlike 2-arylhydrazono-1,3-diketones **I**, reactions of fluorine-containing 3-oxo esters **II** with ethylenediamine in diethyl ether, ethanol, and acetonitrile are accompanied by various side processes to a grater extent. The "acid" cleavage product, arylhydrazone **VIII**, was isolated in the reaction of 2-arylhydrazono-3-oxo ester **IIb** with ethylenediamine, performed in ethanol and diethyl ether.

Fluorinated 2-arylhydrazono-3-oxo esters **II** reacted with ethylenediamine dihydrochloride or the respective perchlorate in the presence of sodium acetate to give an inseparable mixture of products. We also failed to isolate any product from the reaction of ethylenediamine with difluoromethyl-containing 3-oxo ester. In contrast to fluorinated 2-arylhydrazono-3-oxo esters **IIa** and **IIb**, ethyl 2-*p*-tolylhydrazonoacetoacetate (**IIc**) reacted with ethylenediamine to afford compound **IX** (Scheme 5) which, like diamides **VII**, is formed by condensation of one ethylenediamine molecule with two molecules of **IIc**. However, one molecule of the ketoester reacts at the ester fragment, while the other, at the ketone carbonyl. We failed to establish which of the above fragments reacts first, i.e., our attempts to obtain 1 : 1 condensation product were unsuccessful. Even in the reaction with excess ethylenediamine in ethanol at 20°C, we isolated 2 : 1 condensation product **IX**.

It should be noted that under analogous conditions (kinetic control) ethyl acetoacetate reacts with amines at the ketone carbonyl [14], and its reaction with

Scheme 5.



IIc **VIIc** **IX**

ethylenediamine yields diethyl *N*,*N*′-ethylenebis-(3-amino-2-butenoate) [5]. We were thus the first to obtain a mixed condensation product from substituted ethyl acetoacetate. The structure of compound **IX** was confirmed by the data of elemental analysis and IR, ^{1}H NMR, and mass spectra.

As with fluorinated 2-arylhydrazono-3-oxo esters, heating of ester **IIc** with ethylenediamine in ethanol resulted in formation of a mixture of products which were difficult to identify. Under conditions of template synthesis (in the presence of Ni^{2+} ions in methanol at room temperature), from ethyl 2-*p*-tolylhydrazonoacetoacetate (**IIc**) and ethylenediamine we obtained free ligand **VIIc** (Scheme 5) instead of the expected chelate. Presumably, the metal ion orients the molecules of hydrazone **IIc** and ethylenediamine in a way most favorable for the condensation.

Like compounds **IV**, diamides **VII** can give rise to keto–enol, azo–hydrazone, and amide–imide tautomerism, but the number of theoretically possible tautomers increases to six (in addition, unsymmetrical tautomers could also be formed). However, analysis of the ^{1}H and ^{19}F NMR spectra of diamides **VIIa**–**VIIc** revealed the presence of only one symmetric structure. A combination of the IR and ^{1}H NMR spectral data suggests that this structure is keto–-hydrazono–amide. The ^{1}H NMR spectra of **VIIa**–**VIIc** lack signals from CH proton typical of arylazo structure. Their IR spectra contain two absorption bands in the region 1665–1640 cm^{-1}, which correspond to stretching vibrations of the ketone and amide carbonyl groups. The low-frequency shift of these bands is explained, on the one hand, by conjugation with the C=N bond and, on the other, by formation of intramolecular hydrogen bond with the arylhydrazone and ethylenediamine fragments. The existence of such hydrogen bonds is confirmed by the presence in the ^{1}H NMR spectra of **VIIa**–**VIIc** of two downfield broadened signals at δ at ~9 and ~15 ppm, which belong to the NH protons.

Thus, our results show that introduction of an arylhydrazono group into position *2* of 1,3-dicarbonyl compounds essentially affects their reactivity toward ethylenediamine. Unlike unsubstituted analogs, 2-arylhydrazono derivatives almost do not tend to undergo heterocyclizations but prefer to form with ethylenediamine open-chain 2:1 condensation products; fluorine-containing substrates react exclusively at the carbonyl group located in the nonfluorinated part of the molecule. The resulting *N*,*N*′-ethylenebis-(1,3-aminovinyl ketones) are promising as complexing agents.

EXPERIMENTAL

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} using a Specord 75IR spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 instrument at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C; the chemical shifts were measured relative to tetramethylsilane. The ^{19}F NMR spectra were recorded on a Tesla BS-587A instrument at 75 MHz with C_6F_6 as reference. The elemental compositions were determined on a Carlo Erba CHNS-OEA 1108 analyzer. The mass spectra were run on a Varian MAT-311A instrument.

5-Difluoromethyl-7-methyl-6-(*p*-tolylazo)-2,3-dihydro-1*H*-1,4-diazepine (III). *Method A.* 2-Arylhydrazono-1,3-diketone **Ia**, 254 mg (1 mmol), was dissolved in 8 ml of methanol, and 60 mg (1 mmol) of ethylenediamine was added. The mixture was kept for 24 h at room temperature, and the precipitate was filtered off and recrystallized from benzene–hexane (1:10). Yield of **III** 320 mg (60%), mp 172–173°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3430, 1590 (NH); 1625, 1555, 1535 (C=N, C=C, N=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.38 s (3H, CH_3), 2.54 s (3H, CH_3), 3.67 m (2H, CH_2), 4.11 m (2H, CH_2), 5.22 br.s (1H, NH), 6.68 t (1H, HCF_2, $^2J_{HF}$ = 56.0), 7.36 m (4H, C_6H_4). ^{19}F NMR spectrum ($CDCl_3$): δ_F 41.74 ppm, d (4F, $2CHF_2$, $^2J_{FH}$ = 56.0). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 279 (10.06) $[M+1]^+$, 278 (57.52) $[M]^+$, 131 (16.42), 130 (26.52), 120 (26.34) $[HN{=}NC_6H_4CH_3]^+$, 119 (31.09) $[N{=}NC_6H_4CH_3]^+$, 107 (19.91) $[M - NH{=}NC_6H_4Me - CF_2H]^+$, 104 (14.42) $[N{=}NC_6H_4]^+$, 91 (100) $[C_6H_4CH_3]^+$, 65 (13.74). Found, %: C 60.44; H 5.94; F 13.98; N 20.00. $C_{14}H_{16}F_2N_4$. Calculated, %: C 60.43; H 5.80; F 13.65; N 20.13.

***N*,*N*′-Ethylenebis[2-amino-5,5,6,6,7,7,8,8-octafluoro-3-(*p*-tolylazo)2-octen-5-one] (IVb).** Following method *A*, from 404 mg (1 mmol) of 1,3-diketone **Ib** and (30 mg, 0.5 mmol) of ethylenediamine, after recrystallization from benzene–hexane (1:10), we obtained 441 mg (53%) of compound **IVb**, mp 134–135°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3430, 1585 (NH); 1655 (C=O); 1600, 1585 (N=N, C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.29 s (6H, $2CH_3$), 2.59 s (6H, $2CH_3$), 3.92 s (4H, $2CH_2$), 6.20 t.t [2H, $2H(CF_2)_4$, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.7], 7.02 m (8H, $2C_6H_4$), 15.78 br.s (2H, 2NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): 24.58 d.t (4F, $2CHF_2$, $^2J_{FH}$ = 52.0, $^3J_{FF}$ = 7.9), 32.49 m (4F, $2CF_2$), 39.82 m (4F, $2CF_2$), 51.66 m (4F, $2CF_2$). Found, %: C 46.07;

H 3.44; F 36.62; N 10.14. $C_{32}H_{28}F_{16}N_6O_2$. Calculated, %: C 46.16; H 3.39; F 36.51; N 10.09.

***N*,*N*′-Ethylenebis[1-amino-4,4,5,5-tetrafluoro-2-(*p*-methoxyphenylazo)-1-phenyl-1-penten-3-one] (IVc).** Following method *A*, from 382 mg (1 mmol) of 1,3-diketone **Ic** and 30 mg (0.5 mmol) of ethylenediamine, after reprecipitation from chloroform with ethanol, we obtained 434 mg (55%) of compound **IVc**, mp 205–206°C. IR spectrum, ν, cm^{-1}: 3310, 1590 (NH); 1655 (C=O); 1550, 1500 (N=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.42 m (4H, $2CH_2$), 3.84 s (6H, $2OCH_3$), 6.30 t.t [2H, $2CHF_2CF_2$, $^2J_{HF}$ = 53.8, $^3J_{HF}$ = 5.6], 6.87–7.46 m (18H, $2C_6H_4$, $2C_6H_5$), 15.03 br.s (2H, 2NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): 25.20 d.t (4F, $2CHF_2$, $^2J_{FH}$ = 53.8, $^3J_{FF}$ = 7.9), 41.71 m (4F, $2CF_2$). Found, %: C 57.77; H 3.94; F 19.23; N 10.73. $C_{38}H_{32}F_8N_6O_4$. Calculated, %: C 57.87; H 4.09; F 19.27; N 10.66.

***N*,*N*′-Ethylenebis[4-amino-3-(*p*-methoxyphenylazo)-3-penten-2-one] (IVd).** *Method B.* Ethylenediamine, 30 mg (0.5 mmol), was added to a solution of 235 mg (1 mmol) of 1,3-diketone **Id** in 10 ml of diethyl ether, and the mixture was heated for 30 h under reflux. The precipitate was filtered off and recrystallized from acetone. Yield of **IVd** 65 mg (25%), mp 184–185°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3430, 1590 (NH); 1635 (C=O); 1570, 1490 (N=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.49 s (6H, $2CH_3$), 2.55 s (6H, $2CH_3$), 3.78 s (6H, $2OCH_3$), 3.84 s (4H, $2CH_2$), 6.91 m (8H, $2C_6H_4$). Found, %: C 63.05; H 6.77; N 16.75. $C_{26}H_{32}N_6O_4$. Calculated, %: C 63.40; H 6.55; N 17.06.

2-(*p*-Methoxyphenylhydrazono)-1-phenylethan-1-one (V) was synthesized from 382 mg (1 mmol) of 1,3-diketone **Ic** and 30 mg (0.5 mmol) of ethylenediamine, following method *A*. The product was purified by chromatography on a column charged with silica gel (100–250 μm) using chloroform as eluent. Yield 89 mg (35%), mp 107–108°C. IR spectrum, ν, cm^{-1}: 3050, 1555 (NH); 1610 (C=O); 1590, 1520, 1500 (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.82 s (3H, OCH_3), 6.91–7.99 m (9H, C_6H_4, C_6H_5), 7.68 s (1H, CH=), 14.67 br.s (1H, NH). Found, %: C 70.46; H 5.35; N 10.72. $C_{15}H_{14}N_2O_2$. Calculated, %: C 70.85; H 5.55; N 11.02.

[*N*,*N*′-Ethylenebis(1-amino-5,5,6,6,7,7,8,8-octafluoro-3-*p*-tolylazo-2-octen-4-onato)]copper(II) (VIa). *Method C.* Compound **IVb**, 416 mg (0.5 mmol), was dissolved on heating in 5 ml of ethanol, and a solution of 100 mg (0.5 mmol) of copper(II) acetate monohydrate in 3 ml of ethanol was added. The mixture was heated to the boiling point over a period of 10 min, 10 ml of water was added, and the precipitate was filtered off. The product was reprecipitated from chloroform with hexane. Yield 429 mg (96%), mp 164–165°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1660 (C=O); 1605, 1570, 1550, 1500 (N=N, C=C). Found, %: C 43.03; H 2.88; F 34.18; N 9.43. $C_{32}H_{26}CuF_{16}N_6O_2$. Calculated, %: C 42.99; H 2.93; F 34.00; N 9.40.

[*N*,*N*′-Ethylenebis(1-amino-5,5,6,6,7,7,8,8-octafluoro-3-*p*-tolylazo-2-octen-4-onato)]nickel(II) (VIb) was synthesized following method *C* from 416 mg (0.5 mmol) of compound **IVb** and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate. The product was purified by column chromatography using benzene as eluent. Yield 378 mg (85%), mp 190–191°C.

Method D. A mixture of 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate, 404 mg (1 mmol) of 1,3-diketone **Ib**, and 30 mg (0.5 mmol) of ethylenediamine in 10 ml of ethanol was heated for 3 h under reflux. The solvent was removed, and the residue was purified by column chromatography on silica gel (100–250 μm) using methylene chloride as eluent. Yield 289 mg (65%), mp 190–191°C. IR spectrum, ν, cm^{-1}: 1640 (C=O); 1570, 1535, 1490 (N=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.24 s (6H, $2CH_3$), 2.57 s (6H, $2CH_3$), 3.47 br.s (4H, $2CH_2$), 6.22 t.t [2H, $2CHF_2(CF_2)_3$, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.6], 6.98 m (8H, $2C_6H_4$). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): 24.45 d.t (4F, $2CHF_2$, $^2J_{FH}$ = 52.1, $^3J_{FF}$ = 7.9), 32.40 m (4F, $2CF_2$), 39.60 m (4F, $2CF_2$), 51.09 m (4F, $2CF_2$). Found, %: C 43.50; H 2.89; F 33.84; N 9.42. $C_{32}H_{26}F_{16}N_6NiO_2$. Calculated, %: C 43.22; H 2.95; F 34.18; N 9.45.

[*N*,*N*′-Ethylenebis(4-amino-3-*p*-methoxyphenylazo-3-penten-2-onato)]nickel(II) (VIc) was obtained following method *C* from 246 mg (0.5 mmol) of compound **IVd** and 124 mg (0.5 mmol) of nickel acetate tetrahydrate. The product was purified by reprecipitation from chloroform with hexane. Yield 261 mg (95%), mp 204–205°C. Complex **VIc** was also synthesized according to method *D* from 235 mg (1 mmol) of 1,3-diketone **Id**, 30 mg (0.5 mmol) of ethylenediamine, and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate. Purification by column chromatography on silica gel (100–250 μm) using chloroform as eluent gave 157 mg (57%) of the product with mp 204–205°C. IR spectrum, ν, cm^{-1}: 1630 (C=O); 1590, 1525, 1490 (N=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.41 s (6H, $2CH_3$), 2.53 s (6H, $2CH_3$), 3.75 s (6H, $2OCH_3$), 3.39 br.s (4H,

$2CH_2$), 6.87 m (8H, $2C_6H_4$). Found, %: C 56.55; H 5.40; N 15.40. $C_{26}H_{30}N_6NiO_4$. Calculated, %: C 56.86; H 5.51; N 15.30.

***N*,*N*′-Ethylenebis[4,4,5,5-tetrafluoro-3-oxo-2-(*p*-tolylhydrazono)pentanamide] (VIIa)** was synthesized following method *A* from 320 mg (1 mmol) of 3-oxo ester **IIa** and 30 mg (0.5 mmol) of ethylenediamine. The product was purified by reprecipitation from acetone with methanol. Yield 306 mg (48%), mp 190–191°C. IR spectrum, ν, cm^{-1}: 3320, 1580 (NH); 1660, 1650 (C=O); 1620, 1550 sh, 1505 (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.38 s (6H, $2CH_3$), 3.61 m (4H, $2CH_2$), 6.35 t.t [2H, $2CHF_2CF_2$, $^2J_{HF}$ = 53.4, $^3J_{HF}$ = 5.5], 7.27 m (8H, $2C_6H_4$), 9.02 br.s and 15.27 br.s (4H, 4NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): 25.59 d.t (4F, $2CHF_2$, $^2J_{FH}$ = 53.4, $^3J_{FF}$ = 7.9), 42.72 m (4F, $2CF_2$). Found, %: C 48.95; H 4.05; F 23.80; N 13.19. $C_{26}H_{24}F_8N_6O_4$. Calculated, %: C 49.06; H 3.80; F 23.88; N 13.20.

***N*,*N*′-Ethylenebis[4,4,5,5,6,6,7,7,7-nonafluoro-3-oxo-2-(*p*-tolylhydrazono)heptanamide] (VIIb)** was synthesized following method *A* from 438 mg (1 mmol) of 3-oxo ester **IIb** and 30 mg (0.5 mmol) of ethylenediamine. Recrystallization from ethanol gave 166 mg (38%) of the product with mp 76–78°C. IR spectrum, ν, cm^{-1}: 3330, 1575 (NH); 1665, 1650 (C=O); 1515 sh, 1500 (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.37 s (6H, $2CH_3$), 3.62 m (4H, $2CH_2$), 7.28 m (8H, $2C_6H_4$), 9.03 br.s (2H, 2NH), 15.39 br.s (2H, 2NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): 36.59 m (4F, CF_2), 41.14 m (4F, $2CF_2$), 51.21 m (4F, $2CF_2$), 80.93 m (6F, $2CF_3$). Found, %: C 41.02; H 2.50; F 39.00; N 9.48. $C_{30}H_{22}F_{18}N_6O_4$. Calculated, %: C 41.30; H 2.54; F 39.19; N 9.63.

***N*,*N*′-Ethylenebis[3-oxo-2-(*p*-tolylhydrazono)-butanamide] (VIIc).** A mixture of 8 ml of methanol, 249 mg (1 mmol) of nickel(II) acetate tetrahydrate, 496 mg (2 mmol) of 3-oxo ester **IIc**, and 60 mg (1 mmol) of ethylenediamine was kept for 24 h at room temperature. The precipitate was filtered off and purified by chromatography on silica gel (100–250 μm) using chloroform as eluent. Yield of amide **VIIc** 260 mg (56%), mp 216–218°C. IR spectrum, ν, cm^{-1}: 3225, 1575 (NH); 1645 sh, 1640 (C=O); 1610, 1510, 1500 sh (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.35 s (6H, $2CH_3$), 2.49 s (6H, $2CH_3$), 3.57 m (4H, $2CH_2$), 7.23 m (8H, $2C_6H_4$), 9.57 br.s and 14.69 br.s (4H, 4NH). Found, %: C 62.30; H 6.19; N 18.29. $C_{24}H_{28}N_6O_4$. Calculated, %: C 62.05; H 6.08; N 18.09.

Methyl 2-(*p*-tolylhydrazono)etanoate (VIII). Following method *A*, from 320 mg (1 mmol) of ester **IIb** and 30 mg (0.5 mmol) of ethylenediamine in ethanol (or diethyl ether), after recrystallization from benzene–hexane (1:1), we obtained 104 mg (54%) of compound **VIII**, mp 177–178°C. IR spectrum, ν, cm^{-1}: 3240 (NH); 1690 (C=O); 1530, 1500 (C=N, C=C). ^1H NMR spectrum (DMSO-d_6/CCl_4), δ, ppm (*J*, Hz): 2.26 s (3H, $CH_3C_6H_4$), 3.72 s (3H, OCH_3), 7.01 m (4H, C_6H_4), 7.10 s (1H, CH=), 11.02 br.s (1H, NH). Found, %: C 62.47; H 6.23; N 14.81. $C_{10}H_{12}N_2O_2$. Calculated, %: C 62.49; H 6.29; N 14.57.

Ethyl 2-*p*-tolylazo-3-[2-(2-*p*-tolylhydrazono-1,3-dioxobutylamino)ethylamino]-2-butenoate (IX). Following method *A*, from 248 mg (1 mmol) of ester **IIc** and 30 mg (0.5 mmol) of ethylenediamine, after recrystallization from acetone, we isolated 106 mg (43%) of compound **IX**, mp 139–140°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3450, 3250 (NH); 1680, 1640 (C=O); 1575, 1500 (C=N, C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.38 t (3H, OCH_2CH_3, *J* = 7.1), 2.31 s (3H, CH_3), 2.34 s (3H, CH_3), 2.36 s (3H, CH_3), 2.44 s (3H, CH_3), 3.68 m (2H, CH_2), 3.76 m (2H, $2CH_2$), 4.30 q (2H, OCH_2, *J* = 7.1), 7.09–7.34 m (8H, $2C_6H_4$), 9.65 br.s (1H, NH), 14.60 br.s (1H, NH), 15.19 br.s (1H, NH). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 493 (20.24) $[M + 1]^+$, 492 (67.23) $[M]^+$, 246 (13.93) $[CH_3C(=O)C(=NNHC_6H_4CH_3)C(=O)NHCH_2CH_2]^+$ or $[C_2H_5OC(=O)C(=NNHC_6H_4CH_3)C(CH_3)=N]^+$, 155 (13.78) $[CH_3C(=O)C(=NNH_2)C(=O)NHCH=CH_2]^+$ or $[C_2H_5OC(=O)CH=C(CH_3)NHCH=CH_2]^+$, 132 (12.44) $[CH_2=NN=C_6H_4=CH_2]^+$, 119 (41.51) $[N=NC_6H_4CH_3]^+$, 109 (13.05), 107 (75.23) $[H_2NC_6H_4CH_3]^+$, 106 (100) $[NHC_6H_4CH_3]^+$, 97 (12.02) $[HC(=N)C(=O)NHCH=CH_2]^+$ or $[CH_2=N-CH=CHNHC(=O)]^+$, 91 (83.88) $[C_6H_4CH_3]^+$, 79 (12.26). Found, %: C 63.71; H 6.60; N 17.17. $C_{26}H_{32}N_6O_4$. Calculated, %: C 63.40; H 6.55; N 17.06.

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