ISSN 1070-3632, Russian Journal of General Chemistry, 2020, Vol. 90, No. 5, pp. 815–821. © Pleiades Publishing, Ltd., 2020.
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Reactions of *N*'-[2-Oxo-5-R-furan-3(2*H*)-ylidene]acylhydrazides with Primary and Secondary Alcohols

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Received December 13, 2019; revised December 13, 2019; accepted December 22, 2019

Abstract—Reactions of primary and secondary alcohols with *N*'-[2-oxo-5-R-furan-3(2*H*)-ylidene]acylhydrazides resulted in the furan ring decylization to form 2-[2-(arylcarbonyl)hydrazinylidene]-4-alkyl esters of R-4-oxobutanoic acids.

Keywords: *N*'-[2-oxo-5-R-furan-3(2*H*)-ylidene]acylhydrazides, alkyl esters of 2-[2-(arylcarbonyl)hydrazinylidene]-4-R-4-oxobutanoic acids, primary and secondary alcohols

DOI: 10.1134/S1070363220050096

3-Hydrazinylidene(imino)-3*H*-furan-2-ones containing several reaction sites are widely used as polyfunctional synthons in the preparation of acyclic and heterocyclic compounds [1–5]. Reactions of *N*'-[2-oxofuran-3(2*H*)-ylidene]acylhydrazides [6, 7] have been studied only with primary aromatic and heterocyclic amines [8, 9]. To continue the study of the reactivity of *N*'-[2-oxofuran-3(2*H*)-ylidene]aroylhydrazides **1a**–**1i**, herein we investigated their reaction with OH nucleophiles.

Decyclization of the furan ring in compounds **1a**–**1i** upon the action of primary and secondary alcohols proceeds only in the presence of catalytic amounts of triethylamine and leads to the formation of the corresponding alkyl 2-[2-(arylcarbonyl)hydrazinylidene]-4-R-4-oxobutanoates **2a**–**2a'**, existing in solutions as a mixture of tautomeric forms (Scheme 1).

The obtained compounds **2a**–**2a'** are colorless or yellow crystalline substances, soluble in dimethyl sulfoxide, dimethylformamide, poorly soluble in isopropyl alcohol, insoluble in water and hexane.

The IR spectra of the synthesized compounds show absorption bands of stretching vibrations of N–H bonds in (3380–3145 cm^{-1}), an ester carbonyl group (1745–1666 cm^{-1}), and C=N bond (1642–1574 cm^{-1}).

The data of ^1H NMR spectra of the obtained compounds indicate their existence in DMSO-d_6 solution in the form of two hydrazone forms **A** (6–86%) and **B** (2–69%), as well as cyclic form **C** (6–92%), except for compounds **2e**, **2j**, **2q**, and **2t**. These compounds exist in DMSO-d_6 solution as a mixture of hydrazone form **A** and cyclic form **B**. The spectrum of hydrazone form **A** contains the proton signal of the methylene group at 4.07–4.65 ppm and the proton signal of the NH group at 11.07–11.45 ppm. The proton signal of the methylene group of hydrazone **C** is located at 3.86–4.42 ppm; the proton signal of the amino group is recorded at 12.77–13.05 ppm. In the NMR spectrum of cyclic form **C**, two asymmetric doublet signals of the protons of the methylene group are observed at 2.91–3.32 and 3.31–3.46 ppm, and the signal of the proton of the semi-acetal hydroxyl group is in the form of a singlet in the range of 5.73–7.33 ppm or in the field of aromatic protons.

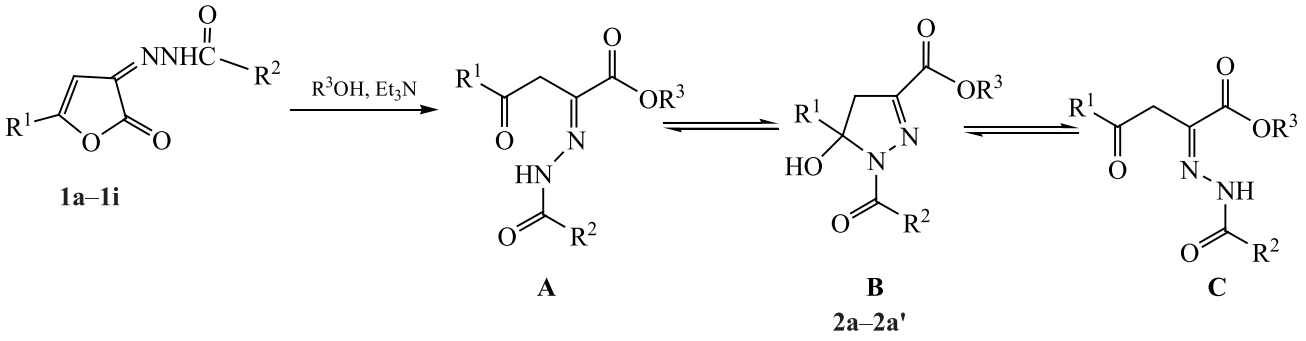
The mass peak of the molecular ion $[M]^+$, *m*/z 395(9.0), and peaks of fragment ions confirming the proposed structure are present in the mass spectrum of compound **2l**.

In summary, the decyclization reaction of *N*'-[2-oxo-5-R-furan-3(2*H*)-ylidene]acylhydrazides under the action of nucleophilic reagents opens up wide possibilities in the synthesis of new derivatives of acylpyruvic acids with potential biological activity.

EXPERIMENTAL

IR spectra were recorded on an FSM-1201 instrument from mineral oil. NMR spectra were recorded on a Bruker

Scheme 1.



R^1 = *t*-Bu (**1a**, **2a**, **2e**, **2i**, **2j**, **2l**, **2u**, **2z**), Ph (**1b 2b**, **2f**, **2j**, **2m**, **2v**), 4-MePh (**1c**, **2g**, 2**n**, **2w**, **2a'**), 4-MeOPh (**1d**, **2c**, **2o**, **2x**), 4-EtOPh (**1e**, **2p**), 3,4-$(MeO)_2$Ph (**1f**, **2q**), 4-BrPh (**1g**, **2d**, **2h**, **2k**, **2r**), 4-FPh (**1h**, **2s**), 4-ClPh (**1i**, **2t**, **2y**); R^2 = Ph (**2a**–**2k**), 2-$PhNHC_6H_4$ (**2l**–**2a'**); R^3 = Me (**2a**–**2d**, **2l**–**2t**), Et (**2e**–**2h**, **2u**–**2y**), $CH(CH_3)_2$ (**2i**–**2k**, **2z**, **2a'**).

Avance III instrument from DMSO-d_6 solutions operating at 400 (^{1}H) and 100 MHz (^{13}C). Purity of the obtained compounds and the reaction progress were monitored by TLC on Sorbfil PTC P-A-UV-254 plates, eluting with diethyl ether–benzene–acetone system (10 : 9 : 1) and detecting with iodine vapor. Elemental analysis was performed on a Leco CHNS-932 instrument. Melting (decomposition) temperatures were determined on an SMP40 instrument. The obtained elemental analysis data correspond to the calculated ones.

Alkyl 2-[(2-arylcarbonyl)hydrazinylidene]-4-oxo-4-R-butanoates 2a–2a'. To a suspension of 0.01 mol of the corresponding 3-hydrazinylidenefuran-2(3*H*)-one were added 20 mL of primary or secondary alcohol and 0.001 mol of triethylamine (catalyst). The mixture was heated for 10–30 min at 64–83°C. After cooling to 0°C, the precipitate was filtered off and recrystallized from propan-2-ol.

Methyl 5,5-dimethyl-4-oxo-2-[2-(phenylcarbonyl)-hydrazinylidene]hexanoate (2a). Yield 0.78 g (51%), yellow crystals, mp 153–154°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3310, 1745, 1705, 1672, 1600. ^{1}H NMR spectrum, δ, ppm: form **A** (71%), 1.17 s (9H, *t*-Bu), 3.71 s (3H, MeO), 4.11 s (2H, CH_2), 7.67 m (5H, H_{Ar}), 11.07 s (NH); form **B** (11%), 1.05 s (9H, *t*-Bu), 2.97 d (1H, C^4H_2, J = 20.0 Hz), 3.45 d (1H, C^4H_2, J = 20.0 Hz), 3.73 s (3H, MeO), 6.33 br. s (1H NMR spectrum, OH), 7.67 m (5H, H_{Ar}); form **C** (18%), 1.15 s (9H, *t*-Bu), 3.78 s (3H, MeO), 3.86 s (2H, CH_2), 7.67 m (5H, H_{Ar}), 12.77 br. s (1H NMR spectrum, NH). Found, %: C 63.14; H 6.62; N 9.20. $C_{16}H_{20}N_2O_4$. Calculated, %: C 63.16; H 6.60; N 9.22.

Methyl 4-oxo-4-phenyl-2-[2-(phenylcarbonyl)-hydrazinylidene]butanoate (2b). Yield 0.94 g (58%), colorless crystals, mp 140–141°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3335, 3269, 1721, 1687, 1637, 1590. ^{1}H NMR spectrum, δ, ppm: form **A** (13%), 3.76 s (3H, MeO), 4.65 s (2H, CH_2), 7.63 m (10H, H_{Ar}), 11.40 br. s (1H, NH); form **B** (74%), 3.32 d (1H, C^4H_2, J = 20.0 Hz), 3.38 d (1H, C^4H_2, J = 20.0 Hz), 3.80 s (3H, MeO), 7.28 br. s (1H, OH), 7.63 m (10H, H_{Ar}); form **C** (13%), 3.79 s (3H, MeO), 4.42 s (2H, CH_2), 7.63 m (10H, H_{Ar}), 13.01 s (1H, NH). Found, %: C 66.67; H 4.94; N 8.64. $C_{18}H_{16}N_2O_4$. Calculated, %: C 66.65; H 4.96; N 8.61.

Methyl 4-(4-methoxyphenyl)-4-oxo-2-[2-(phenyl-carbonyl)hydrazinylidene]butanoate (2c). Yield 0.96 g (54%), yellow crystals, mp 143–145°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3231, 3145, 1721, 1658, 1603. ^{1}H NMR spectrum, δ, ppm: form **A** (59%), 3.76 s (3H, MeO), 4.59 s (2H, CH_2), 7.55 m (9H, H_{Ar}), 11.25 s (1H, NH); form **B** (36%), 3.28 d (1H, C^4H_2, J = 20.0 Hz), 3.40 d (1H, C^4H_2, J = 20.0 Hz), 3.88 s (3H, MeO), 7.55 m (10H, H_{Ar} + OH); form **C** (5%), 3.79 s (3H, MeO), 4.35 s (2H, CH_2), 7.55 m (9H, H_{Ar}), 12.98 br. s (1H, NH). Found, %: C 64.40; H 5.12; N 7.91. $C_{19}H_{18}N_2O_5$. Calculated, %: C 64.42; H 5.15; N 7.93.

Methyl 4-(4-bromophenyl)-4-oxo-2-[2-(phenyl-carbonyl)hydrazinylidene]butanoate (2d). Yield 1.25 g (62%), colorless crystals, mp 148–150°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3310, 1718, 1638, 1586. ^{1}H NMR spectrum, δ, ppm: form **A** (15%), 3.74 s (3H, MeO), 4.59 s (2H, CH_2), 7.60 m (9H, H_{Ar}), 11.25 s (1H NMR spectrum, NH); form **B** (83%), 3.31 d (1H, C^4H_2, J = 20.0 Hz), 3.37 d (1H, C^4H_2, J = 20.0 Hz), 3.78 s (3H, MeO), 7.26 s (1H, OH), 7.60 m

(9H, H_{Ar}); form **C** (2%), 3.77 s (3H, MeO), 4.34 s (2H, CH_2), 7.60 m (9H, H_{Ar}), 12.86 br. s (1H, NH). Found, %: C 53.62; H 3.75; N 6.95. $C_{18}H_{15}BrN_2O_4$. Calculated, %: C 53.64; H 3.73; N 6.97.

Ethyl 5,5-dimethyl-4-oxo-2-[2-(phenylcarbonyl)-hydrazinylidene]hexanoate (2e). Yield 0.81 g (52%), colorless crystals, mp 130–131°C (propan-2-ol). ^{1}H NMR spectrum, δ, ppm: form **A** (88%), 1.18 s (9H, *t*-Bu), 1.24 t (3H, Me, *J* = 7.0 Hz), 4.13 s (2H, CH_2), 4.18 q (2H, CH_2, *J* = 7.0 Hz), 7.63 m (5H, H_{Ar}), 11.27 s (1H, NH); form **B** (12%), 1.06 s (9H, *t*-Bu), 1.20 t (3H, Me, *J* = 7.0 Hz), 2.95 d (1H, C^4H_2, *J* = 20.0 Hz), 3.46 d (1H, C^4H_2, *J* = 20.0 Hz), 4.20 q (2H, CH_2, *J* = 7.0 Hz), 7.67 m (6H, H_{Ar} + OH). ^{13}C NMR spectrum, δ_C, ppm: 13.89, 25.52, 25.93, 35.85, 43.93, 60.94, 61.15, 103.05, 127.70, 128.08, 128.80, 130.82, 131.79, 141.96, 133.16, 163.79, 209.88. Found, %: C 64.13; H 6.97; N 8.80. $C_{17}H_{22}N_2O_4$. Calculated, %: C 64.15; H 6.94; N 8.83.

Ethyl 4-oxo-4-phenyl-2-[2-(phenylcarbonyl)hydrazinylidene]butanoate (2f). Yield 0.93 g (55%), yellow crystals, mp 98–100°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3358, 1709, 1638, 1588. ^{1}H NMR spectrum, δ, ppm: form **A** (17%), 3.77 t (3H, Me, *J* = 7.1 Hz), 4.60 s (2H, CH_2), 7.62 m (10H, H_{Ar}), 11.30 s (1H, NH); form **B** (48%), 3.28 d (1H, C^4H_2, *J* = 20.0 Hz), 3.36 d (1H, C^4H_2, *J* = 20.0 Hz), 7.17 s (OH), 7.62 m (10H, H_{Ar}); form **C** (35%), 1.14 t (3H, Me, *J* = 7.1 Hz), 4.36 s (2H, CH_2), 7.62 m (10H, H_{Ar}), 12.95 br. s (1H, NH). Found, %: C 67.45; H 5.36; N 8.28. $C_{19}H_{18}N_2O_4$. Calculated, %: C 67.47; H 5.33; N 8.29.

Ethyl 4-(4-methylphenyl)-4-oxo-2-[2-(phenylcarbonyl)hydrazinylidene]butanoate (2g). Yield 0.99 g (56%), yellow crystals, mp 119–120°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3236, 3145, 1715, 1683, 1662, 1605. ^{1}H NMR spectrum, δ, ppm: form **A** (36%), 1.23 m (3H, Me), 2.29 s (3H, Me), 4.23 m (2H, CH_2), 4.57 s (2H, CH_2), 7.57 m (9H, H_{Ar}), 11.30 s (1H, NH); form **B** (54%), 1.23 m (3H, Me), 2.40 s (3H, Me), 3.26 d (1H, C^4H_2, *J* = 20.0 Hz), 3.34 d (1H, C^4H_2, *J* = 20.0 Hz), 4.23 m (2H, CH_2), 7.07 br. s (OH), 7.57 m (9H, H_{Ar}); form **C** (10%), 1.14 t (3H, Me, *J* = 20.0 Hz), 2.34 s (3H, Me), 4.23 m (2H, CH_2), 4.32 s (2H, CH_2), 7.57 m (9H, H_{Ar}), 12.95 br. s (1H, NH). Found, %: C 68.17; H 5.72; N 7.95. $C_{20}H_{20}N_2O_4$. Calculated, %: C 68.19; H 5.70; N 7.92.

Ethyl 4-(4-bromophenyl)-4-oxo-2-[2-(phenylcarbonyl)hydrazinylidene]butanoate (2h). Yield 1.38 g (66%), yellow crystals, mp 106–107°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3358, 1710, 1637, 1588. ^{1}H NMR spectrum, δ, ppm: form **A** (13%), 1.24 m (3H, Me), 4.23 m (2H, CH_2), 4.58 s (2H, CH_2), 7.63 m (9H, H_{Ar}), 11.30 s (1H, NH); form **B** (85%), 1.24 m (3H, Me), 3.31 d (1H, C^4H_2, *J* = 20.0 Hz), 3.36 d (1H, C^4H_2, *J* = 20.0 Hz), 4.23 m (2H, CH_2), 7.33 s (OH), 7.63 m (9H, H_{Ar}); form **C** (2%), 1.14 t (3H, Me, *J* = 20.0 Hz), 4.23 m (2H, CH_2), 4.35 s (2H, CH_2), 7.63 m (9H, H_{Ar}), 12.94 br. s (1H, NH). Found, %: C 54.69; H 4.11; N 6.71. $C_{19}H_{17}BrN_2O_4$. Calculated, %: C 54.66; H 4.14; N 6.73.

Isopropyl 5,5-dimethyl-4-oxo-2-[2-(phenylcarbonyl)hydrazinylidene]hexanoate (2i). Yield 1.01 g (61%), colorless crystals, mp 95–96°C (propan-2-ol). ^{1}H NMR spectrum, δ, ppm: form **A** (25%), 1.28 m (15H, *t*-Bu, 2Me), 4.12 s (2H, CH_2), 5.09 m (1H NMR spectrum, CH), 7.70 m (5H, H_{Ar}), 11.08 s (1H, NH); form **B** (6%), 1.10 s (9H, *t*-Bu), 1.21 m (6H, 2Me), 2.98 d (1H, C^4H_2, *J* = 20.0 Hz), 3.45 d (1H, C^4H_2, *J* = 20.0 Hz), 4.23 m (2H, CH_2), 5.09 m (1H, CH), 5.76 br. s (OH), 7.70 m (5H, H_{Ar}); form **C** (69%), 1.21 m (15H, *t*-Bu, 2Me), 3.89 s (2H, CH_2), 5.09 m (1H, CH), 7.70 m (5H, H_{Ar}), 12.96 br. s (1H, NH). Found, %: C 65.04; H 7.28; N 8.43. $C_{18}H_{24}N_2O_4$. Calculated, %: C 65.06; H 7.25; N 8.46.

Isopropyl 4-oxo-4-phenyl-2-[2-(phenylcarbonyl)-hydrazinylidene]butanoate (2j). Yield 1.06 g (60%), yellow crystals, mp 95–96°C (propan-2-ol). ^{1}H NMR spectrum, δ, ppm: form **A** (17%), 1.21 d (6H, 2Me, *J* = 6.3 Hz), 4.59 s (2H, CH_2), 4.99 m (1H, CH), 7.63 m (10H, H_{Ar}), 11.29 s (1H, NH); form **B** (51%), 1.25 t (6H, 2Me, *J* = 5.9 Hz), 3.27 d (1H, C^4H_2, *J* = 20.0 Hz), 3.35 d (1H, C^4H_2, *J* = 20.0 Hz), 5.06 t. d (1H, CH, *J* = 6.2, 4.1 Hz), 7.16 br. s (OH), 7.63 m (10H, H_{Ar}); form **C** (32%), 1.14 d (6H, 2Me, *J* = 6.3 Hz), 4.33 s (2H, CH_2), 5.06 t. d (1H, CH, *J* = 6.2 Hz), 7.63 m (10H, H_{Ar}), 13.01 s (1H, NH). Found, %: C 68.14; H 5.75; N 7.98. $C_{20}H_{20}N_2O_4$. Calculated, %: C 68.16; H 5.73; N 7.96.

Isopropyl 4-(4-bromophenyl)-4-oxo-2-[2-(phenylcarbonyl)hydrazinylidene]butanoate (2k). Yield 1.38 g (64%), yellow crystals, mp 116–117°C (propan-2-ol). ^{1}H NMR spectrum, δ, ppm: form **A** (23%), 1.21 d (6H, 2Me, *J* = 6.3 Hz), 4.56 s (2H, CH_2), 4.99 m (1H, CH), 7.62 m (9H, H_{Ar}), 11.19 s (1H, NH); form **B** (71%),1.25 m (6H, 2Me), 3.29 d (1H, C^4H_2, *J* = 20.0 Hz), 3.34 d (1H, C^4H_2, *J* = 20.0 Hz), 5.05 m (1H, CH), 7.31 br. s (OH), 7.62 m (9H, H_{Ar}); form **C** (6%), 1.14 d (6H, 2Me, *J* = 6.3 Hz), 4.32 s (2H, CH_2), 5.05 m (1H, CH), 7.62 m (9H, H_{Ar}), 12.96 br. s (1H, NH). Found, %: C 55.70; H 4.44; N 6.50. $C_{20}H_{19}BrN_2O_4$. Calculated, %: C 55.73; H 4.42; N 6.53.

Methyl (*Z*)-5,5-dimethyl-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}hexanoate (2l). Yield 1.60 g (81%), yellow crystals, mp 152–154°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3380, 3202, 1722, 1640, 1584. ^1H NMR spectrum, δ, ppm: form **A** (86%), 1.15 s (9H, *t*-Bu), 3.73 s (3H, MeO), 4.08 s (2H, CH_2), 7.24 m (9H, H_{Ar}), 8.50 br. s (1H, NH), 11.32 s (1H, NH); form **B** (14%), 2.91 d (1H, C^4H_2, J = 20.0 Hz), 3.43 d (1H, C^4H_2, J = 20.0 Hz), 3.72 s (3H, MeO), 6.46 br. s (1H, OH), 7.24 m (10H, H_{Ar} + NH). ^{13}C NMR spectrum, δ_C, ppm: 25.41, 25.87, 35.92, 43.96, 52.13, 116.72, 117.7, 118.95, 119.07, 121.47, 129.07, 130.26, 132.33, 141.96, 143.73, 146.25, 161.22, 164.39, 209.79. Mass spectrum, *m/z* (I_{rel}, %): 395 (9.0) $[M]^+$, 336 (4.0) $[M - COOCH_3]^+$, 196 (100.0) $[2\text{-}(PhNH)C_6H_4CO]^+$, 168 (7.0) $[M - COOCH_3 - PhNHPh]^+$. Found, %: C 66.82; H 6.37; N 10.63. $C_{22}H_{25}N_3O_4$. Calculated, %: C 66.84; H 6.34; N 10.65.

Methyl (*Z*)-4-oxo-4-phenyl-2-{2-[2-(phenylamino)-phenylcarbonyl]hydrazinylidene}butanoate (2m). Yield 1.04 g (50%), yellow crystals, mp 100–102°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3341, 1720, 1646, 1594. ^1H NMR spectrum, δ, ppm: form **A** (24%), 3.76 s (3H, MeO), 4.60 s (2H, CH_2), 7.31 m (14H, H_{Ar}), 8.56 br. s (1H, NH), 11.46 s (1H, NH); form **B** (76%), 3.29 d (1H, C^4H_2, J = 20.0 Hz), 3.36 d (1H, C^4H_2, J = 20.0 Hz), 3.79 s (3H, MeO), 7.31 m (16H, H_{Ar} + NH + OH). ^{13}C NMR spectrum, δ_C, ppm: 50.92, 52.34, 94.26, 117.89, 118.31, 119.04, 119.55, 120.94, 121.57, 124.75, 127.39, 127.94, 128.72, 129.15, 129.20, 130.59, 131.46, 132.42, 133.54, 135.98, 141.94, 142.52, 142.85, 143.84, 145.18, 161.48, 164.73, 167.38, 194.11. Found, %: C 69.39; H 5.14; N 10.14. $C_{24}H_{21}N_3O_4$. Calculated, %: C 69.36; H 5.16; N 10.17.

Methyl (*Z*)-4-methylphenyl-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}butanoate (2n). Yield 1.37 g (64%), yellow crystals, mp 135–136°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3351, 1719, 1678, 1642, 1594. ^1H NMR spectrum, δ, ppm: form **A** (19%), 2.41 s (3H, Me), 3.78 s (3H, MeO), 4.56 s (2H, CH_2), 7.24 m (13H, H_{Ar}), 8.56 s (1H, NH), 11.45 s (1H, NH); form **B** (48%), 2.38 s (3H, Me), 3.26 d (1H, C^4H_2, J = 20.0 Hz), 3.34 d (1H, C^4H_2, J = 20.0 Hz), 3.78 s (3H, MeO), 7.24 m (15H, H_{Ar} + NH + OH); form **C** (3%), 2.30 s (3H, Me), 3.72 s (3H, MeO), 4.32 s (2H, CH_2), 7.24 m (14H, H_{Ar} + NH). ^{13}C NMR spectrum, δ_C, ppm: 20.58, 21.16, 37.46, 50.88, 52.31, 94.3, 116.56, 117.83, 118.33, 118.95, 119.05, 119.52, 120.94, 121.58, 123.65, 124.7, 128.36, 128.49, 129.14, 129.26, 130.3, 130.57, 131.42, 133.42, 133.56, 136.58, 139.60, 141.94, 142.53, 142.63, 143.84, 144.02, 145.12, 161.51, 164.73, 167.38, 193.69. Found, %: C 69.92; H 5.40; N 9.78. $C_{25}H_{23}N_3O_4$. Calculated, %: C 69.94; H 5.43; N 9.76.

Methyl (*Z*)-4-(4-methoxyphenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2o). Yield 1.11 g (50%), yellow crystals, mp 100–102°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3356, 1725, 1684, 1673, 1645, 1595. ^1H NMR spectrum, δ, ppm: form **A** (58%), 3.79 s (3H, MeO), 3.87 s (3H, MeO), 4.54 s (2H, CH_2), 7.24 m (13H, H_{Ar}), 8.57 br. s (1H, NH), 11.45 s (1H, NH); form **B** (37%), 3.28 d (1H, C^4H_2, J = 20.0 Hz), 3.34 d (1H, C^4H_2, J = 20.0 Hz), 3.75 s (3H, MeO), 3.85 s (3H, MeO), 7.24 m (15H, H_{Ar} + NH + OH); form **C** (5%), 3.72 s (3H, MeO), 3.79 s (3H, MeO), 4.30 s (2H, CH_2), 7.24 m (14H, H_{Ar} + NH), 12.99 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 37.22, 50.67, 52.29, 55.08, 55.61, 94.25, 113.27, 113.94, 116.58, 117.86, 118.30, 118.97, 119.05, 119.53, 120.91, 121.59, 123.74, 126.10, 128.96, 129.14, 129.26, 130.29, 130.62, 132.42, 141.94, 142.65, 143.85, 145.13, 158.57, 161.53, 163.53, 163.47, 164.74, 167.46, 192.58. Found, %: C 67.41; H 5.20; N 9.43. $C_{25}H_{23}N_3O_5$. Calculated, %: C 67.43; H 5.22; N 9.46.

Methyl (*Z*)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-4-(4-ethoxyphenyl)-butanoate (2p). Yield 1.63 g (71%), yellow crystals, mp 130–132°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3354 br, 3205, 1722, 1667, 1598. ^1H NMR spectrum, δ, ppm: form **A** (39%), 1.32 t (3H, Me, J = 7.0 Hz), 3.79 s (3H, MeO), 4.02 q (2H, OCH_2CH_3, J = 7.0 Hz), 4.54 s (2H, CH_2), 7.27 m (13H, H_{Ar}), 8.57 s (1H, NH), 11.45 s (1H, NH); form **B** (57%), 1.37 t (3H, Me, J = 7.0 Hz), 3.28 d (1H, C^4H_2, J = 20.0 Hz), 3.33 d (1H, C^4H_2, J = 20.0 Hz), 3.75 s (3H, MeO), 4.16 q (2H, OCH_2CH_3, J = 7.0 Hz), 7.24 m (15H, H_{Ar} + NH + OH); form **C** (4%), 1.32 t (3H, Me, J = 7.0 Hz), 3.72 s (3H, MeO), 4.29 s (2H, CH_2), 7.24 m (14H, H_{Ar} + NH), 13.02 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 14.41, 14.62, 37.19, 50.79, 52.28, 63.00, 63.63, 94.28, 113.74, 114.33, 116.57, 117.86, 118.29, 118.96, 119.05, 119.53, 120.91, 121.59, 123.66, 126.08, 128.80, 129.14, 129.26, 130.29, 130.62, 131.41, 132.42, 134.42, 140.99, 141.94, 142.50, 142.64, 143.85, 145.04, 157.82, 161.45, 162.76, 164.75, 167.37, 192.54. Found, %: C 67.96; H 5.48; N 9.14. $C_{26}H_{25}N_3O_5$. Calculated, %: C 67.98; H 5.46; N 9.17.

Methyl (*Z*)-4-(3,4-dimethoxyphenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-

butanoate (2q). Yield 1.31 g (55%), yellow crystals, mp 103–105°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3279, 1714, 1668, 1589. ^1H NMR spectrum, δ, ppm: form **A** (48%), 3.75 s (3H, MeO), 3.75 s (3H, MeO), 4.56 s (2H, CH_2), 7.26 m (12H, H_{Ar}), 8.57 s (1H, NH), 11.14 s (1H, NH); form **A** (52%), 3.27 d (1H, CH_2, *J* = 20.0 Hz), 3.36 d (1H, CH_2, *J* = 20.0 Hz), 3.75 s (3H, MeO), 3.75 s (3H, MeO), 7.24 m (14H, H_{Ar} + NH + OH). ^{13}C NMR spectrum, δ_C, ppm: 37.19, 52.3, 55.47, 55.58, 55.65, 55.86, 94.19, 109.06, 110.62, 111.02, 111.35, 116.59, 117.18, 117.58, 118.45, 118.99, 119.02, 119.37, 121.02, 121.59, 123.23, 123.57, 128.89, 129.15, 129.25, 130.26, 130.54, 131.36, 132.4, 141.93, 142.49, 143.8, 145.22, 148.64, 153.52, 164.7, 167.4, 192.64. Found, %: C 67.96; H 5.48; N 9.14. $C_{26}H_{25}N_3O_5$. Calculated, %: C 67.98; H 5.46; N 9.17.

Methyl (*Z*)-4-(4-bromophenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylylidene}-butanoate (2r). Yield 1.24 g (50%), yellow crystals, mp 133–135°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3257, 1707, 1656, 1574. ^1H NMR spectrum, δ, ppm: form **A** (12%), 3.76 s (3H, MeO), 4.58 s (2H, CH_2), 7.26 m (13H, H_{Ar}), 8.55 br. s (1H, NH), 11.45 s (1H, NH); form **B** (86%), 3.26 d (1H, C^4H_2, *J* = 20.0 Hz), 3.35 d (1H, C^4H_2, *J* = 20.0 Hz), 3.79 s (3H, MeO), 7.26 m (14H, H_{Ar} + OH); form **C** (2%), 3.73 s (3H, MeO), 4.35 s (2H, CH_2), 7.26 m (14H, H_{Ar} + NH), 13.02 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 50.67, 52.35, 61.30, 93.71, 118.21, 118.39, 119.05, 119.70, 120.67, 120.84, 123.92, 127.23, 129.13, 129.25, 130.20, 130.50, 130.78, 131.47, 131.82, 141.94, 142.43, 142.81, 145.27, 161.42,167.30, 193.34. Found, %: C 58.31; H 4.08; N 8.50. $C_{24}H_{20}BrN_3O_4$. Calculated, %: C 58.33; H 4.06; N 8.52.

Methyl (*Z*)-4-(4-fluorophenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2s). Yield 1.10 g (51%), yellow crystals, mp 123–125°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3345 br, 3169 br, 1717, 1692, 1640, 1595. ^1H NMR spectrum, δ, ppm: form **A** (68%), 3.75 s (3H, MeO), 4.58 s (2H, CH_2), 7.36 m (12H, H_{Ar}), 8.56 br. s (1H, NH), 11.44 s (1H, NH); form **B** (24%), 3.21 d (1H, C^4H_2, *J* = 20.0 Hz), 3.37 d (1H, C^4H_2, *J* = 20.0 Hz), 3.79 s (3H, MeO), 7.36 m (14H, H_{Ar} + NH + OH); form **C** (8%), 3.82 s (3H, MeO), 4.32 s (2H, CH_2), 7.36 m (13H, H_{Ar} + NH). ^{13}C NMR spectrum, δ_C, ppm: 37.50, 50.71, 52.27, 93.73, 114.40, 114.62, 115.58, 115.80, 116.56, 118.14, 118.95, 119.59, 120.80, 121.51, 123.82, 126.92, 127.00, 129.07, 129.19, 130.24, 130.46, 131.14, 131.23, 131.38, 132.38, 132.67, 138.50, 141.87, 142.35, 142.68, 143.76, 145.15, 161.39, 164.63, 167.29, 192.69. Found, %: C 66.51; H 4.65; N 9.69. $C_{24}H_{20}FN_3O_4$. Calculated, %: C 66.54; H 4.63; N 9.67.

Methyl (*Z*)-4-(4-chlorophenyl)-4-oxo-2-(2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2t). Yield 1.40 g (62%), yellow crystals, mp 132–134°C (propan-2-ol). ^1H NMR spectrum, δ, ppm: form **A** (24%), 3.79 s (3H, MeO), 4.58 s (2H, CH_2), 7.36 m (13H, H_{Ar}), 8.54 br. s (1H, NH), 11.44 s (1H, NH); form **B** (76%), 3.13 d (1H, C^4H_2, *J* = 20.0 Hz), 3.35 d (1H, C^4H_2, *J* = 20.0 Hz), 3.75 s (3H, MeO), 7.36 m (14H, H_{Ar} + OH), 8.92 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 50.70, 52.35, 93.66, 118.19, 119.03, 119.36, 119.71, 120.83, 123.95, 126.88, 127.84, 128.85, 129.12, 130.10, 130.49, 131.46, 132.09, 141.48, 142.40, 142.81, 145.26, 161.42, 167.29. Found, %: C 64.07; H 4.48; N 9.34. $C_{24}H_{20}ClN_3O_4$. Calculated, %: C 64.05; H 4.46; N 9.37.

Ethyl (*Z*)-5,5-dimethyl-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}hexanoate (2u). Yield 1.76 g (86%), yellow crystals, mp 129–130°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3378, 1709, 1639, 1589. ^1H NMR spectrum, δ, ppm: form **A** (85%), 1.15 s (9H, *t*-Bu), 1.23 m (3H, CH_2CH_3), 4.07 s (2H, CH_2), 4.18 q (2H, CH_2CH_3, *J* = 7.1 Hz), 7.25 m (13H, H_{Ar}), 8.48 br. s (1H, NH), 11.31 s (1H, NH); form **B** (15%), 1.03 s (9H, *t*-Bu), 1.23 m (3H, CH_2CH_3), 2.91 d (1H, C^4H_2, *J* = 20.0 Hz), 3.43 d (1H, C^4H_2, *J* = 20.0 Hz), 4.18 q (2H, CH_2CH_3, *J* = 7.1 Hz), 6.45 br. s (1H, OH), 7.25 m (10H, H_{Ar} + NH). ^{13}C NMR spectrum, δ_C, ppm: 13.97, 25.54, 25.97, 35.98, 43.99, 61.01, 116.78, 119.00, 119.16, 121.50, 129.04, 129.24, 130.36, 132.34, 142.07, 143.75, 163.85, 209.85. Found, %: C 67.46; H 6.65; N 10.26. $C_{23}H_{27}N_3O_4$. Calculated, %: C 67.48; H 6.63; N 10.29.

Ethyl (*Z*)-4-oxo-4-phenyl-2-{2-[2-(phenylamino)-phenylcarbonyl]hydrazinylidene}butanoate (2v). Yield 1.83 g (87%), yellow crystals, mp 142–144°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3380, 3276, 1714, 1684, 1640, 1595. ^1H NMR spectrum, ppm: form **A** (25%), 1.23 t (3H, CH_2CH_3, *J* = 7.1 Hz), 4.23 t (2H, CH_2CH_3, *J* = 7.1 Hz), 4.56 s (2H, CH_2), 7.27 m (14H, H_{Ar}), 8.56 br. s (1H, NH), 11.44 s (1H, NH); form **B** (49%), 1.25 t (3H, CH_2CH_3, *J* =7.1 Hz), 3.26 d (1H, C^4H_2, *J* = 20.0 Hz), 3.33 d (1H, C^4H_2, *J* = 20.0 Hz), 4.23 m (2H, CH_2CH_3), 7.27 m (15H, H_{Ar} + OH), 9.01 br. s (1H, NH); form **C** (6%), 1.12 t (3H, CH_2CH_3, *J* = 7.1 Hz), 4.23 m (2H, CH_2CH_3), 4.30 s (2H, CH_2), 7.27 m (15H, H_{Ar} + NH), 13.05 br. s (1H, NH). ^{13}C NMR spectrum,

δ_C, ppm: 13.52, 13.98, 20.58, 21.15, 37.44, 43.74, 50.93, 61.11, 61.28, 61.72, 94.28, 116.53, 117.31, 117.63, 118.45, 118.94, 119.04, 119.42, 119.53, 119.66, 120.99, 121.58, 121.98, 123.55, 124.69, 128.23, 128.35, 128.49, 128.82, 129.14, 129.25, 129.29, 129.33, 130.31, 130.62, 131.43, 132.37, 133.53, 133.60, 136.53, 139.69, 141.95, 142.57, 142.62, 144.00, 144.14, 161.01, 161.40, 164.18, 167.39, 193.76, 196.31. Found, %: C 69.92; H 5.40; N 9.78. $C_{25}H_{23}N_3O_4$. Calculated, %: C 69.94; H 5.43; N 9.76.

Ethyl (*Z*)-4-oxo-4-methylphenyl-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}butanoate (2w). Yield 1.86 g (84%), yellow crystals, mp 155–157°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3351, 1712, 1685, 1577. ^1H NMR spectrum, δ, ppm: form **A** (23%), 1.23 t (3H, CH_2CH_3, J = 7.1 Hz), 2.30 s (3H, Me), 4.26 m (2H, CH_2CH_3), 7.25 m (13H, H_{Ar}), 8.56 br. s (1H, NH), 11.44 s (1H, NH); form **B** (73%), 1.26 t (3H, CH_2CH_3, J = 7.1 Hz), 2.41 s (3H, Me), 3.26 d (1H, C^4H_2, J = 20.0 Hz), 3.33 d (1H, C^4H_2, J = 20.0 Hz), 7.25 m (15H, H_{Ar} + NH + OH); form **C** (4%), 1.12 t (3H, CH_2CH_3, J = 7.1 Hz), 2.38 s (3H, Me), 4.30 s (2H, CH_2), 7.25 m (14H, H_{Ar} + NH), 13.04 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.98, 20.58, 21.15, 37.45, 50.93, 61.12, 61.26, 94.28, 116.54, 117.63, 118.45, 119.04, 121.00, 123.55, 124.69, 128.35, 128.49, 129.14, 129.25, 129.34, 131.43, 133.60, 136.53, 139.69, 141.95, 142.57, 142.62, 144.00, 145.40, 161.01, 164.18, 167.39, 193.77. Found, %: C 70.41; H 5.68; N 9.47. $C_{26}H_{25}N_3O_4$. Calculated, %: C 70.43; H 5.65; N 9.49.

Ethyl (*Z*)-4-(4-methoxyphenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2x). Yield 1.15 g (50%), yellow crystals, mp 140–142°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3352, 3164, 1706, 1681, 1595. ^1H NMR spectrum, δ, ppm: form **A** (86%), 1.23 m (3H, CH_2CH_3), 3.87 s (3H, MeO), 4.22 m (2H, CH_2CH_3), 4.53 s (2H, CH_2), 7.25 m (13H, H_{Ar}), 8.53 br. s (1H, NH), 11.43 s (1H, NH); form **C** (14%), 1.23 m (3H, CH_2CH_3), 3.75 s (3H, MeO), 4.22 m (2H, CH_2CH_3), 4.26 s (2H, CH_2), 7.25 m (14H, H_{Ar} + NH). ^{13}C NMR spectrum, δ_C, ppm: 13.91, 37.13, 55.01, 55.53, 61.05, 113.20, 113.87, 116.50, 118.34, 118.90, 118.96, 121.50, 126.02, 128.91, 129.07, 129.19, 130.21, 130.54, 131.35, 132.32, 134.53, 141.88, 143.74, 163.40, 164.13, 192.60. Found, %: C 67.96; H 5.48; N 9.14. $C_{26}H_{25}N_3O_5$. Calculated, %: C 67.94; H 5.45; N 9.16.

Ethyl (*Z*)-4-(4-chlorophenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2y). Yield 1.72 g (74%), yellow crystals, mp 112–114°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 3329 br, 3257, 1705, 1666, 1589. ^1H NMR spectrum, δ, ppm: form **A** (6%), 1.23 t (3H, CH_2CH_3, J = 7.1 Hz), 4.26 m (2H, CH_2CH_3), 4.57 s (2H, CH_2), 7.28 m (13H, H_{Ar}), 8.53 br. s (1H, NH), 11.40 s (1H, NH); form **B** (92%), 1.26 t (3H, CH_2CH_3, J = 7.1 Hz), 3.17 d (1H, C^4H_2, J = 20.0 Hz), 3.35 d (1H, C^4H_2, J = 20.0 Hz), 4.26 m (2H, CH_2CH_3), 7.28 m (15H, H_{Ar} + NH + OH); form **C** (2%), 1.12 t (3H, CH_2CH_3, J = 7.1 Hz), 4.26 m (2H, CH_2CH_3), 4.34 s (2H, CH_2), 7.28 m (15H, H_{Ar} + NH), 13.03 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm:13.98, 50.76, 61.30, 93.63, 118.03, 118.32, 120.90, 123.85, 126.69, 127.84, 129.13, 130.53, 131.47, 132.06, 141.50, 142.49, 142.75, 145.54, 160.92, 167.30, 193.21. Found, %: C 64.73; H 4.78; N 9.06. $C_{25}H_{22}ClN_3O_4$. Calculated, %: C 64.71; H 4.76; N 9.03.

Isopropyl 5,5-dimethyl-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}hexanoate (2z). Yield 1.14 g (54%), yellow crystals, mp 105–107°C (propan-2-ol). ^1H NMR spectrum, δ, ppm: form **A** (60%), 1.07 s (9H, *t*-Bu), 1.25 d (6H, 2Me, J = 6.3 Hz), 4.07 s (2H, CH_2), 5.02 m (1H, CH), 7.24 m (5H, H_{Ar}), 8.40 br. s (1H, NH), 11.15 s (1H, NH); form **B** (8%), 1.18 t (6H, Me, J = 3.7 Hz), 2.95 d (1H, C^4H_2, J = 20.0 Hz), 3.41 d (1H, C^4H_2, J = 20.0 Hz), 5.09 m (1H, CH), 5.73 br. s (OH), 7.24 m (6H, H_{Ar} + NH); form **C** (32%), 1.18 t (6H, Me, J = 3.3 Hz), 3.84 s (2H, CH_2), 5.09 m (1H, CH), 7.24 m (5H, H_{Ar}), 8.91 br. s (1H, NH), 12.98 br. s (1H, NH). Found, %: C 68.06; H 6.90; N 9.92. $C_{24}H_{29}N_3O_4$. Calculated, %: C 68.04; H 6.93; N 9.95.

Isopropyl 4-(4-methylphenyl)-4-oxo-2-{2-[2-(phenylamino)phenylcarbonyl]hydrazinylidene}-butanoate (2a'). Yield 1.19 g (52%), yellow crystals, mp 123–125°C (propan-2-ol). ^1H NMR spectrum, δ, ppm: form **A** (40%), 1.24 d (6H, Me, J = 6.3 Hz), 2.43 s (3H, Me), 4.52 s (2H, CH_2), 5.08 m (1H, CH), 7.26 m (9H, H_{Ar}), 8.47 br. s (1H, NH), 11.27 s (1H, NH); form **B** (48%), 1.29 m (6H, Me), 2.32 s (3H, Me), 3.26 d (1H, C^4H_2, J = 20.0 Hz), 3.36 d (1H, C^4H_2, J = 20.0 Hz), 5.02 m (1H, CH), 7.26 m (11H, H_{Ar} + NH + OH); form **C** (32%), 1.17 d (6H, 2Me, J = 6.3 Hz), 2.43 s (3H, Me), 26 s (2H, CH_2), 5.08 m (1H, CH), 7.26 m (9H, H_{Ar}), 8.91 br. s (1H, NH), 12.97 s (1H, NH). Found, %: C 70.88; H 5.95; N 9.18. $C_{27}H_{27}N_3O_4$. Calculated, %: C 70.85; H 5.97; N 9.16.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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