

Iminofuran Chemistry: I. Decyclization of N-Substituted 5-Aryl-3-imino-3H-furan-2-ones by the Action of OH- and NH-Nucleophiles

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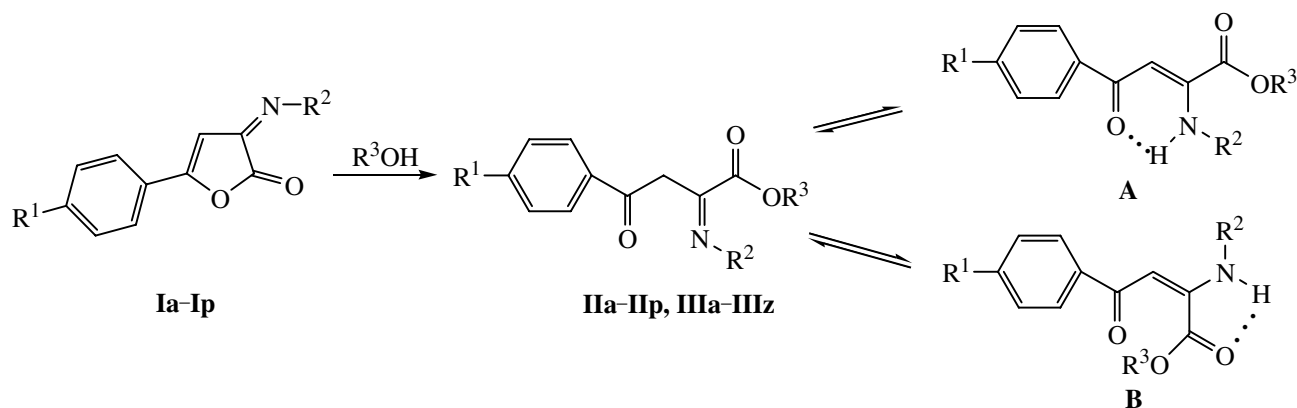
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Abstract—In reactions of N-substituted 5-aryl-3-imino-3H-furan-2-ones with OH- and NH-nucleophiles the nucleophilic reagents attack the carbon atom in the position 2 of the furan ring. All reactions involve the destruction of the furan system.

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Scanty examples are published of the syntheses of compounds containing in the structure 3-imino-3H-furan-2-one [1–6]. The chemical characteristic of this class compounds are virtually not understood apparently because of the lack of reliable procedures for preparation of these substances. We formerly developed a simple method for the synthesis of a series N-substituted 5-aryl-3-imino-3H-furan-2-ones by intramolecular cyclization of N-substituted 2-amino-4-aryl-4-oxo-2-butenic acids under treatment with acetic anhydride [5, 6]. Yet this rare

type of 2-furanone derivatives seems very promising because of high reactivity and possible existence among furan derivatives of biologically active compounds. No reactions of 5-aryl-3-imino-3H-furan-2-ones with nucleophilic reagents were studied before, but analogously to the reactions of 2,3-dihydrofuran-2,3-diones with OH- and NH-nucleophiles [7] these processes might lead to the formation of decyclization and recyclization products resulting from an attack of a nucleophile on C², C³, and C⁵ atoms of the furan ring.



I, II, R³ = H: R¹ = H, R² = 4-ClC₆H₄ (**a**), 4-BrC₆H₄ (**b**), 4-NO₂C₆H₄ (**c**), 1-naphthyl (**d**); R¹ = Me, R² = Ph (**e**), 4-ClC₆H₄ (**f**); R² = 4-antipyryl, R¹ = H (**g**), Me (**h**), MeO (**i**), Cl (**j**), Br (**k**); R² = Ph₂C=N, R¹ = H (**l**), Me (**m**), MeO (**n**), Cl (**o**), Br (**p**); **III**, R³ = Me: R¹ = H, R² = 4-ClC₆H₄ (**a**), 4-BrC₆H₄ (**b**), 4-NO₂C₆H₄ (**c**), 1-naphthyl (**d**); R¹ = CH₃, R² = Ph (**e**), 4-ClC₆H₄ (**f**); R² = 4-antipyryl, R¹ = H (**g**), Me (**h**), CH₃O (**i**), Cl (**j**), Br (**k**); R² = Ph₂C=N, R¹ = H (**l**), Me (**m**), MeO (**n**), Cl (**o**), Br (**p**); R³ = Et: R² = 4-antipyryl, R¹ = H (**q**), CH₃ (**r**), CH₃O (**s**), Cl (**t**), Br (**u**); R² = Ph₂C=N, R¹ = H (**v**), Me (**w**), MeO (**x**), Cl (**y**), Br (**z**).

We established that the reactions of 5-aryl-3-imino-3*H*-furan-2-ones **Ia–Ip** with OH⁻ and NH-nucleophiles proceeded readily and resulted in decyclization of the furan ring. For instance, the reaction of compounds **Ia–If** with air moisture or the recrystallization of compounds **Ia–Ip** from insufficiently dried solvents gave rise to *N*-substituted 4-aryl-2-amino-4-oxo-2-butenoic acids **IIa–IIp** [6].

Alcohols provide the ring opening in compounds **Ia–Ip** resulting in formation of *N*-substituted 4-aryl-2-amino-4-oxo-2-butenoic acids esters **IIIa–IIIz**. Esters **III** like acids **II** exist in solutions in a *cis-trans* equilibrium with the prevalence of the *Z*-enaminoketo form **A** [8, 9].

Esters **IIIa–IIIf** and **IIIg–IIIp** were previously obtained from methyl esters of 4-aryl-2-hydroxy-4-oxo-2-butenoic acids and amines [10–15], and benzophenone hydrazone [15–17].

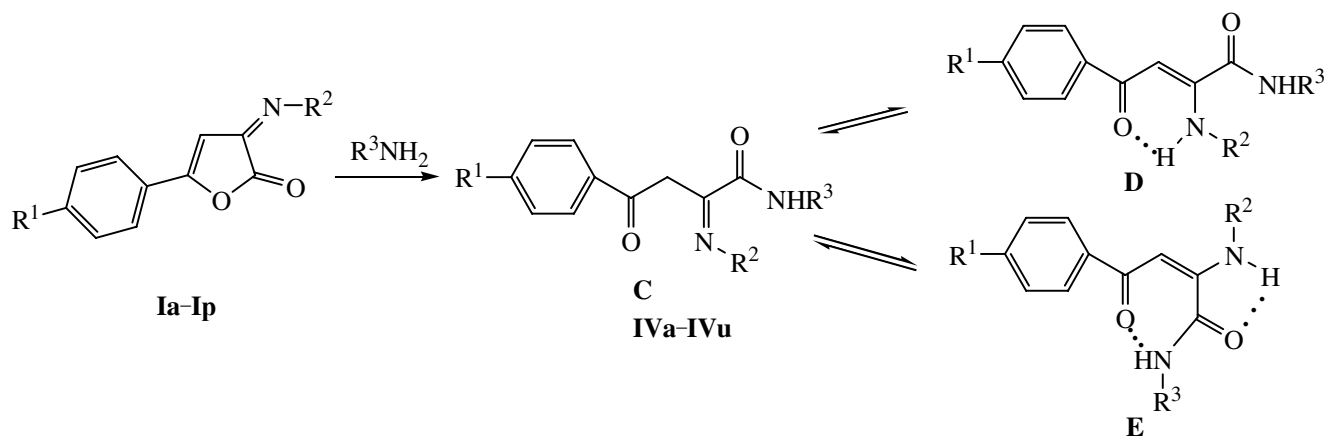
The IR spectra of compounds **III** contain an absorption band in the region 1732–1744 cm⁻¹ characteristic of the stretching vibrations of the ester carbonyl. No definite amino group band was observed in the IR spectra—apparently due to involvement of the amino group hydrogen into an intramolecular hydrogen bond with the oxygen of the C⁴=O group.

We investigated the ¹H NMR spectra of compounds **IIIh–IIIk** and **IIIl–IIIt**. It was established that in DMSO-*d*₆ solution esters **III** existed as equilibrium mixtures of two *Z*-,*E*-isomeric enaminoketo forms with *Z*-isomer **A** prevailing (75–84%). *Z*-isomer **A** is characterized in the spectrum by the presence of a singlet at 11.48–11.64 ppm from the proton of NH group involved in a strong intramolecular hydrogen bond, and of a singlet

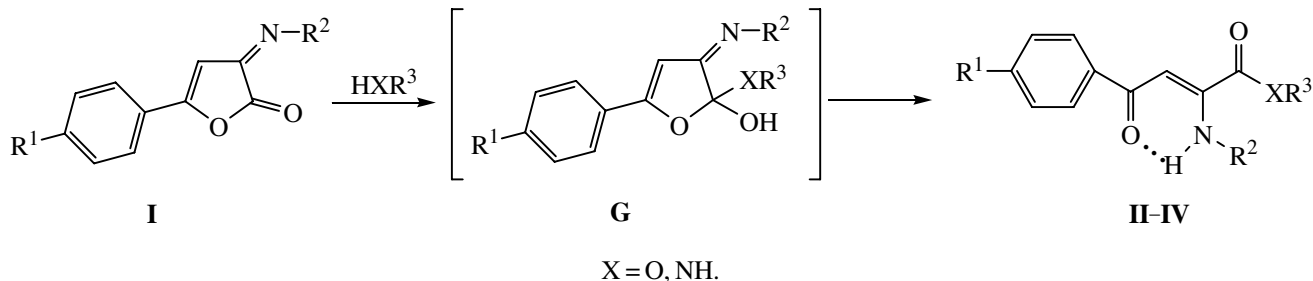
from the proton of CH group at 6.37–6.41 ppm. The proton resonances of the NH and CH groups belonging to *E*-isomer **B** appear upfield at 8.74–9.05 and 5.77–5.79 ppm respectively.

N-Substituted 5-aryl-3-imino-3*H*-furan-2-ones **Ia–Ip** react with aryl(heteryl)amines leading to the formation of *N*-substituted 4-aryl-2-amino-4-oxobut-2-enoic acids amides **IVa–IVu**. Amides **IVk–IVt** in solutions exist in hydrazono-enhydrazone equilibrium, and amides **IVf–IVj** are involved into a *cis-trans* equilibrium of enamino forms, with *Z*-enamino form **D** prevailing.

Amides **IVa–IVf** and **IVi** were formerly obtained from 4-aryl-2-oxy-4-oxo-2-butenoic acids anilides and aryl-(antipyryl)amines [18–23]. In the IR spectra of compounds **IV** appear absorption bands in the region 3250–3280 and 3144–3195 cm⁻¹ characteristic of NH group, and an absorption band in the region 1662–1696 cm⁻¹ from the stretching vibrations of the amide carbonyl. According to ¹H NMR data amides **IVg** and **IVj** exist in the DMSO-*d*₆ solution as equilibrium mixtures of two *Z*-,*E*-isomeric enaminoketo forms with prevailing *Z*-isomer **D** whose content is equal to 85–87%. *Z*-isomer is characterized by the presence in the spectrum of proton singlets of NH groups at 11.38–11.43 and 10.45–10.57 ppm, and of a proton singlet from the CH group at 6.27–6.29 ppm. Peaks of protons belonging to NH and CH groups of *E*-isomer **E** appear upfield at 10.05–10.87, 8.74–8.98, and 5.78–5.85 ppm respectively. The ¹H NMR spectra of compounds **IVm**, **IVo**, **IVq–IVt** in DMSO-*d*₆ reveal the existence of the enhydrazino-hydrazono equilibrium with predominant presence of the enhydrazino isomer. Enhydrazino form **D** is characterised by the



IV, R³ = Ph: R¹ = H, R² = 4-ClC₆H₄ (**a**), 4-BrC₆H₄ (**b**), 4-NO₂C₆H₄ (**c**); R¹ = Me, R² = Ph (**d**), 4-ClC₆H₄ (**e**); R² = 4-antipyryl, R¹ = H (**f**), Me (**g**), MeO (**h**), Cl (**i**), Br (**j**); R² = Ph₂C=N, R¹ = H (**k**), Me (**l**), MeO (**m**), Cl (**n**), Br (**o**); R³ = 2-Py: R² = Ph₂C=N, R¹ = H (**p**), Me (**q**), MeO (**r**), Cl (**s**), Br (**t**); R¹ = H, R³ = 2-thiazolyl, R² = 4-antipyryl (**u**).



presence in the spectrum of singlets from NH protons at 12.75–12.92 and 10.51–10.19 ppm and of a singlet from a proton of CH group at 6.12–6.61 ppm. Hydrazono form **C** contains in the spectrum a singlet of the NH proton at 9.19–10.23 ppm and a proton signal from the CH₂ group at 4.51–4.52 ppm.

In the mass spectrum of compound **IVo** appeared a molecular ion peak with m/z 523 [M]⁺ of intensity 9.5%, and also fragment ion peaks, m/z (I_{rel} , %): 403 (10) [$M - \text{PhNHC=O}$]⁺, 340 (9) [$M - \text{BrC}_6\text{H}_4\text{CO}$]⁺, 219 (5) [$M - \text{BrC}_6\text{H}_4\text{CHO} - \text{PhNHC=O}$]⁺, 184/186 (11) [$\text{BrC}_6\text{H}_4\text{CO}$]⁺, 180 (100) [$\text{Ph}_2\text{C}\equiv\text{N}$]⁺, 77 (100) [Ph]⁺ in conformity with the suggested structure.

Formation of compounds **II–IV** occurs apparently by nucleophilic attack of the NH (OH) group of the nucleophile on the C² atom of the iminofurans followed by a proton transfer from the nitrogen (oxygen) atom of the amino (hydroxy) group to the oxygen atom of the C²=O group leading to the formation of aminoalcohol (hemiacetal) **G**. The latter further transforms into one of enamine forms of amide (ester) by a proton transfer to O' atom or to the nitrogen atom in the imino function and by C²–O' bond rupture.

EXPERIMENTAL

IR spectra were recorded on a spectrometer FSM-1201 from KBr pellets or mulls in mineral oil. ¹H NMR spectra were registered on spectrometers Bruker DRX-500 (500.13 MHz) in DMSO-*d*₆, internal reference HMDS and Varian-Mercury plus 300 (300.05 MHz). Mass spectrum was taken on MKh-1310 instrument at emission current 1000 mA, ionizing electrons energy 70 eV, vaporizer temperature 120°C, ion source temperature 200°C. The completion of reaction and purity of compounds was checked by TLC on Silufol UV-254 plates in a system ether–benzene–acetone, 10:9:1. Melting points and decomposition temperature were measured on a PTP-2 device.

N-substituted 4-aryl-2-amino-4-oxo-2-butenic acids IIa–IIp. An appropriate 5-aryl-3-imino-3H-furan-

2-one **Ia–Ip** (0.01 mol) was recrystallized from 10 ml of a mixture dioxane–water, 10:1. The crystalline precipitate was filtered off. The characteristics of acids **IIa–IIp** are consistent with the published data [6].

N-Substituted 4-aryl-2-amino-4-oxo-2-butenic acids esters IIIa–IIIz. In 10 ml of an appropriate alcohol was heated at reflux 0.01 mol of an appropriate 5-aryl-3-imino-3H-furan-2-one **Ia–Ip** for 3 h. The precipitate was filtered off and recrystallized from acetonitrile. The characteristics of esters **IIIa–IIIf** and **IIIg–IIIp** are in agreement with the published data [13, 17, 18].

Methyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-(4-methylphenyl)-4-oxo-2-butenate (IIIh). Yield 3.4 g (84%), yellow crystals, mp 130–131°C (MeCN). IR spectrum, ν , cm⁻¹: 3445 (NH), 1732 (C=O), 1666, 1593, 1573 (C=O_{pyr.}, C=C). ¹H NMR spectrum, δ , ppm, **A**: 2.26 s (3H, C–CH₃), 2.31 s (3H, C–CH₃), 2.98 s (3H, N–CH₃), 3.64 s (3H, O–CH₃), 6.41 s (1H, CH), 7.5 m (9H_{arom.}), 11.60 s (1H, NH) (78%); **B**: 2.14 s (3H, C–CH₃), 2.27 s (3H, C–CH₃), 3.07 s (3H, N–CH₃), 3.75 s (3H, O–CH₃), 5.79 s (1H, CH), 7.5 m (9H_{arom.}), 8.86 s (1H, NH). Found, %: C 68.20; H 5.68; N 10.30. C₂₃H₂₃N₃O₄. Calculated, %: C 68.13; H 5.72; N 10.36.

Methyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-(4-methoxyphenyl)-4-oxo-2-butenate (IIIi). Yield 3.79 g (90%), yellow crystals, mp 161–163°C (MeCN). IR spectrum, ν , cm⁻¹: 1732 (C=O), 1655, 1601, 1589 (C=O_{pyr.}, C=N). ¹H NMR spectrum, δ , ppm, **A**: 2.23 s (3H, C–CH₃), 2.98 s (3H, N–CH₃), 3.64 s (3H, O–CH₃), 3.78 s (3H, O–CH₃), 6.40 s (1H, CH), 7.4 m (9H_{arom.}), 11.55 s (1H, NH) (81%); **B**: 2.14 s (3H, C–CH₃), 3.08 s (3H, N–CH₃), 3.74 s (3H, O–CH₃), 3.75 s (3H, O–CH₃), 5.80 s (1H, CH), 7.4 m (9H_{arom.}), 8.76 s (1H, NH). Found, %: C 65.50; H 5.46; N 10.00. C₂₃H₂₃N₃O₅. Calculated, %: C 65.55; H 5.50; N 9.97.

Methyl 4-(4-bromophenyl)-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-2-butenate (IIIk). Yield 3.5 g (84%), yellow

crystals, mp 134–136°C (MeCN). IR spectrum, ν , cm^{-1} : 1736 (C=O), 1655, 1574 (C=O_{pyr}, C=N). ¹H NMR spectrum, δ , ppm, **A**: 2.24 s (3H, C–CH₃), 3.00 s (3H, N–CH₃), 3.66 s (3H, O–CH₃), 6.40 s (1H, CH), 7.55 m (9H_{arom}), 11.64 s (1H, NH) (75%); **B**: 2.15 s (3H, C–CH₃), 3.09 s (3H, N–CH₃), 3.77 s (3H, O–CH₃), 5.79 s (1H, CH), 7.55 m (9H_{arom}), 9.05 c (1H, NH). Found, %: C 56.20; H 4.26; Br 17.02; N 8.89. C₂₂H₂₀BrN₃O₄. Calculated, %: C 56.18; H 4.29; Br 16.99; N 8.93.

Ethyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-4-phenyl-2-butenate (IIIq). Yield 3.77 g (93%), yellow crystals, mp 160–162°C (MeCN). IR spectrum, ν , cm^{-1} : 1746 (C=O), 1662, 1607, 1593 (C=O_{pyr}, C=C), 3285 (N–H). ¹H NMR spectrum, δ , ppm, **A**: 1.08 t (3H, C–CH₃), 2.29 s (3H, C–CH₃), 3.07 s (3H, N–CH₃), 4.10 q (2H, O–CH₂), 6.42 s (1H, CH), 7.65 m (10H_{arom}), 11.60 s (1H, NH) (84%); **B**: 1.20 t (3H, C–CH₃), 2.20 s (3H, C–CH₃), 3.29 s (3H, N–CH₃), 4.22 q (2H, O–CH₂), 5.82 s (1H, CH), 7.65 m (10H_{arom}), 8.90 s (1H, NH). Found, %: C 68.10; H 5.76; N 10.38. C₂₃H₂₃N₃O₄. Calculated, %: C 68.13; H 5.72; N 10.36.

Ethyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-(4-methylphenyl)-4-oxo-2-butenate (IIIr). Yield 3.4 g (84%), yellow crystals, mp 147–148°C (MeCN). IR spectrum, ν , cm^{-1} : 3417 (NH), 1726 (C=O), 1663, 1591 (C=O_{pyr}, C=C). ¹H NMR spectrum, δ , ppm, **A**: 1.09 t (3H, C–CH₃), 2.23 s (3H, C–CH₃), 2.44 s (3H, C–CH₃), 3.03 s (3H, N–CH₃), 4.12 q (2H, O–CH₂), 6.37 s (1H, CH), 7.45 m (9H_{arom}), 11.53 s (1H, NH) (80%); **B**: 1.22 t (3H, C–CH₃), 2.14 s (3H, C–CH₃), 2.23 s (3H, C–CH₃), 3.08 s (3H, N–CH₃), 4.22 q (2H, O–CH₂), 5.78 s (1H, CH), 7.4 m (9H_{arom}), 8.93 s (1H, NH). Found, %: C 68.70; H 6.00; N 10.08. C₂₄H₂₅N₃O₄. Calculated, %: C 68.72; H 6.01; N 10.02.

Ethyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-(4-methoxyphenyl)-4-oxo-2-butenate (IIIs). Yield 3.78 g (87%), yellow crystals, mp 156–157°C (MeCN). IR spectrum, ν , cm^{-1} : 3418 (NH), 1716 (C=O), 1667, 1592 (C=O_{pyr}, C=C). ¹H NMR spectrum, δ , ppm, **A**: 1.08 t (3H, C–CH₃), 2.24 s (3H, C–CH₃), 2.99 s (3H, N–CH₃), 3.78 s (3H, O–CH₃), 4.08 q (2H, O–CH₂), 6.38 s (1H, CH), 7.45 m (9H_{arom}), 11.48 s (1H, NH) (84%); **B**: 1.22 t (3H, C–CH₃), 2.14 s (3H, C–CH₃), 3.08 s (3H, N–CH₃), 3.74 s (3H, O–CH₃), 4.21 q (2H, O–CH₂), 5.78 s (1H, CH), 7.4 m (9H_{arom}), 8.74 s (1H, NH). Found, %: C 66.20; H 5.76; N 9.68. C₂₄H₂₅N₃O₅. Calculated, %: C 66.19; H 5.79; N 9.65.

Ethyl 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-4-(4-chlorophenyl)-2-butenate (IIIt). Yield 3.96 g (91%), yellow crystals, mp 145–147°C (MeCN). IR spectrum, ν , cm^{-1} : 1734 (C=O), 1653, 1591 (C=O_{pyr}, C=N). ¹H NMR spectrum, δ , ppm, **A**: 1.09 t (3H, C–CH₃), 2.31 s (3H, C–CH₃), 3.00 s (3H, N–CH₃), 4.09 q (2H, O–CH₂), 6.37 s (1H, CH), 7.45 m (9H_{arom}), 11.53 s (1H, NH) (78%); **B**: 1.23 t (3H, C–CH₃), 2.14 s (3H, C–CH₃), 3.09 s (3H, N–CH₃), 4.22 q (2H, O–CH₂), 5.77 s (1H, CH), 7.4 m (9H_{arom}), 8.93 s (1H, NH). Found, %: C 62.80; H 5.06; Cl 8.10; N 9.60. C₂₃H₂₂ClN₃O₄. Calculated, %: C 62.80; H 5.04; Cl 8.06; N 9.55.

Ethyl 4-(4-bromophenyl)-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-2-butenate (IIIu). Yield 3.42 g (89%), yellow crystals, mp 144–146°C (MeCN). IR spectrum, ν , cm^{-1} : 1739 (C=O), 1653, 1594 (C=O_{pyr}, C=N). Found, %: C 57.00; H 4.46; Br 16.55; N 8.68. C₂₃H₂₂BrN₃O₄. Calculated, %: C 57.04; H 4.58; Br 16.50; N 8.68.

Ethyl 2-(diphenylmethylenhydrazono)-4-oxo-4-phenyl-2-butenate (IIIv). Yield 3.42 g (86%), yellow crystals, mp 140–142°C (MeCN). IR spectrum, ν , cm^{-1} : 1732 (C=O), 1608, 1594 (C=O, C=C, C=N). Found, %: C 75.29; H 5.56; N 7.08. C₂₅H₂₂N₂O₃. Calculated, %: C 75.36; H 5.57; N 7.03.

Ethyl 2-(diphenylmethylenhydrazono)-(4-methylphenyl)-4-oxo-2-butenate (IIIw). Yield 3.87 g (94%), yellow crystals, mp 126–127°C (MeCN). IR spectrum, ν , cm^{-1} : 1730 (C=O), 1604, 1577 (C=O, C=C, C=N). Found, %: C 75.70; H 5.86; N 6.80. C₂₆H₂₄N₂O₃. Calculated, %: C 75.71; H 5.86; N 6.79.

Ethyl 2-(diphenylmethylenhydrazono)-4-(4-methoxyphenyl)-4-oxo-2-butenate (IIIx). Yield 3.77 g (88%), yellow crystals, mp 96–97°C (MeCN). IR spectrum, ν , cm^{-1} : 1729 (C=O), 1612, 1589 (C=O, C=C, C=N). Found, %: C 72.80; H 5.66; N 6.58. C₂₄H₂₅N₃O₅. Calculated, %: C 72.88; H 5.65; N 6.54.

Ethyl 2-(diphenylmethylenhydrazono)-4-oxo-4-(4-chlorophenyl)-2-butenate (IIIy). Yield 3.94 g (91%), yellow crystals, mp 164–165°C (MeCN). IR spectrum, ν , cm^{-1} : 1732 (C=O), 1610, 1591 (C=O, C=C, C=N). ¹H NMR spectrum, δ , ppm, **A**: 1.33 t (3H, C–CH₃), 4.40 q (2H, O–CH₂), 6.18 s (1H, CH), 7.45 m (14H_{arom}), 12.59 s (1H, NH) (89%); **B**: 1.07 t (3H, C–CH₃), 4.10 q (2H, O–CH₂), 6.51 s (1H, CH), 7.5 m (9H_{arom}), 10.39 s (1H, NH). Found, %: C 69.30; H 4.86; Cl 8.27; N 6.48. C₂₅H₂₁ClN₂O₃. Calculated, %: C 69.36; H 4.83; Cl 8.19; N 6.47.

Ethyl 4-(4-bromophenyl)-2-(diphenylmethylenehydrazono)-4-oxo-2-butenoate (IIIz). Yield 4.1 g (86%), yellow crystals, mp 160–163°C (MeCN). IR spectrum, ν , cm^{-1} : 1730 (C=O), 1605, 1589 (C=O, C=C, C=N). Found, %: C 57.06; H 4.53; Br 16.80; N 5.82. $\text{C}_{25}\text{H}_{21}\text{BrN}_2\text{O}_3$. Calculated, %: C 57.04; H 4.58; Br 16.74; N 5.87.

N-Substituted 4-aryl-2-amino-4-oxobut-2-enoic acids amides IVa–IVu. A solution of 0.01 mol of an appropriate 5-aryl-3-imino-3*H*-furan-2-one **Ia–Ip** and 0.01 mol of an appropriate amine in 20 ml of anhydrous toluene was heated at reflux for 3 h. On cooling the precipitate was filtered off and dried. The characteristics of amides **IVa–IVf** and **IVi** are consistent with the published data [18, 21–23].

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylamino)-(4-methylphenyl)-4-oxo-2-butenoic acid anilide (IVg). Yield 3.48 g (89%), yellow crystals, mp 214–215°C (TolH). IR spectrum, ν , cm^{-1} : 3248 (CONH), 3129 (NH), 1659 (CONH), 1653 (C=O_{pyr.}), 1597, 1574 (C⁴=O, C=C, C=N). ¹H NMR spectrum, δ , ppm, **D**: 2.21 s (3H, C–CH₃), 2.31 s (3H, C–CH₃), 2.96 s (3H, N–CH₃), 6.27 s (1H, CH), 7.5 m (14H_{arom.}), 10.45 s (1H, NH), 11.38 s (1H, NH) (85%); **E**: 2.15 s (3H, C–CH₃), 2.28 s (3H, C–CH₃), 3.08 s (3H, N–CH₃), 5.85 s (1H, CH), 7.55 m (14H_{arom.}), 8.74 s (1H, NH), 10.05 s (1H, NH). Found, %: C 67.70; H 5.66; N 14.38. $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_3$. Calculated, %: C 67.68; H 5.68; N 14.35.

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylamino)-4-(4-methoxyphenyl)-4-oxo-2-butenoic acid anilide (IVh). Yield 3.74 g (92%), yellow crystals, mp 194–195°C (MeCN). IR spectrum, ν , cm^{-1} : 3256 (CONH), 3132 (NH), 1660 (CONH), 1653 (C=O_{pyr.}), 1599, 1570 (C⁴=O, C=C, C=N). Found, %: C 65.02; H 5.46; N 13.80. $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4$. Calculated, %: C 65.01; H 5.46; N 13.78.

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-ylamino)-4-oxo-4-(4-bromo-phenyl)-2-butenoic acid anilide (IVj). Yield 3.41 g (75%), yellow crystals, mp 190–191°C (MeCN). IR spectrum, ν , cm^{-1} : 3259 (CONH), 3194 (NH), 1681 (CONH), 1655 (C=O_{pyr.}), 1581, 1539 (C⁴=O, C=C, C=N). ¹H NMR spectrum, δ , ppm, **D**: 2.22 s (3H, C–CH₃), 2.96 s (3H, N–CH₃), 6.29 s (1H, CH), 7.5 m (14H_{arom.}), 10.57 s (1H, NH), 11.43 s (1H, NH) (87%); **E**: 2.01 s (3H, C–CH₃), 3.09 s (3H, N–CH₃), 5.78 s (1H, CH), 7.55 m (14H_{arom.}), 8.98 s (1H, NH), 10.87 s (1H, NH). Found, %: C 55.40; H 4.23;

Br 17.60; N 12.31. $\text{C}_{21}\text{H}_{19}\text{BrN}_4\text{O}_3$. Calculated, %: C 55.40; H 4.21; Br 17.55; N 12.31.

2-(Diphenylmethylenehydrazono)-4-oxo-4-phenyl-2-butenoic acid anilide (IVk). Yield 4.05 g (89%), yellow crystals, mp 148–149°C (toluene). IR spectrum, ν , cm^{-1} : 3352 (CONH), 3287 (NH), 1674 (CONH), 1601, 1578, 1543 (C⁴=O, C=C, C=N). Found, %: C 78.20; H 5.20; N 9.45. $\text{C}_{29}\text{H}_{23}\text{N}_3\text{O}_2$. Calculated, %: C 78.18; H 5.20; N 9.43.

2-(Diphenylmethylenehydrazono)-(4-methylphenyl)-4-oxo-2-butenoic acid anilide (IVl). Yield 3.95 g (86%), yellow crystals, mp 144–146°C (toluene). IR spectrum, ν , cm^{-1} : 3268 (CONH), 3144 (NH), 1674 (CONH), 1604, 1574, 1554 (C⁴=O, C=C, C=N). Found, %: C 78.40; H 5.46; N 9.11. $\text{C}_{30}\text{H}_{25}\text{N}_3\text{O}_2$. Calculated, %: C 78.41; H 5.48; N 9.14.

2-(Diphenylmethylenehydrazono)-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid anilide (IVm). Yield 4.04 g (85%), yellow crystals, mp 141–143°C (toluene). IR spectrum, ν , cm^{-1} : 3260 (CONH), 3202 (NH), 1686 (CONH), 1589, 1574, 1554 (C⁴=O, C=C, C=N). ¹H NMR spectrum, δ , ppm, **D**: 3.73 s (3H, O–CH₃), 6.13 s (1H, CH), 7.4 m (19H_{arom.}), 10.75 s (1H, NH), 12.78 s (1H, NH) (100%). Found, %: C 75.75; H 5.32; N 8.82. $\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_5$. Calculated, %: C 75.77; H 5.30; N 8.84.

2-(Diphenylmethylenehydrazono)-4-oxo-4-(4-chlorophenyl)-2-butenoic acid anilide (IVn). Yield 4.22 g (88%), yellow crystals, mp 160–162°C (toluene). IR spectrum, ν , cm^{-1} : 3250 br (CONH), 1585 (CONH), 1562 (C⁴=O, C=C, C=N). Found, %: C 72.55; H 5.66; Cl 7.43; N 8.78. $\text{C}_{29}\text{H}_{22}\text{ClN}_3\text{O}_2$. Calculated, %: C 72.57; H 4.62; Cl 7.39; N 8.75.

4-(4-Bromophenyl)-2-(diphenylmethylenehydrazono)-4-oxo-2-butenoic acid anilide (IVo). Yield 4.51 g (86%), yellow crystals, mp 137–138°C (tOλσOλ). IR spectrum, ν , cm^{-1} : 3260 (CONH, NH), 1587 (CONH), 1559 (C⁴=O, C=C, C=N). ¹H NMR spectrum, δ , ppm, **D**: 6.61 s (1H, CH), 7.60 m (19H_{arom.}), 10.51 s (1H, NH), 12.92 s (1H, NH) (83%); **C**: 4.52 s (2H, CH₂) 7.60 m (19H_{arom.}), 10.23 s (1H, NH). Found, %: C 66.40; H 4.23; Br 15.29; N 8.02. $\text{C}_{29}\text{H}_{22}\text{BrN}_3\text{O}_2$. Calculated, %: C 66.42; H 4.23; Br 15.24; N 8.01.

2-(Diphenylmethylenehydrazono)-4-oxo-4-phenyl-2-butenoic acid 2-pyridylamide (IVp). Yield 4.05 g (88%), yellow crystals, mp 173–174°C (MeCN). IR spectrum, ν , cm^{-1} : 3163 (CONH), 3121 (NH), 1682 (CONH), 1567, 1577, 1538 (C⁴=O, C=C, C=N). Found, %: C 78.20; H 5.24; N 9.45. $\text{C}_{29}\text{H}_{23}\text{N}_3\text{O}_2$. Calculated, %: C 78.18 H 5.20; N 9.43.

2-(Diphenylmethylenhydrazono)-(4-methylphenyl)-4-oxo-2-butenoic acid 2-pyridylamide (IVq).

Yield 3.95 g (86%), yellow crystals, mp 144–146°C (MeCN). IR spectrum, ν , cm^{-1} : 3268 (CONH), 3144 (NH), 1674 (CONH), 1604, 1574, 1554 ($\text{C}^4=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm: 2.26 s (3H, C–CH₃), 6.13 s (1H, CH), 7.65 m (18H_{arom}), 11.18 s (1H, NH), 12.78 s (1H, NH) (76%); **C**: 2.31 s (3H, C–CH₃), 4.52 s (2H, CH₂) 7.65 m (19H_{arom}), 9.2 s (1H, NH). Found, %: C 78.40; H 5.46; N 9.15. C₃₀H₂₅N₃O₂. Calculated, %: C 78.41; H 5.48; N 9.14.

2-(Diphenylmethylenhydrazono)-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid 2-pyridylamide (IVr).

Yield 4.04 g (85%), yellow crystals, mp 141–143°C (tOλσOλ). IR spectrum, ν , cm^{-1} : 3260 (CONH), 3202 (NH), 1686 (CONH), 1589, 1574, 1554 ($\text{C}^4=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm, **D**: 3.77 s (3H, O–CH₃), 6.12 s (1H, CH), 7.65 m (19H, 2C₆H₅, C₆H₄, C₅H₄N), 11.17 s (1H, NH), 12.75 s (1H, NH), (61%); **C**: 3.78 s (3H, O–CH₃), 4.51 s (2H, CH₂), 7.65 m (19H, 2C₆H₅, C₆H₄, C₅H₄N), 9.19 s (1H, NH). Found, %: C 75.74; H 5.32; N 8.88. C₂₄H₂₅N₃O₅. Calculated, %: C 75.77; H 5.30; N 8.84.

2-(Diphenylmethylenhydrazono)-4-oxo-4-(4-chlorophenyl)-2-butenoic acid 2-pyridylamide (IVs).

Yield 4.22 g (88%), yellow crystals, mp 160–162°C (toluene). IR spectrum, ν , cm^{-1} : 3250 br (CONH), (NH), 1585 (CONH), 1562 ($\text{C}^4=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm, **D**: 6.15 s (1H, CH), 7.65 m (19H, 2C₆H₅, C₆H₄, C₅H₄N), 11.19 s (1H, NH), 12.79 s (1H, NH) (80%); **C**: 4.54 s (2H, CH₂) 7.65 m (19H, 2C₆H₅, C₆H₄, C₅H₄N), 9.2 s (1H, NH). Found, %: C 72.57; H 4.60; Cl 7.42; N 8.78. C₂₉H₂₂ClN₃O₂. Calculated, %: C 72.57; H 4.62; Cl 7.39; N 8.75.

4-(4-Bromophenyl)-2-(diphenylmethylenhydrazono)-4-oxo-2-butenoic acid 2-pyridylamide (IVt).

Yield 4.51 g (86%), yellow crystals, mp 137–138°C (toluene). IR spectrum, ν , cm^{-1} : 3260 (CONH), 1587 (CONH), 1559 ($\text{C}^4=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm, **D**: 6.61 s (1H, CH), 7.60 m (19H, 3C₆H₅, C₆H₄), 10.51 s (1H, NH), 12.92 s (1H, NH) (83%); **C**: 4.52 s (2H, CH₂) 7.60 m (19H, 2C₆H₅, C₆H₄), 10.23 s (1H, NH). Found, %: C 66.40; H 4.23; Br 15.28; N 8.05. C₂₉H₂₂BrN₃O₂. Calculated, %: C 66.42; H 4.23; Br 15.24; N 8.01.

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylamino)-4-oxo-4-(4-tolyl)-2-butenoic acid 2-thiazolylamide (IVu). Yield 3.41 g (75%), yellow crystals, mp 189–190°C. IR spectrum, ν , cm^{-1} : 3457

(CONH), 3194 (NH), 1672 (CONH), 1664 ($\text{C}=\text{O}_{\text{pyr}}$), 1597 ($\text{C}^4=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$). ^1H NMR spectrum, δ , ppm, **D**: 2.24 s (3H, C–CH₃), 2.97 s (3H, N–CH₃), 6.43 s (1H, CH), 7.5 m (10H, 2Ph + 2H, Ht), 11.53 s (1H, NH), 12.84 s (1H, NH) (76%); **E**: 2.01 s (3H, C–CH₃), 3.1 s (3H, N–CH₃), 5.86 s (1H, CH), 7.50 m (10H, 2Ph + 2H, Ht), 9.01 s (1H, NH), 13.2 s (1H, NH). Found, %: C 62.85; H 4.43; N 15.31. C₂₄H₁₀N₅O₃S. Calculated, %: C 62.87; H 4.40; N 15.27.

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